Macromolecules **2001,** *34,* 4299−4301 **4299**

Synthesis of Discotic Microgels by Cross-Linking of Poly(styrene-*block*-4-vinylpyridine)/3-*n*-Pentadecylphenol Blend Film

Reiko Saito*

Department of Organic and Polymeric Materials,
Tokyo Institute of Technology 2-12, Ookayama,
Meguro-ku, Tokyo, 152-8552 Japan

Received December 12, 2000
Revised Manuscript Received April 27, 2001

Introduction. It is possible to synthesize core−shell type microgels with cross-linked core and hairy shell by cross-linking of spherical microdomains in a matrix formed by AB diblock copolymers.[1−4] The following two features are required to synthesize the microgels by this method: First, the microdomains, which are cross-linked, should be isolated in a matrix. Second, the sequence forming a matrix should not form a bridge structure. If these two requirements are satisfied, it will be possible to synthesize microgels from not only AB diblock copolymer but also other systems.

Ikkala and co-workers reported novel morphologies of the microphase separation by blending of poly(styrene-*block*-4-vinylpyridine) [P(S-*block*-4VP)] and 3-*n*-pentadecylphenol (PDP).[5−7] When contents of PS, P4VP, and PDP were optimized, a P4VP/PDP mixture formed cylinders in a PS matrix. Moreover, P4VP and PDP formed lamellae in each cylinder. That structure was named a “lamella-within-cylinder” structure. In the lamella-within-cylinder structure, P4VP microdomains were isolated and discotic; neither PS nor PDP formed a bridge structure. P4VP can be cross-linked with 1,4-dibromobutane or 1,4-diiodibutane without changing of the morphology of the microphase-separated films. Additionally, PDP is not connected to P4VP by covalent bonding but hydrogen bonding.[5,8−10] This suggests that PDP can be removed from the blend of P(S-*block*-4VP) and PDP after the cross-linking. Therefore, by cross-linking of the discotic P4VP domains in the lamella-within-cylinder structure, novel discotic microgels with the discotic P4VP core and the PS shell surrounding the side of the core will be obtained. Figure 1 shows the synthetic concept of the discotic microgels.

The microgel will have an anisotropic surface. Because junction points of PS shells on the P4VP core will exist on the side of the core, the top and bottom of the core will not be completely covered with the PS shells. Anisotropy of the microgel surface induces aggregation of the microgels. The discotic microgels synthesized in this work will re-form P4VP cylinders in a PS matrix by self-aggregation. The length of the P4VP cylinders will be able to be controlled by changing aggregation conditions. By adding polymers that have interaction with P4VP, such as poly(methacrylic acid), novel lamella-within-cylinder structure will be obtained. Thus, the P4VP core-PS shell type discotic microgels will be unique nanomaterials. Expected aggregates are also in Figure 1.

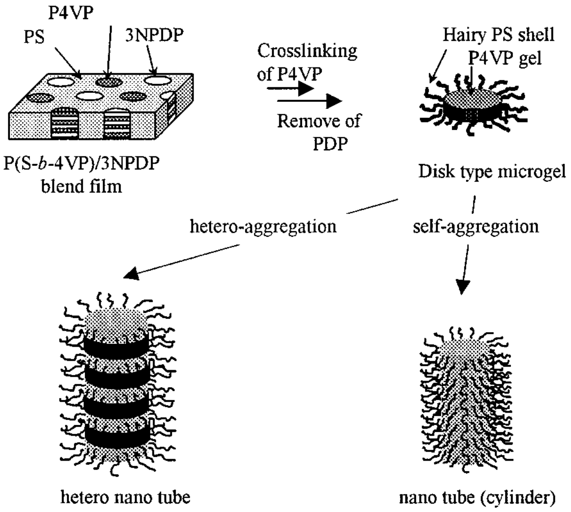

Figure 1. Synthetic concept of discotic microgel by cross-linking of the P(S-*block*-4VP)/PDP blend film.

The purpose of this paper is to synthesize the discotic microgels by cross-linking the discotic P4VP microdomains in the blend film of the P(S-*block*-4VP) and PDP with the lamella-within-cylinder structure with 1,4-diiodobutane. The morphology of the template blend film and structure of the cross-linked products were investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

Experimental Section. P(S-*block*-4VP) diblock copolymer was synthesized with *n*-butyllithium as an initiator in tetrahydrofuran (THF) at −78 °C by an usual additional anionic living polymerization technique.[11] The number-average and dispersion index of P(S-*block*-4VP) diblock copolymer measured with a gel permeation chromatograph (TOSHO, HPLC-8020) with chloroform were 5.38×10^4 and 1.23, respectively. Molar contents of PS and P4VP determined by ^{1}H NMR (JEOL GSX, 500 MHz) were 70.6 and 29.4 mol %, respectively.

Blend films of the P(S-*block*-4VP) diblock copolymer and PDP were prepared from 0.1 g of P(S-*block*-4VP) diblock copolymer, 0.0136 g of PDP, and 11 mL of chloroform solution based on the method proposed by Ikkala and co-workers.[5] To confirm the forming of hydrogen bonding between pyridine and phenol in PDP, Fourier transfer infrared measurements were carried out for the blend films with a Jasco FT-IR/410. To cross-link the film, the film was exposed with 1,4-diiodobutane gas at room temperature for a day. The cross-link density of the P4VP domains was calculated from the degree of quaternization measured by Volharts titration based on equations proposed previously.[3]

To observe the morphology of microphase separation, small-angle X-ray scattering (SAXS) measurements were carried out for the films with a rotating anode X-ray generator (Rigaku Denki, Rotaflex RTP 300 RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized to Cu Kα ($\lambda = 1.52$ Å) radiation. The SAXSA patterns were recorded by using the imaging plate technique.

For TEM observation, the blend film was microtomed with 80 nm thickness with an Ultracut-N (Reihart-Nissein). To increase the contrast, these specimens were stained with methyl iodide gas. To observe external shape of the microgel, the cross-linked product was dissolved in chloroform and sprayed in *n*-hexane. Polymer con-

---

* Phone +81-3-5734-2937; FAX +81-3-5734-2888; e-mail rsaito@polymer.titech.ac.jp.

10.1021/ma002115t CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/24/2001

centration and volume fraction *n*-hexane were 0.001 wt % and 99 vol %, respectively. The solution was cast on the copper microgrid covered with a carbon substrate and quickly evaporated. Some specimens were stained with methyl iodide, and others were sputtered platinum at an angle of 15°. The specimens were observed by a transmission electron microscope (Hitachi, H-500) at 75 kV.

Results and Discussion. In the blend film, weight fractions of PS, P4VP, and PDP were 0.62, 0.258, and 0.122, respectively. Molar fractions of PDP to P4VP were 0.16. To compare with Ikkala and co-workers' work,[5] the molar ratio of PDP to P4VP of this study was lower than their study. However, to avoid the formation of the lamella-within-lamella structure, the PDP content was not increased. To obtain homogeneous morphology, the film was annealed at 110 °C for a week. Since boiling point of PDP is 190−195 °C/1 mmHg, PDP remained in the blend film after the annealing.

Figure 2a,b shows TEM micrographs of the blend film of P(S-*block*-4VP) and PDP with and without annealing. Dark regions in the micrographs are selectively stained P4VP domains with methyl iodide. The morphology of the blend film before annealing seemed to be PS and P4VP lamella (Figure 2a). After annealing (Figure 3b), the spherical P4VP domains seemed to be continued to form cylinders. From Figure 2b, an average diameter of the P4VP domain and an average domain spacing between centers of the lines formed with P4VP domains were 17 and 25 nm, respectively. However, the lamella-within-cylinder structure was not confirmed.

For the detail investigation of the morphology of the blend film, SAXS spectra were measured and are shown in Figure 3. The patterns have clearly distinguishable lattice peaks. By annealing, the peak pattern did not change but became clearer. This suggests that the morphology did not change but became homogeneous by annealing. For the annealing film, the values of $qn/q1$ are 1:1.18:1.41:1.59:1.76:2.06, which are close to $1:(3/2)^{1/2}:2^{1/2}:(5/2)^{1/2}:3^{1/2}:2$. The possitions of these peaks can be indexed as the (110), (111), (200), (210), (211), and (200) reflections of an ordered bicontinuous double diamond (OBDD) structure, respectively.[12,13] For poly(styrene-*block*-isoprene) diblock copolymer, the ODBB structure was observed when PS content was in a range from 0.62 to 0.66 .[14] The PS content of the blend film of this study, 0.62, was close in the range. Thus, the morphology of annealed film was concluded to be the OBDD in a PS matrix.

Another important feature of the SAXS patterns is the appearance of a novel peak at $q = 1.69$ nm^{-1}. As described above, the basic morphology did not change by annealing. However, the TEM micrographs indicated the change of the shape of the P4VP domains. From $q = 1.69$ nm^{-1}, the d spacing was calculated to be 3.72 nm. This agreed well with not only the lamella thickness of the P4VP domains in the blend film used as a template but also the lamella thickness of the P4VP determined by Ikkala et al. by the small-angle X-ray scattering method.[5] Thus, it was concluded that the P4VP and PDP were phase-separated by annealing even though the PDP molar fraction to P4VP was only 0.16. Peaks at higher q could not be observed due to the low performance of the SAXS equipment. From these results, the morphology of the annealed blend film was concluded to be lamella-within-ODBB.

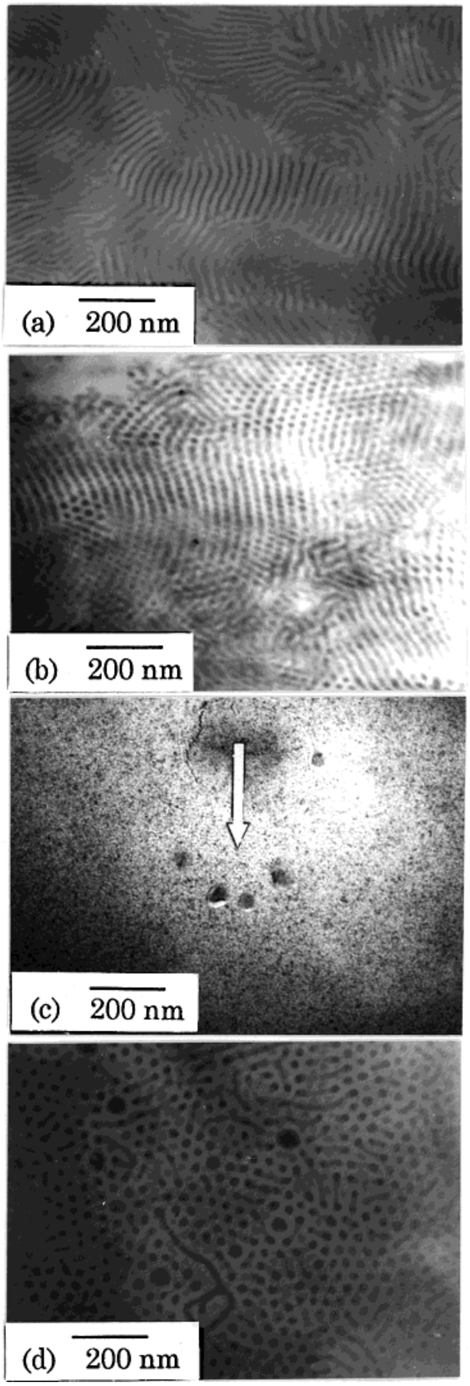

Figure 2. TEM micrographs of the P(S-*block*-4VP)/PDP blend film and cross-linked products stained with methyl iodide: (a) blend film without annealing, (b) blend film with annealing, (c) shadowed specimen of the cross-linked products at an angle of 15°, (b) as-cast specimen of the cross-linked product.

To confirm the hydrogen-bonding formation, FT-IR measurements were carried out. Figure 4 showed the FT-IR profiles of the blend films with and without annealing. After annealing, the peak of the hydrogen-bonded pyridine appeared at 1006 cm^{-1}, and the free pyridine peak at 993 cm^{-1} vanished. Thus, it was concluded that the lamella-within-cylinder structure was formed by blending of the P(S-*block*-4VP) and PDP and annealing of the blend films.

In the OBDD structure, the tetrapod microdomain of PDP and P4VP is constructed with short rods, and P4VP domains would be discotic in the short rods. Thus, the discotic microgel will be obtained by cross-linking of lamella-within-OBDD instead of the lamella-within-OBDD. Then, the P4VP domains were cross-linked with

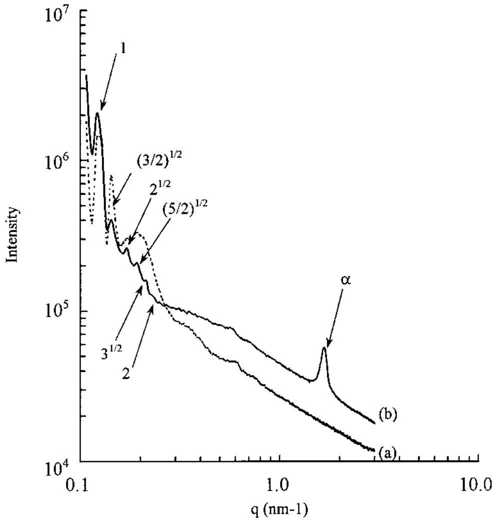

Figure 3. SAXS profiles of the blend films with and without annealing: (a) before annealing; (b) after annealing.

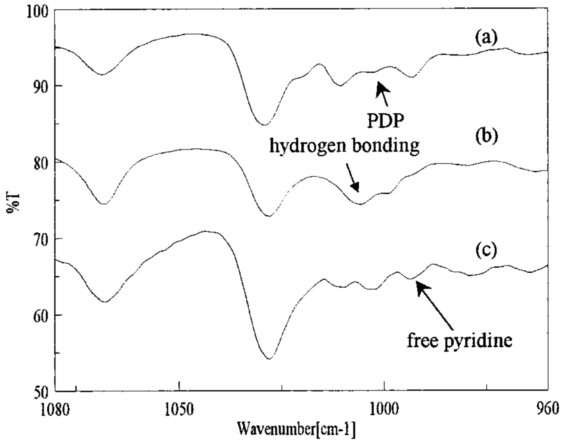

Figure 4. FT-IR profiles of the blend films and cross-linked product: (a) as-cast blend film; (b) annealed blend film; (c) purified product.

1,4-diiodobutane (DIB). After cross-linking, the annealed film was freely dissolved in chloroform, dimethylformamide, and tetrahydrofuran. The cross-link density determined by Volharts' titration was 39.8 mol %. The P4VP domains were tightly cross-linked. Then, PDP was removed from the cross-linked blend film by precipitation with *n*-hexane that is a good solvent for PDP. The removal of PDP was confirmed by FT-IR by vanishing of the peak at 942.5 cm^{-1} originated from the hydroxyl group of PDP (Figure 4).

The TEM micrographs of the purified cross-linked product are shown in Figure 2c,d. To investigate the external shape and height of the cross-linked product, the products were cast from dilute solutions, dried quickly, and observed by TEM by a shadowing technique (Figure 2c). In the micrograph, the white arrow indicates the shadowing direction. It was found that the external shape of the cross-linked product was a flat discotic microgel. On the opposite side of the cross-linked product from arrow, white regions (shadow) were observed. An average external diameter and an average maximum shadow length of the microgel were 44.0 and 10 nm, respectively. Since a shadowing angle was 15°, the height at the edge of the microgel was calculated as 2.7 nm (= 10 nm × tan 15°). Taking account of the *d* spacing measured by SAXS, 3.72 nm, and the volume fraction of P4VP to PDP/P4VP blend, 0.68, the height of the microgel was reasonable. To investigate the inside structure of the microgel, a TEM observation for the as-cast film of the microgel was carried out (Figure 3d). On the micrograph, round P4VP cores were observed. An average diameter of the P4VP core, 18 nm, agreed well with the average diameter of the P4VP microdomains in the blend film and was smaller than the external diameter of the microgel. This indicates that PS shell was surrounding the side of the P4VP cores. The specimens were cast from dilute solutions and dried quickly; the external size of the microgel shows the history of the expansion of PS chains in the solvents. Thus, the size of PS domains could not be discussed quantitatively. An arm number of the PS shell in the microgel that was calculated with the volume of the P4VP core was 14.

It was concluded that the discotic microgel with 2.7 nm height, 18 nm core diameter, and 44 nm external diameter was synthesized by cross-linking of the discotic microdomains in the lamella-within-OBDD. However, structural details of the microgels in solution and in the solid state are unclear. Further investigations are required.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 11650905) from the Ministry of Education, Science, Sports and Culture in Japan.

References and Notes

(1) Ishizu, K. *Polymer* **1989**, *30*, 793−798.
(2) Ishizu, K.; Onen, A. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 3721.
(3) Saito, R.; Kotsubo, H.; Ishizu, K. *Eur. Polym. J.* **1991**, *27*, 1153−1159.
(4) Saito, R.; Kotsubo, H.; Ishizu, K. *Polymer* **1992**, *33*, 1073−1077.
(5) Ruokolainen, J.; Saariaho, M.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1999**, *32*, 1152−1158.
(6) Ikkala, O.; Ruokolainen, J.; Markinen, R.; Tokkeli, M.; Serimaa, R.; Makela, T.; ten Brinke, G. *Synth. Met.* **1999**, *102*, 1498−1501.
(7) Makinen, R.; ten Brinke, G.; Ruokolainen, J.; De Odoric, W.; Ikkala, O.; Stamm, M.; de Moel, K. *Macromolecules* **2000**, *33*, 3441−3446.
(8) Ruokolainen, J.; ten Brinke, G.; Ikkala, O.; Tokkeli, M.; Serimaa, R. *Macromolecules* **1996**, *29*, 3409−3415.
(9) Ruokolainen, J.; Tokkeli, M.; Serimaa, R.; Vahvaselka, S.; Saariaho, M.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1996**, *29*, 6621−6628.
(10) Ruokolainen, J.; Tokkeli, M.; Serimaa, R.; Komanschek, E.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1997**, *30*, 2002−2007.
(11) Scindler, A.; Williams, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1969**, *10*, 832.
(12) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197−2202.
(13) Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651−1662.
(14) Floudas, G.; Pispas, S.; Hadjichristidis, N.; Paukula, T.; Erukhimovich, I. *Macromolecules* **1996**, *29*, 4142−4154.

MA002115T