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# Synthesis and Micellization of Triblock Copolymers Containing MePEG-*b*-PDMAEMA and Fluoropolymer: Effect of Block Lengths on Self-Assembly

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A series of triblock copolymer consisting of a double-hydrophilic diblock and a fluorinated block, namely monomethyl end-capped poly(ethylene glycol)-*b*-poly[2-(dimethylamino)ethyl methacrylate]-*b*-poly(2, 2, 3, 3, 4, 4, 5, 5-octafluoropentyl methacrylate) (MePEG-*b*-PDMAEMA-*b*-POFPMA), was synthesized via oxyanion-initiated copolymerization. The hydroxyl group of poly(ethylene glycol) monomethyl ether (MePEG$_{16}$, $M_n = 750$ g mol$^{-1}$ or MePEG$_{45}$, $M_n = 2000$ g mol$^{-1}$) reacted with potassium methylsulfinyl carbanion (DMSO$^-$K$^+$) and converted into a potassium alcoholate macroinitiator (MePEGO$^-$K$^+$). The lengths of PDMAEMA and POFPMA blocks could be controlled by the original molar ratio of monomers to the macroinitiator. These triblock copolymers were characterized by the measurements of $^1$H-NMR, and gel permeation chromatography (GPC). The results indicated that they had relatively low polydispersities ($M_w/M_n$:1.15–1.36). A significant investigation in this work was the comparison of the effects of the different block lengths, especially for MePEG and PDMAEMA, on the mecellization of copolymers in aqueous solution by the measurements of surface activities and electrical conductivity. The lower critical solution temperatures (LCSTs) of the di- and triblock copolymers varied with different factors, including the chemical structure, the block lengths, and the concentration. The effects of PDMAEMA length on the two kinds of diblock copolymers MePEG-*b*-PDMAEMA, which were initiated respectively by MePEG-2000 or MePEG-750 oxyanions, were studied by turbidimetric measurement. Furthermore, the different morphologies of MePEG-*b*-PDMAEMA-*b*-POFPMA in aqueous solution at pH 7.0 were observed by transmission electron microscopy (TEM).

**Keywords:** Fluorinated amphiphile, oxyanion-initiated polymerization, self-assemble, poly(ethylene glycol), PDMAEMA

## 1 Introduction

Fluorinated amphiphilic copolymers have recently received the attention of many researchers due to their exceptional combination of well-defined amphiphilic polymer moieties and fluorinated polymer segments, which results in the self-assembly behavior in solution (such as gelification in fluorous, organic, and aqueous media), the powerful hydrophobic and lipophobic effects, and the nanocompartamentation within membranes and colloids (1–4). The potential application of these copolymers involves biomedical materials, (5,6) drug and gene delivery systems, (7) oxygen transfers and blood substitutes, (8) fouling resistance, (9) etc.

There are some pioneering studies on the synthesis of fluorine-containing polymers prepared by living anionic polymerizations, (10,11) group transfer polymerizations, (12,13) cationic polymerizations, (14,15) nitroxide-mediated polymerizations (NMP), (16) atom transfer radical polymerizations (ATRP), (17–19) and reversible addition-fragmentation chain transfer polymerization (RAFT), (20,21) however, these controlled/‘living’ polymerization techniques have their individual limitation to prepare some special products. To the best of our knowledge, there have been some reports on the synthesis of water-soluble fluorine-containing amphiphilic block copolymers. Miyamoto et al. (22) reported the first study of a water-soluble fluorine-containing block copolymer, poly(perfluoroalkyloxazoline)-*b*- poly(methyloxazoline). Matsumoto et al. (15,23,24), synthesized a series of water-soluble copolymers containing poly(2-hydroxyethyl vinyl ether) (PHOVE) block and fluorinated block. They investigated the solubility and aggregation of the diblock copolymer in water and the solubilization of various fluoro

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*Address correspondence to: Peihong Ni, Key Laboratory of Organic Chemistry of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: phni@suda.edu.cn and nonfluoro compounds in the aqueous solutions of these polymers.

As an effective living polymerization, oxyanion-initiated polymerization has exhibited its unique advantages: (i) it does not require such strict experimental conditions as anionic polymerization; and (ii) it facilitates the incorporation of polyether blocks with polymethacrylates to give di-, tri-, and pentablock copolymers (25–28). Armes and coworkers have made significant contributions on the chemistry (25,26,29). In their works, tertiary amino methacrylates were considered as more suitable monomers than methyl methacrylate (MMA) with respect to both initiation and narrow polydispersity (29). Moreover, our group extended the synthetic method to MMA and obtained well-defined AB or BA types of PDMAEMA-*b*-PMMA diblock copolymers by a sequential addition of alternative monomers (30).

The incorporation of fluorinated chains with double hydrophilic molecules may be a challenging subject, which would generate stimuli-responsive fluorinated copolymers. Double-hydrophilic block copolymers (DHBCs) are a class of diblock copolymers which consist of two water-soluble blocks of different chemical nature. The most important character of these polymers is that their amphiphilicity in aqueous environments could be induced just in the presence of a substrate or by ion strength, temperature and pH changes, respectively (31).

In our previous study, we have reported on the synthesis of a series of fluorinated copolymers via oxyanion-initiated polymerization, i.e., amphiphilic triblock copolymers, monomethylcapped poly(ethylene glycol)-*b*-poly[2-(dimethylamino) ethyl methacrylate]-*b*-poly(2,2,3, 3,4,4,5,5-octafluoropentyl methacrylate) (MePEG-*b*-PDMAEMA-*b*-POFPMA); (32) amphiphilic hyperbranched star-block copolymers, HP-star-PDMAEMA-*b*-POFMA (HP, hydroxyl-terminated hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane]); (33) a series of fluoroalkyl end-capped diblock copolymers of NFHO-PDMA-*b*-PDEA and NFHO-PDEA-*b*-PDMA; (34) some novel fluorinated pentablock copolymers, POFMA-*b*-F127-*b*-POFMA, based on Pluronic F127 ($PEO_{100}$-$PPO_{65}$-$PEO_{100}$); (35) poly[2-(dimethylamino) ethyl meth acrylate]-*b*-poly(2,2,2-trifluoroethylmethacrylate) (PDMA EMA-*b*-PTFMA), poly[2-(dimethylamino)ethyl metha crylate]-*b*-poly (2,2,3,4,4,4-hexafluorobutyl methacrylate) (PDMAEMA-*b*-PHFMA), (36) etc. Among them, $MePEG_{45}$-*b*-PDMAEMA-*b*-POFPMA was obtained by using potassium alcoholate of monomethyl-capped poly(ethylene glycol) (MePEG-2000, $M_n$ =2000 g mol$^{-1}$) as a macroinitiator to polymerize DMAEMA. If not quenched, the living moiety of MePEG-*b*-PDMAEMA could subsequently be used to yield a triblock copolymer MePEG-*b*-PDMAEMA-*b*-POFPMA with adding the second feed of monomer (OFPMA) to the living system (32).

The present work is an attempt to obtain a series of fluorocarbon-hydrocarbon hybrid triblock copolymers, which combined are the blocks of hydrophilic PEG and pH-responsive PDMAEMA with fluorophilic moieties (POFPMA). Comparing the degree of polymerization of PEG on the self-assembly property, we further selected the other macroinitiator MePEG-750 ($M_n = 750$ g mol$^{-1}$) to synthesize a series of di- and triblock copolymers, i.e., $MePEG_{16}$-*b*-PDMAEMA double hydrophilic diblock copolymers and $MePEG_{16}$-*b*-PDMAEMA-*b*-POFPMA triblock copolymers, via oxyanion-initiated polymerization. We mainly discuss the effects of different lengths of MePEG, PDMAEMA and POFPMA blocks on the aggregation in aqueous solutions, as well as the lower critical solution temperatures (LCSTs). For simplicity, MePEG-*b*-PDMAEMA diblock copolymer was designated as MD, and MePEG-*b*-PDMAEMA-*b*-POFPMA triblock copolymer as MDO.

## 2 Experimental

### 2.1 Materials

2-(***N,N***-Dimethylamino)ethyl methacrylate (DMAEMA) was purchased from Shanghai Chemical Reagent Co., China. The monomer were passed through an activated basic alumina column and distilled immediately in vacuum before use. Dimethyl sulfoxide (DMSO) (Shanghai Wulian Co., China) was dried with anhydrous molecular sieves and distilled before use. Tetrahydrofuran (THF) was initially dried over potassium hydroxide at least overnight and then refluxed over sodium wire for 3 days before use. Potassium hydride (KH, Aldrich) was stored in mineral oil and washed with anhydrous THF in an inert atmosphere before use. 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA, TCI) and triphenylmethane (Aldrich) was used as received. All polymerizations were carried out under a dry argon atmosphere.

The poly(ethylene glycol) monomethyl ether (MePEG-750, Fluka) was heated at 90°C for 4 h with a rotary vacuum distillator for the removal of trace water before use. GPC analyses gave $M_w/M_n$ of 1.17 for MePEG and $^1$H-NMR analysis gave degrees of 16 for PEG part. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta = 3.65$ (m, 65H), 3.39 (s, 3H).

### 2.2 Preparation of Potassium Methylsulfinyl Carbanion ($DMSO^-K^+$)

KH was taken from mineral oil and placed in a preweighed round-bottom flask. The mineral oil was washed three times with anhydrous THF. The resulting white powder was suspended in THF. The suspension was cooled to 0°C using an ice bath before the addition of DMSO (2-fold molar excess based on KH). Then, the suspension was stirred at 30°C for about 1 h until all the KH had reacted, leading to the formation of a homogeneous phase (32,37).

## 2.3 Syntheses of Di- and Triblock Copolymers

In a typical polymerization, the monomethyl-capped poly(ethylene glycol) was dissolved in anhydrous THF along with triphenylmethane indicator. The THF solution of $DMSO^-K^+$ was added until the reaction mixture turned slightly pink due to the formation of triphenylmethyl carbanion and remained for 15 min. Then, the flask was moved into an oil bath at 30°C, freshly distilled monomer DMAEMA was added to the initiator solution. The reaction was stirred for 1 h. If a second monomer OFPMA was used, the polymerization was allowed to proceed for a further 1 h. The polymerization was quenched with methanol. The solvent was then removed with a rotary vacuum distillatory. The copolymer was purified by repeated precipitation into cold *n*-hexane to remove the indicator and unreacted monomers. Finally, the samples were dried in a vacuum oven at 50°C for 3 days.

$^1$H-NMR (400 MHz, $CDCl_3$) for MePEG$_{16}$-*b*-PDMAEMA$_{30}$ copolymer: $\delta = 4.00$ (s, 61H), 3.39 (s, 3H), 2.57 (m, 54H), 2.28 (m, 160H).

$^1$H-NMR (400 MHz, $CDCl_3$) for MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer: $\delta = 6.14$ (m, 7H), 4.0 (s, 59H), 3.39 (s, 3H), 2.57 (m, 58H), 2.28 (m, 163H).

The accurate recipes are summarized in Table 1. The overall yields were in excess of 95%.

## 2.4 $^1$H-NMR Spectroscopy

All copolymer compositions were determined by $^1$H-NMR (INVOA-400) with $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. The successful copolymerization of OFPMA was demonstrated by both $^1$H-NMR measurements.

**Table 1.** Recipes of syntheses of MePEG$_{16}$-*b*-PDMAEMA and MePEG$_{16}$-*b*-PDMAEMA-*b*-POFPMA

| *Sample ID* | *MePEG (mmol)* | *The first monomer DMAEMA (mmol)* | *The second monomer OFPMA (mmol)* |
|---|---|---|---|
| MD-1 | 1.14 | 17.09 | 0 |
| MDO-1-1 | 1.35 | 19.80 | 4.19 |
| MDO-1-2 | 1.16 | 17.30 | 7.11 |
| MD-2 | 1.17 | 35.18 | 0 |
| MDO-2-1 | 1.30 | 39.25 | 4.00 |
| MDO-2-2 | 1.15 | 34.46 | 7.05 |
| MDO-3 | 1.25 | 62.32 | 0 |
| MDO-3-1 | 1.33 | 66.71 | 4.00 |
| MDO-3-2 | 1.04 | 51.75 | 6.18 |
| MDO-4-1 | 1.25 | 36.80 | 7.50 |

## 2.5 GPC Measurements

The molecular weights and molecular weight distributions of di- and triblock copolymers were determined with a gel permeation chromatograph (GPC) instrument (HP-1100) equipped with a PL502 column connected to a refractive-index detector (G1362A). Calibration was carried out with polystyrene standards. THF was used as an eluent at a flow rate of 1.0 mL min$^{-1}$.

## 2.6 Surface Tension

Surface tension measurements were carried out by a JK99C automatic surface tensiometer (Shanghai Zhongchen Co., China) equipped with a platinum ring. Dissolving a copolymer sample in deionized water, and adjusting the solution at desired pH value using dilute hydrochloric acid, and then the aqueous stock solution of the copolymer was obtained. A series of the aqueous copolymer solutions with different concentrations were prepared by diluting the stock solution, held the same pH value. All measurements were carried out at 20°C, and the obtained values were checked gradually through measurement of the surface tension of deionized water (72–73 mN m$^{-1}$).

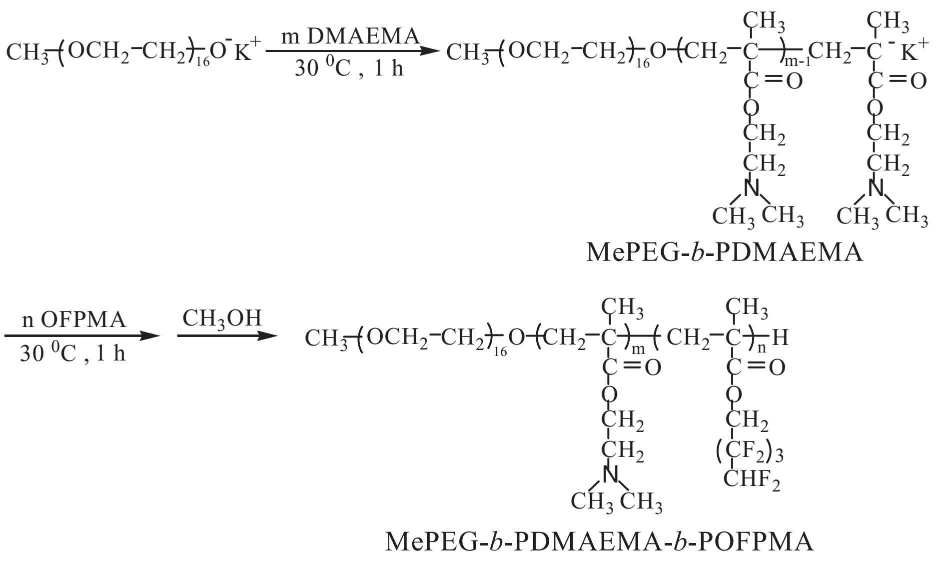
Critical aggregation concentrations (cac) for the diblock and triblock copolymers were determined by surface tensiometry, measuring the surface tension ($\gamma$), as a function of the polymer concentration in water. The value of cac was located at the break point of surface tension vs. concentration curve.

## 2.7 Electrical Conductivity

Electrical conductivities of the diblock and triblock copolymer solutions were measured at different temperature using a DDS-12A conductimeter (Shanghai Kangning Electrooptical Technology Co., China) and a dipping cell with DJS-1C platinum black electrodes. The reproducibility of the instrument was better than 0.1% accuracy.

## 2.8 LCST

Lower critical solution temperatures (LCSTs) of di- and triblock copolymers were obtained by turbidimetric measurements of the copolymer aqueous solutions at various temperatures, using a Shimadzu 3150 UV-VIS-NIR spectrophotometer. The transmittance was measured as a function of temperature at wavelength $\lambda = 278$ nm. The quarts cuvette was thermostated by a Water Bath SB-11 thermocontroller (Tokyo Rikakikai Co., Japan) equipped with a circulating water jacket. Polymer solutions of various concentrations were heated slowly from a starting temperature of 10°C with a heating rate of 0.5°C min$^{-1}$. The LCST was defined as the onset temperature of the cloud point curves, i.e., the temperature at which the absorbance rapidly augmented.



**Sch. 1.** A representative reaction procedure for the synthesis of MD diblock copolymer via oxyanion-initiated polymerization, as well as MDO triblock copolymer by subsequent addition of second monomer.

### 2.9 TEM

Transmission electron microscopy (TEM) images were obtained from the instrument (TECNAI $G^2$ 20, FEI Co.) at an acceleration voltage of 200 kV. The specimen solutions were prepared as follows: copolymers were dissolved in deionized water, and then the pH value was adjusted by adding sodium hydroxide solution to 7.0 .The carbon-coated copper grid (400 mesh) was immersed in the aqueous polymer solution, taken out, and dried at room temperature for 1 day prior to the measurements.

## 3 Results and Discussion

### 3.1 Preparation of Di- and Triblock Copolymers

A series of MePEG-*b*-PDMAEMA diblock (MD) and MePEG-*b*-PDMAEMA-*b*-POFPMA triblock copolymers (MDO) were prepared via oxyanion-initiated polymerization using a potassium alcoholate of oligomer, i.e., monomethyl-capped poly(ethylene glycol) (MePEG-750), as a macroinitiator. Scheme 1 shows a representative reaction procedure for the synthesis of diblock and triblock copolymers via oxyanion-initiated polymerization. In order to control precisely the formation of oligomer oxyanion and further to determine the molecular weight of block copolymers, we used the DMSO carbanion titration method (32). The hydroxyl group of poly(ethylene glycol) monomethyl ether (MePEG) reacted with potassium methylsulfinyl carbanion ($DMSO^-K^+$) and converted into a potassium alcoholate macroinitiator ($MePEGO^-K^+$). It could initiate DMAEMA monomer to yield a hydrophilic-hydrophilic diblock copolymer MePEG-*b*-PDMAEMA (MD). If not quenched, the living chain could be subsequently used to initiate a second fed monomer such as 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) to produce a new triblock copolymer MePEG-*b*-PDMAEMA-*b*-POFPMA (MDO). The living character of oxyanion-initiated polymerization was demonstrated by synthesizing reasonably well-defined MD diblock or MDO triblock copolymers.

As shown in Figure 1, GPC analysis shows the traces of (a) MePEG-750 ($MePEG_{16}$, $M_w/M_n = 1.17$) and (b) the final $MePEG_{16}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_6$ triblock copolymer (Sample MDO-2-2 in Table 2) with degrees of polymerization for PDMAEMA block about 30 units and POFPMA about 6 units, according to the initial molar ratios of monomers to macroinitiator. From

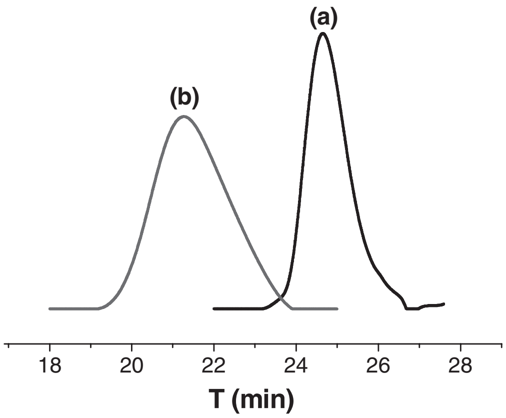


**Fig. 1.** GPC plots showing (a) the original MePEG-750 oligomer and (b) the resulting triblock copolymer $MePEG_{16}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_6$ (Sample MDO-2-2 in Table 2).

**Table 2.** Compositions and molecular weight distributions of di- and triblock copolymers

| *Sample ID* | *Copolymer composition (Theor.)* | *$\bar{M}_n$ of PDMAEMA block ($g\ mol^{-1}$)* Theor. | *$\bar{M}_n$ of PDMAEMA block ($g\ mol^{-1}$)* Actual[a] | *$\bar{M}_n$ of POFPMA block ($g\ mol^{-1}$)* Theor. | *$\bar{M}_n$ of POFPMA block ($g\ mol^{-1}$)* Actual[a] | *$\bar{M}_w/\bar{M}_n^b$ of final copolymers* |
|---|---|---|---|---|---|---|
| MD-1 | $MePEG_{16}$-*b*-$PDMAEMA_{15}$ | 2360 | 2160 | — | — | 1.15 |
| MDO-1-1 | $MePEG_{16}$-*b*-$PDMAEMA_{15}$-*b*-$POFPMA_3$ | 2310 | 2510 | 930 | 840 | 1.21 |
| MDO-1-2 | $MePEG_{16}$-*b*-$PDMAEMA_{15}$-*b*-$POFPMA_6$ | 2340 | 2290 | 1840 | 1570 | 1.15 |
| MD-2 | $MePEG_{16}$-*b*-$PDMAEMA_{30}$ | 4730 | 4250 | — | — | 1.28 |
| MDO-2-1 | $MePEG_{16}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_3$ | 4750 | 4250 | 920 | 1130 | 1.26 |
| MDO-2-2 | $MePEG_{16}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_6$ | 4710 | 4560 | 1840 | 2140 | 1.25 |
| MDO-3 | $MePEG_{16}$-*b*-$PDMAEMA_{50}$ | 7840 | 7590 | — | — | 1.34 |
| MDO-3-1 | $MePEG_{16}$-*b*-$PDMAEMA_{50}$-*b*-$POFPMA_3$ | 7890 | 7120 | 900 | 1010 | 1.28 |
| MDO-3-2 | $MePEG_{16}$-*b*-$PDMAEMA_{50}$-*b*-$POFPMA_6$ | 7820 | 8770 | 1780 | 2000 | 1.36 |
| MDO-4-1 | $MePEG_{45}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_6$ | 4930 | 4980 | 1800 | 1950 | 1.25 |

[a] As calculated by $^1$H NMR spectra, measured in $CDCl_3$.
[b] As measured by GPC in THF.

Figure 1(b), it can be seen that neither MePEG nor the monomers was detected in the lower molecular weight region. The peak in the GPC trace of the MDO triblock copolymer is monomodal, suggesting the absence of unreacted oligomers and an efficient initiation via subsequent addition of both DMAEMA and OFPMA. All samples of MD diblock copolymers and MDO triblock copolymers have narrow molecular weight distributions ($M_w/M_n = 1.15$–$1.36$) as shown in Table 2. For the system of MePEG-2000 ($MePEG_{45}$) macroinitiator, we have also obtained the similar di- and triblock copolymers with narrow molecular weight distributions (32).

Figure 2 depicts two typical $^1$H-NMR spectra (solvent: $CDCl_3$) of $MePEG_{16}$-*b*-$PDMAEMA_{15}$ diblock copolymer and $MePEG_{16}$-*b*-$PDMAEMA_{15}$-*b*- $POFPMA_3$ triblock copolymer. From Figure 2(a), the peak attributed to the protons for methoxy group of MePEG can be observed at $\delta$ 3.39 ppm, and the chemical shift signals of two protons of N-$CH_2$ in PDMAEMA residues at $\delta$ 2.57 ppm. Although only three units of OFPMA in theory were linked with the living chain of $MePEG_{16}$-*b*-$PDMAEMA_{15}$, the proton of –$CHF_2$ for POFPMA in $MePEG_{16}$-*b*-$PDMAEMA_{15}$-*b*-$POFPMA_6$ triblock copolymer was clearly visible at $\delta$ 6.0–6.3 ppm as shown in Figure 2(b), indicating that the very short fluoropolymer chain was successfully linked with the double-hydrophilic diblock copolymer. The relative molecular weights of PDMAEMA and POFPMA can be calculated by comparing integrals of different peaks of character groups. The data of molecular weight and molecular weight distribution for the synthetic copolymers are listed in Table 2.

As derived by $^1$H-NMR, the degrees of polymerization of PDMAEMA block were in reasonable agreement with those expected from the corresponding original [DMAEMA]/[$MePEGO^-K^+$] molar ratios. However, the degree of polymerization of POFPMA block was less accurate in GPC compared with the theoretical values because of the facile aggregation of fluorinated block in solution. Several researchers have found the phenomenon and clarified the reason why the results of GPC for fluorinated polymers were higher than normal polymers (38–41). Krupers et al. found that the GPC trace of the fluorinated copolymer had a higher molecular weight peak along with the expected normal molecular weight peak (38). The appearance of such a peak suggested the formation of micelles in solution. Zhang et al. found that the molecular weights of fluorinated copolymers calculated by GPC were different from the theoretical values. The authors attributed the difference to the aggregation of fluorinated blocks in solution (39,40). Therefore, we only calculated the degree of polymerization of fluorinated block in terms of the integrals in $^1$H-NMR.

## 3.2 Surface Tensions of Di- and Triblock Copolymers

It is known that MePEG-*b*-PDMAEMA diblock copolymer exhibits pH/temperature responsive properties in definite conditions. Armes et al. studied the reversible aggregation of $MePEG_{45}$-*b*-$PDMAEMA_{50}$ diblock copolymer via $^1$H-NMR spectra at 55 and 25°C. They also investigated the pH-responsive properties of $MePEG_{45}$-*b*-$PDMAEMA_{34}$ via $^1$H-NMR spectra at pH 2.0 and 9.0 (25). In our recent study, we explored the aggregation of $MePEG_{45}$-*b*-PDMAEMA diblock copolymer (with 15 or 30 DMAEMA units) and $MePEG_{45}$-*b*-PDMAEMA-*b*-POFPMA triblock copolymer (with the same length of DMAEMA and 6 POFPMA units) in aqueous solutions via the measurements of surface tension and electrical conductivity (32). Herein, we first investigated the effects of pH values in aqueous solution on the micellization of $MePEG_{16}$-*b*-$PDMAEMA_{30}$-*b*-$POFPMA_6$ by measuring the surface tensions as a function of the concentrations.

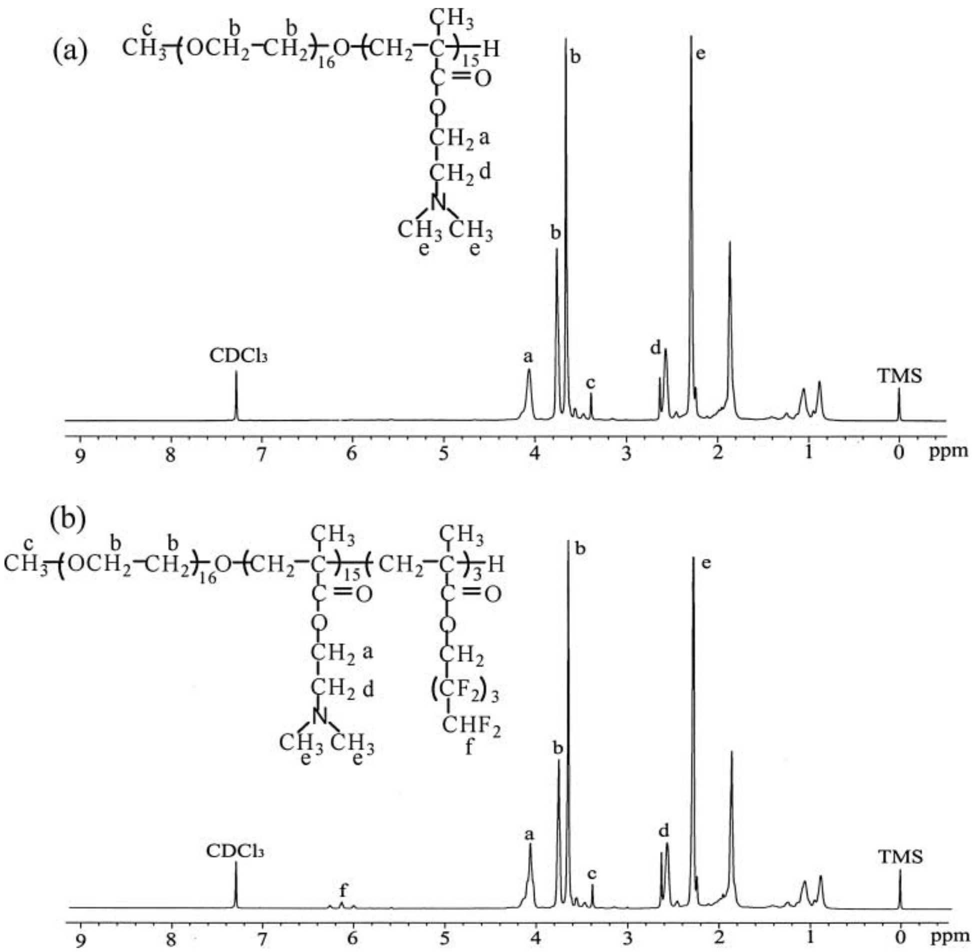


**Fig. 2.** 400 MHz$^1$H-NMR spectra of (a) MePEG$_{16}$-*b*-PDMAEMA$_{15}$ diblock copolymer (MD-1 in Table 2) and (b) MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_3$ triblock copolymer (MDO-1-1 in Table 2).

Under the condition of different pH media, surface tension studies of MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer were carried out. The results obtained from surface tension measurements of the aqueous solution are shown in Figure 3. At the aqueous solution of pH 3.0 and 5.0, the surface tension decreased with the increasing concentration of the triblock copolymer, and finally reached 42.2 mN m$^{-1}$ and 41.7 mN m$^{-1}$ with cac in the range of 7.1–7.3 g L$^{-1}$ and 7.0–7.2 g L$^{-1}$, respectively. The dimethylamino groups of PDMAEMA were protonated in acidic media and led to a repulsion of cationic blocks. The electrostatic interaction between the polymer chains makes them less association in water. With the comparison of the curves obtained at pH 3.0 or 5.0, the surface tension at pH 7.0 fell greatly with the increase of concentration of MDO, falling to 38.0 mN m$^{-1}$. The cac of the aqueous solution was about 6.6–7.0 g L$^{-1}$. This indicates that the fluorinated triblock copolymer containing both non-ionic and cationic parts has very good surface activity at neutral aqueous conditions.

A significant investigation in this work was the comparison of surface activities from two aspects: (i) the

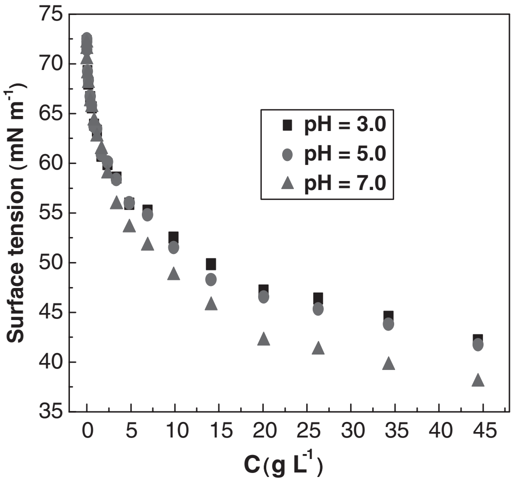
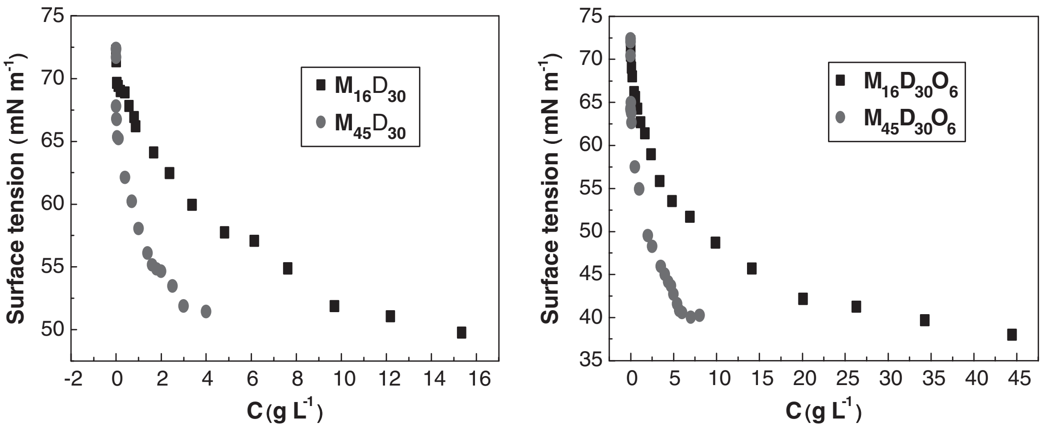


**Fig. 3.** Surface tension curves as the function of polymer concentrations for MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ at pH 3.0, 5.0 and 7.0, respectively. All the measurements were carried out at 20°C.



(a) (b)

**Fig. 4.** Surface tension curves as the function of polymer concentrations for (a) MePEG$_{16}$-*b*-PDMAEMA$_{30}$ and MePEG$_{45}$-*b*-PDMAEMA$_{30}$, and (b) MePEG$_{16}$-*b*- PDMAEMA$_{30}$-*b*-POFPMA$_6$ and MePEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$. All measurements were carried out at 20 °C at pH 7.0.

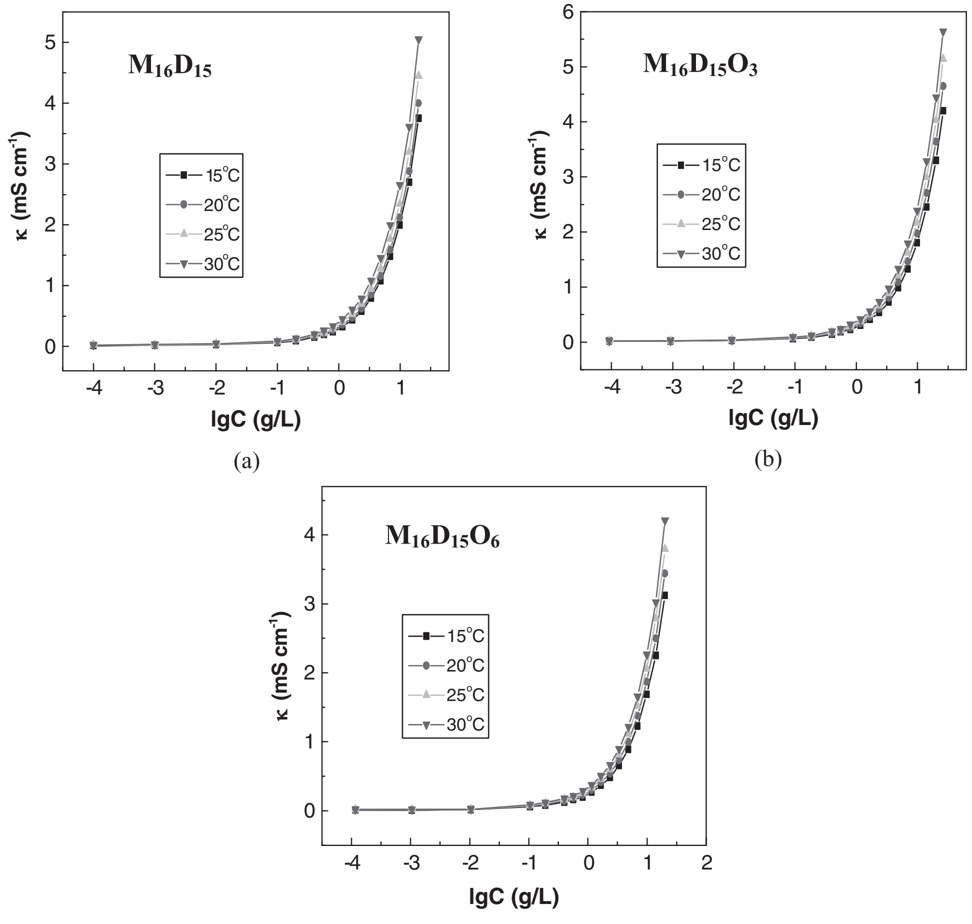
effect of different MePEG lengths on the surface activities of double-hydrophilic diblock copolymer, i.e., comparing MePEG$_{16}$-*b*-PDMAEMA$_{30}$ with MePEG$_{45}$-*b*-PDMAEMA$_{30}$; (ii) the effect of different MePEG lengths on the surface activities of fluorinated triblock copolymer, i.e. comparing MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ with MePEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$. Figure 4(a) shows that the lowest surface tension of MePEG$_{45}$-*b*-PDMAEMA$_{30}$ was 51.4 mN m$^{-1}$ and the critical aggregation concentration (cac) was in the range of 1.8 to 1.9 g L$^{-1}$. The lowest surface tension of MePEG$_{16}$-*b*-PDMAEMA$_{30}$ was 49.8 mN m$^{-1}$ and its cac ranged between 4.4~4.6 g L$^{-1}$. When a short chain of fluoroalkyl methacrylate (about 6 units) was connected with the hydrophilic-hydrophilic diblock copolymer, the surface activity of the new triblock copolymer would be changed greatly. As seen in Figure 4(b), the lowest surface tension of MePEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ declines to 40.0 mN m$^{-1}$. The value of cac was about 5.4~5.5 g L$^{-1}$. For MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$, the lowest surface tension reached 38.0 mN m$^{-1}$ and the value of cac was 6.6~7.0 g L$^{-1}$. The fluorinated block copolymer shows very low surface tension. These results further demonstrate the successful copolymerization of OFPMA monomer with living chain of MePEG-*b*-PDMAEMA.

Figure 4(a) shows that the surface tension of the MePEG$_{45}$-*b*-PDMAEMA$_{30}$fell much faster with the increasing concentration than that of the MePEG$_{16}$-*b*-PDMAEMA$_{30}$. The surface tension of the MePEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$declined much faster with the increasing concentration than that of the MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ as shown in Figure 4(b). These results indicate that the solubility of the MDO triblcok copolymers with MePEG-750 is much better than that of those with MePEG-2000, on the condition that these copolymers contain the same block lengths of PDMAEMA and POFPMA. This may be attributed to the better solubility of MePEG-750 than that of MePEG-2000.

### 3.3 Electrical Conductivity Measurement of Di- and Triblock Copolymers

The critical aggregation concentrations (cac) of MD diblock copolymer and MDO triblock copolymer aqueous solutions have been measured using electrical conductivity at various temperatures and pH media. The results are shown in Figure 5.

Under identical conditions (pH=5.0), the values of electrical conductivity increased with the increasing concentration of copolymers and displayed a sharp increase. Moreover, the electrical conductivity increased slightly as the temperature increased from 15 to 30°C. From the plots of electrical conductivity ($\kappa$) vs. logarithm concentrations, the critical aggregation concentration (cac) could be obtained by tangents, cac=3.6~3.8 g L$^{-1}$ for MePEG$_{16}$-*b*-PDMAEMA$_{15}$, 5.1~5.3 g L$^{-1}$ for MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_3$ and 5.0~5.2 g L$^{-1}$ for MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$, respectively. These results suggest that the fluorinated block leads to higher critical aggregation concentration than that of hydrophilic-hydrophilic diblock copolymers due to the hydrophobic nature of the fluorinated block. The cac of fluorinated triblock copolymers are much higher than that of double hydrophilic diblock copolymers. This may be attributed to the self-aggregation of fluorinated copolymers in aqueous solution. We will confirm it in our further study. In addition, for MDO triblock copolymer, the cac value of MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_3$ is a little higher than that of MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$. This result shows that the influence of the short chain of fluoroalkyl methacrylate on the cac values



(a) (b)

(c)

**Fig. 5.** Plots of the electrical conductivity against logarithm concentrations of (a) MePEG$_{16}$-*b*-PDMAEMA$_{15}$, (b) MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*POFPMA$_3$ and (c) MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$ in water at different temperatures. The pH values of the aqueous solutions were kept at 5.0.

of triblock copolymers may be limited in a restricted length range for the short fluorinated chain.

### 3.4 LCST of Di- and Triblock Copolymers

The effects of polymer composition and different lengths of PDMAEMA on lower critical solution temperatures (LCSTs) in aqueous solution are shown in Table 3.

The aqueous solution of MePEG-750 with concentration at 5.4 g L$^{-1}$ had no clearly visible cloud point, even though the aqueous solution was heated in a boiling water bath. When MePEG-750 linked with about 15, 30 and 50 units of PDMAEMA, LCSTs of the aqueous solutions declined from >100°C of MePEG to 68.5, 56.5 and 49.6 °C, respectively. Compared to the LCST of MePEG$_{16}$-*b*-PDMAEMA$_{50}$ (49.6 °C in Table 3), only 3 or 6 units of fluorinated short chain in MePEG$_{16}$-*b*-PDMAEMA$_{50}$-*b*-POFPMA$_3$ and MePEG$_{16}$-*b*-PDMAEMA$_{50}$-*b*-POFPMA$_6$ would lead the LCSTs to fall to 48.9 and 42.1°C, respectively.

We have conducted similar research on the polymers initiated by potassium alcoholate of monomethyl-capped

**Table 3.** LCST of various polymers of aqueous solutions

| *Sample ID* | *Copolymer composition (Theor.)* | *pH* | *LCST (°C)*$^a$ |
|---|---|---|---|
| 1 | MePEG-750 | 9.0 | >100 |
| 2 | MePEG$_{16}$-*b*-PDMAEMA$_{15}$ | 9.0 | 68.5 |
| 3 | MePEG$_{16}$-*b*-PDMAEMA$_{30}$ | 9.0 | 56.5 |
| 4 | MePEG$_{16}$-*b*-PDMAEMA$_{50}$ | 9.0 | 49.6 |
| 5 | MePEG$_{16}$-*b*-PDMAEMA$_{50}$-*b*-POFPMA$_3$ | 9.0 | 48.9 |
| 6 | MePEG$_{16}$-*b*-PDMAEMA$_{50}$-*b*-POFPMA$_6$ | 9.0 | 42.1 |

$^a$The concentrations of polymer solutions were maintained at 5.4 g L$^{-1}$.

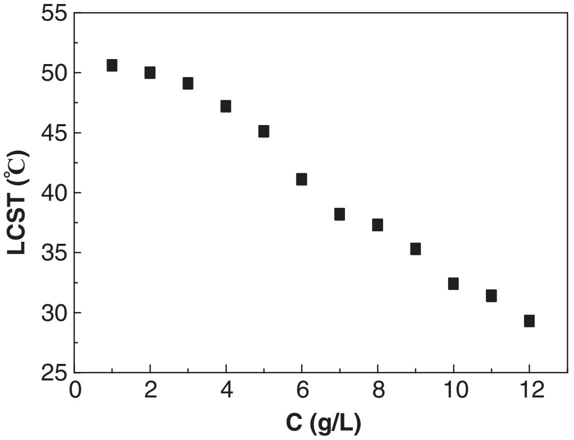


**Fig. 6.** Effect of concentration of MePEG$_{16}$-*b*-PDMAEMA$_{50}$-*b*-POFPMA$_6$ on the LCSTs, measured at pH 9.0.

poly(ethylene glycol) (MePEG-2000). The LCSTs of the aqueous solutions decreased 9.1°C when the units of PDMAEMA linked to MePEG-2000 increased from 15 to 30 (32). In this study, the LCSTs of the aqueous solutions decreased 12.0°C when the units of PDMAEMA connected to MePEG-750 increased from 15 to 30. These results imply that the length of PDMAEMA affects the LCST of MD diblcok copolymers in aqueous solution because of the different mass fractions of PDMAEMA in these diblock copolymers, which contained MePEG-750 or MePEG-2000.

For the identical copolymer, LCST also depended on the concentration of polymer aqueous solution. Figure 6 shows the variation of LCST with the concentrations of MDO at pH 9.0. The LCST changes regularly with the increasing concentrations of triblock copolymer. The appearance of LCST depended on the aggregation of the hydrophobic portions of the polymers at a given temperature. It is thought that the interactions between the polymers were not close in the dilute solution. The LCSTs decreased more slowly at lower copolymer concentrations than that at higher copolymer concentrations. This might be due to the fact that the interactions between the copolymers in aqueous solution are weak in a restricted range of low concentration.

## 3.5 TEM of Triblock Copolymers

Transmission electron microscopy (TEM) is one of the most powerful methods to investigate self-assembly behavior. We used TEM to observe the micelle structures that resulted from the samples by dissolving the copolymers in deionized water at pH 7.0 at different concentrations.

According to Figure 7, we found that the PEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFMA$_6$, PEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ and PEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymers exhibit different micelle morphologies in aqueous solutions at pH 7.0. Figure 7a is the TEM image of micelles for the PEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$, Figure 7b is the TEM image of micelles for the PEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 6 g L$^{-1}$, Figure 7c is the TEM image of micelles for the PEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$, Figure 7d is the TEM image of micelles for the PEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$. Compare Figure 7a with Figure 7c, we can see that at same concentration and pH, longer PDMAEMA block is preferential to form

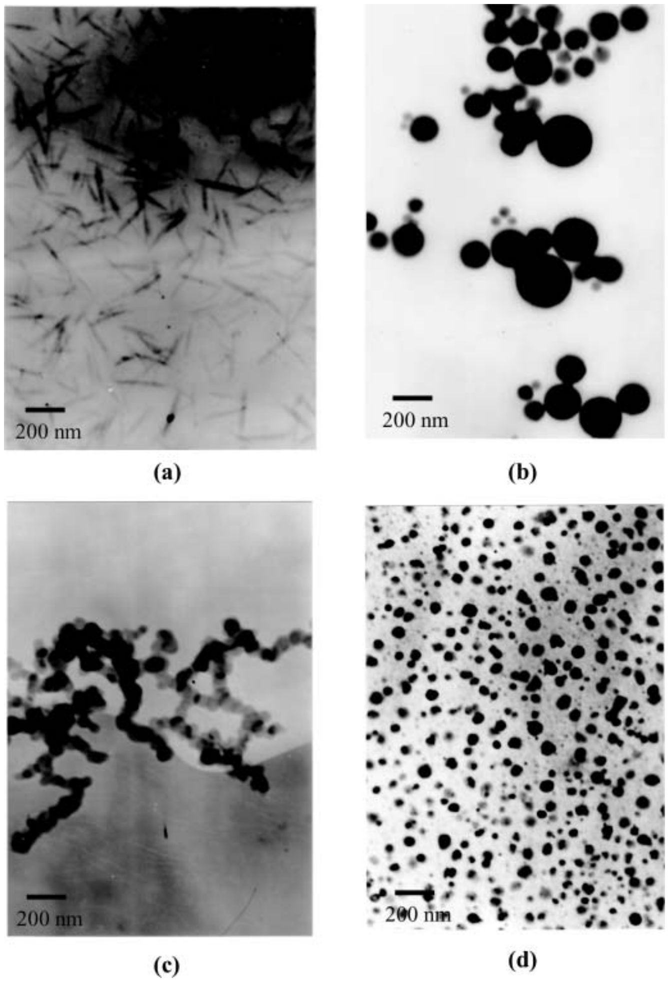


**Fig. 7.** TEM images of self-assembled micelles obtained from (a) MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$, (b) MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 6 g L$^{-1}$, (c) MePEG$_{16}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$, and (d) MePEG$_{45}$-*b*-PDMAEMA$_{30}$-*b*-POFPMA$_6$ copolymer at pH 7.0 with a concentration of 5 g L$^{-1}$, bar= 200 nm.

sphere micelles while Figure 7a appears rod shape. Some papers reported that hydrophilic/hydrophobic block ratios can influence aggregation morphologies of amphiphilic copolymers (42,43). Therefore, we could understand the different micelle morphologies between Figure 7a with Figure 7c. From Figure 7b and Figure 7c, it can be seen that slightly higher concentration results in the more regular sphere micelles. Besides, Figure 7c and Figure 7d indicate that size of micelles from copolymer using MePEG ($M_n = 750$ g mol$^{-1}$) as macroinitiator is about 150 nm, larger than the copolymer using MePEG ($M_n =$ 2000 g mol$^{-1}$) as macroinitiator, which is about 100 nm. In addition, the latter spherical micelles are more dispersed, it can be contributed to the fact that the solubility of the copolymers connected MePEG-750 is much better than that of those linked MePEG-2000, consistent with the results of surface tension measurement.

## 4 Conclusions

A triblock copolymer, MePEG$_{16}$-*b*-PDMAEMA-*b*-POFPMA, containing double-hydrophilic diblock copolymer and fluorinated methacrylate block has been synthesized via oxyanion-initiated polymerization in THF at 30°C, using (dimethyl amino)ethyl methacrylate (DMAEMA) as the first monomer and 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) as the second fed monomer. $^1$H-NMR measurement confirmed that the actual molecular weights of PDMAEMA and POFPMA blocks in copolymers were reasonably close to those corresponding to the original [Monomer]/[MePEGO$^-$K$^+$] molar ratios, suggesting that the polymerization could be controlled. The results of GPC analyses showed that both the diblock and the triblock copolymers had narrow polydispersities ($M_w/M_n$ =1.15–1.36).

For the identical block lengths of PDMAEMA and POFPMA, but different MePEG lengths, the surface tension measurement showed that the solubility of the copolymers connected MePEG-750 was much better than that of those linked MePEG-2000. The cac values obtained by electrical conductivity measurement for MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_3$ and MePEG$_{16}$-*b*-PDMAEMA$_{15}$-*b*-POFPMA$_6$ were 5.1∼5.3 g L$^{-1}$ and 5.0∼5.2 g L$^{-1}$, respectively. The results suggested that the effect of the short chain of fluoroalkyl methacrylate on the triblock copolymers may be limited in a restricted range of the length of the short fluorinated chain. The study of LCST indicated that the effects of the PDMAEMA segment on copolymers initiated by MePEG-750 oxyanion are greater than that on those initiated by MePEG-2000 oxyanion. The results of TEM show that MePEG-*b*-PDMAEMA-*b*-POFPMA can self-assemble different morphologies in aqueous solution at pH 7.0, depending on the block lengths.

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