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Brush-type amphiphilic polystyrene-*g*-poly(2-(dimethylamino)ethyl methacrylate)) copolymers from ATRP and their self-assembly in selective solvents

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Abstract

A series of well-defined brush-type amphiphilic polystyrene-*g*-poly(2-(dimethylamino) ethyl methacrylate)) (PS-*g*-PDMAEMA) copolymers were successfully synthesized via atom transfer radical polymerization (ATRP), using chloromethylated polystyrene (CMPS) as the macroinitiator. The self-assembly behavior of the resulting brush-type copolymers in deionized water and deionized water/acetone (v/v = 2/3) mixture was studied by high performance particle sizer (HPPS). The results showed that the *Z*-average size of the micelles in deionized water increased with the increase of molecular weight of PDMAEMA, and the corresponding size was larger than that in mixed solvent of deionized water and acetone (v/v = 2/3). The morphologies of the micelles self-assembled from PS-*g*-PDMAEMA in selective solvents were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). When the micelles were prepared in water/acetone (v/v = 2/3) mixture and cast them on a glass slide at different temperatures (from 50 up to 200 °C), the transformation of the morphologies of aggregates, from needle-like solid to microcubic particles, was observed using SEM.

Keywords: ATRP; Polymer brush; Amphiphilic

1. Introduction

Brush-type copolymers have recently attracted considerable attention in a broad range of fields, including drug carriers for targeted drug delivery, new class of elastomeric materials, sensitive to environment materials [1–3]. The synthesis of graft copolymers can be accomplished through one of the three routes: 'grafting from' reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), 'grafting through' processes (operating by homo- or copolymerization of a macromonomer) and 'grafting onto' (occurring when the growing chain is attached to a polymer backbone) [4]. More recently, a number of excellent works on polymer brushes on the surfaces of silicon [5–10], intercalated and exfoliated silicate (clay) layers [11] and single-walled carbon nanotubes [12] have been reported. As a novel polymerization approach, atom transfer radical polymerization (ATRP) [13–16] has been attracting increasing interest because of its adaptability to a wide range of functional monomers under less stringent experimental conditions. The ATRP technique offers a new way to form well-defined and predictable multicomponent polymer structures. Up to now, ATRP has been successfully applied not only to the synthesis of well-defined macromolecular architecture such as amphiphilic random, gradient, star, and block copolymers [17–21] but also to the preparation of a wide range of brush-type copolymers [22,23].

2-(Dimethylamino)ethyl methacrylate (DMAEMA) has attracted much attention in recent years due to a variety of applications of PDMAEMA to environmental protection [24,25]. The temperature-sensitive solubility of PDMAEMA in water also renders it potentially applicable in the fields such as drug delivery systems, sensors, etc. Amphiphilic block copolymers with the PDMAEMA as amphiphilic block, such as PSMA-*b*-PDMAEMA [26], PtBUMA-*b*-PDMAEMA [27], PDMAEMA-*b*-PMMA-*b*-

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PDMAEMA [28] and PS-*b*-PDMAEMA [29], can self-assemble into micelles in water, which has the potential to be used as nano-reactors, drug delivery vehicles, or templates for preparing inorganic mesoporous materials. Jayachandran et al. studied the grafting of poly(*N*,*N*-dimethylacrylamide) from negatively charged polystyrene latex via ATRP [30]. Adsorption of dPS-*b*-PMMA and dPS-*b*-PDMAEMA from a PS neutral matrix to the melt/SiO*x* interface was studied using LE-FRES and NR by Costa et al. [31]. Surface-immobilized PS-*b*-PDMAEMA brushes was synthesized on silicate substrates from chlorine-terminated polystyrene (PS) brushes via ATRP and the diblock copolymer brushes underwent self-reorganization in response to environmental changes [32].

The amphiphilic block copolymers, PS-*b*-PDMAEMA, have been studied widely [29–32], however, few works involved the self-assembly from brush-type copolymer (PS-*g*-PDMAEMA) in selective solvents. In the present work, a series of PS with different molecular weights and narrow molecular weight distributions were synthesized via ATRP, and then the PS polymers were functionalized by chloromethylation. Subsequently, the brush-type copolymers, PS-*g*-PDMAEMA, were prepared using chloromethylated PS (CMPS) as the macroinitiator via ATRP. The self-assembled micelles from PS-*g*-PDMAEMA, prepared in various selective solvents or at different temperatures, were studied by high performance particle sizer (HPPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively.

2. Experimental section

2.1. Materials

Styrene (St) (chemically pure, Shanghai Chemical Reagent Co., Ltd) were purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with water and dried with anhydrous sodium sulfate overnight, finally distillated under vacuum. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (chemical pure, Wuxi Xinyu Co. Ltd) was distillated under vacuum. *p*-α,α′-Dichloroxylene (DClX) (chemically pure, Jiangsu Jiangdu Sandeli Co. LTD.) was recrystalyzed twice from ethanol. CuCl (chemically pure, Shanghai Chemical Reagent Co. LTD.) was dissolved in HCl, precipitated into a large amount of water then dried under vacuum. *N*,*N*-Dimethyl formamide (DMF) (analytical reagent, Shanghai No.1 Chemical Reagent Factory) was distillated under vacuum. Tetrahydrofuran (THF) (analytical reagent, Shanghai Chemical Reagent Co. Ltd), 2,2′-bipyridyl (bpy) (analytical reagent, Shanghai Chemical Reagent Co. Ltd), PCl_3 (analytical pure, Shanghai Chemical Reagent Co. LTD.), paraformaldehyde (chemically pure, Shanghai Chemical Reagent Co. LTD.), $ZnCl_2$ (analytical pure, Jiangsu Jincheng Chemical Reagent Co. Ltd) and methanol (commercially available) were used as received.

2.2. Polymerizations

2.2.1. Synthesis of polystyrene

The general procedures of the polymerization are as follows: styrene (20 ml), bpy, CuCl and DClX ($[\text{DClX}]_0$:$[\text{CuCl}]_0$:$[\text{bpy}]_0 = 1:2:6$ (molar ratio)) were added to a dried 50 ml round-bottom flask; three cycles of vacuum-nitrogen were applied in order to remove the dissolved oxygen. Then the flask was sealed using a septum under nitrogen. The polymerization of St was carried out at 120 °C for a desired period of time. At the end of the polymerization reaction, the flask was quenched in cold water and opened, diluted with THF, precipitated into a large amount of methanol and dried under vacuum at 55 °C for 48 h.

2.2.2. Chloromethylation of polystyrene

PS (5 g) was dissolved in $CHCl_3$ (25 ml), paraformaldehyde (1.5 g), PCl_3 (10 g) and $ZnCl_2$ (5 g) were added, respectively, to a three-necked flask equipped with a stirrer and reflex condenser, and the reaction mixture was heated at 60 °C for 10 h under stirring. The product was isolated by precipitating into a large amount of ethanol, filtered. The solid was washed with 5% $NaHCO_3$ and deionized water in turns to remove chlorine ions until no white precipitate was observed when a drop of $AgNO_3$ solution was added to the final filtrate, indicating no chlorine ion remained. The chloromethylated PS, CMPS, was dried under vacuum at 25 °C until a constant weight was obtained.

2.2.3. Synthesis of brush-type amphiphilic PS-g-PDMAEMA copolymer using CMPS as the macroinitiator

Graft copolymerization was performed in the same manner as the typical ATRP procedures for the polymerization of St: DMAEMA (1 ml), toluene (1 ml), CMPS, CuCl, and bpy ($[\text{CMPS}]_0$:$[\text{CuCl}]_0$:$[\text{bpy}]_0 = 1:1:3$ (molar ratio)) were added to a 5 ml ampoule tube; three cycles of vacuum-nitrogen were applied. Then the ampoule tube was sealed with a rubber septum under nitrogen and was placed in an oil bath thermostated at the desired temperature. The polymerizations were carried out for a desired time. At the end of the polymerization reaction, the tube was quenched in cold water and opened, diluted with THF. The brush-type copolymer, PS-*g*-PDMAEMA, was obtained by precipitating into a large amount of hexane and drying under vacuum at 25 °C until a constant weight was obtained.

2.3. Preparation of the micelle solutions

The brush-type amphiphilic PS-*g*-PDMAEMA copolymer (5 mg) was first dissolved in dry DMF (1 ml) at room temperature to give a 5 mg/ml polymer solution. The polymer solution (0.20 ml) was added into selective solvents (4.80 ml, water, acetone or acetone/water mixture) at the rate of one drop every 10 s by a microsyringe under vigorous stirring. The micelle solution with a polymer concentration of about 0.2 mg/ml was used for the *Z*-average size analysis by high performance particle sizer (HPPS) and the subsequent morphological studies by TEM and SEM.

2.4. Characterizations

Conversion of monomers was determined by gravimetrically. Molecular weights and molecular weight distributions of polymers were measured on Waters 1515 gel permeation chromatography (GPC), equipped with microstyragel columns (HR1, HR3, HR4) with THF as a mobile phase at a flow rate of 1 ml/min and operated at 30 °C. The molecular weight was calibrated with narrow polystyrene standards with molecular weights of 1100, 2950, 6690, 9650, 18,600, 43,700, 114,000, 177,000 and 871,000 g mol^{-1}. Molecular weights and molecular weight distributions of polymers were also measured by GPC coupled with Wyatt Technology DAWN EOS multi-angle laser light scattering (MALLS) detector using 30 mW solid laser at 690 nm. ^{1}H NMR spectra were recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Elemental analyses (EA) of C, H and N, were measured on the EA1110 CHNO-S. FT-IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer. The *Z*-average size and the polydispersity index (PDI) of the self-assembled micelles from PS-*g*-PDMAEMA copolymer in selective solvents were measured on a Malvern HPP 5001 high performance particle sizer (HPPS) at 25 °C. Transmission electron microscopy (TEM) was recorded on a Hitachi H-600 TEM at a 100 kV accelerating voltage. The samples were prepared by mounting a drop of the micelle solution (0.05 ml) on a copper EM grid covered with a thin film of formvar. Scanning electron microscopy (SEM) was recorded on a Hitachi S-570 SEM at 20 kV. The samples were prepared by mounting a drop of the micelle solution (0.05 ml) on a clean glass slide thermostated at the desired temperature (80, 100, 115, 130, 150, 180 and 200 °C, respectively). All the glass slides used were first treated with hydrochloric acid (about 33%) for 2 h, and then washed with deionized water and acetone, respectively. A thin layer of gold was sputter-coated on the samples for charge dissipation during SEM imaging.

3. Results and discussion

3.1. ATRP of styrene

The ATRP of St, initiated by DClX/CuCl/bpy, was carried out in bulk as reported in our previous work [33]. The results are listed in Table 1.

3.2. Chloromethylation of polystyrene

To synthesize brush-type PS-*g*-PDMAEMA copolymer via ATRP, we first tried to use polychloromethylstyrene (PCMS) as the macroinitiator, however, it was hard to obtain the soluble copolymer due to higher concentration of benzyl chloride in PCMS, which results in the cross-linking reaction. In some reports, the PCMS-*co*-PS copolymer was used as the macroinitiator in order to lower the number of reactive sites available for grafting. Thus, in the present work, the chloromethylated PS (CMPS) was used as the macroinitiator to give rise to the PS-*g*-PDMAEMA copolymer via ATRP. The synthetic pathway is shown in Scheme 1.

PS with different molecular weights (5500, 16,700 and 26,500 g/mol) was selected to be functionalized by chloromethylation, and the results are shown in Table 2. The contents of Cl in CMPS obtained were less than 5% (measured by elemental analyses). It is found that the contents of Cl are decreased with increasing molecular weight of PS under the same reaction conditions. This may be attributed to the increase of viscosity of the reaction solution. Fig. 1 shows the ^{1}H NMR spectrum of CMPS, the chemical shift at 4.5 ppm is a characteristic peak of chloromethyl group ($-CH_2Cl$) protons. In addition, a new peak at 1238 cm^{-1} in Fig. 2(b) corresponds to the chloromethyl group in CMPS. All these indicate that PS has been partly chloromethylated.

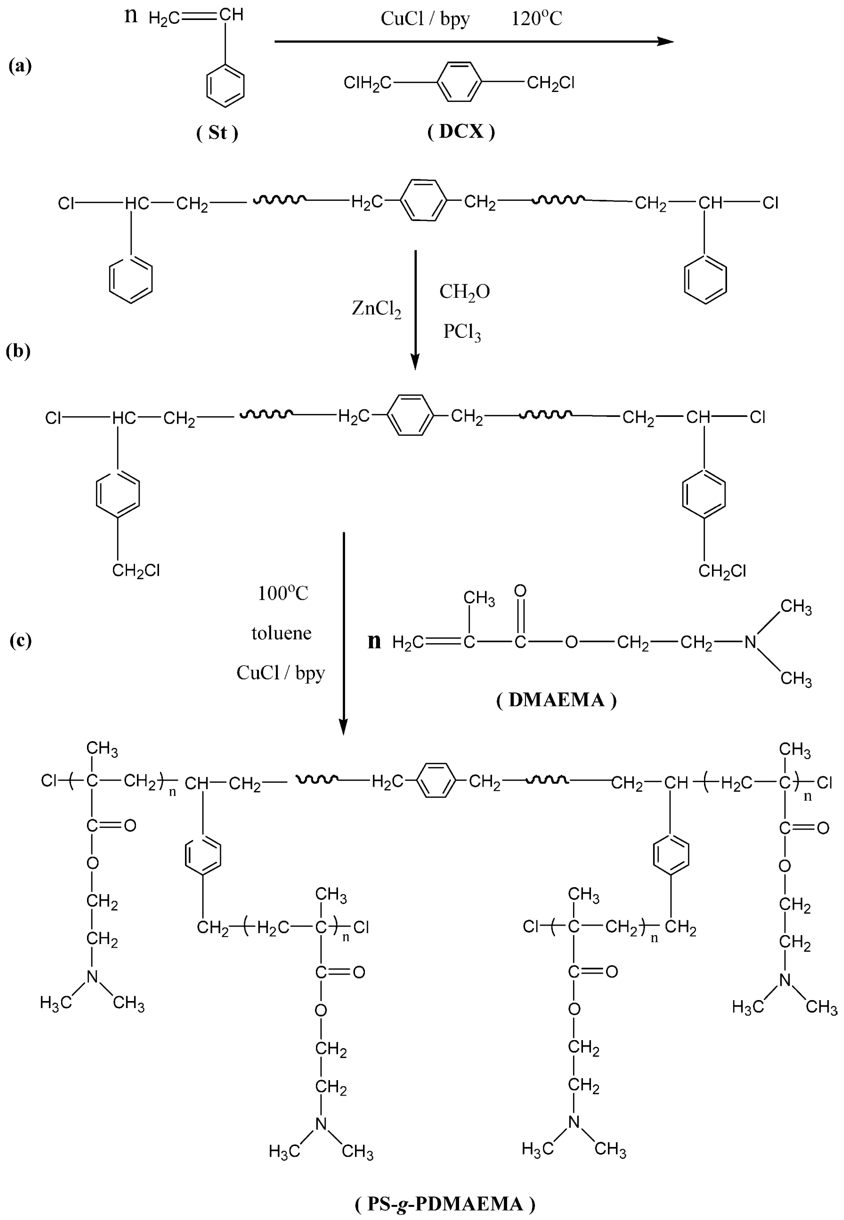
3.3. ATRP of DMAEMA using CMPS as the macroinitiator

A series of brush-type copolymers of PS-*g*-PDMAEMA with different molecular weights were synthesized via ATRP using CMPS as the macroinitiator (Scheme 1(c)) and no cross-linking reaction was observed even the conversion

Table 1
Experimental conditions and results of ATRP of styrene

$[M]_0$:$[I]_0$	*T* (*h*)	Conv. (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
100:1	2.5	48.5	5500	5100	1.33
200:1	11	83.5	16,700	16,600	1.31
300:1	20	83.2	26,500	26,000	1.25

Polymerization conditions: $[DClX]_0$:$[CuCl]_0$:$[bpy]_0$ = 1:2:6, temperature = 120 °C.



Scheme 1. Schematic diagram illustrating the preparation process of the brush-type amphiphilic PS-*g*-PDMAEMA copolymers.

Table 2
Chloromethylation results of polystyrene from EA

PS		CMPS	
$M_{n,GPC}$	$M_{n,cal}$[a]	Cl (%)[b]	*f* (–Cl)[c]
5500	5750	3.8	6
16,700	17,070	2.1	10
26,500	26,980	1.5	12

[a] Molecular weight of CMPS calculated from the results of elemental analyses.
[b] Contents of Cl measured by EA.
[c] Number of chlorine atoms calculated from the results of EA.

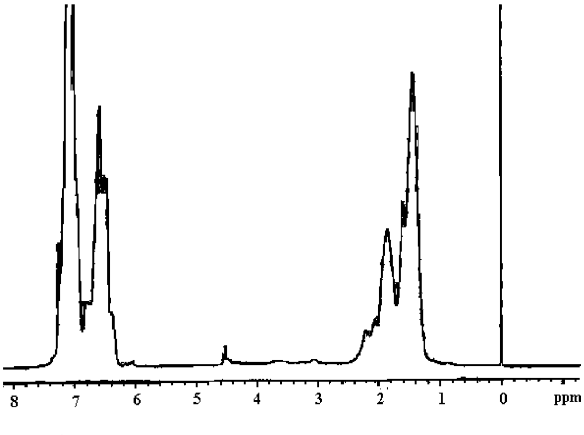


Fig. 1. ^1H NMR spectrum of chloromethylated polystyrene (CMPS).

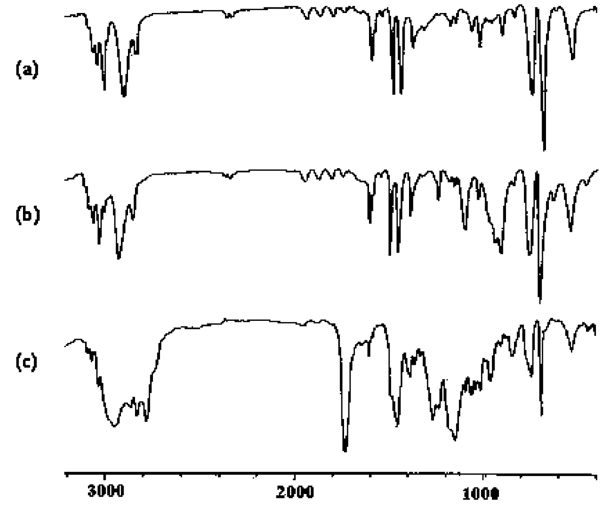


Fig. 2. IR spectra of chloromethylation of PS before (a), after (b) and PS-*g*-PDMAEMA (c).

of DMAEMA up to 80%. The ^{1}H NMR spectrum of PS-*g*-PDMAEMA is shown in Fig. 3. By comparison with Fig. 1, the chemical shift at 4.5 ppm, corresponding to the chloromethyl group, disappears, while a series of new peaks (a, c, d and e in Fig. 3, attributable to the protons of PDMAEMA) appear. Further verification of the secondary molecular structure of the PDMAEMA was established by FT-IR spectroscopy (Fig. 2(c)), in which characteristic peak for ester group is found at 1728 cm^{-1}. These chemical shifts and the characteristic FT-IR absorption band are consistent with the structure of the PS-*g*-PDMAEMA.

The molecular weights ($M_{\mathrm{n,GPC}}$s) and the molecular weight distributions (MWDs) of some PS-*g*-PDMAEMA copolymer samples were first measured by GPC. The MWDs remained very narrow (1.2–1.3), however, the $M_{\mathrm{n,GPC}}$s were much less than the theoretical values ($M_{\mathrm{n,th}}$s) calculated from the feed ratios of monomer to initiator. The deviations may be caused by the facts that the PS-*g*-PDMAEMA was adsorbed by the gel particles in GPC column as documented by Creutz et al. [34] and that the hydrodynamic volumes of the brush-type copolymers probably differ substantially from that of the linear PS standards. The GPC coupled with multi-angle laser light scattering (MALLS) detector was also used to determine the molecular weight and the MWD of PS-*g*-PDMAEMA copolymer, and the result is given in Table 3. The molecular weight ($M_{\mathrm{n,MALLS}}$) measured by GPC coupled with MALLS detector is 164,900, being larger than $M_{\mathrm{n,GPC}}$. However, the MWD (1.18) is in a good agreement with that (1.29) obtained by general GPC. In addition, ^{1}H NMR spectra were also used to estimate the molecular weights of the brush-type copolymers. The molecular weights of the PS-*g*-PDMAEMA copolymers calculated from ^{1}H NMR results are consistent with the $M_{\mathrm{n,th}}$s (Tables 3 and 4). Thus, the molecular weights of PS-*g*-PDMAEMA copolymers were mainly determined from ^{1}H NMR results. These results confirm that the molecular weights and the unit composition of brush-type copolymers can successfully be controlled by the molar ratio of monomer to initiator and by conversion via ATRP using CMPS as the macroinitiator.

3.4. Characterization of micelle solution by HPPS

In this section, we focus our discussion on self-assembled micelles from PS-*g*-PDMAEMA copolymers with different molecular weights in two selective solvents, deionized water and deionized water/acetone (v/v = 2/3). The *Z*-average size and the polydispersity index (PDI) of the micelles in two selective solvents were measured, respectively, using water as dispersant by high performance particle sizer (HPPS), and the results are summarized in Table 4. It has been reported the micelle size depends strongly on the grafting density of the side chain [35,36].

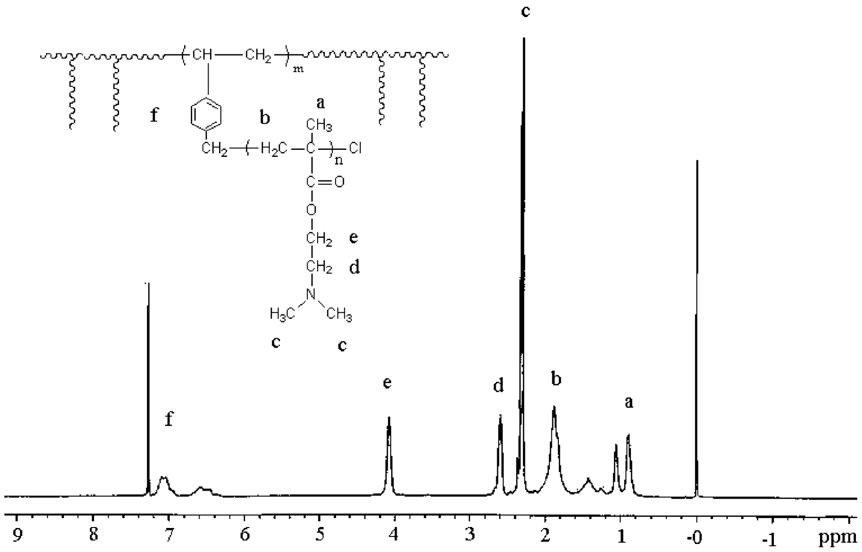


Fig. 3. ^{1}H NMR spectrum of the brush-type amphiphilic PS-*g*-PDMAEMA copolymer.

Table 3
Molecular weights and molecular weight distributions of PS-*g*-PDMAEMA copolymer

Copolymer	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n[a]	$M_{n,NMR}$	$M_{n,MALLS}$	M_w/M_n[b]
PS-*g*-PDMAEMA	117,300	24,990	1.29	91,600	164,900	1.18

[a] Measured by general GPC.
[b] Measured by GPC coupled with multi-angle laser light scattering detector.

The number of branches (*f*) as well as the degree of polymerization (DP) of PDMAEMA in each branch (*n*) are also listed in Table 4. The *Z*-average size of the micelles in deionized water increases with the increase of molecular weights of PDMAEMA side chains. However, in the mixed solvent of deionized water and acetone (v/v = 2/3), all of the *Z*-average sizes of the micelles almost keep constant except that of the PS-*g*-PDMAEMA copolymer with DP = 254 for PS, in which the *Z*-average size of the micelles increase from 85 to 170 nm when the DP of the PDMAEMA side chains increasing from 195 to 628. From Table 4, the *Z*-average sizes of the micelles of the same PS-*g*-PDMAEMA copolymer samples in deionized water are larger than those in the mixed solvent of deionized water and acetone (v/v = 2/3). In addition, there is no obvious discrepancy in the PDIs of micelles in the two different selective solvents, which indicates that there is no obvious discrepancy of the stability of micelles in the two solvents.

3.5. Morphology of micelles

The morphology of brush-type PS-*g*-PDMAEMA copolymer in aqueous solution was studied by TEM at room temperature. It is well known that comb polymers with densely grafted side chains in a good solvent can adopt a wormlike cylinder brush conformations, in which the side chains are stretched in the direction normal to the backbone, owing to the excluded-volume interaction. In our work, the TEM image shows the downy spherical micelles with PDMAEMA coronas and PS cores in water (Fig. 4). It is believed to be mainly due to the relatively low branches of graft copolymer.

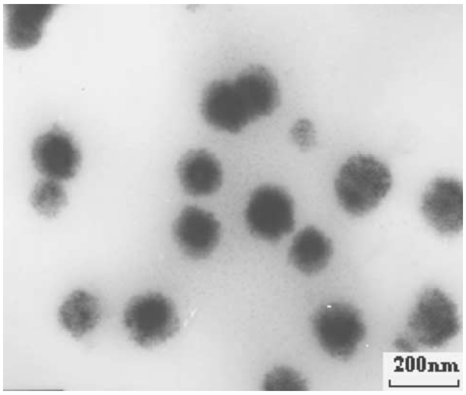


Fig. 4. TEM image of PS_{254}-*g*-$PDMA_{435}$ formed on a formvar film by casting the micelle aqueous solution at room temperature.

It is well known that many factors such as the composition of copolymer, temperature, pH, solvent and additive can affect the morphology of the resultant aggregates in selective solvents. In this work, the effect of the temperature on the morphologies of the micelles from PS-*g*-PDMAEMA copolymer, PS_{160}-*g*-$PDMA_{234}$, in deinoic water/acetone was discussed. Fig. 5 shows the SEM images formed by mounting the micelle solution in water/acetone mixed solvent (v/v = 2/3) on a glass slide at different temperatures. When the temperature increased from room temperature to 200 °C, different morphologies including needle-like, cubic and flower-like aggregates were observed, respectively.

Fig. 5(B) (at 100 °C) shows the needle-like aggregates. Below 100 °C, the morphology of aggregates observed using SEM is unclear, but it can be found that the needle-like aggregates are formed from spherical particles (Fig. 5(A) at 80 °C). The needle-like aggregates at the

Table 4
Micelle characterizations of brush-type amphiphilic PS-*g*-PDMAEMA copolymers with different molecular weights in various selective solvents

S/*D*[a]	*f*[b]	*n*[c]	Conv. (%)	$M_{n,th}$	$M_{n,NMR}$	Solvent[d]		Solvent[e]	
						Z-size (nm)	PDI	*Z*-size (nm)	PDI
53/106	6	18	65.3	26,300	22,400	171	0.40	122	0.46
53/360	6	60	69.3	71,100	62,300	417	0.49	128	0.30
160/234	10	23	83.9	56,600	53,900	122	0.27	103	0.27
160/645	10	65	76.0	124,500	118,500	150	0.35	103	0.40
254/195	12	16	66.5	58,300	57,600	130	0.39	85	0.22
254/628	12	52	75.6	133,900	125,700	193	0.51	170	0.33

[a] *S* means the degree of polymerization of PS in main chain and *D* means the degree of polymerization of PDMAEMA in side chains.
[b] The number of branches of PS-*g*-PDMAEMA.
[c] The degree of polymerization of PDMAEMA in each branch.
[d] In deionized water.
[e] In mixed solvent of deionized water and acetone (v/v = 2/3).

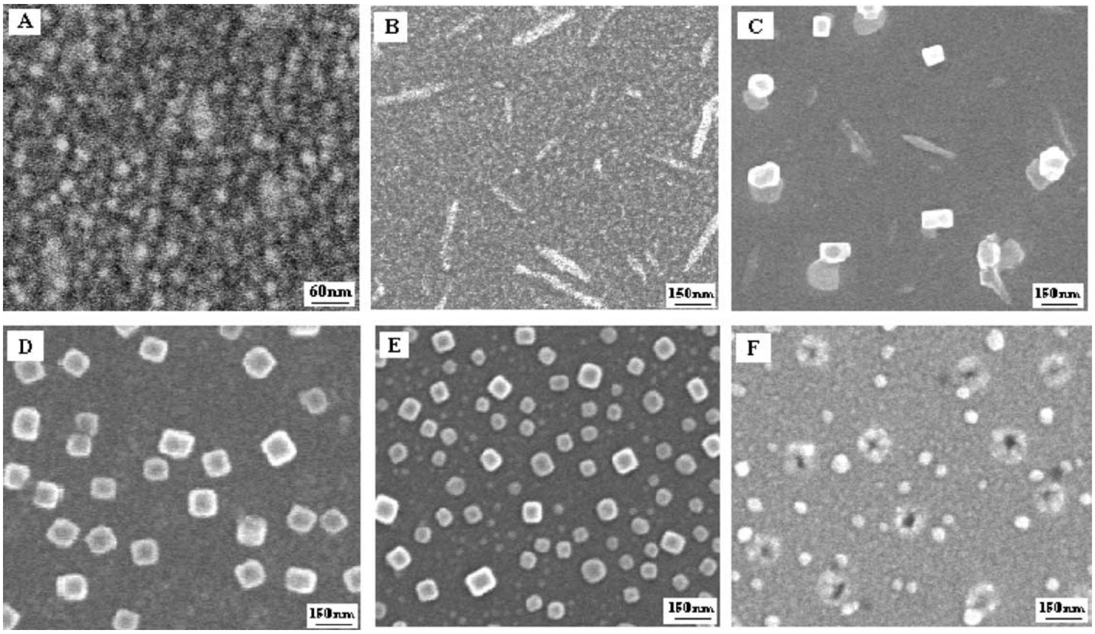


Fig. 5. SEM images formed by casting the micelle solutions of PS_{160}-*g*-$PDMA_{234}$ in water/acetone mixed solvent (v/v = 2/3) on glass slides at 80 °C (A), 100 °C (B), 115 °C (C), 130 °C (D), 180 °C (E) and 200 °C (F).

glass–air interface were also observed by drying an aqueous solution of self-assembled spherical micelles from PS_{180}-*b*-PAA_{28}.[37]

Fig. 5(D) shows the morphology of microcubic particles obtained when the sample was heated at 130 °C to vaporize the solvent mixture quickly. Usually, inorganic compounds and a few organic compounds can form a highly symmetrical crystal. It seems incredible that an amorphous polymer can self-assemble into a highly symmetrical structure. Zhang et al. has reported such highly symmetrical structure of diblock copolymer of PS-*b*-PAA, and that the composition of the microcubic particles has been confirmed by the fact that there was no any inorganic impurity by X-ray fluorescence spectroscopy (XRF) [38]. However, the similar structure of microcubic particles of the brush-type copolymer, PS-*g*-PDMAEMA, was also observed in our work. Furthermore, when the DPs of the PS and PDMAEMA varied, the same structure of microcubic particles were still observed under the same conditions, which indicates that the formation of microcubic particles is prevalent under the experimental conditions. On the other hand, it somewhat demonstrates that the temperature and the selective water/acetone mixed solvent play more important roles in the formation of microcubic particles than the composition of the copolymer. The formation of microcubic particles may be resulted from the fact that the micelle solution forms a ternary system of copolymer/water/acetone. When partly evaporating the acetone and water, a suitable ratio of copolymer/water/acetone may be achieved, resulting in the formation of the nanomicellar cubic phase. In addition, no well-defined morphology was observed by SEM when the sample was cast on a glass slide at 50 °C, which further indicates that the temperature plays a key role in the formation of a variety of aggregates.

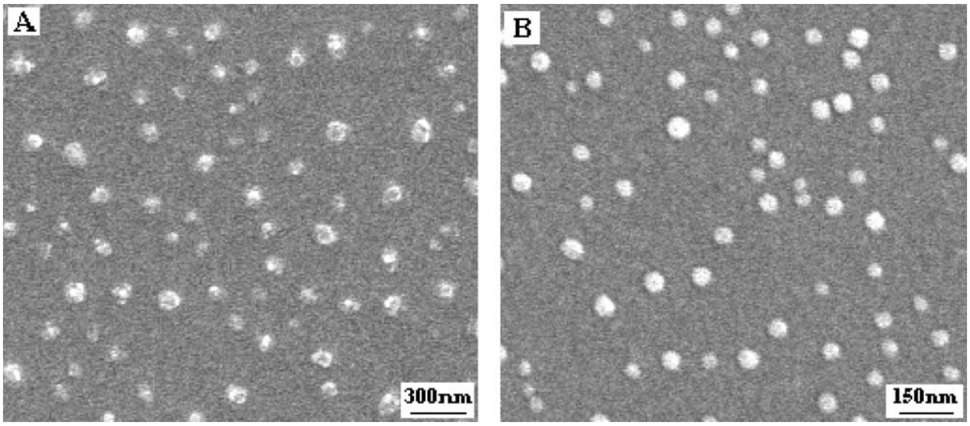


Fig. 6. SEM images formed by casting the respective micelle solutions of PS_{160}-*g*-$PDMA_{234}$ in water (A) and in acetone (B) on glass slides at 150 °C.

In Fig. 5(C) (at 115 °C), the needle-like aggregates coexists together with the cubic particles. Thus, it can be concluded that the temperature of morphology change from needle-like to cubic particles is about 115 °C. The cubic particles were remained when the temperature increased to 150 °C. Further increasing the temperature to 180 °C (Fig. 5(E)), one part of the cubic particles turned into spherical particles. At 200 °C (Fig. 5(F)), another new morphology of flower-like shape was formed. It is noted that all of the samples in Fig. 5 were prepared under the same experimental conditions except temperature, which indicates that the temperature induced the morphology transformation.

Besides, the effect of the ratio of water to acetone in solvent mixture on the formation of cubic particles was also investigated. In pure water or in pure acetone, neither cubic particle structure was observed at 130 °C nor flower-like shape was observed at 200 °C. The self-assembled micelles from the PS-*g*-PDMAEMA copolymer presented disorder aggregates in water and presented spherical particles in acetone as shown in Fig. 6. When the ratio of acetone to water was changed from 1/4, 2/3, 3/2 to 4/1 (v/v) successively, similar cubic particles were observed and no obvious difference in each SEM image. Thus, it is hard to judge which solvent play the main role in the formation of cubic particles. In conclusion, water/acetone solvent mixture and temperature jointly contribute to the cubic particle structure, but the mechanism of such morphology formation needs further study.

4. Conclusions

Chloromethylated polystyrene (CMPS) with different degrees of substitute by chloromethyl group was successfully prepared by chloromethylation of PS synthesized via ATRP. A series of well-defined brush-type PS-*g*-PDMAEMA copolymers could easily be synthesized via ATRP using CMPS as the macroinitiator. The molecular weights of PS-*g*-PDMAEMA copolymers determined from ^{1}H NMR results were in a good agreement with their corresponding theoretical values calculated from the molar ratios of monomer to macroinitiator. The *Z*-average size of the self-assembled micelles in deionized water increases with the increase of molecular weights of PDMAEMA side chains. However, in mixed solvent of deionized water and acetone (v/v = 2/3), the *Z*-average size of the micelles almost keeps constant except that of the PS-*g*-PDMAEMA copolymer with DP = 254 for PS. The *Z*-average size of the micelles in deionized water are larger than that formed in mixed solvent of deionized water and acetone (v/v = 2/3). The casting temperature and subsidiary solvent (such as acetone) have a significant effect on the morphologies of the aggregates from the self-assembled micelle solution of PS-*g*-PDMAEMA copolymer in mixed solvent of deionized water and acetone (v/v = 2/3). The morphology transformation such as from needle-like solids to micro-cubic particles was observed when casting temperature changed from 100 to 130 °C. The temperature of such morphology transformation is about 115 °C.

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References

[1] Xu P, Tang H, Li S, Ren J, Van Kirk E, Murdoch WJ, et al. Biomacromolecules 2004;5(5):1736–44.

[2] Neugebauer D, Zhang Y, Pakula T, Sheiko SS, Matyjaszewski K. Macromolecules 2003;36(18):6746–55.

[3] Kizhakkedathu JN, Kumar KR, Goodman D, Brooks DE. Polymer 2004;45(22):7471–89.

[4] Matyjaszewski K, Xia J. Chem Rev 2001;101(9):2921–90.

[5] Pyun J, Kowalewski T, Matyjaszewski K. Macromol Rapid Commun 2003;24(18):1043–59.

[6] Liu Y, Klep V, Zdyrko B, Luzinov I. Langmuir 2004;20(16):6710–8.

[7] Cheng GL, Bo1ker A, Zhang MF, Krausch G, Muller AHE. Macromolecules 2001;34(20):6883–8.

[8] Iwata R, Suk-In P, Hoven VP, Takahara A, Akiyoshi K, Iwasaki Y. Biomacromolecules 2004;5(6):2308–14.

[9] Yu WH, Kang ET, Neoh KG. Langmuir 2004;20(19):8294–300.

[10] Xu FJ, Yuan ZL, Kang ET, Neoh KG. Langmuir 2004;20(19):8200–8.

[11] Zhao H, Farrell BP, Shipp DA. Polymer 2004;45(13):4473–81.

[12] Qin S, Qin D, Ford WT, Resasco DE, Herrera JE. J Am Chem Soc 2004;126(1):170–6.

[13] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117(20):5614–5.

[14] Koto M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28(5):1721–3.

[15] Malinowska A, Vlcek P, Kříž J, Toman J, Látalová P, Janata M, et al. Polymer 2005;46(1):5–14.

[16] Jiang G, Wang L, Chen T, Yu H. Polymer 2005;46(1):81–7.

[17] Lee SB, Russell AJ, Matyjaszewski K. Biomacromolecules 2003;4(5):1386–93.

[18] Boyes SG, Brittain WJ, Weng X, Cheng SZD. Macromolecules 2002;35(13):4960–7.

[19] Kurjata J, Chojnowski J, Yeoh C-T, Rossi NAA, Holder SJ. Polymer 2004;45(18):6111–21.

[20] Reining B, Keul H, Höcker H. Polymer 2002;43(25):7145–54.

[21] Yao J, Ravi P, Tam KC, Gan LH. Polymer 2004;45(8):2781–91.

[22] Zhang M, Breiner T, Mori H, Müller AHE. Polymer 2003;44(5):1449–58.

[23] Ishizu K, Satoh J, Sogabe A. J Colloid Interf Sci 2004;274(2):472–9.

[24] Zhang X, Xia J, Matyjaszewski K. Macromolecules 1998;31(15):5167–9.

[25] Zeng F, Shen Y, Zhu S, Pelton R. Macromolecules 2000;33(5):1628–35.

[26] Zhang Z, Liu G, Bell S. Macromolecules 2000;33(21):7877–83.

[27] De Cupere VM, Gohy J-F, Jérome R, Rouxhet PG. J Colloid Interf Sci 2004;271(1):60–8.

[28] Zhang X, Matyjaszewski K. Macromolecules 1999;32(6):1763–6.

[29] Pitsikalis M, Siakali-Kioulafa E, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2004;42(17):4177–88.

[30] Jayachandran KN, Takacs-Cox A, Brooks DE. Macromolecules 2002; 35(11):4247–57.

[31] Costa AC, Geoghegan M, Vlček P, Composto RJ. Macromolecules 2003;36(26):9897–904.

[32] Zhao B, Brittain WJ. Macromolecules 2000;33(23):8813–20.

[33] Hu DJ, Cheng ZP, Wang G, Zhu XL. Polymer 2004;45(19):6525–32.

[34] Creutz S, Teyssie P, Jerome R. Macromolecules 1997;30(1):6–9.

[35] Hsu H-P, Nadler W, Grassberger P. Macromolecules 2004;37(12): 4658–63.

[36] Birshtein TM, Zhulina EB. Polymer 1984;25:1453–61.

[37] Zhang L, Eisenberg A. Science 1995;268:1728–31.

[38] Zhang W, Shi L, An Y, Shen X, Guo Y, Gao L, et al. Langmuir 2003; 19(15):6026–31.