Characterization and Processing/Property Relationships of Semiconducting PT and PPV Nanotubes by Template Wetting Nanofabrication

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Abstract

Nanotubules are fabricated from widely studied semiconducting poly(3-hexylthiophene) (P3HT) and a soluble poly(*p*-phenylene vinylene) (PPV) derivative using template wetting procedures. Ultraviolet-visible (UV-Vis) spectroscopy reveals a significant reduction in the bandgap in the non-crystalline PPV derivative when confined in the nanoporous structure. Analysis of space-charge-limited (SCL) currents demonstrated increases in low-field hole mobility by a factor of 10^2. Each of these results are indicative of enhanced molecular ordering in the nanostructure, and neither result was observed in the semi-crystalline P3HT.

Introduction

Poor hole and electron mobilities inherent in disordered systems of conjugated, semiconducting polymers have been shown to limit efficiencies and performance in electronic devices such as polymer light-emitting diodes.[1] In particular, interchain hopping of carriers in the disordered systems found in traditional thin-film devices has been shown as the rate limiting step in carrier transport.[2] Exceptionally high hole mobilities have been observed in systems of self-ordering polymers like P3HT which produce strong interchain π-π orbital overlapping.[3] Thus, improving electronic transport in these materials has been the focus of much research, with specific interest on enhancement of order.

Several techniques including electrospinning,[4] template synthesis,[5] and template wetting[6] have all been demonstrated as viable means of producing nanoscale fibers or tubules from a wide variety of polymers, often with increased molecular order.[7-11] The template wetting approach has proven to be one of the simplest of these methods for the creation of such structures, making use of wetting phenomena to create uniform coatings of low surface energy materials, such as polymer solutions, upon high surface energy pore surfaces such as porous alumina. Steinhart *et. al.* later demonstrated curvature-directed crystallization of poly(vinylidene difluoride) by template wetting which produced a brush structure along the inner wall.[9] Such a structure should improve intermolecular π-π overlap, increasing carrier transport. Here, we examine poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and P3HT nanotubes fabricated using solution-based template wetting nanofabrication. Analysis of spectroscopic properties and space-charge-limited (SCL) currents are used to characterize the nanostructures.

Experimental

Preparation. MEH-PPV and regioregular P3HT were obtained from Sigma-Aldrich and used as received. Solutions of each polymer were created by dissolving in chloroform at a concentration of 2 mg/ml. Highly porous alumina membranes used as templates were 60 μm thick with pore diameters of 100 nm and 200 nm. Templates were wetted with polymer solutions by applying a droplet to the top surface of the membranes, and allowing the solvent to evaporate. Residual polymer on the template surface was subsequently removed by etching in a helium plasma. For spectroscopic analysis, templates were used directly after etching, and thin films were created by spincasting the polymer solutions onto quartz slides. Hole-only electronic devices were created by deposition of Au contacts on either side of the nanoporous membrane.

Characterization. UV-Vis spectroscopy was performed using a Shimadzu UV 1650PC system in order to determine optical absorbance spectra and approximate band gaps of the material in various forms. Absorbance spectra were obtained for energies ranging from 1.5 to 3.5 eV. Current density – voltage (*J*-*V*) measurements were performed using a Keithley 236 source-measure unit. Devices were initially tested by repeatedly sweeping the applied bias between -100 V and 100 V in 1 V steps every 250 ms. Typically, electric fields applied to polymer thin-film devices are on the order of 10^5 ~ 10^7 V/cm^2. Here, we examine devices at significantly lower fields on the order of 10^3 ~ 10^4 V/cm^2 in order to accurately observe the SCL currents which dominate in this field regime.[1]

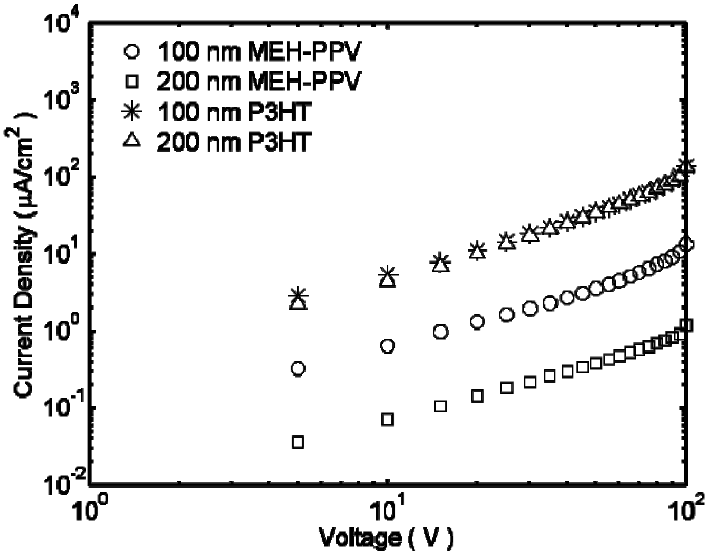

Figure 1. Current-voltage characteristics for MEH-PPV and P3HT. P3HT curves are indistinguishable.

Results and Discussion

Electrical conduction was observed to be quadratic in all samples, indicative of SCL conduction. Fitting *J-V* data to the SCL model,

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_p \frac{V^2}{L^3}$$

where *V* is the applied bias, *L* is the device length, $\varepsilon_0\varepsilon_r$ is the permittivity of the material, and μ_p is the hole mobility.[12] Using this model, hole mobilities for 100 nm and 200 nm MEH-PPV nanotubes were calculated to be 10^{-4} cm^2/V▪s and 10^{-5} cm^2/V▪s, respectively. The mobility commonly noted in thin films of MEH-PPV is 10^{-6} cm^2/V▪s,[13] demonstrating improved mobility through progressive confinement. P3HT devices of both pore diameters produced mobilities of 10^{-2} cm^2/V▪s, in good agreement with values reported elsewhere for thin films.[3] These results are illustrated in Figure 1. The progressive increase in mobility with decreasing pore diameter in MEH-PPV suggests an enhancement of molecular ordering in the non-crystalline polymer, when compared with the thin film, given that similar increases in mobility were not observed in the semicrystalline P3HT.

These observations are further evidenced by UV-Vis spectroscopic analysis. Marked reduction in the bandgap of MEH-PPV was observed in the nanotube samples when compared with similar measurements on thin-films. The bandgap reduction was estimated approximately 0.6 eV in MEH-PPV, and the entire observed absorbance peak was correspondingly shifted. Little or no variation in the bandgap was observed in P3HT, suggesting, again suggesting little difference in the molecular ordering of P3HT nanotubes when compared to the thin-film. This short analysis suggests a more ordered structure in the template than is present in the film.

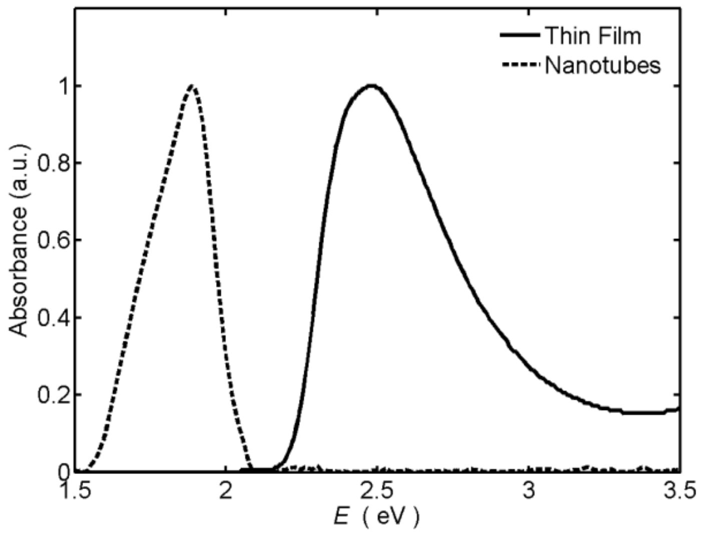

Figure 2. UV-Vis spectroscopy demonstrates significant red shifting of the absorbance in MEH-PPV nanotubes, and a corresponding reduction of the bandgap.

Conclusions

We conclude that template wetting of conjugated polymers can significantly alter their electronic properties. The comparison of observations in materials known to be semicrystalline (P3HT) and amorphous (MEH-PPV) suggests that enhanced ordering of amorphous polymers is possible in template wetted nanostructures, suggesting improved interchain transport in the material. The observation that mobility in MEH-PPV is increased as pore size is reduced further indicates that these improvements are confinement induced.

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