Solvent Effect on the Aggregation Behavior of Rod–Coil Diblock Copolymers

Jie Zhang, Weiran Lin, Anhua Liu, Zhenning Yu, Xinhua Wan,* Dehai Liang,* and Qifeng Zhou

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry & Physics of MOE, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, P. R. China

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The water-induced aggregation behavior of rod–coil diblock copolymers based on poly(ethylene oxide) (PEO) and poly(1,2,5-bis[4-(2-methylbutoxy)phenyl]styrene) (PMBPS), PEO_{302}-b-PMBPS_{53}, was investigated in the common solvent THF and in the selective solvent dioxane. Before adding water, PEO_{302}-b-PMBPS_{53} stayed as single polymer chains no matter what conformation the PEO block took (i.e., either the random coil conformation in THF or the compact globule conformation in dioxane). The critical water content (≈6 wt %) at which PEO_{302}-b-PMBPS_{53} began to aggregate was also similar in both solvents, indicating that PMBPS dominated the aggregation process. However, the size, the size distribution, and the morphology of aggregates in THF/water were quite different from those in dioxane/water. Narrowly distributed spheres with $R_g \approx 20$ nm were observed in dioxane, whereas in THF, a bimodal distribution peaked at 3 and $\sim 300$ nm, was observed. The results from 2D wide-angle X-ray diffraction and polarized optical microscopy demonstrated that the PMBPS blocks packed in a parallel pattern upon aggregation in dioxane/water. The anisotropic disclike structures observed in THF/water also indicated the orientation of the PMBPS blocks upon forming aggregates in dilute solution.

Introduction

The design of unique macromolecular building blocks for ordered nanostructures is an important aspect in materials science, supramolecular chemistry, and biomimetic chemistry. Block copolymers having various immiscible segments covalently connected are capable of self-assembly into a wide range of nanoscale architectures in selective solvents. In the past decade, much effort has been made to understand the relationship between macromolecular structures, hierarchical supramolecular architectures, and the self-assembly process. It is generally believed that three factors (i.e., the stretching entropy of the core-forming blocks, the repulsive interaction of the coronal chains, and the core–corona interfacial energy) govern the structures of the aggregates formed by coil–coil block copolymers in selective solvents. Practically, a variation of solvents, block length, the ratio of one block to another, concentration, additives, and pH value can lead to the formation of a wide range of morphologies such as spheres, rods, lamellae, vesicles, and tubules. Rod–coil block copolymers composed of a rigid rod segment jointed to a flexible coil block exhibit much more distinct self-assembly features than do their coil–coil counterparts because of the orientation of the rigid block during aggregation. Moreover, they are able to form supramolecular architectures endowed with various functionalities through the rod blocks. Several studies on the microphase separation of block copolymers in the bulk have shown that the conformational asymmetry between rod and coil blocks plays a significant role in determining the geometry of the microdomains and the rod block has a tendency to form liquid-crystalline nematic phases with orientational order. Besides their behavior in the bulk, rod–coil block copolymers are also ready to form robust supramolecular structures in solution. For rod–coil diblock copolymers, besides the three contributions mentioned above, the orientation of the rod block also plays an important role during self-organization. Therefore, different ways can be found to change those factors to design interesting aggregates.
(phenylquinoline) (PPQ) in organic solvents upon tuning the rod block length or solvent quality. Among those aggregates, the vesicles had a specific single-layer structure by virtue of enhanced shell stiffness and surface tension due to the high in-plane order of the rigid PPQ block. The liquid-crystalline property of rodlike polymers in the bulk also has a great effect on the morphology of the suprastructure in solution. According to Li’s recent studies on amphiphilic block copolymers containing side-chain liquid-crystalline polymers as the hydrophobic core-forming segment, a smectic structure of block copolymers in bulk is associated with nanoparticle formation in water, whereas the copolymer that does not present a smectic phase in bulk self-assembles into vesicles instead of nanoparticles.

The incorporation of helical chains as rigid segments in rod–coil copolymers is of special interest because of their omnipresence in biological systems. Moreover, it opens a way to create unique supramolecular structures by providing extra-tunable chiral parameters. In a recent communication, we described the synthesis of a series of novel helix–coil diblock copolymers containing poly(ethylene oxide) (PEO) as a hydrophilic, flexible segment and poly[(+)-2,5-bis{4-[[(S)-2-methylbutoxy]-phenyl][styrene} (PMBPS) as a hydrophobic, rigid segment through atom-transfer radical polymerization. The bulky terphenyl group of PMBPS served to enforce a helical conformation of the rigid block, and the excess helical sense was induced by the chiral tails appended to the terphenyl moieties. Because of their amphiphilic nature and unique architecture, the copolymers self-assembled into a variety of suprastructures in aqueous solution, such as micelles, vesicles, and tubules. Moreover, the block copolymers also formed ordered structures from spherical aggregates to cylindrical aggregates depending on the surface pressure and the copolymer composition at the air–water interface.

Herein, we report the aggregation behavior of one of such diblock copolymer, PEO_{104-b-PMBPS}_{53} (where subscripts 104 and 53 denote the number-average degrees of polymerization of PEO and PMBPS, respectively) (Chart 1) in solvent mixtures of both tetrahydrofuran (THF)/water and dioxane/water. Both organic solvents were used to dissolve the copolymer first, and then the selective solvent, water, was added to induce the aggregation of the highly hydrophobic PMBPS block. It is envisioned that the initial conformational difference of the copolymer in the two solvents and its variation upon addition of water will remarkably influence the self-assembly process and the resultant suprastructures. Laser light scattering was used to monitor the changes in size and size distribution during the aggregation process. The morphology of the aggregates and the orientation of the rod block were studied separately by transmission electron microscopy, 2D wide-angle X-ray diffraction, and polarized optical microscopy.

### Experimental Section

#### Sample Preparation

Diblock copolymer PEO_{104-b-PMBPS}_{53} was synthesized and characterized according to the procedure reported previously. It was dissolved in HPLC-grade dioxane or THF to prepare homogeneous solutions at a concentration of 1.0 × 10^{-3} g/mL. For laser light scattering measurements, polymer solutions were filtered directly into dust-free light-scattering cells through Millex filters with a 0.45 μm pore size (Millipore, Billerica, MA). Deionized water (Milli-Q) passed through a filter with 0.22 μm pore size was added dropwise, and each of the water increment steps was about 1–3 wt %. After the addition of water, the polymer solutions were slightly shaken and allowed to sit at 25 °C for at least 20 min to reach equilibrium, which was evaluated by the time dependence of the scattering intensity. For transmission electron microscopy (TEM) measurements, about 35 wt % water was added dropwise at a rate of 0.5 wt %/min to THF and dioxane solutions, and the solutions were transferred to dialysis tubes (Huamei Bio-Engineering Co., molecular weight cutoff of 14 000 Da) and dialyzed against deionized water for 3 days to remove organic solvents. Deionized water was changed three times a day. After dialysis, the final aqueous solutions were further diluted for the sample preparation of TEM.

#### Laser Light Scattering

A commercial Laser light scattering spectrometer (Brookhaven Inc., Holtsville, NY) equipped with a BI-200SM goniometer and a BI-TurboCorr digital correlator was used to perform both static light scattering (SLS) and dynamic light scattering (DLS) over a scattering angle range of 15 to 155°. A 100 mW, vertically polarized solid-state laser (GNI, Changchun, China) operating at 532 nm was used as the light source. In SLS, the angular dependence of the excess absolute time-averaged scattering intensity was measured. In DLS, the intensity–intensity time correlation function G^{(2)}(\tau) in the self-beating mode was measured. It is related to the normalized first-order electric field time correlation function g^{(1)}(\tau) as

\[ G^{(2)}(\tau) = A[1 + \beta g^{(1)}(\tau)] \]  

where \( A \) is the measured baseline, \( \beta \) is a coherence factor, and \( \tau \) is the delay time. \( g^{(1)}(\tau) \) is further related to the line width (\( \Gamma \)) distribution \( G(\Gamma) \) by

\[ g^{(1)}(\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma \tau}d\Gamma \]

By using the CONTIN^{33} Laplace inversion program, the normalized distribution function of the characteristic line width \( G(\Gamma) \) was obtained. The line width \( \Gamma \) is a function of both \( C \) and \( q \), which can be expressed as

\[ \Gamma_q = D(1 + k_d C)[1 + f(R_d q)^2] \]

with \( D, k_d, \) and \( f \) being the translational diffusion coefficient, the diffusion second virial coefficient, and a dimensionless constant, respectively. When the concentration is extremely dilute and \( R_d q \ll 1 \), then \( \Gamma q^2 \) is approximately equal to \( D, D \) can be further converted to the hydrodynamic radius \( R_h \) by using the Stokes–Einstein equation

where $k_B$, $T$, $\eta$ are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

Estimation of the Solubility Parameter of Homo-PMBPS. The solubility parameter ($\delta$) of the homo-PMBPS was estimated according to the group contribution method \(^{(34)}\):

$$\delta = \frac{\rho \sum_j F_j}{M}$$ \hspace{1cm} (5)

where $\rho$ is the polymer density, $M$ is the molecular weight of the polymer, and $F_j$ is the molar attraction constant of functional group $j$ of the polymer, the values of which were given by Hoy. \(^{(34)}\)

The density of the homo-PMBPS sample was measured by a flotation technique. At room temperature, the sample was equilibrated with mixed solvents of different volumes of water and ethanol. At the buoyancy matching point, the sample floated freely for an extended period of time. According to the density of the mixed solvents, the values of which can be found in the literature, \(^{(35)}\), the density of homopolymer PMBPS, 0.978 g/cm$^3$, was obtained.

Transmission Electron Microscopy (TEM). TEM images were obtained on a JEM-100CX TEM operating at an acceleration voltage of 100 kV. A drop of the sample solution was mixed with a drop of 2% (w/v) aqueous solution of uranyl acetate. The mixture was deposited onto a carbon-coated copper EM grid for a few minutes. Excess solutions were blotted away with a strip of filter paper, and the sample grid was dried in air. As for the metal shadowing experiments, one drop of the sample solution was deposited on the grid and dried under vacuum. The sample was then shadowed with platinum at an angle of ca. 30°.

Wide-Angle X-ray Diffraction (WAXD). Two-dimensional WAXD patterns were obtained by using a Bruker D8 Discover diffractometer with a general area detector diffraction system (GADDS) as the detector. The 2D diffraction patterns were recorded in transmission mode at room temperature. The background scattering pattern was recorded and subtracted from the corresponding 2D WAXD patterns of the samples.

Polarized Optical Microscopy (POM). The phase morphology was identified via a Leica DML POM with a Mettler hot stage (FP 82 HT with an FP-90 central processor).

**Results and Discussion**

THF is a good solvent for PEO-b-PMBPS, whereas dioxane is a selective solvent for the PMBPS block. Therefore, the copolymer conformations of PEO$_{104}$-b-PMBPS$_{53}$ in THF and in dioxane should be different. When water, a non-solvent for PMBPS but a good solvent for PEO, is added to solutions to induce the aggregation of the PMBPS block, the copolymer should exhibit different behaviors in THF/water from that in dichloromethane/water.

Figure 1 shows the DLS results of PEO$_{104}$-b-PMBPS$_{53}$ in THF (left panels) and in dioxane (right panels) after adding different amounts of water. In pure THF, only one component with $R_{\text{app}} \approx 3.7$ nm was observed, corresponding to the size of PEO$_{104}$-b-PMBPS$_{53}$ single chains. With increasing water content, the size and the size distribution remained constant. As the water content reached about 6.9 wt%, a larger component that peaked at $\approx 240$ nm was observed at a scattering angle of 90°. Even though only one component was observed at a scattering angle of 90°, its size distribution was significantly broadened, indicating the occurrence of aggregation. With more water added, the aggregation became stronger, not only demonstrated as the appearance of the bimodal distribution at a scattering angle of 90° but also as an increase in the size and area ratio of the larger component measured at 30°. As the water amount reached 19.4 wt%, the $R_{\text{app}}$ value of the larger component was increased to $\approx 295$ nm when measured at 30°. Even though the size of the smaller component remained almost constant with increasing water content, its area ratio was decreased, indicating the transition of single polymer chain to aggregates. Adding more water gave rise to heavy turbidity, making the LLS measurement impractical. Because the excess scattered intensity was roughly proportional to the sixth power of the size, the intensity-averaged peak ratio in Figure 1A indicated that the number of single polymer chains was still much larger than the number of aggregates even at 19.4 wt% water content.

The aggregation behavior of PEO$_{104}$-b-PMBPS$_{53}$ in dioxane/water was quite different from that in THF/water. As shown in the right panels of Figure 1, only one component with $R_{\text{app}} \approx 3$ nm was observed in pure dioxane. As the water content reached about 6.2 wt%, almost all of the single polymer chains in the solution formed micelles with $R_{\text{app}} \approx 18$ nm. Adding more water to the solution has little effect on the size of the micelles. Figure 2 exhibits the changes in size of PEO$_{104}$-b-PMBPS$_{53}$ and its aggregates with increasing water content. In pure dioxane, the size of PEO$_{104}$-b-PMBPS$_{53}$ in a single chain conformation was 3.4 nm, slightly smaller than that in THF. It sharply increased to about 18 nm at the onset of aggregation and the water content reached $\approx 6$ wt%. A further increase in water contents to above 20 wt% has almost no effect on the size of aggregates ($R_v \approx 20$ nm). For a better comparison, Figure 2 also shows the size change of the smaller component observed in THF.

Figure 3 depicts the selected correlation functions measured at a scattering angle of 30° for PEO$_{104}$-b-PMBPS$_{53}$ in pure solvents and in solvent mixtures where aggregation occurred. Note that the measured and calculated baselines have a difference of $\approx 0.1\%$. As shown in Figure 3, PEO$_{104}$-b-PMBPS$_{53}$ solutions in both types of solvent mixtures showed slower relaxations and higher apparent coherences after the occurrence of aggregation than in pure solvents. In THF solution with 8.5 wt% water, two relaxation modes, which corresponded to the bimodal distribution shown in Figure 1, were observed. The different apparent coherences in Figure 3 were mainly caused by the scattering intensities. Figure 4 displays the changes in the absolute excess scattered intensities of PEO$_{104}$-b-PMBPS$_{53}$ at different water contents. Only the data measured at scattering angles of 30 and 90° were shown, and the excess scattering intensity was also corrected by concentration for accuracy and for better comparison. At a water content below 5 wt%, where aggregation had not occurred, the excess scattering intensity showed no angular dependence, and the values in THF/water were very close to that in dioxane/water. At a water content above the critical point ($\approx 6$ wt%), the excess scattering intensity in THF/water increased slowly and a stronger angular dependence was observed at elevated water content, whereas in dioxane the intensity sharply increased from $\approx 1000$ (au) to $\approx 6000$ (au) when the water content increased by 13 wt% and no prominent increase was observed upon increasing the water content to 20 wt%. Although the aggregates with $R_{\text{app}} \approx 20$ nm that formed in dioxane/water were much smaller than those that formed in THF (more than 300 nm), the excess scattering intensity was stronger.

Figure 5 compares the angular dependence of the reciprocal excess scattered intensity of PEO$_{104}$-b-PMBPS$_{53}$ in THF and in dioxane after adding $\approx 20$ wt% water. In the mixture of THF and water, a pronounced downward curvature at low scattering

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angles is observed. This is a typical curve due to the presence of large aggregates, which agreed with the DLS results in Figure 1. The $R_{g,app}$ value of the aggregates was able to be roughly estimated from the scattering intensity at low scattering angles from 20 to 40° by extrapolating to zero angle. As indicated by the solid line in Figure 5, the $R_{g,app}$ value of the aggregates was calculated to be 640 nm. By combining the DLS results in Figure 1, the conformation of the aggregates can be estimated from the $R_g/R_h$ ratio. It was well established in the literature that the $R_g/R_h$ ratios were 0.775 and 1.5 for a solid sphere and random coil, respectively. With the $R_{h,app}$ value of the aggregate being 283 nm after extrapolating to zero angle (data from Figure 1), $R_{g,app}/R_{h,app} = 2.3$, which was much larger than the ideal value for a random coil, indicating the existence of a certain anisotropy of the aggregate. Figure 5 also presents the weak angular dependence of the excess scattering intensity of PEO104-$b$-PMBPS53 in dioxane with a similar amount of water. Actually, the curve was slightly upward at low scattering angles (indicated by the dotted line). Such curvature was also observed at other elevated water contents (data not shown). On one hand, the weak angular dependence suggested that the $R_g$ value of the particles

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was very small, usually less than 5% that of the wavelength of the laser. On the other hand, the negative $R_g$ value obtained at low scattering angles was not rare in the study of copolymers by SLS. Usually, the refractive index of the chosen solvent was somewhere in between those of the different monomers in the copolymer. $^36$ In our case, both of the refractive indices of dioxane (1.422) and water (1.334) were smaller than those of PEO and PMBPS, both of which were larger than 1.45. Therefore, there must be another reason for the abnormality in dioxane/water. According to the findings by Burchard, $^37$ it could be attributed to the water-induced ordering of block copolymers or aggregates (especially the parallel packing of PMBPS segments).

The above LLS results have demonstrated that PEO$_{104}$-b-PMBPS$_{53}$ formed aggregates in either THF or dioxane by adding water to about 6 wt %, and the aggregates in dioxane/water possessed a different morphology and size distribution from those in THF/water. To confirm the above results, we replaced the organic solvent with water by dialysis and visualized the aggregates by TEM. Because of the strong hydrophobicity of the core-forming PMBPS block, the structure of the aggregates formed in the mixed solvent could be “frozen” or maintained during dialysis. Therefore, the structure observed by TEM was able to reflect the real structure in the mixed solvent. As shown in Figure 6A, the aggregates formed in dioxane/water were spheres with an average diameter of ~39 nm, and the size distribution was very narrow, which agreed well with the results from LLS. While in THF/water, besides the spherical disc-like structures with a diameter larger than 100 nm and thickness of ~20 nm, many smaller fragments were observed (Figure 6B). Considering the existence of the large number of single polymer chains (Figure 1A) and the fact that water was not able to “freeze” them, we attributed the small fragments in Figure 6B to the aggregates formed by those single polymer chains during the dialysis process before TEM sample preparation.

A fascinating feature in the field of rod–coil block copolymer self-assembly is the anisotropic aggregation of the molecules. Several studies of the microphase separation of block copolymers in bulk have shown the rod blocks are capable of forming liquid-crystalline nematic phases with orientational order. $^{17,19,20}$ However, a few studies on spherical aggregates formed from rod–coil block copolymers in selective solution give evidence of the ordered structure of the rigid rod in the core. Does the rigid rod PMBPS pack in orientational order during the aggregation process? To clearly answer this question, we investigated the liquid-crystalline property of the spherical aggregate powder, prepared by freeze-drying the polymer aggregate solution, by a combination of the POM and 2D WAXD.

The single polymer chains also formed aggregates in THF/water during dialysis, and the structure of such aggregates was difficult to define. We studied only the orientational behavior of the sample obtained from dioxane/water. Figure 7 presents a 2D WAXD pattern of the aggregate powder at room temperature. Strong diffraction can be seen at $2\theta = 4.6^\circ$ (d spacing of 1.91
which is very close to the characteristic diffraction of the liquid-crystalline phase of PMBPS at high temperature, which suggests that the ordered structure of the rod was developed during the aggregation process. Obvious birefringence was also observed at room temperature, and the intensity of birefringence increased after the aggregate sample was sheared, as shown in the image of POM (Figure 8). Moreover, the intensity of the birefringence did not decrease at a temperature above the melting point of PEO, implying that the birefringence originated from the anisotropic arrangement of the PMBPS segment instead of the crystallization of PEO.

The above observations could be reasonably well explained by using the solvent quality of THF and dioxane. Both THF and dioxane are good solvents for the PMBPS block. The calculated values of the solubility parameter ($\delta$) also indicated that THF ($\delta = 18.6$) should be a slightly better solvent than dioxane ($\delta = 20.5$) for PMBPS ($\delta = 17.4$). In other words, PMBPS chains might adopt a more relaxed conformation in THF than in dioxane. As for the PEO block, it has been well documented that THF is a good solvent but dioxane is a nonsolvent. On the basis of this information, a possible mechanism of the reasonable water-induced aggregation of PEO$_{104}$-b-PMBPS$_{53}$ in THF and dioxane was proposed, as shown in Scheme 1. Because dioxane is a nonsolvent for PEO, a micellar structure with PEO being the core and PMBPS being the corona would be expected for PEO$_{104}$-b-PMBPS$_{53}$ in pure dioxane. However, LLS results showed that $R_{\text{app}}$ of PEO$_{104}$-b-PMBPS$_{53}$ was $\sim 3$ nm (Figure 2) and the excess scattering intensity was relatively weak (Figure 4), indicating that PEO$_{104}$-b-PMBPS$_{53}$ stayed as single polymer chains in pure dioxane. We attribute this to the architecture of the block copolymer. The PMBPS block had a higher molecular weight but a shorter contour length than the PEO chain. Together with the helix conformation, the PMBPS block was bulky and cumbersome. However, the PEO chain was condensed in dioxane, and the diameter of the condensed globule might be smaller or not much larger than the thickness of the PMBPS rod. Therefore, the condensed PEO block was not able to pull PMBPS chains together to form the micellar structure. In other words, the conformation of PEO$_{104}$-b-PMBPS$_{53}$ in pure dioxane was determined predominantly by the PMBPS block. Because of its size and conformation, the PMBPS block was much more sensitive to environmental changes than was the PEO block. When a small amount ($<5$ wt %) of water was added, the decrease in the solvent quality was not enough to induce a conformational change.

Figure 6. Typical TEM images of PEO$_{104}$-b-PMBPS$_{53}$ (A) in dioxane/water and (B) in THF/water. The inset image in B came from the copper grid shadowed with platinum at an angle of ca. 30°.

Figure 7. Two-dimensional WAXD powder pattern of PEO$_{104}$-b-PMBPS$_{53}$ powder obtained from dioxane/water.

Figure 8. POM picture of the powder sample of aggregates formed from PEO$_{104}$-b-PMBPS$_{53}$ observed at room temperature after shearing. The arrow represents the shear direction.

in PEO104-b-PMBPS53. At a water content of ~6 wt %, PMBPS chains started to aggregate, which also facilitated the aggregation of PEO blocks. Therefore, most of the single polymer chains got into the micelles in a short time period, which was demonstrated in the disappearance of the mode at \( R_h \approx 3 \) nm (Figure 1) as well as sharp increases in size (Figure 2) and in excess scattering intensity (Figure 4). Adding more water not only caused the PMBPS blocks to be strongly aggregated but also made the PEO chains more relaxed. Eventually, the size and the excess scattering intensity remained constant with increasing water content.

The water-induced aggregation behavior of PEO104-b-PMBPS53 in THF was quite different from that in dioxane. Because THF is a good solvent for both PEO and PMBPS, the block copolymer was in a more relaxed conformation. Therefore, the size of PEO104-b-PMBPS53 in pure THF was slightly larger than that in dioxane (Figure 2). Adding water changed the solvent quality mainly for the PMBPS block. The critical water content (~6.9 wt %) at which PEO104-b-PMBPS53 starts to aggregate in THF/water was very close to that in dioxane/water (~6.0 wt %), indicating again that PMBPS was sensitive to environmental changes and dominated the aggregation process. Because of the good solubility of PEO in THF and water, the aggregation process of PEO104-b-PMBPS53 was weak and mild. However, once aggregation started, there was the tendency to form large, anisotropic disc-like structures (Figure 6). A possible explanation was as follows. The growth of disc-like structures and their stability were controlled by the orientation of the hydrophobic rod blocks. Once the orientation was formed, more polymer chains would join in, trying to cover the hydrophobic edge of the disc. However, such a process also decreased the stability of the disc. Therefore, the disc-like structure would be destroyed when the size reached a certain value. In other words, equilibrium has been reached between the single polymer chains and disc-like aggregates. Of course, the chance of forming such anisotropic structures was proportional to the water content, which was demonstrated as the increase in size (Figure 2) and in the excess scattering intensity (Figure 4).

As discussed above, it was the PMBPS block that dominated the water-induced aggregation process. However, it was the conformation of PEO that endowed the aggregation of PEO104-b-PMBPS53 with quite different morphology. The packing and orientation of PMBPS blocks in the core of aggregates in dioxane/water were evidenced. The anisotropic behavior observed from LLS and the disc-like structures visualized from TEM also demonstrated the orientation of PMBPS blocks in the aggregates formed in THF/water.

Conclusions

In the common solvent of THF and in the selective solvent of dioxane, the rod–coil diblock copolymer, PEO104-b-PMBPS53, showed quite different aggregation behavior by adding water. In dioxane/water, spherical micelles were confirmed by LLS and TEM, whereas in THF/water, anisotropic disc-like structures coexisted with a large number of single polymer chains. PEO104-b-PMBPS53 formed liquid-crystalline domains in the cores of micelles with PMBPS oriented parallel upon aggregation. It was the rod block that dominated the aggregation process, whereas the initial conformation of the coil block showed a profound effect on the aggregate structure.

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