Effect of Hydrophilic Chain Length on the Aqueous Solution Behavior of Block Amphiphilic Copolymers PMMA-*b*-PDMAEMA

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ABSTRACT: A series of amphiphilic block copolymers, polymethyl methacrylate (PMMA)-*b*-poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA), were synthesized by atom transfer radical polymerization (ATRP) method. Surface tension, dynamic light scattering (DLS), transmission electron microscope (TEM), and atomic force microscopy (AFM) studies were performed to investigate the aqueous micellar behavior of these block amphiphiles. At a fixed degree of polymerization (DP) of PMMA block (DP = 55), the PDMAEMA block length was found to have a significant influence on the critical micelle concentration (cmc) values and hydrodynamic size of aggregates. An increase in the DP of PDMAEMA from 11 to 337, resulted in a decrease in the cmc from 1.44×10^{-5} to 5.81×10^{-7} M (a factor of almost 24.8), and a decrease in the Z ($2R_h$) from 85.5 to 15.5 nm (pH = 4), respectively. TEM and AFM results indicated that by changing the soluble block lengths, spherical, short rod, crew-cut, vesicles or large aggregates can be observed in the solution. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 202–208, 2012

Key words: ATRP; amphiphilic copolymers; phase behavior; aggregate

INTRODUCTION

Amphiphilic block copolymers have been extensively investigated in view of their many applications, especially in nanotechnology and controlled release of bioactive molecules.[1–3] Their solutions and interfacial characteristics have been studied in detail theoretically and experimentally in the past decades. In recent years, block copolymers with poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as hydrophilic segments, such as PSMA-*b*-PDMAEMA,[4] PtBUMA-*b*-PDMAEMA,[5] PDMAEMA-*b*-PMMA-*b*-PDMAEMA,[6] and PS-*b*-PDMAEMA,[7] have attracted much attention due to their applications as nanoreactors,[8] drug delivery vehicles,[9] and dispersion or miniemulsion polymerization stabilizers.[10] These copolymers were prepared usually by the earlier classical living anionic,[11,12] group transfer polymerization (GTP),[13] and the later atom transfer radical polymerization (ATRP).[14]

In the previous article, the solution properties of GTP-synthesized PDMAEMA-*b*-PMMA copolymers and their micelles, have been studied in detail by Baines and Billingham.[15] Later, they also reported the interaction of these diblock copolymers with salt and an anionic surfactant sodium dodecyl sulfate (SDS) in aqueous solution.[16] Recently, amphiphilic diblock and triblock copolymers of PMMA and PDMAEMA have been synthesized by ATRP, and the research indicated that for a fixed degree of polymerization (DP = 52) of the PMMA block in the diblock copolymers, the hydrodynamic diameter of the micelles in methanolic water (water 95 vol%) increases with the DP of the PDMAEMA block (DP = 57, 89, 232).[17]

The amphiphilic diblock copolymers, PMMA-*b*-PDMAEMA, have been studied widely;[18] however, few works involved the systemic investigations of the effects of PMMA or PDMAEMA block length on the solution properties, such as surface tension, cmc, hydrodynamic size, and micromorphology of the formed aggregates. In the present work, a series of PMMA-*b*-PDMAEMA with different molecular weights (DP of PDMAEMA changes from 11 to 337) were synthesized by ATRP method, using an ATRP prepared PMMA-Br macroinitiator (DP = 55). The

aqueous solution behavior of these copolymers, were studied by surface tension measurements, dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM), respectively.

EXPERIMENTAL

Materials

Methyl methacrylate (Sinopharm Chemical Reagent, SCRC) was washed with 5% NaOH water solution and distilled water, then dried with anhydrous calcium chloride and distilled under vacuum. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was purchased from Wuhan Shenshi Chemical company and purified by distilling under vacuum. Finally, the monomers with CaH_2 were stored in the icebox under nitrogen atmosphere at about $-10°C$. CuBr and CuCl were purified by successive washing with glacial acetic acid and isopropanol; then these compounds were dried under vacuum and stored under a purified nitrogen atmosphere. Ethyl 2-bromoisobutyrate (EBIB) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich. All other reagents were purchased from SCRC and used as received.

Preparation of macroinitiator PMMA-Br

PMMA macroinitiator was prepared in the mixture of DMF and anisole at $70°C$. In a typical experiment, $CuBr/CuBr_2$ and a stirring bar were put into a reaction tube. The tube was tightly sealed with a rubber septum and three cycles of evacuating and backfilling with nitrogen were conducted. Then, the mixture of the degassed monomer, solvent and PMDETA was added via a degassed syringe. The tube was immersed in an oil bath. The initiator was added to the mixture until the solution became homogeneous. The reaction was stopped after a suitable time. The product was isolated by passing through a column of basic alumina, precipitation in cold methanol, and drying in vacuum.

Preparation of PMMA-b-PDMAEMA

A representative example is as follows. The PMMA-Br macroinitiator (2.75 g) was dissolved in 20 g 1 : 1 chlorobenzene and DMF mixture (w/w) in a reaction vessel. The above mixture was degassed by high-pure nitrogen for 2 h. Then, CuCl and $2,2'$-bipyridine (bpy) were introduced into the vessel under nitrogen atmosphere followed by 15 min nitrogen purging. Finally, the degassed DMAEMA was added to the vessel by a nitrogen-purged syringe. The vessel was then sealed with a rubber septum and parafilm. The reaction mixture was

stirred at $80°C$ for 12 h. Then, the obtained polymer was diluted with acetone (20 mL), passed through a column of basic alumina, precipitated in petroleum ether and dried under vacuum.

NMR

^1H-NMR spectra were recorded on a Varian Mercury VX-300 MHz instrument using $CDCl_3$ as a lock solvent and TMS as a standard for chemical shifts.

Gel permeation chromatography

Molecular weight and molecular weight distribution were measured on a GPC system consisting of a Waters 515 pump, Wyatt Technology Optilab Dsp and DAWN® EOS™, equipped with MZ gel SDplus linear 5 μm column and 500 Å 5 μm column. HPLC grade THF (Spectrochem, India) mixed with triethylamine (5 vol %) was used as the eluent at a flow rate of 1 mL min^{-1} as reported.[19]

Surface tension

The surface tension (γ) measurements were carried out using a duNoüy tensionometer Krüss K100, equipped with a platinum Wilhelmy plate at $25°C$. The glassware was dipped in a sulfochromic acid solution for at least 6 h, thoroughly rinsed with double distilled water, and dried in an oven at $50°C$. The platinum plate was cleaned with water and chloroform and flamed before each measurement. The cleanness of the glassware was checked by measuring the surface tension of double distilled water, which was measured to be $72 \sim 73$ mN m^{-1}. Each measurement was accepted whenever the values were steady within 0.01 mN m^{-1}. The sample was first dissolved in a pH = 2 HCl solution to obtain a stock solution with 1 mg mL^{-1} and stirred for 24 h, then the solution was adjusted to pH = 9 by $1M$ NaOH, which cannot change the concentration significantly. The different concentration was prepared by diluting the stock solution using double distilled water.

Dynamic light scattering

DLS measurements were carried out with a Malvern Zetasizer Nano-ZS equipped with an argon laser (λ = 633 nm) at a scattering angle of $173°$ at $25°C$. The determination of the hydrodynamic radius was done with the CONTIN algorithm.

Preparations of Micellar solutions were conducted in two ways:

Aqueous preparation

The copolymer samples were dissolved in 0.05 mol L^{-1} HCl solution at a concentration of 1 mg mL^{-1},
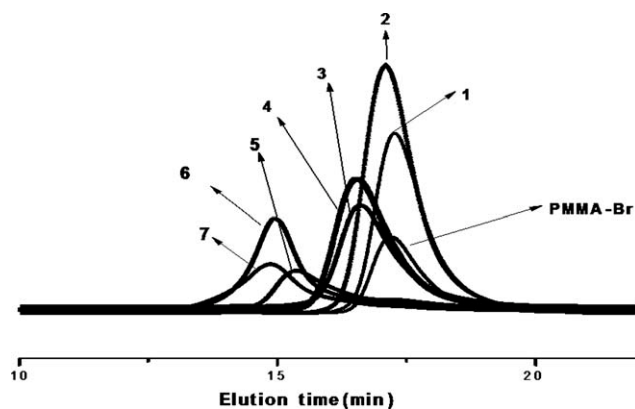
Figure 1 GPC traces for MMA microinitiator and PMMA-*b*-PDMAEMA block copolymers.

and the solution was stirred for 48 h. After filtering the solutions through a 200 nm filter (0.2 μm PVDF), the solution was adjusted to desired pH by the addition of 1*M* NaOH to induce self-assembly. Final polymer concentrations after this adjustment were not significantly changed.

Solvent preparation

Samples (0.1 g) were dissolved in 5 mL acetone. After filtering the solutions through a 200 nm filter, we slowly added distilled water dropwise with gentle agitation between each addition to a final polymer concentration of 1 mg mL^{-1}. All the solutions were stored at room temperature for 48 h and filtered again before analysis.

Transmission electron microscopy

The TEM was done using a JEOL JEM 2010 TEM instrument, operating at 200 kV. The sample preparation was the same procedure of solvent preparation as above. Samples were prepared by dipping mesh copper grids into the aqueous copolymer solution added with a very small amount of 10% ammonium phosphomolybdate. The excess of copolymer solution was wiped off with a paper filter, and the grid was dried under ambient atmosphere for 1 h.

Atomic force microscopy

AFM imaging was conducted with a PicoScan AFM (Molecular Imaging Corporation, Phoenix, Arizona, USA). Freshly prepared samples were mounted on AFM stage and imaged under MAC Mode in air (relative humidity = 40–50%, $T = \sim 25°C$) using MAClever Type II probes (spring constant = 2.8 N m^{-1}, resonant frequency = $\sim$ 85 kHz, Molecular Imaging). Scan rates were about 1.5 line s^{-1}. The images were rastered at 256 × 256 pixels, unfiltered and flattened when needed. A drop of 20 μL of sample solution prepared as above solvent preparation was dropped onto freshly cleaved ruby muscovite mica substrate (Digital Instruments) and allowed to dry about 1 h.

RESULTS AND DISCUSSION

PMMA-*b*-PDMAEMA block copolymers

A series of PMMA-*b*-PDMAEMA block copolymers were prepared via ATRP method, by using the
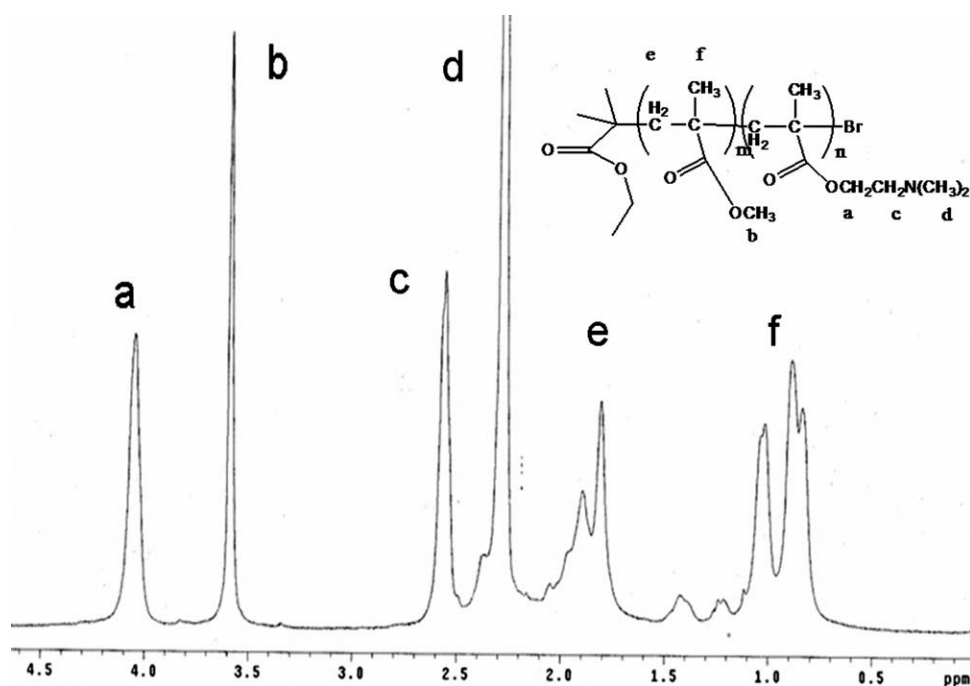
Figure 2 ^{1}H-NMR spectrum of sample 5 in DCCl$_3$.

TABLE I
Characteristics of the PMMA-*b*-PDAMEMA Copolymers Synthesized via ATRP

No.	Compo^{GPC}	M_n^G	M_w/M_n	f^{GPC}	f^{NMR}	Mol % (D)$_{GPC}$
PMMA-Br	M55	5500	1.07			
1	M55-D11	5500-1745	1.05	1 : 0.20	1 : 0.09	16.67
2	M55-D19	5500-2950	1.05	1 : 0.34	1 : 0.12	25.67
3	M55-D38	5500-6000	1.10	1 : 0.69	1 : 0.40	40.86
4	M55-D50	5500-7500	1.05	1 : 0.91	1 : 0.55	47.62
5	M55-D121	5500-19,000	1.20	1 : 2.20	1 : 1.77	68.75
6	M55-D242	5500-38,000	1.25	1 : 4.40	1 : 2.98	81.48
7	M55-D337	5500-53,000	1.39	1 : 6.10	1 : 6.20	85.97

Compo^{GPC} represents the composition of the copolymers determined by GPC.
M_n^G represents the number molecular composition of block copolymers determined by GPC.
f^{GPC} represents the rate of the two blocks of the copolymers determined by GPC.
f^{NMR} represents the monomer rate of the two blocks of the copolymers determined by NMR.
Mol % (D)$_{GPC}$ represents the rate of DMAEMA in the block copolymers (mole ratio) determined by GPC.

different ratio of PMMA-Br macroinitiator and DMAEMA monomer. The GPC analysis has been attempted to characterize the molecular weight and molecular weight distribution of the block copolymers. Figure 1 illustrates the GPC curves of the polymers. After the polymerization, the peak of the starting PMMA-Br macroinitiator shifts towards the left (the region of higher molecular weight). This indicates that the polymerization of DMAEMA is initiated efficiently by the living PMMA-Br.

The molecular weights and compositions of the copolymers were also determined by ^{1}H-NMR spectroscopy. Figure 2 shows the typical ^{1}H-NMR spectrum of the block copolymer 5. The block length and composition were calculated from the peak integrals among the protons (Peak a at 4.05 ppm) in the ethyl groups of PDMAEMA, and the protons (Peak b at 3.58 ppm) in the methyl groups of PMMA. The signals at 2.56, 2.27, 1.75–2.08, and 0.82–1.50 ppm, were attributed to the protons of methylene groups (Peak c), methyl groups(Peak d), methylene groups(Peak e) and methyl groups (Peak f), respectively. Table I summarizes the detailed characteristics of the synthesized copolymers with well-controlled molecular weight and distribution.

Surface tension

The surface activities of these PMMA-*b*-PDMAEMA copolymers in dilute aqueous solution were confirmed by the surface tension measurement (Fig. 3 and Table II). The results show that these block copolymers can decrease the surface tension of aqueous medium considerably. The γ_{cmc}, the value of surface tension at cmc, is in the range of 41.61–45.14 mN m^{-1}, and has a small decrease when the hydrophilic PDAMEMA chain length increases. This

is similar with the surface activities of C_iE_6 as reported.[20] The hydrophobic chain of the surfactants can bend or incline at the air/water interface when it is long enough (such as $C_{16}E_6$, $C_{18}E_6$), and this may decease the density of the hydrophobic chain at the interface and lead to the increase of γ_{cmc}. For this series block copolymers, though the chain length is sufficiently long for bending, the relative length ratio of hydrophilic to hydrophobic chain may also affect the density of the hydrophobic chain on the surface. The arrangement of the PMMA-*b*-PDMAEMA block copolymers was illustrated in Scheme 1.

Moreover, the cmc of these block copolymers are in the range of $5.81 \times 10^{-7} \sim 1.44 \times 10^{-5}$ mol L^{-1} (0.034 $\sim$ 0.122 mg mL^{-1}), which are lower than 0.35 mg mL^{-1} at pH = 7.5 as Chatterjee reported.[17] This may be attributed to the higher pH (pH = 9)
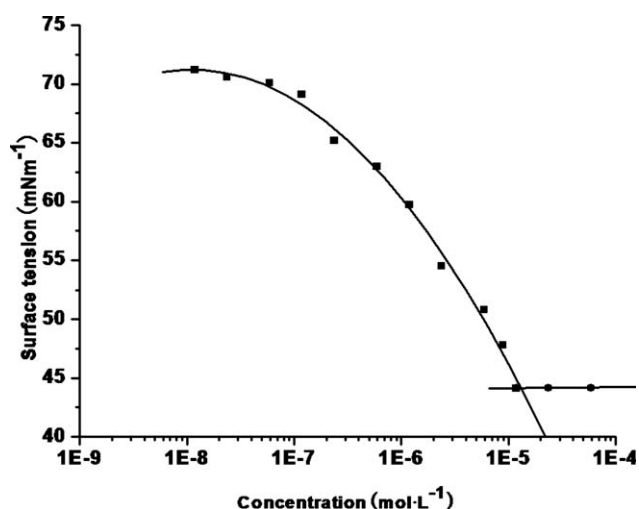
Figure 3 Surface tension versus concentration (mol L^{-1}) of PMMA-*b*-PDMAEMA block copolymers (Sample 2) in pH = 9 solution at 25°C.

TABLE II
**Physicochemical Properties of Block Copolymers in Aqueous Solution at 25°C**

No	Mol % $(D)_{GPC}$	γ_{cmc} (mN m^{-1})	cmc (mol L^{-1})	Γ_{max} (μmol m^{-2})	A_{min} (nm^2 molecule^{-1})	ΔG^0_{mic} (KJ mol^{-1})
2	25.67	44.15	1.44×10^{-5}	7.97	0.21	−27.62
3	40.86	45.14	3.20×10^{-6}	6.28	0.26	−31.35
4	47.62	42.60	1.29×10^{-6}	4.78	0.35	−33.60
5	68.75	42.87	1.18×10^{-6}	3.55	0.47	−33.82
6	81.48	41.76	6.91×10^{-7}	2.96	0.56	−35.14
7	85.97	41.61	5.81×10^{-7}	1.14	1.46	−35.57

$\Gamma_{max} = -(d\gamma/d\ln c)_{T,P}/RT$, $A_{min} = 1/N_A\Gamma_{max}$, $\Delta G^0_{mic} = RT \ln(\text{cmc})$.
Γ_{max} represents surface excess concentration.
A_{min} represents minimum area per copolymer molecule.
ΔG^0_{mic} represents the standard free energy of micellization.
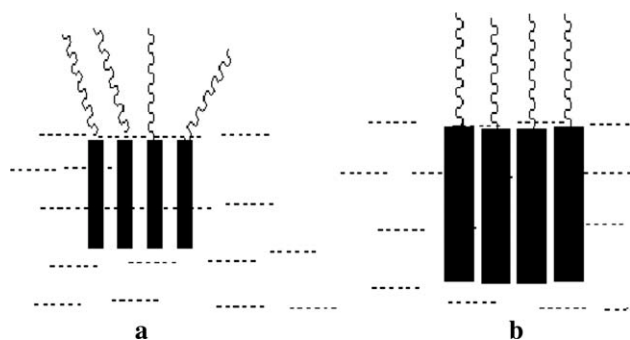
Scheme 1 The arrangement of the block copolymers at the air/water interface. (a) The block copolymers with short PDMAEMA chain and (b) the block copolymers with long PDMAEMA chain.

and the salting out effect produced in the pH adjusting process.[15] Because at pH 7.5, the PMMA-*b*-PDMAEMA chain is partly protonated,[21] and this may increase the solubility of the diblock copolymers in aqueous medium and lead to the increase of cmc. Furthermore, the cmc of these PMMA-*b*-PDMAEMA block polymers in aqueous medium decreases when the PDMAEMA chain length increases (see Table II), this is different from the normal ionic surfactants and the ionic block copolymers. And the reason may be due to the weak hydrophilicity of the PDMAEMA.

Another explanation is that the chain length of the PDMAEMA has little effect on the solubility of the block polymers,[10] but it can change the volume of hydrophilic chain.

The surface excess concentration (Γ_{max}), the minimum surface area per polymer molecule (A_{min}) occupied at the surface and the standard free energy of micellization (ΔG_{mic}), were also listed in Table II. The results show that the Γ_{max} decreases obviously when the PDMAEMA block increases, this is accordant with the normal nonionic surfactant.[22] The longer PDMAEMA chain will occupy more surface area and decrease the number of block copolymers on the surface. The ΔG_{mic} values obtained are lower than the small nonionic surfactants,[20] this indicates that the amphiphilic block copolymers prefer to form aggregates in aqueous medium. The aggregation tendency of these polymers is stronger when the hydrophilic PDMAEMA length increases.

Micellar morphology

The Z-average sizes of the micelles of these amphiphilic block polymers in different solvent were measured by DLS respectively, and the results are summarized in Table III. The data show the micelle size depends strongly on the composition of the

TABLE III
Average Sizes of Block Copolymer Micelles at Different pH in Water and a Water/Acetone Mixture at 1 mg mL^{-1}

No	Z (pH = 4) (nm)	Z (pH = 7) (nm)	Z (pH = 9) (nm)	Z(aceto) (nm)	TEM (aceto) (nm)
1	85.0 + P	137 + P	157 + P	40.0 + P	23.8
2	47.4 + P	49.3 + P	41.4 + P	37.8	25.9
3	43.9	68.2	182	20.8	17.6
4	49.0	65.1	155	19.5	16.1
5	38.0	61.5	94.9	37.7	19.9
6	34.7	62.4	83.0	63.2	−
7	15.5	52.8	83.1	65.5	21.04

"P" represents that there were obviously precipitate in the solution.
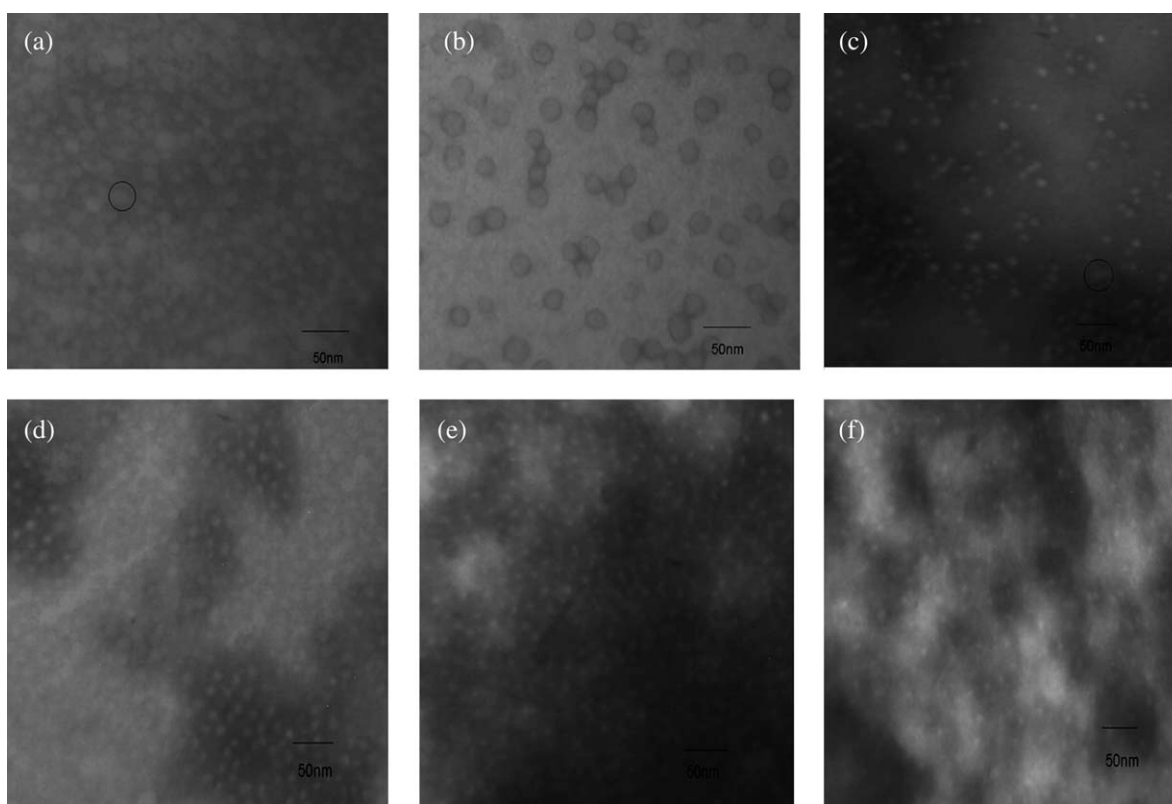
Figure 4 Representative TEM images of the block copolymer micelles prepared in water: acetone (95 : 5 v/v). (a) Sample 1, crew-cut micelle; (b) Sample 2, vesicle; (c) Sample 3, spherical micelle with short rod micelle; (d) Sample 4, spherical micelle; (e) Sample 5, spherical micelle; (f) Sample 7, spherical micelle.

polymer chain and the solvent nature. At pH = 4, the sizes of sample 3 ~ 7 were in the range of 15 ~ 50 nm, and the size of Samples 1 and 2 are 85 nm and 47.4 nm with some precipitate. The sizes of the aggregates decease gradually when the mole ratio of PDMAEMA block increases. This phenomenon can be explained by the packing parameter theory.[23] Longer PDMAEMA chain leads to the bigger hydro-

philic head group and prefer to form small aggregates in solution.

The micellar behavior of these copolymers at pH = 7 are similar to those at pH = 4. But the size of the same sample at pH = 7 was bigger than that at pH = 4. The same phenomenon can also be found at pH = 9. This is due to the relatively less electrostatic repulsion of the head groups at higher pH. For the
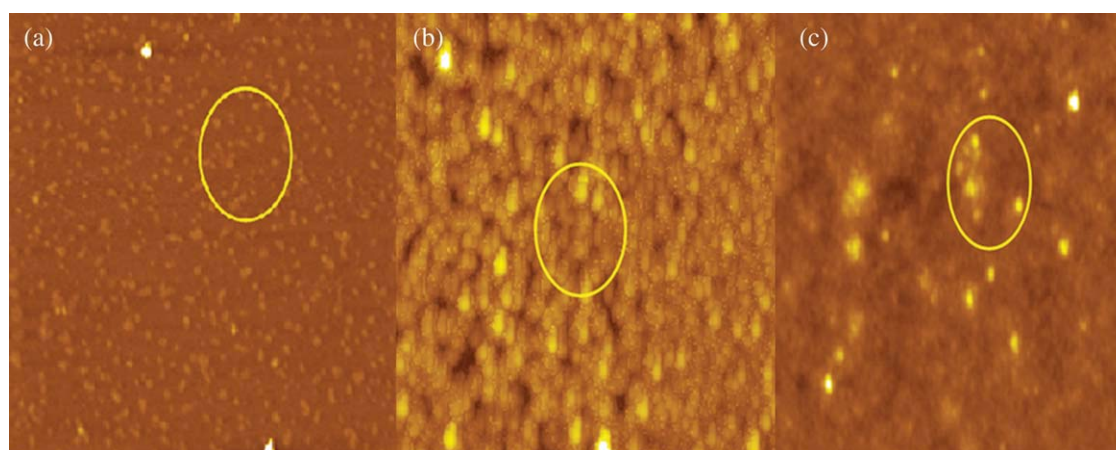
Figure 5 AFM images of a $2 \times 2 \mu m^2$ area on mica of the block copolymer aggregates. (a) Average height is 1.4 nm, data scale = 10 nm (Sample 1); (b) average height is 32.8 nm, data scale = 80 nm (Sample 2); (c) average height is 8.6 nm, data scale = 20 nm (Sample 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

same block copolymers at different pH, the lower pH value is, the more protonated PDMAEMA is, the stronger electrostatic repulsion and smaller aggregate should be obtained.

In the mixture of water and acetone, the average size of the copolymer aggregates is smaller than those in pure water at pH = 9. The size decreases a little and then increases with the hydrophilic chain increasing. This can be confirmed by TEM observations (Fig. 4), and the average sizes measured directly from the TEM images are listed in Table III. The results show that the aggregates of Sample 1 are almost elliptical, and the average size is about 23.8 nm. This should be the crew-cut micelles and was confirmed by measured height derived from AFM [1.4 nm; Fig. 5(a)]. The average aggregation size of Sample 2 is bigger than those (Samples 3, 4, 5, and 7) with longer hydrophilic block, this may be due to the formation of vesicles or large aggregates, which can be confirmed by TEM image [Fig. 4(b)] and obtained height of 32.8 nm from the AFM measurement [Fig. 5(b)]. There are some short rod micelles can be found in the spherical aggregates of sample 3 [Fig. 4(c)], and the biggest height of the aggregates is about 8.6 nm in AFM [Fig. 5(c)]. In samples 4, 5, and 7 [TEM image is Fig. 4(d–f)], small spherical micelles are observed. What should be pointed out is that the average size variability of these samples from TEM observations is similar to the DLS results.

CONCLUSION

Well-defined PMMA-*b*-PDMAEMA with same hydrophobic and different hydrophilic chains lengths can be prepared conveniently via ATRP method. The surface tension measurements indicated that these copolymers possess certain surface activities and could decrease the surface tension of water to nearly 40 mN m^{-1}. Moreover, the cmc decreases obviously with PDMAEMA chain increasing, but the γ_{cmc} decreases a little at the same time. DLS results show that the average aggregate sizes of these block copolymers at different pH in water or in acetone/water (5 : 95, w/w) mixtures, depends strongly on the composition of the polymer chain and the solvent nature. TEM and AFM observations revealed that the increasing of the PDMAEMA chain length has significant influence on the size and the micromorphology of the polymer aggregates.

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