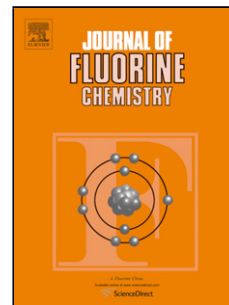


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Authors: Mohammed Ikram, Robert J. Baker



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Correspondence: Dr. Robert Baker
School of Chemistry
University of Dublin, Trinity College
Dublin 2
Ireland
Email: Bakerrj@tcd.ie

**Fluorous Catalyst Recycling Utilising Highly Fluorinated Zinc Compounds: Ring
Opening Polymerisation of ϵ -Caprolactone**

Mohammed Ikram and Robert J. Baker*

School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland.

Received:

Fluorous Catalyst Recycling Utilising Highly Fluorinated Zinc Compounds: Ring Opening Polymerisation of ϵ -Caprolactone

Mohammed Ikram and Robert J. Baker*

School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland.

Abstract

The synthesis of highly fluorinated zinc carboxylates, $[\{\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{CO}_2\}_2\text{Zn}]$, and alkoxides, $[\{\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{O}\}_2\text{Zn}(\text{OEt}_2)_2]$ and their use as catalysts for the ring opening polymerisation of ϵ -caprolactone are described. Quenching the polymerisation reaction with fluorous acids or alcohols regenerates the catalyst which can be recovered by fluorous solvent extractions and the catalytic activity is retained for three cycles. The superior recyclability of the alkoxide to the carboxylate zinc compound is due to the greater partition coefficient between fluorous and organic solvents. Also investigated is the well defined aryloxide compound $[(\text{ArO})_2\text{Zn}(\text{THF})_2]$ which yields very well controlled polymerisation, but cannot be recycled by quenching with a fluorous alcohol.

Keywords: Ring Opening Polymerisation; Perfluorinated Alcohols; ϵ -Caprolactone; Zinc Alkoxides

* Corresponding author. Tel: +353 (0)1 896 3501; fax: +353 (0)1 671 2826; email: bakerrj@tcd.ie.

1. Introduction

Arguably, the major disadvantage of homogeneous catalysis is catalyst recovery. This is particularly important if costly precious metal or synthetically complex ligand architectures are present in the (pre)catalyst. Therefore catalyst recycling or recovery has become an important topic of interest, and there are many methods available in the

literature [1]. One concept that has gained popularity is in the use of biphasic systems, and the temperature dependent miscibility properties of fluorinated and organic solvents have been taken advantage of in the design of fluorophilic catalysts [2]. Typically, a ligand is appended with one or more fluorous ‘ponytails’ to impart substantially enhanced solubility in a fluorous solvent, and above specific temperatures the fluorous and organic phases become miscible and the catalysis has the advantages of homogeneous catalysis, in particular selectivity and activity. Upon cooling, the solutions phase separate and the fluorous catalyst partitions into the fluorous phase whilst the products remain in the organic phase. Phosphine ligands with fluorous ‘pony-tails’ have become popular since the first report by Hovárth and co-workers [3] and there are now a plethora of aryl phosphine ligands with one or more long chain fluorous group substituted onto the aryl ring with a suitable spacer to modulate the electronic effects [4] of the perfluoroalkyl chain. Perfluoroalkyl diarylphosphines R_fPAR_2 are also popular modular ligands [5]. One particularly elegant application of this has been reported by Gladysz and co-workers where a labile fluorinated phosphine ligand on a Grubbs type pre-catalyst has more solubility in a fluorous phase, thus retarding the rate of re-coordination and ultimately increasing the activity of the catalyst which resides exclusively in the organic phase [6]. Fluorous techniques for organic transformations are also on the increase [7]. However the disadvantages of this approach are the environmental impact and bio-accumulation of typical fluorinated solvents [8] and, for potential commercial processes, the cost. This has been mitigated to an extent by the development of thermomorphic catalysts. It has been noted that very heavy fluorinated compounds show appreciable solubility in organic solvents only at high temperatures, and upon cooling these precipitate out of solution allowing for easy catalyst recovery. This has begun to be exploited in a number of organic transformations [9]. Interestingly, the use of fluorous supports apparently aids this precipitation [10], and we have recently shown that non-covalent C-F...F-C interactions need to be considered [11].

Herein, we report on a new concept of catalyst recovery, whereby the quenching reagent added to release the polymer from the metal centre contains a fluorous group, which enables catalyst recovery via solvent extraction. We have chosen the ring opening

polymerisation of cyclic lactones for our initial investigations as the initiating species is typically a metal alkoxide [12], whilst quenching the reaction is carried out by the addition of acidified organic alcohols. The mechanism(s) are well known and the presence of the initiating alkoxide as an end group suggests a coordination-insertion type mechanism that is prevalent for metal-alkoxide based catalysts. It occurred to us that quenching the reaction with a fluorinated alcohol would produce the polymer and a “RfO-M” moiety, which would selectively partition into a fluorinated solvent and could be separated from the reaction mixture and polymer. The addition of further aliquots of monomer to the recovered catalyst should be able to re-initiate polymerisation. Poly(caprolactone) is an important polymer as it is biodegradable and has found applications in various different fields such as scaffolds in tissue engineering, long-term drug delivery, microelectronics, adhesives and in packaging. [12] Due to this, a large number of catalysts and catalytic systems, spanning virtually the whole periodic table have been investigated, with zinc, aluminium and magnesium compounds prevalent. However, there are no examples known using fluorinated catalysts. Herein we report our initial investigations into fluorine recycling of catalysts for the

2. Results and Discussion

Our initial investigations began with the zinc bis-carboxylate complex $[(\text{RfCO}_2)_2\text{Zn}]$, ($\text{Rf} = \text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2$) which is readily prepared by the addition of the perfluorinated acid to $[\text{Zn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (Equation 1). Multinuclear NMR and infrared spectroscopy confirm the formulation, particularly the absence of resonances due to the $\text{N}(\text{SiMe}_3)_2$ groups, indicating that both amides have been replaced. The addition of one equivalent of benzyl alcohol affords the zinc carboxylate alkoxide complex $[\text{RfCO}_2\text{ZnOBn}]$, (Scheme 1) which has been characterised by *in situ* ^1H NMR spectroscopy; the benzyl methylene resonates at $\delta_{\text{H}} = 5.13$ ppm. ϵ -Caprolactone (25 equivalents) was then added to the NMR tube and the NMR spectrum recorded. Insertion of the monomer into the Zn-OBn bond is observed, with a shift in the benzyl methylene resonance to $\delta_{\text{H}} = 5.48$ ppm. No evidence of insertion into the zinc-carboxylate bond was observed, which is in line with the observations that acetate groups are poor initiators for the ring opening polymerisation of

cyclic lactones [13]. After one hour polymer is observed to precipitate out of the solution. In order to confirm that the OBn group is the initiator, this was quenched with acidified MeOH and the polymer analysed by MALDI-ToF mass spectrometry and NMR spectroscopy, with the benzylic methylene resonating at $\delta_{\text{H}} = 5.08$ ppm.

INSERT EQUATION 1 AND SCHEME 1 HERE

Our hypothesis is that if this catalyst is quenched by the addition of an equivalent of RfCO_2H in a fluoruous solvent then the pre-catalyst will be regenerated and preferentially extracted into the fluoruous phase. For this to effectively occur the partition coefficient - the preference for partitioning into the fluoruous phase over the organic phase - must be high. The measured partition coefficient for the zinc carboxylate is 86.1:14.9 in perfluoromethylcyclohexane:toluene. Therefore it may be predicted that this pre-catalyst would not be efficiently recycled and, when the quenching experiment is conducted, NMR spectroscopy confirms that the pre-catalyst is recovered in the fluoruous layer (1,3-bis(trifluoromethyl)benzene), [14] but only in 43% mass balance relative to the first polymerisation. The polymer was isolated and characterised by GPC which is reported as run 1 in Table 1. The calculated and measured number-averaged molecular weights (M_n) are similar which suggests that the polymerisation goes towards completion and the narrow molecular weight distribution suggests that the polymerisation is well controlled with little transesterification side reactions. Upon addition of BnOH and ϵ -caprolactone to the isolated pre-catalyst, very little polymer is produced which has a lower molecular weight (Run 2 in Table 1). A further quench and catalyst recovery cycle afforded a negligible amount of an oil that had a M_n of 427 (run 3 in Table 1). It is worthy of note that bulk polymerisation of ϵ -caprolactone using $[\text{Zn}(\text{OAc})_2]$ has been reported with a PDi of 1.10-1.40 [15].

INSERT TABLE 1 HERE

We next turned our attention to zinc aryloxides and alkoxides as these are well known to be superior catalysts for this reaction. We attempted two different strategies to examine

catalyst recovery. Firstly, a well-defined non-fluorous zinc phenoxide was used without an initiator and the catalyst quenched using a fluorous alcohol. The hypothesis is that this affords a fluorous zinc species, $[(RfO)_2Zn]$, that could be extracted using fluorous solvents. Subsequent protonolysis of the Zn-ORf bond with ArOH would regenerate the catalyst (Scheme 2). For these experiments we chose the zinc phenoxide complex $[Zn(OAr)_2(THF)_2]$ (Ar = 2,6-*t*Bu₂C₆H₃) as it is known to be a good catalyst for the copolymerisation of epoxides and CO₂ [17]. Addition of ϵ -caprolactone to a THF solution of the catalyst at 60 °C afforded a polymer after 1 hour. To this solution was added an excess of CF₃(CF₂)₅CH₂CH₂OH in 1,3-bis(trifluoromethyl)benzene to quench the polymerisation. Separation of the phases and examination of the ¹H and ¹⁹F NMR spectrum of the residue in the fluorous phase showed that a complex mixture of products had formed, so this approach was not continued. It is worthy of note that this is the first time this compound has been shown to ring open polymerise caprolactone and the polydispersity suggests very good control (Run 4 in Table 1). The polymer contains an -OAr end group as evidenced from NMR spectroscopy.

INSERT SCHEME 2 HERE

Our second approach was to intentionally prepare the intermediate fluorinated alkoxide complex of zinc, and then quench the polymerisation with a fluorous alcohol. Thus we prepared the zinc alkoxide complex $[Zn(OCH_2CH_2(CF_2)_5CF_3)_2(OEt_2)_2]$ by the protonolysis reaction of $[Zn\{N(SiMe_3)_2\}_2]$ with the corresponding alcohol in Et₂O (Equation 1). This cleanly produced the expected complex as a colourless oil in good isolated yield after extraction into FC-72 (FC-72 = perfluorohexane) and has been fully characterised. The NMR spectroscopic data show resonances due to the fluorous chains, with the expected coupling patterns [18], and coordinated Et₂O. The absence of resonances at 0.5 ppm in the ¹H NMR spectrum confirms that protonolysis of both amide groups has occurred. The partition coefficient for this complex in perfluoromethylcyclohexane:toluene is 97.3:2.7, which would be predicted to give an improvement in catalyst recycling compared to $[(RfCO_2)_2Zn]$.

Upon addition of ϵ -caprolactone to a THF solution of the catalyst at 60 °C a polymer precipitated out of solution after 1 hour. The polymer shows the expected $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{O}$ - end group as shown by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectroscopy (Figure 2) and mass spectrometry. Most diagnostic are the methylene groups of the end group at 54.67 ($^3J_{\text{C-F}} = 4.8$ Hz) and 30.01 ($^2J_{\text{C-F}} = 23.5$ Hz), and the CF_2 groups that appear as a multiplet between 106-116 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The ^{19}F resonances are not shifted relative to the alcohol, as expected. Quenching the polymerisation with $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OH}$ and extraction with 1,3-bis(trifluoromethyl)benzene afforded, by NMR spectroscopy, only resonances associated with the fluorous alkoxide and no coordinated THF was observed. Therefore the extractable species is likely to be $[\text{Zn}(\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_2]_n$, which probably exists as an oligomeric species. This catalyst could be cycled for three times in total (runs 5-7 in Table 1), before polymerisation activity stopped and no polymer was produced.

INSERT FIGURE 1 HERE

3. Conclusions

In conclusion, we have shown that a new method of catalyst recycling using fluorous groups for quenching polymerisations can be utilised in ring opening polymerisation of caprolactone. In our un-optimised systems the catalyst can be recycled three times before deactivation of the catalyst mixture. This catalyst recovery sequence may hold promise for the combination of fluorous separation techniques and conventional catalysis in order to enhance recovery using little of the expensive, environmentally harmful fluorous solvents.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Toluene and THF were distilled over potassium, whilst diethyl ether was distilled over Na/K. ϵ -Caprolactone, BnOH,

CF₃(CF₂)₅CH₂CH₂OH, 1,3-bis(trifluoromethyl)benzene, perfluoromethylcyclohexane and FC-72 were distilled over CaH₂ immediately before use. [Zn{N(SiMe₃)₂}₂], [Zn(OAr)₂(THF)₂] [16] and CF₃(CF₂)₅CH₂CH₂CO₂H [19] were prepared according to the literature methods. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.13 (¹H), 376.55 (¹⁹F) and 100.65 (¹³C) MHz, and were referenced to the residual ¹H or ¹³C resonances of the solvent used or external CFC₃ (¹⁹F). Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with an ATR accessory. Mass spectra were measured on a MALDI QTOF Premier MS system. GPC data was recorded on a Varian ProStar with a 350 RI detector using a PLgel 5μm MIXED-D column and calibrated with EasiCal polystyrene standards. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Fluorinated solvents were acquired from Fluorochem or Acotta (FC-72) and all other reagents from commercial sources and used as received. Partition coefficients were calculated via ¹⁹F NMR spectroscopy following the method of Gladysz [20].

4.1 {CF₃(CF₂)₅CH₂CH₂CO₂}₂Zn, 1. To a solution of [Zn{N(SiMe₃)₂}₂] (0.50 g, 1.30 mmol) in THF (10 cm³) was added a solution of CF₃(CF₂)₅CH₂CH₂CO₂H (1.10 g, 2.8 mmol) in THF (10 cm³) and the reaction mixture stirred for 3 hours. The solvent was removed in vacuo and the residue washed with hexane (2 x 10 cm³) then extracted into FC-72. Filtration and removal of the solvent afforded an off-white powder that was recrystallised from 1,3-bis(trifluoromethyl)benzene (0.79 g, 72%). ¹H NMR (CDCl₃/1,3-bis(trifluoromethyl)benzene): 1.34 (m, CH₂CF₂), 1.75 (t, ³J_{H-F} = 18.3Hz, CH₂CO₂); ¹³C{¹H} NMR (CDCl₃/1,3-bis(trifluoromethyl)benzene): 18.9 (s, CH₂CO₂); 29.8 (t, ²J_{C-F} = 23Hz, CF₂CH₂, 118-119 (m, CF₃ and CF₂), 153.6 (s, CO₂); ¹⁹F NMR (CDCl₃/1,3-bis(trifluoromethyl)benzene): -117.60 (CH₂CF₂), -124.92 (CF₂), -125.93 (CF₂), -126.33 (CF₂), -129.34 (CF₂), -84.48 (CF₃); ν (ATR, cm⁻¹): 2943 (w), 1630 (s), 1549 (m), 1490 (m), 1457 (m), 1343 (w), 1310 (w), 1246 (w), 1133 (m), 1108 (m), 1078 (m), 982 (m), 944 (w), 763 (s), 700 (s); C₁₈F₂₆H₈O₄Zn requires: C 25.51%, H 0.95%, found C 26.97%, H 1.65%.

4.2 $\{CF_3(CF_2)_5CH_2CH_2O\}_2Zn(OEt)_2$, **2**. To a solution of $[Zn\{N(SiMe_3)_2\}_2]$ (0.50 g, 1.3 mmol) in Et_2O (10 cm^3) was added a solution of $CF_3(CF_2)_5CH_2CH_2OH$ (1.04 g, 2.8 mmol) in Et_2O (10 cm^3) and the reaction mixture refluxed for 3 hours. The solvent was removed in vacuo and the residue washed with hexane ($2 \times 10\text{ cm}^3$) then extracted into FC-72. Filtration and removal of the solvent afforded an off-white powder that was recrystallised from 1,3-bis(trifluoromethyl)benzene (0.88 g, 86%). Mpt = 168-172 °C (dec); 1H NMR (C_6D_6 , 400.13 MHz) 3.74 (m, 4H, OCH_2), 2.20 (m, 4H, CH_2CF_2), 3.34 (q, 8H, $^3J_{H-H} = 7.3\text{ Hz}$, Et_2O), 1.19 (t, 12H, $^3J_{H-H} = 7.2\text{ Hz}$, Et_2O); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100.65 MHz), 118-119 (m, CF_3 and CF_2), 56.1, (s, CH_2O), 31.3, (t, $^2J_{C-F} = 20\text{ Hz}$, CF_2CH_2); ^{19}F NMR (C_6D_6 , 376.55 MHz): -117.70 (CH_2CF_2), -127.73 (CF_2), -125.71 (CF_2), -126.79 (CF_2), -130.41 (CF_2), -85.68 (CF_3); ν (ATR, cm^{-1}): 2917 (w), 1672 (w), 1610 (w), 1583 (w), 1517 (m), 1467 (m), 1414 (m), 1379 (m), 1329 (s), 1211 (w), 1102 (w), 1016 (s), 922 (w), 866 (s), 742 (w), 678 (m); $C_{24}H_{28}F_{26}O_4Zn$ requires: C 30.67%, H 3.00%, found C 31.95%, H 3.10%.

4.3 *Polymerisation Experiments*. In a typical experiment 600 equivalents of ϵ -caprolactone was added to a solution of the catalyst (1.5 mmol) in THF (10 cm^3) held at 60 °C and the reaction stirred for 1 hour. To this mixture was added the fluororous quenching agent (3.75 mmol of $RfCO_2H$ or $RfOH$) in 1,3-bis(trifluoromethyl)benzene (15 cm^3) and the reaction stirred for 15 minutes. The solution was cooled, filtered to isolate the polymer and the phases separated to recover the catalyst in the fluororous layer. The polymer was washed copiously with MeOH and dried *in vacuo* before analysis by GPC.

5. Acknowledgements

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Table and Figure Captions

Table 1. Characterisation data for poly(caprolactone) produced by fluorinated (pre)-catalysts ($R_f = CF_3(CF_2)_5CH_2CH_2$).

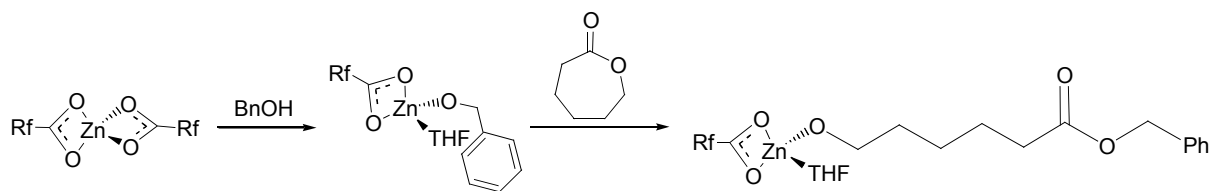
Scheme 1. Ring Opening Polymerisation catalysed by $[(R_fCO_2)_2Zn]$.

Scheme 2. Ring Opening Polymerisation catalysed by $[(ArO)_2Zn(THF)_2]$.

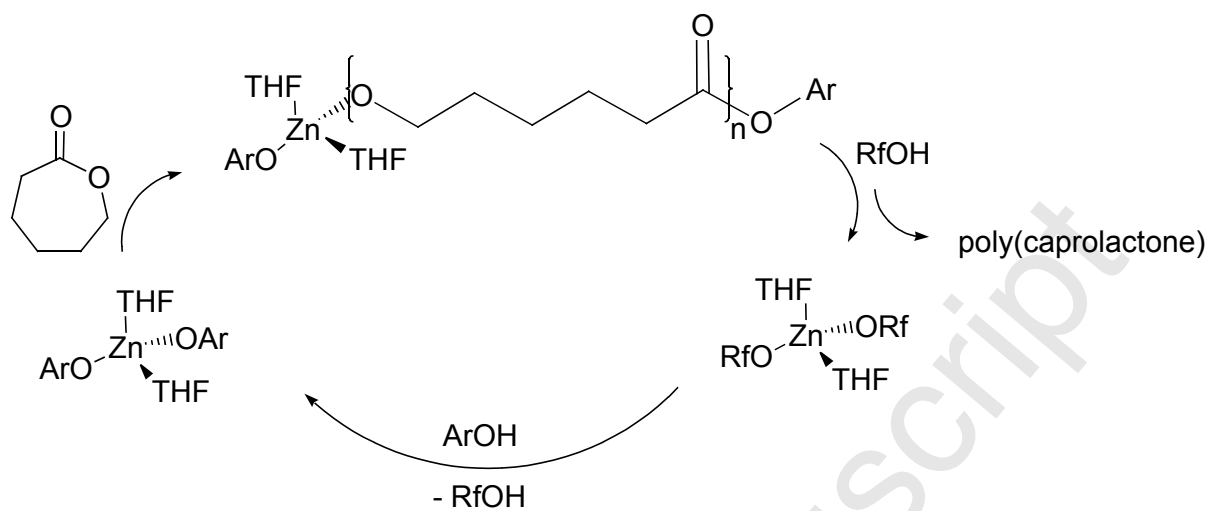
Figure 1. 1H (a), ^{19}F (b) and $^{13}C\{^1H\}$ (c) NMR spectra of poly(caprolactone) obtained from $R_fO_2Zn(OEt)_2$. (* indicates 1,3-bis(trifluoromethyl)benzene impurity)

run	(pre)-catalyst	conditions ^[a]	M_n ^[b]	Calculated M_n	PDi
1	[(RfCO ₂) ₂ Zn]	BnOH initiator	2756	3298	1.03
2		1 st Recycle	1133	3298	1.03
3		2 nd Recycle	427	3298	1.10
4	[(ArO) ₂ Zn(THF) ₂] ^[c]		2560	3769	1.01
5	[(RfO) ₂ Zn(OEt ₂) ₂]		5110	8957	1.21
6		1 st Recycle	2549	8957	1.10
7		2 nd Recycle	1171	8957	1.15

[a] 1:600 catalyst loading, Temp = 60°C, solvent = THF, time = 1hr; [b] Mark-Houwink correction applied [¹⁶]; [c] Ar = 2,6-^tBu₂C₆H₃.



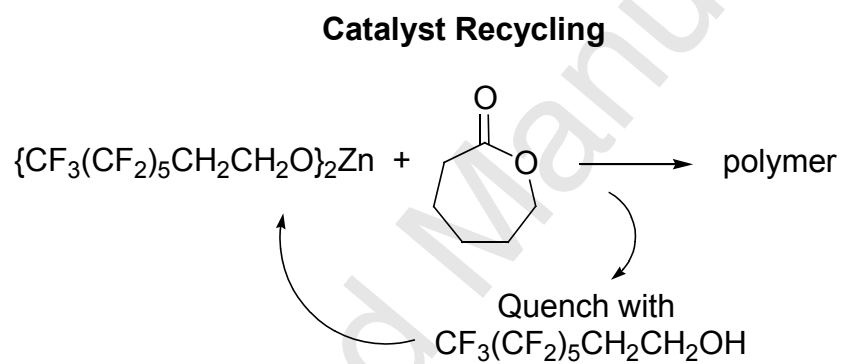
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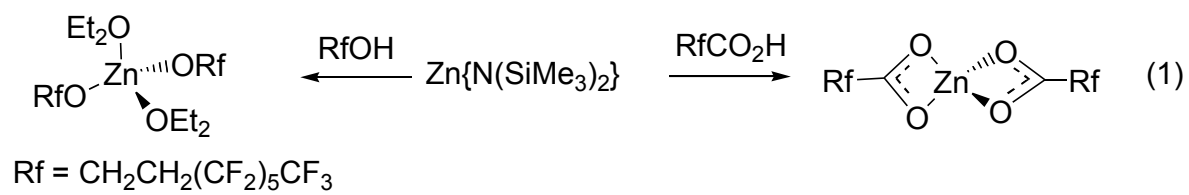


Graphical Abstract Synopsis**Fluorous Catalyst Recycling Utilising Highly Fluorinated Zinc Compounds: Ring
Opening Polymerisation of ϵ -Caprolactone****Mohammed Ikram and Robert J. Baker**

Recycling strategies for a zinc catalysed ring opening polymerisation of caprolactone have been explored. The use of fluorous alkoxide compounds of zinc and quenching with a fluorous alcohol allows the catalyst to be recycled three times before loss of activity.

Graphical Abstract Pictogram

**Fluorous Catalyst Recycling Utilising Highly Fluorinated Zinc Compounds: Ring
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Figure(s)

