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New reactivity of the uranyl ion: ring opening polymerisation of epoxides†

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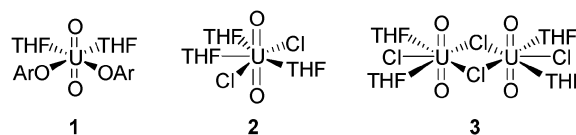
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The uranyl aryloxide, $[\text{UO}_2(\text{OAr})_2(\text{THF})_2]$, and uranyl chloride, $[\text{UO}_2\text{Cl}_2(\text{THF})_3]$ or $[\text{UO}_2\text{Cl}_2(\text{THF})_2]$ act as pre-catalysts for the ring opening polymerization of propylene oxide and cyclohexene oxide. Coordination of the monomers has been investigated using ^1H EXSY spectroscopy and kinetic and thermodynamic parameters reported. NMR analyses of the polymers suggest a bimetallic mechanism for the polymerization.

Our understanding of the coordination and organometallic chemistry of uranium (III) and (IV) has begun to gather pace over the past decade, and fascinating reactivity distinct from that associated with d-block metal complexes has been observed.¹ In contrast, considerably less attention has been paid to the uranyl (UO_2^{2+}) ion in anhydrous media, as such comparatively little is known about its reactivity and potential utility in non-nuclear chemistry, although hints of unusual reactivity have recently emerged.² We therefore became interested in identifying new reactivity patterns for the uranyl cation in order to probe its fundamental chemistry in non-aqueous media. Specifically, we are interested in systematically evaluating its potential in catalytic applications,^{3,4} as it has generally been accepted that due to the hard nature of an oxygen containing monomer, hard actinide ion catalysts are incapable of promoting any reactions.⁵ This thesis has only been challenged very recently with reports of U(IV) catalyzing the ring opening polymerization of ϵ -caprolactones,⁶ and the Tishchenko reaction.⁷ We are not aware of any work which has extended this to the harder uranyl ion. We found this particularly surprising, as an examination of the uranyl ion's coordination geometry allows one to identify enormous inherent potential for use in catalytic applications due to the strictly linear nature of the $\text{O}=\text{U}=\text{O}$ fragment. This restricts the coordination of other ligands to the equatorial plane and forces both ligands and labile solvent molecules to adopt mutually *cis* sites. Thus from a coordination perspective, a catalytically competent complex geometry—which must be engineered through ligand design in transition metal complexes—is 'built in' to the uranyl system *via* a trivial synthesis.

We began our studies with the catalysis of epoxide polymerization. We reasoned that this monomer would be an excellent entry into new uranyl chemistry due to the release of ring strain of the three-membered epoxide ring; this has been implicated in CO_2 /epoxide co-polymerizations.⁸ The literature catalyst systems for this reaction⁹ are generally based upon Al^{3+} , Zn^{2+} and Co^{2+} complexes, and to the best of our knowledge no actinide complex has been reported as a catalyst for this reaction. Moreover, comparisons to *cis*- $[\text{M}^{\text{VI}}\text{O}_2]$ ($\text{M} = \text{Mo}, \text{W}$) are useful as these do not have f-orbitals so the $\text{O}=\text{M}=\text{O}$ fragment is *cis*. Complexes of this type are catalysts for the epoxidation of alkenes, and further ring opening reactions are not observed.¹⁰ Initially we selected three complexes for evaluation (Scheme 1). Uranyl aryloxide **1** $[\text{UO}_2(\text{OAr})_2(\text{THF})_2]$ ($\text{Ar} = 2,6$ -di-*tert*-butylphenyl)¹¹ is a discrete mononuclear compound due to the presence of the sterically bulky aryloxy ligands. Moreover, the thermodynamics of the reaction are expected to be favourable as only U–O bonds are being formed or broken, therefore the polymerization would be entropically controlled. We also wished to investigate the potential influence of nuclearity on the catalytic efficacy (if any) of these systems, hence we also studied the less hindered, easily prepared ion **2**, which is monomeric in THF solution but dimerises to the binuclear analogue **3** in toluene.¹²

The reactivity of **1–3** towards propylene oxide (PO) and cyclohexene oxide (CHO) has been studied in both coordinating and non-coordinating solvents.† All catalyse the ring opening polymerisation of both epoxides at room temperature with 1 mol% of catalyst. Fig. 1 shows the conversion of PO and CHO to the respective polymers with precatalyst **1**. The observed rate constant has been determined (Table 1), and for **1** the increase of CHO over PO is possibly due to the increased ring strain from the additional contribution of the 6 membered ring,⁸ or that CHO is a 'slim' monomer so steric interactions are reduced. **2** and **3** display no significant difference in observed rates, which suggests a similar catalytic centre. In order to probe

Ar = 2,6-di-*tert*-butylphenyl

Scheme 1 Uranium precatalysts for the polymerisation of epoxides.

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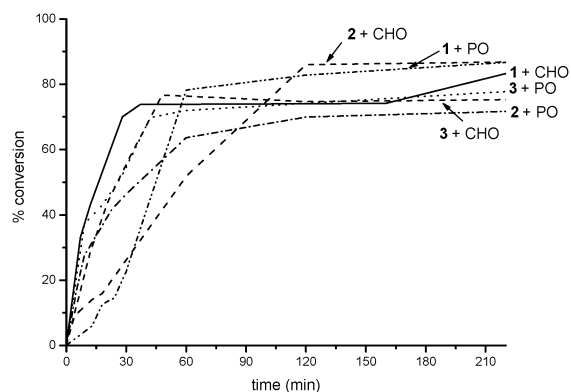


Fig. 1 Conversion of CHO and PO by 1 mol% of precatalyst **1** in THF against time.

Table 1 Characterisation data for polymers obtained from 1 mol% precatalyst in THF (**1** and **2**) or toluene (**3**) and observed rate constants

| Catalyst | Monomer | M_n | M_w | PDI | Calc M_w | k_{obs} ($\times 10^{-2} \text{ min}^{-1}$) |
|----------|---------|-------|-------|------|------------|---|
| 1 | PO | 1605 | 1645 | 1.03 | 6010 | 1.298 ± 0.357 |
| 1 | CHO | 5815 | 6013 | 1.04 | 10013 | 2.708 ± 0.573 |
| 2 | PO | 1000 | 1330 | 1.33 | 5840 | 1.960 ± 0.092 |
| 2 | CHO | 1007 | 1218 | 1.21 | 9843 | 1.039 ± 0.110 |
| 3 | PO | 1380 | 1518 | 1.10 | 5840 | 1.052 ± 0.439 |
| 3 | CHO | 2052 | 2078 | 1.02 | 9843 | 1.242 ± 0.166 |

the steric influence of the epoxide, we have examined the more substituted 2,3-dimethyl-2,3-epoxybutane with all catalysts; no polymerisation was observed under any conditions. Finally, the minimum loading required for this catalysis was found to be 0.5 mol%, albeit with longer reaction times. The resulting polymers were characterized by GPC in order to determine the molecular weights and polydispersities (Table 1). The molecular weights for PO polymerisation are similar for the three catalysts and the polydispersities are narrow, which suggests that these systems are well controlled, but a plot of M_n vs. time does not give a straight line so these cannot be considered as living.

The initial step in the polymerization mechanism would be coordination of the epoxide *via* exchange of THF. The poor solubility of **2** in non-coordinating solvents precluded NMR analysis. However, a ^1H NMR spectrum of **1** with less than 2 equivalents of PO displays broad peaks for THF and PO, indicating that they are slowly exchanging. In order to probe this exchange further we have utilized EXSY spectroscopy and a typical spectrum is shown in Fig. 2. Exchange between the THF and propylene oxide is clearly observed as cross peaks. Moreover, we have determined the rate constants over a range of temperatures and thus the activation energy and thermodynamic parameters for the exchange.¹³ The kinetic data confirm a slow exchange ($k = 0.028 \pm 0.002 \text{ s}^{-1}$ at 296 K) and a small activation energy ($E_{act} = 1.04 \pm 0.03 \text{ kJ mol}^{-1}$). The thermodynamic parameters for the exchange ($\Delta H = 0.71 \pm 0.03 \text{ kJ mol}^{-1}$, $\Delta S = -235.06 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$) suggest an associative transition state. Interestingly, when the bulkier epoxide 2,3-dimethyl-2,3-epoxybutane is examined, exchange with THF is observed, and the rate constant is slower than for PO ($k = 0.007 \pm 0.002 \text{ s}^{-1}$ at 296 K) presumably due to the increase in steric bulk. Attempts to measure the kinetics at

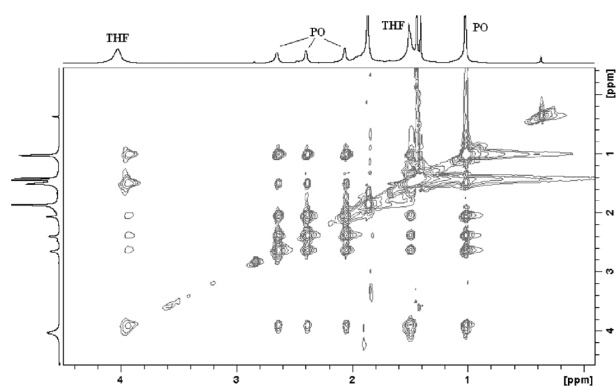


Fig. 2 EXSY spectrum of **1** + >2 equivalents of PO in C_6D_6 at 600 MHz ($T = 298 \text{ K}$, $t_m = 1 \text{ s}$).

variable temperatures were thwarted by decomposition to unidentified products. ^1H and ^1H EXSY spectra of cyclohexene oxide also show exchange (smaller linewidths) but a reliable kinetic analysis was not possible due to overlapping of peaks. When propylene sulfide is used as a monomer, no coordination and no polymerisation has been observed. This would be expected as the enthalpy of the exchange of a strong U–O bond for a weaker U–S bond would be unfavourable. Therefore we can postulate that the rate determining step for the polymerisation is nucleophilic attack at the coordinated epoxide and not coordination of the monomer; however coordination of this is essential.

The microstructure of the resultant polymers has been examined by NMR spectroscopy and MALDI-tof spectroscopy. Mass spectra of the PO polymer catalyzed by **1** shows a series of peaks separated by 58 mass units and correspond to $[\text{ArO}(\text{CH}_2\text{CH}(\text{Me})\text{O})_n\text{CH}_2\text{CH}(\text{Me})\text{OH} + \text{Na}]^+$, clearly indicating that the aryloxy group is incorporated into the polymer. ^1H NMR spectroscopy also confirms this as the aryl protons are observed and connectivity between aryl and alkyl groups can be observed using 2D NMR (Fig. S4). NMR and mass spectrometry confirm the presence of a Cl end group in polymers derived from **2** and **3** (Fig. S5). There are two plausible mechanisms that could operate: either an intramolecular *cis*-migratory insertion as observed for main group lactone ring opening, or an intermolecular backside attack, as seen for all metal catalyzed epoxide polymerisation. Homonuclear *J*-resolved NMR spectroscopy of the polymers obtained from CHO can be used to distinguish between these possibilities (Fig. 3).

If the mechanism is intramolecular then there will be no inversion of stereochemistry, whilst inversion will be observed in the intermolecular case.¹⁴ The coupling constants for the methine protons readily allows the identification of the mechanism. The ddd coupling pattern for the multiplets at 3.51 and 3.22 ppm indicates inversion of stereochemistry as the measured coupling constants agree with experimental and calculated values.¹⁴ Similarly, the polymers obtained from catalysis with both **2** and **3** show essentially identical *J*-resolved NMR spectra. The negligible difference in the observed rate constant also suggests the mechanism is very similar for the monometallic and bimetallic species, and we postulate that upon the addition of epoxide to dimeric **3**, a mononuclear complex is formed with one or more coordinating epoxides.

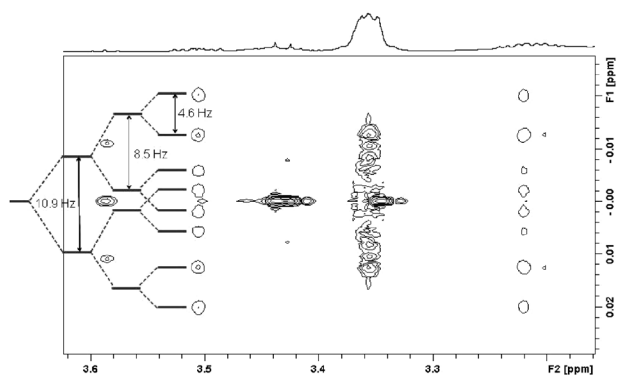


Fig. 3 Homonuclear J -resolved ^1H NMR spectrum of the methine region of poly(cyclohexene oxide) in CDCl_3 at 600 MHz. The resonance at 3.33 ppm is due to the ring methylene protons.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy has been used to identify the microstructure of poly(propylene oxide) from diad to tetrad level.¹⁵ Using established assignments of the methine and methylene carbons of the polymers obtained from *rac*-PO catalyzed by **1**–**3** (Fig. S7), it can be deduced that the polymer is mostly regioregular, but some H–H and T–T diads are observed. There is a bias towards isotactic diads in the regioregular portions of the polymer, suggesting that there is inversion of stereochemistry. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the polymer produced from *s*-PO confirms this observation. If inversion of stereochemistry is involved then the optical rotation of *s*-PO should be quenched;¹⁶ the polymer obtained from **1** and *s*-PO has an optical activity $[\alpha]_{\text{D}}^{20} = 0.002 \text{ deg cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.08 \text{ g cm}^{-3}$ in CH_2Cl_2) {cf. *s*-PO $[\alpha]_{\text{D}}^{20} -0.538$ ($c = 0.10 \text{ g cm}^{-3}$ in CH_2Cl_2)}, which further corroborates our postulated bimetallic mechanism. Taking into account all spectroscopic evidence, we suggest a mechanism (Fig. 4) where an intermolecular nucleophilic aryloxyde or halide attacks at an epoxide coordinated to a uranium(vi) centre in a chain shuttling mechanism as postulated for aluminium compounds.^{9g}

In conclusion, we have shown for the first time that aryloxides of uranium in high oxidation states can polymerize the ring opening of oxygen containing monomers. Spectroscopic evidence for a bimetallic mechanism has been presented.

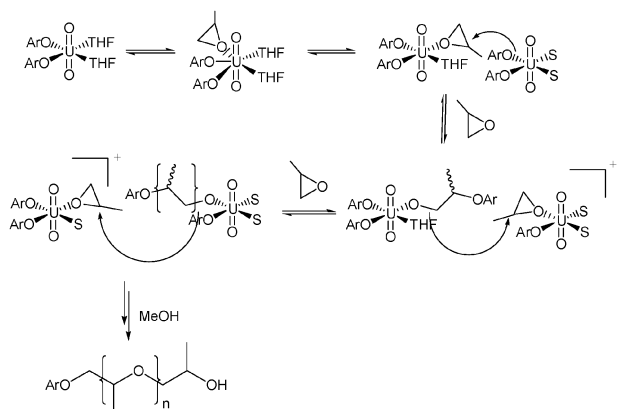


Fig. 4 Postulated mechanism for the polymerization of PO by pre-catalyst **1** ($S = \text{solvent}$).

Significantly, this reactivity can be extended to simple coordination compounds of the uranyl ion. This work emphasizes that hard monomers do not need to be excluded from hard oxophilic catalysts and demonstrates that the uranyl ion has great potential for hitherto unexplored catalysis.

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