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Redox Cationic Polymerisation

A thesis submitted to the University of Dublin
for the degree of
Doctor of Philosophy

by

David J. Farrell

Trinity College Dublin **January 2011**

DECLARATION

This thesis has not been submitted as an exercise for a degree at any other university. Except where stated, I carried out the work described therein alone.

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SUMMARY

The aim of this work is the development of an initiation chemistry that allows preparation of storage stable single-component epoxy compositions, which polymerize when contacted with metallic substrates, at ambient temperatures and without the use of an externally applied energy stimulus such as heat or light. Such epoxy compositions would be considered the cationically initiated analogues of existing radical initiated acrylic systems used commercially as so-called anaerobic machinery adhesives.

Known redox cationic polymerisation systems consist of an iodonium salt latent catalyst and a reducing agent component, typically an ascorbic acid derivative, as the redox couple catalysed by a Cu(II) species. A fundamental investigation of this redox polymerisation chemistry was undertaken looking at the effect of concentration and catalyst-type on redox couple activity, this is reported in Chapter Two. Additionally the influence of residual oxygen and moisture, as well as the nature of the latent catalyst cation, anion and the reducing agent component was assessed. The activity of several cationically polymerisable monomers was also considered. The relative reactivities of the systems studied were quantified using a calorimetric method. The longterm reactivity of an optimised model system was evaluated, and its applicability as an ambient temperature curable, single-component epoxy adhesive was ascertained by a standard tensile strength test method. It was determined that copper catalysed redox cationic polymerisation does not have adequate reactivity or stability to meet the requirements of a commercially useful single-component adhesive.

In Chapter Three a new approach to the surface promoted redox cationic polymeristion of epoxy monomers based on the direct reduction of silver salts of non-nucleophilic anions by metallic substrates was investigated. The various factors influencing the activity of the redox polymerisations were studied including influence of the cation, anion, substrate-type and the monomeric environment. All surface promoted polymerisations were followed using FTIR-ATR. The relative conversion to polymer was determined for each system evaluated. Ag(I) surface promoted redox cationic polymerisation was shown to have the general performance and storage stability of typical redox anaerobic acrylate adhesives, in addition to thermal properties particular to polyethers. An alternative approach to surface promoted cationic polymerisation based on the reduction of onium salts by redox-generated radicals was also explored.

In conclusion patented novel single-component redox cationic polymerisation systems are demonstrated that have potential for development as a commercial adhesives technology.

Dedicated to My Family

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"The greatest obstacle to discovery is not ignorance
– it is the illusion of knowledge."
Daniel J. Boorstin

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LIST OF ABBREVIATIONS

A-6-Hex	L-Ascorbic Acid 6-Hexadecanoate
Ar	Aryl
APH	1-Acetyl-2-Phenyl Hydrazine
ATR	Attenuated Total Reflectance
ATRP	Atom Transfer Radical Polymerisation
BADGE	Diglycidyl Ether of Bisphenol A
BDVE	1,4-Butanediol Divinyl Ether
BENA	Bis(Ethyl-α-Pyridinium Acrylate)
BHT	Butylated Hydroxy Toluene
BPO	Benzoyl Peroxide
C	Coulomb
C	Percentage Conversion Monomer to Polymer (%)
c.	*Circa*: Approximately, Close to
CHO	Cyclohexene Oxide
CHP	Cumene Hydroperoxide
COD	1,5-Cyclooctadiene
CT	Charge Transfer Complexes
DIAP	Diazonium Induced Anchoring Process
DLaTGS	Deuterated L-Alanine Doped Triglycine Sulfate (IR Detector)
DMPT	Dimethyl-*p*-Toluidine
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
DVE3	Triethylene Glycol Divinyl Ether
EB	Electron Beam
EDTA	Ethylenediamine-tetraacetic Acid
ENA	Ethyl-α-Pyridinium Acrylate
EPA	Ethyl-α-Triphenylphosphonium Acrylate
ETM	Ethyl-α-(Tetrahydrothiophenium Methyl)Acrylate
F	Faraday Constant (96,485 C/mol)
FP	Frontal Polymerisation
FTIR	Fourier Transform Infrared Spectroscopy
GBMS	Grit Blasted Mild Steel

GCMS	Gas Chromatography Mass Spectrometry
GEC	General Electric Corporation
HPLC	High Performance Liquid Chromatography
HX	Brønsted Acid
I	Initiator
IFP	Isothermal Frontal Polymerisation
Ini-fer-ter	Initiator–Transfer Agent–Terminator
ITX	2-Isopropylthioxanthone
K	Kelvin (Temperature)
k_{abs}	Rate of Absorption
k_{SET}	Rate of Single Electron Transfer
L	Ligand
LRP	Living Radical Polymerisation
M	Monomer
M	Molar Mass of the Monomer, (g/mol)
M^+	Metal Cation, +1 oxidation state
Mol. Wt.	Molecular Weight, (g/mol)
MS	Mass Spectrometry
MS	Mild Steel
n	Number of Electrons
N	Number of Repeat Units Per Molecule
N	Newton (Force)
N/mm^2	Tensile Strength
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance Spectroscopy
PAG	Photo Acid Generator
PAT	Phenyl Azo Triphenyl Methane
Ph_2I^+	Diphenyliodonium
PMMA	Poly(Methyl Methacrylate)
RAFT	Reversible Addition Fragmentation Chain Transfer
RITP	Reverse Iodine Transfer Polymerisation
RT	Real Time
rt	Room Temperature

SFRP	Stable Free Radical Polymerisation
SHE	Standard Hydrogen Electrode
SPRC	Surface Promoted Redox Cationic (Polymerisation)
SPP	Surface Promoted Polymerisation
STM	Standard Test Method
STP	Standard Temperature (25 °C) and Pressure (1 bar)
SW	Solvent Wiped
T	Time
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl, (Stable Radical)
TFP	Thermal Frontal Polymerisation
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
T_{max}	Maximum Exotherm (°C)
TRIEGMA	Triethylene Glycol Dimethacrylate
UV	Ultra Violet
V	Voltage
VOC	Volatile Organic Carbon (Solvent)
X or X^-	Anion

LIST OF SYMBOLS

1K	One Component / One Part (Adhesive)
2K	Two Component / Two Part (Adhesive)
α	Degree of Conversion Monomer to Polymer (%)
$\alpha_{,t}$	Degree of Conversion Monomer to Polymer at Time (t)
°C	Degree Celcius (Temperature)
ΔE_{rxn}	Potential Difference: $E_{½}^{ox}$ - $E_{½}^{red}$ for Redox Reaction
$\Delta H_{exp,t}$	Experimental Enthalpy of Reaction
ΔH_{T}	Theoretical Enthalpy (J/g)
ΔH_{Tf}	Theoretical Enthalpy of One Reacted Functional Group (J/mol)
ΔT	Change in Temperature (K)
E^{*}	Excitation Energy
$E^{'}$	Loss Modulus
$E^{''}$	Storage Modulus
$E_{½}^{ox}$	Redox Potential, Oxidation
$E_{½}^{red}$	Redox Potential, Reduction
$h\nu$	Wavelength or Photo Irradiation
I^{*}	Initiator in Excited State
λ	Wavelength (nm)
R^{*}	Reactive Species
R·	Radical
S^{*}	Excited Sensitizer
σ	Wavenumber (cm^{-1})
$t_{½}$	Half-Time
Tan δ	Mechanical damping behaviour of a polymer at chosen oscillatory frequency, typically 1 Hz, (E”/E’)

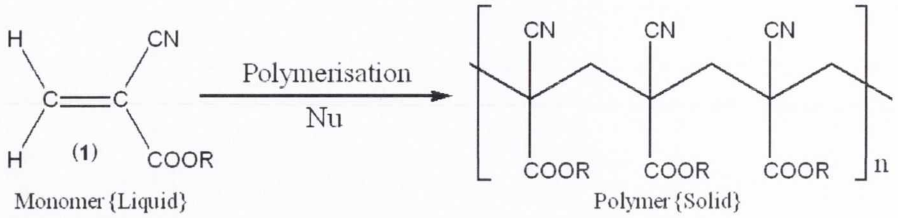
CHAPTER ONE | INTRODUCTION

One of the largest commercial application areas for speciality polymers is adhesives. Throughout the world adhesives find substantial use in both industrial and consumer applications. Adhesives allow the bonding of two or more components or substrates together to form a unit with structural integrity. Adhesives are often used in applications where they function to reinforce the reliability of a mechanical joint e.g. bolt (fastener) thread-locking [1]. Further benefits of adhesives over alternate fixturing methods include weight minimisation, reduced inventory and improved aesthetics. Many adhesives are thermoplastic hot-melts i.e. they already exist as polymerised materials that can be liquefied by re-heating. Others are supplied in what are known as multipart systems, usually two-part or two-component adhesive systems. In this format a catalyst is supplied in one part of the package that requires mixing with the reactive component in the second part of the package prior to adhesive formation. Generally such systems have a "working-time" within which the substrates to be joined can be prepared and coated with the mixture before it polymerises, or "cures".

Still other adhesive systems are supplied as one-part or one-component materials that require the addition of an external stimulus in the form of energy, e.g. heat or light, to activate a catalyst that is held latent within the adhesive matrix. However, there is yet another group of adhesives that requires neither mixing prior to use nor activation by externally applied energy. In these alternative systems the substrate itself typically plays an active role in inducing polymerisation. Such systems offer considerable end-user benefits as they are the most convenient to deploy.

All materials have surfaces. Bringing together the surfaces of any two materials results in the formation of an interface. It is the properties at play in this interfacial region that are crucial for determining the mechanical and other related properties in an adhesive bond or a composite material [2]. Surface induced polymerisations form the basis of two of the world's most successful adhesive chemistries:

- *Cyanoacrylate adhesives*, more commonly known as "Superglues", function as surface curing polymers because their activation relies upon the presence of ubiquitous nucleophilic contaminants on all surfaces such as bound moisture or basic residues. This is an *anionic* polymerisation, Scheme 1.0 [3-10].



… Scheme 1.0

- *Anaerobic acrylate adhesives* on the other hand rely upon a combination of metallic surface impurities, such as copper(II) species, and an oxygen free environment to induce the decomposition of peroxide components formulated within and initiate *radical* polymerisation [11-18].

The attractiveness of surface curing adhesive materials is that they require no additional processing by the end user. They are purchased as single component liquids and are applied directly to the surfaces to be bonded. They require no mixing, they have a virtually infinite open time, i.e. they remain in a liquid state when applied to just one substrate, and therefore processes do not have to be completed immediately or in a single step. These adhesive systems are low cost in use, and they have cure-on-demand properties not possessed by many of the other available options. In addition no externally applied source of energy is required to induce polymerisation, which proceeds at room temperature. The combination of these desirable characteristics brings significant advantages to the consumer.

To date, so far as can be determined, there have been no reports of one-component, room temperature, surface induced *cationic* polymerisations. However the concept of a one-component, room temperature curing cationic adhesive has been proposed [19,20] and the requirements of such a system have been explored [21,22]. It has even been reported that failure to develop workable, rapid curing, shelf-stable, one-component epoxy cure systems has prevented the use of epoxy adhesives in automated assembly processes [23]. Such an advancement, if realised, would lay open the possibility of developing a new adhesive technology based upon epoxy chemistry – bringing together the advantages of a one-component room temperature curing adhesives technology with the additional benefits, such as higher temperature performance and chemical resistance, associated with epoxy chemistry [19].

1.1 Comparison of Radical & Ionic Chain Polymerisations

Chain polymerisations are initiated by a reactive species R^* which originates from a compound called the initiator, I:

$$I \rightarrow R^* \qquad \text{… Scheme 1.1}$$

Typically the reactive species is formed by decomposition of the initiator following its direct or indirect thermal, photo or redox excitation. The reactive species, which can be a radical, a cation or an anion, adds to the monomer molecule typically by reaction with a π-bond forming a new radical, cation or anion centre which continues the chain reaction [24]:

$$R^* + CH_2{=}CHY \rightarrow R\text{-}CH_2\text{-}C^*(HY)$$
$$R\text{-}CH_2\text{-}C^*(HY) + CH_2{=}CHY \rightarrow R\text{-}CH_2\text{-}C(HY)\text{-}CH_2\text{-}C^*(HY)$$
$$R\text{-}CH_2\text{-}C(HY)\text{-}CH_2\text{-}C^*(HY) + CH_2{=}CHY \rightarrow R\text{-}[\text{-}CH_2\text{-}C(HY)\text{-}]_2\text{-}CH_2\text{-}C^*(HY)$$
$$\rightarrow\rightarrow R\text{-}[\text{-}CH_2\text{-}C(HY)\text{-}]_n\text{-}CH_2\text{-}C^*(HY)$$

… Scheme 1.2

Termination of chain polymerisation occurs when the reactive centre is destroyed by a suitable reaction depending on the type of polymerisation and the reaction conditions concerned. Even though radical, cationic and anionic initiators are used for chain polymerisation they cannot be used interchangeably as all three types of initiator do not polymerise all monomers. The majority of monomers that contain carbon–carbon double bonds can undergo radical polymerisation, whereas ionic polymerisations are very much more selective, see Table 1.0. Cationic polymerisation is essentially limited to monomers that contain electron-releasing substituents like alkoxy, phenyl and vinyl. Anionic polymerisation occurs in monomers having multiple electron-withdrawing groups such as cyano, nitrile, carbonyl, etc. The selectivity of ionic polymerisation results from the very strict stabilisation requirements of anionic and cationic propagating species. The commercial applications of cationic and anionic polymerisations are largely limited by this high selectivity of ionic polymerisations as compared to radical polymerisations [25].

Table 1.0: Comparison of Chain Polymerisation Initiation Methods for Various Unsaturated Monomers [24]

	Mode of Initiation		
Monomer	**Radical**	**Cationic**	**Anionic**
Ethylene	+	-	+
1-Alkyl Alkenes (α-Olefins)	-	-	+
1,1-Dialkyl Alkenes	-	+	-
1,3-Dienes	+	+	+
Styrene, α-Methyl Styrene	+	+	+
Halogenated Alkenes	+	-	-
Vinyl Esters (CH_2=CHOCOR)	+	-	-
Acrylates, Methacrylates	+	-	+
Acrylonitrile, Methacrylonitrile	+	-	+
Acrylamide, Methacrylamide	+	-	+
Vinyl Ethers	-	+	-
N-Vinyl Carbazole	+	+	-
N-Vinyl Pyrrolidone	+	+	-
Aldehydes, Ketones	-	+	+

The research that forms the basis of this thesis is principally based on redox reactions, processes that proceed at ambient temperature in the absence of added photo or thermal stimulus. However, there is much to be gained through understanding how related photochemical and thermochemical polymerisations are promoted and what the key controlling factors involved are. Additionally several photo radical generators have been employed to promote redox cationic polymerisations. Therefore, it might be considered that the key initiation aspects of conventional photo and thermal polymerisations may be achieved under ambient thermal and light-free conditions if suitable redox chemistry is developed.

1.2 Free-Radical Polymerisation

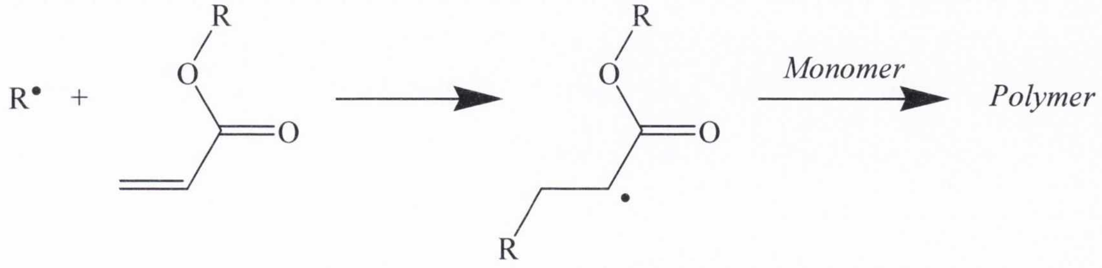
Radical polymerisations are amongst the longest established and widely studied methods of chain polymerisation and many commonly used plastics, enamels, and other polymers are formed from this type of polymerisation [34,35]. The magnitude of this use is demonstrated by the fact that almost 20 million tonnes of polymer were produced by radical polymerisation in the United States in the year 2001 [24].

All polymerisation processes must have initiation, propagation and termination steps and radical polymerisations are no exception, Scheme 1.3:

- *Initiation* of radical polymerisation requires the introduction of a radical species into the monomer matrix. During the process of initiation this radical attacks a monomer molecule converting it into a radical.

- *Propagation* occurs when the monomer-converted-to-radical, which is also an active species, adds to further monomer molecules while the growing chain preserves its radical character.

- *Termination* of the radical chain reaction occurs when one active radical species reacts with another active radical species eliminating both active radicals. Termination is the only way that a radical can be removed from the system. In general terms peroxide initiation systems are not easily inhibited and this is distinctly advantageous for use in variable industrial and engineering applications where robust adhesive systems are essential [36].



… Scheme 1.3

As outlined in Table 1.0 different monomers display varying degrees of selectivity relative to the variety of reactive centres that can cause their polymerisation. Monomers based upon highly polarised carbonyl groups, e.g. formaldehyde, are not generally susceptible to polymerisation by radical initiators. While virtually all monomers that contain carbon–carbon double bonds can undergo radical polymerisation albeit at varying rates [24].

Radical initiating species are often neutral and thus a wide range of substituents can stabilise the propagating radical by delocalisation over two or more atoms. Several radical initiators used for photo, thermal and redox radical polymerisations are presented in Table 1.1.

1.2.1 Overview of Modes of Radical Polymerisation

- *Photoinitiated Radical Polymerisation*

Photopolymerisation offers a means of rapidly converting a liquid monomer system to a solid polymer using radical or ionic initiating species typically generated by UV or electron beam (EB) irradiation at ambient temperatures, with low energy consumption and without using organic solvents [26-28]. As such photopolymerisation finds wide application in such applications as coatings, varnishes, inks, electronics, photolithography and adhesives [26-29]. The features of photoinitiated radical polymerisation are described in several publications [30-33,45].

- *Thermal Radical Polymerisation*

A wide variety of radical generators have been employed in thermal radical polymerisation, Table 1.1. Such initiators can be used across a range of temperatures due to the different dissociation energies of each species [42,46]. The various aspects of thermally activated radical polymerisation are described in several publications [40,42-48].

- *Frontal Radical Polymerisation*

Chechilo and co-workers first reported frontal polymerisation in 1972 using methyl methacrylate under high pressure [49]. Frontal polymerisation is a form of thermal polymerisation in which a spatially localized reaction zone propagates while converting monomer into polymer due to the relationship between thermal conduction and temperature-dependent reaction rates [50,51]. Frontal radical polymerisations have been the subject of several recent publications and reviews [52-59]. The three principal forms of frontal polymerisation are:

i. *Thermal Frontal Polymerisation* (TFP) requires a point source of heat to ignite the polymerisation front [60].

ii. *Photo-Frontal Polymerisation* in which the localized reaction is activated by an externally applied electromagnetic source typically UV light [61].

iii. *Isothermal Frontal Polymerisation* (IFP), which occurs when a solution of monomer and a thermal initiator contacts a polymer seed, i.e. a small piece of polymer, a viscous region is formed in which the polymerisation rate is faster because of the Tromsdorf gel effect [62].

- *Living Radical Polymerisation*

Chain polymerisations normally progress with associated chain-breaking reactions, and irreversible chain transfers and terminations with the initiating species having limited lifetimes [24]. Living polymerisation is a form of addition polymerisation in which the growing polymer chain is unable to terminate [63]. The original living polymerisation techniques, developed in the mid-1950s, were anionic polymerisation systems [64]. Living radical polymerisations are generally thermally activated processes. All controlled radical polymerisation methods include activation and deactivation steps. The generated radicals propagate and terminate as in conventional polymerisation. However, the contribution of termination processes is very small, hence the living character of these polymerisations [65]. This leads to uniform polymer chain growth and a low polydispersity. There are many reviews on the various forms of LRP [24,65-92]:

i. *Iniferters* (Initiator–Transfer Agent–Terminator), originally introduced by Otsu, function as radical initiators that induce polymerisation, which proceeds by initiation, propagation, primary radical termination, and transfer to initiator [70,71].

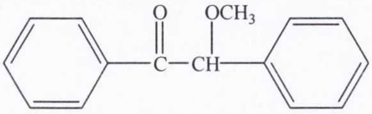
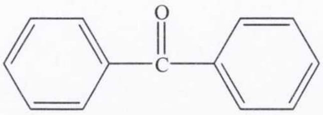
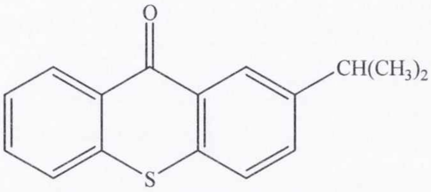
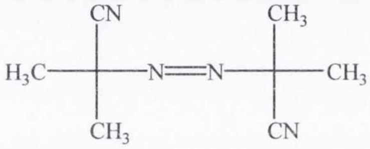
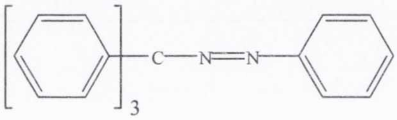
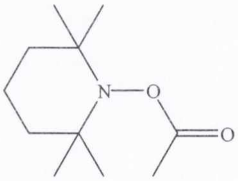
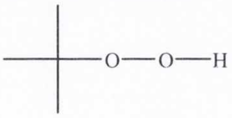
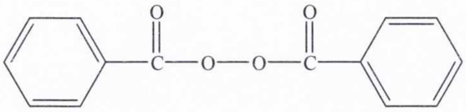
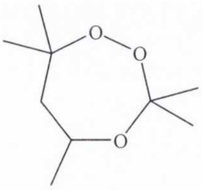
ii. *Stable Free Radical Polymerisation* (SFRP) makes possible the preparation of linear or branched polymers having narrow molecular weight distributions while retaining reactive end groups [72-76].

iii. *Atom Transfer Radical Polymerisation* (ATRP), originally described by Matyjaszewski *et al.*, is a method of forming C–C bonds using transition metal catalysts, Scheme 1.10 [65,77-87]. ATRP has links with redox radical processes although in atom transfer systems transition metals also have a significant inhibitory function [78].

iv. *Reversible Addition Fragmentation Chain Transfer* (RAFT) polymerisation, originally described by Rizzardo *et al.*, is an LRP techniques used in the preparation of materials with such complex architectures as block, star, comb and brush co-polymers [88-91].

v. Recently *reverse iodine transfer polymerisation* (RITP) has been developed. RITP is a controlled radical polymerisation technique based on the use of molecular iodine, I_2, as a control agent [92].

Table 1.1: Overview of Various Classes of Radical Initiators

	Photo-Radical Generators		
2		Benzoin Methyl Ether	[37]
3		Benzophenone	[38]
4		2-Isopropylthioxanthone (ITX)	[39]
	Thermal-Radical Generators		
5		α,α'-Azoisobutyronitrile (AIBN)	[40]
6		Phenyl Azo Triphenyl Methane (PAT)	[41]
7		*N*-Acyloxyamine	[42]
8	$M^{++}\ S_2O_8^{2-}$	Persulfate, where M^{++} = Divalent Cation	[43]
	Per-oxy Compounds Used as Thermal and Redox Radical Initiators		
9		*tert*-Butyl Hydroperoxide	-
10		Benzoyl Peroxide (BPO)	[40]
11		3,3,5,7,7-Pentamethyl-1,2,4-Trioxepane (Trigonox 311)	[44]

1.2.2 Redox Radical Polymerisation

Redox radical polymerisation, in the form of anaerobic acrylate adhesives, is a long established chemical technology [93-96]. The original anaerobic adhesive systems, developed during the 1950s and 1960s in the General Electric Corporation (GE), were known as "Anaerobic Permafil" and required the continuous bubbling of air through a bath of polyethylene glycol dimethacrylate monomer [93]. Subsequently Krieble discovered a solution to the inherent instability of the original anaerobic formulations through the use of a hydroperoxide initiator combined with partially filled air-permeable polyethylene packaging [94]. This system permitted the convenient and widespread use of these adhesives and still forms the basis of the anaerobic acrylate products seen today.

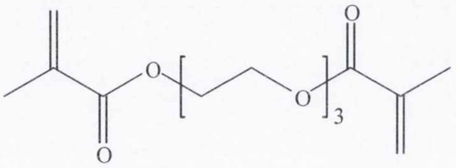
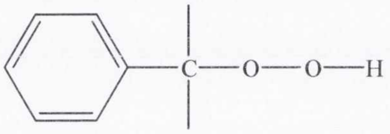
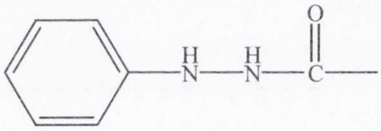
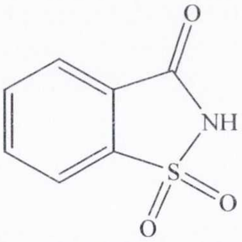
Anaerobic adhesives are single component acrylic adhesives that have inherent stability during aerobic storage at room temperature but polymerise rapidly when confined between two closely fitting metallic substrates. Transition metal ions on the surface of substrates to be bonded play a key role in catalysing the decomposition of polymerisation initiators to create free radicals [14,97,98]. Anaerobic adhesive systems are composed of readily reduced organic peroxides, e.g. hydroperoxides and perbenzoates, which are the most commonly applied initiators, used in combination with reducing agents with or without the presence of an organic acid and tertiary amine as accelerators, see Table 1.2 [97].

Surfaces play a major role in the performance of anaerobic adhesives. Anaerobics are extremely sensitive to the nature of the substrate they are applied to i.e. they polymerise quickly on iron and copper rich surfaces but slowly or not at all on zinc, aluminium and non-metallic surfaces *in spite* of an anaerobic bondline environment. Anaerobic adhesive formulations are used in a wide range of industrial applications including the thread locking of bolts, flange sealing, structural bonding, and engine block sealing amongst others [99]. They are subject to continuous development in order to meet the increasing demands of modern technologies [100-103]. Several reviews have been published on redox polymerisation, anaerobic adhesive systems and their applications [15,97,104-108].

1.2.2.1 Major Components of Redox Radical Systems

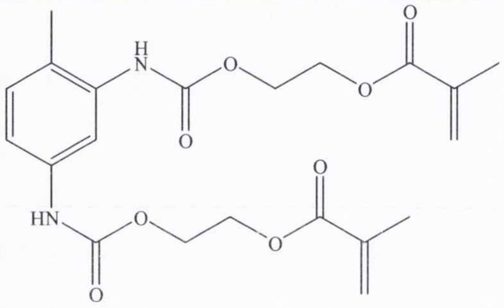
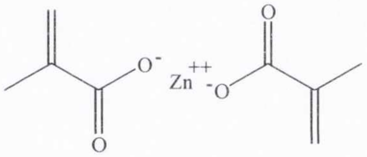
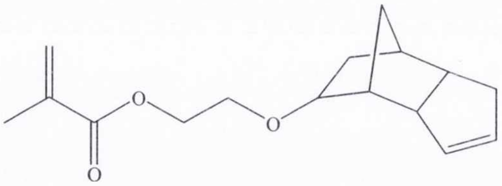
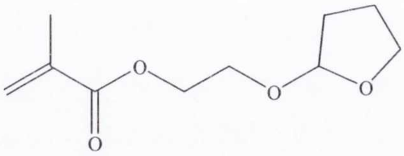
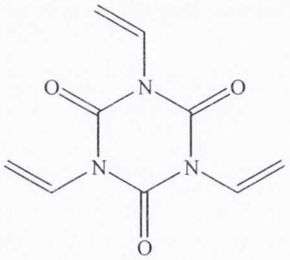
The diversity of materials that have found use in redox anaerobic polymerisation systems is extremely varied. However the four major components that will almost certainly be present in some form are listed Table 1.2 with typical example for each.

Table 1.2: Major Components of Anaerobic Adhesive Systems

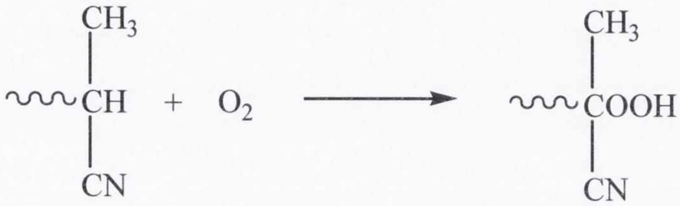
Component	**Typical Example**	**Structure**		**[Ref]**
Monomer	Triethylene Glycol Dimethacrylate (TRIEGMA)		**12**	[94,109]
Initiator (Oxidant)	Cumene Hydroperoxide (CHP)		**13**	[110]
Reducing Agent	Acetyl Phenyl Hydrazine (APH)		**14**	[111-115]
Accelerator	Saccharin		**15**	[116,117]

- *Monomers:* Monomers are central to the usefulness of any polymerisation system. Various properties and performance characteristics can be conferred on the final polymer formed through careful selection of the monomer system. The first anaerobic monomers were based on polyethyleneglycol dimethacrylates e.g. triethylene glycol dimethacrylate, see Table 1.2 [93,94,109]. Even today methacrylic esters are used almost exclusively in anaerobic adhesive systems due their ease of preparation, reliable performance, low toxicity, rapid cure speed, good environmental resistance and a lower sensitivity to oxygen as compared to their acrylate counterparts [15]. Acrylic and methacrylic acids as well as some other vinyl monomers may also be used depending on the properties required. Short chain methacrylate monomers have the limitations that they form brittle products, which are of limited value in adhesive bonds that are subject to impact, cleavage or peel forces [15]. Many acrylate and methacrylate monomers aimed at addressing these limitations and encompassing a diverse range of properties have been developed and have found widespread use in anaerobic adhesives technologies, see Table 1.3.

Table 1.3: A Selection of Monomers used in Redox Anaerobic Systems

	Structure	***Monomer Type*:** **Function**	**[Ref]**
16		*Polyurethane Acrylate*: Long-chain, flexible monomers useful for high-temperature performance, gap filling, and structural adhesives.	[101, 118-122]
17		*Methacrylate Half Ester* *e.g. Zinc Methacrylate*: Methacrylic acid replacement. Giving improved adhesion to metal through carboxylic functionality, improved thermal resistance, oil cutting, and reduced rust formation.	[123,124]
18		*Dicyclopentenyl Methacrylates*: Low odour, low shrinkage, good oil tolerance.	[125]
19		*Tetrahydrofurfuryl Methacrylates*: Thermal performance, water resistance, oil tolerance and low shrinkage.	[96]
20		*Triallylisocyanurate*: Improved thermal performance, water resistance, photo-stability and reduced shrinkage.	[126]

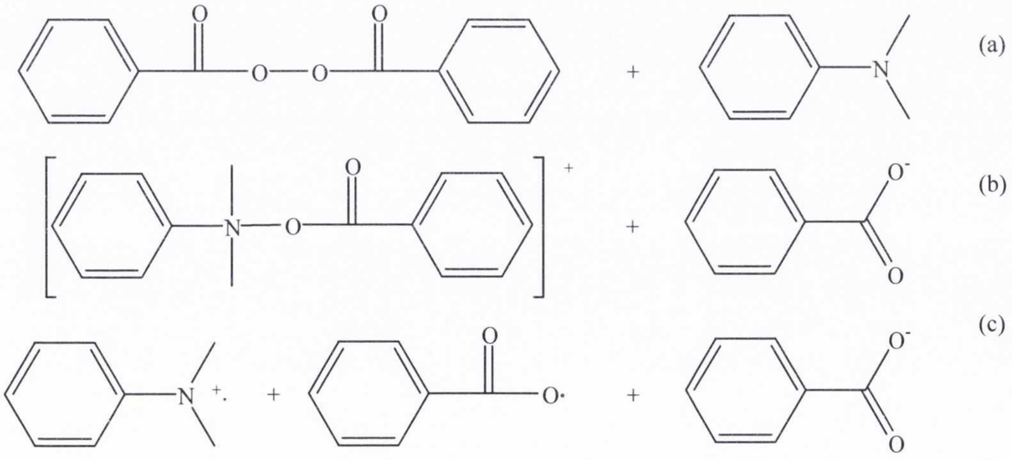
- *Initiators:* In early redox radical systems it was found that bubbling oxygen through methacrylate monomer at elevated temperature induced oxidation of the monomer and subsequent removal of the oxygen supply brought about polymerisation [11]. The reaction between oxygen and the monomer led to formation of hydroperoxides at certain active hydrogen sites on the monomer, Scheme 1.4 [127].



$$\sim\!\sim\!\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{CH}} + O_2 \longrightarrow \sim\!\sim\!\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{COOH}}$$

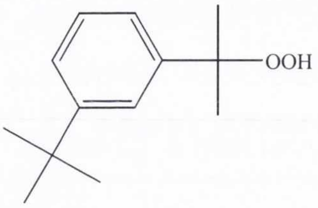
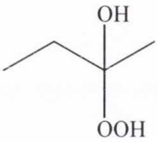
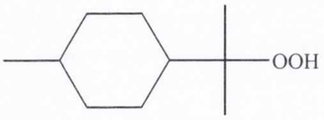
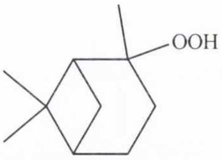
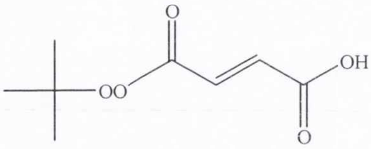
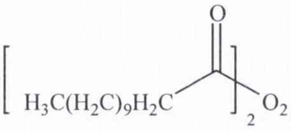
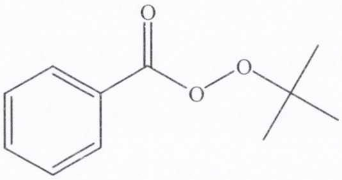
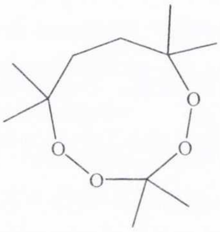
... Scheme 1.4

In modern anaerobic systems hydroperoxides are added directly to the monomer to form air stabilised compositions. Cumene hydroperoxide and *tert*-butyl hydroperoxide are the most widely used peroxy initiators in anaerobic systems. A large number of other anaerobic radical initiators have been described, see Table 1.4. Redox anaerobic systems have been described which do not require the addition of peroxy compounds as initiators and there is evidence to suggest they may rely on the formation of radical ions, see Scheme 1.5, or residual oxygen in or peroxy species on the monomer to promote the polymerisation [15,17,97,127].



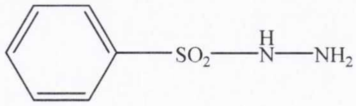
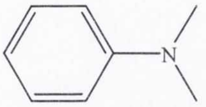
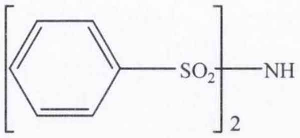
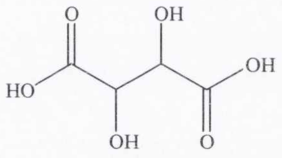
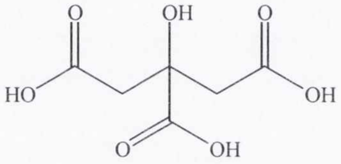
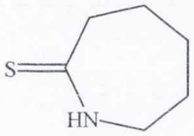
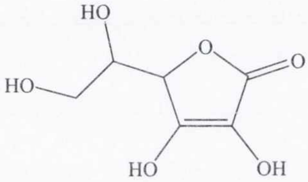
... Scheme 1.5

Table 1.4: Examples of Initiators, which have found use in Redox Anaerobic Systems

	Structure	**Name:**		**Structure**	**Name:**
21		Diisopropyl-benzene Hydroperoxide	**22**		Methyl Ethyl Ketone Hydroperoxide [128]
23		*p*-Mentane Hydroperoxide	**24**		Pinene Hydroperoxide
25		*tert*-Butyl-peroxymaleic Acid [129]	**26**		Lauroyl Peroxide
27		*tert*-Butyl Perbenzoate [113]	**28**		Cyclic Diperoxide [130]

- *Reducing Agents & Accelerators:* The accelerating components of anaerobic compositions are species, which promote the decomposition of the oxidising component under anaerobic conditions or in the presence of a transition metal catalyst, Table 1.5. One of the first materials used as an accelerator was tributylamine [109]. In contemporary composition the reducing agents commonly consist of a mixture of an amine such as *N,N*-dimethyl-*p*-toluidine (DMPT) and saccharin. This combination is known to form the reducing species aminal [98]. Otherwise acetylphenylhydrazine (APH) is used to replace DMPT [97]. Okamoto *et al.* have investigated the use of amine salts of saccharin as accelerators [13]. Accelerators, in the form of aromatic amines, are known to lower the decomposition temperature of peroxide initiators [131]. The reaction of tertiary aromatic amines with peroxides proceeds with a similar mechanism to that of metallic ions, Scheme 1.9 [132]. Sun *et al.* conducted a study on the reaction mechanism of organic hydroperoxides and tertiary aromatic amines [133]. Several α-hydroxy ketones [134-139] and thio [128,140] compounds have also been studied for their applicability in the role as reducing agents and accelerators.

Table 1.5: Several accelerators, which have found use in redox anaerobic systems

	Structure	Name		Structure	Name
29		Tributyl Amine [109]	**30**		Benzene Sulfonyl Hydrazide [141]
31		*N,N*-dimethyl-p-toluidine (DMPT) [98]	**32**		Dibenzene-sulfonimide [142]
33		Tartaric Acid [137,138]	**34**		Citric Acid [139]
35		Thiocaprolactam [128]	**36**		Ascorbic Acid & Derivatives [134-136]

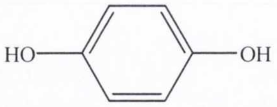
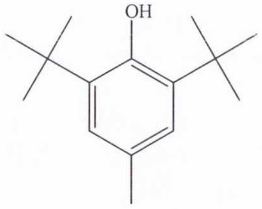
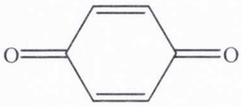
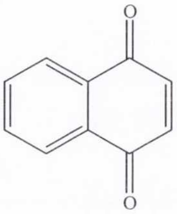
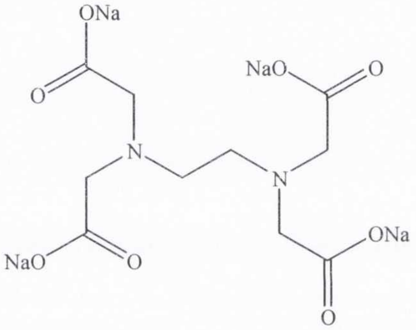
- *Stabilisers:* In addition to stabilisation by oxygen several compounds are usually present in commercially sourced acrylate monomers and may be added to redox anaerobic formulations to prevent the untimely formation and propagation of free radicals, Table 1.6. Free radical stabilisers, such as hydroquinone, *p*-methoxyphenol and butylated hydroxy toluene (BHT), are routinely added to the radically susceptible monomers that are used in redox anaerobic systems. These additives and related compounds e.g. benzoquinone and naphthoquinone, have been shown to improve the stability of anaerobic compositions without impeding performance [143]. Additionally the chelator tetrasodium EDTA and its analogues have been used to stabilize redox anaerobic systems against contamination by trace amounts of metal ions [144]. The concentration of transition metals inherent in anaerobic systems has been studied using HPLC and voltametry [16,145]. Okamoto suggests that chelators achieve stabilisation of anaerobic adhesives for the following reasons [146]:

i. Formation of insoluble metal chelating complexes.

ii. They alter the redox potential of metal ions and prevent them acting as catalysts.

iii. They form sterically hindered complexes, which cannot partake in redox reactions.

Table 1.6: Examples of Stabilizers, which have found use in Redox Anaerobic Systems

	Structure	Name		Structure	Name
37		Hydroquinone	**38**		Butylated Hydroxy Toluene (BHT)
39		1,4-Benzo-quinone [143]	**40**		1,4-Naphtho-quinone [143]
41				Ethylenediamine-tetraacetic acid (EDTA) Tetrasodium Salt [144]	

1.2.2.2 Mechanism of Redox Radical Polymerisation

Redox anaerobic systems have been used extensively in adhesive applications over several decades and have been the focus of extensive industrial research. Accordingly there has been much effort aimed at elucidating cure mechanisms involved. However as anaerobic technology is of significant commercial value it has been the subject of limited academic study with a majority of published information in the patent literature. In recent years several groups and individuals have studied and published research on the various mechanisms at play in anaerobic cure chemistry. The role of bonding surfaces and the effects of various accelerators form the bulk of literature discussing the mechanism of redox anaerobic polymerisation [50]. Studies into the roles of the reducing and oxidising agent components as well as various transition metal catalysed processes by Okamoto, in particular, have affirmed the redox mechanism of anaerobic acrylate systems [17,18].

- *Redox Radical Stabilisation or "Anaerobic" Mechanism & the Role of Oxygen:* Oxygen plays a unique role in redox anaerobic systems as an inhibitor used to delay the onset of polymerisation and subsequently in the activation of polymerisation that occurs at active metallic surfaces [50]. When anaerobic adhesives are stored in air, typically in half filled air permeable polyethylene bottles, the continuously forming radicals are intercepted and quenched by oxygen to form unreactive peroxy radicals, Scheme 1.6(c). Oxygen has a high reaction rate with free radicals and the peroxy radical formed is a poor initiating species [50]. Therefore anaerobic adhesives remain stable and in the uncured liquid state.

When the oxygen supply is depleted, for example in an adhesive bondline, the continuously forming radicals are no longer eliminated and add directly to the acrylate monomer to initiate polymerisation, Scheme 1.6(d). This process is greatly accelerated by the presence of metal ions, which facilitate electron transfer.

Initiation	$I \rightarrow I\cdot$	*Reactive Radicals*	(a)
	$I\cdot + M \rightarrow M\cdot$		(b)
Inhibition	$M\cdot + O_2 \rightarrow MOO\cdot$	*Weak Radical with low reactivity*	(c)
Propagation	$M\cdot + (n\text{-}1)M \rightarrow M_n\cdot$	*Reactive Radical*	(d)
Termination	$M\cdot + M\cdot \rightarrow M_2$	*Free Radical Eliminated*	(e)
	$M\cdot + I\cdot \rightarrow MI$		(f)

… Scheme 1.6

In redox polymerisation studies oxygenated monomers were shown to react more quickly than deoxygenated monomers [13]. Hydroperoxides whether added directly to or formed in-situ through oxygen absorption effects serve as latent initiators in redox anaerobic systems. Hydroperoxides can function as oxidants, reductants or even both, Scheme 1.7 [132]. Several mechanisms for the oxidising action of a hydroperoxide include abstraction of a single electron, abstraction of a pair of electrons from an electron donor or through the donation of an oxygen atom to an acceptor [147,148].

$$\mathrm{RO{-}OH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{RO\cdot} + \mathrm{OH}^{-} + \mathrm{Fe}^{+3} \quad \text{(a)}$$

$$\mathrm{RO{-}OH} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{ROO\cdot} + \mathrm{H}^{+} + \mathrm{Fe}^{+2} \quad \text{(b)}$$

... Scheme 1.7

- *Redox Radical Polymerisation Mechanism & the Role of Transition Metals:* Redox anaerobic systems rely very much on surface chemistry to catalyse the polymerisation process [19]. Anaerobic adhesive polymerisation is promoted by the metal ion catalysed redox generation of radicals, Figure 1.0.

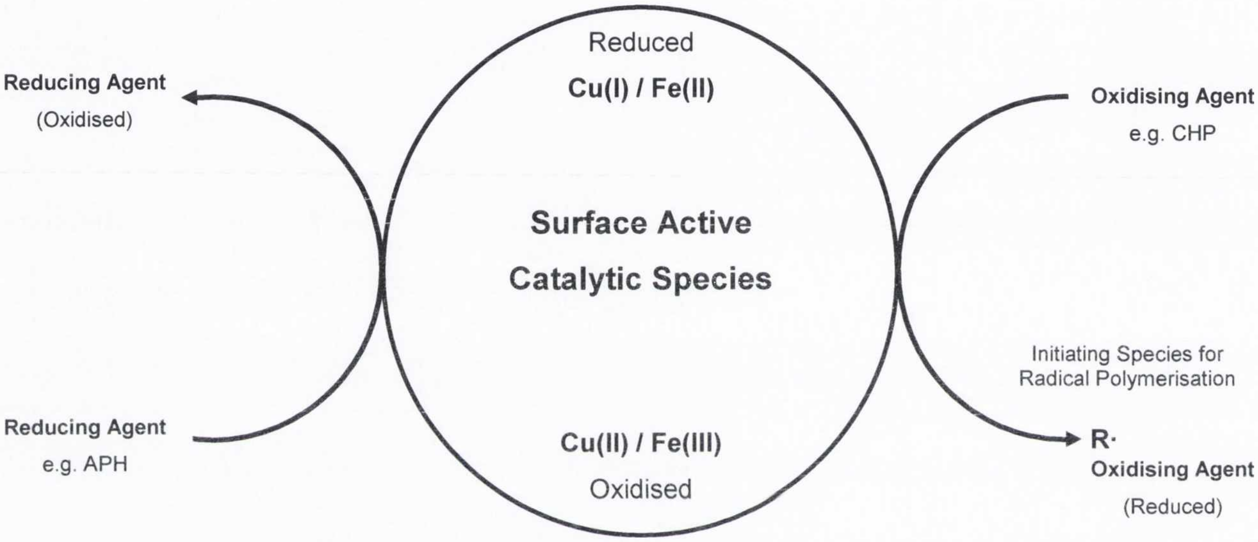
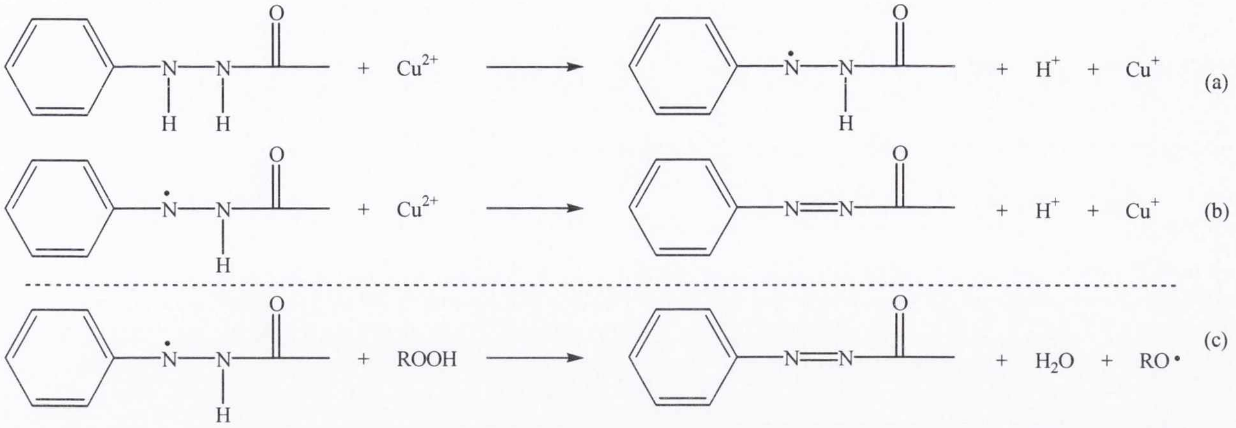


Figure 1.0: Transition metal catalysed radical generating anaerobic adhesive redox cycle

In a typical anaerobic acrylate system radical formation begins as soon as the reducing and oxidising components are brought together and continues until the reducing or oxidising components are completely consumed [146]. Oxidation and reduction processes always occur simultaneously [149]. Leonard has investigated the mechanistic role of 1-aceto-2-phenyl-hydrazine (APH) as a reducing agent in anaerobic adhesive systems [113], Scheme 1.8. APH causes reduction of Cu(II) to Cu(I), Scheme 1.8(a), the hydrazine radical generated in step (a) can react with further Cu(II) to generate additional Cu(I) species, Scheme 1.8(b). In addition the hydrazine may react directly with peroxide to generate further radicals, Scheme 1.8(c), The mechanistic role of saccharin as been studied by Moane *et al.* [98]. While it has been shown that saccharin can contribute to the formation of active reducing species e.g. aminal [98] its major function is as a mild acid. A mildly acidic environment assists the activation of metal surfaces and it has been shown that saccharin may be substituted for other mild acids such as acrylic, methacrylic and propionic acids [146,150].



... Scheme 1.8

The redox reaction between hydroperoxide and transition metals in adjacent oxidation states is a key feature of anaerobic adhesive cure [81]. Several chemical models have been used in the study of the anaerobic adhesive cure mechanism. The simplest model of redox radical generation is Fenton's reagent, which is composed of a mixture of hydrogen peroxide and ferrous salts. This is a well-known reagent in organic chemistry used for radical oxidation reactions [151]. At room temperature this mixture decomposes through reaction of a ferrous ion, Fe(II), with hydrogen peroxide to yield one radical and a ferric ion, Fe(III), Scheme 1.9.

$$\mathrm{HO{-}OH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{OH}\cdot + \mathrm{OH}^{-} + \mathrm{Fe}^{3+}$$ ... Scheme 1.9

In the presence of a monomer susceptible to radical polymerisation, the hydroxyl radical will act as an initiator [152]. Several different transition metal species, including copper, cobalt, manganese and vanadium amongst others, in both their higher and lower oxidation states can decompose hydroperoxides [132]. As a result only a small amount of metal is required for catalytic decomposition [153].

- *Combined Mechanisms:* As described there are several mechanisms involved in the stabilisation, polymerisation and acceleration of redox anaerobic systems. The rate of stabilisation is influenced by the type of monomer used, system viscosity, bulk volume and temperature. While factors influencing the rate of polymerisation include the nature of the redox couple employed, monomer, presence of active metals, degree of radical stabilisation and temperature. A schematic diagram outlining these processes is presented in Figure 1.1 [146].

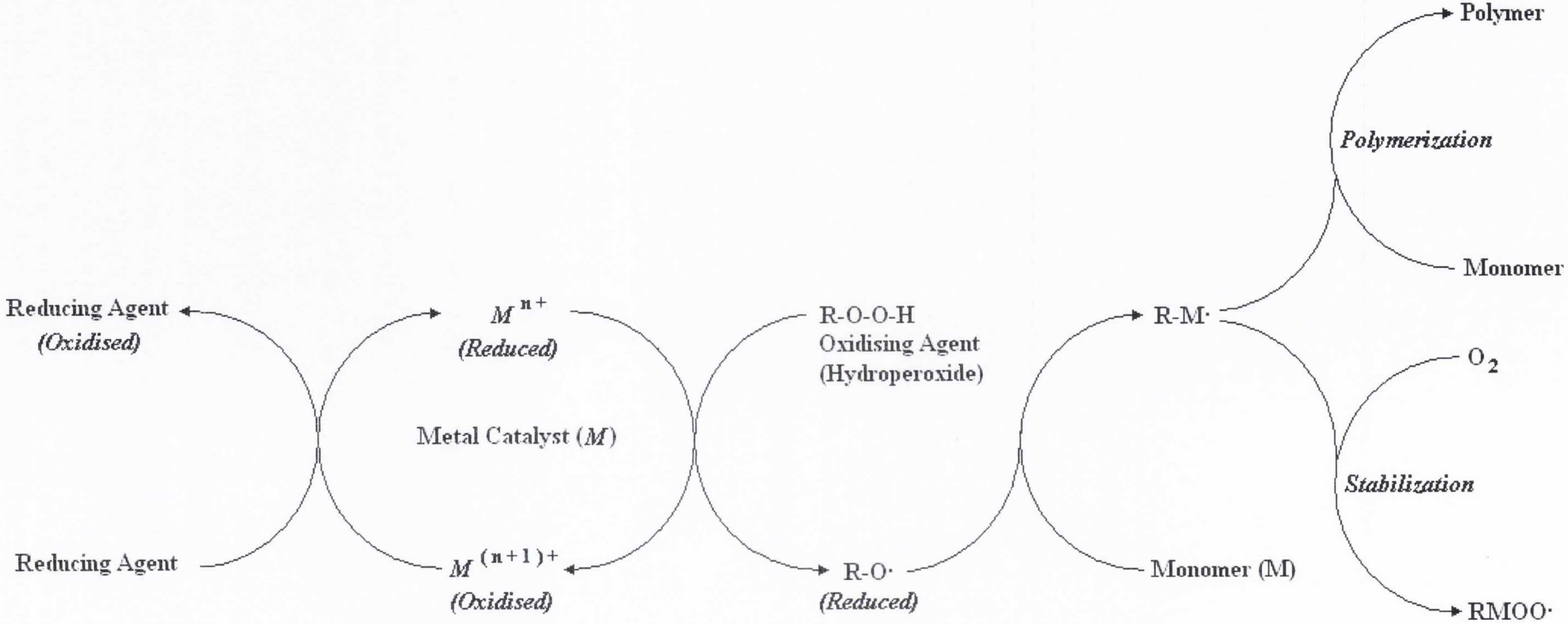
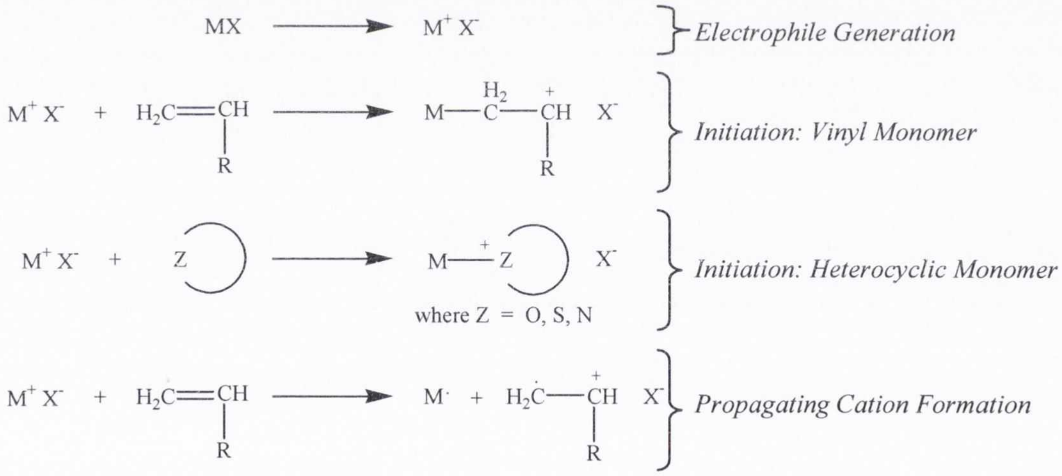


Figure 1.1: Schematic diagram of the combined mechanisms that contribute to activation and stabilisation of redox anaerobic systems [146]

1.3 Cationic Polymerisation

Cationic polymerisations are used for manufacture of several commercially important polymers e.g. isobutene based polymers [154], halocarbon resins [155], polyvinyl ethers [156] and siloxanes [157]. However some of the increasingly important applications of cationic polymerisation are in speciality applications, photoresists, adhesives and surface coatings technology areas [158].

The principal modes of cationic polymerisation that are used in industrial applications are direct Lewis acid initiation, as well as indirect initiation using latent thermal- and photo-cationic initiators. The initiation step requires the addition or in-situ generation of a positively charged electrophile with an attendant counterion e.g. Brønsted acid, Lewis acid, carbocation or trialkyloxonium salt [159]. The charged electrophile can then add to a susceptible monomer to yield a positively charged reactive centre, or it can accept an electron thereby yielding a propagating cation, Scheme 1.10 [160].



… Scheme 1.10 [160]

The classical cationic initiators instantly dissociate into an initiating cation and its allied counter anion once added to the polymerisable system. Latent cationic initiation systems, e.g. systems based on thermal or photo labile initiators, remain stable in the polymerisable monomer system until stimulated by an appropriate energy source e.g. heat or photo radiation. In all cationic polymerisation systems the counter anion must be sufficiently non-nucleophilic to prevent termination of growing chains by cation-anion recombination [159]. Direct initiation of cationic initiation is subject to several inherent limitations:

- Handling of highly acidic and even gaseous Brønsted acids used as direct initiation catalysts prior to addition to the polymerisable systems may present significant difficulties.

- Direct initiation systems initiate polymerisation immediately upon addition to the monomer system; therefore the concentration of the initiator throughout the course of the reaction is uncontrolled.

- Direct initiation results in rapid generation of a significant polymerisation exotherm. Therefore is necessary to work at relatively low temperatures in order to control the reaction. This leads to relatively low rates of polymerisation [159].

Latent cationic polymerisation initiators on the other hand eliminate these difficulties, allowing significantly improved control over cationic polymerisations and for these reasons are often by end users especially for speciality applications. The advantages of latent cationic initiation systems include:

- Stable polymerisable compositions can be prepared and stored for extended periods prior to use.

- Application of externally applied energy is required in order to promote polymerisation therefore fine control is maintained over the polymerisation process.

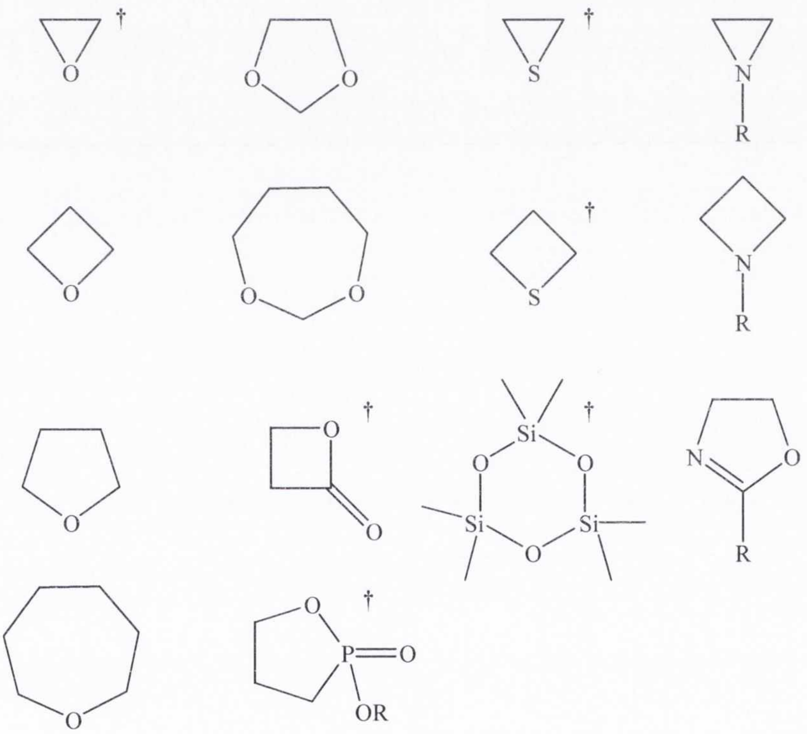
- The concentration of the initiating species generated can be regulated by careful control of the energy applied to the system [159].

In all cationic polymerisations the rate of polymerisation is significantly influenced by temperature, the reactivity of the monomer being used and by the presence of any impurities [161].

1.3.1 Cationically Polymerisable Monomers

Radical polymerisations are typically non-specific. However for ionic polymerisations this is not the case as the formation and stabilisation of a charged ion is largely dependent upon the nature of the monomer. Therefore cationic initiation is generally limited to vinyl monomers having electron-donating groups, which assist in stabilisation through delocalisation of the positive charge in the π-orbitals of the double bond. When there is a combination of mesomeric and inductive effects the stability is significantly enhanced. Since these ions have a counter ion associated with them solvent effects can have a profound influence on these polymerisations [162].

Table 1.7: Heterocyclic Monomers that can be Cationically Polymerised [163]



† These compounds can also be polymerised anionically.

Both vinyl and heterocyclic monomers can be polymerised cationically, see Tables 1.0 and 1.7. The two systems differ in that the active centres for polymerisation of vinyl monomers are carbenium ions while onium ions are the active centres for polymerisation of heterocycles. Polymers prepared by ring opening polymerisation always contain heteroatoms or other reactive functional groups along the backbone e.g. ether, sulfide, ester, amide, double bonds etc. [158]. Oxirane monomers in particular are favoured for use with cationic initiation systems since when cured epoxy resins form heavily cross-linked polyethers, which are mechanically very tough [164]. In commercial applications monomers are often multifunctional i.e. contain more than one polymerisable group per molecule e.g. diglycidyl ether of bisphenol A (BADGE) an epoxide, or 1,4-butanediol divinyl ether (BDVE) [165].

As a result of their relatively high ring strain energy cyclic ethers with three, four and five members are the most interesting monomers for polymerisation. Six-membered cyclic ethers have low ring strain and therefore do not undergo polymerisation [166,167]. Cyclic ether monomers with seven and more members have not been studied as extensively as those cyclic ethers with fewer members [168]. The number of atoms in the ring directs ring geometry. Ring strain results from the difference between the angles, which result from the normal overlapping of atomic orbitals and the angles that result from the requirements that are imposed upon the molecule by the size of the ring, see Table 1.8 [169]. The interactions between non-bonded atoms in close proximity to one another are another factor that contributes to the molecular strain.

Table 1.8: Ring Strain Values of Some Typical Unsubstituted Cyclic Ethers [170]

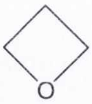
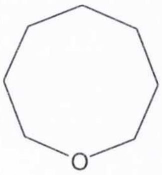
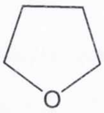
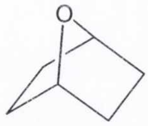
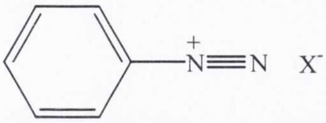
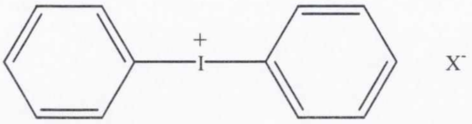
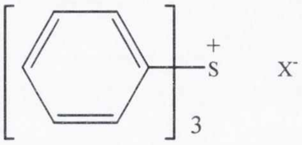
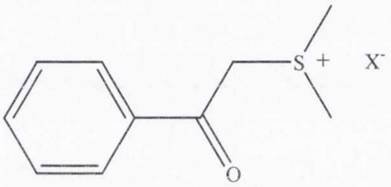
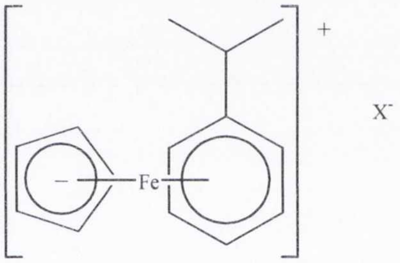
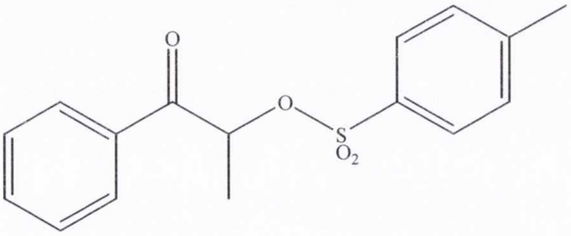
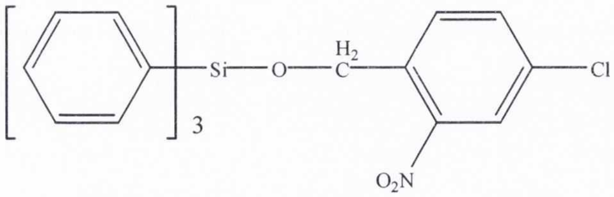
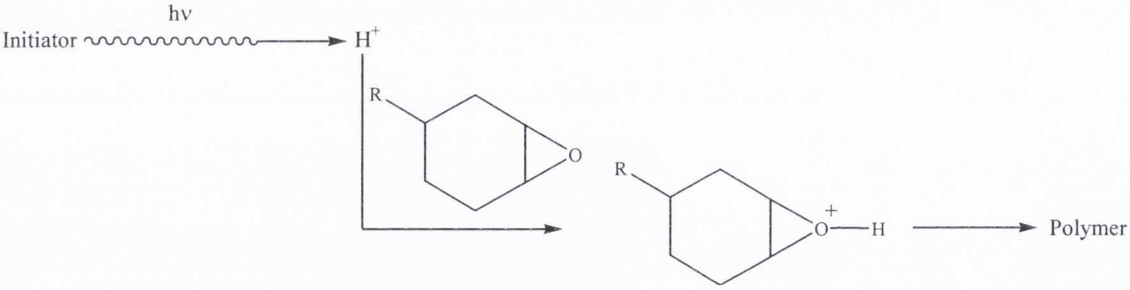
Cyclic Ether Monomer		***Ring Strain*** **(kJ mol^{-1})**	**Cyclic Ether Monomer**		***Ring Strain*** **(kJ mol^{-1})**
Oxirane (Ethylene Oxide)		114	Oxirane (Ethylene Oxide)		5
Oxetane (Trimethylene Oxide)		107	Oxocane		107
Oxolane (Tetrahydrofuran)		23	7-oxabicyclo[2.2.1]heptane		23

Table 1.9: The Major Classes of Photo Acid Generators used in Cationic Polymerisation [159]

	Ionic Cationic Photoinitiators		
42		Aryldiazonium Salts	[171,172]
43		Diaryliodonium Salts	[173]
44		Triarylsulphonium Salts	[174]
45		Dialkyl Phenacyl-Sulphonium Salts	[175]
46		Ferrocenium Salts	[176]
	Where X^- = Non-nucleophilic anion, typically: BF_4^-, AsF_4^-, PF_6^-, SbF_6^-		
	Non-ionic Cationic Photoinitiators		
47		α-Sulfonyloxy Ketones	[177]
48		Silyl Benzyl Ethers	[178-180]

1.3.2 Photo-initiated Cationic Polymerisation

Interest in cationic photopolymerisation has grown significantly in recent decades [181-184]. Unlike radical photopolymerisation, cationic photopolymerisation is not subject to oxygen inhibition therefore dry to touch UV cured coatings can be readily formed under a normal atmosphere. Cationic photopolymerisation are used in a growing array of applications including coatings, printing inks, adhesives, release coatings, stereolithography, holographic recording, microelectronic resists, and photocurable composites [185]. As a result of this interest much effort has been devoted to the development of a broad range of photoinitiators for cationic polymerisation [159]. Cationic photoinitiators are latent initiators that remain inactive until decomposed by photo-radiation of appropriate energy to generate the actual initiating species typically a Brønsted acid or Brønsted acid precursor, Scheme 1.11. Cationic photoinitiators may be referred to as photo acid generators (PAGs). It is essential that the emission spectrum of the irradiation source used will correspond to the absorption characteristics of the photoinitiator being used [161]. Cationic photoinitiators can be classified according to their general structure, see Table 1.9. Cationic photopolymerisation can be broken down into direct and indirect modes of initiation.



... Scheme 1.11

1.3.2.1 Direct Photolysis

Direct photolysis comprises those systems in which the incident irradiation acts directly on the latent initiator component to cause irreversible photolysis that generates the key initiating cation radical or Brønsted acid species. In the case of onium salts light with wavelengths in the region of 225 and 350 nm are typically used in order to achieve maximum absorption of incident radiation [186-188].

➢ **Onium Salts**

Onium ions are deemed to be the positively charged higher-valency compounds of the non-metallic elements [189]. Onium salts include some of the most widely used initiators for photo-induced cationic polymerisations. The general structure common to onium salts is presented in Table 1.10. The use of inorganic complex anions is necessary as any cationic species generated during photolysis or during polymerisation would rapidly recombine with any nucleophilic anion present thus terminating polymerisation. In the polymerisation of oxirane-type monomers the order of reactivity for non-nucleophilic anions is $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$. As the nucleophilic character of the anion decreases in the order $SbF_6^- < AsF_6^- < PF_6^- < BF_4^-$ the degree of separation between the initiating and propagating ion pairs increases and the reactivity increases and the susceptibility towards termination decreases [161]. An overview of the several classes of onium salt follows.

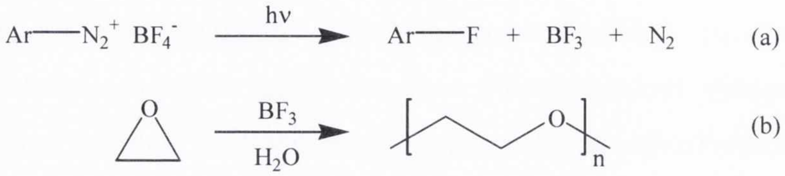
Table 1.10: Anatomy of Onium Salt Cationic Photoinitiator [185]

$$\left[R \right]_n M^+ \quad X^-$$

where typically; R = Ar, Alkyl
$M^+ = I^+, S^+, N^+, P^+$
$X^- = BF_4^-, AsF_4^-, PF_6^-, SbF_6^-$

Cation	Anion
Determines Photochemistry	Determines Polymer Chemistry
λ_{max}	Acid Strength
Molar Absorption Co-efficient	Nucleophilicity (Ion Pairing)
Quantum Yield	Anion Stability
Photosensitisation	Initiation Efficiency
Thermal Stability	Propagation Rate Constants

- *Aryldiazonium Salts:* Azonium ions, the ions of nitrogen compounds, encompass a variety of ions besides the most frequently considered ammonium ions. Aryldiazonium photo initiators of non-nucleophilic anions were used in the earliest commercial photoinitiated cationic polymerisation coating systems, Scheme 1.12 [171,190-194]. This development made use of the known sensitivity of aryldiazonium salts as exemplified by their use in diazo blueprints [195]. However, the inherent thermal instability of these salts limited their use. Also the generation of nitrogen gas as a by-product of their photodecomposition led to bubble formation in all but the thinnest of polymer films. The limitations associated with aryldiazonium salts ultimately led to the development of diaryliodonium and triarylsulfonium salts as cationic photoinitiators [173,174].



... Scheme 1.12 [185]

- *Diaryliodonium Salts* and their bromonium and chloronium analogues are organic polyvalent halogen compounds [196]. The positively charged halogen atom is in the +3 oxidation state. Whilst all three types of halonium salts are useful cationic initiators the iodonium salts are preferred as they are easily prepared and have superior stability [197,198]. Iodonium compounds of non-nucleophilic anions are ionic salts, but those of simple halide anions are somewhat covalent in character [199]. Ledwith made a study of the conductivity of iodonium salts and found that there is greater dissociation when larger anions are used i.e. the PF_6^- anions are more highly dissociated than BF_4^- anions. Ledwith surmises that this variation in dissociation explains the greater efficiency of cationic polymerisations by salts with larger diameter anions [200]. In most diaryliodonium salt reactions the positively charged iodine atom is attacked by nucleophiles causing displacement of an aryl group. The positively charged iodine is also susceptible to reduction by conventional reductants [161]. The broader uses and applications of diaryliodonium salts have been the subject of a recent review [201].

Several groups have investigated the photolysis of diaryliodonioum salts and reported on the primary products of photodecomposition [202-204]. Crivello and Lam have performed mechanistic investigations of diaryliodonium salt photo decomposition and proposed the pathway depicted in Scheme 1.13 [205,206]:

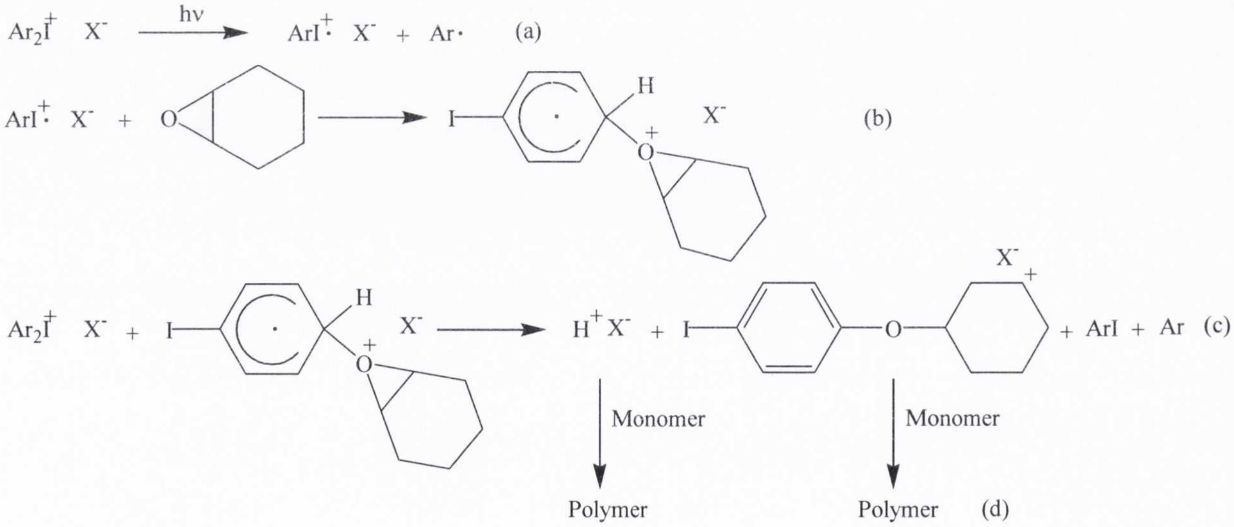
$$Ar_2\overset{+}{I}\!-\!X^- \xrightarrow{h\nu} \left[Ar_2\overset{+}{I}\!-\!X^-\right]^* \qquad (a)$$

$$\left[Ar_2\overset{+}{I}\!-\!X^-\right]^* \longrightarrow Ar\overset{+}{I}\cdot \; X^- + Ar\cdot \qquad (b)$$

... Scheme 1.13

Irradiation of the diaryliodonium salt induces homolytic cleavage of Ar–I bond yielding an aryliodinium radical cation and an aryl radical. Flash photolysis studies have provided direct evidence for this homolytic bond cleavage [184]. The resultant radical cations have been shown to react directly with nucleophiles such as cyclohexene oxide (CHO) and vinyl ethers, Scheme 1.8 [184,207,208]. This reaction Scheme is consistent with both flash photolysis and end group analysis studies which support direct cationic intiation of cyclohexene oxide by the radical cation species derived from the photolysed diaryliodonium salt. The main features of Scheme 1.14 are:

(a) Photolysis of the iodonium salt to yield an aryliodinium radical cation.
(b) Direct reaction of the aryliodinium radical cation with the epoxy monomer.
(c) A second diaryliodonium cation oxidises the adduct formed in (b).
(d) The resulting protonic acid and the activated epoxide can both promote cationic polymerisation of the monomer.



... Scheme 1.14

- *Triarylsulfonium Salts* and their oxonium, selenium and tellurium analogues have been prepared and characterised [161]. However only triarylsulfonium and triarylselenonium have been studied for photoinitiation of cationic polymerisation [209-211]. Of these triarylsulfonium salts have become widely used as they show excellent thermal stability, are efficient initiators and are readily prepared in high yield. Ledwith has shown that the ionic triarylsulfonium salts of hexafluorophosphate are even more highly dissociated than the corresponding diaryliodonium salts [200]. Irradiation of the triarylsulfonium salt induces homolytic cleavage of the Ar–S bond, similar to that seen for diaryliodonium salts, yielding a diarylsulfinium radical cation and an aryl radical, Scheme 1.15.

$$\mathrm{Ar_3\overset{+}{S}{-}X^-} \xrightarrow{h\nu} \left[\mathrm{Ar_3\overset{+}{S}{-}X^-}\right]^* \qquad \text{(a)}$$

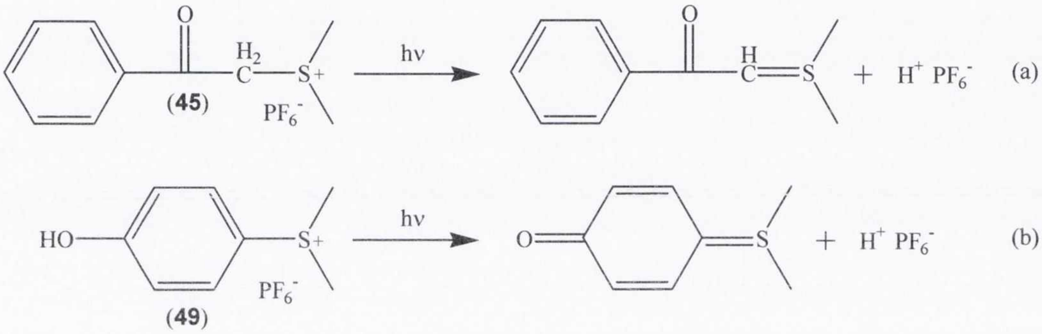
$$\left[\mathrm{Ar_3\overset{+}{S}{-}X^-}\right]^* \longrightarrow \mathrm{Ar_2\overset{+}{S}\cdot\ \ X^-} + \mathrm{Ar}\cdot \qquad \text{(b)}$$

... Scheme 1.15

Following removal of the initiation stimulus, i.e. heat or light, cationic ring-opening polymerisations are recognised as proceeding for prolonged periods in the absence of terminating impurities until ring-chain equilibria are established [212]. These "dark cure" reactions have been observed to proceed for long periods after irradiation has ceased in photo-polymerisations of THF, oxiranes, e-caprolactone and cyclic acetals employing iodonium and sulfonium cationic initiators having non-nucleophilic anions [213,214]. In these examples the long post cure effect has been attributed to slow termination processes [213,214].

The photodecomposition reactions of diaryliodonium and triarylsulfonium salts are generally considered to be irreversible reactions. The various modes of iodonium salt decomposition proposed for cationic polymerisation, are discussed further in Chapter Two of this work.

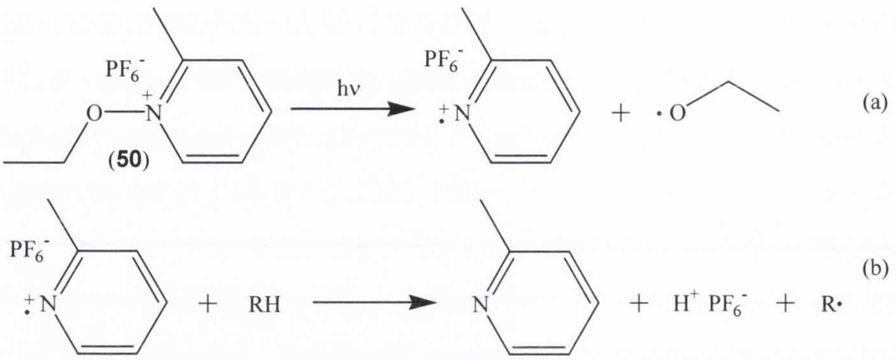
- *Dialkylphenacylsulfonium and Dialkyl-4-Hydroxyphenylsulfonium Salts* are another further type of onium salt photoinitiator used in cationic photopolymerisation. In the case of these initiators polymerisation terminates rapidly as soon as exposure to light is discontinued [215]. Both dialkylphenacylsulfonium & dialkyl-4-hydroxyphenylsulfonium may be considered as reversible photo-acid generators as it has been shown that their photodecomposition is reversible in the absence of cationically susceptible monomer, Scheme 1.16 [216].



… Scheme 1.16

In the case of dialkylphenacylsulfonium salts ylide ($R_2C=SR_2$) formation proceeds by intramolecular abstraction of H by the ketone from the α carbon [216]. In both systems cationically susceptible monomers are able to compete with the highly basic ylide species and undergo polymerisation however in the absence of monomer the protonic lifetime is greatly reduced [216].

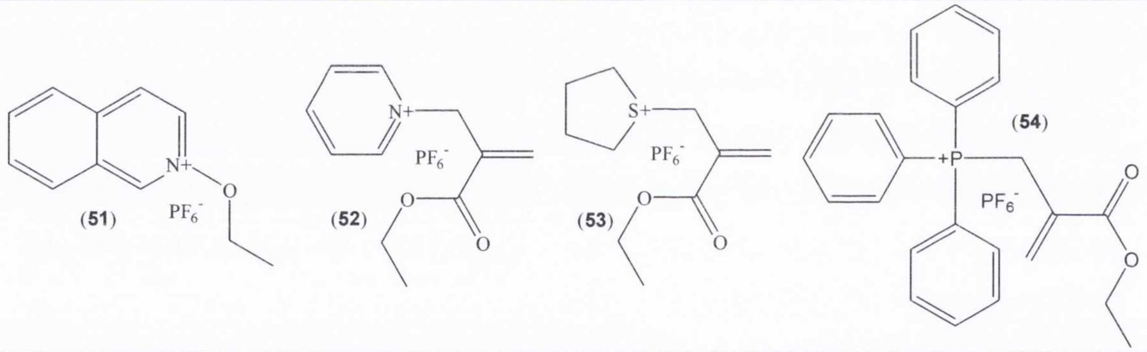
- *N-Alkoxy-Pyridinium Salts* have been reported as cationic initiators by Yagci and co-workers [188,217-220]. The mode by which these salts initiate cationic polymerisation is outlined in Scheme 1.17 [188]. Following photolysis the N–O bond of the initiator cleaves into a pyridinium radical cation and an alkoxy radical, Scheme 1.17(a). The radical cation has been found to have high reactivity with a range of cationically polymerisable monomers [221]. Along with the radical cation, Brønsted acid, formed by abstraction of protons from the monomer may also promote cationic polymerisation, Scheme 1.17(b).



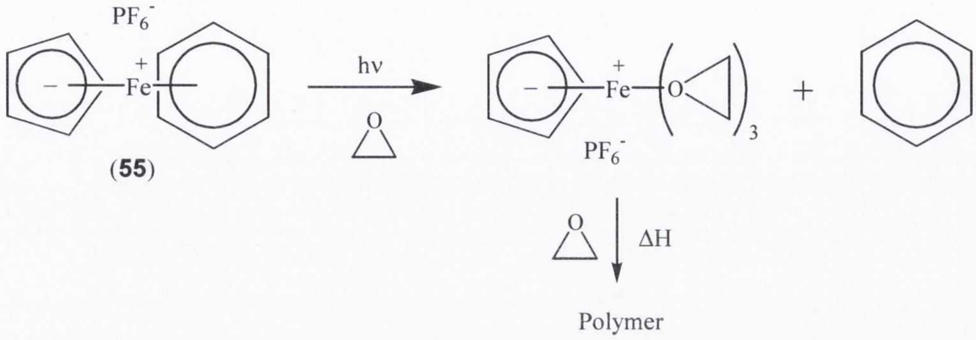
… Scheme 1.17

In addition to *N*-alkoxy-pyridinium salts several other salts in this general family of alkylonium salts have been described and studied as cationic photoinitiators including alkoxy-quinolinium (**51**) [188,222], allylic-pyridinium (**52**) [223], allylic-sulphonium (**53**) [224-226] and allylic-phosphonium (**54**) [227,228] salts, Table 1.11.

Table 1.11: Several Alkyl-onium Photo Acid Generators [222-228]

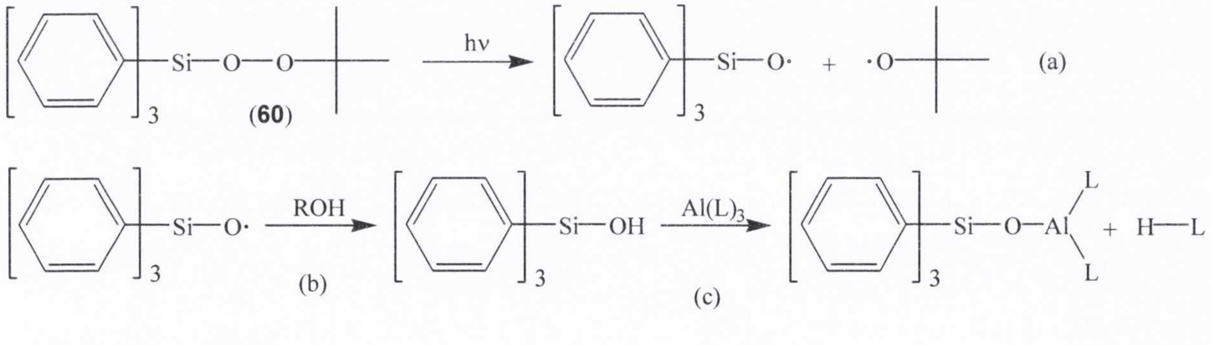


- *Organometallic Salts:* More recently organometallic salts have found use as photoinitiators for cationic polymerisation. One such group are the mixed ligand arene cyclopentadienyl metal salts of complex metal halide anions e.g. (η^6-benzene)(η^5-cyclopentadienyl)Fe^{II} hexafluorophosphate (**55**) [229]. The mechanism proposed for cationic photopolymerisation of oxirane monomers by (**55**) is depicted in Scheme 1.18 [28,230,231]. The photo-induced exchange of the benzene ligand for three oxirane groups was proposed in ligand exchange studies [232]. Cycloaliphatic epoxides, e.g. cyclohexene oxide, undergo spontaneous polymerisation at room temperature, while moderate heat is required for activation of less reactive glycidyl ethers. The presence of efficient oxidising agents, e.g. peroxide, which promote oxidation of Fe(II) to more reactive Fe(III) allow significant reduction of the thermal energy required to promote the reaction.



... Scheme 1.18

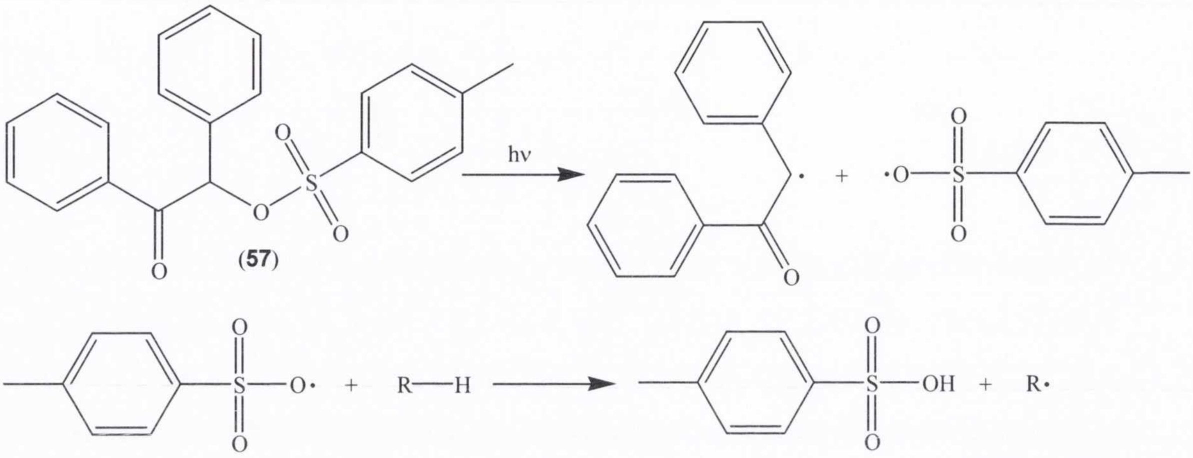
- *Latent Silanol–Aluminium Complex Catalysts* have been reported by Hayase *et al.* to function as efficient cationic photopolymerisation initiators [180,233-236]. The combination of silanol and aluminium(III) complexes of β-keto esters or β-diketones can be used to initiate the thermal polymerisation of cycloaliphatic epoxy monomers [233-235]. Triarylsilyl *tert*-butyl peroxides (**56**), which are reported to be thermally and shock stable, undergo photolytic homolysis of the O–O bond, Scheme 1.19(a). Silanol forms via hydrogen abstraction in the presence of the bulk monomer or added alcohol solvent, Scheme 1.19(b) [237,238]. A subsequent reaction between an aluminium(III) complex , e.g. $Al(acac)_3$ and the photogenerated silanol yields the cationic initiating Brønsted acid species, Scheme 1.19(c).



Where; ROH = Alcohol
L = Ligand

... Scheme 1.19

- *Latent Sulphonic Acids:* Sulphonic acids are nucleophilic acids that are poor cationic polymerisation initiators. However they have found use as catalysts for polymerisation of aminoplast resin coatings [159]. α-Sulphonyloxy ketones (**57**) in particular readily produce sulphonic acid following irradiation, Scheme 1.20 [239].



(**57**)

… Scheme 1.20

1.3.2.2 Indirect Photolysis

Unless incident photo-energy is absorbed photochemical processes cannot occur [159]. Some high-energy light sources provide emissions at 313 and 366 nm. However if lower energy visible light is to be used for photopolymerisation, light absorption at wavelengths greater than 400 nm is desirable. Indirect photolysis of cationic initiators is used to extend the spectral sensitivity of photoinitiators and onium salt initiators in particular. Several routes, all of which involve electron transfer reactions, have been developed to achieve indirect cationic photolysis:

➢ **Photoexcited Sensitizers for Cationic Polymerisation**

- *Classical energy transfer* involves electronic excitation of a sensitizer to its excited state. Energy is transferred either by resonance excitation or energy transfer from the excited sensitizer (S*) the onium salt initiator (I) and may proceed in the excited singlet or triplet state, Scheme 1.21.

$$S \xrightarrow{h\nu} S^*$$

$$S^* + I \longrightarrow S + I^* \qquad \text{… Scheme 1.21}$$

As a consequence of the transfer process the sensitizer returns to its original ground state (S) and the excited onium species (I*) is formed. This mechanism of onium salt decomposition may differ from that observed for the direct photolysis process, in which the initiator is primarily excited to the singlet state, this inference is based on analyses of the decomposition products [240-242]. Successful energy transfer requires the excitation energy of the sensitizer E*(S) to be at least as large as that of the onium salt initiator E*(I). Commonly used photo-sensitizers for onium salts are thioxanthone, acetophenone and naphthalene.

- *Electron Transfer by Exciplex:* In many instances sensitisation does not proceed by energy transfer as many onium salts effectively oxidize the sensitizer molecules following formation of an exciplex. The sensitisation of iodonium and sulfonium salts has by anthracene has been investigated in Yagci and co-workers [217,243,244]. The exciplex is formed between the excited state sensitizer and the ground state onium salt. In the complex one electron transfers from the sensitizer to the onium salt following homolytic cleavage of the corresponding onium species resulting in formation of a sensitizer radical cation [159]. It is the radical cation in conjunction with Bronsted acid formed by proton abstraction that initiate cationic polymerisation, Scheme 1.22.

$$\mathrm{PS} \xrightarrow{h\nu} \mathrm{PS^*} \xrightarrow{\mathrm{On^+X^-}} [\mathrm{PS^* \ldots\ldots On^+X^-}] \longrightarrow \mathrm{PS^{+\cdot}X^-} + \mathrm{On^{\cdot}}$$

$$\mathrm{PS^{+\cdot}X^-} + \mathrm{RH} \longrightarrow \mathrm{HPS^+X^-} + \mathrm{R^{\cdot}}$$

$$\mathrm{HPS^+X^-} \longrightarrow \mathrm{H^+X^-} + \mathrm{PS}$$

… Scheme 1.22

➢ Cationic Polymerisation Promoted by Photo-Generated Free Radicals

- *Oxidation of Radicals:* Several photo-generated radicals can reduce onium cations thereby forming cationic initiating carbocations, Scheme 1.23 [245,246].

$$[\mathrm{R}]_3\mathrm{C}\bullet + \mathrm{On^+} \longrightarrow [\mathrm{R}]_3\mathrm{C^+} + \mathrm{On}\bullet$$

… Scheme 1.23

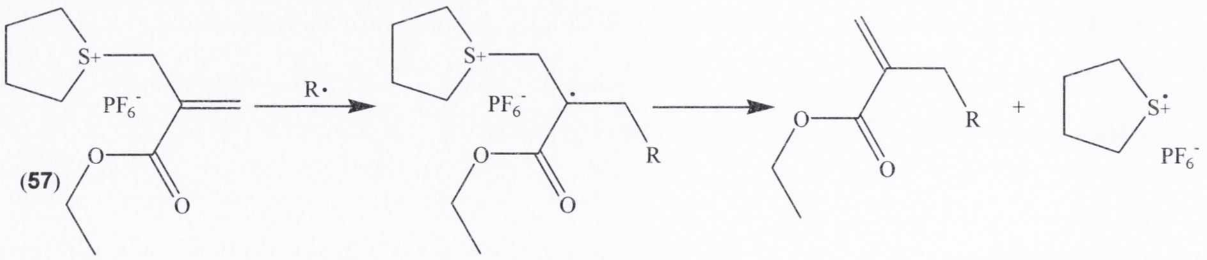
The electron affinity of onium salt cations determines their relative efficiency as oxidising agents. The higher the redox potential ($E_{½}^{red}$) the higher the relative oxidising power of onium cations e.g. aryldiazonium > diaryl iodonium > alkoxy pyridinium > triphenyl sulfonium [188,217,225,247-251]. Iodonium salts have been most frequently used as for the oxidation of photogenerated free radicals due to their relatively high redox potential [252-254]. In contrast the redox potential of trialrylsulphonium cations does not favour oxidation of the majority of radicals [255]. In theory the Rehm-Weller equation, Equation 1.0, can be used to estimate the ability of a particular onium cation to oxidise a radical species once the reduction and oxidation potentials of both species are known [257].

$$\Delta G = F\,[E_{½}^{ox}(R\cdot) - E_{½}^{red}(On^{+})] \qquad \text{...Equation 1.0}$$

where; F = Faraday Constant

However actual calculation of ΔG for *radical* processes is rarely practicable as the accurate oxidation potentials of most radicals $E_{½}^{ox}$ (R·) used in radical promoted polymerisation are not known [258].

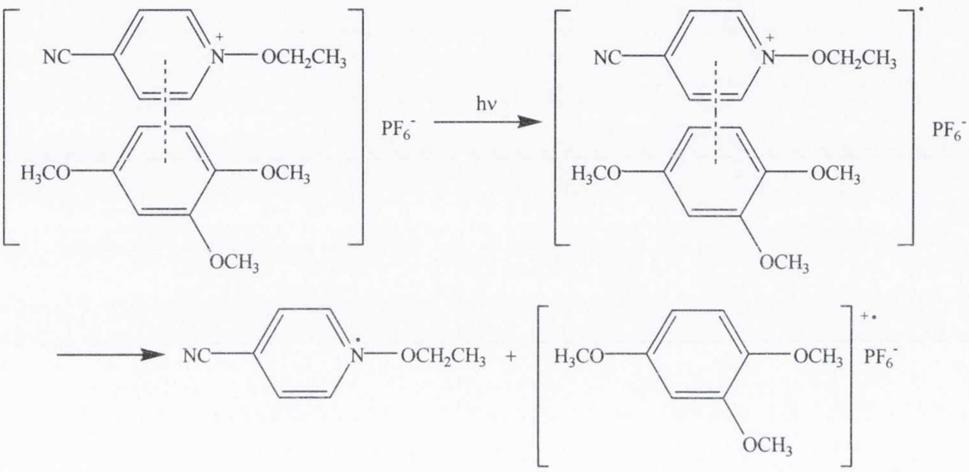
- *Addition fragmentation reactions* have been investigated extensively by Yagci and co-workers and have principally been applied to the allylic salts, Table 1.11 [222-227]. In theory addition fragmentation can be used with a wider range of radical species than the simple oxidation of radicals by onium cations already described. The mechanism of addition-fragmentation as applied to an allyic thiophenium salt is depicted in Scheme 1.24. Radicals add to the double bond of the allylic onium salt resulting in a radical forming β to the heteroatom of the onium cation. Subsequently the molecule fragments to yield the initiating radical cation [222-227].



... Scheme 1.24

- **Excited Charge Transfer Complexes for Cationic Photo-Polymerisation**

Charge transfer (CT) complexes formed between pyridinium salts and electron rich donors such as methyl- and methoxy- substituted benzenes have been reported to cationic photo initiators [259]. The absorption characteristics of these CT complexes are at relatively long wavelengths (420 nm) whereas the individual components have absorption maxima at much lower wavelengths (*c.* 265 nm). The charge transfer complex functions as an efficient latent photoinitiator for polymerisation of epoxide monomers by generation of an initiating radical cation species, Scheme 1.25 [259].



… Scheme 1.25

1.3.3 Thermal Initiation of Cationic Polymerisation

In general terms thermally initiated cationic polymerisation is of secondary interest to photoinitiated cationic polymerisation. Many of the same latent initiators and systems can be used for both thermal and photo cationic initiation. Such initiators as triarylsulfonium [260,261], diaryliodonium [262] salts have been investigated as latent thermal initiators for cationic polymerisation. Additionally thermally generated radicals have been shown to be oxidisable by onium salt cations and capable of addition fragmentation processes following mechanisms analogous to the equivalent indirect photolysis processes already described [245,246].

1.3.3.1 Frontal Cationic Polymerisation

Frontal polymerisation of epoxy resins by amines was described during the 1970's [263-265]. More recently several examples of photo [266] and thermally triggered cationic frontal polymerisation have been described in the literature. As with radical frontal polymerisation, propagation of the polymer front is always by auto-generation of thermal energy. Several patents and publications describe the chemistry and applications of cationic frontal polymerisations [267,268], including recent investigations from Crivello and co-workers on the cationic frontal polymerisation of oxetane monomers [269-273].

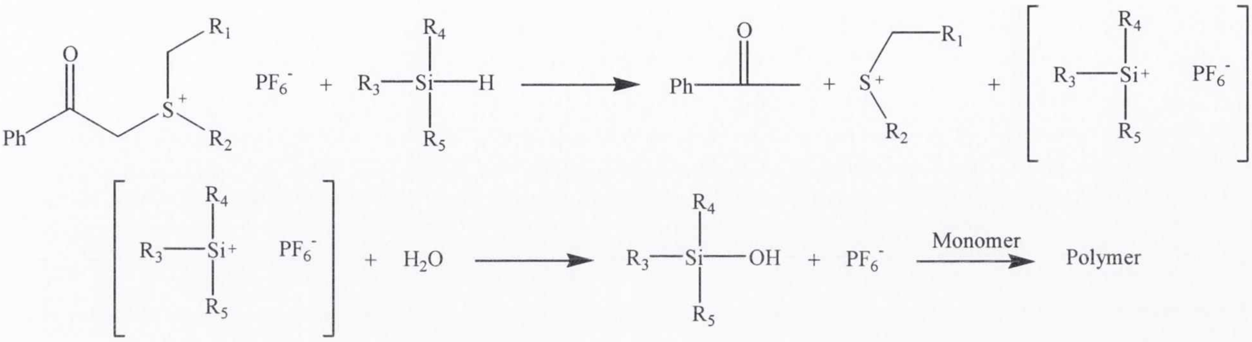
1.3.3.2 Living Cationic Polymerisation (LCP)

First reported in 1984 [274-277], living polymerisation is a form of addition polymerisation in which the growing the carbocation centre is stabilised by a nucleophilic counterion that originates from an initiator and catalyst species. Typically a Brønsted acid, e.g. hydrogen iodide, is employed as the initiator while a Lewis acid, e.g. zinc iodide, is employed as the catalyst [278-280]. Kwon and co-workers have demonstrated photoinduced living cationic polymerisation using a range of diphenyliodonium (Ph_2I) salts of nucleophilic anions in the presense of zinc halides [281,282].

1.3.4 Redox Cationic Polymerisation

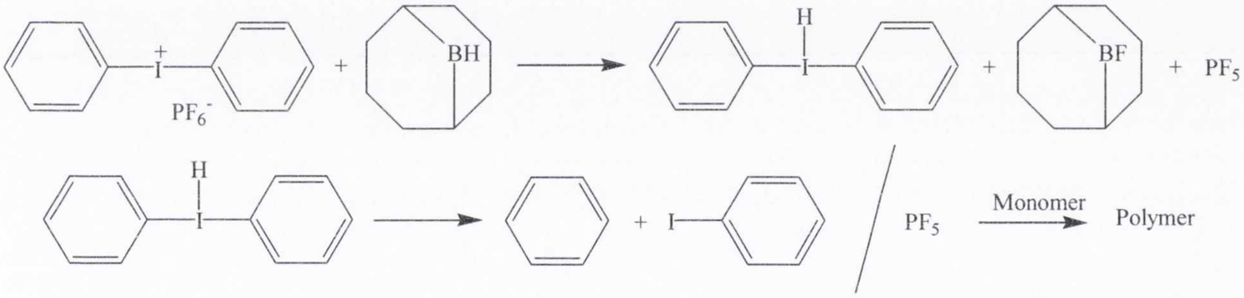
Such sources of energy as electricity, heat and light can all perform the function of reductants in chemical reactions [283]. Crivello has for example demonstrated electro-initiated cationic polymerisation in the presence of sulfonium and iodonium salts [284]. However the subject of redox cationic polymerisation achieved through the use of chemical reducing agents is a relatively little studied aspect of cationic polymerisation. Certainly it has not been developed or used to the extent of its redox radical counterpart. The first reports of redox cationic polymerisation came from Crivello and co-workers in 1981 and involved the transition metal catalysed decomposition of iodonium salts, using ascorbic acid as an efficient chemical reducing agent, to invoke cationic polymerisations at room temperature [285]. Transition metal catalysed redox cationic polymerisation is reviewed in more detail in chapter two of this work.

Recently Crivello has published some alternative redox cationic polymerisation systems. One system is based upon the silane promoted redox cationic polymerisations using sulfonium salts [255]. The proposed mechanism for the dialkylphenacylsulphonium salt : silane redox couple is presented in Scheme 1.26 [255].



… Scheme 1.26

An alternative system employs the direct reduction of iodonium salts by 9-borabicyclo[3.3.1]nonane, see Scheme 1.27 [256].



… Scheme 1.35

1.4 Benefits & Limitations of Radical & Cationic Polymerisation

Several advantages are commonly reported for cationic polymerisation over radical polymerisation processes although both processes have distinct advantages and disadvantages depending on the application areas where they are to be used:

i. Cationic polymerisation processes are not inhibited by oxygen [26,27,286]. Oxygen does not quench the excited state of the photoinitiator nor does it interfere with the initiating or propagating cations [161]. Most free-radical polymerisations on the other hand can be severely inhibited by oxygen, especially when curing thin films.

ii. The cationic polymerisation mechanism allows the continued polymerisation of any residual uncured monomers via a process referred to as "dark cure" [161]. The initiating species, a Brønsted or Lewis acid, is typically a chemically stable entity, which, unless neutralised by a basic species, has an unlimited lifetime unlike free radicals that typically have short lifetimes. In photo and thermal free-radical systems polymerisation ceases once the activation energy is removed.

iii. However, thermal post-curing of cationically polymerised systems is often required in addition to photo-activation in order attain full cure of all but the most reactive monomers. Free radical initiation systems rarely need a thermal post-cure to achieve full conversion.

iv. Cationic polymerisations may be inhibited by and can be very sensitive to the presence of protic agents and basic or nucleophilic contaminants [287]. Water and other hydroxyl compounds depending on their concentration and the type of monomer used can act as inhibitors or chain transfer agents for cationic polymerisations [161]. Radical polymerisations once activated are rarely affected by surface inhibition.

v. Cationically cured polymers may contain residual acid. Free-radically cured polymers may contain trapped radical species.

1.5 Aim of this Research

As outlined in the introduction, surface curing adhesives bring great benefits to manufacturing and repair applications. Currently adhesive technologies that function on the basis of surface induced polymerisation are *exclusively* limited to radical (anaerobic acrylate) and anionic (cyanoacrylate) polymerisation processes. To date it has not been possible to induce the polymerisation of epoxy monomers at room temperature from a stable one-component system without using an additional source of energy as a stimulus. This therefore remains a gap in adhesion technology and more widely in polymer chemistry.

There is precedent in the literature for redox curable epoxies. It would seem however that the existing redox cationic systems have never been developed into a commercial technology. Perhaps this is due to their inherent instability, particularly for more reactive systems, and a need for significant levels of catalysts to promote initiation of polymerisation. The high levels of catalysts required for these existing redox cationic polymerisations means that they are essentially three component systems based upon an oxidising agent, a reducing agent and a catalyst. The huge benefit of redox chemistry however is that it does allow activation of polymerisation with low or no input of externally applied energy i.e. heat or light. ***The possibility of developing cationic polymerisation systems that are stable but which can be activated on command by the substrate itself is a very important goal.***

In the light of this background information, ***the aim of this research is to achieve that goal*** **and point a direction to development of a new class of surface curable adhesive systems and related technologies on the basis of a thorough understanding of academic precedent.**

1.6 Thesis Structure (Approach)

Chapter Two: Fundamental Study of Copper Catalysed Redox Cationic Polymerisation

Chapter Three: Surface Promoted Redox Polymerisation: An Approach to Achieving Ambient Temperature Polymerisation of Epoxy Monomers

- Stoichiometric Reduction of Metal Salts of Non-nucleophilic Anions by Chemical Reducing Agents (*Calorimetric Experiment*)

- Surface Promoted Redox Cationic Polymerisation Employing Silver(I) Salts as Latent Cationic Initiators (*FTIR-ATR*)

- Use of Alternative Latent Cationic Initiators for Achieveing Surface Promoted Redox Cationic Polymerisation is also Investigated

Chapter Four: Experimental & Synthetic Procedures

Chapter Five: Summary of Achievement and Possibilities for Further Study

CHAPTER TWO | FUNDAMENTAL STUDY OF COPPER CATALYSED REDOX CATIONIC POLYMERISATION

2.1 Extrapolation of Photocationic Polymerisation into Redox Catalysed Cationic Polymerisation

Polymerisation of epoxide groups can be achieved through the use of Lewis and Brønsted acids, which are in many cases generated photochemically. Polymerisations catalysed by this type of initiator are typically termed cationic polymerisations. The photochemical polymerisation of cationically polymerisable monomers, including epoxide rings has long been achieved through the use of onium salts [260,294-299]. Diaryliodonium salts of non-nucleophilic anions in particular, first reported by Crivello and Lam, have been studied extensively as catalysts for cationic polymerisation, Figure 2.0 [161,300-302].

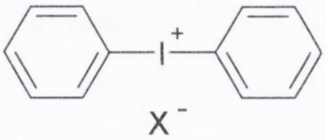


Figure 2.0: Generic structure for a diaryliodonium salt cationic initiator

Having performed a mechanistic study of the photochemical decomposition of iodonium salt cationic photoinitiators Crivello *et al.* proposed that the irradiation of Ph_2I salt with light of appropriate wavelength liberates a radical cation intermediate and a subsequent series of reactions results in reduction of the iodonium centre, Scheme 2.0 [285]. The phenyliodonium cation radical generated during the photolysis process is an extremely reactive species and reacts with solvents, monomers, or impurities (denoted S-H in the reaction Scheme) to generate a Brønsted super acid species, which is a very efficient cationic initiator. The photodecomposition process of diaryliodonium salts is presented in greater detail in section 2.1.1.

$$\begin{array}{lclll}
Ar_2I^+X^- & \xrightarrow{h\nu} & [Ar_2I^+X^-]^* & \text{(a)} & \\
[Ar_2IX^-]^* & \rightarrow & Ar\text{–}I^{+\bullet} + Ar\bullet + X^- & \text{(b)} & \\
Ar\text{–}I^{+\bullet} + S\text{-}H & \rightarrow & Ar\text{–}I^+\text{-}H + S\bullet & \text{(c)} & \\
ArI^+\text{-}H & \rightarrow & Ar\text{–}I + H^+ & \text{(d)} & \\
H^+ + X^- & \rightarrow & HX & \text{(e)} & \text{… Scheme 2.0}
\end{array}$$

The protonic acid in turn reacts with the cationically curable monomer resulting in polymerisation. Studies have shown that such reactions work best when X^- is a non-nucleophilic, or weakly coordinating, counteranion *e.g.* BF_4^-, PF_6^- and SbF_6^- [303,304]. Nucleophilic counterions such as Cl^- result in quenching of the polymerisation reaction and are considered undesirable.

In view of this understanding Crivello investigated the possibility of using diaryliodonium salts as initiators of cationic polymerisation by means of redox-type chemistry [305,306]. The iodonium salt could act as the oxidising component in a redox couple employing a sufficiently strong reductant [149,307]. Therefore instead of direct photochemical reduction a chemical reducing agent could be used to achieve the same goal of diaryliodonium salt reduction in order to generate the protonic acid HX, which is a key initiator of cationic polymerisation, Scheme 2.1.

$$AH_2 + 2\ Ar_2I^+X^- \rightarrow DA + 2ArI + 2\ Ar\bullet + 2\ HX \qquad \text{… Scheme 2.1}$$

Using this theory Crivello and Lam demonstrated a series of three diaryliodonium salt / reducing agent redox couples incorporating ascorbic acid [285], benzoin [308], and tin(II) ethylhexanoate [309]. It was found that the direct reduction of the iodonium salt by the reducing agent was extremely inefficient. Consequently, an inherent feature of these diaryliodonium salt / reducing agent redox couples developed by Crivello *et al.* is the need to incorporate a copper catalyst in order to achieve efficient polymerisation, Scheme 2.2. (These developments in non-photochemical ambient temperature redox cationic polymerisation are particularly relevant to the aims of the current work.)

$AH_2 + 2\ CuY_2 \rightarrow DA + 2\ CuY + 2\ HY$ (a)

$Ar_2I^+X^- + CuY \rightarrow CuXY + ArI + Ar\cdot$ (b)

$AH_2 + 2\ CuXY \rightarrow DA + 2\ CuY + 2HX$ (c)

$nM + HX \rightarrow H(M)_{n-1}M^+X^-$ (d) … Scheme 2.2

Copper salts in particular have been widely used as catalysts to accelerate the decomposition of such oxidising agents as peroxides in the presence of a strong antioxidant [310-313]. Lockhart *et al.* have also described the copper-catalysed reactions of iodonium salts [314] and the use of Cu(II)/Aryliodonium combinations as a latent thermal cationic initiation system [315]. (This is described in more depth later, page 48, section 2.1.2). Such copper catalysed redox cationic initiation packages are effectively three component systems i.e. necessitating the onium salt initiator, the reducing agent and also the catalyst, Figure 2.1. Note the similarity between this redox cationic polymerisation process and a typical anaerobic redox process for radical polymerisation as shown in Figure 1.0.

In addition to the original Crivello-type redox cationic initiation systems Yagci and co-workers have also demonstrated a number of cationic redox couples. These alternative systems were based upon a series of allylic sulfonium [316] and alkoxy pyridinium [249] cationic initiators, which were used in place of the iodonium salt oxidising agent of Crivello. These alternative systems, while clearly demonstrating the applicability of redox cationic polymerisations using initiators based upon alternative heteroatom centres where found not to be as efficient as those based upon the iodonium systems previously demonstrated. The lower efficiency is explained by the lower relative oxidation potential of iodonium salts when compared with the oxidation potentials of other heteroatom onium salt species; see Table 2.0 [249,316,317].

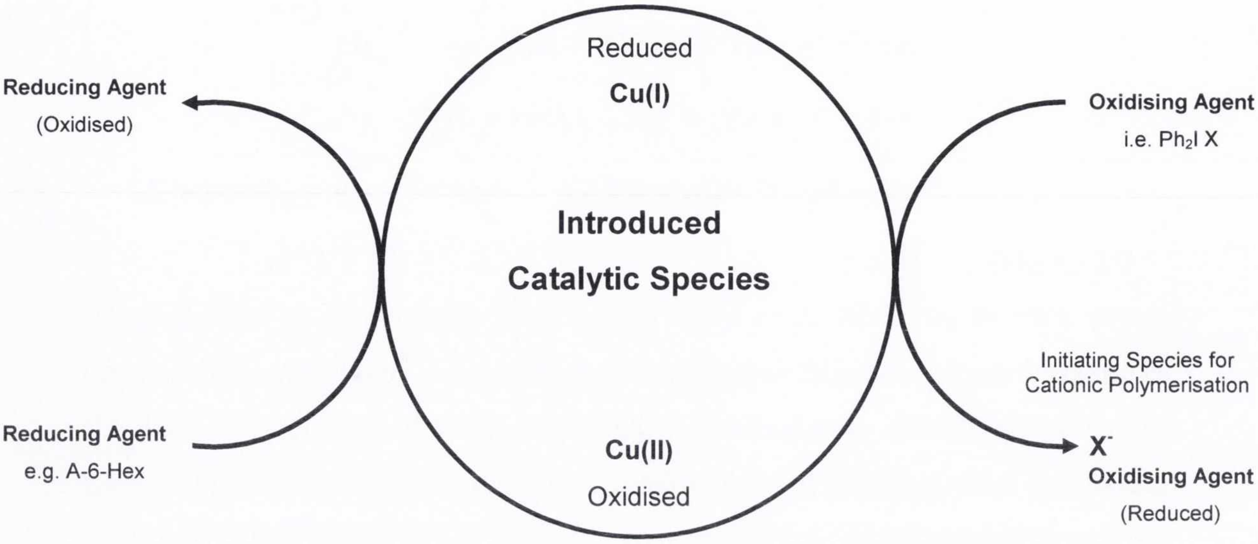
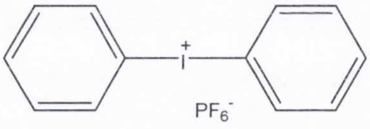
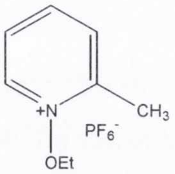
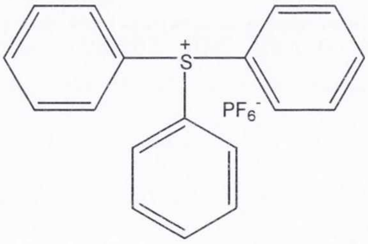


Figure 2.1: Typical "Crivello-type" Copper(II) catalysed cationic redox cycle

Table 2.0: Onium Salt Cation Reduction Potentials ($E_{1/2}$) & the Associated Cu(II) Catalysed Conversion[a] (%) of Cyclohexene Oxide for Each of these Salts [248,249].

		$E_{1/2}^{red}$, SCE[*] (*V*)	**Conversion (%)[a]**
43	 PF$_6^-$	-0.2	33
50		-0.7	17
44		-1.06	6.6

[*] Saturated Calomel Electrode

[a] Salt 2.43 x 10^{-2} mol l^{-1}, A-6-Hex 7.48 x 10^{-2} mol l^{-1}, Cu(II) benzoate 6.1 x 10^{-3} mol l^{-1}, CHO 9.88 mol l^{-1}, temperature 25 °C, time 40 min.

Recently Crivello also described a series of new cationic redox couples catalysed by noble metal complexes and employing a range of onium salts as the oxidising agents with an organosilane having a Si-H group as the reducing agent [255,318,319]. Crivello and Mowers have also shown, through measurement of relative reduction $E_{1/2}$ potentials, that the greater the diameter of the anion associated with the cationic initiator species the more readily reduced the cation will be [320], Table 2.1. Ren *et al.* have extended this Table with a series of even larger anions that increase the propensity of the cationic initiator for reduction even further, Table 2.2 [321].

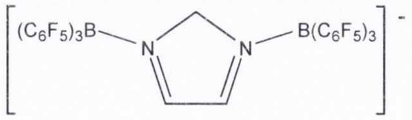
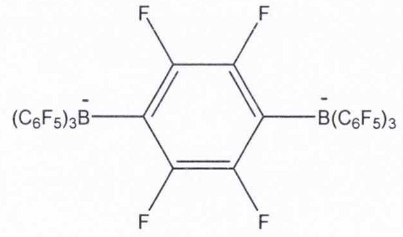
Table 2.1: $E_{1/2}$ potentials of various diphenyliodonium salts (**43**) in 1,2-Dichloroethane [320]

Anion	$E_{1/2}$ (V) [a)]	$\Delta E_{1/2}$ (V) [b)]
ClO_4^-	1.24	0.30
BF_4^-	1.27	0.35
PF_6^-	1.44	0.80
AsF_6^-	1.56	0.70
SbF_6^-	1.60	0.70

[a)] Measured potential at ½ the peak current.

[b)] Change in $E_{1/2}$ potential from the initial CV scan to the sixth scan.

Table 2.2: Impact of various anions on diphenyliodonium salt (**43**) reactivity [321]

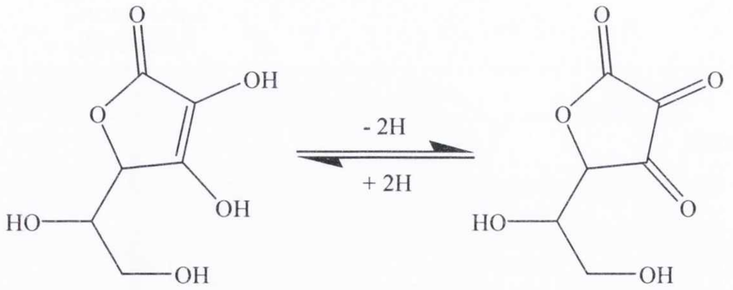
	Anion	Decreasing Reactivity	Ref.
Imidazolide		↓	[322]
Dianion			[323-328]
Carborane	$CB_{11}H_6Br_6^-$		[329-333]
Borate	$B(C_6F_5)_4^-$		[334]
Gallate	$Ga(C_6F_5)_4^-$		[335-337]
Antimonate	SbF_6^-		[304]
Chloride	Cl^-		[57]

2.2 Overview of Various Modes of Iodonium Salt Decomposition Proposed for Cationic Polymerisations with Emphasis on Redox Processes

The chemistry of iodonium salts has been the subject of much research due to their use in organic synthesis [338-340], as cationic initiators [300-302] and for mechanistic reasons [241,285,294,314,341-344]. Iodonium salt chemistry is complicated by the presence of closely balanced yet competing ionic and radical processes [345-347]. Consequently several mechanisms have been proposed for the cationic polymerisation of epoxy monomers promoted by onium salts and iodonium salts in particular.

2.2.1 Copper-Catalysed Reactions of Diphenyliodonium Salts: Crivello-Type Redox Cationic Polymerisation

During the course of the photochemical reaction iodine is photo-reduced from an oxidation state of +3 to +1. This inferred that it might be possible to achieve this reduction by chemical rather than photochemical means [285]. Such a chemical reducing agent must be non-basic as this would inhibit cationic polymerisation and equally it must not be highly acidic as this could promote direct cationic polymerisation. Based on these constraints Crivello chose ascorbic acid (**59**), known to be a strong reducing agent, as an ideal candidate reducing agent, Figure 2.2.



AH$_2$ **DA**

Figure 2.2: Oxidation of ascorbic acid (AH$_2$) to dehydroascorbic acid (DA)

As outlined in the introduction, an inherent feature of diaryliodonium salt : reducing agent redox couples as developed by Crivello *et al.* is the need to incorporate a copper catalyst in order to achieve an efficient polymerisation. Crivello proposed the mechanism presented earlier in Scheme 2.2 to explain the process of copper catalysed redox cationic polymerisation employing the iodonium : ascorbic acid redox couple. The basis of this mechanism is the preliminary reduction of copper(II) by the reducing agent, in this case ascorbic acid (AH_2), to give copper(I), dehydroascorbic acid (DA) and the weak acid HY, see Scheme 2.2 (a). This reaction was demonstrated in aqueous solution yielding an isolable copper(I) ascorbate complex [352]. The copper(I) compound was shown to be an efficient reducing agent for diaryliodonium salts, Scheme 2.2 (b), yielding the mixed copper(II) salt, CuXY, aryl iodide and an aryl radical. The mixed copper(II) salt is then understood to be further reduced by ascorbic acid to generate the strong Brønsted acid, HX, Scheme 2.2 (c). Attack by this strong Brønsted acid on the monomer initiates cationic polymerisation, Scheme 2.2 (d), in a process equivalent to that described for the photochemical reaction, Scheme 2.0. In Scheme 2.2 the copper species functions as an electron carrier for the reduction of the iodonium salt by the ascorbate. There the copper salt is continuously cycled between lower and higher oxidation states and as such it serves as a catalyst for the reaction. Thus the overall reaction can be represented as shown in Scheme 2.3.

$$AH_2 + 2Ar_2I^+X^- \xrightarrow{\text{Cu(I) or Cu(II)}} DA + 2ArI + 2Ar\cdot + 2HX \quad \text{... Scheme 2.3}$$

2.2.2 Copper-Catalysed Reactions of Diphenyliodonium Salts: A Mechanistic Investigation

Lockhart has undertaken a mechanistic investigation of the copper-benzoate catalysed reactions of Ph_2I salts [314]. Some general features of the mechanism by which copper salts catalyse the reactions of iodonium salts have been described previously [353-355]. Lockhart firmly established Cu(I) as the key species responsible for copper reaction with iodonium salt species. First proposed was that the similarity of the iodonium salt reaction with other organic copper catalysed reactions could explain the mechanism of the reaction. The Sandmeyer reaction in particular has been proposed to account for the reaction of diazonium salts with copper halides, see Scheme 2.4(A) [356]. Electron transfer from Cu(I), which has been generated in the reaction medium, to the diazonium cation generates an aryl radical which abstracts an anion from Cu(II) yielding the aryl halide. If water is used as the reaction medium the aryl halide cannot form [357], Scheme 2.4(B), and the aryl radical is oxidised by Cu(II) followed by nucleophilic attack on water giving

ArOH and Cu(I). Lockhart proposed that an aryl copper complex, ArCu(III), may be an intermediate of aryl radical oxidation due to charge balancing considerations and as similar complexes are known to form as intermediates in other reactions [358-361]. There are several features that suggest similarity between copper catalysed diazonium and iodonium, Scheme 2.5, reaction systems and which advocate such a comparison:

i. The reduction potentials of both organic salts are similar [247,362].

ii. Cu(I) is the active species in both reactions.

iii. Similar reactivity for reactions performed in nucleophilic solvents in the absence of halide.

iv. Formation of benzene in iodonium salt reactions indicates consistency with the presence of phenyl radicals on the reaction pathway.

Mechanism for the Copper Catalysed Diazonium Salt Reaction:

$$\mathrm{ArN_2^+X^-} + \mathrm{Cu(I)X} \xrightarrow{\text{electron transfer}} \mathrm{ArN_2CuX_2}$$

$$\mathrm{ArN_2CuX_2} \rightarrow \mathrm{Ar\cdot} + \mathrm{N_2} + \mathrm{Cu(II)X_2}$$

$$\mathrm{Ar\cdot} + \mathrm{Cu(II)X_2} \rightarrow \mathrm{ArX} + \mathrm{Cu(I)X} \qquad \text{(A)}$$

$$\mathrm{ArN_2^+} + \mathrm{Cu(I)} \xrightarrow{\text{electron transfer}} \mathrm{Ar\cdot} + \mathrm{N_2} + \mathrm{Cu(II)}$$

$$\mathrm{Ar\cdot} + \mathrm{Cu(II)} \xrightarrow{\mathrm{H_2O}} \mathrm{ArOH} + \mathrm{Cu(I)} + \mathrm{H^+} \qquad \text{(B)}$$

... Scheme 2.4

Proposed Mechanism, Modelled on the Diazonium Salt System, for the Copper Catalysed Reaction of Iodonium Salt:

$$\mathrm{CuY_2} \rightarrow \mathrm{Cu(I)Y}$$

$$\mathrm{Ar_2I^+X^-} + \mathrm{Cu(I)Y} \rightarrow \mathrm{Ar\cdot} + \mathrm{Cu(II)XY} + \mathrm{ArI}$$

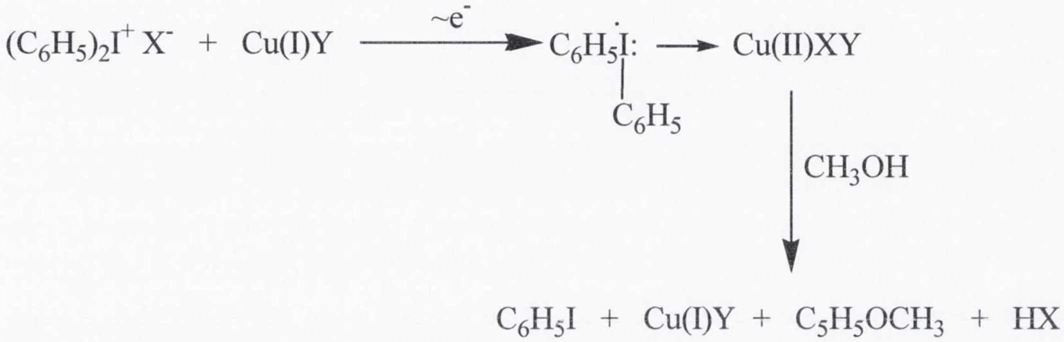
$$\mathrm{Ar\cdot} + \mathrm{Cu(II)XY} \rightarrow \mathrm{ArCu(III)XY}$$

$$\mathrm{ArCu(III)XY} + \mathrm{CH_3OH} \rightarrow \mathrm{Cu(I)Y} + \mathrm{HX} + \mathrm{ArOCH_3}$$

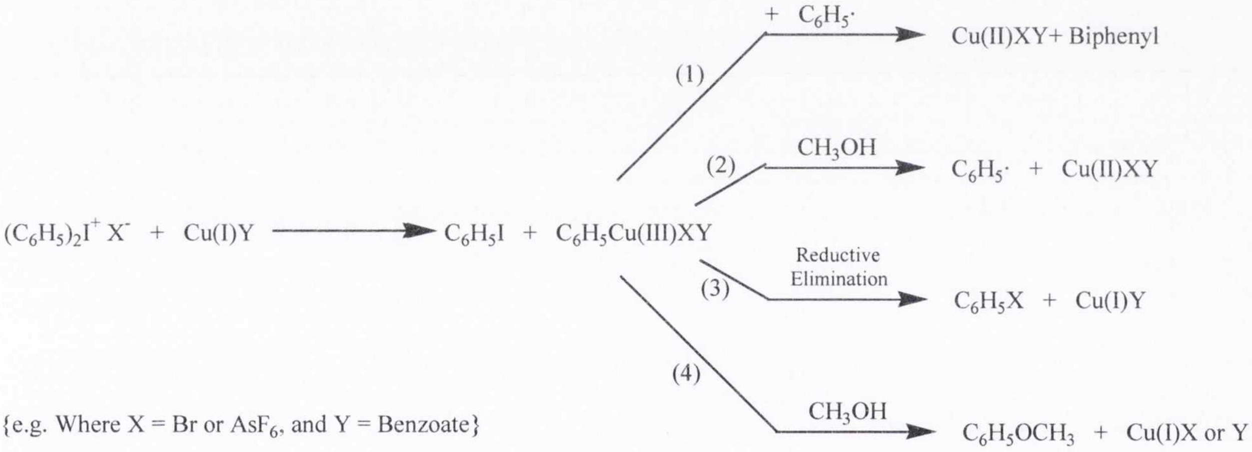
$$\mathrm{Ar\cdot} + \mathrm{CH_3OH} \rightarrow \mathrm{Ar} + \mathrm{\cdot CH_2OH}$$

... Scheme 2.5

Such a mechanism as that proposed does not however take into account the reaction products observed through experiment in polar solvents e.g. methanol. Therefore Lockhart made several additional mechanistic proposals to account for these variations, Scheme 2.6 and 2.7. Of the postulated mechanisms none fit the copper-catalysed reactions of Ph_2I salts emphatically [314].



... Scheme 2.6



... Scheme 2.7

In addition to the work by Crivello *et al.* outlined above, Ledwith proposed an alternative radical-chain mechanism for the decomposition of iodonium salt [252-254]. This alternative mechanism is introduced in more detail in Chapter Three.

It is pertinent to mention in passing that the redox potential of the diazonium cation is higher than that of the iodonium cation (page 102) and therefore potentially more readily activated in latent redox cationic initiating systems. This point will be revisited later.

2.3 Aims of Chapter

With reference to academic precedent it is important to recognise any shortcomings of existing redox catalysed cationic polymerisation with a view to identifying areas for improvement through theory, by design and then experimentation. With this in mind the aim of the work reported in this Chapter is to obtain an intimate understanding of "Crivello-type" redox epoxy cure systems. The ultimate objective being to evaluate this redox cationic cure chemistry for the development of an epoxy analogue of exisiting redox radical anaerobic acrylates. The objectives of this assessment are:

1. To judiciously select a redox catalyst according to some essential criteria, such as: i) a high degree of activity, ii) ready solubility in the preferred monomer and iii) demonstrate a high degree of reproducibility between experiments.
2. To identify a preferred ratio of components for a typical copper(II) catalysed acid generating redox couple as reported by Crivello for use in subsequent investigations.
3. To determine if atmospheric oxygen plays an important role in copper(II) catalysed redox cationic polymerisation.
4. To study the effect of residual water on copper(II) catalysed redox cationic polymerisation.
5. To investigate the influence of a series of Ph_2I salts with anions of increasing non-nucleophilic character on copper(II) catalysed redox cationic polymerisation, see Table 2.1 and 2.2.

6. With the learnings gained from 1 to 5 above further studies, including an in-depth consideration of specially designed oxidising and reducing agents, will aim to improve upon existing Crivello-type copper(II) catalysed redox cationic polymerisation.

For convenience the structures of all compounds used to study these phenomena are given in the following experimental section, see Tables 2.3 to 2.7.

2.4 Experimental

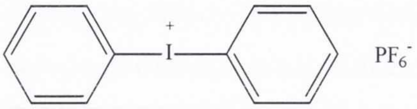
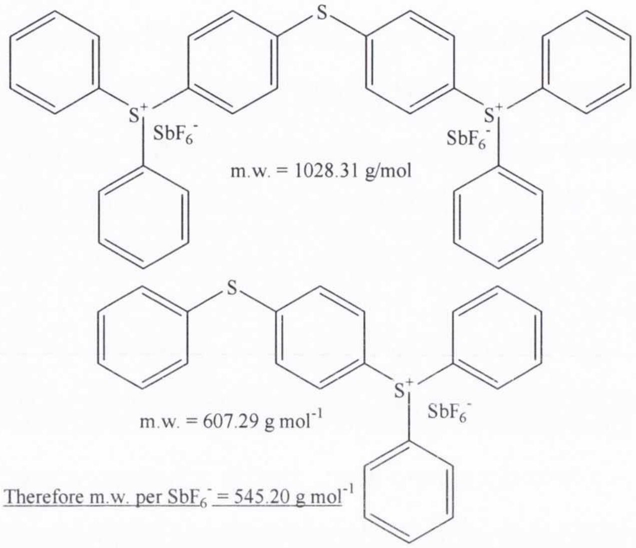
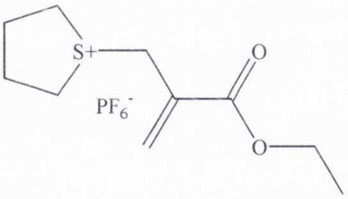
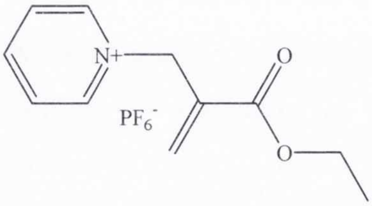
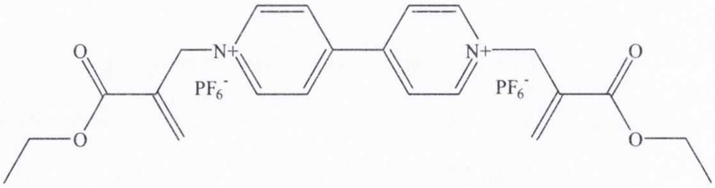
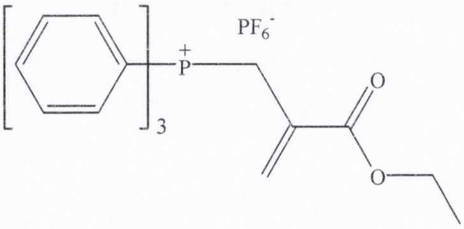
2.4.1 Materials

Cyclohexene oxide (**73**) is a readily polymerised monomeric solvent that is widely used for cationic polymerisation studies. However, while it is indicative of the effectiveness of an initiation system it is not truly representative of the applicability of such a system to the successful polymerisation of commercially useful monomers and resins. It was for this reason that the cycloaliphatic monomer 3,4-epoxy cyclohexyl methyl-3,4-epoxycyclohexane carboxylate (**72**), from Dow Chemical Company, was employed in this study. The cycloaliphatic epoxy siloxane monomer PC-1000 (**75**) was purchased from Polyset. Other monomers used were purchased from Sigma-Aldrich and used as received.

The onium salts Ph_2I PF_6 (**43**) and mixed triaryl sulfonium SbF_6 salts, UVI-6976 (**44**), the reducing agents L-ascorbyl-6-hexadecanoate (**64**), tin(II) ethylhexanoate (**66**), benzoin (**65**), acetyl-phenyl hydrazine (**43**) and α-tocopherol (**67**) were purchased from Sigma-Aldrich. The high boiling point solvent propylene carbonate (**90**), metal salts and drying agents were purchased from Sigma-Aldrich. (Tolylcumyl)iodonium tetrakis(pentafluorophenyl) borate (**58**) was purchased from Rhodia Silicones Europe.

Allylic salts and metal complexes employed as latent cationic intiators were prepared according to literature procedures. Where deviations to published preparative procedures exist details are given in Chapter Four of this thesis. Unless otherwise stated in the text all materials were used as received. The structures of all compounds used are presented in Tables 2.3 to 2.7.

Table 2.3: Structures of the cationic initiators used in this study

	Cationic Initiators (Oxidising Agents)*		
43		Diphenyliodonium PF$_6$ "Ph$_2$I PF$_6$" (426.08 g mol^{-1})	[285]
44		Mixed Salts of Triphenyl Sulphonium SbF$_6$, 50% in Propylene Carbonate (545.20 g mol^{-1})	[174]
53		Ethyl-α-(Tetrahydrothiophenium Methyl)Acrylate PF$_6$ "ETA" (346.27 g mol^{-1})	[225]
52		Ethyl-α-Pyridinium Acrylate PF$_6$ "ENA" (337.20 g mol^{-1})	[250]
60		Bis(Ethyl-α-Pyridinium Acrylate) PF$_6$ "BENA" (672.38 g mol^{-1})	
54		Ethyl-α-Triphenyl Phosphonium Acrylate PF$_6$ "EPA" (520.38 g mol^{-1})	[227]

* Nomenclature commonly used in the literature

Table 2.4: Structures of the metal-based cationic initiators used in this study

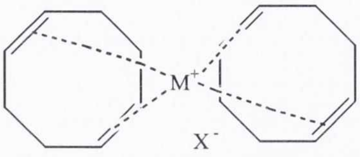
61		[Copper(1,5-Cyclooctadiene)$_2$] Tetrafluoroborate (366.71 g mol^{-1})	[375]
62		[Copper(1,5-Cyclooctadiene) $_2$] Perchlorate (376.36 g mol^{-1})	[375]
63	Where Where Where M = Cu(I) or Ag(I) Where Where Where X = BF_4^- or ClO_4^-	[Silver(1,5-Cyclooctadiene)$_2$] Tetrafluoroborate (411.03 g mol^{-1})	[375]

Table 2.5: Structures of the reducing agents used in this study

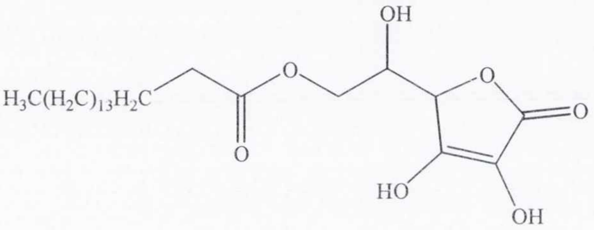
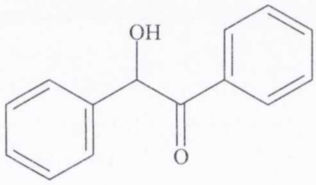
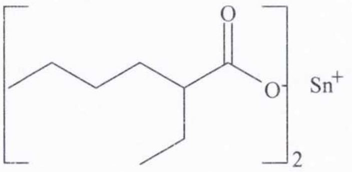
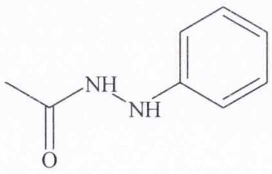
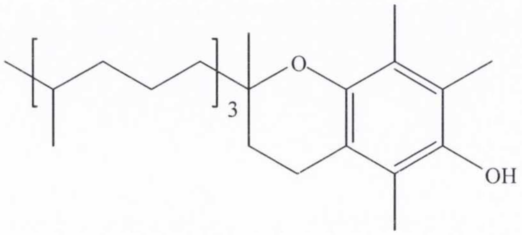
64		L-Ascorbic Acid 6-Hexadecanoate "A-6-Hex" (414.53 g mol^{-1})	[285]
65		Benzoin (212.24 g mol^{-1})	[305]
66		Tin(II) 2-Ethylhexanoate (405.12 g mol^{-1})	[309]
14		Acetylphenyl Hydrazine (150.18 g mol^{-1})	[377]
67		α-Tocopherol (430.71 g mol^{-1})	[378]

Table 2.6: Structures of some further reducing agents investigated in this study

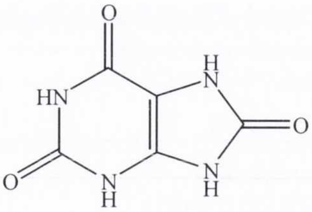
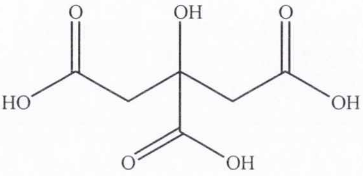
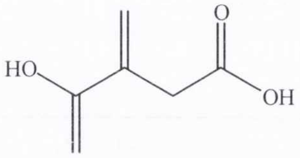
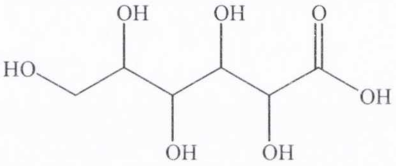
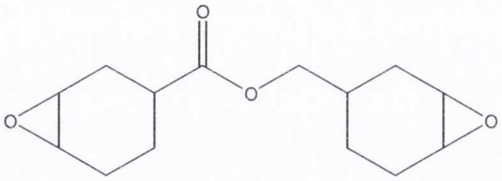
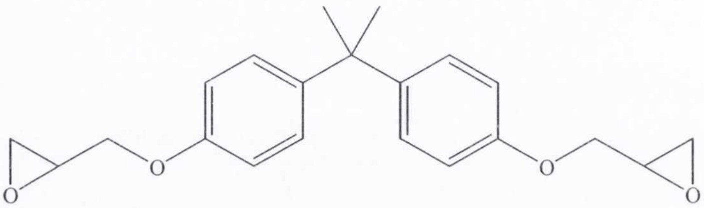
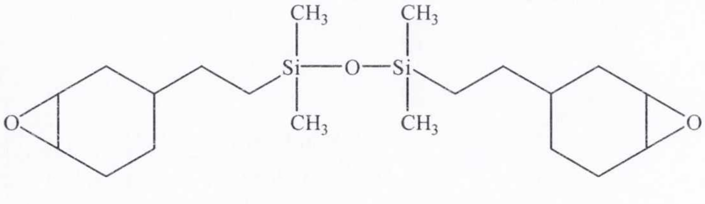
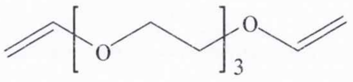
68		Uric Acid (168.11 g mol^{-1})	[379]
69		Citric Acid (192.12 g mol^{-1})	[283]
70		Itaconic Acid (130.10 g mol^{-1})	[380,381]
71		Gluconic Acid (178.14 g mol^{-1})	[382]

Table 2.7: Structures of the cationically polymerisable monomers used in this study

72		3,4-epoxycyclo-hexylmethyl-3,4-epoxycyclohexane carboxylate (252.31 g mol^{-1})
74		4,4'-Isopropylidenediphenol diglycidal ether (340.41 g mol^{-1})
75		1,3-Bis[2-(3,4-epoxycyclohexyl)ethyl]-1,1,3,3-tetramethyldisiloxane (382.68 g mol^{-1})
76		Triethylene glycol divinyl ether "DVE3" (202.25 g mol^{-1})

2.4.2 Calorimetry

The experiments in this Chapter were initially aimed at familiarisation with Crivello-type redox couples and quantification of their relative reactivity in commercially useful cationically curable resins. The relative reactivity of the various systems under study were quantified on the basis of the measured exotherm, the time taken for the system to reach its maximum exotherm and the conversion to polymer as calculated from the recorded exotherm. Typically a higher exotherm of polymerisation equates to a higher degree of conversion for the monomer system under study. Similarly, the more quickly the maximum exotherm of polymerisation is reached, the higher the relative efficiency of the system under study. An equivalent methodology has previously been employed to determine the relative reactivity of several anaerobic acrylate redox couples similarly catalysed by an introduced transition metal catalyst [19].

The polymerisation cure profiles for each of the redox cationic initiation systems under study were followed by measuring the heat of polymerisation using a Comark Diligence EV N2014 data logging device using a type T adaptor with a PTM22M thermocouple probe giving a thermal sensing range from -200°C up to +400°C using a N2000 USB computer interface cradle for data transfer from S.W. Carty & Sons, Dublin, and EVSW logger software, as supplied with this instrumentation, was used for quantification and recording of these measurements before transfer to Microsoft Excel for analysis.

2.4.2.1 Typical Experiment

In a typical calorimetric experiment predetermined amounts of cationic initiator and reducing agent were weighed along with the required amount of monomer **72** (10 g, 39.63 mmol), into 20 ml volume glass vials containing a magnetic stirring bar and sealed using a rubber septa. All mixtures were stirred overnight by which time the solid components were fully dissolved and a homogeneous clear solution was obtained. Due to the potential photosensitivty of the solutions all samples were mixed and stored in darkness.

The solutions thus prepared were purged with argon, unless otherwise stated. All samples were allowed to equilibrate at 25°C with stirring for 10 minutes before initiation of polymerisation. T_0 was taken as the moment of copper(II) catalyst addition to the reaction vessel. The preferred catalyst in these tests was a solution of $Cu(NO_3)_2$ in propylene carbonate (0.1 g/ml). Propylene carbonate was chosen, as it is a polar solvent with a suitably high boiling point. The procedure used for catalyst selection is outlined in a subsequent section. A typical experimental layout is depicted in Figure 2.3.

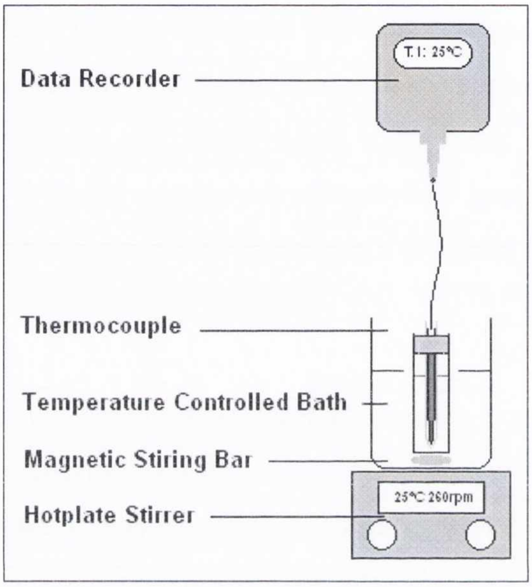


Figure 2.3: Typical experimental layout for redox cationic cure study

2.4.2.2 Quantifying the Degree of Conversion to Polymer [383]

The heat energy, Q, for a copper(II) catalysed redox polymerisation reaction was determined using Equation 2.0:

$$Q = m \cdot c \cdot \Delta T \qquad \text{... Equation 2.0}$$

where Q is heat energy (J)

m is mass of the substance heated (g)

c is specific heat capacity ($J\ g^{-1}\ K^{-1}$); and

ΔT is the temperature rise of the system (K).

Subsequently, the extent of polymerisation or degree of conversion of the monomer to polymer was calculated from the theoretical enthalpy of the system under study and is given as:

$$\alpha = \Delta H_{exp} / \Delta H_T \qquad \text{... Equation 2.1}$$

where α is the degree of monomer conversion

ΔH_{exp} is the experimental enthalpy of reaction (J g^{-1}); and

ΔH_T is the theoretical enthalpy (J g^{-1}).

The theoretical enthalpy was calculated using the following relationship:

$$\Delta H_T = (\Delta H_{Tf} / M)f \qquad \text{... Equation 2.2}$$

where f is the functionality of the monomer used

ΔH_{Tf} is the theoretical enthalpy of one reacted functional group (J mol^{-1})

M is the molar mass of the monomer, (g mol^{-1})

From Ionescu-Vasii and Abadie the theoretical enthalpy for reaction of an epoxy functional group, $\Delta H_{Tf} = 94.47$ kJ mol^{-1} [384], and for vinyl ether $\Delta H_{Tf} = 59.84$ kJ mol^{-1} [385,386]. Therefore, using Equation 2.2 a theoretical enthalpy of 748.84 J g^{-1} is obtained for the epoxy monomer (**72**). The specific heat capacity of the epoxy monomer (**72**) as determined by differential scanning calorimetry (DSC) was found to be 1.58 J g^{-1} (STP) [387-389]. Using the calorimetric method, the polymerisation process is measured as heat flow, which is proportional to the conversion rate.

Consequently conversion can be defined as [390-392]:

$$d\alpha / dt = (dH / dt) / \Delta H_T \qquad \text{... Equation 2.3}$$

where $d\alpha / dt$ – the conversion or the polymerisation rate

dH / dt or $\Delta H_{exp,t}$ – experimental enthalpy (heat flow of reaction at time t)

ΔH_T – theoretical enthalpy (J g^{-1})

The conversion at time t (s) is determined from the integrated form of Equation 2.3:

$$\alpha_{,t} = \Delta H_{exp,t} / \Delta H_T \qquad \text{... Equation 2.4}$$

where $\alpha_{,t}$ – the degree of conversion at time t

$\Delta H_{exp,t}$ – the experimental heat of the reaction at time t

2.4.3 Tensile Strength Testing of Adhesives

The mechanical characteristics of adhesive polymerisation are routinely evaluated by measuring tensile shear bonding strength. Typically tensile strength is determined by bonding metal parts with the adhesive of interest and performing the appropriate test using a tension-testing machine, equipped with a suitable load cell. Although this method of assessing the relative degree of conversion to polymer is subject to certain limitations since bond strength relates not only to the degree of cure but also to various surface-related parameters, it does allow the relative performance of adhesive samples to be evaluated under given cure parameters [393,394]. The standard test method described below was followed for all tensile tests performed [395,396].

- *Apparatus:* Instron 5500R (tension testing machine).

- *Test specimens:* Steel tokens (RS-14), 1.6 mm x 25 mm x 102 mm [397]

- *Assembly procedure:* Five test specimens were used for each test. The specimen surface was prepared where necessary, i.e. mild steel lap-shears are grit blasted with silicon carbide. All test specimens were cleaned by wiping with isopropanol before assembly. The bond area on each lap-shear was 322.6 mm^2. This was marked before applying the adhesive sample. A sufficient quantity of adhesive was applied to the prepared surface of one lap-shear. A second lap-shear was placed onto the adhesive and the assembly was clamped on each side of the bond area. All substrates to be bonded were freshly prepared before use. All specimens were assembled, cured and tested at ambient temperature i.e. 20-25°C.

- *Typical test procedure:* After allowing for cure as specified in the test program the shear strength was determined as follows. The test specimen was placed in the grips of the testing machine so that the jaws held the outer 25.4 mm of each end. The long axis of the test specimen coincided with the direction of applied tensile force through the centre line of the grip assembly. The assembly was tested at a crosshead speed of 2.0 mm/min. The load at failure was recorded in N/mm^2. Each quoted shear strength result is the average result of five replicate tests.

2.5 Results & Discussion

In the early copper catalysed redox cationic polymerisation investigations of Crivello and Lam diphenyl iodonium salts were employed as the oxidising agent component and a series of reducing agents were studied to determine their relative efficiencies in such redox couples [305,306]. The Ph_2I salt (**43**) : A-6-Hex (**64**) redox couple was found to be most efficient of the redox couples in those studies. Subsequently Yagci and co-workers began investigating alternative oxidising agent components in similar redox cationic polymerisations using some of the reducing agent species already demonstrated to be efficient by Crivello [249,316]. In the investigations of Yagci *et al.* it was again shown that the Ph_2I salt (**43**) : A-6-Hex (**64**) redox couple was the most efficient of the couples studied up to that point. In the cited investigations cyclohexene oxide (CHO) (**74**), a cationically polymerisable oxirane solvent, was the monomer of choice. However while CHO is readily polymerised and can be indicative of the effectiveness of a cationic redox initiation couple it is not truly representative of the real world applicability of such an initiation system to the cationic polymerisation of commercially useful monomers and resins. Therefore, in this current study many of the published copper catalysed redox couples were revisited with a view to determining their relative efficiencies in commercially useful epoxy resin systems.

A typical curve depicting the exothermic redox polymerisation of monomer (**72**), using (**43**) as the cationic initiator and (**64**) as the reducing agent catalysed by 0.5 ml $Cu(NO_3)_2$ in propylene carbonate (0.1 g / ml) is shown in Figure 2.4. From the curve it can be seen that there is an induction period before bulk polymerisation proceeds, which culminates in a peak exotherm followed by an exponential drop. In this example bulk polymerisation appears to reach completion within 60 s. The amount of heat released (ΔT), the half time ($t_{½}$) as defined by the time taken to reach half of the maximum exotherm (T_{max}) and the percentage conversion (C) can be derived from this curve.

During this study it was observed that the initial phase of the polymerisation reaction is characterized by an induction period that is indicative of an equilibrium reaction, during which time an active initiation complex between the monomer and redox catalyst system forms [398]. When the concentration of the initiating species has built up to a threshold level, rapid polymerisation follows. These observations reflect those previously noted by Crivello *et al.* [309]. The duration of this induction period is related to the efficiency of the redox couple being studied. A typical redox cationic initiation sequence as proposed by Crivello & Lam was presented earlier in Scheme 2.2. Bottcher *et al.* proposed that the induction period in cationic polymerisation may result from the presence of an impurity, which reacts with the carbocations generated in the initial stage of the polymerisation [217]. The monomer (**72**) used in these preliminary studies is analytically pure (one peak by GC/GC-MS) and had a moisture content as received of 570 ppm by Karl Fisher titration, so this second possibility seems less likely in this instance.

The dramatic change in shape of the curve, which accompanies a large exotherm, is related to the Tromsdorf or gel effect in which the reaction displays auto-acceleration reflected by the steep curve [399-401]. The gel effect is associated with a dramatic decrease in the rate of termination associated with low transport rates of chains and the fact that as the temperature increases the mobility of active species also increases and contributes to an increase in the degree of polymerisation of the system under study [402]. In the absence of strong termination the rate of conversion increases and becomes auto-accelerating due to the exothermic nature of the reaction. Figure 2.5 shows a plot of conversion, %, versus time following catalyst addition, which has been derived from the data presented in Table 2.8, using Equations 2.1, 2.2 and 2.3.

The reproducibility of these experiments was investigated by repeating a typical experiment, as outlined above, several times. The results of this repeatability study are presented in Table 2.9. There is good correlation between the data recorded for each replicate experiment performed.

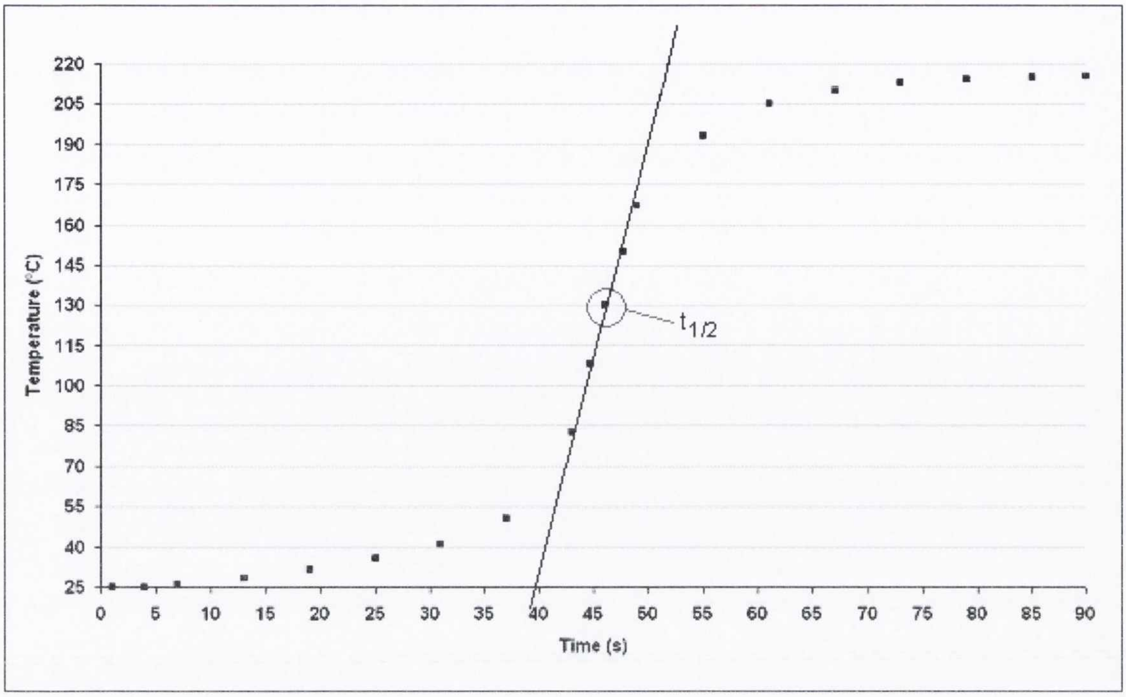


Figure 2.4: Typical exotherm of polymerisation versus time (s) for monomer (**72**), 39.63 mmol, initiated by the Ph_2I PF_6 (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

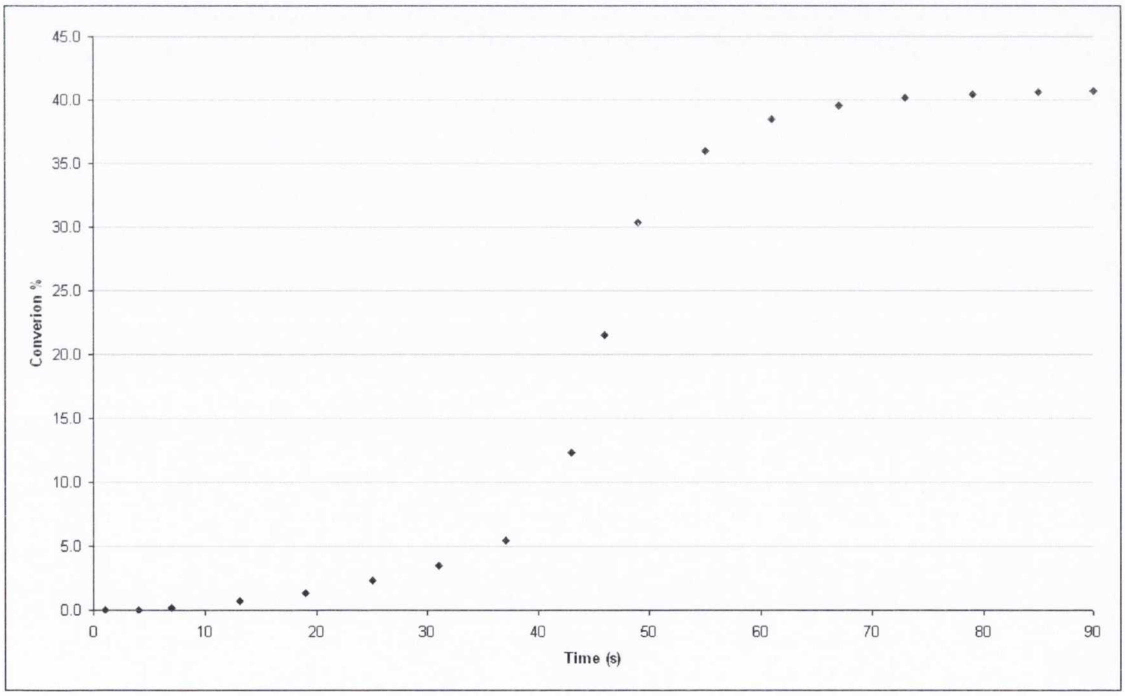


Figure 2.5: Conversion (%) versus Time (s) for monomer (**72**), 39.63 mmol, initiated by the Ph_2I PF_6 (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Table 2.8: Data from a typical calorimetric experiment: monomer (**72**), 39.63 mmol, initiated by the Ph_2I PF_6 (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol (Please see Appendices for a worked calculation example.)

Time (s)	**Q (J)**	**Monomer (g)**	**Reaction Temp. (°C)**	**ΔT (K)**	**c ($Jg^{-1}K^{-1}$)**	**ΔH_{exp} ($J\ mol^{-1}$)**	**ΔH_{exp} ($J\ g^{-1}$)**	**Conversion (%)**
1	**0.0**	**10**	**25.0**	**0.0**	**1.6**	**0.0**	**0.0**	**0.0**
2	0.0	10	25.0	0.0	1.6	0.0	0.0	0.0
4	3.2	10	25.2	0.2	1.6	80.7	0.3	0.0
7	16.0	10	26.0	1.0	1.6	403.7	1.6	0.2
13	54.4	10	28.4	3.4	1.6	1372.6	5.4	0.7
19	102.4	10	31.4	6.4	1.6	2583.7	10.2	1.4
25	172.8	10	35.8	10.8	1.6	4359.9	17.3	2.3
31	259.2	10	41.2	16.2	1.6	6539.9	25.9	3.5
37	409.6	10	50.6	25.6	1.6	10334.6	41.0	5.5
43	921.6	10	82.6	57.6	1.6	23252.9	92.2	12.3
46	1612.8	10	125.8	100.8	1.6	40692.6	161.3	21.5
49	2275.2	10	167.2	142.2	1.6	57405.6	227.5	30.4
55	2691.2	10	193.2	168.2	1.6	67901.7	269.1	35.9
61	2880.0	10	205.0	180.0	1.6	72665.3	288.0	38.5
67	2963.2	10	210.2	185.2	1.6	74764.5	296.3	39.6
73	3008.0	10	213.0	188.0	1.6	75894.8	300.8	40.2
79	3030.4	10	214.4	189.4	1.6	76460.0	303.0	40.5
85	3043.2	10	215.2	190.2	1.6	76783.0	304.3	40.6
90	3046.4	10	215.4	190.4	1.6	76863.7	304.6	40.7
97	3046.4	10	215.4	190.4	1.6	76863.7	304.6	40.7
103	3043.2	10	215.2	190.2	1.6	76783.0	304.3	40.6
109	**3033.6**	**10**	**214.6**	**189.6**	**1.6**	**76540.8**	**303.4**	**40.5**

Table 2.9: Reproducibility & repeatability of a typical experiment: Monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Monomer (mmol)	Oxidising Agent (mmol)	Reducing Agent (mmol)	Replicate	ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	A-6-Hex (0.24)	1	196.6	50	221.6	131.6	42.0
			2	190.4	47	215.4	131.2	40.7
			3	193.7	49	218.6	131.8	41.4

2.5.1 Choice of Catalyst for Redox Cationic Polymerisation

Choice of copper(II) catalyst for activation of the cationic polymerisation redox couples in this study was based on a preliminary screening of the relative efficiencies of several copper(II) and some other transition metal salts, see Table 2.10. It was found to be more convenient to use a minimum amount of solvent carrier for each salt tested. This allowed rapid homogenisation of the catalyst in the reactive system and no delay in redox reaction was then encountered due to poor or slow solvation of the copper species in the bulk monomer. Although the typical calorimetric method, as described previously, was also employed in this catalyst screening no detailed study of polymerisation was undertaken. The data recorded to classify the relative copper(II) salt activities in a model redox cationic polymerisation were T_{max} (°C) and the time (s) to reach $t_{½}$.

Due to its rapid activation of the model redox cationic initiation system, relative to the other species studied, and its ready solubility in propylene carbonate, a high boiling point polar solvent, which allowed convenient handling and addition, copper(II) nitrate was selected as the preferred catalyst in this study

Table 2.10: Metal salts investigated for their relative efficiencies as redox catalysts in a model system: Monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple

	Metal Salt (0.027 mmol)	**Mol. Wt.**	**Solvent Carrier**	**$t_{1/2}$ (s)**	**T_{max} (°C)**	**Relative Activity**
77	Copper(II) Nitrate	187.56	1% in Propylene Carbonate (0.5 ml)	50	221.6	↑
78	Copper(II) Naphthenates	~ 300	8% in White Oil (as received), mixture of naphthenates, not well defined	215	218.4	
79	Copper(II) Ethylhexanoate	349.95	Neat – Good / Rapid Solubility in the Reactive System	387	81.2	
80	Copper(II) Benzoate [285]	305.77	Neat – Good / Rapid Solubility in the Reactive System	434	78.6	
Other Transition Metal Salts – Eliminated due to extreme reactivity, poor solubility and poor activity						
81	Copper(II) Tetrafluoroborate Hydrate	237.16	Propylene Carbonate	Good solubility, but highly reactive even with neat epoxy monomer. Drying difficult. Inherently a strong Lewis acid.		
82	Copper(II) Sulfate	159.61	Propylene Carbonate / Alcohol	Poor solubility: Limited activity		
83	Cobalt(II) Naphthenates	-	White Oil (as received)	Limited activity even at higher concentration.		

2.5.2 Determination of a Preferred Ratio of Redox Components in a Typical Copper(II) Catalysed Redox Cationic Polymerisation

First the $Ph_2I\ PF_6$ (**43**): A-6-Hex (**64**) system was studied by treating it as a model redox couple in monomer (**72**). In all cases the catalyst employed was 0.5 ml of $Cu(NO_3)_2$ as a 0.1g/ml solution in propylene carbonate. When the catalyst is added to the iodonium/ascorbic acid system the colour turns blue then rapidly disappears before turning dark brown as the exothermic polymerisation reaction proceeds.

2.5.2.1 Effect of Concentration of Oxidising & Reducing Agent Components on Efficiency of Conversion to Polymer

It was found that a threshold concentration of $Ph_2I\ PF_6$ (**43**) was required to achieve the maximum degree of polymerisation, above this concentration it was found that the rate of polymerisation does not increase significantly, Table 2.11. Similarly a threshold concentration of reducing agent, A-6-Hex (**64**), was required to achieve the most favourable polymerisation; above this concentration the rate of polymerisation does not increase significantly, Table 2.12.

2.5.2.2 Possible Redox Polymerisation Mechanism Inferred by Initial Studies

The following reaction Scheme 2.8 outlines the reactions that occur in a typical experiment performed in this study as modelled on the Crivello mechanism, Scheme 2.2. The experimental observations most closely support a reaction stoichiometry of one ascorbic acid molecule to two iodonium salt moieties, Scheme 2.8(d1).

$$AH_2 + 2Cu^{II}(NO_3)_2 \rightarrow DA + 2Cu^{I}NO_3 + 2\,HNO_3 \qquad (a)$$

$$Ph_2I\,PF_6 + Cu^{I}NO_3 \rightarrow Cu^{II}(NO_3)(PF_6) + PhI + Ph\cdot \qquad (b)$$

$$AH_2 + 2Cu^{II}(NO_3)(PF_6) \rightarrow DA + 2\,Cu^{I}NO_3 + 2H\,PF_6 \qquad (c)$$

$$AH_2 + 2Ph\cdot \rightarrow DA + 2\,PhH \qquad \text{(Additional Rxn)}$$

Where AH_2 is Ascorbic Acid and DA is Dehydroascorbic Acid

Overall Redox Rxn eq. (a) to (c) 1 : 2 Ratio Reducing Agent + $Ph_2I X$: (d1)

$$AH_2 + 2Ph_2I\,PF_6 \rightarrow DA + 2PhI + 2PhH + DA + 2H^+\,PF_6^-$$

If Overall Redox Rxn eq. 1 : 1 Ratio Reducing Agent + $Ph_2I X$: (d2)

$$AH_2 + Ph_2I\,PF_6 \rightarrow DAH + PhI + PhH + H^+\,PF_6^-$$

… Scheme 2.8

Table 2.11: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**) : A-6-Hex (**64**) redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. The onium salt concentration was varied (0.12 – 1.44 mmol) while the reducing agent was maintained at 0.24 mmol.

	Monomer (mmol)		Oxidising Agent (mmol)		Reducing Agent (mmol)		ΔT (K)	$t_{1/2}$ (s)	T_{max} (°C)	$T_{1/2}$ (°C)	C (%)
1	**72**	(39.63)	**43**	(0.12)	**64**	(0.24)	113.2	88	138.2	72.6	24.2
2	**72**	(39.63)	**43**	(0.16)	**64**	(0.24)	128.4	76	149.4	88.2	27.4
3	**72**	(39.63)	**43**	(0.20)	**64**	(0.24)	142.8	65	167.8	103.0	30.5
4	**72**	(39.63)	**43**	(0.24)	**64**	(0.24)	154.0	52	184.6	132.4	34.1
5	**72**	(39.63)	**43**	(0.48)	**64**	(0.24)	198.2	51	223.2	140.0	42.4
6	**72**	(39.63)	**43**	(0.96)	**64**	(0.24)	180.4	23	205.4	135.2	38.5
7	**72**	(39.63)	**43**	(1.44)	**64**	(0.24)	183.4	16	208.4	126.8	39.1

Table 2.12: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**) : A-6-Hex (**64**) redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. The oxidising agent (onium salt) concentration was maintained at 0.48 mmol, while the reducing agent concentration was varied (0.08 – 0.96 mmol).

	Monomer (mmol)		Oxidising Agent (mmol)		Reducing Agent (mmol)		ΔT (K)	$t_{1/2}$ (s)	T_{max} (°C)	$T_{1/2}$ (°C)	C (%)
1	**72**	(39.63)	**43**	(0.48)	**64**	(0.08)	178.6	38	203.2	124.2	38.0
2	**72**	(39.63)	**43**	(0.48)	**64**	(0.16)	188.2	46	213.2	123.6	40.2
3	**72**	(39.63)	**43**	(0.48)	**64**	(0.24)	198.2	51	223.2	140.0	42.4
4	**72**	(39.63)	**43**	(0.48)	**64**	(0.48)	183.8	39	207.8	125.0	38.9
5	**72**	(39.63)	**43**	(0.48)	**64**	(0.96)	186.0	45	210.0	130.2	39.5

2.5.3 Influence of Oxygen on Copper Catalysed Redox Polymerisations

Molecular oxygen is known to inhibit radical polymerisations [403]. However, unlike their radical polymerisation counterparts, cationic polymerisations are not inhibited by oxygen and indeed may be promoted by its presence [404]. Decker and co-workers for example report that such oxidation products as hydroperoxides, which are known to be good proton donors, form in the monomer due to the presence of oxygen and are expected to accelerate the production of initiating species for cationic polymerisations carried out in the presence of air, Scheme 2.9 [405]. Thus facilitating the efficient formation of the key Brønsted acid initiator following the initial decomposition of the latent onium salt species.

$$\mathrm{ROO{-}H} \rightarrow \mathrm{ROO^-} + \mathrm{H^+}$$

$$\mathrm{H^+} + \mathrm{X^-} \rightarrow \mathrm{H^+X^-}\ \textit{(Brønsted Acid Initiator)} \qquad \text{...Scheme 2.9}$$

During preliminary copper(II) catalysed redox cationic experiments it was observed that under a normal atmosphere the copper catalysed redox cationic polymerisations described here consistently react from the surface of the bulk reaction mixture with the polymerisation front propagating throughout the bulk in a manner reminiscent of an isothermal frontal polymerisation. For this reason it was deemed prudent to determine if this observation was due to an acceleration of the polymerisation reaction by atmospheric oxygen at the surface of the reaction mixture. In order to corroborate these observations two replicates for each of redox couples shown in Table 2.12 were prepared and oxygenated or de-oxygenated respectively by sparging one replicate with oxygen for a period of 25 minutes in order to saturate the system with the gas, while the second replicate was bubbled through with argon for a period of 25 minutes in order to eliminate oxygen from the system. In all cases the catalyst employed was 0.5 ml of $Cu(NO_3)_2$ as a 0.1g/ml solution in propylene carbonate and this was also deoxygenated by bubbling with argon.

The resulting polymerisation exotherms for these experiments are shown as plots in Figures 2.6 and Figure 2.7 and the data are presented in Table 2.12.

- The first redox system investigated under these conditions was the *$Ph_2I\ PF_6$ **(43)**: A-6-Hex **(64)*** couple. As is evident the presence of higher concentrations of oxygen significantly accelerated the copper catalysed reaction for this redox couple. Interestingly, oxygen accelerates this copper(II) catalysed redox cationic polymerisation as seen by the much reduced induction period, $t_{½}$ = 30 s as compared to 51 s, and a higher degree of conversion, 50.3 % as compared to 42.4 % for the oxygenated and de-oxygenated conditions respectively.

- The second redox system investigated under these conditions was the *$Ph_2I\ PF_6$ (43): α-tocopherol (67)* couple. Similarly higher concentrations of oxygen also accelerate the copper(II) catalysed redox cationic polymerisation with this alternative redox couple resulting in a much reduced induction period, $t_{½}$ = 322 s as compared to 435 s, although there is little change in the degree of conversion attained, 41.1 % as compared to 40.8 % for the oxygenated and de-oxygenated conditions respectively.

Table 2.13: Comparison of polymerisation data obtained for argon and oxygen sparged systems: Monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Monomer (mmol)		Oxidising Agent (mmol)		Reducing Agent (mmol)		Gas	ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
72	(39.63)	$Ph_2I\ PF_6$ **(43)**	(0.48)	A-6-Hex **(64)**	(0.24)	Ar	198	51	223	140	42.4
						O_2	235	30	260	135	50.3
72	(39.63)	$Ph_2I\ PF_6$ **(43)**	(0.48)	α-Tocopherol **(67)**	(0.24)	Ar	191	435	216	128	40.8
						O_2	192	322	217	90	41.1

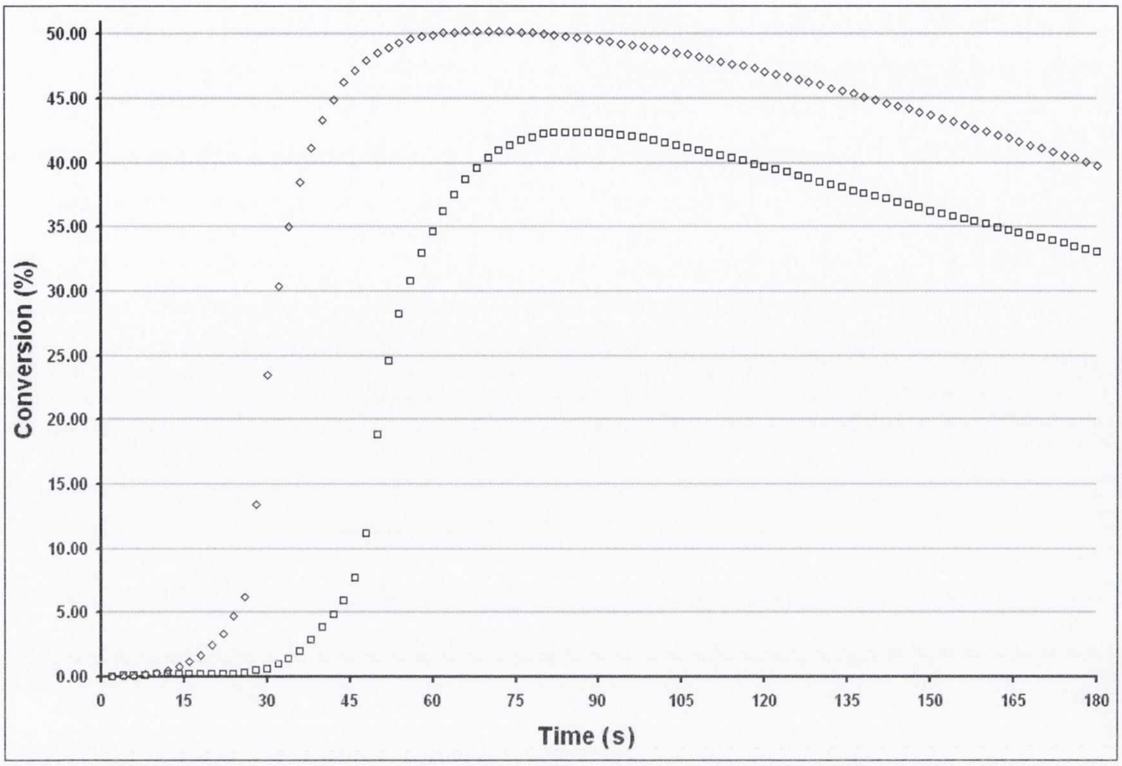


Figure 2.6: Effect of oxygen on conversion (%) of monomer (**72**), 39.63 mmol, initiated by the redox couple $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol and catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. Oxygenated (◇), De-oxygenated (□)

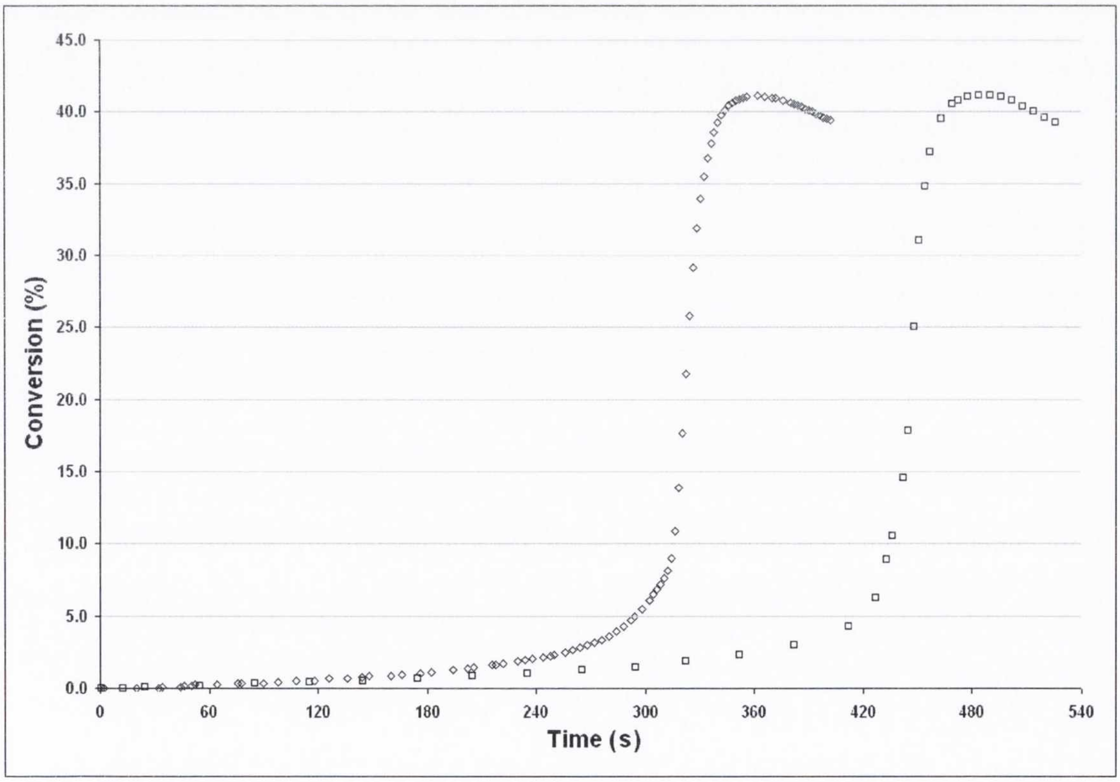


Figure 2.7: Effect of oxygen on conversion (%) of monomer (**72**), 39.63 mmol, initiated by the redox couple $Ph_2I\ PF_6$ (**43**), 0.48 mmol : α-Tocopherol (**67**), 0.24 mmol and catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. Oxygenated (◇), De-oxygenated (□)

2.5.3.1 Possible Mechanism Inferred by Oxygen Promotion of Copper(II) Catalysed Redox Cationic Polymerisation

From the above it is apparent that the presence of oxygen can increase the efficiency of copper catalysed redox cationic polymerisations i.e. increases the rate at which the key initiating species in generated. It may be inferred that the presence of oxygen should have an accelerative effect on the oxidation steps involved in the redox cationic process. Therefore the Ph_2I salt decomposition step, a process of reduction, should not be accelerated directly by oxygen. However the oxidation of the reduced form of the copper catalyst from the Cu(I) to the higher Cu(II) oxidation state may be greatly accelerated thereby promoting formation of strongly Lewis acidic Cu(II)XY or Cu(II)XX species. Such Lewis acids are efficient initiators or co-initiators of cationic polymerisation, see Scheme 2.2c and Table 2.9 line 7 [351]. The copper(II) catalysed oxidation of ascorbic acid is known [406,407].

$AH_2 + 2Cu^{II}(NO_3)_2 \rightarrow DA + 2Cu^{I}NO_3 + 2\,HNO_3$ ...Scheme 2.10

$Ph_2I\,PF_6 + Cu^{I}NO_3 \rightarrow Cu^{II}(NO_3)(PF_6) + PhI + Ph\cdot$ ...Scheme 2.11

$AH_2 + 2Cu^{II}(NO_3)(PF_6) \rightarrow DA + 2\,Cu^{I}PF_6 + 2\,HNO_3$ ...Scheme 2.12

$AH_2 + 2Cu^{II}(NO_3)(PF_6) \rightarrow DA + 2\,Cu^{I}NO_3 + 2\,HPF_6$ ...Scheme 2.13

Oxidation of Cu(I) by Oxygen:

$4Cu^{I}PF_6 + O_2 \rightarrow 2CuO + 2Cu^{II}(PF_6)_2$ ...Scheme 2.14

$4Cu^{I}NO_3 + O_2 \rightarrow 2CuO + 2Cu^{II}(NO_3)_2$ ...Scheme 2.15

$4Cu^{I}NO_3 + O_2 + PF_6^-{}_{(Solution)} \rightarrow 2CuO + 2Cu^{II}(NO_3)(PF_6)$ ...Scheme 2.16

Investigation of the Roles of Cu(I) & Cu(II) in Redox Cationic Polymerisation

The +II oxidation state is the most stable for Cu [408]. However, Cu(I) species are generally unstable and a lifetime of *c*.1 second in aqueous solution and disproportionate spontaneously into Cu(II) and Cu(0), Scheme 2.17 [408,409]. Transient Cu(I) species may be intercepted upon formation however by reaction with another chemical species such as $Ph_2I\,PF_6$ (**43**) as in the case of the copper catalysed redox cationic polymerisation systems under study, Scheme 2.18.

$2Cu^{I}X \rightarrow Cu^{II}X_2 + Cu^{0}$ ...Scheme 2.17

$Cu^{I}X + [Ox]^{n}X \rightarrow Cu^{II}X_2 + [Ox]^{n-1}$ ...Scheme 2.18

In order to elucidate the contribution of the copper catalyst, in the higher +2 and lower +1 oxidation states, during initiation of redox cationic polymerisation a series of experiments were performed as follows:

i. Firstly the redox half-reaction entailing direct reduction of $Cu^{II}(NO_3)_2$ by A-6-Hex (**64**) was performed to determine if there was any significant contribution to cationic polymerisation by the nucleophilic reaction product HNO_3, Scheme 2.10 and Table 2.14.

ii. Direct initiation by Cu(II) salts of nucleophilic, NO_3^-, and non-nucleophilic, BF_4^-, anions Table 2.15 and Figure 2.8.

iii. Copper species in the +I oxidation state can be prepared as isolable complexes with alkenes and alkynes as ligands [408]. The stable complexes of Cu(I) and 1,5-Cyclooctadiene (COD), $[Cu(COD)_2]BF_4$ and $[Cu(COD)_2]ClO_4$, were prepared as model Cu(I) compounds of non-nucleophilic anions [375]. These compounds were then studied in a series of "uncatalysed" redox couples to determine if they could be further reduced or oxidised in order to promote redox cationic polymerisation as Lewis acid initiators or co-initiators, see Table 2.16 and Figure 2.9.

The general parameters of a typical calorimetric experiment remained unchanged however the following adjustments were made:

i. For direct initiation experiments the required amount of monomer **72** (10 g, 39.63 mmol) was weighed neat into 20 ml glass vials containing a magnetic stirring bar, sealed using a rubber septa and purged with argon. T_0 was taken as the moment of copper(II) salt (0.027 mmol) addition to the reaction vessel with stirring. pH of aqueous solutions was determined using universal indicator strips.

ii. In "uncatalysed" redox initiation experiments aliquots of monomer **72** (5 g, 15.88 mmol) were prepared in 20 ml glass vials containing a magnetic stirring bar, sealed using a rubber septa and purged with argon. To each vial was added double the required concentration of either the reducing or oxidising agent component. When ready to proceed with the reaction 5 g of the monomer solution containing the reducing agent component was transferred via syringe into the vial containing the oxidising agent component. T_0 was taken as the moment of first mixing the two monomer solutions.

iii. For experiments where the objective was to demonstrate oxidation of the latent cationic initiator by the strong oxidising agent H_20_2, 30% (w/w) the required amount of monomer **72** (10 g, 39.63 mmol) was weighed into 20 ml glass vials containing a magnetic stirring bar and the required amount of latent initiator. The initiator was dissolved with stirring for c. 16 hr at ambient temperature. The vial was sealed using a rubber septum, purged with argon and brought to 25°C using a water bath. Directly before performing the experiment the vial was removed from the water bath and secured by clamping to a retort stand due to potential for boiling of the added aqueous component during an exothermic polymerisation reaction. The rapid cooling observed in the thermal profiles for these experiments is due to cooling in air. T_0 was taken as the moment of addition of the specified amount of H_20_2, 30% (w/w) or deionised water (as in controls) to the reaction vessel with stirring.

N.B. Hydrogen peroxide can function as both a reducing agent and an oxidising agent [410]. The reductive ability of hydrogen peroxide is pH dependant e.g. in alkaline solution hydrogen peroxide oxidises chromium(III) to chromium(IV) and cerium(III) to cerium (IV) while in acid solution hydrogen peroxide reduces chromium(III) to chromium(II) and cerium(III) to cerium (II) [410].

Table 2.14: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, initiated by the $Cu(NO_3)_2$: A-6-Hex (**64**) redox couple

Monomer (mmol)	Oxidising Agent (mmol)	Reducing Agent (mmol)	ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
72 (39.63)	$Cu(NO_3)_2.6H_2O$ (0.027)	**64** (0.24)	2.6	-	27.6	-	0.6

Table 2.15: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, following direct initiation by the following Copper(II) Lewis acids: $Cu(NO_3)_2$ (**77**), 0.027 mmol & $Cu(BF_4)_2$ (**81**), 0.027 mmol. *N.B.* where Y = Nucleophilic, and X = Non-nucleophilic anions

Cu^{II}	Monomer (mmol)	Direct Initiation (mmol)	pH 2.7×10^{-3} M	ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
Cu^{II} YY	**72** (39.63)	$Cu(NO_3)_2.6H_2O$ (0.027)	5	3	-	28	-	0.7
Cu^{II} XY	**72** (39.63)	$Cu(BF_4)(NO_3).6H_2O$ (0.027)	2	59	46	84	54	12.7
Cu^{II} XX	**72** (39.63)	$Cu(BF_4)_2.6H_2O$ (0.027)	1	56	18	81	53	11.9

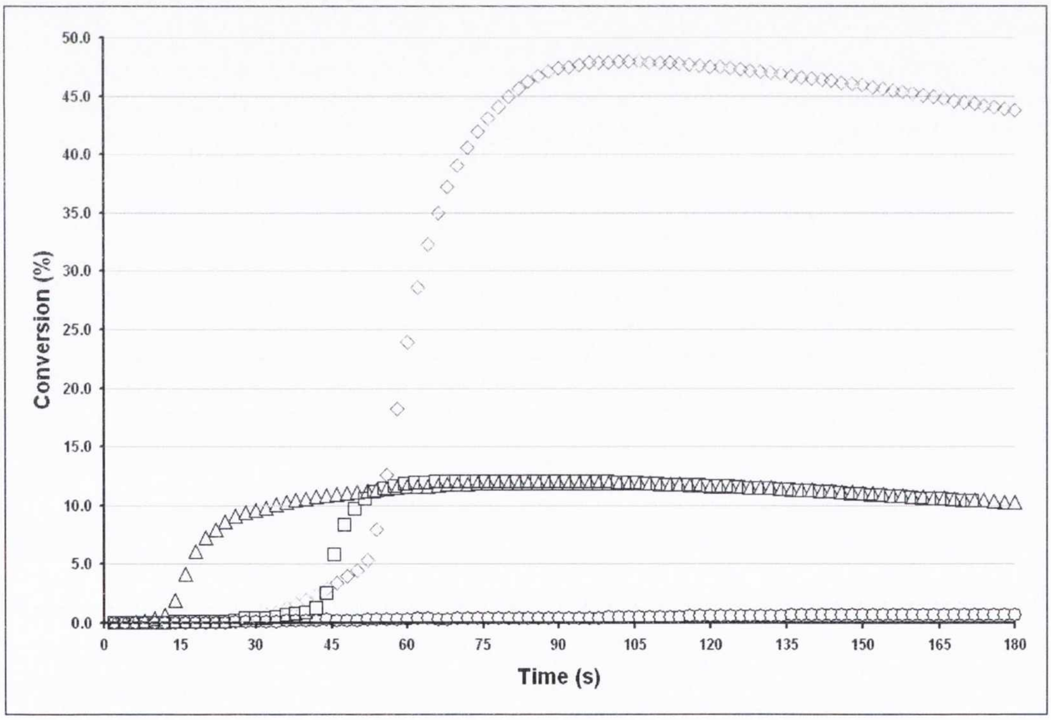


Figure 2.8: Exotherm of polymerisation versus time (s) for direct cationic initiation of monomer (**72**), 39.63 mmol, by $Cu(NO_3)_2$ (○), 0.027 mmol; $Cu(BF_4)(NO_3)$ (□), 0.027 mmol & $Cu(BF_4)_2$ (△), 0.027 mmol. Also shown for comparison is the cure profile for the optimised redox couple Ph_2I PF_6 (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol (◇).

Direct initiation by a catalytic quantity, 0.027 mmol, of the strongly Lewis acidic Cu(II) species, $Cu(BF_4)_2$, resulted in a much reduced induction period with a $t_{1/2}$ of just 18 seconds and a conversion to polymer of *c.* 12 %. In contrast the weaker Lewis acid, $Cu(NO_3)_2$, has induced a minimal conversion to polymer of just 0.7% under equivalent experimental conditions and is very inefficient at promoting cationic polymerisation.

The key feature of these experiments is the practical demonstration of promotion of cationic polymerisation by the catalyst-derived component CuX_2, where X is a non-nucleophilic anion. While when X is a nucleophilic anion there is minimal contribution to the conversion of the bulk monomer.

Table 2.16: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, initiated by a series of H_2O_2, 30% (w/w) : Cu(I) redox couples, plus controls

Mon. (mmol)	**Oxidising Agent (mmol)**		**Reducing Agent (mmol)**		**ΔT (K)**	**$t_{1/2}$ (s)**	**T_{max} (°C)**	**$T_{1/2}$ (°C)**	**C (%)**
72 (39.63)	-	-	$[Cu(COD)_2]BF_4$	(0.48)	Liquid >> 1 week, c. 20°C				-
	O_2	-	$[Cu(COD)_2]BF_4$	(0.48)	Slow gelation, days				-
	$Ph_2I\ PF_6$	(0.48)	$[Cu(COD)_2]BF_4$	(0.48)	Slow gelation, days				-
	$[Cu(COD)_2]BF_4$	(0.48)	A-6-Hex	(0.24)	Slow gelation, days				-
72 (39.63)	H_2O (0.7g)	(42.0)	$[Cu(COD)_2]BF_4$	(0.48)	Slow gelation, days				-
	H_2O_2, 30% (0.7g)	(6.2)	$Ph_2I\ PF_6$	(0.48)	Liquid >> 1 week, c. 20°C				-
	H_2O_2, 30% (0.7g)	(6.2)	$[Cu(COD)_2]BF_4$*	(0.48)	92	135	117	68	19.7
	H_2O_2, 30% (0.7g)	(6.2)	$[Cu(COD)_2]\ ClO_4$*	(0.48)	103	512	128	66	22.0
	-	-	$[Cu(COD)_2]BF_4$	(0.48)	Liquid >> 1 week, c. 20°C				-
	H_2O_2, 30% (0.7g)	(6.2)	$[Ag(COD)_2]BF_4$*	(0.48)	Liquid >> 1 week, c. 20°C				-

* All $[Cu(COD)_2]$ and $[Ag(COD)_2]$ solutions in monomer (**72**) had a pH c. 5 before*H_2O_2 addition.

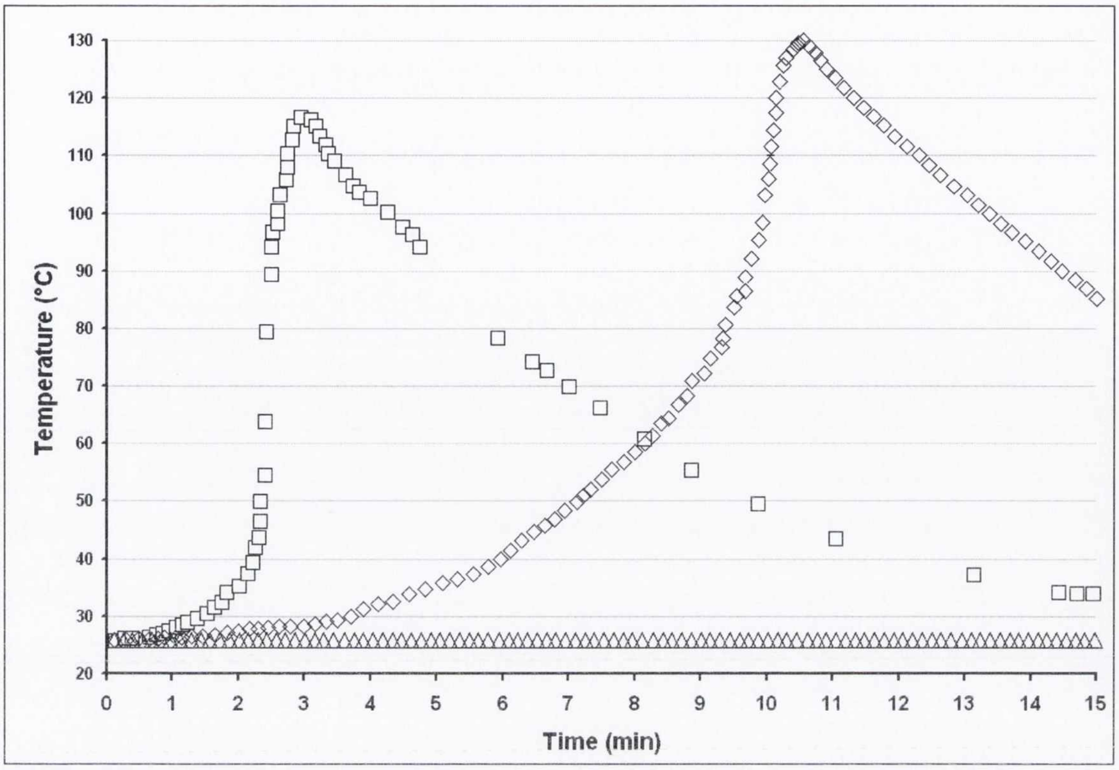


Figure 2.9: Exotherm of polymerisation versus time (min) for monomer (**72**), 39.63 mmol, initiated by oxidation of $[Cu(COD)_2]BF_4$ (□), 0.48 mmol, $[Cu(COD)_2]ClO_4$ (◇), 0.48 mmol, $[Ag(COD)_2]BF_4$ (△), 0.48 mmol with H_2O_2 30%, 6.2 mmol. These polymerisation reactions were cooled in air.

The Cu(I) COD complexes of the non-nucleophilic anions BF_4 and ClO_4, were found not to promote direct cationic polymerisation of the cationically polymerisable monomer (**72**). When an equivalent solution was sparged with oxygen, 20 mins, and the sample was stored in a sealed vial the monomer solution gelled slowly over several days indicating a formation of a species capable of cationic polymerisation, Scheme 2.19. Correspondingly $Ph_2I\ PF_6$ (**43**) did not promote rapid conversion of the monomer in the presence of the $[Cu(COD)_2]BF_4$ complex, but gelation was observed to occur over several days, Scheme 2.20. In both of the instances where an oxidising species was added to a colourless solution of $[Cu(COD)_2]BF_4$ in monomer (**72**), the colour became increasingly blue/green indicating formation of the higher oxidation state Cu(II) species. Neither oxygen nor the iodonium salt species were sufficiently strong oxidising agents to promote rapid oxidation of the Cu(I) COD complexes.

$$4[\mathrm{Cu^{I}(COD)_2}]\mathrm{BF_4} + \mathrm{O_2} \xrightarrow{\textit{slow}} 2\mathrm{Cu^{II}(BF_4)_2} + 2\mathrm{Cu^{II}O} + 8\,[\mathrm{COD}]$$

...Scheme 2.19

$$[\mathrm{Cu^{I}(COD)_2}]\mathrm{BF_4} + \mathrm{Ph_2I\,PF_6} \xrightarrow{\textit{slow}} \mathrm{Cu^{II}(BF_4)(PF_6)} + \mathrm{PhI} + \mathrm{Ph}\cdot + 2[\mathrm{COD}]$$

...Scheme 2.20

In a further control experiment an attempt was made to cause direct reduction of the Cu(I) complex to Cu(0) using the strong reducing agent A-6-Hex (**64**) with a view to generating free anion BF_4^- a Brønsted acid precursor. Direct reduction of the Cu(I) complex was not favourable and proceeded only slowly as evidenced by gelation of the bulk solution over a period of several days, Scheme 2.21.

$$[\mathrm{Cu^{I}(COD)_2}]\mathrm{BF_4} + \mathrm{AH_2} \xrightarrow{\textit{slow}} \mathrm{Cu^{II}(BF_4)(PF_6)} + \mathrm{PhI} + \mathrm{Ph}\cdot + 2[\mathrm{COD}]$$

...Scheme 2.21

As $[Cu^{I}(COD)_2]BF_4$ was found to be relatively stable in the presence of moderate oxidising agents, it was necessary to use a strong oxidising agent, in this instance H_2O_2 (aq. 30% w/w) with a view to better modelling the oxidation process involved in the copper catalysed redox cationic polymerisation process. When an excess of H_2O_2, 30% was introduced into a typical solution of $[Cu^{I}(COD)_2]BF_4$ in monomer (**72**) a strong polymerisation exotherm occurred with a $t_{½}$ of 135 seconds and a conversion of *c*. 20% indicating efficient generation of a cationic initiating species, Scheme 2.22.

A further experiment using the $[Cu^{I}(COD)_2]ClO_4$ complex followed a similar pattern although the $t_{½}$ was consistently longer at 512 seconds with a similar degree of conversion. This observed order of reactivity is consistent with the theoretical relative activity of these anions i.e. $BF_4 > ClO_4$.

$$2[\mathrm{Cu^{I}(COD)_2}]\mathrm{BF_4} + \mathrm{H_2O_2} \xrightarrow{\textit{fast}} \mathrm{Cu^{II}(BF_4)_2} + \mathrm{Cu^{II}O} + \mathrm{H_2O} + 4\,[\mathrm{COD}]$$

...Scheme 2.22

To demonstrate that few if any reductive processes were occurring during reaction of the $[Cu^I(COD)_2]BF_4$ complex with H_2O_2 the copper salt complex was substituted by an analogous silver complex: $[Ag^I(COD)_2]BF_4$. In contrast to copper, silver favours the +I oxidation state and is not readily oxidised to the +II state, moreover silver(I) is readily reduced to silver(0) by relatively mild reducing agents [408]. $[Ag^I(COD)_2]BF_4$ was also shown to be a weak Lewis acid that did not to promote direct cationic polymerisation of the cationically polymerisable monomer (**72**) without further reaction. Even in a strongly oxidising environment, containing an excess of H_2O_2, 30%, no gelation of monomer (**72**) was noted even after several days, which indicated that no strongly acidic initiating species was formed. In addition no precipitation of Ag(0) was noted following this period indicating that no significant reduction of the Ag(I) species had occurred during this time, Scheme 2.23.

$2[Ag^I(COD)_2]BF_4 \quad + \quad H_2O_2 \quad \rightarrow \quad$ *No Reaction* ...Scheme 2.23

In summary, in addition to facilitating the formation of the key Brønsted acid initiator species as proposed by Decker [405], it is also reasonable to suggest that oxygen may play a role in promoting the cycling of the copper catalyst between lower and higher oxidation states. In so doing the conversion of the weaker Lewis acid Cu(I) Y salt species, an inefficient cationic initiator, to the stronger Lewis acid species Cu(II) XY and XX which can promote the polymerisation of the cationically susceptible monomer independently of and in addition to the iodonium salt decomposition process as originally proposed by Crivello, see Figure 2.2 [285].

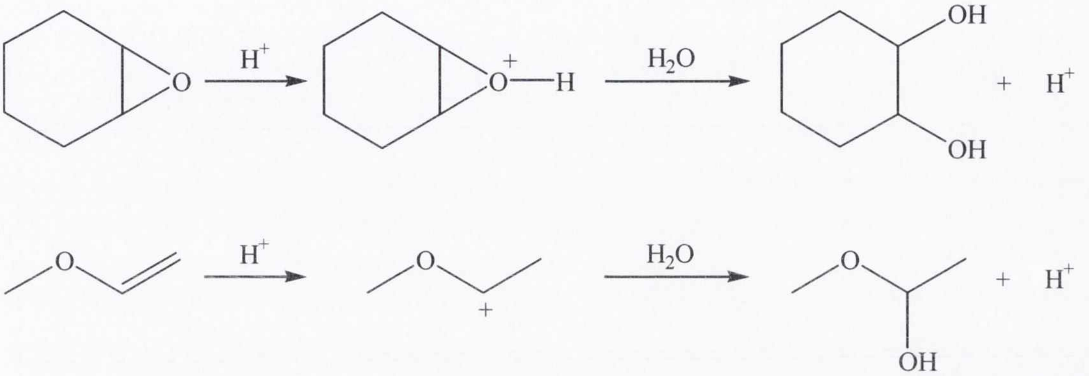
2.5.4 Influence of Water on Copper Catalysed Redox Polymerisations

It is known that cationic polymerisation is influenced by the presence of nucleophilic species such as water [404,411]. The presence of moisture can be both advantageous and disadvantageous with water promoting catalyst formation and also playing a role in chain transfer / termination processes [411]. In real world applications moisture is a ubiquitous and uncontrolled parameter that is subject to seasonal variation. Moisture is almost universally present in commercially available monomers and resins and typically little is done to remove it from formulations. In this study moisture content of the monomers of interest is inherently low with as received moisture content of monomer (**72**) as used in this study being 570 ppm (c. 0.06 %) by Karl Fisher titration. As a comparator, and in order to determine the influence of water on the copper catalysed redox cationic polymerisation systems under study, additional monomer (**72**) was dried by storage over $CaCl_2$ granules for a period of two weeks prior to use resulting in a moisture content of *c.* 100 ppm by Karl Fisher titration. Using the dried monomer, a series of samples were prepared with water contents ranging from c. 3,000 to 16,000 ppm. The cloud point was reached at the c. 16,000 ppm level of water addition to the monomer. All monomer samples were mixed overnight following water addition and prior to addition of the redox initiation system.

The data recorded in Table 2.13 indicate that relatively low concentrations of water have a limited impact on the copper catalysed redox cationic polymerisation system under study. In contrast high concentrations of water result in a significantly lengthened induction period and a general reduction in monomer conversion i.e. 44.5 % at 100 ppm and 40.7% at 16,000 ppm, Figure 2.10.

Several studies have documented the effects of nucleophiles such as water [411-415] and alcohols [416-418] on UV-cationic polymerisations. In typical cationic polymerisation systems oxonium cations derived from epoxy groups and carbonium cations produced from vinyl ether monomers react with water to yield hydroxy terminated species and Brønsted acid. The water thus acts as a chain transfer agent and the Brønsted acid formed is available to react with additional molecules of cationically susceptible monomer thereby generating further propagation sites, Scheme 2.24. Water is generally considered to retard cationic polymerisation

[20,412414]. However, Crivello has also demonstrated that at relatively low concentrations nucleophilic species, such as alcohols, can be useful accelerators of cationic polymerisation. In contrast, at higher concentrations these same nucleophilic species tend to inhibit cationic polymerisation [417,418].



... Scheme 2.24

Table 2.17: Comparison of polymerisation data for monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol with various concentrations of added H_2O

Monomer (mmol)	**Oxidising Agent (mmol)**	**Reducing Agent (mmol)**	**Water (ppm)**	**ΔT (K)**	**$t_{½}$ (s)**	**T_{max} (°C)**	**$T_{½}$ (°C)**	**C (%)**
72 (39.63)	$Ph_2I\ PF_6$ **43** (0.48)	A-6-Hex **64** (0.24)	100	208	57	233	130	44.5
			570	202	59	227	128	43.2
			3,000	205	58	230	129	43.9
			6,000	199	61	224	129	42.5
			10,000	199	67	224	128	42.6
			13,000	197	74	222	125	42.0
			16,000	191	117	216	123	40.7

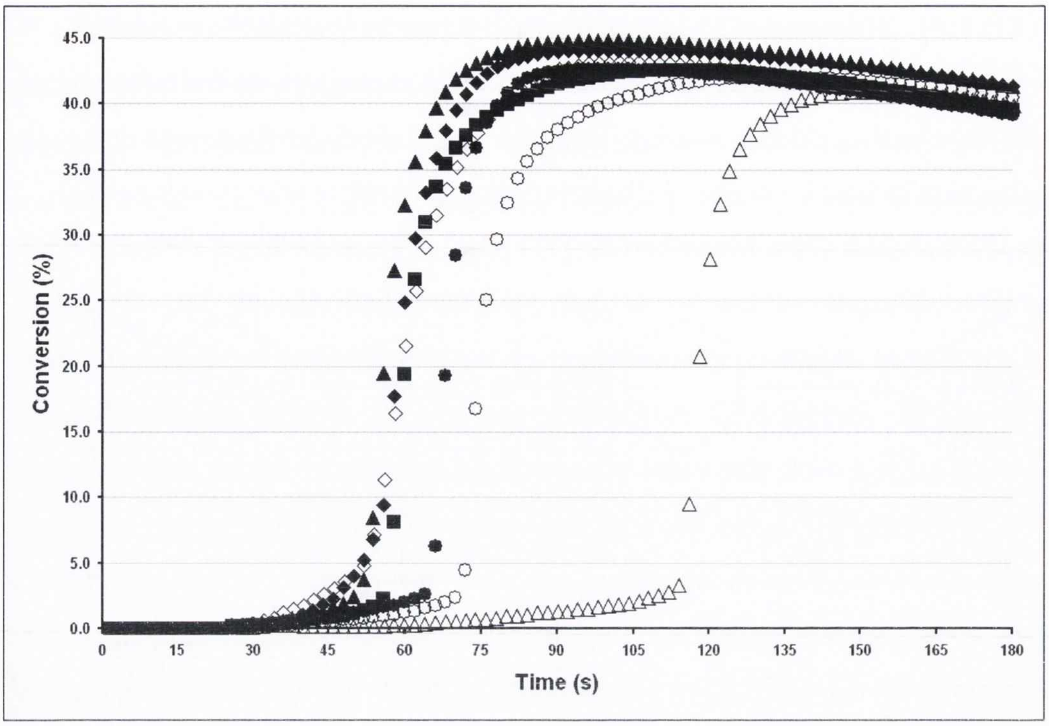


Figure 2.10: Effect of various concentrations of water on conversion (%) of monomer (**72**), 39.63 mmol, initiated by the redox couple $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol and catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. H_2O Content: 100 ppm (▲), 570 ppm (◇); 3,000 ppm (◆); 6,000 ppm (■); 10,000 ppm (●); 13,000 ppm (○) & 16,000 ppm (△)

2.5.5 Influence of the Anion on the Redox Polymerisation Process

Given that the redox potential of the associated cation varies markedly with changing nucleophilicity of the associated counterion, see Table 2.1, and that the larger the diameter of the non-nucleophilic anion the higher the associated conversion to polymer, see Table 2.2. A series of commercially available iodonium salts with increasing strength of the superacid anion were investigated [320,321,334].

The data recorded in Table 2.14 and % conversion profiles depicted in Figure 2.11, confirm that as the nucleophilic character of the anion decreases the degree of conversion to polymer increases. In all cases there is a minimal change in induction period with increasing non-nucleophilic character of the onium salt anion. The order of anion reactivity increases, with % conversion to polymer in parenthesis, is as follows: hexafluorophosphate (42.4 %) < hexafluoroantimonate (46.8 %) < tetrakispentafluoro borate (56.5 %).

Table 2.18: Comparison of data for the redox polymerisation of monomer (**72**), 39.63 mmol, initiated by the Ph_2I cation (**43**) with various anions, 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

	Monomer (mmol)	Oxidising Agent (mmol)	$E_{1/2}$ (V) [320]	Increasing Acidity [334]	Reducing Agent (mmol)	ΔT (K)	$t_{1/2}$ (s)	T_{max} (°C)	$T_{1/2}$ (°C)	C (%)
1	**72** (39.63)	$Ph_2I\ PF_6$ (0.48)	1.44	↓	**64** (0.24)	198	51	223	169	42.4
2	**72** (39.63)	$Ph_2I\ SbF_6$ (0.48)	1.60		**64** (0.24)	219	52	244	169	46.8
3	**72** (39.63)	$Ph_2I\ B(C_6F_5)_4$ (0.48)	- [423]		**64** (0.24)	265	57	290	182	56.5

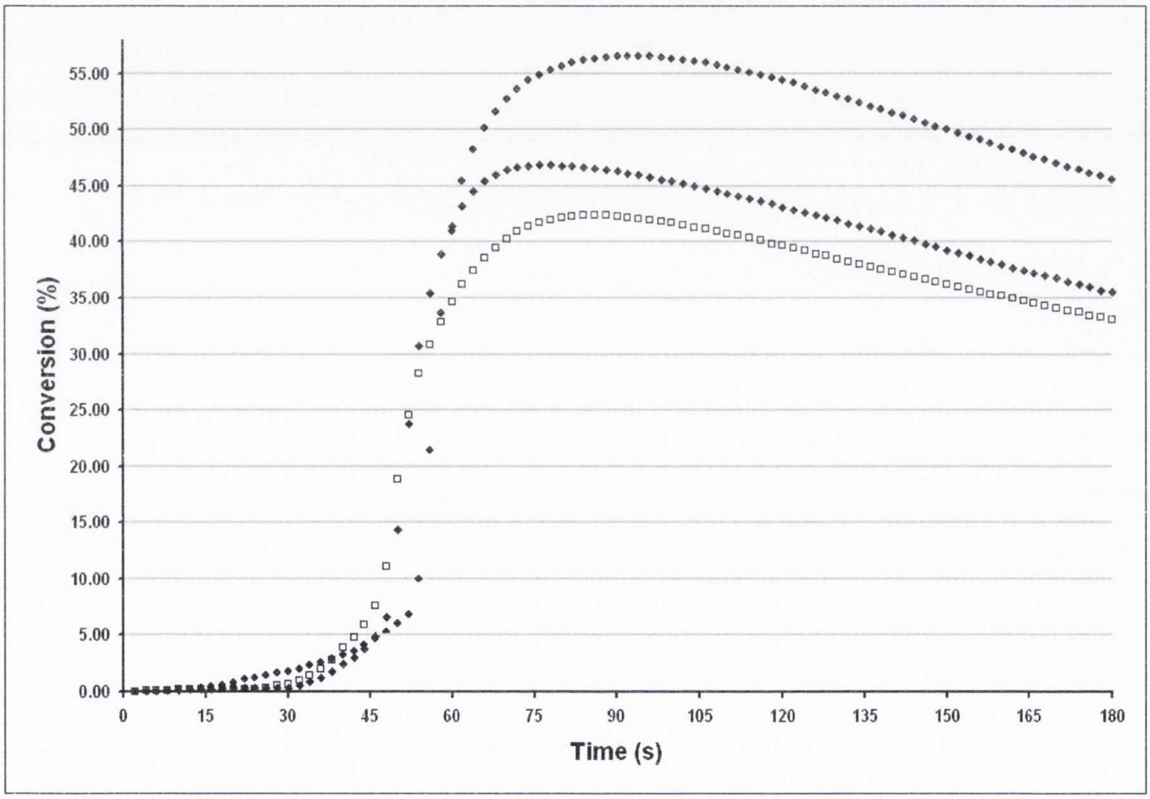
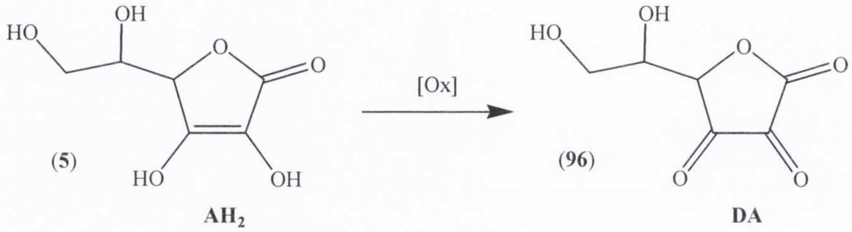


Figure 2.11: Effect of anion type on conversion (%) of monomer (**72**), 39.63 mmol, initiated by the redox couple $Ph_2I\ PF_6$ (**43**) cation with □ PF_6^-, ◆ SbF_6^- & ◆ $B(C_6F_5)_4^-$ anions : A-6-Hex (**64**), 0.24 mmol and catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

2.5.6 The Role of Dehydroascorbyl-6-Hexadecanoate

Ascorbic acid (**59**) is a weak acid and a strong reducing agent, Scheme 2.25. Several attempts were made during this study to prepare and characterise dehydro-ascorbic acid (DA) directly by NMR in a deuterated solvent. While a reaction was observed both visually and spectroscopically, indicating successful oxidation of ascorbic acid, it was difficult to accurately determine the reaction product in-situ.



... Scheme 2.25

Several further experiments were performed in order to prepare and isolate larger quantities of dehydro-ascorbic acid on the bench, following oxidation of ascorbic acid and its derivative A-6-Hex (**64**) with two equivalents of an Ag(I) salt e.g. $AgSbF_6$ and $AgNO_3$ in an organic solvent, typically acetone, Scheme 2.26.

$AH_2 + 2\,AgX \rightarrow DA$ (**87**) $+ 2\,Ag_{(s)} + 2\,HX$ ... Scheme 2.26

While these reactions were also observed to proceed quickly, as indicated by the deposition of Ag(0) on the walls of the reaction vessel, the reaction products were highly acidic and incompatible with cationically polymerisable monomers even following purification by column chromatography. In the case of silver nitrate oxidation of ascorbic acid, the nitric acid by-product of the reaction, which was present in the reaction product, was observed to decompose to the red gas, nitrogen dioxide after short-term storage of the isolated reaction products, Scheme 2.27.

$4\,HNO_3 \rightarrow 4\,NO_2 + 2\,H_2O + O_2$ ... Scheme 2.27

For this reason dehydro-ascorbic acid was prepared via air oxidation catalyzed by Cu(II), based on the procedure developed by Koliou and Ioannou, Scheme 2.28 [406]. The reaction products were isolated for characterisation by FT-IR, MS and NMR.

$$AH_2 + O_{2\,(air)} + MeOH \xrightarrow{Cu(II)} DA\ (\mathbf{88}) + H_2O_2 \quad \ldots \text{Scheme 2.28}$$

The structure of dehydroascorbic acid is very much dependant on the on the solvent in which ascorbic acid is oxidized. Therefore the structure of dehydroascorbic acid is not completely represented by structures **84** or **85**, but it may also be **86** [419], **87** [188,420421] or **88** [249] depending on the oxidation environment.

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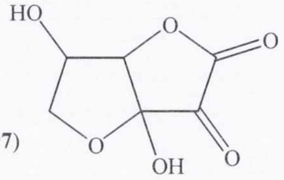

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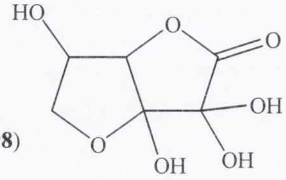

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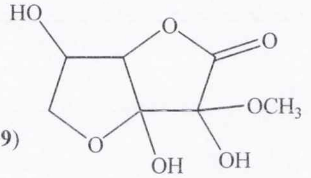

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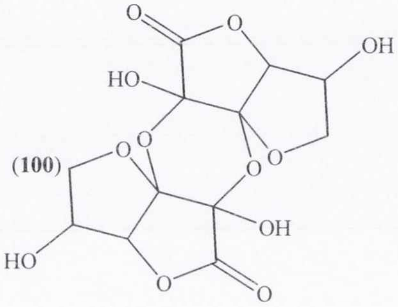


Dehydro-ascorbyl-6-hexadecanoate thus prepared was tested for activity in copper catalysed redox cationic polymerisation, Table 2.19. No significant activity was noted, ΔT: 4 K. This is consistent with a loss in anti-oxidant properties as compared to the A-6-Hex (**64**) starting material.

Table 2.19: Exotherm of polymerisation data for monomer (**72**), 39.63 mmol, initiated by the $Ph_2I\ PF_6$ (**43**) : A-6-Hex (**64**) redox couple & an equivalent couple composed of $Ph_2I\ PF_6$ (**43**) : Dehydro-Ascorbyl-6-Hexadecanoate (**84**) both catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol.

Monomer (mmol)		**Oxidising Agent (mmol)**		**Reducing Agent (mmol)**		**ΔT (K)**	**t½ (s)**	**T_{max} (°C)**	**T½ (°C)**	**C (%)**
72	(39.63)	$Ph_2I\ PF_6$ **43**	(0.48)	A-6-Hex **64**	(0.24)	198.2	51	223.2	169.2	42.4
72	(39.63)	$Ph_2I\ PF_6$ **43**	(0.48)	Dehydro- A-6-Hex **84**	(0.24)	4.0	-	29.0	-	0.8

2.5.7 Reactivity of a Series of Reducing Agents in Copper Catalysed Redox Cationic Polymerisation

Using the optimised model system determined previously the iodonium salt component was maintained constant while the series of reducing agents previously reported by Crivello *et al.* i.e. A-6-Hex (**64**), benzoin (**65**) and tin(II) ethylhexanoate (**66**) were studied to determine their relative efficiencies as reducing agents in redox cationic polymerisation [285,308,309]. No other reducing agents cited in the context of copper catalysed redox cationic polymerisation were found in the literature. As a result a wide range of candidate reducing agents were screened in order to find alternatives that could also be used in the context of redox cationic polymerisation, see Table 2.4 and 2.6. The principle criterion required by candidate reducing agents was the need for non-basic or only mildly basic character so that there would not be significant inhibition of acid catalysed cationic polymerisation. Of the alternative reducing agent investigated only acetyl phenyl hydrazine (APH) and α-tocopherol were found to act efficiently in copper catalysed redox cationic polymerisation, see Table 2.20.

Table 2.20: Comparison of polymerisation data for monomer (**72**), 39.63 mmol, initiated by $Ph_2I\ PF_6$ (**43**), 0.48 mmol : with a series of reducing agents, 0.24 & 0.48 mmol, catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Monomer (mmol)	Oxidising Agent (mmol)	Reducing Agent (mmol)		ΔT (K)	$t_{1/2}$ (s)	T_{max} (°C)	$T_{1/2}$ (°C)	C (%)
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	A-6-Hex (**64**)	(0.24)	198	51	223	169	42.4
			(0.48)	184	39	209	125	38.9
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	Acetylphenyl Hydrazine (**14**)	(0.24)	195	121	220	130	41.7
			(0.48)	190	134	215	117	40.7
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	Sn(II) Ethylhexanoate (**66**)	(0.24)	192	166	217	126	41.0
			(0.48)	187	278	212	117	40.0
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	α-Tocopherol (**67**)	(0.24)	191	435	216	128	40.8
			(0.48)	197	218	222	96	42.0
72 (39.63)	$Ph_2I\ PF_6$ (0.48)	Benzoin (**65**)	(0.24)	164	607	189	101	35.0
			(0.48)	182	576	207	111	39.8

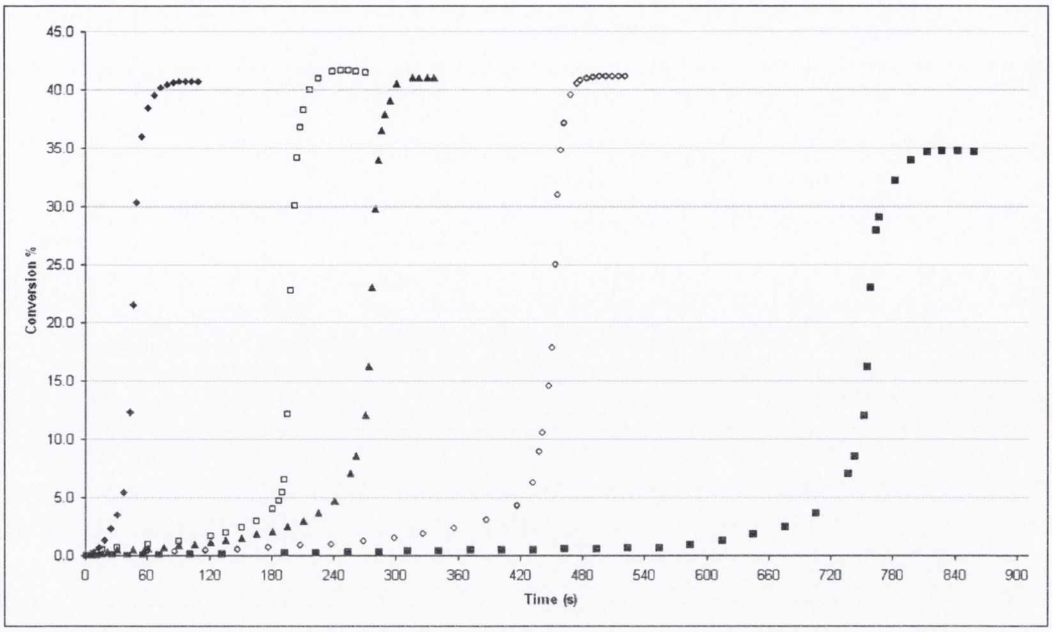


Figure 2.12: Conversion (%) of monomer (**72**), 39.63 mmol, initiated by a series of redox couples employing $Ph_2I\ PF_6$ (**43**), 0.48 mmol as oxidising agent and several reducing agents, 0.24 mmol, catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. ◆ A-6-Hex (**64**); □ Acetyl Phenyl Hydradrazine (**14**); ▲ Tin(II) Ethylhexanoate (**66**); ○ α-Tocopherol (**67**); ■ Benzoin (**65**)

The plot of degree of conversion versus time for the range of reducing agents successfully tested is presented in Figure 2.12. Each species results in a similar degree of conversion to polymer of the bi-functional cycloaliphatic monomer, i.e. c. 41%, although benzoin does show slightly reduced conversion efficiency. The relative efficiencies as defined by the half-time, $t_{½}$ (s), found for the five reducing agents in decreasing order of effectiveness is: A-6-Hex **(64)** > Acetyl Phenyl Hydrazine (**14**) > Tin(II) Ethylhexanoate (**66**) > α-Tocopherol (**67**) > Benzoin (**65**).

2.5.8 Reactivity of a Series of Cationic Initiators as Oxidising Agents in Copper Catalysed Redox Cationic Polymerisation

Using the *$Ph_2I\ PF_6$ (43): A-6-Hex (64)* couple determined previously as a control a series of cationic initiator species substituted for the oxidising agent were studied to determine their relative efficiencies in copper(II) catalysed redox cationic polymerisation, Table 2.21.

Table 2.21: Comparison of polymerisation data for monomer (**72**), 39.63 mmol, initiated with a series of Oxidising Agents, 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Monomer (mmol)		Oxidising Agent (mmol)		Reducing Agent (mmol)		ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
72	(39.63)	$Ph_2I\ PF_6$ **43**	(0.48)	A-6-Hex	(0.24)	198	51	223	169	42.4
72	(39.63)	$Ph_3S\ SbF_6$ **44**	(0.48)	A-6-Hex	(0.24)	4.5	-	29.5	-	0.9
72	(39.63)	ETA PF_6 **53**	(0.48)	A-6-Hex	(0.24)	4.0	-	29.0	-	0.8
72	(39.63)	ENA PF_6 **52**	(0.48)	A-6-Hex	(0.24)	6.0	-	31.0	-	1.3
72	(39.63)	BENA PF_6 **60**	(0.48)	A-6-Hex	(0.24)	4.5	-	29.5	-	0.9
72	(39.63)	EPA PF_6 **54**	(0.48)	A-6-Hex	(0.24)	3.8	-	28.8	-	0.8

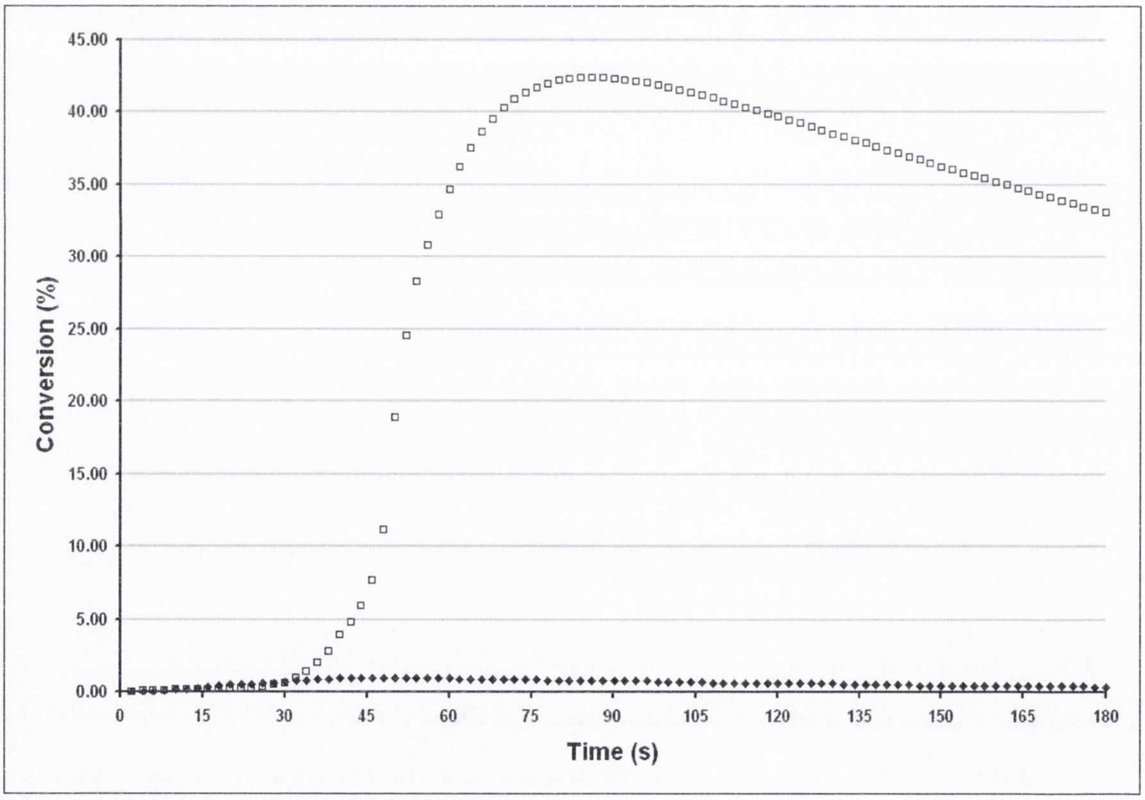


Figure 2.13: Conversion (%) of monomer (**72**), 39.63 mmol, initiated by a series of redox couples employing A-6-Hex (**64**), 0.24 mmol as reducing agent and several oxidising agents, 0.48 mmol, catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. □ $Ph_2I\ PF_6$ (**43**); ◆ Typical cure profile for the remaining cationic initiators investigated

None of the typical cationic initiator species examined showed promise as an alternative to Ph_2I salts in the copper catalysed redox cationic polymerisation of the bi-functional epoxy monomer, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate. A typical plot for conversion (%) versus time (s) for the range of oxidising agent components studied are presented in Figure 2.13. Each of the alternative cationic initiator species resulted in <1% conversion of the of the bi-functional cycloaliphatic monomer to polymer. This confirms the literature determination that Ph_2I salts have a redox potential that is favourable for reduction in these copper catalysed redox systems while triaryl sulphonium, allyl thiophenium, allyl pyridinium and allyl triphenyl phosphonium were all shown to be extremely inefficient.

2.5.9 Relative Reactivity of a Range of Cationically Polymerisable Monomers using the Diphenyliodonium Hexafluorophosphate : Ascorbyl-6-hexadecanoate Redox Couple

The major factors understood to contribute to the reactivity of cationically susceptible monomers are the relative nucleophilicity (reflects the ability to combine with an electrophilic substrate), basicity, ring-strain and steric hindrence [168]. The lower reactivity of this cycloaliphatic epoxy bisepoxide, relative to cyclohexene oxide, has been attributed the interaction of the ester carbonyl group with the initially formed protonated or alkylated oxonium cation to give bicylic dialkoxycarbenium ions. These species are more sterically hindered as well as having lower reactivity than the oxonium cation precursor and undergo propagation at a significantly reduced rate [425,426].

For industrial applications a large number of cationically susceptible monomers and resins are frequently used when developing UV curing epoxy products. Of these cycloaliphatic epoxies, e.g. monomer (**72**), are most commonly used. Additionally, epoxy resins are often blended with other epoxies or cationically curable resins and additives [427]. This allows better overall performance to be achieved through tuning cure speed, thermal stability, mechanical perfomance, as well as environmental resistance. PC-1000 (**75**), a cyclopaliphatic epoxy siloxane, for example is considered to be one of the most reactive difunctional cycloaliphatic epoxide monomers used in photoinitiated cationic polymerisation [428]. Vinyl ethers are commonly used as accelerators of cationic polymerisation [429,430]. Also such conventional epoxy resins such as diglycidal ether of bisphenol-A, while not widely used in cationically polymerisable compositions due to their relatively low cationic susceptibility, may impart beneficial properties if used as an additive [431].

The *Ph_2I PF_6 **(43)**: A-6-Hex **(64)*** redox couple was prepared in a series of cationically susceptible monomers as detailed in Table 2.17. The theoretical enthalpies (ΔH_T) for the various monomers under investigation were calculated using the method described in section 2.3.3. The relative reactivity of this range of monomers was determined by monitoring their exotherm of polymerisation and relating this to the degree of conversion to polymer, %, versus time using Equations 2.1, 2.2 and 2.3. The results obtained are presented in Table 2.22 and Figure 2.14.

Table 2.22: Comparison of polymerisation data for a series of commercially useful monomer (**72**), 39.63 mmol, initiated by the Ph_2I PF_6 (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, redox couple catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol

Monomer (mmol)	ΔH_T (Jg^{-1})	Oxidising Agent (mmol)	Reducing Agent (mmol)	ΔT (K)	$t_{½}$ (s)	T_{max} (°C)	$T_{½}$ (°C)	C (%)
72 (39.63)	748.8	Ph_2I PF_6 **43** (0.48)	A-6-Hex **64** (0.24)	198	51	223	169	42.4
74 (39.63)	555.0	Ph_2I PF_6 **43** (0.48)	A-6-Hex **64** (0.24)	4.2	-	29.2	-	1.2
75 (39.63)	493.7	Ph_2I PF_6 **43** (0.48)	A-6-Hex **64** (0.24)	97	47	122	68.5	31.6
76 (39.63)	591.7	Ph_2I PF_6 **43** (0.48)	A-6-Hex **64** (0.24)	287	114	312	189	77.7

The relative copper(II) catalysed redox cationic reactivity of the four monomers investigated, as determined by conversion %, decreased in the order triethylene glycol divinyl ether (**76**) > 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (**72**) > 1,3-Bis[2-(3,4-epoxycyclohexyl)ethyl]-1,1,3,3-tetramethyl disiloxane (**75**) > 4,4'-Isopropyl-idenediphenol diglycidal ether (**74**). This general trend is reasonable and supports literature precedent. The vinyl ether species undergoes significantly higher conversion than the other cationically polymerisable monomers, while both cycloaliphatic monomers have relatively similar cure profiles.

In contrast the bisphenol A epoxy monomer has a very poor degree of conversion which is also consistent with the theoretical susceptibility of such monomers to initiation by a cationic mechanism. While there was no strong exotherm of polymerisation the bulk bisphenol A epoxy monomer containing the optimised redox couple was observed to gel and convert to solid polymer during a period of 24 hrs following copper(II) catalysis.

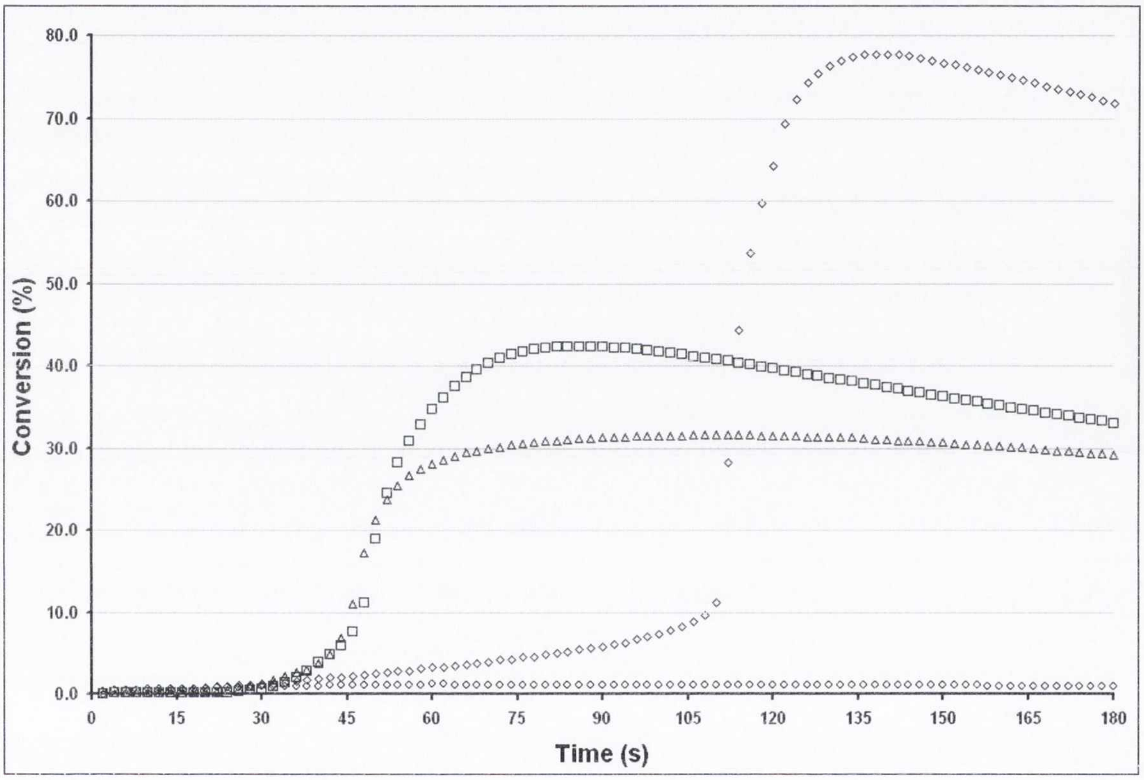


Figure 2.14: Conversion (%) of a series of monomers, 39.63 mmol, initiated by the redox couple $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol and catalysed by $Cu(NO_3)_2$ (**77**), 0.027 mmol. □ 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (**72**), ◇ 4,4'-Isopropyl-idenediphenol diglycidal ether (**74**), △ 1,3-Bis[2-(3,4-epoxycyclohexyl) ethyl]-1,1,3,3-tetramethyldisiloxane (**75**) & ◇ DVE3 (**76**)

2.5.10 Surface Promoted *Catalysis* Properties of Copper(II) Catalysed Crivello-type Redox Couples

In order for transition metal salt catalysed redox cationic initiation chemistry to be deemed useful for development of a one-component room temperature curing adhesive technology, analogous to existing radically polymerisable redox anaerobic adhesive systems, it is not sufficient for the optimised redox couples to show reactivity in bulk matrices as described thus far. The polymerisable system must also be able to cure in a two-dimensional bondline without mixing with the activating catalyst and ideally the surface to be bonded should be sufficiently active to promote catalysis of the redox reaction without addition of further activator. Tensile strength cure profiles for the optimised redox couple Ph_2I PF_6 (**43**) : A-6-Hex (**64**) in monomer (**72**) on standard grit blasted mild steel surfaces were recorded using the described procedure. Two experimental treatments were investigated:

- Solvent wiped grit blasted mild steel.
- Copper(II) primed grit blasted mild steel. The primer used in this study for promotion of redox cationic polymerisation was a commercial product originally developed for use with radically polymerisable anaerobic acrylate adhesives [432]. The primer consisted of a 1 % solution of copper(II) ethylhexanoate in acetone.

As can be seen from the tensile strength cure profile presented in Figure 2.15 and data in Table 2.23, the optimised Ph_2I PF_6 (**43**) : A-6-Hex (**64**) redox couple developed in the study is not sufficiently reactive to promote cationic polymerisation even over a 72 hour period at room temperature in the absence of a catalytic amount of copper(II) primer on the substrate surface. It is therefore apparent that this redox couple configuration is of necessity composed of two-parts, a copper catalyst solution for activation of surfaces and the redox couple containing monomer solution. This indicates that the redox potential of the Ph_2I PF_6 (**43**) : A-6-Hex (**64**) redox couple alone is not favourable for activation by substrate impurities alone. This contrasts sharply with the commercially useful redox anaerobic adhesive chemistry, polymerised by radical cure mechanism, which is readily activated by the presence of surface impurities in mild steel albeit combined with a secondary anaerobic cure mechanism.

Table 2.23: Tensile adhesive strength unprimed and Cu(II) primed grit blasted mild steel (GBMS) substrates using the redox couple $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, in the monomer (**72**), 39.63 mmol. The adhesive strength of neat Monomer (**72**) on a Copper primed GBMS substrate is also shown as a control experiment.

Test Samples		Neat Monomer (**72**) *Control*	(**43**) 0.48 mmol : (**64**), 0.24 mmol in Monomer (**72**) 39.63 mmol	
Substrate		Cu(II) / GBMS	GBMS	Cu(II) / GBMS
		Tensile Strength (N/mm^2)		
Time (Hours)	**0**	0.0	0.0	0.0
	12	0.0	0.0	3.0
	24	0.0	0.0	9.0
	72	0.0	0.0	14.0

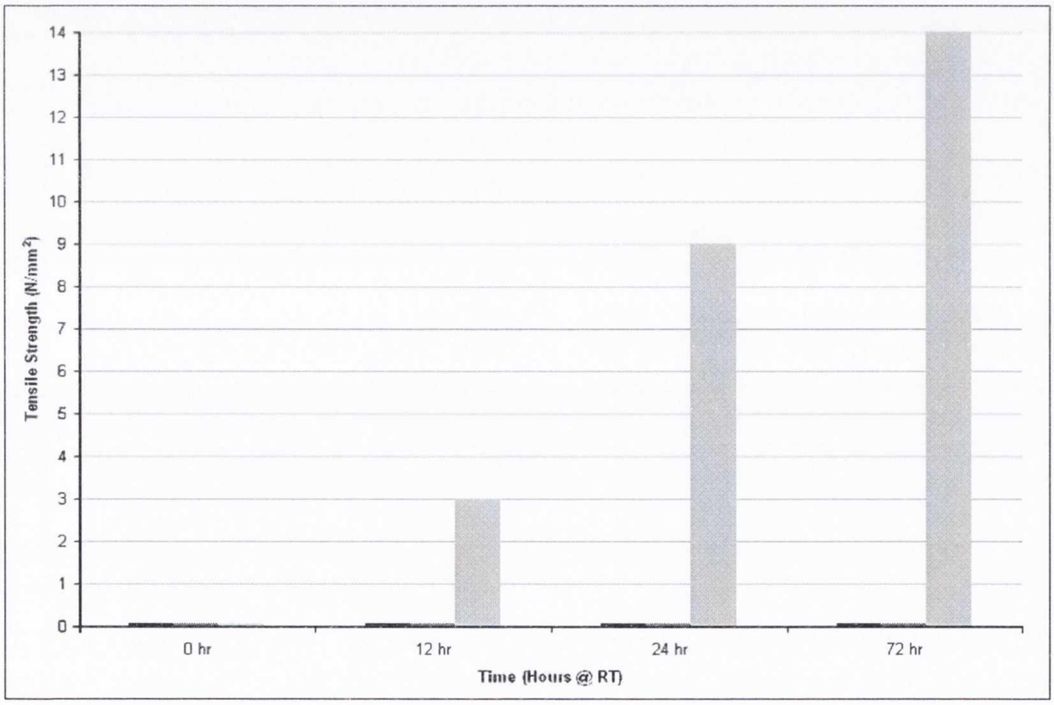


Figure 2.15: Room temperature tensile strength cure profile for unprimed (▩) and Cu(II) primed (░) grit blasted mild steel substrates using the optimised redox couple, $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, in the monomer (**72**), 39.63 mmol. A control showing activity of neat Monomer (**72**) on a Copper primed GBMS substrate is also shown (■).

2.5.11 Activity of Copper(II) Catalysed Crivello-type Redox Couples over Time

The activity of the preferred $Ph_2I\ PF_6$ (**43**) : A-6-Hex (**64**) redox couple as a function of time (days) in monomer (**72**) was investigated by preparing several replicates which could be tested for reactivity at pre-determined intervals following storage at 25 °C or refrigeration at 5 °C, Figure 2.16.

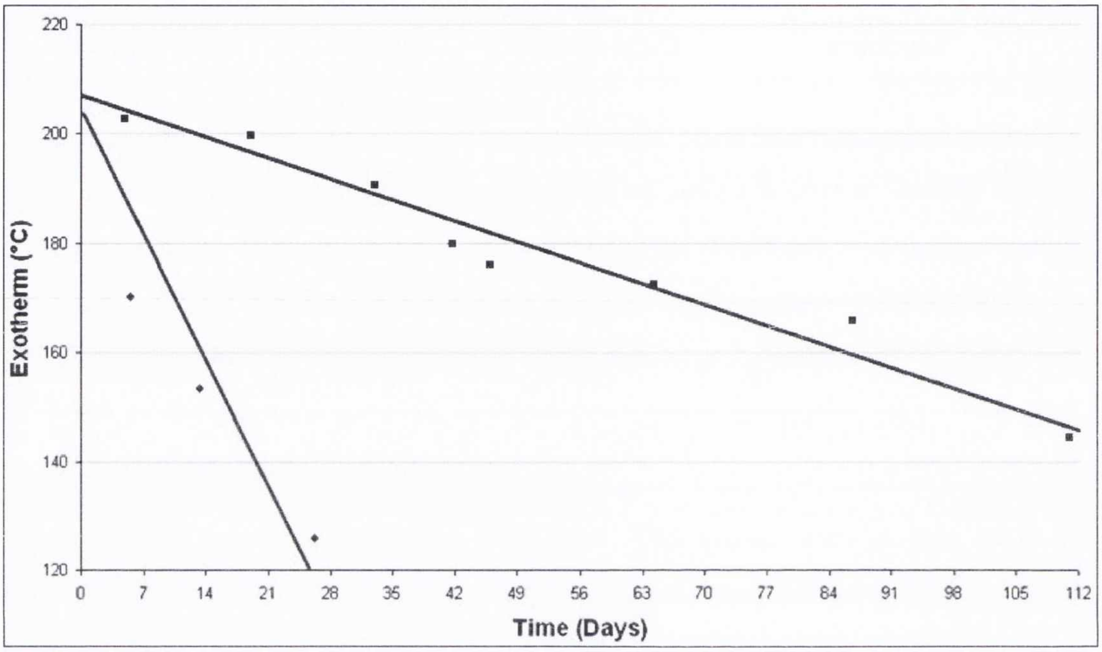


Figure 2.16: Loss in reactivity as measured by T_{max} polymerisation (°C) versus time (days) for the optimised redox couple, $Ph_2I\ PF_6$ (**43**), 0.48 mmol : A-6-Hex (**64**), 0.24 mmol, in the monomer (**72**), 39.63 mmol following storage at ambient temperature, 25°C (■) and under refrigeration, 5°C (◆).

Unlike redox radical polymerisation, the reducing and oxidising component in cationic redox couples as currently known are not by air stabilised. Consequently there is a slow but on-going release of Brønsted acid into the monomer, which polymerises gradually (gels) over several weeks. **Therefore Crivello-type redox cationic systems have an inherent instability and are not suitable for long-term storage.** Stabilisation of redox cationic systems is not straightforward as the addition of proton sponges; for example, in the form of amines to eliminate any acid produced tends to inhibit polymerisation of the monomer itself. There is a very fine balance between addition of too much stabiliser and insufficient stabiliser to maintain the long-term polymerisability of the system.

2.6 Conclusion

The major conclusions from the current study may be summarised as follows:

1. Direct reduction of iodonium salts by a reducing agent is an inefficient process.

2. Previous work has circumvented the shortcoming in (1) through incorporation of a copper(II) catalyst species to effect efficient electron transfer, thereby promoting efficient cationic polymerisation.

3. Copper catalysed redox cationic polymerisation systems are inherently unstable and this was due to slow electron transfer between the reducing agent and the onium salt. Consequently there is a dramatic decrease in reactivity over a relatively short period of time.

4. The presence of oxygen in the monomer was shown to increase the rate of polymerisation of copper catalysed redox cationic initiation systems relative to systems that have been thoroughly de-oxygenated. Experimental evidence suggests that the presence of oxygen may promote rapid formation of strongly Lewis acidic Cu(II) XY and XX species (X is a non-nucleophilic anion), which have been shown to be efficient initiators or co-initiators of cationic polymerisation.

5. In the presence of water at concentrations up to 6,000 ppm little difference was observed in the polymerisation characteristics versus equivalent dry systems. However, at higher concentrations of water, >10,000 ppm, there was a significant increase in $t_{½}$ although the impact on conversion % was minimal.

6. Varying the non-nucleophilic character of the anion associated with the iodonium salt showed:
    a. The non-nucleophilic character of the anion had only a limited influence on the induction period for copper catalysed redox cationic polymerisation.
    b. However as the anion becomes increasingly non-nucleophilic in character the degree of conversion to polymer also increases: tetrakispentafluoro borate (56.5 %) > hexafluoroantimonate (46.8 %) > hexafluorophosphate (42.4 %).

7. It has been shown that the reducing agents acetyl phenyl hydrazine and α-tocopherol can also be employed in analogous copper(II) catalysed redox couples with Ph_2I salts.

8. However, the original Crivello redox couple based on iodonium salt and ascorbic acid *is* the most efficient of the copper catalysed redox systems studied. Even having given consideration to several alternative candidate oxidising agent cations.

It is clear from the experimentation conducted that the existing copper(II) catalysed redox cationic initiation systems are rather crude, and in their current form are of no importance in commercial adhesive systems, since a third component, the catalyst, must be added to effect cure and these systems are inherently unstable with time. These findings have not been reported previously in the literature but perhaps go some way to explain the exisiting gap in the development of a stable single component redox activated cationic adhesive. On the basis of these findings a clear goal exists to develop novel approaches to ambient temperature surface promoted redox cationic polymerisation and thereby improve this poisiton.

CHAPTER THREE | A NOVEL APPROACH TO AMBIENT TEMPERATURE SURFACE PROMOTED REDOX CATIONIC POLYMERISATION

While known for several decades the original Crivello-type [285,308,309], and subsequent Yagci-type [249,316], redox cationic polymerisation systems, introduced in detail in Chapter Two, are ostensibly the closest existing chemical technology with the potential for realising the goal of a "one-component, room temperature curing epoxy". However, as demonstrated, Crivello-type redox systems are not sufficiently sensitive to achieve room temperature polymerisation without the use of a copper(II) primer to promote efficient electron transfer between the redox couple components. A further obstacle to their real-world development is the limited storage stability of these systems due to continual albeit slow electron transfer between the reducing agent and the onium salt oxidant, even in the absence of added catalyst. These limitations need to be addressed.

3.1 Exploiting the Redox Potential of Substrates: An Approach to Surface Promoted Redox Cationic Polymerisation

Given the important role played by the substrate in anaerobic redox radical polymerisation (page 10) it was of interest to consider in what way a metallic substrate could participate in activation of a stable single-component cationic cure system. In the former the effect is catalytic and the polymerisations are extremely efficient. In addition to known anaerobic redox radical polymerisations which may be considered a form of surface promoted polymerisation (SPP), the literature also describes several alternative modes for achieving SPP: Copper-catalysed azide-alkyne cycloaddition [434], and the diazonium induced anchoring process (DIAP) a method of radical polymerisation at iron surfaces [435,436]. Additionally several instances of surface initiated living polymerisations have also been reported including radical [437,438], cationic [439] and anionic [440] mechanisms.

A key feature of surface promoted polymerisation processes is that the substrate forms an integral part of the redox chemistry by playing either a catalytic role or by functioning as a reducing agent. Notwithstanding that scientific precedent points towards catalysis as a means of activating redox cationic polymerisation, a number of considerations are important:

1. Oxygen does not contribute to the stabilisation of redox *cationic* systems. Consequently only a surface promoted mechanism can be relied upon to invoke redox cationic polymerisation.

2. A latent cationic redox couple cannot be held indefinitely as a stable unit in a cationically polymerisable matrix.

3. The high substrate catalyst concentration required for activation of redox cationic polymerisation, relative to anaerobic redox radical polymerisation, indicates that catalysis alone cannot be relied upon as a means of promoting cure of redox cationic systems.

However, one could speculate that if a suitable redox potential gap could be designed into an alternative redox cationic initiation system then a judiciously selected latent cationic initiator, the oxidant, could be reduced stoichiometrically when contacted with an appropriate substrate, the reductant.

3.1.1 The Reduction Potentials of Onium Salt Latent Cationic Initiators

The majority of latent cationic initiators are ionic species. The ease with which each of these can be reduced by photochemical or thermal means to release the initiating species is related to their reduction potential, Table 3.0 [20].

No reports have been found for surface induced *cationic* polymerisations employing onium salts, including systems analogous to those used in the diazonium induced anchoring process [435]. With the exception of the diazonium salts, which are not favoured for typical adhesive applications due to their inherent thermal instability, the diphenyliodonium cation (Ph_2I^+) is acknowledged as the most readily reducible onium salt cationic initiator [20]. Yet when dissolved in a polymerisable monomer and applied to the surface of a desired substrate, cationic polymerisation has not been reported to occur unless additional stimulus in the form of thermal or photo energy is used. The surface is accepted as being passive in these polymerisation processes.

Table 3.0: Literature $E_{1/2}^{red}$ values for a Series of Latent Cationic Initiator Species

Cation Species	**$E_{1/2}^{red}$ (SCE) *V***	**$E_{1/2}^{red}$ (NHE)* *V***	**Ref.**
Phenyl Diazonium	+ 0.35	+ 0.59	[247]
Diphenyliodonium	- 0.2	+ 0.04	[248]
N-Ethoxy Isoquinolinium	- 0.4	- 0.16	[188,249]
N-Ethoxy-*p*-Phenyl Pyridinium	- 0.46	- 0.22	[249]
Ethyl-α-(Tetrahydrothiophenium Methyl) Acrylate	- 0.58	- 0.34	[225]
N-Ethoxy-2-Methyl Pyridinium	- 0.7	- 0.46	[217]
Ethyl-α-Triphenylphosphonium Acrylate	- 0.95	- 0.71	[250]
Triphenylsulphonium	- 1.06	- 0.82	[251]

*NHE values are obtained according to the relationship E (NHE) = E (SCE) + 0.24 V, from the literature experimental potentials V vs. SCE [441]

3.1.2 The Reduction Potential of Selected Metallic Substrates

However, as evidenced by the surface promoted polymerisations described (page 99), e.g. the diazonium induced anchoring process, *metallic* substrates can function as reducing agents. This property may be employed to realize the surface promoted cationic polymerisations sought. The reduction potentials of several metallic elements commonly used as substrates in adhesive bonding are shown in Table 3.1

Table 3.1: Literature $E_{1/2}^{red}$ values for a Series of Metals Used as Adhesive Substrates [443]

Metal Species	**$E_{1/2}^{red}$ (NHE) *V***
$Al^{3+} + 3e^- \rightleftharpoons Al$	- 1.66
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	- 0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	- 0.44
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34

N.B. The values apply to STP conditions, employing standard 1 M *aqueous* solutions

3.1.3 The Reduction Potentials of Selected Metal Cations

In fact not only are metals widely used as substrates for adhesive bonding but many metal salts, or Lewis acids, have also been employed as initiators for cationic polymerisation [450-452]. Furthermore, metal salts typically have even more favourable redox potentials than the majority of onium cations, Table 3.2.

Table 3.2: Literature values for the $E_{½}^{red}$ for a Series of Metal Cations [443,444]

Metal Species	**$E_{½}^{red}$ (NHE)* *V***
$Ag^{+} + e^{-} \rightleftharpoons Ag$	+ 0.80
$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	+ 0.77
$Cu^{+} + e^{-} \rightleftharpoons Cu$	+ 0.52
$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$	+ 0.16

N.B. The values apply to STP conditions, employing standard 1 M *aqueous* solutions

3.1.4 Overview of the Reduction of Latent Initiators in Cationic Polymerisations

Diphenyliodonium salts have high reduction potentials when compared to alternative onium salt latent catalysts, Table 3.0. They are considered to be relatively good oxidants, and they have been used frequently for the oxidation of photo-generated free radicals. By contrast, triphenylsulphonium salts have a much lower reduction potential which significantly limits their use as oxidants. The most strongly oxidising latent cationic initiators including those that have been studied in radical promoted cationic polymerisations include:

i. *Diphenyliodonium salts*, of non-nucleophilic anions, are typically used as photoinitiators for cationic polymerisation. In addition to the work by Crivello *et al.* outlined in Chapter Two [173,204], Ledwith proposed an alternative redox radical-chain mechanism for the decomposition of iodonium salts [252-254]. Due to their relatively high redox potential, $E_{½}^{red} = +0.04$ V vs NHE, iodonium salts are more often used in the presence of photo radical generators in order to facilitate onium salt decomposition at longer, lower energy wavelengths. Experiments employing thermally generated radicals in the presence of onium salt electron acceptors and a kinetic analysis of the cationic polymerisation were published in support of this second cationic initiation pathway, Scheme 3.0 [287,366].

$$\begin{array}{llllll}
\mathrm{Ar_2I^+} & \xrightarrow{h\nu} & \mathrm{Ar{-}I^{+}\cdot + Ar\cdot} & \text{(a)} & & \\
\mathrm{Ar\cdot + MH} & \xrightarrow{k_{\mathrm{abs}}} & \mathrm{ArH + M\cdot} & \text{(b)} & \textit{where } \mathrm{M} = \textit{Monomer} & \\
\mathrm{M\cdot + Ar2I^+} & \xrightarrow{k_{\mathrm{SET}}} & \mathrm{M^+ + Ar_2I\cdot} & \text{(b)} & & \\
\mathrm{Ar_2I\cdot} & \rightarrow & \mathrm{ArI + Ar\cdot} & \text{(c)} & & \\
\mathrm{ArI^+\text{-}H} & \rightarrow & \mathrm{Ar{-}I + H^+} & \text{(d)} & & \\
\mathrm{M^+ + MH} & \rightarrow & \text{Polymer} & \text{(e)} & & \text{… Scheme 3.0}
\end{array}$$

Kampmeier and Nalli have also demonstrated that non-photochemical initiators can promote the same modes of onium salt decomposition and that the typically used photochemical step is solely a commencement step leading to the decomposition of the onium salt [342,343].

ii. *N-alkoxy pyridinium, allyl thiophenium and related salts* of non-nucleophilic anions, were developed with a view to enhancing the radical susceptibility of onium type salts to radical promoted cationic polymerisation. These salts have been studied extensively by Yagci and co-workers [188,217,250].

iii. *Diazonium salts*, of non-nucleophilic anions, were one of the first latent initiators used for cationic photo-initiation [459]. Diazonium salts are generally understood to be relatively unstable compounds and for this reason their use as cationic initiators has been limited in favour of other more stable onium salt initiators. However, 4-alkoxysubstituted diazonium salts with non-nucleophilic anions e.g. BF_4^-, PF_6^-, SbF_6^- etc. have been shown to possess good thermal stability in several solvents [461]. Even though they possess the most positive redox potential of the onium salts they have not received as much attention for radical promoted cationic polymerisations [247,460].

iv. Ledwith has also studied analogous systems employing *silver salts* ($E_{1/2}^{\mathrm{red}} = +0.8$ V), of non-nucleophilic anions, as latent initiators of cationic polymerisation that are reduced by radical species as a precursor to Brønsted acid generation [376].

3.1.5 Identification of Redox Couples with a view to achieving Surface Promoted Redox Cationic Polymerisation

A crucial aspect of the controlled initiation of cationic polymerisation is the generation of a strongly acidic initiator species within the monomer system on-demand. The major objective of this chapter is to seek ways of generating the required strong acid using a one-component, stable, yet readily polymerisable system with the only additional contributor to the polymerisation being the surface to which the formulation will be applied – without the use of any form of external energy i.e. heat or light. In order to realise this objective it is essential to understand and be able to predict which latent cationic initiators will lend themselves, at least in principle, to reduction by selected metallic substrates.

The efficiency of an oxidising agent is directly related to its affinity for electrons. As such the higher the oxidation power of the oxidising species the more positive or higher is its associated reduction potential, $E_{½}^{red}$ [23]. By way of contrast the better the reducing power of a reductant the more negative or lower is its associated reduction potential. Only if the difference between the reduction potentials of the reducing species and the oxidizing species, i.e. ΔE^0 or E_{cell}, is positive is the redox reaction thermodynamically feasible, Equation 3.0 [258].

$$E_{cell} = E_{½}^{red}{}_{(Oxidant)} - E_{½}^{red}{}_{(Reductant)} > 0 \qquad \text{... Equation 3.0}$$

Using iron, ostensibly Fe(0), as a theoretical model substrate for adhesion, one can observe from Table 3.3 that the predicted redox activity trend for the selected cations would be Ag(I) > RN_2^+ > Cu(I) > Ph_2I^+. Therefore it is to be expected that silver(I) cations should in principle facilitate realisation of the aforementioned objective.

Table 3.3: Thermodynamic feasibility, based on theoretical E_{cell} values for the reduction of a series of potential latent cationic initiator cations by Fe(0), (V vs NHE)

Oxidant (Substrate)	$E_{½}^{red}$ *V*	Reductant (Substrate)	$E_{½}^{red}$ *V*	E_{cell} (*V*)	Thermodynamic Feasibility
Ag^+	+ 0.80	Fe(0)	- 0.44	+ 1.24	Higher
RN_2^+	+ 0.59	Fe(0)	- 0.44	+ 1.03	↓
Cu^+	+ 0.52	Fe(0)	- 0.44	+ 0.96	
Ph_2I^+	+ 0.04	Fe(0)	- 0.44	+ 0.48	
Ph_3S^+	- 0.82	Fe(0)	- 0.44	- 0.38	Lower

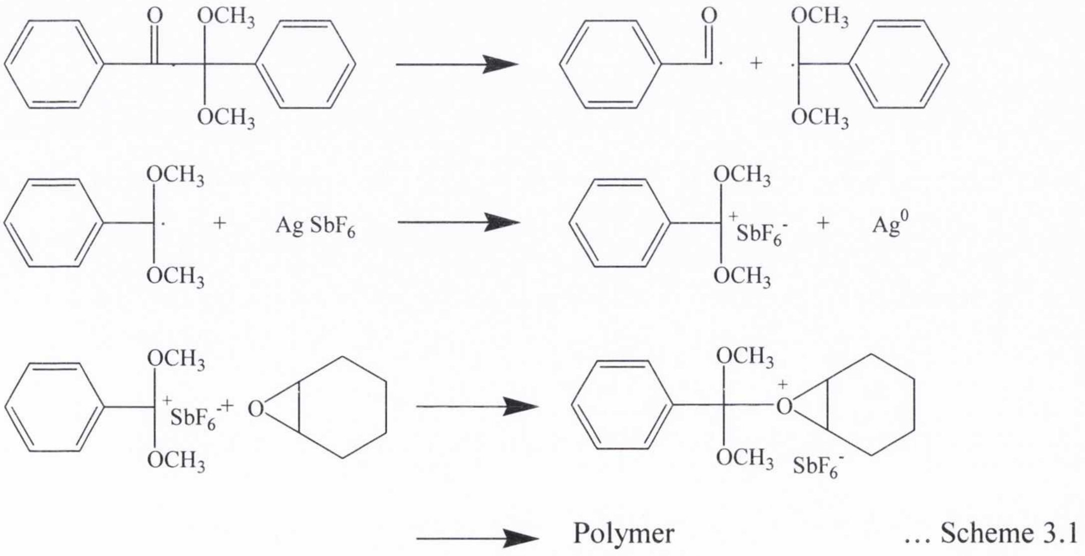
The thermodynamic feasibilities (E_{cell}) presented in the theoretical redox couples above provide a *guide* to initial selection of a preferred candidate latent cationic initiator species, i.e. *silver(I)*, for study in the context of surface promoted redox cationic polymerisation.

Nonetheless, while these figures are indicative of redox couple compatibility other factors including inherent surface oxides and the ability to regulate reduction potentials by means of such factors as solvent environment, anion type and ligand selection etc. must also be considered. Such aspects clearly require careful evaluation and scrutiny during the course of experimental validation of the concepts presented here.

3.2 Silver(I) Salts as Latent Initiators of Cationic Polymerisation

Silver(I) salts of non-nucleophilic anions have been employed by several research groups as initiators for cationic polymerisation [453-458]. Ledwith and co-workers have reported silver(I) salts as suitable oxidants for radical promoted cationic polymerisations, Scheme 3.1 [376]. In such polymerisations Ag(I) functions as a one electron oxidant for electron donor radicals in a manner similar to that previously established for organic cation salts [376].

Yagci *et al.* have used the reduction of silver salts of non-nucleophilic anions by photo-generated radicals for the preparation of silver-epoxy nano-composites [455,456].



... Scheme 3.1

Silver(I) olefin complexes have been reported by Barriau *et al.* as storage stable yet efficient latent initiators for the electron-beam (EB) curing of cationically polymerisable compositions [457]. In this instance epoxy polymerisation is reported to be initiated by Lewis acidic and oxophilic Ag^+ species that form upon irradiation by the electron-beam source.

More recently Fouassier and co-workers have described the *redox* cationic polymerisation of epoxy and vinyl ether compositions by employing a silane : silver(I) salt redox couple in which the silane species is the reductant and the silver(I) salt of a non-nucleophilic anion is the oxidant, Scheme 3.2 [458].

$$2R_3SiH \quad + \quad 2AgSbF_6 \quad \rightarrow \quad 2R_3Si^+SbF_6^- \quad + \quad 2Ag(0) \quad + \quad H_2$$

$$2R_3SiH \quad + \quad 2AgSbF_6 \quad \rightarrow \quad 2R_3Si^+SbF_6^- \quad + \quad 2Ag(0) \quad + \quad H^+SbF_6^-$$

… Scheme 3.2

Given the many instances of silver(I) being employed as a latent catalyst for cationic polymerisation and the prior discussion on redox potentials it is worth noting the lack of reports on its use in the context of *surface promoted redox cationic polymerisation.*

3.3 An Overview of Lewis Acids as Initiators of Cationic Polymerisation

Lewis acids are amongst the most important initiators for cationic polymerisation, and they can form high-molecular-weight polymers in high yield, usually at low temperatures. Lewis acids initiators include many metal halides e.g. $AlCl_3$, BF_3 and SbF_5; and their organometallic counterparts e.g. $R{-}AlCl_2$ [446]. Cationic initiation by Lewis acids generally requires and proceeds more quickly in the presence of proton donors (*protogen*) e.g. water, or a carbocation donor (*cationogen*) e.g. alkyl halide [446, 447]. For example dry isobutylene is unaffected by dry boron trifluoride, however in the presence of even trace amounts of water polymerisation occurs immediately [448]. The initiator and co-initiator are an initiating system that reacts to form an initiator– co-initiator complex that proceeds to donate a proton or carbocation to the monomer and thereby initiate propagation, Scheme 3.3 [449].

$$BF_3 + H_2O \rightleftharpoons BF_3 . H_2O \quad \text{or} \quad H^+ (BF_3OH)^-$$

$$H^+ (BF_3OH)^- + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+ (BF_3OH)^-$$

... Scheme 3.3

Self-ionisation of Lewis acids may also promote direct initiation of cationic polymerisation, Scheme 3.4 [450,451]. However, self-ionisation is difficult to distinguish from co-initiation as even trace levels of protogens or cationogens can exert significant influence on the initiation processes. The stronger the acidic character of the metal salt the more pronounced is its initiating power [446].

... Scheme 3.4

Not all Lewis acid metal salts react spontaneously with cationically polymerisable monomers. Many can be formulated as the latent initiating component in storage stable one-component cationically polymerisable systems [452]. In these instances decomposition of the initiator and activation of polymerisation is typically achieved by thermal or electromagnetic radiation curing processes e.g. silver(I) salts of non-nucleophilic counterions [452,457].

3.4 Aims of Chapter

The aim of this chapter is to overcome the severe limitations discussed after studying the copper catalysed redox cationic polymerisation systems in Chapter Two. This is to be achieved by means of a new principle that exploits the disparate redox potentials of a latent catalyst held in a cationically polymerisable matrix and the substrate upon which such a monomer system is to be applied. To achieve this the design of the following experiments is necessary:

1. To demonstrate the direct reduction of a silver(I) latent cationic initiator by a judiciously selected reducing agent.

2. Using the favourable redox potential of silver(I) salts a key objective is to demonstrate surface promoted cationic polymerisation on metallic substrates, Demonstrating how substrates can fulfil the role of an efficient reducing agent.

3. Investigate which features of a demonstrated surface promoted redox cationic polymerisation can be adjusted with a view to enhancing the efficacy of the described systems.

Further objectives were to consider the overall performance of optimised systems in terms of perceived potential benefits in end use appliation.

For convenience the structures of all compounds used to study these phenomena are given in Tables 3.4 to 3.9.

3.5 Experimental

3.5.1 Materials

The cycloaliphatic monomer 3,4-epoxy cyclohexyl methyl-3,4-epoxycyclohexane carboxylate (**72**), from Dow Chemical Company, was employed in this study.

The onium salt $Ph_2I\ PF_6$ (**43**), the reducing agent L-ascorbyl-6-hexadecanoate (**64**), the simple silver and copper salts, organic ligands, additional monomers and benzoyl peroxide were purchased from Sigma-Aldrich. (Tolylcumyl) iodonium tetrakis(pentafluorophenyl) borate (**58**) was purchased from Rhodia Silicones Europe. The monomer 3-Hydroxymethyl-3-methyl-oxetane (**94**) was obtained from Toagosei.

Allylic salts and metal complexes were prepared according to literature procedures. Where deviations to published preparative procedures exist details are given in Chapter Four of this thesis. Unless otherwise stated in the text all materials were used as received.

Table 3.4: Structures of the metal salt complexes (oxidising agents) used in this study

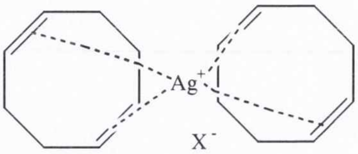
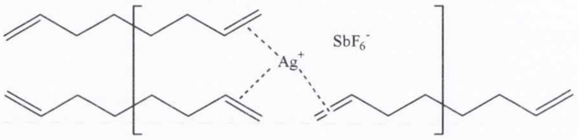
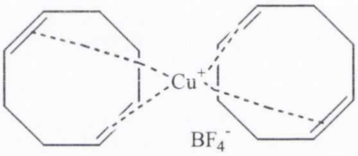
101		[Ag(COD)$_2$] NO$_3$ (386.23 g mol^{-1})	[457]
63		[Ag(COD)$_2$] BF$_4$ (411.03 g mol^{-1})	
102		[Ag(COD)$_2$] PF$_6$ (469.19 g mol^{-1})	
103		[Ag(COD)$_2$] SbF$_6$ (559.98 g mol^{-1})	
104		[Ag(1,7-Octadiene)$_{1.5}$] SbF$_6$ (509.92 g mol^{-1})	[457]
105		Tetrakis(acetonitrole)Ag(I) BF$_4$ (360.90 g mol^{-1})	
61		[Cu(COD)$_2$] BF$_4$ (366.71 g mol^{-1})	[375]

Table 3.5: The metal salts (oxidising agents) used in this study

106	Ag SbF$_6$	Silver(I) Hexafluoroantimonate (343.62 g mol^{-1})
107	Ag PF$_6$	Silver(I) Hexafluorophosphate (252.83 g mol^{-1})
108	Ag BF$_4$	Silver(I) Tetrafluoroborate (194.67 g mol^{-1})
109	Ag CF$_3$ SO$_3$	Silver(I) Trifluoromethane-Sulfonate (256.94 g mol^{-1})
81	Cu (BF$_4$)$_2$	Copper(II) Tetrafluoroborate (236.95 g mol^{-1})

Table 3.6: Structures of the cationically polymerisable monomers used in this study

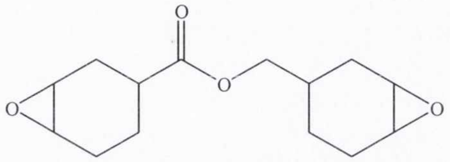
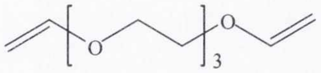
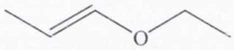
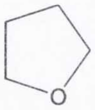
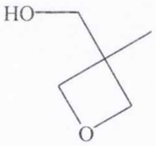
72		3,4-epoxycyclo-hexylmethyl-3,4-epoxy cyclohexane carboxylate (252.31 g mol^{-1})
76		Triethylene glycol divinyl ether "DVE3" (202.25 g mol^{-1})
91		1,4-Butane diol divinyl ether (142.20 g mol^{-1})
92		Ethyl-1-propenyl ether (86.13 g mol^{-1})
93		Tetrahydrofuran (72.11 g mol^{-1})
94		3-Hydroxymethyl-3-methyl-oxetane (102.13 g mol^{-1})

Table 3.7: Structure of the reducing agent used in this study

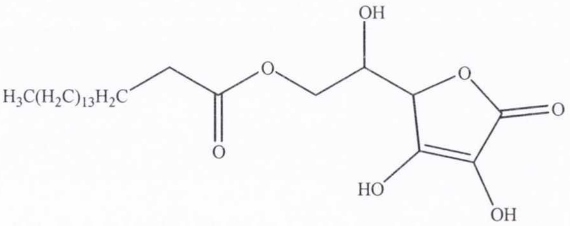
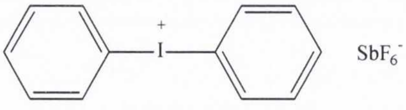
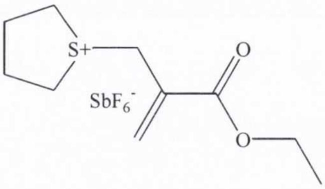
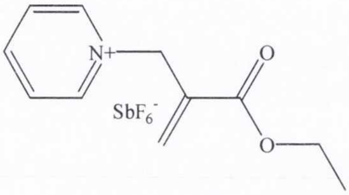
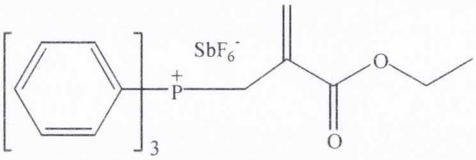
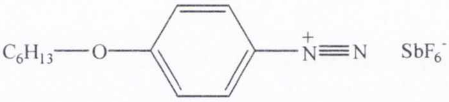
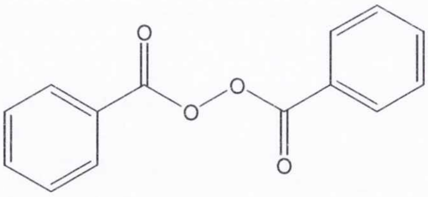
64		L-Ascorbic acid 6-Hexadecanoate "A-6-Hex" (414.53 g mol^{-1})	[285]

Table 3.8: Structures of the onium salt initiators (oxidising agents) used in this study

43		Diphenyliodonium SbF_6 "Ph_2I SbF_6" (516.86 g mol^{-1})
53		Ethyl-α-(Tetrahydrothiophenium Methyl) Acrylate SbF_6 "ETA" (437.06 g mol^{-1})
52		Ethyl-α-Pyridinium Acrylate SbF_6 "ENA" 427.98 g mol^{-1})
54		Ethyl-α-Triphenyl Phosphonium Acrylate SbF_6 "EPA" (611.17 g mol^{-1})
96		Hexyloxyphenyl diazonium SbF_6 (441.03 g mol^{-1}) [453]

* Nomenclature commonly used in the literature

Table 3.9: Structure of the peroxide used in this study

89		Benzoyl Peroxide (242.23g mol^{-1})

3.5.2 Calorimetry

All calorimetry experiments were performed using the techniques described in Chapter two with the following modifications: In "uncatalysed" redox initiation experiments aliquots of monomer **72** (5 g, 15.88 mmol) were prepared in 20 ml glass vials containing a magnetic stirring bar, sealed using a rubber septa and purged with argon. To each vial was added twice the required final concentration of either the reducing or oxidising agent component. When ready to proceed with the reaction 5 g of the monomer solution containing the reducing agent component was transferred via syringe into the vial containing the oxidising agent component. T_0 was taken as the moment of first mixing the two monomer solutions.

3.5.3 Tensile Strength Testing of Adhesives

All tensile strength tests were performed using the method described in Chapter two. Where alternative substrates are used details are provided in the text.

3.5.4 Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) is a non-destructive test method which can be used to characterize materials e.g. polymers in terms of their modulus, elasticity, viscosity, damping behavior, and glass transition temperature, and the changes of these properties with strain, strain rate, temperature, and oscillatory frequency [469]. Of primary interest for this study is determination of the glass transition temperature for polyethers formed by the surface promoted redox cationic polymerisation of epoxy monomers at ambient temperatures and the effects on the polymers glass transition temperature of additional thermal activation. DMTA is a particularly sensitive method for measuring a material's glass transition temperature [470]. The glass transition is detected as a sudden and significant change in the elastic modulus and an attendant peak in the tan δ curve.

DMTA studies were performed using a Tritec 200 dynamic mechanical analyser from Triton Technology Ltd. Typical experiments were performed at a frequency of 1 Hz and a thermal ramp rate of 4°C/min. Typical surface promoted redox cationic polymerisation samples were cured before testing for a period of 24 hours at ambient temperature in a mild steel pouch, from Triton Technology Ltd.

3.5.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which a sample of the material of interest is heated, along with a reference material, and the energy required to maintain both materials at the same temperature is monitored as the surrounding temperature is increased. As a material melts thermal energy is absorbed, while as a material combusts or thermally decomposes energy is released. Absorption of heat results in an endothermic peak while release of heat results in an exothermic peak. Several peaks on a DSC scan are indicative of an impure material or a material with more than one phase transition [471]. DSC can be used for determination of melting points [471] and thermal decomposition temperatures of compounds e.g. exothermic decompsotion of silver oxalate [472]. DSC analyses were recorded using a DSC Plus, Rheometric Scientific Inc. calorimeter.

3.5.6 FTIR-ATR

The benefit of using real-time Fourier transform infrared (RT-FTIR) spectroscopy for kinetic studies is based on its ability to monitor the change of characteristic functional groups of reacting molecules directly during the reaction [393]. Thus, infrared spectroscopy permits quantitative determination of both the degree of cross-linking and the rate of polymerisation from the change in peak absorbance of the characteristic functional group of the monomer or oligomer being investigated. Real-time infrared spectroscopy is appropriate for investigating the kinetics of cationic polymerisations of epoxy and vinyl monomers [473]. These monomers can be followed in real-time by monitoring the decrease of the IR absorbance at 770 cm^{-1} to 790 cm^{-1} and 1635 cm^{-1}, respectively. There have been several reports on the use of FTIR spectroscopy for monitoring cationic polymerisations typically following UV activation [474-476].

Attenuated total reflectance (ATR) has been used for the study of surface promoted redox radical polymerisations [393,477,481]. In ATR a beam of light is passed through the ATR crystal so that it reflects off the internal surface that is in intimate contact with the sample. This reflection forms an evanescent wave, which reaches into the surface of the sample. The infrared detector collects the reflected beam as it leaves the crystal. Several materials e.g. diamond, germanium and zinc selenide, have found use as ATR crystals. Diamond is particularly useful for use as a crystal in ATR due to its hardness, spectral range (25,000 cm^{-1} to 200 cm^{-1}) and chemical inertness [482].

3.5.6.1 Typical FTIR-ATR Experiment

All real-time FT-IR ATR polymerisation experiments were performed with the use of a ThermoElectron Nicolet 380 FTIR fitted with a Smart Orbit™ attenuated total reflectance (ATR) accessory employing a diamond crystal, using a DLaTGS detector and OMNIC version 7.4.127 software. Sixteen scans were recorded per spectrum with a resolution of 4 cm^{-1}. A program for recording multiple scans of polymerisations as a function of time was prepared using OMNIC Macros Basic version 7.4. The experimental methods used here are an adaptation of those described previously by Decker and Mousa [473], and Allen et al. [477]. A background spectrum was collected before beginning each polymerisation experiment.

In a typical experiment a single drop of polymerisable solution was applied to the ATR crystal. Time zero was taken as the time when the activating surface was applied on top of the drop of polymerisable liquid. Uniform pressure was applied to the substrate using the clamping tool attached to the ATR plate so as to ensure intimate contact and reproducible film thickness. The detection of the IR signal was made by operating the spectrophotometer in the absorbance mode. Changes in peak maxima were recorded for the carbonyl peak, which acts as an internal standard, between 1715 and 1735 cm^{-1} and for oxirane decay between 770 and 800 cm^{-1}. When the reducing or activating substrate was applied to a typical polymerisable solution the IR absorbance at *c*. 790 cm^{-1} decayed gradually as a result of oxirane ring opening. This decrease, which reflects the extent of the polymerisation process, was monitored continuously and in real time by the spectrophotometer. Typically spectra were recorded once every minute for the first ten minutes, then once every ten minutes for the next 290 minutes and finally once per hour for the following 19 hours. All experiments were performed under ambient temperature conditions, typically 20 °C, and under a normal atmosphere.

3.5.6.2 Quantifying the Degree of Conversion to Polymer by FTIR [473,477]

The degree of epoxy monomer consumption is directly related to the decrease of the IR absorbance band at 790 cm^{-1}, see Figure 3.1 and the % conversion (C) for the system under study was calculated using the Equation 3.1.

$$\% = [(A_{790})_0 - (A_{790})_t / (A_{790})_0] \times 100\ \% \qquad \text{Equation 3.1}$$

where; $(A_{790})_0$ represents absorbance at 790 cm^{-1} at time zero

$(A_{790})_t$ represents absorbance at 790 cm^{-1} at time *t*

3.6 Results & Discussion

A typical conversion curve for the redox cationic polymerisation of monomers (**72**), 25.4mmols and (**76**), 14.07 mmol, using (**102**) , 0.48 mmol as the cationic initiator and grit blasted mild steel as the reducing substrate monitored by real-time FT-IR ATR is shown in Figure 3.0. This curve was derived from the data presented in Table 3.11, using Equation 3.1 and the overlaid time-interval scan spectra from which this data was obtained are presented in Figure 3.1.

While conversion to a highly cross-linked and insoluble material takes several hours the reaction kinetics show a steady polymerisation from time zero until a plateau is reached at c. 25 % conversion. These two characteristics are suggestive of i) the absence of an induction period which indicates no oxygen inhibition in this cure chemistry as is typical of cationic polymerisations and ii) the gradual slowing down typically observed at degrees of conversion above 20 % is likely a consequence of polymer network formation and the subsequent gelification which reduces the segmental mobility of the growing polymer chains and of remaining unreacted oxirane moieties.

The reproducibility of these experiments was investigated by repeating a typical experiment, as outlined above, several times. The results of this repeatability study are presented in Table 3.10. There is good correlation between the data recorded for each replicate experiment performed.

Table 3.10: Reproducibility & repeatability of a typical FTIR-ATR experiment: Monomers (**72**), 25.4mmols and (**76**), 14.07mmol monitoring oxirane decay at 790 cm^{-1} and using $[Ag(COD)_2]SbF_6$ (**102**), 0.48 mmol as initiator while employing grit blasted mild steel as the reducing substrate

Monomer (mmol)	Co-Monomer (mmol)	Oxidising Agent (mmol)	Replicate	$t_{½}$ (h)	C (%)
72 (39.63)	**76** (14.07)	**102** (0.24)	1	8.1	24.7
			2	7.5	22.6
			3	7.7	24.2

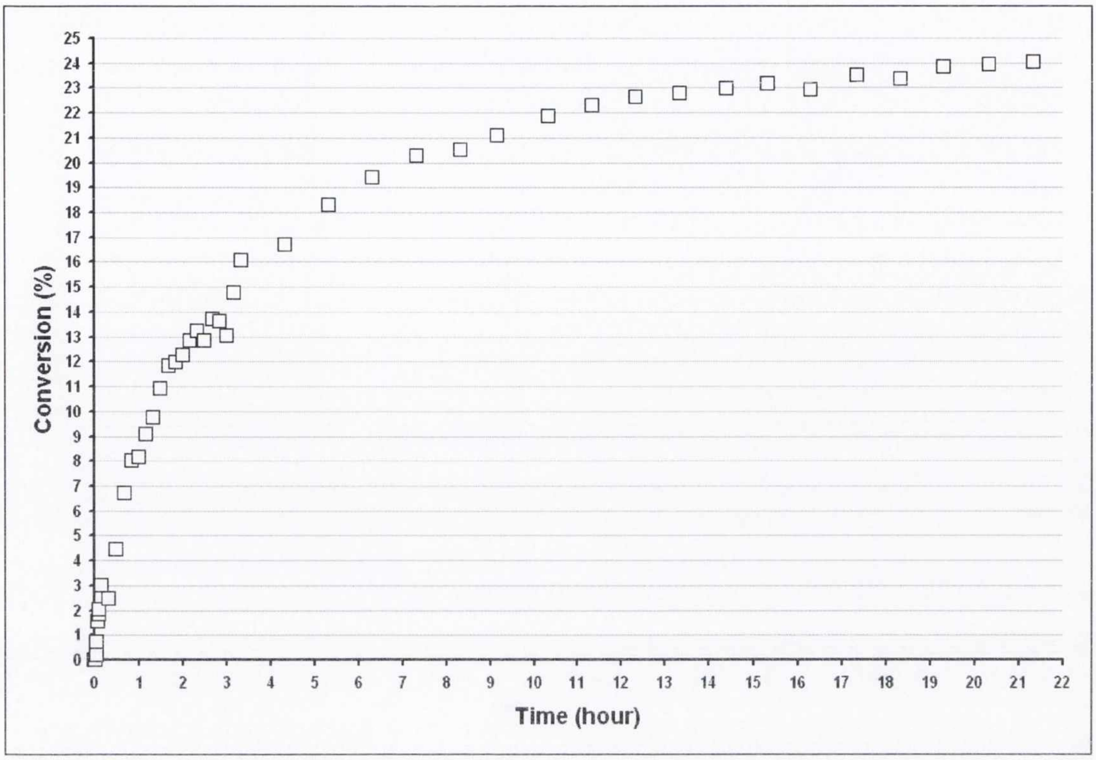


Figure 3.0: Typical conversion (%) versus time (hour) for the redox cationic polymerisation of monomers (**72**), 25.4mmols and (**76**), 14.07mmol monitoring oxirane decay at 790 cm^{-1} and using [Ag(COD)$_2$]SbF$_6$ (**102**), 0.48 mmol as initiator while employing grit blasted mild steel as the reducing substrate

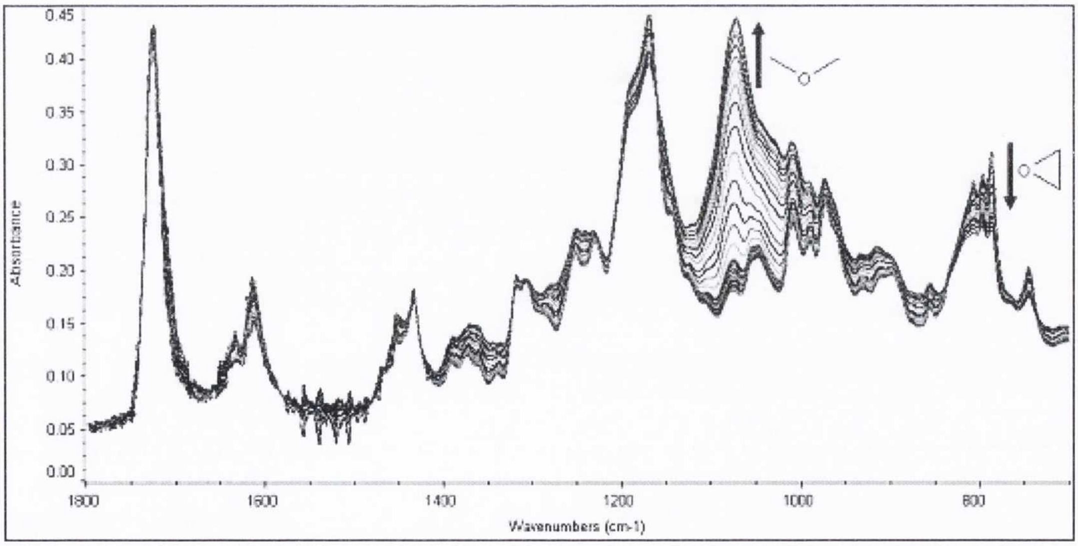


Figure 3.1: Typical FTIR-ATR interval scan spectrum for the redox cationic polymerisation of monomers (**72**), 25.4mmols and (**76**), 14.07mmol showing oxirane decay at 790 cm^{-1} and using [Ag(COD)$_2$]SbF$_6$ (**102**), 0.48 mmol as initiator while employing grit blasted mild steel as the reducing substrate

Table 3.11: Data from a typical FT-IR ATR experiment, at 20°C: monomers (**72**), 25.4mmols and (**76**), 14.07mmol and using [Ag(COD)$_2$]SbF$_6$ (**102**), 0.48 mmol as initiator on a grit blasted mild steel substrate and measurement of oxirane decay at 790 cm^{-1}

Time (hr)	**C=O Abs$_{1725cm-1}$**	**Oxirane Abs$_{790cm}$**	**Abs$_0$ (Abs$_{0\ 790}$/Abs$_{1725}$)**	**Abs$_t$ (Abs$_{t\ 790}$/Abs$_{1725}$)**	**(A$_0$-A$_t$)/A$_0$**	**C %**
0.00	**0.4394**	**0.3228**	**1.361**	**1.361**	**0.000**	**0.00**
0.02	0.4361	0.3214	1.361	1.357	-0.003	0.00
0.03	0.4340	0.3194	1.361	1.359	-0.002	0.00
0.05	0.4332	0.3177	1.361	1.364	0.002	0.21
0.07	0.4337	0.3165	1.361	1.371	0.007	0.70
0.08	0.4345	0.3144	1.361	1.382	0.015	1.54
0.33	0.4352	0.3121	1.361	1.394	0.025	2.45
0.50	0.4355	0.3064	1.361	1.421	0.044	4.42
0.67	0.4404	0.3032	1.361	1.452	0.067	6.70
0.83	0.4399	0.2993	1.361	1.470	0.080	8.01
1.67	0.4376	0.2876	1.361	1.522	0.118	11.80
3.33	0.4309	0.2728	1.361	1.580	0.161	16.07
8.33	0.4334	0.2660	1.361	1.629	0.197	19.70
9.33	0.4323	0.2636	1.361	1.640	0.205	20.50
10.33	0.4362	0.2630	1.361	1.659	0.219	21.87
11.33	0.4361	0.2642	1.361	1.651	0.213	21.29
12.33	0.4363	0.2633	1.361	1.657	0.217	21.73
14.33	0.4374	0.2630	1.361	1.663	0.222	22.20
15.33	0.4388	0.2640	1.361	1.662	0.221	22.13
17.33	0.4410	0.2624	1.361	1.681	0.235	23.51
18.33	0.4393	0.2617	1.361	1.679	0.233	23.35
19.33	0.4396	0.2624	1.361	1.675	0.231	23.11
20.33	0.4391	0.2616	1.361	1.678	0.233	23.33
21.33	0.4394	0.2592	1.361	1.695	0.245	24.54
22.33	**0.4396**	**0.2590**	**1.361**	**1.698**	**0.247**	**24.73**

3.7 *Calorimetric Study:* Novel Cationic Polymerisation Redox Couples Based on the Stoichiometric Reduction of Metal Salts of Non-nucleophilic Anions by Chemical Reducing Agents

Silver(I) cations have more positive redox potentials than typical onium salts and consequently they are readily reduced by a wide range of reducing agents [478-480]. Therefore it is of interest to demonstrate the efficient *direct* reduction of silver salts of non-nucleophilic anions by a typical organic reducing agent, such as ascorbyl-6-hexadecanoate (**64**) as a means of promoting *bulk* redox cationic polymerisation. Such a mode of promoting redox cationic polymerisation is in direct contrast to the inefficient copper(II) catalysed redox cationic polymerisations investigated in Chapter Two. This demonstration of the activity of silver(I) salts as latent cationic initiators provides a clear indication of their potential for achieving the central objective of this work.

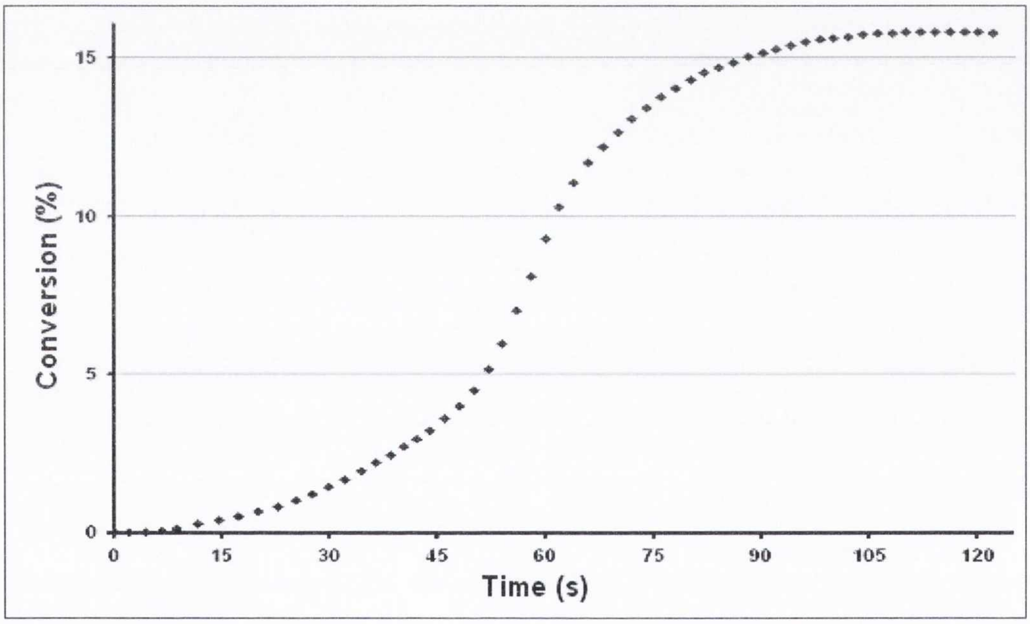


Figure 3.2: Cure profile following direct reduction of $AgBF_4$ (**108**), 0.48 mmol by ascorbyl-6-hexadecanoate (**64**), 0.24 mmol in order to promote the redox cationic polymerisation of monomer (**72**), 39.63 mmol by calorimetry

In this study a series of silver(I) salts of non-nucleophilic anions have been investigated as initiators in *bulk* redox cationic polymerisations using A-6-Hex (**64**) as the reducing agent. The reactions were monitored using the calorimetric method described. A typical curve depicting the exothermic redox cationic polymerisation of monomer (**72**), using $AgBF_4$ (**108**) as the latent cationic initiator and A-6-Hex (**64**) as the reducing agent is shown in Figure 3.2. The results from this investigation are presented in Table 3.12. The example in Figure 3.2 reaches maximum conversion after 100 s. The amount of heat released (ΔT), the induction time ($t_{½}$) as defined by the time taken to reach half of the maximum exotherm (T_{max}) and the percentage conversion (C) can all be derived from this curve. From the curve it can be seen that there is no distinct induction period, which indicates that there are few inhibitory processes. The steep profile of this conversion curve is typical of related redox polymerisations as demonstrated in Chapter Two and is indicative of an auto-accelerating reaction.

Table 3.12: Reduction of latent cationic initiators (oxidants), 0.48 mmmol by A-6-Hex (**64**), 0.24 mmol to promote redox cationic polymerisation of monomer (**72**), 39.63 mmol, followed by calorimetry

Monomer (mmol)		**Oxidising Agent (mmol)**		**Reducing Agent (mmol)**		**ΔT (K)**	**$t_{½}$ (s)**	**T_{max} (°C)**	**$T_{½}$ (°C)**	**C (%)**
72	(39.63)	**43** $Ph_2I\ PF_6$	(0.48)	**64**	(0.24)	-	-	25	-	0
72	(39.63)	**108** $Ag\ BF_4$	(0.48)	**64**	(0.24)	85	59	99	63	15.8
72	(39.63)	**106** $Ag\ SbF_6$	(0.48)	**64**	(0.24)	121	66	146	74	31.2
72	(39.63)	**103** $[Ag(COD)_2]SbF_6$	(0.48)	**64**	(0.24)	133	58	158	77	33.7
72	(39.63)	**104** $[Ag(1,7\text{-}Oct)_{1.5}]SbF_6$	(0.48)	**64**	(0.24)	149	106	174	89	37.2
72	(39.63)	**61** $[Cu(COD)_2]BF_4$	(0.48)	**64**	(0.24)	-	-	27	-	0

Examination of the data in Table 3.14 shows that neither the iodonium salt (**43**) or copper(I) salt (**61**) of non-nucleophilic anions are liable to efficient decomposition by the reducing agent ascorbyl-6-hexadecanoate (**64**). However, all silver(I) salts of non-nucleophilic anions studied do undergo efficient direct reduction by ascorbyl-6-hexadecanoate (**64**) to promote redox cationic polymerisation. In line with previous studies the larger the non-nucleophilic anion the more efficient the reaction and the higher the relative degree of conversion to polymer i.e. $SbF_6 > BF_4$. The effect of various ligands on silver(I) salt activity was also investigated while maintaining the anion unchanged in each case.

In this instance the redox reactivity was observed to increase with increasing solubility of the silver(I) species in the bulk monomer i.e. [Ag(1,7-Octadiene)$_{1.5}$]SbF_6 > [Ag(COD)$_2$]SbF_6 > $AgSbF_6$.

The mechanism inferred by the described silver(I) : ascorbyl-6-hexadecanoate redox couple studies is consistent with that of typical Ag(I) reduction to Ag(0), Scheme 3.5. In this instance the resulting non-nucleophilic Brønsted acid (HX) is an efficient initiator of cationic polymerisation.

$$AH_2 + 2Ag\,X \rightarrow DA + 2Ag(0) + 2HX \qquad \text{... Scheme 3.5}$$

3.8 *FTIR-ATR* *Studies:* Surface Promoted Redox Cationic Polymerisation Employing Silver(I) Salts

The aspiration of the following series of experiments was to demonstrate that a solution comprising a cationically polymerisable monomer and a Silver(I) salt of a non-nucleophilic anion, e.g. $AgSbF_6$ (**106**), could be applied to a metallic substrate which would act as a stimulus for reduction of the Silver(I) Lewis acid and in the process form a stronger Lewis acid on the metallic substrate, *cf.* reduction of Ag(I) in aqueous solution by metallic substrates, Table 3.13. This strongly Lewis acidic species could in turn act as an initiator for promotion of cationic polymerisation of the monomer particularly in the confines of an adhesive bondline. Scheme 3.6 shows a straight forward redox reaction in which metallic iron, Fe(0), acts as a reductant for the oxidant Ag(I) in solution to yield oxidised Fe(II)/(III) and reduced metallic Silver [483].

$$Fe(0) + 2Ag(I) \rightarrow Fe(II) + 2Ag(0)$$
$$Fe(0) + 3Ag(I) \rightarrow Fe(III) + 3Ag(0) \qquad \text{... Scheme 3.6}$$

Table 3.13: Demonstration of surface induced pH change of aqueous solution following metal substrate reduction of Ag(I) SbF_6, at time zero and at 24 hour immersion in dark

Ag(I) Solution	Substrate	pH t_0	pH t_{24}	Ag(0) ↓	Solution Colour $t_0 \rightarrow t_{24}$
2.7×10^{-3} M	Iron, Fe(0)	5	1	Yes	Colourless → Colourless
2.7×10^{-3} M	Copper, Cu(0)	5	1	Yes	Colourless → Blue
2.7×10^{-3} M	Glass	5	5	No	Colourless → Colourless

The experimental investigation that follows outlines studies which demonstrate the efficient ambient temperature activation of redox cationic polymerisation of an epoxy monomer at metallic surfaces and adhesive bondline interfaces having employed the principle of redox activation to promote formation of a strong Lewis acid cationic polymerisation initiator or co-initiator from a latent or mild Lewis acid catalyst e.g. Ag(I) salts of non-nucleophilic anions.

In the first instance a cationically polymerisable monomer system containing the Lewis acid $[Ag(COD)_2]SbF_6$ was applied to a freshly prepared mild steel, Fe(0), substrate. The latent cationic initiation properties of the displacement of Ag(I) cations by their reduction at the metallic interface to Ag(0) with the concomitant oxidation of the Fe(0) substrate to the higher oxidation state, and more strongly Lewis acidic cationic initiating species Fe(II)/Fe(III), was studied by monitoring the degree of polymerisation (%) attained by a cycloaliphatic monomer. The polymerisation reaction was followed FTIR-ATR.

3.8.1 Determination of the $[Ag(COD)_2]SbF_6$ Threshold Catalyst Concentration for Surface Promoted Cationic Polymerisation

In this study it was observed the degree of polymerisation of monomer (**72**) was found to increase with increasing $[Ag(COD)_2]SbF_6$ (**103**) concentration, Table 3.14 and Figure 3.3. Of the initiator concentrations investigated (**103**) 0.48 mmol gave the highest 22-hour conversion (11 %) based on decay of oxirane monomer functionality. The degree of polymerisation increased marginally with increasing initiator concentration. Higher concentrations of initiator could not be studied with accuracy, as 0.48 mmol was also on the threshold of initiator solubility in monomer (**72**). Further studies were therefore carried out aimed at increasing the room temperature activity of these systems and increasing initiator solubility.

From Table 3.14 it is also shown that while conversion to polymer occurs successfully on the grit blasted mild steel substrates used no conversion to polymer was observed in the absence of a substrate or if a glass substrate was employed. The surface dependant reactivity of these redox polymerisations is examined later in this Chapter.

Table 3.14: Conversion (%) of monomer (**72**), 39.63 mmol, in the presence of various concentrations of $[Ag(COD)_2]SbF_6$ (**103**) using grit blasted mild steel and glass as substrate. Polymerisation was monitored by FT-IR ATR

Monomer (mmol)	**Substrate**	**Oxidising Agent**	**(mmol)**	**$t_{1/2}$ (h)**	**C (%)**
72 (39.63)	GBMS	**103** $[Ag(COD)_2]SbF_6$	(0.00)	-	0
72 (39.63)	GBMS	**103** $[Ag(COD)_2]SbF_6$	(0.12)	9.7	9.1
72 (39.63)	GBMS	**103** $[Ag(COD)_2]SbF_6$	(0.24)	9.7	8.7
72 (39.63)	GBMS	**103** $[Ag(COD)_2]SbF_6$	(0.48)	7.8	11.1
72 (39.63)	Glass	**103** $[Ag(COD)_2]SbF_6$	(0.48)	-	0
72 (39.63)	*No Substrate*	**103** $[Ag(COD)_2]SbF_6$	(0.48)	-	0

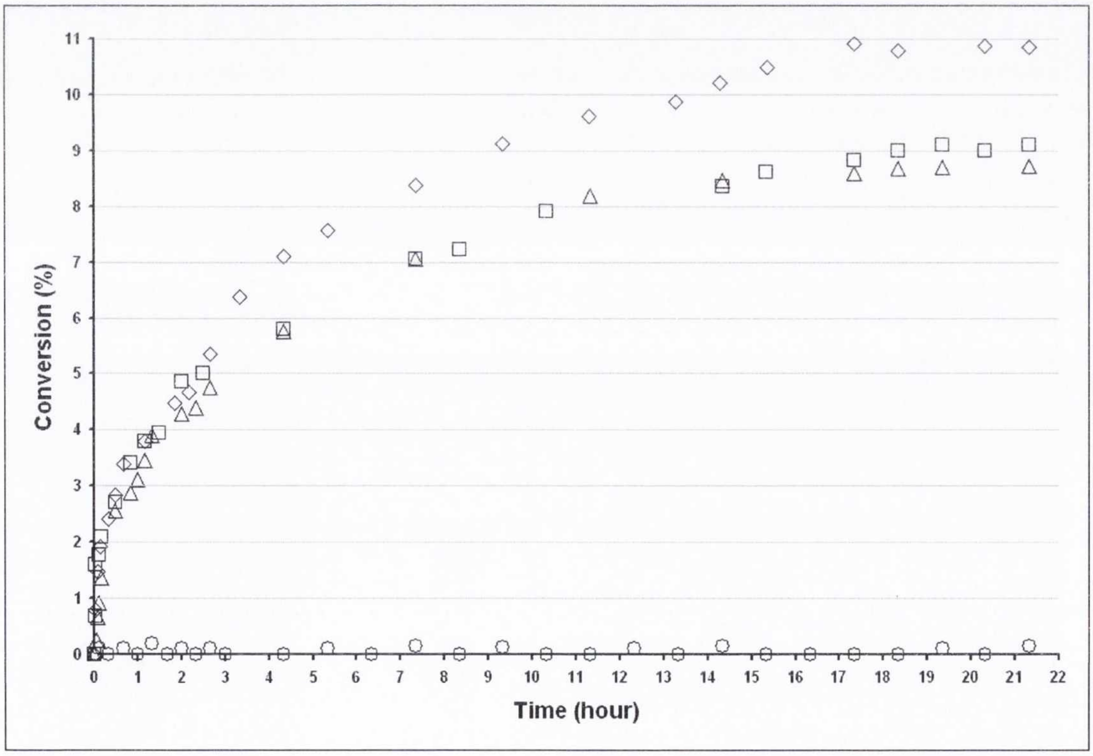


Figure 3.3: Conversion (%) of monomer (**72**), 39.63 mmol, containing various concentrations of $[Ag(COD)_2]SbF_6$ (**103**): 0.00 mmol ○, 0.12 mmol □, 0.24 mmol △ & 0.48 mmol ◇ on a grit blasted mild steel substrate monitored by FT-IR ATR

3.8.2 Surface Promoted Cationic Polymerisation Mediated by a Co-Monomer

Surface promoted redox cationic polymerisation, employing Ag(I) salts of non-nucleophilic anions, as described thus far is an interesting mode of inducing polymerisation of epoxy monomers on metallic substrates at ambient temperatures. However, in order for this mode of polymerisation to become a viable adhesives technology it must be able to compete with its long established and commercially successful anaerobic acrylate adhesive counterparts. To this end an adhesive based on surface promoted redox cationic polymerisation must be able to demonstrate at least comparable cure speed and final adhesive performance. Figure 3.4 shows the adhesive cure profile, on grit blasted mild steel, of a model surface promoted redox cationic polymerisation system comprising the cycloaliphatic monomer (**72**) and $[Ag(COD)_2]SbF_6$ (**103**) as latent catalyst, comparison is made with a typical commercial anaerobic acrylate adhesive. As can be seen, in this configuration, surface promoted redox cationic polymerisation is significantly slower and achieves a lower final adhesive performance than the commercial adhesive. Consequently a study was performed with a view to increasing the efficiency of surface promoted redox cationic polymerisation and degree conversion to polymer of the major cycloaliphatic epoxy monomer component (**72**).

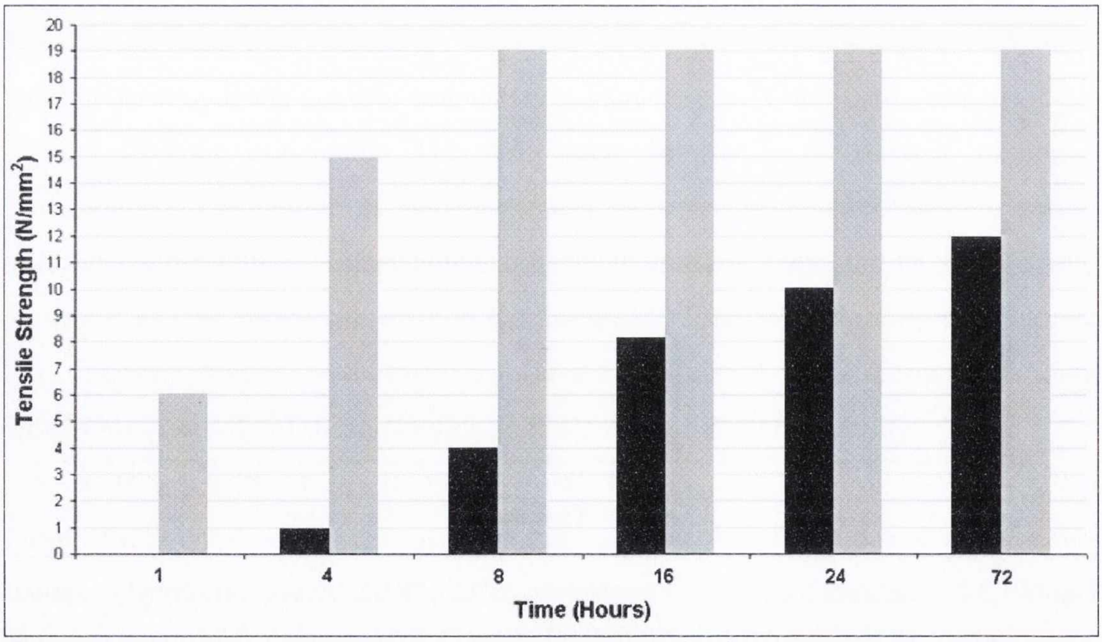
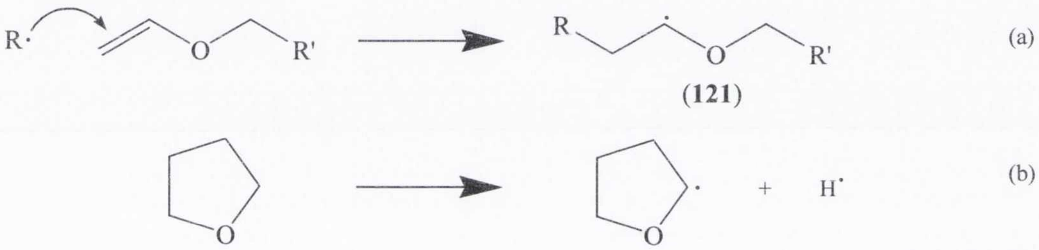


Figure 3.4: Room temperature tensile strength cure profile for monomer (**72**), 39.63 mmol, with $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol as initiator (■) compared with the tensile strength cure profile for a typical commercial anaerobic acrylate adhesive Loctite® 2701 (□). All tests were performed on grit blasted mild steel substrates.

Epoxy resins are often blended with other cationically curable resins and additives [427]. Several cationically polymerisable monomers have found use as accelerators for the photo-cationic polymerisation of cycloaliphatic epoxy monomers. Such co-monomers may include oxetanes [484], vinyl ethers [430] and propenyl ethers [485,486]. In addition to their inherent susceptibility to cationic polymerisation the roles of vinyl ether and cyclic ether, e.g. oxetane and tetrahydrofuran, monomers as accelerants may be additionally understood due to their propensity to form α-ether radicals that can directly reduce suitable oxidising species such as Ph_2I^+ latent initiators. Aliphatic α-ether radicals are known to be good reducing agent species due to the presence of a three-electron interaction i.e. interaction between the oxygen lone-pair electrons and an easily removable single electron in a high-energy antibonding orbital [465].



… Scheme 3.7

Aliphatic α-ether radicals (**99**) may be formed by both addition of radicals (e.g. derived from peroxide inherently present on the bulk ether monomer) to a vinyl ether double bond and / or through hydrogen abstraction from the monomer, Scheme 3.7 (a) and (b) [467]. The reduction potential, $E_{½}^{red}$, of α-ether radicals has been determined to be – 0.56 V (NHE) [466]. If one considers the thermodynamic feasibility for reaction between the onium and metal salt of interest in this study and typical α-ether donor radicals all such cations may in theory be expected to function as efficient one-electron oxidants, Table 3.14 [376]. Scheme 3.8 illustrates single electron oxidation of an α-ether radical by silver(I) to yield the cationic initiator species $\alpha\text{-}E^+ X^-$.

$$\alpha\text{-}E\cdot + Ag\,X \xrightarrow{k_{SET}} \alpha\text{-}E^+ X^- + Ag(0) \qquad (a)$$

$$\alpha\text{-}E^+ X^- + M \xrightarrow{\textit{Monomer}} \text{Polymer} \qquad \text{… Scheme 3.8}$$

Table 3.14: Thermodynamic feasibility, based on theoretical E_{cell} values for the reduction of a series of latent cationic initiator cations by an α-ether radical (V vs NHE)

Oxidant (Substrate)	$E_{½}^{red}$ *V*	**Reductant**	$E_{½}^{red}$ *V*	ΔE_{rxn} (*V*)	**Thermodynamic Feasibility**
Ag^+	+ 0.80	α-ether radical	- 0.56	+ 1.36	Higher
RN_2^+	+ 0.59	α-ether radical	- 0.56	+ 1.15	↓
Cu^+	+ 0.52	α-ether radical	- 0.56	+ 1.08	↓
Ph_2I^+	+ 0.04	α-ether radical	- 0.56	+ 0.60	Lower

The structures of the co-monomers studied in this series of experiments are presented in Table 3.6. The relative reactivity of this range of monomers was determined by monitoring the relative degree of conversion (%) of monomer (**72**) as a function of time. The results obtained are presented in Table 3.15 and Figure 3.5.

Table 3.15: Effect on conversion (%) and $t_{½}$ of monomer (**72**) in presence of various co-monomers, using $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol. The substrate employed was grit blasted mild steel, polymerisation was monitored by FT-IR ATR

Monomer (mmol)	**Mediator (mmol)**	**Oxidising Agent**	**(mmol)**	$t_{½}$ **(h)**	**C (%)**
72 (39.63)	(0.00)	**103** $[Ag(COD)_2]SbF_6$	0.48	7.8	11.1
72 (31.71)	**76** (9.88)	**103** $[Ag(COD)_2]SbF_6$	0.48	8.1	24.7
72 (31.71)	**91** (9.88)	**103** $[Ag(COD)_2]SbF_6$	0.48	6.3	20.5
72 (31.71)	**92** (9.88)	**103** $[Ag(COD)_2]SbF_6$	0.48	6.3	20.6
72 (31.71)	**93** (9.88)	**103** $[Ag(COD)_2]SbF_6$	0.48	7.5	22.4
72 (31.71)	**94** (9.88)	**103** $[Ag(COD)_2]SbF_6$	0.48	6.7	22.8

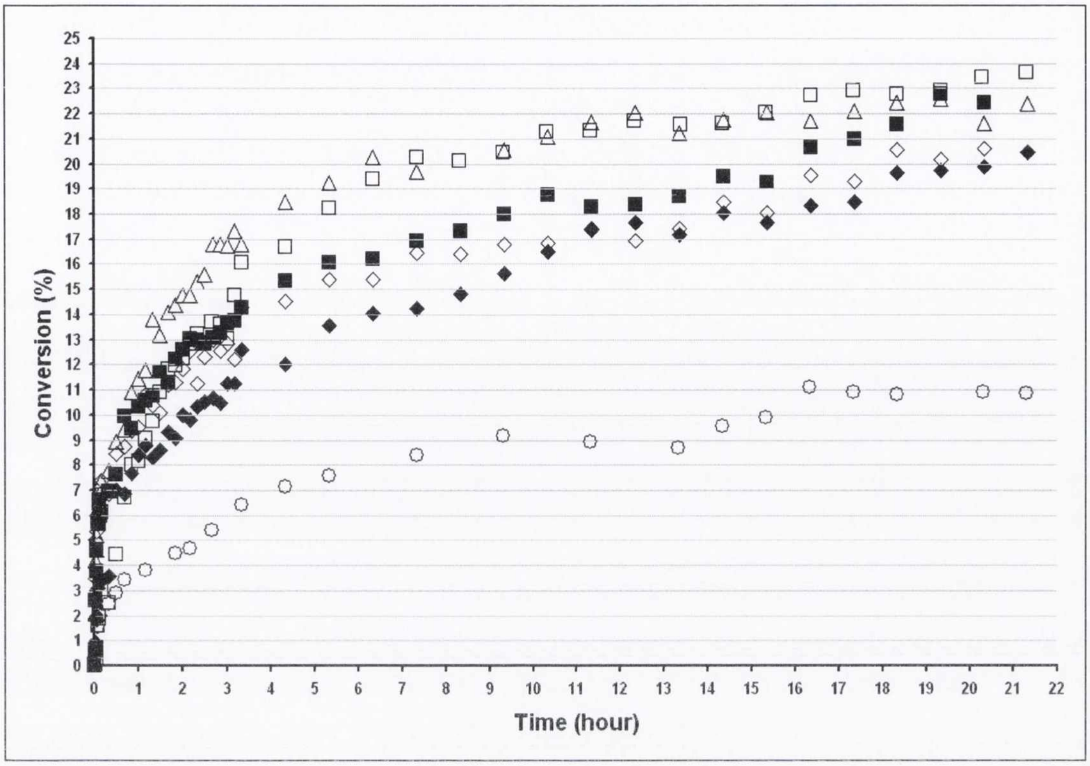


Figure 3.5: Effect on conversion (%) of monomer (**72**), 31.71 mmol in presence of various co-monomers, 9.88 mmol: DVE3 (**76**) □, 1,4-butane diol divinyl ether (**91**) ◆, ethyl-1-propenyl ether (**92**) ◇, tetrahydrofuran (**93**) △, 3-hydroxymethyl-3-methyl-oxetane (**94**) ■, control with no added co-monomer ○. In each experiment $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol was used as initiator and polymerisation was performed on a grit blasted mild steel substrate, monitored by FT-IR ATR.

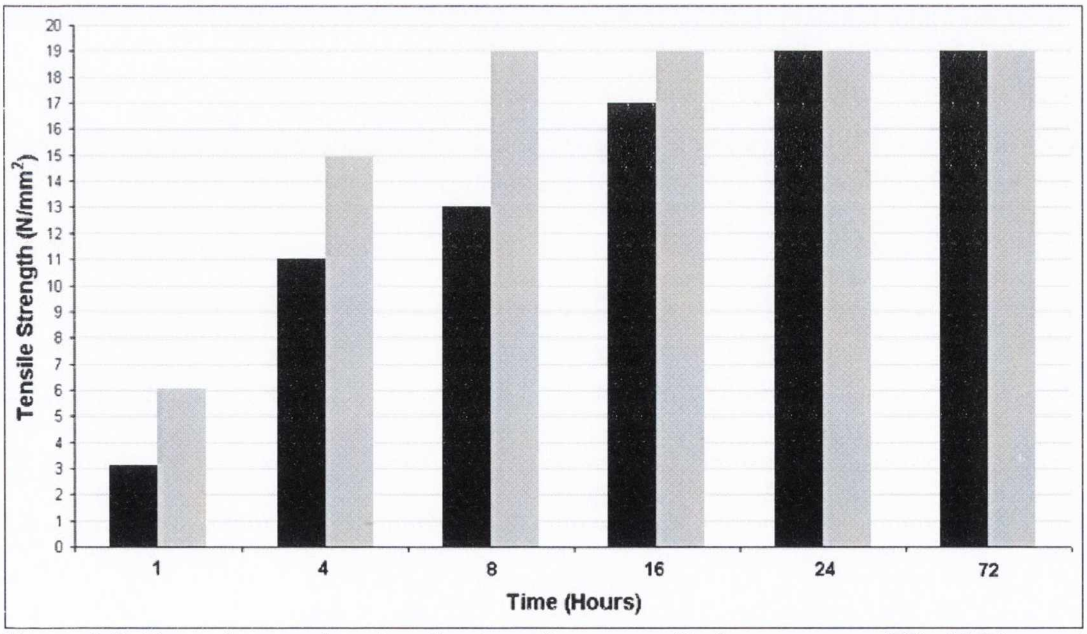


Figure 3.6: Room temperature tensile strength cure profile for monomer (**72**), 31.71 mmol, mediated by DVE3 (**76**) 9.88 mmol using $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol as initiator (■) compared with the tensile strength cure profile for a typical commercial anaerobic acrylate adhesive Loctite® 2701 (▨). All tests were performed on grit blasted mild steel substrates.

From the data in Table 3.17 it can be seen that all of the co-monomers, when used at a level of c. 20%, have enhanced the degree of conversion of the major monomer (**72**) component. Similarly, incorporation of a co-monomer has resulted in a reduced $t_{½}$ (h). There are several possible reasons for these observed improvements in $t_{½}$ (h) and conversion (%) including; higher relative reactivity of the co-monomer, improved solvation of the latent catalyst and even reduction in viscosity of the bulk solution which may facilitate transport of the active initiation species at the substrate interface.

Triethylene glycol divinyl ether (**76**) has provided the best overall improvement in $t_{½}$ and conversion to polymer (24.7%). Figure 3.6 shows the adhesive cure profile, on grit blasted mild steel, for this DVE3 (**76**) mediated surface promoted redox cationic polymerisation system in which cycloaliphatic monomer (**72**) is the major polymerisable component and $[Ag(COD)_2]SbF_6$ (**103**) is the latent catalyst. Once again comparison is made with the cure profile for a typical commercial anaerobic adhesive. In this example adhesive bond strength builds more rapidly in the presence of the vinyl ether component, corresponding with the higher observed efficiency (C %) for this reaction. Similarly an approximate doubling of the 24 h and 72 h adhesive bond strength also corroborates the higher final degree of conversion to polymer observed from the ATR study.

3.8.3 Determination of a Preferred Concentration of Vinyl-Ether as a Mediator of Surface Promoted Redox Cationic Polymerisation

DVE3 (**76**) is a useful accelerator for surface promoted cationic polymerisation. The accelerative effect of (**76**) as a function of concentration on the $t_{½}$ and conversion (%) of cycloaliphatic epoxy monomer (**72**) is shown in Table 3.16 and Figure 3.7. Substitution of 5 % of (**72**) with the vinyl ether mediator (**76**) results in a 60% jump in monomer conversion. However, maximum benefit was obtained by substitution of as much as 20% (9.88 mmol) of (**72**) with the vinyl ether mediator (**76**), this gave a significant reduction in $t_{½}$ (7.52 h) coupled with a doubling in conversion (%). No significant benefit was observed at higher levels of substitution.

Table 3.16: Effect on conversion (%) of monomer (**72**), 31.71 mmol by varying the relative concentration of the co-monomer DVE3 (**76**). In each case polymerisation was promoted on a grit blasted mild steel substrate, conversion to polymer was monitored by FT-IR ATR.

Monomer (mmol)	**Mediator (mmol)**	**Oxidising Agent**	**(mmol)**	**$t_{½}$ (h)**	**C (%)**
72 (39.63)	**76** (0.00)	$[Ag(COD)_2]SbF_6$	0.48	7.8	11.1
72 (37.65)	**76** (2.47)	$[Ag(COD)_2]SbF_6$	0.48	6.5	17.9
72 (35.67)	**76** (4.94)	$[Ag(COD)_2]SbF_6$	0.48	7.5	20.7
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	0.48	8.1	24.7
72 (27.74)	**76** (14.83)	$[Ag(COD)_2]SbF_6$	0.48	8.0	23.9

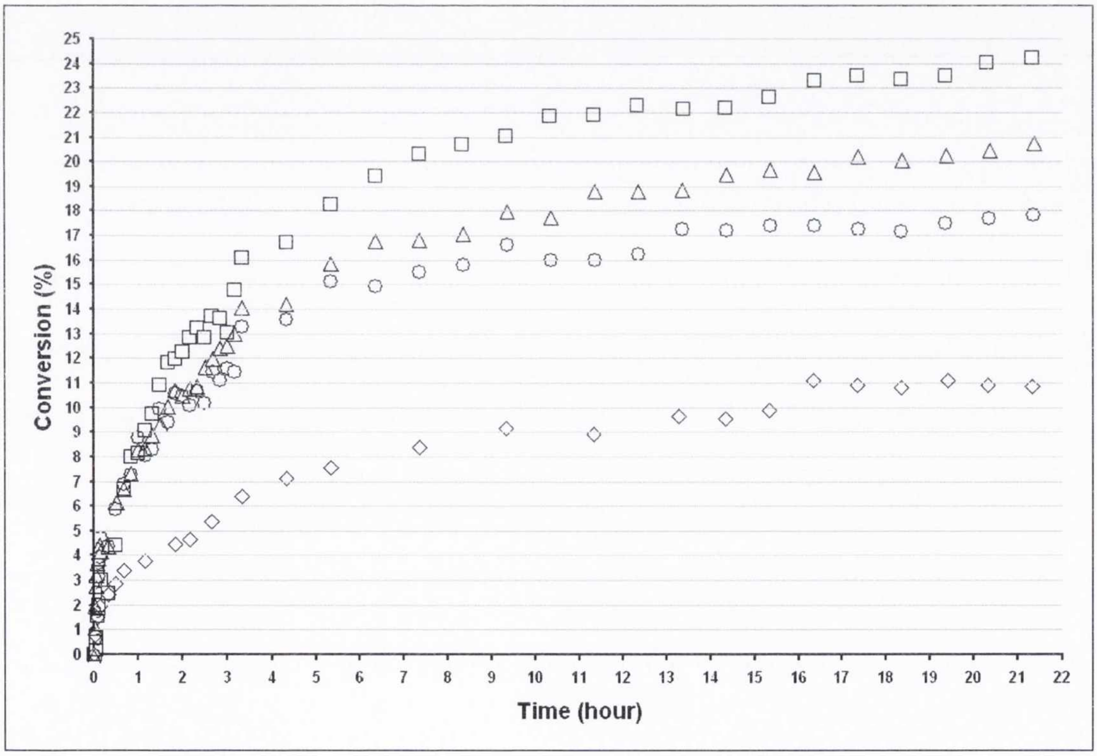


Figure 3.7: Effect on conversion (%) of monomer (**72**) while varying the relative concentration of the co-monomer DVE3 (**76**): 0.00 mmol ◇, 2.47 mmol ○, 4.94 mmol △, 9.88 mmol □. In each experiment $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol was used as initiator on a grit blasted mild steel substrate and conversion to polymer was monitored by FT-IR ATR.

3.8.4 Determination of the [Ag(COD)$_2$]SbF$_6$ Threshold Ag(I) Catalyst Concentration for Vinyl-Ether Mediated Surface Promoted Redox Cationic Polymerisation

Using a preferred monomer system comprising cycloaliphatic epoxy monomer (**72**), 31.71 mmol, and DVE3 (**76**), 9.88 mmol, as an accelerative component the optimum concentration of latent catalyst [Ag(COD)$_2$]SbF$_6$ (**103**) was re-evaluated. It was noted that addition of DVE3 (**76**) facilitated dissolution of the AgSbF$_6$ (**106**) in both its neat and ligated forms. The ligated [Ag(COD)$_2$]SbF$_6$ (**103**) was the preferred form of Ag(I) salt for these experiments as it had low hygroscopicity and could be prepared readily and in high purity.

As before it was observed the degree of conversion to polymer increased with increasing [Ag(COD)$_2$]SbF$_6$ (**103**) concentration, Table 3.17. An [Ag(COD)$_2$]SbF$_6$ (**103**) concentration of 0.48 mmol gave the highest 22 hr conversion at 24.7 %. In general the efficiency of polymerisation also increased with increasing initiator concentration. In this instance, although the initiator showed a high degree of solubility in the chosen monomer system, there was little benefit observed for initiator concentration > 0.48 mmol.

Table 3.17: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol in the presence of various concentrations of [Ag(COD)$_2$]SbF$_6$ (**103**) using grit blasted mild steel and monitored by FT-IR ATR

Monomer (mmol)	Mediator (mmol)	Oxidising Agent	(mmol)	$t_{1/2}$ (h)	C (%)
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.06	6.9	18.4
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.12	7.5	21.8
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.24	7.6	21.8
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.42	7.9	22.3
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.48	8.1	24.7
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	0.54	7.8	21.6

3.8.5 Influence of Anion (X^-) on Vinyl-Ether Mediated Surface Promoted Redox Cationic Polymerisation

Having identified a surface promoted redox cationic polymerisation system demonstrating both reasonsable surface activation and adhesive performance it is of further interest to identify those factors that influence this efficacy. As shown in Chapter two the redox potential of a cationic initiator varies according to the nucleophilicity of its associated counterion, see Table 2.1. Consequently the larger the diameter of the non-nucleophilic anion the higher the theoretical conversion to polymer, see Table 2.2. Therefore in this investigation a series of silver(I) salts with correspondingly more non-nucleophilic anions were studied to determine the impact of this property on surface promoted redox cationic polymerisation.

The data in Table 3.18 and the conversion profiles (%) depicted in Figure 3.8 confirm that as nucleophilicity of the anion increases there is a corresponding decrease in conversion (%) to polymer i.e. hexafluoroantimonate (19.9 %) > hexafluorophosphate (8.3 %) > tetrafluoroborate (6.3 %) > trifluoromethanesulfonate (0.4 %)

Table 3.18: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol in the presence of Ag(I) 0.48 mmol associated with the following anions: SbF_6 (**106**), PF_6 (**107**), BF_4 (**108**) and CF_3SO_3 (**109**) using grit blasted mild steel as substrate and monitored by FT-IR ATR

Monomer (mmol)	**Mediator (mmol)**	**Oxidant**	**(mmol)**	**Increasing Nucleophilic Character**	**$t_{1/2}$ (h)**	**C (%)**
72 (31.71)	**76** (9.88)	Ag SbF_6	(0.48)	↓	6.5	19.9
72 (31.71)	**76** (9.88)	Ag PF_6	(0.48)		2.8	8.3
72 (31.71)	**76** (9.88)	Ag BF_4	(0.48)		2.8	6.3
72 (31.71)	**76** (9.88)	Ag CF_3SO_3	(0.48)		-	0.4

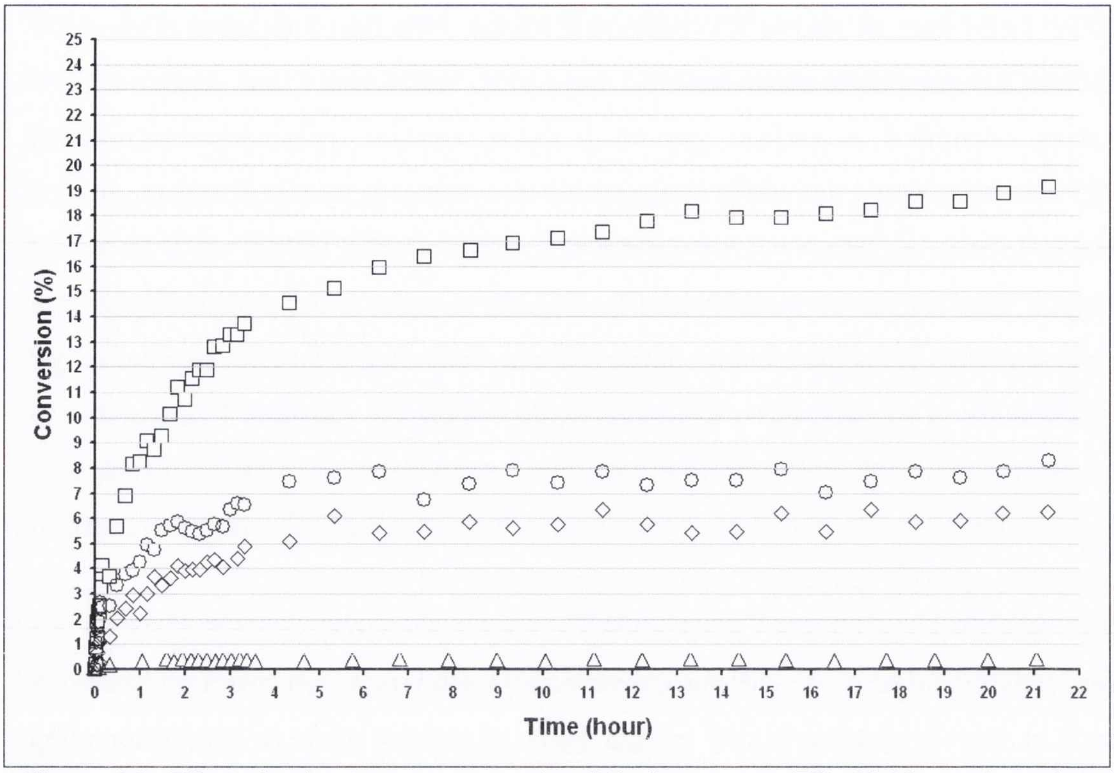


Figure 3.8: Effect of anion type on conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol, initiated by 0.48 mmol of □ $AgSbF_6$ (**106**), ○ $AgPF_6$ (**107**), ◇ $AgBF_4$ (**108**) and △ $AgCF_3SO_3$ (**109**) using grit blasted mild steel as substrate and monitored by FT-IR ATR

3.8.6 Influence of Ligand (L) on Vinyl-Ether Mediated Surface Promoted Redox Cationic Polymerisation

Ligated complexes of silver(I) salts have found use as latent initiators for the e-beam curing of cationically polymerisable monomers [457]. Similarly here it was established that the use of a selection of ligands for the preparation of silver(I) complexes enabled isolation of useful latent catalysts in high purity and with increased solubility in the cationically polymerisable monomers used. A further benefit of using various ligands was a significant improvement in formulation stability without adversely affecting reactivity.

Several ligands, including those listed in Table 3.19, where examined for their applicability in the preparation of stable, efficient and high purity silver(I) catalysts. From this study COD was determined to be the preferred ligand in terms of yield and purity of the resultant complex, adequate solubility in the bulk monomer, improved storage stability of the catalyst monomer solution and reproducible reactivity in the context of vinyl-ether mediated surface promoted redox cationic polymerisation.

Table 3.19: Structures of ligands used in this study

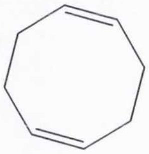
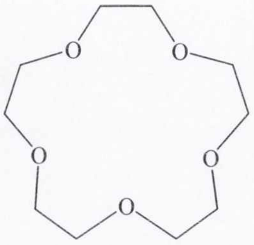
110		1,5-Cyclooctadiene "COD" (108.18 g mol^{-1})
111		1,7-Octadiene (124.22 g mol^{-1})
112		15-Crown-5 (220.26 g mol^{-1})
113		1,5-Hexadiene (82.14 g mol^{-1})

Table 3.20: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol in the presence of Ag SbF$_6$, 0.48 mmol, associated with various ligands & using grit blasted mild steel as substrate and monitored by FT-IR ATR

Monomer (mmol)	**Mediator (mmol)**	**Oxidising Agent**	**(mmol)**	**$t_{½}$ (h)**	**C (%)**
72 (31.71)	**76** (9.88)	Ag SbF$_6$	(0.48)	6.5	19.9
72 (31.71)	**76** (9.88)	[Ag(1,7-Octadiene)$_n$]SbF$_6$	(0.48)	8.0	24.3
72 (31.71)	**76** (9.88)	[Ag(COD)$_2$]SbF$_6$	(0.48)	8.1	24.7
72 (31.71)	**76** (9.88)	[Ag(CH3CN)$_4$]BF$_4$	(0.48)	-	-

The complexes of ligands other than COD (**110**) i.e 1,7-octadiene (**111**), 15-Crown-5 (**112**) and 1,5-Hexadiene (**113**), were difficult to isolate in high yield and adequate purity. Lower purity typically resulted in reduced storage stability although the effect on reactivity in vinyl-ether mediated surface promoted redox cationic polymerisation was minimal, Table 3.20. Similarly the use of unligated, as received, AgSbF$_6$ (**106**) resulted in reduced storage stability, Figure 3.9, and the conversion to polymer was lessened perhaps due to lower mobility of the neat salt in the organic phase.

It was found that the acetonitrile complex of silver(I), $[Ag(CH_3CN)_4]BF_4$, purchased from Sigma-Aldrich and used as received had very low solubilty in the chosen resins. This complex was associated with a tetrafluroborate anion and no attempts were made to prepare the equivalent complex of hexafluoroantimonate in the lab. These two factors and low solubilty in particular contributed to the very limited activity observed for this Ag(I) complex.

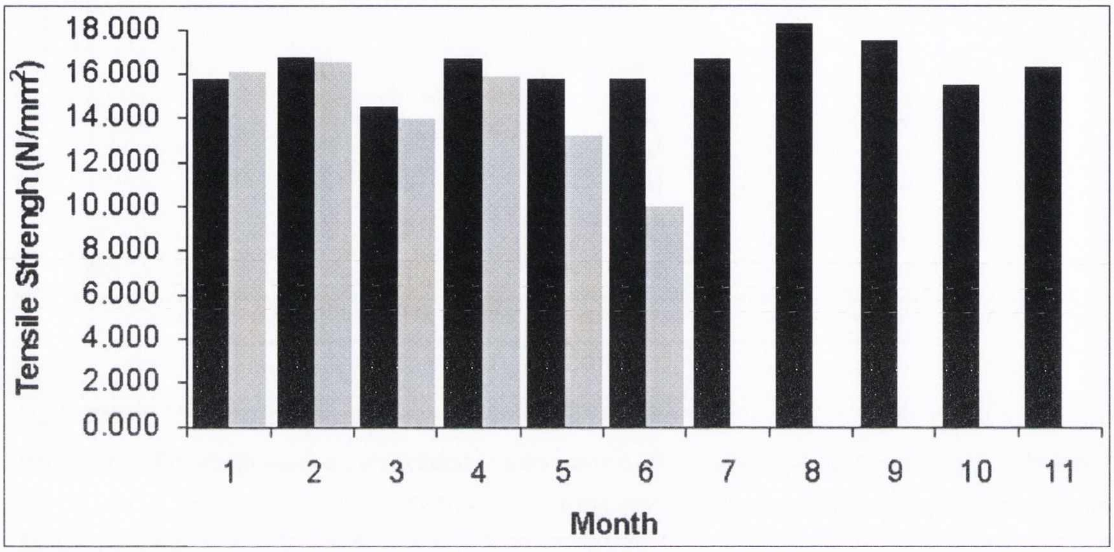


Figure 3.9: Tensile strength following 24 hr cure at ambient temperature using grit blasted mild steel as substrate versus time (months) as measured for monomer (**72**), 31.71 mmol, mediated by DVE3 (**76**) 9.88 mmol comparing the initiators: $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol (■) and Ag SbF_6 (**103**) 0.48 mmol (□). Following six months of storage at room temperature the system based on Ag SbF_6 could no longer be tested due to bulk gelation.

3.8.7 Influence of Cation (M^+) on Vinyl-Ether Mediated Surface Promoted Redox Cationic Polymerisation

Taking the optimised monomer system cycloaliphatic epoxy (**72**), 31.71 mmol, DVE3 (**76**), 9.88 mmol employing the latent initiator $[Ag(COD)_2]SbF_6$ (**103**) , 0.48 mmol as a reference point a series of alternative cationic initiator species, were studied to determine their relative efficiencies in vinyl-ether mediated surface promoted redox cationic polymerisation. The results from this investigation are presented in Table 3.24 and Figure 3.10.

In common with previous redox cationic polymerisation investigations it was found that allyl thiophenium, allyl pyridinium and allyl triphenyl phosphonium hexafluoroantimonate were also inefficient initiators for surface promoted redox cationic polymerisation at a grit blasted mild steel surface. In this study $Ph_2I\ SbF_6$ (**43**), even with its more positive redox potential, was also ineffective as a latent initiator for surface promoted redox cationic polymerisation at a grit blasted mild steel surface.

The three remaining latent catalysts employed in this study based on the following cations: Ag^+ (**103**), Cu^+ (**61**) and $R–N≡N^+$ (**96**); each displayed varying degrees of efficiency as latent initiators for vinyl-ether mediated surface promoted redox cationic polymerisation. This group of latent catalysts all have redox potentials intrinsically more positive than that of Ph_2I and therefore are more liable to undergo reduction processes and this is exemplified in their reactivity on the grit blasted mild steel substrates employed in these polymerisations. Schemes 3.9 to 3.11 outline the probable redox mechanisms involved in cationic initiator generation for these surface promoted polymerisations. In each case the cationic initiator which is believed to play the major role in the observed cationic polymerisations is the strongly Lewis acidic high oxidation state iron salt $Fe(SbF_6)_3$.

$2\ [Ag(COD)_2]SbF_6 + Fe(0) \rightarrow 2\ Ag(0) + 4\ (COD) + Fe(SbF_6)_2$
$3\ [Ag(COD)_2]SbF_6 + Fe(0) \rightarrow 3\ Ag(0) + 6\ (COD) + Fe(SbF_6)_3$ … Scheme 3.9

$2\ [Cu(COD)_2]SbF_6 + Fe(0) \rightarrow 2\ Cu(0) + 4\ (COD) + Fe(SbF_6)_2$
$3\ [Cu(COD)_2]SbF_6 + Fe(0) \rightarrow 3\ Cu(0) + 6\ (COD) + Fe(SbF_6)_3$ … Scheme 3.10

$2\ RPh\ N_2\ SbF_6 + Fe(0) \rightarrow 2\ RPh^{+\bullet} + 2\ N_2 + Fe(SbF_6)_2$
$3\ RPh\ N_2\ SbF_6 + Fe(0) \rightarrow 3\ RPh^{+\bullet} + 3\ N_2 + Fe(SbF_6)_3$ … Scheme 3.11

It was observed that when a sample of Hexyloxyphenyl diazonium SbF_6 (**96**) in isopropyl alcohol solution was applied to a mild steel substrate and a glass microscope slide was used as the second substrate to form a typical bondline configuration loss of the red colour due to reduction of the diazonium component at the iron interface was noted while the simultaneous formation of small gas bubbles (N_2) was also observed. If two glass microscope slides were employed for this simple experiment no colour loss or bubble formation was discerned within an equivalent experimental period. These observations correlate with those reported for the diazonium induced anchoring process (DIAP) [435,436]. When the solvent was replaced with a cationically polymerisable monomer for this experiment polymerisation proceeded rapidly when the monomer /

diazonium mixture was applied in an adhesive bondline on grit blasted mild steel substrates. The $t_{½}$ and conversion to polymer (22.2 %) was very comparable to the results obtained for an equivalent $[Ag(COD)_2]SbF_6$ experiment.

The Cu(I) complex employed in this investigation, $[Cu(COD)_2]BF_4$ (**61**), was associated with a BF_4 anion. This anion is known to be less efficient in the promotion of cationic polymerisations than its SbF_6 counterpart, which was used in conjunction with the other latent catalysts investigated. Several attempts were made to prepare the $[Cu(COD)_2]SbF_6$ complex however these efforts were unsuccessful. The strongly Lewis acidic $Cu(SbF_6)_2$ has been widely used as a catalyst in organic synthesis, however this is typically prepared in situ as the isolated salt requires handling in an inert atmosphere [487]. From the results shown in Table 3.24 it can be seen that $[Cu(COD)_2]BF_4$ gave a somewhat higher $t_{½}$ and polymer conversion (13.8%) when compared to the $[Ag(COD)_2]SbF_6$ used in an equivalent experiment. However, these results do correlate with the results obtained for direct chemical reduction of the $[Cu(COD)_2]BF_4$ by A-6-Hex (**64**) in section 3.6 in which no strong reaction was noted although slow conversion to polymer did occur over time.

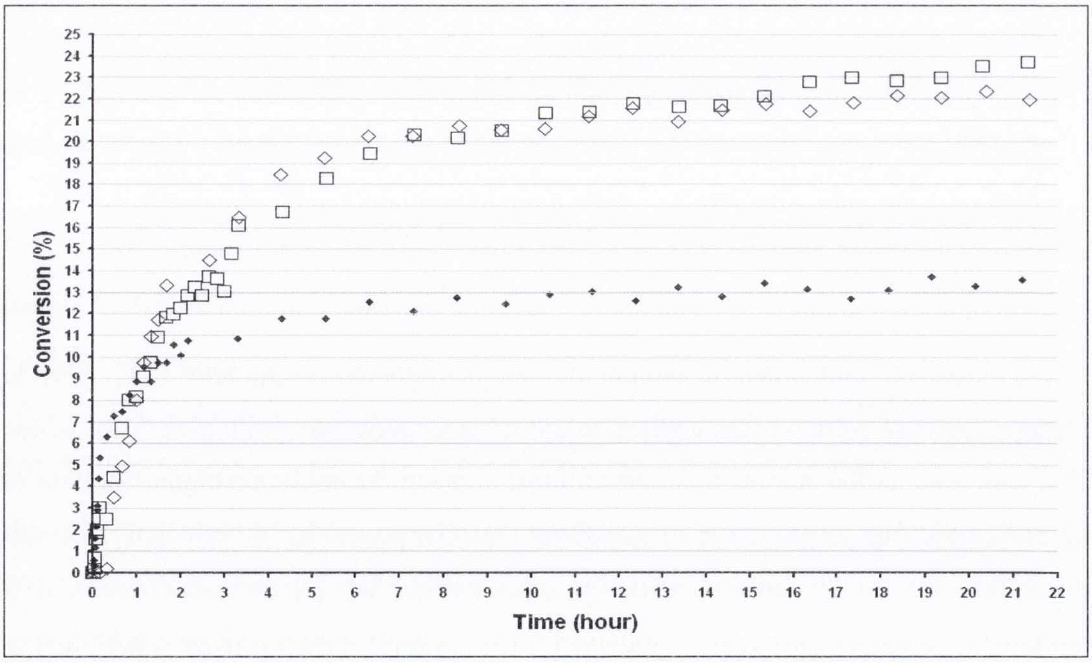


Figure 3.10: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol with the following latent initiators, 9.88 mmol: $[Ag(COD)_2]SbF_6$ (**103**) ◇, $[Cu(COD)_2]BF_4$ (**61**) ◆, Hexyloxyphenyl diazonium SbF_6 (**96**) □. Each polymerisation was performed on a grit blasted mild steel substrate and conversion to polymer was monitored by FT-IR ATR.

Table 3.21: $E_{1/2}^{red}$ for a range of latent cationic initiators, 9.88 mmol, and their associated conversion (%) for monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol, using grit blasted mild steel and monitored by FT-IR ATR

Cation X (mmol) *	**Monomer (mmol)**	**Mediator (mmol)**	**$E_{1/2}^{red}$ (NHE)$^{\#}$ *V***	**$t_{1/2}$ (h)**	**C (%)**
103 $[Ag^{I}(COD)_2]SbF_6$ (0.48)	**72** (31.71)	**76** (9.88)	+ 0.80	8.1	24.7
61 $[Cu^{I}(COD)_2]BF_4$ (0.48)	**72** (31.71)	**76** (9.88)	+ 0.52	1.6	13.8*
96 Hexyloxyphenyl diazonium SbF_6 (0.48)	**72** (31.71)	**76** (9.88)	+ 0.59	8.0	22.2
43 Diphenyliodonium PF_6 (0.48)	**72** (31.71)	**76** (9.88)	- 0.04	-	0
53 Ethyl-α-(Tetrahydrothiophenium Methyl)Acrylate SbF_6 (0.48)	**72** (31.71)	**76** (9.88)	- 0.34	-	0
52 Ethyl-α-Pyridinium Acrylate SbF_6 (0.48)	**72** (31.71)	**76** (9.88)	- 0.46	-	0
54 Ethyl-α-Triphenyl Phosphonium Acrylate SbF_6 (0.48)	**72** (31.71)	**76** (9.88)	- 0.71	-	0

* With the exception of the Cu(I) salt, hexafluoroantimonate was the anion employed in each case. Cu(II) salts of non-nucleophilic anions were not included here as they were observed to be strongly Lewis acidic and catalysed cationic polymerisation upon contact with epoxy monomer. Isolable Cu(I) salts of anions larger than tetrafluoroborate were not prepared [487], see Chapter six.

\# NHE, literature cation values [217,225,247,248,250,251,443,444]

It should be noted, as experimentally indicated in Section 3.8.5 and shown in Table 2.1, that the redox potential for a particular cation tends to become more positive as the associated anion becomes larger or more non-nucleophilic. This may be achieved by shifting the anion associated with a particular onium salt to a suitably non-nucleophilic species (Table 2.2) thereby modulating the redox potentials of the latent initator so that its reduction by a chosen active substrate is favourable. In effect this should enable activation of several of the apparently ineffective onium cations, particularly Ph_2I^+, for surface promoted redox cationic polymerization.

Indeed the ability to attenuate the redox potential of the ostensibly inactive Ph_2I cation was indicated by using the commercially available $Ph_2I\ B(C_6F_5)_4$ (**58**) latent catalyst, 0.48 mmol, in a typical experimental monomer system employing 3,4-epoxycyclohexylmethyl-3,4-epoxy cyclohexane carboxylate monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol and using freshly grit blasted mild steel as substrate. There was no detectable peroxide present in the monomers employed. Activity of samples was tested using the described tensile test method. Tensile test results demonstrated poor reproduciblity between prepared samples and adhesion (10 – 12 N/mm^2, GBMS) was lower than that achieved for an equivalent $[Ag(COD)_2]SbF_6$ system (*c.* 19 N/mm^2, GBMS) even following a 72 hr cure at ambient temperature, Figure 3.11. No successful FT-IR analyses could be performed using the described system. The reasons for this are undecided however this system clearly has lower inherent activity when compared to an equivalent $[Ag(COD)_2]SbF_6$ based system. This system clearly warrants further investigation.

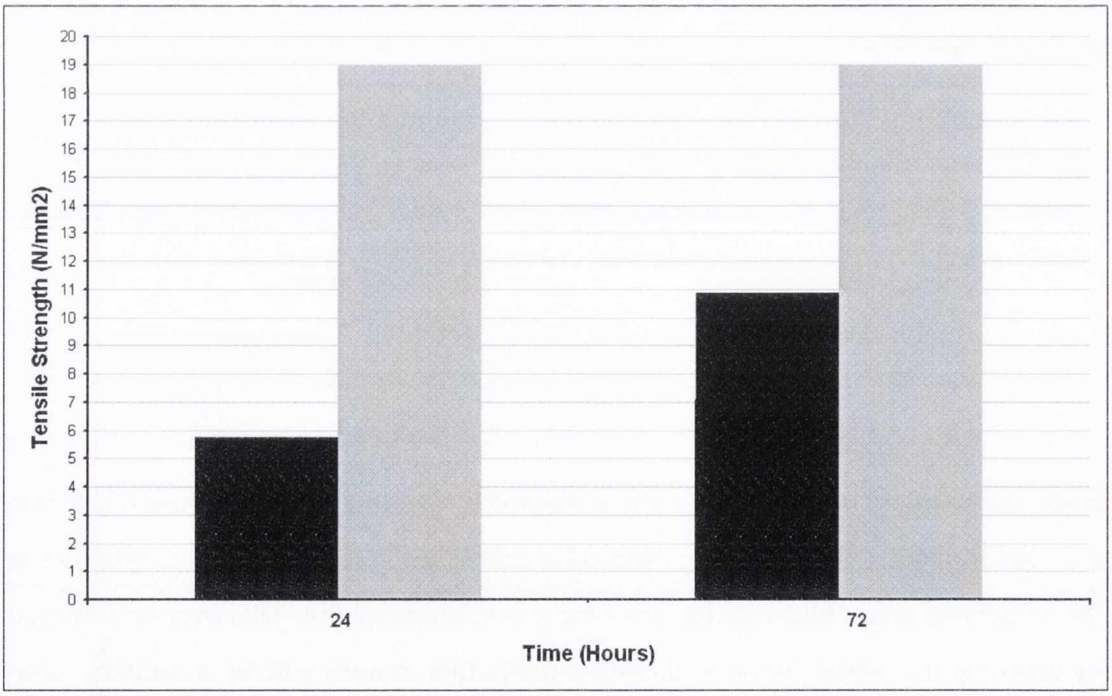
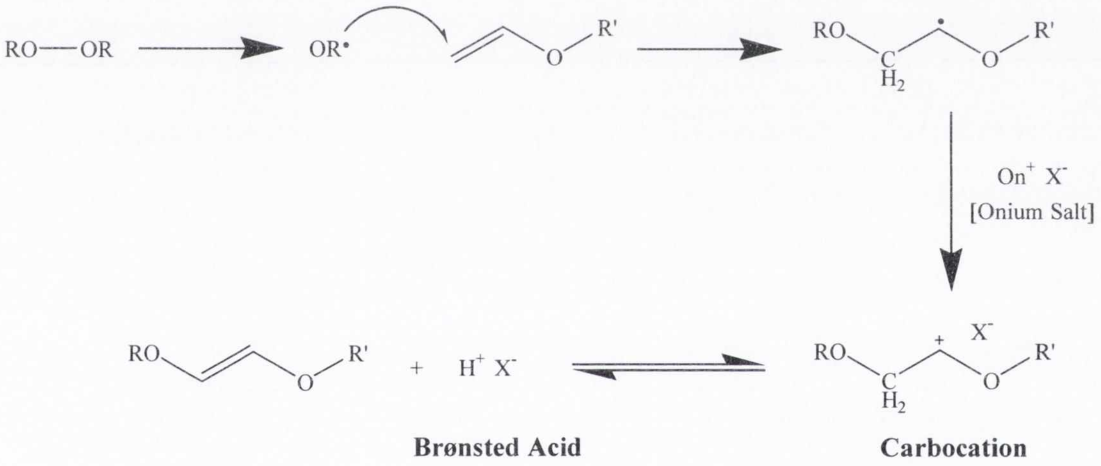


Figure 3.11: RT tensile cure strengths for monomer (**72**), 31.71 mmol, mediated by DVE3 (**76**) 9.88 mmol using Ph_2I cation with $B(C_6F_5)_4^-$ anion (**58**) ■, and $[Ag(COD)_2]SbF_6$ (**103**) ▨, as initiators, 0.48 mmol on GBMS substrates.

3.8.8 Redox Radical Promoted Cationic Polymerisation

The reductive decomposition of onium salts by free radicals, as originally proposed by Ledwith, may provide a further route to preparation of one-component room temperature curable epoxy adhesives [254]. Radical promoted cationic polymerisation means the polymerisation of cationically polymerisable monomers with radical initiators in the presence of an electron acceptor, typically an iodonium salt [463,464]. Several research groups have demonstrated free radical promoted cationic polymerisation using a range of photo and thermal radical generators [342-344,367-374]. In many ways the bringing together of redox radical and redox cationic initiation chemistries would be a clear demonstration of the power of redox reactions. From the preceding discussion, it is reasonable to infer that surface promoted redox radical and radical promoted redox cationic polymerisation can be brought together, Scheme 3.12.



… Scheme 3.12

With this as a further goal the experimental investigation outlined in Table 3.22 was undertaken. Anaerobic sensitivity of this redox radical promoted cationic polymerisation was observed following storage in glass vessels for several days. In such instances gelation was observed to occur in the lower regions of the storage vial while the surface material remained fully liquid i.e. the region of lowest oxygen content cures first. This is a profile typical of bulk anaerobic polymerisations. The adhesive cure profile for this redox radical promoted cationic cure system on a grit blasted mild steel substrate is presented in Figure 3.12. This mode of redox cationic initiation requires further study.

The steps involved in this radical promoted redox cationic polymerisation may be outlined in the following stages:

(a) The redox or anaerobic generation of electron-donating free radicals.

(b) Aliphatic α-ether radical formation following oxidation by free radical addition to vinyl ether double bond.

(c) Electron transfer of α-ether radical to suitable oxidizing agents, e.g. iodonium salt, producing cationic initiator species e.g. carbocation or Brønsted acid.

(d) Initiation of cationic polymerisation by these species.

Table 3.22: Identification of the reactive species required for achieving anaerobic or redox radical promoted cationic polymerisation. Surface polymerisations were performed on grit blasted mild steel and monitored by FT-IR ATR

Cation X (mmol) *	Redox Radical Source	Monomer (mmol)	Mediator (mmol)	Anaerobicity*	C (%)
43 Diphenyliodonium PF_6 (0.48)	**89** BPO **(0.00)**	**72** (31.71)	**76** (9.88)	No	0
43 Diphenyliodonium PF_6 (0.48)	**89** BPO (0.48)	**72** (31.71)	**76 (0.00)**	No	0
43 Diphenyliodonium PF_6 **(0.00)**	**89** BPO (0.48)	**72** (31.71)	**76** (9.88)	No	0
43 Diphenyliodonium PF_6 (0.48)	**89** BPO (0.48)	**72** (31.71)	**76** (9.88)	**Yes**	**15.6**

* In order to ascertain if the solutions detailed above displayed anaerobicity sample vials were sealed with a rubber septum and purged with argon for 20 minutes. Samples displaying anaerobic polymerisation formed a gel in less than *c.* 24 hours following the de-oxygenation procedure under ambient temperature and while stored in the dark. Non-anaerobic samples remained in an uncured liquid state even following several days under identical storage conditions.

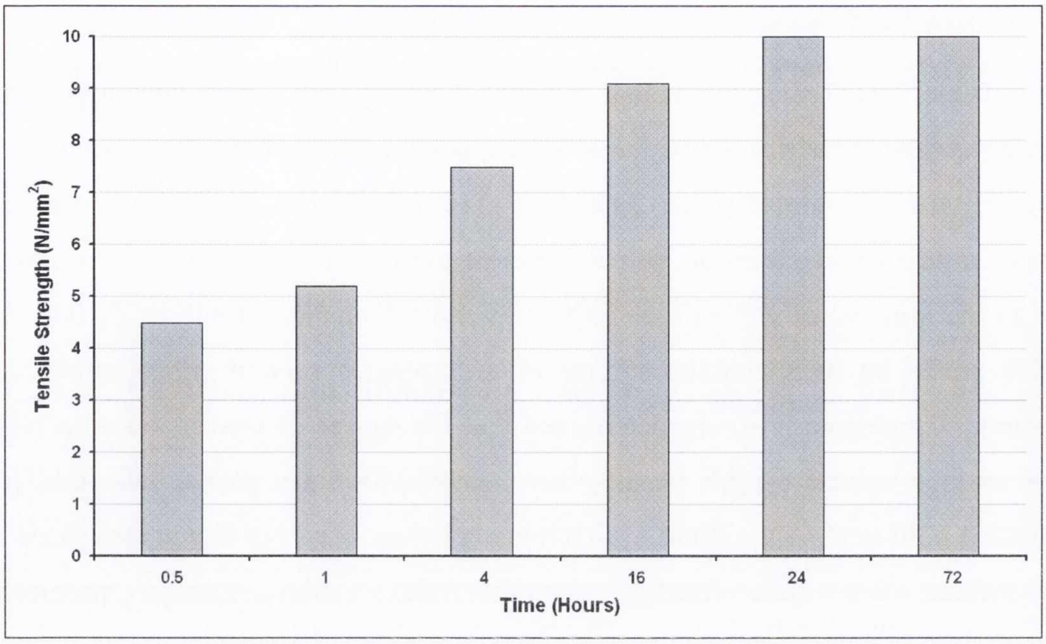


Figure 3.12: Room temperature tensile strength cure profile for monomer (**72**), 31.71 mmol, mediated by DVE3 (**76**) 9.88 mmol using $Ph_2I\ PF_6$ (**43**), 0.48 mmol as cationic initiator and Benzoyl Peroxide (**89**), 0.48 mmol as radical generator (▨). All tests were performed on grit blasted mild steel substrates.

3.8.9 Vinyl-Ether Mediated Surface Promoted Redox Cationic Polymerisation on a Range of Metallic and Non-Metallic Substrates

A wide range of materials including various metals, plastics and ceramics are used in industrial adhesives applications. Iron is of particular interest as an adhesive substrate as it is one of the most widely used metals in industrial adhesives applications [445]. Iron is also one of the more chemically reactive metals, as demonstrated by its ready oxidation (Fe_2O_3). Other engineering metals show varying reactivity. Aluminium is more reactive than iron although this property is not readily apparent as when exposed to atmospheric oxygen it quickly forms an aluminium oxide (Al_2O_3) layer, which is colourless and adheres strongly to the native metal underneath thereby passivating the exposed surface. Surface promoted redox cationic polymerisation as described thus far relies on the reducing ability of the substrate to be bonded to promote formation of the key acidic cationic initiating species. In this study a range of substrates many of which can be found in industrial adhesives applications were investigated to determine their relative efficacy as promoters of surface promoted redox cationic polymerisation. The two broad categories investigated were metals and non-metals; the results of this study are presented in Table 3.26 and 3.27 respectively.

3.8.9.1 Metallic Substrates

From Table 3.21 it is apparent that metallic substrates are active substrates, with varying degrees of efficacy, for the room temperature promotion of redox cationic polymerisations employing $[Ag(COD)_2]SbF_6$ (**103**) as catalyst. In general terms grit blasted mild steel is a very active substrate for promotion of these reactions, likely due to the removal of any surface impurities and elimination of any oxide barriers which are to be found on the surface of an untreated solvent wiped mild steel substrate. Consequently it was determined that the degree of conversion on a mild steel surface treated by grit blasting was almost 2.5 times greater than that for untreated mild steel. Aluminium, which inherently has a layer of aluminium oxide at its surface, was quite inactive towards redox cationic surface promoted polymerisation unless subjected to further pre-treatment before use.

During this study it was observed that the use of copper as a substrate for the promotion of redox cationic polymerisations employing $[Ag(COD)_2]SbF_6$ (**103**) resulted in an induction period before following the typical conversion cure profile as recorded for other active substrates, Figure 3.13. An induction period such as this was not noted for any of the other surface promoted redox cationic polymerisations in this study. This induction period may be rationalised when one considers the possible interaction between the $[Ag(COD)_2]SbF_6$ initiator and Cu(0), Scheme 3.13.

$$[Ag(COD)_2]SbF_6 + Cu(0) \rightarrow [Cu(COD)_2]SbF_6 + Ag(0)$$

$$[Ag(COD)_2]SbF_6 + [Cu(COD)_2]SbF_6 \rightarrow Ag(0) + 4(COD) + Cu(SbF_6)_2$$

… Scheme 3.13

Therefore, it is proposed that the observed induction period may be due to the transient formation of a COD ligand stabilised Cu(I) salt, during an equilibrium period, prior to further oxidation or disproportionation of the Cu(I) species to the more strongly Lewis acidic Cu(II) species that is understood to promote cationic polymerisation.

Table 3.23: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol in the presence of $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol using several metallic substrates as monitored by FT-IR ATR

Monomer (mmol)	**Mediator (mmol)**	**Oxidant**	**(mmol)**	**Substrate**	**$t_{\frac{1}{2}}$ (h)**	**C (%)**
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Copper	4.5	27.5
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Grit Blasted Mild Steel	8.1	24.7
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Mild Steel	6.4	10.8
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Aluminium	7.2	7.8

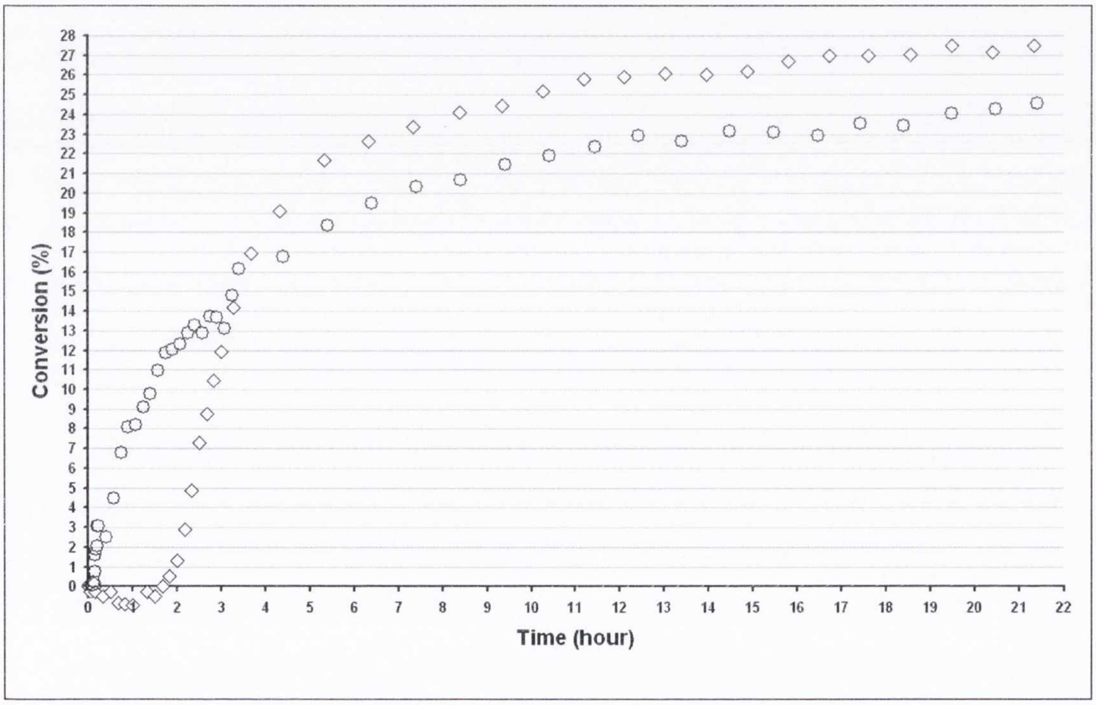


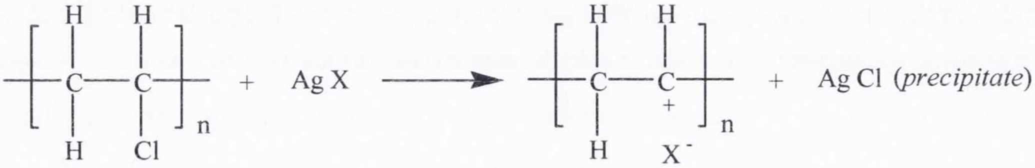
Figure 3.13: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol using $[Ag(COD)_2]SbF_6$ (**103**) 9.88 mmol as initiator on solvent wiped Copper (◇) and grit blasted mild steel (○) substrates. Conversion to polymer was monitored by FT-IR ATR.

Table 3.24: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol in the presence of $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol using various non-metallic substrates as monitored by FT-IR ATR

Monomer (mmol)	**Mediator (mmol)**	**Oxidant**	**(mmol)**	**Substrate**	**$t_{½}$ (h)**	**C (%)**
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Glass	-	0
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Polycarbonate	-	0
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Perspex	-	0
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	PVC	7.5	28.7
72 (31.71)	**76** (9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Teflon	-	0

3.8.9.2 Non-Metallic Substrates

The majority of non-metallic substrates, i.e. glass and plastics, induced no polymerisation reaction when contacted with a typical cationically polymerisable formulation containing $[Ag(COD)_2]SbF_6$ (**103**) as initiator, Table 3.24. However, it was observed that polyvinyl chloride, a commercially important material, was a good substrate for promotion of room temperature cationic polymerisation employing silver(I) salts of non-nucleophilic anions, Figure 3.14. Figure 3.15 shows the *adhesive* cure profile on polyvinyl chloride of a model surface promoted redox cationic polymerisation system comprising the cycloaliphatic monomer (**72**) mediated by DVE3 (**76**) employing $[Ag(COD)_2]SbF_6$ (**103**) as latent catalyst. It is proposed that the mechanism involved in this example of surface promoted cationic polymerisation is based on anion exchange or halide abstraction, Scheme 3.14.



... Scheme 3.14

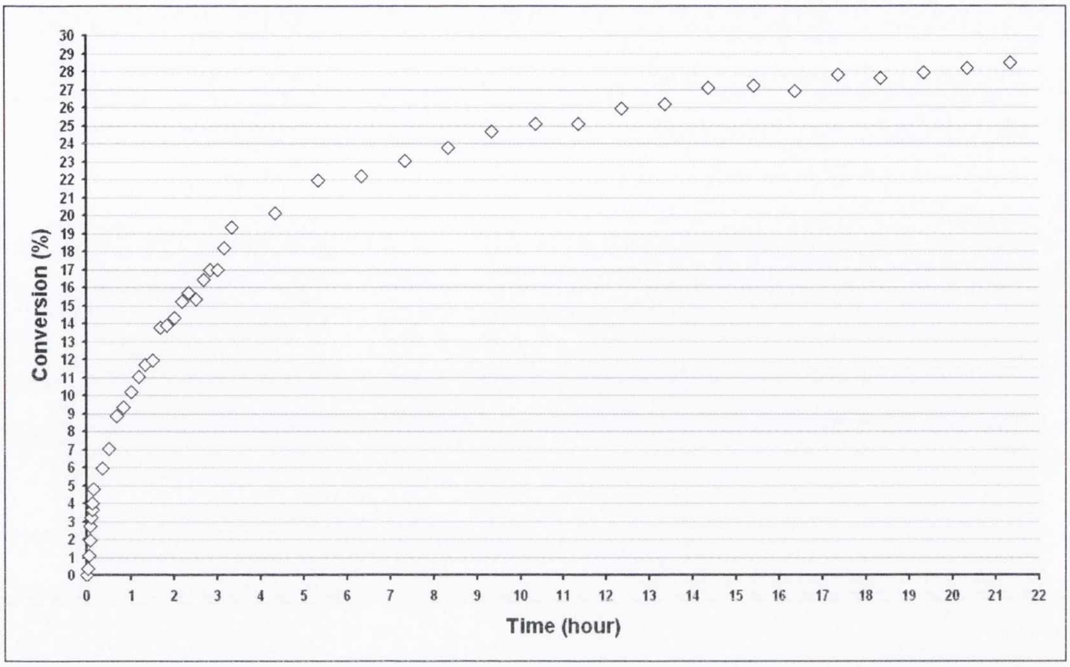


Figure 3.14: Conversion (%) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol using $[Ag(COD)_2]SbF_6$ (**103**) 9.88 mmol as initiator on a PVC (◇) substrate. Conversion to polymer was monitored by FT-IR ATR.

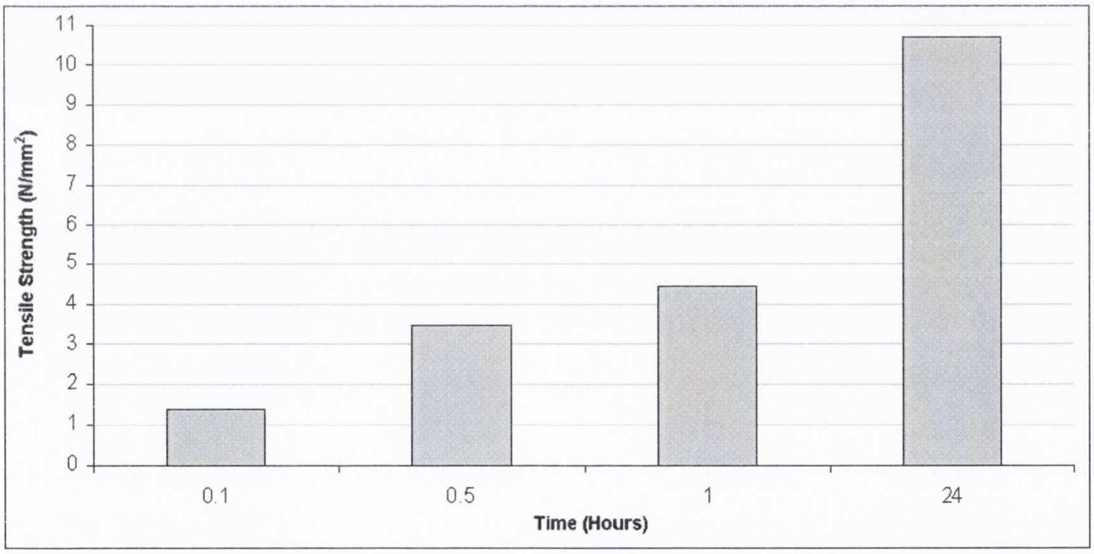
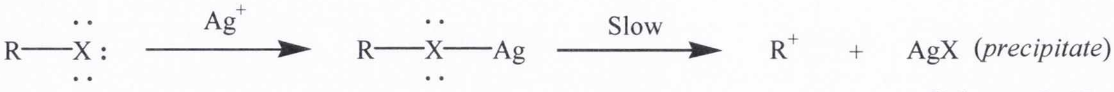


Figure 3.15: Room temperature tensile strength cure profile for monomer (**72**), 31.71 mmol, mediated by DVE3 (**76**) 9.88 mmol using $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol as initiator on a polyvinyl chloride substrate.

Support for this proposed mechanism comes from the known reactions of silver salts with alkyl halides. Such a reaction forms the basis of the alcoholic silver nitrate test for alkyl halides, Scheme 3.15. The driving force for this reaction is the formation of insoluble silver halides, with the exception of fluoride. Silver salts catalyse SN1 reactions of alkyl halides through complexation with the lone-pair of electrons on the halide atoms, and the resultant leaving group is a silver halide rather than a halide ion.

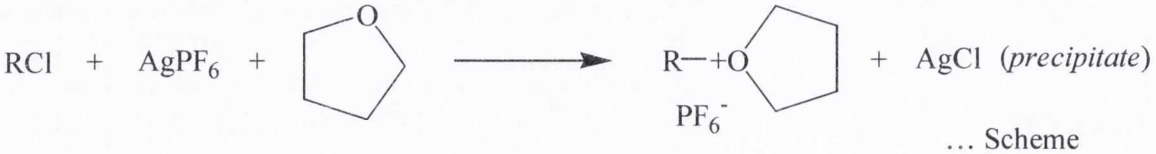


$$R-\ddot{\underset{..}{X}}: \xrightarrow{Ag^+} R-\ddot{\underset{..}{X}}-Ag \xrightarrow{\text{Slow}} R^+ + AgX\ (\textit{precipitate})$$

... Scheme 3.15

The rate of reaction (silver halide precipitation) depends on both the halide leaving group where I > Br > Cl and also on the structure of the alkyl moiety. Structural elements that stabilise the formation of the electron deficient carbocation serve to promote the reaction. The expected order of reactivity for halide abstraction by Ag(I) is: Benzyl ≈ allyl > 3° > 2° > 1° > methyl > vinyl ≈ aryl.

Dreyfuss and co-workers have previously exploited this type of reaction in solution as a means of initiating cationic polymerisation by mixing a silver salt of a non-nucleophilic anion, an alkyl halide and a cationically polymerisable monomer, Scheme 3.16 [489,490]. Similarly, Drain and co-workers have also demonstrated a two-component cationic adhesive based on this initiation mechanism in which an alkyl halide is incorporated into the cationically polymerisable monomer and a second solution containing the silver salt of a non-nucleophilic anion [491-493]. Upon mixing a silver halide is removed from solution by precipitation leaving a cationic polymerisation initiating carbocation centre and associated non-nucleophilic anion.



... Scheme 3.16

Of most interest in the context of surface promoted is the observation that a poly-alkyl halide in the form of an important structural material and substrate, i.e. PVC, can be harnessed to promote solvent free, no-mix and ambient temperature activated cationic polymerisation of an epoxy monomer. This could be of significant benefit for many commercial applications including substitution for existing high VOC adhesives or energy saving in applications that currently employ hot-melt adhesives for lamination.

3.8.10 Investigation of the Thermal Properties of Surface Promoted Redox Cationic Polymerisation Systems Employing Ag(I) as Latent Initiator

A significant motivation for development of a one-component room temperature polymerisable epoxy adhesive is to leverage the thermal performance that is understood to be inherent to thermally cured polyether polymers [19]. It is therefore of benefit to quantify the thermal performance that can be achieved by a model polyether formed from surface promoted redox cationic polymerisation including the adhesive strength at elevated temperatures, adhesive strength following thermal aging of the cured polymer and the glass transition temperature (T_g). Additionally the thermal stability of Ag(I) based surface promoted redox cationic formulations is of critical importance in the development of a commercially viable product. Such a stability study will provide a general indication of the safety of such a product for preparation in large volume and during periods of prolonged storage.

3.8.10.1 Thermal Adhesive Performance of a Model System

The inherent thermal perfomance and properties possessed by an unformulated model surface promoted redox cationic adhesive are presented in Table 3.25. From this study it is clear that the data lend support to the reasoning behind development of a redox cationic polymerisation response to anaerobic acrylate adhesives.

The unformulated redox cationic adhesive employed here shows significant thermal performance when tested at elevated temperatures, i.e. 150 °C, 175 °C and 200 °C. In contrast the formulated commercial anaerobic methacrylate adhesives demonstrate significantly less adhesive performance at these elevated temperatures.

The data presented in Table 3.25 also shows that even following one week of thermal aging at 150 °C, 175 °C and 200 °C the unformulated model surface promoted redox cationic adhesive system can compete with the commercial anaerobic methacrylate adhesive systems.

Table 3.25: Thermal performance (tensile strength, N/mm^2) of a typical polyether formed by surface promoted redox cationic (SPRC) polymerisation, using two commercial anaerobic acrylate products (Loctite® 620 and Loctite® 2701) for comparison. Substrate in all tests is aluminium pins and collars.

		SPRC Polyether (N/mm^2)	**Loctite® 620* (N/mm^2)**	**Loctite® 2701* (N/mm^2)**
Ambient Cure, 24 hr		4.6	3.4	4.9
Hot Strength (After 24 hr RT Cure)	150 °C	10.0	5.9	3.3
	175 °C	10.0	5.9	3.6
	200 °C	11.5	4.5	2.6
Thermally Aged, 1 week (After 24 hr RT Cure) Tested at RT	150 °C	13.0	12.5	21.4
	175 °C	11.7	10.7	15.8
	200 °C	9.3	9.1	14.9

*N.B. Loctite® 620 is classified as a medium to high-strength retaining adhesive
Loctite® 2701 is classified as a high-strength threadlocking adhesive
Technical data sheets for both Loctite® 620 and Loctite® 2701 are included in the appendices of this thesis

3.8.10.2 Glass Transition Temperature (T_g)

The T_g of the model polyether formed by ambient temperature surface promoted redox cationic polymerisation in these studies was determined to be 137 °C, Table 3.26 and Figure 3.16. Subsequent thermal post baking for periods of 30 minutes at 180 °C and also 250 °C, Figures 3.17 and 3.18 respectively, did not invoke a change in the determined glass transition temperature although such treatment undoubtedly promoted conversion of available unpolymerised material.

It was interesting to note that the ambient temperature cured and 180 °C thermally treated surface promoted redox cationic polymers both contained a second peak at around 200 °C. This peak however was absent following thermal treatment for 30 minutes at 250 °C. Subsequent investigation suggested that this secondary peak corresponds to the thermal decomposition of the ligand associated with the latent catalyst employed in these experiments, $[Ag(COD)_2]SbF_6$, which occurs in the region of 220°C, Figure 3.19.

The glass transition temperature determined for such a simple surface promoted redox cationic polyether was favourable particularly when compared to a formulated commercial anaerobic acrylate adhesive, Table 3.26. It must of course be noted that the Loctite® 2701 anaerobic adhesive used here for comparative purposes has not been developed for thermal resistence rather it was chosen as a representative off-the-shelf material.

By way of additional comparison typical two-part epoxy adhesives are comprised of an epoxy monomer and an aliphatic amine curative, which are mixed before curing at room temperature. Typically such two-part adhesives are understood to yield polymers with limited thermal resistance, T_g of 50 – 105 °C [494]. A thermal post bake treatment to accelerate the polymerisation process of such two-part epoxy adhesives is not unusual.

Table 3.26: Glass transition temperature (T_g) of a typical polyether formed by surface promoted redox cationic (SPRC) polymerisation, using a commercial anaerobic acrylate product (Loctite® 2701) as a comparison and PMMA homopolymer as a control

Monomer (mmol)	**Experimental**	**Theoretical**	**[Ref]**
SPRC Polyether*	137 °C	-	-
Loctite® 2701 (Polymethacrylate) Commercial Anaerobic Adhesive	108 °C	-	-
PMMA (Control)	133 °C	*c.* 135 °C	[495]

*Polyether formed from a model system comprising: monomer (**72**), 39.63 mmol, mediated by DVE3 (76) 9.88 mmol in the presence of $[Ag(COD)_2]SbF_6$ (**103**) 0.48 mmol as initiator.

Polymerisation for both the polyether and commercial polymethacrylate specimens was achieved as a thin film within a folded mild steel pouch, T_g was determined directly from the samples formed.

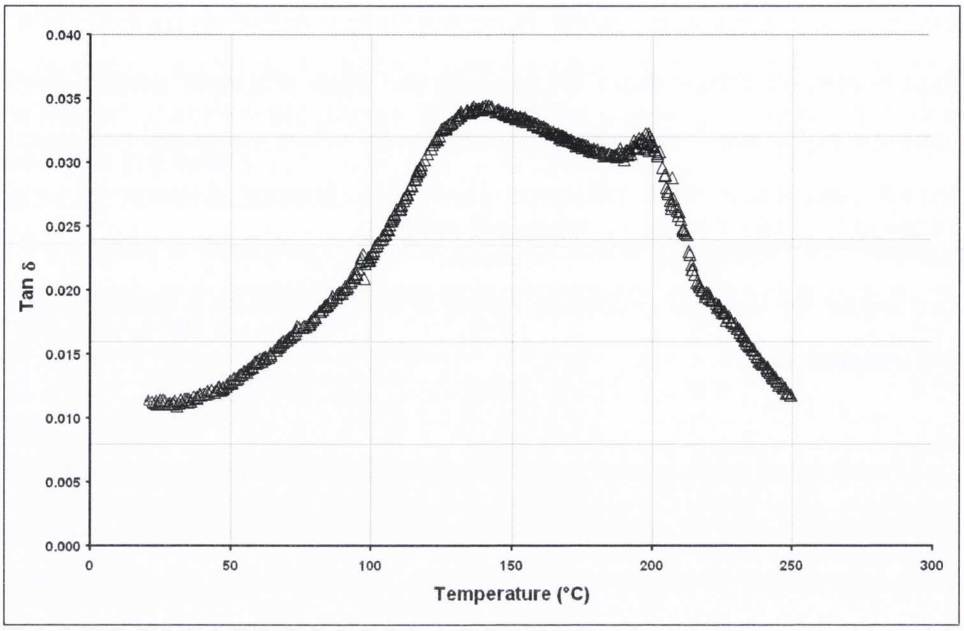


Figure 3.16: Dynamic mechanical (1 Hz) properties versus temperature for polymer formed following 24 hr cure at ambient temperature in a mild steel pouch. Using monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol employing [Ag(COD)$_2$]SbF$_6$ (**103**), 9.88 mmol as initiator.

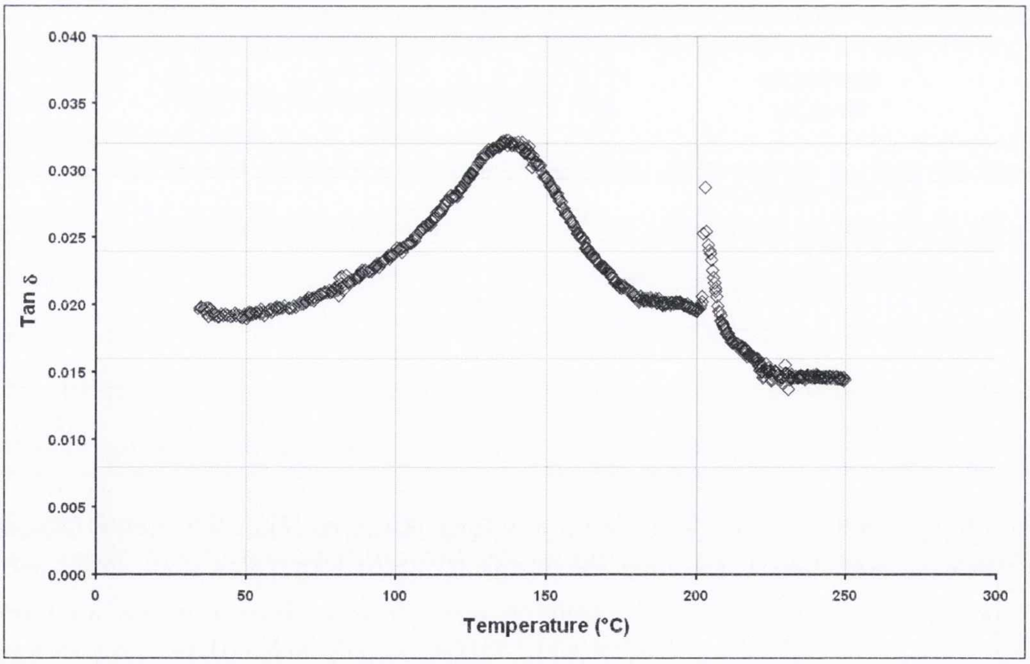


Figure 3.17: Dynamic mechanical (1 Hz) properties versus temperature for polymer formed following 24 hr cure at ambient temperature and 30 min cure at 180°C in a mild steel pouch. Using monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol employing [Ag(COD)$_2$]SbF$_6$ (**103**), 9.88 mmol as initiator.

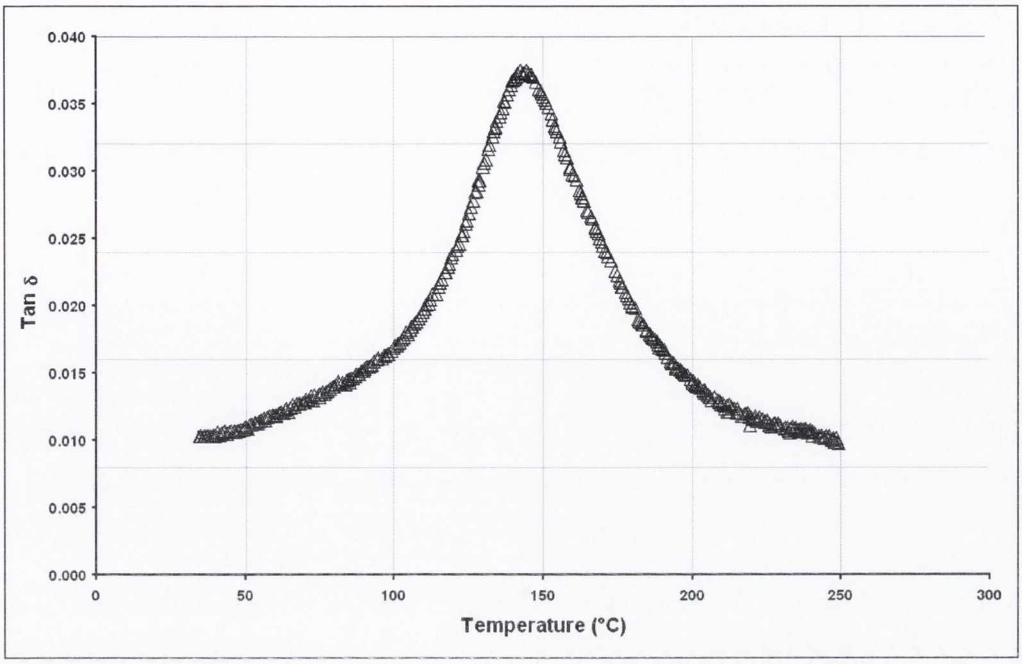


Figure 3.18: Dynamic mechanical (1 Hz) properties versus temperature for polymer formed following 24 hr cure at ambient temperature and subsequent thermal cure at 250°C for 30 min in a mild steel pouch. Using monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol employing $[Ag(COD)_2]SbF_6$ (**103**), 9.88 mmol.

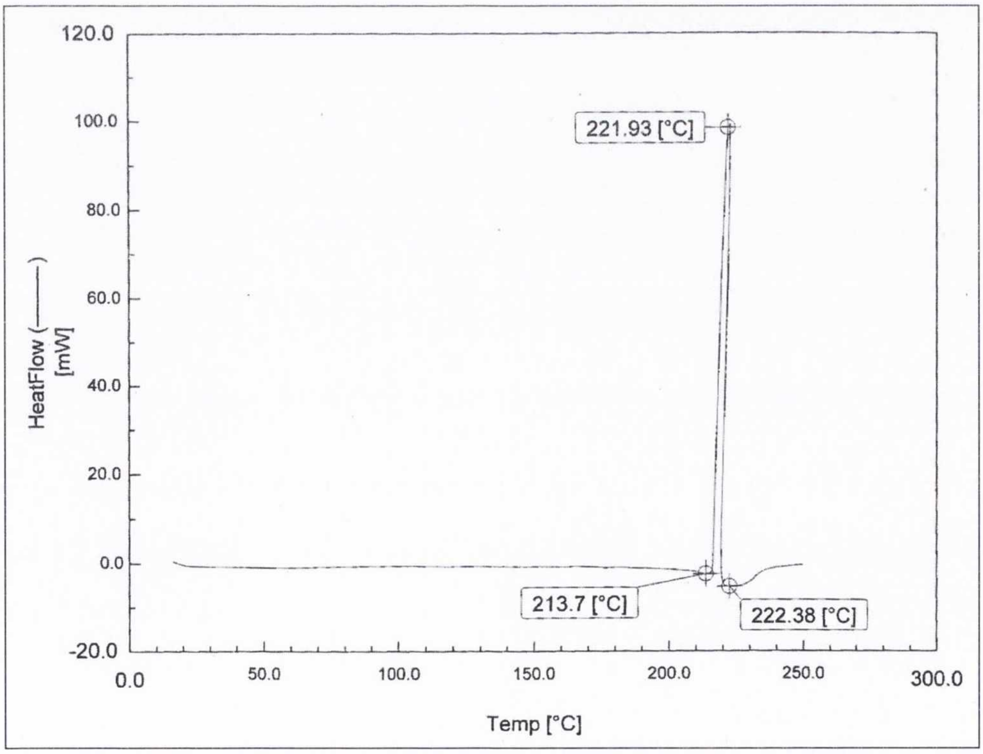


Figure 3.19: Differential Scanning Coulometry (DSC) of $[Ag(COD)_2]SbF_6$ (**103**) showing its thermal decomposition temperature at 221.9 °C

3.8.10.3 Thermal Stability of Initiator & Polymerisable Composition

A further study was undertaken to investigate the thermal stability of the latent initiator within the polymerisable monomer composition. The neat latent catalyst $[Ag(COD)_2]SbF_6$ (**103**) has a thermal decomposition temperature of 222 °C, Figure 3.19. However the thermal stability of this species when present in a polymerisable matrix decreases considerably with increasing temperature, Figure 3.20. So, while polymerisation is readily activated at ambient temperatures when contacted with suitable substrates, polymerisation can also be activated thermally for these polymerisable systems. This ability to activate thermally needs to be taken into consideration if this chemistry is to be used successfully in a commercial application.

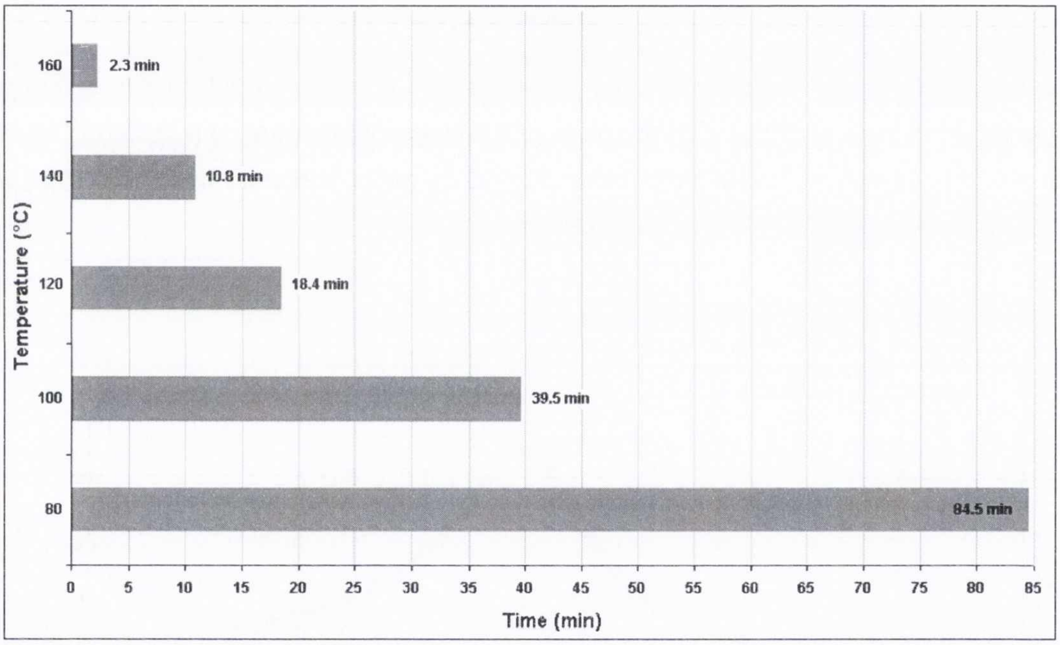


Figure 3.20: Time to 95% conversion with increasing temperature by Isothermal DSC (STM 2116) of monomer (**72**), 39.63 mmol, mediated by DVE3 (**76**) 9.88 mmol employing $[Ag(COD)_2]SbF_6$ (**103**), 9.88 mmol

In summary the data presented here for thermal adhesive performance, glass transition temperature and the thermal stability of the bulk formulation for surface promoted redox cationic polymerisation systems employing $[Ag(COD)_2]SbF_6$ (**103**) as latent initiator clearly show the speculated thermal performance of polymers formed by surface promoted redox cationic polymerisation. As such, much scope must be presented for development of commercially useful ambient temperature curing one-component epoxy adhesive systems.

3.10 Conclusion

The major conclusions from this novel approach to surface promoted redox cationic polymerisation may be summarised as follows:

1. Direct reduction of silver(I) salts of non-nucleophilic anions, employed here as latent cationic initiators, by selected reducing agents *is* an efficient process.

2. Silver(I) was selected due to its favourable reduction potential. This facility for reduction has allowed realisation of the key objective of this study i.e. demonstration of surface promoted cationic polymerisation on metallic substrates at ambient temperatures.

3. Co-monomers such as vinyl ethers, which have a propesnsity α-ether radicals via a proton abstraction mechanism, were found to accelerate the redox decompostion of the latent catalyst and further enhanced the efficiency of the described systems.

4. The nature of the non-nucleophilic anion associated with the latent catalyst was confirmed to be important in the context of surface promoted redox cationic polymerisation. Surface promoted polymerisation was found to proceed more readily as the non-nucleophilicity of the anion increased i.e. $SbF_6 > PF_6 > BF_4 > CF_3SO_3$.

5. Several cations were shown to be useful in the described surface promoted redox cationic polymerisations. The efficacy of the cations decreased broadly in line with calculated theoretical free energies for activity on ferrous substrates i.e. Ag(I) > RN_2^+ > Cu(I) > Ph_2I^+. In the case of copper(I) the inability to prepare the hexafluorantimonate salt is likely to have resulted in its lower efficiency relative to the diazonium hexafluoroantimonate catalyst.

6. Surface activity of the silver(I) surface promoted redox catonic polymerisation was shown to decrease in the order Cu > Fe > Al, corresponding with lower oxidation potential of the substrate and also the propensity for surface oxides to be present. An alternative surface promoted redox cationic initiation mechanism on polyvinyl chloride substrates was also demonstrated.

7. Polymers formed using model surface promoted redox cationic cure systems were confirmed to have inherent thermal properties widely attributed to polyethers.

In summary *an efficient and stable one-component ambient temperature curable surface activated redox cationic cure system with attractive thermal properties has been demonstrated.* Such a system has not been described previously. Additionally this approach addresses the inherent limitations of previously described redox cationic intiation systems and as such has potential for further development into a practical adhesives technology.

CHAPTER FOUR | EXPERIMENTAL & SYNTHETIC PROCEDURES

This chapter describes general experimental techniques employed during the course of this research. When very specific experimental techniques have been used these have been described during the experimental sections of the chapters concerned. Also described are the synthetic procedures followed in this work for the preparation of a range of latent cationic initiators and other materials. Where materials have been prepared using previously published methodologies relevant citations have been included in the main body of text and those preparations are not repeated here.

4.1 Experimental Techniques

4.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectra were collected using a ThermoElectron Nicolet 380 FTIR fitted with a Smart Orbit^{TM} attenuated total reflectance (ATR) accessory employing a diamond crystal, using a DLaTGS detector and OMNIC version 7.4.127 software.

4.1.2 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA studies were performed using a Tritec 200 dynamic mechanical analyser from Triton Technology Ltd. Typical experiments were performed at a frequency of 1 Hz and a thermal ramp rate of 4°C/min.

4.1.3 Differential Scanning Calorimetry (DSC)

DSC analyses were recorded using a DSC Plus, Rheometric Scientific Inc. calorimeter.

4.1.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR experiments were typically performed by Dr. John O'Brien, School of Chemistry, Trinitiy College Dublin. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a Brucker Avance DPX 400 MHz spectrometer.

4.1.5 Mass Spectrometry (MS)

Mass spectrometric analyses were performed by Mr. Dermot Heatley, Analytical Department, Henkel Ireland Ltd. Samples were studied using a using a PE-GCMS Clarus 500, Perkin Elmer GCMS spectrometer.

4.1.6 X-Ray Crystallography

All X-ray crystallographic determinations were performed Dr. Thomas McCabe, School of Chemistry, Trinitiy College Dublin. Samples were studied using a Rigaku Saturn-724 CCD X-ray diffractometer equipped with both CuKα and MoKα radiation sources.

4.1.7 Elemental Analysis

All carbon, hydrogen and nitrogen (C, H, N) elemental analyses were performed in the elemental analysis laboratory of University College Dublin. Samples were studied using an Exeter Analytical CE440 elemental analyser. A sample of 1.6 to 1.8 mg was loaded into a carousel containing conditioners, blanks and standards. Throughout the run standards were inserted following each batch of 8 to 10 samples to ensure consistent performance of the instrument. The determined elemental analysis values were deemed acceptable if they fell within 0.3% of the theoretical values.

4.2 Synthetic Procedures

The purity of synthesised products was determined by chromatographic methods, and melting point analysis where appropriate. When further purification was deemed necessary this was achieved by recrystalisation. Qualitative characterisation of synthesised materials was achieved by means of spectroscopic methodologies i.e. NMR, IR, and MS. All of the data presented correlate well with theoretical values and, where available, literature values for these compounds.

4.2.1 Anion Exchange Metathesis

Metathesis or double-displacement reactions occur when two soluble ionic compounds exchange parts [499]. A metathesis reaction can be expected to occur when an insoluble precipitate, a volatile gas, a non-electrolyte or a weak electrolyte is formed as the product. The driving force for the formation of any of these product types is the net removal of ions from the solution. In a precipitation-type reaction the precipitate forms because the electrostatic attraction between the ions is greater than the affinity of the ions for the solvent molecules i.e. they cannot become solvated. When two solutions of suitable ions are mixed the ions collide and remain together forming a solid that falls out of solution.

4.2.2 Preparation of Initiators for Redox Cationic Polymerisation

4.2.2.1 Bis(Ethyl-α-Bipyridinium Acrylate Hexafluorophosphate) (**60**) [223]

Following the general procedure of Yagci *et al.* to 4,4'-bipyridal (3.35 g, 21.5 mmol) in acetonitrile (50 ml) was added with stirring ethyl-α-(bromomethyl)acrylate (8.4 g, 43 mmol). The reaction was stirred for 15 hours at room temperature. The solvent was removed by rotary evaporation and the yellow residue was washed copiously with diethyl ether.

Hexafluorophosphate anion metathesis was achieved by dissolving the bromide salt (4.0 g, 7.63 mmol) in miniumum amount of distilled water. To this aqueous solution was added dropwise sodium hexafluorophosphate (2.56 g, 15.3 mmol) also dissolved in a minimum quanitity of water. A white precipitate was obtained dried in vacuo and recrystallised from ethanol.

Similarly, hexafluoroantimonate anion metathesis was achieved by dissolving the bromide salt (4.0 g, 7.63 mmol) in miniumum amount of distilled water. To this aqueous solution was added dropwise sodium hexafluoroantimonate (3.94 g, 15.3 mmol) also dissolved in a minimum quanitity of water. A white precipitate was obtained dried in vacuo and recrystallised from ethanol.

Elemental Analysis, Actual (Theory):

Br^-: % C 47.04 (48.73), % H 4.97 (4.83), % N 4.87 (5.17)
PF_6^-: % C 39.12 (39.3), % H 3.82 (3.90), % N 4.00 (4.17)
SbF_6^-: % C 31.00 (30.94), % H 3.10 (3.07), % N 3.10 (3.28)

Melting Point (DSC): 221.8 °C (Br^-), 218.0 °C (PF_6^-), 155.8 °C (SbF_6^-),

4.2.3 Preparation of Silver(I) & Copper(I) Complexes [375,457,503-505]

Preliminary samples of ligated silver(I) complexes used were prepared by the Universtiy of Karlsruhe, Germany and were provided by Dr. R. Schoenfeld and Dr. E. Barriau, VTR Corporate Research, Henkel Duesseldorf. Further samples of silver(I) and additional copper(I) salts were prepared as described below.

4.2.3.1 Bis(1,5-Cyclooctadiene)Silver(I) Hexafluoroantimonate

To ethanol (40 ml) in a clean dry 250 ml glass vessel was added 1,5-Cyclooctadiene (15.74 g, 145.5 mmol). This solution was warmed, using a water bath, to 30 °C with stirring. In another vessel silver hexafluoroantimonate (25.0 g, 72.25 mmol) was dissolved in a minimum volume of ethanol. When fully dissolved this silver salt solution was added dropwise with stirring to the solution of 1,5-Cyclooctadiene in ethanol prepared above. A white precipitate forms rapidly. One hour after the final addition of the silver hexafluoroantimonate solution, the precipitate should be removed from the solvent and dried by vacuum filtration. The filtered solid was washed several times with 10 ml quantities of cold ethanol followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (1.0 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The white crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle. Yield: 72.7 %

Elemental Analysis, Actual (Theory): % C 33.7 (34.3), % H 4.3 (4.3)

AAS-ICP, Actual (Theory): % Ag 19.4 (19.3), % Cu 0.1 (0.0)

Decomposition Temperature (DSC): 214 – 222 °C

FT-IR ATR: 2948, 2891, 2844, 1604, 1448, 1451, 1431, 1325, 1238, 1200, 1086, 1004, 988, 911, 823, 751, 725, 645

4.2.3.2 Bis(1,5-Cyclooctadiene)Silver(I) Hexafluorophosphate

To ethanol (40 ml) in a clean dry 250 ml glass vessel was added 1,5-Cyclooctadiene (8.55 g, 79.1 mmol). This solution was warmed, using a water bath, to 30 °C with stirring. In another vessel silver hexafluorophosphate (10.0 g, 39.6 mmol) was dissolved in a minimum volume of ethanol. When fully dissolved the silver salt solution was added dropwise with stirring to the solution of 1,5-Cyclooctadiene in ethanol prepared above. A white precipitate forms rapidly. One hour after the final addition of the silver hexafluorophosphate solution, the precipitate should be removed from the solvent and dried by vacuum filtration. The filtered solid was washed several times with 10 ml quantities of cold ethanol followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (0.5 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The white crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle. Yield: 64.1 %

Elemental Analysis, Actual (Theory): % C 40.9 (41.0), % H 5.0 (5.2)

FT-IR ATR: 2950,2893,2040,1604,1484,1449.5,1431.5,1326,1265,1239,1202,1087 1051,1004.5,983,678,815.5,748.5,724,655.5

4.2.3.3 Bis(1,5-Cyclooctadiene)Silver(I) Perchloroate

To ethanol (40 ml) in a clean dry 250 ml glass vessel was added 1,5-Cyclooctadiene (10.44 g, 94.5 mmol). This solution was warmed, using a water bath, to 30 °C with stirring. In another vessel silver perchlorate (10.0 g, 48.2 mmol) was dissolved in a minimum volume of ethanol. When fully dissolved this silver salt solution was added dropwise with stirring to the solution of 1,5-Cyclooctadiene in ethanol prepared above. A white precipitate forms rapidly. One hour after the final addition of the silver perchlorate solution, the precipitate should be removed from the solvent and dried by vacuum filtration. The filtered solid was washed several times with 10 ml quantities of cold ethanol followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (0.5 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The white crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle. Yield: 84.1 %

Elemental Analysis, Actual (Theory): % C 45.1 (45.4), % H 5.6 (5.71)

FT-IR ATR: 2499,2891,2841,1603,1484,1451,1428,1391,1325,1238,1075,1003, 985,910,848,822,751,727,654,618

4.2.3.4 Bis(1,5-Cyclooctadiene)Silver(I) Tetrafluoroborate

To ethanol (40 ml) in a clean dry 250 ml glass vessel was added 1,5-Cyclooctadiene (11.1 g, 102.7 mmol). This solution was warmed, using a water bath, to 30 °C with stirring. In another vessel silver tetrafluoroborate (10.0 g, 51.4 mmol) was dissolved in a minimum volume of ethanol. When fully dissolved this silver salt solution was added dropwise with stirring to the solution of 1,5-Cyclooctadiene in ethanol prepared above. A white precipitate forms rapidly. One hour after the final addition of the silver tetrafluoroborate solution, the precipitate should be removed from the solvent and dried by vacuum filtration. The filtered solid was washed several times with 10 ml quantities of cold ethanol followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (0.5 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The white crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle. Yield: 70.2 %

Elemental Analysis, Actual (Theory): % C 46.69 (46.75), % H 5.84 (5.89)

FT-IR ATR: 2952, 2893.5, 2843.5, 1603, 1486, 1451, 1429, 1281.5, 1263, 1239, 1194.5, 1090.5,1029.5,910.5,847.7,822,751,727.5,676.5,655

4.2.3.5 Bis(1,5-Cyclooctadiene)Copper(I) Tetrafluoroborate

To acetone (50 ml) in a clean dry 250 ml glass vessel was added acetyl phenyl hydrazine (8.0g, 54mmol) and 1,5-Cyclooctadiene (?? g, 108 mmol). This solution was warmed to 30 °C to assist dissolution of these two components. Copper(II) tetrafluoroborate hydrate (11.86 g, 50 mmol) as solid was then added to the reaction vessel with constant stirring. After 16 hr the stirring was discontinued and a white salt precipitated to the bottom of the solution. The solid was collected by filtration and washed with several 10 ml quantities of cold acetone followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (1.0 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle.

Elemental Analysis, Actual (Theory): % C 52.32 (52.40), % H 6.56 (6.60)
AAS-ICP, Actual (Theory): % Cu 17.12 (17.33)

4.2.3.6 Bis(1,5-Cyclooctadiene)Copper(I) Perchlorate

To acetone (50 ml) in a clean dry 250 ml glass vessel was added acetyl phenyl hydrazine (8.0g, 54mmol) and 1,5-Cyclooctadiene (11.7 g, 108 mmol). This solution was warmed to 30 °C to assist dissolution of these two components. Copper(II) perchlorate hydrate (11.86 g, 50 mmol) as solid was then added to the reaction vessel with constant stirring. After 16 hr the stirring was discontinued and a white salt precipitated to the bottom of the solution. The solid was collected by filtration and washed with several 10 ml quantities of cold acetone followed by a further two 20 ml aliquots of cold diethyl ether. The salt was dried in vacuo.

Recrystalisation: The crude product was dissolved in warm acetone and carbon black (1.0 g) was added to remove soluble impurities. The warm solution was filtered using a warm filtration apparatus and the collected filtrate was placed in the fridge where it was allowed to recrystallise overnight. The crystals formed were recovered by filtration washed with a minimum amount of cold ethanol and dried in vacuo. Where necessary salts were recrystallised twice to achieve higher purity. Before use in cationic polymerisations the recrystallised salts were homogenised with a mortar and pestle.

Elemental Analysis, Actual (Theory): % C 50.4 (50.66), % H 6.2 (6.38)

AAS-ICP, Actual (Theory): % Cu 16.6 (16.75)

4.2.4 Preparation of Dehydro-Ascorbic Acid & Dehydro-Ascorbyl-6-Hexadecanoate

4.2.4.1 Preparation of Dehydroascorbyl-6-Hexadecanoate by Air Oxidation Catalyzed by Cu(II) in Methanol

$$AH_2 + O_{2\,(air)} + MeOH \xrightarrow{Cu(II)} DA\ (\mathbf{88}) + H_2O_2 \quad \ldots \text{Scheme 2.28}$$

Following the method of Koliou and Ioannou [406]. To a solution of dehydroascorbyl-6-hexadecanoate (8.2 g, 20 mmol) in methanol (100 ml) in a 250 ml beaker, a dark blue methanolic solution (15 ml) containing copper(II) ethylhexanoate (0.12 g, 0.33 mmol) and pyridine (0.11 ml, 1.33 mmol) and solid copper(II) ethylhexanoate (0.24 g, 0.667 mmol) were added to give a brown-green solution, which was vigorously stirred at room temperature for 16 hours. The reaction progress was monitored by TLC and tested for hydrogen peroxide (using peroxide indicator sticks), which was no longer detected after this time. A thin film of copper(0) was visible as a deposit on the walls of the reaction vessel. The methanol solvent was removed by rotary evaporation and the resultant green solid was re-dissolved in a minimum amount of ethyl acetate loaded onto a silica gel column (30g, 2 x 17 cm) and eluted with ethyl acetate. Following elution the copper salt remains in the upper two thirds of the column and the recovered colourless solution was evaporated to dryness on the rotary evaporator. This chromatographic cleaning step was repeated for a second time followed by removal of the solvent on the rotary evaporator. The product was an off-white waxy solid. Yield: 1.34 g.

FT-IR ATR (cm^{-1}): 3400, 2956, 2915, 2850, 1800, 1728, 1467, 1165, 1110, 1044, 720

MS (m/z) – Quadrupole Detector: 201, 172, 156, 144, 117, 115, 105, 91, 89, 77, 68, 63, 57, 51, 39

NMR (500 MHz), ^{1}H (ppm), *d*-Acetone: 0.86-0.88 (t), 1.28 (m), 1.58-1.62 (q), 2.34-2.37 (t), 3.85-4.78 (m), 6.32 (d)

4.2.4.2 Preparation of Dehydro-Ascorbic Acid by Stoichiometric Oxidation with Ag(I) in Acetone

Ascorbic Acid (18 mg, 0.1mmol) and in excess of two equivalents of silver hexafluoroantimonate (86 mg, 0.25 mmol) were added to a 20 ml glass reaction vessel. 1 ml of anhydrous acetone was then added to these reactants with stirring. A reaction, noted by the colour change from white / yellow starting reagents forming a black reaction product and a silver mirror on the vessel walls, occurred instantly upon addition of the solvent. The ascorbic acid had limited solubility in acetone. The mixture was stirred continuously at ambient temperature for 30 minutes, following which the solution was filtered under gravity. The filtrate had a slight yellow colour. The solvent was removed by evaporation under a flow of nitrogen. The recovered product was an off-white solid.

FT-IR ATR (cm^{-1}): 3399,2985.5,2669,1736.5,1666,1376,1270,1095,1041,927,849, 772.5,681.5,634.3,610.5,446

NMR (500 MHz): 1H (ppm), *d*-Acetone 1.29 (s), 3.83-4.93 (m)

4.2.4.3 Preparation of Dehydro-Ascorbyl-6-Hexadecanoate by Stoichiometric Oxidation with Ag(I) in Acetone

Ascorbyl-6-hexadecaoate (42 mg, 0.1mmol) and in excess of two equivalents of silver hexafluoroantimonate (86 mg, 0.25 mmol) were added to a 20 ml glass reaction vessel. 1 ml of anhydrous acetone was then added to these reactants with stirring. A reaction, noted by the colour change from white / yellow starting reagents forming a black reaction product and a limited silver mirror in some replicates, occurred instantly upon addition of the solvent. The solution was stirred continuously at ambient temperature for 30 minutes, following which the solution was filtered under gravity. The filtrate had a slight yellow colour. The solvent was removed by evaporation under a flow of nitrogen. The product was a waxy yellow solid.

FT-IR ATR (cm^{-1}): 3400, 3200, 2958, 2920, 2848, 2505, 1732, 1687, 1655, 1467, 1176, 723, 657

NMR (500 MHz): 1H (ppm), *d*-Acetone 0.86-0.88 (t), 1.28 (m), 1.58-1.62 (quar), 2.34-2.37 (t), 3.85-4.78 (m), 4.32 (s)

CHAPTER FIVE | SUMMARY AND FUTURE WORK

It is well recognised that the market potential for surface induced polymerisation at ambient tempearature is significant. For example, a market estimate for acrylic machinery adhesives was in excess of €17 million for Europe alone in 2008 [506]. Nevertheless radical cure systems do have shortcomings; especially with regard to thermal performance and oxygen inhibition of wet exudates from bondlines. A means of addressing these limitations through development of a redox system capable of promoting *cationic* polymerisation when contacted with an active substrate is of considerable importance. Suitable systems to affect that goal have been presented and evaluated in this current study.

However, although the original objective has been realised, the demonstrated redox cationc systems are still not optimal for practical application. For example, initiation systems based on silver(I) latent catalysts may be prohibitively expensive from a commercial perspective even when used at levels of <2 %. Also, while vinyl ether mediation considerably accelerates these cationic polymerisations they are still relatively sluggish when compared with their redox radical counterparts. Further work in this area would allow opportunity to develop greater understanding and improve these features of surface promoted redox cationic polymerisation. The foremost areas for consideration are:

1. Investigation of the use of non-metal latent catalysts in stable surface promoted redox cationic polymerisations. Of particular interest would be development of stable chemistries based on diazonium or even iodonium species.

2. To explore methods for uniting both redox radical and redox cationic polymerisation in stable single-part systems with a view to leveraging the benefits of both processes.

3. To evaluate and investigate the possibility of employing alternative mechanisms also needs to be given consideration. Such approaches may include:
    a. Radical to cation transformation initation [462-464].
    b. Further investigation of radical promoted cationic polymerisation.

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COMPOUNDS USED IN CHAPTER TWO

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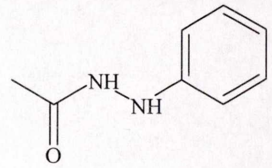

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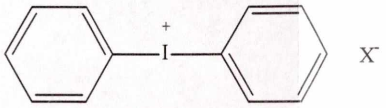
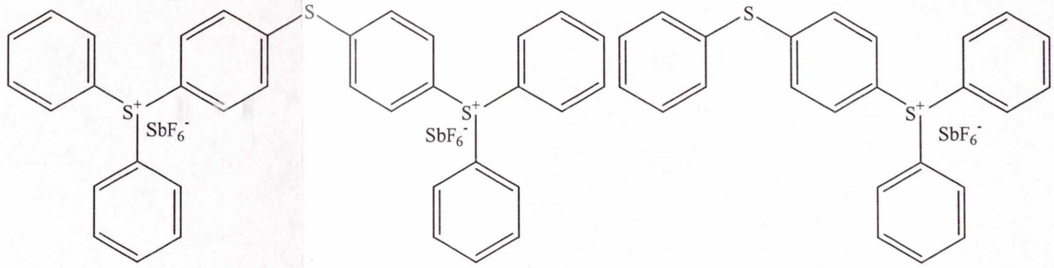


Where X = PF_6^- or SbF_6^-

44



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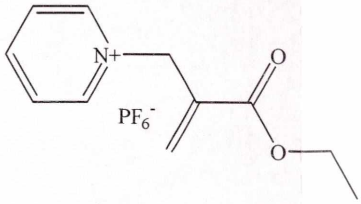

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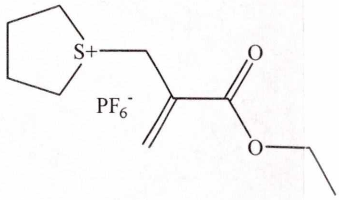

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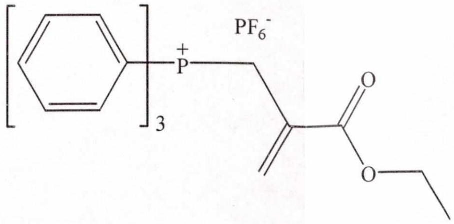

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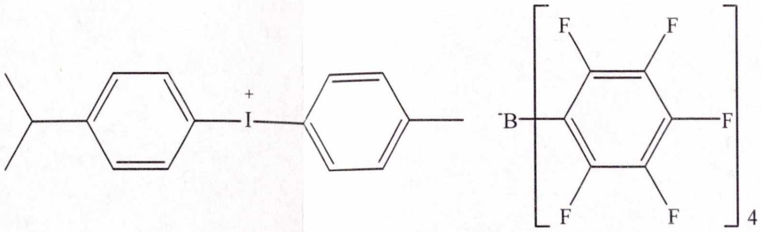

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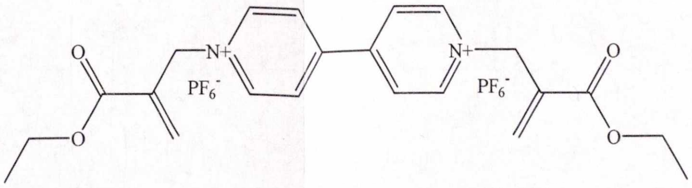

COMPOUNDS USED IN CHAPTER TWO (Continued)

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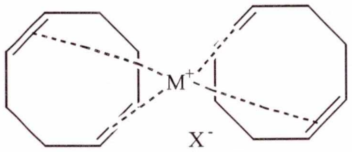
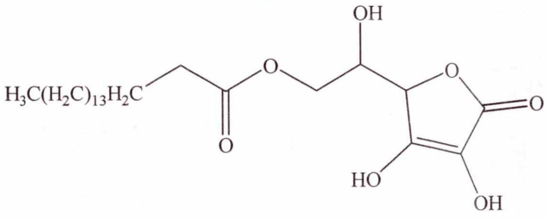
62,
63



Where M = Cu(I) or Ag(I)
Where X = BF_4^- or ClO_4^-

64



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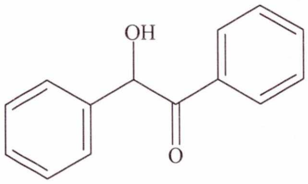

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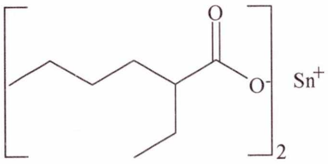

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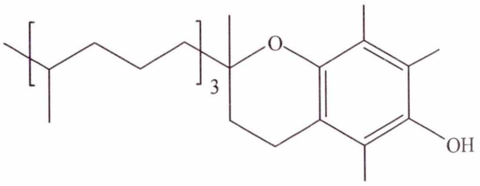

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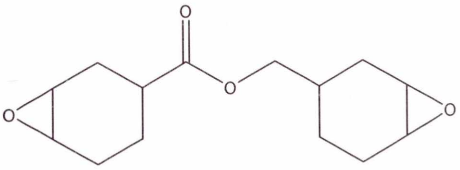

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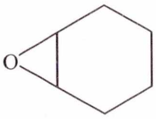

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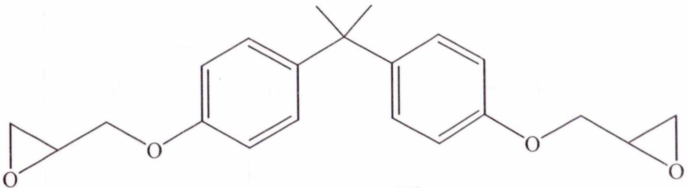

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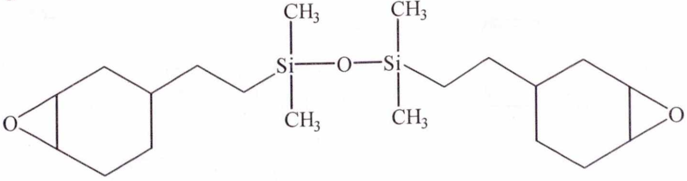

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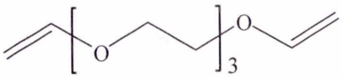

COMPOUNDS USED IN CHAPTER THREE

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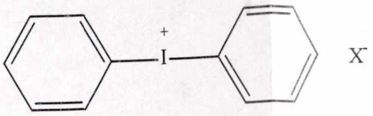

Where X = PF_6^- or SbF_6^-

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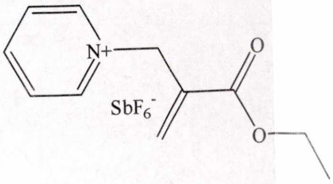

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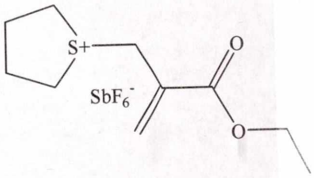

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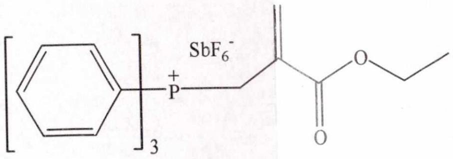

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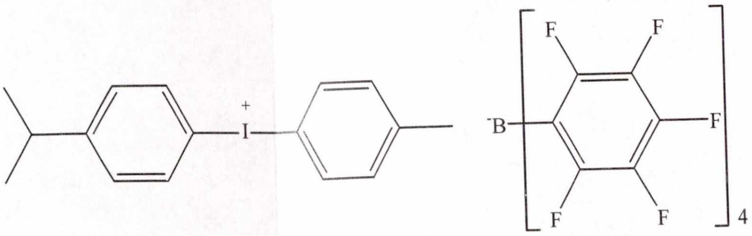

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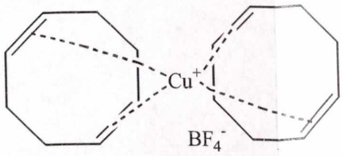

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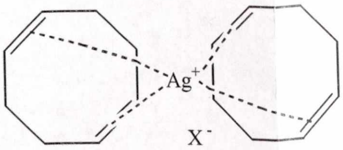

Where X = BF_4^-

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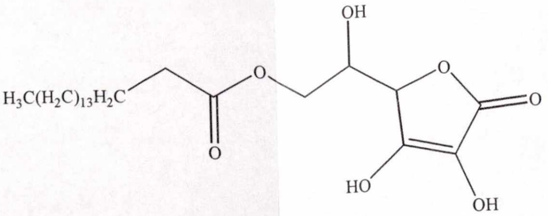

COMPOUNDS USED IN CHAPTER THREE (Continued)

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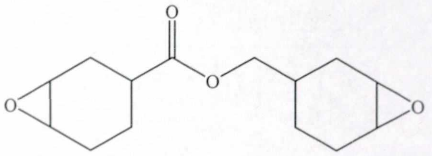

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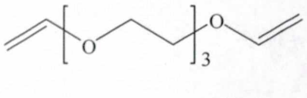

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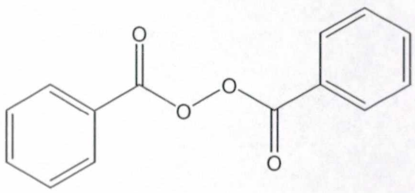

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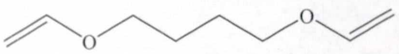

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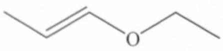

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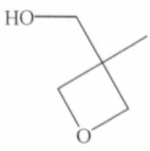

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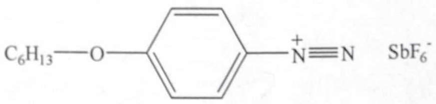

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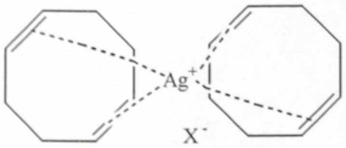
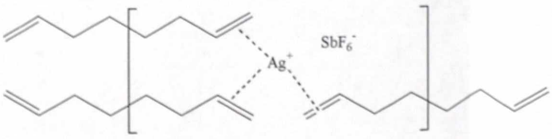


Where X = NO_3^-, PF_6^- or SbF_6^-

104



105

$[CH_3C{\equiv}N]_4Ag^+\ BF_4^-$

LIST OF PATENTS & PUBLICATIONS DERIVED FROM THIS THESIS

1. US Patent Application **2009**0288769
   Surface-Promoted Cure of Cationically Curable Compositions Comprising Vinyl Ethers
2. US Patent Application **2009**0288770
   Surface-Promoted Cure of One-Part Cationically Curable Compositions
3. US Patent Application **2009**0288771
   Surface-Promoted Cure of One-Part Radically Curable Compositions
4. World Intellectual Property Organization Patent WO**2010**094599A1:
   Metal to Polymer Bonding Using an Adhesive Based on Epoxides
5. United Kingdom Patent Office Application No. GB1013201.7, **2010**
   Adhesive Composition with Enhanced Cure Through Volume

Title: Surface Promoted Redox Cationic Polymerisation

Status: Draft

Target Journal: *Macromolecules or Journal Polymer Science: Polymer Chemistry*

Abstract: An investigation aimed at realizing ambient temperature polymerisation of epoxy monomers in the absence of such stimuli as heat or light was undertaken. It was found that silver(I) salts of non-nucleophilic anions are capable of oxidising ferrous substrates to form Lewis acids which are efficient promoters of cationic polymerisation. FTIR ATR was used to study the factors influencing the redox reactivity of this system. The glass transition temperature of polymers formed was evaluated using DMTA. Adhesive properties of the polymers were evaluated by a tensile test method.

APPENDIX

WORKED EXAMPLE OF CALCULATIONS FOR QUANTIFYING THE DEGREE OF CONVERSION (%) OF MONOMER (72) TO POLYMER BY A CALORIMETRIC METHOD (SEE SECTION 2.4.2.2 PAGE 58)

The experimental conditions and data recorded in Table 2.8 are used for the following calculations.

Conversion of ΔT to $\Delta H_{exp,t}$:

Determination of Heat Energy, Q, for a Typical Copper(II) Catalysed Redox Cationic Polymerisation

$$Q = m \cdot c \cdot \Delta T \qquad \text{... Equation 2.0}$$

Where Q is heat energy (J)

m is mass of the substance heated (g)

i.e. from Table 2.5 $m = 10$ g

c is specific heat capacity ($J\ g^{-1}$)

i.e. for monomer (**72**) $c = 1.6\ J\ g^{-1}$

ΔT is the temperature rise of the system (K)

e.g. from Table 2.5 $\Delta T = 189.6$ K at 109 seconds

Therefore $Q = 10\ g \cdot 1.6\ J\ g^{-1}\ K^{-1} \cdot 189.6\ K$

$Q = 3033.6\ J$

Calculation of Theoretical Enthalpy, ΔH_T, for a Typical Copper(II) Catalysed Redox Cationic Polymerisation

$$\Delta H_T = (\Delta H_{Tf} \ / \ M) f \qquad \text{... Equation 2.2}$$

Where ΔH_T is the theoretical enthalpy (J g^{-1})

f is the functionality of the monomer used i.e. 2 for (**72**)

ΔH_{Tf} is the theoretical enthalpy of one functional group (J mol^{-1}) i.e. ΔH_{Tf} = 94.47 kJ mol^{-1} for epoxy [384]

M is the molar mass of the monomer, (g mol^{-1}) i.e. 252.31 g mol^{-1} for (**72**)

Therefore $\Delta H_T = (94{,}470 \text{ J mol}^{-1} \ / \ 252.31 \text{ g mol}^{-1})$

$\Delta H_T = 748.8 \text{ J g}^{-1}$

Calculation of Experimental Enthalpy, $\Delta H_{exp,t}$, at time t for a Typical Copper(II) Catalysed Redox Cationic Polymerisation

$$\Delta H_{exp,t} = Q_t \ / \ m$$

Where $\Delta H_{exp,t}$ is the experimental enthalpy (J g^{-1})

Q_t is the heat energy of the reaction at time t (J) i.e. as calculated from Table 2.2 Q = 3033.6 J at 109 s

m is the mass of the substance heated (g) i.e. from Table 2.5 m = 10 g

Therefore $\Delta H_{exp,t} = 3033.6 \text{ J} \ / \ 10 \text{ g}$

$\Delta H_{exp,t} = 303.4 \text{ J g}^{-1}$

Degree of Conversion (%) of Monomer (72) to Polymer at time t (s) is determined from the Theoretical Enthalpy, ΔH_T, and Experimental Enthalpy, $\Delta H_{exp,t}$, as follows:

$$\alpha_{,t} = \Delta H_{exp,t} / \Delta H_T \qquad \text{… Equation 2.4}$$

where $\alpha_{,t}$ is the degree of conversion at time t

$\Delta H_{exp,t}$ is the Experimental Enthalpy of the reaction at time t

i.e. from Table 2.2 $\Delta H_{exp,t} = 303.4\ \mathrm{J\ g^{-1}}$ at time 109 s

ΔH_T is the Theoretical Enthalpy of the reaction at time t

i.e. from Table 2.2 $\Delta H_T = 748.8\ \mathrm{J\ g^{-1}}$ at time 109 s

Therefore $\alpha_{,t} = 303.4\ \mathrm{J\ g^{-1}}\ /\ 748.8\ \mathrm{J\ g^{-1}}$

$\alpha_{,t} = 0.405$ and

% Conversion = 40.5 %

Technical Data Sheet

LOCTITE® 2701

June 2004

PRODUCT DESCRIPTION

LOCTITE® 2701 provides the following product characteristics:

Technology	Acrylic
Chemical Type	Dimethacrylate ester
Appearance (uncured)	Green liquid^{LMS}
Fluorescence	Positive under UV light^{LMS}
Components	One component - requires no mixing
Viscosity	Low
Cure	Anaerobic
Secondary Cure	Activator
Application	Threadlocking
Strength	High

LOCTITE® 2701 is designed for the permanent locking and sealing of threaded fasteners. The product cures when confined in the absence of air between close fitting metal surfaces and prevents loosening and leakage from shock and vibration. This product is particularly suited for use on inactive substrates and/or where maximum resistance to hot oil is required.

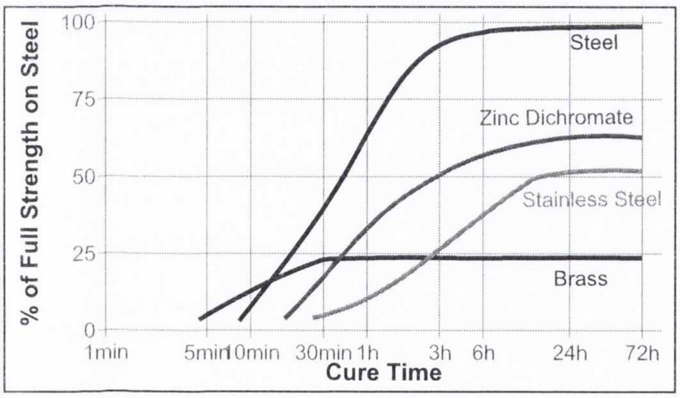
TYPICAL PROPERTIES OF UNCURED MATERIAL

Specific Gravity @ 25 °C	1.08
Flash Point - See MSDS	
Viscosity, Brookfield - RVT, 25 °C, mPa·s (cP):	
Spindle 2, speed 20 rpm	500 to 900^{LMS}

TYPICAL CURING PERFORMANCE

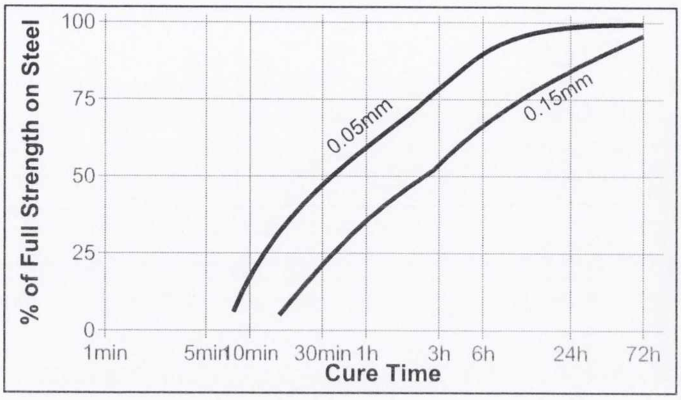
Cure Speed vs. Substrate

The rate of cure will depend on the substrate used. The graph below shows the shear strength developed with time on steel pins and collars compared to different materials and tested according to ISO 10123.



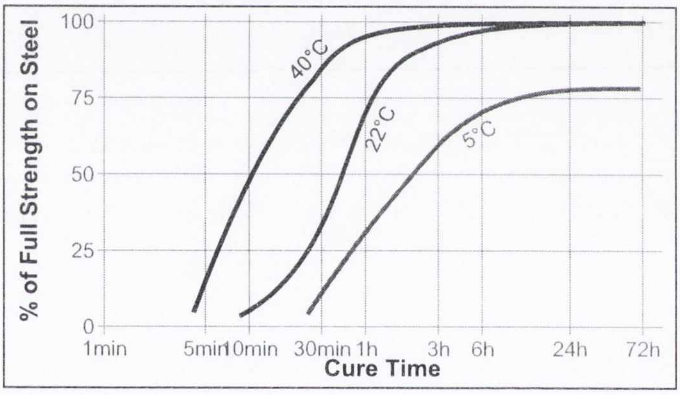
Cure Speed vs. Bond Gap

The rate of cure will depend on the bondline gap. The following graph shows shear strength developed with time on steel pins and collars at different controlled gaps and tested according to ISO 10123.



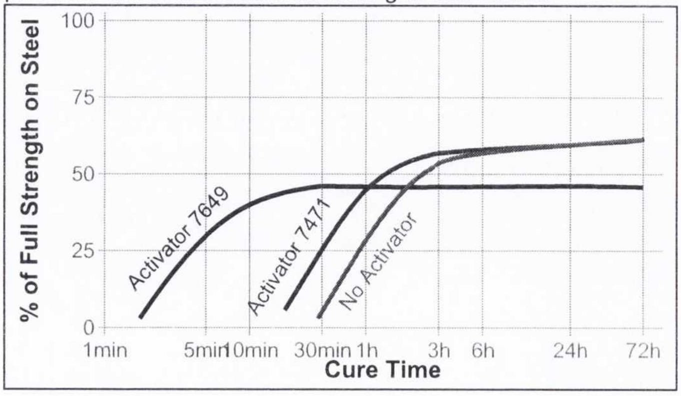
Cure Speed vs. Temperature

The rate of cure will depend on the temperature. The graph below shows the shear strength developed with time at different temperatures on steel pins and collars and tested according to ISO 10123.



Cure Speed vs. Activator

Where cure speed is unacceptably long, or large gaps are present, applying activator to the surface will improve cure speed. The graph below shows shear strength developed with time using Activator 7471 and 7649 on zinc dichromate steel pins and collars and tested according to ISO 10123.



TYPICAL PROPERTIES OF CURED MATERIAL

Physical Properties:

Coefficient of Thermal Expansion, ASTM D 696, K^{-1}	100×10^{-6}
Coefficient of Thermal Conductivity, ASTM C 177, W/(m·K)	0.10
Specific Heat, kJ/(kg·K)	0.30

TYPICAL PERFORMANCE OF CURED MATERIAL

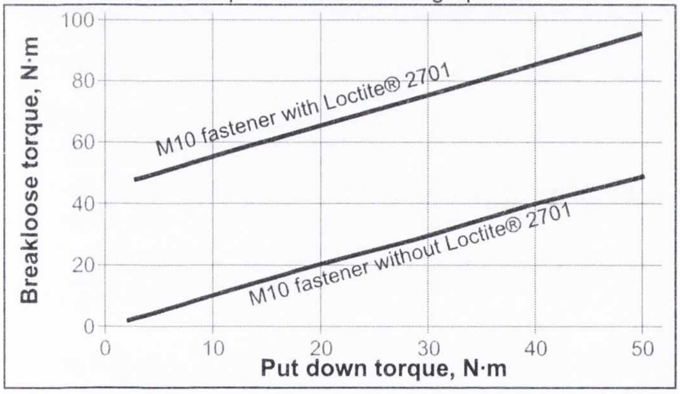
Adhesive Properties

After 24 hours @ 22 °C

Breakaway Torque, ISO 10964:		
M10 black oxide steel nuts and bolts	N·m (lb.in.)	26 to 50 (230 to 440)
Prevail Torque, ISO 10964:		
M10 black oxide steel nuts and bolts	N·m (lb.in.)	≥15^{LMS} (≥132)
Breakloose Torque, ISO 10964, Pre-torqued to 5 N·m:		
M10 black oxide steel nuts and bolts	N·m (lb.in.)	30 to 60 (265 to 530)
Max. Prevail Torque, ISO 10964, Pre-torqued to 5 N·m:		
M10 black oxide steel nuts and bolts	N·m (lb.in.)	36 to 60 (320 to 530)
Compressive Shear Strength, ISO 10123:		
Steel pins and collars	N/mm^2 (psi)	18 to 30 (2,610 to 4,350)

Torque Augmentation

Breakloose torque of an uncoated fastener will normally be 15 to 30% less than the on-torque. The effect of LOCTITE® 2701 on the breakloose toque is shown in the graph below.



TYPICAL ENVIRONMENTAL RESISTANCE

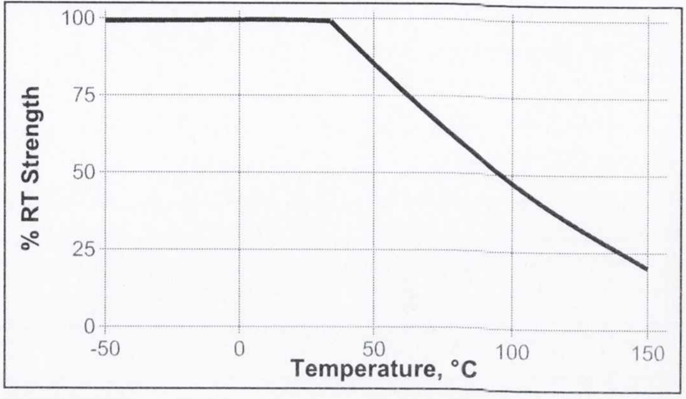
Cured for 1 week @ 22 °C

Breakloose Torque, ISO 10964, Pre-torqued to 5 N·m:

M10 zinc phosphate steel nuts and bolts

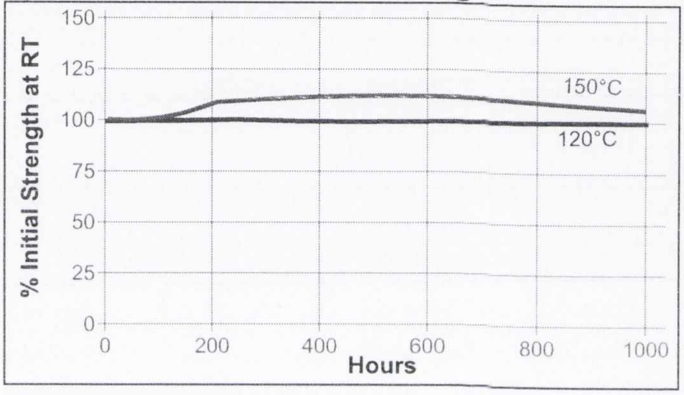
Hot Strength

Tested at temperature



Heat Aging

Aged at temperature indicated and tested @ 22 °C



Chemical/Solvent Resistance

Aged under conditions indicated and tested @ 22°C.

		% of initial strength		
Environment	**°C**	**100 hr**	**500 hr**	**1000 hr**
Motor Oil	125	95	100	110
Gasoline	22	100	110	115
Brake fluid	22	100	100	105
Ethanol	22	95	95	95
Acetone	22	100	100	100
1,1,1 Trichloroethane	22	100	110	110
Water Glycol 50/50	87	100	100	100

GENERAL INFORMATION

This product is not recommended for use in pure oxygen and/or oxygen rich systems and should not be selected as a sealant for chlorine or other strong oxidizing materials.

For safe handling information on this product, consult the Material Safety Data Sheet (MSDS).

Where aqueous washing systems are used to clean the surfaces before bonding, it is important to check for compatibility of the washing solution with the adhesive. In some cases these aqueous washes can affect the cure and performance of the adhesive.

This product is not normally recommended for use on plastics (particularly thermoplastic materials where stress cracking of the plastic could result). Users are recommended to confirm compatibility of the product with such substrates.

Directions for use

For Assembly

1. For best results, clean all surfaces (external and internal) with a Loctite cleaning solvent and allow to dry.
2. If the material is an inactive metal or the cure speed is to slow, spray all threads with Activator 7471 or 7649 and allow to dry.
3. To prevent the product from clogging in the nozzle, do not allow the tip to touch metal surfaces during application.
4. **For Thru Holes**, apply several drops of the product onto the bolt at the nut engagement area.
5. **For Blind Holes**, apply several drops of the product down the internal threads to the bottom of the hole.
6. **For Sealing Applications**, apply a 360° bead of product to the leading threads of the male fitting, leaving the first thread free. Force the material into the threads to thouroughly fill the voids. For bigger threads and voids, adjust product amount accordingly and apply a 360° bead of product on the female threads also.
7. Assemble and tighten as required.

For Disassembly

1. Apply localized heat to nut or bolt to approximately 250 °C. Disassemble while hot.

For Cleanup

1. Cured product can be removed with a combination of soaking in a Loctite solvent and mechanical abrasion such as a wire brush.

Loctite Material Specification^{LMS}

LMS dated February 27, 1998. Test reports for each batch are available for the indicated properties. LMS test reports include selected QC test parameters considered appropriate to specifications for customer use. Additionally, comprehensive controls are in place to assure product quality and consistency. Special customer specification requirements may be coordinated through Henkel Loctite Quality.

Storage

Store product in the unopened container in a dry location. Storage information may be indicated on the product container labeling.

Optimal Storage: 8 °C to 21 °C. Storage below 8 °C or greater than 28 °C can adversely affect product properties. Material removed from containers may be contaminated during use. Do not return product to the original container. Henkel Corporation cannot assume responsibility for product which has been contaminated or stored under conditions other than those previously indicated. If additional information is required, please contact your local Technical Service Center or Customer Service Representative.

Conversions

(°C x 1.8) + 32 = °F
kV/mm x 25.4 = V/mil
mm / 25.4 = inches
N x 0.225 = lb
N/mm x 5.71 = lb/in
N/mm² x 145 = psi
MPa x 145 = psi
N·m x 8.851 = lb·in
N·mm x 0.142 = oz·in
mPa·s = cP

Note

The data contained herein are furnished for information only and are believed to be reliable. We cannot assume responsibility for the results obtained by others over whose methods we have no control. It is the user's responsibility to determine suitability for the user's purpose of any production methods mentioned herein and to adopt such precautions as may be advisable for the protection of property and of persons against any hazards that may be involved in the handling and use thereof. In light of the foregoing, **Henkel Corporation specifically disclaims all warranties expressed or implied, including warranties of merchantability or fitness for a particular purpose, arising from sale or use of Henkel Corporation's products. Henkel Corporation specifically disclaims any liability for consequential or incidental damages of any kind, including lost profits.** The discussion herein of various processes or compositions is not to be interpreted as representation that they are free from domination of patents owned by others or as a license under any Henkel Corporation patents that may cover such processes or compositions. We recommend that each prospective user test his proposed application before repetitive use, using this data as a guide. This product may be covered by one or more United States or foreign patents or patent applications.

Trademark usage

LOCTITE is a trademark of Henkel Corporation

Reference 1

Technical Data Sheet

LOCTITE® 620

May 2004

PRODUCT DESCRIPTION

LOCTITE® 620 provides the following product characteristics:

Technology	Acrylic
Chemical Type	Methacrylate Ester
Appearance (uncured)	Green liquid^{LMS}
Components	One component - requires no mixing
Viscosity	High
Cure	Anaerobic
Secondary Cure	Activator
Application	Retaining
Strength	Medium to High

LOCTITE® 620 is designed for the bonding of cylindrical fitting parts. The product cures when confined in the absence of air between close fitting metal surfaces and prevents loosening and leakage from shock and vibration. Typical applications include locating pins in radiator assemblies, sleeves into pump housings and bearings in auto transmissions. Particularly suitable for applications where temperature resistance up to 200°C is required.

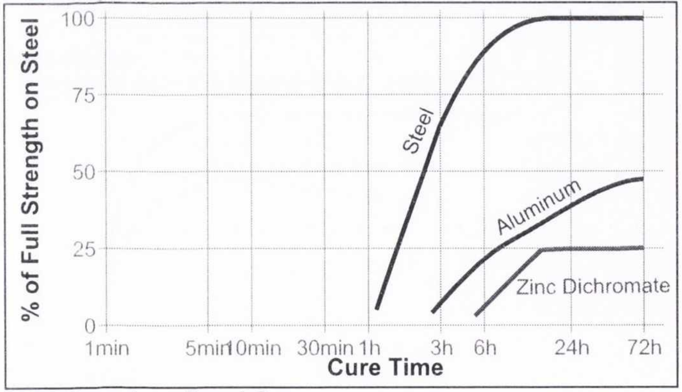
TYPICAL PROPERTIES OF UNCURED MATERIAL

Specific Gravity @ 25 °C	1.16
Flash Point - See MSDS	
Viscosity, Brookfield - RVT, 25 °C, mPa·s (cP):	
Spindle 5, speed 20 rpm	5,000 to 12,000^{LMS}
Viscosity, EN 12092 - MV, 25 °C, after 180 s, mPa·s (cP):	
Shear rate 129 s^{-1}	1,200 to 2,400

TYPICAL CURING PERFORMANCE

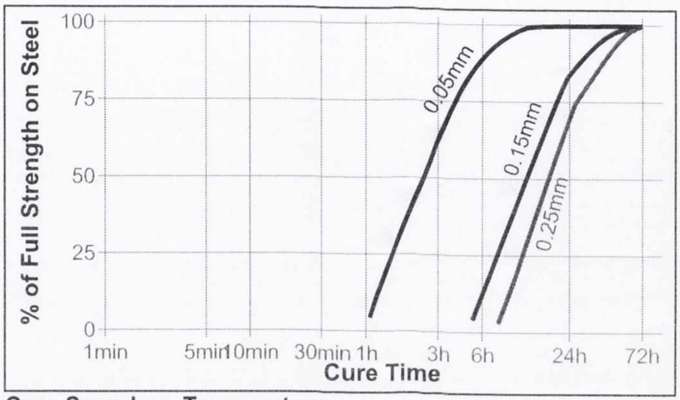
Cure Speed vs. Substrate

The rate of cure will depend on the substrate used. The graph below shows the shear strength developed with time on steel pins and collars compared to different materials and tested according to ISO 10123.



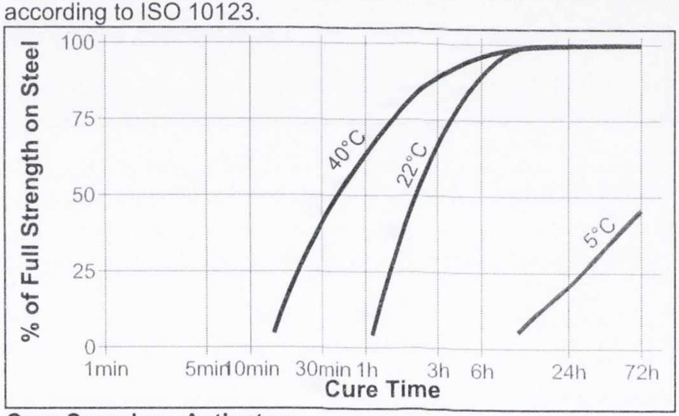
Cure Speed vs. Bond Gap

The rate of cure will depend on the bondline gap. The following graph shows shear strength developed with time on steel pins and collars at different controlled gaps and tested according to ISO 10123.



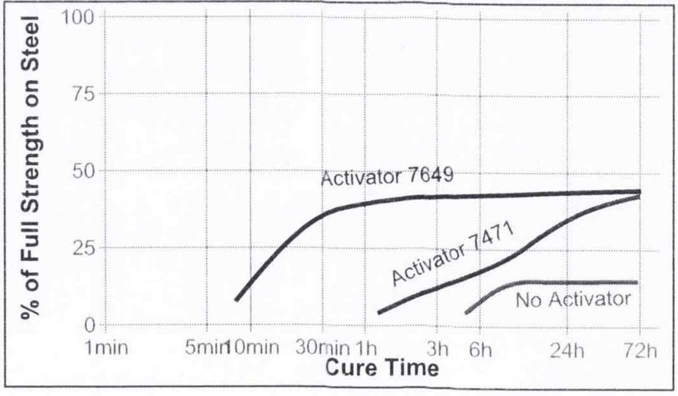
Cure Speed vs. Temperature

The rate of cure will depend on the temperature. The graph below shows the shear strength developed with time at different temperatures on steel pins and collars and tested according to ISO 10123.



Cure Speed vs. Activator

Where cure speed is unacceptably long, or large gaps are present, applying activator to the surface will improve cure speed. The graph below shows shear strength developed with time using Activator 7471 and 7649 on Zinc Dichromate steel pins and collars and tested according to ISO 10123.



TYPICAL PROPERTIES OF CURED MATERIAL

Physical Properties:

Coefficient of Thermal Expansion, ASTM D 696, K^{-1}	80×10^{-6}
Coefficient of Thermal Conductivity, ASTM C 177, W/(m·K)	0.10
Specific Heat, kJ/(kg·K)	0.30
Elongation, at break, ASTM D 412, %	<1

TYPICAL PERFORMANCE OF CURED MATERIAL

Adhesive Properties

After 24 hours @ 22 °C

Compressive Shear Strength, ISO 10123:

Steel pins and collars	N/mm²	$\geq 17.20^{LMS}$
	(psi)	(2,495)

Cured for 24 hours @ 22 °C, followed by 24 hours @ 177 °C, tested @ 22 °C

Compressive Shear Strength, ISO 10123:

Steel pins and collars	N/mm²	$\geq 24.10^{LMS}$
	(psi)	(3,495)

TYPICAL ENVIRONMENTAL RESISTANCE

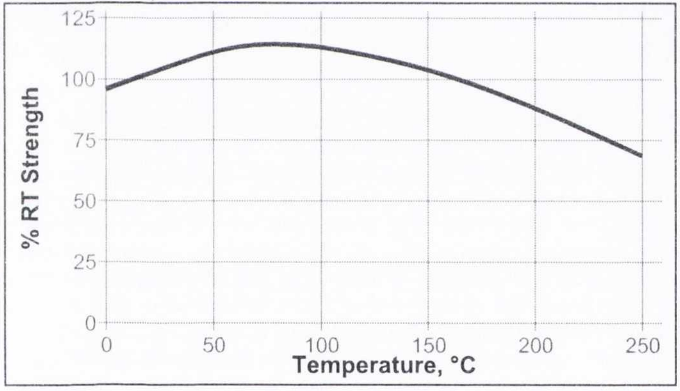
Cured for 1 week @ 22 °C

Compressive Shear Strength, ISO 10123:

Steel pins and collars

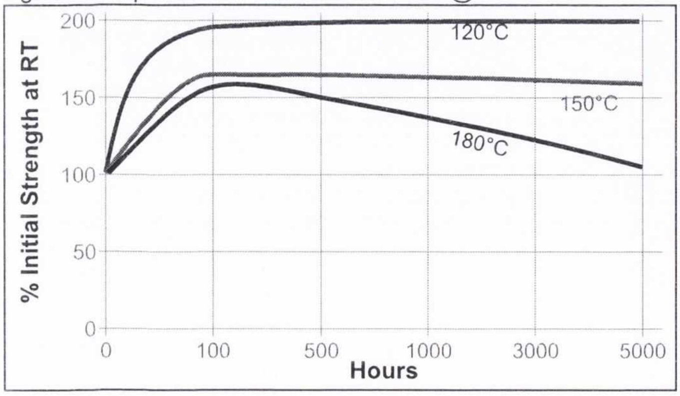
Hot Strength

Tested at temperature



Heat Aging

Aged at temperature indicated and tested @ 22 °C



Chemical/Solvent Resistance

Aged under conditions indicated and tested @ 22 °C.

		% of initial strength		
Environment	**°C**	**100 hr**	**500 hr**	**1000 hr**
Motor Oil	125	100	100	100
Unleaded Petrol	22	95	95	95
Brake fluid	22	100	100	100
Water Glycol 50/50	87	95	80	80
Ethanol	22	100	100	75
Acetone	22	95	95	95

GENERAL INFORMATION

This product is not recommended for use in pure oxygen and/or oxygen rich systems and should not be selected as a sealant for chlorine or other strong oxidizing materials.

For safe handling information on this product, consult the Material Safety Data Sheet (MSDS).

Where aqueous washing systems are used to clean the surfaces before bonding, it is important to check for compatibility of the washing solution with the adhesive. In some cases these aqueous washes can affect the cure and performance of the adhesive.

This product is not normally recommended for use on plastics (particularly thermoplastic materials where stress cracking of the plastic could result). Users are recommended to confirm compatibility of the product with such substrates.

Directions for use

For Assembly

1. For best results, clean all surfaces (external and internal) with a Loctite cleaning solvent and allow to dry.
2. If the material is an inactive metal or the cure speed is to slow, spray with Activator 7471 or 7649 and allow to dry.
3. Shake the product thoroughly before use.
4. **For Slip Fitted Assemblies**, apply adhesive around the leading edge of the pin and the inside of the collar and use a rotating motion during assembly to ensure good coverage.
5. **For Press Fitted Assemblies**, apply adhesive thoroughly to both bond surfaces and assemble at high press on rates.
6. **For Shrink Fitted Assemblies** the adhesive should be coated onto the pin, the collar should then be heated to create sufficient clearance for free assembly.
7. Parts should not be disturbed until sufficient handling strength is achieved.

For Disassembly

1. Apply localized heat to the assembly to approximately 250 °C. Disassemble while hot.

For Cleanup

1. Cured product can be removed with a combination of soaking in a Loctite solvent and mechanical abrasion such as a wire brush.

Loctite Material Specification^{LMS}

LMS dated August 20, 1997. Test reports for each batch are available for the indicated properties. LMS test reports include selected QC test parameters considered appropriate to specifications for customer use. Additionally, comprehensive controls are in place to assure product quality and consistency. Special customer specification requirements may be coordinated through Henkel Loctite Quality.

Storage

Store product in the unopened container in a dry location. Storage information may be indicated on the product container labeling.

Optimal Storage: 8 °C to 21 °C. Storage below 8 °C or greater than 28 °C can adversely affect product properties. Material removed from containers may be contaminated during use. Do not return product to the original container. Henkel Corporation cannot assume responsibility for product which has been contaminated or stored under conditions other than those previously indicated. If additional information is required, please contact your local Technical Service Center or Customer Service Representative.

Conversions

(°C x 1.8) + 32 = °F
kV/mm x 25.4 = V/mil
mm / 25.4 = inches
N x 0.225 = lb
N/mm x 5.71 = lb/in
N/mm^2 x 145 = psi
MPa x 145 = psi
N·m x 8.851 = lb.in
N·mm x 0.142 = oz.in
mPa·s = cP

Note

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Trademark usage

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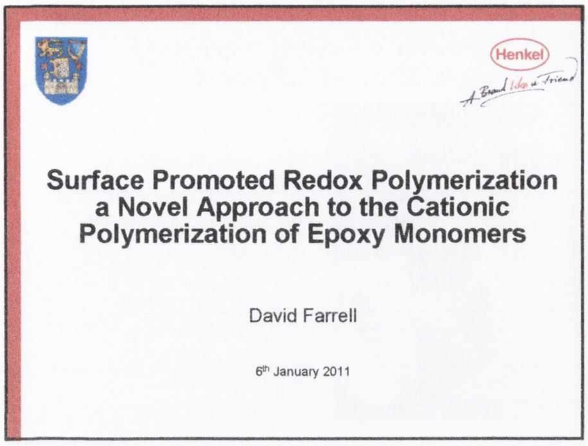
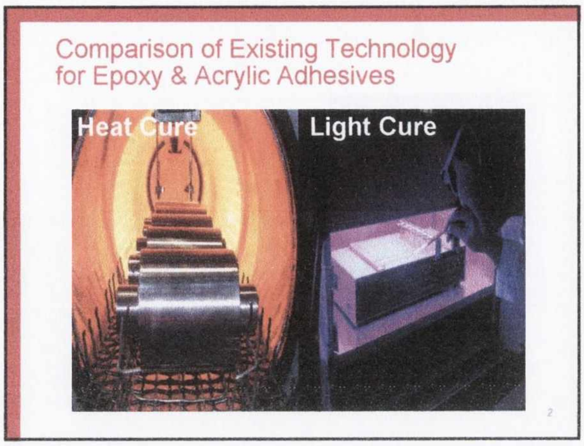
Reference 0.3



Surface Promoted Redox Polymerization a Novel Approach to the Cationic Polymerization of Epoxy Monomers

David Farrell

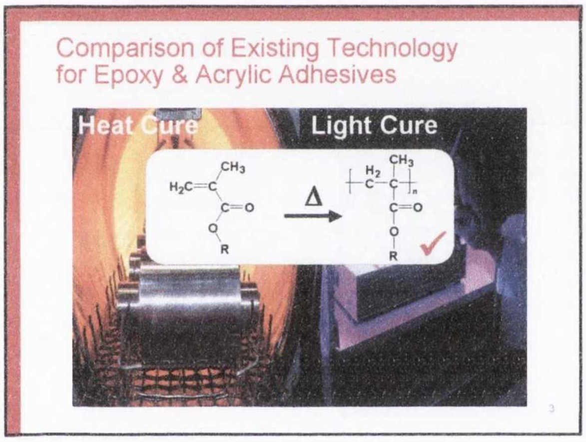
6th January 2011



Comparison of Existing Technology for Epoxy & Acrylic Adhesives

Heat Cure

Light Cure



Comparison of Existing Technology for Epoxy & Acrylic Adhesives

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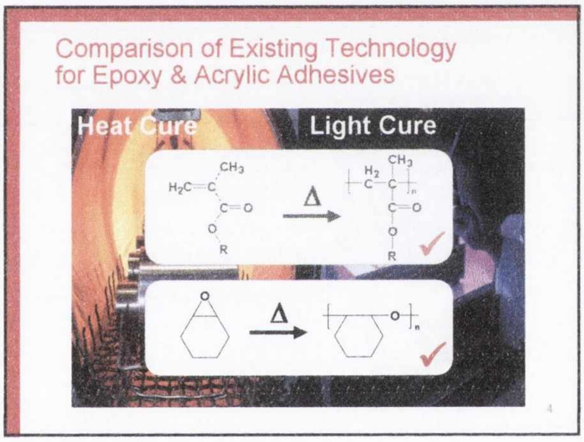


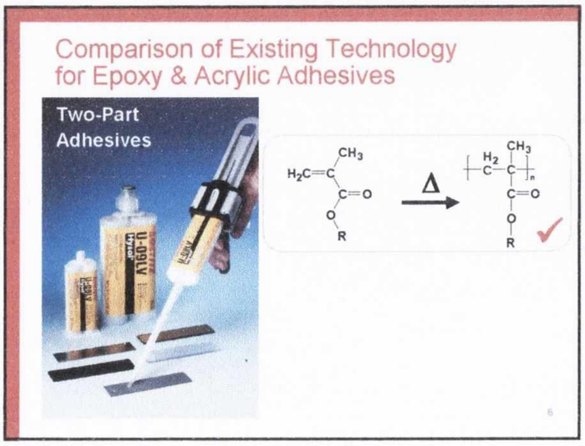
Comparison of Existing Technology for Epoxy & Acrylic Adhesives

Heat Cure

Light Cure

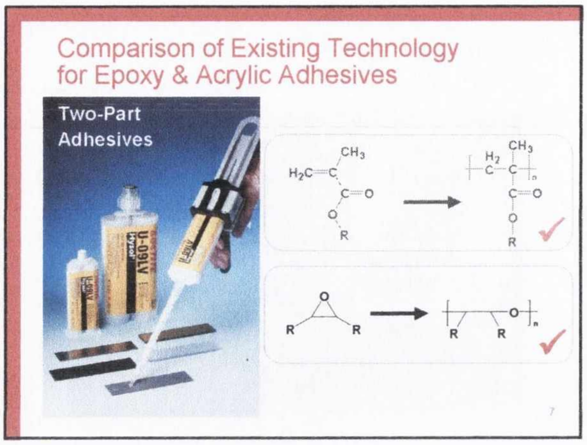
Comparison of Existing Technology for Epoxy & Acrylic Adhesives

Two-Part Adhesives



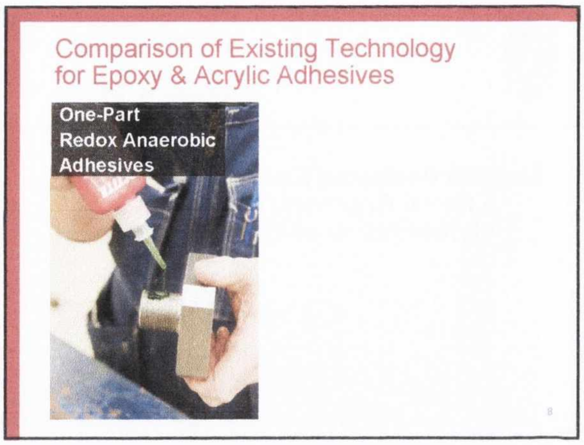
Comparison of Existing Technology for Epoxy & Acrylic Adhesives

Two-Part Adhesives



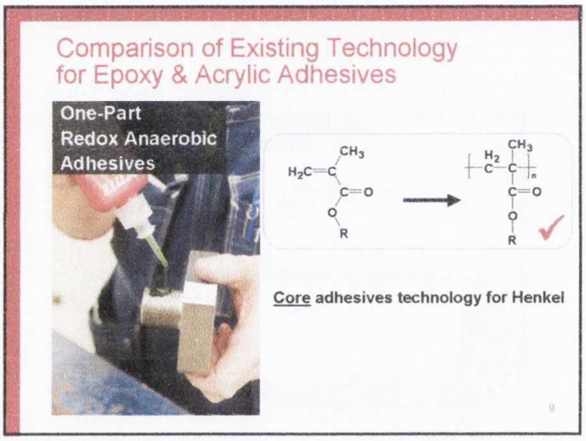
Comparison of Existing Technology for Epoxy & Acrylic Adhesives

Two-Part Adhesives



Comparison of Existing Technology for Epoxy & Acrylic Adhesives

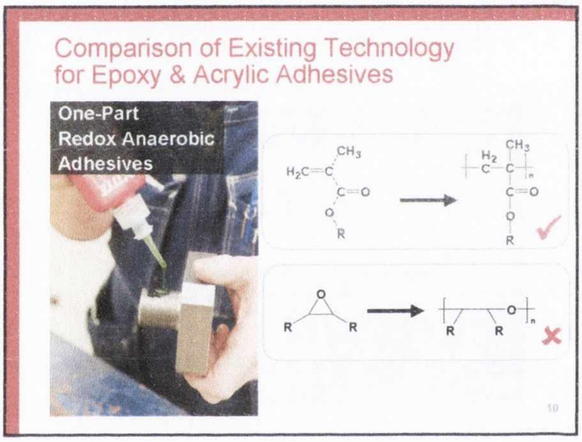
One-Part Redox Anaerobic Adhesives



Comparison of Existing Technology for Epoxy & Acrylic Adhesives

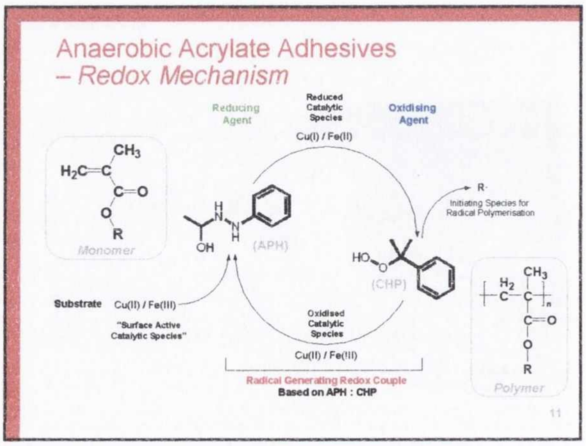
One-Part Redox Anaerobic Adhesives

Core adhesives technology for Henkel



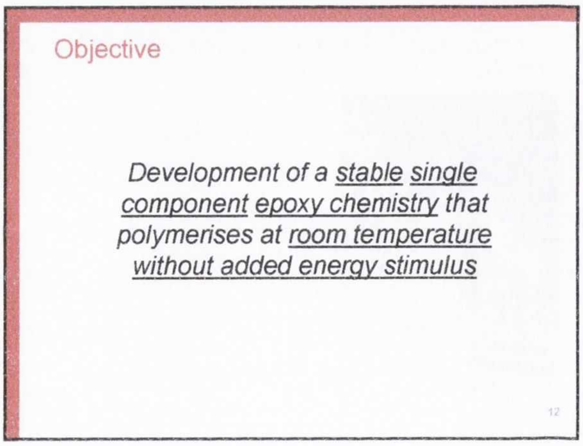
Comparison of Existing Technology for Epoxy & Acrylic Adhesives

One-Part Redox Anaerobic Adhesives



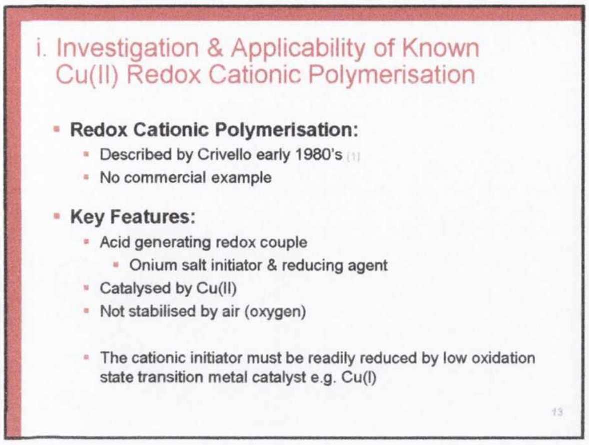
Anaerobic Acrylate Adhesives – *Redox Mechanism*

Radical Generating Redox Couple
Based on APH : CHP



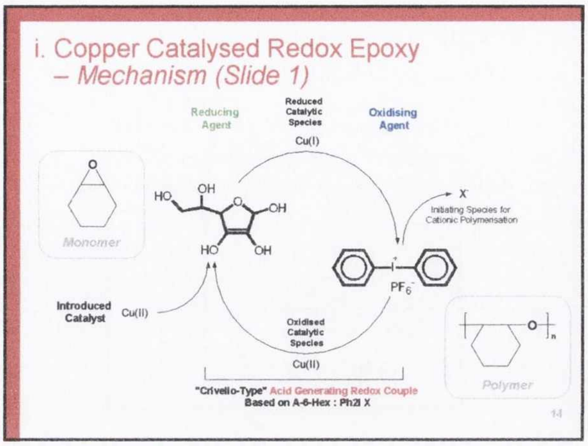
Objective

Development of a stable single component epoxy chemistry that polymerises at room temperature without added energy stimulus



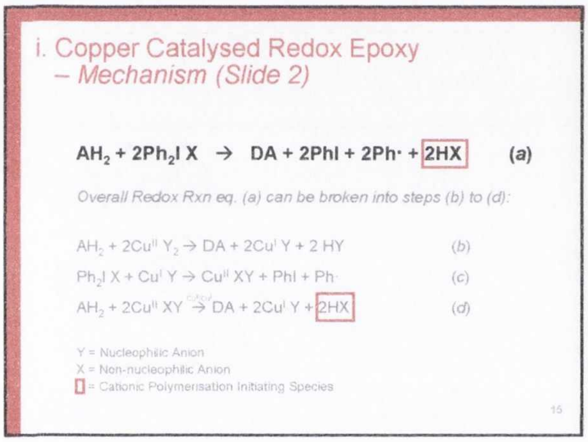
i. Investigation & Applicability of Known Cu(II) Redox Cationic Polymerisation

- **Redox Cationic Polymerisation:**
  - Described by Crivello early 1980's (1)
  - No commercial example
- **Key Features:**
  - Acid generating redox couple
    - Onium salt initiator & reducing agent
  - Catalysed by Cu(II)
  - Not stabilised by air (oxygen)
  - The cationic initiator must be readily reduced by low oxidation state transition metal catalyst e.g. Cu(I)



i. Copper Catalysed Redox Epoxy – *Mechanism (Slide 1)*

"Crivello-Type" Acid Generating Redox Couple
Based on A-6-Hex : Ph2I X



i. Copper Catalysed Redox Epoxy – *Mechanism (Slide 2)*

$$AH_2 + 2Ph_2I\,X \rightarrow DA + 2PhI + 2Ph\cdot + \boxed{2HX} \qquad (a)$$

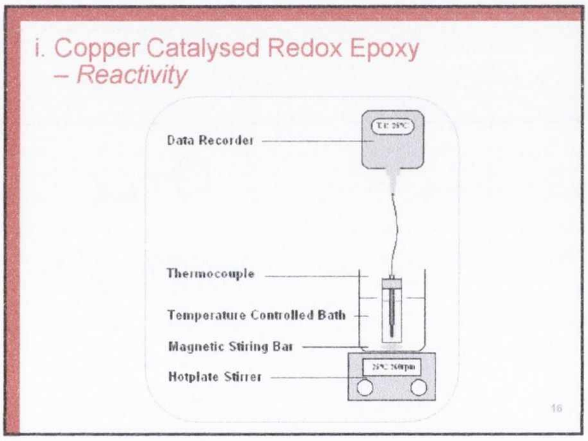
Overall Redox Rxn eq. (a) can be broken into steps (b) to (d):

$$AH_2 + 2Cu^{II}\,Y_2 \rightarrow DA + 2Cu^{I}\,Y + 2\,HY \qquad (b)$$

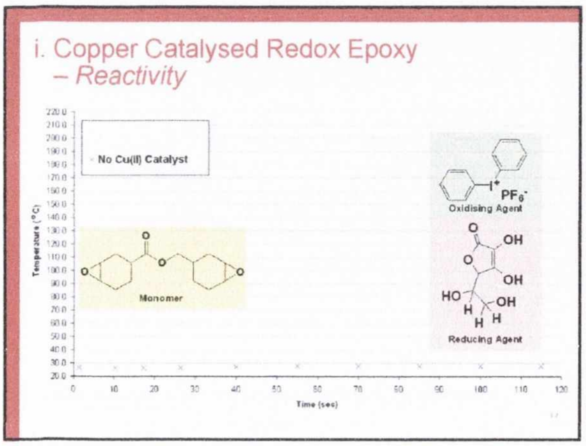
$$Ph_2I\,X + Cu^{I}\,Y \rightarrow Cu^{II}\,XY + PhI + Ph\cdot \qquad (c)$$

$$AH_2 + 2Cu^{II}\,XY \xrightarrow{Cu^{II}/Cu^{I}} DA + 2Cu^{I}\,Y + \boxed{2HX} \qquad (d)$$

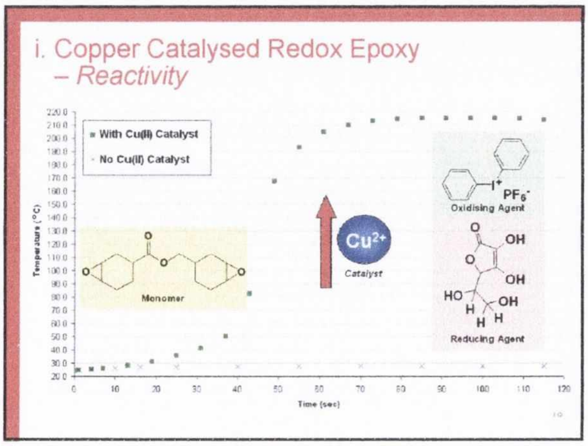
Y = Nucleophilic Anion
X = Non-nucleophilic Anion
▯ = Cationic Polymerisation Initiating Species



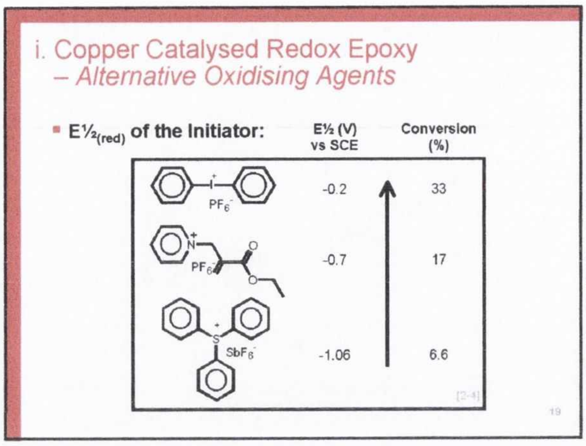
i. Copper Catalysed Redox Epoxy – *Reactivity*



i. Copper Catalysed Redox Epoxy – *Reactivity*



i. Copper Catalysed Redox Epoxy – *Reactivity*

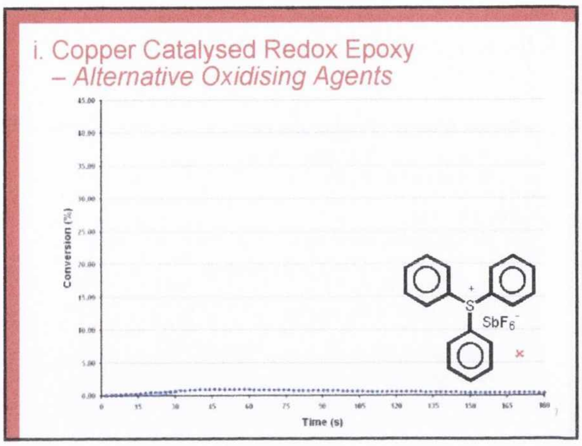


i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*

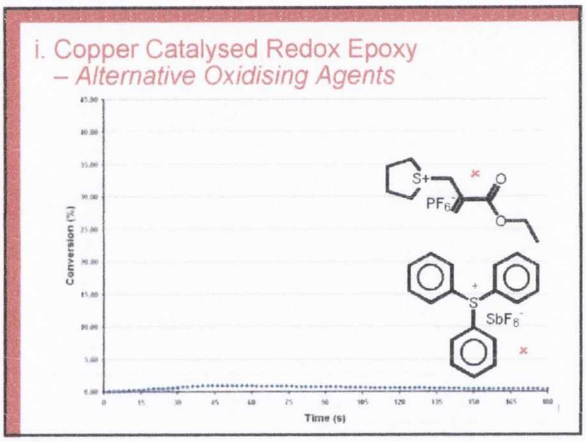
- **E½$_{(red)}$ of the Initiator:**

	E½ (V) vs SCE	Conversion (%)
	-0.2	33
	-0.7	17
	-1.06	6.6

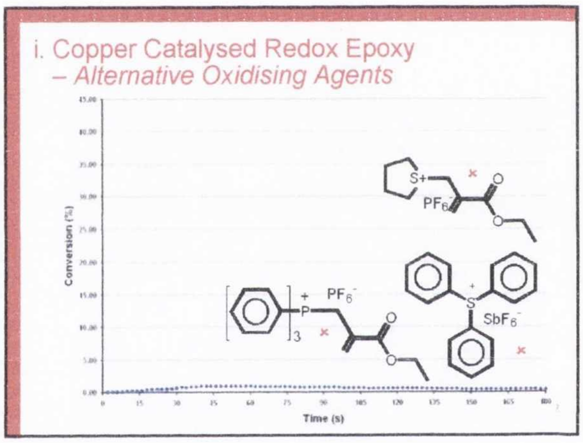
[2-4]



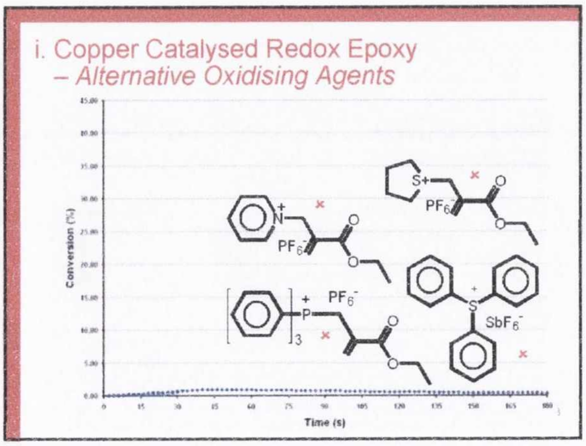
i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*



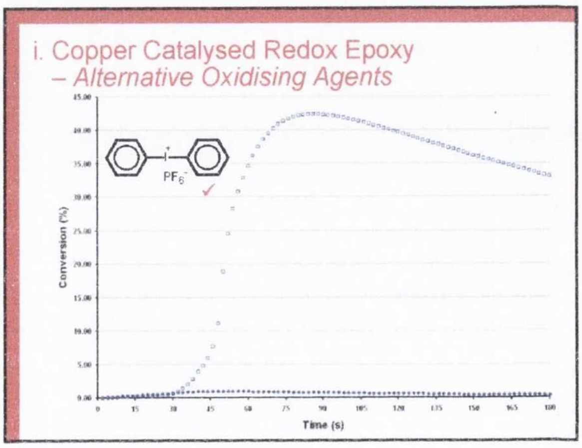
i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*



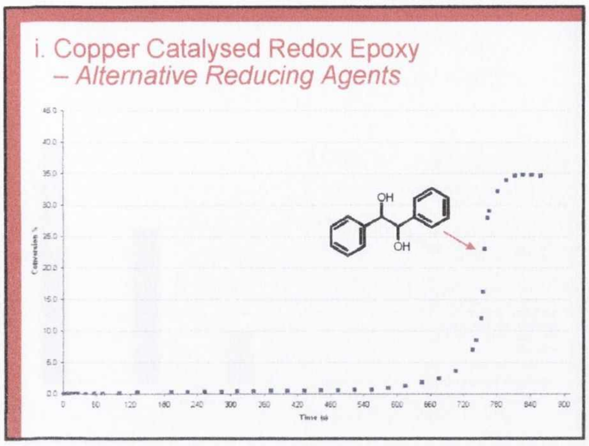
i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*



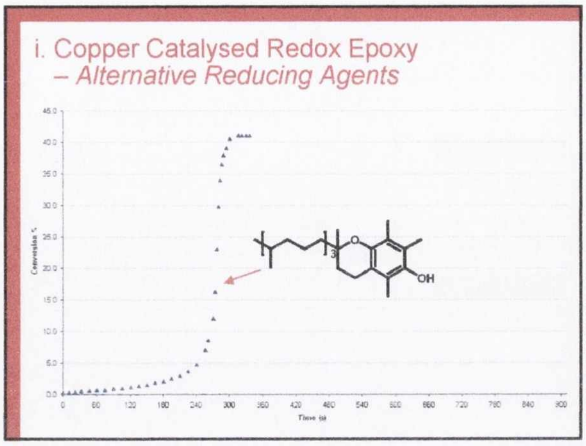
i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*



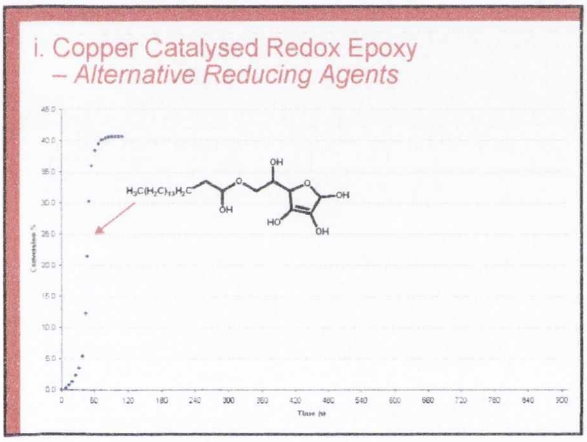
i. Copper Catalysed Redox Epoxy – *Alternative Oxidising Agents*



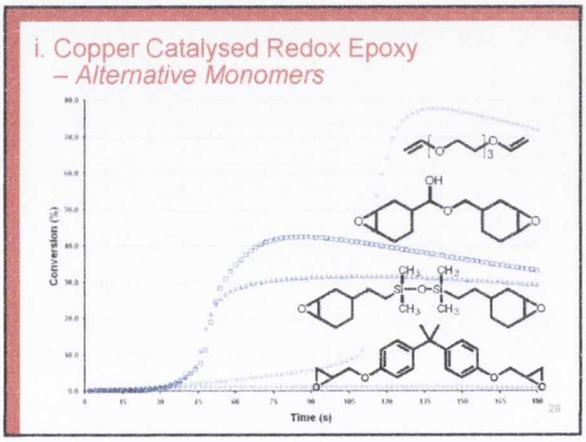
i. Copper Catalysed Redox Epoxy
– Alternative Reducing Agents



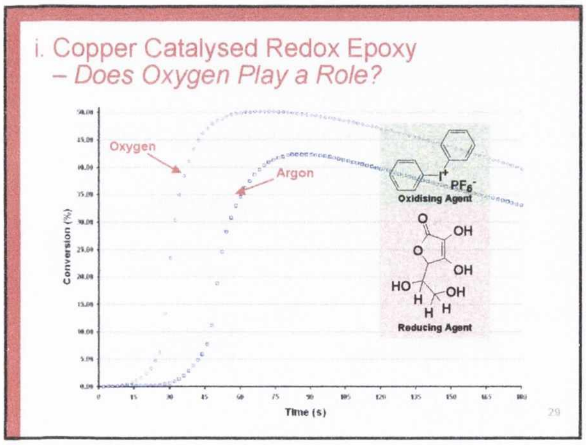
i. Copper Catalysed Redox Epoxy
– Alternative Reducing Agents



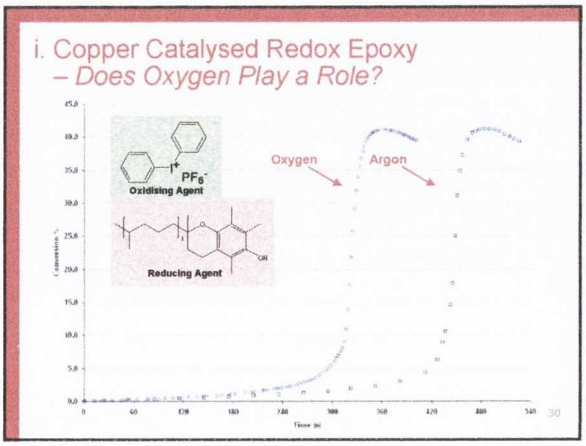
i. Copper Catalysed Redox Epoxy
– Alternative Reducing Agents



i. Copper Catalysed Redox Epoxy
– Alternative Monomers



i. Copper Catalysed Redox Epoxy
– Does Oxygen Play a Role?



i. Copper Catalysed Redox Epoxy
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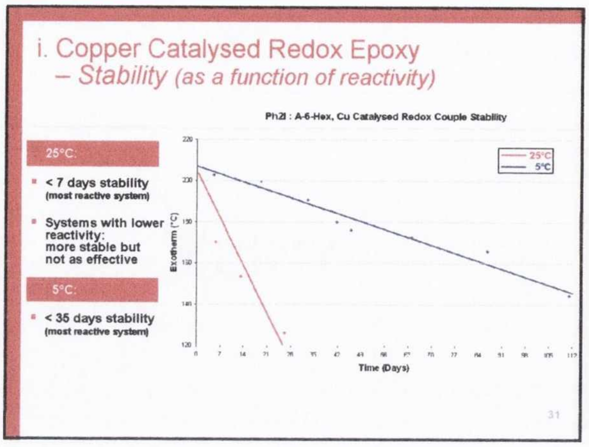


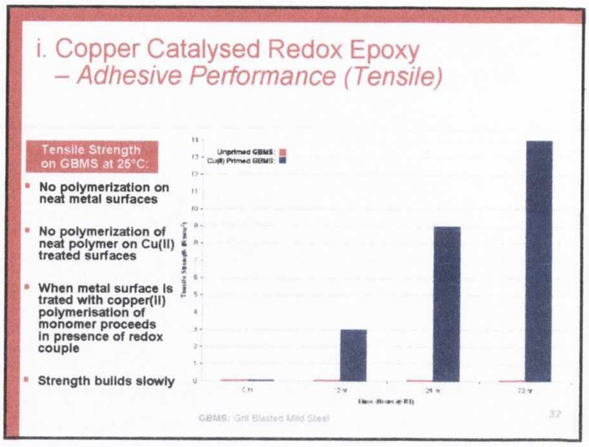
i. Copper Catalysed Redox Epoxy
– *Stability (as a function of reactivity)*

25°C:

- **< 7 days stability**
  (most reactive system)
- **Systems with lower reactivity: more stable but not as effective**

5°C:

- **< 35 days stability**
  (most reactive system)

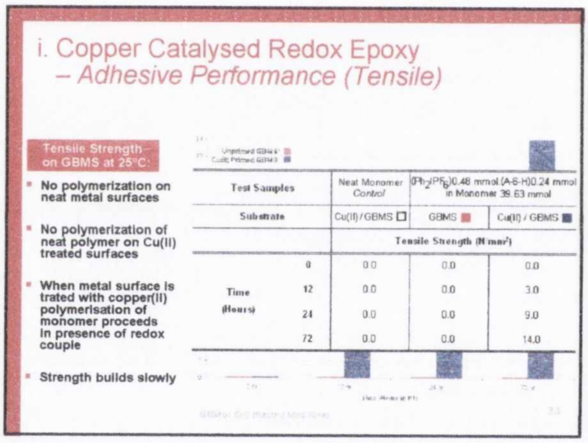


i. Copper Catalysed Redox Epoxy
– *Adhesive Performance (Tensile)*

Tensile Strength on GBMS at 25°C:

- **No polymerization on neat metal surfaces**
- **No polymerization of neat polymer on Cu(II) treated surfaces**
- **When metal surface is trated with copper(II) polymerisation of monomer proceeds in presence of redox couple**
- **Strength builds slowly**

GBMS: Grit Blasted Mild Steel



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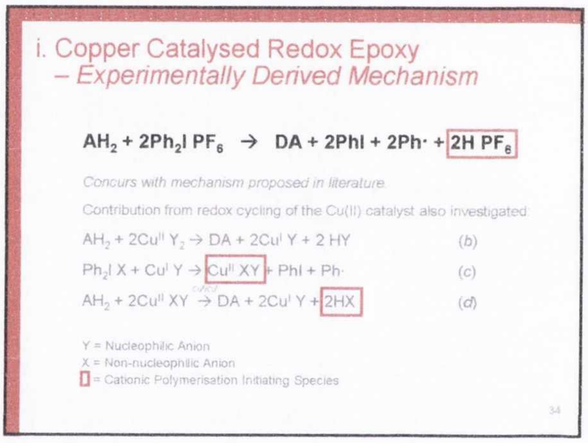
- **Strength builds slowly**

Test Samples		Neat Monomer *Control*	(Ph_2IPF_6)0.48 mmol (A-6-H)0.24 mmol in Monomer 39.63 mmol	
Substrate		Cu(II) / GBMS ☐	GBMS 🟥	Cu(II) / GBMS 🟦
		Tensile Strength (N/mm²)		
Time (Hours)	0	0.0	0.0	0.0
	12	0.0	0.0	3.0
	24	0.0	0.0	9.0
	72	0.0	0.0	14.0

GBMS: Grit Blasted Mild Steel



i. Copper Catalysed Redox Epoxy
– *Experimentally Derived Mechanism*

$$AH_2 + 2Ph_2I\,PF_6 \rightarrow DA + 2PhI + 2Ph\cdot + \boxed{2H\,PF_6}$$

Concurs with mechanism proposed in literature.

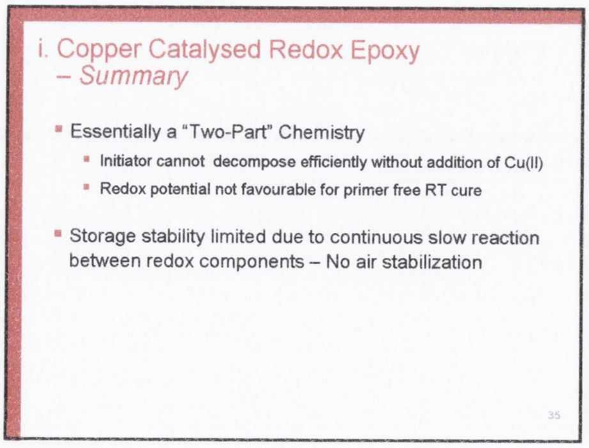
Contribution from redox cycling of the Cu(II) catalyst also investigated:

$$AH_2 + 2Cu^{II}\,Y_2 \rightarrow DA + 2Cu^{I}\,Y + 2\,HY \qquad (b)$$

$$Ph_2I\,X + Cu^{I}\,Y \rightarrow \boxed{Cu^{II}\,XY} + PhI + Ph\cdot \qquad (c)$$

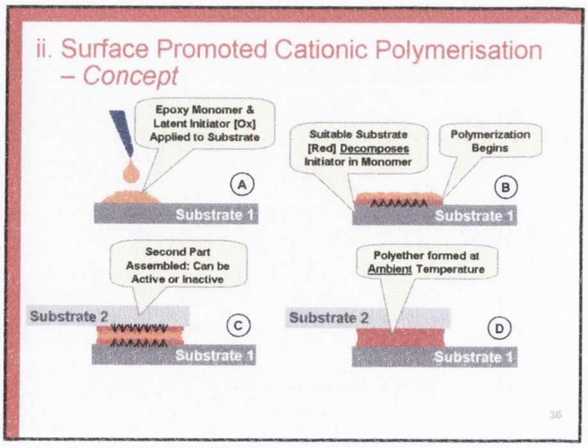
$$AH_2 + 2Cu^{II}\,XY \xrightarrow{cyclic} DA + 2Cu^{I}\,Y + \boxed{2HX} \qquad (d)$$

Y = Nucleophilic Anion
X = Non-nucleophilic Anion
▯ = Cationic Polymerisation Initiating Species

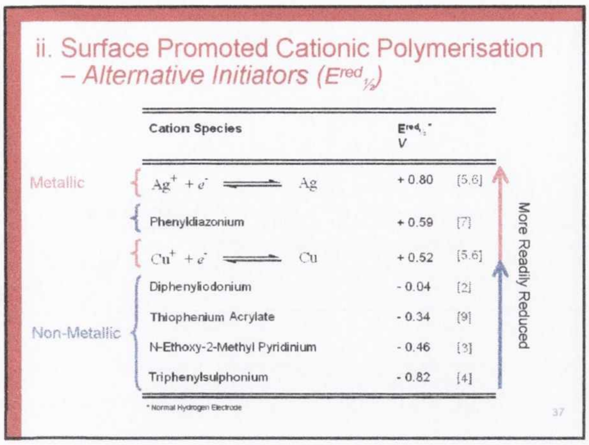


i. Copper Catalysed Redox Epoxy
– *Summary*

- Essentially a "Two-Part" Chemistry
  - Initiator cannot decompose efficiently without addition of Cu(II)
  - Redox potential not favourable for primer free RT cure
- Storage stability limited due to continuous slow reaction between redox components – No air stabilization



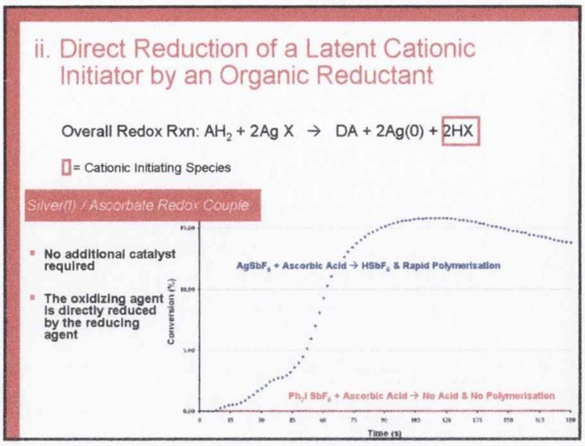
ii. Surface Promoted Cationic Polymerisation
– *Concept*



ii. Surface Promoted Cationic Polymerisation – *Alternative Initiators ($E^{red}_{1/2}$)*

	Cation Species	$E^{red}_{1/2}$ * V	
Metallic	$Ag^+ + e^- \rightleftharpoons Ag$	+ 0.80	[5,6]
	Phenyldiazonium	+ 0.59	[7]
	$Cu^+ + e^- \rightleftharpoons Cu$	+ 0.52	[5,6]
Non-Metallic	Diphenyliodonium	- 0.04	[2]
	Thiophenium Acrylate	- 0.34	[9]
	N-Ethoxy-2-Methyl Pyridinium	- 0.46	[3]
	Triphenylsulphonium	- 0.82	[4]

* Normal Hydrogen Electrode



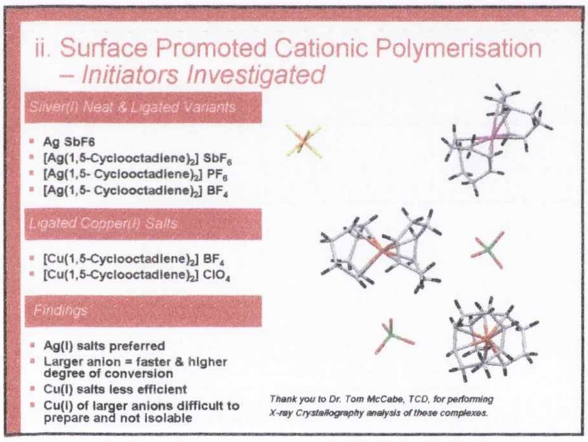
ii. Direct Reduction of a Latent Cationic Initiator by an Organic Reductant

Overall Redox Rxn: $AH_2 + 2Ag\,X \rightarrow DA + 2Ag(0) + \boxed{2HX}$

▯ = Cationic Initiating Species

Silver(I) / Ascorbate Redox Couple

- No additional catalyst required
- The oxidizing agent is directly reduced by the reducing agent



ii. Surface Promoted Cationic Polymerisation – *Initiators Investigated*

Silver(I) Neat & Ligated Variants

- Ag SbF6
- $[Ag(1,5\text{-Cyclooctadiene})_2]\ SbF_6$
- $[Ag(1,5\text{- Cyclooctadiene})_2]\ PF_6$
- $[Ag(1,5\text{- Cyclooctadiene})_2]\ BF_4$

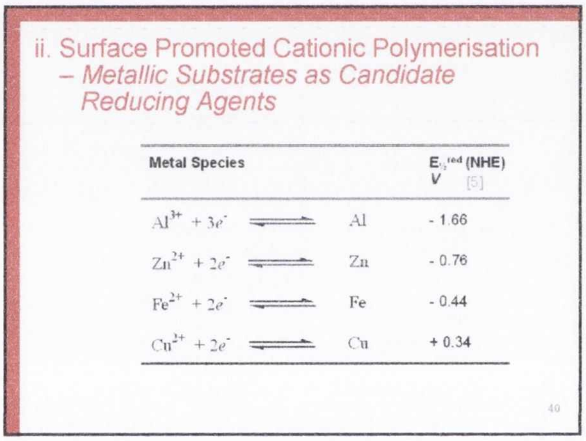
Ligated Copper(I) Salts

- $[Cu(1,5\text{-Cyclooctadiene})_2]\ BF_4$
- $[Cu(1,5\text{-Cyclooctadiene})_2]\ ClO_4$

Findings

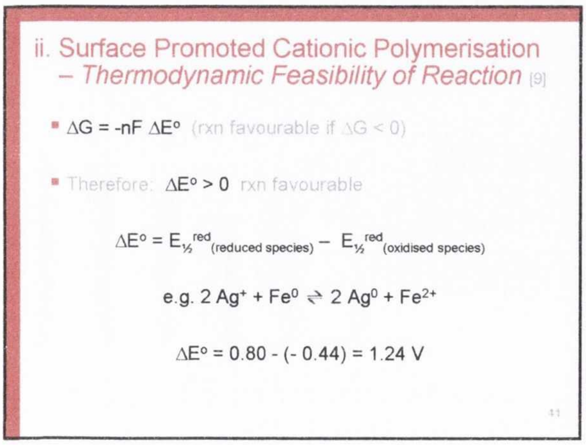
- Ag(I) salts preferred
- Larger anion = faster & higher degree of conversion
- Cu(I) salts less efficient
- Cu(I) of larger anions difficult to prepare and not isolable

Thank you to Dr. Tom McCabe, TCD, for performing X-ray Crystallography analysis of these complexes.



ii. Surface Promoted Cationic Polymerisation – *Metallic Substrates as Candidate Reducing Agents*

Metal Species	$E_{1/2}^{red}$ (NHE) V [5]
$Al^{3+} + 3e^- \rightleftharpoons Al$	- 1.66
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	- 0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	- 0.44
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34



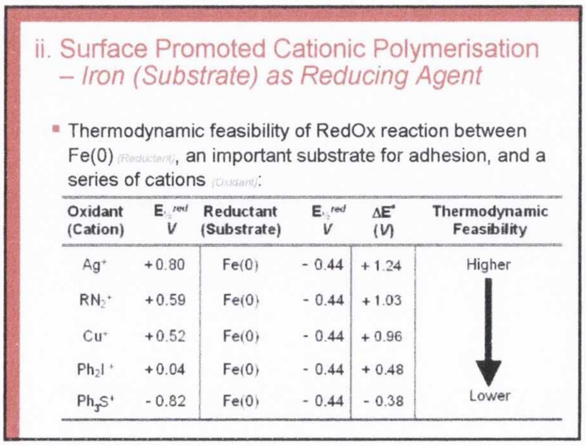
ii. Surface Promoted Cationic Polymerisation – *Thermodynamic Feasibility of Reaction* [9]

- $\Delta G = -nF\,\Delta E^o$ (rxn favourable if $\Delta G < 0$)
- Therefore: $\Delta E^o > 0$ rxn favourable

$$\Delta E^o = E_{1/2}{}^{red}{}_{(\text{reduced species})} - E_{1/2}{}^{red}{}_{(\text{oxidised species})}$$

$$\text{e.g. } 2\,Ag^+ + Fe^0 \rightleftharpoons 2\,Ag^0 + Fe^{2+}$$

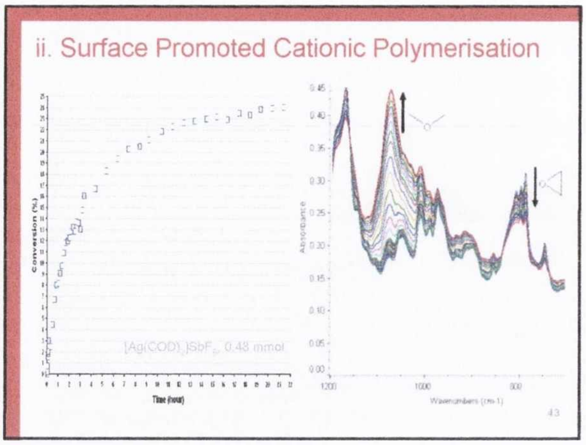
$$\Delta E^o = 0.80 - (-\,0.44) = 1.24\ V$$



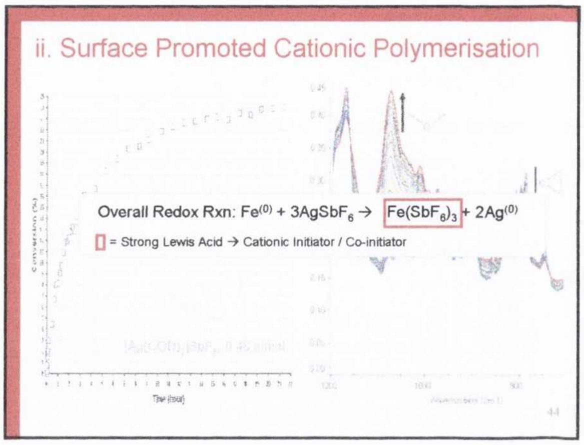
ii. Surface Promoted Cationic Polymerisation – *Iron (Substrate) as Reducing Agent*

- Thermodynamic feasibility of RedOx reaction between Fe(0) (Reductant), an important substrate for adhesion, and a series of cations (Oxidant):

Oxidant (Cation)	$E_{1/2}^{red}$ V	Reductant (Substrate)	$E_{1/2}^{red}$ V	ΔE° (V)	Thermodynamic Feasibility
Ag^+	+0.80	Fe(0)	- 0.44	+ 1.24	Higher
RN_2^+	+0.59	Fe(0)	- 0.44	+ 1.03	↓
Cu^+	+0.52	Fe(0)	- 0.44	+ 0.96	
Ph_2I^+	+0.04	Fe(0)	- 0.44	+ 0.48	
Ph_3S^+	- 0.82	Fe(0)	- 0.44	- 0.38	Lower



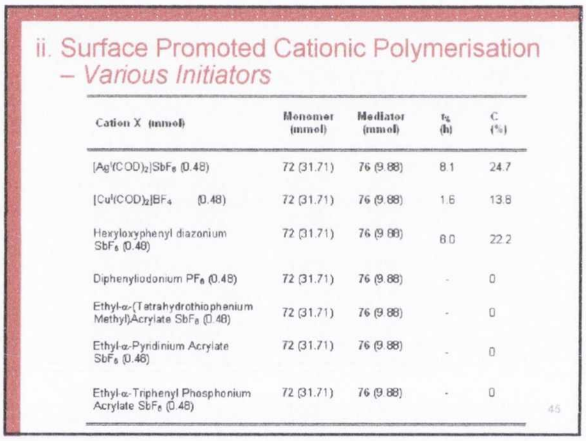
ii. Surface Promoted Cationic Polymerisation



ii. Surface Promoted Cationic Polymerisation

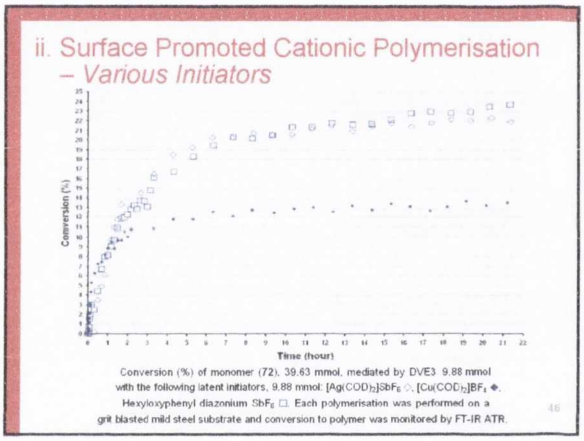
Overall Redox Rxn: $Fe^{(0)} + 3AgSbF_6 \rightarrow \boxed{Fe(SbF_6)_3} + 2Ag^{(0)}$

🟥 = Strong Lewis Acid → Cationic Initiator / Co-initiator



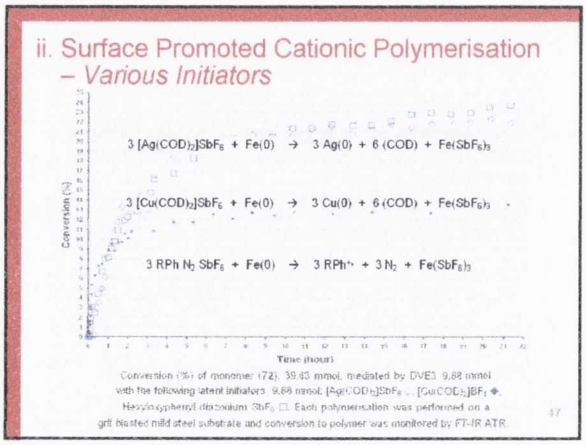
ii. Surface Promoted Cationic Polymerisation – *Various Initiators*

Cation X (mmol)	Monomer (mmol)	Mediator (mmol)	$t_{½}$ (h)	C (%)
[Ag^I(COD)$_2$]SbF$_6$ (0.48)	72 (31.71)	76 (9.88)	8.1	24.7
[Cu^I(COD)$_2$]BF$_4$ (0.48)	72 (31.71)	76 (9.88)	1.6	13.8
Hexyloxyphenyl diazonium SbF$_6$ (0.48)	72 (31.71)	76 (9.88)	8.0	22.2
Diphenyliodonium PF$_6$ (0.48)	72 (31.71)	76 (9.88)	-	0
Ethyl-α-(Tetrahydrothiophenium Methyl)Acrylate SbF$_6$ (0.48)	72 (31.71)	76 (9.88)	-	0
Ethyl-α-Pyridinium Acrylate SbF$_6$ (0.48)	72 (31.71)	76 (9.88)	-	0
Ethyl-α-Triphenyl Phosphonium Acrylate SbF$_6$ (0.48)	72 (31.71)	76 (9.88)	-	0



ii. Surface Promoted Cationic Polymerisation – *Various Initiators*

Conversion (%) of monomer (72), 39.63 mmol, mediated by DVE3 9.88 mmol with the following latent initiators, 9.88 mmol: [Ag(COD)$_2$]SbF$_6$ ◇, [Cu(COD)$_2$]BF$_4$ ◆, Hexyloxyphenyl diazonium SbF$_6$ □. Each polymerisation was performed on a grit blasted mild steel substrate and conversion to polymer was monitored by FT-IR ATR.



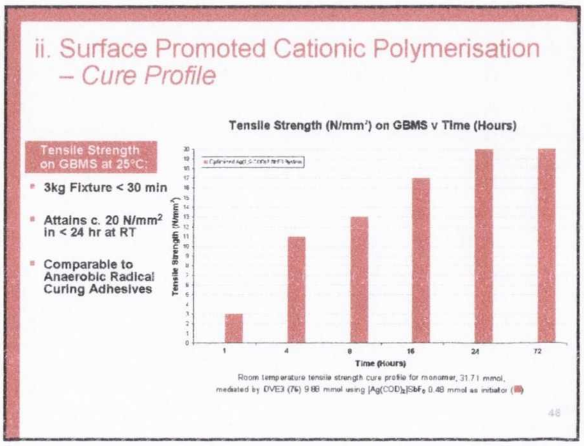
ii. Surface Promoted Cationic Polymerisation – *Various Initiators*

$3\,[Ag(COD)_2]SbF_6 + Fe(0) \rightarrow 3\,Ag(0) + 6\,(COD) + Fe(SbF_6)_3$

$3\,[Cu(COD)_2]SbF_6 + Fe(0) \rightarrow 3\,Cu(0) + 6\,(COD) + Fe(SbF_6)_3$

$3\,RPh\,N_2\,SbF_6 + Fe(0) \rightarrow 3\,RPh^{+\cdot} + 3\,N_2 + Fe(SbF_6)_3$

Conversion (%) of monomer (72), 39.63 mmol, mediated by DVE3 9.88 mmol with the following latent initiators, 9.88 mmol: [Ag(COD)$_2$]SbF$_6$ ◇, [Cu(COD)$_2$]BF$_4$ ◆, Hexyloxyphenyl diazonium SbF$_6$ □. Each polymerisation was performed on a grit blasted mild steel substrate and conversion to polymer was monitored by FT-IR ATR.



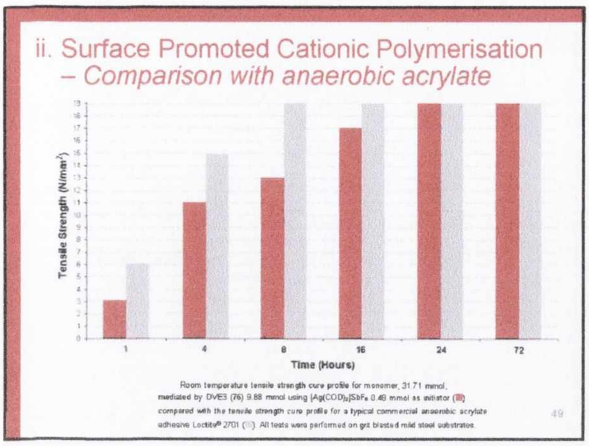
ii. Surface Promoted Cationic Polymerisation – *Cure Profile*

Tensile Strength on GBMS at 25°C:

- **3kg Fixture < 30 min**
- **Attains c. 20 N/mm^2 in < 24 hr at RT**
- **Comparable to Anaerobic Radical Curing Adhesives**

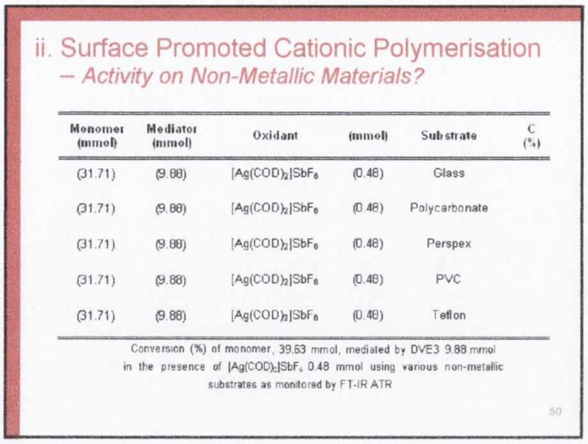
Tensile Strength (N/mm^2) on GBMS v Time (Hours)

Room temperature tensile strength cure profile for monomer, 31.71 mmol, mediated by DVE3 (76) 9.88 mmol using [Ag(COD)$_2$]SbF$_6$ 0.48 mmol as initiator (🟥)



ii. Surface Promoted Cationic Polymerisation – *Comparison with anaerobic acrylate*

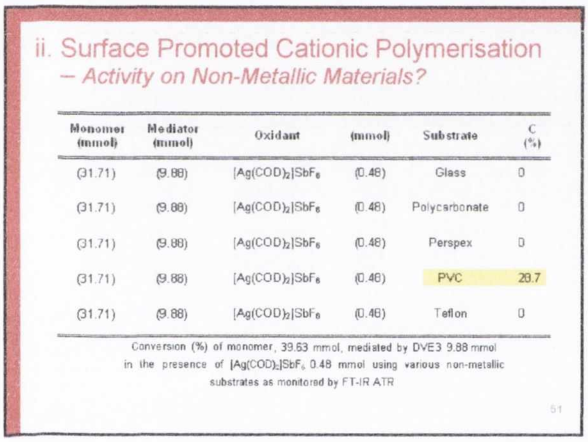
Room temperature tensile strength cure profile for monomer, 31.71 mmol, mediated by DVE3 (76) 9.88 mmol using $[Ag(COD)_2]SbF_6$ 0.48 mmol as initiator (🟥) compared with the tensile strength cure profile for a typical commercial anaerobic acrylate adhesive Loctite® 2701 (⬜). All tests were performed on grit blasted mild steel substrates.



ii. Surface Promoted Cationic Polymerisation – *Activity on Non-Metallic Materials?*

Monomer (mmol)	Mediator (mmol)	Oxidant	(mmol)	Substrate	C (%)
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Glass	
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Polycarbonate	
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Perspex	
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	PVC	
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Teflon	

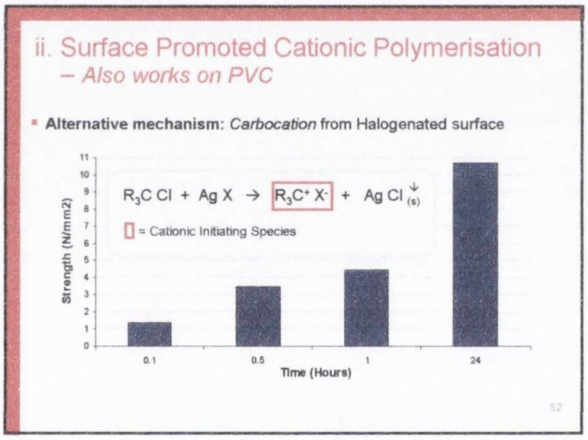
Conversion (%) of monomer, 39.63 mmol, mediated by DVE3 9.88 mmol in the presence of $[Ag(COD)_2]SbF_6$ 0.48 mmol using various non-metallic substrates as monitored by FT-IR ATR



ii. Surface Promoted Cationic Polymerisation – *Activity on Non-Metallic Materials?*

Monomer (mmol)	Mediator (mmol)	Oxidant	(mmol)	Substrate	C (%)
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Glass	0
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Polycarbonate	0
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Perspex	0
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	PVC	28.7
(31.71)	(9.88)	$[Ag(COD)_2]SbF_6$	(0.48)	Teflon	0

Conversion (%) of monomer, 39.63 mmol, mediated by DVE3 9.88 mmol in the presence of $[Ag(COD)_2]SbF_6$ 0.48 mmol using various non-metallic substrates as monitored by FT-IR ATR

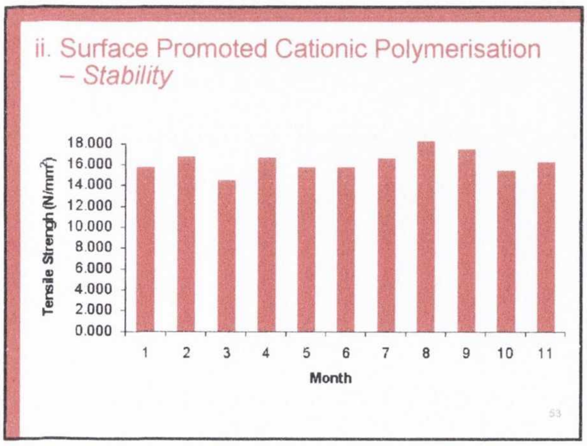


ii. Surface Promoted Cationic Polymerisation – *Also works on PVC*

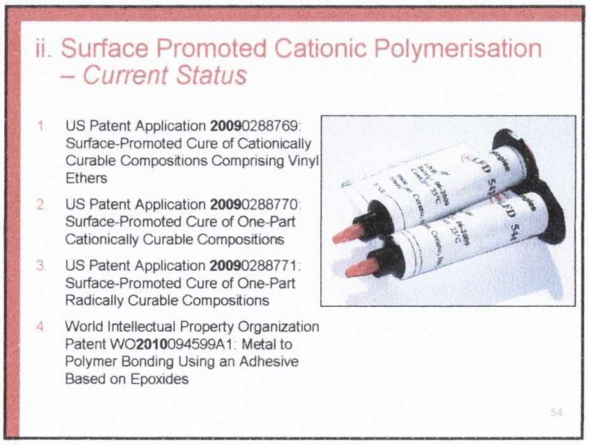
- **Alternative mechanism:** *Carbocation* from Halogenated surface

$$R_3C\,Cl + Ag\,X \rightarrow \boxed{R_3C^+ X^-} + Ag\,Cl_{(s)}\downarrow$$

▭ = Cationic Initiating Species

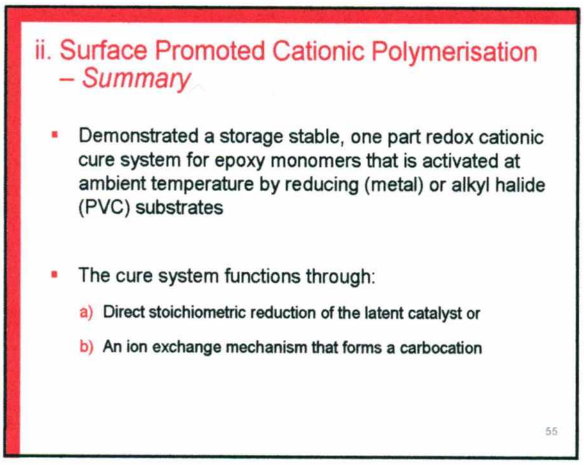


ii. Surface Promoted Cationic Polymerisation – *Stability*



ii. Surface Promoted Cationic Polymerisation – *Current Status*

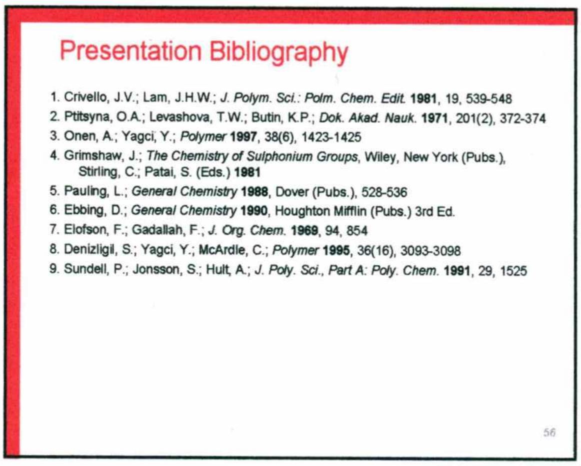
1. US Patent Application **2009**0288769: Surface-Promoted Cure of Cationically Curable Compositions Comprising Vinyl Ethers
2. US Patent Application **2009**0288770: Surface-Promoted Cure of One-Part Cationically Curable Compositions
3. US Patent Application **2009**0288771: Surface-Promoted Cure of One-Part Radically Curable Compositions
4. World Intellectual Property Organization Patent WO**2010**094599A1: Metal to Polymer Bonding Using an Adhesive Based on Epoxides



ii. Surface Promoted Cationic Polymerisation – *Summary*

- Demonstrated a storage stable, one part redox cationic cure system for epoxy monomers that is activated at ambient temperature by reducing (metal) or alkyl halide (PVC) substrates

- The cure system functions through:
  - a) Direct stoichiometric reduction of the latent catalyst or
  - b) An ion exchange mechanism that forms a carbocation



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