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Synthesis and characterization of perfluorocyclobutyl aryl ether-based amphiphilic diblock copolymer

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ABSTRACT

Perfluorocyclobutyl aryl ether-based amphiphilic diblock copolymer containing hydrophilic poly (ethylene glycol) segment was synthesized by atom transfer radical polymerization (ATRP). Perfluorocyclobutyl-containing methacrylate-based monomer, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate, was prepared firstly, which can be polymerized by ATRP in a controlled way to obtain well-defined homopolymers with narrow molecular weight distributions ($M_w/M_n \leq 1.30$). The molecular weights increased linearly with the conversions of monomer and the apparent polymerization rate exhibited first-order relation with respect to the concentration of monomer. ATRP of 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate was initiated by PEG-based macroinitiators with different molecular weights to obtain amphiphilic diblock copolymers with narrow molecular weight distributions ($M_w/M_n < 1.35$) and the number of perfluorocyclobutyl linkage can be tuned by the feed ratio and the conversion of the fluorine-containing methacrylate monomer. The critical micelle concentrations of these amphiphilic diblock copolymers in water and brine were determined by fluorescence probe technique. The morphologies of the micelles were found to be spheres by TEM.

1. Introduction

It is well-known that fluoropolymer has many advantages compared with conventional carbon hydrogen polymer due to the incorporation of fluorocarbon functionality, such as increased thermal and oxidative stability, optical transparency, solvent compatibility, environmental stability, etc. [1]. Thus, many researchers studied the applications of fluoropolymer with high performance in recent years. However, the use of fluoropolymer was limited by its low solubility and processability. Therefore, fluoropolymers including polychlorotrifluoroethlene (PCTFE), Teflon-AF, Cytop and various copolymers of polytetrafluoroethylene (PTFE) with low crystallinity have been modified to improve the processability. A recent advance in the incorporation of fluorine into polymers with high performance involved a step-growth cycloaddition polymerization of trifluorovinyl aryl ether monomers to provide a kind of fluoropolymer containing perfluorocyclobutyl (PFCB) linkage, which was first synthesized by Dow Chemical Co. in 1993 [2]. Many recent studies reported new thermoplastic and thermoset PFCB polymers by thermal chain extension of bis- and tri-functionalized trifluorovinyl aryl ether monomers [3–5]. The traditional homopolymerization and random copolymerization of trifluorovinyl aryl ether monomer normally proceed above 150 °C without any initiator and catalyst, either as a melt or in solution that using solvent with high boiling point.

PFCB aryl ether polymer provides the conventional properties of fluoropolymer such as high thermal/oxidative stability, high chemical resistance, low dielectric constant, low moisture absorption and low surface energy, on the other hand, it also possesses many other advantages including optical transparency, improved processability [6]. These semi-fluorinated polymers are tunable to a variety of applications based on the substitution groups of bisphenol segment, such as curing additive [7], proton exchange membrane for fuel cell [8] and light emitting polymers [9].

Due to the normal high polymerization temperature (>150 °C) and unusual polymerization mechanism ([2 + 2] cycloaddition) compared to those of commercially available monomers, only few literatures reported the synthesis of copolymers via trifluorovinyl aryl ether monomers and other commonly used monomers, in addition, the number of PFCB linkage in copolymers was very difficult to be tuned [10–13]. This certainly confined the application of PFCB aryl ether polymer.

In order to enlarge its application range, it is necessary to combine the high performance of PFCB aryl ether polymer with other commercial polymers. To realize this, block copolymer with a stable covalent-bonded linkage between two different segments

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is a good and convenient choice, which can be synthesized by sequential feeding of different monomers via living polymerization [14] including anionic polymerization [15–17], cationic polymerization [18,19], group transfer polymerization [20] and living radical polymerization [21–24] or the mechanism transformation strategy using different polymerization methods [25–31]. In particular, amphiphilic block copolymers have attracted much attention during the past decade [32,33], which can be easily synthesized by ATRP [34–36]. Many researches focused on the self-assembly behavior of block copolymer, which was found to be affected by many factors such as pH value, ionic strength, micelle's preparation conditions, concentration of the copolymer, molecular weight and composition of the copolymer [37], due to the potential applications in the fields of solubilizer [38], drug delivery [39,40], catalysis [41] and microelectronics [34,42]. Poly(ethylene glycol) (PEG) has been widely selected as the hydrophilic block in building block copolymers for its good biocompatibility, low toxicity and good solubility in aqueous media and organic solvents [43–45]. Different amphiphilic block copolymers containing hydrophilic PEG segment were synthesized by atom transfer radical polymerization (ATRP) of hydrophobic monomers initiated by PEG-based macroinitiator which can be easily prepared by converting the hydroxyl end group of PEG into halogen-containing ATRP initiation group [46–49].

In this work, we present the first example of amphiphilic diblock copolymer containing PFCB segment. PFCB linkage was incorporated into methacrylate monomer as a side group using commercially available 4-methylphenol as starting material. This new monomer, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate, can be polymerized by ATRP in a controlled way. Poly(ethylene glycol)-*b*-poly(4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate) diblock copolymers (PEG-*b*-PTPFCBBMA) with narrow molecular weight distributions were obtained by ATRP of this new fluorine-containing methacrylate monomer initiated by PEG-based macroinitiators as shown in Scheme 1. Self-assembly behavior of this kind of amphiphilic diblock copolymer was studied. Their critical micelle concentrations (cmc) were measured using *N*-phenyl-1-naphthylamine as fluorescence probe. The morphologies of the micelles formed from them were studied by transmission electron microscopy (TEM) and found to be spheres.

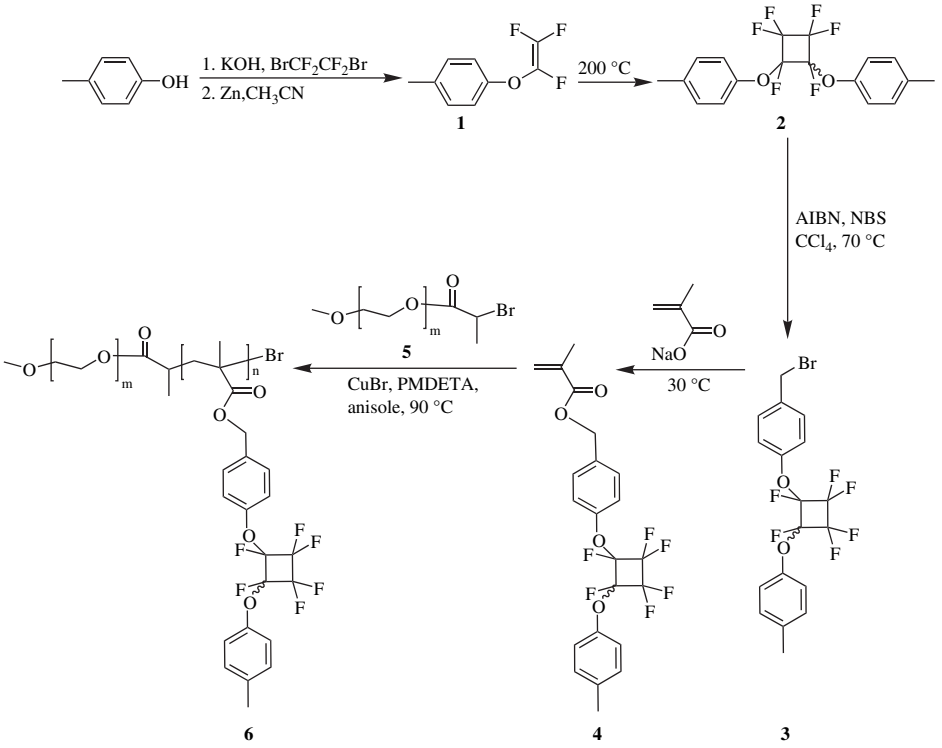
2. Experimental section

2.1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol for three times. 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 vacuo* for 1 day. $BrCF_2CF_2Br$ was prepared by condensing equimolar amounts of bromine and tetrafluoroethylene at −195 °C followed by warming up to 22 °C [50]. Granular zinc was activated by washing in 0.1 N HCl followed by drying at 140 °C *in vacuo* overnight. Anisole (Aldrich, 99%) was dried over CaH_2 and distilled *in vacuo* prior to use. Poly(ethylene glycol) monomethyl ether (mPEG, $M_n = 5000$, Aldrich, 99%), methyl 2-bromopropionate (2-MBP, Aldrich, 99%), 4-methylphenol (Aldrich, 99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), methacrylic acid (Aldrich, 99%), 2-bromopropionyl chloride (Aldrich), dimethyl sulfoxide (DMSO, Aldrich, 99.9%), *N*-bromosuccinimide (NBS, Aldrich, 99%), CCl_4 (Aldrich, 99.5%) and 2-bromopropionyl chloride (Acros, 98%) were used as received.

2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. All NMR analyses were performed on a Bruker Avance 500 spectrometer (500 MHz) in $CDCl_3$, TMS (^1H 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. ESI-MS was measured by an Agilent LC/MSD SL system. Conversions



Scheme 1. Synthesis of PEG-*b*-PTPFCBBMA amphiphilic diblock copolymer.

of 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate were determined by GC using a HP 6890 system with SE-54 column. 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) 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 flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Steady-state fluorescent spectra of PNA were measured on a Hitachi FL-4500 spectrofluorometer with the band width of 5 nm for excitation and emission, the emission intensity at 418 nm was recorded to determine the cmc with a $\lambda_{ex} = 340$ nm. Thermal properties were characterized on a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) under N_2 purge with a heating rate of 10 °C/min. The glass transition temperature (T_g) was recorded from the second heating process after a quick cooling. TEM images were obtained using a Philips CM120 instrument operated at 80 kV.

2.3. Preparation of p-trifluorovinyloxytoluene

p-Trifluorovinyloxytoluene **1** was prepared by fluoroalkylation of 4-methylphenol with $BrCF_2CF_2Br$ followed by Zn-mediated elimination with a yield of 49.0%, the procedures were similar to those in previous literature [2]. ^{1}H NMR: δ (ppm): 2.34 (3H, CH_3), 7.02 (2H, $C_6H_4CH_3$), 7.16 (2H, $C_6H_4OCF{=}CF_2$). ^{19}F NMR: δ (ppm): −120.6, −128.0, −133.7 (3F, OC*F*=C*F*$_2$).

2.4. Thermal [2 + 2] cycloaddition of trifluorovinyl aryl ether 1

p-Trifluorovinyloxytoluene **1** (92.0 g, 0.49 mol) was added to a 250 mL dried flask under N_2. The flask was heated to 200 °C and the reaction lasted for 14 h with reflux. Next, a colorless liquid, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)toluene **2** (85.0 g, 92.0% yield), was obtained by silica column chromatography. ^{1}H NMR: δ (ppm): 2.33 (3H, CH_3), 7.01 (4H, $C_6H_4CH_3$), 7.12 (4H, C_6H_4–OC_4F_6O–C_6H_4). ^{13}C NMR: δ (ppm): 20.6 (*C*H$_3$), 105.0–115.2 (4C, perfluorocyclobutyl), 118.3, 130.2, 135.0, 150.5. ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, perfluorocyclobutyl).

2.5. Bromination of dimer 2

4-(4′-*p*-Tolyloxyperfluorocyclobutoxy)toluene **2** (27.56 g, 73.3 mmol) and 100 mL of CCl_4 were added to a 250 mL flask for deoxygenating under N_2. Next, the solution was heated to 70 °C followed by introducing NBS (13.0 g, 73.3 mmol) and AIBN (0.6010 g, 3.75 mmol). The reaction lasted for 12 h. Finally, a light yellow liquid, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl bromide **3** (14.0 g, 42.0% yield), was obtained by silica column chromatography. ^{1}H NMR: δ (ppm): 2.34 (3H, CH_3), 4.48 (2H, CH_2Br), 7.02 (2H, $C_6H_4CH_3$), 7.12 (4H, C_6H_4–OC_4F_6O–C_6H_4), 7.36 (2H, $C_6H_4CH_2Br$). ^{13}C NMR: δ (ppm): 20.6 (*C*H$_3$), 39.4 (*C*H$_2$Br), 105.0–115.2 (4C, perfluorocyclobutyl), 118.5, 130.5, 134.9, 150.3. ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, perfluorocyclobutyl).

2.6. Esterification of 3

4-(4′-*p*-Tolyloxyperfluorocyclobutoxy)benzyl bromide **3** (35.2 g, 77.5 mmol) and sodium methacrylate (16.7 g, 154.9 mmol) were added to 200 mL of DMSO at room temperature for deoxygenating under N_2. The solution was heated to 30 °C for 20 h. Next, 300 mL of water was added and the aqueous mixture was extracted with ether. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solution and brine followed by drying over $MgSO_4$. Finally, a colorless liquid, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate **4** (20.5 g, 57.6% yield), was obtained by silica chromatography. ESI-MS (*m*/*z*): calcd $(M + Na)^+$ 483.1, found 483.1. FT-IR: ν (cm^{-1}): 3060, 2950, 1722, 1639, 1600, 1509, 1456, 1320, 1201, 1157, 1118, 963, 817. ^{1}H NMR: δ (ppm): 1.97 (3H, $CH_2{=}C{-}CH_3$), 2.33 (3H, $C_6H_4CH_3$), 5.17 (2H, $C_6H_4CH_2O$), 5.60, 6.16 (1H, $CH_2{=}C{-}CH_3$), 7.02 (2H, $C_6H_4CH_3$), 7.11 (4H, C_6H_4–OC_4F_6O–C_6H_4), 7.35 (2H, $C_6H_4CH_2O$). ^{13}C NMR: δ (ppm): 18.3 ($CH_2{=}C{-}CH_3$), 20.6 ($C_6H_4CH_3$), 65.6 ($C_6H_4CH_2O$), 105.0–115.2 (4C, perfluorocyclobutyl), 118.3, 126.0 ($CH_2{=}C{-}CH_3$), 130.3, 134.9, 136.2 ($CH_2{=}C{-}CH_3$), 150.5, 167.2 (*C*=O). ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, perfluorocyclobutyl).

2.7. ATRP homopolymerization of fluorine-containing methacrylate monomer 4

ATRP of 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate **4** was initiated by 2-MBP using PMDETA/CuBr as catalysis system in anisole to get the corresponding homopolymer with narrow molecular weight distribution. To a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum, CuBr (0.0128 g, 0.089 mmol) was first added for degassing and kept under N_2. Next, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate **4** (1.024 g, 2.23 mmol), PMDETA (37 μL, 0.178 mmol), 2-MBP (4.97 μL, 0.0445 mmol) and anisole (2.23 mL) which were stored under N_2, were introduced via a gastight syringe. The solution was degassed by three cycles of freezing–pumping–thawing and 0.40 mL of solution taken as the first data point (time = 0) was withdrawn from the flask using a gastight syringe. The flask was immersed into an oil bath thermostated at 90 °C to start the polymerization. ATRP kinetics was studied by taking 0.40 mL of solution with a gastight syringe at every time interval (1.0 h). The conversions of monomer **4** were determined by GC. The molecular weights and molecular weight distributions were measured by GPC.

The polymerization was terminated by immersing the flask into liquid nitrogen after 6 h. THF was added to the flask for dilution and the solution was filtered through a short Al_2O_3 column to remove the copper catalyst. The resulting solution was concentrated and precipitated into *n*-hexane. After repeated purification by dissolving in THF and precipitating in *n*-hexane for three times, a white solid, poly[4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate], was obtained. Conversion of monomer **4**: 93.8%. GPC: $M_n = 31{,}400$, $M_w/M_n = 1.05$. T_g: 135.3 °C. FI-IR: ν (cm^{-1}): 3040, 2950, 1722, 1600, 1509, 1456, 1320, 1201, 1157, 1114, 963, 817. ^{1}H NMR: δ (ppm): 0.65, 0.89 (3H, CCH_3), 1.27, 1.61, 1.79 (CH_2C), 2.25 (3H, $C_6H_4CH_3$), 3.56 (3H, COOCH_3 of ATRP initiation group), 4.81 (2H, $C_6H_4CH_2O$), 6.94 (2H, $C_6H_4CH_3$), 7.03 (4H, C_6H_4–OC_4F_6O–C_6H_4), 7.20 (2H, $C_6H_4CH_2O$). ^{13}C NMR: δ (ppm): 20.1 (*C*H$_3$), 29.3 (*C*H$_2$C), 44.1 (*C*H$_2$C), 64.9 ($C_6H_4CH_2O$), 105.0–115.2 (4C, perfluorocyclobutyl), 117.2, 129.2, 134.8, 149.3, 175.8 (*C*=O). ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, perfluorocyclobutyl).

2.8. Block copolymerization of fluorine-containing methacrylate monomer 4

Block copolymerization of **4** was initiated by PEG-based macroinitiator **5** to obtain well-defined PEG-*b*-PTPFCBBMA **6** diblock copolymer. PEG-based macroinitiator **5** was prepared by reacting mPEG ($M_n = 5000$) with 2-bromopropionyl chloride according to previous literature [51].

CuBr (0.0029 g, 0.02 mmol) and PEG-based macroinitiator **5** (0.0500 g, 0.01 mmol ATRP initiation group) in 0.2 mL of anisole were added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum under N_2. After three cycles of evacuating and purging with N_2, PMDETA (8.35 μL, 0.04 mmol), 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate **4** (0.2300 g, 0.5 mmol), and anisole (0.8 mL) were charged via a gastight syringe. The flask was degassed by three cycles of

freezing–pumping–thawing followed by immersing the flask into an oil bath set at 90 °C. The polymerization was terminated by putting the flask into liquid nitrogen after 24 h. The reaction mixture was diluted with THF and passed through an alumina column to remove the copper catalyst. The solution was concentrated and precipitated into cold methanol. The final product, poly(ethylene glycol)-*b*-poly(4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate) **6c**, was obtained after drying *in vacuo* overnight. GPC: $M_n = 14{,}200$, $M_w/M_n = 1.22$. FI-IR: ν (cm^{-1}): 3040, 2950, 2885, 1734, 1600, 1509, 1456, 1322, 1268, 1201, 1157, 1114, 962, 817. ^{1}H NMR: δ (ppm): 0.67, 0.88 (3H, CCH_3), 1.25, 1.81 (CH_2C), 2.26 (3H, $C_6H_4CH_3$), 3.41 (3H, OCH_3), 3.65 (4H, OCH_2CH_2O), 4.83 (2H, $C_6H_4CH_2O$), 6.94 (2H, $C_6H_4CH_3$), 7.03 (4H, C_6H_4–OC_4F_6O–C_6H_4), 7.20 (2H, $C_6H_4CH_2O$). ^{13}C NMR: δ (ppm): 20.5 (CH_3), 30.3 (CH_2C), 44.8 (CH_2C), 68.9 ($C_6H_4CH_2O$), 70.6 (OCH_2), 105.0–115.2 (4C, perfluorocyclobutyl), 118.1, 130.1, 134.8, 150.3, 175.6. ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, perfluorocyclobutyl).

2.9. Determination of critical micelle concentration

Acetone solution of PNA (1.15×10^{-3} mol/L) was added to a large amount of water until the concentration of PNA reached 6×10^{-7} mol/L. Different amounts of THF solutions of PEG-*b*-PTPFCBBMA **6** (10 mg/mL) were added to water containing PNA ([PNA] = 6×10^{-7} mol/L). All fluorescence spectra were recorded at 25 °C.

2.10. Micelle morphology

THF solution of PEG-*b*-PTPFCBBMA **6** diblock copolymer (1 mg/mL) was added dropwise to water with vigorous stirring until the concentration of diblock copolymer was 0.01 mg/mL. THF was evaporated by stirring for another several hours. For TEM studies, a drop of micellar solution was deposited on an electron microscopy copper grid coated with carbon film and the water evaporated at room temperature.

3. Results and discussion

3.1. Preparation of fluorine-containing methacrylate monomer with PFCB linkage

Trifluorovinyl aryl ether **1** was prepared firstly by the traditional approach in two steps from commercially available 4-methylphenol via fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn-mediated elimination [2]. In the following step, thermal [2 + 2] cycloaddition of **1** was carried out to give dimer **2** containing PFCB linkage. Finally, sodium methacrylate was used to esterify compound **3**, mono-brominated product of dimer **2**, to give PFCB-containing methacrylate monomer **4**.

The chemical structure of methacrylate monomer **4** was characterized by FT-IR, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR. Fig. 1A shows FT-IR spectrum of **4**. Typical signals of double bond and carbonyl appeared at 1639 and 1722 cm^{-1}, respectively. The sharp peak at 963 cm^{-1} demonstrated the successful incorporation of PFCB linkage. The peaks at 1456, 1509 and 1600 cm^{-1} were attributed to benzene ring of PFCB aryl ether unit. In particular, *para*-disubstituted benzene ring structure of PFCB aryl ether unit was confirmed by the sharp band centered at 817 cm^{-1}.

^{1}H NMR spectrum of monomer **4** is shown in Fig. 2A. Typical resonance signals of double bond were found to appear at 5.60 and 6.16 ppm. The peaks at 7.02, 7.11 and 7.25 ppm were attributed to the protons of benzene ring in PFCB aryl ether unit. The resonance signals of 2 carbons of double bond appeared at 126.0 and 136.2 ppm in ^{13}C NMR spectrum of **4**. The peak at 167.2 ppm represented the carbon of carbonyl. A series of peaks between 105.0 and 115.2 ppm came from 4 carbons of PFCB linkage. In addition, the existence of PFCB linkage in monomer **4** was verified by a series of peaks between −127.3 and −132.6 ppm in ^{19}F NMR spectrum of **4** as shown in Fig. 2B.

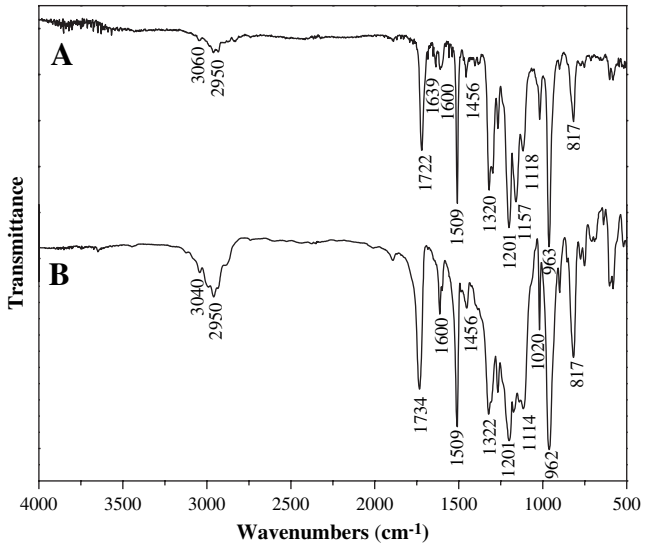


Fig. 1. FT-IR spectra of TPFCBBMA **4** (A) and PEG-*b*-PTPFCBBMA **6** (B).

All the above results evidenced the successful synthesis of PFCB-containing methacrylate monomer **4**.

3.2. ATRP of 4-(4′-p-tolyloxyperfluorocyclobutoxy)benzyl methacrylate

ATRP of PFCB-containing methacrylate monomer **4** was initiated by 2-MBP in solution similar to previous report [52]. ^{1}H NMR spectrum after homopolymerization showed the disappearance of the signals of double bond (Fig. 3). ATRP mechanism was confirmed by a minor peak at 3.56 ppm, which was attributed to 3 protons of $COOCH_3$ in ATRP initiation group. In addition, the presence of PFCB linkage in homopolymer was visioned by the peaks between 105.0 and 115.2 ppm in ^{13}C NMR spectrum and the peaks ranged from −127.3 to −132.6 ppm in ^{19}F NMR spectrum.

The semilogarithmic plot of $\ln([M]_0/[M])$ *vs.* time, based from the data of conversions of monomer **4** measured by GC, was drawn in Fig. 4. It can be concluded that the apparent polymerization rate is first-order with respect to the concentration of monomer **4**, which is the characteristic of ATRP.

The evolution of molecular weights and molecular weight distributions of PTPFCBBMA homopolymer with the conversions of

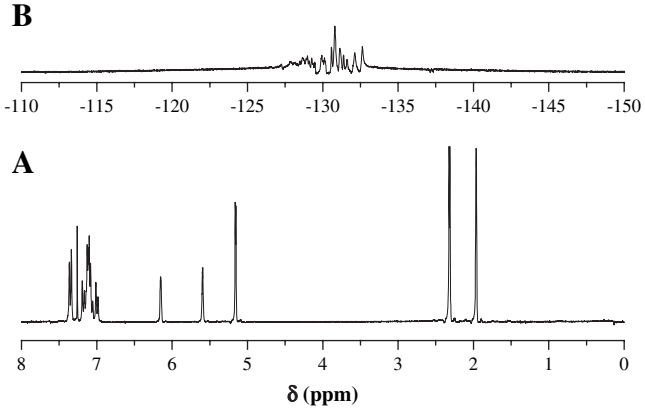


Fig. 2. ^{1}H NMR (A) and ^{19}F NMR (B) spectra of TPFCBBMA **4** in $CDCl_3$.

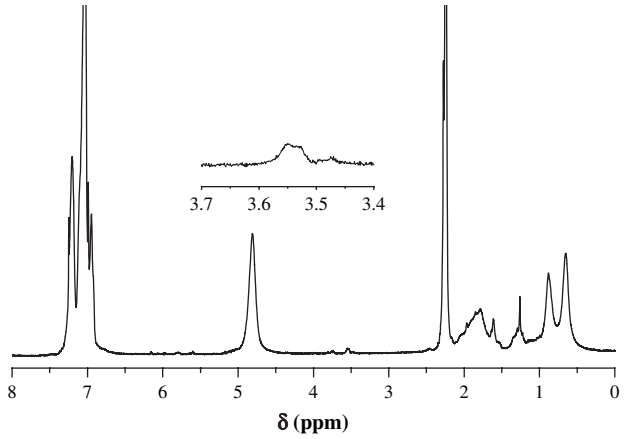


Fig. 3. ^{1}H NMR spectrum of PTPFCBBMA homopolymer.

monomer **4** were plotted in Fig. 5. It is clear that molecular weights increased linearly with the conversions of monomer **4**. In addition, the molecular weight distributions kept narrow throughout the homopolymerization ($M_w/M_n \leq 1.30$). These two phenomena also accorded with the characteristics of ATRP.

Therefore, ATRP of PFCB-containing methacrylate monomer **4** was carried out successfully and PTPFCBBMA homopolymers with narrow molecular weight distributions were obtained.

PTPFCBBMA homopolymer is soluble in common organic solvents such as THF, CH_2Cl_2, chloroform, DMSO, acetone, etc. However, it is insoluble in water and was deemed hydrophobic.

PTPFCBBMA homopolymer has a high decomposition temperature (T_d) around 320 °C, which indicates the excellent thermal stability of PTPFCBBA containing PFCB aryl ether unit. Glass transition temperature (T_g) was found to be 135 °C, which is much higher than that of PMMA due to the incorporation of PFCB aryl ether unit. This implies that PFCB aryl ether unit can be introduced into methacrylate monomer to increase T_g for future application while keeping the transparence.

3.3. Synthesis of perfluorocyclobutyl aromatic ether-based diblock copolymer

A series of PEG-*b*-PTPFCBBMA diblock copolymer were synthesize by ATRP of PFCB-containing methacrylate monomer **4** initiated by PEG-based macroinitiators and the results were listed in Table 1.

All diblock copolymers' molecular weights were much higher than that of PEG-based macroinitiator, which meant PFCB-containing methacrylate monomer **4** was initiated for polymerization. The molecular weights of diblock copolymers increased with the extending of polymerization time, which is the characteristic of ATRP. In addition, all diblock copolymers showed unimodal and symmetrical GPC curves with narrow molecular weight distributions ($M_w/M_n < 1.35$), which are characteristic of ATRP [53] and also indicated that intermolecular coupling reactions could be neglected [54].

PEG-*b*-PTPFCBBMA **6** was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR, respectively. FT-IR spectrum of PEG-*b*-

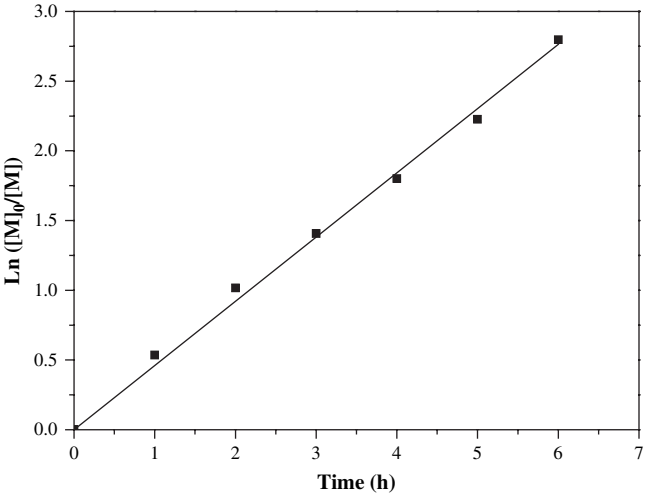


Fig. 4. Kinetic plot for solution ATRP of TPFCBBMA **4** initiated by 2-MBP.

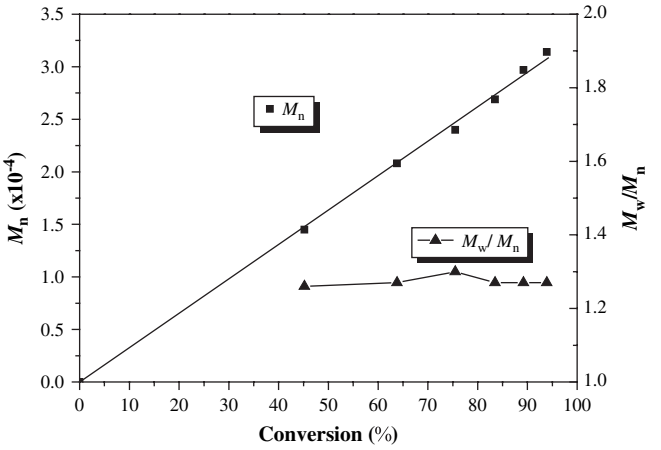


Fig. 5. Dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) on the conversion of **4** for solution ATRP of **4** initiated by 2-MBP.

Table 1
Synthesis of PEG-*b*-PTPFCBBMA diblock copolymer[a]

	Time (h)	M_n[d] (g/mol)	M_w/M_n[d]	cmc[e] (g/mol)
6a[b]	3	6,600	1.24	3.16×10^{-6}
6b[b]	9	8,200	1.16	2.50×10^{-6}
6c[b]	24	14,200	1.22	1.95×10^{-6}
6d[c]	36	12,000	1.33	3.98×10^{-6}

[a] Initiated by PEG-based macroinitiator **5**, [**4**]:[Br group]:[CuBr]:[PMDETA] = 50:1:2:4.
[b] Initiated by macroinitiator **5a** (M_n = 5,000).
[c] Initiated by macroinitiator **5b** (M_n = 2,000).
[d] Measured by GPC in THF.
[e] Critical micelle concentration determined by fluorescence spectroscopy.

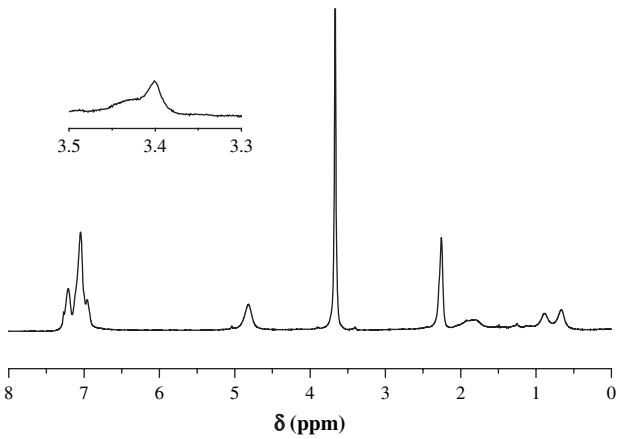


Fig. 6. ^{1}H NMR spectrum of PEG-*b*-PTPFCBBMA **6**.

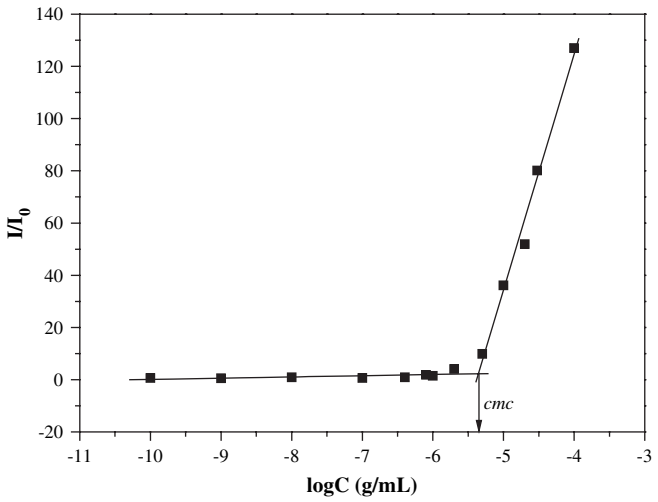


Fig. 7. Dependence of fluorescence intensity ratio of PNA emission band at 418 nm on the concentration of PEG-*b*-PTPFCBBMA **6c**.

PTPFCBBMA **6** is shown in Fig. 1B. The signal of double bond disappeared and the peak of carbonyl remained at 1734 cm^{-1} compared to that of TPFCBBMA **4**. The peaks at 817, 962, 1456, 1509 and 1600 cm^{-1} were attributed to PFCB aryl ether unit. The signals at 1114 and 1020 cm^{-1} demonstrated the incorporation of poly(ethylene glycol) segment.

Fig. 6 shows ^{1}H NMR spectrum of PEG-*b*-PTPFCBBMA **6**. The signal of double bond disappeared. The peaks at 6.94, 7.03 and 7.20 ppm illustrated the existence of PFCB aryl ether unit. The peaks at 3.41 and 3.65 ppm were attributed to the protons of terminal OCH_3 and OCH_2CH_2 groups of PEG segment, respectively. In particular, the signal of 2 protons of $C_6H_4CH_2O$ group shifted to 4.83 ppm due to the disappearance of double bond, which appeared at 5.17 ppm before copolymerization as shown in Fig. 2A. In addition, the presence of PFCB aryl ether unit were confirmed by the signals between 105.0 and 115.2 ppm in ^{13}C NMR spectrum and the peaks ranged from −127.3 to −132.6 ppm in ^{19}F NMR spectrum, respectively. Thus, the structure of PEG-*b*-PTPFCBBMA **6** diblock copolymer was affirmed.

3.4. Self-assembly of PEG-b-PTPFCBBMA amphiphilic diblock copolymer

PNA was used as fluorescence probe to determine cmc of PEG-*b*-PTPFCBBMA **6** in aqueous solution (Fig. 7). PNA is a more suitable fluorescent probe than pyrene in terms of reproducibility since it displays higher fluorescence activity in nonpolar environments and the fluorescence can be very easily quenched by polar solvents such as water [55]. The relationship of the fluorescence intensity ratio (I/I_0) of PNA as a function of the concentration of PEG-*b*-PTPFCBBMA **6c** at 25 °C is shown in Fig. 7. The fluorescence intensity ratios were almost constant while the concentration was below a certain value. However, I/I_0 increased sharply when the concentration exceeded that value, which demonstrated the incorporation of PNA probe into the hydrophobic region of micelles. Therefore, cmc of PEG-*b*-PTPFCBBMA **6c** was determined to be the intersection of 2 straight lines with a value of 1.95×10^{-6} g/mL.

The cmc values of PEG-*b*-PTPFCBBMA **6** diblock copolymers are summarized in Table 1. These values were comparable with those of polymeric amphiphiles [29,33,34,56]. It was found that cmc values of PEG-*b*-PTPFCBBMA **6** decreased when the molecular weights increased due to the increase of the content of hydrophobic PTPFCBBMA block.

Finally, the micelle structures were preliminarily explored by TEM. Typical TEM images of the micelles of PEG-*b*-PTPFCBBMA **6** in fresh aqueous solution are shown in Fig. 8. The micelles formed by

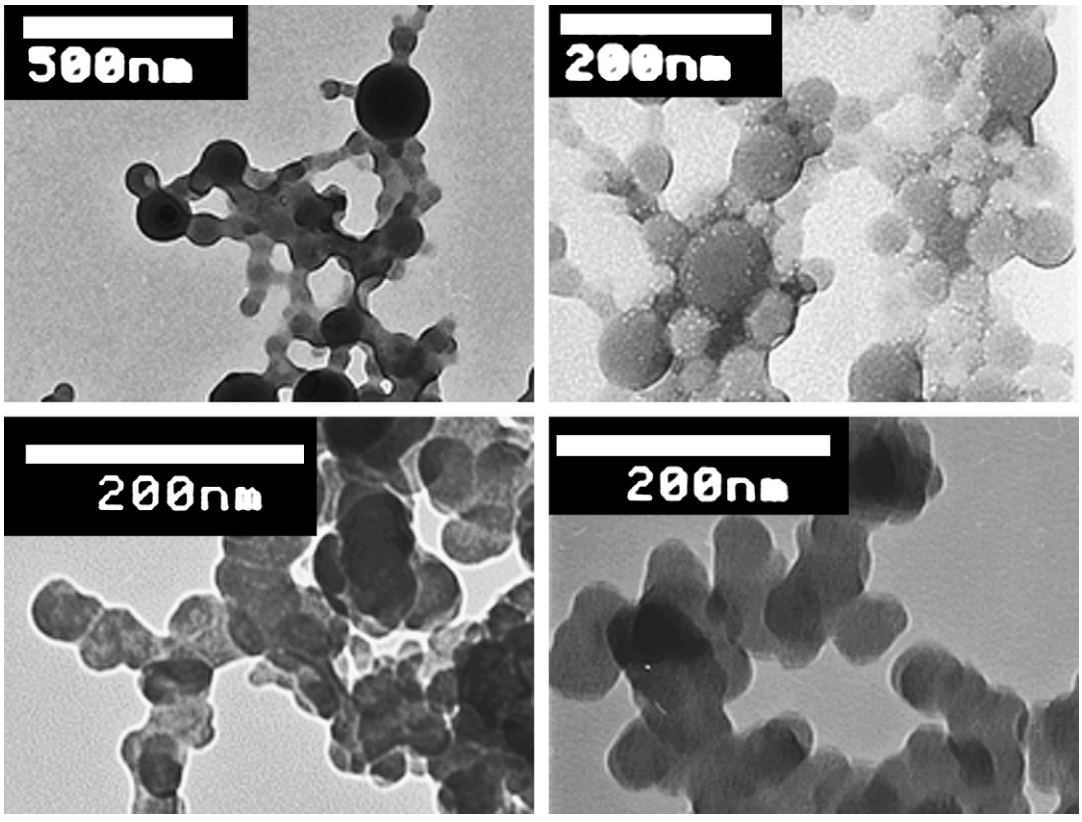


Fig. 8. TEM images of micelles formed from PEG-*b*-PTPFCBBMA **6a** (A), **6b** (B), **6c** (C) and **6d** (D) in pure water.

PEG-*b*-PTPFCBBMA **6** in pure water with different molecular weights were all spheres (ca. 70–170 nm).

4. Conclusion

We presented the first example of successful synthesizing amphiphilic diblock copolymer containing PFCB segment using ATRP. PFCB linkage was incorporated into methacrylate monomer as a side group using commercially available 4-methylphenol as starting material. This kind of PFCB-containing methacrylate monomer can be polymerized by ATRP in a controlled way and the apparent polymerization rate exhibited first-order relation with respect to the concentration of monomer. PTPFCBBMA homopolymer shows excellent thermal properties with high T_g and T_d, and excellent solubility in common organic solvents.

PEG-*b*-PTPFCBBMA diblock copolymers were obtained by ATRP of this new fluorine-containing methacrylate monomer initiated by PEG-based macroinitiators. This kind of diblock copolymer can self-assemble in water. PNA was used as fluorescence probe to determine cmc of these amphiphilic copolymers and TEM was employed to study the morphologies of the micelles, which was found to be spheres.

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