Communications to the Editor

Polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate) Vesicles and Their Aggregates

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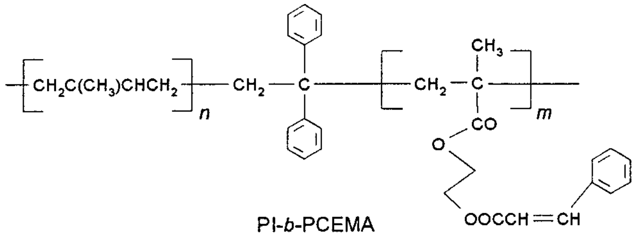
In a block-selective solvent, a diblock copolymer may form micelles with the soluble block in contact with the solvent to stabilize the collapsed insoluble block. The micelles can be spherical,[1,2] cylindrical,[3,4] or vesicular.[5] Formation of vesicular micelles has been reported only recently by Eisenberg and co-workers in water from polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA).[5]

As far as we know, the preparation of vesicles of block copolymers in organic solvents has not been reported. In this paper, we communicate the preparation of vesicles from a polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate) (PI-*b*-PCEMA) sample with 1.6 × 10^2 units of CEMA and isoprene, respectively, in hexanes and THF mixtures. Also reported is the preparation of various aggregates from these vesicles.



PI-*b*-PCEMA

The precursor polymer, PI-*b*-P(HEMA−TMS), to PI-*b*-PCEMA was synthesized by the sequential anionic polymerization of isoprene of 2-(trimethylsilyl)ethyl methacrylate (HEMA−TMS).[6] Isoprene was polymerized in hexane at room temperature using *sec*-butyllithium as the initiator. After the addition of freshly distilled 1,1-diphenylethylene, at ~3 molar equiv to *sec*-butyllithium, hexane was removed and dry THF was added by cryodistillation. HEMA−TMS was polymerized at −78 °C for 2 h before being terminated by the addition of methanol. The TMS group of the P(HEMA−TMS) block was hydrolyzed at room temperature overnight in a THF/methanol mixture containing ~25% methanol by volume. PI-*b*-PCEMA was obtained by reacting PI-*b*-PHEMA with excess cinnamoyl chloride in pyridine.[2,6−8]

By ratioing the intensities of the peaks for the PI to those of the PCEMA block, the n/m value determined from ^{1}H NMR was 0.99. The PI block normally possessed a GPC polydispersity index <1.10 and that for the diblock was 1.24 against polystyrene standards in THF. The specific refractive index increment of the polymer determined in chloroform using a differential refractometer (Precision Instruments Co.) was 0.150 mL/g. Following the Zimm method, the weight-average molar mass determined from light scattering was 5.2 × 10^4 g/mol. Using the n/m value of 0.99 and light scattering $\bar{M}_w$ of 5.2 × 10^4, the n and m values for the polymer are all 1.6 × 10^2, respectively.

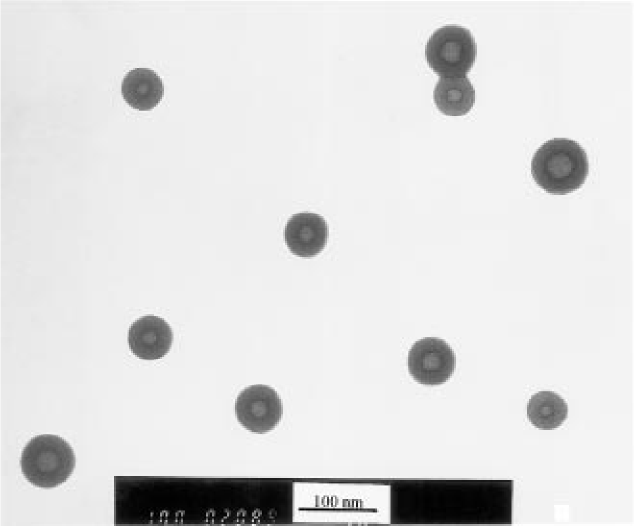


Figure 1. Vesicles of PI-*b*-PCEMA prepared in hexanes/THF with 40% THF. The TEM sample was prepared by spraying the vesicle solution on a carbon-coated copper grid.

To prepare micelles from PI-*b*-PCEMA, the polymer was dissolved in distilled THF before a designated amount of hexanes, a selective precipitant for PCEMA, was added to get a final polymer concentration of ~1.0 mg/mL. The solution was heated to 50 °C for 2 h and then stirred at room temperature for 2 days. Several drops of a micellar solution were then added into a tube containing a capillary open end and a male ground joint at the other end. The tube was then inserted into a socket with the capillary end located at the narrowed exit end of the socket. As the solution dripped out of the capillary, air, introduced from the other end of the socket and gushing out of the exit, broke the fine droplet and brought the particles into contact with a carbon grid. Sprayed micelles were stained with OsO_4 overnight and viewed by a Hitachi-7000 transmission electron microscope (TEM) operated at 10^5 V.

Illustrated in Figure 1 is a TEM photograph of such micelles prepared in hexanes/THF with 40% THF by volume. That the micelles were spherical was unambiguously verified by the fact that the size of the circular images of the micelles did not change when the tilt angle of the TEM sample stage changed from 0 to 45°. The circular image consists of a dark ring separating a light core from a shell of intermediate darkness. To differentiate the reactivity of PCEMA and PI toward OsO_4, a film containing 10% PI and 90% PCEMA homopolymers was prepared. The film was then sliced, and the slices were stained with OsO_4 and viewed by TEM. Since the domains of the minor PI component appeared darker, this suggested that PI reacted with OsO_4 more favorably.

The particles of Figure 1 are not spheres with PCEMA as the core and PI as the shell, as this assignment cannot explain the presence of a dark ring between the shell and the core. Then, the weight fraction of 21% for PI is simply too low to explain the observed thickness of the shell. Similar structures were observed from PS-*b*-PAA in water by TEM and the structures were shown by Zhang and Eisenberg to be vesicles.[5] Thus, the lighter centers of the particles in Figure 1 correspond to the locations of the cavities. The dark ring represents the location of a collapsed PI layer. The cavities should have originally been filled with swollen PI chains in equilibrium with the THF/hexanes mixture. It is surprising to see that the cavity remained stable in the vacuum chamber of the TEM after the PI chains collapsed and the solvent evaporated.

Although not seen in Figure 1, a PI layer must have existed on the outer surface of the PCEMA shell for the vesicles to be stable in THF/hexanes. The outer PI layer is not discernible here probably because the PI layer on the outer surface was very thin. The outer PI layer could be thin, as the outer layer occupies a much larger surface area. Drawing a very thin layer around a large sphere and lines through this thin layer, one will find that the path lengths of the lines through the thin layer are indeed short. Such short path lengths will not enable the efficient blockage of the TEM beams for the formation of a dark ring in the TEM image.

The TEM sample shown in Figure 1 was prepared by aspirating a fine spray of PI-*b*-PCEMA in hexanes/THF on carbon grids. Due to the fast solvent evaporation rate, significant morphological change in the micelles during solvent evaporation should not have been possible. PI-*b*-PCEMA micelles in hexanes/THF mixtures with 40% THF were also irradiated with UV light from a 500-W mercury lamp which had passed through a 260-nm cutoff filter to cross-link the PCEMA phase. As judged from the CEMA double bond conversion estimated from UV spectrophotometer at 274 nm, we prepared micelles with the cross-linking densities of ~13%, ~30%, and 45%.[2] Using these micelles, similar TEM images were obtained. Since cross-linked micelles are very unlikely to undergo a fast morphological transition with solvent composition change, the vesicles of Figure 1 must have been present in the original hexanes/THF mixture.

What are more interesting are the morphologies of the films formed on water surfaces. Such films were prepared by evaporating solvent, for 5−10 s, from a drop of a PI-*b*-PCEMA micellar solution carefully dispensed on the surface of water contained in a 100-mL beaker. Illustrated in Figure 2 is such a film formed from vesicles prepared in hexanes/THF with 40% THF. The unit cells here are hexagonal. The film possesses an overall honeycomb morphology with some intervesicle voids. Also, there seems to exist a distribution in the unit cell sizes.

The disappearance of solvents on the water surface may not only involve solvent evaporation but also their dissolution in water. The dissolution of solvent in water can be preferential for THF. As solvent disappeared gradually, a thin cloudy film was eventually seen on the water surface. Solvent disappearance in this case normally took 5−10 s, which should be considerably slower than in the case when the vesicle solution was sprayed on carbon-coated copper grids for TEM studies. Because of this, one may wonder if the hexagonal objects were new species formed because of the solvent composition change during film formation. PI-*b*-PCEMA vesicles with a photo-cross-linking density of ~13% were also used to prepare a film on the water surface. Such films possessed a similar morphology as shown in Figure 2. At this cross-linking density, vesicles were shown to retain their integrity even in THF, a good solvent for both PCEMA and PI. Since the cross-linked vesicles were not expected to rupture during film formation, this suggested that the hexagonal objects in Figure 2 were derived from the vesicles which were originally present in hexanes/THF with 40% THF.

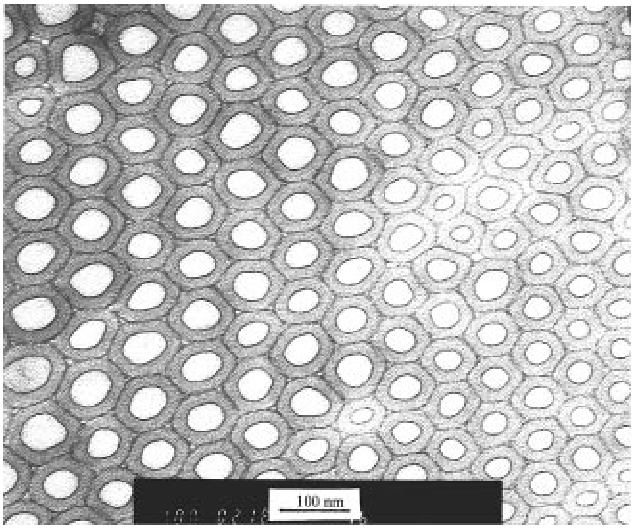


Figure 2. Film formed from PI-*b*-PCEMA vesicles prepared in hexanes/THF with 40% THF. The film was prepared by evaporating the vesicle solution on water surfaces.

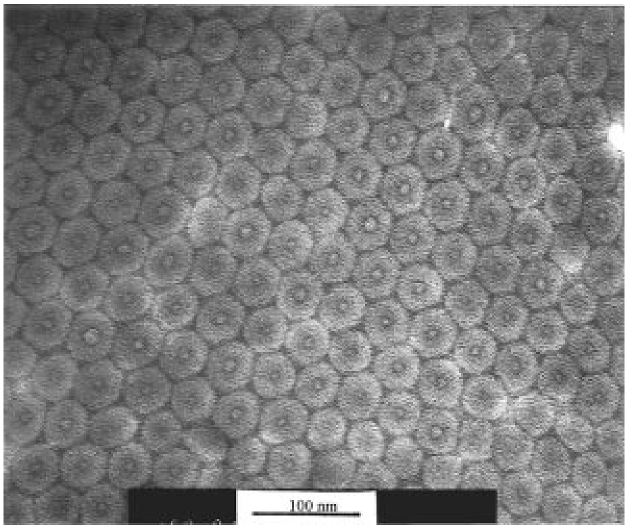


Figure 3. Film of PI-*b*-PCEMA vesicles prepared in hexanes/THF with 10% of THF.

Although the morphologies of the films formed from cross-linked and un-cross-linked vesicles were similar, the basic unit in the film of the cross-linked vesicles was overall more circular than those in Figure 2. This is expected, as the cross-linked vesicles were more resistant to deformation. As the PCEMA cross-linking density increased to 30%, the vesicles were found not to form compact films any more as the vesicles refused to deform.

The vesicles in Figure 2 have not only changed their shape, from being spherical to hexagonal, but the cavity regions also look much thinner than those in Figure 1. A dark layer between different “vesicles” is now evident, suggesting the presence of the expected PI layer on the vesicle outer surfaces. When the TEM sample stage tilt angle changed from 0 to 45°, we saw a ~25% decrease

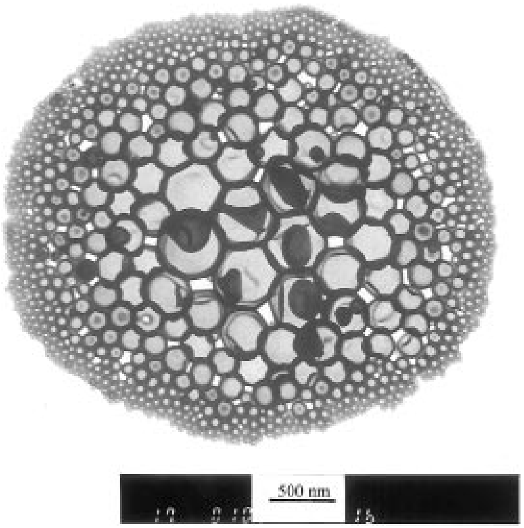


Figure 4. Coral flower aggregate of PI-*b*-PCEMA vesicles prepared in hexanes/THF with 50% of THF.

in the length of each hexagonal unit along the tilting direction. That the image size changed with the observation angle clearly demonstrated that the vesicles were flattened.

Since individual vesicles were seen not to deform in the TEM vacuum chamber, we believe that the extensive vesicle deformation observed occurred on water surfaces. This deformation was possible, because the fusion of vesicles significantly decreased the PI and water contact area. A film consisting of undeformed vesicles would have had a wavy interface between water and the PI outer layer. This deformation was also facilitated by the gradual disappearance of the solvent, the presence of which should have helped to improve the mobility of the vesicles and the polymer chains.

Figure 3 illustrates a film formed from vesicles prepared in hexane/THF with 10% THF. As the THF content decreased, the vesicle size and cavity both decreased. Thus, changing solvent composition provided a convenient method for vesicle size tuning.

Vesicles started to form in hexanes/THF with hexanes content $\sim$50% as judged from the turbidity change of the solution upon adding more and more hexanes. In hexanes/THF with hexanes content $\sim$50%, the vesicles formed had a relatively wide size distribution. Also, the vesicles did not self-assemble to form films with sizes $\sim 10^3\ \mu\text{m}^2$. Instead, coral flower-shaped structures were formed, as illustrated in Figure 4. In such structures, the relatively large vesicles are packed in the center. The vesicles get smaller farther away from the center.

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References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1992**, *15*, 1.
(2) Guo, A.; Liu, G.; Tao, J. *Macromolecules* **1996**, *29*, 2487.
(3) Price, P. *Pure Appl. Chem.* **1983**, *55*, 1563.
(4) Tao, J.; Stewart, S.; Liu, G.; Yang, M. *Macromolecules*, in press.
(5) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(6) Tao, J.; Liu, G.; Ding, J.; Yang, M. Highly Crosslinked Nanospheres of Poly(2-cinnamoylethyl methacrylate) with Surface Functional Groups. Submitted to *Macromolecules*.
(7) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. *Macromolecules* **1996**, *29*, 220.
(8) Tao, J.; Guo, A.; Liu, G. *Macromolecules* **1996**, *29*, 1618.

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