Semiconducting Nanocomposites

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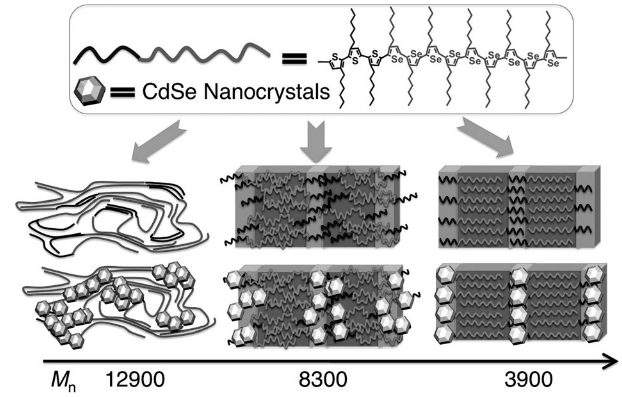
Nanocrystal Self-Assembly with Rod–Rod Block Copolymers[**]

Lianshan Li, Jon Hollinger, Neil Coombs, Srebri Petrov, and Dwight S. Seferos[*]

The assembly of isotropic nanomaterials into anisotropic hierarchical structures is a fundamental challenge in nanochemistry.[1] This challenge is akin to imparting chirality into achiral molecules, which has been one of the main objectives of organic chemistry for over a century.[2] In nanoscience, methods have been developed for organizing inorganic nanomaterials at a range of length scales. Specific examples include the use of biological synthons, such as DNA and proteins[3] or peptides,[4] the use of immiscible liquid–liquid interfaces,[5] the use of ligands or surfactants,[6] and the use of diblock copolymers.[7] The self-assembly of block copolymers is particularly attractive because it is an inexpensive and scalable process that can be rationally designed to produce a stable solid-state composite.[8] In general, polymers can be designed to self-assemble through phase separation by synthesizing block copolymers that contain regions of distinct functional groups.[9] When combined with nanoparticles, block copolymer self-assembly offers a means to control the organization of nanoparticles within a film.[7b,10] This strategy has been demonstrated for several coil–coil block copolymers, including poly(styrene)-*b*-poly(ethylene propylene),[11] poly(styrene)-*b*-poly(methylmethacrylate),[12] and poly(styrene)-*b*-poly(vinyl pyridine).[13] On the other hand, although there is considerable interest in the co-self-assembly of conjugated polymers, such as polythiophene, with nanoparticles, such as quantum dots and fullerene derivatives for electronics applications,[14] to the best of our knowledge, conjugated rod–rod diblock copolymers[15] have not been tested for their ability to co-self-assemble with nanoparticles.

Recently, our group has introduced selenophene–thiophene block copolymers as a class of conjugated block copolymer that undergoes phase separation according to their different heterocycle constituents.[16] From this work, the question arose as to whether rod–rod block copolymers can be used to assemble nanoparticles. Herein we describe a study that tests the ability of selenophene–thiophene block copolymers to self-assemble spherical CdSe nanocrystals (NCs). Of particular interest to us was the morphology of polymer/NC composites and how the molecular weight of the polymer influences morphology (Scheme 1). We also establish whether rod–rod polymers of distinct molecular weight crystallize in a distinct manner, and how that influences composite morphology.



Scheme 1. A depiction of the selenophene–thiophene copolymer structure and possible self-assembled composites of copolymers with and without CdSe NCs.

Selenophene–thiophene block copolymers were synthesized according our previously published procedure.[16] Herein, the selenophene–thiophene block copolymers have a ratio of selenophene to thiophene of about 75:25, which was confirmed by NMR spectroscopy (Supporting Information, Figure S1). Three polymers with number average molecular weights M_n of 3.9, 8.3, and 12.9 kg mol^{-1} were prepared using this method. Combined NMR and GPC analysis shows that the average polymer chain is composed of approximately 5 thiophene and 15 selenophene units, 9 thiophene and 30 selenophene units, and 14 thiophene and 45 selenophene units for the 3.9, 8.3, and 12.9 kg mol^{-1} polymers, respectively. Although GPC tends to overestimate the true weight of rod–rod copolymers by a factor of 1.2–2.3,[17] the analysis shows that we were successful in synthesizing three distinct distributions of macromolecules. While some samples have low molecular weights, we will refer to all chain lengths as polymers for the sake of clarity in the discussion.

Films prepared from high molecular weight (M_n = 12.9 kg mol^{-1}) polymers were examined first. All of the films were prepared by drop-casting from chlorobenzene (5 g L^{-1}). Scanning transmission electron microscopy (STEM) was then used to investigate morphology. Accordingly, large-area STEM imaging (Figure 1 a) shows that the high-molecular-weight block-copolymer-only film has a needle-like structure. A magnified image (Figure 1 b) reveals small bright nanowires that are about 10 nm in diameter and randomly arranged throughout the surface. This morphology is consistent with microphase separation in crystalline rod–rod copolymers.[15a,16] Next, the same polymer solution was mixed with NCs (ca. 6 nm trioctylphosphine oxide (TOPO)

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[*] Dr. L. Li, J. Hollinger, Dr. N. Coombs, Dr. S. Petrov,
Prof. D. S. Seferos
Department of Chemistry, University of Toronto
80 St. George Street, Toronto, Ontario, M5S 3H6 (Canada)
E-mail: dseferos@chem.utoronto.ca
Homepage: http://www.chem.utoronto.ca/staff/seferos/

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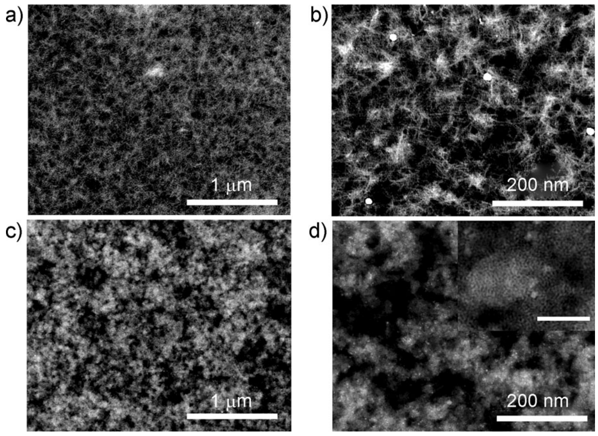

Figure 1. Dark-field STEM images of polymer fibers ($M_n = 12.9$ kg mol^{-1}) self-assembled without (a,b) and with (c,d) CdSe NCs. The inset in (d) is a magnified image; scale bar: 100 nm.

coated CdSe, 1:1 w/w) and deposited. In this case, new features are observed. These features are most likely due to NC mixing and intercalation into the polymer film. The magnified image (Figure 1 d) shows mainly spherical domains rather than nanowires. Overall, the analysis shows that the high-molecular-weight polymer produces a NC composite that is distinct from the polymer-alone form but is relatively unstructured.

We next turned our attention to the medium-molecular-weight sample ($M_n = 8.3$ kg mol^{-1}). In this case, fibers that are several hundreds of nanometers long and up to 100 nm wide are formed by the polymer using the same drop-casting methods (Figure 2 a,b). Compared with the needles formed by the high-molecular-weight sample, the size of the features are dramatically increased. In previous work on poly(3-hexyl)thiophene (P3HT) homopolymers, it has been shown that polymer chains transition from folded to extended when M_n is below a critical value (about 10 kg mol^{-1}), and this leads to the formation of highly ordered two-dimensional nanoribbons.[18] Our results are consistent with a size increase caused by a decrease in M_n. Because the diameter of the fiber is greater than the estimated length of the polymer (ca. 16 nm),[19] these fibers most likely consist of end-on aggregated polymer molecules (Scheme 1, $M_n = 8.3$ kg mol^{-1}). Next, NC composites were prepared using this medium-molecular-weight polymer. Interestingly, the NCs do not arrange completely randomly, but are associated with the polymer fibers, rather than the interstitial spaces where no polymer is present (Figure 2 c,d). Because the samples were prepared by mixing and drop-casting, this association shows that there is an affinity between the NCs and polymer.

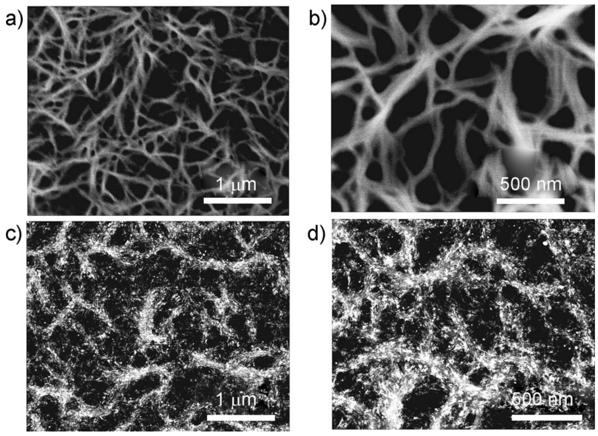

Figure 2. Dark-field STEM images of polymer fibers ($M_n = 8.3$ kg mol^{-1}) self-assembled without (a,b) and with (c,d) CdSe NCs.

Motivated by this result, we decreased polymer molecular weight further to $M_n = 3.9$ kg mol^{-1} and again investigated the self-assembled structure of the polymer-only films. The STEM images (Figure 3 f) show that polymers fibers are again quite large. In this case, the microstructure of the fibers can be seen, and it is composed of several bright and dark areas (Figure 3 f). A magnified STEM image (Figure 3 g) shows that the width of the bright region is about 10 nm, which is slightly larger than the length of the selenophene block within this copolymer (6.5 nm).[19] This 10 nm domain size is a very reasonable value for the selenophene region considering that the selenophene regions should overlap from different polymer molecules, and thus the width of the selenophene regions should range from 6.5 nm (totally overlapped) to 13 nm (non-overlapped). Topographic elemental linescans (Supporting Information, Figure S2) confirm that the bright regions are rich in selenium and deficient in sulfur, while the dark regions are rich in sulfur and deficient in selenium, and these observations lend further support to the proposed structure (Scheme 1, $M_n = 3.9$ kg mol^{-1}).

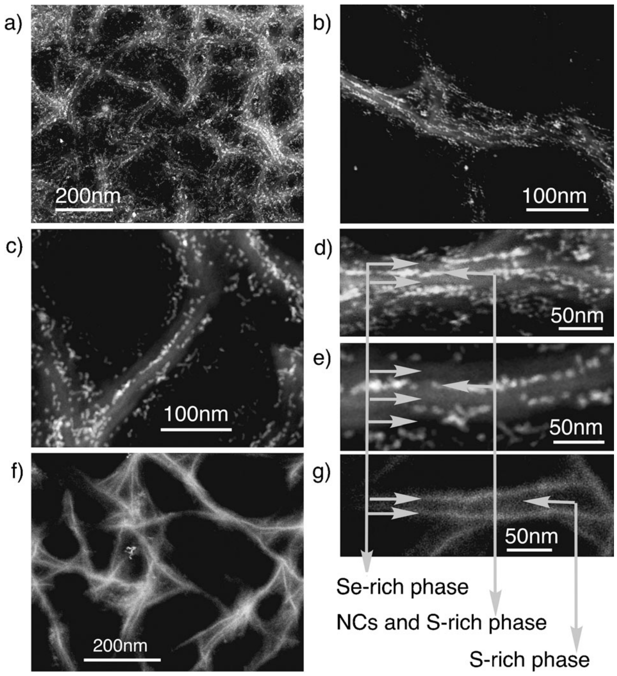

Figure 3. Dark-field STEM images of polymer nanofibers ($M_n = 3.9$ kg mol^{-1}) self-assembled with (a–e) and without (f,g) CdSe NCs.

Having established that low-molecular-weight selenophene–thiophene rod–rod copolymers ($M_n = 3.9\ \mathrm{kg\,mol^{-1}}$) form large aggregate fibers with an observable phase separation occurring within, we next prepared blends using the low-molecular-weight polymer and NCs in the hope of using this phase separation to align NCs along the phase domains. In this case, a pronounced co-self-assembly of NCs with polymer fibers is observed. Specifically, the NCs appear as new features that are decorated along the nanofibers (Figure 3a). A magnified image shows that the new features arrange in a non-continuous linear path (Figure 3b–e). When comparing the composite with the fibers formed by the block copolymer alone, it is reasonable to assume that the NCs are either selectively associated with one of the polymer phases (either selenophene or thiophene), or selectively associated with the interface between the two phases (Figure 3d,e). Elemental linescans (Supporting Information, Figure S3) of the aligned NCs show that the Cd peaks do not overlap with the broad Se peaks (from the polymer), thus showing that the NCs are more selectively associated with the thiophene phase.

Having determined that selenophene–thiophene block copolymers can be used to self-assemble NCs in a molecular-weight-dependent fashion, we next investigated whether the rod–rod polymers used in this study are crystalline, and if there were any differences in their crystalline structure. Drop-cast films of block copolymers were investigated by wide-angle X-ray scattering (WAXS). The analysis shows that the high-molecular-weight block copolymer film is crystalline, showing a characteristic diffraction peak at $2\theta = 5.64°$ corresponding to 15.5 Å spacing (Figure 4a, gray line). The 15.5 Å spacing is due to the interlayer stacking of both the hexylthiophene and hexyselenophene phases. This value is very close to the reported structure of P3HT, which has a (16.0 ± 0.2) Å[20] interlayer spacing, and poly(3-hexyl)selenophene (P3HS), which has a 15.2 Å[21] interlayer spacing (Figure 4b). The observed value of 15.5 Å lies between these two values and is most likely a convolution of both values. We refer to the crystalline phase characterized by this diffraction peak as type 1 (Figure 4b).

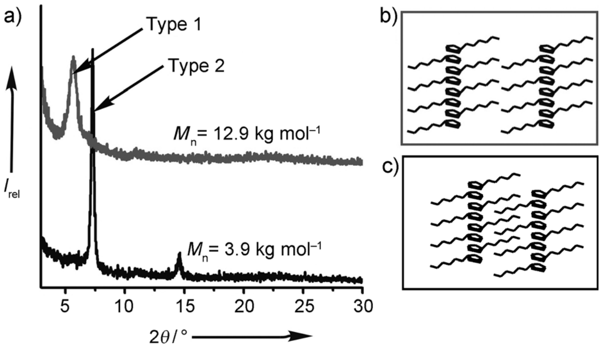

Figure 4. a) WAXS pattern of polymer films with different molecular weight. b,c) Layered structures of b) type 1 and c) type 2 phases.

Upon going from the high-molecular-weight to low-molecular-weight samples, a distinct diffraction peak appears. This peak, which occurs at a $2\theta = 7.30°$, corresponding to a 12.1 Å spacing (Figure 4a black line), is even sharper than the first, again indicating that the polymer is crystalline. The origin of this peak was puzzling to us at first, but we eventually ascribed it to a second polymorph in the low-molecular-weight sample (both phases are present in the medium-molecular-weight samples; Supporting Information, Figure S4). The origin of the second polymorph (type 2) of P3HT is observed exclusively in low-molecular-weight polymers, often with longer side-chains than P3HT (C8 and C10, for example),[22] and has smaller interlayer spacing.[19] Presently, literature models that account for this second polymorph are based on either a more interdigitated arrangement side-chains (Figure 4c)[22] or a greater degree of side-chain tilting.[23] Based on this, the high- and low-molecular-weight polymers have clearly distinct packing structures.

We next wondered if this difference in crystal type played a role in the difference in co-self-assembled structure. In control experiments, we observe a pure type 2 phase (Supporting Information, Figure S4) in low-molecular-weight polyselenophene ($M_n = 4.2\ \mathrm{kg\,mol^{-1}}$) as well as the formation of large fibers (Supporting Information, Figure S7). In co-assembled films, however, NCs are dispersed randomly throughout the polyselenophene fibers (Supporting Information, Figure S7). This result shows that the type 2 polymorph alone cannot account for the organization of NCs in the manner that we observe with the selenophene–thiophene block copolymers (Supporting Information, Figure S3), showing that phase separation is critical for self-assembly.

A series of photoluminescence quenching experiments were conducted to gain more insight into the physical interaction between the selenophene–thiophene block copolymers and NCs. In general, conjugated polymer/NC composites have potential use as light-harvesting materials because both the conjugated polymer and NCs are strong light absorbers, and the LUMO level of the polymer is positioned above the conduction band of CdSe while the HOMO level of the polymer is positioned above the valence band of CdSe.[24] From an energy-transfer perspective, photoinduced charge separation is expected based on this energy-level alignment and the physical contact of the two materials. Because photoinduced charge separation also leads to luminescence quenching, fluorescence can be used as a measure of the physical contact of these two materials. Accordingly, upon illumination at $\lambda = 470$ nm, a film of NCs emits strongly at $\lambda = 602$ nm. When the NCs are mixed with selenophene–thiophene block copolymers ($M_n = 3.9\ \mathrm{kg\,mol^{-1}}$) prior to casting, emission is quenched by 72% (Supporting Information, Figure S5d). Quenching is observed even at a relatively low loading of polymer (1.2%; w/w) and without TOPO ligands removed, which indicates efficient energy transfer. Furthermore, at this low polymer loading, the absorption spectra of the blend is nearly identical to the NC-only film, which shows that the diminished luminescence is not due to increased absorption (Supporting Information, Figure S5a). Although the ratio of polymer to NC is different in self-assembled composites, these quenching studies provide strong evidence of the close contact between selenophene–thiophene polymer and NCs. Even when different wavelengths (400 nm, 440 nm, 530 nm) were used to excite the

NCs, efficient quenching is observed in these blends (Supporting Information, Figure S5b, c, e).

Next, quenching experiments were carried out on NCs that were blended with P3HT and P3HS homopolymers to determine which material quenches more strongly. In this case, we observed that polythiophene is a more efficient quencher of NC emission than polyselenophene (Supporting Information, Figure S6). Because polythiophene and polyselenophene have nearly identical HOMO levels,[21] meaning that they are energetically equal hole acceptors, this result was not expected. However, because quenching efficiency is distance-dependent, the fact that polythiophene is a better quencher is therefore illustrative of the stronger affinity between NCs and polythiophene. These observations are consistent with the selective association of the NCs with the thiophene phase of the block copolymer.

In conclusion, we have carried out a series of experiments to test the ability of selenophene–thiophene block copolymers to co-assemble NCs. Block copolymer/nanoparticle co-self-assembly had previously been shown for several coil–coil polymers. We have established that selenophene–thiophene rod–rod block copolymers can be used to organize spherical NCs into two types of hierarchical structures depending on the molecular weight of the polymer. In high-molecular-weight samples, phase separation occurs at the nanoscale and the polymer film adopts a needle-like structure. When high-molecular-weight polymer is co-self-assembled with NCs, NCs disperse throughout the film, resulting in spherical domains. In low-molecular-weight samples, phase separation also occurs at the nanoscale, however larger self-assembled polymer fibers are observed that are composed of several phase-separate domains. When the low-molecular-weight polymer is co-self-assembled with NCs, NCs are aligned within the thiophene-rich phases of the fibers. A different crystalline polymorph was observed for the low-molecular-weight selenophene–thiophene block copolymers; however, homopolymers that crystallize in this polymorph could not be used to drive NC self-assembly in the same manner that was observed for the block copolymer, showing that block copolymer structure is critical for self-assembly in these systems. These results should motivate researchers to continue to develop semiconducting rod–rod block copolymers in applications where the co-organization of a conjugated polymer and nanoparticle are important, such as in organic optoelectronic devices.

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