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Short communication

Fluorous catalyst recycling utilising highly fluorinated zinc compounds: Ring opening polymerisation of ε-caprolactone

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ABSTRACT

The synthesis of highly fluorinated zinc carboxylates [$\{CF_3(CF_2)_5CH_2CH_2CO_2\}_2Zn$], and alkoxides [$\{CF_3(CF_2)_5CH_2CH_2O\}_2Zn(OEt_2)_2$] 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 [$(ArO)_2Zn(THF)_2$] which yields very well controlled polymerisation, but cannot be recycled by quenching with a fluorous alcohol.

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 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 in the design of fluorophilic catalysts [2]. Typically, a ligand is appended with one or more fluorous 'pony-tails' 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 Horváth and Rabai [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 $RfPAr_2$ 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

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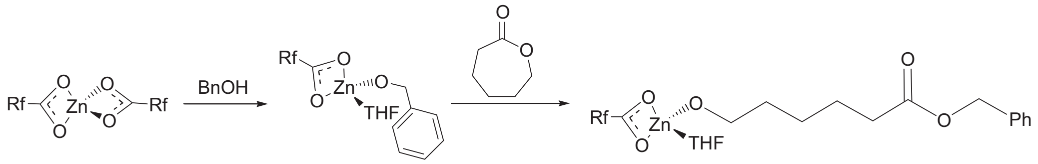


Scheme 1. Ring opening polymerisation catalysed by [($RfCO_2$)$_2$Zn].

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

Run	(Pre)-catalyst	Conditions[a]	M_n[b]	Calculated M_n	PDi
1	[$(RfCO_2)_2Zn$]	BnOH initiator	2756	3298	1.03
2		1st recycle	1133	3298	1.03
3		2nd recycle	427	3298	1.10
4	[$(ArO)_2Zn(THF)_2$][c]		2560	3769	1.01
5	[$(RfO)_2Zn(OEt_2)_2$]		5110	8957	1.21
6		1st recycle	2549	8957	1.10
7		2nd recycle	1171	8957	1.15

[a] 1:600 catalyst loading, temp = 60 °C; solvent = THF; time = 1 h.

[b] Mark–Houwink correction applied [16].

[c] Ar = 2,6-^{t}$Bu_2C_6H_3$.

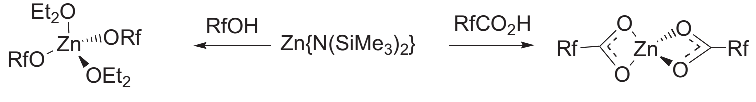
fluorinated solvent and could be separated from the reaction mixture and polymer. The addition of further aliquots of monomer to the recovered catalyst should be able to re-initiate polymerisation. Poly(caprolactone) is an important polymer as it is biodegradable and has found applications in various 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 fluorous recycling of catalysts for the ring opening polymerisation of ε-caprolactone.

2. Results and discussion

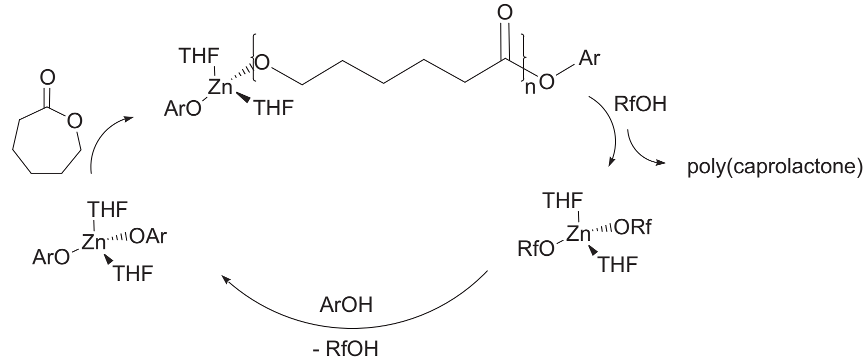
Our initial investigations began with the zinc bis-carboxylate complex [$(RfCO_2)_2Zn$] ($Rf = CF_3(CF_2)_5CH_2CH_2$), which is readily prepared by the addition of the perfluorinated acid to [$Zn\{N(SiMe_3)_2\}_2$] (Eq. (1)). Multinuclear NMR and infrared spectroscopy confirm the formulation, particularly the absence of resonances due to the $N(SiMe_3)_2$ groups, indicating that both amides have been replaced. The addition of one equivalent of benzyl alcohol affords the zinc carboxylate alkoxide complex [$RfCO_2ZnOBn$] (Scheme 1), which has been characterised by in situ ^1H NMR spectroscopy; the benzyl methylene resonates at $\delta_H = 5.13$ 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 $\delta_H = 5.48$ 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 1 h 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 $\delta_H = 5.08$ ppm.

Our hypothesis is that if this catalyst is quenched by the addition of an equivalent of $RfCO_2H$ in a fluorous solvent then the pre-catalyst will be regenerated and preferentially extracted into the fluorous phase. For this to effectively occur the partition coefficient – the preference for partitioning into the fluorous 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 fluorous 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 [$Zn(OAc)_2$] has been reported with a PDi of 1.10–1.40 [15].

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}$Bu_2C_6H_3$) as it is known to be a good catalyst for the copolymerisation of epoxides and CO_2 [17]. Addition of ε-caprolactone to a THF solution of the catalyst at 60 °C afforded a

 (1)

$Rf = CH_2CH_2(CF_2)_5CF_3$



Scheme 2. Ring opening polymerisation catalysed by $[(ArO)_2Zn(THF)_2]$.

polymer after 1 h. To this solution was added an excess of $CF_3(CF_2)_5CH_2CH_2OH$ in 1,3-bis(trifluoromethyl)benzene to quench the polymerisation. Separation of the phases and examination of the ^1H and ^{19}F 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.

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 Et_2O (Eq. (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 Et_2O. 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 h. The polymer shows the expected $CF_3(CF_2)_5CH_2CH_2O$– end group as shown by ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectroscopy (Fig. 1) and mass

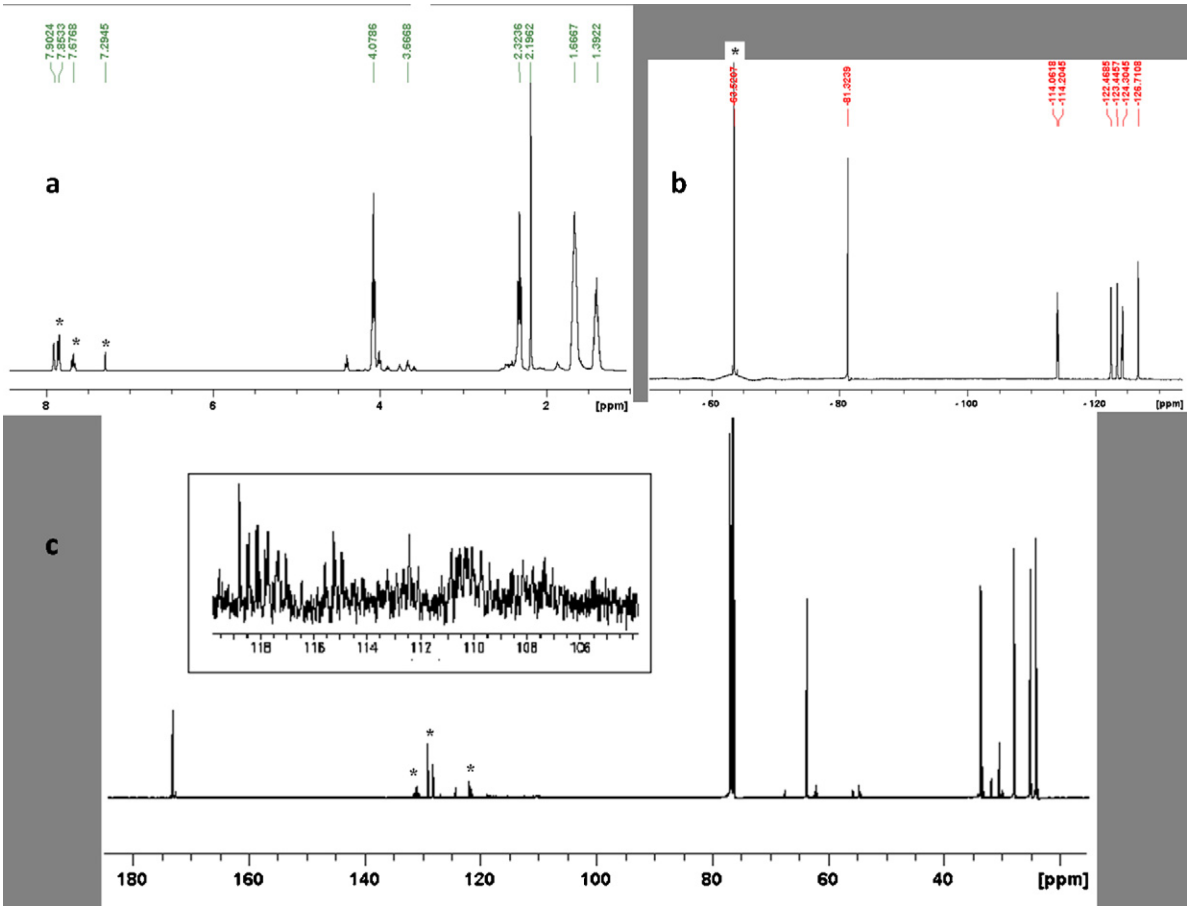


Fig. 1. ^1H (a), ^{19}F (b) and $^{13}C\{^1H\}$ (c) NMR spectra of poly(caprolactone) obtained from $RfO_2Zn(OEt_2)_2$. (*Indicates 1,3-bis(trifluoromethyl)benzene impurity).

spectrometry. Most diagnostic are the methylene groups of the end group at 54.67 ($^3J_{C-F}$ = 4.8 Hz) and 30.01 ($^2J_{C-F}$ = 23.5 Hz), and the CF_2 groups that appear as a multiplet between 106 and 116 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The ^{19}F resonances are not shifted relative to the alcohol, as expected. Quenching the polymerisation with $CF_3(CF_2)_5CH_2CH_2OH$ 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 $[Zn(OCH_2CH_2(CF_2)_5CF_3)_2]_n$, 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.

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, $CF_3(CF_2)_5CH_2CH_2OH$, 1,3-bis(trifluoromethyl)benzene, perfluoromethylcyclohexane and FC-72 were distilled over CaH_2 immediately before use. $[Zn\{N(SiMe_3)_2\}_2]$, $[Zn(OAr)_2(THF)_2]$ [16] and $CF_3(CF_2)_5CH_2CH_2CO_2H$ [19] were prepared according to the literature methods. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.13 (^1H), 376.55 (^{19}F) and 100.65 (^{13}C) MHz, and were referenced to the residual ^1H or ^{13}C resonances of the solvent used or external $CFCl_3$ (^{19}F). 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 5 μm 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 ^{19}F NMR spectroscopy following the method of Gladysz [20].

4.1. *$\{CF_3(CF_2)_5CH_2CH_2CO_2\}_2Zn$*, 1

To a solution of $[Zn\{N(SiMe_3)_2\}_2]$ (0.50 g, 1.30 mmol) in THF (10 cm^3) was added a solution of $CF_3(CF_2)_5CH_2CH_2CO_2H$ (1.10 g, 2.8 mmol) in THF (10 cm^3) and the reaction mixture stirred for 3 h. The solvent was removed in vacuo and the residue washed with hexane (2 × 10 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 (0.79 g, 72%). ^1H NMR ($CDCl_3$/1,3-bis(trifluoromethyl)benzene): 1.34 (m, CH_2CF_2), 1.75 (t, $^3J_{H-F}$ = 18.3 Hz, CH_2CO_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$/1,3-bis(trifluoromethyl)benzene): 18.9 (s, CH_2CO_2); 29.8 (t, $^2J_{C-F}$ = 23 Hz, $CF_2\mathbf{C}H_2$), 118–119 (m, CF_3 and CF_2), 153.6 (s, CO_2); ^{19}F NMR ($CDCl_3$/1,3-bis(trifluoromethyl)benzene): −117.60 ($CH_2C\mathbf{F}_2$), −124.92 (CF_2), −125.93 (CF_2), −126.33 (CF_2), −129.34 (CF_2), −84.48 (CF_3); 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); $C_{18}F_{26}H_8O_4Zn$ requires: C 25.51%, H 0.95%, found C 26.97%, H 1.65%.

4.2. *$\{CF_3(CF_2)_5CH_2CH_2O\}_2Zn(OEt_2)_2$*, 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 h. The solvent was removed in vacuo and the residue washed with hexane (2 × 10 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, $OC\mathbf{H}_2$), 2.20 (m, 4H, CH_2CF_2), 3.34 (q, 8H, $^3J_{H-H}$ = 7.3 Hz, Et_2O), 1.19 (t, 12H, $^3J_{H-H}$ = 7.2 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 Hz, $CF_2\mathbf{C}H_2$); ^{19}F NMR (C_6D_6, 376.55 MHz): −117.70 ($CH_2C\mathbf{F}_2$), −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 h. To this mixture was added the fluorous 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 min. The solution was cooled, filtered to isolate the polymer and the phases separated to recover the catalyst in the fluorous layer. The polymer was washed copiously with MeOH and dried in vacuo before analysis by GPC.

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References

[1] M. Benaglia (Ed.), Recoverable and Recyclable Catalysts, John Wiley & Sons, Chichester, UK, 2009.
[2] (a) J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley VCH, Weinheim, 2004;
(b) A.E.C. Collis, I.T. Horváth, Catalysis Science and Technology 1 (2011) 912–919;
(c) L.P. Barthel-Rosa, J.A. Gladysz, Coordination Chemistry Reviews 190–192 (1999) 587–605.
[3] I.T. Horváth, J. Rabai, Science 266 (1994) 72–75.
[4] (a) I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai, E.J. Mozeleski, Journal of the American Chemical Society 120 (1998) 3133–3143;
(b) H. Jiao, S. Le Stang, T. Soós, R. Meier, K. Kowski, P. Rademacher, L. Jafarpour, J.-B. Hamard, S.P. Nolan, J.A. Gladysz, Journal of the American Chemical Society 124 (2002) 1516–1523;
(c) L.J. Alvey, R. Meier, T. Soós, P. Bernatis, J.A. Gladysz, European Journal of Inorganic Chemistry (2000) 1975–1983.
[5] D. Gudmunsen, E.G. Hope, D.R. Paige, A.M. Stuart, Journal of Fluorine Chemistry 130 (2009) 942–950, and references therein.
[6] R.C. da Costa, J.A. Gladysz, Advanced Synthesis and Catalysis 349 (2007) 243–254.
[7] (a) W. Zhang, Green Chemistry 11 (2009) 911–920;
(b) W. Zhang, Combinatorial Chemistry and High Throughput Screening 10 (2007) 219–229;
(c) W. Zhang, Chemical Reviews 104 (2004) 2531–2556.
[8] A.B. Lindstrom, M.J. Strynar, E.L. Libelo, Environmental Science and Technology 45 (2011) 7954–7961.
[9] (a) M. Wende, R. Meier, J.A. Gladysz, Journal of the American Chemical Society 123 (2001) 11490–11491;
(b) M. Wende, J.A. Gladysz, Journal of the American Chemical Society 125 (2003) 5861–5872;

(c) K. Ishihara, S. Kondo, H. Yamamoto, Synlett (2001) 1371–1374;
(d) K. Ishihara, A. Hasegawa, H. Yamamoto, Synlett (2002) 1299–1301;
(e) K. Mikami, Y. Mikami, H. Matsuzawa, Y. Matsumoto, J. Nishikido, F. Yamamoto, H. Nakajima, Tetrahedron 58 (2002) 4015–4021;
(f) J. Otera, Accounts of Chemical Research 37 (2004) 288–296;
(g) G. Maayan, R.H. Fish, R. Neumann, Organic Letters 5 (2003) 3547–3550;
(h) J.A. Gladysz, V. Tesevic, Topics in Organometallic Chemistry 23 (2008) 67–89;
(i) D. Mandal, M. Jurisch, C. Consorti, J.A. Gladysz, Chemistry – An Asian Journal 3 (2008) 1772–1782.

[10] F.O. Seidel, J.A. Gladysz, Advanced Synthesis and Catalysis 350 (2008) 2443–2449.

[11] R.J. Baker, P.E. Colavita, D. Murphy, J.A. Platts, J.D. Wallis, Journal of Physical Chemistry A 116 (2012) 1435–1444.

[12] (a) For recent reviews see: M.J. Stanford, A.P. Dove, Chemical Society Reviews, 39 (2010) 486–494;
(b) M. Labet, W. Thielemans, Chemical Society Reviews 38 (2009) 3484–3504;
(c) C.A. Wheaton, P.G. Hayes, B.J. Ireland, Dalton Transactions (2009) 4832–4846;
(d) N.E. Kamber, W. Jeong, R.M. Waymouth, R.C. Pratt, B.G.G. Lohmeijer, J.L. Hedrick, Chemical Reviews 107 (2007) 5813–5840;
(e) C.-T. Chen, C.-C. Lin, Coordination Chemistry Reviews 250 (2006) 602–626.

[13] B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, Journal of the American Chemical Society 123 (2001) 3229–3238.

[14] It should be noted that 1,3-bis(trifluoromethyl)benzene is an amphiphillic solvent that can dissolve both organic and fluorous compounds. We carefully checked the purity of our extracted species by multinuclear NMR spectroscopy to ensure only the fluorinated compounds were extracted. Poly(caprolactone) shows no solubility in this solvent.

[15] R.R. Gowda, D. Chakraborty, Journal of Molecular Catalysis A: Chemical 333 (2010) 167–172.

[16] (a) A. Kowalski, A. Duda, S. Penczek, Macromolecules 31 (1998) 2114;
(b) A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski, S. Penczek, Macromolecules 23 (1990) 1640.

[17] D.J. Darensbourg, M.W. Holtcamp, G.E. Struck, M.S. Zimmer, S.A. Niezgoda, P. Rainey, J.B. Robertson, J.D. Draper, J.H. Reibenspies, Journal of the American Chemical Society 121 (1999) 107–116.

[18] A.A. Ribeiro Mag, Magnetic Resonance in Chemistry 35 (1997) 215–221.

[19] R.J. Baker, T. McCabe, J.E. O'Brien, H.V. Ogilvie, Journal of Fluorine Chemistry 131 (2010) 621–626.

[20] C.S. Consorti, F. Hampel, J.A. Gladysz, Inorganica Chimica Acta 359 (2006) 4874–4884.