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Synthesis and characterization of amphiphilic centipede-like copolymer PS-PS-PMAA

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A well-defined amphiphilic centipede-like copolymer of styrene and methacrylic acid (PS-PS-PMAA) was synthesized by the combination of living anionic polymerization and atom transfer radical polymerization (ATRP). The synthetic approach involves the first coupling reaction of polystyrene (PS) backbone bearing 1,1-diphenylethene (DPE) pendant groups with living polystyryllithium (PSLi), and sequential anionic polymerization of *t*-butyl methacrylate (*t*BMA) initiated by resulting 1,1-diphenylmethyl anion, and final hydrolysis of obtained PS-PS-P*t*BMA. The centipede-like copolymer PS-PS-PMAA was characterized by ^{1}H NMR, IR, GPC, and SLS measurements. The critical micelle concentration (CMC) of PS-PS-PMAA in water was determined by fluorescence probe technique. The self-assembly behavior of PS-PS-PMAA in water-THF mixture was observed by TEM. The results showed that the micellar morphology can be varied, such as vesicle, sphere, and agglomerate, depending on the THF content. These phenomena are worthy of further research in polymer physics field.

atom transfer radical polymerization, living anionic polymerization, amphiphilc centipede-like copolymer, self-assembly

1 Introduction

Compared with the simple linear polymer, the graft polymer with complex architecture can give an insight into the structure-property relationship and have versatile self-assembling behaviors. Therefore, since Hadjichristidis and Mays *et al.* first reported a new type of complex graft polymer named centipede-like polymer [1], it has stimulated a great deal of interest.

Hirao and coworkers reported the synthesis of centipede-like homopolymer or A_2B type copolymer by coupling reaction of a PS backbone bearing two benzyl bromide groups at each repeating unit with polymer anions [2, 3], or bearing one benzyl bromide at the middle of homopolymer or at the junction of diblock copolymer with polymer anions [4, 5]. Recently, Huang synthesized a series of well-defined centipede-like copolymers containing polyacrylate backbone, PS and poly(ethylene glycol) side chains by successive ATRPs [6]. More recently, Pan synthesized centipede-like copolymers with poly(glycidyl methacrylate) as the main chain and poly(L-lactide) (PLLA) and PS as graft chains by combination of ring-opening polymerization and ATRP [7]. Liu reported on the synthesis and self-assembly of coil-rod double hydrophilic diblock copolymer PEO-*b*-[PGMA-g-(PDEA)(PMEO$_2$MA)] with pH- and thermo-responsive asymmetric centipede-shaped polymer brush as the rod segment via a combination of ATRP and click chemistry [8].

In our earlier work, a series of hydrophobic centipede-like copolymers such as ABC type PI-PS-PMMA, and A_2B type PS-PS-PMMA has been synthesized via ATRP and anionic polymerization [9, 10]. Herein, we extend the hydrophobic structure into amphiphilic structure inducing polyelectrolyte chains such as PMAA. Specifically, the amphiphilic centipede-like copolymer PS-PS-PMAA was synthesized by the coupling reaction of living polystyryl-

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*Corresponding author (email: z.lu@sdu.edu.cn) lithium (PSLi) with polystyrene (PS) backbone bearing 1,1-diphenylethene (DPE) pendant groups, sequential polymerization of *t*BMA, and hydrolysis reaction of obtained PS-PS-P*t*BMA. The self-assembly behavior of PS-PS-PMAA in THF-water mixture was also preliminary investigated.

2 Experimental

2.1 Materials

Styrene was purified by distillation over calcium hydride. *t*BMA was purified by distillation over calcium hydride and dibutyl magnesium. Tetrahydrofuran (THF) was refluxed with a Na-K alloy and benzophenone until a characteristic blue color was evident. Lithium chloride (LiCl, 99.7%) was dried in a vacuum oven at 120 ℃ for 1 d. *n*-Butyllithium (*n*-BuLi, Aldrich, 1.6 M in hexane) and other reagents were used as received.

2.2 Synthesis of PS backbone bearing DPE pendant groups (2)

PS backbone bearing DPE pendant groups (**2**) was synthesized according to the method reported in our earlier work [9].

To a three-necked flask, 4-hydroxybenzophenone, 4-vinylbenzyl chloride, sodium bicarbonate, and *N*,*N*-dimethylformamide were added. The reaction was carried out at 105 °C for 3 h with stirring under nitrogen flow. Upon cooling, the red-brown reaction mixture was poured into water, and this was followed by extraction with dichloromethane. After recrystallization from petroleum ether, white 4-vinylbenzyloxy benzophenone was obtained in 80% yield.

^{1}H NMR ($CDCl_3$, δ, ppm): 5.13 (s, 2H, $-C\underline{H}_2O-$), 5.25, 5.28 (d, 1H, $C\underline{H}_2{=}CH-$), 5.74, 5.79 (d, 1H, $C\underline{H}_2{=}CH-$), 6.69–6.71 (q, 1H, $CH_2{=}C\underline{H}-$). IR (KBr, cm^{-1}): 1640 (C=O), 1604, 1503 (aryl), 1250, 1173 ($-CH_2O-$), 1604, 1015 (vinyl).

To an ampole charged with nitrogen, 4-vinylbenzyloxy benzophenone, $PhCH_2Cl$, CuCl, 2,2'-bipyridine, and diphenyl ether were added. After three freeze-vacuum-thaw cycles, the ample was sealed *in vacuo*. The reaction was performed at 130 °C for 24 h and terminated by quenching in liquid nitrogen. The polymer was isolated by precipitation into methanol and was dissolved/precipitated with dichloromethane /methanol three times. The final product (**1**) was dried in vacuo at 50 °C for 12 h.

^{1}H NMR ($CDCl_3$, δ, ppm): 0.80–2.40 ($-C\underline{H}_2-C\underline{H}-Ph$), 4.75–5.10 ($-C\underline{H}_2-O-$), 6.2–7.3 (phenyl ring). IR (KBr, cm^{-1}): 1650 (C=O), 1600, and 1506 (aryl), 1250 ($-CH_2O-$).

Methyltriphenylphosphonium iodide and equal molar sodium hydride were suspended in anhydrous THF, and the mixture was refluxed for 12 h under argon. Thereafter, the solution of polymer **1** in THF was added dropwise at 0 °C. After 12 h of refluxing, the reaction was terminated by acetone. After filtration, the liquid was concentrated and precipitated into methanol. The polymer **2** was dissolved/ precipitated with dichloromethane/methanol three times and dried in vacuo at 50 ℃ for 12 h. The conversion of C=O to C=C is nearly quantitative indicated by ^{1}H NMR spectrum and IR spectrum of **2** as reported in ref. [9].

^{1}H NMR ($CDCl_3$, δ, ppm): 1.15–2.40 ($-C\underline{H}_2-C\underline{H}-Ph$), 4.75–4.95 ($-C\underline{H}_2-O-$), 5.20–5.40 ($C\underline{H}_2{=}CPh_2$), 6.2–7.3 (phenyl ring). IR (KBr, cm^{-1}): 1604, and 1508 (aryl), 1242 ($-CH_2O-$).

2.3 Synthesis of centipede-like copolymer PS-PS-PtBMA (4)

The anionic polymerization of styrene was performed at –78 ℃ using n-BuLi as an initiator and THF as a solvent. After 0.5 h, an aliquot of polymer solution was taken out for gel permeation chromatography (GPC) measurement. Subsequently the living PSLi was introduced quickly into the solution of PS backbone bearing DPE pendant groups **2**. The reaction was carried out for 1 h and the cooled *t*BMA was injected into the reactor rapidly. The polymerization of *t*BMA was terminated by addition of degassed methanol after 40 min. The polymer **4** was isolated by precipitation into methanol and dried in vacuum at 50 ℃ for 12 h.

2.4 Synthesis of amphiphilic centipede-like copolymer PS-PS-PMAA (5)

1.0 g centipede-like copolymer PS-PS-P*t*BMA was dissolved in 40 mL dioxane. The excess trifluoracetic acid (TFA) was added dropwise to the reaction solution (based on the ester groups presented). The hydrolysis reaction was carried out at 65 °C for 24 h. The product was precipitated in hexane and then dried under vacuum.

2.5 Preparation of PS-PS-PMAA micellar solution

THF solution of PS-PS-PMAA (**5**) graft copolymer (3 mg/mL) was added dropwise to water or water-THF solution with vigorous stirring to obtain micellar solution.

2.6 Characterization

All ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal reference. FTIR spectra were recorded on a 20SX IR spectrometer using KBr pellets. GPC measurements were carried out in THF (1 mL/min) at 35 °C using a Waters 515 liquid chromatography equipped with three linear Styragel columns (HR3, HR4, and HR6) and a 2414 refractive index detector. Monodisperse PS samples were used as standards for calibration. Static Light Scattering (SLS) measurements were performed in THF at 25 °C with a DAWN HELEOS 18-angle light scattering detector with a 50 mW solid-state laser operating at 658 nm.

Pyrene was used as fluorescence probe to measure the determination of critical micelle concentration (CMC) of the micelle solution formed from PS-PS-PMAA centipede-like copolymers (5). The concentration of pyrene was 5×10^{-7} g/mL. Fluorescence spectra was recorded on a PerkinElmer LS-55 fluorescence spectrophotometer at 25 °C. Transmission Electron Microscopy (TEM) observations were conducted on a JEM-100CX II electron microscope. The sample was prepared by placing a drop of micellar solution on copper grids coated with carbon films and evaporating the solvent at room temperature.

3 Results and discussion

Scheme 1 illustrates the strategy for the preparation of the amphiphilic comb-like copolymer PS-PS-PMAA. ATRP of 4-vinylbenzyloxy benzophenone led to polymer **1** with benzophenone pendant groups. This precursor was then converted to the corresponding polymer **2** bearing DPE pendant groups via Wittig reaction and used as a polymer backbone. The PSLi chains coupled with the DPE groups along the PS backbone (**2**), and the resulting carbanions (**3**) further initiated and polymerized *t*BMA monomers to yield well-defined centipede-like copolymer PS-PS-P*t*BMA (**4**). After hydrolysis, amphiphilic centipede-like copolymer PS-PS-PMAA (**5**) with a PS backbone and PS and PMAA side chains was obtained.

3.1 Synthesis of centipede-like copolymer PS-PS-PtBMA (4)

Living PSLi was prepared by anionic polymerization of styrene in THF at –78 °C using *n*-BuLi as the initiator. The coupling reaction was carried out at –78 °C by quick addition of PSLi solution into the THF solution containing a known amount of **2** which was previously vacuum-dried. A small excess amount of DPE functions of **2** was used ($[PSLi]_0/[DPE]_0 = 0.95$) to convert all the PSLi into diphenylmethyl carbanions and suppress the side reactions in the next step. A rapid colour change from orange to deep red was observed, suggesting that the formation of diphenylmethyl carbanions occurred rapidly.

Figure 1(b) shows the GPC trace of the graft polymer precursor (PS-*g*-PS) obtained from **3** by quenching with methanol. The GPC trace ascribed to PS-*g*-PS is sharp, monomodal, and very narrow (M_w/M_n = 1.14), suggesting homogeneous and clean grafting.

Figure 2 shows the ^{1}H NMR spectrum of graft polymer precursor (PS-*g*-PS). The resonance at 5.29 ppm corresponding to vinyl protons diminished dramatically. Instead, a new signal at 3.52 ppm corresponding to the terminal methine proton was observed. The integrated area ratio of this resonance to the resonance at 4.91 ppm for methylene protons adjacent to the ether linkage is 0.470:1 (theoretical ratio is 0.475:1), suggesting the graft efficiency (GE) is 94.0% (theoretical value is 95% based on feeding amounts). In order to get more accurate value, we used SLS technique to determine the absolute molecular weight M_w of PS-*g*-PS (see Table 1), and calculated the GE from the formula as follows,

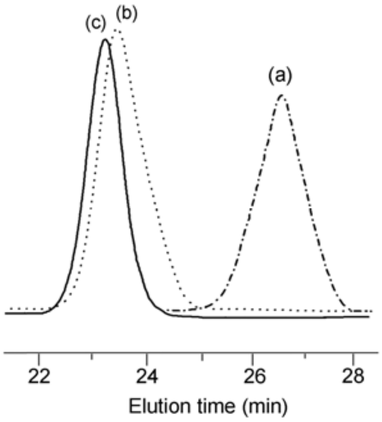
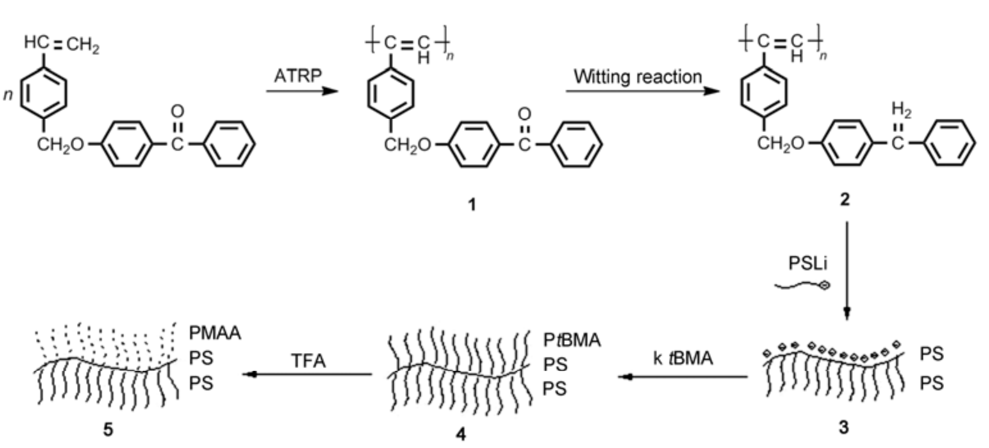


Figure 1 GPC traces of comb-like copolymer PS-PS-P*t*BMA: (a) PS precursor obtained from PSLi by quenching with methanol; (b) graft polymer precursor PS-*g*-PS obtained from **3** by quenching with methanol; (c) PS-PS-P*t*BMA.



Scheme 1 Synthetic route to amphiphilic centipede-like copolymer PS-PS-PMAA.

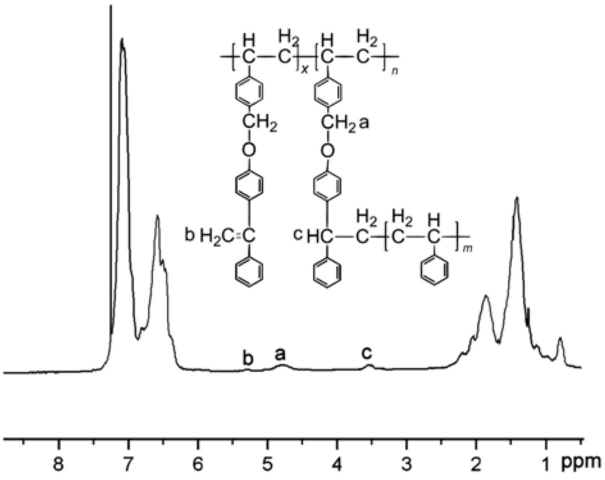


Figure 2 ^{1}H NMR of PS-*g*-PS obtained from **2** by quenching with methanol.

Table 1 Characteristics of the centipede-like copolymer PS-PS-PMAA (**5**)

Polymers	M_n ($\times 10^{-3}$)			M_w/M_n $^{c)}$
	Theo.	GPC ^{a}	SLS + GPC $^{b)}$	
2	5.00	5.10	–	1.17
PSLi	4.50	4.22	–	1.25
PS-*g*-PS	73.53	70.0	69.2	1.17
4	115.0	96.4	109.7	1.15
5	98.5 $^{d)}$	87.3	93.9	1.15

a) Determined by GPC with linear polystyrene as calibration standards; b) Caculated from $M_n=M_w/(M_w/M_n)$, where M_w is examined by SLS and M_w/M_n is examined by GPC; c) Determined by GPC; d) Calculated from the formula.

$$\mathrm{GE} = \frac{\dfrac{M_{\mathrm{n,\ Ps\text{-}}g\mathrm{\text{-}Ps}} - M_{\mathrm{n,\ Ps}}}{M_{\mathrm{n,\,PSLi}}}}{\dfrac{M_{\mathrm{n,\ PS}}}{312}}$$

where $M_{\mathrm{n,\,PS}\text{-}g\text{-}\mathrm{PS}}$, $M_{\mathrm{n,\,PS}}$, and $M_{\mathrm{n,\,PSLi}}$ are the number-average molecular weights of graft polymer, backbone chain, and graft chain, respectively. The $M_{\mathrm{n,\,PS}\text{-}g\text{-}\mathrm{PS}}$ is calculated using $M_w/(M_w/M_n)$, where M_w is examined by SLS and M_w/M_n is examined by GPC. The $M_{\mathrm{n,\,PS}}$ and $M_{\mathrm{n,\,PSLi}}$ are examined by GPC. The calculated value is 93%.

When *t*BMA monomers were added, the deep red color of diphenylmethyl anions changed to light yellow immediately, and the viscosity of the solution rose, indicating that the initiation and polymerization of *t*BMA was very quickly. It should be noted that the addition of LiCl is necessary. Some studies have demonstrated that the occurrence of side reactions is effectively suppressed when the living chain end is associated with LiCl [11]. Moreover, the narrow molecular weight distribution and high initiator efficiency are obtained [12].

Figure 1(c) shows the GPC trace of PS-PS-P*t*BMA (**4**). A sharp peak shifting to a higher molecular weight can be observed, and this suggested that the growth of P*t*BMA branches was effective and homogeneous. The peaks at a low molecular weight were invisible, indicating the possible byproducts and PS homopolymer were negligible.

The characteristics of **5** are given in Table 1. Due to its branched architecture, the apparent molecular weight of **4** determined by GPC using linear polystyrenes as standards for calibration is not reliable. After measuring the specific d*n*/d*c* value of centipede-like copolymer, the absolute molecular weight of **4** was measured to be 109700 by SLS. Assuming that all diphenylmethyl anions initiated quantitatively *t*BMA monomers to polymerize, we can calculate the theoretical molecular weight of **4** in the following formula.

$$M_{\mathrm{n,\,Ps\text{-}Ps\text{-}PtBMA}} = M_{\mathrm{n,\,Ps\text{-}}g\mathrm{\text{-}Ps}} + \frac{W_{\mathrm{t,\,tBMA}} \times \mathrm{Conversion}}{\dfrac{W_{\mathrm{t,\,Ps}}}{M_{\mathrm{n,\,Ps}}} \times GE}$$

where $M_{\mathrm{n,\,PS}\text{-}g\text{-}\mathrm{PS}}$ and $M_{\mathrm{n,\,PS}}$ are the number-average molecular weights of graft polymer and backbone chain, respectively. The $M_{\mathrm{n,PS}\text{-}g\text{-}\mathrm{PS}}$ is calculated using $M_w/(M_w/M_n)$, where M_w is examined by SLS and M_w/M_n is examined by GPC. The $M_{\mathrm{n,\,PS}}$ is examined by GPC. $W_{\mathrm{t},\,t\mathrm{BMA}}$ and $W_{\mathrm{t,\,PS}}$ is the feed weights of *t*BMA and backbone polymer **2**, respectively. The conversion of *t*BMA is 99% by weight. The calculated value is 110100, which is closed to 109700. This result supports that the sample possess the designed centipede-like architecture.

Figure 3 shows the ^{1}H NMR spectrum of **4**. The characteristic resonances for PS and P*t*BMA segments are observed clearly. 6.40–7.30 (c, phenyl ring) for PS, 1.25 (f, $-C\underline{H}_2-C(CH_3)-COO-$), 1.07 (d, $-C(C\underline{H}_3)COO-$), and 1.45 ppm (e, $-COOC(C\underline{H}_3)_3$) for P*t*BMA. From ^{1}H NMR spectrum, the composition of PS-PS-P*t*BMA was calculated to

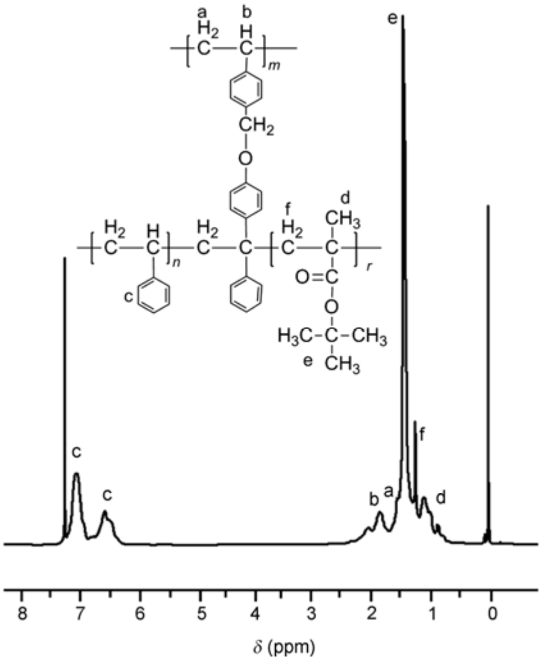


Figure 3 ^{1}H NMR of PS-PS-P*t*BMA (**4**).

be as follows: PS, 57.1 wt%, and P*t*BMA, 42.9 wt%, consistent with the feed weight ratio.

3.2 Synthesis of amphiphilic centipede-like copolymer PS-PS-PMAA (5)

Since *t*-butyl groups on P*t*BMA branch of **4** are sensitive to acid, PMAA branches can be obtained by acid hydrolysis. The amphiphilic centipede-like copolymer PS-PS-PMAA was prepared from **4** by adding excess TFA at 65 °C for 24 h.

Figure 4 shows the GPC traces of **4** and **5** respectively. Compared with trace (a), trace (b) shifted to lower molecular weight clearly, also suggesting successful hydrolysis.

Figure 5 shows the ^{1}H NMR spectrum of **5**. The characteristic resonances corresponding to carboxyl proton at 8.3 ppm suggested the formation of PMAA branches after hydrolysis. The resonance at 1.45 ppm corresponding to *t*-butyl proton was diminished completely, indicating the quantitative hydrolysis had occurred.

3.3 CMC of PS-PS-PMAA micelles in aqueous solution

Amphiphilic copolymers often self assemble into micelles with a hydrophilic shell and a hydrophobic core in aqueous solution. Their critical micelle concentrations (CMCs) were often determined by fluorescence technique using pyrene as probe. This is because the fluorescence spectrum of pyrene is sensitively affected by the environment and the polarity of its surrounding [13, 14]. When the micelles of **5** began to form, the pyrene was solubilized within the interior of the hydrophobic part. As a result, the values of I_1/I_3 of the emission spectrum changed sharply. The intensity ratios (I_1/I_3) against the logarithm of polymer concentrations were plotted to determine the CMC of **5** (Figure 6). The calculated CMC value is 1.78×10^{-3} g/L.

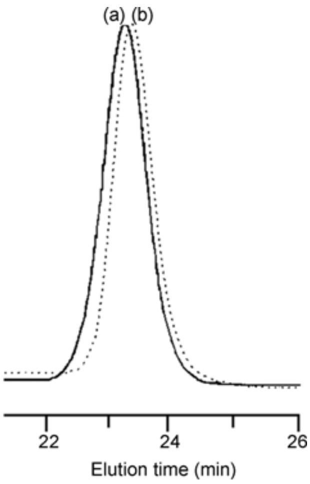


Figure 4 GPC traces of PS-PS-P*t*BMA (trace (a)) and PS-PS-PMAA (trace (b)).

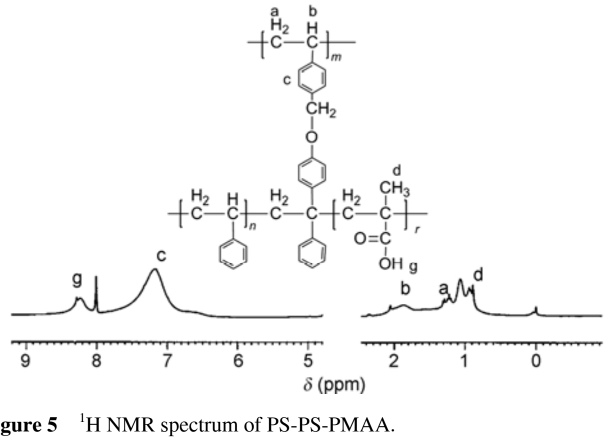


Figure 5 ^{1}H NMR spectrum of PS-PS-PMAA.

3.4 Self-assembly behavior of PS-PS-PMAA in water-THF solution

It is well known that the structure and size of micelles are greatly affected by the polarity of solvents. In such a way, we investigated the influence of mixed solvents on PS-PS-PMAA micelle morphology when mixing THF and water at different volume ratios.

Figure 7 shows the TEM images of self-assembled micelles from PS-PS-PMAA at different volume ratios (*r*) of THF/water. At the low THF content (*r* = 1:9), the vesicle micelles were clearly observed (see Figure 7(a)), and the average radius was 35 ± 5 nm obtained from TEM. At *r* = 2:8, the shape exhibited spherical micelles (see Figure 7(b)). Obviously, the micellar size also significantly increased, and the average radius was 45 ± 5 nm. At high THF contents (r = 3:7 and 4:6, respectively), the agglomerates of the spherical micelles were formed (see in Figure 7(c) and 7(d)). These visible morphology changes suggested that solvent polarity played a key role during PS-PS-PMAA micelle self-assembly. The reason could be the swollen status of PS grafts varied with increasing THF contents. This caused the increase of stretching degree and aggregation number of PS grafts [15], and thus different morphologies were formed. However, the details of the kinetic process related to the formation of micellar morphology so far are unclear. Further

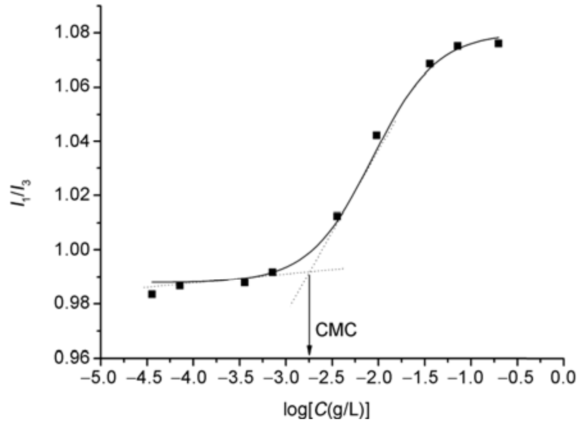


Figure 6 Dependence of fluorescence intensity ratios of pyrene emission bands on the concentration of PS-PS-PMAA (**5**).

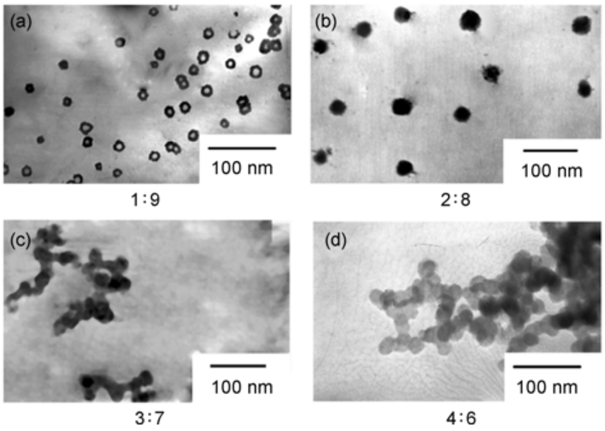


Figure 7 TEM images of self-assembled micells from PS-PS-PMAA at different volume ratios (r) of THF/water. The concentration of PS-PS-PMAA is 0.0045 g/L.

studies are needed as the understanding will enable us to control the structure and properties of PS-PS-PMAA micelles.

4 Conclusions

A well-defined amphiphilic centipede-like copolymer of styrene and methacrylic acid (PS-PS-PMAA) was successfully designed and synthesized by the combination of living anionic polymerization and ATRP.

The CMC of PS-PS-PMAA in aqueous solution is measured to be 1.78×10^{-3} g/L by fluorescence probe technique. The self-assembly behavior of PS-PS-PMAA was greatly affected by the solvent polarity. It self-assembled into vesicle, sphere, and agglomerate with increasing THF content in THF-water mixed solvent. These morphology changes and polyelectrolyte nature of PMAA grafts would attract much interest in polymer physics.

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