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A novel semi-fluorinated graft copolymer containing perfluorocyclobutyl aryl ether-based backbone

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ABSTRACT

The synthesis of a series of novel semi-fluorinated graft copolymers bearing perfluorocyclobutyl (PFCB) aryl ether-based backbone and polystyrene side chains is described. This work initially focused on the synthesis of a trifluorovinyl ether (TFVE) monomer containing a bromine atom, which could be employed as an initiating site for atom transfer radical polymerization (ATRP). Thermal cyclopolymerization of this TFVE monomer provided a macromolecular initiator followed by subsequent initiating ATRP of styrene to afford the desired PFCB aryl ether-based graft copolymers.

1. Introduction

The incorporation of fluorine into polymers for advanced materials continues to be attractive in recent decades because of the unique properties of fluorinated polymers [1]. In particular, partially fluorinated polymers exhibit dramatic and tailorable changing in property with controlled incorporation of fluorine. Perfluorocyclobutyl (PFCB) aryl ether polymers are a class of amorphous partially fluorinated polymers which not only provide the conventional properties of fluoropolymer such as high thermal and thermal oxidative stability, chemical resistance, but also possess many other advantages including optical transparency and improved processability; thus, they can be applied in optics, aerospace coatings, and battery electrolyte [2–5].

PFCB aryl ether polymers are generally prepared by thermal [2π + 2π] cycloaddition polymerization of trifluorovinyl ether (TFVE) monomers above 150 °C in bulk or in solution without any initiator or catalyst as shown in Scheme 1. TFVE monomers are stable and may be synthesized from a variety of commercially available phenols. Alternatively, a variety of TFVE monomers have been synthesized via the intermediate strategy [6–8]. This methodology has worked well for incorporating functionality into the monomers. However, this technology is currently still restricted by the cost and availability. Direct polymerization of functional TFVE monomers only offers limited possibility of PFCB aryl ether homopolymers. Meanwhile, the relatively high polymerization temperature (>150 °C) makes it difficult for the copolymerization of commonly used monomers (styrene, acrylate, etc.) with TFVE monomers. Thus, the application of PFCB aryl ether polymers has been obviously confined.

For enlarging its application range, it is significant to combine the high performance of PFCB aryl ether polymer with other commercial polymers. Recently, a few examples of modified PFCB aryl ether-based block copolymers have been reported [9–12]. Graft copolymers with a stable covalent-bonded linkage between the backbone and side chains may be also a good choice. Graft copolymers offer the unique possibility of tailoring materials properties through their numerous structural variables that can be modified such as composition and density of the grafts [13–15]. Properties such as morphology, order–disorder transitions, phase behavior and compatibility with other polymers can be greatly changed by post-modification of the backbone of fluoropolymers. Depending on the nature of the copolymer, graft polymers may possess specific properties while retaining the desirable properties of the parent fluoropolymers.

The synthesis of graft fluoropolymers, however, can still pose a significant challenge. Generally, three strategies including grafting-through, grafting-onto, and grafting-from were used for the synthesis of graft copolymers [16]. The grafting-onto technique is the grafting of side chains onto the backbone by a coupling reaction. Ligon et al. directly grafted fluoroalkyl side chains onto PFCB aryl ether polymers with Umemoto's FITS reagents [12]. The fluoroalkylated PFCB polymers (20% functionalized) showed

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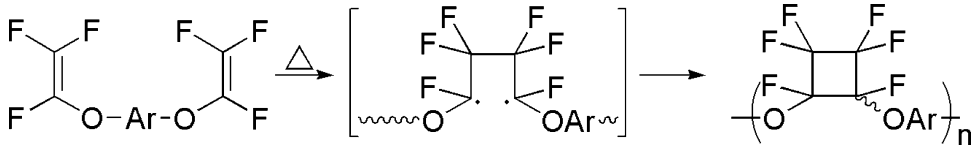
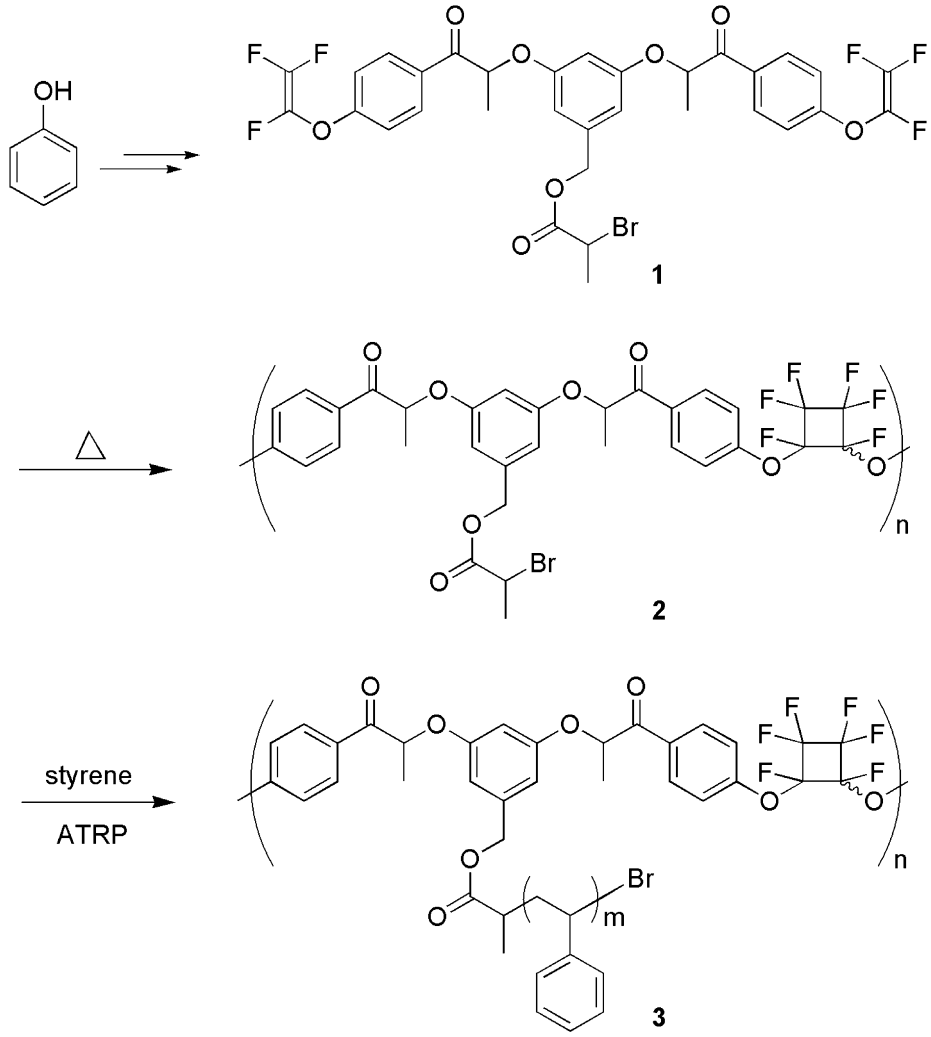


Scheme 1. Thermal cyclopolymerization of trifluorovinyl aryl ether monomer.



Scheme 2. Synthesis of PFCB aryl ether-based graft copolymer **3**.

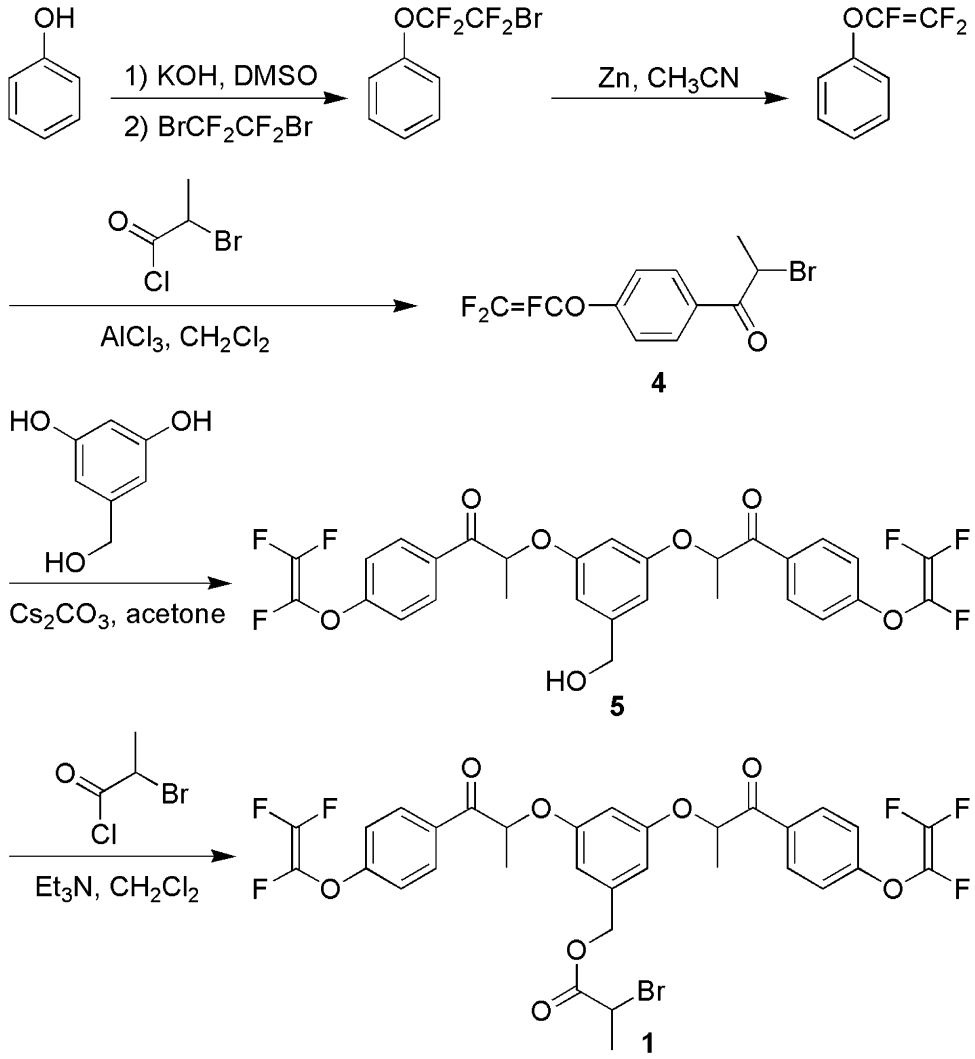
increases in both hydrophobicity and oleophobicity. This strategy provides a relatively simple method of synthesizing graft fluoropolymers; however, this functionalization reaction was undergoing normally in an uncontrolled way, with an insufficient grafting efficiency, resulting in limited grafting density. Recently, atom transfer radical polymerization (ATRP) has been successfully used to prepare the graft copolymers based on the grafting-from method, i.e., side chains are grafted from the backbone via ATRP initiated by the pendant initiating groups on the backbone polymers [17,18]. Specifically, the living characteristic of ATRP enables it to control both the molecular weights and molecular weight distributions of side chains. Mayes et al. succeeded in performing the direct graft copolymerization of methacrylates via ATRP using secondary fluorine on PVDF backbone as initiating sites [19]. Zhang and Russell grafted polystyrene and poly(*tert*-butyl acrylate) from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) via ATRP [20]. Their synthetic approaches offer a convenient way to modify fluoropolymers.

In this paper, we utilized the intermediate strategy to prepare a TFVE monomer **1** with a secondary bromine atom as ATRP initiating group as shown in Scheme 2. Thermal cyclopolymerization of monomer **1** gave a PFCB aryl ether homopolymer **2** possessing pendant ATRP initiating groups in every repeating unit, i.e., PFCB macroinitiator **2** was formed. ATRP of styrene initiated by macroinitiator **2** through the grafting-from strategy afforded a novel semi-fluorinated graft copolymer **3** containing a PFCB aryl ether polymeric backbone and polystyrene side chains. All compounds in this paper were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS, and GPC in detail.

2. Results and discussion

2.1. Design and synthesis of monomer 1

In ATRP, alkyl bromide with radical stabilizing substituent (such as carbonyl group) on the α-carbon has been widely used as



Scheme 3. Synthesis of TFVE monomer **1**.

initiators. Preparation of graft copolymer through the grafting-from strategy requires the polymeric backbone comprising monomer units with pendant ATRP initiating groups. 2-Bromopropionate group is a kind of commonly used ATRP initiating group and it is easily introduced into molecules by esterification. And it was reported that this type of ATRP initiating group is stable at a high temperature (200 °C) [10]. Thus, a new TFVE monomer **1** containing a 2-bromopropionate group was designed and the intermediate strategy was utilized to synthesize TFVE monomer **1** (Scheme 3). Trifluorovinyloxybenzene was first prepared by fluoroalkylation of phenol with $BrCF_2CF_2Br$ followed by subsequent elimination of BrF with zinc. Next, a secondary bromine atom (–$COCHBrCH_3$) was introduced into the 4-position of trifluorovinyl aryl ether by Friedel-Crafts reaction with 2-bromopropionyl chloride and the key intermediate **4** was obtained in good yield. The ^{1}H NMR spectrum of **4** is shown in Fig. 1A. The peaks at 7.18 and 8.07 ppm were attributed to 4 protons of benzene ring, and the signals at 1.89 (–$COCH(CH_3)Br$) and 5.24 (–$COCH(CH_3)Br$) ppm belonged to the protons of 2-bromopropionate group, respectively. The sharp peak at 1834 cm^{-1} (–$OCF{=}CF_2$) in FT-IR spectrum and the signals at −119.0, −125.6 and −135.0 ppm in ^{19}F NMR spectrum gave a clue of the existence of trifluorovinyl group.

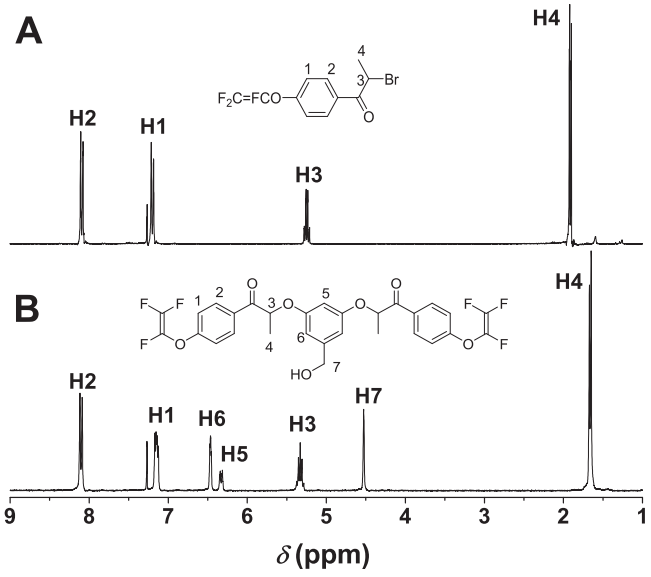


Fig. 1. ^{1}H NMR spectra of **4** (A) and **5** (B).

3,5-Dihydroxybenzyl alcohol is a versatile building block for organic synthesis, having two different hydroxyl groups in it. One is phenol hydroxyl and the other is benzyl hydroxyl. The phenol hydroxyl is more reactive and would make nucleophilic attack on the secondary bromine and the benzyl hydroxyl would keep inertness. Thus, compound **5** was prepared in the presence of

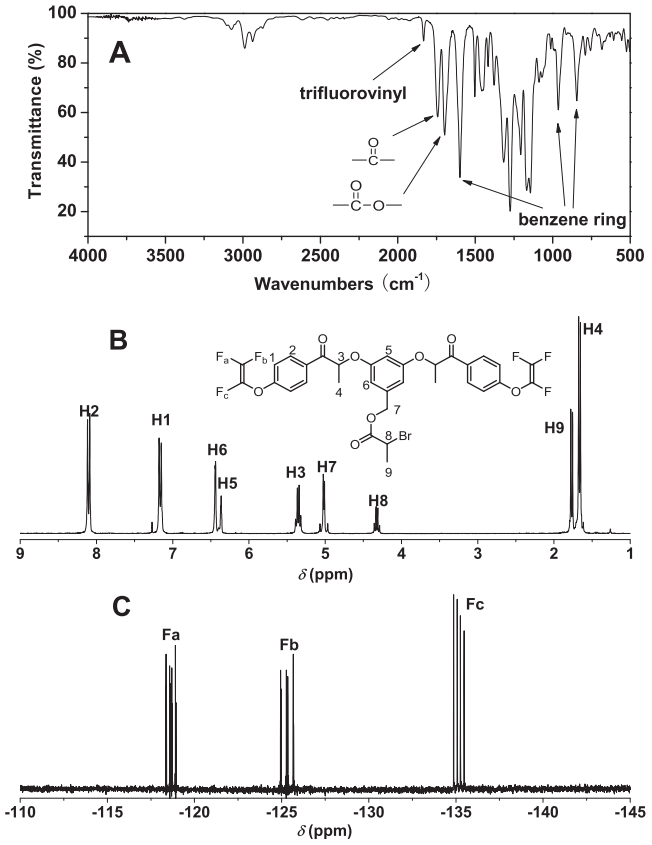


Fig. 2. FT-IR (A), ^{1}H NMR (B) and ^{19}F NMR (C) spectra of TFVE monomer **1**.

Cs_2CO_3 by nucleophilic substitution reaction and it was easily separated by silica chromatography as a light yellow oil. Fig. 1B shows ^{1}H NMR spectrum of **5** and new peaks at 6.46, 6.33 (C_6H_6) and 4.53 (–CH_2–OH) ppm were found in comparison with that of **4** (Fig. 1A). This result indicated that two phenol hydroxyls were both transformed into ether linkage while benzyl hydroxyl was remained under the current reaction condition. The sharp peak at 1834 cm^{-1} (–OCF=CF_2) in FT-IR spectrum and the signals at −119.0, −125.6 and −135.0 ppm in ^{19}F NMR spectrum after the nucleophilic reaction demonstrated that shows the vinyl group was not affected during the reaction.

Finally, compound **5** was esterified with 2-bromopropionyl chloride in dichloromethane to afford the desired monomer **1**, which was characterized by FT-IR, ^{1}H NMR, and ^{19}F NMR. Typical signals of the carbonyl group appeared at 1743 and 1698 cm^{-1} in FT-IR spectrum (Fig. 2A). As shown in Fig. 2B, two new peaks at 4.32 and 1.76 ppm corresponded to the newly introduced –COC*H*(CH_3)Br group. Furthermore, the peak at 1834 cm^{-1} (–OCF=CF_2) in FT-IR spectrum and the signals at −119.0, −125.6 and −135.0 ppm in ^{19}F NMR spectrum (Fig. 2C) illustrated the remaining of trifluorovinyl groups. From the above results, it can be concluded that we have successfully synthesized TFVE monomer **1** containing an ATRP initiating group.

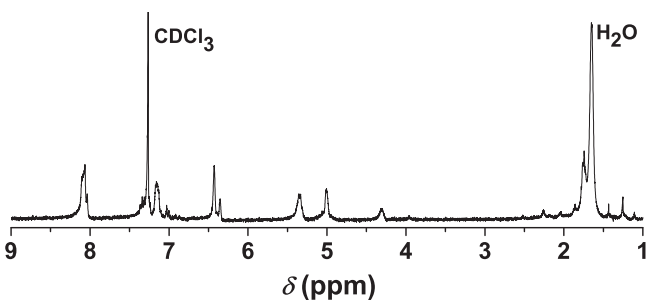


Fig. 3. ^{1}H NMR spectrum of macroinitiator **2**.

Table 1
Synthesis of graft copolymer **3** initiated by macroinitiator **2**.[a]

Sample	Temperature (°C)	Time (h)	M_n[b] (g/mol)	M_w/M_n[b]
3a	110	4	58,100	2.31
3b	110	5	56,800	2.39
3c	110	6	62,500	3.14
3d	110	7	77,000	2.45

[a] Initiated by macroinitiator **2** (M_n = 8600 g/mol, M_w/M_n = 2.10) in diphenyl ether, [St]:[Br group]:[CuBr]:[PMDETA] = 100:1:1:2.
[b] Measured by GPC in THF at 35 °C.

2.2. Preparation of macroinitiator 2

PFCB macroinitiator **2** was prepared by thermal cyclopolymerization of TFVE monomer **1** (Scheme 2). The homopolymerization was carried out in diphenyl ether at 180 °C. ^{1}H NMR and ^{19}F NMR were employed to examine the chemical structure of macroinitiator **2**. We still found the peaks of –COC*H*(CH_3)Br group at 4.31 and 1.70 ppm and the protons of benzene rings at 8.09, 7.15, 6.43, and 6.35 ppm as shown in Fig. 3, which are similar with that of monomer **1**. Br atom kept inert during the thermal cyclopolymerization according to previous report [10]. The existence of PFCB linkage was also affirmed by the typical multiplets ranging from −128 to −134 ppm in ^{19}F NMR spectrum. In addition, TFVE end group signals were found at −119.0, −125.6 and −135.0 ppm. All these evidence showed that a PFCB aryl ether-based macroinitiator bearing ATRP initiating groups in every repeating unit was successfully synthesized.

2.3. Synthesis of graft copolymer 3

The graft copolymer **3** was prepared by the grafting-from strategy via ATRP of styrene using homopolymer **2** as macroinitiator (M_n = 8600, M_w/M_n = 2.10) and CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalytic system. The polymerization was performed in diphenyl ether at 110 °C and the results are listed in Table 1. All products' molecular weights are much higher than that of the macroinitiator, indicating the occurrence of the polymerization of styrene. Moreover, the molecular weights of graft copolymers increased with the ascending of polymerization time, which accorded with the living nature of ATRP.

The copolymer **3c** (M_n = 62,500) was also hydrolyzed with KOH to cleave polystyrene side chains according to previous report [21]. GPC measurement was run for the cleaved PS side chains and the result indicated that $M_{n,GPC}$ of the cleaved polystyrene side chains was 4200. The narrow molecular weight distribution (M_w/M_n = 1.26) of the cleaved polystyrene side chains obtained from GPC is the evidence that polystyrene side chains were well-defined.

The graft copolymers were characterized by FT-IR, ^{1}H NMR, and ^{19}F NMR. A sharp band at 962 cm^{-1} attributed to perfluorocyclobutyl unit was found in FT-IR spectrum and two sharp peaks at 698 and 757 cm^{-1} confirmed the existence of *mono*-substituted benzene ring of polystyrene segment. Fig. 4A presents ^{1}H NMR spectrum of the graft copolymer in $CDCl_3$. The peaks at 8.10 and 6.40 ppm were attributed to the protons of benzene ring of PFCB aryl ether-based backbone, and the typical signals of polystyrene side chains were found to appear at 1.43 (–CH_2–), 1.79 (–C*H*–), and 6.53, 6.93 ppm (benzene ring). ^{19}F NMR of graft copolymer **3** was

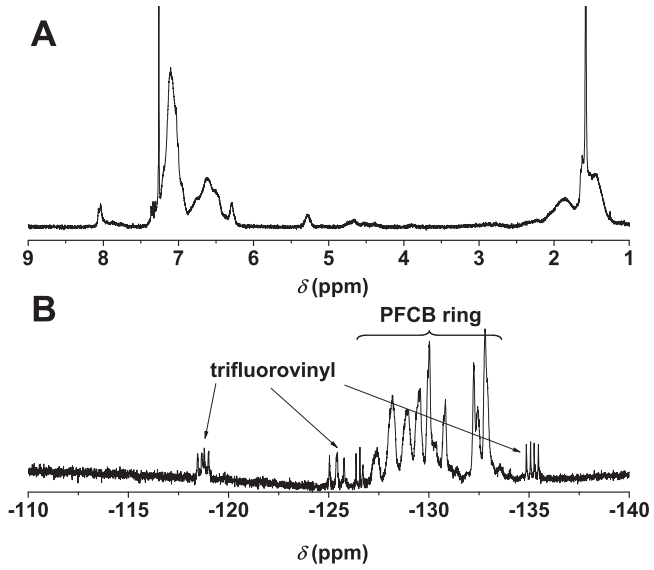


Fig. 4. ^{1}H NMR (A) and ^{19}F NMR (B) spectra of graft copolymer **1**.

similar to that of macroinitiator **2** (Fig. 4B), which illustrated that PFCB-based polymeric backbone was stable under ATRP condition.

Solubility test for copolymer **3** was performed in four kinds of solvents with low boiling point, tetrahydrofuran, chloroform, dichloromethane, and acetone. The graft copolymer **3** shows excellent solubility in the above solvents, which was similar to the result of corresponding ABA triblock copolymer containing 2 polystyrene segments [10].

3. Conclusion

A new TFVE monomer **1** with ATRP initiating group was synthesized via intermediate strategy. The thermal cyclopolymerization of monomer **1** provided a PFCB aryl ether polymer with pendent ATRP initiating groups, i.e., macroinitiator **2**. ATRP of styrene initiated by macroinitiator **2** formed the graft copolymer **3**, which contained PFCB polymer backbone and polystyrene side chains. The resulting graft copolymer **3** shows good solubility in common used solvents.

4. Experimental

4.1. 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 in vacuum for 1 day. Granular zinc was activated by washing in 0.1 M HCl followed by drying at 140 °C *in vacuo* for 10 h. 1,2-Dibromotetrafluoroethane was prepared by condensing equimolar amounts of Br_2 and tetrafluoroethylene at −195 °C followed by warming up to 22 °C [22]. All solvents were purified by standard methods prior to use. Phenol (Aldrich, 99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (Acros, 98%), and 2-bromopropionyl chloride (Acros, 98%) were used as received. All other chemicals and reagents were purchased from Alfa Aesar or Sigma Aldrich and used as received unless otherwise stated.

4.2. Measurements

^{1}H and ^{13}C NMR spectra were obtained with a Varian Mercury 300 spectrometer (300 MHz). ^{19}F NMR spectroscopy measurements were collected on a Bruker AM-300 spectrometer (282 MHz). All NMR spectra were collected in $CDCl_3$, TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards and CF_3CO_2H was used as external standard for ^{19}F NMR. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. EI-MS was measured by an Agilent 5937N system. HRMS were recorded on a Waters Micromass GCT instrument. 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 (RI) detector and a set of Waters Styragel columns (HR3 (500–30,000), HR4 (5000–600,000) and HR5 (50,000–4,000,000), 7.8 mm × 300 mm, particle size: 5 μm). GPC measurements were carried out at 35 °C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

4.3. Synthesis of compound 4

The compound **4** was synthesized according to Scheme 3 by three steps using phenol as starting material [10]. Synthesis of (1,2,2-trifluorovinyloxy)benzene was similar to those reported procedures in previous literature [23].

To a 250 mL dried three-neck round-bottom flask fitted with a condenser and a thermometer, (1,2,2-trifluorovinyloxy)benzene (11.7971 g, 68 mmol) and CH_2Cl_2 (100 mL) were added under N_2 followed by adding 2-bromopropionyl chloride (7 mL, 69 mmol) and aluminum chloride ($AlCl_3$) (9.94 g, 74 mmol). The solution was heated to 30 °C for 8 h, then the flask was cooled to 0 °C, and granular ice was added to terminate the reaction. 1 M HCl (80 mL) was added to the solution and the organic layer was washed by brine (3× 50 mL) followed by drying over $MgSO_4$. A straw yellow solid, 2-bromo-1-(*p*-trifluorovinyloxy)phenylpropan-1-one **4** (17.5765 g, 83.6%), was obtained by flash 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). FT-IR (KBr): ν (cm^{-1}): 3023, 2983, 2923, 1834 (OCF=CF_2), 1689, 1601, 1505, 847.

4.4. Synthesis of compound 5

To a 250 mL dried three-neck round-bottom flask fitted with a condenser, 3,5-dihydroxybenzyl alcohol (6.44 g, 46 mmol), K_2CO_3 (19.06 g, 138 mmol), Cs_2CO_3 (0.456 g, 1.38 mmol) and acetone (150 mL) were added under N_2 followed by adding compound **4** (28.44 g, 92 mol). The solution was heated to 60 °C for 10 h, then the flask was cooled to room temperature. One hundred milliliters of water and 50 mL of diethyl ether were added into the solution, and the organic layer was washed by brine (3× 50 mL) followed by drying over $MgSO_4$. A light yellow oil (19.19 g, 70%) was obtained by flash column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.66 (d, *J* = 6.6 Hz, 6H), 4.53 (s, 2H), 5.33 (q, *J* = 6.6 Hz, 2H), 6.33 (s, 1H), 6.46 (s, 2H), 7.15 (d, *J* = 8.1 Hz, 4H), 8.10 (d, *J* = 8.1 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.0 (dd, 1F), −125.6 (dd, 1F), −135.0 (dd, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 18.54, 64.79, 101.6, 106.4, 115.7, 130.6, 131.5, 134.3, 144.1, 146.8, 149.6, 158.6, 197.2. FT-IR (KBr): ν (cm^{-1}): 3503, 2988, 2936, 1834, 1697, 1600, 1503, 1457, 1317, 1275, 1207, 1167, 1144, 964, 845. EI-MS *m*/*z*: 596. HRMS: $C_{29}H_{22}F_6O_7$, Calcd. 596.1270, Found 596.1271.

4.5. Synthesis of TFVE monomer 1

In a 50 mL dried three-neck round-bottom flask, **5** (1.0715 g, 1.80 mmol) and triethylamine (0.5 mL, 3.6 mmol) were dissolved in 25 mL of dichloromethane and the mixture was stirred at 0–5 °C. 2-Bromopropionyl chloride (0.18 mL, 1.80 mmol) was added and the mixture was stirred for another 1 h. Finally, the mixture was stirred at room temperature for 1 h. The precipitated triethylammonium chloride was filtered and the filtrate was washed twice with water. The solution was dried over $MgSO_4$ followed by the concentration to remove solvent. The desired product **1** of yellow oil was obtained by flash column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.66 (d, J = 6.6 Hz, 6H), 1.76 (d, J = 7.2 Hz, 3H), 4.32 (q, J = 7.2 Hz, 1H), 5.00 (q, J = 6.6 Hz, 2H), 5.33 (s, 2H), 6.35 (s, 1H), 6.43 (s, 2H), 7.15 (d, J = 8.4 Hz, 4H), 8.09 (d, J = 8.4 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.0 (dd, 1F), −125.6 (dd, 1F), −135.0 (dd, 1F). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 18.5, 21.3, 39.8, 66.8, 102.5, 107.3, 130.6, 131.2, 134.7, 138.0, 143.1, 146.4, 150.5, 158.6, 169.7, 196.8. FT-IR (KBr): ν (cm^{-1}): 3074, 2988, 2937, 1834, 1743, 1698, 1599, 1503, 1458, 1317, 1275, 1207, 1168, 1144, 964, 845. EI-MS m/z: 730. HRMS: $C_{32}H_{25}BrF_6O_8$, Calcd. 730.0637, Found 730.0641.

4.6. Preparation of PFCB aryl ether-based macroinitiator 2

To a predried 25 mL Schlenk flask sealed with a rubber septum, trifluorovinyl ether monomer **1** (0.77 g, 1.05 mmol) and diphenyl ether (6 mL) were added under N_2 and followed by three cycles of freezing–pumping–thawing. The flask was placed in an oil bath at 180 °C for polymerization. The reaction lasted for another 12 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, followed by drying under vacuum to obtain 0.54 g of solid. GPC: M_n = 8600, M_w/M_n = 2.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.70, 4.31, 5.00, 5.33, 6.35, 6.43, 7.15, 8.09. ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.0 (dd), −125.6 (dd), −128.2 to −133.5 (m, cyclobutyl-F_6), −135.0 (dd). FT-IR (KBr): ν (cm^{-1}) 2923, 2852, 1834, 1735, 1695, 1599, 960, 846.

4.7. Synthesis of graft copolymer 3

A typical procedure of synthesis of graft copolymer **3** is listed as follows: ATRP macroinitiator **2** (0.2 g, M_n = 8600 g/mol) and CuBr (19 mg, 0.12 mmol) were added to a 25 mL Schlenk flask (flame-dried under vacuum just before use) sealed with a rubber septum under N_2. After three cycles of evacuating and backfilling with N_2, styrene (1.3 mL, 12.0 mmol), PMDETA (0.05 mL, 0.24 mmol), and diphenyl ether (2 mL) 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 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 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 crude product was purified by three times of dissolution and precipitation, followed by drying under vacuum to obtain 0.51 g of graft copolymer **3c**. GPC: M_n = 62,500, M_w/M_n = 3.14. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.43, 1.79, 6.35, 6.53, 6.93, 8.09. ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.0 (dd), −125.6 (dd), −128.2 to −133.5 (m, cyclobutyl-F6), −135.0 (dd). FT-IR (KBr): ν (cm^{-1}) 2924, 1735, 1695, 1600, 1495, 1453, 962, 846, 757, 698.

4.8. Cleavage of polystyrene side chains

The graft copolymer **3c** (0.10 g, M_n = 62,500, M_w/M_n = 3.14) was dissolved in 5 mL of THF. Next, 3 mL of KOH solution (1 M in ethanol) was added and the mixture was refluxed for 2 days. The solution was concentrated and precipitated into acetonitrile to obtain the cleaved polystyrene side chains since the backbone is soluble in acetonitrile. GPC: M_n = 4,200, M_w/M_n = 1.26. FT-IR: ν (cm^{-1}): 3025, 2983, 2923, 1601, 1493, 1452, 757, 698.

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