

Note

SELF-ASSEMBLY OF ROD-COIL DIBLOCK COPOLYMERS —
INFLUENCE OF THE ROD LENGTH*Ying-feng Tu^{a,b}, Xin-hua Wan^a, Hai-liang Zhang^a, Xin-he Fan^a, Dong-ning Lü^a,
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Abstract The self-assembly of five narrowly distributed novel rod-coil diblock copolymers, poly(styrene-*block*-(2,5-bis[4-methoxy-phenyl]oxycarbonyl)styrene) (PS-*b*-PMPCS), in *p*-xylene, a selective solvent at room temperature, was studied. The rod-coil copolymers, which have the same PS length but different PMPCS length, were synthesized by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated living free radical polymerization. The influence of the rod length on the self-assembly morphology was studied by transmission electron microscopy (TEM). At a concentration of 2.0 mg/mL, those copolymers with relatively shorter PMPCS length (copolymers 1 and 2) form individual spherical micelles; those with relatively longer PMPCS length (copolymer 3 and 4) form “pearl chains” coexisting with individual spherical micelles; the ones with longest PMPCS length form “pearl chains” coexisting with occasionally formed nanofibers. The diameter of all the morphologies was controlled by the rod length. This gives us a way to govern the self-assembly morphology by altering the length of one block in the block copolymer.

Keywords Self-assembly, Rod-coil copolymer, Living free radical polymerization

Spontaneous self-assembly of macromolecules through non-covalent bonds including hydrogen bonding and electrostatic or hydrophilic and hydrophobic interactions is an area of current interest because of its potential for creating supramolecular architectures in nanoscale dimensions with well-defined shapes and functions^[1–3]. Rod-coil copolymers, which have the ability to form liquid crystalline phases in melts as well as in solutions, have recently attracted much attention^[4–14] due to their tendency to form a variety of supramolecular structures. Stupp *et al.* reported on rod-coil copolymers consisting of an elongated mesogenic rod and a monodisperse polyisoprene and they proposed that these rod-coil copolymers can self-assemble into fascinating mushroom-shaped supramolecular structures^[5a]. Jenekhe and Chen reported the influence of solvent mixture on self-assembly of PPQ-PS rod-coil block copolymer. They found that the block copolymer can form spherical, vesicular, cylindrical, and lamellar aggregates when the solvent composition was changed^[6]. Lee *et al.* reported the synthesis of rod-coil copolymer consisting of two biphenyls and PPO block, studied their self-assembly in bulk state and the influence of the coil length, and found that they can form columnar (honeycomb-like) and bicontinuous cubic assemblies^[8]. However, reports on the influence of the rod length on the self-assembly of rod-coil copolymers are scarce and need further exploration. Recently, Zubarev *et al.* reported the influence of the rod length on the self-assembly of dendron rod-coils (DRC). Typically, the copolymers can self-assemble to form ribbonlike structures^[5b]. However, their rods consisted of small biphenyl molecules and the total molar mass of

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the rod is only about 1,000 Dalton. Here, we report our investigation of the influence of rod length on the self-assembly process and the morphology of rod-coil copolymers with long rods by transmission electron microscopy (TEM).

Recently, we have explored a way to synthesize a kind of novel rod-coil block copolymer by using 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) mediated living free radical polymerization^[15]. In the selective solvent *p*-xylene and at dilute concentrations, the block copolymer forms core-shell nanostructures as observed by static and dynamic laser light scattering (LLS)^[16]. When the concentration is increased, more rods insert into the core while the soluble coils in the shell stretch and elongate due to the repulsions between themselves. In this study we synthesized a series of rod-coil block copolymers (Fig. 1) in order to study the influence of rod length on the morphology of self-assembled structures. The copolymers consist of polystyrene (PS) as coil segment and poly(2,5-bis[4-methoxy-phenyl]oxycarbonyl)styrene) (PMPCS) as rod segment. The PS-*b*-PMPCS block copolymers were synthesized by the procedure we previously reported^[15], using TEMPO-polystyrene as initiator that consists of 620 repeating styrene units on average with a polydispersity index of 1.20. The rod-coil molecule 1, and its analogues with longer PMPCS rods, 2, 3, 4 and 5, respectively contain 90, 180, 310, 1000 and 1890 PMPCS repeating units as determined by ¹H-NMR as presented in Fig. 1, and have a polydispersity index of 1.22, 1.24, 1.25, 1.35 and 1.38, respectively, as determined by gel permeation chromatography (GPC) using standard polystyrene calibration.

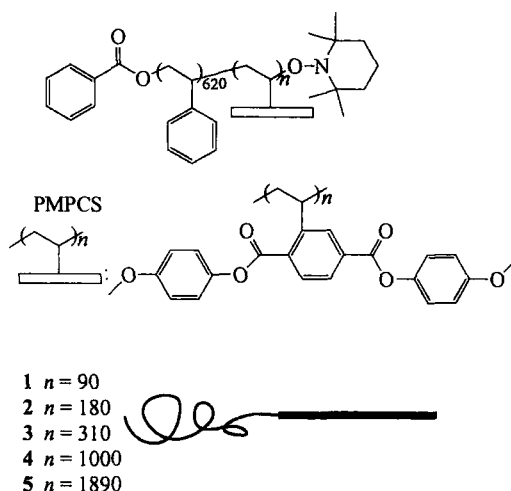


Fig. 1 Chemical structure and schematic drawing of rod-coil copolymers 1–5

p-Xylene is a good solvent for PS coils at any temperature but for PMPCS rods this is true only at temperatures higher than 100 °C. Thus the temperature-induced self-assembly takes place when a *p*-xylene solution of PS-*b*-PMPCS copolymer is cooled from high temperatures (> 110 °C) to room temperature. In this study, the solutions of the five copolymers at the concentration of 2.0 mg/mL were heated to 120 °C and kept at this temperature for 12 h to ensure complete dissolution. After quenching to 20 °C, the solutions were conditioned at room temperature for 2 days to completely remove the heat history. For TEM studies, the solution of the copolymer was dropped onto the carbon coated copper grid, stored for 5 min, and the residual solution was absorbed by tissue paper.

Figures 2–4 are the typical TEM images for the self-assembled structures of five rod-coil copolymers, directly observed without any staining. Because PMPCS rods contain heavier atoms (oxygen) while the PS coils contain only the lighter hydrogen and carbon atoms, and because the density of PMPCS ($\approx 1.3 \text{ g/cm}^3$) is much higher than that of PS coils ($\approx 1.0 \text{ g/cm}^3$) in the bulk state, the PMPCS domains scatter electrons much more strongly than the PS domains. Thus, the dark regions in the TEM image are formed by PMPCS while the gray regions around the dark regions should be attributed to PS.

In Fig. 2(a) for copolymer 1 and Fig. 2(b) for copolymer 2, only individual spherical micelles having diameters of about 25–35 nm for copolymer 1 and about 35–45 nm for copolymer 2 were observed. The micelle structure is consistent with our previously reported core-shell structure demonstrated by laser light scattering^[16]. This core-shell structure also dominates in self-assembly of coil-coil copolymers in selective solvents^[3, 17, 18]. The low contrast of the TEM images seen for copolymer 1 is due to the small volume fraction of PMPCS rods.

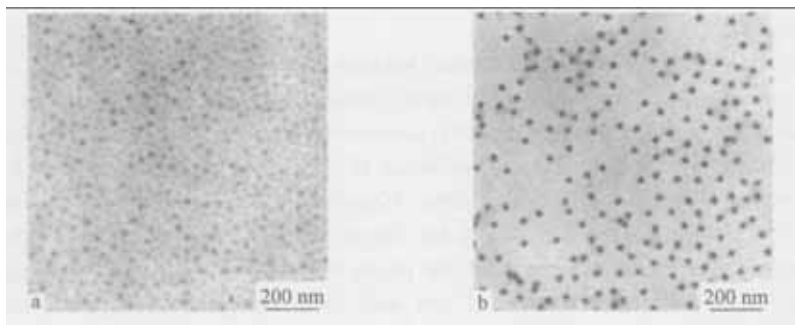


Fig. 2 Transmission electron microscopy of self-assembled morphologies for rod-coil copolymers 1 and 2 at a concentration of 2.0 mg/mL. Figure 2(a) for copolymer 1 and 2(b) for copolymer 2 revealed self-assembled spherical micelles.

When the PMPCS rods became longer and the volume fraction increased, a morphology with individual spherical micelles coexisting with “pearl chains” was clearly observed, as shown in Fig. 3(a) for copolymer 3 and Fig. 3(b) for copolymer 4. For copolymer 3, the diameter of the spheres is about 50–60 nm, while for copolymer 4 it is about 75–90 nm. The “pearls” in the “pearl chains” have almost the same diameter as the individual spheres, and are connected by gray regions. These findings elucidate that the “pearl chains” are formed by aggregation of spheres due to interactions of the coronal PS coils, which appear gray in the images, with the dark cores remaining unchanged.

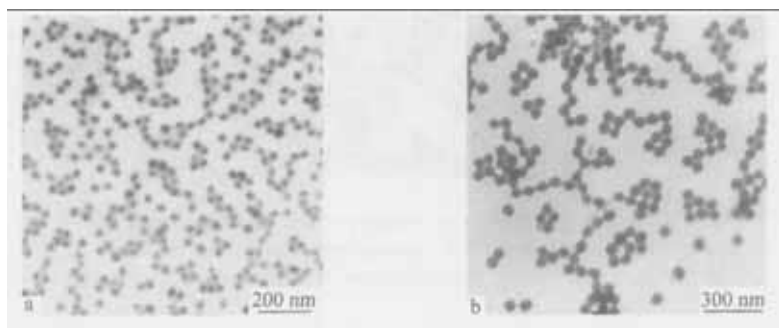


Fig. 3 Transmission electron microscopy of self-assembled morphologies for rod-coil copolymer 3 and 4 at a concentration of 2.0 mg/mL. Figure 3(a) for copolymer 3 and Fig. 3(b) for copolymer 4 revealed self-assembled “pearl chains”.

We used a 0.45 μm Millipore LCR filter to clarify the solutions in order to decide whether the “pearl chains” were formed in the solution or formed in the preparation of TEM samples during the solvent evaporation. For copolymers 1 and 2, the solution can pass through the filter readily. However, for copolymers 3 and 4, the filter was soon blocked, which meant there existed large aggregates exceeding 0.45 μm , and as indicated by TEM here, these aggregates should be the “pearl chains”.

Generally, when block copolymers self-assemble in a selective solvent in dilute solutions, individual core-

shell micelles are formed without “pearl chain” morphologies, due to the repulsions between the coils in the shell^[3, 17, 18]. The “pearl chain” morphologies were considered to be formed during the transition from the spheres to rods or nanofibers when the micelles aggregated to reduce the free surface energy^[17]. In our rod-coil copolymers, the core radius of the micelles increases with increasing PMPCS rod length while the PS coil length remains unaltered. As a result, the surface area occupied per PS coils increases and the repulsions between the PS coils decrease. The PS coils of the adjacent micelles can entangle with each other to form “pearl chains” and the surface energy is reduced.

A spherical micelle is stable in most of the cases because of the repulsion between the coils and the need to reduce the surface curvature^[3, 17]. However, if the surface area per PS coil occupied further increases as a result of the rod elongation, the repulsion between the coils decreases and the insertion of PMPCS rods into the micelle becomes possible; in other words, micelles are no longer the most stable form of morphology and other forms such as nanofibers or pearl-chains may become stable. Eisenberg reported this first and called these “crew-cut” aggregates^[18]. This is the case as shown in Fig. 4 for copolymer 5, where the “pearl chains” are dominated by occasionally formed nanofibers. The diameter of the pearls is about 130–150 nm as estimated from the TEM images. The length of the nanofiber is about 1 μm with diameter of about 160–170 nm. The ends of the nanofibers are hemispherical.

Recently, we reported the self-assembly of PS-*b*-PMPCS copolymer in *p*-xylene morphologies forming core-shell nanostructures^[16]. We found that the value of the core radius calculated from laser light scattering was sufficiently close to the contour length of the PMPCS block. However, we find that this is not applicable here, especially to the copolymers containing high molecular weight PMPCS rods. The contour length for copolymers 1–5 is about 22 nm, 43 nm, 74 nm, 240 nm and 450 nm, respectively. They are all larger than the core radius displayed in TEM images. This indicates that PMPCS copolymers contain no zigzag conformation in the core, as we previously thought.

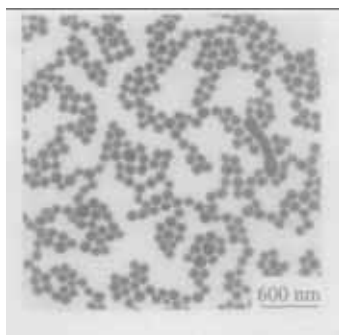


Fig. 4 Transmission electron microscopy of self-assembled morphologies for rod-coil copolymer 5 at a concentration of 2.0 mg/mL. Dominating “pearl chains” coexisting with a “nanofiber” was observed

To find if we can attain a nanofiber-dominated morphology, we changed the cooling rate of copolymer solution. However, it seems that changing the temperature has no influence on the self-assembly morphology. We have also synthesized another block copolymer with a larger number of PMPCS repeating units of about 3000. But this block copolymer is insoluble in *p*-xylene even at 130 °C; therefore, no information can be obtained from it. Nevertheless, the results for the five block copolymers have already revealed that the self-assembly morphology changes from spherical micelles to “pearl chains” when the length of the rod block increases. It is also possible to form nanofibers if the length of the rod block is large enough. This provides us a way to control the self-assembly morphology by altering the length of one block in the block copolymer.

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