Synthesis and Self-Assembly of Rod-Coil Diblock Molecules of Oligophenylenevinylene-Poly(ethylene oxide)

Huiming Xiong, Lidong Qin, Jingzhi Sun, Xi Zhang,* and Jiacong Shen
Key Lab of Supramolecular Structure & Spectroscopy, Department of Chemistry, Jilin University, Changchun 130023, P. R. China

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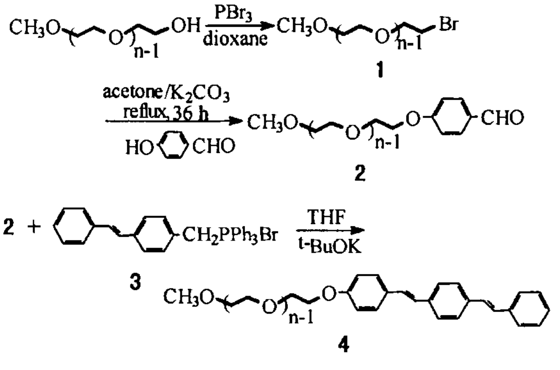
A series of amphiphilic rod-coil diblock molecules containing oligophenylenevinylene have been synthesized and demonstrated various aggregate behaviors in selected solvents. They can nano-separate to form either domain structures or stripes in as-cast state.

Rod-coil diblock copolymers consisting of a rigid rod and a flexible coil have been studied both experimentally and theoretically in recent years.[1] The unique self-assembly behaviors of rod-coil diblock copolymers exhibit as they can form various supramolecular structures. Incorporation of functional group into rod-coil system is anticipated to create a new class of material. Recently, poly(phenylene vinylene) (PPV) and its derivatives have attracted considerable attention due to their applications and fundamental research interest.[2] It is shown that chains aggregation and intermolecular interaction have dramatic effects on the photophysical properties of the polymers.[3] So, design and control of supramolecular structure and morphology become critically important. Conjugated oligomers as models for the related polymer have aroused extensive interest.[4] Here, we report synthesis of a series of amphiphilic rod-coil diblock molecules, the rod is oligophenylene vinylene(OPV-3), the coil is poly(ethylene oxide)(PEO). It will then discuss the spectroscopic studies of aggregates of this kind of rod-coil amphiphilic diblock molecule in selected solvents and its supramolecular structures based on nanophase separation in as-cast state.



Scheme 1. The synthetic route of OPV-3/PEO. (n=7, 16 corresponding to PEO350, PEO750)

The synthetic route is shown in Scheme 1. All the solvents were dried, freshly distilled and bubbled with nitrogen before used. The methyloxy poly(ethyleneoxy) ethyl bromide **1** was originally prepared via bromination of the corresponding methyloxypoly(ethyleneoxy)ethyl alcohol (20 mmol) with PBr_3 (30 mmol) in 30 mL dry dioxane. The methyloxypoly(ethyleneoxy)-ethyl alcohol (Mw 350, 750) were commercially obtained from Fluka and dried under vacuum at 60 °C overnight before used. The 4-[methyloxypoly(ethyleneoxy)]-benzaldehyde **2** was obtained by mixing compound **1** (6.4 mmol) with *p*-hydroxybenzaldehyde (7.2 mmol) and anhydrous potassium carbonate (12.8 mmol) in 50 mL dry acetone. A little amount of 18-crown-6 was added as phase-transition catalyst. The mixture was heated under reflux for 36 h under nitrogen and then filtered after cooled to room temperature. The solvent was removed, 15 mL of water added to the residue and the resulting solution was extracted with methylene choloride. The organic extract was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel G, anhydrous chloroform-methanol (3:1) as eluent). The synthesis of 4-styrylbenzyltriphenylphosphonium bromide **3** was according to reference.[5] The target compound **4** (abbreviated as OPV-3/PEO350) was obtained by using Wittig reaction: compound **2** (1.3 mmol) and **3** (1.3 mmol) were mixed in 40 mL dry tetrahydrofuran. Potassium *tert*-butoxide (2 mmol) was dissolved in dry tetrahydrofuran and added dropwise to the suspension on an ice-bath for about 2 h. The mixture was stirred on ice-bath for 36 h, then filtered. The solvent was removed under vacuum at room temperature. Yellow compound was obtained and purified by column chromatography (silica gel G, anhydrous chloroform-cyclohexane (5:1) as eluent), recrystallized at least three times from ethanol and dried under vacuum to give the desired product. (Yield, 30-40%). OPV-3/PEO750 was purified by recrystallized from anhydrous diethyl ether. The purity of compounds was confirmed by ^1H NMR, GPC and IR spectroscopy.[6]

Little work has been reported on aggregation of poly(phenylenevinylene) oligomers in solution because of their solubility problem. However, the solubility of this kind of rod-coil system is greatly enhanced due to the connection of the PEO coil, which enables us to investigate their self-assembly behaviors in selected solvents. The compounds can dissolve in chloroform well, and in water or cyclohexane up to a concentration of an order of 10^{-5} M. The UV-Vis absorption spectra of OPV-

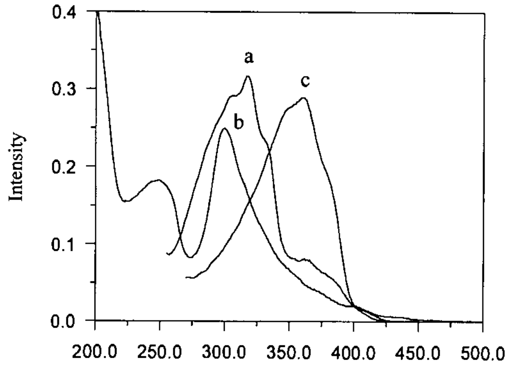


Figure 1. The UV-Vis spectra of OPV-3/PEO350 in chloroform (a), water (b) and cyclohexane (c) in a concentration of 1×10^{-5} M.

3/PEO350 show large difference depending on the solvents, as shown in Figure1. From the UV-Vis absorption spectrum in chloroform (Figure 1a), we can find two absorption bands peaked around 316 nm and 361 nm, respectively. In water the absorption maximum is at about 300 nm (Figure 1b). In cyclohexane, the absorption band peaked at about 361 nm (Figure 1c). For OPV-3/PEO750, it shows minor substituent effect on absorbance and almost similar spectroscopic behaviors.

To identify these absorption bands which originate from different aggregate states, we examine temperature dependent UV-Vis absorption and host-guest complexes of OPV-3/PEO350 with β-cyclodextrin (β-CD) in aqueous solution. It is believed that β-CD can only form 1:1 inclusion complex with oligo(phenylene vinylene).[7] OPV-3/PEO350 and β-CD (mole ratio 1:200) were dissolved in water and stirred for two weeks, however, the absorption spectrum was not found any change. The peak positions of spectra remained almost the same even to relatively low concentration or upon heating, which suggests that this species may be pretty stable. To adjust the polarity of the solvent, ethanol was added. By increasing the solution temperature from 23 °C to 84 °C, we found that the absorption band peaking around 300 nm decreased, meanwhile a absorption band at about 361 nm appeared and its intensity increased gradually, as shown in Figure 2. This suggests that absorption around 361 nm should originate from monomers. An isosbectic point was also found from the temperature dependent absorption spectra. It indicated a direct conversion of these two species. Furthermore, when we added the β-CD to the mixed solution (water : ethanol 3:1), stirred overnight and precipitated β-CD from the solution by chloroform, washed the precipitates several times, dried it under vacuum, then dissolved the β-CD into water again, we found that besides the absorption at 300 nm, there still existed an absorption band peaked around 361 nm. It was greatly different from that in pure water without β-CD since the aggregates are stable and can't exist as monomers in it. This can also support the conclusion that the absorption at about 361 nm originates from monomers. In this case it formed 1:1 inclusion complex with β-CD. In water, the absorption peaking around 300nm which is much blue-shifted compared to that of monomers is indicative of formation of H-aggregates. It is very similar to those obtained for LB films.[8] In cyclohexane, the rod-coil compound absorbing at about 361 nm exists majorly as monomers. In chloroform, the absorption is blue-shifted to 316 nm compared to that of monomers, suggesting formation of a type of H-aggregate.

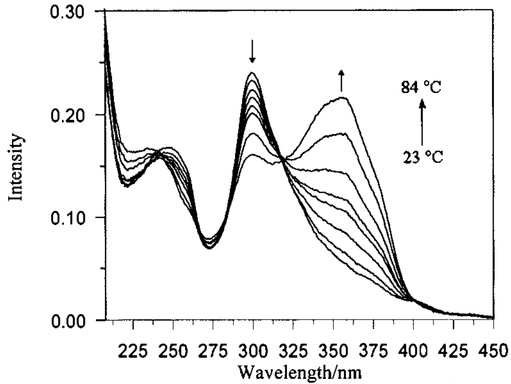


Figure 2. The UV-Vis spectra of OPV-3/PEO350 (1×10^{-5} M) in C_2H_5OH-H_2O (1:3) mixed solvent at different temperatures: 23, 33, 41, 49, 56, 65, 75, 84 °C.

The microphase separation behaviors of the copolymers were studied by using transmission electron micrograph (TEM). For TEM studies, thin films were prepared by casting the cyclohexane solution (1×10^{-5} M) on carbon-coated copper grid and evaporating in a solvent atmosphere, then exposing it to vacuum for about one day and not staining. As shown in Figure 3, the micrograph of OPV-3/PEO750 clearly shows aggregate domains that are approximate 3-4 nm in diameter. It is also found that the morphology is dependent on coil fraction. For OPV-3/PEO350, it can form stripes on the scale of nanometer and the length can extend to several tens of nanometers. These patterned materials based on nanophase separation are anticipated leading to novel photophysical and electronic properties and further research is underway.

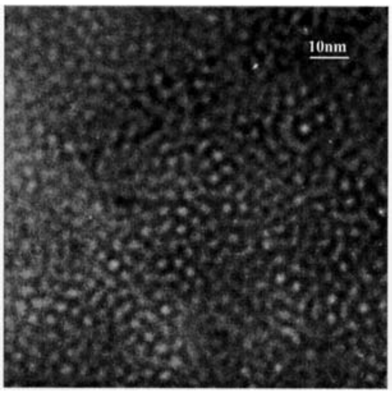


Figure 3. TEM of OPV-3/PEO750 thin film on carbon-coated copper grid

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References and Notes

1 a) A. Haperin, *Macromolecules*, **23**, 2724 (1990). b) D. R. M. Williams and G. H. Fredrickson, *Macromolecules*, **25**, 3561 (1992). c) L. H. Radzilowski and S. I. Stupp, *Macromoleules*, **27**, 7747 (1994). d) S. A. Jenekhe and X. L. Chen, *Science*, **279**, 1903 (1998). e) M. Lee, B. K. Cho, H. Kim, J. Y. Yoon, and W. C. Zin, *J. Am. Chem. Soc.* **120**. 9168 (1998). f) J. T. Chen, E. L. Thomas, C. K. Ober, and G. –p. Mao, *Science,* **273**, 343 (1996). g) W. J. Li, H. B. Wang, L. P. Yu, T. L. Morkved, and H. M. Jaeger, *Macromolecules*, **32**, 3034 (1999).

2 a) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B.Holmes, *Nature*, **347,** 539 (1990). b) D. Braun and A. J. Heeger, *Appl. Phys. Lett*., **58**, 1982 (1991).

3 J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, and J. L. Brédas, *J. Am. Chem. Soc*., **120**, 1289 (1998).

4 K. Müllen and G. Wegner, *Adv. Mater.*, **10**, 433 (1998).

5 R. Schenk, H. Gregorius, K. Meerholz, J. Heinze, and K. Müllen, *J. Am. Chem. Soc.*, **113**, 2634 (1991).

6 Selected data OPV-3/PEO350: Mw/Mn = 1.10; (^{1}H NMR 400 MHz, $CDCl_3$): É¬3.379 (s,3H), 3.5-3.8 (24H), 3.871 (t,2H,J=4.4 Hz), 4.146 (t, 2H, *J* = 4.4 Hz), 6.916 (d, 2H, *J* = 8.4 Hz), 6.952-7.114 (4H), 7.257 (t, 1H, *J* = 7.6 Hz), 7.364 (t, 2H, *J* = 7.6 Hz), 7.448 (d, 2H, *J* = 8.8 Hz), 7.490 (s, 4H), 7.523 (d, 2H, *J* = 7.6 Hz); IR(KBr cm^{-1}): CH_2 2871, 2924, C-O-C 1113, 1063, C-O-Ar 1251, *trans* –CH=CH- 968, 3022; OPV-3/PEO750: Mw/Mn = 1.09; É¬3.379 (s, 3H) 3.5-3.8 (60H), 3.872 (t, 2H, *J* = 4.8 Hz), 4.158 (t, 2H, *J* = 4.8 Hz), 6.917 (d, 2H, *J* = 8.4 Hz), 6.953-7.115 (4H), 7.259 (t, 1H, *J* = 7.2 Hz), 7.364 (t, 2H, *J* = 7.6 Hz), 7.449 (d, 2H, *J* = 8.8 Hz) 7.491 (s, 4H), 7.524 (d, 2H, *J* = 7.2 Hz); IR(KBr cm^{-1}): CH_2 2870, 2924, C-O-C 1113, 1062, C-O-Ar 1253, *trans* –CH=CH- 968, 3024.

7 X. D. Song, C. Geiger, M. Farahat, J. Perlstein, and D. G. Whitten, *J. Am. Chem. Soc.*, **119**, 12481 (1997).

8 a) A. Watakabe, H. Okada, and T. Kunitake, *Langmuir*, **10**, 2722 (1994). b) Results unpublished.