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Multiple morphologies of polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate) and polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) micelles in organic solvents

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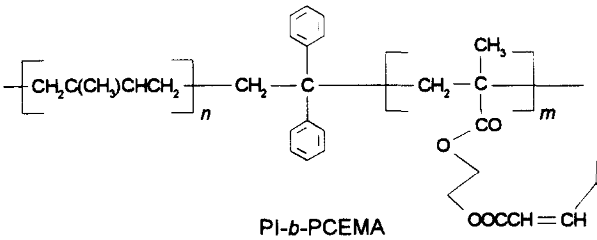
Polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate) (PI-*b*-PCEMA) and polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) formed micelles in solvents, such as cylcopentane (CP), which were selectively poor for PCEMA. Decreasing the length of the soluble blocks relative to that of PCEMA, the shape of the micelles changed from spheres, to cylinders, and to vesicles for both families of diblock copolymers. When a binary solvent mixture was used, the same micellar morphological transitions could be induced for the same diblock by increasing the content of the block selective solvent in the mixture. For PI-*b*-PCEMA, this meant an increase in the content of hexanes (HX) in THF/HX where HX was good only for PI. Similar trend was observed for PS-*b*-PCEMA in THF/CP. This represented the first observation of multiple morphologies of diblock copolymer micelles formed in organic solvents. © 1997 Elsevier Science Ltd.

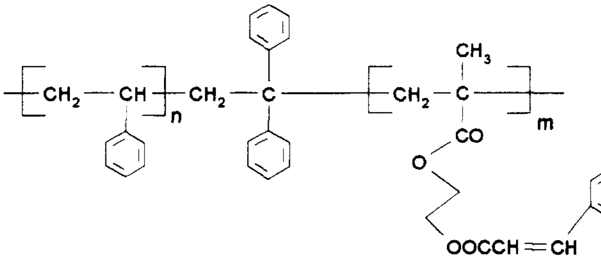
(Keywords: block copolymer micelles; vesicles; cylinders)

Depending on the structure of the 'head' and 'tail', a small-molecule surfactant in water may form micelles of different shapes including spheres, cylinders, branched cylinders, discs, and vesicles[1]. Diblock copolymers also form micelles of different shapes[2]. In bulk, the two blocks of a diblock copolymer segregate to form different domains packed with long-range order. The domain structure for the minor component can be spherical, cyndrical, gyroidal, or lamellar depending on the volume fraction of the minor component. Multiple morphologies have also been established for micelles of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) and PEO-*b*-PPO in concentrated solutions, e.g. > 10 wt%, in water and in water/organic solvent mixtures[3]. In these cases, the long range ordering of the micelles gave the solutions liquid crystalline properties.

It was only recently that the formation of vesicular micelles, the equivalent of the lamallar phase in bulk, was observed in dilute block copolymer solutions, e.g. ~ 0.1% by weight[4–6]. This expanded the morphologies of micelles formed in dilute polymer solutions to include spheres[7,8], cylinders[4,5,9,10], and vesicles[4–6]. To our knowledge, Eisenberg and coworkers were the only ones who saw multiple micellar morphologies, i.e. spheres, cylinders, and vesicles, from the same block copolymer family in dilute polymer solutions. These were micelles formed in water from polystyrene-*block*-poly(acrylic acid) and polystyrene-*block*-poly(ethylene oxide)[4–5].



PI-*b*-PCEMA



PS-*b*-PCEMA

Water is a unique medium. Due to the intricate interplay of hydrophobic and electrostatic interactions, block copolymers and small-molecule surfactants formed complex architecture in water. To show the generality of multiple morphologies of block copolymer micelles in dilute solutions, diblock copolymer solutions in organic solvents should be studied. In this paper, we communicate the formation of various micelles in organic solvents from PI-*b*-PCEMA and PS-*b*-PCEMA.

The polymers were synthesized by anionic polymerization as described previously[11,12] or to be described elsewhere[13]. The polymers all had polydispersity indices ~ 1.10 as determined by g.p.c. against polystyrene standards. The *n*/*m* values were determined by ^{1}H n.m.r. and the weight-average molar masses by light scattering. The characteristics of the polymers examined are summarized in *Table 1*. A PI-*b*-PCEMA sample in this communication is denoted by I*n*–C*m*, where *n* and *m* stand for the numbers of isoprene and CEMA units in a

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Table 1 Polymer and micelle characteristics of PI-*b*-PCEMA and PS-*b*-PCEMA

Code	*n*/*m* from n.m.r.	$\bar{M}_w/\bar{M}_n$ by g.p.c.	10^{-2} *n*	10^{-2} *m*	w_{PCEMA}	Morphology/solvent
I350–C179	1.94	1.11	3.5	1.8	0.66	Spherical/{THF/HX(50–95%)}
I350–C179						Cylindrical/{CP or cyclohexane)
I260–C174	1.50	1.11	2.6	1.7	0.72	Spherical/{THF/HX(50–95%)}
I260–C174						Cylindrical/{CP or cyclohexane)
I200–C200	0.99	1.19	2.0	2.0	0.79	Vesicular/{THF/HX(50–95%)}
I99–C174	0.57	1.09	0.99	1.7	0.87	Vesicular/{THF/HX(50–95%)}
I200–C680	0.25	1.11	2.0	6.8	0.93	Vesicular/{THF/HX(50–95%)}
S838–C61	13.8	1.17	8.4×10^2	6.1	0.15	Spherical/CP
S211–C23	9.6	1.09	2.11	0.23	0.21	Spherical/CP
S309–C38	8.2	1.10	3.09	0.38	0.23	Cylindrical/CP[a]
S309–C38						Spherical/{CP(97%)/THF}
S1253–C158	7.9	1.10	12.5	1.58	0.24	Cylindrical/CP[a]
S1253–C158						Spherical/{CP(97%)/THF}
S777–C111	7.0	1.12	0.78	1.11	0.26	Cylindrical/CP[a]
S777–C111						Spherical/{CP(97%)/THF}
S1321–C383	3.5	1.08	13.2	3.8	0.42	Cylindrical/CP[a]
S1077–C1158	0.93	1.10	10.8	11.6	0.73	Cylindrical/{CP(88–96%)/THF}[a]
S302–C570	0.53	1.07	3.0	5.7	0.83	Vesicular/{CP(85–95%)/THF}[a]

[a] Coexist with spherical micelles

chain, respectively. S*n*–C*m* denotes a PS-*b*-PCEMA sample containing *n* units of styrene and *m* units of CEMA.

Micelles of PI-*b*-PCEMA and PS-*b*-PCEMA were prepared in solvents or solvent mixtures in which PCEMA was insoluble. PI-*b*-PCEMA micelles were typically prepared in THF/hexanes (HX) or in clycopentane (CP, 95%, Aldrich). To prepare a THF/HX solution, PI-*b*-PCEMA was dissolved in THF first and then a designated amount of HX was added. CP or CP/THF was the solvent used to prepare PS-*b*-PCEMA micelles.

TEM was used to identify the morphology of the micelles. TEM specimens were prepared by either spraying a micellar solution at a concentration $\sim 1.10\,\mathrm{mg\,ml^{-1}}$ on a carbon coated copper grid or transferring a micellar film, prepared on water surface due to solvent evaporation from a dilute micellar solution, onto a copper grid. To spray micellar solution, several drops of the solution were added into a tube containing a capillary open end and a male ground joint at the other end. The tube was 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. The specimens prepared were then stained by OsO_4 vapour overnight before viewing with a Hitachi-7000 electron microscope operated at 100 kV.

The morphologies observed for the micelles of different diblock copolymers under various experimental conditions are summarized in *Table 1*. I350–C179 and I260–C174 formed spherical micelles in THF/HX over the HX contents of 50 to ~ 95%. Illustrated in *Figure 1* is the TEM image of I350–C179 micelles in THF/HX with 10% THF. The spheres clearly had dark PI shells and light PCEMA cores. The thin shells were expected as the weight fraction of PI in I350–C179 was only 34%.

The PI layer appeared darker, because PI was a rubber and PCEMA was a glassy polymer at room temperature which made PI more susceptible to OsO_4 staining. We also prepared a film containing 10% of PI and 90% of PCEMA homopolymers. The film was then sliced, the slices were stained with OsO_4 and viewed by TEM. Since the domains of the minor component in this sample appeared darker, this experimentally verified that PI reacted with OsO_4 more favourably.

Large white regions with no polymers are seen in *Figure 1*. This occurred as the TEM specimen was prepared by transferring a nanosphere film formed on a water surface to a copper grid. On water surfaces, nanospheres aggregated to minimize the interfacial area between water and polymer.

As *n*/*m* or the relative length of the soluble block decreased, the micelles became vesicular for I200–C200, I99–C174, and I178–C682. Illustrated in *Figure 2* are the vesicular micelles formed from I99–C174 in THF/HX with 10% THF. The image of each micelle consisted of a dark ring separating a light core from a shell of intermediate darkness.

That the micelles were vesicular could be appreciated from the following considerations. First, the micelles were spherical as the size of the circular images of the micelles did not change when the tilt angle of our TEM sample stage changed from 0 to 45°. Then, the particles of *Figure 2* were not spheres with PCEMA as the core and PI as the shell, as this assignment could not explain the presence of a dark ring between the shell and the core. Furthermore, the weight fraction of 13% for PI was 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[4]. Thus, the lighter centres of the particles in *Figure 2* corresponded to the locations of the cavities. The dark ring represented the location of a collapsed PI layer. The cavities should have originally been filled with swollen

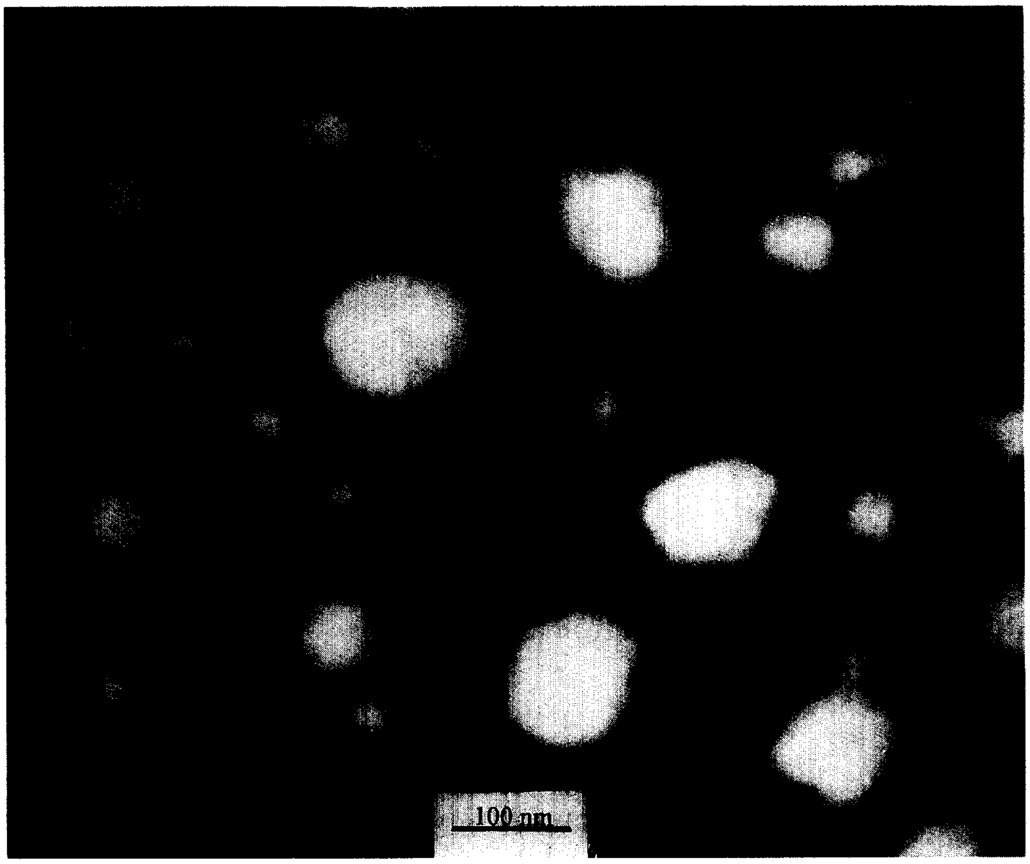

Figure 1 Spherical micelles of I350–C179 prepared in HX/THF with 10% of THF. This TEM specimen was obtained by transferring a thin micelle film prepared on water to a carbon-coated copper grid

PI chains in equilibrium with the THF/hexanes mixture. It was surprising to see that the cavities remained stable in the vacuum chamber of the TEM even after the PI chains collapsed and the solvent evaporated.

Although not seen in *Figure 2*, 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 was not discernible probably because the PI layer on the outer surface was thin. The outer PI layer could be thin, as the outer layer occupied 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 pathlengths of the lines through the thin layer are indeed short. Such short pathlengths will not enable the efficient blockage of the TEM beams for the formation of a dark ring in the TEM image.

The TEM sample imaged in *Figure 2* was prepared by aspirating a fine spray PI-*b*-PCEMA in hexanes/THF on a carbon grid. Due to the fast solvent evaporation rate, a morphological change in the micelles during solvent evaporation should not have been possible and the vesicles of *Figure 2* must have been present in the original hexanes/THF mixture with 10% THF.

Evidence for the absence of a micelle shape change during TEM sample preparation for I200–C200 micelles was obtained from the following experiment. I200–C200 micelles in hexanes/THF with 40% THF were irradiated with u.v. light from a 500-W mercury lamp which had passed through a 260-nm cut-off filter to crosslink the PCEMA phase. As judged from the CEMA double bond conversion estimated from u.v. specrophometry at 274 nm, micelles with crosslinking densities of ~ 13%, ~ 30%, and 45% were prepared[8]. TEM images similar to those of uncrosslinked samples were obtained from these micelles. Since the photocrosslinking was unlikely to change the morphology of the micelles in a solution[8,10], and the crosslinked micelles were unlikely to undergo a fast morphological transition with a solvent composition change during solvent evaporation when TEM specimens were prepared, the vesicles imaged must have existed in the original THF/HX mixture and could not have resulted during TEM sample preparation.

As *n*/*m* decreased in the PI-*b*-PCEMA series, no cylindrical micelle formation was observed in THF/HX with HX below 95%. This could have been due to the limited number of samples we examined. At any rate, the *n*/*m* range over which cylindrical micelles form should be very narrow for PI-*b*-PCEMA, if cylindrical micelles form at all in THF/HX with HX below 95%.

Cylindrical micelle formation was induced by increasing the HX content in THF/HX to above ~ 97% for I350–C179 and I260–174. Similarly, cylindrical micelles were formed from the samples in CP or cyclohexane. Illustrated in *Figure 3* is the TEM image of cylindrical micelles of I350–C179 formed in CP.

Similar trends were observed for PS-*b*-PCEMA. In cyclopentane, S838–C61 and S211–C23 with *n*/*m* larger than 9.6 formed star micelles. S309–C38 to S1321–C383 in *Table 1* with *n*/*m* between 3.5 and 8.2 formed mixtures of long cylindrical micelles and star micelles. The preparation of micelles in CP from samples with even smaller *n*/*m* values became progressively difficult due to their decreasing solubility. For easy micelle preparation

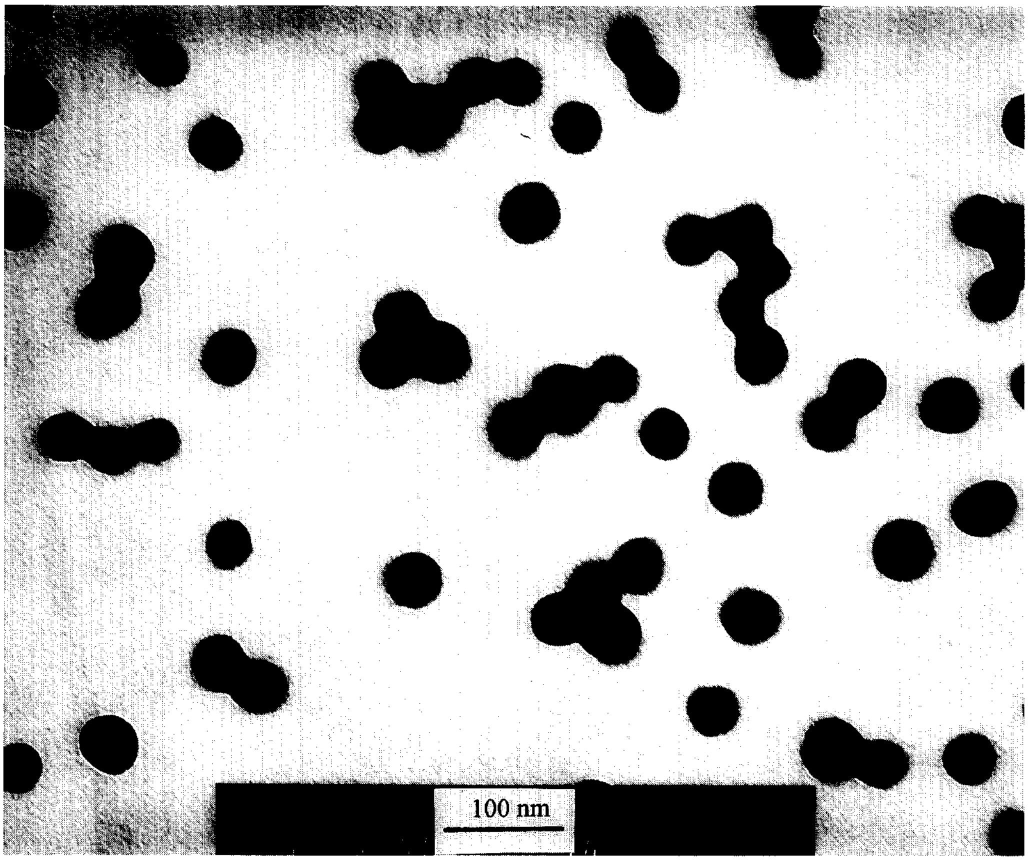

Figure 2 Vesicles of I99–C174 prepared in HX/THF with 10% of THF. The TEM specimen was prepared by directly spraying a micellar solution onto a carbon-coated copper grid

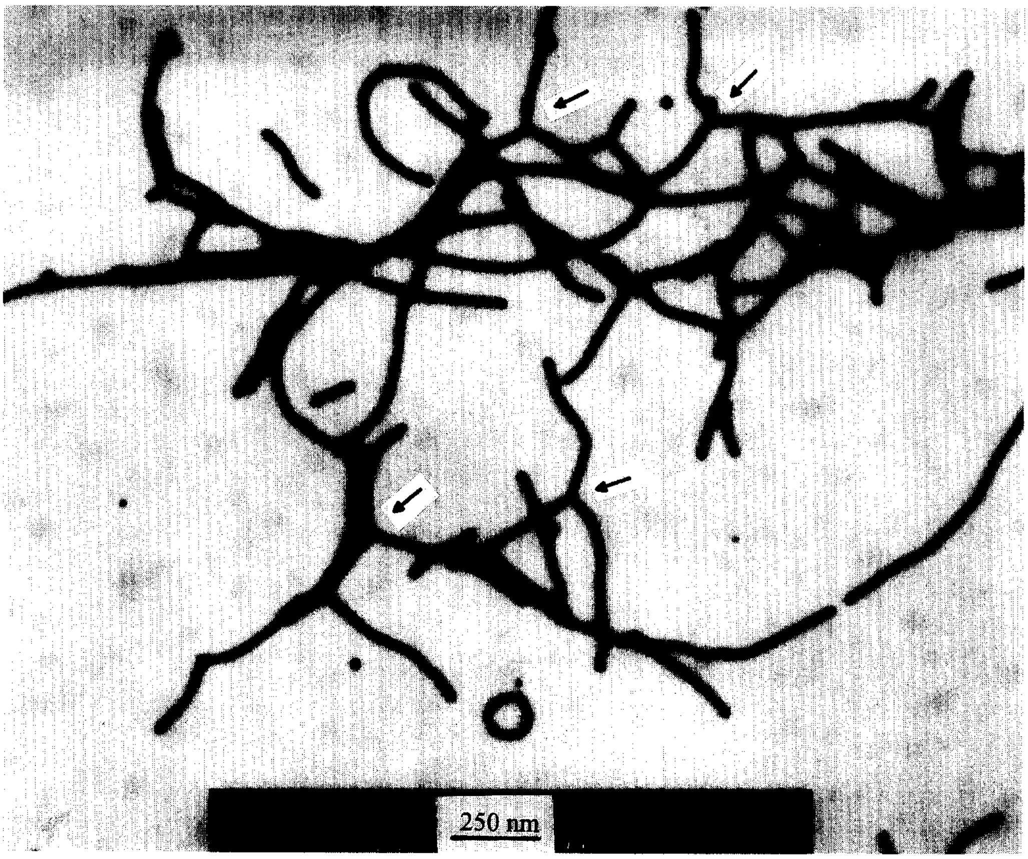

Figure 3 Cylindrical micelles of I350–C179 prepared in CP. Also present are some branched cylinders (some branching points are marked by arrows) and a doughnut-shaped micelle (slightly above the scale bar). The TEM specimen was prepared by directly spraying a micellar solution onto a carbon-coated copper grid

from these samples, THF had to be used to dissolve the polymer first and CP was then added. In CP/THF containing 85% to 95% CP, vesicular micelles formed from S302–C570 with $n/m = 0.53$.

Similarly, the amount of CP in the THF/CP affected the morphology of PS-*b*-PCEMA micelles. Increasing CP content in THF/CP had the same effect as decreasing n/m. S309–C38, S1253–C158, S777–C111 formed star micelles in THF/CP with 97% CP. Removing the 3% of THF by extraction with water induced significant cylindrical micelle formation[10]. S302–C570 formed spherical micelles when CP content was low, e.g. <60%, vesicles were observed in THF/CP when CP content was above ~ 85%.

A close examination of *Figure 3* shows that a doughnut-shaped micelle co-exists with the cylindrical micelles of I350–C179. Doughnuts were also found to co-exist with the cylindrical micelles of S1077–C1158 in CP/THF with CP greater than ~ 92%. A doughnut appears to form due to the folding together by the two ends of a cylindrical micelle. The conditions for increasing the doughnut micelle population are currently being explored.

Also clear from *Figure 3* is the formation of some branched cylinders, an observation in agreement with that of Danino *et al.* made on a small-molecule surfactant system[14].

In summary, both PI-*b*-PCEMA and PS-*b*-PCEMA formed spherical, cylindrical, vesicular, and some doughnut-shaped micelles in organic solvents. Multiple morphologies of micelles are probably the intrinsic properties of diblock copolymers. They occur not only in water but also in organic solvents.

The obvious reason for the formation of micelles of different shapes is the requirement for a micellar system to minimize its free energy. At relatively large n/m values, PI-*b*-PCEMA or PS-*b*-PCEMA micelles had relatively large positive curvature or were spherical so that the large PI or PS 'heads' could enjoy more lateral areas than the PCEMA 'tails' to reduce the stretching energy of the shell block. As n/m decreased or the head became smaller and the tail became larger, a large positive curvature could not be tolerated and the spheres changed to cylinders or vesicles. The effect of the solvent composition change was somewhat counter-intuitive. Upon decreasing THF content, one expected the core size to decrease due to reduced core swelling by THF. This effect should be equivalent to decreasing the size of the insoluble block and favour the formation of spherical micelles. That decreasing the THF content favoured the formation of cylinders and vesicles was probably caused by the fact that the size of the PI or PS chains decreased more drastically than the core size as THF content decreased. This was understandable as THF was a good solvent for PI and PS and the quality of hexanes and cyclopentane was only comparable to that of a theta solvent for PI and PS, respectively.

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