Self-assembly of polystyrene-b-poly(4-vinylpyridine) in deoxycholic acid melt

Cheng-Hao Yu, Yu-Hao Chuang, Shih-Huang Tung*

Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

ABSTRACT

It is well known that amphiphilic block copolymers in selective solvents self-assemble into micellar structures, where solvophilic blocks tend to contact with solvents while solvophobic blocks are shielded from the solvents. Different from the conventional micellization in liquid systems, we report that the block copolymer, polystyrene-b-(4-vinylpyridine) (PS-b-P4VP), can self-assemble in melted deoxycholic acid (DCA) at high temperatures and the structures are retained in "solid state" after being cooled down to room temperature. Probing by transmission electron microscopy (TEM), we found that a series of self-assembled structures, including spherical micelles, wormlike micelles and vesicles can be obtained by varying the length of the block copolymers and the morphologies are dependent on the annealing temperature and time. We also demonstrate how to extract the structures that are trapped in solid state by removing DCA using appropriate solvents. The extracted vesicles, which are loaded with solid molecules, are potential for applications in nanocapsules and controlled release.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Amphiphilic molecules, such as surfactants or lipids, which are molecules with distinct hydrophilic and hydrophobic portions can spontaneously organize into structures in aqueous or organic solutions [1]. Much similar to amphiphilic molecules, block copolymers comprised of two or more homopolymers linked by covalent bonds, when dispersed in selective solvents, self-assemble into a variety of structures due to the interplay of solvents with the solvophilic and solvophobic blocks [2–9]. One major difference between surfactants and block copolymers is their molecular weight: common surfactants have ∼ 10-carbon alkyl tails while block copolymers typically have tens or more repeat units. Upon micellization, surfactants are able to rapidly exchange between the micellar state and the unimer state in solvents due to their low molecular weight and furthermore, the alkyl tails are liquid-like in the aggregates so that the structures can adopt shapes with minimum free energy [10]. The exchange process, however, is very slow for block copolymers since the thermal energy in mild conditions is insufficient to transfer bulky chains from micelles into solvents [11]. In other words, the entropic gain of mixing solvophobic chains with solvents is quite small compared to the free energy loss of breaking structures. Thus, once self-assembled structures are formed, they are more or less locked, which implies that more structures other than those commonly seen in surfactant systems can be kinetically frozen during micellization [6]. Moreover, the long chains could lead to entanglements, which in turn reduces the chain mobility and enhances the mechanical properties of the structures [12]. The designable molecular architectures, the kinetic stability and the robustness of the self-assembled structures provide block copolymers the potency for applications in nanomaterial synthesis [13–16] and control release [5,17].

While most micellization of block copolymers were studied in liquid aqueous or organic media near room temperature, a couple of systems have been reported in special conditions. He et al. reported the amphiphilic block copolymer, polybutadiene-b-poly(ethylene oxide), form micelles and vesicles in ionic liquids and their shapes are dependent on the length of PEO block [18]. Several groups have created block copolymer micelles and vesicles in supercritical fluids at high pressure, such as CO_2 [19–21]. Supercritical fluids were then vented and the structures formed at high pressure retained after being re-dispersed in analogous selective solvents under ambient conditions. In addition to the above fluidic systems, the micellization of block copolymers was found in polymeric media [22,23]. When blending block copolymers with a large amount of homopolymers which are compatible with one of the blocks, the homopolymers mix with the compatible block while repel the others above the glass transitions of the polymers, leading to the micellization of block copolymers. Kinning et al. has reported

a variety of structures, including spherical micelles, wormlike micelles and vesicles, in polystyrene-*b*-polybutadiene/polystyrene blends [24]. Note that polystyrene is in glassy state at room temperature, which means that the structures formed in melted state can be trapped in solids after cooling down. Moreover, the introduction of polystyrene block covalently bonded with polybutadiene promotes the dispersion of polybutadiene in originally immiscible polystyrene. This strategy is useful to produce well-dispersed composites and can efficiently improve the properties of homopolymers [25].

In this study, we produced self-assembled structures by a new route, that is, instead of liquid and polymeric media, a low-mass molecule which is a crystalline solid at room temperature was used as a "solvent." The molecule we used is a bile acid, deoxycholic acid (DCA), whose structure is schemed in Fig. 1. The melting temperature of DCA is 175 °C. Since the hydroxyl and carboxyl groups lie on the same side of the four-ring structure (steroid ring), DCA is an unusual amphiphiles: unlike typical surfactants, which present a polar head and a non-polar tail, DCA is a facial amphiphile, with a polar and a non-polar face [26]. We mixed polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) in a large amount of DCA and heated it above the melting temperature of DCA. Interestingly, PS-*b*-P4VP self-assemble in DCA melt and the structures formed at high temperature could be retained in crystalline solids after being cooled down to room temperature.

The supramolecules formed by block copolymers and low-mass molecules via secondary bonding, such as hydrogen bonding and electrostatic interactions, have been widely studied, especially the PS-*b*-P4VP-based systems [27–29]. The microphase separation behaviors of block copolymers were tailored by the addition of low-mass molecules due to the association of the molecules with one of the blocks and more interestingly, many hierarchical structure-*within*-structure morphologies were observed. In such systems, the amounts of added low-mass molecules are normally in stoichiometric ratio to the repeat units of the associated block. The present system, in a sense, can be regarded as an extension of the supramolecular assembly, where various structures different from those in conventional block copolymer-based supramolecules are formed in the presence of a much greater amount of low-mass molecules which similarly interact with one of the blocks. Since the self-assembly process in this system is very slow, it provides a platform to study the evolution of the structures.

In addition to the scientific curiosity about the mechanism of the self-assembly, this technique provides some advantages over others in applications. For example, low-mass molecules here serve as "solvent" that can fill the entire enclosed portions of vesicles, which may give high encapsulation efficiency of the low-mass molecules in vesicles. Furthermore, since low-mass molecules inside the vesicles are protected by bilayers while the exterior ones can be washed away by proper solvents, the vesicles filled with low-mass molecules can be extracted in an intact form. We will show that the PS-*b*-P4VP structures in solid DCA can be successfully extracted by alcohol or sodium hydroxide (NaOH) aqueous solutions.
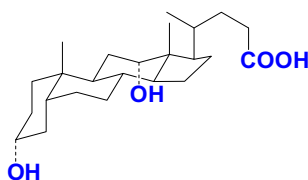
2. Experimental section

2.1. Materials

PS(40000)-*b*-P4VP(5600) (PDI = 1.09), PS(41500)-*b*-P4VP-(17500) (PDI = 1.07) and PS(20000)-*b*-P4VP(17000) (PDI = 1.08) were purchased from Polymer Source Inc. Deoxycholic acid (DCA) was purchased from Sigma Aldrich. Tetrahydrofuran (THF) was purchased from Mallinckrodt Chemicals. All chemicals were used as received.

2.2. Sample preparation

The diblock copolymer PS-*b*-P4VP and DCA were first dried in vacuum oven for 1 day and then dissolved in THF with desired amounts, followed by stirring for 2 days at room temperature. After well-mixed, the polymer/DCA solutions were placed in Teflon beakers covered by an inverted dish and THF was allowed to evaporate slowly at room temperature for several days. Samples were further dried and annealed in an oven purged with nitrogen at 175 °C or 185 °C for 1–4 days. After being annealed, the samples were either quenched in liquid nitrogen or slowly cooled down to room temperature. The morphologies are basically the same using these two cooling processes, as described later in the paper. The samples of PS-*b*-P4VP without DCA were also dissolved in THF first and after the removal of THF, the samples were annealed at 175 °C for 2 days. The characteristics of all samples used in this paper were listed in Table 1.

2.3. Fourier transform infrared spectra (FT-IR)

FT-IR samples were prepared by mixing ground powders of PS-*b*-P4VP/DCA mixtures in KBr with a ratio of 1:30. The spectra were recorded in the transmission mode at room temperature by a PerkinElmer Spectrum 100 Model FT-IR spectrometer.

2.4. Transmission electron microscopy (TEM)

Pieces of non-annealed or annealed solid samples were embedded in resin and cured at 60 °C overnight and then were sectioned to a thickness ∼ 80 nm. The thin sections were exposed to iodine vapor for 2 h that selectively stains the P4VP block to enhance the contrast. To image the extracted structures, a small piece of self-assembled PS-*b*-P4VP/DCA mixtures was placed in methanol, ethanol or NaOH aqueous solutions where DCA was dissolved while the structures were suspended. The solutions were further diluted and then dropped onto a carbon-coated copper grid, followed by air-drying before imaging was conducted. TEM images were collected on a Joel JEM-1230 transmission electron microscope at an accelerating voltage of 100 kV.

Fig. 1. Molecular structure of deoxycholic acid (DCA). The hydrophilic groups are all on the same side, i.e. a facial amphiphile.

Table 1
Characteristics of Samples.

Sample	$M_{n,PS}$ (g/mole)	$M_{n,P4VP}$ (g/mole)	Morphology[a]	
			Without DCA	In DCA
PS(40000)-*b*-P4VP(5600)	40,000	5600	Sphere	Vesicle
PS(41500)-*b*-P4VP(17500)	41,500	17,500	Gyroid	Wormlike micelle
PS(20000)-*b*-P4VP(17000)	20,000	17,000	Lamella	Spherical micelle

[a] Samples were annealed at 175 °C in nitrogen atmosphere for 2 days.

3. Results and discussion

3.1. Morphology of non-annealed mixtures

We first used FT-IR to study the interaction between DCA and PS-*b*-P4VP. Fig. 2 shows the FT-IR spectra of PS-*b*-P4VP, DCA and mixtures of PS-*b*-P4VP/DCA in which molar ratio of DCA to 4VP is 1:1. Free pyridine groups of P4VP contribute to the absorption at 993 cm^{-1} (Spectrum A). In the non-annealed PS-*b*-P4VP/DCA mixture, the absorption at 993 cm^{-1} disappeared (Spectrum B), implying that the pyridine groups of P4VP interact with DCA. This interaction should be hydrogen bonding formed by the carboxyl and hydroxyl groups of DCA with the pyridine groups of P4VP [30].

Similar to many other supramolecular systems [27–29], DCA molecules associate with P4VP blocks and thus increase the volume fraction of P4VP(DCA) complexes, which in turn, leads to a morphological change. Taking PS(40000)-*b*-P4VP(5600) as an example, without DCA, P4VP blocks form spherical microdomains in PS matrix, shown in Fig. 3a. After mixed with DCA, the morphology is completely different. Fig. 3b shows the TEM image of a non-annealed sample with 11 wt% of PS-*b*-P4VP in DCA. The sample macroscopically phase separates into block copolymer-rich regions where ordered structures are formed and DCA-rich regions, i.e. the pale regions in the image. In the block copolymer-rich regions, lamellar microdomains were predominantly observed, instead of spherical ones shown in Fig. 3a, suggesting that a certain amount of DCA associate with P4VP blocks and the swelling of P4VP blocks transforms the morphology from spheres to lamellae. The microdomains, however, are not regularly packed, possibly due to the uneven distribution of a great amount of excess DCA. The morphologies of PS-*b*-P4VP in DCA are essentially the same for the samples annealed at temperatures below melting point of DCA (175 °C) since the mobility of PS-*b*-P4VP is retarded by the frozen DCA molecules.

3.2. Morphology of annealed mixtures

We then turn our focus to samples annealed at 175 °C where DCA crystals start to melt and the melt can be regarded as liquid solvents that dissolve polymers. Furthermore, this temperature is higher than the glass transition points of PS (~102 °C) and P4VP (~136 °C) where the polymer chains are able to move toward their thermodynamically-stable states. On the other hand, it is well known that the hydrogen bonding interactions decay with temperature [31]. We therefore firstly need to know the strength of hydrogen bonds between P4VP and DCA in the melt state. Spectrum
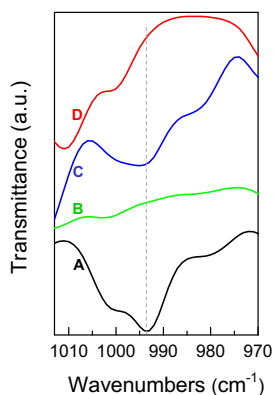

Fig. 2. FT-IR spectra of (A) PS-*b*-P4VP, (B) a non-annealed PS-*b*-P4VP/DCA mixture, (C) a PS-*b*-P4VP/DCA mixture annealed at 175 °C for 2 days, and (D) DCA.
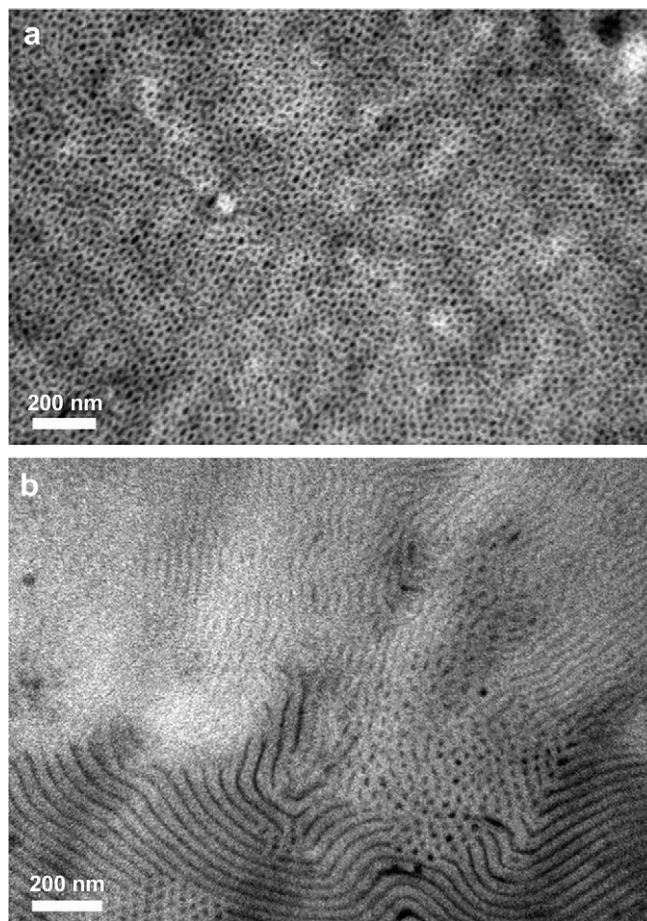

Fig. 3. TEM images of (a) PS(40000)-*b*-P4VP(5600) alone, (b) a non-annealed mixture with 11 wt% PS(40000)-*b*-P4VP(5600) in DCA.

C in Fig. 2 represents the FT-IR data of a PS-*b*-P4VP/DCA mixture (DCA:P4VP = 1:1) which was annealed at 175 °C for 2 days before being measured at room temperature. The characteristic absorption at 993 cm^{-1} attributed to the free pyridine groups of P4VP which disappears in non-annealed samples now appears, indicating that the hydrogen bonding interactions are weakened and the DCA molecules are dissociated from P4VP at 175 °C. Upon cooling, DCA melt is rapidly frozen so that the hydrogen bonds between DCA and P4VP are unable to recover at room temperature where the FT-IR measurements were made. It is possible that DCA molecules prefer to form hydrogen bonds with each other rather than with P4VP during annealing and cooling [30]. Despite the weakening of hydrogen bonds, DCA still plays an important role in the self-assembly behavior of PS-*b*-P4VP, which we will discuss as follows.

We now present a mixture of 11 wt% PS(40000)-*b*-P4VP(5600) in DCA annealed at 175 °C for 2 days and then cooled to room temperature, where the samples were solidified and could be microtomed for TEM imaging. The TEM image, shown in Fig. 4a, surprisingly reveals that PS(40000)-*b*-P4VP(5600) self-assembles into bilayered vesicles in DCA melt. The diameters of the vesicles mostly range from 100 nm to 200 nm. The P4VP blocks were stained with iodine so that the dark concentric rings on the sectioned vesicles are made up of P4VP while the light regions between rings are formed by PS. DCA is partitioned by the bilayers and fills both the interiors and exteriors of the vesicles to solvate the P4VP brushes. The formation of vesicles is also observed in concentrated and dilute mixtures. The vesicular structures of a 42 wt% and a 1.5 wt% mixture are shown in Figure S2 and S3 in
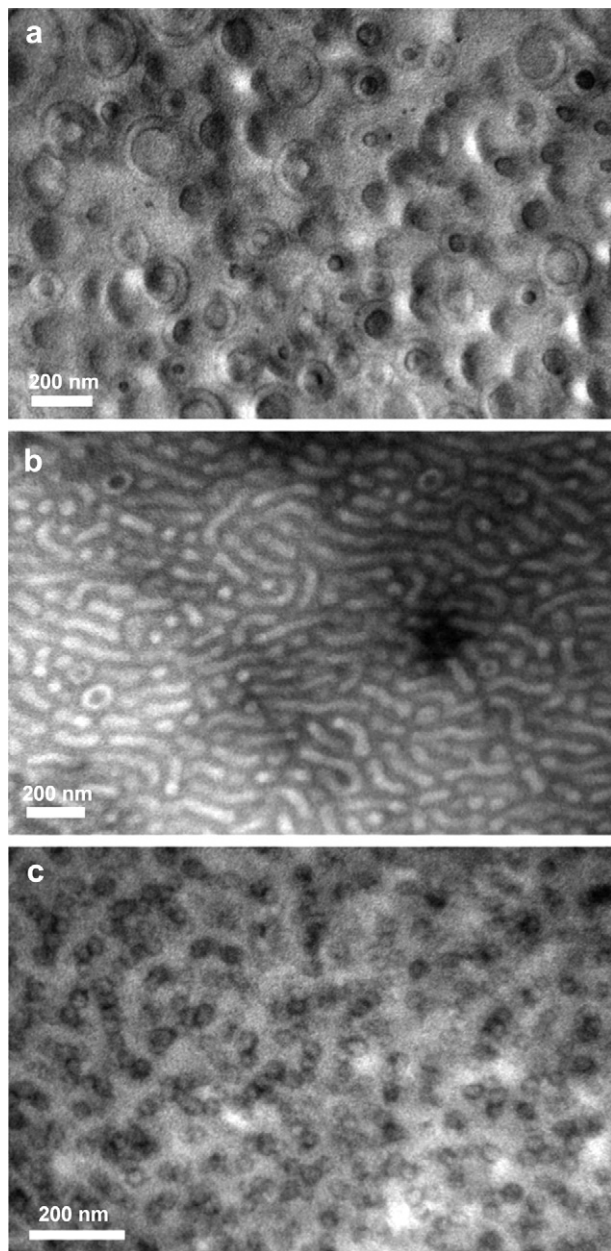
Fig. 4. TEM images of (a) a mixture with 11 wt% PS(40000)-*b*-P4VP(5600) in DCA, (b) a mixture with 11 wt% PS(41500)-*b*-P4VP(17500) in DCA, and (c) a mixture with 18 wt% PS(20000)-*b*-P4VP(17000) in DCA. All samples were annealed at 175 °C for 2 days.

supplementary material. The vesicles are supposed to be formed in melt state at 175 °C and interestingly, these structures can be retained in solid DCA after samples are either slowly cooled or quenched by liquid nitrogen. The mobility of the polymer chains is slow and also DCA molecules quickly crystallize below 175 °C such that the cooling rate has no significant effects on the final structures.

We have also characterized the morphologies of copolymers with varying lengths of PS and P4VP. PS(41000)-*b*-P4VP(17500), which has higher volume fraction of P4VP, alone microphase-separates into bicontinuous gyroid structure (Figure S1a in supplementary material). When mixed in DCA following the same treatment, the sample shows mostly wormlike micelles along with a few spherical micelles and vesicles in an 11 wt% mixture, as illustrated in Fig. 4b. The length of most worms is less than 500 nm

and it is apparent that PS forms the cores surrounded by P4VP blocks. Following this scenario, a further increase in the volume fraction of P4VP blocks is expected to result in the formation of spherical micelles. This is demonstrated in Fig. 4c for PS(20000)-*b*-P4VP(17000) in an 18 wt% mixture, where discrete spherical micelles with PS cores and P4VP coronas can be clearly seen. Note that PS(20000)-*b*-P4VP(17000) alone forms lamellar structures since the two blocks are approximately symmetric (Figure S1b in supplementary material).

The above results reveal a new self-assembly behavior: spherical micelles, cylindrical micelles, and vesicles which are commonly observed in amphiphilic molecule/solvent solutions can be formed in the melts of low-mass molecules as well. When amphiphiles are mixed in regular liquid solvents, the self-assembly process occurs in order to reach a more stable state, driven either by hydrophobic interaction which is arisen exclusively in aqueous systems, or by specific interactions between components in the micellar core, which is normally found in non-polar organic solvents [32]. For amphiphilic block copolymers mixed in organic solvents, the interaction between polymer chains and solvents is the dominant factor that governs the micellization behavior of block copolymers [33]. For example, the micellization of a diblock copolymer is normally carried out by firstly dissolving the copolymer in a common solvent, i.e. a good solvent for both blocks, followed by gradually adding a selective solvent that is a precipitant of one of the blocks [34]. Or a morphological transition can be induced by adjusting temperature [35], pH values, or salt concentration [36] that alter the solvent quality for the blocks. In the present case, the principle behind the process should be similar, that is, the interaction between DCA and P4VP plays a crucial role, except that the temperature window is quite different from regular systems. At 175 °C, although the hydrogen bonding interactions are weakened, the DCA melt still preferentially interacts with P4VP and works as a good solvent for P4VP, but a poor or non-solvent for PS. On the other hand, the high temperature imparts thermal energy for PS and P4VP chains to diffuse in the melt, thereby leading to the formation of the self-assembled structures. The P4VP blocks swell in DCA melt and the aggregates are thus stabilized through steric repulsion.

The next question is why various structures can be formed by changing the chain lengths. This length-shape relationship has also been found in many other copolymer-based micellar systems [18,24,34,37–39]. In classical description for surfactant systems, the shape of self-assembled structures is governed by the size of the hydrophobic tail relative to the hydrophilic headgroup [1]. This connection is usually expressed in terms of the packing parameter $p = v_t/a_h l_t$, where v_t is the tail volume, a_h the headgroup area, and l_t the tail length. The ratio v_t/l_t can be regarded as the tail area a_t, namely $p = a_t/a_h$. It has been shown that the self-assembled structures of flexible coil–coil amphiphilic block copolymers in regular solvents are regulated by p as well [4,40]. In the case of PS-*b*-P4VP/DCA systems, p can be simply interpreted as a_{PS}/a_{P4VP}. Since DCA interacts with P4VP and can penetrate into P4VP blocks, the cross-sectional area of P4VP increases due to the swelling of P4VP chains. PS(40000)-*b*-P4VP(5600) alone has a long PS and a short P4VP chain and its a_{PS} should be larger than a_{P4VP}. When mixed in the DCA melt, the swollen P4VP chains cause a_{P4VP} to increase and once a_{P4VP} is increased to be comparable with a_{PS}, vesicles are more stable than other shapes (Fig. 4a). In PS(41000)-*b*-P4VP(17500)/DCA mixtures, the volume fraction of P4VP blocks is higher and a_{P4VP} of swollen P4VP chains exceeds a_{PS}, which leads to cylindrical micelles (Fig. 4b). A further increase of P4VP volume fraction, as shown in the case of PS(20000)-*b*-P4VP(17000)/DCA mixtures, then gives rise to the formation of spherical micelles (Fig. 4c). Thus, relatively longer length of P4VP affects the cross-sectional area of
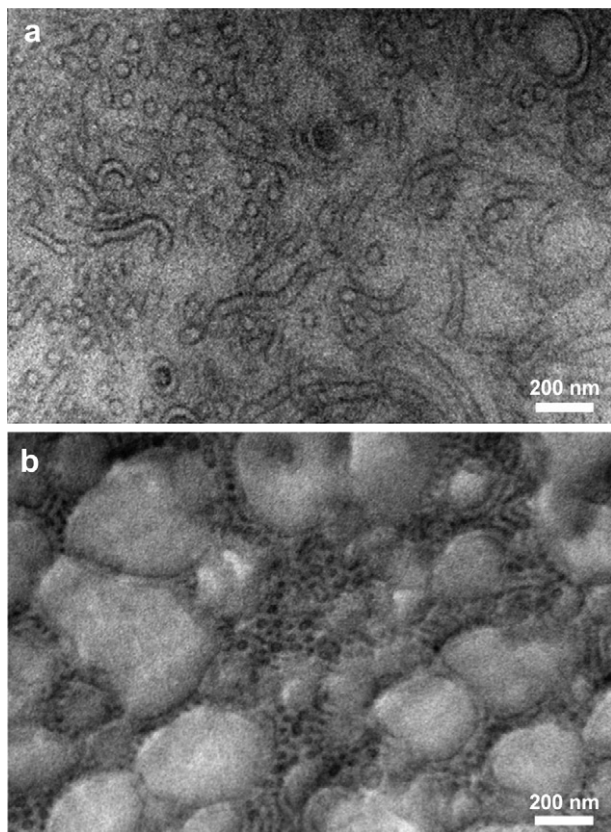
Fig. 5. TEM images of a mixture with 11 wt% PS(40000)-*b*-P4VP(5600) in DCA annealed (a) at 175 °C for 4 days and (b) at 185 °C for 2 days.

P4VP in ways that cause a decrease in *p* and hence the structures are transformed from vesicles to wormlike micelles and then to spherical micelles. Note that *p* varies with annealing time, which will be elaborated in the next section. The packing parameter discussed here is used to describe the geometry of PS-*b*-P4VP during the slow process, not based on the thermodynamic equilibrium.

3.3. Effects of annealing time and temperature

Compared to surfactants, the diffusivity of polymer chains in regular solvents is much smaller and it takes much longer time for polymeric systems to reach thermodynamic equilibrium. The motion of polymer chains is even slower in highly viscous melts and thus annealing time could be an important factor. In the preceding section, the samples were annealed at 175 °C for 2 days. We then extended the annealing time while maintaining temperature to see the time effect on the self-assembled behaviors. Fig. 5a shows the TEM image of the mixture of 11 wt% PS(40000)-*b*-P4VP(5600) in DCA annealed at 175 °C for 4 days. Instead of the dominant vesicular structures, it shows a coexistence of spherical micelles, wormlike micelles and vesicles. This transition can be rationally understood, since at high temperature, P4VP and DCA tend to further mix to enhance the system entropy and the P4VP chains gradually swell with time in DCA melt. The packing parameter *p* thus decreases with time, leading to the formation of spherical or cylindrical micelles. On the other hand, the interfacial free energy between PS and P4VP/DCA reduces at high temperature, which counteracts the increase of surface area per chain upon the transition from bilayers to micelles. The morphologies of PS(41500)-*b*-P4VP(17500) and PS(20000)-*b*-P4VP(17000) annealed

at 175 °C for 4 days are different from those annealed for 2 days as well. Both form mostly spherical micelles as shown in Figure S4 and S5 in supplementary material. The transition from wormlike to spherical micelles of PS(41500)-*b*-P4VP(17500)/DCA mixtures is consistent with the trend that the packing parameter *p* decreases with annealing time. It can thus be concluded that the structures appeared in 2-day-annealed samples are kinetically trapped, not thermodynamically stabilized; even so, the various structures are highly reproducible since the assembly process is so slow that the transitional structures can be easily controlled and captured.

The temperature 175 °C is near the melting point of DCA. We further examined the effect of higher annealing temperature, which is expected to decrease the viscosity of DCA melt and increase the mobility of polymer chains. After the PS-*b*-P4VP/DCA samples were annealed at 185 °C for one day, the assembled structures were similar to those annealed at 175 °C for 2 days, shown in Figure S6 and S7 in supplementary material. Higher annealing temperature can indeed facilitate the assembling process and reduce annealing time. Longer annealing time at 185 °C, however, gives rise to a completely different structure. Shown in Fig. 5b, block copolymer-rich phase and DCA-rich phase were observed after 2-day annealing at 185 °C for an 11 wt% PS(40000)-*b*-P4VP(5600)/DCA mixture, which is typical of macrophase separation. In the block copolymer-rich phase, P4VP forms spherical microdomains, consistent with the morphology of PS(40000)-*b*-P4VP(5600) without DCA shown in Fig. 3a. The appearance of the macrophase separation indicates that P4VP and DCA are no longer miscible at 185 °C, specifically after long-time annealing. It has been reported that bile salts, including DCA, can be polymerized through catalyzed esterification of carboxyl groups and hydroxyl groups [41]. This reaction is highly possible to occur at high temperature in spite of the absence of catalysts and hence causes the phase-separation.

We used FT-IR to examine whether DCA can esterify at high temperature. The spectra for pure DCA under different heat treatments are shown in Fig. 6. The stretching mode of C=O bonds on carboxyl groups of non-annealed DCA has an absorption at 1715 cm^{-1}. After annealed at 175 °C for 1 day, the peak position does not change (Spectrum B). In fact, no significant change for the adsorption peak even if samples are annealed at 175 °C for 4 days. On the other hand, for the sample annealed at 185 °C for 1 day, a new peak at 1731 cm^{-1} is observed (Spectrum C), which corresponds to the stretching of C=O bonds in esters. FT-IR thus confirmed the esterification of DCA at 185 °C. Such condensation reaction results in the consumption of hydroxyl and carboxyl
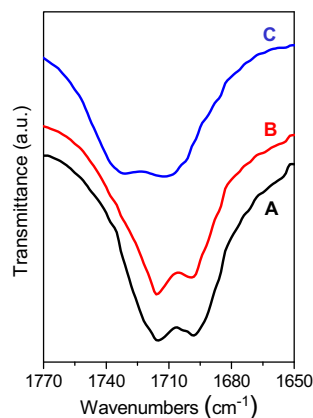
Fig. 6. FT-IR spectra of (A) non-annealed DCA, (B) DCA annealed at 175 °C for 1 day and (C) DCA annealed at 185 °C for 1 day.

groups and the formation of DCA oligomers or even polymers, which therefore decreases the P4VP-DCA interactions as well as the mixing entropy of P4VP in reacted DCA, ultimately leading to the macrophase separation. The GPC measurements also reveal that the molecular weight of DCA increases with annealing time at 185 °C, data shown in Figure S8 in supplementary material, evidencing the polymerization of DCA.

3.4. Extraction of self-assembled structures

For the conventional micellization in liquid solvents, as the solvents are evaporated, the self-assembled structures collapse [42]. For example, once the interior solvents of vesicles are removed, the vesicles cannot hold their original shapes. The present system, interestingly, provides an opportunity to extract the whole structures. The PS-b-P4VP micelles or vesicles formed in DCA melt at 175 °C are retained at room temperature in DCA crystals. The solid DCA is soluble in alcohol or strong basic aqueous solutions, which, however, are non-solvent to PS. Thus, as PS-b-P4VP/DCA mixtures are placed in such solvents, DCA molecules are dissolved while the self-assembled PS-b-P4VP structures still maintain. Fig. 7a shows the TEM image of the wormlike micelles formed by PS(41500)-b-P4VP(17500), which were extracted in ethanol. More interestingly, for PS(40000)-b-P4VP(5600)/DCA mixtures, the vesicles with interiors filled with DCA and outer surface covered by DCA were entirely extracted, shown in Fig. 7b. The structures extracted by sodium hydroxide (NaOH) basic aqueous solutions are shown in Figure S9 in supplementary

material. The solid DCA inside vesicles prevents the vesicles from collapsing and the diffusion of interior DCA is very slow due to the barrier of the bilayers so that the vesicles can last in alcohol or NaOH solutions for a long period of time.

The above advantage brings this new type of self-assembly systems potential for applications. The first one we think of is that drugs or nanoparticles with electronically, optically or magnetically-active properties can be encapsulated inside vesicles. The extracted vesicles with encapsulated substances can be re-dispersed in solvents and serve for controlled release or for opto-electronic and magnetic-responsive devices [43]. It has been shown that the encapsulation ability of vesicles formed by block copolymers in liquid systems is inefficient [44]. The present route provides a highly efficient way to enclose substances in vesicles. Furthermore, following this route, we believe that there should be other pairs of block copolymers and low-mass molecules that have similar self-assembly behaviors. The potency can then be expanded if more systems are discovered. For example, instead of DCA, other functional molecules can be used and directly encapsulated in vesicles. Also, the biological applications are practicable if water-soluble molecules or drugs and biocompatible copolymers are properly designed and synthesized. This strategy paves a way toward new classes of nanomaterials and may expand the applications of the existed nanotechnologies.

4. Conclusions

This study has demonstrated that block copolymers can self-assembly into a variety of structures in the melted state of low-mass molecules which are crystalline solids at room temperature. We show that polystyrene-b-(4-vinylpyridine) (PS-b-P4VP) forms spherical micelles, wormlike micelles and vesicles in a large amount deoxycholic acid (DCA) at a temperature above the melting point of DCA, where DCA melt works as a selective solvent for P4VP. Similar to self-assembly in regular solvents, the shapes of the structures in the melt depend on the lengths of PS and P4VP blocks. This self-assembly is a slow process due to the low diffusivity of copolymers and high viscosity of the melt so that these structures are kinetically captured in the melt and can be frozen in the crystalline solid upon cooling. We also show that the trapped structures can be entirely extracted from the solid by using proper solvents to remove low-mass molecules. This study provides the first step toward designing block copolymers/melt systems for producing new nano-scaled structures in melts and the potential applications of nanocapsules and controlled release.
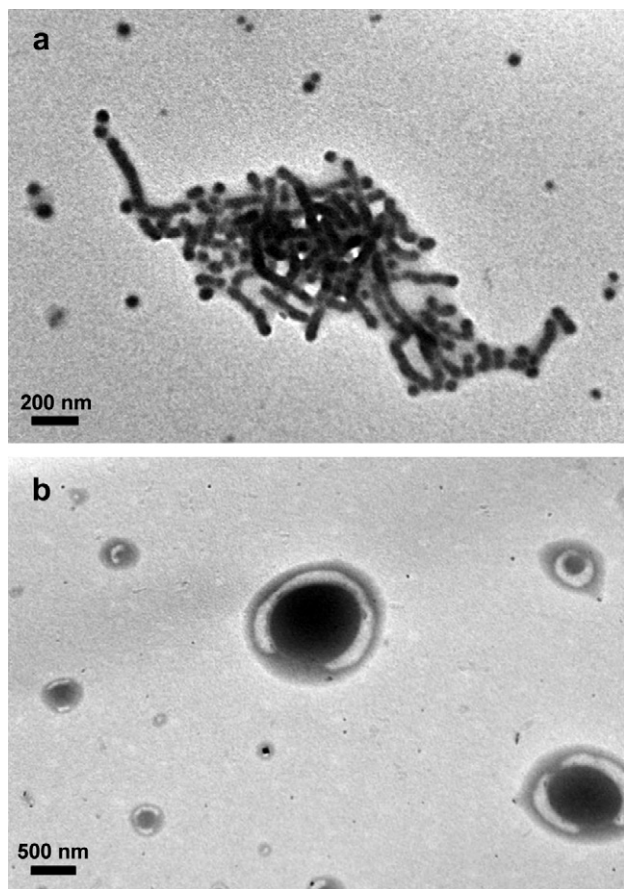
Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.07.014.

Fig. 7. TEM images of structures extracted by ethanol: (a) wormlike micelles from a PS(41500)-b-P4VP(17500)/DCA mixture and (b) vesicles from a PS(40000)-b-P4VP(5600)/DCA mixture annealed at 175 °C for 2 days.

References

[1] Israelachvili J. Intermolecular and surface forces. 3rd ed. San Diego: Academic Press; 2011.
[2] Discher DE, Eisenberg A. Science 2002;297(5583):967–73.
[3] Soo PL, Eisenberg A. Journal of Polymer Science Part B-Polymer Physics 2004; 42(6):923–38.
[4] Antonietti M, Forster S. Advanced Materials 2003;15(16):1323–33.
[5] Blanazs A, Armes SP, Ryan AJ. Macromolecular Rapid Communications 2009; 30(4–5):267–77.
[6] Hayward RC, Pochan DJ. Macromolecules 2010;43(8):3577–84.

[7] Riess G. Progress in Polymer Science 2003;28(7):1107–70.
[8] Lodge TP, Bang JA, Li ZB, Hillmyer MA, Talmon Y. Faraday Discussions 2005;128:1–12.
[9] Hamley IW. Soft Matter 2005;1(1):36–43.
[10] Aniansson EAG, Wall SN, Almgren M, Hoffmann H, Kielmann I, Ulbricht W, et al. Journal of Physical Chemistry 1976;80(9):905–22.
[11] Jain S, Bates FS. Macromolecules 2004;37(4):1511–23.
[12] Discher BM, Won YY, Ege DS, Lee JCM, Bates FS, Discher DE, et al. Science 1999;284(5417):1143–6.
[13] Jaramillo TF, Baeck SH, Cuenya BR, McFarland EW. Journal of the American Chemical Society 2003;125(24):7148–9.
[14] Massey JA, Winnik MA, Manners I, Chan VZH, Ostermann JM, Enchelmaier R, et al. Journal of the American Chemical Society 2001;123(13):3147–8.
[15] Sohn BH, Choi JM, Yoo SI, Yun SH, Zin WC, Jung JC, et al. Journal of the American Chemical Society 2003;125(21):6368–9.
[16] Mai Y, Eisenberg A. Journal of the American Chemical Society 2010;132(29):10078–84.
[17] Savic R, Eisenberg A, Maysinger D. Journal of Drug Targeting 2006;14(6):343–55.
[18] He YY, Li ZB, Simone P, Lodge TP. Journal of the American Chemical Society 2006;128(8):2745–50.
[19] McClain JB, Betts DE, Canelas DA, Samulski ET, DeSimone JM, Londono JD, et al. Science 1996;274(5295):2049–52.
[20] Edmonds WF, Hillmyer MA, Lodge TP. Macromolecules 2007;40(14):4917–23.
[21] Xu LM, Zhang XK, Yang H, Li X, Li CS, Zhang SX. Polymer 2010;51(16):3808–3813.
[22] Leibler L, Orland H, Wheeler JC. Journal of Chemical Physics 1983;79(7):3550–7.
[23] Dean JM, Verghese NE, Pham HQ, Bates FS. Macromolecules 2003;36(25):9267–70.
[24] Kinning DJ, Winey KI, Thomas EL. Macromolecules 1988;21(12):3502–6.
[25] Ruzette AV, Leibler L. Nature Materials 2005;4(1):19–31.
[26] Hofmann AF, Small DM. Annual Review of Medicine 1967;18:333–76.
[27] Ruokolainen J, Saariaho M, Ikkala O, ten Brinke G, Thomas EL, Torkkeli M, et al. Macromolecules 1999;32(4):1152–8.
[28] Ikkala O, ten Brinke G. Chemical Communications 2004;(19):2131–7.
[29] Valkama S, Ruotsalainen T, Nykanen A, Laiho A, Kosonen H, ten Brinke G, et al. Macromolecules 2006;39(26):9327–36.
[30] Ruokolainen J, Torkkeli M, Serimaa R, Vahvaselka S, Saariaho M, tenBrinke G, et al. Macromolecules 1996;29(20):6621–8.
[31] Sun L, Wick CD, Siepmann JI, Schure MR. Journal of Physical Chemistry B 2005;109(31):15118–25.
[32] Hiemenz PC, Rajagopalan R. Principles of colloid and surface chemistry. 3rd ed. Boca Raton: CRC Press; 1997.
[33] Liu T, Liu LZ, Chu B. Amphiphilic Block Copolymers: Self-Assembly and Applications; 2000:115–49.
[34] Zhang LF, Eisenberg A. Science 1995;268(5218):1728–31.
[35] LaRue I, Adam M, Pitsikalis M, Hadjichristidis N, Rubinstein M, Sheiko SS. Macromolecules 2006;39(1):309–14.
[36] Zhang LF, Eisenberg A. Macromolecules 1996;29(27):8805–15.
[37] Jain S, Bates FS. Science 2003;300:460–4.
[38] Shen HW, Eisenberg A. Macromolecules 2000;33(7):2561–72.
[39] Ding JF, Liu GJ, Yang ML. Polymer 1997;38(21):5497–501.
[40] Forster S, Zisenis M, Wenz E, Antonietti M. Journal of Chemical Physics 1996;104(24):9956–70.
[41] Zuluaga F, Valderruten NE, Wagener KB. Polymer Bulletin 1999;42(1):41–6.
[42] Azzam T, Eisenberg A. Langmuir 2010;26(13):10513–23.
[43] Bai ZF, Lodge TP. Journal of the American Chemical Society 2010;132(45):16265–70.
[44] Adams DJ, Adams S, Atkins D, Butler MF, Furzeland S. Journal of Controlled Release 2008;128(2):165–70.