

New Process for Synthesizing Fluorinated Polymers in Supercritical Carbon Dioxide

Zhao-Tie Liu,^{*,†,‡} Jian-Gang Chen,^{†,‡} Zhong-Wen Liu,^{†,‡} and Jian Lu[†]

Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Xi'an 710062, China, and School of Chemistry & Materials Science, Shaanxi Normal University, Xi'an 710062, China

Received January 27, 2008; Revised Manuscript Received August 3, 2008

ABSTRACT: The typical polymerization process in supercritical fluids (SCFs) was improved through modifying the reaction system and designing and using sampling tubes. The efficacy of the newly developed procedure was demonstrated by the free radical homopolymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) and copolymerization of TFEMA and *N*-vinylpyrrolidone (NVP) in supercritical carbon dioxide (scCO₂). Results indicate that the newly developed procedure has the characteristics of minimum loss of reactants and polymerization starting at the desired temperature and pressure. Furthermore, the polymerization process can be well tracked by analyzing the reaction mixtures online sampled from the reactor at certain reaction times by FT-IR, ¹H NMR, and GPC. The reaction time and the product properties can be optimized based on the tracking results. For the first time, block copolymers by free radical polymerization in scCO₂ was successfully synthesized by sequential addition of TFEMA and methyl methacrylate (MMA) into the reactor at different reaction stages. The synthesized polymers were characterized by FT-IR, ¹H NMR, ¹³C NMR, GPC, TGA, and DSC, respectively. It was proved that the losing of monomer, pollution to the environment, and distribution of the molecular weight of the synthesized polymers decreased while the yield of product, the reproducibility, and the controllability of polymerization increased after improvement of the polymerization process.

Introduction

Owing to the superiority of supercritical fluids (SCFs) to conventional liquid solvents such as high diffusivity, high compressibility, low viscosity, low surface tension, and the continuously tunable physical properties (e.g., density, solubility, dielectric constant, etc), SCFs have become the most attractive solvents and are extensively applied in the fields of extraction,¹ catalysis,² synthesis of nanoparticles,^{3,4} processing and synthesis of polymers,^{5–8} and so on in recent years. Among different SCFs, supercritical carbon dioxide (scCO₂) is commonly used for the synthesis of polymers attributed to its easily accessible critical conditions ($T_c = 31.06$ °C, $P_c = 7.38$ MPa), low cost, low toxicity, and, most importantly, inertness enough that there is no detectable chain transfer reaction to CO₂.⁹ To date, among the known polymers, fluorinated polymers exhibit superior performance of chemical inertness, high thermal stability, excellent weatherability, low flammability, low dielectric constant, low refractive index, and special surface properties.¹⁰ 2,2,2-Trifluoroethyl methacrylate (TFEMA) has the features of both typical methacrylate monomers and fluorine-containing monomers, and the homopolymer (PTFEMA), having excellent capacity for water repellence and stain resistance, is extensively used in various applications.^{11,12}

By detailed examining of the reported experimental procedures^{6–8,11} that are commonly used for the laboratory investigation on the polymerization in scCO₂^{6,7,11} or in trifluoromethane,⁸ we find that the following main defects are unavoidable, which may shadow the accuracy of the experimental results. First, because of charging the volatile reactants before purging the reactor by CO₂, Ar, or N₂, the added reactants cannot be accurately counted due to the unmeasurable loss of the volatile monomer(s), which produces errors in calculating monomer feed

ratio, conversion, or product yield. Moreover, adding the initiator before the desired reaction temperature results in that the polymerization occurs at wide temperature ranges at the initial reaction stage, leading to a relative broader distribution of the molecular weights and poor reproducibility. Finally, the time for polymerization is conceptually ambiguous when all the reactants are added in the reactor before the desired temperature. These problems are mainly resulted from the difficulty in putting into/taking out the reactants/products during the polymerization, especially at a relatively higher pressure.

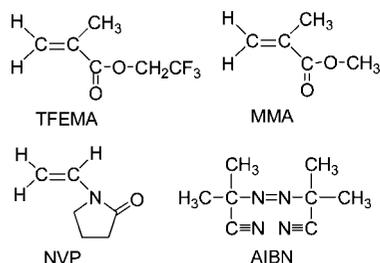
Some efforts have been made to overcome these problems for polymerization in SCFs.^{13,14} During the precipitation polymerization of acrylic acid,¹³ the initiator of AIBN was added through a tube at the desired reaction temperature. However, limited by the poor solubility of the polymeric product and the resulting heterogeneous process, the molecular weight distributions were broad (3.8–3.9). Thus, differences induced by the addition sequence of initiator cannot be differentiated. In the copolymerization of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole,¹⁴ the volatile monomers were charged after purging the reactor for safety purpose, but the product yield was relatively low (34–74%), maybe owing to an insufficient reaction time of 5 h.

In this work, an experimental apparatus targeted for the laboratory investigation on polymerization in SCF was purposefully designed to overcome the above-mentioned problems. Based on our developed experimental procedure, the polymerization in SCF can be reasonably controlled, that is, minimum loss of reactants, polymerization starting at the desired temperature and pressure, and the easy tracking of the polymerization process. The efficacy of the newly developed procedure was confirmed by comparatively studying on the polymerization of TFEMA in scCO₂. Moreover, a new process for the synthesis of copolymers of P(TFEMA-*r*-NVP) and (PTFEMA-*b*-PMMA) in scCO₂ was demonstrated by free radical polymerization. The synthesized polymers were quantitatively characterized by FT-IR, ¹H NMR, ¹³C NMR, gel permeation chromatograph (GPC),

* To whom correspondence should be addressed. Tel./fax: +86-29-85303682. E-mail: ztliu@snnu.edu.cn.

[†] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education.

[‡] School of Chemistry & Materials Science, Shaanxi Normal University.

Scheme 1. Structures of Monomers (TFEMA, MMA, NVP) and Initiator (AIBN) Used

thermal gravity analysis (TGA), and differential scanning calorimeters (DSC).

Experimental Section

Materials. 2,2,2-Trifluoroethyl methacrylate (TFEMA, minimum 99.7% purity) was kindly provided by Weihai New Era Chemical Co. Ltd. (China). Before use, it was pretreated through an alumina column to remove inhibitor (4-methoxyphenol, MEHQ) and then purified by vacuum distillation. Before use, the commercial products (analytical purity) of methyl methacrylate (MMA) and *N*-vinylpyrrolidone (NVP) were further distilled under vacuum. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol, dried under vacuum at 20 °C for 24 h, and stored at 0 °C before use. Methanol and anhydrous ethanol of analytical purity were used as received. Tetrahydrofuran (THF, HPLC grade) was filtrated through a membrane with 0.45 μm pore size before use. Carbon dioxide (99.99% purity) was purchased from Messer (China) and used as received. The structures of the main chemicals used in this work are given in Scheme 1.

Apparatus. To overcome the above-mentioned problems, two sets of sampling tubes were designed as shown in Figure 1. The sample-in tubes having volumes from 1 to 30 mL were manufactured with internally conic surfaces at the two ends and used to add monomer(s) and initiator at different reaction stages. The sample-out tubes (0.6–2.5 mL) composed of a pressure vessel with internally hemispheric surface at the end was designed for online sampling from the high pressure reactor. In this case, the products at different reaction stages were off-line analyzed, and the monomer conversion and the distribution of molecular weight were traced. As shown in Figure 1, by connecting the sampling tubes to inlet 10 and outlet 11 in the reactor, the polymerization in SCF was controllable and trackable. The detailed description of the procedure was depicted in the following. The procedure of free radical polymerization of TFEMA in scCO₂ is shown in Scheme 2.

Free Radical Homopolymerization. The improved polymerization procedure was illustrated with the homopolymerization of TFEMA in scCO₂. A variable volume view cell was purged with low-pressure CO₂ (or Ar) and degassed by a vacuum pump alternatively for several times to eliminate the air in the system. After sealing the outlets of the reaction system, the desired amount of TFEMA was added to the view cell via a sample-in tube equipped with a syringe pump. After this, the pressurized CO₂ was filled until about one-third of the cell volume and started to heat the reactor. Upon the desired polymerization temperature of 70 °C, AIBN was pumped into the cell carried by a suitable flow rate of CO₂ through the sample-in tube line. Finally, the desired system pressure was conditioned by feeding additional CO₂, and the polymerization started at this point. The mixture in the cell was sampled periodically during the process of polymerization, and the reaction was stopped until the monomer conversion was about 90%. After every sampling, the system pressure was kept the same either by moving the piston to reduce the cell volume or by filling additional pressurized CO₂ to the cell.¹⁵ After reaction, the cell was cooled by ice/water or dry ice/acetone, and the CO₂ was released slowly and selectively. The raw product was collected, detected by ¹H NMR spectroscopy to analyze the conversion of TFEMA, and subjected to exhaustive washing with ethanol in a

Soxhlet extractor to remove the residue of the reactants. Finally, the polymer was dried in vacuum at 50 °C overnight (entries 1–6, Table 1). For a comparison purpose, homopolymerization of TFEMA was also done under the same conditions as mentioned above but with the commonly used procedure reported in the references^{5–8,11} (entries 7–9, Table 1).

Free Radical Copolymerization. The free radical copolymerization of TFEMA and a nonfluorinated monomer (NVP or MMA) in scCO₂ is investigated in two ways. One is the one-step-one-pot polymerization of TFEMA and NVP, with the same procedure as that of TFEMA homopolymerization mentioned above except that TFEMA and NVP were added simultaneously. As a result, random copolymer, P(TFEMA-*r*-NVP) was obtained (entry 10, Table 1). The other is the two-step-one-pot polymerization for the synthesis of diblock copolymer of P(TFEMA-*b*-MMA). In the first step, it was exactly the same as that of the TFEMA homopolymerization. After approaching complete consumption of TFEMA (about 90% conversion), the second step was started by pumping the desired amount of MMA monomer into the view cell through a sample-in tube, as shown in Figure 1. In this case, the temperature was kept while the system pressure was conditioned by moving the piston in the cell. When the conversion of MMA was close to 90% (determined by ¹H NMR spectroscopy), the reaction was stopped. The cell was cooled and decompressed. The raw product, PTFEMA-*b*-PMMA, was collected and subjected to exhaustive washing and extraction with ethanol/benzene (5:1, v/v) so as to remove the residue of the reactants and homopolymer(s). The product was dried under reduced pressure at a room temperature for at least 24 h until a constant weight was obtained (entry 11, Table 1).

Characterization. FT-IR spectra were measured on a Nicolet Avatar 360 FT-IR spectrometer in a KBr disk. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCF300 superconducting Fourier digital NMR spectrometer (300 MHz) in CDCl₃. Tetramethylsilican (TMS) and the residual chloroform in CDCl₃ were used as internal references at 0.00 ppm and 7.27 ppm in ¹H NMR and 0.00 ppm and 77.5 ppm in ¹³C NMR, respectively. GPC was performed at 35 °C using THF as the eluent at a flow rate of 1.0 mL min⁻¹. The GPC instrument was equipped with a Waters 717 plus autosampler, a Waters 1515 HPLC pump, three μ-Styragel columns, and a Waters 2414 refractive index (RI) detector. The columns were calibrated using polystyrene standards in molecular weight ranges of 500–500000. TGA and DSC measurements were carried out at a heating rate of 10 °C·min⁻¹ from 20–600 °C with about a 10 mg sample on a Q600SDT (TA) and a Q1000DSC (TA) under a nitrogen atmosphere.

Results and Discussion

The FT-IR and NMR spectra (Figure 2) indicate the successful polymerization of TFEMA in scCO₂. The results are summarized in Table 1 (entry 6). As shown in Figure 2A, the strong peak of 1753 cm⁻¹ is assigned to the stretching vibration of C=O groups. In addition, the bands at 1284 and 655 cm⁻¹ are attributed to the stretching and bending vibration of C–F groups, respectively, whereas the peak at 1639 cm⁻¹, which is attributed to the stretching vibration of C=C group, disappears, indicating the exhausting of TFEMA after polymerization.

In the ¹³C NMR spectrum of PTFEMA (Figure 1B), peaks attributed to the six kinds of carbon atoms in PTFEMA are well assigned. Influenced by the spin–spin coupling of the three F atoms in the molecule, the signal of –CF₃ centered at 125 ppm is split into four peaks. The signals at 19.5 ppm and 17.8 ppm are assigned to –CH₃, attributed to the head–head and head–tail combination of TFEMA in the polymer chain, respectively.

¹H NMR spectra of TFEMA and PTFEMA are shown in Figure 3a and Figure 2C, respectively. Owing to the exhausting of C=C after polymerization, the descreening effect disappeared, resulting in a dramatic decline in chemical shift of CH₂ (vinyl end group) protons from 6.23 and 5.71 ppm to 2.17 ppm. The

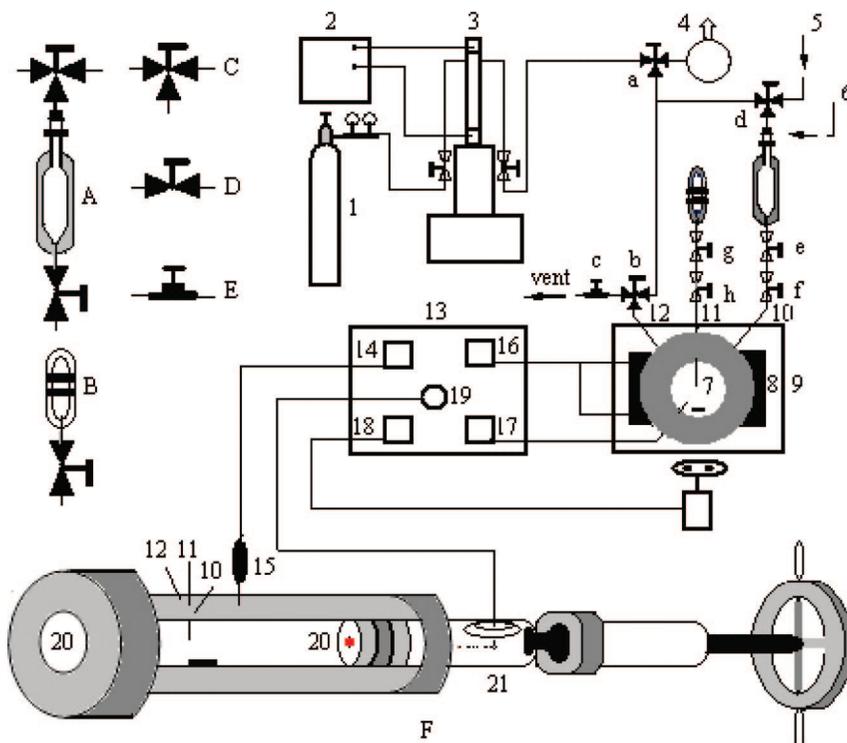
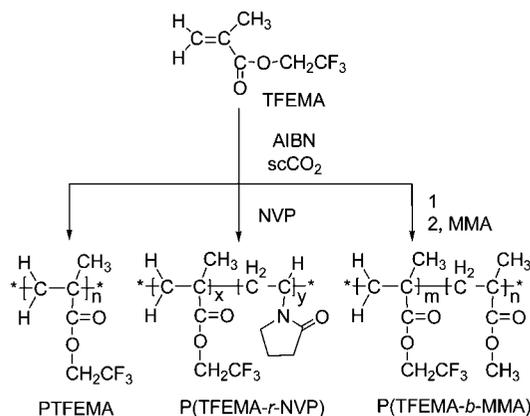


Figure 1. Schematic diagram of the experimental apparatus. 1, cylinder (CO₂); 2, cryostat; 3, syringe pump (ISCO 260D); 4, vacuum pump; 5, inlet for gaseous/liquid reactant; 6, inlet for solid reactant; 7, view cell with variable volumes; 8, heater; 9, asbestos attenuator; 10, inlet for reactants; 11, outlet for sample; 12, inlet/outlet for gases and fluid; 13, control box; 14, pressure gauge (China Academy of Aerospace Aerodynamics, model TS-5, 0.05 MPa accuracy, 0.01 MPa resolution); 15, digital pressure transducer (China Academy of Aerospace Aerodynamics, type AK-4); 16, temperature controller (WEST 6400); 17, digital thermometer; 18, magnetic stirrer; 19, light source; 20, view windows (synthesized sapphire); 21, piston. A, sample-in tube; B, sample-out tube; C, three-way valve; D, two-way valve; E, micrometering valve; F, side view of the variable volume view cell (7).

Scheme 2. Free Radical Polymerization of TFEMA in scCO₂



chemical shift of CH₃ protons also decreased, from a single peak of 2.00 ppm to double peaks of 1.09 and 0.93 ppm, attributed to the head–head and head–tail combination of TFEMA in the polymer chain. Moreover, the previous *p*– π conjugation effect in TFEMA was weakened, therefore, the chemical shift of –OCH₂CF₃ protons declined slightly from 4.62 ppm to 4.35 ppm.

Tracking the Polymerization of TFEMA. Tracking the polymerization process to monitor the conversion of monomer(s), the molecular weight and its distribution of polymer, is vital to control the quality of polymeric product in both laboratory and industrial practice. However, to the best of our knowledge, there is no report on this aspect, which limits the further application of SCFs in polymer synthesis. Thus, we developed a method for tracking the polymerization process in scCO₂ with a procedure as follows.

Table 1. Reaction Conditions and Results for Free Radical Polymerization in scCO₂^{a,b}

entry	reaction conditions		reaction results					
	Monomer(s)	time/h	feed ratio ^b	% conv. ^c	% yield ^d	ratio ^e	<i>M_n</i> , GPC	PDI ^f
1	TFEMA	6	100/1	50.6			19430	1.24
2	TFEMA	12		63.7			20944	1.28
3	TFEMA	24		83.8			19747	1.35
4	TFEMA	36		89.6			18138	1.36
5	TFEMA	48		90.5	77		19706	1.36
6	TFEMA	25	100/1	86.7	81		25619	1.32
7	TFEMA	24	100/1	^g	56		23676	1.53
8	TFEMA	24	100/1	^g	52		15294	1.62
9	TFEMA	25	100/1	^g	60		23060	1.63
10	TFEMA	36	100/100/1	94/99	87	0.9/1	39416	1.80
11	TFEMA MMA	24	100/90/1	96/99	86	1.2/1	18893 ^h	1.34 ^h
		40					28588	1.53

^a Free radical polymerization was carried out at 70 °C and 25.0 MPa: homopolymerization (entries 1–6, the tracking results were shown in entries 1–5), homopolymerization in common process^{5–8,11} (entries 7–9), copolymerization in one-step-one-pot for 36 h (entry 10), and copolymerization in two-step-one-pot for (24 + 16) h (entry 11). ^b Feed ratio was the initial molar ratio of TFEMA/AIBN in homopolymerization or TFEMA/comonomer/AIBN in copolymerization. ^c Conversion was calculated from ¹H NMR according to eq 1 before purification and was listed as TFEMA/comonomer. ^d Yield was obtained gravimetrically from the dried copolymer after purification. ^e Ratio was calculated from ¹H NMR from the dried copolymer after purification. ^f PDI was calculated according to the equation PDI = *M_w*/*M_n*, and was obtained from GPC after purification. ^g The conversion can not be detected exactly because of the unavoidable losing of monomer during the purging procedure. ^h *M_n* and PDI of the synthesized polymer sampled at 24 h before adding MMA.

First, a small portion (about 1–2.5%) of the reaction mixtures at a series of selected polymerization times was withdrawn by using a sample-out tube. Then, the conversion of monomer, the molecular weight and its distribution of the synthesized polymer at the corresponding reaction time were determined by off-line

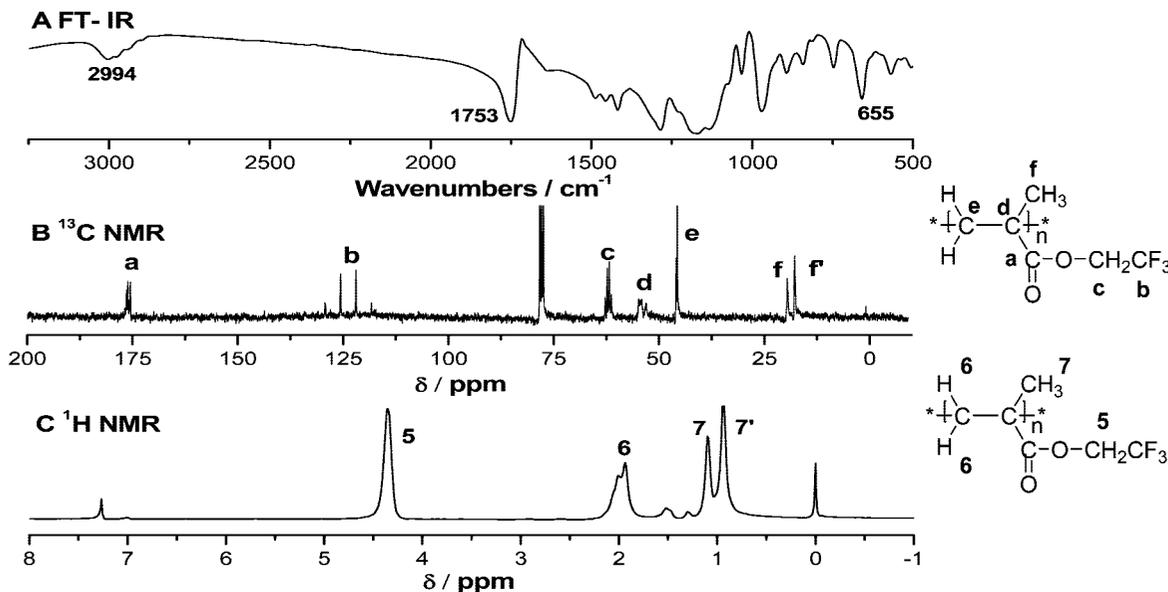


Figure 2. FT-IR (A), ^{13}C NMR (B), and ^1H NMR (C) spectra of PTFEMA synthesized at 70°C and 25.0 MPa in scCO_2 for 25 h. The molar ratio of the TFEMA and AIBN was 100:1.

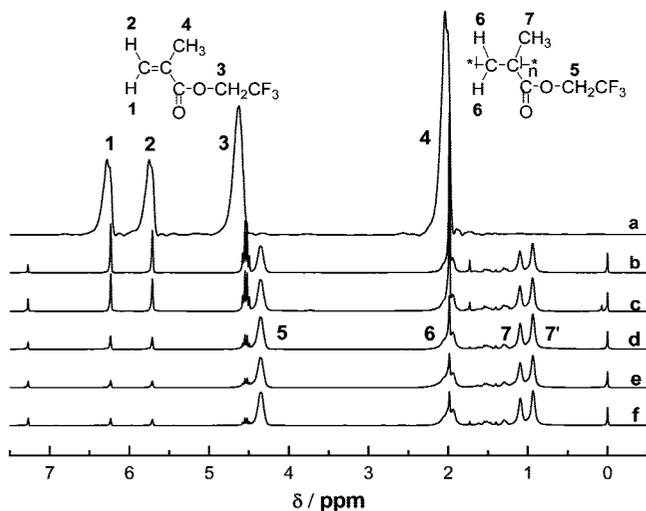


Figure 3. ^1H NMR spectra of TFEMA (a) and reaction mixture sampled from the view cell at reaction times of 6 h (b), 12 h (c), 24 h (d), 36 h (e), and 48 h (f). The polymerization was carried out at 70°C and 25.0 MPa in scCO_2 . The molar ratio of the TFEMA and AIBN was 100:1.

analysis of NMR and GPC. Finally, the polymerization process was traced by plotting the evolution curves of monomer conversion and the distribution of molecular weight. The evolution curve could be at least used to optimize the reaction time.

When a polymerization was carried out in SCFs, such as scCO_2 , the reaction medium could be removed without apparent loss of the reaction mixture after cooling the sampling tube(s) and the reactor by ice/water or dry ice/acetone and deflating slowly. Thus, the residual monomer and the synthesized polymer could be well reserved in the raw product. This could hardly be actualized when polymerization was carried out in traditional organic solvents. Additionally, the spectra (IR, NMR) of the monomer and the resulting polymer changed distinctly and regularly. Therefore, the spectrum technique, especially the qualitative and quantitative function of ^1H NMR, could be used to analyze the content and the conversion of the monomer in the raw product before purification. The ^1H NMR spectra of

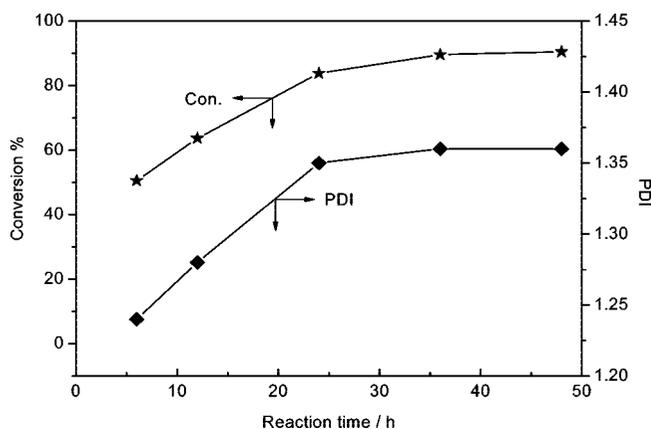


Figure 4. Conversion of TFEMA and PDI of PTFEMA synthesized in scCO_2 at 70°C and 25.0 MPa at different reaction times.

TFEMA and PTFEMA synthesized at 70°C and 25.0 MPa in scCO_2 at different reaction times are shown in Figure 3.

As shown in Figure 3, with the increase of reaction time, the signals at 6.23 and 5.71 ppm, which are assigned to the H atoms in $=\text{CH}_2$ of TFEMA, decreased gradually, while those at 4.35 ppm, assigned to CH_2 in $-\text{OCH}_2\text{CF}_3$ of PTFEMA, increased steadily. This directly illuminated the conversion from TFEMA to PTFEMA, that is, the polymerization process. The conversion of TFEMA could be calculated from ^1H NMR spectra of the raw PTFEMA product according to eq 1.

$$\text{conv}_t\% = \frac{\int(-\text{OCH}_2)_t}{\int(-\text{OCH}_2)_t + \int(=\text{CH}_2)_t} \times 100 \quad (1)$$

where $\int(-\text{OCH}_2)_t$ and $\int(=\text{CH}_2)_t$ represent the integrals of the peaks assigned to CH_2 in OCH_2CF_3 of PTFEMA and the 2 H atoms in $=\text{CH}_2$ of the residual TFEMA, respectively, at t times. $\text{Conv}_t\%$ represents the conversion of TFEMA at t time. The molecular weight and its distribution could be determined by GPC from the dried polymer after purification. The calculated conversion of TFEMA and the measured polydispersity index (PDI) are plotted versus reaction time as shown in Figure 4.

Both the monomer conversion and PDI increased with the increase of polymerization time (Figure 4). Interestingly, the

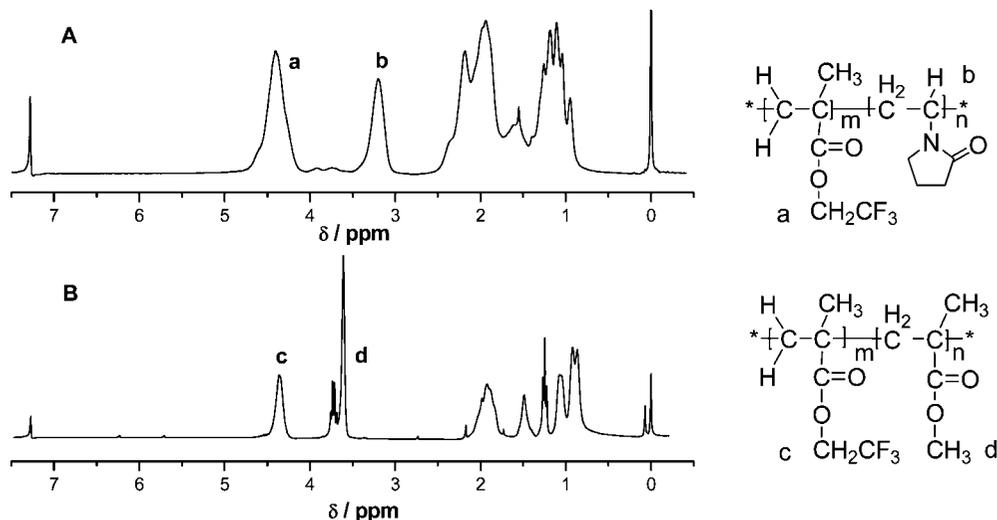


Figure 5. ^1H NMR spectra of P(TFEMA-*r*-NVP) (A) and P(TFEMA-*b*-MMA) (B).

PDI changed slightly with the further increase of TFEMA conversion by extending the reaction time from 24 to 48 h. Thus, the optimal values of conversion of TFEMA and the PDI of PTFEMA were obtained at the reaction time of 24–48 h, that is, PDI of 1.3–1.4 and monomer conversion of 80–90%. Increasing the reaction time would certainly achieve a higher monomer conversion but a lower efficiency and, probably, a broader PDI can be reasonably expected. In this way, the polymerization of TFEMA in scCO_2 was tracked. Therefore, the utilization of the sample-out tubes and the resulting reaction tracking method made the choice of reaction time feasible, reliable and relatively convenient, and can be extended to the polymerization of different monomers in SCFs. Additionally, the results of entries 3 and 6 shown in Table 1 indicate that our newly developed procedure is highly reproducible.

Copolymerization. The conditions and the results of the one-step-one-pot copolymerization of TFEMA and NVP in scCO_2 are shown in Table 1 (entry 10). In the ^1H NMR spectrum of P(TFEMA-*r*-NVP), as shown in Figure 5A, the peaks at 4.35 and 3.20 ppm are assigned to CH_2 in $-\text{OCH}_2\text{CF}_3$ of TFEMA segment and CH in $-\text{CH}(\text{N})$ of NVP segment, indicating the successful polymerization of both monomers. There is only one weight losing stage centered at 410 $^\circ\text{C}$ in TGA and DSC curves (Figure 6A), indicating the distribution of the two segments in the copolymer chain is homogeneous and no distinct phase separation. It could be confirmed that a random copolymer, P(TFEMA-*r*-NVP), was obtained.

The technique by sequentially adding different monomers is of great importance to synthesis block copolymers in CO_2 , both for cationic polymerization and atom transfer radical polymerization (ATRP), as reported in the references.^{16,17} In this work, using the sample-in tubes to add TFEMA and MMA sequentially, we also demonstrated a two-step-one-pot free radical copolymerization method to synthesize a novel diblock copolymer containing a semifluorinated block in scCO_2 . In the second step, MMA was added into the cell without any separation, isolation or other intermediate steps. The conditions and the results of the copolymerization are shown in Table 1 (entry 11). In the ^1H NMR spectrum of the synthesized copolymer (Figure 5B), the peaks at 4.35 and 3.60 ppm are attributed to $-\text{OCH}_2\text{CF}_3$ in TFEMA segment and $-\text{OCH}_3$ in MMA segment, indicating the successful polymerization of both monomers. Moreover, in the TGA and DSC analysis (Figure 6B), there are two weight losing stages centered at 290 and 390 $^\circ\text{C}$, respectively, indicating that these two segments are distributed heterogeneously in the copolymer chain and a distinct phase separation occurs.

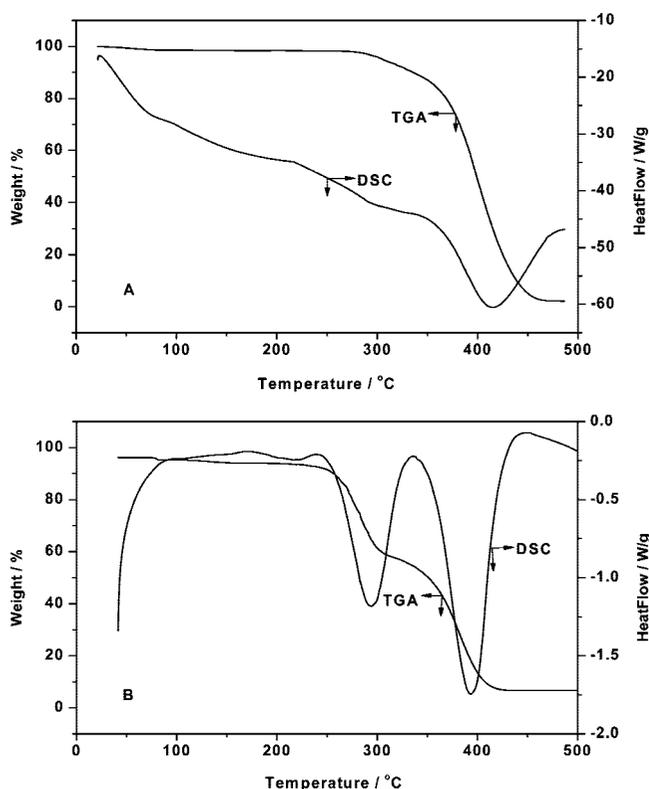


Figure 6. TGA and DSC analysis of P(TFEMA-*r*-NVP) (A) and P(TFEMA-*b*-MMA).

Comparing with the GPC results at 24 and 40 h (entry 11), M_n is found to increase dramatically, indicating further polymerization occurs after the sequential addition of MMA in the second step. It could be inferred that a diblock copolymer, P(TFEMA-*b*-MMA), was obtained. More characterization details are under taken to confirm the structure of this copolymer.

Discussion on the Newly Developed Procedure. As reported in the reference,¹¹ the PDI of TFEMA homopolymer obtained in scCO_2 was obviously lower than that synthesized in the typical organic solvents. As a matter of fact, amorphous fluorinated polymers such as PTFEMA are soluble in scCO_2 .^{6a,12} In this case, the homopolymerization of TFEMA in scCO_2 occurred in a homogeneous way. Moreover, there was no detectable chain transfer reaction to CO_2 due to its perfect inertness.⁹ Thus, these factors are responsible for the relatively

lower PDI of PTFEMA synthesized in scCO₂. By comparing the results in Table 1, under the same conditions, the PDI of PTFEMA synthesized by using our newly developed method (entries 3 and 6) is clearly lower than those by using the commonly used procedure (entries 7–9), which may be explained mainly as that the polymerization starts at the desired temperature. Moreover, the TFEMA yield in entry 6, which can be accurately measured, is much higher than those in entries 7–9 owing to the unavoidable losing of monomer during the purging procedure. Thus, in comparison with the commonly used procedure for the polymerization reaction in SCFs, our newly developed method showed a lower PDI together with accurately measured monomer conversion and polymer yield. In our newly developed process, volatile reactant(s) was charged after purging the reactor, avoiding the losing of monomer(s) and minimizing the pollution to the environment.

Conclusions

A new process for synthesizing fluorinated polymers in scCO₂ was exploited by improving the polymerization apparatus and modifying the reaction system. The polymerization was effectively tracked in scCO₂ in this improved process. Fluorinated polymers were successfully synthesized in scCO₂ by using the sampling tube(s) with a relative lower PDI, higher conversion, and higher yield. It also indicated that diblock copolymers could be synthesized in a two-step-one-pot copolymerization using the sampling tubes and a sequential monomer addition technique to add the second needed monomer.

This improved process, which was originally targeted for the laboratory investigation on polymerization in SCFs, can also be viewed as a model of industrial production of fluorinated polymer(s) in SCFs and are expected to upgrade the quality of resultant polymeric products. The further improvement and application of this new process in scCO₂ and other SCFs to synthesize novel polymers, especially some fluorinated block copolymers, is still going on, and will be presented later.

Acknowledgment. The authors gratefully acknowledge the financial support of the Specialized Research Fund for the Doctoral Program of Higher Education (20070718003) and the Natural Science Foundation of Shaanxi Province (2007B07).

Supporting Information Available: The relationship between PDI and the molecular weight of PTFEMA and the impact of pressure on TFEMA conversion and PTFEMA molecular weight. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA800193V