

Nanostructured Block Copolymers*

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NANOSTRUCTURED BLOCK COPOLYMERS

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ABSTRACT

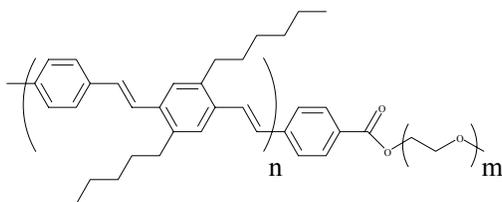
Block copolymers are well known to undergo micro-phase separation. Typical domain sizes range from a few to about 100 nanometers. With use of OPV_n-PEG_m diblock copolymers, long nanofiber, short nanorod, and lamella morphologies have been observed. OPV is oligo(phenylenevinylene) and PEG is poly(ethyleneglycol). The OPV segment is photoluminescent as well as electroluminescent. The micrometer long OPV₁₃-PEG₄₅ nanofiber consists of OPV₁₃ inner core with radius of 5.2 nm, and PEG₄₅ outer shell with overall fiber radius of 7.9 nm. The nanorod has similar core-shell composition but with much shorter length of ~100 nm. Lamella morphology consists of alternating OPV and PEG layers. The structural characterization and physical properties of these nanostructured materials and their implication are summarized.

INTRODUCTION

Diblock copolymers are a special class of material that consist of two covalently linked homopolymer segments. When these two segments are made from polymers with incompatible chemical affinities, such as hydrophilic versus hydrophobic in nature, it is well known that diblock copolymers undergo micro-phase separation due to the intrinsic incompatibility. While a water-oil mixture shows macro-phase separation, diblock copolymers are constrained by covalent linkages and only lead to microphase separation in the 1 to 100 nm regions. The resulting morphologies will be dependent upon the segment-segment interaction energy that is proportional to the heat of mixing, degree of polymerization, and the molar fraction of the two segments. [1] In general, repulsion between two different segments and a large degree of polymerization favor phase separation, while higher temperatures promote mixing. Known morphologies include three-dimensional spatially confined spheres, two-dimensional spatially confined cylinders, and one-dimensional spatially confined lamellae. Under comparable segment-segment interaction and degree of polymerization, the morphologies will be driven by the molar fraction. For example, an A-B diblock copolymer with 10-90% molar fraction will

result in spherical domains A in a matrix B. An A-B diblock copolymer with 30-70% molar fraction will favor cylinders A in a matrix B, and 50-50 molar fraction will lead to an alternating A-B lamella structure. [2] The length scale of these spheres, cylinders, and layers are typically in the nm range. Therefore, diblock copolymers provide a very interesting platform for nano-scale control and manipulation.

Our interest in diblock copolymers stemmed from two motivations. The first one is to search for quantum confinement effects in organic materials and the second is to carry out rational design and synthesis of controlled structures with desired physical properties. While the first goal is still elusive, we have made significant progress toward the second goal. The system under detailed study consists of OPV_n - PEG_m diblock copolymers, where OPV is oligo(phenylenevinylene) and PEG is poly(ethyleneglycol), n and m stand for the number of repeating unit of the monomers. The chemical drawing of OPV_n - PEG_m is shown below. [3]



OPV_n - PEG_m

The OPV is a conjugated and unsaturated segment. It is hydrophobic and rigid. The OPV is known to be photoluminescent and electroluminescent. It provides the built-in functionalities for electronic and photonic properties. Two hexyl side chains are attached to every other phenyl ring in order to increase the solubility and processability. The PEG is a saturated segment. It is hydrophilic and flexible. It is commonly used to support ion transport in rechargeable batteries. For this project, PEG is applied for its hydrophilic nature to induce microphase separation.

EXPERIMENTAL

The OPV_n oligomers were prepared with stepwise organic synthesis. [3] They are well defined and monodispersed. The PEG segments were purchased from Aldrich and the polydispersities of OPV_n - PEG_m are <1.05 . Neutron scatterings were carried out on solution samples (d_8 -tetrahydrofuran solvent) with the SANS instrument at Intense Pulsed Neutron Source. X-ray scatterings were carried out on solution or melt samples with SAXS equipment at the Advanced Photon Source (APS), BESSRC 12-ID-C beam line. Typical energy ranges were between 8 and 12 KeV. Silver behenate powders were used as a scattering calibration standard. X-ray powder diffractions were performed at APS BESSRC 12-BM-B beam line due to limited amount of samples. Molecular mechanics calculations (MM2 level) were performed with commercial Chem3D software (CambridgeSoft).

RESULTS AND DISCUSSION

Self Assembly of OPV_n-PEG_m In Organic Solvents

The OPV_n-PEG_m diblock copolymers undergo self assembly in organic solvents, such as chloroform and tetrahydrofuran (THF). The Small Angle Neutron Scattering (SANS) data of OPV₁₃-PEG_m in d₈-THF showed a form factor typical of infinitely long rod-like micelles. With modified Guinier analysis for rod-like objects, which involves plotting $\ln[Q \times I(Q)]$ versus Q^2 , the radius of the rod is obtained as $R = \sqrt{2} \times \sqrt{-2 \times \text{slope}}$. The averaged radius of OPV₁₃-PEG₄₅ under several different concentrations gave a value of 7.9 nm. There are two possible ways for OPV_n-PEG_m diblock copolymers to self-assemble in THF, i.e., the OPV segment can be either the outer shell or the inner core. Based on the hydrophobicity of the OPV segment and the hydrophilicity of both PEG and solvent THF, the expected packing consists of a hydrophobic OPV inner core and a hydrophilic PEG outer shell. In order to verify the model, we carried out a contrast matching experiment. The neutron and x-ray scattering length densities of the solvent and block copolymer segments are listed in the following Table.

Table 1. Neutron and X-ray scattering length density (10^{10} cm^{-2})

Compound	Neutron	X-ray
THF	–	8.35
d ₈ -THF	6.35	–
PEG	0.58	9.40
OPV	0.79	8.80
d-PEG	6.26	–

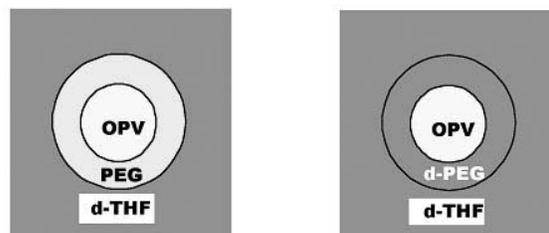


Figure 1 Schematic representation of neutron scattering (see text).

In deuterated THF, SANS measures the contributions from both OPV and PEG due to the contrast difference (Table 1 and Figure 1 Left). With fully deuterated PEG segment (d-PEG), the neutron scattering density of d-PEG is comparable to that of the d₈-THF solvent and neutron scattering measures the OPV contribution only (Table 1 and Figure 1 Right). If OPV is the outer shell of the rod-like micelle, OPV-d-PEG will give a radius about the same as that of the OPV-PEG. However, if OPV is the inner core, OPV-d-PEG will reflect a much smaller radius. SANS measurements on OPV₁₃-d-PEG₅₂ in d₈-THF gave a radius of 5.2 nm that was significantly smaller than 7.9 nm of OPV₁₃-PEG₄₅. The result clearly indicated that the OPV-PEG micelles consisted of OPV inner cores with PEG outer shells, and the radii of the OPV₁₃ inner cores are 5.2 nm. The contrast difference among OPV, PEG, and THF, under x-ray scattering condition is small but measurable with the strong synchrotron source. We modeled the small angle x-ray scattering (SAXS) data of OPV₁₃-PEG₄₅ in THF solution with a core-shell cylinder and an elliptical cross section. The two semi axes are approximately 50 and 100 Å with a shell thickness of ~20 Å. The neutron and x-ray scattering intensity versus scattering vector plots as well as modeling have been published previously. [4]

In addition to the direct measurement of the OPV₁₃ inner core radius, the contrast matching experiment also provides other important information. Since we are measuring the inner core only, the mass per unit length of the inner core can be extracted from the neutron scattering intensity. For OPV₁₃-d-PEG₅₂ nanofibers, the mass per Å was determined to be 2070 amu/Å. As a crude estimation, a 10 nm long nanofiber contains about 87 OPV₁₃ segments. If the nanofiber axis is along the OPV₁₃ side-by-side direction, and the side-by-side repeat distance is ~12 Å, approximately 11 OPV₁₃ segments per cross section is estimated.

Packing of the OPV Inner Cores

Another issue to address is that how do OPV segments pack in the cylinders. A schematic drawing of the cross section of a nanofiber is shown in Figure 2. Rectangular bars indicate the rigid OPV segments and curly lines indicate the flexible PEG chains. Head-to-tail (monolayer) and head-to-head (bilayer) packing motifs are shown in the left and right, respectively. Both packing motifs provide the same cross sectional area and hydrophobic inner core with hydrophilic outer shell. Theory suggested that both packing motifs are energetically favorable. [5]

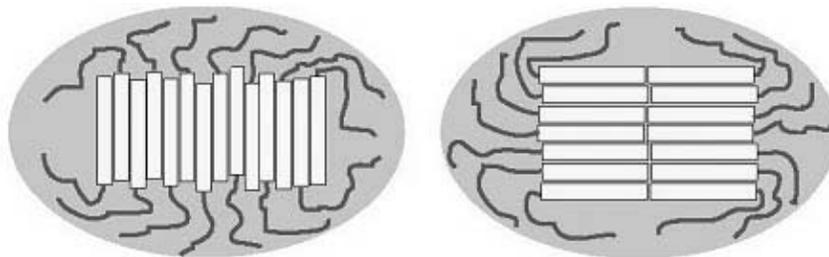
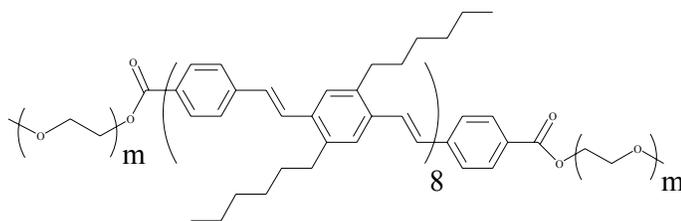


Figure 2 Possible packing motifs of a nanofiber

In order to differentiate the two packing motifs, we designed and synthesized a new triblock copolymer, PEG₁₁₄-OPV₁₇-PEG₁₁₄, with PEG segments attached to both ends of the OPV segment (see drawing below).



PEG_m-OPV₁₇-PEG_m

Since the head-to-head packing was not possible for the triblock copolymer, the experiment was to determine whether similar nanofiber formation occurred. The triblock copolymer was first dissolved in d₈-THF. Without water and with 3% water (Figure 3 two lower traces), the scattering intensities were quite weak that suggested no micelle in

the solution. However, with 7% water added (top trace), the scattering intensities increased by one order of magnitude that was indicative of micelle formation. With modified Guinier analysis for rod-like objects, a radius of 8.9 nm was obtained. The result directly supported triblock nanofibers in solution. Due to steric hindrance of the two bulky PEG₁₁₄ tails, it is more difficult for the triblock copolymer to assemble. Increasing water concentration in the solution mixture increases the hydrophilic environment and forces the OPV segments to aggregate. The observation that the triblock copolymers do form similar nanofibers leads to the conclusion that the monolayer packing is the predominant packing in these nanostructured copolymeric materials.

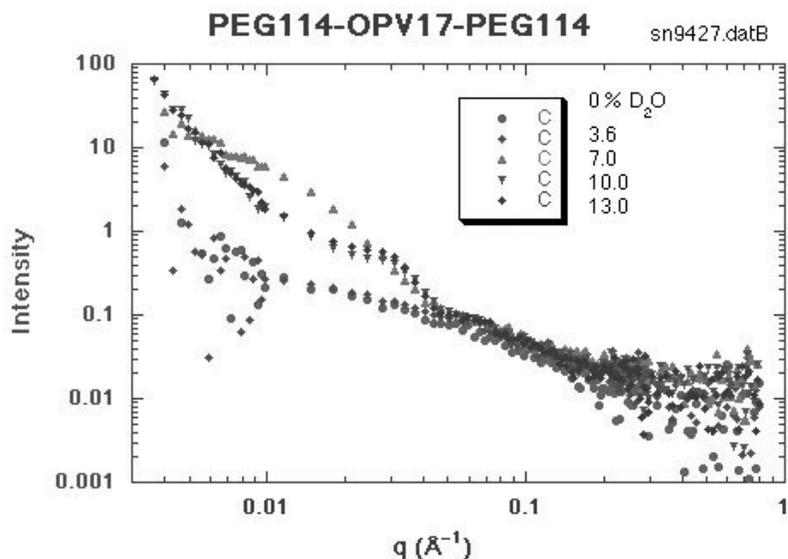


Figure 3 SAXS results from triblock copolymer in d₈-THF with D₂O addition

Crystallinity in Nanofibers

Short OPV_n oligomers ($n < 7$) form well defined crystals, and long OPV_n oligomers become liquid crystalline materials. The phenylenevinylene function groups provide a rigid backbone. Although all trans configuration is rigorously maintained in the vinylene groups through stepwise organic synthesis, it is possible to have conformational isomers through out the block segment especially for the longer OPV_n due to the presence of many single bonds. The inner cores of the OPV₁₃-PEG_m nanofibers consist of monolayers of OPV₁₃ segments as described above. It is interesting to find out whether liquid crystalline nature remains in the nanofibers. As a first step, we carried out x-ray powder diffraction on the OPV₁₃-PEG₄₅ material. The experiments were carried out at ambient temperature with powder samples on a special low background quartz substrate. The results are shown in Figure 4.

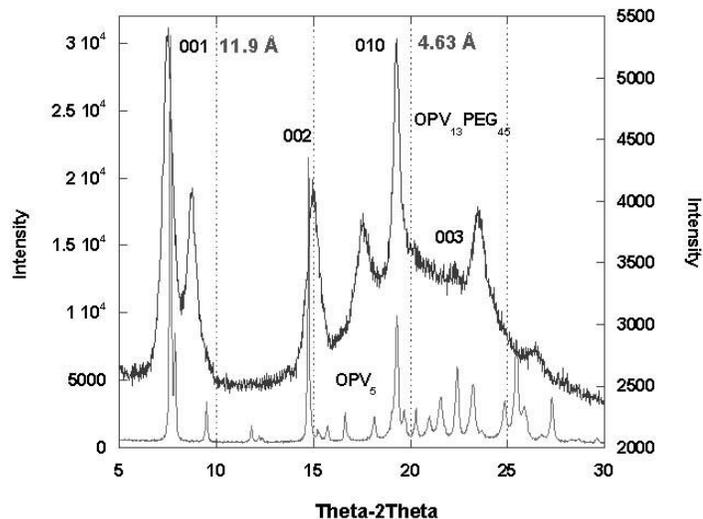


Figure 4 θ - 2θ x-ray powder diffractions of OPV₅ and OPV₁₃-PEG₄₅

As shown in Figure 4, small oligomer, OPV₅, diffracts very well due to its highly crystalline nature. The diblock copolymer, OPV₁₃-PEG₄₅, also diffracts but with low peak intensity, uneven background, and much broader peak widths. A few major peaks have been assigned. The $2\theta = 19.3^\circ$ peak in OPV₁₃-PEG₄₅ corresponds to $d = 4.63\text{\AA}$, distance along the OPV stacking direction, and $2\theta = 7.5^\circ$ peak corresponds to $d = 11.9\text{\AA}$, distance along the inter-stack direction. For these peaks, the positions are nearly the same for the oligomer, OPV₅, and the block copolymer, OPV₁₃-PEG₄₅, suggesting that the OPV packing motifs are very similar in both samples. These results clearly indicate that the packing order for the OPV segments is retained in the OPV₁₃-PEG₄₅ diblock copolymer. This result is quite significant because the optical properties of the nanofibers are expected to be anisotropic.

TEM Studies of OPV_n-PEG_m

We have carried out TEM studies on OPV_n-PEG_m nanostructured materials. The diblock copolymers were first dissolved in THF. The concentrations of the polymers were kept above the critical micelle concentration at about 0.05%. Under these conditions, the OPV_n-PEG_m copolymers undergo self-assembly in solutions to form nano-scaled aggregates that are randomly distributed in solution mixture. These aggregates can be partially aligned by mixing in ten weight percent of water. The resulting mixture was then dropped onto TEM grids for direct observation. The TEM images of OPV₁₃-PEG_m ($m = 13$ and 45) are shown below.

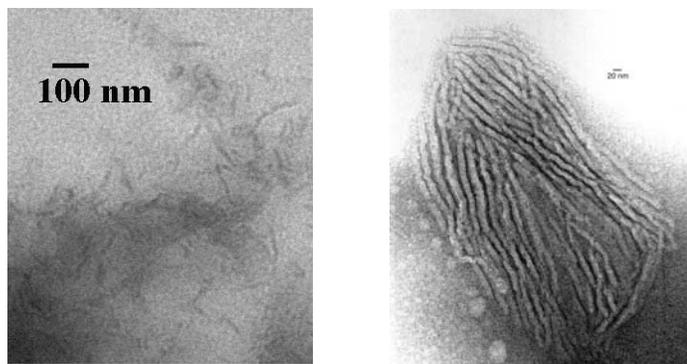


Figure 5 TEM images of OPV₁₃-PEG₁₃ (Left) with 100 nm scale bar and OPV₁₃-PEG₄₅ (Right) with 20 nm scale bar.

The OPV₁₃PEG₄₅ block copolymer self-assembles into micrometer long nanofibers. The diameter of the fibers is consistent with the value determined from SANS measurements. These nanofibers also form partially aligned aggregates. In contrast to OPV₁₃-PEG₄₅, only short rods were observed for OPV₁₃-PEG₁₃. Typical length of the rods was around 100 nm. These rods were randomly dispersed on the TEM grid and no ordered aggregates were found. This finding is very interesting because it provides a possible route to control the third dimension, i.e., the length of the nanofibers. The radii of the nanofibers can be regulated with the length of the OPV segments through designed synthesis, but there was no other known controlling factor for the length of the nanofibers. With the use of short PEG segments, apparently, there is a pronounced effect on the resulting nano-structures.

CONCLUSION

We carried out detailed studies on the self-assembly of OPV_n-PEG_m diblock copolymers in organic solution. Nanofibers with radii around 8 nm were observed in all samples. The structure of the nanofibers consisted of OPV_n inner cores and PEG_m outer shells. The packing motif of the OPV_n inner core was that of a head-to-tail monolayer. The crystalline nature of the inner cores was observed through the use of x-ray powder diffraction. The OPV₁₃-PEG_m ($m = 45$ and 114) forms nanofibers on the order of a few micrometers as directly measured with TEM, while OPV₁₃-PEG₁₃ form short rods around 100 nm in length. The nanofibers can be easily attached to a hydrophilic area for surface patterning and sensor application. The nanorod formation will help us gain insight in terms of how would the PEG segment length control the resulting morphologies.

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