Living polymers allow for the synthesis of well-defined and complex macromolecular architectures.1 Currently, controlled/living radical polymerization has attracted much attention since radical polymerization is generally more tolerant toward polar functionalities and impurities than ionic and coordination polymerizations.2 Among the approaches developed, transition-metal-catalyzed atom transfer radical polymerization (ATRP) has been extensively studied. By employing alkyl-substituted 2,2′-bipyridines (bpy), homogeneous ATRP was achieved which resulted in well-controlled polymerization for a variety of monomers.2,3 Under these conditions, the degree of polymerization (DP) was predetermined by the ratio of the change in monomer concentration and initial initiator concentration (DPn = Δ[monomer]/[initiator]0), and low polydispersities (Mw/Mn < 1.1) were obtained.3,4

Recently, the use of supercritical carbon dioxide (scCO2) as a polymerization medium has attracted considerable interest. In addition to being an environmentally benign alternative to volatile organic and aqueous solvents, scCO2 offers several advantages as a solvent, e.g., low solution viscosity, an effectively inert solution medium (no detectable chain transfer to solvent), and tunable solvent strength. Previous work has shown that CO2 is an excellent medium for performing radical polymerizations. Solution, dispersion, precipitation, and emulsion radical polymerizations have been successfully performed in scCO2.5

There have been very few reports about living polymerizations carried out in CO2. DeSimone et al. reported the “living” carbocations polymerization of vinyl ethers in CO2.6 High polydispersities were obtained for the polymerization of isobutyl vinyl ether largely due to the heterogeneous nature of the polymerization system. The lowest polydispersity (Mw/Mn = 1.6) was obtained when a vinyl ether bearing a fluorinated side chain was polymerized. Odell et al. recently reported the controlled radical polymerization of styrene in scCO2 using the 2,2′,6,6′-tetramethylpiperidine-N-oxyl (TEMPO)-mediated stable free radical polymerization (SFRP) process.7 The polymerizations were carried out at high temperature (125 °C). When the concentration of styrene was low (10% of the reactor volume), polystyrene was produced at low conversion and had a molecular weight (Mn) of about 3000 and Mw/Mn < 1.3.

As part of the effort toward applying ATRP in a more environmentally friendly medium, in this paper we report our initial work on controlled/living radical polymerization carried out in CO2. The polymerization of fluorinated (meth)acrylates, the subsequent synthesis of block copolymers, and the dispersion polymerization of methyl methacrylate (MMA) by ATRP in scCO2 are presented.

On the basis of the solubility in CO2, polymers can be categorized into either “CO2-philic” (amorphous fluoropolymers and silicone polymers) or “CO2-phobic” materials (conventional organic polymers, either hydrophilic or lipophilic).8 We first chose to polymerize two fluorinated monomers, 1,1-dihydroperfluoroctyl methacrylate (FOMA) and 1,1-dihydroperfluoroctyl acrylate (FOA), by ATRP as both the monomers and the resultant polymers are soluble in scCO2. The structures of the two fluorinated monomers and the three ligands used in this study are shown in Figure 1.

The effect of using different ligands in the copper-mediated ATRP of FOMA in scCO2 was studied, and the results are summarized in Table 1.9 Cu(0) was added in the polymerization to accelerate the reaction.10 The highest yield and best agreement between the measured molecular weights and the calculated values were obtained when 4,4′-di(tridecafluoro-1,1,2,2,3,3-hexahydroronyl)-2,2′-bipyridine (dR6bpy) was used as the ligand.11 We attribute this to the enhanced catalyst solubility in scCO2. The high-pressure polymerizations were carried out in a view cell equipped with sapphire windows to visually observe the phase behavior during the polymerization. When bpy or 4,4′-di(5-nonyl)-2,2′-bipyridine (dN6bpy) was used as the ligand, the catalyst appeared as a brown oil on the interior walls and windows of the view cell, and the view cell was transparent with light yellow color. In contrast, with dR6bpy
The system resulted in polymers with lower polydispersity than previous results where a homogeneous ATRP catalyst appeared dark brown with no visible precipitation. Analogous to previous results where a homogenous ATRP system resulted in polymers with lower polydispersity, the fluorinated alkyl chain contained ca. 25% CF₃ branches.

Table 1. Effect of Ligands on Copper-Mediated ATRP of FOMA in scCO₂

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Conv (%)</th>
<th>Mₙ,Cal</th>
<th>Mₙ,NMR</th>
<th>Mₚ,LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>54</td>
<td>11000</td>
<td>N/A</td>
<td>65000</td>
</tr>
<tr>
<td>dNbpy</td>
<td>64</td>
<td>13000</td>
<td>21800</td>
<td>18000</td>
</tr>
<tr>
<td>dR₆bpy</td>
<td>83</td>
<td>16800</td>
<td>19000</td>
<td>17000</td>
</tr>
</tbody>
</table>

* All polymerizations were conducted at 85 °C under a pressure of 4900 psi. [FOMA]₀ = 1.40 M; [FOMA]₀/[MBP]₀ = 42 (MBP = methyl 2-bromopropionate). * Conversions were obtained gravimetrically after purification and drying of the synthesized polymers. * Calculated according to the following equation: Mₙ,Cal = ([M]₀/[n]₀) × (MW)₀ × conversion + MW_MBP, where [M]₀ and [n]₀ represent the initial concentrations of monomer and initiator, (MW)₀ is the molecular weight of the monomer, and MW_MBP is the molecular weight of the initiator. * Determined by ¹H NMR. * Determined by light scattering with Vertrel as the solvent and dn/dc = 0.18 (estimated value). * [MBP]₀/[Cu(0)]₀/[CuCl]₀/[dR₆bpy]₀ = 1.0/0.5/0.5/2 for 17 h. * End group was not detectable by ¹H NMR. * [MBP]₀/[Cu(0)]₀/[CuCl]₀/[dNbpy]₀ = 1.0/0.5/0.5/1.0 for 18 h. * [MBP]₀/[Cu(0)]₀/[CuCl]₀/[dR₆bpy]₀ = 1.0/0.5/0.5/1.0 for 18 h.

as the ligand, the whole polymerization medium appeared dark brown with no visible precipitation. Analogous to previous results where a homogenous ATRP system resulted in polymers with lower polydispersities, greater solubility of the catalyst in scCO₂ yielded better controlled polymerizations. It should be noted that, for the dR₆bpy ligand, the presence of a propylene spacer between the strong electron-withdrawing perfluorinated chain and the pyridine ring serves to minimize any unfavorable electronic effects.

To examine the "living" nature of the polymerization, poly(FOMA-b-MMA)° and poly(FOMA-b-DMAEMA)° block copolymers were synthesized in scCO₂ by the polymerization of MMA or 2-(dimethylamino)ethyl methacrylate (DMAEMA) using the above poly(FOMA) as a macroinitiator. In all cases, dR₆bpy was used as the ligand to gain better control of the polymerization. All the polymers were characterized by ¹H NMR after purification by Soxhlet extraction with THF. Figure 2A shows the ¹H NMR spectrum of the poly(FOMA) obtained by ATRP in scCO₂. The signal at 4.45 ppm corresponds to the ester methylene protons of poly(FOMA), and the resonance at 3.60 ppm corresponds to the ester methyl protons originating from the initiator (methyl 2-bromopropionate). The degree of polymerization (DP) for poly(FOMA) was determined from the peak integration ratio of the methylene protons to the methyl ester protons (a/b). The peak integration ratio of the methylene protons to the methyl ester protons is 5:1 (Table 2).

Figure 2. ¹H NMR spectra of (A) poly(FOMA), (B) poly(FOMA-b-MMA), and (C) poly(FOMA-b-DMAEMA) synthesized by ATRP in scCO₂. For the synthesis of the poly(FOMA) macronitiator: [FOMA]₀ = 1.40 M; [FOMA]₀/[MBP]₀ = 42; [MBP]₀/[Cu(0)]₀/[CuCl]₀/[dR₆bpy]₀ = 1/0.5/1.0; 85 °C and 4900 psi for 16 h. For the synthesis of poly(FOMA-b-MMA): [MMA]₀ = 1.03 M; [MMA]₀/[poly(FOMA)]₀ = 78; [poly(FOMA)]₀/[Cu(0)]₀/[CuBr]₀/[dR₆bpy]₀ = 1/1.2/1.2/4; 85 °C and 4900 psi for 14 h; MMA conversion = 64%. For the synthesis of poly(FOMA-b-DMAEMA): [DMAEMA]₀ = 0.47 M; [DMAEMA]₀/[poly(FOMA)]₀ = 47; [poly(FOMA)]₀/[Cu(0)]₀/[CuBr]₀/[dR₆bpy]₀ = 1/1/1/2; 65 °C and 4900 psi for 17 h; DMAEMA conversion = 61%.

Table 2. Synthesis of PFOMA Block Copolymers by Copper-Mediated ATRP in scCO₂ and Their Solubility Studies

<table>
<thead>
<tr>
<th>Block</th>
<th>Mₙ,Cal</th>
<th>Mₙ,NMR</th>
<th>mol %</th>
<th>Solubility in CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>5000</td>
<td>6400</td>
<td>61</td>
<td>l ~ C</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>4500</td>
<td>2800</td>
<td>31</td>
<td>C ~ S</td>
</tr>
</tbody>
</table>

* The PFOMA macronitiator had Mₙ,NMR = 19 000. See Figure 2B for reaction conditions. ° 4% (w/w) polymer; l = insoluble; C = cloudy; S = soluble.

show the ¹H NMR spectra of the poly(FOMA-b-MMA) and poly(FOMA-b-DMAEMA) block copolymers, respectively. The methyl ester group assigned to the MMA repeating unit was observed at 3.60 ppm (Figure 2B). The resonances originating from the DMAEMA repeating unit were seen at 4.20, 2.65, and 2.35 ppm, corresponding to the methylene protons adjacent to the ester (CO2CH2CH2NMe2), the methylene protons adjacent to the amine (CO2CH2CH2NMe2), and the methyl substituents on the nitrogen (CO2CH2CH2NMe2), respectively (Figure 2C). On the basis of the ratio of the area of the two peaks (a/b or a/a) and the molar mass of poly(FOMA), the chemical compositions and the molar masses were calculated and are summarized in Table 2. In all cases, measured molecular weights by ¹H NMR (Mₙ,NMR) were close to the calculated values (Mₙ,Cal), indicating that controlled polymerizations were achieved using ATRP in scCO₂.

Table 2 also shows the solubilities of the block copolymers in CO₂ after isolation and purification.
Although the poly(FOMA) macroinitiator was soluble in CO$_2$, the poly(FOMA-b-MMA) block copolymer was insoluble in CO$_2$, and the CO$_2$ phase became cloudy only at higher temperature and pressure. In contrast, the poly(FOMA-b-DMAEMA) block copolymer was initially poorly soluble in CO$_2$, but as temperature and pressure were increased, the block copolymer became soluble in CO$_2$, displaying a clear solution.

The differential scanning calorimetry (DSC) thermogram of the poly(FOMA-b-MMA) block copolymer displayed two glass transition temperatures, suggesting microphase separation in the solid state. $T_g^1$ (48.0 °C) corresponded to the glass transition of the poly(FOMA) microdomains, and $T_g^2$ (123.7 °C) corresponded to the glass transition of the poly(MMA) microdomains.

Similarly, the polymerization of FOMA (Figure 1) by ATRP in scCO$_2$ was carried out. Using a difunctional initiator, 1,2-bis(bromopropionyloxy)ethane, poly(FOA) with $M_{n,NMR}$ = 12,000 was obtained. Subsequent polymerization of MMA in scCO$_2$ using this poly(FOA) as a macroinitiator afforded a block copolymer where the MMA segment had $M_{n,NMR}$ = 4900. The structure of the block copolymer is currently under investigation. In general, ABA type triblock copolymers containing a fluorinated center block are of interest as they could potentially be used as fluorinated thermoplastic elastomers.

In contrast to “CO$_2$-philic” polymers, conventional polymers, such as poly(MMA), have very limited solubilities in scCO$_2$. Among the heterogeneous polymerization techniques, dispersion polymerization has proven very useful for CO$_2$-based systems. In dispersion polymerization, latex particles are formed in the presence of a suitable stabilizer from an initially homogeneous reaction mixture. Particles typically range in size from 1 to 50 μm. Previous work has shown that poly(FOA) is an effective stabilizer for the poly(MMA)–CO$_2$ system. Thus, the dispersion polymerization of MMA by ATRP in scCO$_2$ was carried out using low molecular weight poly(FOA) as the steric stabilizer. The precipitation polymerization of MMA in scCO$_2$ by ATRP under similar conditions in the absence of the stabilizer was also carried out. All polymerizations were initially homogeneous, as the MMA monomer is soluble in scCO$_2$ under the reaction conditions. In the absence of the poly(FOA) stabilizer, the forming poly(MMA) precipitated out of the CO$_2$ phase, and limited conversion (conversion = 55%) and $M_{n,SEC}$ = 12,000 was obtained. In contrast, the dispersion ATRP of MMA conducted in the presence of the stabilizer started homogeneously and became progressively more cloudy and formed a kinetically stable colloidal dispersion after ca. 4 h. The resulting product was easily isolated as a free-flowing powder after venting of the CO$_2$ into methanol. The obtained poly(MMA) had a measured molecular weight ($M_{n,SEC}$ = 13,400) close to the calculated value and relatively narrow molecular weight distribution, $M_w/M_n$ = 1.41.

Scanning electron microscopy (SEM) was used to determine the morphology of the poly(MMA) synthesized by ATRP in scCO$_2$. Particles made by dispersion polymerization were more spherical than those made by precipitation polymerization but were somewhat coagulated. In previous work, it has been determined that low molecular weight poly(FOA) as a polymeric stabilizer for poly(MMA) results in more coagulation and less single particle formation. However, the use of high molecular weight poly(FOA) produces more uniform particles. We are currently investigating the use of high molecular weight poly(FOA) with this system to examine the effect on particle formation.

In conclusion, ATRP has been successfully carried out in scCO$_2$ for the polymerization of both FOMA and FOA. Using the poly(FOMA) prepared in scCO$_2$ as a macroinitiator, block copolymers were prepared by the ATRP of either MMA or DMAEMA in scCO$_2$. Similarly, a triblock copolymer of poly(MMA-b-FOA-b-MMA) was prepared by ATRP using a difunctional poly(FOA) macroinitiator. In addition, the dispersion polymerization of MMA in scCO$_2$ using ATRP in the presence of a fluorinated polymeric surfactant was successfully performed to yield stable poly(MMA) latex particles with controlled molecular weights and narrow molecular weight distribution. The use of ATRP in scCO$_2$ for the synthesis of other well-defined polymers is in progress.

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Supporting Information Available: DSC thermogram of poly(FOA-b-MMA), table of poly(MMA) made by dispersion and precipitation ATRP in scCO$_2$, and SEM micrograph of poly(MMA) particles made by dispersion ATRP. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(9) Fluorinated monomers (FOMA and FOA) were obtained from 3M Inc. and purified by passing through alumina columns. All polymerizations in scCO$_2$ were conducted in a 10 mL, high-pressure view cell equipped with a high pressure view cell equipped with sapphire windows to permit the visual observation of the reaction mixture. A representative example is as follows. The reactor was charged with Cu(0) (10 mg), CuCl (16.3 mg), and dR (130 mg). It was then purged with a flow of argon for at least 15 min. A degassed solution of FOMA (4 mL) and methyl 2-bromopropionate (36.0 μL) was added using a degassed syringe under argon. An ISCO model no. 2600 automatic syringe pump was used to pressurize the reactor with CO$_2$ to approximately 2000 psi, and the reaction mixture was heated to the desired temperature of 85 ± 0.1 °C. Then, the remaining CO$_2$ was slowly added to the system until the desired temperature (85 °C) and pressure (4900 psi) were reached. Once the final reaction conditions were obtained, the reaction was allowed to proceed with stirring for 16 h. At the end of the reaction, CO$_2$ was slowly vented from the cell into a solution of MeOH, while maintaining a pressure of 4000 psi inside the reactor using the automatic syringe pump. The white polymer was collected by vacuum filtration over a Hirsch funnel.
(11) The dR6bpy ligand was synthesized as follows. To a stirred solution of dry THF (4.4 mL) and diisopropylamine (0.44 mL) under Ar at −78 °C was added dropwise n-butyllithium (2.5 M in hexane, 1.2 mL). After 15 min, the solution was warmed to 0 °C where it was allowed to stir for 15 min. The mixture was cooled to −78 °C again, and a solution of 4,4′-dimethyl-2,2′-bipyridine (250 mg) in dry THF (10 mL) was added slowly. After 3 h, a solution of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (1.0 mL) in dry THF (16.0 mL) was added. The solution was allowed to warm to room temperature overnight and then poured into ice-cold water (20 mL). The aqueous phase was extracted with ether (3 × 20 mL). The combined organic phase was dried over Na2SO4, filtered, and concentrated in vacuo to give a yellow solid. Recrystallization from MeOH afforded a pale white solid (50% yield). Physical data: mp 113–115 °C; 1H NMR (300 MHz, CDCl3) δ: 8.6 (d, 2H, ArH), 8.3 (s, 2H, ArH), 7.2 (d, 2H, ArH), 2.8 (t, 4H, CH2CF2), 2.1–2.0 (m, 8H, CH2CH2CH2CF2) ppm; 13C NMR (75.5 MHz, CDCl3) δ: 156.3, 150.6, 149.4, 123.8, and 121.1 (aromatic C), 34.6 (CH2CH2CH2CF2), 30.4 (t, JF-C = 22 Hz, CH2CF2), 21.0 (CH2CH2CF2) ppm. Electrospray ionization mass spectroscopy (ESI MS) m/z calculated for C28H18F26N2 [M + H]+: 877.1; observed: 877.0.


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