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Synthesis and self-assembly of amphiphilic maleic anhydride–stearyl methacrylate copolymer

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Abstract

Amphiphilic maleic anhydride–stearyl methacrylate (MA–SMA) random copolymer was synthesized via the free radical copolymerization and its amide was prepared through the MA moieties being reacted with morpholine. Polymers obtained were characterized by GPC and ^{1}H NMR. The aggregating behaviors of copolymers were investigated by first dissolving them in tetrahydrofuran (THF) and then adding water to induce association of the long alkyl chains and observed over the range of copolymer concentrations from 0.028 to 0.22 wt% and water content from 5.32 to 34.85 wt%. Resultant aggregates show new potential application in the fields of drug delivery systems, microcapsules and so on.

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Keywords: Maleic anhydride; Stearyl methacrylate; Self-assembly

1. Introduction

Amphiphilic molecules have received considerable attention due to their ability to self-assemble in bulk and in solution forming a range of different morphologies (e.g. spheres, rods, lamellae and large compound vesicles) and sizes through weak non-covalent interactions (hydrogen bonding, π–π interaction, van der Waals, coordination, and charge-transfer interaction) [1–7]. Amphiphilic micellar systems have very interesting particular properties, so they have many potential applications in areas such as micro-reactors, microcapsules, and drug delivery systems, encapsulation of various kinds of guest molecules [8–12]. Many investigations had begun on the thermodynamic and kinetic aspects that induced morphogenesis [13–15]. And many factors were found to alter the aggregation architectures, for example, temperature, solvent, concentration [16], solvent composition and water content [17], and pH [18], among other factors [19].

Maleic anhydride (MA) is an excellent monomer which can provide reactive anhydride or carboxylic groups, and amphiphilic molecules can be obtained easily via the copolymerization of MA and hydrophobic monomer. Recently, extensive studies have been performed on the radical copolymerization of MA with other monomer and the self-assembly of their copolymers [20–27]. For example, Stover et al. [20] studied that the self-assembly of lightly cross-linked, swellable poly(divinylbenzene-*alt*-maleic anhydride) microgels at the oil–water interfaces of a propyl acetate–water suspension. Li et al. [21] prepared a well-defined block copolymer having alternating maleic anhydride/styrene segments and polystyrene segments and studied the self-assembly aggregating behavior of its hydrolyzed amphiphilic product in water. Li et al. [22] also reported on the synthesis of a diblock copolymer containing a block of alternately structured maleic anhydride with 4-vinylbenzyl chloride (VBC) and PVBC block. It was found that the copolymer can form stable inverse micelles in THF after the MA moieties being reacted with 2-mercaptoethyl amine. In general, the studies mentioned above mainly focused on the self-assembly of alternate copolymers or diblock copolymers containing one alternate block and other hydrophobic block.

Stearyl methacrylate (SMA) is an interesting monomer because it has a pendent long alkyl side chain which can form crystalline domain [28]. Many studies have appeared in the literature concerning the micelle properties of copolymers consisting of a PSMA block. Hadjichristidis et al. [29] reported on the synthesis of polystyrene-*b*-polystearyl methacrylate (PS-*b*-PSMA) using anionic polymerization high-vacuum techniques. And it was found that the copolymer could self-assemble into aggregates in organic solvents.

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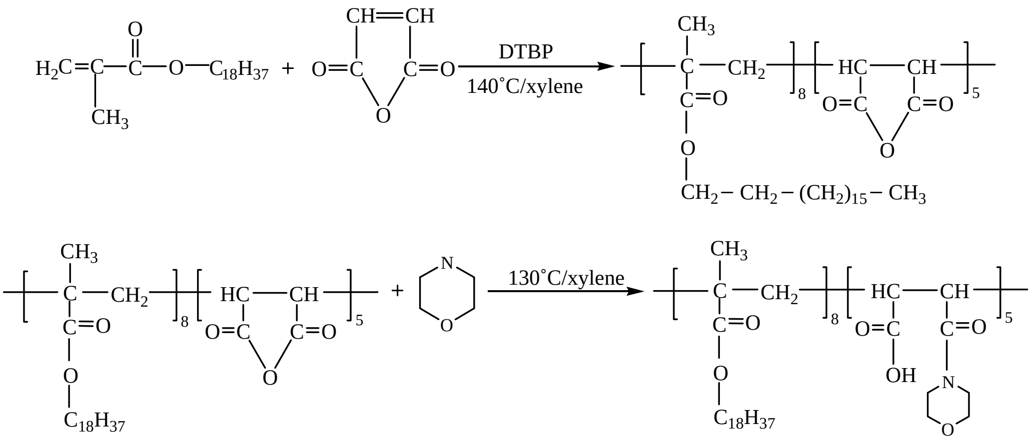


Scheme 1. Synthesis procedure of P(MA-*co*-SMA) and its amide.

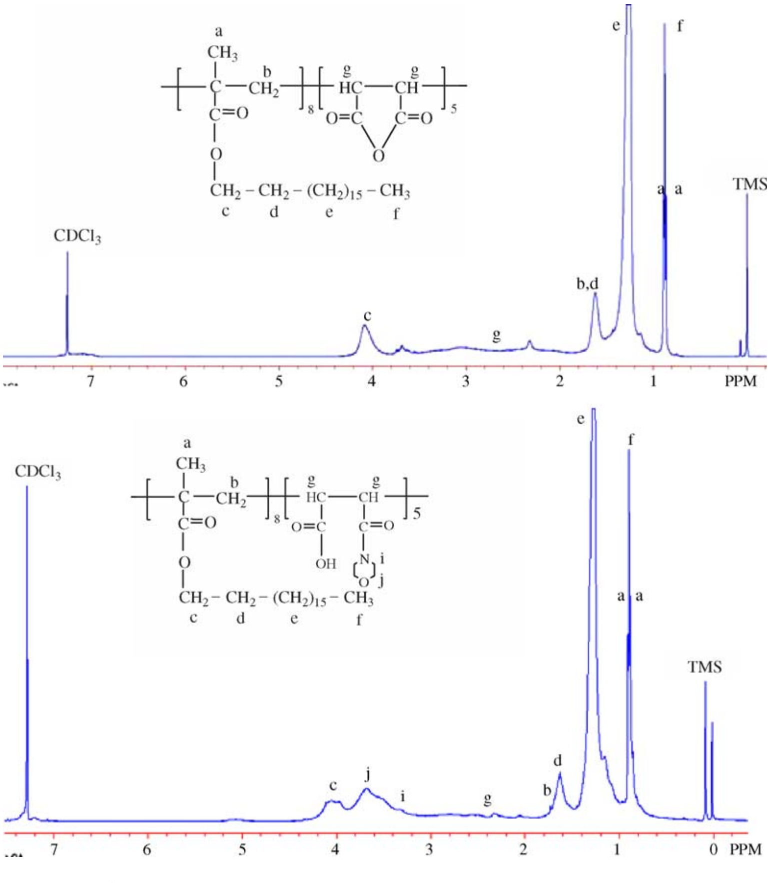


Fig. 1. ^{1}H NMR spectra of P(MA-*co*-SMA) and the amide of P(MA-*co*-SMA).

The copolymer of MA and SMA should combine the reactive anhydride property of MA and crystalline property of SMA together. The polymeric micelles formed from MA and SMA copolymer are of interest in further chemical or biological modification. If the hydrophilicity of the resultant copolymer was regulated through amination, the self-assembly behaviors of it would changed. The synthesis of MA-*co*-SMA was first reported by Gargallo et al. [30]. In Gargallo's work, an alternating (1:1) copolymer of MA-*co*-SMA was synthesized

Table 1
Molecular weight and molecular weight distribution of copolymers

Copolymer	M_n[a] (g/mol)	M_w/M_n[a]
P(MA-*co*-SMA)	3.1×10^3	1.45
Amide of P(MA-*co*-SMA)	4.3×10^3	1.34

[a] M_n determined by GPC.

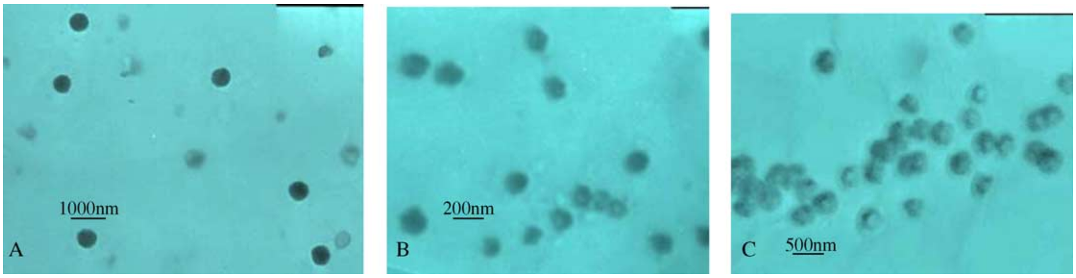


Fig. 2. TEM images of aggregates made by dissolution of P(MA-*co*-SMA) in a 89.9/10.1 (w/w) THF/water mixture to different final copolymer concentrations. P(MA-*co*-SMA) wt%: (A) 0.028 wt%, (B) 0.096 wt%, (C) 0.22 wt%.

by the radical polymerization and some aspects of the solution behavior of the copolymer were studied.

Herein, we reported on the synthesis and characterization of maleic anhydride-*co*-stearyl methacrylate copolymer (P(MA-*co*-SMA)) and its amide and investigated the self-assembly behaviors of the resultant polymers in mixed solvents.

2. Experimental

2.1. Materials

MA, SMA, di-tert-butyl peroxide(DTBP), xylene, *n*-dodecanethiol, ethyl acetate, methanol, morpholine were all purchased from Shanghai No.1 Chemical reagent factory. MA was recrystallized in chloroform before use. SMA was washed using 5 wt% NaOH solution. DTBP was treated by the literature method [31]. Xylene, morpholine and *n*-dodecanethiol were all used as received.

2.2. Synthesis of P(MA-co-SMA) copolymer [32]

The P(MA-*co*-SMA) copolymer was obtained by solution copolymerization of MA/SMA. The polymerization was carried out in a 50 ml four necked round bottom flask immersed in a constant temperature oil bath at 140 °C and equipped with a reflux condenser, an efficient stirrer, two dropping funnels and a nitrogen inlet. 1.20 g of MA (1.23×10^{-2} mol) was dissolved in 1.8 ml of xylene in the flask, and 4.2 g of SMA (1.23×10^{-2} mol) and 0.35 ml of *n*-dodecanethiol (1.45×10^{-3} mol) in 6.0 ml of xylene were added dropwise over a period of 2 h and 0.28 ml of DTBP (1.52×10^{-3} mol) in 0.43 ml of xylene was added dropwise over a period of 3 h. The reaction processed continuously for another 3 h. The copolymer product was precipitated in excess methanol. The polymer was purified by using ethyl acetate as the solvent for MA-*co*-SMA copolymer while as the non-solvent for homopolymer contamination at 25 °C. 4.5532 g of product was obtained, in a yield of 84.32%.

^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (3H, in $CH_3(CH_2)_{15}$–), 0.86 and 0.90 (3H, in CH_3C–), 1.20–1.40 (30H, in –$(CH_2)_{15}CH_3$), 1.58–1.78 (2H, in –$CH_2(CH_2)_{15}CH_3$, 2H, in –CH_2C–), 2.2–3.8 (2H, in –*CH*–*CH*–), 4.13 (2H, in –OCH_2–).

2.3. Synthesis of the amide of P(MA-co-SMA) copolymer [33]

The resultant copolymer was amidated successively with morpholine in a molar ratio of 1:1, on the basis of maleic anhydride in the copolymer. Amidation was conducted by heating to 130 °C while vigorous stirring in the presence of an excess volume of xylene as a solvent and under nitrogen atmosphere for 3 h. The amidated copolymer was purified by evaporation at reduced pressure, then purified by repeated precipitations with 250 ml of methanol and dried in a vacuum.

^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (3H, in $CH_3(CH_2)_{15}$–), 0.86 and 0.90 (3H, in CH_3C–), 1.20–1.40 (30H, in –$(CH_2)_{15}CH_3$), 1.58–1.78 (2H, in –$CH_2(CH_2)_{15}CH_3$, 2H, in –CH_2C–), 2.2–3.8 (2H, in –*CH*–*CH*–), 3.25–3.82 (2H, in –CH_2N–, 2H, in –CH_2O–), 4.13 (2H, in –OCH_2–).

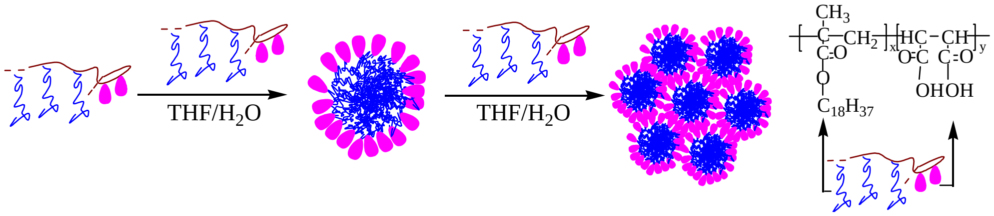
2.4. Self-assembly of amphiphiles

Extremely dilute solutions (containing 0.028, 0.096, 0.11, 0.22 wt% copolymers, respectively) were prepared by dissolving P(MA-*co*-SMA) or its amide in distilled THF which was a common solvent for both segments at room temperature (25 °C) without sonication, mechanical stirring or other forms of applied energy. And subsequently deionized water was added to the solution to induce association of the long alkyl chains. The micelles in THF/H_2O mixtures with 10.1 wt% H_2O were prepared.

The self-assembly structures with different sizes and morphologies formed spontaneously upon the addition of deionized water were studied. The copolymers were first dissolved in the THF to the desire concentrations (0.11 wt%). After that, deionized water was added at a rate of 0.5 wt% per minute, until the pre-determined contents (water content from

Table 2
Dimensions of aggregates of varying P(MA-*co*-SMA) concentration in the THF/H_2O mixtures

Concentration of copolymer (wt%)	0.028	0.096	0.22
Average micelle size (TEM) (nm)	600±110	350±150	400±60
Average micelle size (LLS) (nm)	655±60	659±50	585±100



Scheme 2. Schematic model of the aggregates with the increase of concentration.

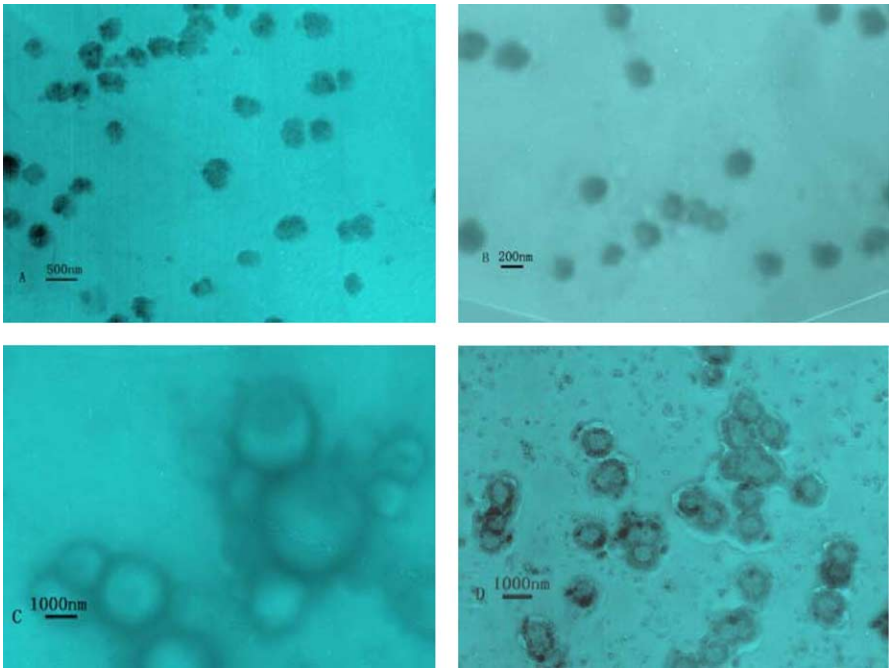


Fig. 3. TEM images of aggregates from P(MA-*co*-SMA) at different water contents in the THF/water mixture. The initial copolymer concentration in THF is 0.11 wt% when 0% water. H_2O wt%: (A) 5.32 wt%, (B) 10.11 wt%, (C) 18.35 wt% and (D) 32.8 wt%.

5.32 to 34.85 wt%). As the addition of water, the aggregates were formed gradually.

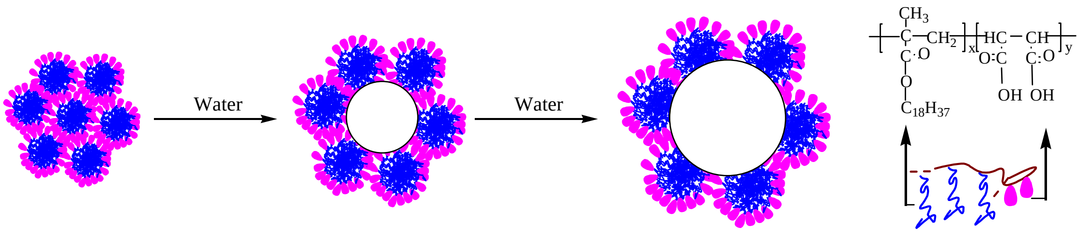
Samples for TEM measurement were prepared by aerosol spraying a dilute micellar solution (ca. 10 μL) onto 200-mesh gilder copper TEM grids. The samples were air-dried before introduction into TEM. The morphology and structure of the prepared samples were examined with TEM.

2.5. Characterizations

^{1}H NMR spectra of polymers were recorded with a 500 MHz AVANCE NMR spectrometer (Model DMX500) in $CDCl_3$, using TMS as the standard. The molecular weight of these copolymers was determined by gel permeation chromatography (GPC) with laser scattering detector, ultrastyragel column with pore sizes of 10^3–10^5 Å. The eluent was THF at a flow rate of 1.0 mL/min. A detection wavelength of 632.8 nm and the refraction index increment value of the polymer solutions dn/dc = 0.20 were used for laser scattering detection. TEM were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV. Infrared spectrum was recorded on Nicolet 5700 infrared spectrophotometer. Light scattering experiments were performed on a Zetasizer 3000HSA zeta potential and laser nanometer particle size analyzer equipped with a He–Ne laser (633 nm). The scattering angle used for the measurements was 90°. A refractive index matching bath of filtered decalin surrounded the scattering cell, and the temperature was controlled usually at 30 °C. All the glass vessels were cleaned with detergent and rinsed abundantly with water and dried at 60 °C.

Table 3
Dimensions of aggregates of varying water content in the THF/H_2O mixture

Water content (wt%)	5.32	10.11	18.35	32.80
Average micelle size (TEM) (nm)	400 ± 100	350 ± 100	1100 ± 150	1000 ± 50
Average micelle size (LLS) (nm)	450 ± 50	423 ± 75	1222 ± 110	1289 ± 80



Scheme 3. Schematic model of the aggregates with the increase of water content.

3. Results and discussion

3.1. Synthesis and characterization of P(MA-co-SMA) and its amide

P(MA-*co*-SMA) was synthesized via the free radical copolymerization and its amide was prepared through the MA moieties in copolymer chain being reacted with morpholine. The synthetical route was depicted in Scheme 1.

The chemical structures of the prepared polymers were characterized by ^{1}H NMR analysis, as shown in Fig. 1. The ^{1}H NMR spectrum of P(MA-*co*-SMA) showed peaks with following shift [34]: the H of C–H in polymeric state maleic anhydride showed a chemical shift of 2.2–3.8 ppm; the H of methylene group adjacent to the oxygen atom of stearyl showed a chemical shift of 4.13 ppm, the H of the methylene in backbone and the H of the methylene adjacent to the methylene connected with oxygen atom of stearyl showed a chemical shift of 1.78–1.58 ppm, the H in the long-chain methylene bands exhibited a chemical shift of 1.40–1.20 ppm, and the chemical shifts for the methyl groups were ranged within 0.90–0.86. NMR spectrum of product indicated that there existed stearyl methacrylate moiety, and maleic anhydride moiety in the prepared copolymer.

Compared with the spectrum of P(MA-*co*-SMA), the peak at 3.82–3.25 ppm corresponding to methylene proton next to oxygen atom and next to nitrogen atom appeared. This indicated the amide of P(MA-*co*-SMA) was successfully prepared. The molecular weight of copolymers was shown in Table 1.

3.2. Self-assembly behaviors of P(MA-co-SMA)

The self-assembly behaviors of the hydrolyzed amphiphilic product of P(MA-*co*-SMA) in THF/H_2O were investigated. P(MA-*co*-SMA) could easily be hydrolyzed resulting in an amphiphile which could form uniform nanoscale particles by self-assembly [21]. These architectural particles in nanoscale size constructed by the long chain alkyl segment as a core, and the other segment as a corona, which provided reactive or carboxylic groups on the surface of particles, were of interest in further chemical or biological modification.

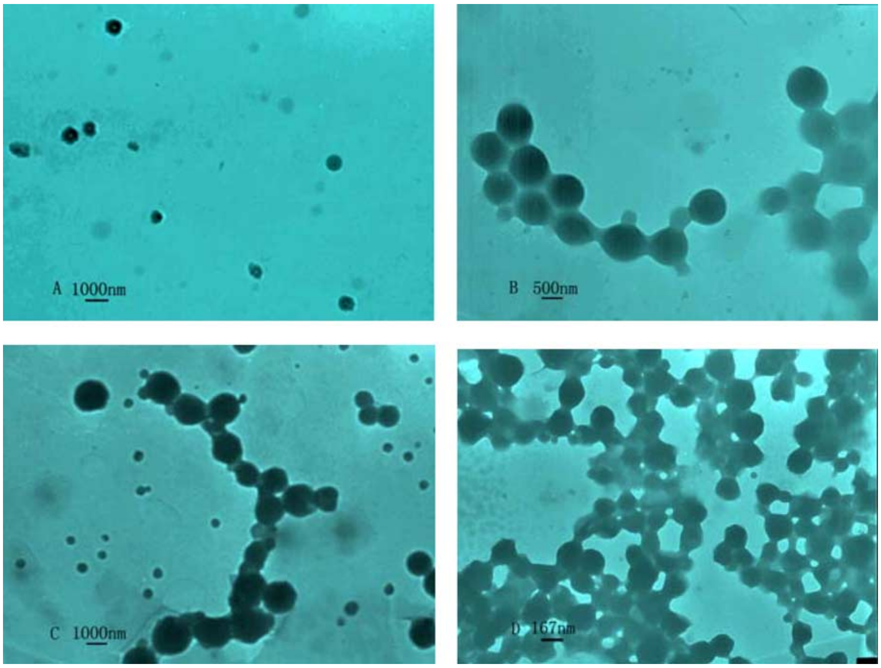


Fig. 4. Aggregates made by dissolution of the amide of P(MA-*co*-SMA) in a 89.9/10.1 (w/w) THF/water mixture to different final copolymer concentrations. The amide of P(MA-*co*-SMA) wt%: (A) 0.028 wt%, (B) 0.084 wt%, (C) 0.11 wt%, (D) 0.22 wt%.

Table 4
Dimensions of aggregates of varying the amide of P(MA-*co*-SMA) concentration in the THF/H_2O mixture

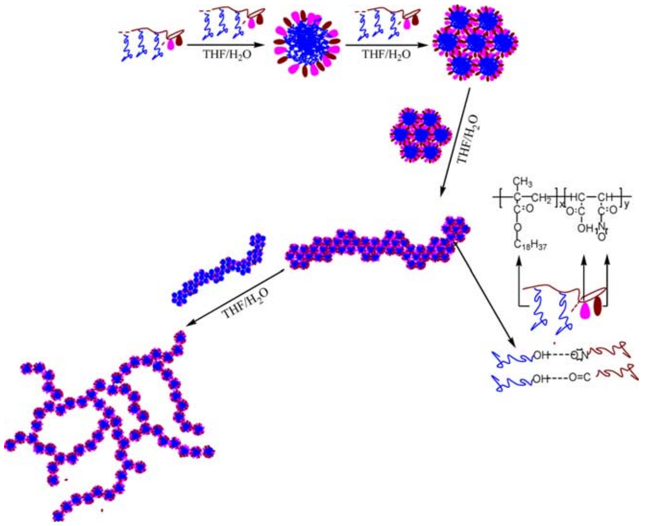
Concentration of copolymer (wt%)	0.028	0.096	0.11	0.22
Average micelle size (TEM) (nm)	500 ± 100	600 ± 50	1200 ± 150	200 ± 50
Average micelle size (LLS) (nm)	504 ± 100	663 ± 80	1310 ± 200	291 ± 130

To gain insight into the role of concentration of P(MA-*co*-SMA), we prepared a series of systems with different concentrations to probe the self-assembly behaviors. Fig. 2 showed the aggregates formed by direct dissolution of P(MA-*co*-SMA) to different final concentrations. Clearly, the aggregating morphology depended strongly on the copolymer concentration.

When the copolymer concentration was 0.028 wt%, large compound micelles (LCMs) were formed (Fig. 2(A)). The LCMs had a diameter of 600 nm and a high narrow polydispersity. With the polymer concentration increasing further (Fig. 2(A)–(C)), the population of LCMs could be enhanced.

Laser light scattering (LLS) was also used to investigate the aggregation behaviors of P(MA-*co*-SMA) in THF/water mixture. The results were given in Table 2. From the data in Table 2 one could see that, the average size from P(MA-*co*-SMA), as measured by TEM, was smaller than that measured by LLS. Because the LLS measurements were carried out in solution where the corona (the maleci acid units) of the aggregates would stretched out to some centent due to the solubility of maleic acid units in the water, while the TEM measurements were made on the solid aggregates in which the corona were collapsed [35].

It was well-known that the self-assembly of amphiphile in selective solvents could result in LCMs [36–38]. Eisenberg et al. [39–42] had reported that the formation of LCMs could be explained by considering a balance between three major forces acting on the system: The stretching of the core-forming segments, the interfacial tension between the core and the solvent, and the intercorona repulsion. In the present study, the formation of LCMs in THF/H_2O mixture could be explained by the following model of self-assembly (shown in Scheme 2). P(MA-*co*-SMA) was first dissolved in THF suitable for both segments, and then water which was a precipitant for the long alkyl chains but which was simultaneously a good solvent for maleic acid units was added. This induced the long alkyl chains forming the core and the maleic acid units forming the corona of spherical micelle. The number of the spherical micelles was increased due to an increase of the copolymer concentration. When the number of the spherical micelles reached some critical value, they would collide, fuse and undergo a secondary aggregation, and thus formed into LCMs finally because the soluble maleic acid units were very short, the interactions between the corona chains and the solvent could no longer stabilize the spherical aggregates.



Scheme 4. Schematic model of the morphological transition from alone spheres to pearl-necklace and networks.

Aggregates arising from P(MA-*co*-SMA) in mixtures of THF and water, with different ratios, were studied. Fig. 3 showed that P(MA-*co*-SMA) aggregates in THF at the initial copolymer concentration of 0.11 wt% when 0 wt% water exhibited various morphologies when adding water of various content. At water content of 5.32 wt% and 10.11 wt% (Fig. 3(A)–(B)), LCMs were seen. At high water content, 18.35 wt% (Fig. 3(C)), the morphology changed to large vesicles. With a further increase in the water content, and 32.8 wt% (Fig. 3(D)), the morphology went to large vesicles coexisting with spheres. LLS was also used to measure the size of the aggregates of varying water content in the THF/water system. The results were shown in Table 3. All but one of the averages were higher than those from the corresponding TEM data (Fig. 3); this observation was similar to what has been found in the above section.

Eisenberg et al. [16,17] had studied the influence of water content on turning the morphologies of the micelles

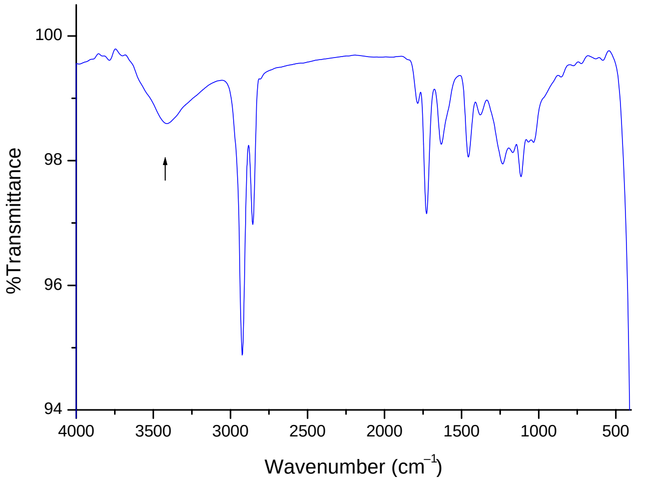


Fig. 5. FT-IR spectrum of dried micelles from the amide of P(MA-*co*-SMA).

Table 5
Dimensions of aggregates from the amide of P(MA-*co*-SMA) of varying water content in the THF/H_2O mixture

Water content (wt%)	5.32	10.11	18.35	32.80
Average micelle size (TEM) (nm)	1300±200	1200±150	600±50	1200±200
Average micelle size (LLS) (nm)	1356±80	1310±200	876±90	1611±150

self-assembled by PS-*b*-PAA in dioxane/H_2O. It is well known that a balance of attractive and repulsive forces among segments and solvents could mediate the formation of supermolecular units. We believed the possible mechanism of the transition from LCMs to large vesicles was shown in Scheme 3. With water added, the mixture became poorer for the SMA chains, and the interfacial energy between the core and the corona increased. To reduce the total interfacial area in response to the increasing interfacial energy, there was an increase in the micelle diameter. But the increase of both the SMA chains stretching and the maleic acid units repulsion was entropically unfavorable, so the high penalty for the SMA chains stretching and the maleic acid units repulsion forced the aggregates to change morphology from LCMs to large vesicles in order to decrease the free energy of micellization.

3.3. Self-assembly behaviors of the amide of P(MA-co-SMA)

The hydrophilicity of P(MA-*co*-SMA) was regulated through amination, and the aggregating behaviors of the amide of P(MA-*co*-SMA) in THF/H_2O mixture was also investigated.

Fig. 4 showed a set of TEM pictures demonstrating the morphologies of the aggregates made by dissolution of the amide of P(MA-*co*-SMA) to THF/H_2O mixture to different final polymer concentrations. At a low polymer concentration, as shown in Fig. 4(A) for 0.028 wt% polymer, a few LCMs were formed. Most of LCMs were around 500 nm in diameter. As the polymer concentration increased to 0.084 and 0.11 wt%, as shown in Fig. 4(B) and (C), besides a few LCMs, pearl-necklace aggregates were formed. The length and diameters of pearl-necklace micelles formed in this case were not uniform. As the polymer concentration increased further to 0.22 wt% (Fig. 4(D)), more and more pearl-necklace micelles formed led to the formation of the networks.

The characterization data of the aggregates obtained by LLS measurements were given in Table 4. This supported the TEM observations (Fig. 4).

Compared with P(MA-*co*-SMA), the amide of P(MA-*co*-SMA) could provide more groups such as ether link and tertiary amine group, thus hydrogen bonds could be formed easily between them. According to previous studies [42–45], the possible mechanism of the morphological transition from alone LCMs to pearl-necklace and networks was shown in Scheme 4. As the total polymer concentration increased, the number of LCMs in the solution would increase. Thus, when the distance among LCMs reached some critical value, the O–H···O hydrogen bonds would be formed, thus self-associate

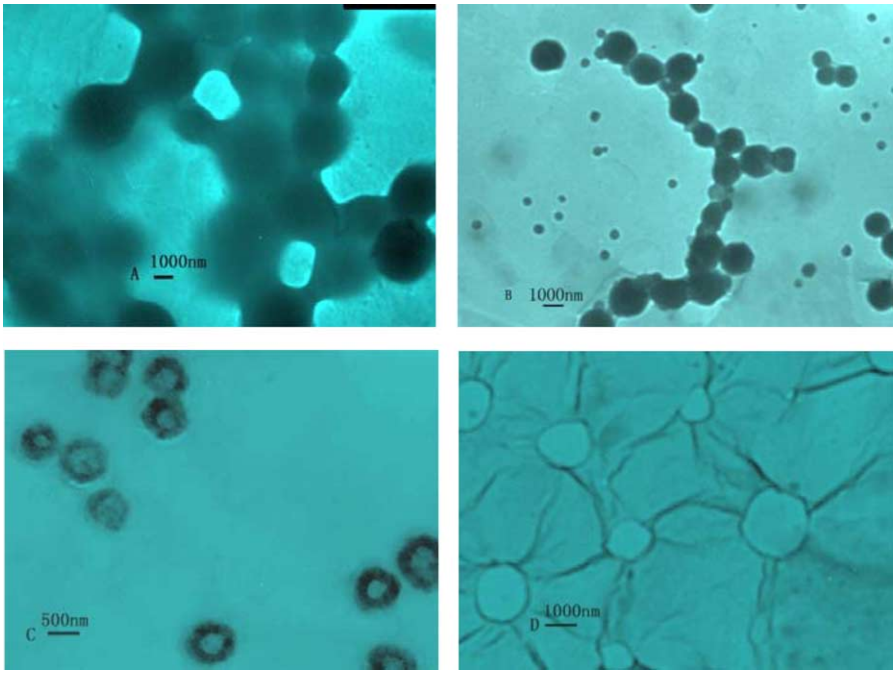


Fig. 6. TEM images of aggregates from the amide of P(MA-*co*-SMA) at different water contents in the THF/water mixture. The initial copolymer concentration in THF is 0.11 wt% when 0% water. H_2O wt%: (A) 5.32 wt%, (B) 10.11 wt%, (C) 18.35 wt% and (D) 32.8 wt%.

via two strong O–H···O hydrogen bonds had lent itself for a reliable supermolecular structure. Eventually, primary structural aggregates, such as pearl-necklaces, networks were formed. These aggregates showed a high degree of uniformity in the diameter. Therefore, hydrogen bonds played a key role in the formation of the pearl-necklaces and networks.

Here, FT-IR was used to detect the hydrogen bonds in the resulting dried micelles [46,47]. The detail of the vibration bands of dried micelles from the amide of P(MA-*co*-SMA) was shown in Fig. 5. The characteristic absorptions in the range of 3000–3750 cm^{-1} could indicate that a certain amount of hydroxyl groups had formed hydrogen bonds in the micelles originated from the self-assembly of the amide of P(MA-*co*-SMA) molecules because the free hydroxyl groups show a very sharp absorption peak at 3600–3650 cm^{-1} and the hydroxyl groups forming hydrogen bonds show a very wide absorption peak at 3200–3500 cm^{-1}.

Fig. 5 showed the TEM images of the aggregates formed by adding different water content into 0.11 wt% THF solution of the amide of P(MA-*co*-SMA). The results showed that at lower water content, the resulting aggregates were LCMs in Fig. 5(A) and (B). At high water content, 18.35 wt% (Fig. 5(C)), the morphology changed to large vesicles. With a further increase in the water content, and 32.8 wt% (Fig. 5(D)), the particle number density is sufficiently high for the onset of micellar ordering to be visible in regions of a monolayer film with regular pores.

Table 5 showed the dimensions of aggregates from the amide of P(MA-*co*-SMA) of varying water content in the THF/ H_2O mixture, the data measured by LLS supported the results obtained by TEM (Fig. 6).

The mechanism of the transition from LCMs to vesicles could be explained by that presented in previous section 'self-assembly behavior of P(MA-*co*-SMA)'. But the possible mechanism of the morphology of a monolayer film with regular pores suggested that, on water addition, the interactions between the corona chains and the solvent could no longer stabilize the aggregates since the soluble maleic acid units were short, which resulted in the vesicles undergoing a secondary aggregation due to adhensive collisions, thus a monolayer film with regular pores were formed.

4. Conclusion

In this paper, P(MA-*co*-SMA) copolymer was synthesized via the free radical copolymerization and its amide was prepared through the MA moieties being reacted with morpholine. It was found that the resultant polymers could form different sizes and morphologies of micelles in the selective solvents with adjusting the copolymer concentrations and water content. The micelles formation mechanisms through self-assembly process were discussed. These micelles might become important in the new opportunities for applications in the fields of drug delivery systems and microcapsules and so on.

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