

FORMATION OF FLOWER-LIKE AGGREGATES FROM SELF-ASSEMBLING OF MICELLES WITH PEO SHELLS AND CROSS-LINKED POLYACRYLAMIDE CORES*

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Abstract Amphiphilic block copolymers, poly(ethylene oxide)-*b*-poly(*N*-acryloxysuccinimide) (PEO-*b*-PNAS) with various molecular weights have been successfully synthesized by atom transfer radical polymerization (ATRP) of NAS using functionalized PEO (PEO-Br) as ATRP macroinitiator. The self-assembling of the block copolymers in water, which is a good solvent for PEO and a non-solvent for PNAS, yielded spherical core-shell micelles with PNAS as core and PEO as shell. The cross-linked reaction of oxysuccinimide in PNAS chains with ethylenediamine occurred in the core of micelles, and the core cross-linked micelles were formed. The flower-like and dendritic aggregates were formed by self-assembling of the core cross-linked micelles on the glass slides or silicon wafers. Longer PNAS block in the block copolymers and higher evaporation temperature formed bigger spherical particles. The optical microscope was used to follow the formation and growth of the flower-like aggregates from the colloidal solution and the main driving forces for the self-assembling are solution fluid and interactions between PEO chains.

Keywords: Amphiphilic diblock copolymer; Micelles; Atom transfer radical polymerization.

INTRODUCTION

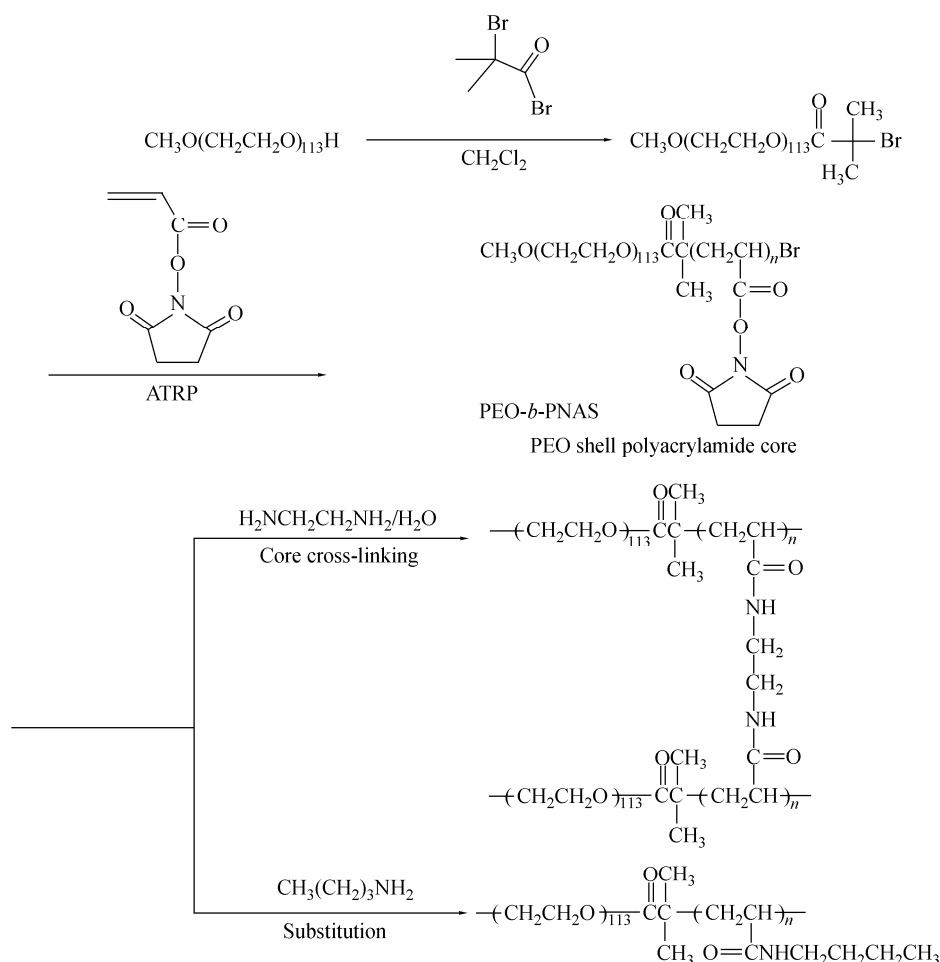
In the recent decade, architectures, morphologies and patterns of the chemical materials at all dimensions from the nanoscale to macroscopic scale have received much attention because of their potential applications in advanced technologies^[1]. The self-assembling of semiconductor, metal and metal oxide nanoparticles has been extensively studied, and the aggregates formed usually show different electronic and optical properties from those of isolated nanoparticles^[2–4]. Different morphologies and patterns were formed from self-assembling of polymeric nanoparticles during the evaporation process of liquid media, and they were found to have potential for microreactors, separation, sensing or optical applications^[5–7]. However, only a few papers reported the investigation of self-assembling of micelles. For examples, different morphologies were formed by self-assembling of the amphiphilic block or graft copolymers micelles with variation of the self-assembling conditions^[8–10]. Very nice cubic aggregates were produced by evaporation of the solvent mixture from the solution of diblock copolymer, polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) micelles in water and low molecular weight additives^[8]. Self-assembling of spherical PS-*b*-PAA micelles on glass slide at 0°C formed spindle-like aggregates, and their further aggregation *via* freeze-thaw cycles yielded flower-like arrays^[9]. However, the micelles used in those studies were not core or shell cross-linked, they might change their shape and size with variation of environments, such as solvent, concentration, pH and temperature. However, during the formation of various morphologies induced by solvent evaporation from micelles solution, the variation of micelles' size and shape might influence the resultant morphologies. For investigation on the influence of various parameters on the morphologies and patterns formed, use of the core or shell cross-linked micelles is necessary.

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Generally, micelles with core-shell structure are formed by self-assembly of block copolymers in selective solvents^[11–16]. For stabilization of the micelles obtained, big efforts on investigation of cross-linking the cores or shells of micelles have been made^[17–24]. Polymeric micelles were stabilized by shell cross-linking with gold nanoparticles^[17]. Two synthetic approaches for cross-linked core of the micelles are used generally: one is the polymerization of vinyl groups in the cores initiated by thermal or photo initiators^[18–22]. For example, maleic groups in the poly(D,L-lactide) core of the micelles with poly(ethylene glycol) shell underwent cross-linking reaction in the presence of $K_2S_2O_8$ at $50^\circ C$ ^[20]. The cross-linking reaction between the vinyl groups in the poly(glycidyl methacrylate) core of the micelles with PEG shell was successfully performed by ultraviolet radiation and heat^[22]. The other is the introduction of special cross-linkable reagents into the cores of micelles, following cross-linking reaction^[23, 24]. For example, poly(4-vinylpyridine) in the core of micelles with PS shell was cross-linked using 1,4-dibromobutane as cross-linker^[23]. For efficient cross-linked core, our group developed a cross-linked approach *via* reaction of diamine with *p*-nitrophenyl group in the poly(*p*-nitrophenyl methacrylate) core, but atom transfer radical polymerization (ATRP) of *p*-nitrophenyl acrylate was not successful^[24]. The ATRP of *N*-acryloxysuccinimide (NAS) is of controlled radical polymerization characters^[25]. The oxysuccinimide group in poly(*N*-acryloxysuccinimide) (PNAS) is easier to be substituted by amines, and the resultant polymers will become water soluble. Although the micelles prepared from double hydrophilic block copolymers have received attention^[26], up to now, all core or shell cross-linked micelles prepared from amphiphilic block copolymers have hydrophilic shell (or core) and hydrophobic core (or shell), preparation of the micelles with hydrophilic core and shell should be challenging.



Scheme 1 The synthesis of micelles with PEO shells and cross-linked polyacrylamide cores, and the substitution reactions of *N*-oxysuccinimide groups in PNAS with *n*-butylamine

Herein, we report the synthesis of double hydrophilic core-shell micelles from PEO-*b*-PNAS and their self-assembling. The synthetic procedures are outlined in Scheme 1.

EXPERIMENTAL

Materials

Poly(ethylene oxide) monomethyl ether with $M_n = 5000$ and $M_w/M_n = 1.01$ was purchased from Aldrich, and further freed of water by azeotropic distillation in anhydrous benzene. Triethylamine (TEA) and ethylenediamine were dried with potassium hydroxide, and then distilled. CuBr (AR, Shanghai Chemical Reagent Plant) was purified by stirring in glacial acetic acid for half an hour, washing with methanol, and then drying in a vacuum oven. Dichloromethane was dried with CaH_2 and distilled prior to use. The α -bromoisobutyryl bromide (Fluka, assay $\geq 97\%$), *N*-hydroxysuccinimide (Fluka, 97%), diethyl ether, ethanol, benzene, 2,2'-bipyridine (bpy) were used as received without further purification. *N*-acryloxysuccinimide was prepared in 73% yield according to the procedure reported^[27]. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS, δ): 6.15–6.74 (m, 3H, $\text{CH}_2=\text{CH}$), 2.87 (s, 4H, CH_2CH_2).

Synthesis of PEO ATRP Macroinitiator

A solution of TEA (0.7 mL, 5 mmol) in anhydrous dichloromethane (10 mL) was transferred into a 250 mL three-necked round bottom flask equipped with a dropping funnel and a magnetic stirrer. After cooling to 0°C , α -bromoisobutyryl bromide (0.928 g, 5 mmol) solution in dry dichloromethane (10 mL) was added. Into the reaction mixture, a PEO (5 g, 1 mmol) solution in dichloromethane (50 mL) was added dropwise in 1 h. Subsequently the solution was warmed to room temperature and the reaction continued for 24 h. After the salt of TEA formed was filtered, the reaction solution was concentrated, the residue was added into cold diethyl ether and the product was precipitated. The PEO macro initiator (PEO-Br) was collected by filtration, and then it was dried in a vacuum oven at 30°C for 24 h. $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{113}\text{COC}(\text{CH}_3)_2\text{Br}$, $M_n(\text{GPC})$: 5200, $M_w/M_n = 1.01$. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS, δ): 4.32 (t, 2H, $-\text{CH}_2\text{OCO}-$), 3.62 (m, 448H, $\text{OCH}_2\text{CH}_2\text{O}-$), 3.3 (m, 6H, OCH_3), 1.94 (s, 6H, 2CH_3).

Preparation of Diblock Copolymer, PEO-*b*-PNAS

The synthetic procedure of PEO-*b*-PNAS is as follows. A glass tube with a magnetic stirrer was charged with PEO-Br (0.50 g, 0.097 mmol), CuBr (0.014 g, 0.097 mmol), bpy (0.046 g, 0.291 mmol) and NAS (1.641 g, 9.7 mmol). After three freeze-evacuate-thaw cycles, the tube was sealed under vacuum, and then placed in an oil bath thermostated at 110°C for prescribed time. After reaction was finished, about 20 mg reaction mixtures were dissolved in DMSO-d_6 for measurement of $^1\text{H-NMR}$, and monomer conversions were calculated according to Eq. (1).

$$\text{Conversion (\%)} = 1.5 \times I_{2.04} / (1.5 \times I_{2.04} + I_{6.3-6.7}) \times 100\% \quad (1)$$

Here, $I_{2.04}$ and $I_{6.3-6.7}$ are the integral intensities of signals corresponding to protons of methylene units in the main chain of PNAS and vinyl protons of unreacted NAS respectively. The residual reaction mixture was dissolved in DMSO, and then poured into excess of ethanol. The precipitate was filtered and the block copolymer was dried in a vacuum oven at 40°C for 24 h.

Preparation of the Core Cross-Linked Micelles and the Formation of Ordered Allays

Micelles with PNAS core and PEO shell were formed by addition of water (8 mL) into the PNAS-*b*-PEO (20 mg) solution in DMSO (2 mL), and this solution was sonicated for 10 min to obtain a solution of micelles with concentration of 2 g/L. Ethylenediamine ($\text{NH}_2/\text{succinimide} = 2:1$, molar ratio) was added into the aqueous solution obtained. After the reaction was carried out at ambient temperature for 5 days, the reaction solution was dialyzed against water for 4 days for removal of small molecules. A drop of the final micellar solution was placed on a freshly cleaned silicon wafer. Subsequently the wafer was put in an airproof container, and the solvent was evaporated slowly. Finally, the samples were put into a vacuum oven at room temperature for 24 h.

before observation on optical microscopy (OM) and scanning electron microscopy (SEM). In order to clarify the growth of assemblies, the self-assembling process was followed by observation on OM at prescribed time intervals.

Analysis

^1H -NMR spectra were recorded on a Bruker DRX-300 nuclear magnetic resonance (NMR) instrument with CDCl_3 or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. The molecular weight and molecular weight distribution were determined on a Waters-150C gel permeation chromatograph (GPC) equipped with microstyragel columns (50, 10^2 and 10^3 nm) at 30°C . Narrow polystyrene standards were used in the calculation of molecular weights. THF was used as eluent at a flow rate of 1.0 mL/min. Fourier transform infrared spectra (FTIR) were recorded on a Bruker VECTOR-22 IR spectrometer. The size measurement of micelles was performed on a JEM100-SX transmission electron microscopy (TEM) and a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Malvern, UK) with 90° optics and a He-Ne Laser (4.0 mW, 633 nm). The OM images were taken using an Olympus Polarizing Microscope with BX51M System. SEM was carried out on a KYKY-1000B scanning electron microscope. The sample was sputtered with a thin gold layer before SEM observation.

RESULTS AND DISCUSSION

Although the synthesis of PNAS-*b*-PEO has not been reported based on our knowledge, high reactivity of *N*-oxysuccinimide ester group to amine substitution and hydrolysis reactions was investigated^[28, 29]. The advantages of PNAS-*b*-PEO micelles are that the cross-linking reaction of NAS units in the cores with diamine is more efficient in mild conditions in comparison with other core cross-linking reactions reported, and the hydrophobic PNAS core is easily transformed to hydrophilic core after substitution reaction of NAS units with ethylenediamine, forming double hydrophilic micelles. Thus the amphiphilic block copolymer, PNAS-*b*-PEO was selected as precursor in the preparation of core cross-linked micelles. As we mentioned in introduction, ATRP of NAS can yield well-defined polymers. So the PNAS-*b*-PEO was prepared by ATRP of NAS using PEO-Br as macro initiator.

Preparation of Core Cross-Linked PNAS-*b*-PEO

The macroinitiator, PEO-Br used in this study was prepared by reaction of PEO with α -bromoisobutyryl bromide (BiB). To ensure one initiating site in every PEO chain, an excess of BiB was used in the reaction, and the residual BiB can be removed during the precipitation in diethyl ether. An evidence for the formation of PEO-Br is its FT-IR spectrum. Comparing the FT-IR spectra of PEO before and after reaction with BiB, we can see a characteristic carbonyl-stretching band of ester at $\nu = 1737\text{ cm}^{-1}$ of the PEO-Br obtained from esterification reaction. Its ^1H -NMR spectrum can verify further its structure. Figure 1(A) represents a typical ^1H -NMR spectrum of PEO-Br and we can see the signal at $\delta = 3.62$ (b) corresponding to the methylene protons in the PEO main chain and two new signals at $\delta = 4.31\text{--}4.34$ (a), and 1.94 (c) corresponding to ester methylene protons and two methyl protons of terminal BiB unit. The integration ratio (1:226) of signals a to b indicates that almost all terminal hydroxyl groups were capped with α -bromoisobutyryl groups.

The PEO-Br with $M_n(\text{NMR}) = 5150$, $M_w/M_n = 1.01$ was applied in the bulk ATRP of NAS with CuBr/bpy as catalyst and ligand. The conditions and results are listed in Table 1. Similar to the result that complexation of PEO with copper ion did not affect the polymerization of vinyl monomers^[30], the results listed in Table 1 show increase of molecular weight with the evolution of polymerization. The molecular weight and molecular weight distribution of the resultant block copolymers could not be measured by GPC method using tetrahydrofuran (THF) eluent because they are insoluble in THF. So the block copolymers, PNAS-*b*-PEOs were treated with *n*-butylamine before GPC measurements for improving the polymer solubility in THF, and the M_w/M_n values in Table 1 is that of poly(*N*-*n*-butyl acrylamide)-*b*-PEO.

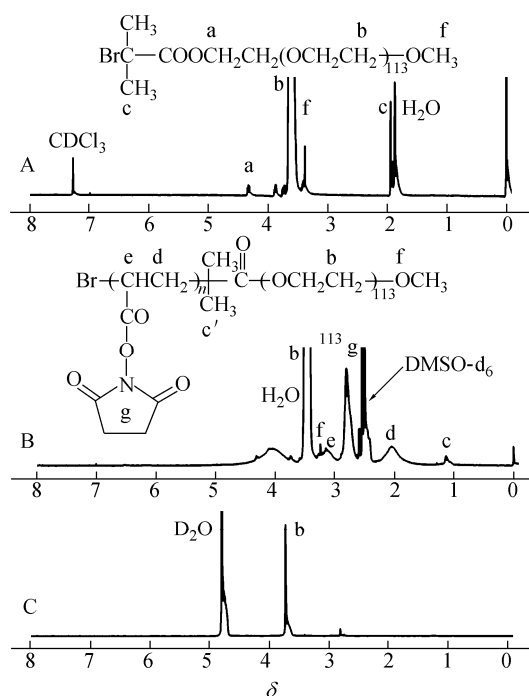


Fig. 1 ^1H -NMR spectra of (A) PEO-Br, (B) diblock copolymer PEO-*b*-PNAS (sample 4 in Table 1) in DMSO-d_6 and (C) diblock copolymer after substitution with *n*-butylamine in D_2O

Table 1. Results and conditions for ATRP of NAS using PEO-Br as macro initiator^a

No.	$[\text{M}]_0/[\text{I}]_0$ (molar ratio)	Time (h)	Conv. (%)	$M_n(\text{th})^b$	$M_n(\text{NMR})^c$	M_w/M_n^d	d^e (nm)	n/m^f
1	40:1	1	17	6290	6350	—	—	113/7
2	40:1	4	25	6820	7000	1.03	174	113/11
3	100:1	2	26	9540	9040	—	—	113/23
4	100:1	5	47	13060	11230	1.03	248	113/36
5	100:1	11.3	52	13940	14950	1.05	375	113/58

^a NAS was polymerized at 110°C in bulk with the molar ratio in feed: PEO-Br/CuBr/bpy = 1/1/3; ^b The number-average molecular weight of block copolymers, $M_n(\text{th}) = 5150 + ([\text{NAS}]_0/[\text{I}]_0) \times \text{conv} \times 169$, where $[\text{NAS}]_0$ and $[\text{I}]_0$ are initial molar concentrations of NAS and PEO-Br, 5150 and 169 are the molecular weights of PEO-Br and NAS respectively; ^c Calculated according to Eq. (2); ^d Measured by GPC method after substitution of NAS unit in PNAS-*b*-PEO with *n*-butylamine; ^e Measured by a Zetasizer nano ZS90 instrument after core cross-linking with ethylenediamine and dialysis against water; ^f n = degree of polymerization (DP) of PEO and m = DP of PNAS in the block copolymers, PEO-*n*-*b*-PNAS_{*m*}

For determination of the resultant polymer structure, ^1H -NMR spectra were measured, and Fig. 1(B) represents a typical ^1H -NMR spectrum of PEO-*b*-PNAS (sample 4 in Table 1) in DMSO-d_6 since DMSO is a good solvent of both polymers, PNAS and PEO. The signals at $\delta = 3.45$ and 2.79 are characteristic signals of PEO and PNAS respectively. The signals at $\delta = 2.04$ and 1.14 are corresponding to methylene protons in the PNAS main chain and two methyl protons at the conjunction between PNAS and PEO blocks respectively. Thus the number-average molecular weight, $M_n(\text{NMR})$ of the block copolymer can be calculated according to Eq. (2).

$$M_n(\text{NMR}) = 5150 + (I_{2.04}/2)/(I_{1.14}/6) \times 169 \quad (2)$$

Here $I_{2.04}$ and $I_{1.14}$ are the integral values of the signals at $\delta = 2.04$ and 1.14 respectively, 169 is the molecular weight of NAS. The results are listed in Table 1. The theoretical molecular weights, M_n (th)s agree well with M_n (NMR)s (Table 1), thus the block copolymers with various molecular weights' PNAS were easily prepared by feed molar ratio and conversion. When ^1H -NMR spectrum of PEO-*b*-PNAS after substitution with *n*-butylamine was measured in D_2O as shown in Fig. 1(C), only the characteristic signal of PEO at $\delta = 3.62$ was observed, and the characteristic signals of PNAS at $\delta = 3.1$, 2.79 and 2.04 disappeared completely. This can be explained by the formation of micelles with compact PNAS core stabilized by PEO shell in D_2O .

To prepare the core-shell micelles, the amphiphilic block copolymers, PNAS-*b*-PEO, were dissolved in DMSO, and then water was slowly added into the polymer solution for formation of micelles with PNAS core and PEO shell. The core cross-linking reaction was performed in water using ethylenediamine as cross-linker. For estimating the reaction efficiency, FT-IR spectra of the micelles before and after cross-linking reaction were measured; and typical spectra are shown in Fig. 2. The absorption bands at $\nu = 1811$, 1781 and 1738 cm^{-1} in Fig. 2(a) are ascribed to carbonyl groups of NAS units of PNAS chains. After treated with ethylenediamine, these carbonyl absorption bands disappeared completely, and two new secondary amide N—H absorption bands at $\nu = 3304$ and 3073 cm^{-1} , amide carbonyl absorption bands at $\nu = 1655$ and 1546 cm^{-1} appeared in Fig. 2(b). These facts indicate the removal of most of *N*-oxysuccinimide groups in the core of micelles and the formation of cross-linked amides (Scheme 1) due to their cross-linking reaction with ethylenediamine. When considering the reaction between neighboring *N*-oxysuccinimide groups in the same chain, the cross-linkage of the micelles should be less than the content of *N*-oxysuccinimide groups in the micelles.

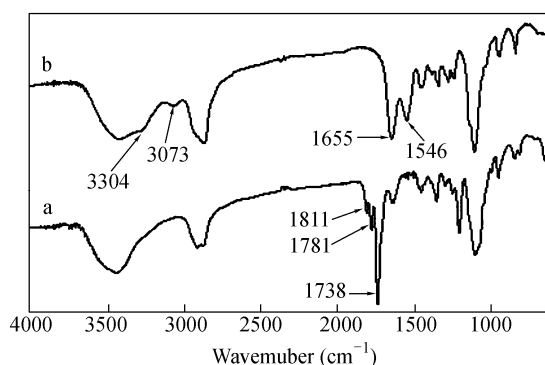


Fig. 2 FTIR spectra of the PEO-*b*-PNAS prepared from PEO₁₁₃-*b*-PNAS₃₆ (sample 4 in Table 1) before (a) and after (b) core cross-linking reaction with ethylenediamine at ambient temperature for 5 days

The size of core cross-linked micelles was measured on a Zetasizer nano ZS90 instrument and the results are listed in Table 1. Since water is a selective solvent of PEO in the PEO-*b*-PNAS, the spherical micelles can be formed with PNAS core and PEO shell in the water. The higher molecular weight PNAS induced the formation of larger micelles due to the aggregation of more PNAS molecules. Thus result in Table 1 demonstrates that the size of micelles formed after the core cross-linking reaction increases with the molecular weight increase of the PNAS block (see Nos. 2, 4 and 5 in Table 1). The core cross-linked micelles can be confirmed further by their TEM image. Figure 3 is a typical TEM image of the core cross-linked micelles obtained from the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles (the sample 4 in Table 1), and their diameters ranged from 80 to 100 nm. The micellar size is substantially smaller than that (248 nm) measured on Zetasizer nano ZS90 in water. One probable reason is that the micelles in water are well swollen, but they are highly shrunk in the TEM measurements.

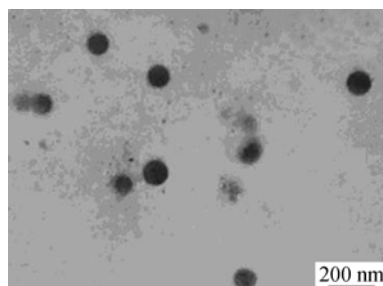


Fig. 3. TEM image of the core cross-linked micelles prepared from PEO₁₁₃-*b*-PNAS₃₆ (sample 4 in Table 1) using ethylenediamine as cross-linker

Self-Assembling of the Core Cross-Linked PNAS-*b*-PEO Micelles

The OM images in Figs. 4(a) and 4(b) show the flower-like aggregates with $300\ \mu\text{m} \times 425\ \mu\text{m}$ prepared from self-assembling of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles on a silicon wafer, and this was performed by slow evaporation of a drop of aqueous micellar solution until dried. Every aggregate is composed of several branches (Fig. 4b), and every branch is of dendritic structure (Fig. 4a). Clearly, the high ordered aggregates, which are quite different from TEM photos of the micelles shown in Fig. 3, were formed from self-assembling of the cross-linked micelles. To understand the detailed structure of the aggregates, the same sample used in OM espial was observed on SEM, and Figs. 5(b–d) show the SEM images with different magnifications. Although both Fig. 5(a) and Fig. 4(b) are OM photos, their shapes are different slightly because the sample observed in Fig. 4 was not dried completely. From Figs. 5(b) and 5(c) we can see many flowers with different shapes and sizes on the branches. Every individual flower possesses many radically out-extending thin petals with a thickness of about 200 nm as shown in Fig. 5(d). Similar petal structure was reported, but it was formed from complete removal of zeolite in the polystyrene/zeolite composite after treated with HF aqueous solution for 36 h^[31]. For the aggregates in Fig. 5(b) formed from the pure core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles, the formation of petals in Fig. 5(d) may be ascribed to slow evaporation of the solvent swollen in the aggregates at last drying stage, and the cross-linked micelles were assembled further to form thin petals. The flowers were not as big as that formed by removal of Zeolite method, which may be related to lower content of water in the aggregates. The core cross-linking of the PNAS₃₆-*b*-PEO₁₁₃ micelles is important for the formation of the highly ordered aggregates because the uncross-linked micelles will change their shape and size due to the

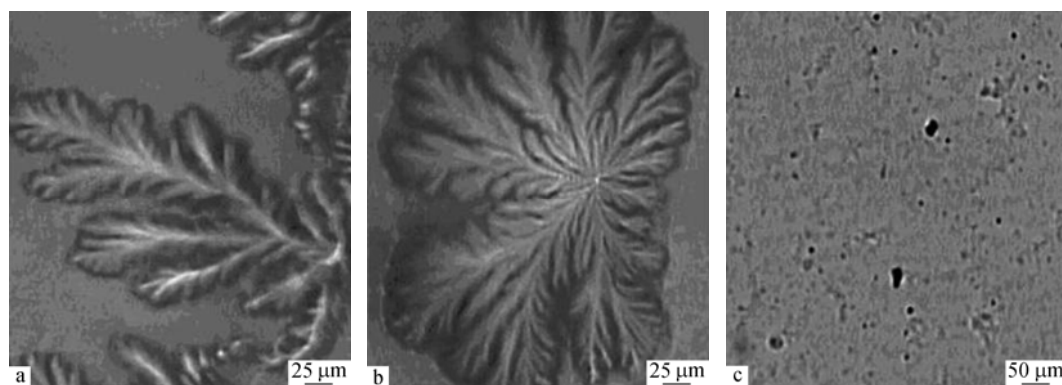


Fig. 4 Optical microscopy photos of the aggregates obtained from the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles formed from water evaporation of the aqueous core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles solution (2 mg/mL) on silicon wafer and at room temperature until dried

a) The image on the fringe of aggregate; b) The image of one whole aggregate; c) The aggregates formed from the uncross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles solution (1 mg/mL) on a glass slide in airproof condition at 30°C until dried completely

variations of concentration and temperature during the evaporation of solvent. If the cores of the PNAS₃₆-*b*-PEO₁₁₃ micelles were not cross-linked, their self-assembling on a glass slide with the same self-assembling conditions of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles formed bigger size micellar morphology as shown in OM image of Fig. 4(c).

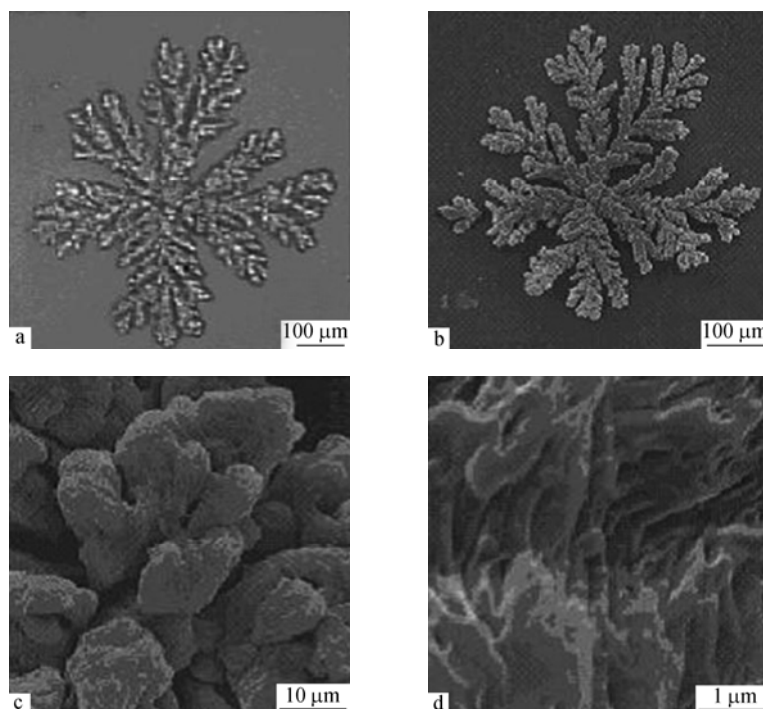


Fig. 5 Optical microscope photo (a) and SEM images of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micellar assembly with different magnifications: (b) $\times 204$, (c) $\times 2040$, (d) $\times 20400$

The sample was formed by slow evaporation of aqueous solution (2 mg/mL) on a silicon wafer in a container at room temperature until dried completely.

Generally, nanoparticles, such as colloids or micelles, dispersed in solvent tend to aggregate into random structures upon evaporation of solvent because of the high specific surface energy and irregular aggregation of micelles. In order to illustrate how the highly ordered flower-like aggregates were formed, the OM observation was used to follow the formation of the aggregates. This was performed by putting drops of aqueous solution of the core cross-linked micelles on glass slide, and then it was placed in a container for slow evaporation of the solvent. The OM observation was carried out at various time intervals. The results are shown in Fig. 6. With the evaporation of solvent, the core cross-linked micelles were assembled during the solvent evaporation process. At the beginning of solvent evaporation, no aggregates were observed (Fig. 6a). Continuous evaporation of solvent led to increase of micellar concentration to a critical value, the interaction between the PEO chains in the shell of micelles induced the micelles to aggregate, and big aggregates formed were deposited on the substrate surface (Fig. 6b). Generally, those aggregates have uneven edge as shown in Fig. 6(c). Similar to the explanation for the formation of crystal ring^[31–33], faster evaporation of solvent at the borderline between the micelle solution and solid assemblies led to significant increase of the micelles' concentration, and the aggregates grew from the protruding parts of the aggregate edge. With the continuous flow of polymer solution to the edge of aggregates for compensation of evaporation loss, the flower-like assemblies became bigger and bigger as shown in Figs. 6(d)–6(i). The final size of the aggregate in Fig. 6(i) is $450\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$. The aggregates shown in Fig. 6 are not dried completely; they are swollen with water, and water in the polymers was not easier to be removed completely because both core poly(*n*-butyl acrylamide) and shell PEO are hydrophilic. After dried in a vacuum oven over P₂O₅ at room temperature for 24 h, the flowers with petals were formed as we discussed already.

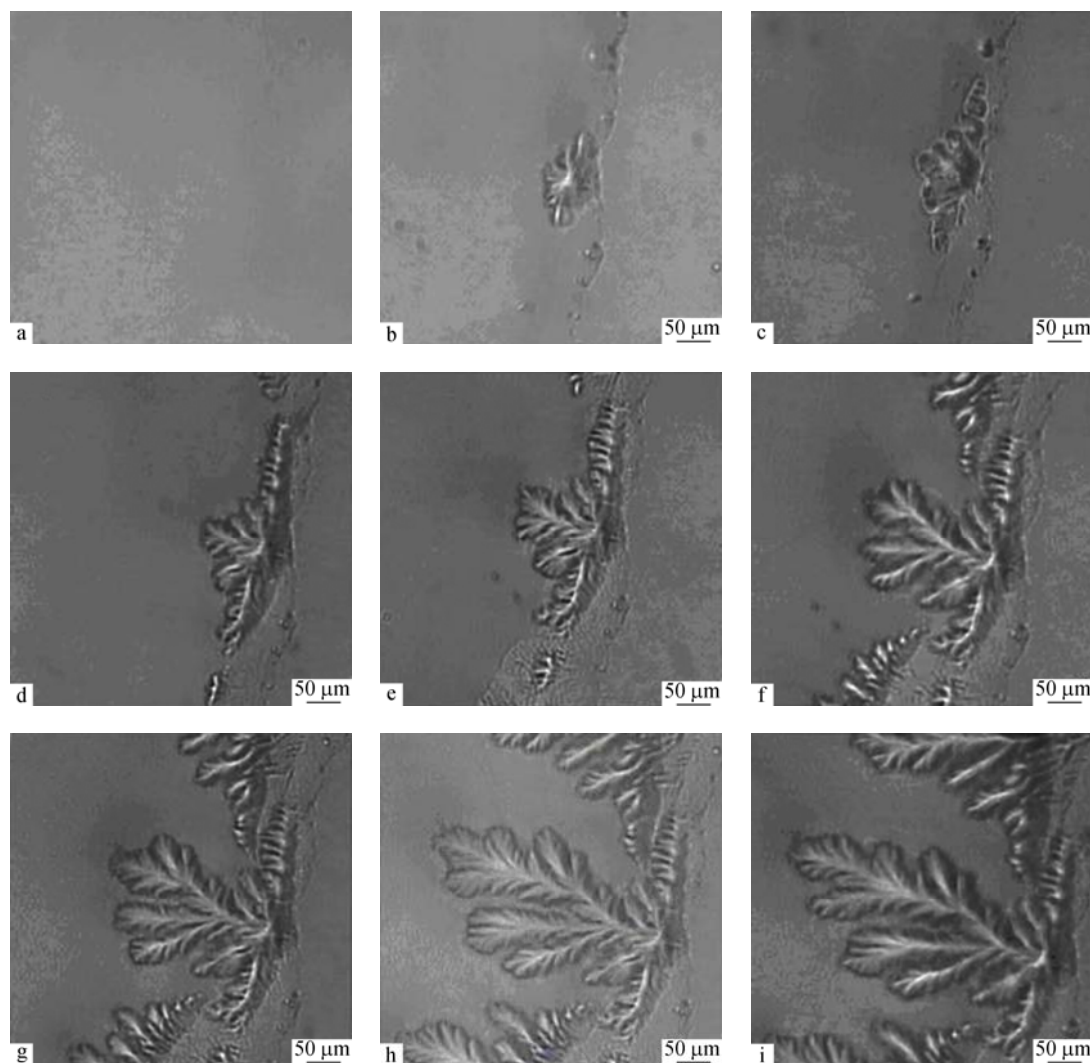


Fig. 6 Optical microscope photos for the formation of flower-like aggregates on a glass slide from aqueous solution of the core cross-linked micelles (2 mg/mL) at different times
a) 0 h; b) 3 h; c) 3.3 h; d) 3.7 h; e) 4.1 h; f) 4.9 h; g) 5.4 h; h) 7.1 h; i) 8.1 h

There are several factors influenced the formation of flower-like aggregates, such as the evaporation rate of solvent during the self-assembling, the hydrophobicity of PEO at 90°C and crystallization of PEO. In those factors, the temperature is more important. Consider the core cross-linked micelles used in this study, their shape and size are not influenced by temperature significantly. Thus the effect of temperature on the morphologies should not be due to variation of micelles' shape and size. Figures 7(a)–7(c) are OM photos of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micellar aggregates formed from self-assembling on glass slides under atmosphere at 90°C, 50°C, and in airproof condition at 30°C respectively, and different morphologies were observed. Figure 7(a) shows bigger spherical particles with average diameter of 10 μm; and Fig. 7(b) displays small spherical particles with diameter of approximate 3 μm concentrated in several separated round areas. All these particles are the aggregates of the core cross-linked micelles. Fast solvent evaporation at 90°C caused the fast increase of the micelles' concentration, and rapid aggregation of the micelles, the lower interaction between PEO shells may be the reason for the formation of the bigger particles. Continuous self-assembling to form flower-like aggregates was impossible due to dryness of spherical particles. At 50°C, slower solvent evaporation

led to slow increase of micelles' concentration, and the gradual self-assembling of micelles formed small particles, and those particles were concentrated in several separated round areas as shown in Fig. 7(b). Therefore, further lowering evaporation rate of solvent is necessary for formation of flower-like aggregates. When the self-assembling was carried out in the airproof condition at 30°C, the flower-like aggregates were formed as shown in Fig. 7(c).

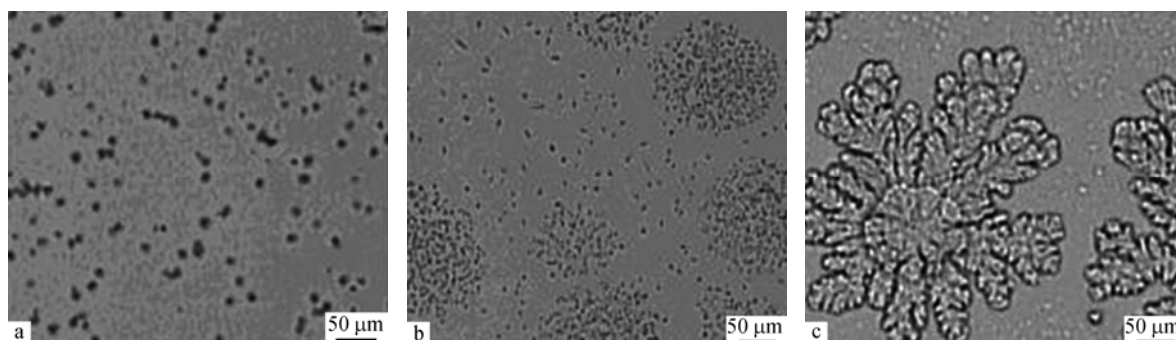


Fig. 7 Optical microscope photos of core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micellar aggregates formed from aqueous solution of the core cross-linked micelles (2 mg/mL) on glass slides in atmosphere at various temperatures a) 90°C; b) 50°C; c) In airproof condition at 30°C

As we discussed, the main driving forces for self-assembling are the solution fluid and the interaction between PEO chains including their crystallization. Variation of block copolymers' composition should affect the self-assembling morphologies. The OM photos in Fig. 8 show the aggregates formed from aqueous solutions of the core cross-linked PNAS₅₈-*b*-PEO₁₁₃ (Fig. 8a) and PEO₁₁₃-*b*-PNAS₂₃ (Fig. 8b) micelles on glass slide in airproof condition at 30°C. Different from flower-like aggregates formed from core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles, the self-assembling of core cross-linked PNAS₅₈-*b*-PEO₁₁₃ micelles at the same conditions afforded the spherical aggregates with average diameter of about 2.5 μm (Fig. 8a), the PNAS with higher molecular weight induced the formation of big micelles with the larger PNAS cores (the average diameters of the core cross-linked PNAS₅₈-*b*-PEO₁₁₃ and PNAS₃₆-*b*-PEO₁₁₃ micelles in water are 375 and 248 nm, respectively). Probably the interaction between the PEO shells is a driving force for the formation of spheric aggregates, and the solution fluid is not big enough to move the big micelles or small aggregates of the micelles in the order directions for the formation of flower-like aggregates. Whereas, self-assembling of the core cross-linked PNAS₂₃-*b*-PEO₁₁₃ micelles formed flower-like aggregates as shown in Fig. 8(b), which is similar to the result obtained from self-assembling of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles.

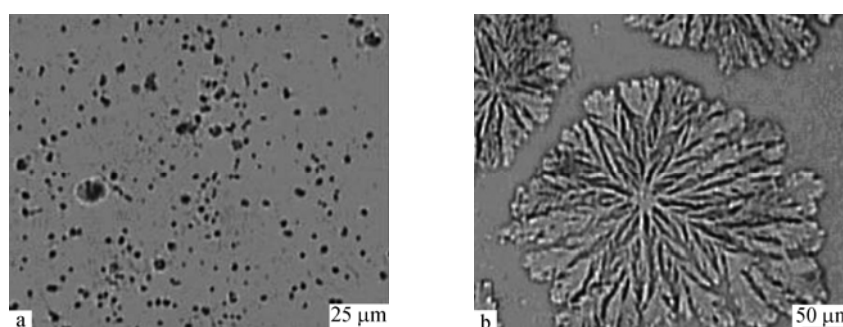


Fig. 8 Optical microscope photos of the micellar aggregates of (a) PNAS₅₈-*b*-PEO₁₁₃ and (b) PNAS₂₃-*b*-PEO₁₁₃ formed from aqueous solution of the core cross-linked micelles (2 mg/mL) on glass slides in airproof condition at 30°C until dried completely

The effect of various substrates on the morphology was investigated. The self-assembling of core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles on glass slide and silicon wafer was carried out at the same conditions, and their OM photos are shown in Figs. 5(a) and 7(c) respectively. In comparison with those aggregates formed on silicon wafers (Fig. 5a), the flower-like aggregates formed in glass slide seem to have two or more layers. The possible reason is the higher surface hydrophilicity of the glass slide, which restricts the mobility of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles. Thus formation of the bigger grains shown in Fig. 5(a) is difficult.

CONCLUSIONS

Amphiphilic block copolymers, PEO-*b*-PNAS with various compositions have been successfully prepared by ATRP of NAS using PEO-Br as macro initiator. The core cross-linking reaction of PEO-*b*-PNAS micelles can be achieved by the substitution reaction of oxysuccinimide of NAS units in the cores of micelles by ethylenediamine. The self-assembling of the core cross-linked PNAS₃₆-*b*-PEO₁₁₃ micelles on silicon wafers or glass slides formed flower-like aggregates, which are composed of several branches with many flowers on those branches. The driving forces for self-assembling in this system are the solution fluid and interaction between PEO chains, and they are competitive in formation of flower-like aggregates or spheric aggregates. Evaporation rate of solvents is one of the determined factors to form highly ordered aggregates. Relative chain length ratio of the PNAS and PEO blocks is another important factor for the formation of morphologies and the block copolymers with longer PNAS chains is difficult to form flower-like aggregates. Therefore, one route is provided for preparation of the various interesting morphologies and this study will help to understand the relationship between morphologies prepared from the micelles and self-assembling conditions.

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