Pergamon

Tetrahedron 58 (2002) 4053–4059

TETRAHEDRON

Preparation of fluorinated methacrylic copolymers by copper mediated living radical polymerization

Sébastien Perrier,[a] Stuart G. Jackson,[a] David M. Haddleton,[a,*] Bruno Ameduri[b] and Bernard Boutevin[b]

[a]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[b]*UMR 5076 CNRS, 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France*

Received 22 November 2001; accepted 5 February 2002

Abstract—The synthesis of fluorinated macroinitiators and macromonomers for copper mediated living radical polymerization is reported. In a first approach, various fluorinated telomers showing one or two hydroxy groups are transformed into initiators via esterification. The resultant macroinitiators are used for the polymerization of methyl methacrylate (MMA) to give well-defined block copolymers. In a second approach, the same telomers were transformed into methacrylic monomers and subsequently polymerised using living radical polymerization. In both cases, the final products of polymerization show molecular weights close to expected, assuming living polymerization, with polydispersities of approximately 1.1–1.2. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Fluorinated polymers exhibit an unique combination of high thermal stability, chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low water absorptivities, low refractive indices, excellent weatherability, a good resistance to oxidation and aging, low flammabilities, and very interesting surface properties.[1–3]

The diversity of polymerization methods available enables a number of strategies for the incorporation of fluorine into polymers to be used. The resultant fluorinated chains are generally pendant from the main polymer chain and can be introduced by a variety of linking units.[4–9] In other cases, the polymer backbone itself can be the fluorinated portion of the macromolecule. The polymer micro-architecture greatly influences all surface active properties. Thus, controlling the distribution of fluorine atoms within the polymer is of interest. It has been shown that the effect of fluorine on the surface energy can be maximized when fluorinated monomers are polymerised by radicals under special conditions, leading to the formation of fluorinated blocks on the end of hydrocarbon chains.

Well defined polymer architectures can be prepared from living radical polymerization, polycondensation or via polyaddition. In polycondensation and polyaddition, telechelic or α,ω-difunctional (i.e. the functional groups are located at both extremities of the chain) precursors are required to obtain high molecular weight materials with satisfactory properties. In the case of fluorinated telechelics, there is an abundant literature describing their synthesis.[10–13]

Transition metal living radical polymerization (LRP)[14] is a versatile method of synthesising well defined polymers which was first reported, almost simultaneously, by two research groups.[15,16] In this process, the degree of control of a living polymerization is combined with the versatility and robust character of a radical process. The most widely employed system for transition metal mediated LRP utilizes Cu(I)X (X=Cl, Br) as the catalyst which is rendered almost totally soluble in the reaction media by a suitable ligand. Other transition metals which have been investigated for LRP include Ru(II),[15,17] Ni(II),[18] Rh(I),[19] Re(V),[20] Pd(0),[21] and Fe(II).[22,23] As the process is living, polymers produced are ω-functionalised with a halogen atom, which is reversibly abstracted to allow addition of new monomer.[24] Isolated polymers can be subsequently used as macroinitiators to give well-defined block co-polymers.[25] Fluorinated polymers from metal-mediated polymerization have previously been reported.[26–28] The ability to form well defined random and block co-polymers by copper mediated LRP have been investigated in this current work.

2. Results and discussion

2.1. Copper mediated LRP initiated by fluorinated macroinitiators

2.1.1. Synthesis of fluorinated initiators. Living radical

Keywords: copper mediated living radical polymerization; methacrylate; styrene; perfluorononane; α-perfluoroalkyl initiator; α-perfluoroalkyl monomer.

* Corresponding author. Tel.: +44-2476-523256; fax: +44-2476-528267; e-mail: d.m.haddleton@warwick.ac.uk

PII: S0040-4020(02)00274-0

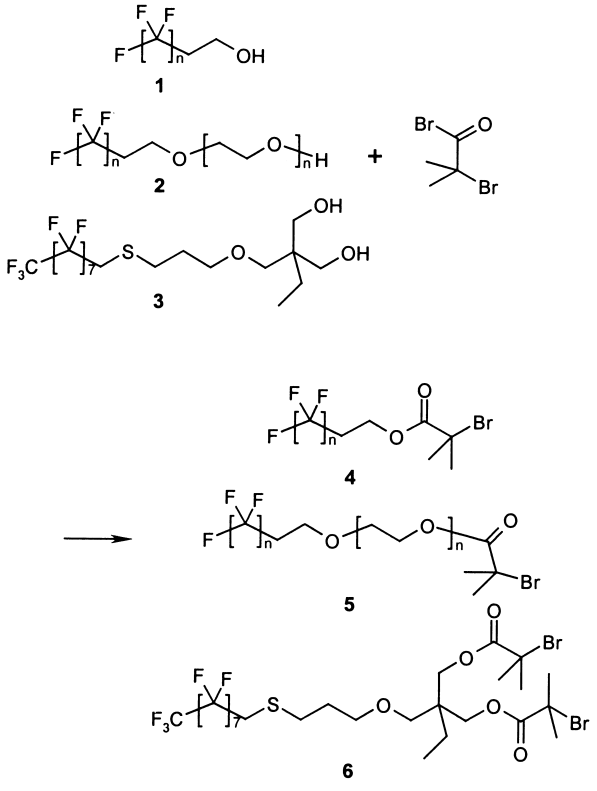

Figure 1. Synthesis of α-perfluoroalkyl LRP initiators.

polymerization is a facile synthetic route to α-functionalised polymers[29–34] and block copolymers[35,36] through the use of initiators bearing a secondary functionality that is unreactive under the polymerization conditions. Functional LRP initiators can be synthesized by the reaction of an appropriate alcohol, or amine, with a α-bromo functional acid bromide.

Perfluoroalkyl ethanol (ZONYL BA®, Du Pont) was used to synthesize a semi-fluorinated LRP initiator, **4** (Fig. 1). This

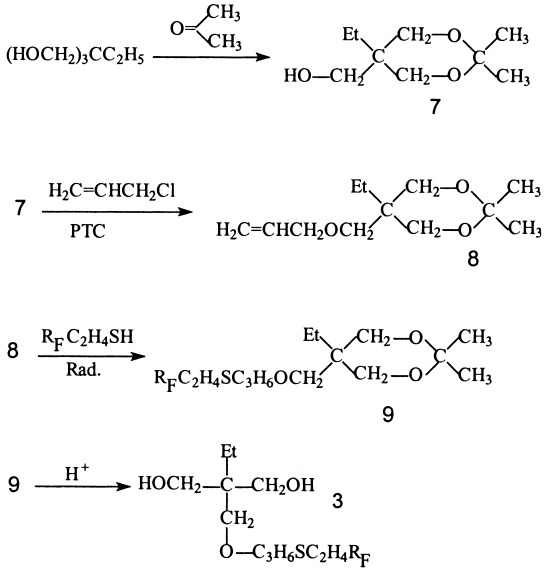

Figure 2. Synthesis of the fluorinated telechelic diol.

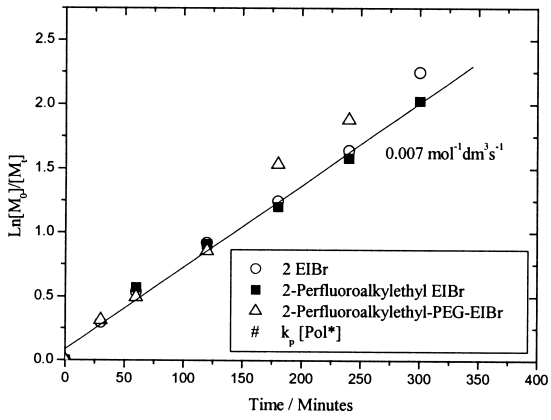

Figure 3. First order plot for the LRP of MMA at 90°C initiated (a) 2EIBr, (b) 2-perfluoroalkyl EIBr, (c) 2-perfluoroalkyl-PEG-EIBr and mediated by Cu(I)Br/*N*-pentyl-2-pyridinalmethanimine ([M]/[I]/[Cu]/[L]=100:1:1:2) in toluene solution.

alcohol is produced commercially via the telomerization of tetrafluoroethylene[37,38] and results in a product with a range of linear chain lengths. ^{19}F NMR indicated that the average number of CF_2 units (n) was ~8. A second initiator containing a similar perfluoroalkyl group bound to a polyethylene glycol unit (DP~8, ^{1}H NMR) was synthesized from ZONYL FSO® fluorinated surfactant, **5**. The use of this initiator results in ABC tri-block copolymers.

A third fluorinated initiator was synthesized from di-hydroxy functional telomer, **3**. The telomer was synthesized using a 4-step reaction starting from the formation of an acetal, **7**, from trimethylol propane (Fig. 2) catalyzed by paratoluene sulfonic acid at ambient temperature[33] leading to 78% yield for **7**. This was confirmed by FTIR (ν_{OH}= 3457 cm^{-1}) and ^{1}H NMR (see Experimental). The second step was via a phase transfer catalyzed Williamson reaction in the presence of tetrabutyl ammonium hydrogenosulfate leading to 90% yield of **8**. The formation of this product was seen by the absence of peaks at 3457 and 1640 cm^{-1} in the FTIR from the vinyl group. In a further step, the radical addition of a fluorinated thiol to the **8** occurred in 70% yield of **9**. The final step was the opening of the acetal leading to the fluorinated diol, **3** in 81%. The overall yield of the synthesis of **3** was 40% from trimethyl propane.

2.1.2. Copper mediated LRP of MMA. LRP of MMA initiated by 2-perfluoroalkyl ethyl bromoisobutyrate (perfluoroalkyl EIBr) occurs at a similar rate to ethyl-2-bromoisobutyrate (2-EIBr) initiation. Little termination is observed as seen by the linear first order rate plot (Fig. 3). The M_n increased linearly with conversion and were slightly lower than theoretical values (N.B. FW of initiator ~700 g mol^{-1}) (Fig. 4).

The rates of polymerization were also similar for the PEG containing initiator, **5**, although in this case there was evidence of an increase in the rate of polymerization towards the end of the reaction. The M_n increased linearly with conversion in each case, although were lower than the theoretical values at all stages of polymerization. Polydispersity indices (PDI) were slightly higher than for the **4** although in general, control of molecular weight was good.

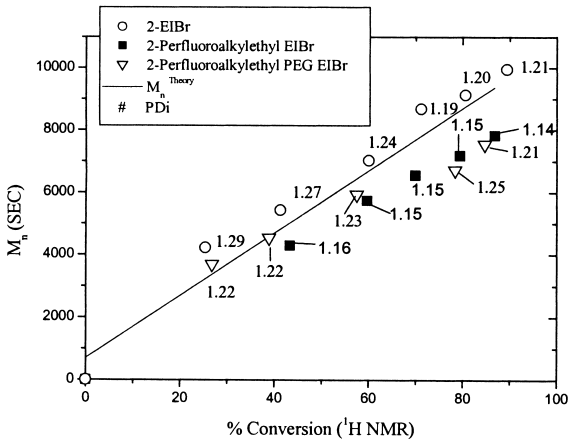

Figure 4. Evolution of molecular weight for the LRP of MMA at 90°C initiated by (a) 2-EIBr, (b) 2-perfluoroalkyl EIBr, (c) 2-perfluoroalkyl-PEG-EIBr and mediated by Cu(I)Br/*N*-pentyl-2-pyridinalmethanimine ([M]/[I]/[Cu]/[L]=100:1:1:2) in toluene solution.

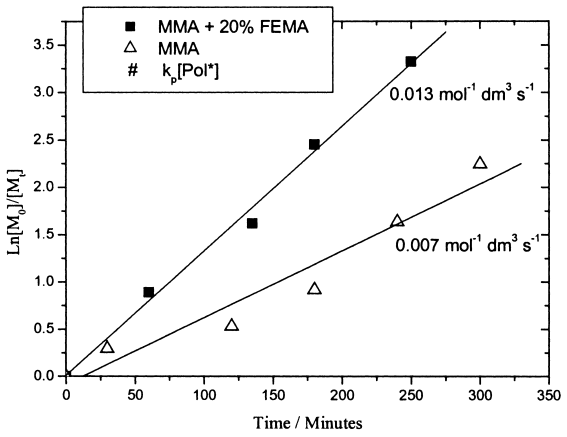

Figure 6. First order rate plot for the LRP statistical copolymerization of MMA and FEMA (20%) at 90°C initiated by phenyl-2-bromoisobutyrate and mediated by Cu(I)Br/*N*-pentyl-2-pyridinalmethanimine ([M]/[I]/[Cu]/[L]=100:1:1:2) performed in toluene.

Table 1. Summary of the final properties of PMMA polymers initiated by fluorinated initiators

Initiator	[M]/[I]	M_n	PDI
6	200	26,000	1.16
4	200	17,100	1.30
	100	12,000	1.08

Interestingly, molecular weight control seemed better for the **4** than with 2-EIBr as initiator, as seen by lower PDI at all stages of polymerization, despite the variation in its own perfluoroalkyl chain length (Fig. 4). Polymerization using the telomer di-initiator, **6**, led to well-defined copolymers with molecular weight close to theory and PDI=1.16. It is remarkable that the presence of the sulfur atom in the initiator has little effect on the polymerization.

The final products exhibited narrow PDI with molecular weights in good agreement with theory. A broader molecular weight distribution (PDI) is observed for DP=200 (Table 1).

2.2. LRP of perfluoroalkyl ethyl methacrylate

2.2.1. Synthesis and polymerization of perfluoroalkyl ethyl methacrylate (FEMA). FEMA was synthesized by the reaction of the fluoroalcohol, described above, with methacryloyl chloride (Fig. 5, yield=47.5% after basic alumina column and aqueous work up). It is noted that the monomer is also commercially available (ZONYL TM®, Du Pont).

In the attempted homopolymerization of FEMA by LRP at [M]/[I]/[Cu]/[L]=100:1:1:2 in toluene, the initial reactions were homogenous. However, as polymerization proceeds, phase separation occurs once vigorous agitation is stopped.

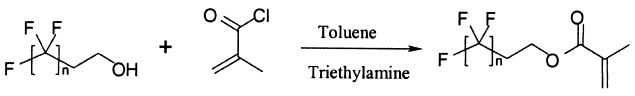

Figure 5. Synthesis of perfluoroalkyl ethyl methacrylate ($n\sim8$).

Samples removed from the Schlenk tubes settled into a solid lower layer and an upper liquid layer. ^{1}H NMR showed that the upper layer consisted of toluene, unreacted FEMA and only a tiny amount of polymer. As the reaction continued, the level of free monomer in the top layer was observed to decrease relative to the toluene. The lower solid layers were not soluble in any common organic solvents but dissolved in highly fluorinated solvents such as FC77, perfluoromethyl cyclohexane and 1,1,1,3,3,3-hexafluoro isopropanol (HFIPA).

The final polymer sample was stirred vigorously in hot toluene and then allowed to phase separate at reaction temperature. The toluene layer, which contained most of the green/brown color associated with the catalyst, was siphoned off. Repeated washing in this manner followed by high vacuum evaporation and cooling yielded an almost colorless glassy solid. ICP analysis of the product indicated that only 5% of the Cu added to the polymerization mixture had been retained within the polymer.

2.2.2. Statistical copolymerization of FEMA with MMA using LRP. Phase separation of PFEMA from FEMA monomer and organic soluble reagents means that LRP is likely to be uncontrolled and the usual methodologies for characterization of successful LRP impossible to perform. In order to show that LRP of FEMA is possible, statistical copolymers of FEMA and MMA (20% FEMA) were synthesized and in this case phase separation did not occur.

FEMA copolymerized well with MMA and at all stages, conversion of each monomer was almost identical indicating similar reactivity ratios. The rate of polymerization was higher than for PMMA homopolymer and there was no evidence of termination reactions in the first order rate plots (Fig. 6). Control of molecular weight distribution was good during the polymerization. M_n values increased linearly with conversion and the PDI remained low throughout the reaction (<1.2), Fig. 7, an initial flux of radicals at the start of the reaction as the copper(II) concentration is built up explains the initial high molecular weight and results in the graphs not passing through the origin.

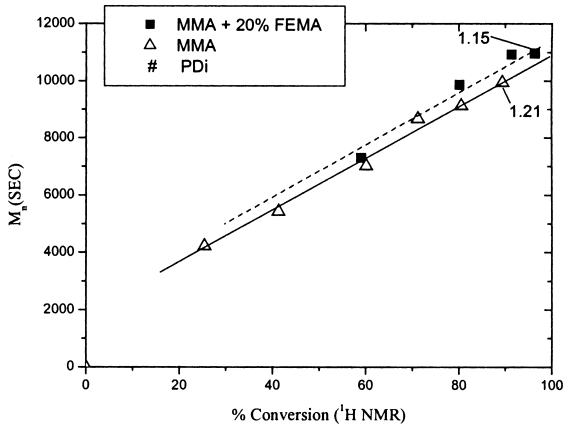

Figure 7. Evolution of molecular weight distribution for the statistical copolymerization of MMA and FEMA (20%) at 90°C initiated by phenyl-2-bromoisobutyrate and mediated by Cu(I)Br/*N*-pentyl-2-pyridinalmethanimine ([M]/[I]/[Cu]/[L]=100:1:1:2) performed in toluene.

3. Summary

A series of narrow molecular weight distribution fluorinated polymers have been prepared via copper mediated living radical polymerization. The presence of fluorine does not affect the product properties. This is a versatile route to a range of interesting, surface active materials. The use of living radical polymerization as opposed to conventional radical polymerization results in polymers with narrow molecular weight distribution and controlled molecular weights.

4. Experimental

4.1. General procedures

Experiments were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. NMR spectra were recorded on Bruker AC400 and DPX300 spectrometers. Molar mass distributions were measured using size exclusion chromatography (SEC) at ambient temperature, on a system equipped with a guard column and one 3 μm mixed E column (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran as eluent, at a flow rate of 1 mL min^{-1}. Poly(MMA) standards in the range (6×104–200 g mol^{-1}) were used for specific calibration.

For the fluorinated telechelic diol, after reaction and evaporation of the solvent, the total product mixture was worked up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 3 m×1/8″ (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260 and 255°C, respectively. The temperature program started from 50°C and reached 250°C at a heating rate of 15°C min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390). FTIR spectra were recorded onto Nicolet SP581 apparatus and the error on the frequency was ±2 cm^{-1}. The products were characterized by ^{1}H and ^{19}F NMR spectroscopy at 20°C. Spectra in this case were recorded on Bruker AC-200, AC-250 or WM-360 instruments, using deuterated chloroform or acetone as solvent. All chemical shifts are given in ppm/TMS for ^{1}H and in ppm/$CFCl_3$ for ^{19}F NMR, the coupling constants being in Hz. Hydroxyl titration was realized by acetylation.

4.2. Reagents

N-(*n*-Alkyl)-2-pyridylmethanimine was synthesized as previously reported[39] and stored under anhydrous conditions prior to use. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[40] MMA and DMAEMA were obtained from Aldrich and filtered before utilization through a basic alumina column to remove the radical inhibitor. MeOPEG-MA was obtained from Aldrich and used as received. 2-Bromo-2-methylpropionyl bromide (Lancaster, 98%) was stored under dry nitrogen. Triethylamine (BDH, 99%) was stored over sodium hydroxide pellets and 4 Å molecular sieves for 48 h and then filtered before use. Anhydrous THF (Romil 'Hi-Dry', 99.99%) were stored over activated 4 Å molecular sieves under dry nitrogen.

For the synthesis of the fluorinated telechelic diol, 1-thio-1*H*,1*H*,2*H*,2*H*-perfluorodecanol (or perfluoro-*n*-octyl ethanethiol) was kindly supplied by Atofina (Pierre Benite, France). 2,2-Azobisisobutyronitrile (AIBN) was purchased from Merck, trimethylolpropane, allyl chloride and paratoluenesulfonic acid from Aldrich. All other reagents (except allyl chloride, distilled) were used as received.

4.2.1. Esterification of 2-perfluoroalkyl ethanol. ZONYL BA® {Du Pont, $R_f=(CF_2)_n$, $n\sim8$ from ^{19}F analysis} (4 g, 0.0086 mol) and dimethylamino pyridine (0.048 g, 0.0004 mol) were suspended in anhydrous toluene {Romil Hi Dry} (10 mL). The mixture was heated and stirred until the ZONYL BA® dissolved. Triethylamine (1.226 mL, 0.0088 mol) and 2-bromoisobutyroyl bromide {Aldrich, 98%} (1.44 mL, 0.0088 mol) were added slowly and the suspension was stirred at room temperature for 8 h. The suspension was filtered and toluene was removed by rotary evaporation. The waxy solids were dissolved in dichloromethane and washed extensively with saturated $NaHCO_3$ solution, 1 M HCl, and distilled water. The product was dried over $MgSO_4$ and dichloromethane was removed by rotary evaporation to leave a pale yellow gelatinous solid, **4**. Yield=73%, FW=613; CH Theoretical 27.10, 1.50 found 27.74, 1.66; ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ (ppm from TMS)=4.45 (t, 2H, J=6.03 Hz), 2.49 (tt, 2H, J_1=6.03 Hz, J_2=18.1 Hz), 1.90 (s, 6H); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz) δ (ppm from TMS) 171.6, 121–107 (heavily split CF signals), 58, 55, 30.5 (t), 30.7; ^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz) δ (ppm from TMS) −81.4, −114.1, −122.3, −122.5, −123.3, −124.2, 126.7; IR absorption ν (cm^{-1}) 3308, 2969, 2871, (Alk. C–H stretch), 1738, 1636 (C=O stretch), 1549, 1524, 1466, 1435, 1370, 1296, 1265, 1228, 1216, 1204, 1068.

4.2.2. Esterification of ZONYL FSO®. A second initiator, **5**, containing a perfluoroalkyl group bound to a polyethylene glycol unit (DP∼8 by ^{1}H NMR) was synthesized from ZONYL FSO® fluorinated surfactant. $R_f=(CF_2)_n$, $n\sim8$ from ^{19}F analysis, $(CH_2CH_2O)_y$, $y\sim8$ from ^{1}H NMR analysis.

ZONYL FSO® {Aldrich} (10 g) was dissolved in toluene (100 mL). Approximately 50 mL of solvent was distilled off at room temperature to dry the reagent. The remaining solvent removed by rotary evaporation. Dried ZONYL FSO® (3 g, 0.004 mol) was dissolved in perfluoromethyl cyclohexane (4 mL). Dimethylaminopyridine (0.024 g, 0.0002 mol), triethylamine (0.613 mL, 0.0044 mol) and 2-bromoisobutyroyl bromide (0.719 mL, 0.0044 mol) were added. The mixture was stirred at room temperature for 12 h and subsequently extracted with dichloromethane. The upper orange dichloromethane layer was washed extensively with saturated $NaHCO_3$ solution, 0.1 M HCl and distilled water. The solution was dried over $MgSO_4$ and dichloromethane was removed by rotary evaporation to give the product, **5**, as a clear yellow oil. Yield=34.4%, FW=921; CH Theoretical 27.10, 1.50, found 26.92, 1.93; ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ (ppm from TMS)= 4.30 (t, 2H, J=4.88 Hz), 3.73 (m, 4H), 3.62 (m, 22H), 2.40 (tt, 2H, J_1=7.03 Hz, J_2=18.63 Hz), 1.91 (s, 6H); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz) δ (ppm from TMS)=171.6, 121–107 (heavily split CF signals), 70.3, 64.8, 62.8, 30.4; ^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz) δ (ppm from TMS) −81.4, −114.1, −122.3, −122.5, −123.3, −124.2, 126.7; IR absorption ν (cm^{-1}) 2870, 1735, 1466, 1351, 1275, 1236, 1203, 1143, 1105, 1087.

4.3. Synthesis of the fluorinated telechelic diol initiator

4.3.1. Synthesis of acetal, 7. Trimethylolpropane (67.09 g, 0.50 mol) were dissolved in 400 mL of acetone in a three necked round bottomed flask equipped with a condenser and a mechanical stirrer. When the mixture became homogeneous, 0.5 g of paratoluene sulfonic acid was added. The medium was stirred at room temperature for 16 h. Potassium carbonate (1.0 g) was subsequently added and left stirring at room temperature for 1 h. After evaporation of acetone, the total product mixture was distilled and 68.0 g (0.39 mol) of the acetal, **7**, was obtained. Yield=78%; bp=83–86°C/ 0.1 mbar; ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ: 0.8 (t, $^3J_{HH}$=6 Hz, CH_3CH$_2$, 3H), 1.25 (q, $^3J_{HH}$=6 Hz, CH$_3$CH_2, 2H), 1.35–1.40 (s, CH_3, 6H), 2.7 shifted with dilution (broad s, HO, 1H); 3.6 (s, CH_2O, 2H); 3.7 (s, CH_2O, 2H); IR (KBr) ν: 3457, 2980–2910, 1510, 1180, 1140, 1110, 1080, 1050, 1010, 980, 910, 890, 760.

4.3.2. Synthesis of 8. Acetal, **8**, (50.0 g, 0.287 mol), tetrabutyl ammonium hydrogenosulfate (9.7 g, 0.029 mol) and 250 mL of a caustic solution (50 wt% NaOH) were placed into a 500 mL round bottomed flask equipped with a condenser and a mechanical stirrer. Allyl chloride (87.9 g, 1.14 mol) was added dropwise with stirring. The mixture was heated to 40°C for 16 h and 200 mL of methylene chloride was subsequently added. After the reaction was cooled to room temperature, both organic and aqueous layers were separated. The former layer was extracted with water and dried over $MgSO_4$. Then, the excess of allyl chloride was evaporated and 56.6 g (0.28 mol) of acetal, **8**, were distilled in 90% yield (bp=69–72°C/0.1 mbar; ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ: 0.8 (t, $^3J_{HH}$=6 Hz, CH_3CH$_2$, 3H); 1.25 (q, $^3J_{HH}$=6 Hz, CH$_3$CH_2, 2H); 1.4 (2s, 2CH_3, 6H); 3.4 (s, CH_2O, 2H); 3.6 (2AB systems, 2CH_2OC(CH$_3$)$_2$, 4H); 3.95 (dd, CH_2CH=CH$_2$, 2H); 5.15 (2dd, =CH_2, 2H); 5.85 (m, HC=CH, 1H);); IR (KBr, cm^{-1}): 3035, 2985, 1640, 1450, 1380, 1320, 1250, 1150, 1100, 1020, 950, 910, 835, 720, 520.

4.3.3. Radical addition of fluorinated thiol onto 8. Perfluoro *n*-octyl ethanethiol (57.20 g, 0.119 mol) and 250 mL of acetonitrile were placed into a 500 mL three necked round bottomed flask. The mixture was refluxed under a nitrogen flow. Then 0.5 g of AIBN was added followed by a dropwise addition of 25.1 g (0.117 mol) of **8**. After complete addition, the mixture was stirred at 82°C for 6 h. After cooling to room temperature the acetonitrile was evaporated and the unreacted starting materials distilled. 58.6 g (0.085 mol) of the fluorinated acetal, **9**, was obtained (yield=70%). ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ: 0.8 (t, $^3J_{HH}$=6 Hz, CH_3CH$_2$, 3H); 1.25 (q, $^3J_{HH}$=6 Hz, CH$_3$CH_2, 2H); 1.4 (2s, 2CH_3, 6H); 1.7–2.1 (m, CH$_2$CH_2CH$_2$S, 2H); 2.5–3 (t, $^3J_{HH}$=6.5 Hz, C$_2$H$_4$CH_2S, 2H); 2.5–3 (t, $^3J_{HH}$=6 Hz, SCH_2CH$_2$C$_8$F$_{17}$, 2H); 2.7–3 (tt, $^3J_{HF}$=22 Hz, $^3J_{HH}$=6.5 Hz, CH_2C$_8$F$_{17}$, 2H); 3.4 (s, CH_2O, 2H); 3.5 (d, $^3J_{HH}$=6.8 Hz, OCH_2CH$_2$, 2H); 3.6 (2AB systems, 2CH_2OC(CH$_3$)$_3$, 2H). ^{19}F NMR ($CDCl_3$) δ: −83.7 (m, CF_3, 3F); −115.2 (m, CF_2CH$_2$, 2F); −122.3 (m, CF_2CF$_2$CH$_2$, 2F); −123.1 (m, CF_2(CF$_2$)$_2$CH$_2$, 2F); −124.4 (m, CF_2(CF$_2$)$_3$CH$_2$, 2F); −126.2 (m, CF_2(CF$_2$)$_4$CH$_2$, 2F).

4.3.4. Synthesis of fluorinated diol 3. The fluorina ted acetal, **9**, (58.6 g, 0.085 mol), 107 mL of methanol, 19 mL of deionized water and 1 mL of HCl 37% were placed into a two necked round bottomed flask equipped with a condenser. The reaction mixture was heated up to 30°C for 24 h. After the reaction, methanol was evaporated and the residue dissolved in diethyl ether and extracted with water until neutral pH. The organic layer was dried and after solvent removed by evaporation, 45 g (0.069 mol) of the diol were recovered as a beige wax. Yield=81%. ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz): 0.7 (t, $^3J_{HH}$=6 Hz, CH_3CH$_2$, 3H); 1.15–1.35 (q, $^3J_{HH}$=6 Hz, CH$_3$CH_2, 2H); 1.7–1.9 (qi, CH$_2$CH_2CH$_2$, 2H); 2.1–2.45 (td, $^3J_{HF}$=22 Hz, $^3J_{HH}$=7 Hz, CH$_2$C$_8$F$_{17}$, 2H); 2.5–2.7 (t, $^3J_{HH}$=6.5 Hz, SCH_2CH$_2$R$_F$, 2H); 2.6–2.8 (m, C$_2$H$_4$CH_2S, 2H); 3.2–3.7 (m, 3CH_2O, 6H).

The ^{19}F NMR spectrum was identical to that of the above fluorinated acetal. HO titration (exp): 4.7% (th. 5.2%); F titration (exp): 49.5% (th. 49.4%)

4.3.5. Synthesis of 6. The telomer, **3**, (5.00 g, 0.00764 mol) was dissolved in anhydrous THF {Romil Hi Dry} (50 mL). Triethylamine (2.60 mL, 0.01834 mol) and 2-bromoisobutyroyl bromide {Aldrich, 98%} (2.20 mL, 0.01834 mol) were added slowly and the suspension was stirred at room temperature for 8 h. The suspension was filtered and toluene removed by rotary evaporation. The yellow liquid was dissolved in dichloromethane and washed extensively with saturated $NaHCO_3$ solution, 1 M HCl, and distilled water. The product was dried over $MgSO_4$ and dichloromethane was removed in vacuo to leave a pale yellow viscous liquid. Yield=81%, FW=654; CH Theoretical C 38.01%, H 4.36%, found 38.2%, H 4.4%; ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ (ppm from TMS)=3.35 (m, 8H), 2.49 (m, 4H), 1.90 (s, 6H), 1.67 (q, 2H), 1.11 (m, 2H), 0.63 (t, 3H); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz) δ (ppm from TMS) 171.6, 121–107 (heavily split CF signals), 76.2, 74.5,

70.2, 43.3, 40.46, 32.3 (t), 29.5 (m), 23.6, 23.3, 21.5, 18.5, 7.8; ^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz) δ (ppm from TMS) −81.5, −114.9, −122.4, −122.5, −123.3, −124.0, 126.8; IR absorption ν (cm^{-1}) 3303, 2938, 2882, (Alk. C–H stretch), 2360, 2341, 1636 (C=O stretch), 1367, 1331, 1308, 1068, 997, 954, 871, 779, 764, 736, 724, 703, 682, 618, 604, 588, 573, 511.

4.4. Copper mediated LRP of MMA initiated by fluorinated initiators

4.4.1. LRP initiated by 4. Cu(I)Br, (a) 0.134 g, 9.32×10^{-4} mol, (b) 0.223 g, 1.56×10^{-3} mol, (c) 0.334 g, 2.34×10^{-3} mol), **4**. (a) 0.641 g, 9.36×10^{-4} mol, (b) 1.07 g, 1.56×10^{-3} mol, (c) 1.60 g, 2.34×10^{-3} mol) and a dry magnetic follower were charged to a dry Schlenk tube. The tube was sealed with a rubber septum prior to three vacuum/N_2 cycles. Toluene (10 mL), MMA (10 mL, 9.36×10^{-2} mol) and *N*-^{n}pentyl-2-pyridinalmethanimine, (a) 0.35 mL, 1.87×10^{-2} mol, (b) 0.58 mL, 3.12×10^{-2} mol, (c) 0.87 mL, 4.68×10^{-2} mol) were added under N_2. The Schlenk tube was subjected to three freeze pump thaw cycles and subsequently heated to 90°C with constant stirring (t=0). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis. The final polymers were passed down a small basic alumina column prior to precipitation into heptane. Volatiles were removed in vacuo overnight.

4.4.2. LRP initiated by 5. Cu(I)Br (0.072 g, 5.0×10^{-4} mol), **5** (0.50 g, 5.4×10^{-4} mol) and a dry magnetic follower were charged to a dry Schlenk tube. The tube was sealed with a rubber septum prior to three vacuum/N_2 cycles. Toluene (5 mL), MMA (5.34 mL, 5.0×10^{-2} mol) and *N*-^{n}pentyl-2-pyridinalmethanimine (0.195 mL, 1.0×10^{-3} mol) were added under N_2. The Schlenk tube was subjected to three freeze pump thaw cycles and subsequently was heated to 90°C with constant stirring (t=0). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis.

The final polymer was passed down a small basic alumina column prior to precipitation into heptane. Volatiles were removed by drying in a vacuum oven overnight. M_n=8700, PDI=1.15, T_g=102.4°C; TGA 70% wt loss at 300°C, 100% wt loss at 380°C.

4.4.3. LRP initiated by 6. Cu(I)Br (0.142 g, 1.00×10^{-3} mol), **6** (0.400 g, 0.50×10^{-3} mol) and a dry magnetic follower were charged to a dry Schlenk tube. The tube was sealed with a rubber septum prior to three vacuum/N_2 cycles. Toluene (10.8 mL), MMA (10.8 mL, 10.00×10^{-2} mol) and *N*-^{n}pentyl-2-pyridinalmethanimine (0.32 mL, 2.00×10^{-3} mol) were added under N_2. The Schlenk tube was subjected to three freeze pump thaw cycles and subsequently was heated to 90°C with constant stirring (t=0). Molecular weight and conversion were calculated as described above. The final purification was undertaken as above.

4.5. LRP of perfluoroalkyl ethyl methacrylate

4.5.1. Synthesis of FEMA. ZONYL BA® {Du Pont} (50 g, 0.0932 mol) and triethylamine (13 mL, 0.0932 mol) were dissolved in anhydrous toluene {Romil Hi Dry} (200 mL). Methacryloyl chloride (9.74 mL, 0.0932 mol) was added slowly and the solution refluxed for 16 h. Toluene was removed in vacuo and the resulting orange oil dissolved in dichloromethane and passed down a basic alumina column. The product was concentrated and the solution washed extensively with saturated $NaHCO_3$ solution, 0.1 M HCl, distilled water and finally dried over $MgSO_4$. Dichloromethane was removed by thin film evaporation to give a clear, straw colored viscous liquid. Yield=47.5% (FW=531); CHN Theoretical 30.9, 1.50, 0 found 30.86, 1.62, 0; ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ (ppm from TMS)=6.10 (t, 1H, J=1.1 Hz), 5.56 (q, 1H, J=1.7 Hz), 4.42 (t, 2H, J=6.4 Hz), 2.48 (tt, 2H, J_1=6.4 Hz, J_2=18.3 Hz), 1.91 (t, 3H, J=1.2 Hz); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz) δ (ppm from TMS)=166.8, 135.74, 126.0, 120–108 (heavily split CF signals), 56.4, 30.5 (t), 18.8; ^{19}F NMR ($CDCl_3$, 298 K, 282.2 MHz) δ (ppm from TMS)=−82.0, −114.6, −122.8, −123.7, −124.5, 127.2; IR absorption ν (cm^{-1}) 2893, 1726, 1640, 1456, 1323, 1298, 1198, 1143, 1081, 1013, 944.

4.6. Polymerization procedure

In the attempted homopolymerization of FEMA by LRP at [M]/[I]/[Cu]/[L]=100:1:1:2 were dissolved in toluene. Cu(I)Br (0.012 g, 8.29×10^{-5} mol) and a magnetic follower were placed in a Schlenk tube which was evacuated and re-filled with N_2 three times. Toluene (4.25 mL), *N*-^{n}pentyl pyridinalmethanimine (0.031 mL, 1.66×10^{-4} mol) and FEMA (4.25 mL, 8.29×10^{-3} mol) were added and the solution subjected to three freeze pump thaw cycles. The solution was stirred and heated to 90°C. Once the reaction temperature was reached, 2-EIBr (0.013 mL, 8.29×10^{-5} mol) was added (t=0). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis. The product was not soluble in any common organic solvents (including *m*-cresol and 1,2 dichlorobenzene), consequently (high temperature) SEC analysis was not possible. DSC—indicates melting point at 65.6°C; ICP analysis measured 5.4×10^{-3} % by weight of Cu (5% retention); TGA—9.5% loss at 200°C, 81% loss at 300°C, 91% loss at 435°C.

4.7. Statistical copolymerization of FEMA with MMA using LRP

4.7.1. Synthesis of phenyl-2-bromoisobutyrate. Phenol 18.85 g (0.20 mol) was dissolved in anhydrous THF (400 mL) with triethylamine (30.6 mL, 0.22 mol). 2-Bromo-2-methylpropionyl bromide 26.4 mL, 0.22 mol) was added dropwise under an atmosphere of dry nitrogen. The reaction was left for 6 h at 25°C before the solution was taken up in dichloromethane (100 mL) and washed successively with saturated, aqueous sodium hydrogen carbonate solution (3×100 mL). The resultant organic phase was dried over anhydrous magnesium sulfate and the solvent removed under vacuum to give a slightly yellow/brown liquid. This was vacuum distilled at 58°C and 0.2 Torr to give a colorless liquid. Yield=28.9 g (72.7%); ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ (ppm from TMS)=7.41 (t, J=7.6 Hz, 2H), 7.26 (t, J=6.9 Hz, 1H), 7.13 (d, J=8.7 Hz, 2H), 1.93 (s,

6H); ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz) δ (ppm from TMS)=169.40, 150.38, 129.09, 125.74, 120.74, 64.14, 29.09; IR absorption ν (cm^{-1}) 3044, 2985, 2936, 1754, 1591, 1456, 1389, 1371, 1265, 1186, 1161, 1140, 1107, 1070, 1006, 938, 911, 859, 745, 688; Mass spectrum: m/z=200, 198 (mass peaks) 131, 94, 77, 65, 41; Elemental analysis: 60.36 %C, 5.58 %H, (theoretical; 60.46 %C, 5.58 %H).

4.8. Polymerization procedure

Cu(I)Br (0.067 g, 4.68×10^{-4} mol) and a, dry magnetic follower were placed in a Schlenk tube which was evacuated and re-filled with N_2 three times. Toluene (5 mL), *N*-^{n}pentyl pyridinalmethanimine (0.173 mL, 9.36×10^{-4} mol), FEMA (2.5 mL, 7.53×10^{-3} mol) and MMA (3.0 mL, 3.75×10^{-2} mol) were added and the Schlenk was subjected to three freeze pump thaw cycles. The solution was stirred and heated to 90°C. Once the reaction temperature had been reached, phenyl-2-bromoisobutyrate (0.074 mL, 4.68×10^{-4} mol) was added (t=0). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis. Selected samples were passed down a basic alumina column prior to precipitation in heptane. The resulting white powders were dried overnight in a vacuum oven.

Acknowledgements

The authors would like to thank Uniqema (SP) for funding and Atofina for providing the fluorinated thiol.

References

1. Smart, B. E. In *Properties of Fluorinated Compounds, Physical and Physiochemical Properties*; Hudlicky, M., Pavlath, S. E., Eds.; ACS: Washington, 1995; p. 979.
2. Scheirs, J. *Modern Fluoropolymers*; Wiley: New York, 1997.
3. Hougham, G.; Johns, K.; Cassidy, P. E. *Fluoropolymers: Synthesis and Properties*; Plenum: New York, 1999.
4. Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G. *Macromolecules* **1997**, *30*, 2883.
5. Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Stika, K. M. *Macromolecules* **1998**, *31*, 4595.
6. Jariwala, C. P.; Mathias, L. J. *Macromolecules* **1993**, *26*, 5129.
7. Hoyle, C. E.; Matias, L. J.; Jariwala, C.; Sheng, D. *Macromolecules* **1996**, *29*, 3182.
8. Feiring, A. E.; Wonchoba, E. R. *Macromolecules* **1998**, *31*, 7103.
9. Yuan, Y.; Shoichet, M. S. *Macromolecules* **2000**, *33*, 4926.
10. Ameduri, B.; Boutevin, B. *J. Fluorine Chem.* **1999**, *100*, 97.
11. Boutevin, B.; Robin, J. J. *Adv. Polym. Sci.* **1992**, *102*, 105.
12. Ameduri, B.; Boutevin, B. *Adv. Polym. Sci.* **1992**, *102*, 133.
13. Couvret, D.; Brosse, J. C.; Chevalier, S.; Senet, J. P. *Eur. Polym. J.* **1991**, *27*, 193.
14. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
15. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
16. Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
17. Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820.
18. Granel, C.; Teyssie, P.; DuBois, P.; Jerome, P. *Macromolecules* **1996**, *29*, 8576.
19. Moineau, G.; Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1998**, *31*, 542.
20. Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 2420.
21. Lecomte, P.; Drapier, I.; DuBois, P.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 7631.
22. Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.
23. Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.
24. Feiring, A. E.; Wonchoba, E. R.; Davidson, F.; Percec, V.; Barboiu, B. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 3313.
25. Huan, K.; Bes, L.; Haddleton, D. M.; Khoshdel, E. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1833.
26. Xia, J. H.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802.
27. Zhang, Z. B.; Ying, S. K.; Shi, Z. Q. *Polymer* **1999**, 40.
28. Zhang, Z. B.; Ying, S. K.; Zhang, Q. L.; Xu, X. D. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 2670.
29. Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36*, 811.
30. Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36*, 653.
31. Haddleton, D. M.; Waterson, C.; Derrick, P. J.; Jasieczek, C. B.; Shooter, A. J. *Chem. Commun.* **1997**, 683.
32. Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
33. Matyjaszewski, K.; Coca, S.; Nakagawa, Y.; Xia, J. H. *Abstr. Pap. Am. Chem. Soc.* **1997**, *213* 83-PMSE.
34. Haddleton, D. M.; Derrick, P. J.; Waterson, C.; Eason, M. D. *Abstr. Pap. Am. Chem. Soc.* **1999**, *218* 284-POLY.
35. Jankova, K.; Chen, X. Y.; Kops, J.; Batsberg, W. *Macromolecules* **1998**, *31*, 538.
36. Ashford, E. J.; Naldi, V.; Odell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285.
37. Banks, R. E. et-al., *Organofluorine Chemistry: Principles and Commercial Applications*; Plenum: New York, 1994.
38. Boutevin, B. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 3235.
39. Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.
40. Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1947**, *2*, 1.