Synthesis and Solution Aggregation of Polystyrene−Oligo(*p*-phenyleneethynylene)−Polystyrene Triblock Copolymer

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Received October 6, 2003

Revised Manuscript Received December 16, 2003

The supramolecular organization of π-conjugated polymers is a topic of great importance because it has a profound effect on the macroscopic properties of the materials such as luminescence quantum efficiency and charge-carrier mobility.[1,2] One of the most promising strategies to manipulate supramolecular structures is the incorporation of conjugated polymer chains into rod−coil block copolymer architectures as the rodlike component.[3] Aggregation and microphase separation of rod−coil block copolymers containing π-conjugated polymers and oligomers have yielded a number of nanoscale morphologies, such as lamellar, spherical, cylindrical, and vesicular structures with tunable optical and electronic proprieties.[4−9] Variation of physicochemical interactions between the constituent blocks and the relative lengths of the blocks will allow a tailoring of morphologies and formation of well-defined conductive domains in nanoscale dimensions. Compared to the effort directed at understanding the self-assembly of rod−coil diblock copolymers, triblock copolymers containing conjugated moieties are much less studied.[10,11] In this Communication, we describe the synthesis of a coil−rod−coil triblock copolymer consisting of oligo(*p*-phenyleneethynylene) (OPE) as the rod segment and polystyrene as the coil segment. It is found that this triblock copolymer exhibits unique solvatochromatic behaviors through aggregation-induced $\pi-\pi$ stacking and planarization of the conjugated backbone.

The phenyleneethynylene polymers (PPEs) and oligomers are a class of materials with demonstrated applications in displays, sensors, and molecular electronics.[12] Its unique optoelectronic properties associated with strong aggregation behavior spark the ideas of the incorporation of OPEs into block copolymer architectures.[13−15] Most approaches to OPE containing block copolymers include the introduction of alkyl or alkyoxy side chains, generally at α-positions of the phenyl rings in OPEs, to increase solubility and processability. Recently, Coudret and co-workers reported the synthesis of unsubstituted OPE designed for self-assembly monolayers.[16] Scheme 1 outlines our synthetic route used to prepare the triblock copolymer containing unsubstituted OPEs. This convergent approach circumvents the insolubility problem of OPEs without introducing the α-position substituents and allows extension of the chemistry to longer OPEs and other architectures. A large χ value (the Flory−Huggins segment−segment interaction parameter) due to significant differences in structures and solubility parameters between the highly rigid unsubstituted OPEs and flexible polystyrene is expected to induce the formation of novel supramolecular assemblies through the microphase separation in the solid state and selective solvation in solution.

As shown in Scheme 1, a bifunctional phenyleneethynylene trimer, **1**, with an amino end group and an iodo terminal group was synthesized and then coupled with a carboxyl acid-terminated polystyrene (PS-COOH, **2**) to yield a polystyryl-OPE, **3**.[17] Carboxyl terminal polystyrene was prepared by anionic polymerization initiated with *sec*-BuLi and subsequently adding ultrapure carbon dioxide into the polymerization solution.[18] The formation of the triblock copolymer, **4**, was accomplished under Pd/Cu cross-coupling condition, using 1,4-diethynylbenzene to connect two polystyryl-OPE together. The incorporation of rigid block into polymeric chain was proven by spectroscopic studies. After the coupling reaction of **1** and **2**, the ^{1}H NMR spectrum of **3** shows no signal for residual amine groups at 3.92 ppm and affords a doublet at 7.75 ppm and a singlet at 7.54 ppm, which are characteristic signals of benzylic protons from OPE. Four signals at 90−94 ppm in the ^{13}C NMR spectrum of **3** are assigned to ethine carbons from OPE. In the ^{1}H NMR spectrum of **4**, the absence of a doublet around 7.75 ppm corresponding to aromatic protons adjacent to the iodo group, and the increased intensity of a singlet at 7.54 ppm indicates the presence of heptamer OPE in the triblock copolymer. The Raman spectrum of **4** reveals an intense signal at 2205 cm^{-1} attributed to the C≡C bonds. The proposed structures were proved by gel permeation chromatography (GPC) studies as well. For **2**, the number-average molecular weight (M_n) was calculated to be 2791 with a polydispersity (PDI) of 1.10 using THF as the eluent and polystyrenes as standards. For **3**, a M_n of 3141 (PDI = 1.14) was determined. Dimerization of polystyryl-OPE results in the triblock copolymer with an approximately double M_n of 6128 (PDI = 1.17). The transformation of **1** into **2** was accompanied by a blue shift of the absorption maximum from 345 to 335 nm in the UV/vis spectra. This 10 nm shift is attributed to the electron-withdrawing effect of amido bonds, which further confirmed the formation of polystyryl-OPE, rather than the mixture of two starting materials. Since there was no special steric or push−pull effect present in the triblock copolymer, as expected, the $\pi-\pi^*$ absorption of **4** is red-shifted to 368 nm due to the increase in conjugation length. The fluorescence spectrum of **4** in toluene gives an emission maximum at 406 nm with two small shoulders at about 424 and 467 nm derived from low−energy vibronic sidebands and a quantum yield of 0.78.

The intermolecular aggregation of OPE derivatives has been generally observed in both solution and solid states with a substantial influence on optical properties.[19−21] We investigated the solvatochromism of **4** to study its aggregation behavior in solution. The copolymer **4** is found to dissolve readily in solvents such as THF, dichloromethane, chloroform, toluene, and 1,1,2,2-tetrachloroethane (TCE) at room temperature to give a clear, colorless solution. The absorption spectra are independent of concentration. Even in relatively concentrated solutions (1.5 g/L, measured in a 1 mm cell), only one broad band is detected. However, the

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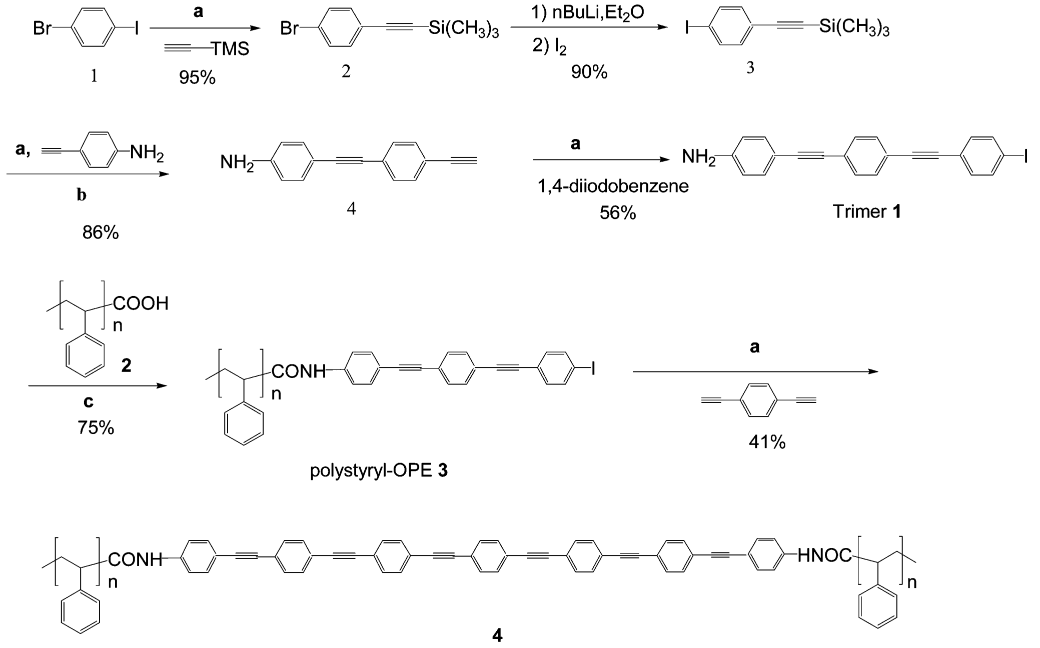
10.1021/ma035503e CCC: $27.50

Scheme 1. Synthesis of Triblock Copolymer 4



Reagents: **a**. $PdCl_2(PPh_3)_2$ (3mol%), CuI (1mol%), Et_3N/THF (1:1).
b. K_2CO_3, CH_3OH, CH_2Cl_2
c. i) $SOCl_2$, reflux 5 hours; ii) Trimer **1**, THF/ Pyridine (2:1)

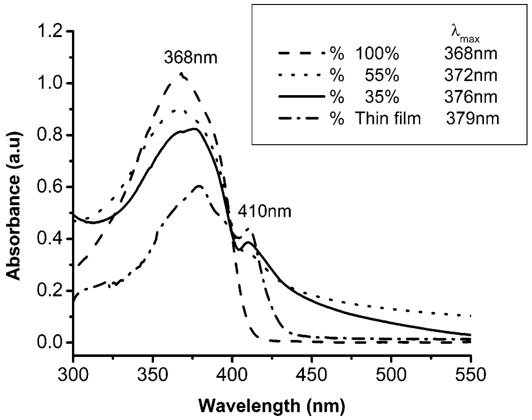


Figure 1. UV/vis absorption spectra of PS−OPE−PS, **4**, in toluene/MeOH mixtures and thin film at room temperature. The "aggregate band" is observed at 410 nm. The solvent composition is marked by the volume percentage of toluene.

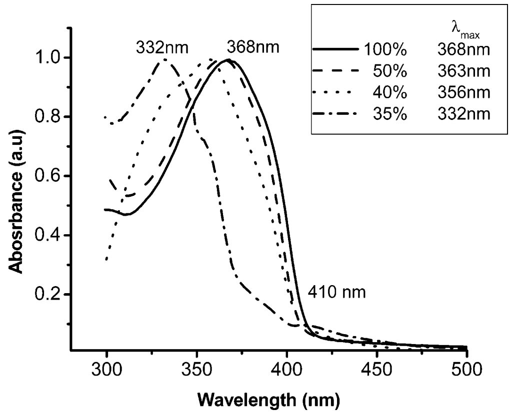


Figure 2. UV/vis absorption spectra of **4** in TCE/MeOH mixtures. The solvent composition is marked by the volume percentage of TCE.

absorption spectrum changes dramatically if a nonsolvent such as methanol is added. As shown in Figure 1, addition of methanol to a solution of **4** in toluene leads to the main transition band (λ_{max}) red-shifted from 368 to 376 nm and, concomitantly, with the development of an additional aggregate-induced band at 410 nm. At about 65 vol % methanol, the aggregate band is completely developed, and the solution spectrum of **4** is almost superimposable to that of thin films. Similar effects have been observed in dialkyl- and dialkoxy-substituted poly(phenyleneethynylene)s as well as other conjugated polymers such as poly(alkylthiophene)s.[22−24] The general consensus about the bathochromic shift in λ_{max} is caused by the increased effective conjugated length as a result of the conjugated chain backbone becoming more planar due to the formation of aggregates in solution or solid states.[18,25−27]

It is noteworthy that the triblock copolymer **4** exhibits different solvatochromatic behaviors in different solvent systems, which reveals the fact that **4** can readily adopt diverse assemblies in response to the external stimuli. Addition of methanol to a solution of **4** in TCE leads to the reverse solvatochromatic shift (Figure 2). When more than 50 vol % methanol is added, the PS−OPE−PS TCE solution begins to show the hypsochromic shift behavior. At a 1:2 TCE/methanol ratio, the λ_{max} is blue-shifted to 332 nm with the formation of an aggregation peak at 410 nm. The observed hypsochromic shift (36 nm) is considerable and can be interpreted by the molecular exciton model, assuming H-type aggregates formed by a parallel orientation of OPE segments.[28,29] The observed blue shift is a consequence of interchain $\pi-\pi$ interaction between parallel OPE segments raised from aggregates, which accompanied by strong fluorescence quenching. Fluorescence spectroscopy of **4** (Figure 3) illustrated that upon increasing the methanol content

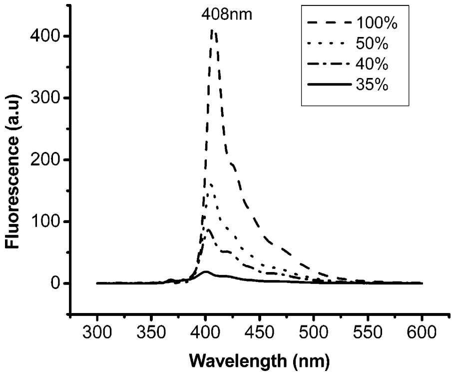


Figure 3. Fluorescence spectra of **4** in TCE/MeOH mixtures at room temperature. The solvent composition is marked by the volume percentage of TCE. Excitation was performed at 332 nm.

of the TCE/methanol mixture from 0 to 65 vol % the fluorescence intensity decreases and the quantum yield declines from 0.78 to 0.17. Although reduced photoluminescence quantum yields have also been observed in toluene/methanol mixtures, the TCE/methanol system exhibits larger decrease of fluorescent efficiency. This is due to the presence of densely packed aggregates, further confirming the H-type aggregate formation in TCE/MeOH. Small-angle neutron scattering (SANS) experiments were performed to rationalize the observed solvatochromatic properties. SANS in toluene evidenced the presence of nanoscopic aggregates of **4**, and the calculated average aggregation number is about 5 (see Supporting Information for details). As for the case of TCE, no supramolecular aggregates were observed, and **4** appears as individual chains. These results indicate that TCE is a better solvent for **4** than toluene. The polymer chains of **4** in TCE take an open, extended conformation which, relative to toluene solutions, facilitates interchain cofacial $\pi-\pi$ interactions during aggregation. Without the steric repulsion from α-position substituents, the strong tendency for $\pi-\pi$ stacking among unsubstituted OPE segments promotes the formation of parallel aligned OPE assemblies as well. This aggregation behavior is distinctive and, to our knowledge, has not been observed in PPEs derivatives. The polymer chains of **4** in toluene, on the other hand, take a compact conformation and thus, relative to TCE, tend to resist interchain $\pi-\pi$ stacking and form relatively disordered aggregates. The effect of single-chain planarization of the phenyleneethynylene moieties is responsible for the red shift of $\lambda_{\max}$, similar to aggregation behaviors of alkyl-substituted PPEs.[22]

In conclusion, we described the synthesis, characterization, and solution aggregation of a coil−rod−coil triblock copolymer **4**. It has been demonstrated that the use of the solvent composition to influence chain conformations and thus to manipulate the packing of the conjugated polymer blocks is important for achieving control in the assembly of conducting polymers and associated optical characteristics. Our ongoing work aims to elucidate aggregate morphologies and solid-state microscopic phase separation of this novel triblock copolymer.

Acknowledgment. This work was supported by the Pennsylvania State University, the Center for Optical Technologies, and the Pennsylvania Department of Community and Economic. Assistance with SANS studies by Drs. L. Guo and P. Thiyagarajan at Argonne National Laboratory is appreciated.

Supporting Information Available: Synthetic procedures and characterization data for trimer **1**, PS-COOH **2**, polystyryl-OPE **3**, and triblock copolymer **4**; fluorescence spectra of **4** in TCE, TCE/MeOH, and toluene/MeOH; the quantum yield of **4** in TCE/MeOH mixtures as a function of volume fraction of methanol; SANS studies of **4** in TCE and toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035503E