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Synthesis, characterization and self-assembly of ion-bonded amphiphilic A_2B miktoarm star copolymers containing an azobenzene unit at the core

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ABSTRACT

An azobenzene-containing supramolecular copolymers, consisted of two polystyrene (PSt) arms and one poly(ethylene oxide) (PEO) arm linked via ionic bond, has been designed and successfully synthesized. Monomethoxy PEO with phenylazobenzenesulfonic acid as the terminus (PEO-N=N-SO_3H) was utilized to react with polystyrene carrying tertiary amino group at the middle of the polymer chain (PSt_2-$N(CH_3)_2$) to form ion-bonded supramolecular star copolymers (PSt_2-N=N-PEO) with an azobenzene group at the core based on the interaction between sulfonic acid group and amino group. The obtained copolymers were characterized by ^1H nuclear magnetic resonance (^1H NMR) and gel permeation chromatography (GPC) techniques. The self-assembly behavior of the copolymers with different molecular weight of PSt was investigated, which shows solid spherical aggregates in water. The aggregation leads to the lower isomerization degree (54%) at the photostationary state in water compared with that in 1,4-dioxane (82%).

1. Introduction

Amphiphilic block/star copolymers have attracted a great deal of attention in the realm of polymer science [1–12]. One of the mean reasons is their ability to form organized micellar aggregates with different morphologies in polymer solution, in bulk state, and in thin polymer layers at surfaces and interfaces [1–10]. During the past few decades, important progress has been made on the synthesis, characterization and application of block/star copolymers. Various polymerization techniques have been successfully used to prepare amphiphilic block/star copolymers, e.g., anionic [13], group transfer [14], metathesis [15], and controlled radical polymerization [16–20]. Most of the prepared copolymers are based on the concept of covalent bond to link different building blocks.

On the other hand, recent development in the filed of supramolecular chemistry provides an alternative concept for the preparation of block/star copolymers. That is, the building blocks are connected through noncovalent interactions. Based on this concept, polymer chains with specific end groups combine with each other to form supramolecular block/star copolymer through the noncovalent interactions, such as hydrogen bond [21–23], coordination bond [24–27] and ionic bond [28–34]. For example, Schubert's group has prepared hydrophilic and hydrophobic blocks with terpyridine end groups, and combined these two blocks via metal–ligand interactions [24]. Using a similar way, amphiphlic diblock copolymers linked via multiple-hydrogen bonds were also obtained by Yang et al. [21]. However, the synthesis of polymer chains end-capped with terpyridine or hydrogen bonding complementary associating units is complicated. Ionic bond is stronger than others [35] and feasible to be obtained in comparison with coordination bond and multiple-hydrogen bond, which may lead to its broad application. To the best of our knowledge,

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researches on the synthesis and self-assembly of ion-bonded amphiphilic block/star copolymers are few, especially in selective solvent [31–34]. Very recently, we have developed two methods to synthesize ion-bonded (miktoarm) star copolymers: one involves reversible addition-fragmentation chain transfer (RAFT) polymerization of monomers (styrene, *tert*-butylacrylate and N-isopropylacrylamide) in the presence of supramolecular RAFT agent [31,32] and the other is based on complementary functional group reaction of building blocks [33].

Azobenzene-containing polymers (azo polymers) are currently attracted considerable attention because of their unique reversible photoisomerization between trans- and cis-isomers of chromophore upon irradiation with UV light [36–38] and potential optical applications [39–42]. Although extensive studies have been conducted on azo polymers, there has been recently growing interest for azo copolymers with amphiphilic properties [43–45].

In this contribution, a novel ion-bonded amphiphilic A_2B miktoarm star copolymers containing an azobenzene moiety at the core was synthesized and studied. As shown in Scheme 1, PEO end-capped with 4-(4′-hydroxyphenylazo)-benzenesulfonic acid (PEO-N=N-SO_3H) was used to form ionic bond with amino-functionalized polystyrene (PSt_2-$N(CH_3)_2$) to provide ion-bonded PSt_2-N=N-PEO. It was found that sulfonic acid group of PEO was an efficient functional group to construct supramolecular amphiphilic copolymers with amino-functionalized PSt. The photoresponsive and self-assembly behaviors of ion-bonded PSt_2-N=N-PEO in water were investigated.

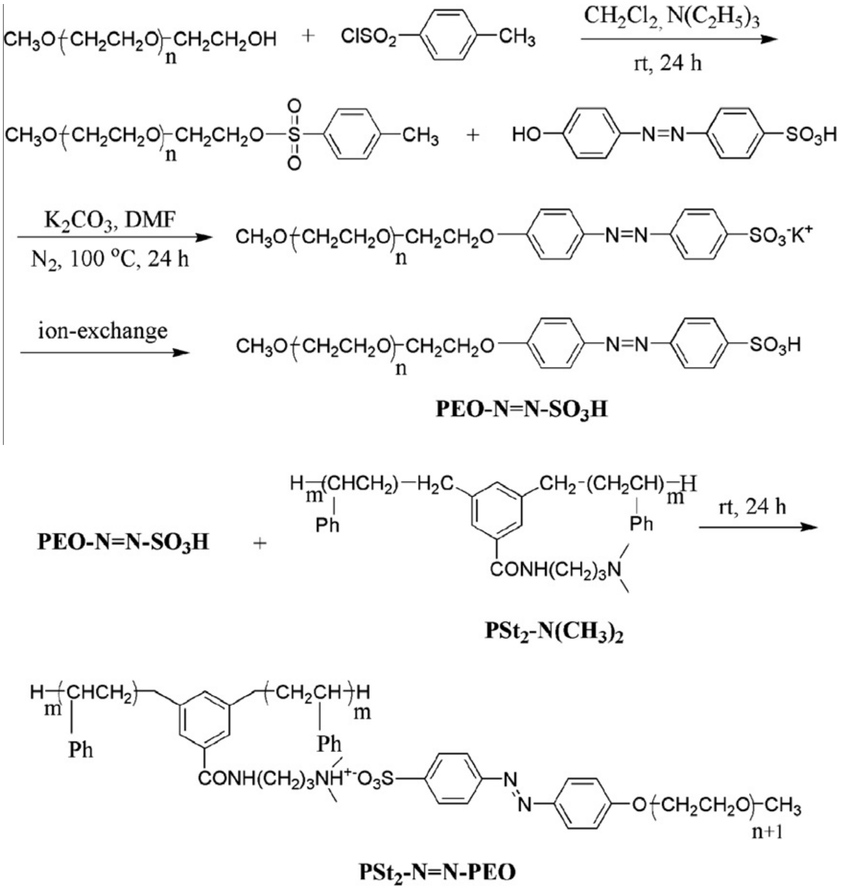
2. Experimental part

2.1. Materials

Monomethoxy poly(ethylene oxide) (PEO, Fluka, $M_n = 5000$, $M_w/M_n = 1.02$) was dried by azeotropic distillation of its toluene solution. 4-(4′-Hydroxyphenylazo)-benzenesulfonic acid (HPB) was synthesized according to the literature [46]. Polystyrene carrying tertiary amino group at the middle of polymer chain, PSt_2-$N(CH_3)_2$, and the precursor monoester polystyrene was premade in our previous work [33]. All other chemical reagents were analytical grade and used as received without further purification.

2.2. Synthesis of PEO-N=N-SO_3H

To a solution of PEO (5.0 g, 1.0 mmol) in 15 mL of CH_2Cl_2 and triethyl amine (NEt_3) (0.67 mL, 5.0 mmol), tosyl chloride (TyCl) (0.92 g, 5 mmol) in 10 mL of CH_2Cl_2 was



Scheme 1. Synthetic route of ion-bonded PSt_2-N=N-PEO copolymer.

added dropwise at 0 °C and stirred at room temperature for 24 h. After concentration and precipitation in diethyl ether, the precipitate was collected and redissolved in CH_2Cl_2. The solution was then passed through a short neutral alumina column using CH_2Cl_2 as the eluent. After evaporating the solvent, the solution was precipitated in diethyl ether twice. The precipitate was collected and dried to afford PEO–Ty (4.60 g, yield: 89%). ^1H NMR ($CDCl_3$): $\delta = 7.79$ (d, 2H, Ar*H*), 7.33 (d, 2H, Ar*H*), 4.15 (t, 2H, TsO-C*H*$_2$–), 3.64 (m, –OC*H*$_2$C*H*$_2$O–), 3.38 (s, 3H, C*H*$_3$–O–), 2.44 (s, 3H, C*H*$_3$–Ar–).

Under N_2 atmosphere, a mixture of PEO–Ty (2.06 g, 0.4 mmol), HPB (0.33 g, 1.2 mmol) and K_2CO_3 (1.66 g, 12 mmol) in 20 mL of N,N-dimethylformamide (DMF) was stirred at 100 °C for 24 h. After filtration, the polymer solution was concentrated under reduced pressure and precipitated in diethyl ether. The solid was dissolved in CH_2Cl_2 again and filtrated to remove the excess HPB. After evaporating the solvent, the concentrated solution was precipitated in diethyl ether to provide PEO-N=N $-$ $SO_3^-K^+$. The product was then ion-exchanged using Dowen 1 × 8-400 ion-exchange resin in methanol. The polymer solution was precipitated in diethyl ether to give PEO-N=N-SO_3H (1.66 g, yield: 79%). ^1H NMR ($CDCl_3$): $\delta = 8.03$ (*d*, 2H, Ar*H*), 7.87 (*d*, 2H, Ar*H*), 7.79 (*d*, 2H, Ar*H*), 7.00 (*d*, 2H, Ar*H*), 4.23 (*t*, 2H, ArO–C*H*$_2$–), 3.64 (*m*, –OC*H*$_2$C*H*$_2$O–), 3.38 (*s*, 3H, C*H*$_3$–O–).

2.3. Synthesis of ion-bonded PSt_2-N=N-PEO

PSt_2-$N(CH_3)_2$ (400 mg) (no. 2 in Table 1) and 223 mg of PEO-N=N-SO_3H (1 mol ratio) were dissolved in 20 mL of CH_2Cl_2 and the solution was stirred at room temperature for 24 h. After concentration and precipitation in petroleum ether (bp 30–60 °C), the precipitate was collected and dried at room temperature for 3 days to afford ion-bonded PSt_2-N=N-PEO. ^1H NMR: see Fig. 1.

2.4. Preparation of micelles

PSt_2-N=N-PEO (18 mg) (no. 2 in Table 1) was dissolved in 1,4-dioxane (6 mL) and deionized water (9 ml) was added at a rate of one drop every 10 s using a syringe under vigorous stirring. The solution was then stirred at room temperature for 3 days and dialyzed against deionized water for 3 days. Finally, the micelles solution was diluted to 0.36 mg/mL (2.5×10^{-5} M).

Table 1
Data of polystyrene precursor and PSt_2-N=N-PEO.[a]

No.	PSt				A_2B copolymer	
	M_n (NMR)[b]	M_n (GPC)[c]	M_w/M_n[c]	m[d]	M_n (GPC)[c]	M_w/M_n[c]
1	6170	6150	1.17	28	7720	1.12
2	9560	9230	1.13	44	13,170	1.13
3	16,200	16,290	1.09	76	20,350	1.20

[a] The same PEO chain was used and the degree of PEO is 113.
[b] Calculated according to ^1H NMR spectra [33].
[c] Obtained from gel permeation chromatography (GPC).
[d] Degree of PSt (Scheme 1).

2.5. Characterization

^1H nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker DMX-300 instrument with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was performed at 30 °C using THF as eluent on a Waters 150C instrument equipped with 10^3, 10^4, 10^5 Å columns and a Waters refractive index detector. The UV–vis absorbance spectra were obtained with a UV-2401 PC instrument. Transmission electron microscopy (TEM) measurement was carried out on a Japan Hitachi Model H-800 microscopy.

3. Results and discussion

3.1. Synthesis of PSt_2-N=N-PEO

As stated in the introduction part, we aimed to prepare azobenzene core containing A_2B type miktoarm star copolymer composed of two hydrophobic PSt arms and one hydrophilic PEO arm. In our recent work, it has been demonstrated that ionic bond is an efficient way to construct supramolecular miktoarm star rod-coil copolymer whose components are all hydrophobic [33]. The synthetic route of ion-bonded amphiphilic PSt_2-N=N-PEO is outlined in Scheme 1. The first step is the synthesis of PEO-N=N-SO_3H, monomethoxy poly(ethylene oxide) with phenylazobenzenesulfonic acid as the terminus. Tosylation of PEO with tosyl chloride at room temperature provided PEO–Ty, as confirmed by ^1H NMR spectrum. Signals at 7.79, 7.33 and 2.44 ppm correspond to aromatic protons and methyl protons of tosylate group while signals at 4.15 and 3.38 ppm are attributed to methylene protons adjacent to tosylate group and methyl protons of monomethoxy group. The etherification was performed by stirring PEO–Ty and HPB together with K_2CO_3 at 100 °C in DMF under N_2 condition. To ensure the complete reaction of PEO–Ty, an excess of HPB was added. The product PEO-N=N $-$ $SO_3^-K^+$ was then ion-exchanged using Dowen 1 × 8-400 ion-exchange resin to afford PEO-N=N-SO_3H. The end-functionalization was proved by comparing ^1H NMR spectrum of PEO–Ty with that of PEO-N=N-SO_3H. In ^1H NMR spectrum of PEO-N=N-SO_3H, the characteristic signal at 2.44 ppm corresponding to methyl protons of tosylate group disappeared completely and new signals at 8.03, 7.87, 7.79 and 7.00 ppm ascribed to aromatic protons of azobenzene group emerged.

The next step is to prepare ion-bonded PSt_2-N=N-PEO from tertiary amino-functionalized polystyrene ($(PSt)_2$-$N(CH_3)_2$) and PEO-N=N-SO_3H based on the formation of ionic bond between –$N(CH_3)_2$ and –SO_3H. $(PSt)_2$-$N(CH_3)_2$ was previously synthesized and fully characterized [33]. The process was carried out under mild condition, at room temperature for 24 h. The amino and sulfonic acid groups were exactly adjusted at 1:1 M ratio. The formation of ionic bond and ion-bonded miktoarm star copolymer was confirmed by ^1H NMR and GPC techniques. As shown in Fig. 1B, besides the typical signals of PSt, new signal appears at 3.64 attributed to methylene protons of PEO backbone. The peaks at 7.79–8.05 ppm correspond to partial aromatic protons of azobenzene unit. The other character-

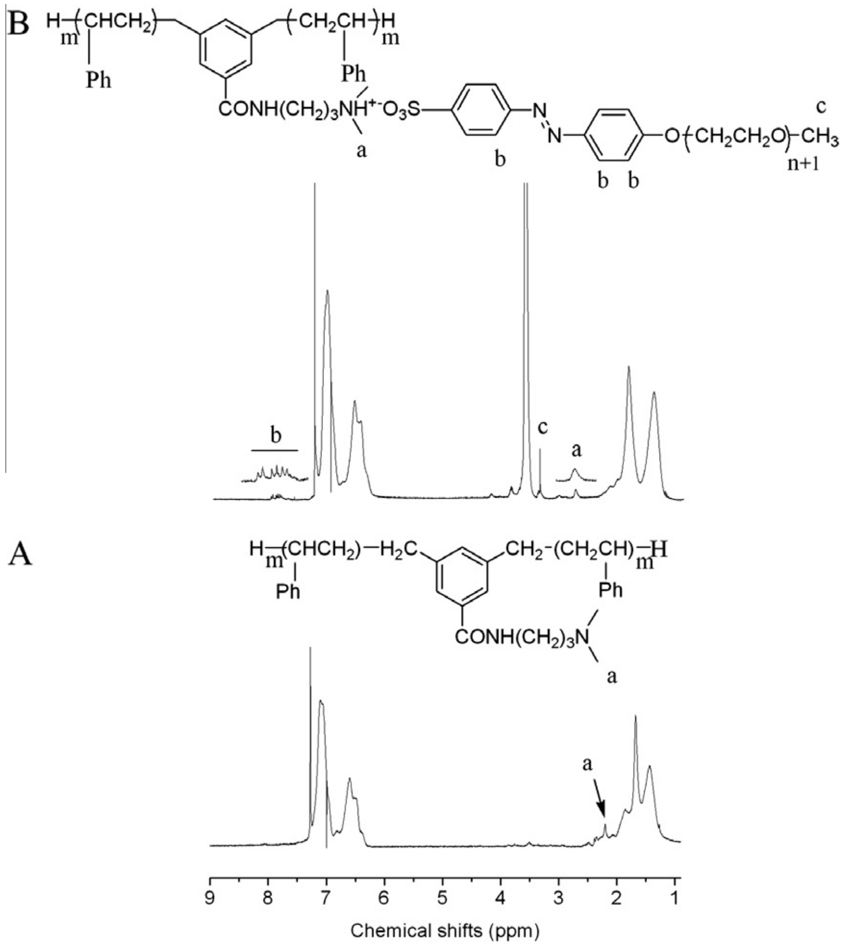


Fig. 1. ^{1}H NMR spectra of amino-functionalized PSt (A) and ion-bonded PSt$_2$-N=N-PEO copolymer (B, no. 2 in Table 1).

istic peak of aromatic protons in azobenzene unit is overlapped by the broad peaks of phenyl protons of PSt. The signal at 2.30 ppm in Fig. 1A is ascribed to methyl protons of amino group ($-N(CH_3)_2$), which is shifted to 2.76 ppm after the formation of ionic bond with sulfonic acid group ($-N(CH_3)_2H^+$) (Fig. 1B). The integral ratio of peaks at 3.38 and 2.76 ppm is 3.1:6.0, which is about 3:6 within ±5% of experiment error. GPC traces of the resulting copolymer and precursors were given in Fig. 2. The GPC peak of PEO-N=N-SO$_3$H shifts to low molecular weight side in comparison with PEO–Ty due to that sulfonic acid group interacts strongly with stationary phase. Such phenomenon was also observed in our early investigation [31]. However, GPC traces of PSt$_2$-N=N-PEO copolymers reveal only one single symmetrical peak for the miktoarm star copolymers with narrow molecular weight distribution (Table 1). This clearly shows that the ion-bonded miktoarm star copolymers were formed and no homopolymers are present. All the evidences mentioned above suggest that ion-bonded PSt$_2$-N=N-PEO containing azobenzene unit at the core was successfully synthesized from the polystyrene carrying tertiary amino group and PEO-N=N-SO$_3$H.

It is reported in the literature that proton transfer from the carboxy group of PEO to the amino group of PSt was partly hindered because of the steric effect and hydrogen bond between carboxy group and oxygen atoms of the PEO chain [29,47]. On the other hand, increasing the acid strength of guest molecules can promote the binding of

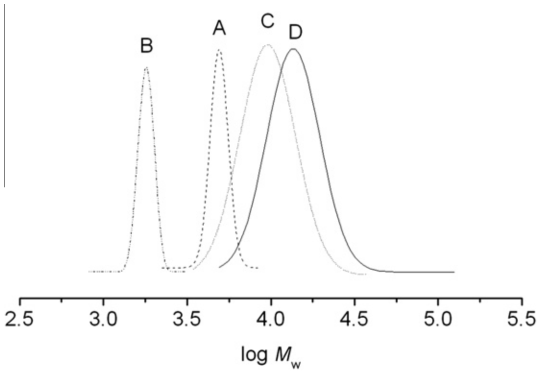


Fig. 2. GPC traces of PEO–Ty (A, $M_n = 4790$, $M_w/M_n = 1.02$), PEO-N=N-SO$_3$H (B, $M_n = 1810$, $M_w/M_n = 1.02$), amino-functionalized PSt (C, $M_n = 9180$, $M_w/M_n = 1.13$) and ion-bonded PSt$_2$-N=N-PEO copolymer (D, no. 2 in Table 1).

guest molecules and adamantyl-urea-functionalized poly(propylene imine) dendrimer to provide supramolecular dendrimers linked via ionic bond, as reported by Meijer and coworkers [48,49]. The number of guests that bind to the dendrimer is mainly governed by the acid–base interaction. For example, the amount of guests (oligo(ethylene oxide)) that bind to the dendrimer and the binding strength increased when the carboxy group was replaced by a phosphonic group [48]. Herein, we found that the formation of ionic bond between sulfonic acid group of PEO and amino group of PSt occurred effectively. Since the acidity of sulfonic acid group is much stronger than that of carboxy group [50], increasing the acid strength of functional group of PEO may promote the binding of acid and amino groups and lead the equilibrium toward the formation of amphiphilic A_2B copolymers.

3.2. Photoresponsive properties and self-assembly behavior of PSt$_2$-N=N-PEO in water

It is well known that azobenzene and their derivatives undergo conversion from trans- to cis-form under irradiation of UV light. The process could be restrainted by the aggregation of copolymers in selective solvent, in which the hydrophobic azobenzene group was entangled in the core of micelles [43,44]. Herein, photoresponsive property of the azo miktoarm star copolymers was first determined by UV–vis absorption spectrum with UV light at 365 nm in 1,4-dioxane, which is good solvent for the two components. Fig. 3 shows the photoisomerization process with the irradiation time. During the irradiation, the absorption maximum at 353 nm ascribed to π–π^* transition of trans-azobenzene was decreased and a weak band at 444 nm ascribed to n–π^* transition increased gradually. Thus, upon irradiation of PSt$_2$-N=N-PEO solution with λ = 365 nm UV light, energetically preferred trans-form changed to cis-form (photochemical isomerization procedure).

The micellization is studied in deionized water since the amphiphilic copolymers contain PEO block which is soluble in water. 1,4-Dioxane was chosen to facilitate the self-assembly as the common solvent. The aggregates were prepared by adding water to the copolymer solution in 1,4-dioxane slowly. As shown in Fig. 4, the diminution of absorption band at 254 nm attributed to phenyl groups of PSt is found, suggesting that PSt chains were aggregated as the core and micelles were formed. Moreover, the absorption maximum at 353 nm in 1,4-dioxane shifts to 349 nm in water. This 4 nm hypsochromic shift indicates the formation of the H-type (face-to-face) aggregates of azobenzene group which is located at the interface between the core and the shell of micelles.

The photoisomerization of the micelles from PSt$_2$-N=N-PEO was also studied and the results are given in Fig. 5A. Similarly, the absorption maximum at 349 nm ascribed to π–π^* transition of trans-azobenzene was decreased and a weak band at 439 nm ascribed to n–π^* transition increased gradually. The azo copolymer in 1,4-dioxane and water reached to the photostationary state with the approximately same time. However, the percentages of cis-azobenzene at the photostationary state in the two systems are different. It can be estimated from the following equation:

$$\%\mathrm{cis} = 100(A_0 - A_S)/A_0 \tag{1}$$

where A_0 is the absorbance at the absorption maximum measured before irradiation and A_S is the absorbance at the corresponding absorption wavelength at the photostationary state. The isomerization degrees of the azo copolymer in 1,4-dioxane and water are 82% and 54%, respectively. Wang et al. also reported the decrease of the isomerization degree of amphiphilic random azo copolymers, poly{2-[4-(phenylazo)phenoxy]ethyl acrylate-*co*-acrylic acid}, in water because of the polymer chain collapse and entanglement of the azobenzene unit [43,44]. In this case, the azobenzene group was arrayed at the interface between the core and the shell of the micelles after the self-assembly of the amphiphilic copolymer in water. The isomerization was hindered by the confinement of azobenzene group at the interface of micelles as well as the π-stacking of azobenzene group (H-aggregates). Thus, the isomerization degree of the azo copolymer in water is lower than that in 1,4-dioxane, in which the copolymer is molecularly dissolved.

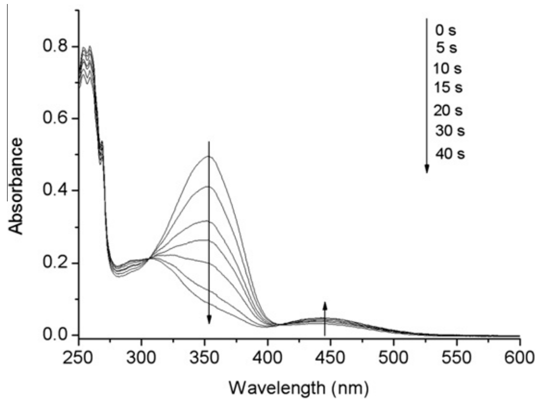


Fig. 3. UV–vis absorption changes of PSt$_2$-N=N-PEO (no. 2 in Table 1) in 1,4-dioxane (2.5×10^{-5} M) under the irradiation with 365 nm UV light at room temperature.

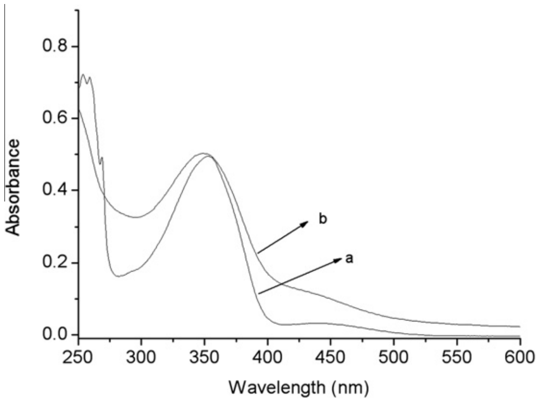


Fig. 4. UV–vis absorption of PSt$_2$-N=N-PEO (no. 2 in Table 1) in 1,4-dioxane (2.5×10^{-5} M, a) and water (2.5×10^{-5} M, b) before irradiation.

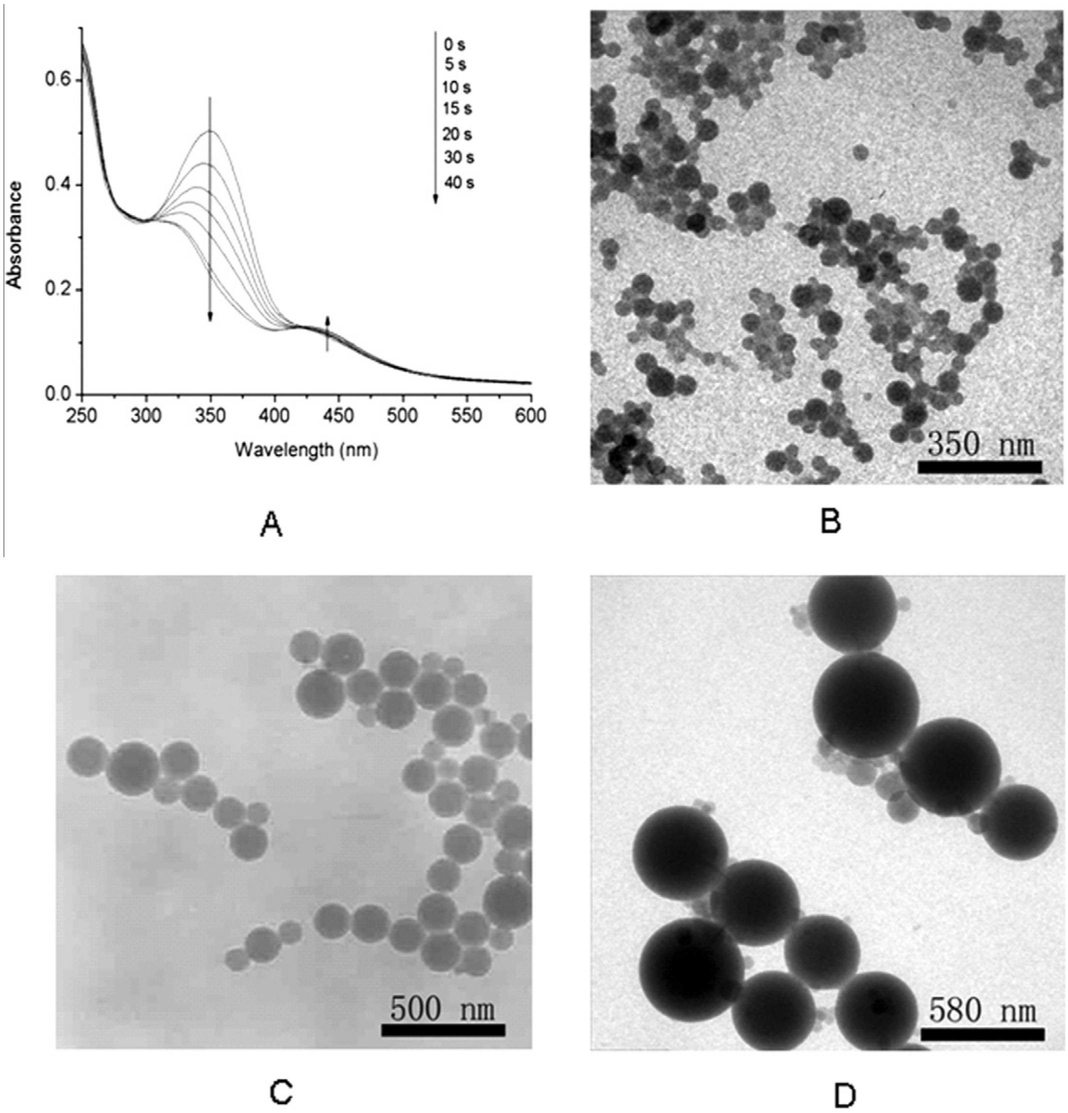


Fig. 5. UV–vis absorption changes of PSt_2-N=N-PEO in water under the irradiation with 365 nm UV light at room temperature (A, no. 2 in table, 2.5×10^{-5} M) and TEM image of the micelles obtain from the self-assembly of PSt_2-N=N-PEO with different molecular weight of PSt (B, no. 1 in table; C, no. 2 in table; C, no. 3 in table).

The morphology of the micelles was characterized by transmission electron microscopy (TEM). All the miktoarm star copolymers shows solid spherical particles formed from the self-assembly in deionized water. As exhibited in Fig. 5, the diameter of the particles increases with increasing the molecular weight of PSt block. For example, the diameters of sample 1 and sample 2 are in the range of 20–95 and 64–210 nm, respectively. Sample 3 is mainly composed of large compound micelles with the diameter in the range of 315–560 nm. The morphology of micelles after UV irradiation was also characterized by TEM. However, no obvious change was found. This may be attributed to that the azobenzene groups in the star polymers are minor and very local. The micelle solution is stable over 6 months. It should be noted that ionic bond is sensitive to the ionic strength, when 0.10 M NaCl aqueous solution was used as poor solvent instead of deionized water, only precipitate was obtained instead of spherical micelles. This phenomenon indicated that ionic bond plays the important role in the formation of organized aggregates.

4. Conclusions

In summary, a novel ion-bonded amphiphilic A_2B miktoarm star copolymers containing and azobenzene group at the core, PSt_2-N=N-PEO, has been designed and successfully synthesized. The resulting copolymers possess well-defined structure, controlled molecular weight, and narrow molecular weight distribution, which were confirmed by ^{1}H NMR and GPC. The amphiphilic copolymers form solid spherical micelles with azobenzene group located at the interface between the shell and the core of the spheres after self-assembly in water and the diameter increased with increasing the molecular weight of PSt. The photoisomerization of the azo copolymers in water was hindered by the confinement and the π-stacking of azobenzene group (H-aggregates) located at the interface between the core and the shell of the micelles. This is the first detailed studies on the self-assembly of supramolecular amphiphilic star copolymers linked via ionic bond in selective solvent.

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