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Syntheses of Amphiphilic Diblock Copolymers Containing a Conjugated Block and Their Self-Assembling Properties

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Abstract: An efficient approach to the syntheses of amphiphilic rod−coil diblock and coil−rod−coil triblock copolymers was developed. Each diblock copolymer consists of a perfectly monodispersed oligo(phenylene vinylene) covalently bonded to a poly(ethylene glycol) block with a very low polydispersity ($<$1.05). The structure and basic physical properties of these copolymers were characterized by various spectroscopic techniques such as NMR, MALDI-TOF, GPC, DSC, UV/vis, and the fluorescence study. These diblock copolymers were shown to possess remarkable self-assembling abilities, and long cylindrical micelles ($>$1 μm) were formed. TEM, SANS, and AFM studies showed that the core of the micelles has a diameter of ∼8−10 nm and was composed of an OPV block. TEM and SANS studies revealed that these OPV-PEG micelles have a cylindrical OPV core surrounded by a PEG corona. Cryo-TEM and SANS studies indicate that fibers were formed even in very dilute THF/H_2O solutions. Since the conjugated OPV blocks exhibit liquid crystallinity and electric and optical properties, these micelles are interesting for studying the electroactive effect in a nanometer scale.

During the past few decades, scientists have been fascinated by the microphase separation properties of block copolymers, especially diblock copolymers.[1−12] Because the two covalently connected blocks are physically incompatible, the system will undergo a phase separation to form a highly symmetric morphology of repeated structures, such as spheres, cylinders, or lamellae, formed on nanometer scales. Diblock copolymers that have flexible chains in both blocks have been extensively studied.[1−7] Our current understanding of the phase behavior of diblock copolymers is largely based on these systems.[2,8] However, in recent years, there has been a growing interest in diblock copolymers with rod−coil structures, based on which new morphologies and phase separation behaviors have been observed.[9−12] Our group is interested in this area because the self-assembling ability of the diblock copolymers offers a chance to organize functional species into nanometer domains. This research area provides an opportunity to synthesize functional polymers with well-defined supramolecular architectures. New materials with promising physical, chemical, electronic, and optical properties can be generated. One kind of functional species in which we are interested is conjugated polymers because of their unique electrical and optical properties, such as high electrical conductivity upon doping, high third-order optical nonlinearity, and electroluminescent properties.[13−16] Incorporation of a conjugated polymer chain into heterogeneous diblock copolymers creates a new class of self-assembling electroactive materials in which the classical lamella, cylindrical, and spherical morphologies of diblock copolymers allow for one-, two-, and three-dimensional confinement of the electroactive regions. All of these morphologies may be useful for the fabrication of novel dielectric and electrically conductive polymer devices.

Recently, we have succeeded in synthesizing OPV−polyisoprene diblock copolymers via a two-stage approach.[17] Both blocks in this copolymer system are hydrophobic and are found to form lamella structures in a wide range of composition. An interesting question is whether this trend applies to the am-

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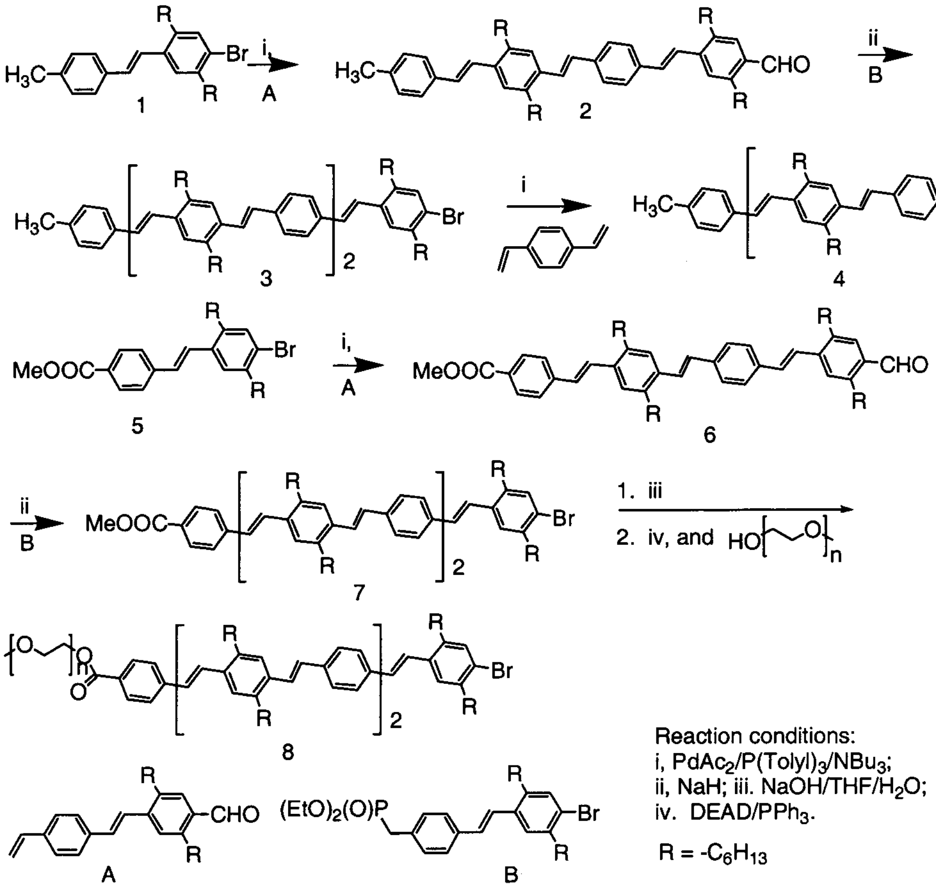
Scheme 1. Synthesis of Building Blocks for Diblock Copolymers



phiphilic type of rod−coil diblock copolymer. In this paper, we describe a new approach for the synthesis of a diblock copolymer system consisting of an oligo(phenylene vinylene) and poly(ethylene glycol), an amphiphilic type of rod−coil diblock copolymer. It was found that these diblock copolymers exhibit remarkable self-assembling capabilities, particularly the capability to form wormlike cylindrical micelles even at very low concentrations.

Experimental Section

Materials. 1,4-Dichlorobezene, 1-bromohexane, methyl 4-methylbenzoate, triethyl phosphite, poly(ethylene glycol) methyl ether (average M_n ca. 1900, 5000) and the other conventional reagents were used as received. Divinylbenzene was purified according to a literature procedure.[10] Tetrahydrofuran was dried by distillation from sodium metal. Ethylene glycol dimethyl ether and *N*,*N*-dimethylformamide were purified by distillation from calcium hydride.

^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer. A differential scanning calorimeter (TA instruments DSC 10) was used to determine the thermal transitions in a heating rate of 10 °C min^{-1}. The results were reported as the maxima and minima of their endothermic or exothermic peaks. A polarized optical microscopy (Nikon Optiphoto-2, magnification ×400) equipped with a high-temperature stage (Creative devices 50-600) was used to observe the thermal transitions and to analyze the anisotropic texture. Molecular weight distributions were determined by using gel permeation chromatography (GPC) with a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, Waters 410 differential refractometer, and Waters 486 tunable absorbance detector. THF was used as the eluent and polystyrene as the standard. Elemental analyses were performed by Atlantic Microlab, INC. MALDI-TOF spectra were performed by Washington University Resource for Biomedical and Bioorganic Mass Spectrometry lab with dithranol as the matrix. UV−vis spectra were collected by using a Shimadzu UV-2401PC recording spectrophotometer. Emission spectra were collected by using a Shimadzu RF-5301PC spectrofluorophotometer.

Transmission Electron Microscopy. Films were prepared by placing a drop of the copolymer solution onto carbon-coated or holey TEM grids. The grids were dried in the air or with the atmosphere of a solvent. The specimen may be exposed to osmium tetraoxide overnight or washed with a drop of phosphotungstic acid to get a stain effect. The specimen was then examined in a Philips CM120 electron microscope operated at 120 KV.

Small-Angle Neutron Scattering. Scattering experiments were performed by using the time-of-flight instrument SAND at the Intense Pulsed Neutron Source at Argonne National Laboratory. By using neutrons with wavelengths in the range of 0.5−14.0 Å by time-of-flight and a 40 × 40 cm^2 position sensitive proportional counter at a fixed sample-to-detector distance of 2 m, SAND produces data in the scattering vector q ($q = 4\pi \sin(\theta/\lambda)$, where θ is half the scattering angle and λ is the wavelength of the incident neutrons) range of 0.004−0.8 Å^{-1} in a single measurement. To obtain best contrast for the SANS signals, deuterated THF was used as a solvent. In addition D_2O was used for the investigation of the effect of water on the self-assembly of the diblock copolymer in deuterated THF. The solutions were measured in Suprasil (quartz) cylindrical cells with 2 mm path length. The data for each sample were corrected for the backgrounds from the instrument, the Suprasil cell, solvent, and sample transmission and placed on an absolute scale by using the routine procedures at IPNS.[18]

Synthesis. A general synthetic procedure is outlined in Scheme 1. Compounds **A** and **B** were synthesized by similar procedures described previously.[17]

General Procedure for the Heck Reaction. **A** (0.83 g, 2.06 mmol), tri-*o*-tolylphosphine (0.125 g, 0.412 mmol), NBu_3 (0.74 mL, 4.12 mmol), $Pd(OAc)_2$ (0.023 g, 0.103 mmol), and **5** (1.00 g, 2.06 mmol) were dissolved in anhydrous DMF (10 mL). The mixture was heated

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at 90 °C for 12 h and poured into 100 mL of methanol after being cooled to room temperature. The precipitate was collected by suction filtration and washed with methanol. The product was purified by column chromatography using a mixture of chloroform and hexane as the eluent, yielding pure **6** as a yellowish orange solid.

General Procedure for the Wittig Reaction. Compound **B** (0.95 g, 1.65 mmol) was dissolved in anhydrous DME (10 mL), then dropped slowly into the mixture of compound **6** (1.00 g, 1.24 mmol), NaH (0.041 g, 1.70 mmol), and DME (10 mL). The resulting solution was stirred under reflux for 5 h and poured into 100 mL of methanol after being cooled to 0 °C. The precipitate was collected by suction filtration and washed with methanol. The product was purified by column chromatography by using a mixture of chloroform and hexane as the eluent to give pure **7** as a yellowish orange solid.

Compound A. ^{1}H NMR ($CDCl_3$, ppm): δ10.25 (s, 1 H), 7.64 (s, 1 H), 7.51 (d, $J = 8.3$ Hz, 2 H), 7.48, (s, 1 H), 7.44 (d, $J = 8.3$ Hz, 2 H), 7.34 (d, $J = 16.1$ Hz, 1 H), 7.12 (d, $J = 16.1$ Hz, 1 H), 6.74 (dd, $J = 10.9$ Hz, 1 H), 5.80 (d, $J = 17.6$ Hz, 1 H), 5.29 (d, $J = 10.9$ Hz, 1 H), 3.01 (t, $J = 7.8$ Hz, 2 H), 2.77 (t, $J = 7.8$ Hz, 2 H), 1.62 (m, 4 H), 1.40 (m, 4 H), 1.33 (m, 8 H), 0.89 (m, 6 H). Anal. Calcd for $C_{28}H_{38}O$: C, 86.52; H, 9.51. Found: C, 86.37; H, 9.48.

Compound B. ^{1}H NMR ($CDCl_3$, ppm): 7.46 (d, $J = 8.1$ Hz, 2 H), 7.41 (s, 1 H), 7.32 (s, 1 H), 7.31 (dd, $J_1 = 8.1$ Hz, $J_2 = 2.3$ Hz, 2 H), 7.24 (d, $J = 16.1$ Hz, 1 H), 6.95 (d, $J = 16.1$ Hz, 1 H), 4.03 (m, 4 H), 3.17 (d, $J = 21.8$ Hz, 2 H), 2.68 (m, 4 H), 1.61 (m, 4 H), 1.33 (m, 4 H), 1.26 (m, 8 H), (0.89 (m, 6 H). Anal. Calcd for $C_{31}H_{46}BrO_3P$: C, 64.46; H, 8.03. Found: C, 64.46; H, 8.04.

Compound 1. ^{1}H NMR ($CDCl_3$, ppm): 7.41 (s, 1 H), 7.40 (d, $J = 7.9$ Hz, 2 H), 7.32 (s, 1 H), 7.20 (d, $J = 15.9$ Hz, 1 H), 7.17 (d, $J = 7.8$ Hz, 2 H), 6.95 (d, $J = 15.9$ Hz, 1 H), 2.68 (m, 4 H), 2.36 (s, 3 H), 1.59 (m, 4 H), 1.33 (m, 8 H), 0.90 (m, 6 H). Anal. Calcd for $C_{27}H_{37}Br$: C, 73.45; H, 8.46; Br, 18.10. Found: C, 73.39; H, 8.46; Br, 17.98.

Compound 2. ^{1}H NMR ($CDCl_3$, ppm): 10.25 (s, 1 H), 7.65 (s, 1 H), 7.55 (s, 4 H), 7.50 (s, 1 H), 7.45−7.42 (m, 4 H), 7.40 (d, 1 H), 7.37 (d, $J = 16.0$ Hz, 1 H), 7.31 (d, $J = 16.1$ Hz, 1 H), 7.19 (d, $J = 8.0$ Hz, 2 H), 7.15 (d, $J = 16.1$ Hz, 1 H), 7.05 (d, $J = 16.1$ Hz, 1 H), 7.02 (d, $J = 16.0$ Hz, 1 H), 3.03 (t, 2 H), 2.77 (m, 6 H), 2.38 (s, 3 H), 1.64 (m, 8 H), 1.42 (m, 8 H), 1.34 (m, 16 H), 0.90 (m, 12 H). Anal. Calcd for $C_{56}H_{74}O$: C, 86.32; H, 9.57. Found: C, 87.44; H, 9.75.

Compound 3. ^{1}H NMR ($CDCl_3$, ppm): 7.54−7.51 (m, 8 H), 7.46−7.42 (m, 7 H), 7.39 (d, $J = 16$ Hz, 1 H), 7.38 (d, $J = 16$ Hz, 2 H), 7.34 (s, 1 H), 7.31 (d, $J = 16$ Hz, 1 H), 7.28 (d, $J = 16$ Hz, 1 H), 7.20 (d, $J = 8$ Hz, 2 H), 7.054 (d, $J = 16$ Hz, 1 H), 7.048 (d, $J = 16$ Hz, 1 H), 7.042 (d, $J = 16$ Hz, 7.01 (d, $J = 16$ Hz, 1 H), 6.99 (d, $J = 16$ Hz, 1 H), 2.77 (m, 8 H), 2.73 (m, 4 H), 2.38 (s 3 H), 1.65 (m, 12 H), 1.43 (m, 12 H), 1.34 (m, 24 H), 0.90 (m, 18 H). Anal. Calcd for $C_{84}H_{109}Br$: C, 84.01; H, 9.26. Found: C, 83.76; H, 9.35.

Compound 4. ^{1}H NMR ($CDCl_3$, ppm): 7.54 (b, 8 H), 7.49 (d, $J = 8$ Hz, 2 H), 7.46−7.34 (m, 15 H), 7.31 (d, $J = 16$ Hz, 1 H), 7.18 (d, $J = 8$ Hz, 2 H), 7.06−6.99 (m, 6 H), 6.71 (dd, $J_1 = 18$ Hz, $J_2 = 10$ Hz, 1 H)), 5.77 (d, $J = 18$ Hz, 1 H), 5.25 (d, $Jj = 10$ Hz, 1 H), 2.76 (m, 12 H), 2.37 (s, 3 H), 1.66 (m, 12 H), 1.35 (m, 24 H), 0.90 (m, 18 H). Anal. Calcd for $C_{93}H_{118}$: C, 90.38; H, 9.62. Found: C, 90.16, H, 9.67.

Compound 5. ^{1}H NMR ($CDCl_3$, ppm): 8.04 (d, $J = 8.3$ Hz, 2 H), 7.56 (d, $J = 8.3$ Hz, 2 H), 7.43 (s, 1 H), 7.37 (d, $J = 15.2$ Hz, 1 H), 7.35 (s, 1 H), 7.01 (d, $J = 16.1$ Hz, 1 H), 3.93 (s, 3 H), 2.69 (m, 4 H), 1.57 (m, 4 H), 1.43 (m, 4 H), 1.32 (m, 6 H), 0.90 (m, 6 H). Anal. Calcd for $C_{28}H_{37}BrO_2$: C, 69.27; H, 7.68; Br, 16.46. Found: C, 69.54; H, 7.79; Br, 16.33.

Compound 6. ^{1}H NMR ($CDCl_3$, ppm): 10.25 (s, 1 H), 8.04 (d, $J = 8.3$ Hz, 2 H), 7.66 (s, 1 H), 7.60 (d, 2 H), 7.57 (s, 4 H), 7.51 (s, 1 H), 7.48 (d, 1 H), 7.47 (s, 1 H), 7.46 (s, 1 H), 7.41 (d, $J = 16.1$ Hz, 1 H), 7.38 (d, $J = 16.1$ Hz, 1 H), 7.15 (d, $J = 16.1$ Hz, 1 H), 7.07 (d, $J = 16.1$ Hz, 2 H), 3.94 (s, 3 H), 3.03 (t, $J = 7.8$ Hz, 2 H), 2.78 (m, 6 H), 1.64 (m, 8 H), 1.42 (m, 8 H), 1.34 (m, 16 H), 0.91 (m, 12 H). Anal. Calcd for $C_{57}H_{74}O_3$: C, 84.82; H, 9.24. Found: C, 84.57; H, 9.31.

Compound 7. ^{1}H NMR ($CDCl_3$, ppm): 8.04 (d, $J = 8$ Hz, 2 H), 7.58 (d, $J = 8$ Hz, 2 H), 7.54−7.52 (m, 8 H), 7.49−7.46 (m, 5 H), 7.44 (s, 1 H), 7.39 (d, $J = 16$ Hz, 2 H), 7.39 (d, $J = 16$ Hz, 1 H), 7.28 (d, $J = 16$ Hz, 1 H), 7.06 (d, $J = 16$ Hz, 2 H), 7.056 (d, $J = 16$ Hz, 1 H), 7.05 (d, $J = 16$ Hz, 1 H), 7.00 (d, $J = 16$ Hz, 1 H), 3.93 (s, 3 H), 2.78 (m, 8 H), 2.70 (m, 4 H), 1.64 (m, 12 H), 1.42 (m, 12 H), 1.35 (m, 24 H), 0.90 (m, 18 H). Anal. Calcd for $C_{84}H_{109}BrO_2$: C, 81.98; H, 8.93; Br, 6.49. Found: C 81.62; H, 8.85.

Compound 9. ^{1}H NMR ($CDCl_3$, ppm): 7.54 (s, 4 H), 7.50 (d, $J = 8.3$ Hz, 4 H), 7.46 (s, 2 H), 7.45 (s, 2 H), 7.43 (d, $J = 8.3$ Hz, 4 H), 7.39 (d, $J = 16.1$ Hz, 2 H), 7.36 (d, $J = 16.1$ Hz, 2 H), 7.05 (d, $J = 16.1$ Hz, 2 H), 7.03 (d, $J = 16.1$ Hz, 2 H), 6.74 (dd, $J_1 = 11.0$ Hz, $J_2 = 17.5$ Hz, 2 H), 5.78 (d, $J = 17.5$ Hz, 2 H), 5.26 (d, $J = 11.0$ Hz, 2 H), 2.77 (m, 8 H), 1.64 (m, 8 H), 1.35 (m, 8 H), 1.25 (m, 16 H), 0.90 (m, 12 H). Anal. Calcd for $C_{66}H_{82}$: C, 90.56; H, 9.44. Found: C, 90.29; H, 9.43.

Preparation of Diblock Copolymer Precursors. Compound **7** (0.8355 g, 0.679 mmol) and KOH (0.183 g, 3.4 mmol) were dissolved in THF (15 mL) and 0.6 mL of H_2O was added. The resulting solution was heated to reflux for 12 h, and then poured into 100 mL of methanol at room temperature. The precipitate was collected by suction filtration and washed with methanol. The product was further purified by flash chromatography using a mixture of chloroform and methanol as the eluent to give a yellow solid (OPV6-acid).

The mixture of poly(ethylene glycol) monomethyl ether (MW = 1900) (0.63 g 0.33 mmol), OPV6-acid (0.368 g, 0.3 mmol), and PPh_3 (87 mg, 0.33 mmol) in 15 mL of THF was heated to 80 °C. When all the starting material dissolved, the solution was cooled to 35 °C and DEAD (63 mg, 0.36 mmol) was added. After the resulting solution was stirred at 35 °C for 24 h, the THF was distilled out by vacuum distillation. The product was further purified by flash chromatography using a mixture of chloroform and methanol as the eluent to give compound **8** as a yellow solid.

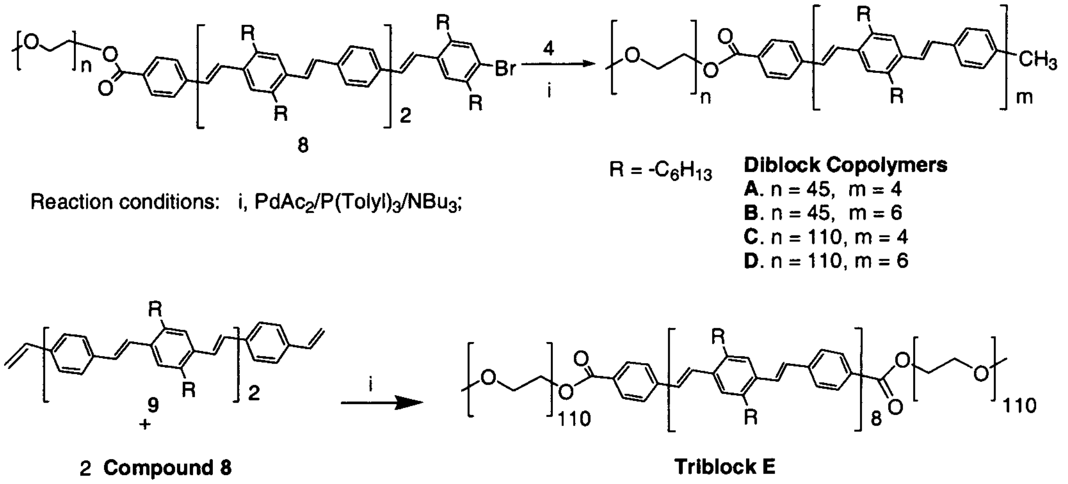
Compound 8 (*n* = 110). ^{1}H NMR ($CDCl_3$, ppm): 8.06 (d, $J = 8$ Hz, 2 H), 7.58 (d, $J = 8$ Hz, 2 H), 7.54−7.52 (m, 8 H), 7.49−7.46 (m, 5 H), 7.44 (s, 1 H), 7.39 (d, $J = 16$ Hz, 2 H), 7.39 (d, $J = 16$ Hz, 1 H), 7.28 (d, $J = 16$ Hz, 1 H), 7.06 (d, $J = 16$ Hz, 2 H), 7.056 (d, $J = 16$ Hz, 1 H), 7.05 (d, $J = 16$ Hz, 1 H), 7.00 (d, $J = 16$ Hz, 1 H), 4.49 (t, $J = 5.1$ Hz, 2 H), 3.85 (t, $J = 5.1$ Hz, 2 H), 3.82 (t, $J = 5.1$ Hz, 4 H), 3.64 (m, 432 H), 3.46 (t, $J = 5.1$ Hz, 4 H), 3.38 (s, 3 H), 2.78 (m, 8 H), 2.68 (m, 4 H), 1.64 (m, 12 H), 1.42 (m, 12 H), 1.35 (m, 24 H), 0.91 (m, 18 H).

Result and Discussion

Synthesis. In our two-stage approach, we had to synthesize long conjugated molecules such as oligothiophene, oligo(phenylene vinylene) with mono- or difunctionalities.[10,16,17] These oligomers were then coupled with living polymeric species. It became apparent that this approach has several limitations. The most critical one is the limited solubility of OPVs, which causes difficulty in purification and lowers the efficiency in any further coupling reaction. To overcome this problem, we developed a convergent approach to the diblock copolymers. Scheme 1 shows the synthesis of asymmetric building blocks. Scheme 2 shows the coupling of these blocks at the final step to the block copolymers. The advantage of this approach is that the solubility of the smaller pieces of the conjugated block is sufficient for coupling and the resulting block copolymers are soluble in the reaction medium. Therefore, the coupling reaction became more efficient. The product and the starting materials were found to have enough contrast in solubility and polarity that the purification became much easier than with the previous approach. This approach also permits easy synthesis of triblock copolymers and other architectures (Scheme 2).

As outlined in Scheme 1, a monofunctionalized OPV block with a vinyl end functional group (Compound **4**) and a difunctionalized OPV block with bromide and methyl ester end functional groups (**7**) were synthesized stepwise. The R group (a hexyl hydrocarbon chain) located at the para positions of phenyl rings in the OPV block is introduced to increase the solubility and render the block hydrophobic. These OPVs show

Scheme 2. Convergent Approach for the Syntheses of Diblock Copolymers



the typical physical properties observed in corresponding polyphenylene vinylenes, such as strong photoluminescence and electroluminescent properties.[16] Hydrolysis of compound **4** yielded an OPV containing a carboxylic acid group, which was later reacted with commercially available monodispersed poly(ethylene glycol) monomethyl ether to yield compounds **8**. Two PEGs with Mn of 1900 and 5000 were used. The PEG chain is flexible and strongly hydrophilic. PEG also exhibits some special properties, such as water solubility and complexation capacity with alkali metal cations, which can induce various liquid crystalline supramolecular structures.[19−21] Further coupling between compounds **8** and **4** yielded the final diblock copolymers. Five diblock copolymers (copolymers **A−D, 8**) with three types of OPV blocks were synthesized. When a divinyl compound was used to couple with compound **8**, a triblock copolymer was obtained. The resulting copolymers were purified by column chromatography (silica gel) using a chloroform/methanol mixture as the eluent. Preliminary results show that the triblock copolymer behaves similarly with diblock copolymers (its detailed studies will be published elsewhere).

All of the resulting block copolymers showed a narrow molecular weight distribution with polydispersity of less than 1.05, as determined from GPC (inset in Figure 1). MS spectroscopic studies using MALDI-TOF showed a close match between calculated and experimental molecular weights (Figure 1). Fine peaks in the mass spectrum vary by the mass of one ethylene oxide unit (44.01), indicating that the polydispersity of the copolymer mirrors that of the PEG used in the synthesis.

The chemical structures of these copolymers were confirmed by using ^{1}H NMR. All of the chemical shifts corresponding to the OPV and PEG blocks appear in the ^{1}H NMR spectrum. The ratio of ethylene oxide protons to the aromatic protons is consistent with the ratio calculated according to the number of repeating units in poly(ethylene glycol) and the OPV blocks.

Thermotropic Phase Behavior. Because the *all-trans*-OPVs are rigid molecules,[22,23] it was observed that all of the copolymers manifest a reversible thermotropic liquid crystalline phase. Table 1 presents the thermal transition temperatures of the diblock copolymers, deduced from DSC traces. The first transition, Tm1, corresponds to the melting point of the PEG block and the third thermal transition, Tm3, corresponds to the LC-isotropic transition. A visible crystalline melting peak corresponding to the OPV block can be observed only for an OPV with 13 benzene rings.[24] Optical polarized microscopic studies of these copolymers revealed a Schlieren texture and also confirmed that the Tm3 is the LC-isotropic phase transition temperature.

Table 1. Thermal Transition Temperatures of Diblock Copolymers

	8 (n=45)	diblock **A**	diblock **B**	diblock **C**	diblock **D**
Tm1 (°C)	43	39	39	46	55
Tm2 (°C)	NA	NA	150	NA	150
Tm3 (°C)	126	175	234	NA	235

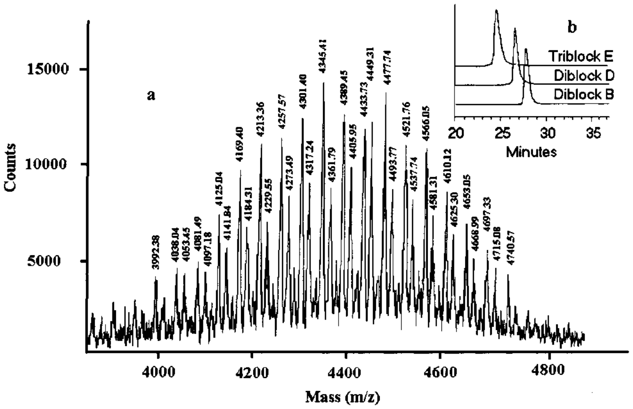


Figure 1. (a) MALDI-TOF spectrum of diblock copolymer **B**. (b) GPC traces of three copolymers.

Electronic Properties. UV−vis and Emission spectra of the copolymer **B** solution in THF and THF/water mixture solvents (0.02 mg/ml) are shown in Figure 2. In pure THF, the copolymer exhibited an intense transition with absorption maximum at 418 nm resulting from the OPV block (inset to Figure 2). Small-angle neutron scattering studies show that the diblock copolymer molecules self-assemble into cylindrical micelles at this concentration. Addition of water as a nonsolvent for the OPV block results in a significant solvatochromic effect. At a THF/H_2O ratio (v/v) of 1:1, the absorption maximum was blue-shifted to 393 nm, accompanied by a slight decrease in the absorption

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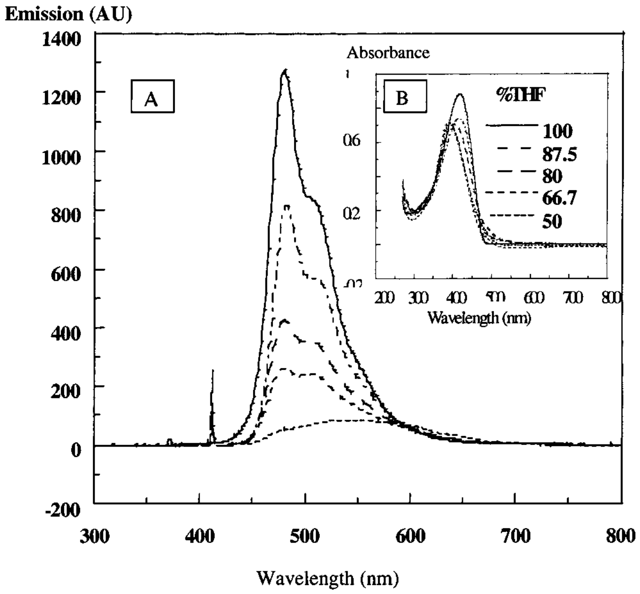

Figure 2. (A) Fluorescence spectra of diblock copolymer **B** in THF/H_2O mixtures (excited at 410 nm). (B) UV−vis absorption spectra of copolymer **B** in THF/H_2O mixtures.

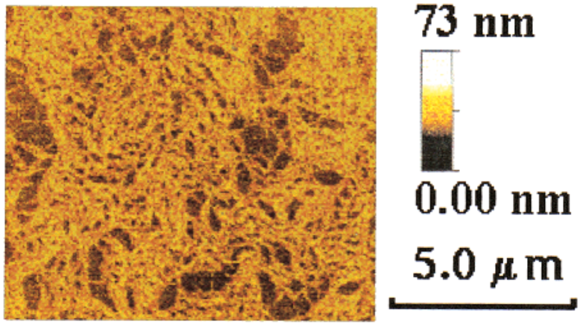

Figure 4. AFM image of diblock copolymer **B** film (TopMatrix Discoverer, on Mica substrate, Contact mode).

intensity caused by the formation of aggregates in solution. The formation of aggregates also dramatically reduces the fluorescence intensity with a concurrent reversal of the relative intensities of the three emissions. At a 1:1 THF/H_2O (v/v) ratio, the fluorescence maximum red-shifted to 542 nm. Photoemission of the copolymer in a THF solution, excited at 410 nm, produces a typical spectrum for poly(phenylene vinylene) in solution: a strong fluorescence at 480 nm with two small shoulders at about 508 and 555 nm derived from low-energy vibronic sidebands.[25−27]

Phase Separation Behavior. Diluted solutions of these diblock copolymers in mixed THF/water solvents at various volume ratios were used for the self-assembling studies. A THF/water mixture solvent was used because the copolymers do not have good solubility in pure water. Both THF and H_2O are good solvents for the PEG, but the OPV is insoluble in H_2O and only has limited solubility in THF.

Films cast from solution (0.5 mg/mL) were studied by transmission electron microscopy (TEM) under various conditions. Figure 3a shows the TEM image of copolymer **B** obtained when a Holey grid was used as the substrate for the casting film. It can be seen that the whole film is composed of interwoven fibers several thousands nanometers in length. Because the micelles are entangled with each other, they can support themselves over holes as wide as a micrometer in the holey grid. In various solvent conditions, cylindrical micelles with different lengths were observed and no staining was needed. The diameters of the fibers are all identical (8−10 nm) and long fibers (several micrometers) can be obtained when the samples are air-dried. All copolymers show identical behavior except copolymer **A** & **C** which forms fibers with smaller diameters because of its short OPV block. AFM studies also indicated the formation of fibers, as shown in Figure 4. However, the fibers are obviously aggregated to form bundles.

These fibers can be observed in films as cast from a diluted solution. This seems to indicate that the fiber may have been formed in the diluted solution state. Cryo-TEM (CTEM) images of the copolymers in vitrified solutions (THF/water 1:10) confirmed this hypothesis (Figure 3b). Cylindrical micelles were observed in these samples with the same diameter. It is interesting to note that after the copolymer solution was solidified by freezing, the micelles were not straight, rather they were often curved, looped, and entangled with each other. This deformation of fibers may be due to the effect of the matrix or may reflect a snapshot of fiber motion in solution. Although the TEM micrographs are two-dimensional projections of microstructures in three-dimensional specimens, it is hard to tell where a micelle begins and ends. Continuous strands with lengths of thousands of nanometers were identified.

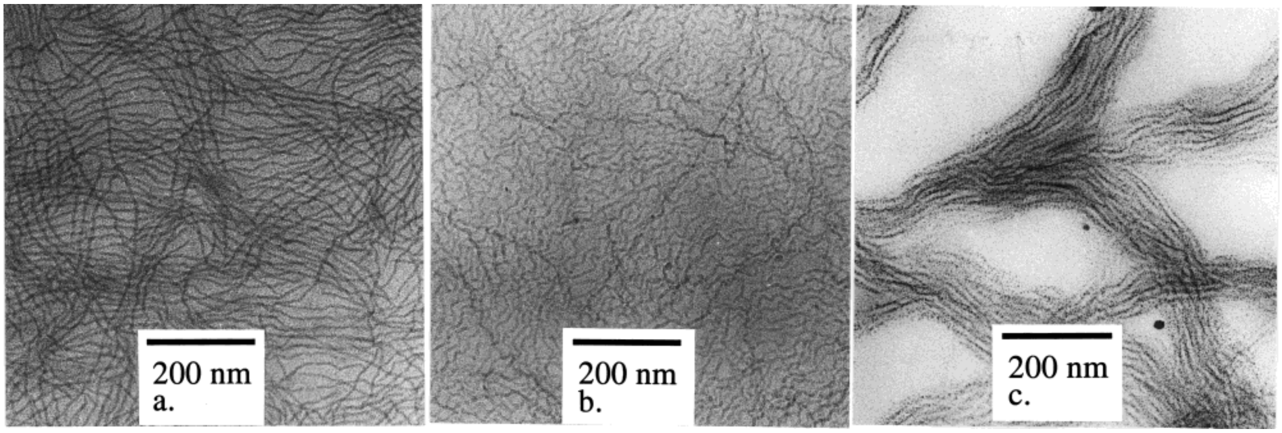

Figure 3. (a) TEM images of copolymer **B** films prepared by placing a drop of the copolymer solution onto holey TEM grids. The grids were dried in the air or atmosphere of a solvent. The specimen was then examined in a Philips CM120 electron microscope operated at 120 kV. (b) Cryo-TEM Images. Cryo-TEM samples were prepared by placing a drop of the copolymer solution on a copper grid and vitrified by rapidly plunging into liquid ethane (90 K). It was subsequently transferred under liquid nitrogen to a grid box and mounted in a Gatan cryo specimen holder (model 626, Gatan Inc., Warrendale, PA) and examined at low temperature (−172 °C) in a Philips CM120 electron microscope operated at 100 kV. (c) TEM images of the AgTf complex of copolymer **B**.

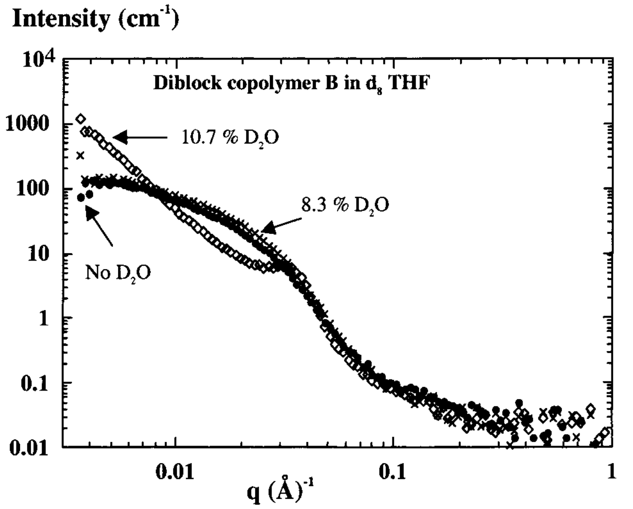

Figure 5. Neutron scattering intensity versus scattering vector (q, Å^{-1}) of copolymer **B** in d_8-THF showing three different conditions: no water, 8.3% D_2O, and 10.7% D_2O. The sharp peak in the presence of 10% D_2O indicates the spatial correlation between the rods.

The formation of cylindrical micelles in solution is further confirmed by SANS studies. SANS is a nondestructive technique that can provide information on size, shape, and interactions among particles from the size of 1 to 100 nm at relevant solution conditions. It was found that solutions of copolymer **B** showed strong neutron scattering intensities (Figure 5, curve without the addition of D_2O). The data show a form factor typical of infinitely long, rodlike objects. From a Modified Guinier analysis for rodlike objects of the SANS data we obtained a rod radius of 7.71 ± 0.07 nm for the diblock copolymer **B**.[28] This result indicates that copolymer molecules in solution self-assemble into cylindrical micelles at concentrations of 0.05−2.5 wt % in d_8-THF. More detailed analysis of the SANS data revealed that the cross-section of an elliptical shell characterized with 5.0 and 10.0 nm semiaxis and 2.0 nm shell thickness.[29]

Moreover, interesting results were observed when D_2O was added into the d_8-THF solution (0.05 mg/mL) of diblock copolymer **B**. A sudden and dramatic change in the scattering pattern was observed upon addition of 10.7 wt % D_2O (Figure 5): the forward neutron scattering intensity increased by an order of magnitude in the low q region, indicating that the cylindrical micelles formed by copolymer **B** become less entangled and orient parallel to each other. Furthermore, a correlation peak appears at a q value (length scale of 19.6 nm) that corresponds to the center-to-center correlation between the cross-sections of the rodlike particles. Thus, the originally distinct and randomly oriented rodlike particles condense into a phase of more ordered packed rods. Further addition of water continuously shifts the peak position to smaller scattering vectors (Figure 6). This indicates that the addition of water swells the system such that the distance between the center of the rods monotonic increases from 19 nm (at 10% water) to 23 nm (at 27% water) (Figure 7). It is interesting to note the linear relationship between water content and the distance between the centers of the rods with a slope of 0.74 nm/g. The aggregation is also accompanied by the change in their electronic absorption and emission spectra.

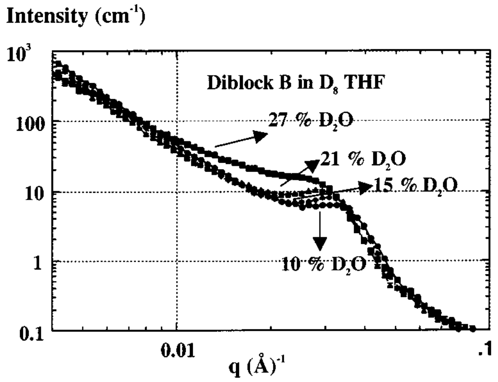

Figure 6. Scattering intensity versus q of copolymer **B** in d_8-THF/D_2O mixture showing the correlation peak shifts to a smaller value with increasing water concentration.

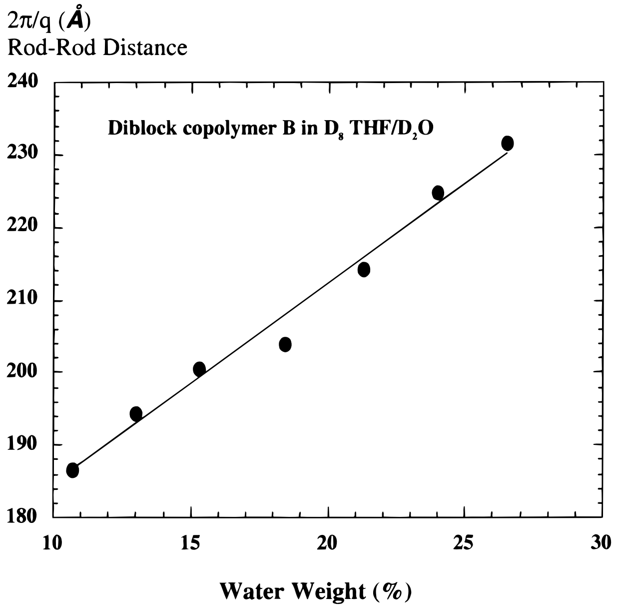

Figure 7. Plot of the rod-rod distance ($2\pi/q$) against D_2O weight percent of copolymer **B** in THF/ D_2O mixture showing a linear relationship.

These fibers are much like the giant wormlike micelles observed in the coil−coil diblock system.[30] An important question about these fibers is the packing structure of the diblock molecules, especially that of the OPV block in the core of the fiber. Traditional micelle organization is not consistent with the TEM and SANS results and thermodynamically not favored since the length of the conjugated block is about 8.5 nm corresponding to the diameter of the fiber obtained from TEM studies. A layered structure is a possible packing mode, as shown in other “hairy-rod” molecules.[31] However, identification of detailed molecular packing requires more extensive scattering work and will be the topic of our next publication.

Complexation with Metal Ions. One of the special properties of PEG is its complexion capability with metal cations.[19,32] It is thus interesting to dope metal cations into the copolymer solution. Complex copolymers were prepared by mixing THF solutions of OPV-PEG$_{114}$ (0.05 wt %) with an appropriate ratio

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of silver triflate salt ($R = 0.33$, R is the ratio of the salt to the EO repeating unit). It was found that silver triflate induced a strong aggregation of the cylindrical micelles, packing them into parallel fiber bundles (Figure 3c). The silver ions selectively chelate with the poly(ethylene glycol) block, causing a sharp contrast in the TEM micrograph (Figure 3c). The PEG block became much darker than the OPV block (the central block). The diameter of the whole fiber is about 15−17 nm and the size of the core (∼8−10 nm) is about the same size as the diameter of micelles observed without salt. When the sample was stained with osmium tetraoxide, a similar internal structure such as Figure 3c was observed because osmium tetraoxide will not stain the OPV block but will selectively stain the PEG block.[33] The result is interesting because it indicates the possibility of preparing an ionic conductive wire with an electronic conductive core.

Conclusion

A novel series of amphiphilic rod−coil copolymers with different lengths of oligo(phenylene vinylene) as the rod block and poly(ethylene oxide) as the coil block were synthesized. These copolymers organize into cylindrical micelles in solution and in cast films on a nanometer scale, as observed by using TEM, AFM, and SANS. These OPV-PEG micelles have a cylindrical OPV core surrounded by a PEG corona. The detailed fiber structure is still unknown and needs further study. These nanometer-sized micelles are interesting because the OPV blocks exhibit liquid crystallinity, electric, and optical properties. These built-in physical properties distinguish these diblock copolymers from others. It is possible to further manipulate these nanofibers. For example, a magnetic field may be used to align these fibers because these diblock copolymers are liquid crystalline materials. Studies on electric and optical properties are in progress.

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