Synthesis and Characterization of a Novel Perfluorocyclobutyl Aromatic Ether-Based ABA Triblock Copolymer

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ABSTRACT: A novel perfluorocyclobutyl aromatic ether-based ABA triblock copolymer (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block) was synthesized by combination of atom transfer radical polymerization (ATRP) of styrene and thermal step-growth cycloaddition polymerization of trifluorovinyl monomer. We first synthesized a new ATRP initiator containing the trifluorovinyl group, which can initiate ATRP of styrene in a controlled way to obtain well-defined polystyrene with narrow molecular weight distribution (M_w/M_n < 1.10). The apparent polymerization rate exhibited first-order relation with respect to the concentration of monomer and the molecular weight increases linearly with the conversion of monomer. Second, fluoropolymer containing a perfluorocyclobutyl aromatic ether unit was prepared by solution polymerization and followed by reacting with ATRP initiator containing a trifluorovinyl group to get ATRP macroinitiator with two initiation groups at both ends. The macroinitiator-initiated ATRP of styrene to obtain ABA triblock copolymer. The copolymer shows excellent solubility in conventional solvents.

Introduction

It is well-known that fluoropolymers have many advantages compared with general commercial polymers only containing carbon, hydrogen, and oxygen due to the incorporation of fluorocarbon functionality, including increased thermal and oxidative stability, optical transparency, solvent compatibility, environmental stability, etc.[1] So the application of fluoropolymers with high performance have taken on great significance in recent years. However, low processability limited the use of fluoroplymers.[2] Recently, some scientists of The Dow Chemical Co. obtained fluoropolymers containing perfluorocyclobutane (PFCB) linkage by step-growth cycloaddition polymerization of aryl trifluorovinyl ether monomers.[3]

PFCB polymers have the conventional properties of fluoropolymer such as low dielectric constant, low moisture absorption, low surface energy, high thermal/oxidative stability, and high chemical resistance, also possessing many other advantages including optical transparency, improved processability, and thermal mechanical properties.[4−6] PFCB aromatic ether polymers are generally synthesized by step-growth cycloaddition polymerization of trifluorovinyl monomers in bulk or solution above 150 °C without any initiator and catalyst. Recent studies of PFCB polymers focused on the use of the thermal polymerization of different aryl trifluorovinyl ether monomers to obtain different homopolymers and random copolymers containing PFCB aromatic ether linkage.[7−9] Monomers containing two trifluorovinyl groups were synthesized from commercially available raw materials, such as 1,3-dihydroxybenzene, 4,4′-biphenol, and 2,2-bis(*p*-hydroxyphenyl)perfluoropropane, and were polymerized to form different PFCB thermoplastic polymers. Also, thermoset PFCB polymers were prepared from the monomers containing three trifluorovinyl groups, which were also synthesized from 1,3,5-trihydroxybenzene and 1,1,1-tri(4-hydroxyphenyl)ethane. So the synthesis strategy using PFCB combined the flexible, yet thermally robust, aromatic ethers with fluorocarbon linkage, thereby providing fluoropolymers which are easily processed from solution or melt.

Because of much higher polymerization temperature (>150 °C) and much different polymerization mechanism ([2 + 2] cycloaddition) without any initiator compared with those of common used monomers, polymer chemists only studied the homopolymerization and random copolymerization of different trifluorovinyl monomers. Research about combining trifluorovinyl monomer and common used monomer (styrene, acrylate, etc.) into block copolymer has never been reported until now. So the application of PFCB fluoropolymers has been obviously limited.

Generally, two strategies have been employed to synthesis block copolymer: sequential feeding of different monomers through living polymerization, including anionic polymerization,[10] cationic polymerization,[11] group transfer polymerization,[12] living radical polymerization,[13] etc.; also mechanism transformation strategy[14] was used to synthesize block copolymers containing the blocks with different polymerization mechanisms. Because the polymerization mechanism of trifluorovinyl monomer is entirely different from the common used monomer, only mechanism transformation strategy can be used to prepare block copolymer from trifluorovinyl monomer and the common used monomer.

In this paper, we reported the synthesis of a novel perfluorocyclobutyl aromatic ether-based ABA triblock copolymer **1** (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block) (Scheme 1) through mechanism transform strategy. This kind of triblock copolymer is the first example of block copoly-

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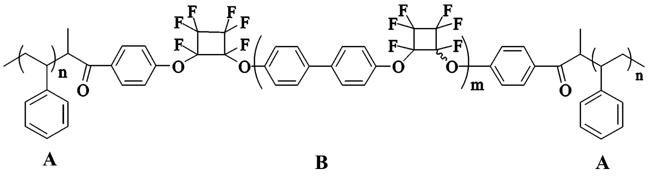
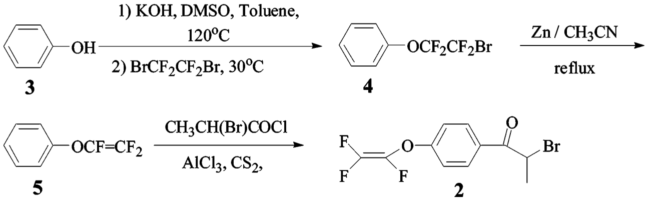
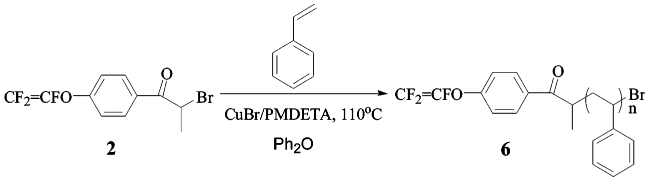
Scheme 1. ABA Triblock Copolymer 1



Scheme 2. Synthesis of ATRP Initiator 2



Scheme 3. Synthesis of Model Polystyrene 6



mer containing perfluorocyclobutyl aromatic ether unit. All compounds in this paper were characterized by FT-IR, GPC, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS, and element analysis in detail.

Experimental Section

Materials. Styrene (St, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove inhibitor and then with water, dried with $MgSO_4$, and distilled twice over CaH_2 under reduced pressure before use. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying at 40 °C under vacuum for 1 day. 4,4′-Biphenol (97%) was purchased from Aldrich and purified by recrystallization before use. 1,2-Dibromotetrafluoroethane was prepared by condensing equimolar amounts of bromine and tetrafluoroethylene at −195 °C followed by warming up to 22 °C.[15] Granular zinc was activated by washing in 0.1 N HCl followed by drying at 140 °C under vacuum for 10 h. Phenol (Aldrich, 99+%), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and 2-bromopropionyl chloride (Acros, 98%) were used as received.

Measurements. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. ^{1}H NMR and ^{13}C NMR were performed on a Varian Mercury 300 spectrometer (300 MHz). ^{19}F NMR was collected on a Bruker AM-300 spectrometer using trifluoroacetic acid as external standard. ESI-MS were measured by an Agilent LC/MSD SL system. Relative molecular weights and molecular weight distributions (M_w/M_n) were measured by a Waters gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual λ absorbance detector (UV), and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using tetrahydrofuran (THF) as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Elemental analysis was carried out on a Carlo-Erba1106 system. Monomer conversion was determined by GC using a HP 6890 system with an SE-54 column.

ATRP Initiator 2. ATRP initiator **2** was synthesized according to Scheme 2 by three steps using phenol as starting material. Synthesis of (1,2,2-trifluorovinyloxy)benzene (**5**) was similar to those reported procedures in previous literature.[16] The yield is 47.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.09 (d, J = 8.4 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −120.5 (dd, 1F), −127.2 (dd, 1F), −134.2 (dd, 1F). Anal. Calcd for $C_8H_5F_3O$: C, 55.18%; H, 2.89%. Found: C, 55.15%; H, 2.90%. ESI-MS (*m/z*): calcd 174.1; found 174.0.

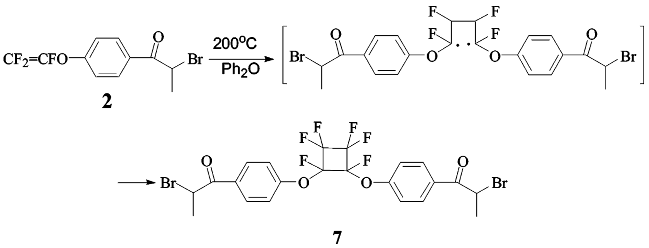
To a 250 mL dried three-neck round-bottom flask fitted with a condenser and a thermometer, (1,2,2-trifluorovinyloxy)-benzene (**5**) (3.2665 g, 18.8 mmol) and carbon disulfide (CS_2) (50 mL) were added under a N_2 atmosphere followed by adding 2-bromopropionyl chloride (2.2 mL, 3.74 g, 21.8 mmol) and aluminum chloride ($AlCl_3$) (3.1268 g, 23.4 mmol). The solution was heated to reflux for 8 h, then the flask was cooled to 0 °C, and granular ice was added to terminate the reaction. 1 N HCl (80 mL) was added, and the organic layer was separated. The organic layer was washed by brine (50 mL × 3) followed by drying over $MgSO_4$. A straw yellow solid, ATRP initiator **2**, 2-bromo-1-(*p*-trifluorovinyloxy)phenylpropan-1-one (2.5566 g, 44.0%), was obtained by silica column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.89 (d, J = 6.3 Hz, 3H), 5.24 (q, J = 6.6 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.0 (dd, 1F), −125.6 (dd, 1F), −135.0 (dd, 1F). ^{13}C NMR (300 MHz, acetone-d_6): δ (ppm): 20.2 ($-CH_3$), 42.9 ($-C$HBr), 116.5, 129.7, 132.0, 132.4, 129.7−136.3 ($-CF{=}CF_2$), 143.9−152.0 ($-CF{=}CF_2$), 159.0, 192.0 ($-C{=}O$). FT-IR (KBr): ν (cm^{-1}): 3023, 2983, 2923, 1835 ($OCF{=}CF_2$), 1689, 1601, 1505, 847. Anal. Calcd for $C_{11}H_8F_3BrO_2$: C, 42.75%; H, 2.61%; F, 18.44%; Br, 25.85%. Found: C, 42.79%; H, 2.64%; F, 18.59%; Br, 25.77%. ESI-MS (*m/z*): calcd 309.1; found 309.2.

Model Polystyrene 6 Initiated by 2. ATRP of styrene can be initiated by **2** (Scheme 3) to get polystyrene with narrow molecular weight distribution. A typical procedure of synthesis of model polystyrene **6** by bulk polymerization is listed as follows: to a 25 mL Schlenk flask (flame-dried under vacuum just before use) sealed with a rubber septum, CuBr (0.1342 g, 0.936 mmol) was charged under a N_2 atmosphere. After three cycles of evacuating and backfilling with N_2, styrene (10 mL, 87.0 mmol), PMDETA (0.196 mL, 0.939 mmol), and **2** (0.2889 g, 0.935 mmol) were introduced via a gastight syringe followed by three cycles of freezing−pumping−thawing. The mixture was stirred at room temperature for 30 min so that the mixture became homogeneous. The flask was placed in an oil bath at 110 °C for polymerization. The polymerization was quenched by immersing the flask in liquid N_2 after 8 h. THF was added to dissolve the viscous crude product, and the solution was filtered through a short Al_2O_3 column to remove the catalyst. The resulting solution was concentrated and precipitated in methanol. The solid was purified by three times of dissolution and precipitation, followed by drying under vacuum to obtain 7.9261 g of polystyrene of 87.5% yield, M_n = 15 100, M_w/M_n = 1.12. FT-IR (KBr): ν (cm^{-1}): 3025, 2983, 2923, 1601, 1493, 1452, 757, 698.

ATRP Kinetics. ATRP kinetics of styrene initiated by **2** was studied in solution polymerization using diphenyl ether as solvent.[17] CuBr (0.0824 g, 0.575 mmol) and diphenyl ether (10 mL) were charged to a 25 mL Schlenk flask sealed with a rubber septum under a N_2 atmosphere. After three cycles of evacuating and backfilling with N_2, styrene (5 mL, 43.5 mmol), PMDETA (0.12 mL, 0.575 mmol), and ATRP initiator **2** (0.1778 g, 0.575 mmol) were introduced via a gastight syringe followed by three cycles of freezing−pumping−thawing. The mixture was stirred at room temperature for 30 min until the mixture became homogeneous. Then, the first sample taken as a time = 0 data point was obtained by withdrawing 0.50 mL of solution from the flask using a purged syringe and adding to 2.00 mL of THF. The flask was immersed into an oil bath at 110 °C. At every time interval (1.0 h), a 0.50 mL sample solution was taken and added to 2.00 mL of THF.

Every sample solution in THF taken at different time was injected into GC to determine the monomer conversion compared with the time = 0 data point. The remaining solution was filtered through a short Al_2O_3 column to remove the catalyst and then used for GPC measurement to determine the molecular weight and molecular weight distribution.

Scheme 4. Synthesis of Model Dimer 7



Model Dimer 7. Model dimer **7** was synthesized through intramolecular [2 + 2] cycloaddition of the trifluorovinyl ether group of ATRP initiator **2** (Scheme 4).

To a 10 mL predried Schlenk flask, ATRP initiator **2** (0.3740 g, 1.21 mmol) and diphenyl ether (1.50 mL) were added under a N_2 atmosphere followed by three cycles of freezing−pumping−thawing. The solution was heated at 200 °C for 6 h. The reaction was quenched by immersing the flask in liquid N_2. Model dimer **7** (0.3180 g, 85.0%), a light yellow liquid, was obtained by silica column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.90 (d, J = 6.6 Hz, 6H), 5.23 (q, J = 6.3 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 8.07 (t, J = 8.4 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −127.2 to −132.8 (m, cyclobutyl-F_6). ^{13}C NMR (300 MHz, acetone-d_6): δ (ppm): 20.0 ($-C$H$_3$), 42.2 ($-C$HBr), 105.0−115.2 (m, cyclobutyl), 116.5, 129.7, 132.0, 132.4, 159.0, 191.7 ($-C$=O). λ_{max} = 327 nm. Anal. Calcd for $C_{22}H_{16}F_6Br_2O_4$: C, 42.75%; H, 2.61%. Found: C, 42.82%; H, 2.57%. ESI-MS (*m/z*): calcd 618.2; found 618.3.

Trifluorovinyl Monomer 8. Trifluorovinyl monomer **8**, 4,4′-bis(trifluorovinyloxy)biphenyl, was synthesized according to Scheme 5. The procedure was similar to those of previous literature.[18] The product was separated by column chromatography with a yield of 42.8%. Next, it was purified by recrystallization from ethanol/water to obtain the trifluorovinyl monomer **8** of 99.8% purity measured by GC. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.19 (d, J = 9.0 Hz, 4H), 7.55 (d, J = 8.7 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.8 (dd, 2F), −126.8 (dd, 2F), −134.3 (dd, 2F). Anal. Calcd for $C_{16}H_8F_6O_2$: C, 55.50%; H, 2.33%. Found: C, 55.47%; H, 2.30%. ESI-MS (*m/z*): calcd 346.2; found 346.3.

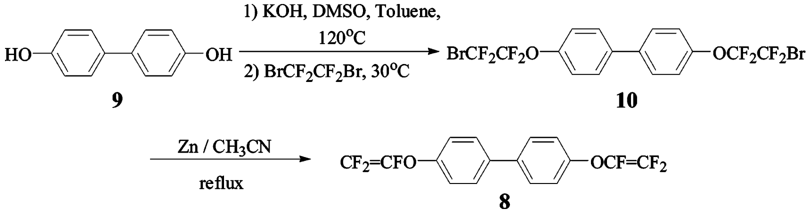
ATRP Macroinitiator 11. ATRP macroinitiator **11** was synthesized through intramolecular [2 + 2] cycloaddition of the trifluorovinyl ether group of ATRP initiator **2** and the trifluorovinyl ether end group of propagating chain of poly(4,4′-bis(trifluorovinyloxy)biphenyl) at both ends (Scheme 6).

A typical procedure of synthesis of ATRP macroinitiator **11** is listed as follows: To a predried 25 mL Schlenk flask sealed with a rubber septum, trifluorovinyl monomer **8** (4.0855 g, 11.8 mmol) and diphenyl ether (6 mL) were added under a N_2 atmosphere and followed by three cycles of freezing−pumping−thawing. The flask was placed in an oil bath at 200 °C for polymerization. After 4 h, ATRP initiator **2** (3.9000 g, 12.6 mmol) in 5 mL of diphenyl ether was charged using a gastight syringe. The reaction lasted for another 6 h and was quenched by immersing the flask in liquid N_2. Dichloromethane (20 mL) was added to dilute the solution, and the solution was added to 300 mL of methanol to precipitate the solid product. The crude product was purified by three times of dissolution and precipitation to separate any possible dimer **7**, followed by drying under vacuum to obtain 7.2395 g of solid. M_n = 7500, M_w/M_n = 1.31, Br% = 2.18%. FT-IR (KBr): ν (cm^{-1}) 1693 ($-$C=O), 1607, 1497, 962, 824.

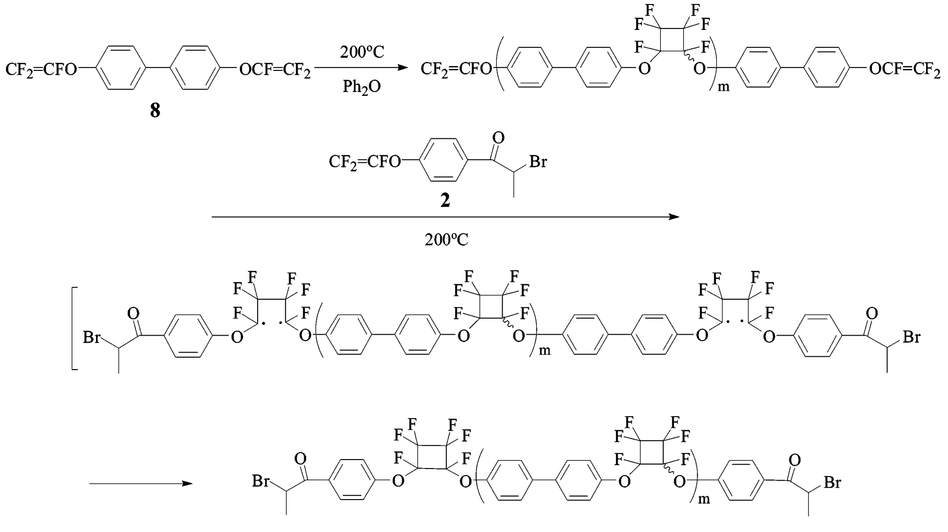
ABA Triblock Copolymer 1. Perfluorocyclobutyl aromatic ether-based ABA triblock copolymer **1** (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block) was synthesized by ATRP of styrene initiated by ATRP macroinitiator **11** (Scheme 7).

The procedure of synthesis of ABA triblock copolymer initiated by **11** is similar to that of synthesis of model polystyrene initiated by **2**: ATRP macroinitiator **11** and CuBr were added to a 25 mL Schlenk flask (flame-dried under vacuum just before use) sealed with a rubber septum under a N_2 atmosphere. After three cycles of evacuating and backfilling with N_2, styrene, PMDETA, and diphenyl ether were introduced via a gastight syringe followed by three cycles of freezing−pumping−thawing. The mixture was stirred at room temperature for 10 min so that the mixture became homoge-

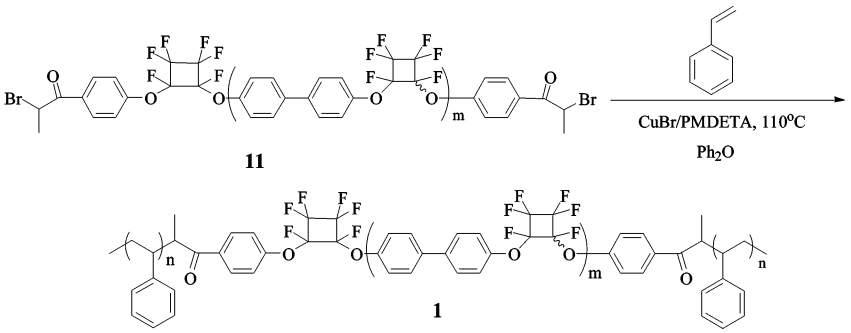
Scheme 5. Synthesis of Trifluorovinyl Monomer 8



Scheme 6. Synthesis of ATRP Macroinitiator 11



Scheme 7. Synthesis of ABA Triblock Copolymer 1



neous. The flask was placed in an oil bath at 110 °C for polymerization. The polymerization was quenched by immersing the flask in liquid N_2 after 6 h. THF was added to dilute the solution, and the solution was filtered through a short Al_2O_3 column to remove the catalyst. The resulting solution was concentrated and precipitated in methanol. The solid was purified by three times of dissolution and precipitation, followed by drying under vacuum.

Results and Discussion

ATRP of Styrene Initiated by 2. We used the traditional method to synthesize compound **5** containing trifluorovinyl in two steps from commercially available phenol via fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn-mediated elimination.[19,20] Next, the ATRP initiation group $-COCHBrCH_3$ was introduced by Friedel−Crafts reaction so that compound **5** was transformed into ATRP initiator **2** with trifluorovinyl.

Compound **2** initiated the polymerization of styrene to obtain model polystyrene **6** with narrow molecular weight distribution. Model polystyrene **6** was characterized by ^{1}H NMR and ^{19}F NMR. As shown in Figure 1A, we can find the typical ^{1}H NMR signals of polystyrene: the peaks at 6.60 and 7.09 ppm attributed to the benzene ring of polystyrene and the peaks at 1.45 and 1.84 ppm attributed to the $-CH_2-$ and $-CH-$ units of polystyrene. We also can find a minor peak at 4.40 ppm, the signal of $-C\mathit{H}Br$ end group of polystyrene, and a peak at 0.90 ppm, the signal of methyl of $-COCH(C\mathit{H}_3)-PS$. Figure 1B depicts its ^{19}F NMR spectrum of model polystyrene **6** in $CDCl_3$; the resonance signals of the $-OCF{=}CF_2$ group appeared, including −117.6, −124.3, and −134.3 ppm. We also found that model polystyrene **6** ($M_n = 15\,100$, $M_w/M_n = 1.12$) comprised 0.35% of fluorine and 0.42% of bromine determined by titration. All these evidences confirmed that model polystyrene **6** was initiated by **2** and contained a trifluorovinyl end group.

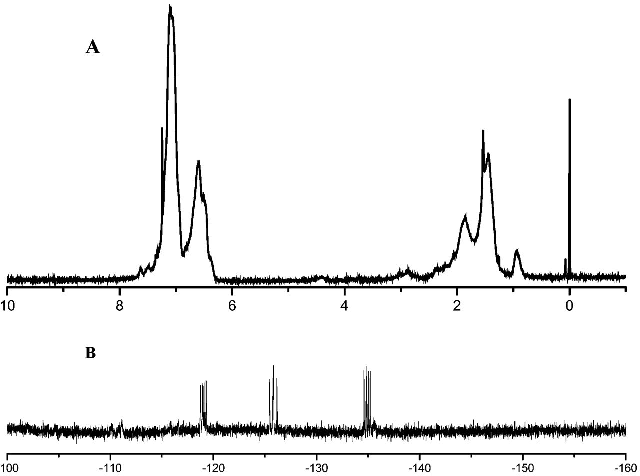


Figure 1. ^{1}H NMR (A) and ^{19}F NMR (B) of model polystyrene **6** in $CDCl_3$.

To make sure whether the polymerization of styrene initiated by **2** is atom transfer radical polymerization, we studied polymerization kinetics by GC to obtain a semilogarithmic plot of $\ln([M]_0/[M])$ vs time (Figure 2). From Figure 2, we can conclude that the apparent polymerization rate is first order with respect to the monomer concentration, which is same as the common ATRP. The apparent rate coefficient ($k_{app} = 7.3 \times 10^{-5}$ s^{-1}) is determined from the slope of the kinetic plot.

The evolution of molecular weights and molecular weight distributions with monomer conversion is shown in Figure 3. It is obvious that molecular weights increase linearly with monomer conversion and are very close to the expected molecular weights (solid line in Figure 3). Also, the molecular weight distributions remained low throughout the polymerization ($M_w/M_n <$ 1.15). These two phenomena also accord with the characteristics of ATRP.

So we can confirm that ATRP of styrene can be initiated by **2** to obtain polystyrene containing trifluorovinyl end group with narrow molecular weight distribution.

Synthesis and Characterization of Macroinitiator. Since we must employ a mechanism transformation

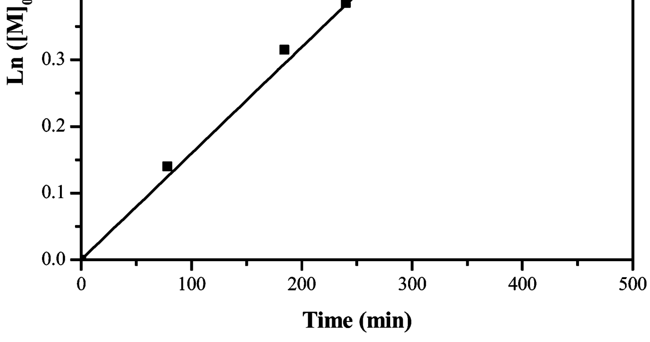


Figure 2. Kinetic plot for solution ATRP of styrene initiated by **2** at 110 °C: $[styrene]_0 = 4.35$ M, $[CuBr]_0 = [PMDETA]_0 = [initiator]_0 = 0.0575$ M, $k_{app} = 7.3 \times 10^{-5}$ s^{-1}.

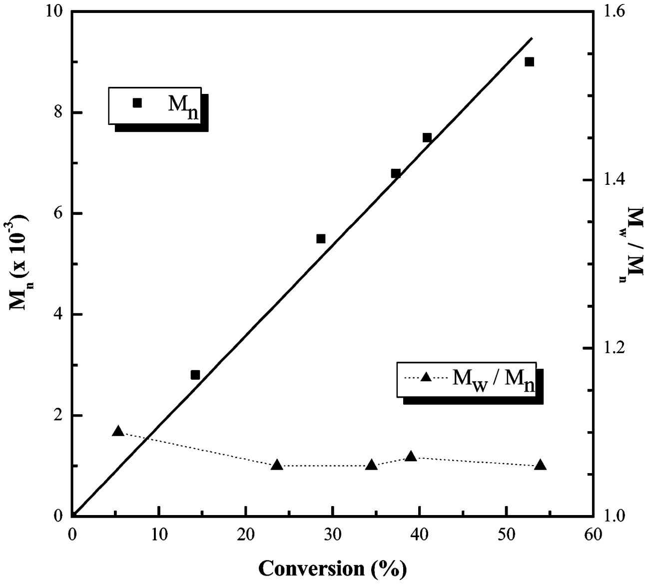


Figure 3. Dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) on monomer conversion for solution ATRP of styrene initiated by **2** at 110 °C: $[\text{styrene}]_0 = 4.35$ M, $[\text{CuBr}]_0 = [\text{PMDETA}]_0 = [\text{initiator}]_0 = 0.0575$ M.

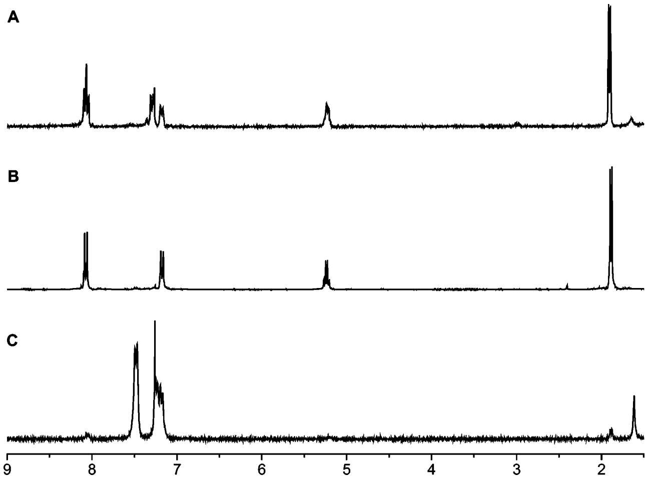


Figure 4. ^{1}H NMR of model dimer **7** (A), ATRP initiator **2** (B), and macroinitiator **11** (C) in $CDCl_3$.

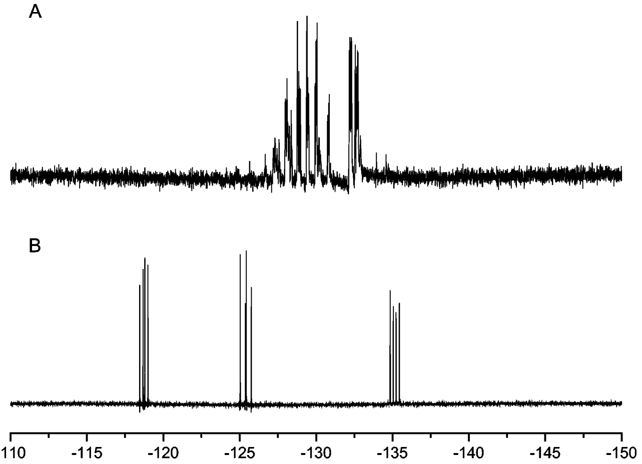


Figure 5. ^{19}F NMR of model dimer **7** (A) and ATRP initiator **2** (B) in $CDCl_3$.

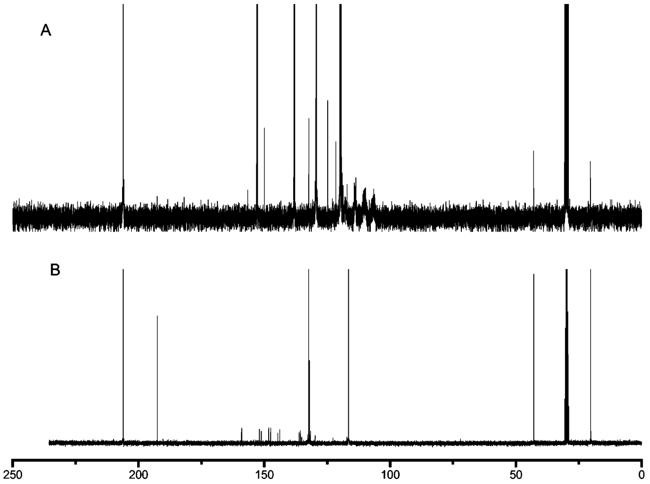


Figure 6. ^{13}C NMR of macroinitiator **11** (A) and ATRP initiator **2** (B) in acetone-d_6.

strategy to synthesize perfluorocyclobutyl aromatic ether-based ABA triblock copolymer (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block), we need to synthesize perfluorocyclobutyl aromatic ether-based prepolymer with ATRP initiation groups at both ends, which can initiate ATRP of styrene to obtain the polymer we desired. We designed the synthesis route as shown in Scheme 6, so the key points are whether the ATRP initiation groups of compound **2** are stable at a high temperature (200 °C) for some time and whether the trifluorovinyl of compound **2** can react with the trifluorovinyl of propagating chain at both ends. The easiest way to get answers is to run model reaction of compound **2** by heating at 200 °C for 6 h. We obtained a dimeric product **7** containing two ATRP initiation groups at both ends and perfluorocyclobutyl with high yield (85.0%). The dimeric product **7** was characterized by ^{1}H NMR and ^{19}F NMR. Figure 4A shows the ^{1}H NMR spectrum of model dimer **7**; the peaks of $-COCH(CH_3)-Br$ and $-COCH(CH_3)-Br$ and the protons of benzene ring close to the carbonyl appeared at 1.90, 5.23, and 8.07 ppm, which are same as those of ATRP initiator **2** shown in Figure 4B. We also find two peaks at 7.18 and 7.30 ppm attributed to other protons of benzene ring close to the perfluorocyclobutyl. Figure 5A depicts the ^{19}F NMR spectrum of model dimer **7**. A series of peaks between −127.2 and −132.8 ppm appeared which denoted perfluorocyclobutyl; compared with the ^{19}F NMR spectrum of ATRP initiator **2** shown in Figure 5B, we cannot find the resonance signals of trifluorovinyl including −119.0, −125.6, and −134.3 ppm. So we can confirm that ATRP initiation group, $-COCH(CH_3)-Br$, is stable at 200 °C, and the trifluorovinyl of compound **2** is easy to run intermolecular [2 + 2] cycloaddition to form perfluorocyclobutyl by heating.

Next, we synthesized ATRP macroinitiator **11** with two initiation groups at both ends by reacting ATRP initiator **2** with propagating chain of trifluorovinyl monomer **8** according to Scheme 6. Its chemistry structure was confirmed by ^{1}H NMR and ^{13}C NMR. As shown in Figure 4C, we still find the minor peaks of $-COCH(CH_3)-Br$, $-COCH(CH_3)-Br$, and the protons of benzene ring close to the carbonyl at both ends at 1.88, 5.21, and 8.05 ppm, which are the same as those of ATRP initiator **2**. We also find two new strong peaks at 7.21 and 7.48 ppm attributed to the protons of benzene ring of 4,4′-biphenylene perfluorocyclobutyl ether repeating unit. Figure 6A displays the ^{13}C NMR spectrum of ATRP macroinitiator **11** in acetone-d_6; the

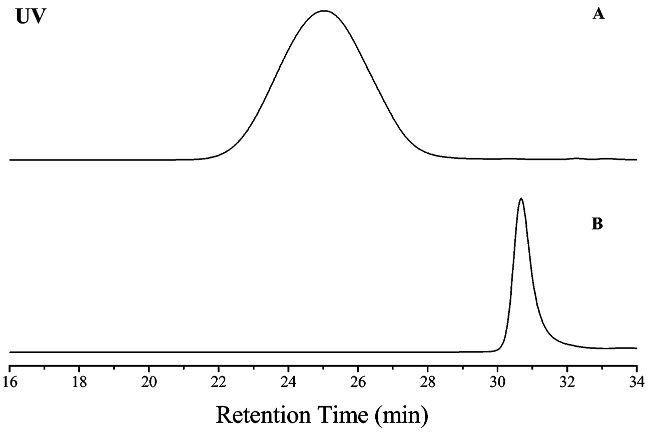


Figure 7. GPC curve of macroinitiator **11** (A) and model dimer **7** (B).

Table 1. Synthesis of ABA Triblock Copolymers 1 by Solution Polymerization[a]

run	[M]:[I][b]	time (h)	temp (°C)	M_n (g/mol)[c]	M_w/M_n[c]
1	100:1	8	110	8 300	1.34
2	300:1	8	110	8 900	1.29
3	300:1	17	110	15 500	1.27
4	300:1	48	110	17 900	1.24

[a] Macroinitiator: $M_n = 7500$, $M_w/M_n = 1.31$, Br = 2.18%. [b] The ratio of the moles of monomer and ATRP initiation group. [c] Measured by GPC under 35 °C.

peaks at 20.0, 43.0, and 192.0 ppm are attributed to $-CH_3$, $-CHBr$, and $-C{=}O$, which are the same as those of ATRP initiator **2** shown in Figure 6B. A series of new peaks between 105.0 and 115.0 ppm appeared, which are typical signals of perfluorocyclobutyl. To make sure whether dimer **7** was separated from macroinitiator **11** after repeated dissolution and precipitation, GPC measurement was run using a UV detector, and the detection wavelength was set at 327 nm. Only one peak appeared in the GPC curve (Figure 7A) of macroinitiator **11** (M_n = 7500), and we cannot find any peak in the area of lower molecular weight compared with that of dimer **7** (Figure 7B). This means we obtained a pure macroinitiator **11** without any dimer **7**. FT-IR assured the presence of $-C{=}O$ at 1693 cm^{-1}. Also, the titration result demonstrated that 2.18% of Br existed in the reaction product (M_n = 7500, M_w/M_n = 1.31) of ATRP initiator **2** with propagating chain of trifluorovinyl monomer **8**, and the titration result is identical with the theory value (2 × 80/7500 = 2.13%). Now, we can make sure that we successfully synthesized perfluorocyclobutyl aromatic ether-based macroinitiator with two ATRP initiation groups at both ends.

Synthesis and Characterization of ABA Triblock Copolymer. A series of ABA triblock copolymers were prepared under different polymerization conditions. The polymerization results are listed in Table 1. We can find that all products' molecular weights are higher than that of macroinitiator, which means styrene is initiated for polymerization. It is obvious that the molecular weight increases with lifting of polymerization time and feed ratio. This is a typical phenomenon of ATRP.

The polymerization products were characterized by ^1H NMR and FT-IR. Figure 8 presents a ^1H NMR spectrum of the polymerization product in acetone-d_6, the peaks at 7.14 and 7.50 ppm are attributed to the protons of benzene ring of 4,4′-biphenylene perfluorocyclobutyl ether repeating unit, and the typical signals of polystyrene appeared at 1.43 ($-CH_2-$), 1.79 ($-CH-$), and 6.53, 6.93 ppm (benzene ring). The polymerization product was also characterized by FT-IR to find a sharp band at 962 cm^{-1} attributed to perfluorocyclobutyl unit, and the typical signals of polystyrene segment appeared at 3026, 2924, 2850, 1603, 1495, and 1453 cm^{-1}. Also, the sharp band at 825 cm^{-1} demonstrated the para-disubstituted benzene ring of the PFCB block; other two sharp peaks at 698 and 757 cm^{-1} confirmed the mono-substituted benzene ring of polystyrene block.

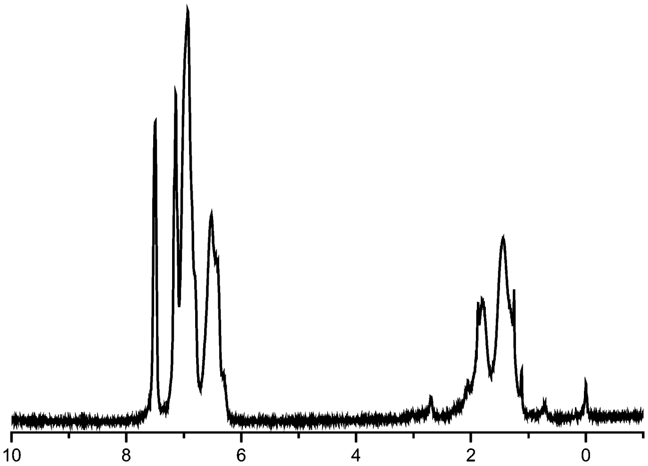


Figure 8. ^1H NMR of ABA triblock copolymer **1** in acetone-d_6.

All these evidence confirmed the synthesis of ABA triblock copolymer **1** (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block).

Solubility Tests. Solubility tests were performed for ABA triblock copolymer **1** with different molecular weights in four conventional solvents with low boiling point: tetrahydrofuran, chloroform, dichloromethane, and acetone. The results indicated that ABA triblock copolymer **1** exhibits excellent solubility in the above four solvents.

Conclusion

A new ATRP initiator containing a trifluorovinyl group, which can initiate ATRP of styrene in a controlled way to obtain well-defined polystyrene with narrow molecular weight distribution ($M_w/M_n < 1.10$), was synthesized. Next, a novel perfluorocyclobutyl aromatic ether-based ABA triblock copolymer (A: polystyrene block; B: perfluorocyclobutyl aromatic ether-based fluoropolymer block) was synthesized by combination of atom transfer radical polymerization of styrene and thermal step-growth cycloaddition polymerization of trifluorovinyl monomer. The copolymer shows excellent solubility in conventional solvents.

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