Vesicles Prepared from Supramolecular Block Copolymers

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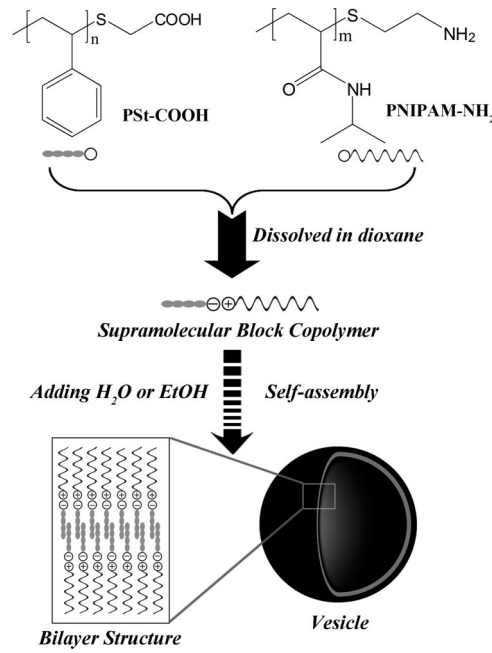
ABSTRACT: Polymeric vesicles were prepared through self-assembly of amphiphilic supramolecular block copolymers (SBP). Hydrophilic poly(*N*-isopropylacrylamide) with amino end groups (PNIPAM-NH_2) and hydrophobic polystyrene with carboxylic end groups (PSt-COOH) were prepared by free radical polymerization using cysteamine hydrochloride and thioglycolic acid as chain transfer reagents, respectively. These two polymer chains could be connected through the ionic interaction of the amino groups and carboxylic groups in dioxane to form an amphiphilic SBP. The self-assembly behavior of SBP was investigated in dioxane/H_2O and dioxane/ethanol systems. In the dioxane/H_2O system, these amphiphilic SBP could self-assemble to form spherical vesicles. In the dioxane/ethanol system, the morphologies of the formed aggregates were dependent on the SBP concentration. As the SBP concentration increased from 0.01 to 0.075 g mL^{-1}, the aggregates changed from wormlike vesicles to spherical vesicles. A temperature-induced morphological transition was observed in the dioxane/ethanol system. Increasing the temperature of the wormlike vesicular solution led to the transformation of the aggregates from wormlike vesicles to spherical vesicles.

Introduction

In recent years, polymeric vesicles have gained much attention due to the variety of potential applications, such as pharmaceuticals, biomimetic materials, and cosmetics.[1−6] The polymeric vesicles were mostly prepared via self-assembly of the amphiphilic block copolymers.[1,2,7,8] To prepare these amphiphilic block copolymers, important advances have been made in the past few decades. Various polymerization techniques such as anionic,[9] controlled radical,[10] group transfer,[11] and metathesis polymerization[12,13] have all been used successfully to prepare the block copolymers. All of these techniques are based on the concept of using covalent bonds to connect the substructural polymer blocks. On the other hand, developments in the field of supramolecular chemistry, particularly those concerning noncovalent interactions, provide an alternative concept for preparing copolymers with specific architectures. Pioneering work by several research groups has shown that polymers functionalized with specific groups can further self-assemble and form a supramolecular organization of macromolecules via noncovalent interactions of these groups, such as ionic interactions,[14−16] hydrogen bonds,[17−23] and metal−ligand interactions.[24] Based on this concept, several polymer chains with specific end groups can combine with each other to form supramolecular block copolymers (SBPs) through the supramolecular interactions of these end groups.[14,25−27] For instance, Schubert's group have prepared hydrophilic and hydrophobic blocks with terpyridine end groups, and combined these two blocks to form an SBP via metal−ligand interactions.[28,29] It was found that these SBPs could self-assemble to form micelles in selected solvents. However, the synthetic strategies of these end functionalized polymers are complicated, and the preparation of vesicles from these SBPs has not yet been reported. Furthermore, the detailed self-assembly behavior of these SBPs and the morphological control of the as-formed aggregates have not been widely investigated. Therefore, exploring a facile way to synthesize SBPs and utilize them to prepare polymeric vesicles remains a challenge. A detailed investigation of the self-assembly behavior of SBPs in selected solvents is therefore necessary.

The chain transfer reaction in free radical polymerization provides a facile and high-yield way to prepare end functionalized polymers.[30] Herein, hydrophilic poly(*N*-isopropylacrylamide) with amino end groups (PNIPAM-NH_2) and hydrophobic polystyrene with carboxylic end groups (PSt-COOH) were prepared by free radical polymerization using cysteamine hydrochloride and thioglycolic acid as chain transfer reagents, respectively. As shown in Scheme 1, when dissolving the two end functionalized polymers in a suitable cosolvent, the ionic interaction of the -NH_2 groups and -COOH groups would cause the two polymers to combine to form the corresponding SBP.

Scheme 1. Schematic Illustration of Vesicle Formation from SBP



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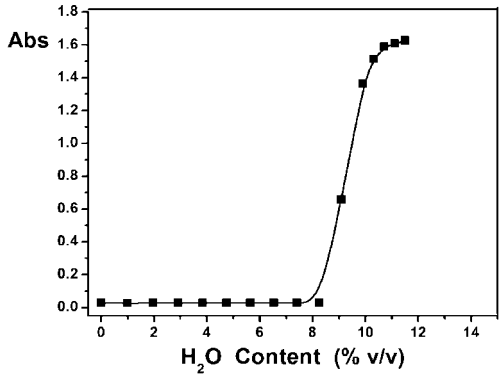


Figure 1. Turbidity diagram of the SBP (0.01 g mL^{-1}) in a dioxane/H_2O system.

As conventional block copolymers, these SBPs could also self-assemble to form vesicular aggregates in both dioxane/H_2O and dioxane/ethanol systems. The dependence of the morphological transition of the vesicular aggregates on the polymer concentration and temperature has also been investigated in the dioxane/ethanol system.

Results and Discussion

Preparation and Characterization of the End Functionalized Polymers. The hydrophilic poly(*N*-isopropylacrylamide) with amino end groups (PNIPAM-NH_2) and hydrophobic polystyrene with carboxylic end groups (PSt-COOH) were prepared by free radical polymerization using cysteamine hydrochloride and thioglycolic acid as chain transfer reagents, respectively. The element analysis shows that the sulfur contents of the PNIPAM-NH_2 and PSt-COOH are 0.34 wt % and 0.14 wt %, respectively. This result indicates that the two polymers are end functionalized. GPC measurements of PNIPAM-NH_2 and PSt-COOH revealed weight-average molecular weights (M_w) of 9976 and 16732, respectively, and polydispersity indices of 2.76 and 1.66, respectively.

Self-Assembly of the SBP in the Dioxane/H_2O System. The phase separation behaviors of PNIPAM-NH_2 and PSt-COOH were investigated in the dioxane/H_2O system. PNIPAM-NH_2 and PSt-COOH (molar ratio: 1/1) were first dissolved in dioxane with polymer concentrations of 0.01 g mL^{-1}, and then deionized water was added to this polymer solution to the desired water content. The turbidity diagram (Figure 1) shows that the critical water content (CWC) was about 8% (v/v). When the water content was above the CWC, the absorbance increased dramatically, indicating that the polymers self-assembled to form aggregates. The aggregates were investigated by transmission electron microscopy (TEM) analysis. From the TEM image (Figure 2A), it could be seen that the aggregates display a vesicular structure of about 100 nm in diameter, and the coronas and walls of the vesicles could be easily distinguished (Figure 2B). The vesicular structure was also confirmed by freeze fracture TEM analysis (Figure 2C). It is also clearly shown that the membrane of the vesicle shows a bilayer structure (Figure 2B), which is similar to the structure formed by conventional polystyrene-*block*-poly(*N*-isopropylacrylamide) (PSt-*b*-PNIPAM) in a THF/H_2O system.[31] However, the two block polymers of PSt-*b*-PNIPAM are connected via covalent bonds, while in the present work, PSt-COOH and PNIPAM-NH_2 dissolved in dioxane connect with each other through ionic interactions to form an SBP. As shown in Scheme 1, when water is added into the polymer solution, the PSt-COOH blocks aggregate to form the walls of the vesicles, while the PNIPAM-NH_2 blocks are anchored around the PSt-COOH walls through ionic bonds to form the corona and maintain the stability of the vesicles. It should be noted that, as the ionic bonds are nonfixed bonds, the two blocks could be exchanged between different supramolecular block copolymers, so these supramolecular block copolymers just dynamically exist. It is well-known that the ionic strength of the solution could weaken the strength of the ionic bonds, so the number of the dynamically formed supramolecular block polymers was reduced. When using 0.075 M NaCl solution instead of the pure water to be the poor solvent, only precipitate was obtained instead of the vesicles. This result indicated that the ionic bonds play important roles in the formation of the ordered polymer organizations, the supramolecular block copolymers, and only these dynamically formed supramolecular block copolymers could self-assemble to form the vesicles.

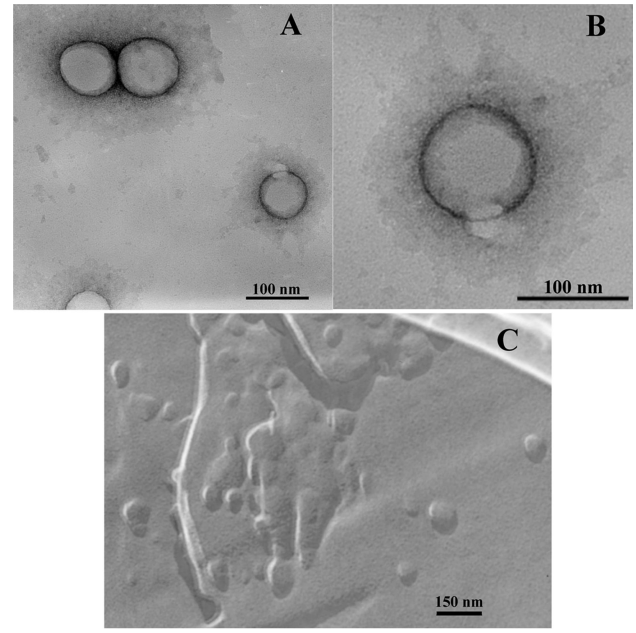


Figure 2. TEM (A and B) and freeze fracture TEM (C) images of the vesicles.

Table 1. Data from the ζ-Potential and Light Scatting Analyses before and after Treatment with NaOH

analysis	as-prepared	treated with NaOH
ζ-potential	0.5 mV	−7.7 mV
polydispersity index	0.08	0.07

The ζ-potential and size distribution of the vesicles in aqueous solution were investigated through ζ-potential analysis and light scatting investigation, respectively. The experiments showed that the ζ-potential of the vesicles is about 0.5 mV, while after the vesicular solution was treated with NaOH, the ζ-potential decreased to about −7.7 mV. When the vesicles were treated with NaOH, the ionic bonds formed between the -NH_2 and -COOH groups were broken, causing the -COOH groups to ionize. The PNIPAM-NH_2 blocks, which are the coronas of the vesicles, were disassociated, leaving behind ionized carboxylic groups on the surfaces of the vesicles and resulting in a decrease in the ζ-potential (Table 1). This result confirms that the SBPs self-assemble to form aggregates with an ordered bilayer structure. The light scatting investigation shows that the polydispersity index (PDI) of the vesicles is 0.08, which indicates that the vesicles have a relatively narrow size distribution. Though the GPC measurement has already shown that both of the polymers are polydisperse, it is possible that the vesicle membrane could be a more interdigitated structure, rather than a bilayer with a well-defined midplane,[1] so that the formed vesicles still could be monodisperse.

It was found that the size of the vesicles was dependent on the concentration of the SBP. Figure 3 shows the variation of

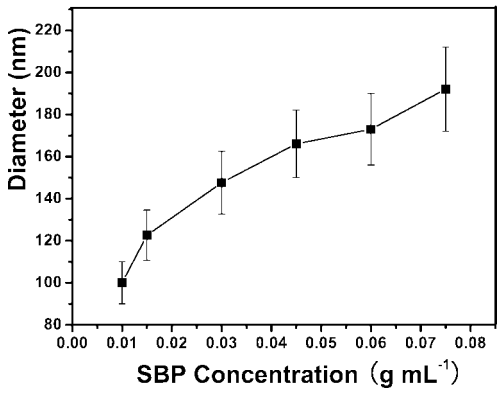


Figure 3. Influence of SBP concentration on the diameter of the vesicles.

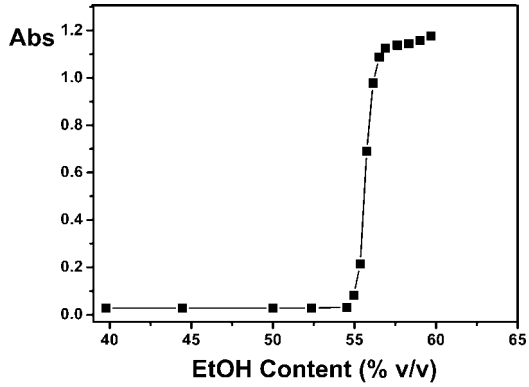


Figure 4. Turbidity diagram of the SBP (0.01 g mL^{-1}) in a dioxane/ethanol system.

the hydrodynamic diameters for the vesicles obtained at different concentrations but with a fixed water content (8% v/v). It could be seen that, as the concentration of the SBP increased from 0.01 to 0.075 g mL^{-1}, the hydrodynamic diameter of the obtained vesicles also increased from about 100 to 200 nm. As the polymer concentration increased, more supramolecular block copolymers were formed, and the average aggregation number of the vesicles could be increased.

Self-Assembly of the SBP in the Dioxane/Ethanol System. The self-assembling behavior of the SBP was also investigated in the dioxane/ethanol system. The turbidity diagram (Figure 4) shows that the critical ethanol content (CEC) is about 54% (v/v), which is much higher than the CWC. As is well-known, though ethanol is a poor solvent for PSt blocks, it is a better solvent than H_2O. Consequently, PSt blocks are more soluble in ethanol than in water, and a higher ethanol content was needed for the phase separation.

TEM and SEM analyses indicate that SBPs aggregate to form vesicles whose morphologies are dependent on the concentration of SBP. The TEM and SEM images of the aggregates formed at various SBP concentrations are shown in Figure 5. At a low polymer concentration (0.01 g mL^{-1}), besides a few spherical vesicles, most of the aggregates show wormlike vesicular structures (Figure 5A). At a median polymer concentration (0.03 g mL^{-1}), as shown in Figure 5B, more spherical vesicles were observed, and the formed wormlike vesicles were shorter than the ones formed at 0.01 g mL^{-1}. At a high polymer concentration (0.075 g mL^{-1}), all of the aggregates show spherical vesicular structures, and no wormlike vesicles were found (Figure 5C).

A temperature-induced morphological transition of the vesicular aggregates was observed in the dioxane/ethanol system

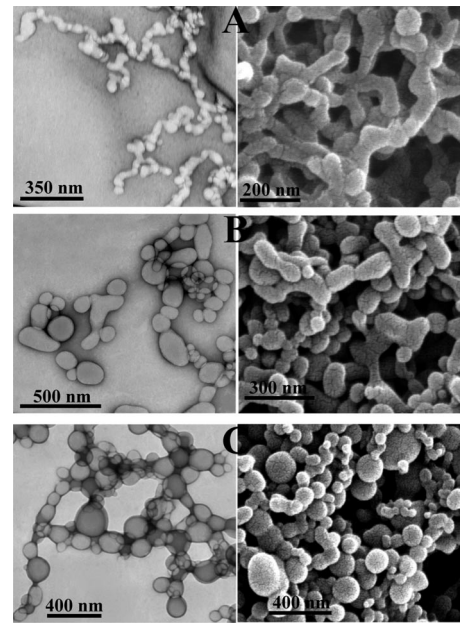


Figure 5. TEM and SEM images of the vesicular aggregates at different SBP concentrations (A, 0.01 g mL^{-1}; B, 0.03 g mL^{-1}; C, 0.075 g mL^{-1}) in a dioxane/ethanol system.

via TEM and SEM analyses. It was found that the wormlike vesicles formed at the low SBP concentration could be transformed to spherical vesicles via increasing the temperature of the wormlike vesicular solution. Figure 6 shows the morphological changes induced by increasing temperature for a system with a 0.01 g mL^{-1} polymer concentration and a 54% (v/v) ethanol content. At 30 and 40 °C, the morphologies of the aggregates were mostly wormlike vesicular structures, as shown in Figure 6A and B, respectively. When the temperature was increased to 50 °C, spherical vesicles with polydispersity were formed exclusively (Figure 6C), and finally, at 60 °C, monodisperse spherical vesicles were obtained (Figure 6D). It should be noted that the observed morphological transition is not reversible, and that the spherical vesicles formed at high temperature could not be transformed back to wormlike vesicles when the temperature was cooled back to room temperature. This irreversible transition indicates that the spherical vesicular structure is more stable than the wormlike vesicular structure for the aggregates in ethanol. The mechanism of the temperature-induced morphological transition could also be deduced from the SEM analysis. From the SEM image at 50 °C (the rectangular part of Figure 6C), we could find an intermediate state of the transition which shows how the wormlike vesicles change to form spherical vesicles. It could be seen that the wormlike vesicles are "cut" to form several conterminous small pieces, which do not have a regular sphericity. When the temperature was increased to 60 °C, these small pieces were further transformed to form relatively monodisperse spherical vesicles. As is well-known, PSt chains are more flexible in ethanol at high temperatures, so that the PSt chains of the SBPs could reorganize to form more stable structures. As illustrated in Scheme 2, at 50 °C, this temperature is just high enough for the partial reorganization of PSt chains, so the aggregates maintain an intermediate morphology (irregular spherical vesicles); while at 60 °C, this temperature is already high enough for the thorough reorganization of the PSt chains to form the more stable structures (regular spherical vesicles). This morphological transition coincides with the conclusion from the work on the self-assembly behavior of the polystyrene-*b*-poly(acrylic acid) by Eisenberg's group.[32,33] It was reported that the better the solvent for the PSt blocks (the solvent quality of ethanol

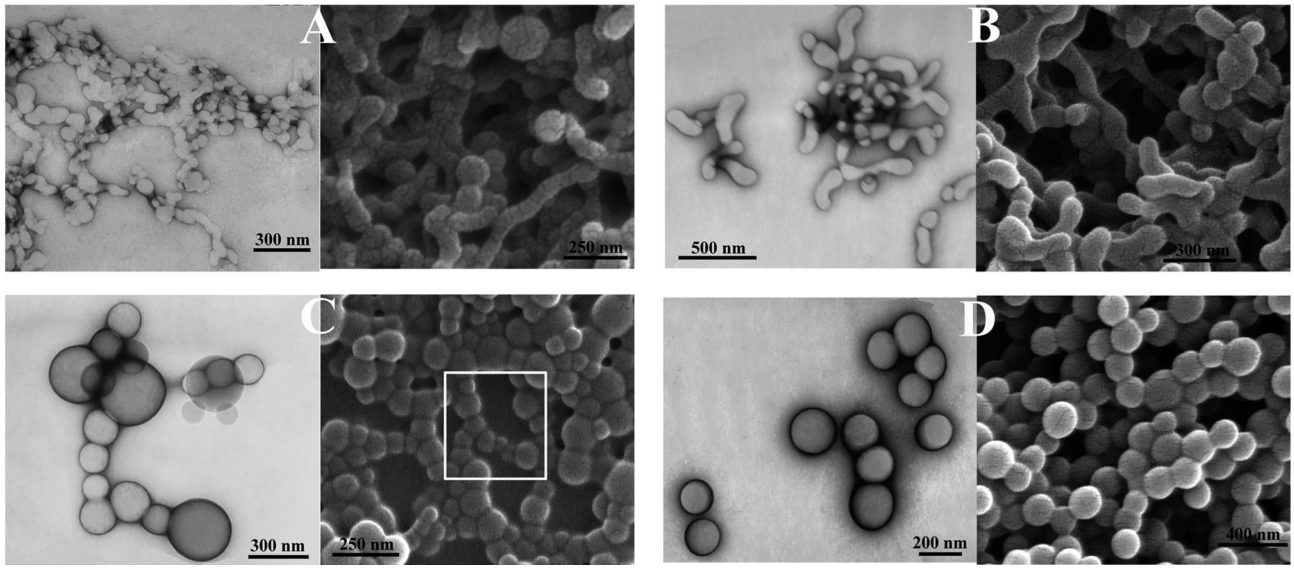
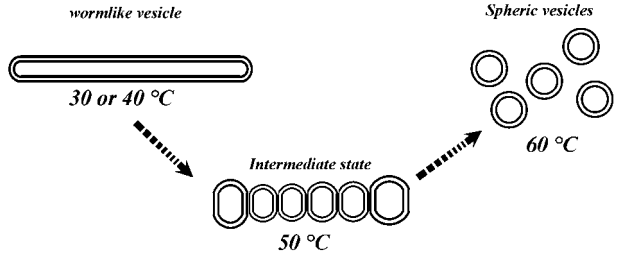


Figure 6. TEM and SEM images of the vesicular aggregates treated at 30 (A), 40 (B), 50 (C), and 60 °C (D).

Scheme 2. Schematic Illustration of the Morphological Transition in Dioxane/Ethanol System



improves as the temperature increases), the more likely it is to form spherical aggregates.

Light scatting analysis of the vesicular solution treated at different temperatures could also prove the temperature-induced morphological transition observed in the TEM and SEM analyses. Figure 7 shows the size distribution of the vesicular solution treated at different temperatures. At 30 (Figure 7A) and 40 °C (Figure 7B), the vesicular aggregates in the solution are polydisperse, and the PDI of the aggregates at the two temperatures are 0.94 and 0.45, respectively. Because of the aggregation of the wormlike vesicles, large aggregates (diameters above 500 nm) are also observed. When the temperature is increased to 50 °C, as shown in Figure 7C, the vesicular aggregates in the solution are less polydisperse (PDI: 0.15). Only small aggregates with diameters of around 200 nm are observed, and the big aggregates disappear. This result indicates that the wormlike vesicles are transformed to form small pieces, which coincides with the results from the TEM and SEM analyses. At 60 °C, only small aggregates with relative monodispersity (PDI: 0.07) are observed (Figure 7D). This result indicates that the polydisperse small pieces are further transformed to form relatively monodisperse spherical vesicles, as confirmed by TEM and SEM analyses.

It should be noted that, the temperature-induced morphological transition in the dioxane/ethanol system was not observed in the dioxane/H_2O system, which may result from the difference in the solubilities of the PSt blocks in H_2O and ethanol. Though ethanol is a poor solvent for PSt blocks, it is a better solvent than H_2O and much better at high temperatures. Consequently, the morphology of the aggregates in the dioxane/ethanol system could be changed through the reorganization of the PSt blocks, while in the dioxane/H_2O system, as the PSt blocks are highly

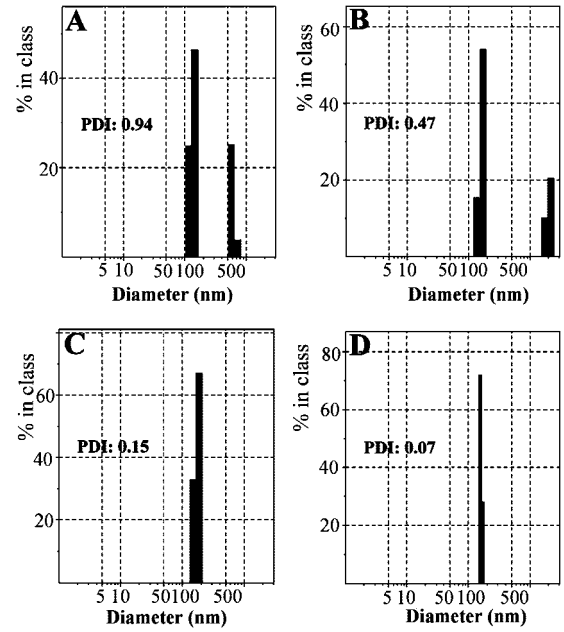


Figure 7. Size distribution of the vesicular aggregates treated at 30 (A), 40 (B), 50 (C), and 60 °C (D).

"frozen" in the presence of H_2O, the spherical vesicular structure of the aggregates could be maintained despite the variation in temperature.

Conclusion

In conclusion, end functionalized polymer blocks of PSt-COOH and PNIPAM-NH_2 were prepared by the chain transfer reaction in free radical polymerization. These two polymer chains could be connected through the ionic interaction of the amino groups and carboxylic groups to form an amphiphilic supramolecular block copolymer (SBP). These SBPs could self-assemble to form vesicles both in dioxane/H_2O and dioxane/ethanol systems. In the dioxane/H_2O system, spherical vesicles were obtained, and the size of these vesicles could be controlled by modulating the SBP concentration. In the dioxane/ethanol system, the morphologies of the formed aggregates were dependent on the SBP concentration. As the SBP concentration increased from 0.01 to 0.075 g mL^{-1}, the aggregates changed

from wormlike to spherical vesicles. A temperature-induced morphological transition was observed in the dioxane/ethanol system. The wormlike vesicles could be transformed to form monodisperse spherical vesicles by increasing the temperature of the solution. In this study, instead of using complex controlled living polymerization, all of the end functionalized polymers were prepared by the simple and high-yield free radical polymerization method. The size and morphology of the vesicles could be controlled by modulating the concentration of SBP and the temperature of the solution. This strategy based on the supramolecular technique provides a facile way to prepare polymeric vesicles.

Experimental Section

Synthesis of the End Functionalized Polymers. For the preparation of PSt-COOH, styrene (10.4 g) thioglycolic acid (0.46 g; **Caution!** It is toxic and caustic), and the initiator AIBN (0.164 g) were dissolved in 50 mL of dioxane. After the solution was purged with nitrogen for 20 min, the vessel was sealed and the polymerization was allowed to proceed at 60 °C for 24 h. The polymers were precipitated by adding excess ethanol, and purified by dissolving in dioxane and precipitating with ethanol for 2 times. The purified polymers were dried in vacuum at 50 °C for several hours. For the preparation of PNIPAM-NH_2, *N*-isopropylacrylamide (3.39 g) cysteamine hydrochloride (0.1703 g) and AIBN (0.0492 g) were dissolved in 50 mL of ethanol. After the solution was purged with nitrogen for 20 min, the vessel was sealed and the polymerization was allowed to proceed at 60 °C for 24 h. After the solution was condensed to about 20 mL, KOH (0.084 g; dissolved in 10 mL ethanol), and anhydrous Na_2SO_4 (3 g) were added into the solution. After 3 h, the solution was filtrated and the polymers in the filtrate were precipitated by petroleum ether. The polymers were purified by dissolving in dioxane and precipitating with petroleum ether two times. The purified polymers were dried in vacuum at 50 °C for several hours.

Turbidity Diagram. PSt-COOH (0.15 g) and PNIPAM-NH_2 (0.1 g) were dissolved in 25 mL of dioxane. The deionized water (or ethanol) was dropwise added into the polymer solution to the desired water (or ethanol) content. The turbidity measurement was carried out at 500 nm by the UV/vis spectrophotometer.

Preparation of the Vesicles. Two solvent systems were used for the preparation of vesicles. The first one is dioxane/water system, and the second one is dioxane/ethanol system. For the dioxane/water system, PSt-COOH and PNIPAM-NH_2 (mass ratio, 3/2; molar ratio, 1/1) were dissolved in dioxane to the desired polymer concentration (0.01−0.075 g mL^{-1}). The deionized water was dropwise added into the polymer solution to 8% (v/v) water content. Then the solution was quenched into excess water (20-fold) to quickly vitrify the PSt blocks. A little precipitate in the solution was filtrated to obtain the final vesicle solution. For the dioxane/ethanol system, PSt-COOH and PNIPAM-NH_2 (mass ratio, 3/2; molar ratio, 1/1)) were dissolved in dioxane to the desired concentration (0.01−0.075 g mL^{-1}). Ethanol was added dropwise into the polymer solution to 54% (v/v) ethanol content. Then the solution was quenched into excess ethanol (20-fold) to vitrify the PSt blocks.

Temperature-Induced Morphological Transition. The wormlike vesicles were first prepared. PSt-COOH (0.15 g) and PNIPAM-NH_2 (0.10 g) were dissolved in 25 mL of dioxane. Ethanol was dropwise added into the polymer solution to 54% (v/v) ethanol content. Then the solution was quenched into excess ethanol (20-fold) to obtain the wormlike vesicular solution. The wormlike vesicular solution was sealed and kept in water bath at desired temperature (30, 40, 50, and 60 °C). After 3 h, the solution was cooled to room temperature freely.

TEM Analysis. TEM images were obtained by using a JEM200CX transmission electron microscope operating at 160 kV. The preparation of the samples for TEM measurement was as follows: one drop of vesicular solution was put onto a carbon-coated copper grid and was stained with uranyl acetate. Then the sample was dried freely at room temperature.

Freeze Fracture TEM. A small amount of sample was placed on a thin copper sheet and rapidly quenched in liquid nitrogen. Fracturing and replication were carried out in a freeze-fracture apparatus (Balzers BAF 400D) at a temperature of −140 °C. Pt/C was deposited at an angle of 45°. The replicas were washed with deionized water and then observed with a JEM200CX transmission electron microscope.

SEM Analysis. SEM images were obtained using a Hitachi S-4300 scanning electron microscope. A drop of vesicle solution was placed on the aluminum stub and dried at the room temperature, then sputter-coated with gold.

Light Scatting Analysis. The hydrodynamic diameters and polydisperse indices of the vesicles were determined using a Malvern Zeta Nano-ZS system.

ζ-Potential Analysis. The ζ-potential of the vesicles was investigated using a Malvern Zeta Nano-ZS system.

Supporting Information Available: ζ-Potential profile of the vesicles prepared from dioxane/H_2O system. This material is available free of charge via the Internet at http://pubs.acs.org.

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