Self-Assembled Nanostructure of a Novel Coil−Rod Diblock Copolymer in Dilute Solution

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Abstract: A novel narrowly distributed rod−coil diblock copolymer, poly(styrene-*block*-(2,5-bis[4-methoxyphenyl]oxycarbonyl)styrene) (PS-*b*-PMPCS), was synthesized by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated living free radical polymerization. The rodlike PMPCS block is a mesogen-jacked liquid crystalline polymer and is soluble in *p*-xylene at temperatures higher than 100 °C. When a PS-*b*-PMPCS dilute solution is cooled, the copolymer chains can self-assemble into a core−shell nanostructure. The temperature-induced self-assembly was studied. We showed, *for the first time*, that instead of a neutron scattering, a combination of static and dynamic laser light scattering results could also lead to the core radius (R_c) and the shell thickness (ΔR). Using this novel method, we found that when more chains were assembled into the nanostructure, R_c remained as a constant, close to the contour length of the PMPCS block, but the shell became thicker, indicating that the attraction between the insoluble rigid rodlike PMPCS blocks led to their insertion into the core, while the repulsion between the soluble coillike PS blocks forced them to stretch in the shell.

Introduction

Diblock copolymers in a selective solvent could self-assemble into a variety of supramolecular structures through mutual interaction between polymer segments and solvent.[1−7] Multiple morphologies, i.e., spherical micelles,[1−3] rods,[4,5] vesicles,[4,6] and lamellae,[7] were recently found. The formation of specific morphology could be controlled by the relative block length, the solvent composition, the polymer concentration, additives (salts, homopolymers, etc.), and temperature.[1,4,6,7] The core−shell model was often used when the copolymer solution was dilute.[2,4,7−9] Diblock copolymers consisting of a flexible coil block and a rigid rod block are a new kind of fantasizing materials, which have attracted a lot of research interests.[10−16]

It is important to control the supramolecular nanostructure of a self-organizing material for its desired functions and properties.[11−15] Most of the past studies in this aspect were focused on final morphologies and less attention has been paid to the detail of how these rod−coil block copolymers are self-assembled together in solution.[4,13,17]

Recently, we have developed a novel coil−rod diblock copolymer poly(styrene-*block*-(2,5-bis[4-methoxyphenyl]oxycarbonyl)styrene) (PS-*b*-PMPCS). The rodlike PMPCS block is a novel mesogen-jacked liquid crystalline polymer[18−20] soluble in *p*-xylene at temperatures higher than 100 °C. Therefore, *p*-xylene at lower temperatures is a selective solvent for PS-*b*-PMPCS. In the present study, we took PS-*b*-PMPCS as a model system for the study of the self-assembly of coil−rod diblock copolymers in solution. Using a recently developed method, we have shown that a combination of static and dynamic laser light scattering (LLS) can be used to obtain not only the average association number of the chains (n_{chain}) in the self-assembly and the average size of the nanostructures, but also the core radius, the shell thickness, and the core and shell densities on the basis of the core−shell model. Our focus in this study was

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† The Chinese University of Hong Kong.
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(1) Henslewood, F.; Liu, G. *Macromolecules* **1997**, *30*, 488−493 and references therein.
(2) Harada, A.; Kataoka, K. *Science* **1999**, *283*, 65−67 and references therein.
(3) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728−1731 and references therein.
(4) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372−375 and references therein.
(5) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960−963.
(6) Discher, B. M.; Discher, D. E.; Hammer, D. A. et al. *Science* **1999**, *284*, 1143−1146.
(7) Svensson, M.; Alexandridis, P.; Linse, P. *Macromolecules* **1999**, *32*, 637−645.
(8) Kriz, J. et al. *Macromolecules* **1999**, *32*, 397−410.
(9) Matsumoto, K.; Kubota, M.; Matsuoka, H.; Yamaoka, H. *Macromolecules* **1999**, *32*, 7122−7127.
(10) Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225−1232.
(11) Chan, V. Z.-H.; Hoffman, J.; Thomas, E. L. et al. *Science* **1999**, *286*, 1716−1719.
(12) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384−389.

(13) Zubarev, E. R.; Pralle, M. U.; Li, L.; Stupp, S. I. *Science* **1999**, *283*, 523−526.
(14) Lee, M.; Cho, B.-K.; Kang, Y.-S.; Zin, W.-C. *Macromolecules* **1999**, *32*, 7688−7691.
(15) Schneider, A.; Zanna, J.-J.; Yamada, M.; Finkelmann, H.; Thomann, R. *Macromolecules* **2000**, *33*, 649−651.
(16) Yamada, M.; Itoh, T.; Nakagawa, R.; Hirao, A.; Nakahama, S.-I.; Watanabe, J. *Macromolecules* **1999**, *32*, 282−289.
(17) Wu, C.; Niu, A.; Leung, L. M.; Lam, T. S. *J. Am. Chem. Soc.* **1999**, *121*, 1954−1955.
(18) Zhou, Q.-F.; Zhu, X.; Wen, Z. *Macromolecules* **1989**, *22*, 491−493 and references therein.
(19) Liu, Y. X.; Zhang, D.; Wan, X. H.; Zhou, Q.-F. *Chin. J. Polym. Sci.* **1998**, *16*, 283−288.
(20) Wan, X.; Tu, Y.; Zhang, D.; Zhou, Q.-F. *Chin. J. Polym. Sci.* **1998**, *16*, 377−380.

Scheme 1. Synthesis Route of the Coil−Rod Diblock Copolymer Poly(styrene-*block*-(2,5-bis[4-mathoxyphenyl]-oxycarbonyl)styrene) (PS-*b*-PMPCS)
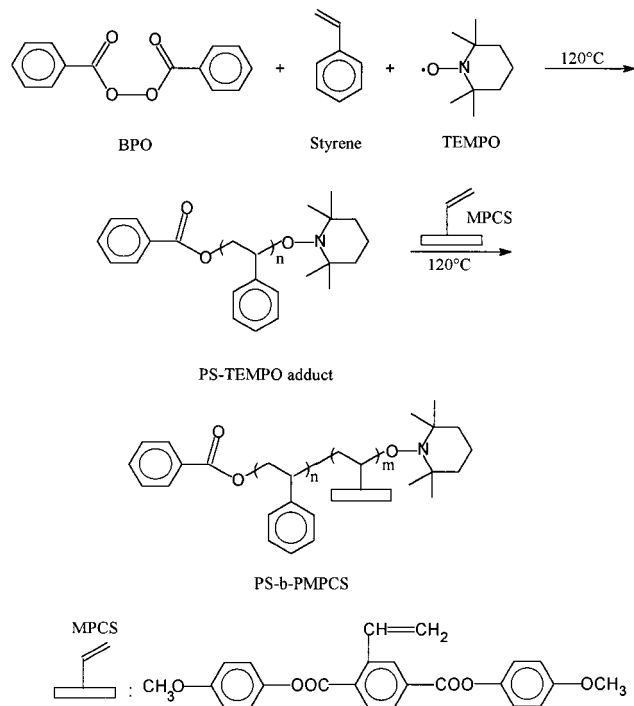
on how these microscopic parameters were affected by the copolymer concentration.

Experimental Section

Sample Preparation. In PMPCS, the mesogenic units are directly attached to the chain backbone at the waist.[18] MPCS was prepared by an established method.[19] PS-*b*-PMPCS was synthesized by TEMPO mediated radical polymerization, as shown in Scheme 1.[20] Freshly distilled styrene, benzoyl peroxide (BPO), and TEMPO were charged into a polymerization tube. After being degassed with 3 freeze−thaw cycles, the tube was sealed off under vacuum. The reaction mixture was kept at 90 °C for 3 h to ensure a complete decomposition of BPO. The reaction was carried at 120 °C for 15 h. The PS-TEMPO adduct was precipitated in methanol and dried overnight in a vacuum. Using *p*-xylene as solvent and PS-TEMPO adduct as initiator, we were able to polymerize MPCS at 120 °C. The solution was clear and colorless during the polymerization. The diblock copolymer was harvested in methanol and dried overnight in a vacuum. The unreacted substances was removed by a cyclohexane extraction.

The PS initiator has a number-average molar mass of 52 000 g/mol and a polydispersity index of 1.34 determined by size exclusion chromatography. The copolymer composition was attained by nuclear magnetic resonance (¹H NMR, DPX300) with dichloromethane-d_2 as solvent. The block lengths were estimated from the intensity ratio of methoxy ($\delta = 3.3-3.8$) and the aromatic ($\delta = 6.3-7.2$) groups. The diblock copolymer used in this work, on average, contained 520 styrene and 119 MPCS repeating units and had a polydispersity index of ∼1.3 estimated from the line width measured in dynamic LLS. A stock solution (5.00×10^{-4} g/mL) was prepared by dissolving PS-*b*-PMPCS in *p*-xylene at 110 °C. A subsequent dilution resulted in a series of solutions with different designed concentrations. Before being cooled to 25 °C, the dilute solutions were kept at 110 °C to ensure complete dissolution. The solutions were left to stand at 25 °C for 24 h before the LLS measurement. All the solutions were clarified by a 0.45 μm Millipore LCR filter to remove dust.

Laser Light Scattering. In static LLS,[21] we were able to obtain the weight-average molar mass (M_w) and the *z*-average root-mean-square

(21) Chu, B. *Laser light scattering*, 2nd ed.; Academic Press: New York, 1991.
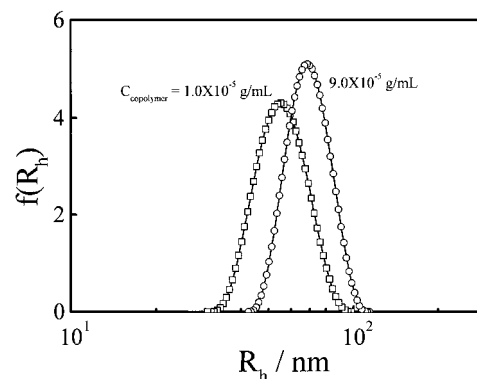

Figure 1. Concentration dependence of hydrodynamic radius distribution f(R_h) of self-assembled PS-*b*-PMPCS nanostructures in *p*-xylene at 25 °C.

radius of gyration ($\langle R_g^2 \rangle^{1/2}$ or written as $\langle R_g \rangle$) of the scattering objects in a very dilute dispersion from the angular dependence of the excess absolute scattering intensity, known as the Rayleigh ratio $R_{vv}(q)$, where q is the scattering vector. The specific refractive index increment (dn/dC) was determined by a novel and precise differential refractometer.[22] The refractive index increments of PS and PMPCS in *p*-xylene are nearly identical (dn/d$C = 0.112 \pm 0.002$ mL/g at 25 °C and 532 nm). Therefore, we were able to determine the true weight-average molar mass of the self-assembled PS-*b*-PMPCS nanostructures. In dynamic LLS,[23] the cumulants analysis of the measured intensity−intensity time correlation function of a narrowly distributed scattering object could lead to an accurate average line width $\langle \Gamma \rangle$. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $D = (\Gamma/q^2)_{q\to0,c\to0}$ or the hydrodynamic radius R_h by $R_h = k_BT/(6\pi\eta D)$ with k_B, η, and T being the Boltzmann constant, solvent viscosity, and the absolute temperature, respectively. The details of our LLS instrumentation can be found elsewhere.[24] In this study, the solutions were so dilute (∼10^{-5} g/mL) that the extrapolation of $C \to 0$ was not necessary.

Results and Discussion

The size distribution in Figure 1 shows a clear self-assembly of PS-*b*-PMPCS in *p*-xylene at 25 °C because the hydrodynamic radius in the range 30−100 nm is larger than that of individual chains. These self-assembled PS-*b*-PMPCS nanostructures are narrowly distributed with a relative line width ($u_2/\langle\Gamma\rangle^2$) no more than 0.03, implying that they are well-defined, presumably micelle-like core−shell nanostructures with the insoluble PMPCS and soluble PS blocks respectively as the core and shell. The size of the nanostructures increases with the copolymer concentration. The self-assembly can be better viewed in terms of the change of the average molar mass of such formed nanostructures.

Figure 2 shows that the weight average molar mass of the nanostructures increases with the copolymer concentration in the range $(1.0-9.0) \times 10^{-5}$ g/mL, different from the self-assembly of poly(styrene-*block*-3-hydroxymethylsilacyclobutane) in toluene or methanol reported by Yamaoka et al.;[25] namely, they found that the size was nearly independent of the copolymer concentration in the 0.5−3.0 wt % range. It is worth noting that it is not easy to study the concentration dependence of the self-assembly of diblock copolymer chains in an extremely dilute solution. Most of the reports in the literature

(22) Wu, C.; Xia, K.-Q. *Rev. Sci. Instrum.* **1994**, *65*, 587−590.

(23) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.

(24) Wu, C.; Zhou, S. Q. *Macromolecules* **1995**, *28*, 8381−8387. Wu, C.; Zhou, S. Q. *Macromolecule* **1996**, *29*, 1574−1578.

(25) Matsumoto, K.; Miyagawa, K.; Matsuoka, H.; Yamaoka, H. *Polym. J.* **1999**, *31*, 609−613.
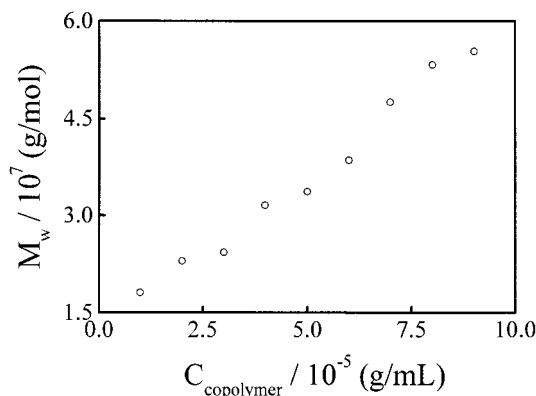
Figure 2. Concentration dependence of weight-average molar mass (M_w) of self-assembled PS-*b*-PMPCS nanostructures in *p*-xylene at 25 °C.
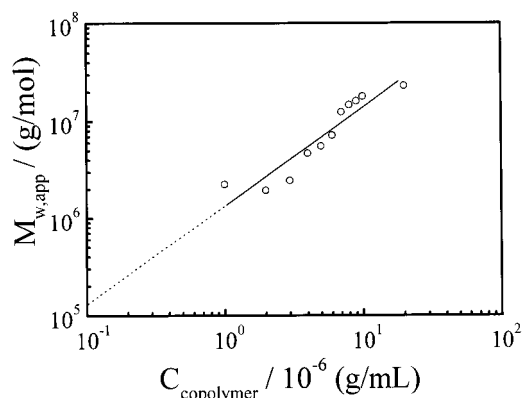

Figure 3. Concentration dependence of apparent weight-average molar mass ($M_{w,app}$) of PS-*b*-PMPCS in an extreme dilute region. The extrapolation leads to an estimate of critical association concentration of PS-*b*-PMPCS in *p*-xylene at 25 °C.
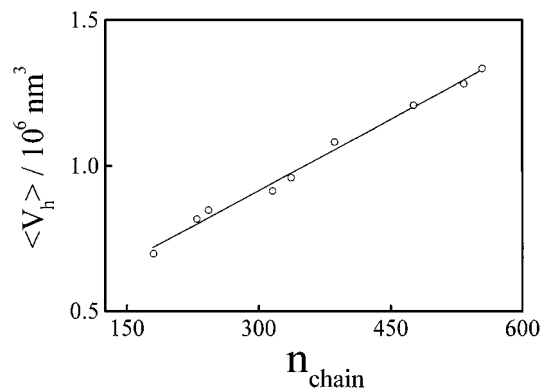

Figure 4. Association chain number (n_{chain}) dependence of average hydrodynamic volume $\langle V_h \rangle$ of self-assembled PS-*b*-PMPCS nanostructures in *p*-xylene at 25 °C.
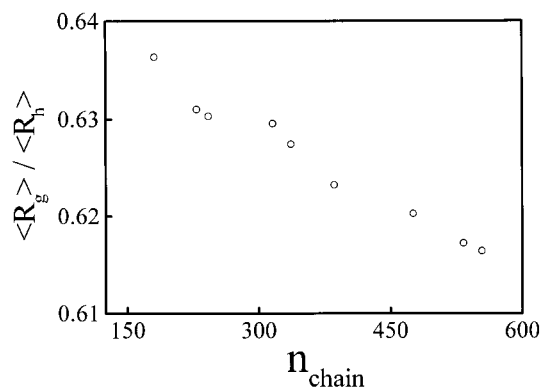

Figure 5. Association chain number (n_{chain}) dependence of $\langle R_g \rangle / \langle R_h \rangle$ of self-assembled PS-*b*-PMPCS nanostructures in *p*-xylene at 25 °C, where $\langle R_g \rangle$ and $\langle R_h \rangle$ are average radius of gyration and average hydrodynamic radius, respectively.

were limited to the range of $> 10^{-4}$ g/mL. Moreover, the critical association concentration (CAC) of diblock copolymers in a selective solvent is usually so low that its determination is extremely difficult, if not impossible.

Figure 3 shows that the extrapolation of the apparent weight-average molar mass of PS-*b*-PMPCS to that of individual copolymer chains ($\sim 10^5$ g/mol) reveals that PS-*b*-PMPCS in *p*-xylene has a CAC lower than $\sim 10^{-7}$ g/mL at 25 °C. This method of estimating CAC was previously used by Zhou et al.[26] and Iyama et al.[27] Therefore, when working in the range $10^{-5}-10^{-4}$ g/mL, we could neglect the effect of this small CAC in all the LLS calculations. From the weight-average molar masses of the nanostructures and individual copolymer chains, we were able to calculate the average association number of the chains inside each nanostructure.

Figure 4 shows that the average hydrodynamic volume ($\langle V_h \rangle$) of the PS-*b*-PMPCS nanostructures increases linearly with n_{chain}. The average chain density estimated from the slope of "$\langle V_h \rangle$ vs n_{chain}" is ~ 0.1 g/cm^3, much lower than that of the corresponding bulk copolymer, but higher than the copolymer chains swollen in a good solvent. This density probably reflects the packing of the insoluble PMPCS blocks in the core and the stretching of the swollen PS blocks in the shell. The questions are (1) in which way the copolymer chains are self-assembled into the core and the shell and (2) how the core size and the shell thickness are influenced by the copolymer concentration. The

chain density distribution and conformation change can also be viewed in terms of the ratio of the radius of gyration to the hydrodynamic radius.

Figure 5 shows that $\langle R_g \rangle / \langle R_h \rangle$ decreases when more chains are assembled together. This is because $\langle R_h \rangle$ increases faster than $\langle R_g \rangle$. It is known that for a random coil chain in a good solvent, $\langle R_g \rangle / \langle R_h \rangle \sim 1.5$, and for a uniform sphere, $\langle R_g \rangle / \langle R_h \rangle \sim 0.775$. Figure 5 shows that $\langle R_g \rangle / \langle R_h \rangle < 0.775$, indicating that the center of the nanostructure has a higher density, which agrees with the presumed core−shell nanostructure. Previously, a similar low $\langle R_g \rangle / \langle R_h \rangle$ ratio was also observed for other self-assembled structures,[28] the adsorption of polymer chains on colloid particles,[29] and the molten globule state of a collapsed single homopolymer chain.[30] Unfortunately, this low value of $\langle R_g \rangle / \langle R_h \rangle$ has not been properly explained and attributed to the self-assembly of diblock copolymers in solution.

The core−shell nanostructure can be described by two concentric spheres.[31] The center is made of the insoluble blocks, while the outer corona consists of the soluble blocks swollen by solvent. For the first approximation, one can assume that the core and the shell have different, but uniform densities (ρ_c and ρ_s). Noolandi et al.[32] and Leibler et al.[33] used it to model

(26) Zhou, Z.; Chu, B.; Peiffer, D. G. *Macromolecules* **1993**, *26*, 1876−1883.

(27) Iyama, K.; Nose, T. *Polymer* **1998**, *39*, 651−658.

(28) Moffitt, M.; Yu, Y.; Nguyen, D.; Graziano, V.; Schneider, D. K.; Eisenberg, A. *Macromolecules* **1998**, *31*, 2190−2197.

(29) Wu, C.; Gao, J. *Macromolecules* **1999**, *32*, 1704−1705.

(30) Wu, C.; Wang, X. *Phys. Rev. Lett.* **1998**, *80*, 4092−4094.

(31) de Gennes, P.-G. In *Solid State Physics*; Liebert, L., Ed.; Academic: New York, 1978; Suppl. 14.

(32) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443−1448.

(33) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550−3557.
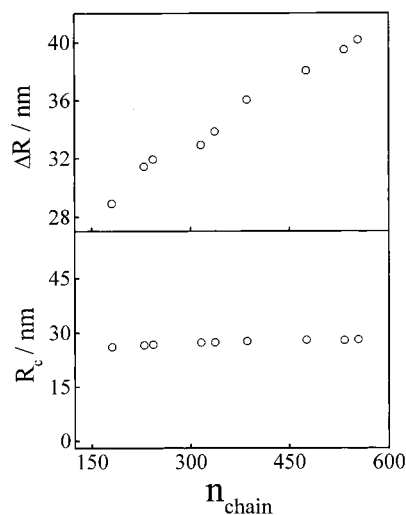
Figure 6. Association chain number (n_{chain}) dependence of the average radius of the PMPCS core (R_c) and average thickness of the PS shell (ΔR) of the self-assembled PS-*b*-PMPCS nanostructure at 25 °C.

the self-assembly of diblock copolymers in dilute solution and got some results in good agreement with the experimental data. Normally, neutron scattering is required to measure the core radius (R_c) and the shell thickness (ΔR). In the following, we like to show that a combination of static and dynamic LLS can also be used to estimate R_c and ΔR from the ratio of $\langle R_g \rangle / \langle R_h \rangle$. In the core−shell model, the masses of the core (M_c) and the shell (M_s) are

$$M_c = \frac{4}{3}\pi\rho_c R_c^3 \quad \text{and} \quad M_s = \frac{4}{3}\pi\rho_s(R^3 - R_c^3) \qquad (1)$$

where R is the radius of the outside sphere. Substituting eq 1 into the definition of R_g for a sphere, we obtain:

$$R_g^2 = \frac{\int_v \rho(r)r^2 \, dv}{\int_v \rho(r) \, dv} = \frac{\int_0^{R_c} 4\pi\rho_c r^4 \, dr + \int_{R_c}^R 4\pi\rho_s r^4 \, dr}{M_c + M_s} =$$

$$\frac{3[M_c R_c^2 R^3 - (M_c + M_s)R_c^5 + M_s R^5]}{5(M_c + M_s)(R^3 - R_c^3)} \qquad (2)$$

Setting the mass ratio $M_c/M_s = A$ and the radius ratio $R_c/R = x$, we can rewrite eq 2 as:

$$R_g^2 = \frac{3R^2[Ax^2 - (1 + A)x^5 + 1]}{5(1 + A)(1 - x^3)} \qquad (3)$$

Replacing R with R_h, we have

$$\frac{R_g}{R_h} = \left\{\frac{3[Ax^2 - (1 + A)x^5 + 1]}{5(1 + A)(1 - x^3)}\right\}^{1/2} \qquad (4)$$

Note that M_c/M_s equals to the mass ratio of the insoluble block and soluble blocks, a constant for a given diblock copolymer, independent of the actual density distributions of the core and shell. Therefore, for each measured $\langle R_g \rangle / \langle R_h \rangle$ in Figure 5, we are able to find a corresponding x according to eq 4 and further calculate R_c and ΔR since $R_c = \langle R_h \rangle x$ and $\Delta R = \langle R_h \rangle - R_c = \langle R_h \rangle (1 - x)$.

Figure 6 shows that R_c is nearly independent of n_{chain}, but ΔR increases with n_{chain}. It is worth noting that the values of R_c are sufficiently close to the contour length of the PMPCS block ($\sim$31 nm). This clearly reveals that when more copolymer chains
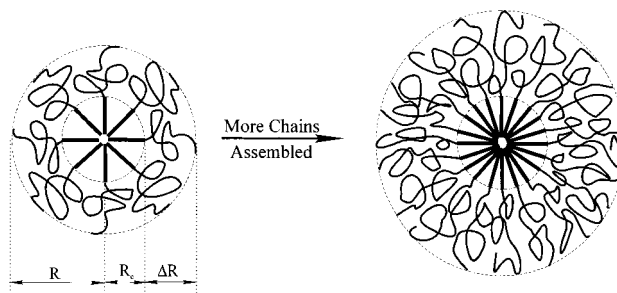

Figure 7. Schematic of a core−shell nanostructure formed by a self-assembly of coil−rod diblock copolymer chains in a selective solvent.
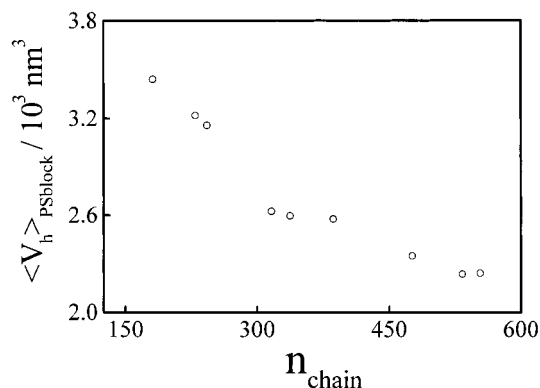

Figure 8. Association chain number (n_{chain}) dependence of average hydrodynamic volume per PS block in the shell ($\langle V_h \rangle_{PSblock}$) of the self-assembled PS-*b*-PMPCS nanostructure.

are self-assembled into the core−shell nanostructure, the insoluble rodlike PMPCS blocks are simply inserted into the core while the soluble coillike PS blocks are forced to stretch in the shell due to the repulsion in a good solvent. Further calculation shows that as n_{chain} increases from 180 to 554, the surface area occupied per PS block decreases from 47 to 18 nm^2 and the core density increases from 0.19 to 0.47 g/cm^3, further indicating the packing of the PMPCS blocks in the core and the elongation of the PS blocks in the shell, as shown in Figure 7.

The stretching of a coillike chain in the shell has previously been reported.[29] However, to our knowledge, a core with a constant size is observed for the first time. In the past, it was always assumed that the core had a chain density close to that of bulk polymer ($\sim$1 g/cm^3). However, our results clearly indicate that the core actually contains more than 50% of the solvent even in its highly packed state. Figure 8 shows that the average hydrodynamic volume per PS block in the shell decreases as n_{chain} increases. In other words, the average density of the shell increases as more diblock copolymer chains are inserted into the nanostructure. It reveals that the PS blocks are not only stretched, but also squeezed. The swollen PS blocks behave very similar to the polymer chains grafted on a given surface,[34−36] but very different from the adsorption of long polymer chains on a given surface because the average volume per adsorbed chain increased with the adsorption.[29]

Conclusions

The novel coil−rod diblock copolymer PS-*b*-PMPCS in a selective solvent, *p*-xylene, can self-assemble into a core−shell

(34) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069−1075.
(35) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051−1059.
(36) Jones, R. L.; Spontak, R. J. *J. Chem. Phys.* **1995**, *103*, 5137−5143.

nanostructure when the solution is cooled from 110 °C to room temperature. In this nanostructure, the rodlike thermotropic liquid crystal PMPCS blocks are closely packed in the core, while the swollen PS blocks act as the polymer chains grafted on the core. A combination of static and dynamic laser light scattering studies reveals that the average number of chains assembled in each nanostructure increases with the copolymer concentration, different from the self-assembly of normal diblock copolymers in a selective solvent. This difference can be attributed to a strong attraction between the insoluble rodlike thermotropic liquid crystalline PMPCS blocks. We observed, *for the first time*, that when more copolymer chains were assembled into the nanostructure, the size of the core remained a constant, very close to the contour length of the PMPCS block, but the PS blocks in the shell were stretched and compressed, because of the rigidity of the insoluble PMPCS block.