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A novel well-defined amphiphilic diblock copolymer containing perfluorocyclobutyl aryl ether-based hydrophobic segment

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ABSTRACT

A series of well-defined binary hydrophilic-fluorophilic diblock copolymers were synthesized by successive atom transfer radical polymerization (ATRP) of methoxylmethyl acrylate (MOMA) and 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate (TPFCBBMA) followed by the acidic selective hydrolysis of the hydrophobic poly(methoxymethyl acrylate) (PMOMA) segment into the hydrophilic poly (acrylic acid) (PAA) segment. ATRP of MOMA was initiated by 2-MBP at 50 °C in bulk to give two different PMOMA homopolymers with narrow molecular weight distributions ($M_w/M_n \leq 1.15$). PMOMA-*b*-PTPFCBBMA well-defined diblock copolymers were synthesized by ATRP of TPFCBBMA at 90 °C in anisole using Br-end-functionalized PMOMA homopolymer as macroinitiator and CuBr/PMDETA as catalytic system. The final PAA-*b*-PTPFCBBMA amphiphilic diblock copolymers were obtained via the selective hydrolysis of PMOMA block in dilute HCl without affecting PTPFCBBMA block. The critical micelle concentrations (*cmc*) of PAA-*b*-PTPFCBBMA amphiphilic copolymers in aqueous media were determined by fluorescence spectroscopy using pyrene as probe and these diblock copolymers showed different micellar morphologies with the changing of the composition.

1. Introduction

Fluoropolymers have been found to possess many advantages though their solubility and processability are generally low, such as the increased thermal and oxidative stability, optical transparency, solvent compatibility and environmental stability etc., compared to the conventional carbon-hydrogen-containing polymers because of the incorporation of fluorocarbon functionality [1]. Therefore, fluoropolymers including polychlorotrifluoroethylene, Teflon-AF, Cytop and various copolymers of polytetrafluoroethylene with low crystallinity have been modified to improve the processability [1]. Recently, perfluorocyclobutyl (PFCB) aryl ether polymer has received considerable attention since its discovery by Dow Chemical Co. in early 1990s [1,2]. The predominant head-to-head thermal [2π + 2π] cyclopolymerization of aryl trifluorovinyl ethers (TFVE) proceed to form a stable diradical intermediate followed by rapid ring closure to afford a mixture of *cis*- and *trans*-1,2-disubstituted perfluorocyclobutanes [3–7]. The stereo-random PFCB rings provided amorphous polymers with excellent solubility and processability compared with the ordinary fluoropolymers. PFCB aryl ether polymers have the common properties of fluoropolymer and they also possess many other advantages including optical transparency and improved processability [8,9]. Thus, PFCB polymers are attractive for a multitude of new applications often inaccessible using commercial fluoropolymer preparative routes due to the combination of solution processability and thermal stability as reviewed by Smith *et al* [9].

Most recent studies of PFCB-based polymers focused on the synthesis of homopolymers and random copolymers via the thermal polymerization of different TFVE monomers in which PFCB connection was employed as a way to link different functionalities [10–14]. However, the unusual polymerization mechanism ([2π + 2π] cycloaddition) and relatively high polymerization temperature (at least >150 °C) made the studies on the synthesis of the copolymers via TFVE and commonly used vinyl monomers very limited and it was found to be difficult to regulate the number of PFCB unit in copolymers in those cases [15–18]. Thus, it is necessary to combine the high performance of PFCB-based fluoropolymer with other commercial polymer to enlarge the application range of PFCB-based fluoropolymer.

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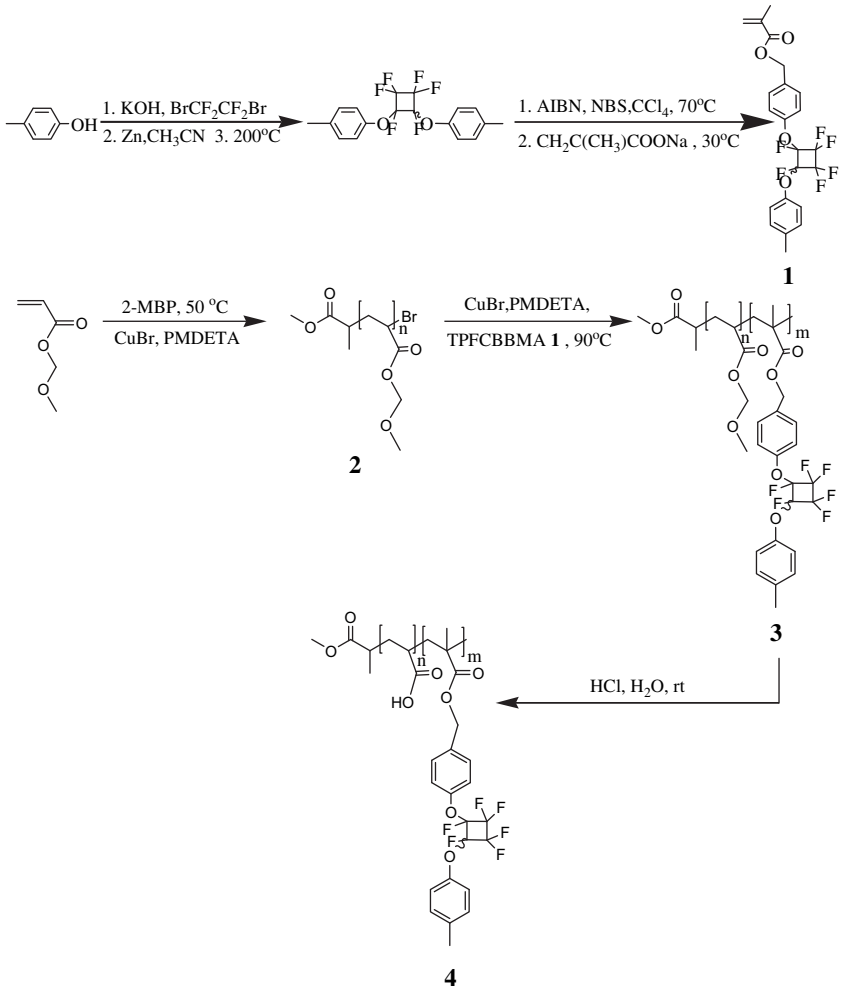

Scheme 1. Synthesis of PAA-*b*-PTPFCBBMA amphiphilic diblock copolymer.

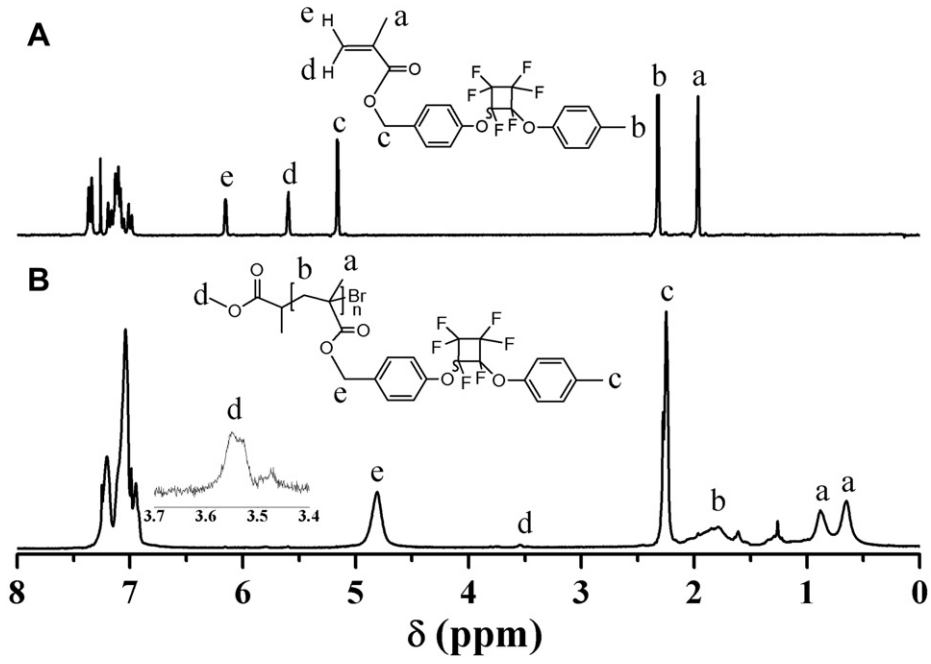

Fig. 1. ^{1}H NMR spectra of TPFCBBMA **1** (A) and PTPFCBBMA (B) in $CDCl_3$.

Table 1
Synthesis of PMOMA **2** macroinitiator.[a]

Sample	[MOMA]:[2-MBP]	Time (h)	M_n[b] (g/mol)	M_w/M_n[b]
2a	50:1	3	2800	1.13
2b	50:1	9	4300	1.15

[a] Polymerization temperature: 50 °C, [2-MBP]:[PMDETA]:[CuBr] = 1:1:1.
[b] Measured by GPC in THF at 35 °C.

Block copolymer with a stable connection between two different segments may be a suitable choice to realize the above consideration. Generally, block copolymer is synthesized by the sequential feeding of different monomers via living polymerization [19] including anionic polymerization [20,21], cationic polymerization [22,23], group transfer polymerization [24] and living radical polymerization [25–28] or the strategy of mechanism transformation via different polymerization approaches [29–31]. In particular, atom transfer radical polymerization (ATRP) has been easily employed to synthesize amphiphilic block copolymers [32,33]. However, the synthesis of well-defined semi-fluorinated amphiphilic block copolymers as well as their self-assembly behaviors in aqueous media were rarely reported [34–37].

In this work, we report the synthesis of a new well-defined PFCB-based amphiphilic diblock copolymer consisting of hydrophilic PAA segment and hydrophobic PTPFCBBMA segment synthesized by sequential ATRP of methoxy- methyl acrylate (MOMA) and 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)benzyl methacrylate (TPFCBBMA) followed by the selective hydrolysis of PMOMA block as shown in Scheme 1. Moreover, the self-assembly behavior of PAA-*b*-PTPFCBBMA amphiphilic diblock copolymer in pure water was preliminarily explored by measuring the critical micelle concentration and visualizing the diverse micellar morphologies Scheme 1.

2. Experimental section

2.1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol. Granular zinc was activated by washing in 0.1 N HCl followed by drying at 140 °C *in vacuo* overnight. 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. Pyrene (Aldrich, 98%) was purified by recrystallization in ethanol for three times. Anisole (Aldrich, 99%) was dried over CaH_2 and distilled *in vacuo* prior to use. $BrCF_2CF_2Br$ was prepared by condensing equimolar amounts of Br_2 and CF_2CH_2 at −195 °C followed by warming up to 22 °C [38]. 4-Methylphenol (Aldrich, 99%), methyl 2-bromopropionate (2-MBP, Aldrich, 99%), methacrylic acid (Aldrich, 99%), acrylic acid (Aldrich, 99%), chloromethyl methyl ether (Aldrich, 99%), α-bromoisobutyryl bromide (Aldrich, 98%), *N*-bromosuccinimide (NBS, Aldrich, 99%), *N,N,N′,N′,N″*- pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), CCl_4 (Aldrich, 99.5%) and dimethyl sulfoxide (DMSO, Aldrich, 99.9%) were used as received.

2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. All ^1H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) analyses were performed on a Bruker Avance 500 spectrometer. TMS (^1H NMR) and $CDCl_3$ and acetone-d_6 (^{13}C NMR) were used as internal standards, respectively; CF_3CO_2H was used as external standard for ^{19}F NMR. ESI-MS was 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) and a set of Waters Styragel columns (HR3 (500–30,000), HR4 (5000–600,000) and HR5 (50,000–4,000,000), 7.8 × 300 mm, particle size: 5 μm). 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 pyrene were recorded on a HITACHI F-4500 spectrofluorometer with the band widths of 10 nm for excitation and 2.5 nm for emission, where the excitation wavelength (λ_{ex}) was

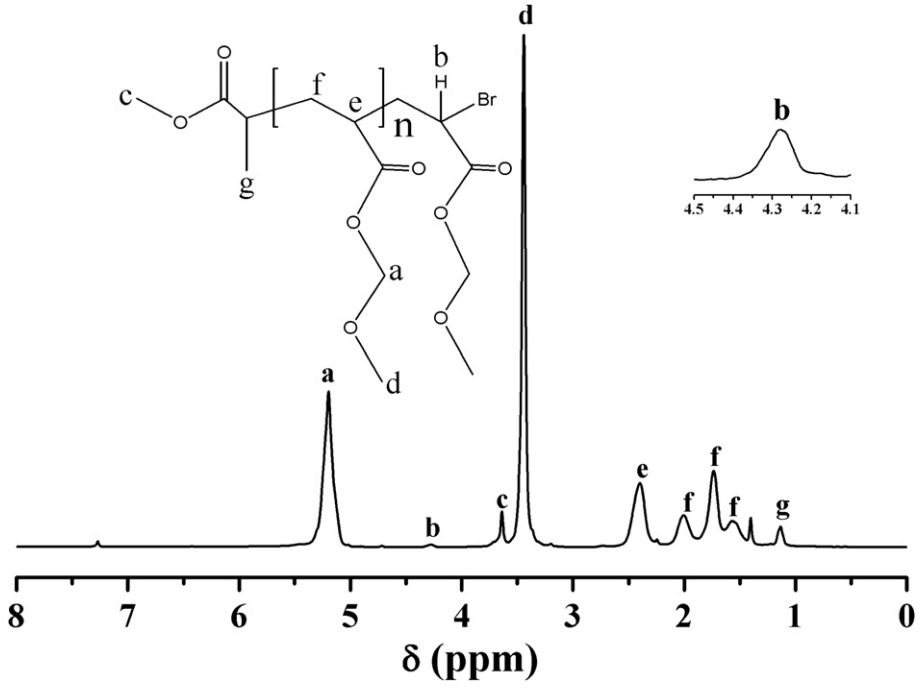

Fig. 2. ^1H NMR spectrum of PMOMA **2** macroinitiator in $CDCl_3$.

Table 2
Synthesis of PMOMA-*b*-PTPFCBBMA **3** using PMOMA **2** macroinitiator.[a]

Sample	Macroinitiator	[1] : [2]	Time (h)	M_n[b] (g/mol)	M_w/M_n[b]
3a	2a	40:1	12	12,700	1.33
3b	2a	40:1	18	14,200	1.36
3c	2a	40:1	24	16,900	1.30
3d	2a	40:1	48	18,600	1.28
3e	2b	100:1	9	18,200	1.32

[a] Polymerization temperature: 90 °C, [**2**]:[PMDETA]:[CuBr] = 1:4:4.
[b] Measured by GPC in THF at 35 °C.

339 nm. Transmission electron microscope (TEM) images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

2.3. Preparation of TPFCBBMA 1

The intermediate, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy) toluene, was first prepared via the bulk thermal [2π + 2π] cycloaddition (200 °C) of *p*-trifluorovinyloxytoluene obtained by the fluoroalkylation of 4-methylphenol with $BrCF_2CF_2Br$ followed by Zn-mediated elimination [2]. The dimer was obtained by silica column chromatography with a yield of 92.0%. ^{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 (CH_3), 105.0–115.2 (4C, PFCB). ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, PFCB).

TPFCBBMA **1** monomer was obtained through the bromination of 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)toluene with NBS and AIBN in CCl_4 (yield: 42.0%) followed by reacting with sodium methacrylate in DMSO (yield: 57.6%). ESI-MS (*m*/*z*): calcd $(M + Na)^+$ 483.1, found 483.1. FT-IR: ν (cm^{-1}): 3060, 2950, 1722, 1639, 1600, 1509, 1456, 1201, 1157, 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, PFCB), 118.3, 126.0 (CH_2=C–CH_3), 130.3 (phenyl), 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, PFCB).

2.4. Preparation of MOMA

MOMA monomer was prepared by reacting acrylic acid with chloromethyl methyl ether in CH_2Cl_2 at room temperature according to our previous reports [39–41]. ^{1}H NMR: δ (ppm): 3.50 (3H, CH_3O), 5.34 (2H, $COOCH_2O$), 5.91, 6.50 (2H, CH_2=CH), 6.17 (1H, CH_2=CH).

2.5. ATRP homopolymerization of MOMA

In a typical procedure, CuBr (0.0507 g, 0.353 mmol) was first 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, MOMA (2 mL, 17.6 mmol), PMDETA (0.0737 mL, 0.353 mmol) and 2-MBP (0.0393 mL, 0.353 mmol) 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 thermostated at 50 °C. The polymerization lasted 3 h and was terminated by putting the flask into liquid N_2. THF was added to dissolve the viscous crude product and the solution was passed through a short Al_2O_3 column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold *n*-hexane. The precipitation was dried *in vacuo* overnight to afford 1.435 g of glassy solid, poly(methoxymethyl acrylate) (PMOMA) **2a**. GPC: M_n = 2800, M_w/M_n = 1.13. ^{1}H NMR: δ (ppm): 1.13 (3H, CH_3CH), 1.57, 1.74, 2.01 (2H, CH_2CH), 2.39 (1H, CH_2CH), 3.44 (3H, OCH_3), 3.63 (3H, $COOCH_3$), 4.28 (1H, CHBr), 5.20 (2H, $COOCH_2O$). ^{13}C NMR: δ (ppm): 31.7 (CH_2CH), 41.4 (CH_2CH), 57.9 (OCH_3), 92.0 ($COOCH_2O$), 174.1 ($COOCH_2$).

2.6. ATRP block copolymerization of TPFCBBMA *1*

ATRP block copolymerization of TPFCBBMA **1** was initiated by PMOMA **2** macroinitiator to provide a series of well-defined PMOMA-*b*-PTPFCBBMA **3** diblock copolymers. In a typical procedure, CuBr (0.0258 g, 0.18 mmol) and PMOMA **2a** (0.126 g, 0.045 mmol of ATRP initiation group, M_n = 2800, M_w/M_n = 1.13) in 1.8 mL of anisole were first 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, TPFCBBMA **1** (0.828 g, 1.8 mmol) and PMDETA (0.0376 mL, 0.18 mmol) were introduced via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath preset at 90 °C. The polymerization was terminated by putting the flask into liquid N_2 after 48 h. THF was added to the flask for dilution and the solution

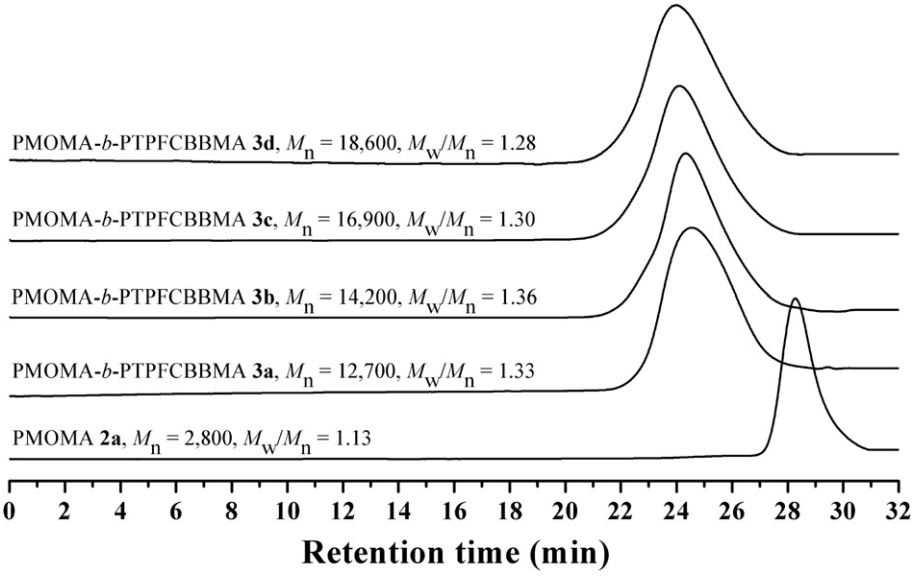

Fig. 3. GPC traces of PMOMA **2a**, PMOMA-g-PTPFCBBMA **3a**, **3b**, **3c** and **3d**.

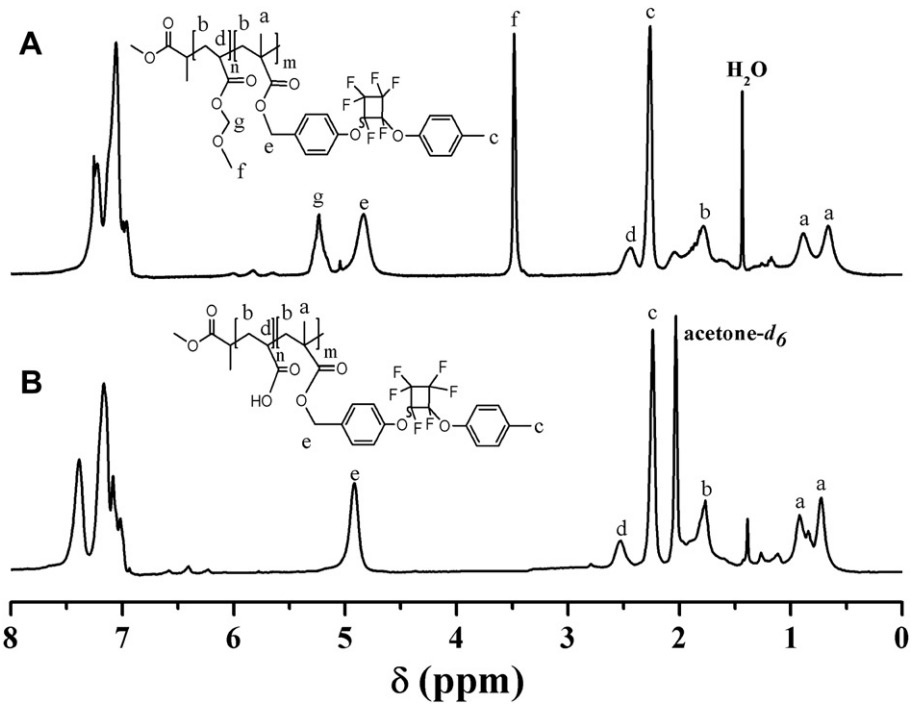

Fig. 4. ^{1}H NMR spectra of PMOMA-*b*-PTPFCBBMA **3** in $CDCl_3$ (A) and PAA-*b*-PTPFCBBMA **4** in acetone-d_6 (B).

was filtered through a short Al_2O_3 column to remove the residual copper catalyst. The resulting solution was concentrated and precipitated into cold *n*-hexane. After repeated purification by dissolving in THF and precipitating in cold *n*-hexane for three times, the final product, PMOMA-*b*-PTPFCBBMA **3d**, was obtained after drying *in vacuo* overnight. GPC: $M_n = 18{,}600$, $M_w/M_n = 1.28$. FI-IR: ν (cm^{-1}): 2948, 2926, 2837, 1735, 1612, 1509, 1452, 1407, 1324, 1198, 1142, 963. ^{1}H NMR: δ (ppm): 0.67, 0.88 (3H, CCH_3), 1.78 (2H, CH_2C), 2.26 (3H, $C_6H_4CH_3$), 2.44 (1H, CH_2CH), 3.47 (3H, OCH_3), 4.84 (2H, $C_6H_4CH_2O$), 5.23 (2H, $COOCH_2O$), 6.97 (2H, $C_6H_4CH_3$), 7.06 (4H, C_6H_4—OC_4F_6O—C_6H_4), 7.22 (2H, $C_6H_4CH_2O$). ^{13}C NMR: δ (ppm): 21.4 (CH_3), 30.5 (CH_2C), 41.7 (CH_2C), 44.6 (CH_2C), 58.0 (OCH_3), 68.2 ($C_6H_4CH_2O$), 91.1 (OCH_2O), 105.0–115.0 (4C, PFCB), 118.1, 130.4, 135.0, 150.5, 174.1, 176.4, 177.1. ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, PFCB).

2.7. Acidic selective hydrolysis of PMOMA-*b*-PTPFCBBMA *3*

PMOMA-*b*-PTPFCBBMA **3** was dissolved in THF and treated with excess 1 M HCl for 2 h at room temperature. The reaction mixture

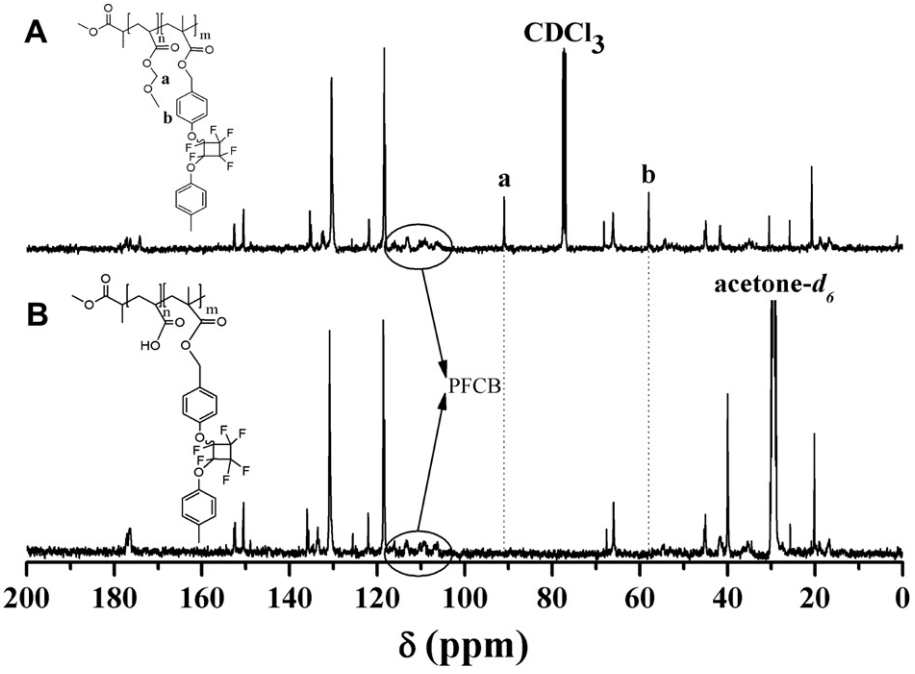

Fig. 5. ^{13}C NMR spectra of PMOMA-*b*-PTPFCBBMA **3** in $CDCl_3$ (A) and PAA-*b*-PTPFCBBMA **4** in acetone-d_6 (B).

was washed with water until the aqueous phase became neutral and then with brine followed by drying over anhydrous $MgSO_4$. Next, the solution was concentrated and precipitated into cold *n*-hexane. After filtration PAA-*b*-PTPFCBBMA **4** amphiphilic diblock copolymer was obtained after drying *in vacuo* overnight. FT-IR: ν (cm^{-1}): 3422 (COOH), 2961, 1734, 1612, 1510, 1451, 1320, 1198, 1119, 962. ^1H NMR (acetone-d_6): δ (ppm): 0.73, 0.92 (3H, CCH_3), 1.77 (2H, CH_2C), 2.24 (3H, $C_6H_4CH_3$), 2.51 (1H, CH_2CH), 4.92 (2H, $C_6H_4CH_2O$), 7.06 (2H, $C_6H_4CH_3$), 7.17 (4H, $C_6H_4{-}OC_4F_6O{-}C_6H_4$), 7.39 (2H, $C_6H_4CH_2O$). ^{13}C NMR: δ (ppm): 20.0 (CH_3), 25.5 (CH_3), 29.5 (CH_2C), 39.9 (CH_2C), 44.8 (CH_2C), 66.0 ($C_6H_4CH_2O$), 105.0–116.3 (4C, PFCB), 118.0, 130.3, 135.9, 150.6, 176.5, 177.1. ^{19}F NMR: δ (ppm): −127.3 to −132.6 (6F, PFCB).

2.8. Determination of critical micelle concentration

Pyrene was used as fluorescence probe to measure the critical micelle concentration (*cmc*) of PAA-*b*-PTPFCBBMA **4** amphiphilic block copolymer. Acetone solution of pyrene (0.3 mM) was added to a large amount of water until the concentration of pyrene reached 0.0006 mM. Different amounts of THF solutions of PAA-*b*-PTPFCBBMA **4** (20 mg/mL) were added to pyrene-containing water ([pyrene] = 0.0006 mM). All fluorescence spectra were recorded at 25 °C.

2.9. TEM images

THF solution of PAA-*b*-PTPFCBBMA **4** (20 mg/mL) was added dropwise to water with vigorous stirring until the concentration of the copolymer was 0.1 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 was evaporated at room temperature.

3. Results and discussion

3.1. TPFCBBMA *1* semi-fluorinated methacrylate monomer

Commercially available 4-methylphenol was used as starting material to prepare *p*-trifluorovinyloxytoluene in two steps via the fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn-mediated elimination according to the standard procedure [2]. The dimer, 4-(4′-*p*-tolyloxyperfluorocyclobutoxy)toluene, was obtained by the thermal [2π + 2π] cycloaddition of *p*-trifluorovinyloxytoluene. Finally, the mono-brominated product of the dimer reacted with sodium methacrylate to provide the desired PFCB-linkage-containing methacrylate monomer, TPFCBBMA **1**.

The chemical structure of TPFCBBMA **1** was characterized by FT-IR, ^1H NMR, ^{19}F NMR and ^{13}C NMR in detail. The typical signals of the double bond and the carbonyl appeared at 1639 and 1722 cm^{-1} in FT-IR spectrum, respectively. The peaks at 963, 1456, 1509 and 1600 cm^{-1} demonstrated the successful incorporation of PFCB linkage. Moreover, the *para*-disubstituted benzene ring structure of PFCB aryl ether unit was confirmed by the sharp band centered at 817 cm^{-1} ^1H NMR spectrum of TPFCBBMA **1** is shown in Fig. 1A and the typical resonance signals of the double bond were found to locate at 5.60 and 6.16 ppm. The peaks at 7.02, 7.11 and 7.25 ppm were attributed to 8 protons of benzene ring in PFCB aryl ether unit. The resonance signals of 2 carbons of the double bond also appeared at 126.0 and 136.2 ppm in ^{13}C NMR spectrum of **1**. The peak at 167.2 ppm corresponded to the carbon of the carbonyl and a series of peaks between 105.0 and 115.2 ppm belonged to 4 carbons of PFCB linkage. Furthermore, the presence of PFCB linkage was illustrated by the peaks between −127.3 and −132.6 ppm in ^{19}F NMR spectrum of **1**. All the above results showed the successful synthesis of PFCB-linkage-containing monomer **1**.

This semi-fluorinated methacrylate monomer is suitable for ATRP. Its ATRP homopolymerization can be initiated by 2-MBP at 90 °C in anisole using PMDETA/CuBr as catalytic system. When the feed ratio of [TPFCBBMA]:[2-MBP]:[PMDETA]:[CuBr] was 50:1:4:2, a well-defined PTPFCBBMA homopolymer (M_n = 31,400, M_w/M_n = 1.05) was obtained after 6 h with a high conversion of 93.8% determined by GC. ATRP mechanism was confirmed by the minor peak at 3.55 ppm attributed to 3 protons of $COOCH_3$ in ATRP initiation group as shown in Fig. 1B.

Table 3
cmc of PAA-*b*-PTPFCBBMA **4** diblock copolymers.[a]

Sample	$N_{hydrophilic}/N_{fluorophilic}$	*cmc* (g/mL)
4a	22.7/21.5	3.78×10^{-6}
4b	22.7/24.8	1.76×10^{-6}
4c	22.7/30.7	6.31×10^{-7}
4d	22.7/34.3	5.67×10^{-7}
4e	35.6/30.2	5.61×10^{-6}

[a] Critical micelle concentration determined by fluorescence spectroscopy.

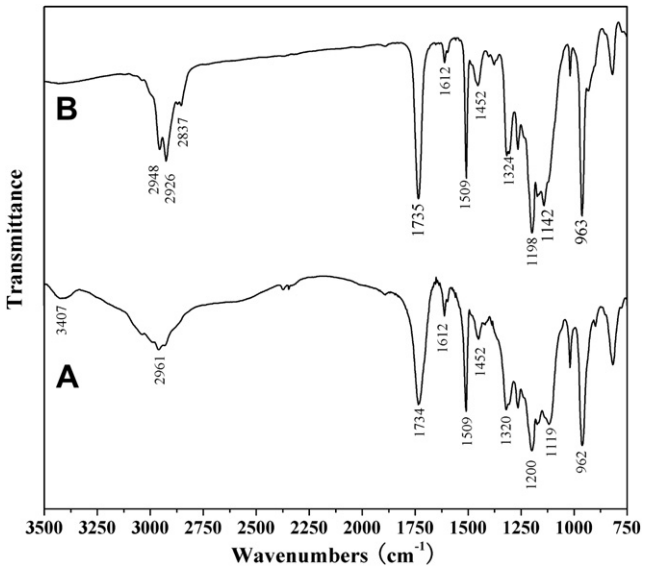

Fig. 6. FT-IR spectra of PAA-*b*-PTPFCBBMA **4** (A) and PMOMA-*b*-PTPFCBBMA **3** (B).

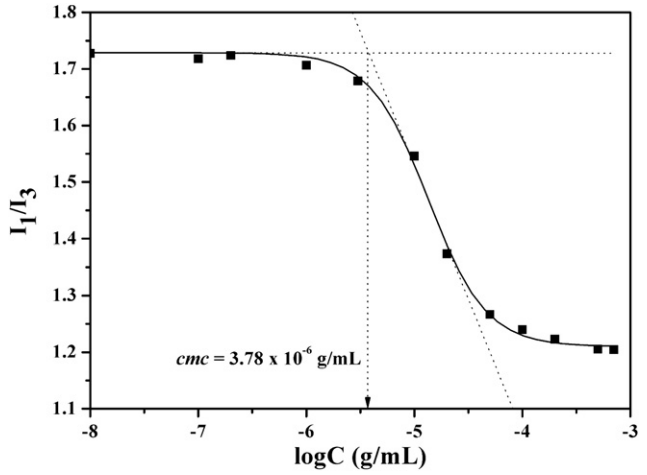

Fig. 7. Dependence of fluorescence intensity ratios of pyrene emission bands on the concentration of PAA-*b*-PTPFCBBMA **4a**.

3.2. Br-end-functionalized PMOMA **2** macroinitiator

It was found that the ester group of PTPFCBBMA homopolymer could be hydrolyzed into the carboxyl in basic surrounding; however, it was stable in acidic environment. Moreover, acrylic acid can not be polymerized by ATRP. For the targeted PAA-*b*-PTPFCBBMA diblock copolymer, a suitable polyacrylate segment which can be easily hydrolyzed into poly(acrylic acid) segment under mild acidic conditions should be chosen. Thus, MOMA was selected due to its mild acidic hydrolysis conditions without steric effect [39–41].

PMOMA **2** homopolymers with narrow molecular weight distributions ($M_w/M_n \leq 1.15$) were obtained via bulk ATRP at 50 °C using 2-MBP as initiator and CuBr/PMDETA as catalytic system (Table 1). From the data of molecular weight, it was estimated that every PMOMA **2a** and **2b** chain possess 22.7 and 35.6 MOMA repeating units, respectively. Fig. 2 shows ^{1}H NMR spectrum of PMOMA **2**. The peaks of 3 protons of the double bond at 5.90, 6.17

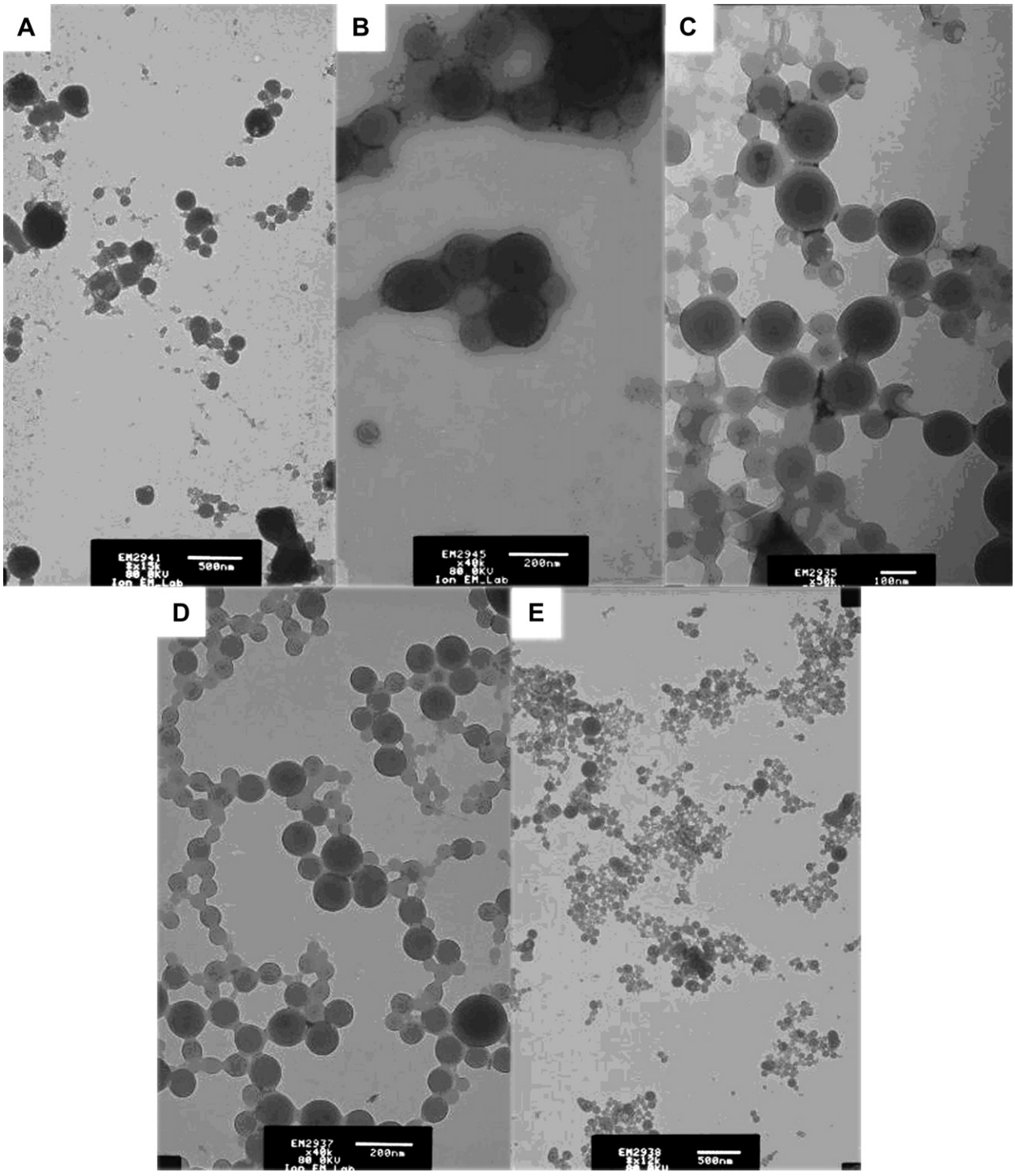

Fig. 8. TEM images of PAA-*b*-PTPFCBBMA **4a** (A), **4b** (B), **4c** (C), **4d** (D) and **4e** (E) in aqueous media, [copolymer] = 0.1 mg/mL.

and 6.50 ppm disappeared after ATRP homopolymerization and the resonance signals of polyacrylate backbone appeared at 1.57, 1.74, 2.01 and 2.39 ppm. The peaks "b" (4.29 ppm), "c" (3.63 ppm) and "g" (1.13 ppm) were attributed to the protons of ATRP initiation group, this verifying ATRP mechanism of the homopolymerization. In particular, the peak at 4.29 ppm indicated the existence of active ATRP initiation group as end group of PMOMA **2**, which meant PMOMA **2** can initiate ATRP of another monomer to obtain PMOMA-containing block copolymer.

3.3. Synthesis of PMOMA-*b*-PTPFCBBMA **3** diblock copolymer

PMOMA-*b*-PTPFCBBMA **3** diblock copolymers were synthesized via ATRP of TPFCBBMA **1** initiated by Br-end-functionalized PMOMA **2** at 90 °C in anisole using CuBr/PMDETA as catalytic system and the results are listed in Table 2. All obtained diblock copolymers' molecular weights were much higher than those of PMOMA **2**, this indicating the occurring of ATRP of TPFCBBMA **1**. The molecular weights of the copolymers increased with the extending of polymerization time and all copolymers showed unimodal and symmetrical GPC curves (Fig. 3) with narrow molecular weight distributions ($M_w/M_n \leq 1.36$), which were the characteristics of ATRP [42,43].

FT-IR, ^{1}H NMR and ^{13}C NMR were employed to characterize PMOMA-*b*-PTPFCBBMA **3** diblock copolymer. The signal of the double bond at 1639 cm^{-1} in FT-IR spectrum disappeared after the copolymerization and the bands at 963, 1452, 1509 and 1612 cm^{-1} demonstrated the existence of PFCB aryl ether unit. The peaks at 3.47 and 5.23 ppm in ^{1}H NMR spectrum (Fig. 4A), and the peaks at 58.0 and 91.1 ppm in ^{13}C NMR spectrum (Fig. 5A) corresponded to the methoxymethyls of PMOMA block. The presence of PFCB aryl ether unit was also verified by the resonance signals at 6.97, 7.06 and 7.22 ppm in ^{1}H NMR spectrum and a series of peaks between 105.0 and 115.0 ppm in ^{13}C NMR spectrum. Specially, the peak of 2 protons of $C_6H_4CH_2O$ in PTPFCBBMA segment shifted to 4.84 ppm compared to that of TPFCBBMA **1** at 5.17 ppm because the double bonds disappeared after ATRP of **1**. All these results confirmed the chemical structure of PMOMA-*b*-PTPFCBBMA **3**.

3.4. Selective hydrolysis of PMOMA-*b*-PTPFCBBMA **3**

Dilute HCl was employed to hydrolyze PMOMA-*b*-PTPFCBBMA **3** diblock copolymers into PAA-*b*-PTPFCBBMA **4** diblock copolymers at room temperature in THF according to previous literatures [39–41]. ^{1}H NMR (3.47 and 5.23 ppm) and ^{13}C NMR (58.0 and 91.1 ppm) signals of the methoxymethyls disappeared after the hydrolysis as shown in Figs. 4B and 5B, this confirming the complete hydrolysis of PMOMA block. The resonance signals of PFCB aryl ether units remained in Figs. 4B and 5B, which meant that PTPFCBBMA segment was not affected during the hydrolysis. In addition, it was found that a new broad peak appeared at 3407 cm^{-1} in FT-IR spectrum after the hydrolysis (Fig. 6A) compared to that before the hydrolysis as shown in Fig. 6B, this indicating the formation of PAA block.

3.5. Self-assembly of PAA-*b*-PTPFCBBMA **4** in aqueous media

In current case, pyrene was used as fluorescence probe to determine the critical micelle concentrations of PAA-*b*-PTPFCBBMA **4** amphiphilic diblock copolymers in aqueous media and the results are summarized in Table 3. It is well-known that fluorescence spectrum of pyrene is sensitively affected by the environment and the polarity of its surroundings [44–46]. In the existence of micelles, pyrene is solubilized within the interior of the hydrophobic part. Thus, the values of I_1/I_3 of the emission spectrum would change sharply as a result, which showed pyrene probes transferred to a more hydrophobic micro-environment. The ratios of the intensity (I_1/I_3) against the logarithm of the concentration of the copolymer are plotted in Fig. 7. The I_1/I_3 ratios almost kept constant ranging from 1.7 to 1.8 when the concentration of PAA-*b*-PTPFCBBMA **4a** was low, which meant that pyrene probes located in a hydrophilic environment. With the increasing of the concentration of **4a**, I_1/I_3 ratios dropped quickly and an inflection point ([**4a**] = 3.78 × 10^{-6} g/mL) appeared in the curve, which was determined to be the *cmc* of PAA-*b*-PTPFCBBMA **4a**. The *cmc* values of PAA-*b*-PTPFCBBMA **4** are all around 10^{-7} g/mL as listed in Table 3 which is very low compared to the common surfactants or polymeric amphiphiles [47–50]. These low *cmc* values are related with the semi-fluorinated PTPFCBBMA segment. Moreover, the values of *cmc* decreased with the raising of the length of fluorophilic PTPFCBBMA segment (**4d** < **4c** < **4b** < **4a**) while keeping the length of hydrophilic PAA block constant; when the lengths of PTPFCBBMA segment were similar ($N_{TPFCBBMA}$ = 30.7 and 30.2 for **4c** and **4e**, respectively), *cmc* values increased with the rising of the length of PAA block (**4c** < **4e**).

Micellar morphologies were visualized under TEM. Fig. 8 show micellar morphologies formed by PAA-*b*-PTPFCBBMA **4** with different compositions in aqueous media. When the content of fluorophilic TPFCBBMA unit was low (**4a**, **4b** and **4e**), the copolymers aggregated to form spherical micelles as shown in Fig. 8A, B and E. With the increasing of the content of TPFCBBMA unit (**4c** and **4d**), spherical micelles turned to pearl-necklace-like micelles (Fig. 8C and D).

4. Conclusion

In summary, we present the synthesis and self-assembly of a well-defined semi-fluorinated amphiphilic diblock copolymer with hydrophilic PAA and fluorophilic PTPFCBBMA segments. A new PFCB-based methacrylate monomer was first prepared in 5 steps using 4-methylphenol as starting material and this monomer is suitable for ATRP. Well-defined PMOMA-*b*-PTPFCBBMA diblock copolymers with narrow molecular weight distributions were obtained by sequential ATRP of MOMA and TPFCBBMA and they were selectively hydrolyzed into PAA-*b*-PTPFCBBMA diblock copolymers in acidic environment. Pyrene was used as fluorescence probe to determine the *cmc*s of these amphiphilic copolymers and they aggregated to form micelles with different morphologies while changing the compositions.

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