Preparation of Fluorinated Copolymers by Copper-Mediated Living Radical Polymerization

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ABSTRACT: Copper-mediated living radical polymerization mediated with pyridine imine ligands has been used for the synthesis of poly(methacrylate)s and polystyrene incorporating fluorinated moieties as either initiators or monomers as well as in the presence of fluorinated solvents. It was found that fluorinated organics do not interfere detrimentally in the polymerization mechanism. α-Perfluoroalkyl initiators have been used for the polymerization of MMA initiated by both 2-perfluoroalkyl ethyl 2-bromoisobutyrate (ZONYL BA initiator) and 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (ZONYL FSO initiator) initiators which occurs at an almost identical rate to that initiated by ethyl 2-bromoisobutyrate (EIBr). The M_n increased linearly with conversion, and the polydispersity indices were low throughout all polymerizations (<1.20). Polymerization of MeOPEG-MA initiated by 2-perfluoroalkyl ethyl 2-bromoisobutyrate (ZONYL BA initiator) at 60 °C results in a water-soluble/dispersible polymer with $M_n = 6700$ g mol^{-1} and PDI = 1.07. Perfluoroalkylethyl methacrylate (FEMA) proves difficult to homopolymerize due to solubility problems but has been used to form statistical copolymers with MMA and styrene. Synthesis of AB block copolymers using fluorinated macroinitiators with a methacrylate B block gives both hydrophobic, MMA, and hydrophilic, MeOPEG-MA, polymers with well-defined α-terminal block copolymers and PDI as low as 1.10. Copper-mediated living radical polymerization was found to be an effective method for the synthesis of fluorine-containing synthetic polymers.

Introduction

Polymer films are used in a diverse range of applications, and the ability to control their surface properties is often desirable. Incorporation of fluorine atoms into polymer films, by a variety of methods,[1−7] has been shown to be an effective means to reduce the surface energy and hence to produce nonwettable surfaces. The incorporation of fluorine into polymers can be achieved by a variety of synthetic polymerization techniques.[8,9] Fluorinated chains can be introduced by a variety of linking units and therefore be pendant from the main polymer chain[3−7,10] or, in other cases, the polymer backbone itself can be fluorinated. Moreover, polymer architecture can also greatly influence any surface-active properties as it enables to control the distribution of fluorine atoms within the polymer. For instance, the effect of fluorine on the surface energy can be maximized when fluorinated monomers are polymerized by free radical polymerization under conditions leading to the formation of fluorinated blocks on the terminus of hydrocarbon chains.

Transition metal mediated living radical polymerization[11−13] is a versatile method of synthesizing well-defined polymers which was first reported almost simultaneously by two research groups.[14,15] In this process, the degree of control of a living polymerization is combined with the versatility and robust character of a free radical process. Polymerization is initiated by an appropriate alkyl halide and catalyzed by a low valent transition metal. The exact mechanism of propagation is uncertain, but it seems likely that the transition metal reversibly abstracts the halogen atom from the initiator, which is then able to react with substituted vinyl monomers. The halogen atom is then able to cap the propagating end to form a dormant oligomer. This dormant species can then be activated once more by the removal of the halogen to enable further propagation. The equilibrium between dormant and active species lies far to the dormant side, and so the concentration of propagating species at any time is kept low and constant. This low concentration effectively eliminates bimolecular termination reactions, and the system shows "living" character. The molecular weight is predetermined by the ratio [M]/[I] ([M] = concentration of monomer, [I] = concentration of initiator), and the polydispersity generally remains low.

The most widely employed system for transition-metal-mediated living radical polymerization utilizes Cu(I)X (X = Cl, Br) as the catalyst which is rendered almost totally soluble in the reaction media by a suitable ligand.[14,16] Other transition metals that have been investigated include Ru,[17] Rh,[18] Fe,[19] Ni,[20,21] and Pd.[22] As the polymerization process is a living process, polymers produced are ω-functionalized with a halogen atom, which can then be abstracted to allow addition of new monomer. Isolated polymers can be used as

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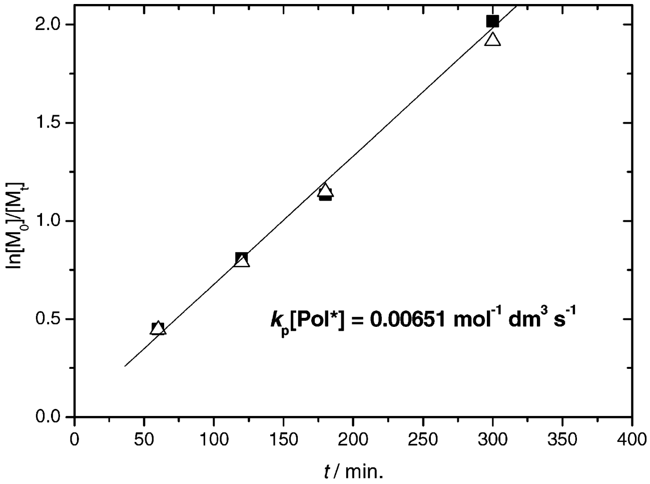

Figure 1. First-order plot for the polymerization of MMA at 90 °C initiated by ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine in toluene solution with [M]:[I]:[Cu]:[L]:[perfluorononane] = 100:1:1:2:1 (■) and [M]:[I]:[Cu]:[L]:[perfluorononane] = 100:1:1:2:0 (△).

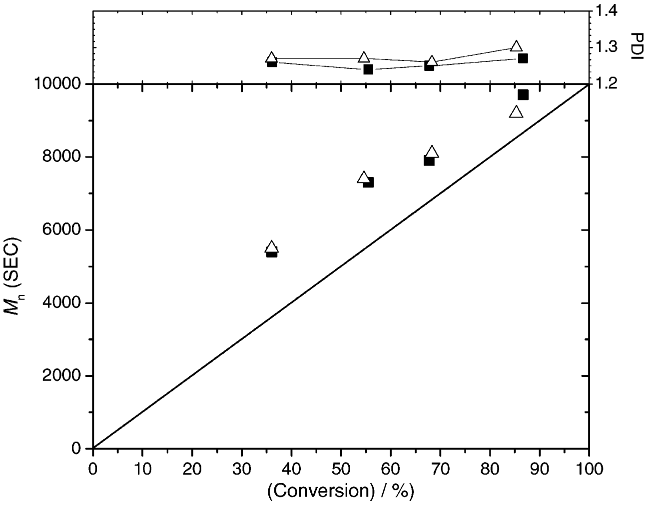

Figure 2. Evolution of molecular weight distributions vs conversion for the polymerization of MMA at 90 °C initiated by ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-octyl)-2-pyridylmethanimine with [M]:[I]:[Cu]:[L]:[perfluorononane] = 100:1:1:2:1 (■), [M]:[I]:[Cu]:[L]:[perfluorononane] = 100:1:1:2:0 (△), and theoretical M_n (−).

macroinitiators, which produce well-defined block copolymers.[23,24] A number of fluorine-containing polymers have previously been reported,[25,26] including semifluorinated fluorocarbon diblock copolymer poly(butyl methacrylate-*co*-perfluoroalkyl acrylate)[27] and homopolymers and diblock copolymers containing 4-fluorostyrene and methyl acrylate.[28] Indeed, there has been a previous report of the use of perfluoroalkylsulfonyl chlorides and bromides to initiate the metal-catalyzed free radical polymerization of both hydrocarbon and fluorocarbon monomers affording polymers with perfluoroalkyl end groups.[29] The ability to form well-defined random and block copolymers by polymerization containing fluorine atoms has been investigated in this current work. The reaction conditions have been optimized and kinetic parameters determined for a range of polymerization conditions.

Experimental Section

General Procedures. Experiments were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. NMR spectra were recorded on a Bruker AC400 and DPX300 spectrometer. Molar mass distributions were measured from crude samples (before precipitation) 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}. PMMA standards in the range (200−6 × 10^4 g mol^{-1}) were used for specific calibration with a second-order polynomial fit. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 51 under nitrogen and in air at 5 °C min^{-1}. DSC measurements were carried out on a Perkin-Elmer DSC Pyris 1 calibrated with indium and cyclohexane.

Reagents. *N*-(*n*-Alkyl)-2-pyridylmethanimines were synthesized as reported previously[13] and stored under anhydrous conditions prior to use. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[30] Methyl methacrylate (MMA) and styrene (STY) were obtained from Aldrich and filtered before utilization through a basic alumina column to remove the inhibitor. Methyl ether poly(ethylene glycol) methacrylate (MeOPEG-MA) and ethyl 2-bromoisobutyrate (EIBr) were obtained from Aldrich and used as received. 2-Perfluoroalkyl ethyl 2-bromoisobutyrate (**4**, Figure 3) and 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (**5**, Figure 3) were synthesized from ZONYL BA (DuPont, $R_f = (CF_2)_n$, $n \sim 8$, from ^{19}F NMR analysis) and ZONYL FSO (DuPont, $R_f = (CF_2)_n$, $n \sim 8$, from ^{19}F NMR analysis and $(CH_2CH_2O)_x$, $x \sim 8$, from ^{1}H NMR analysis), respectively, as described previously.[31] The fluorinated telechelic di-initiator **6** ($R_f = (CF_2)_n$, $n \sim 7$, from ^{19}F NMR analysis)[25] and phenyl 2-bromoisobutyrate[31] were synthesized as described previously. Previous works in our laboratories have shown that phenyl 2-bromoisobutyrate and ethyl 2-bromoisobutyrate have the same effect on polymerizations. However, phenyl 2-bromoisobutyrate was preferred to ethyl 2-bromoisobutyrate when polymerizing nonconventional monomers. In these cases, the aromatic protons introduced when using phenyl-2-bromisobutyrate were used as reference when calculating the molecular weight of the final polymer by ^{1}H NMR.[31] All other reagents and solvents were obtained from Aldrich at the highest purity available and used without further purification.

Polymerization of MMA in the Presence of Perfluorononane. Cu(I)Br (0.134 g, 9.32 × 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 (10 mL), MMA (10 mL, 9.36 × 10^{-2} mol), *N*-(*n*-octyl)-2-pyridylmethanimine (0.453 mL, 1.872 × 10^{-3} mol), and perfluorononane (Aldrich, 97%) (0.254 mL, 9.36 × 10^{-4} mol) were added under nitrogen. The Schlenk tube was subjected to three freeze−pump−thaw cycles and subsequently heated to 90 °C with constant magnetic stirring. Once the reaction temperature was reached, ethyl-2-(EIBr) (0.136 mL, 9.36 × 10^{-4} mol) was added under nitrogen (t = 0). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis.

Polymerization Initiated by 2-Perfluoroalkyl Ethyl 2-Bromoisobutyrate (4, Figure 3). 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), 2-perfluoroalkyl ethyl 2-bromoisobutyrate ((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-pyridylmethanimine ((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 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 polymers were passed down a small basic alumina column

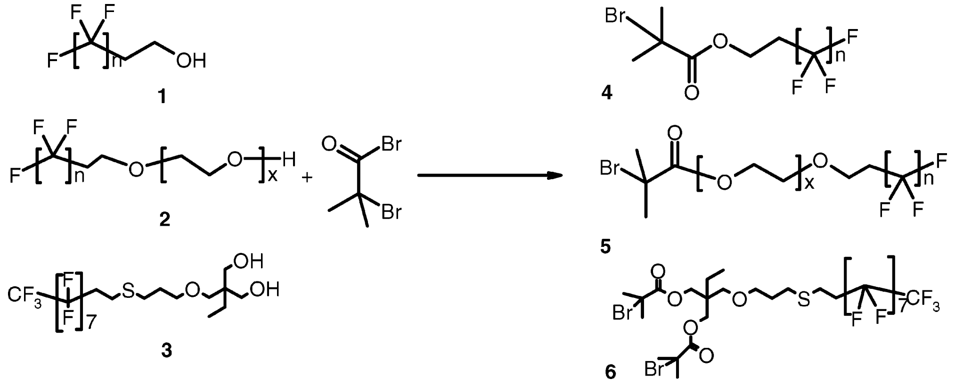

Figure 3. Synthesis of fluorinated polymerization initiators.

prior to precipitation into heptane. Volatiles were removed by drying in a vacuum oven overnight.

Polymerization Initiated by 2-Perfluoroalkyl Ethyl-*co*-Poly(ethylene glycol) 2-Bromoisobutyrate (5, Figure 3). Cu(I)Br (0.072 g, 5.0×10^{-4} mol), 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (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-pyridylmethanimine (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 solution was passed down a small basic alumina column prior to precipitation into heptane. Volatiles were removed by drying in a vacuum oven overnight. $M_n = 8700$ g mol^{-1}, PDI = 1.15, $T_g = 102$ °C; TGA 70 wt % loss at 300 °C, 100 wt % loss at 380 °C.

Polymerization Initiated by Fluorinated Telechelic Di-initiator (6, Figure 3). Cu(I)Br (0.142 g, 1.00×10^{-3} mol), **6** (Figure 3, 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-pyridylmethanimine (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 purifications were undertaken as described above.

Copper-Mediated Polymerization of MeOPEG-MA Initiated by 2-Perfluoroalkyl Ethyl 2-Bromoisobutyrate (4, Figure 3), Targeted Degree of Polymerization, $DP_{Theo} = 10$. CuBr (0.442 g, 3.1 mmol) was placed in a Schlenk tube and placed under a nitrogen atmosphere. Deoxygenated MeO-(PEG)MA (10 mL, 0.031 mol), toluene (50 vol %), and α-perfluoroalkyl 2-bromoisobutyrate (1.9003 g, 3.1 mmol) were added at ambient temperature. The mixture was deoxygenated by three freeze–pump–thaw cycles after which the *N*-(*n*-propyl)-2-pyridylmethanimine ligand was added (2 mol equiv to CuBr, 6.2 mmol, 0.97 mL). The Schlenk tube was then immersed in a thermostated oil bath at the reaction temperature (time = 0 s). Samples for analysis of the molar mass distribution (MMD) and monomer conversion were taken at different intervals throughout the reaction. Catalyst residues were removed by passing the samples through a short column of basic alumina prior to SEC and NMR analysis.

Polymerization of Perfluoroalkylethyl Methacrylate (FEMA). FEMA was synthesized from Zonyl BA as described previously.[25] In the attempted homopolymerization of FEMA by polymerization at [M]:[I]:[Cu]:[L] = 100:1:1:2 in toluene, the initial reaction conditions were homogeneous. Cu(I)Br (0.012 g, 8.29×10^{-5} mol) and a clean, dry magnetic follower were placed in a Schlenk tube which was evacuated and refilled with N_2 three times. Toluene (4.25 mL), *N*-(*n*-pentyl)-2-pyridylmethanimine (0.031 mL, 1.66×10^{-4} mol), and FEMA (4.25 mL, 8.29×10^{-3} mol) were added, and the Schlenk tube was subjected to three freeze–pump–thaw cycles. The solution was stirred and heated to 90 °C, once the reaction temperature was reached; 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.

Statistical Copolymerization of FEMA with MMA Using Polymerization. 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 refilled with N_2 three times. Toluene (5 mL), *N*-(*n*-pentyl)-2-pyridylmethanimine (0.173 mL, 9.36×10^{-4} mol), FEMA ((a) 0.78 mL, 2.34×10^{-3} mol, (b) 1.56 mL, 4.68×10^{-3} mol, (c) 2.0 mL, 6.00×10^{-3} mol, (d) 2.5 mL, 7.53×10^{-3} mol) and MMA ((a) 4.5 mL, 4.45×10^{-2} mol, (b) 4.0 mL, 4.21×10^{-2} mol, (c) 3.5 mL, 3.98×10^{-2} mol, (d) 3.0 mL, 3.75×10^{-2} mol) were added, and the Schlenk tube 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.

Statistical Copolymerization of FEMA with Styrene Using Polymerization. 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 refilled with N_2 three times. Toluene (5 mL), *N*-(*n*-pentyl)-2-pyridylmethanimine (0.173 mL, 9.36×10^{-4} mol), FEMA ((a) 0.70 mL, 2.10×10^{-3} mol, (b) 1.40 mL, 4.20×10^{-3} mol, (c) 2.1 mL, 6.23×10^{-3} mol, (d) 2.5 mL, 7.53×10^{-3} mol) and STY ((a) 4.8 mL, 4.20×10^{-2} mol, (b) 4.28 mL, 3.75×10^{-2} mol, (c) 3.75 mL, 3.28×10^{-2} mol, (d) 3.5 mL, 3.0×10^{-2} mol) were added, and the Schlenk tube underwent three freeze–pump–thaw cycles. The solution was stirred and heated to 90 °C. Once the reaction temperature was 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.

Results and Discussion

Polymerization of MMA in the Presence of Perfluorononane. Halogen atom exchange can take place if mixed systems of halogenated initiator/Cu(I)X are used during the living radical polymerization of MMA.[32] Formation of a terminal C–Cl is preferred with the effect of reducing the rate of polymerization in systems containing both Br and Cl atoms to a similar rate observed with pure chlorine-containing polymerizations. To ensure that polymerization would be unaffected by

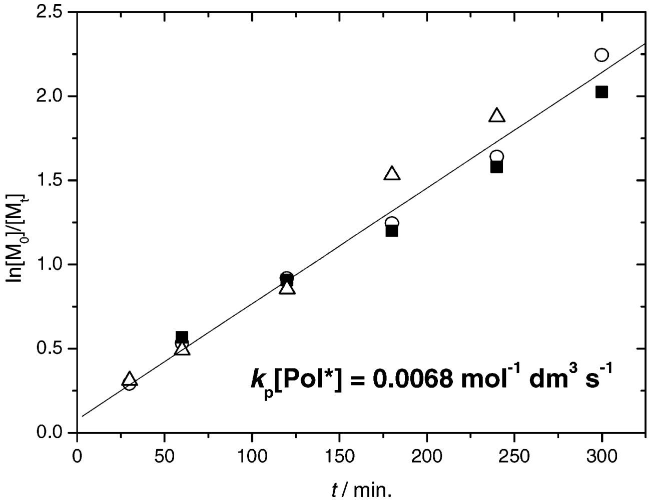

Figure 4. First-order plot for the polymerization of MMA at 90 °C initiated by 2-EIBr (○), 2-perfluoroalkyl ethyl 2-bromoisobutyrate (■), and 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (△) and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) in toluene solution.

the presence of fluorinated moieties via a similar process, MMA was polymerized in the presence of perfluorononane with [M]:[I]:[CuBr]:[L]:perfluorononane (PFN) = 100:1:1:2:1. The first-order rate plot (Figure 1) shows no detrimental effect with the addition on perfluorononane with a similar rate of polymerization to the control polymerization in conventional organic solvents. As expected for a polymerization process, molecular weight distributions were narrow; M_n values increased in a linear fashion with conversion and agreed well with theoretical values (Figure 2). This evidence shows that perfluoroalkyl chains are chemically inert under the reaction conditions.

Copper(I)-Mediated Polymerization Initiated by Perfluoroalkyl Initiators (4, 5, and 6, Figure 3). The synthesis of fluorinated block copolymers has attracted a great deal of attention in the recent years.[39−43] Living radical polymerization has been shown to be an easy synthetic route to α-functionalized polymers[34−37] and indeed block copolymers[23,38] through the use of initiators bearing a secondary functionality that is unreactive under the polymerization conditions. Functional polymerization initiators can be synthesized by the reaction of an appropriate alcohol or amine with a α-bromo acid bromide. Zonyl BA, Zonyl FSO, and a telechelic fluorinated telomer were used to synthesize semifluorinated polymerization initiators (Figure 3).[25] These initiators were then used to initiate polymerization to produce AB block copolymers (from **4**, where A is a perfluoroalkyl chain and B a PMMA chain), ABC block copolymers (from **5**, where A is a perfluoroalkyl chain, B a PEG chain, and C a PMMA chain), and graft diblock copolymers (“Y” shape polymer, from **6**, where the backbone is a PMMA chain and the pendent chain is a perfluoroalkyl chain).

The polymerization of MMA initiated by both 2-perfluoroalkyl ethyl 2-bromoisobutyrate (**4**, Figure 3) and 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (**5**, Figure 3) occurs at an almost identical rate to that initiated by ethyl 2-bromoisobutyrate (EIBr). No evidence of termination reactions was observed in any reaction, each reaction following excellent first-order kinetics (Figure 4). The M_n values increased

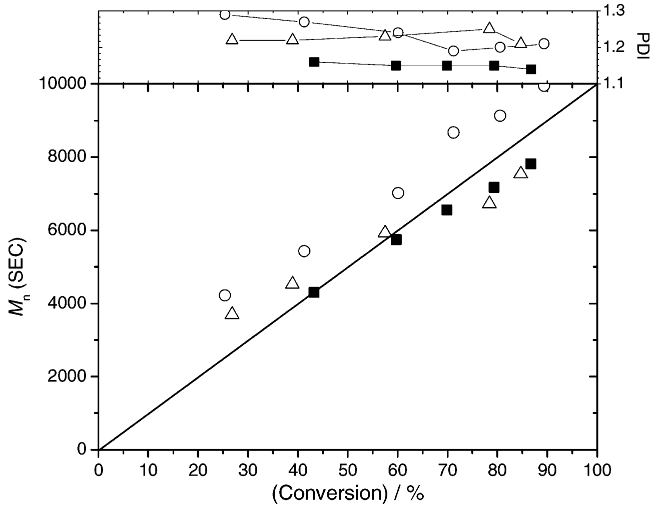

Figure 5. Evolution of molecular weight distribution for the polymerization of MMA at 90 °C initiated by 2-EIBr (○), 2-perfluoroalkyl ethyl 2-bromoisobutyrate (■), and 2-perfluoroalkyl ethyl-*co*-poly(ethylene glycol) 2-bromoisobutyrate (△) mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) in toluene solution and theoretical M_n (—).

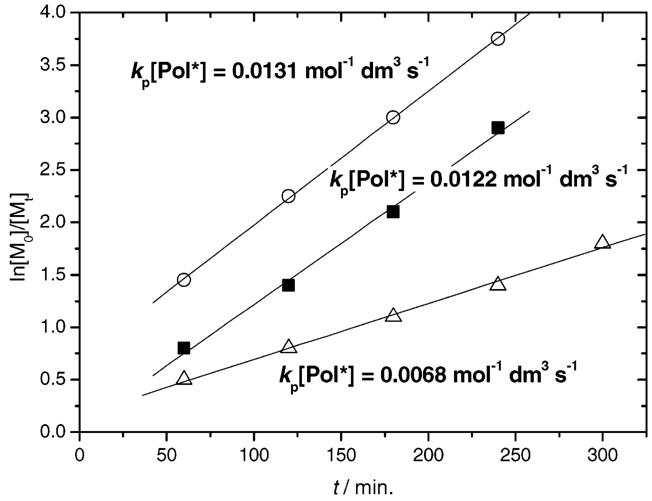

Figure 6. First-order rate plot for the polymerization of MMA at 90 °C initiated by 2-perfluoroalkyl ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine in toluene solution ([M]:[I]:[Cu]:[L] = 40:1:1:2 (○), 60:1:1:2 (■) and 100:1:1:2 (△)).

linearly with conversion in all cases and were slightly lower than theoretical for the polymerization with both fluorinated initiators toward the end of the reaction (Figure 5) with polydispersity remaining low. Methyl methacrylate was polymerized at different target molecular weights [M]:[I]:[Cu]:[L] = 100:1:1:2, 60:1:1:2 and 40:1:1:2 with 2-perfluoroalkyl ethyl 2-bromoisobutyrate initiator (Figure 6). The rates of polymerization increased as the monomer/initiator ratio decreased as expected. The first-order rate plots for [M]:[I] = 100 and 60 indicated that no significant termination was occurring even though there was an increase in the number of active species present. In the polymerization with [M]:[I] = 40, a faster initial rate was observed, and after a significant number of termination events, the concentration of reactive species remains almost identical to that of the polymerization with [M]:[I] = 60. The M_n increased linearly with conversion (Figure 7), and the polydispersity indices were low throughout all polymer-

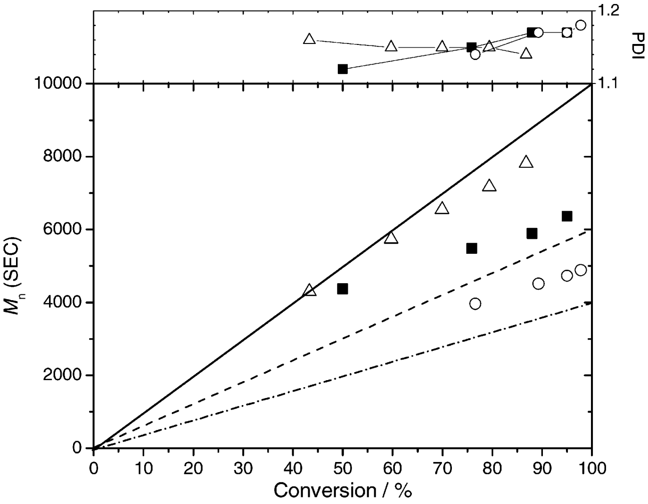

Figure 7. Evolution of molecular weight distribution for the polymerization of MMA at 90 °C initiated by 2-perfluoroalkyl ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine in toluene and theoretical M_n ([M]:[I]:[Cu]:[L] = 40:1:1:2 [(○), $M_{n,theo}$ (—)], 60:1:1:2 [(■), $M_{n,theo}$ (- - -)] and 100:1:1:2 [(△), $M_{n,theo}$ (– ·–)]).

izations (<1.20). Termination reactions evident in the first-order rate plot at [M]:[I] = 40 do not significantly affect the degree of control exhibited over the polymerization with regards molecular weight and polydispersity control. Higher degrees of polymerization were targeted with both 2-perfluoroalkyl ethyl 2-bromoisobutyrate and the fluorinated telechelic telomer (DP = 200). In each case approximately 90% conversion was reached in 7 h for both initiators. All three reactions led to polymers showing a molecular weight close to the theoretical value.

The polymerization of MMA initiated by **6** led to well-defined copolymers with molecular weight close to that expected and low PDI (e.g., M_n = 26 000 ($M_{n,theo}$ = 20 000 g mol^{-1}) and PDI = 1.6). This reaction shows further the great versatility of the polymerization system, as the sulfur atom present in the initiator did not influence the reaction (Figure 3). The resulting product shows a "Y" shape, with a fluorinated chain attached to two PMMA chains of equal length. The properties of this novel structure and its comparison to block copolymers obtained from MMA polymerization with **4** will be reported in a forthcoming publication.

Polymerization of MeOPEG-MA initiated by 2-Perfluoroalkyl Ethyl 2-Bromoisobutyrate (4, Figure 3). Polymerization of MeOPEG-MA initiated by 2-perfluoroalkyl ethyl-2-bromoisobutyrate at 60 °C results in 95% conversion after approximately 2 h (Figure 8). The rate of polymerization increases after approximately 20 min (20% conversion) and stays constant up to conversion over 90%. At high conversion, termination, chain transfer reactions, and the resulting high viscosity of the solution result in the rate slowing. Figure 9 shows the evolution of the molecular weight as a function of the conversion, measured by SEC, which seems to stay constant. When polymerized with a more traditional initiator (phenyl 2-bromoisobutyrate), the molecular weight of MeOPEG-MA increases according to theory, as observed by SEC or ^{1}H NMR. Therefore, we believe that in the specific case of using a fluorinated initiator phase separation might occur, isolating the hydrophobic α-terminus from the fluorinated initiator away from the solvent and resulting in a fairly constant hydrodynamic volume for the product, which would be independent of the poly(MeOPEG-MA) degree of polymerization. To test this hypothesis, we added the fluorinated polymer to a THF solution, and as expected, we observed formation of aggregates. The water-soluble copolymer was purified by dialysis, to give a polymer with M_n^{SEC} = 6700 g mol^{-1} and PDI = 1.07.

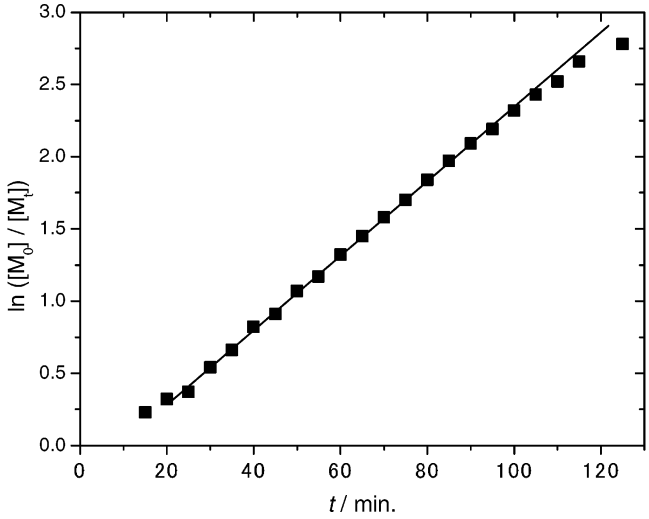

Figure 8. First-order rate plot for the polymerization of MeOPEG-MA in toluene at 60 °C initiated by 2-perfluoroalkyl ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-propyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 10:1:1:2).

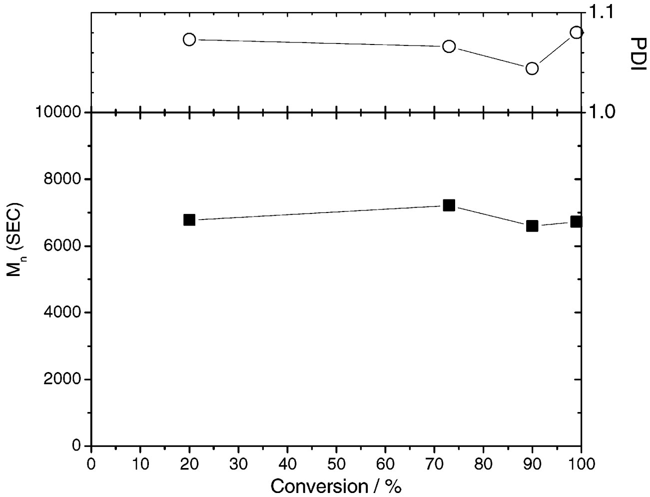

Figure 9. Evolution of molecular weight distribution and PDI for the polymerization of MeO(PEG)-MA in toluene (50% v/v) at 60 °C initiated by 2-perfluoroalkyl ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-propyl)-2-pyridylmethanimine.

Copper(I)-Mediated Polymerization of 2,2,2-Trifluoroethyl Methacrylate. As polymerization occurs readily in the presence of perfluoroalkyl groups, we rationalized that it should be possible to polymerize monomers bearing perfluoroalkyl chains. 2,2,2-Trifluoroethyl methacrylate is a commercially available monomer, with a low level of fluorination, which is fully soluble in many organic solvents. The fully homogeneous polymerization of 2,2,2- trifluoroethyl methacrylate resulted in polymers with relatively low polydispersity at all stages of reaction (PDI ~ 1.30). Although the M_n increased linearly with conversion (Figure 10), measured values of M_n were higher than the theoretical values, indicating poor initiator efficiency with this monomer. The initial rate of polymerization is similar

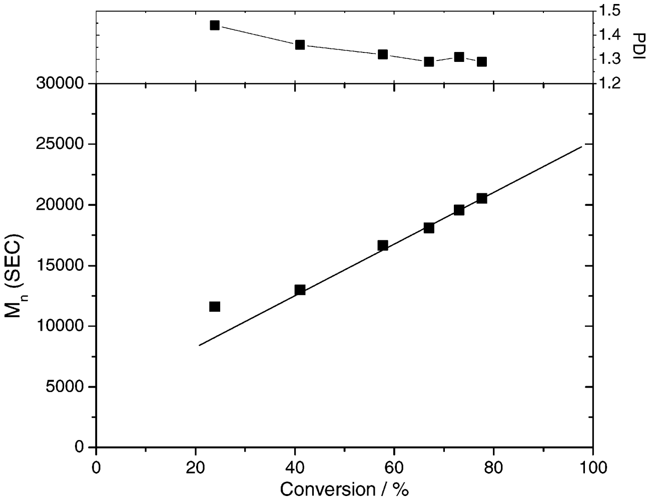

Figure 10. Evolution of molecular weight distribution for the polymerization of 2,2,2-trifluoroethyl methacrylate at 90 °C initiated by ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine in toluene ([M]:[I]:[Cu]:[L] = 100:1:1:2).

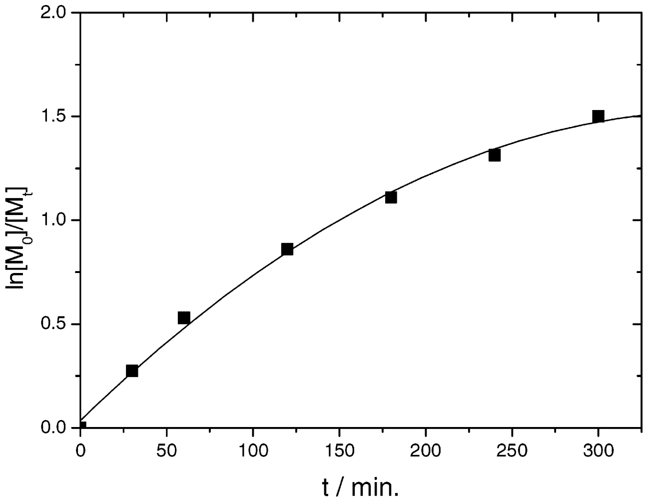

Figure 11. First-order rate plot for the polymerization of 2,2,2-trifluoroethyl methacrylate at 90 °C initiated by ethyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) in toluene solution.

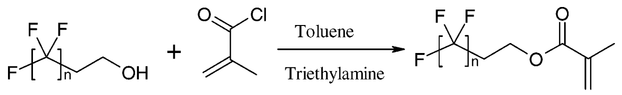

Figure 12. Scheme of the synthesis of perfluoroalkyl ethyl methacrylate ($n \sim 8$).

to that of MMA under comparable conditions, but a gradual loss of reactive species resulting from irreversible termination can be seen in the first-order plot, and this may account for the larger polydispersity indices observed (Figure 11).

Copper(I)-Mediated Polymerization of Perfluoroalkylethyl Methacrylate (FEMA). Perfluoroalkylethyl methacrylate (FEMA) was synthesized by the esterification of ZONYL BA with methacryloyl chloride (Figure 12, yield = 47.5% after a basic alumina column and aqueous work-up). The attempted homopolymerization of FEMA by polymerization with [M]:[I]:[Cu]:[L] = 100:1:1:2 in toluene led to a phase separation during the reaction due to the nonmiscibility of the fluorinated and organic phases.[25] The resulting product was insoluble in all common organic solvents but was soluble in highly fluorinated solvents, e.g. FC77, perfluoromethylcyclohexane, and HFIPA.

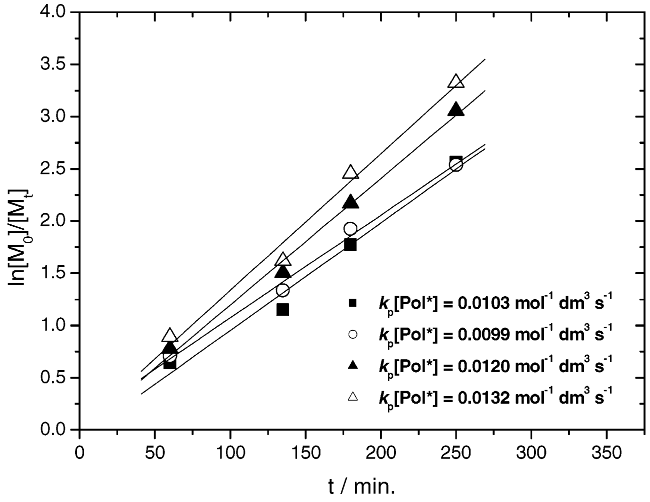

Figure 13. First-order rate plot for the polymerization statistical copolymerization of MMA and FEMA (5 (■), 10 (○), 15 (▲), 20% (△)) at 90 °C initiated by phenyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) performed in toluene solution.

Statistical Copolymerization of FEMA with MMA. Statistical copolymers of FEMA and MMA (5, 10, 15, and 20 mol % FEMA) were carried out in order to circumvent solubility problems. In each case, phase separation did not occur. In all cases, the conversion of each monomer was almost identical throughout the reaction, indicating reactivity ratios close to unity (see Supporting Information for full reaction details). The rate of polymerization increased marginally with increasing levels of FEMA, and the first-order rate plots indicated no significant termination occurring (Figure 13). Although the SEC molecular weight will be different than the "real" molecular weight of the statistical copolymer, results suggest a good control of the molecular weight distribution at all levels of FEMA incorporation, with M_n values increasing reasonably linearly with conversion (Figure 14). Polydispersity indices of the final products are all below 1.20 (see Supporting Information).

Statistical Copolymerization of FEMA with Styrene. The homopolymerization of styrene at 90 °C follows good first-order kinetics but is significantly slower than the polymerization of MMA under identical conditions. The M_n increased linearly with conversion being slightly higher than the calculated values with relatively narrow distributions (PDI ~ 1.3). Again, an increase in rate was observed with an increase in the percent FEMA content with no evidence of termination reactions up to 15% FEMA (Figure 15). At 20% FEMA, deviation from first-order kinetics is observed after approximately 300 min (decrease in polymerization rate) ascribed to radical–radical termination reactions. However, it is noted that this is not conclusive since difficulties in measuring the individual conversions for this copolymer system reduce the accuracy of the experiment. The M_n values increased linearly with conversion (see Figure 16 and Supporting Information). Thus, copolymerization of FEMA with styrene is possible with this polymerization system, but the reaction is not as controlled as the copolymerization of FEMA with methacrylates (see Supporting Informa-

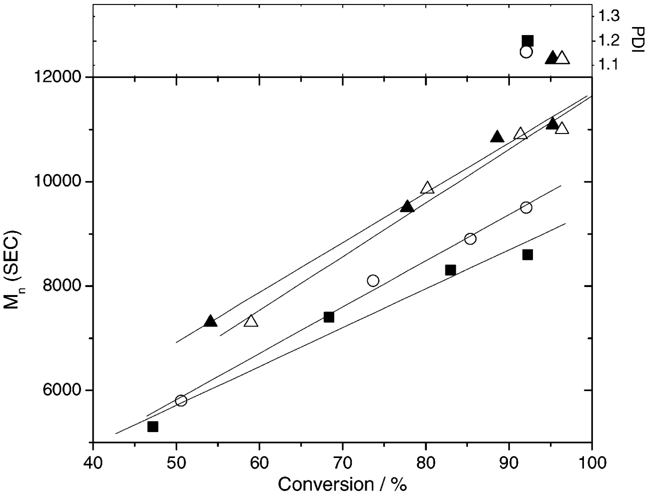

Figure 14. Evolution of molecular weight distribution for the statistical copolymerization of MMA and FEMA (5 (■), 10 (○), 15 (▲), 20% (△)) at 90 °C initiated by phenyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) in toluene solution.

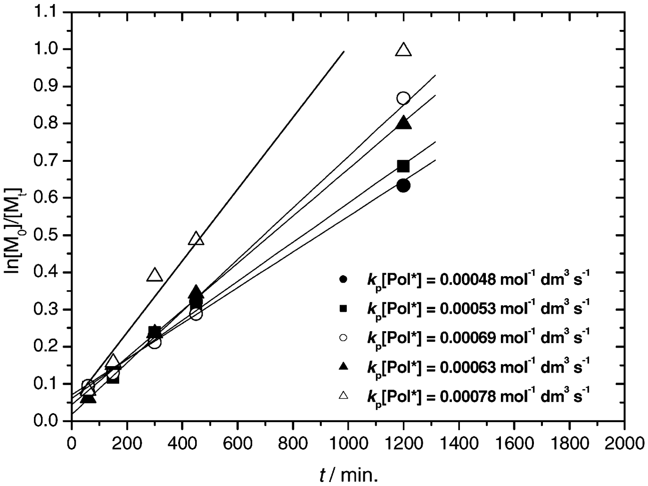

Figure 15. First-order kinetic plot for the statistical copolymerization of styrene and FEMA (0 (●), 5 (■), 10 (○), 15 (▲), 20% (△)) at 90 °C initiated by phenyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) performed in toluene

tion). The reactivity ratios, as would be expected, are significantly different, resulting in styrene and FEMA not polymerizing at the same rate, leading to a heterogeneous polymer and monomer feed composition of the polymer throughout the reaction (see Supporting Information).

Conclusions

Copper-mediated living radical polymerization mediated with pyridinimine ligands has been shown to be efficient for the synthesis of poly(methacrylate)s and polystyrene in the presence of fluorinated species. After having shown that the fluorine atoms do not exchange with the bromine atoms present in the polymerization mechanism, the synthesis of AB block copolymers using fluorinated macroinitiators with a methacrylate B block giving both hydrophobic, MMA, and hydrophilic, MeOPEG-MA, was carried out. This resulted in well-defined α-terminal block copolymers with PDI as low as 1.10. Fluorine was also incorporated into polymers with controlled molecular weight and narrow PDI through the use of fluorine containing monomers by both homopolymerization and copolymerization with MMA and STY. While homopolymerization appeared difficult to control due to solubility problems in conventional organic solvents, statistical copolymerization of fluorinated macromonomers and methyl methacrylate or styrene led to final products exhibiting well-controlled molecular weight distribution.

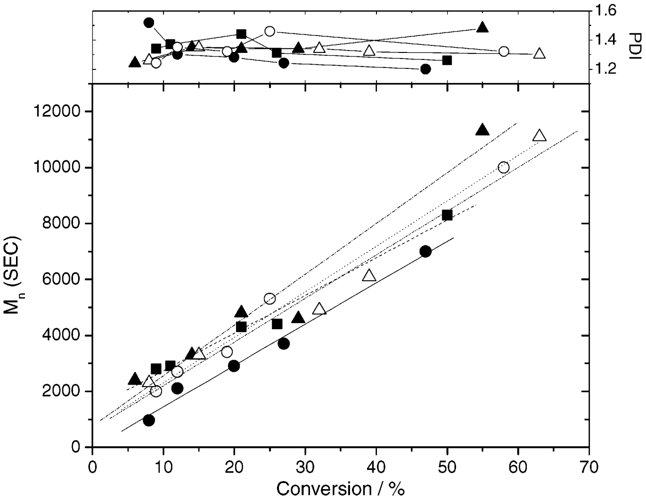

Figure 16. Evolution of molecular weight distribution for the statistical copolymerization of styrene and FEMA (0 (●), 5 (■), 10 (○), 15 (▲), 20% (△)) at 90 °C initiated by phenyl 2-bromoisobutyrate and mediated by Cu(I)Br/*N*-(*n*-pentyl)-2-pyridylmethanimine ([M]:[I]:[Cu]:[L] = 100:1:1:2) in toluene solution.

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Supporting Information Available: Tables summarizing the data for all the polymerization reactions reported in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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