Novel Perfluorocyclobutyl Aryl Ether-Based Well-Defined Amphiphilic Block Copolymer

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ABSTRACT: A series of fluorine-containing amphiphilic diblock copolymers comprising hydrophobic poly(*p*-(2-(*p*-tolyloxy)perfluorocyclobutoxy)phenyl methacrylate) (PTPFCBPMA) and hydrophilic poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) segments were synthesized via successive reversible addition fragmentation chain transfer (RAFT) polymerizations. RAFT homopolymerization of *p*-(2-(*p*-tolyloxy)perfluorocyclobutoxy)-phenyl methacrylate was first initiated by 2,2′-azobisisobutyronitrile using cumyl dithiobenzoate as chain transfer agent, and the results show that the procedure was conducted in a controlled way as confirmed by the fact that the number-average molecular weights increased linearly with the conversions of the monomer while the polydispersity indices kept below 1.30. Dithiobenzoate-capped PTPFCHPMA homopolymer was then used as macro-RAFT agent to mediate RAFT polymerization of 2-(diethylamino)ethyl methacrylate, which afforded PTPFCBPMA-*b*-PDEAEMA amphiphilic diblock copolymers with different block lengths and narrow molecular weight distributions ($M_w/M_n \leq 1.28$). The critical micelle concentrations of the obtained amphiphilic diblock copolymers were determined by fluorescence spectroscopy technique using *N*-phenyl-1-naphthylamine as probe. The morphology and size of the formed micelles were investigated by transmission electron microscopy and dynamic light scattering, respectively. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4433–4440, 2011

KEYWORDS: block copolymers; perfluorocyclobutyl; RAFT; self-assembly; synthesis

INTRODUCTION Most block copolymers containing a fluorinated segment have unconventional phase behaviors.[1,2] In comparison with the usual hydrocarbon-based polymers, the fluorinated relevant polymers are more rigid and less miscible for their fluorophobic effect. Therefore, the replacement of hydrocarbon block with fluorinated block in amphiphilic copolymers can imbue favorable properties to nanomaterials such as thermal stability, chemical resistance, low surface energy, low refractive index, and high insulating ability.[3–5] In particular, the incorporation of fluorinated segments into amphiphilic block copolymers can result in interesting self-assembly characteristics due to the combination of hydrophobicity and lipophobicity in fluorinated polymers.[6,7] Percec et al. reported fluorinated liquid crystal molecules with perfluorinated alkane chains, which can produce a microsegregation at the molecular level, and this process can be alone responsible for the formation of lamellar thermotropic and lyotropic mesophases.[8–21] Ni and coworkers[22] prepared amphiphilic hyperbranched star-block copolymers containing polycations and fluoropolymer segment, which can directly self-organize into supramolecular multicompartment micelles with different diameters. Although these interesting results were concerned with the polymers with flexible fluorinated alkane side chains, seldom have been reported on the self-assembly behaviors of amphiphilic copolymers bearing rigid fluorine-containing side groups, which may self-assemble into more different nanostructures.

A new kind of partially fluorinated polymer, perfluorocyclobutyl (PFCB) aryl ether polymers, which was discovered by Babb et al. of Dow Chemical in early 1990s,[23–26] has attracted much interests in many fields such as photonics,[27] polymer light-emitting diodes,[28,29] and proton exchange membranes for fuel cells.[30] Because of their low crystallinity, PFCB aryl ether-based polymers have improved processability, which have solved to some extent the manufacturing problems of fluoropolymers compared with traditional fluoropolymers.[31] PFCB aryl ether-based homopolymers or copolymers are commonly synthesized by free radical-mediated [$2\pi + 2\pi$] step-growth thermal cyclopolymerization of monomers bearing two or three trifluorovinyl ether functionalities at a temperature region of 150–200 °C.[32–35] However, because of the unusual polymerization mechanism and relative higher polymerization temperature, seldom has reported the incorporation of PFCB groups into commonly used monomers, which can be polymerized by conventional chain

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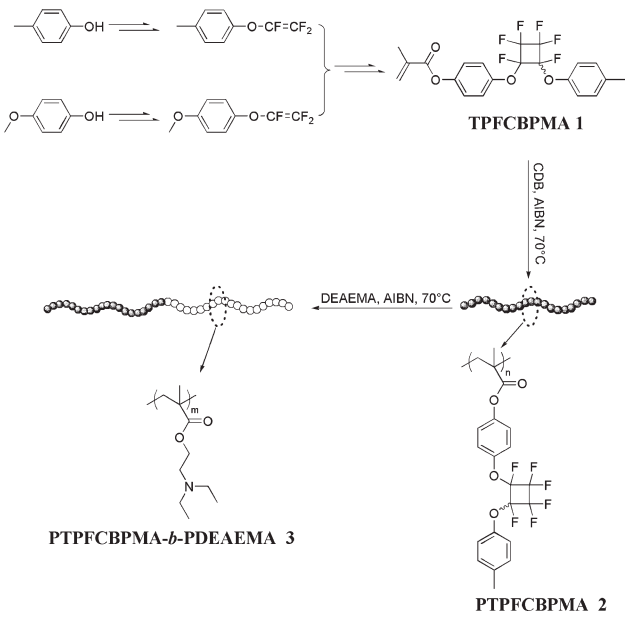
growth polymerization approaches. Therefore, it obviously poses a limitation in the variety and application of PFCB aryl ether-based polymers. Recently, our group has developed a novel type of (meth)acrylate monomers with PFCB-containing ester group,[36–39] which can be polymerized via traditional or living/controlled radical polymerization, it enabled us to obtain tailor-made PFCB aryl ether-based homopolymers or copolymers with well-defined architecture and function, which has certainly widen the application of PFCB aryl ether-based fluoropolymers.

Amphiphilic block copolymers are macromolecules composed of hydrophilic and hydrophobic chains connected at their terminal. The covalently connected thermodynamically incompatible segments give rise to self-assembly of the components into ordered structures with periodicity or compositional heterogeneityon.[40,41] Synthesis of amphiphilic block copolymers can be conducted by anionic,[42,43] cationic,[44,45] and living/controlled radical polymerization.[46,47] The living/controlled radical polymerization, including stable free radical polymerization,[48] atom transfer radical polymerization,[49–51] reversible addition fragmentation chain transfer (RAFT)[52,53] polymerization, and single electron transfer-living radical polymerization,[54–58] has become a powerful tool in the preparation of well-defined polymers. Specially, RAFT polymerization has many advantages such as more tolerant to a wide range of monomers and milder polymerization condition over other methods.[59]

The objectives of this article concern the synthesis and solution behavior of a new well-defined PFCB aryl ether-based amphiphilic block copolymer, poly(*p*-(2-(*p*-tolyloxy)perfluorocyclobutoxy)phenyl methacrylate)-*b*-poly(2-(diethylamino)ethyl methacrylate) (PTPFCBPMA-*b*-PDEAEMA), which were synthesized via successive RAFT of *p*-(2-(*p*-tolyloxy)-perfluorocyclobutoxy)phenyl methacrylate (TPFCBPMA) and 2-(diethylamino)ethyl methacrylate (DEAEMA) as shown in Scheme 1. The aqueous self-assembly behavior of the amphiphilic diblock copolymers have been investigated by measuring the critical micelle concentrations (CMCs) and the size of the micelles and visualizing the micellar morphologies.



SCHEME 1 Synthesis of PTPFCBPMA-*b*-PDEAEMA amphiphilic diblock copolymer.

EXPERIMENTAL

Materials

2,2′-Azobisisobutyronitrile (AIBN, 99%; Aldrich) was recrystallized twice from ethanol. l,2-(Diethylamino)ethyl methacrylate (DEAEMA, 97%; Alfa Aesar) was purified by distilling under vacuum. Granular zinc was activated by washing in 0.1 M HCl followed by drying at 140 °C *in vacuo* for 10 h. *N*-Phenyl-1-naphthylamine (PNA, 97%; Alfa Aesar) was purified by recrystallization in ethanol for three times. 2-Butanone (99%; Aldrich) was dried with $CaCl_2$ and then distilled under vacuum. 1,4-Dioxane (99%; Aldrich) was dried with CaH_2 and then distilled under vacuum. 1,2-Dibromotetrafluoroethane was prepared by condensing equimolar amounts of Br_2 and tetrafluoroethylene at −195 °C followed by warming up to 22 °C according to previous literature.[60] RAFT agent, cumyl dithiobenzoate (CDB), was prepared according to the reported procedures.[61] 4-Methoxyphenol (99%; Aldrich), *p*-cresol (99%; Aldrich), BBr_3 (1.0 M in CH_2Cl_2; Aldrich), and methacryloyl chloride (97%; Alfa Aesar) were used as received.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet AVATAR-360 FTIR spectrophotometer with a resolution of 4 cm^{-1}. All NMR analyses were performed on a Bruker Avance 500 spectrometer (500 MHz). Tetramethylsilane (^1H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards, and CF_3CO_2H was used as an external standard for ^{19}F NMR. EI-MS was measured by an Agilent 5937N system. Conversions of TPFCBPMA were determined by ^1H NMR. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns [HR3 (500–30,000), HR4 (5,000–600,000), and HR5 (50,000–4,000,000), 7.8 × 300 mm^2, 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, and the system was calibrated with linear polystyrene standards. Steady-state fluorescence spectra of PNA were measured on a Hitachi F-4500 spectrofluorometer with the bandwidth of 5 nm for excitation and emission; the emission intensity at 418 nm was recorded to determine the CMC with an excitation wavelength (λ_{ex}) of 340 nm. Transmission electron microscope (TEM) images were obtained by a JEOL JEM-1230 instrument operated at 80 kV. Hydrodynamic diameter (D_h) was measured by dynamic light scattering (DLS) with a Malvern Nano-ZS90 Zetasizer.

Synthesis of TPFCBPMA

p-(Trifluorovinyloxy)toluene and *p*-(trifluorovinyloxy)anisole were first prepared from 4-methoxyphenol and *p*-cresol, respectively, via standard fluoroalkylation followed by Zn-mediated dehalogenation.[32] *p*-(Trifluorovinyloxy)toluene (41.2 mL, 0.22 mol) and *p*-(trifluorovinyloxy)anisole (50.1 g, 0.25 mol) were added to a predried flask, and the mixture was heated at 150 °C for 1 day under N_2. The cross-dimer, a colorless oil of 4-(2-(*p*-tolyloxy)perfluorocyclobutoxy)anisole (38.9 g, yield: 45.3%), was obtained by column chromatography (eluent: hexane: ethyl acetate = 100:1).

^{1}H NMR: δ (ppm): 2.31 (s, 3H), 3.78 (d, 3H), 6.89 (dd, 2H), 7.10 (m, 6H). ^{19}F NMR: δ (ppm): −127.5 to −133.2 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 20.8, 20.9, 55.4, 55.5, 114.5, 114.6, 118.2, 118.6, 119.8, 120.1, 122.9, 130.0, 135.4, 135.9, 145.9, 146.2, 150.3, 150.5, 156.9, 157.1, 157.9. FTIR (KBr): ν (cm^{-1}): 2956, 2860, 1507, 1193, 962 (PFCB). EI-MS: m/z 392.

Demethylation of 4-(2-(*p*-tolyloxy)perfluorocyclobutoxy)anisole was carried out by treating with BBr_3 to provide 4-(2-(*p*-tolyloxy)perfluorocyclobutoxy)phenol. The above-prepared phenol (3.16 g, 0.0084 mol) and triethylamine (1.35 mL, 0.0096 mol) were dissolved in 25 mL of 2-butanone, and the mixture was stirred at 0–5 °C. Methacryloyl chloride (0.95 mL, 0.0096 mol) in 2-butanone (10 mL) was added dropwise within 30 min, and the mixture was stirred for another 1 h. The organic phase was washed twice with water after filtration. The solution was dried over $MgSO_4$ and purified by column chromatography (eluent: hexane: ethyl acetate = 50:1) after concentration. The monomer, TPFCBPMA **1** (colorless oil), was obtained with a yield of 81.2%.

FTIR (KBr): ν (cm^{-1}): 2930, 1740, 1638, 1503, 1319, 1187, 1123, 962 (PFCB), 817. ^{1}H NMR: δ (ppm): 2.04 (s, 3H), 2.31 (s, 3H), 5.75 (s, 1H), 6.33 (s, 1H), 7.10 (m, 8H). ^{19}F NMR: δ (ppm): −127.7 to −133.2 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 18.6, 20.9, 118.2, 118.6, 119.4, 119.8, 123.0, 127.7, 130.4, 130.5, 135.4, 135.9, 148.3, 149.9, 150.2, 165.9. EI-MS: m/z 446.

RAFT Homopolymerization of TPFCBPMA

In a typical procedure of RAFT homopolymerization of TPFCBPMA, CDB (109.0 mg, 0.40 mmol) and AIBN (32.8 mg, 0.20 mmol) were first added to a 10-mL Schlenk flask (flame-dried under vacuum prior to use) with a magnetic stir bar. The contents were purged with N_2 for 10 min to eliminate the dissolved oxygen for three times, and TPFCBPMA (2.67 g, 6.0 mmol) and 2-butanone (5.0 mL) were then charged via a gastight syringe. After three freezing-pumping-thawing cycles, the Schlenk flask was placed in an oil bath thermostated at 70 °C for 1 day. The polymerization was terminated by placing the flask into liquid N_2. The contents were dissolved in THF and precipitated in 200 mL of methanol twice. The obtained polymer, PTPFCBPMA **2a**, was dried at room temperature *in vacuo* overnight.

GPC: M_n = 8,200, M_w/M_n = 1.14. ^{1}H NMR: δ (ppm): 0.87, 1.36 (3H, CCH_3), 1.27 (6H, C(CH_3)$_2$ of CDB moiety), 1.46, 1.75 (2H, CH_2), 2.25 (3H, ArCH_3), 6.98, 7.06 (4H, phenyl). ^{19}F NMR: δ (ppm): −127.6 to −133.3 (m, cyclobutyl-F_6).

TABLE 1 RAFT Homopolymerization of TPFCBPMA **1**[a]

Sample	[**1**]:[CDB]:[AIBN]	M_n[b] (KDa)	M_w/M_n[b]	$N_{TPFCBMA}$[c]
2a	30:2:1	8.2	1.14	18
2b	80:2:1	13.9	1.16	31

[a] Polymerization temperature: 70 °C, polymerization time: 24 hours, solvent: 2-butanone.
[b] Measured by GPC in THF at 35 °C.
[c] The number of TPFCBPMA repeating unit obtained from GPC.

RAFT Block Copolymerization of DEAEMA

The procedures used for block copolymerization of DEAEMA were similar to the RAFT homopolymerization of TPFCBPMA. A 10-mL Schlenk flask (flame-dried under vacuum prior to use) was first filled with AIBN (1.1 mg, 0.0067 mmol) and PTPFCBPMA **2a** (M_n = 8,200 g/mol, M_w/M_n = 1.14, 0.164 g, 0.020 mmol). The contents were purged with N_2 for 10 min to eliminate the dissolved oxygen for three times, and DEAEMA (0.40 mL, 2.0 mmol) and 1,4-dioxane (4.0 mL) were charged via a gastight syringe. The flask was degassed by three cycles of freezing–pumping–thawing, and it was placed in an oil bath preset at 70 °C for 1 day. The polymerization was quenched by putting the flask into liquid N_2. The mixture was dissolved in THF and precipitated into 100 mL of cold *n*-hexane for three times. The obtained white solid, PTPFCBPMA-*b*-PDEAEMA, **3c**, was again washed with a small amount of *n*-hexane and then dried *in vacuo* overnight.

GPC: M_n = 12,200, M_w/M_n = 1.28. FTIR (KBr): ν (cm^{-1}): 2972, 2875, 1766, 1606, 1507, 1320, 1204, 1140, 962. ^{1}H NMR: δ (ppm): 0.89, 1.36 (3H, CCH_3), 1.06 (6H, NCH$_2$CH_3) 1.48, 1.81, 1.90 (2H, CH_2), 2.26 (3H, ArCH_3), 2.61 (4H, NCH_2CH$_3$), 2.73 (2H, COOCH$_2$CH_2), 4.02 (2H, COOCH_2CH$_2$), 6.99, 7.05 (4H, phenyl). ^{19}F NMR: δ (ppm): −127.8 to −133.8 (m, cyclobutyl-F_6)

Determination of CMC

PNA was used as fluorescence probe to measure the CMC of PTPFCBPMA-*b*-PDEAEMA **3**. Acetone solution of PNA (1 mg/mL) was added to a large amount of water until the concentration of PNA reached 0.001 mg/mL. Then, different amounts of THF solutions of PTPFCBPMA-*b*-PDEAEMA **3** (1, 0.1, or 0.01 mg/mL) were added to water containing PNA ([PNA] = 0.001 mg/mL). All fluorescence spectra were recorded at 20 °C.

TEM Images

A total of 0.5 mL of water was added slowly (0.36 mL/h) to 0.5 mL of THF solution of PTPFCBPMA-*b*-PDEAEMA **3** (1 mg/mL), and THF was removed by dialysis. The copper grid (400 meshes) was immersed in a drop of the aqueous polymer solution and then dried at room temperature for 1 day prior to measurement.

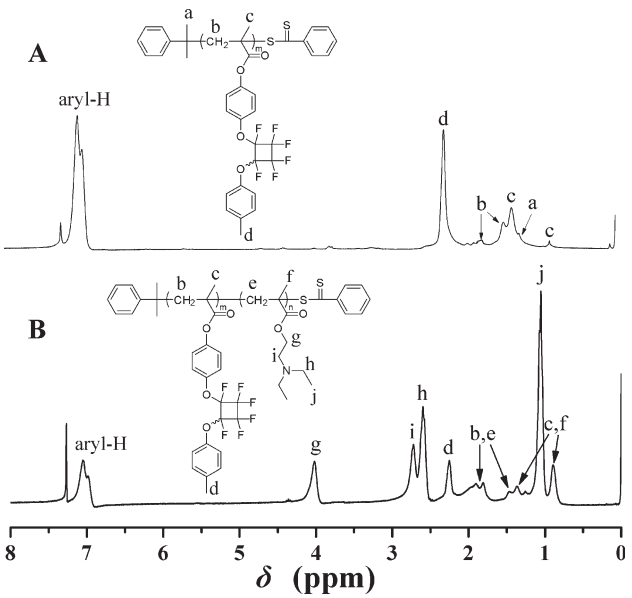


FIGURE 1 ^{1}H NMR spectra of PTPFCBPMA **2** (A) and PTPFCBPMA-*b*-PDEAEMA **3** (B).

RESULTS AND DISCUSSION

Synthesis of PTPFCBPMA

TPFCBPMA **1** monomer was prepared from 4-methoxyphenol and *p*-cresol following the previously reported procedure.[36–39] RAFT homopolymerization of TPFCBPMA was carried out in 2-butanone at 70 °C using AIBN as initiator and CDB as chain transfer agent (CTA). The molecular weights of the resulting PTPFCBPMA **2** homopolymers with narrow molecular weight distributions ($M_w/M_n \leq 1.16$) were tuned by the feeding ratios of TPFCBPMA to CDB as listed in Table 1. The homopolymers were characterized by ^{1}H NMR as shown in Figure 1(A). The signals of the vinylidene of TPFCBPMA monomer at 5.75 and 6.33 ppm disappeared after polymerization, this indicating the occurrence of RAFT homopolymerization. The peaks at 0.87, 1.36, 1.46, and 1.75 ppm belonged to the protons of polymethacrylate backbone. Moreover, the sharp peak at 2.28 ppm corresponded to three protons of tolyl.

To confirm the controlled nature of AIBN-initiated and CDB-mediated RAFT homopolymerization of TPFCBPMA, we studied the polymerization kinetics by ^{1}H NMR to draw the semilogarithmic plot of $\ln([M]_0/[M])$ ($[M]_0$ is the initial monomer concentration and [M] is the monomer concentration) versus time in Figure 2(A). The linearity between $\ln([M]_0/[M])$ and the polymerization time indicated a constant number of propagating species throughout the polymerization and the apparent first-order polymerization rate with respect to the concentration of the monomer. Furthermore, the molecular weights increased linearly with the conversions of monomer, whereas the molecular weight distributions kept narrow throughout the polymerization ($M_w/M_n \leq 1.30$) as shown in Figure 2(B). All these observations suggested that the RAFT homopolymerization of TPFCBPMA is seen to be well controlled.[62]

Synthesis of PTPFCBPMA-*b*-PDEAEMA

After the discovery of living radical polymerizations, sequential addition of the monomers is more widely used than coupling of two appropriately end-functionalized chains[63,64] and mechanism transformation strategy[65–67] to synthesize the block copolymers. We adopted RAFT, which is one method of living radical polymerizations discovered recently, to synthesize PTPFCBPMA-*b*-PDEAEMA diblock copolymers for its more tolerance to a wide range of monomers and solvents, conservation of end groups, and well control over molecular weights.

PDEAEMA is a member of amino-containing polymethacrylates family and a biocompatible weak polyelectrolyte, and it is soluble in acidic solution as a weak cationic polyelectrolyte due to the protonation of tertiary amine group. Its block copolymers often exhibit interesting associative behaviors.[68–70] In this work, we chose DEAEMA as the hydrophilic monomer to prepare the amphiphilic diblock copolymers using the hydrophobic PTPFCBPMA with two different molecular weights as macro-CTA agent. The block length of PDEAEMA

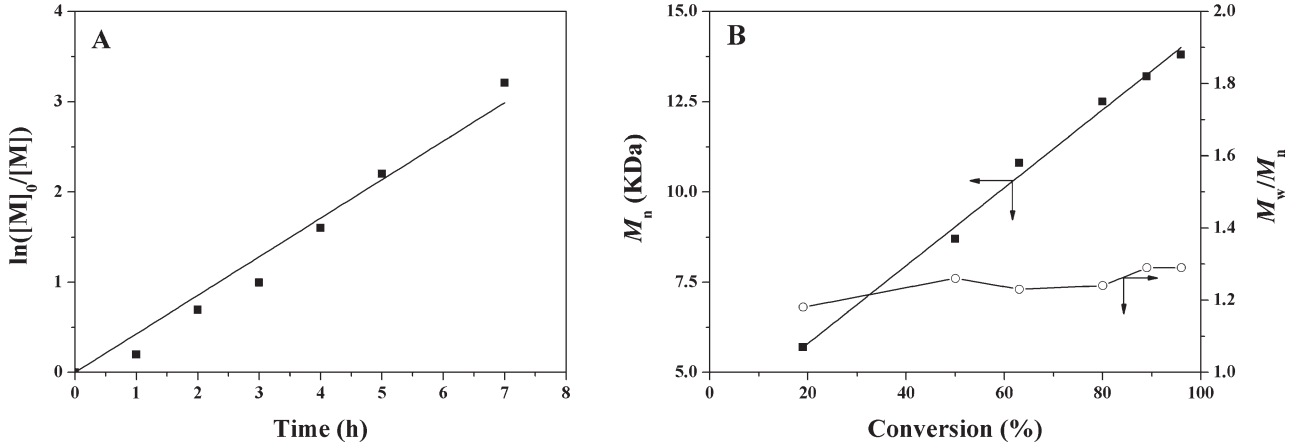


FIGURE 2 Kinetic plot (A) and dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) on the conversion of monomer (B) for RAFT polymerization of TPFCBPMA **2** mediated by CDB.

TABLE 2 Synthesis of PTFCBPMA-*b*-PDEAEMA **3** Diblock Copolymer[a]

Sample	[DEAEMA]:[**2**]:[AIBN]	M_n[d] (KDa)	M_w/M_n[d]	N_{DEAEMA}[e]
3a[b]	90: 3:1	9.3	1.13	6
3b[b]	150: 3:1	10.6	1.18	13
3c[b]	300: 3:1	12.2	1.28	22
3d[c]	90: 3:1	15.1	1.20	6
3e[c]	150: 3:1	16.0	1.17	11
3f[c]	300: 3:1	18.2	1.27	23

[a] Polymerization temperature: 70 °C, polymerization time: 24 hours, solvent: dioxane.
[b] Initiated by PTPFCBPMA **2a** macroinitiator (M_n = 8,200, M_w/M_n= 1.14).
[c] Initiated by PTPFCBPMA **2b** macroinitiator (M_n = 13,900, M_w/M_n= 1.16).
[d] Measured by GPC in THF at 35 °C.
[e] The number of DEAEMA repeating unit obtained from GPC.

segment was tuned by varying the feeding ratio of DEAEMA to PTPFCBPMA macro-CTA as summarized in Table 2. Two series of PDEAEMA-*b*-PTPFCBPMA **3** diblock copolymers with the same hydrophobic segment length and the different hydrophilic block length were obtained and well characterized by ^{1}H NMR, FTIR, and GPC.

Figure 1(B) shows ^{1}H NMR spectrum of PDEAEMA-*b*-PTPFCBPMA diblock copolymer. The peaks at 0.89 and 1.36 ppm were attributed to the respective methyl protons (C(CH_3)) of the polymethacrylate backbone. The signals at 1.48, 1.81, and 1.90 ppm originated from the methylene protons of the main chain. The signals of the ester group of PDEAEMA segment were located at 1.06, 2.61, 2.73, and 4.02 ppm, respectively. GPC traces of PTPFCBPMA macro-CTAs and PTPFCBPMA-*b*-PDEAEMA block copolymers are shown in Figure 3. The molecular weights of all copolymers are much higher than those of macro-CTAs, which demonstrated that RAFT-polymerized PTPFCBPMA can act as macro-CTA to mediate RAFT polymerization of DEAEMA. In addition, all GPC curves of macro-CTAs and diblock copolymers exhibited unimodal and symmetrical peaks with narrow molecular weight distributions ($M_w/M_n \leq 1.28$), which meant an almost 100% efficiency of PTPFCBPMA macro-CTA. From the above-mentioned results, it can be concluded that PDEAEMA-*b*-PTPFCBPMA well-defined diblock copolymers have been successfully synthesized.

Self-assembly of PTPFCBPMA-*b*-PDEAEMA in Aqueous Media

CMCs of PTPFCBPMA-*b*-PDEAEMA **3** diblock copolymers in aqueous solution were determined by fluorescence technique using PNA as probe. PNA can display higher fluorescence activity in nonpolar surroundings, and its fluorescence can be very easily quenched by polar solvents, such as water.[71–74] Figure 4 shows the relationship of the fluorescence intensity ratio (I/I_0) and the concentration of PTPFCBPMA-*b*-PDEAEMA **3c** at 20 °C. We can clearly see from the figure that I/I_0 increased sharply when the concentration of PTPFCBPMA-*b*-PDEAEMA **3c** exceeded a certain value, which meant PNA probe was incorporated into the hydrophobic region of micelles. Thus, the intersection of two straight lines with a value of 3.98×10^{-6} g/mL was determined to be the CMC of PTPFCBPMA-*b*-PDEAEMA **3c**. Diblock copolymers form micelles above the critical concentration and below this concentration, micelles disaggregate into unimers. The CMC values of PTPFCBPMA-*b*-PDEAEMA **3** are listed in Table 3, which are slightly lower than those of the common surfactants or polymeric amphiphiles.[75–78] It was found that the CMC values of PTPFCBPMA-*b*-PDEAEMA **3** rose with the increasing of the block length of hydrophilic PDEAEMA segment.

DLS was used to analyze the size of the micelles prepared via direct dissolution method. As shown in Figure 5(A), when the number of DEAEMA repeating unit increased from 6 of **3a** to 22 of **3c**, the diameter of the micelles enlarged

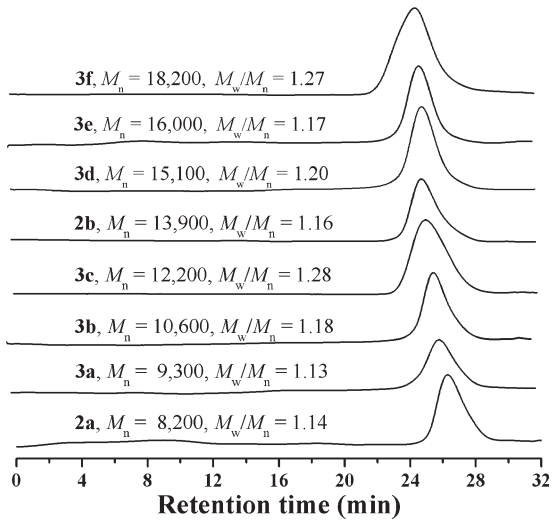


FIGURE 3 GPC curves of PTPFCBPMA **2** and PTPFCBPMA-*b*-PDEAEMA **3** in THF.

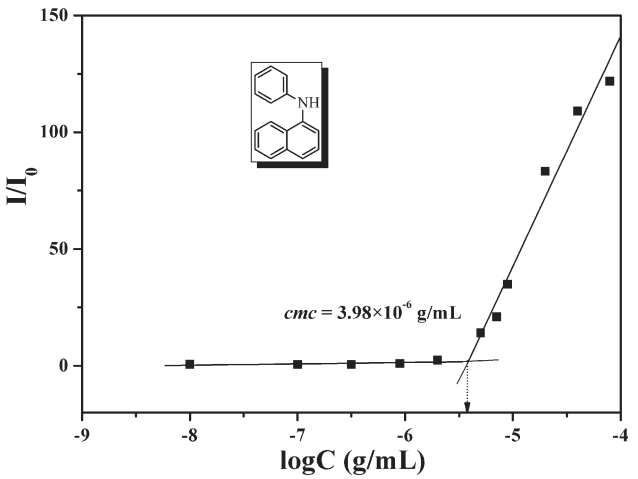


FIGURE 4 Dependence of fluorescence intensity ratio of PNA emission band at 418 nm on the concentration of PTPFCBPMA-*b*-PDEAEMA **3c**.

TABLE 3 Self-assembly of PTFCBPMA-*b*-PDEAEMA **3** in Aqueous Solution

Sample	$N_{TFCBPMA}$-*b*-N_{DEAEMA}[a]	CMC[b] (g/mL)	D_h[c] (nm)
3a	18-*b*-6	3.56×10^{-6}	246.9
3b	18-*b*-13	3.80×10^{-6}	303.1
3c	18-*b*-22	3.98×10^{-6}	332.8
3d	31-*b*-6	3.31×10^{-6}	182.1
3e	31-*b*-11	3.61×10^{-6}	326.7
3f	31-*b*-23	4.07×10^{-6}	372.2

[a] The composition of the block copolymer obtained from GPC.
[b] Critical micelle concentration determined by fluorescence spectroscopy using PNA as probe.
[c] Hydrodynamic diameter determined by DLS.

from 246.9 to 332.8 nm; when the number of DEAEMA repeating unit increased from 6 of **3d** to 23 of **3f**, the diameter of the micelles also shifted from 182.1 nm to 372.2 nm [Fig. 5(B)]. It was found that the size of the micelles was raised as the length of PDEAEMA segment ascended. As the length of PDEAEMA segment lifts, the hydrophilic segment coronas become thicker. As a result, the size of micelles was heightened.

Amphiphilic block copolymers can self-assemble into micelles, vesicles, and other morphologies in selective solution according to their different chemical compositions and molecular architectures.[79–81] In particular, amphiphilic diblock copolymers can spontaneously form micelles with hydrophobic segment as core and hydrophilic segment as corona in aqueous solution. The micellar solution of PTPFCBPMA-*b*-PDEAEMA **3** amphiphilic diblock copolymers with different block lengths were prepared by adding deionized water into the THF solution of the copolymers with vigorous stirring. After removal of THF via dialysis, the micellar morphologies were visualized by TEM (Fig. 6). Under the same condition, all copolymers mainly aggregated into well-ordered spherical large compound micelles (LCMs) with diameters of 400–600 nm and no other morphology was observed. Eisenberg et al. have shown that LCMs are reverse micelles in an almost continuous insoluble blocks in the bulk and surrounded by a hydrophilic surface, which provide colloidal stabilization.[82,83] Although LCMs have been considered no longer in their thermodynamic equilibrium, the formation of LCMs is favored because of the higher glass transition temperature, T_g,[36] of the core-forming segment PTPFCBPMA.[83] When adding water into the copolymer solution, the solvent becomes progressively worse for PTPFCBPMA block, which resulted in the microphase separation of the copolymer solution; and after the formation of the polymer aggregates and subsequent isolation into water, the structures of the aggregates become locked because PTPFCBPMA chains are below their T_g.[83] With the continuous adding of water, the interactions between the corona chains and the solvent can no longer stabilize the aggregates, therefore the aggregates undergo a secondary aggregation to form large compound micelles to minimize free energy.

CONCLUSIONS

Amphiphilic diblock copolymers based on fluorine-containing monomer TPFCBPMA and hydrophilic monomer DEAEMA have been successfully synthesized via two steps of successive RAFT polymerizations. PTPFCBPMA was first synthesized via CDB-mediated and AIBN-initiated RAFT polymerizations. Then, well-defined PTPFCBPMA-*b*-PDEAEMA diblock copolymers with narrow molecular weight distribution ($M_w/M_n \leq 1.28$) was synthesized via RAFT polymerization of DEAEMA mediated by PTPFCBPMA capped with dithiobenzoate. Self-assembly of PTPFCBPMA-*b*-PDEAEMA in aqueous solution was studied by fluorescence spectroscopy, dynamic laser light scattering, and TEM. The CMC values of PTPFCBPMA-*b*-PDEAEMA increased with the rising of the content of hydrophilic segment. The diameter of the micelles raised as the length of PDEAEMA segment lifted. All copolymers we obtained could self-assemble into spherical large compound micelles in deionized water. This type of micelles would throw light on the potential application of PFCB-containing polymers.

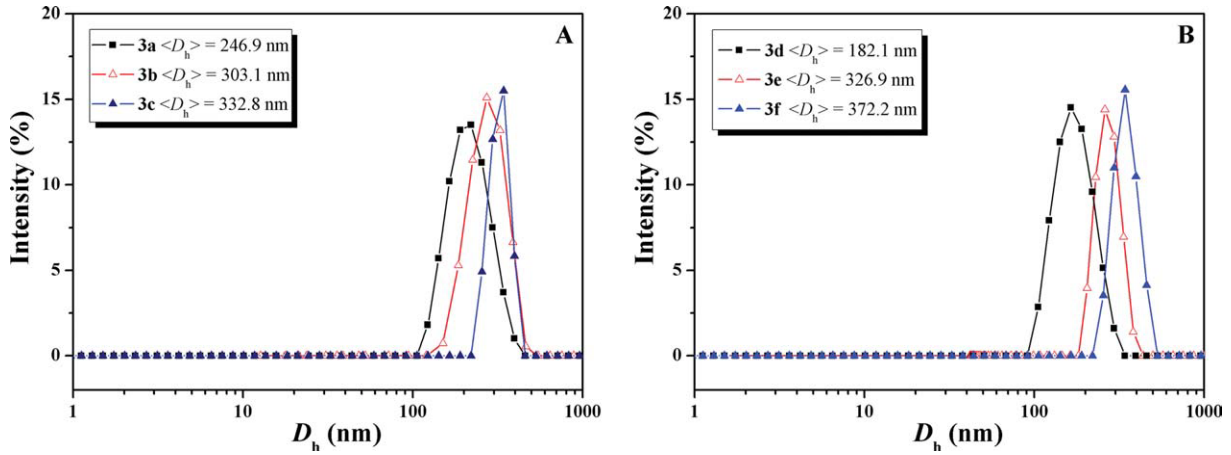


FIGURE 5 Hydrodynamic diameter distributions of micelles formed by PTPFCBPMA-*b*-PDEAEMA **3**, (A) **3a**, **3b**, and **3c** and (B) **3d** and **3f**.

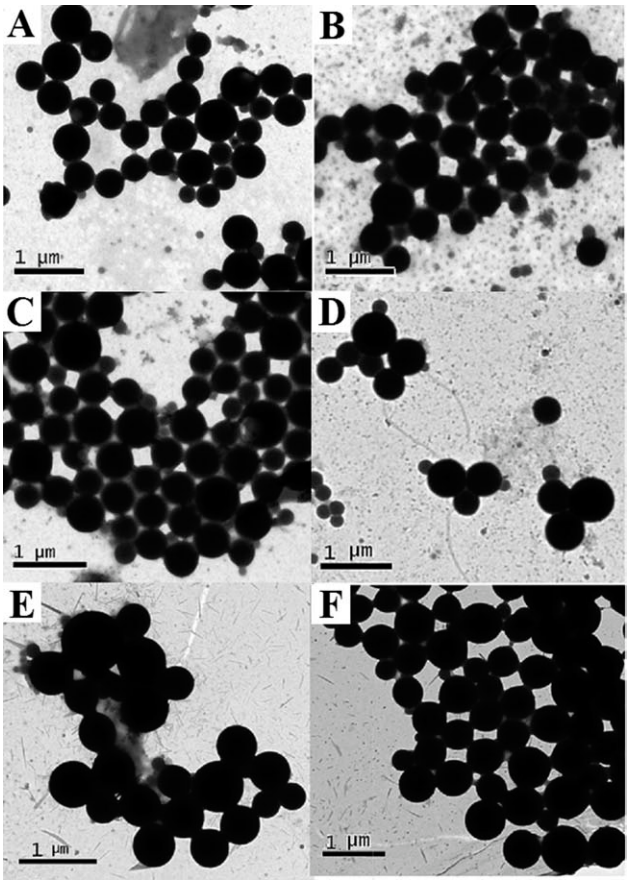


FIGURE 6 TEM images of micelles formed by PTPFCBPMA-*b*-PDEAEMA **3a** (a), **3b** (B), **3c** (C), **3d** (D), **3e** (E), and **3f** (F) in pure water.

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REFERENCES AND NOTES

1 Semenov, A. N.; Nyrkova, I. A.; Khokhlov, A. R. Macromolecules 1995, 28, 7491–7500.

2 Davidock, D. A.; Hillmyer, M. A.; Lodge, T. P. Macromolecules 2004, 37, 397–407.

3 Souzy, R.; Ameduri, B.; Boutevin, B. Prog Polym Sci 2004, 29, 75–106.

4 Li, H.; Zhang, Y. M.; Zhang, H.; Xue, M. Z.; Liu, Y. G. J Polym Sci Part A: Polym Chem 2006, 44, 3853–3858.

5 Krafft, M. P.; Riess, J. G. J Polym Sci Part A: Polym Chem 2007, 45, 1185–1198.

6 Zhou, Z.; Li, Z.; Ren, Y.; Hillmyer, M. A.; Lodge, T. P. J Am Chem Soc 2003, 125, 10182–10183.

7 Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. Science 2004, 306, 98–101.

8 Percec, V.; Lee, M. J Macromol Sci Pure Appl Chem A 1992, 29, 723–740.

9 Hudsom, S. D.; Jung, H. T.; Percec, V.; Cho, W. D.; Johanssom, G.; Ungar, G.; Balagurusamy, V. S. K. Science 1997, 248, 449–452.

10 Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudsonk, S. D.; Duank, H. Nature 2002, 419, 384–388.

11 Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. P. J Am Chem Soc 1996, 118, 9855–9866.

12 Dukeson, D. R.; Ungar, G.; Balagurusamy, V. S. K.; Percec, V.; Johansson, G. A.; Glodde, M. J Am Chem Soc 2003, 125, 15974–15980.

13 Percec, V.; Glodde, M.; Johansson, G.; Balagurusamy, V. S. K.; Heiney, P. A. Angew Chem Int Ed Engl 2003, 42, 4338–4342.

14 Percec, V.; Imam, M. R.; Bera, T. K.; Balagurusamy, V. S. K.; Peterca, M.; Heiney, P. A. Angew Chem Int Ed Engl 2005, 44, 4739–4745.

15 Percec, V.; Schlueter, D.; Kwon, Y. K.; Blackwell, J.; Moller, M.; Slangen, P. J. Macromolecules 1995, 28, 8807–8818.

16 Johansson, G.; Percec, V.; Ungar, G.; Zhou, J. P. Macromolecules 1996, 29, 646–660.

17 Percec, V.; Schlueter, D.; Ungar, G. Macromolecules 1997, 30, 645–648.

18 Wilson, C. J.; Wilson, D. A.; Feiring, A. E.; Percec, V. J Polym Sci Part A: Polym Chem 2010, 48, 2498–2508.

19 Johansson, G.; Percec, V.; Ungar, G.; Smith, K. Chem Mater 1997, 9, 164–175.

20 Percec, V.; Glodde, M.; Peterca, M.; Rapp, A.; Schnell, I.; Spiess, H. W.; Bera, T. K.; Miura, Y.; Balagurusamy, V. S. K.; Aqad, E.; Heiney, P. A. Chem Eur J 2006, 12, 6298–6314.

21 Percec, V.; Aqad, E.; Peterca, M.; Imam, M. R.; Glodde, M.; Bera, T. K.; Miura, Y.; Balagurusamy, V. S. K.; Ewbank, P. C.; Wurthner, F.; Heiney, P. A. Chem Eur J 2007, 13, 3330–3345.

22 Mao, J.; Ni, P. H.; Mai, Y. Y.; Yan, D. Y. Langmuir 2007, 23, 5127–5134.

23 Babb, D. A.; Ezzell, B. R.; Clement, K. S.; Richey, W. F.; Kennedy, A. P. J Polym Sci Part A: Polym Chem 1993, 31, 3465–3477.

24 (a) Babb, D. A.; Clement, K. S.; Richey, W. F.; Ezzell, B. R. (Dow Chemical Co.). U.S. Patent 5,037,917, 1991; (b) Babb, D. A.; Clement, K. S.; Richey, W. F.; Ezzell, B. R. Chem Abstr 1995, 122, 291788.

25 Clement, K. S.; Babb, D. A.; Ezzell, B. R. (Dow Chemical Co.). U.S. Patent 5,210,265, 1993; Chem Abstr 1991, 115, 231753.

26 Kennedy, A. P.; Babb, D. A.; Bermmer, J. N.; Pasztor, A. J. J Polym Sci Part A: Polym Chem 1995, 33, 1859–1865.

27 Fischbeck, G.; Moosburger, R.; Kostrzema, C.; Achen, A.; Petermann, K. Electron Lett 1997, 33, 518–519.

28 Jiang, X.; Liu, S.; Liu, M. S.; Herguth, P.; Jen, A. K. Y.; Fong, H.; Sarikaya, M. Adv Funct Mater 2002, 12, 745–751.

29 Gong, X.; Moses, D.; Heeger, A. J.; Liu, S.; Jen, A. K. Y. Appl Phys Lett 2003, 83, 183–185.

30 Ford, L. A.; Desmarteau, D. D.; Smith, D. W. J Fluorine Chem 2005, 126, 653–660.

31 Babb, D. A.; Snelgrove, R. V.; Smith, D. W.; Mudrich, S. F. Step-Growth Polymers for High-Performance Materials; American Chemical Society: Washington, DC, 1996; p 431.

32 Babb, D. A.; Clement, K. A.; Richey, W. F. In Polymeric Materials Encyclopedia; Salmone, J. C., Ed.; CRC Press: Boca Raton, 1996; pp 4911–4920.

33 Iacono, S. T.; Budy, S. M.; Jin, J. Y.; Smith, D. W. J Polym Sci Part A: Polym Chem 2007, 45, 5705–5721.

34 Zhang, S.; Li, Y. J.; Tong, L.; Lu, G. L.; Huang, X. Y. Acta Chim Sinica 2009, 67, 425–434.

35 Lv, X. L.; He, C.; Li, Y. G.; Jia, Q.; Gong, C. Q. Acta Chim Sinica 2010, 68, 697–702.

36 Li, Y. J.; Zhang, S.; Tong, L.; Li, Q. N.; Li, W. X.; Lu, G. L.; Liu, H.; Huang, X. Y. J Fluorine Chem 2009, 130, 354–360.

37 Li, Y. J.; Chen, S.; Zhang, S.; Li, Q. N.; Lu, G. L.; Li, W. X.; Liu, H.; Huang, X. Y. Polymer 2009, 50, 5192–5299.

38 Li, Y. J.; Zhang, S.; Feng, C.; Zhang, Y. Q.; LI, Q. N.; Li, W. X.; Huang, X. Y. Chin J Chem 2009, 27, 2261–2266.

39 Li, Y. J.; Zhang, S.; Liu, H.; Li, Q. N.; Li, W. X.; Huang, X. Y. J Polym Sci Part A: Polym Chem 2010, 45, 5419–5429.

40 Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H. In Block Copolymers I; Abetz, V., Ed.; Spring-Verlag: Berlin, 2005; pp 1–124.

41 Ryan, A. J.; Mai, S. M.; Fairclough, J. P. A.; Hamley, I. W.; In Amphiphilic Block Copolymers; Alexandridis, P.; Lindman, B., Eds; Elsevier: Amsterdam, 2000; pp 151–190.

42 Raghunadh, V.; Baskaran, D.; Sivaram, S. J Polym Sci Part A: Polym Chem 2004, 42, 875–882.

43 Hillmyer, M. A.; Schmuhl, N. W.; Lodge, T. P. Macromol Symp 2004, 215, 51–56.

44 Aoshima, S.; Sugihara, S.; Shibayama, M.; Kanaoka, S. Macromol Symp 2004, 215, 151–164.

45 Wu, C. M.; Liou, W.; Chen, H. L.; Lin, T. L.; Jeng, U. S. Macromolecules 2004, 37, 4974–4980.

46 Schilli, C. M.; Zhang, M.; Rizzardo, E.; Thang, S. H.; Chong, Y. K.; Edwards, K.; Karlsson, G.; Muller, A. H. E. Macromolecules 2004, 37, 7861–7866.

47 Albertin, L.; Stenzel, M.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P. Macromolecules 2004, 37, 7530–7537.

48 Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 5316–5320.

49 Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614–5615.

50 Percec, V.; Barboiu, B. Macromolecules 1995, 28, 7970–7972.

51 Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721–1723.

52 Moad, G.; Rizzardo, E.; Thang, S. H. Aust J Chem 2005, 58, 379–410.

53 Moad, G.; Rizzardo, E.; Thang, S. H. Polymer 2008, 49, 1079–1131.

54 Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. J Am Chem Soc 2006, 128, 14156–14165.

55 Rosen, B. M.; Percec, V. Chem Rev 2009, 109, 5069–5119.

56 Fleischmann, S.; Rosen, B. M.; Percec, V. J Polym Sci Part A: Polym Chem 2010, 48, 1990–1996.

57 Fleischmann, S.; Percec, V. J Polym Sci Part A: Polym Chem 2010, 48, 2236–2242.

58 Nguyen, N. H.; Rosen, B. M.; Lligadas, G.; Percec, V. Macromolecules 2009, 42, 2379–2386.

59 Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. Macromol Symp 2003, 192, 1–12.

60 Kastsuhara, Y.; DesMatteau, D. D. J Am Chem Soc 1980, 102, 2681–2686.

61 Fan, D. Q.; He, J. P.; Xu, J. T.; Tang, W.; Liu, Y.; Yang, Y. L. J Polym Sci Polym Chem 2006, 44, 2260–2269.

62 Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. Macromolecules 2003, 36, 2273–2283.

63 Higashihara, T.; Feng, D. S.; Faust, R. Macromolecules 2006, 39, 5275–5279.

64 Huang, H. H.; Niu, H.; Dong, J. Y. J Polym Sci Part A: Polym Chem 2011, 49, 2222–2232

65 Chen, J. Z.; Cui, K.; Zhang, S. Y.; Xie, P.; Zhao, Q. L.; Huang, J.; Shi, L. P.; Li, G. Y.; Ma, Z. Macromol Rapid Commun 2009, 30, 532–538.

66 Chen, J. Z.; Zhao, Q. L.; Lu, H. C.; Huang, J.; Cao, S. K.; Ma, Z. J Polym Sci Part A: Polym Chem 2010, 48, 1894–1900.

67 Li, Q. Z.; Zhang, G. Y.; Chen, J. Z.; Zhao, Q. L.; Lu, H. C.; Huang, J.; Wei, L. H.; D'Agosto, F.; Boisson, C.; Ma, Z. J Polym Sci Part A: Polym Chem 2011, 49, 511–517.

68 Butun, V.; Bennett, C. E.; Vamvakaki, M.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. J Mater Chem 1997, 7, 1693–1695.

69 Butun, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. J Am Chem Soc 1999, 121, 4288–4289.

70 Liu, S. Y.; Billingham, N. C.; Armes, S. P. Angew Chem Int Ed Engl 2001, 40, 2328–2331.

71 Akiyoshi, K.; Deguchi, S.; Moriguchi, N.; Yamaguchi, S.; Sunamoto, J. Macromolecules 1993, 26, 3062–3068.

72 You, L. C.; Lu, F. Z.; Li, Z. C.; Zhang, W.; Li, F. Macromolecules 2003, 36, 1–4.

73 Xu, P. S.; Tang, H.; Li, S.; Ren, J.; Kirk, E. V.; Murdoch, W. J.; Radosz, M.; Shen, Y. Q. Biomacromolecules 2004, 5, 1736–1744.

74 Astafieva, I.; Khougaz, K.; Eisenberg, A. Macromolecules 1995, 28, 7127–7134.

75 Thurmond, K. B.; Kowalewski, T.; Wooley, K. L. J Am Chem Soc 1997, 119, 6656–6665.

76 Whitesides, G. M.; Grzybowski, B. Science 2002, 295, 2418–2421.

77 Clendenning, S. B.; Fournier-Bidoz, S.; Pietrangelo, A.; Yang, G. C.; Han, S. J.; Brodersen, P. M.; Yip, C. M.; Lu, Z. H.; Ozin, G. A.; Manners, I. J Mater Chem 2004, 14, 1686–1690.

78 Yagci, Y.; Tasdelen, M. A. Prog Polym Sci 2006, 31, 1133–1170.

79 Nakano, M.; Matsuoka, H.; Yamaoka, H.; Poppe, A.; Richter, D. Macromolecules 1999, 32, 697–703.

80 Xu, R. L.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. Macromolecules 1992, 25, 644–652.

81 Germack, D. S.; Harrisson, S.; Brown, G. O.; Wooley, K. L. J Polym Sci Part A: Polym Chem 2006, 44, 5218–5228.

82 Zhang, L. F.; Eisenberg, A. Science 1995, 268, 1728–1731.

83 Zhang, L. F.; Eisenberg, A. J Am Chem Soc 1996, 118, 3168–3181.