Aggregation, crystallization, and resistance properties of poly(3-hexylthiophene-2,5-diyl) solid films gel-cast from CHCl₃/p-xylene mixed solvents

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1. Introduction

Crystallinity and a well-controlled morphology are desirable characteristics for obtaining high charge mobility from semi-rigid poly(3-alkyl thiophene)s (P3AT)s. Several methods and techniques—including vapor treatment, drop casting [1], thermal annealing [2,3], surface treatment [4], control over the rate of solvent evaporation [5], and electro-spinning [6]—have been used to improve the aggregation behavior of poly(3-hexylthiophene-2,5-diyl) (P3HT) to achieve a higher degree of π–π stacking in lamella-type thiophene ring aggregation and, thereby, enhance the electronic properties of P3ATs. The excellent mobility of P3HT is believed to be due to the lamella-type stacking of its thiophene rings and, thus, strong inter-chain interactions.

It has been reported that films of P3HT exhibit nanowhisker or nanowire morphologies when cast directly from solutions of poor solvents [4] or when subjected to post-treatment with solvent vapor [1]. The morphology of a polymeric thin film is affected significantly by controlling the rate of solvent evaporation or through aging with mixtures of aromatic and non-aromatic solvents; using such approaches, the optical, physical, and morphological properties [7] of P3HT-based semi-rigid polymer thin films can be modified to enhance the performance of corresponding devices [8,9]. The solvation properties of mixtures of non-aromatic and aromatic solvents can affect not only the crystallinity [10] of polymers but also the quality of the interfacial area between materials [11,12].

The key factor influencing the morphology of a semi-rigid P3AT polymer is the kinetic and/or thermodynamic balance in the aggregation behavior of its side chains and main chain. Several investigations of the influence of solvent mixtures on device performance have demonstrated...
that the organization of P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is strongly affected by changing the composition of the solvent [13–16]. The implication is that mixing of solvents is a promising technique for modifying the layer morphology and, hence, improving the performance of semi-rigid P3HT–type solar cells.

Recently, from a study of the conductivity of P3HT gel films cast from p-xylene, toluene, and benzene, Pozzo and coworkers [17] demonstrated that it is possible to tune the electronic properties of organogels by adjusting the conditions for self-assembly. They achieved films with different mechanical and electrical properties when performing the gelation of P3HT in different solvents. Understanding the structural and mechanical features that contribute to enhancing electronic properties is critical for the engineering of gel structures specifically for particular applications.

Although many separate investigations have been made into the phase transitions of P3AT’s rigid thiophene main chains [18–21] or alkyl side chains [22,23], few reports have discussed the kinetic balance of the aggregation of hexyl side chains (flexible) and thiophene main chains (rigid) simultaneously. Furthermore, the solid–solid phase transition behavior of the hexyl side chains of P3HT in the temperature range 30–60 °C has been studied by controlling the evaporation rate of solvents, but without discussing the phase transition behavior of main chain crystallization in the approximate temperature range 220–230 °C [23]. Recently, Smith and coworkers [24] demonstrated that the thermal and structural characteristics of P3HTs can be characterized into two distinct classical polymorphs: Form I, in which the hexyl side-chains are not interdigitated, and Form II, in which they are; they did not, however, discuss the difference in resistance between the two forms.

For this present study, we suspected that careful control over the gelation behavior of P3HT, in pure solvents and in CHCl3/p-xylene mixed cosolvents [25], would allow us to modify the solid–solid phase transition and crystallinity behavior of semi-rigid P3HT gel films, thereby potentially improving the π–π stacking of the thiophene main chains and decreasing the resistance of the gel-cast P3HT films [21]. To date, it has remained a great challenge to achieve ultimate control over both the film morphology and crystallinity for semi-rigid P3HT through favorable π–π stacking of its thiophene units [26]. By controlling these parameters, we should be able to optimize semi-rigid P3HT–based devices, particularly through the screening of potentially high-performing semi-rigid P3HT materials whose π–π stacking morphologies and crystallinity are not optimized under the crystallization conditions imposed by drop-casting.

2. Experimental section

2.1. Materials

Regioregular P3HT (Mw: ca. 48,000; PDI: 2.1; regioregularity: 90–94%; Uniregion Biotech), p-xylene (Aldrich), and CHCl3 (Aldrich) were used without further purification. Clear P3HT solutions were obtained after adding P3HT (10 mg) to various solvents (1 mL) and heating at 40 °C for 10 min. These clear P3HT solutions were then aged in N2-filled vials for 36 h at ambient temperature. Dried films were obtained by drop-casting the aged solutions onto glass surfaces patterned with two indium tin oxide (ITO) electrodes separated by 200 μm and then placing them in a N2-filled cubic box (15 × 15 × 15 cm) for further vacuum drying.

2.2. Measurements

Differential scanning calorimetry (DSC) was performed using a PerkinElmer Pyris Jade DSC instrument operated at a heating rate of 10 °C min⁻¹ and a N2 flow rate of 40 mL min⁻¹. UV–Vis spectra were recorded using a PerkinElmer Lambda 35 UV/Vis spectrometer; solutions were prepared from P3HT dissolved in p-xylene, CHCl3, and various ratios of CHCl3 and p-xylene, while films were prepared by drop-coating various long-time-aged gel solutions onto ITO (featuring two parallel electrodes). A polarized optical microscope (POM, Nikon Optiphot) was employed to observe the morphological textures of the polymer sols and gels. Grazing incidence X-ray diffraction (GIXRD) measurements were conducted using a Bruker D8 multi-function X-ray diffractometer and an X-ray beam wavelength (λ) of 1.541 Å (Cu Kα radiation). Because P3HT is a conjugated polymer that becomes p-doped after exposure to O2 and/or moisture [27,28], impedance measurements were performed in a N2-filled box at room temperature, using an Zahner Zennium apparatus equipped with a frequency analyzer module, over the frequency range from 1 Hz to 1 MHz, with voltage modulation of 500 mV.

By capturing the appropriate parameters of the sample, we calculated the complex resistance:

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Z = R_S + \frac{R_P}{1 + (i\omega)^\eta R_P C_P}
\]

where R, C, and ω denote the measured resistance, capacitance, and frequency, respectively. The real part of the complex resistance, plotted with respect to the imaginary part, gives the Cole–Cole plot, also known as a Nyquist plot [29]. The ITO contact contributes to the serial resistance (R_S).

3. Results and discussion

3.1. Gelation behavior of P3HT in various solvent mixtures

For this study we chose CHCl3 and p-xylene as solvents because of their widely different boiling points (ca. 61 and 138 °C, respectively) and different solubility parameters (ca. 9.3 and 8.75 eal¹/² cm⁻³/², respectively). Different boiling points are advantageous when studying aggregation behavior from cosolvent solutions because they prevent thermodynamic effects from influencing the formation of thin films. Indeed, rapid vaporization of one solvent results in earlier quenching of the materials in the mixtures [10] and, consequently, changes their degrees of stacking and
interchain overlapping prior to vaporization of the second solvent, and analysis of the properties of film will be more interesting. Changing the ratio of CHCl$_3$ and p-xylene in the P3HT solutions enabled us to investigate the phase transitions and π–π stacking behavior of the thiophene units in solution as well as the film morphology after casting. Fig. 1a displays photographic images of P3HT solutions at various CHCl$_3$/p-xylene ratios during a gelation period of 36 h. Three phases are evident (Fig 1b): clear, turbid, and dark, which represent the random coil phase, the planarization (liquid-crystalline) phase, and the gelation phase, respectively. The solutions containing pure p-xylene and 20 and 40 vol% CHCl$_3$ ultimately formed the dark color (e.g., gel state). The 60 vol% CHCl$_3$ solution became turbid; it represented the liquid crystal state. Clear solutions were ultimately obtained for P3HT dissolved in 80 vol% and pure CHCl$_3$. Interestingly, the P3HT films cast from these gels after long-time aging exhibited these same aggregation behaviors; they could be identified through appropriate instrumental measurements. Notably, the gelation time of the P3HT solution could be adjusted by changing the CHCl$_3$/p-xylene ratio of the mixed solvent [30,31].

Fig. 2 displays POM images of the P3HT samples subjected to gelation in the various cosolvents for 36 h. Increasing the amount of CHCl$_3$ in the solvent led to a decrease in the crystallite size. In pure p-xylene, some of the P3HT crystallites had aggregated to sizes in the range 100–300 µm (Fig. 2a). This behavior implies that P3HT coexisted as both ordered and random coil aggregates in p-xylene, which can be considered a marginal solvent for the P3HT rigid polymer; it helps the random-coil P3HT chains transform into planarized structures and favors gel formation.

When we increased the CHCl$_3$ ratio to 20 vol%, lamellar aggregation sheets of P3HT crystallites were formed with domain sizes of greater than 500 µm. CHCl$_3$ is the good solvent for P3HT in these cosolvent systems; it can be considered as a lubricant or helper to maintain kinetic balance between good and poor solvents, as has been discussed extensively in the literature [26,32,33].

Fig. 2c reveals that the crystallites in the 40 vol% CHCl$_3$ solution formed a continuous, smooth crystal structure in the gel phase. The turbidity of the 60 vol% CHCl$_3$ solution implies that the P3HT crystallites had sizes of less than 100 µm (Fig. 2d). We observed no crystallites in the clear solutions obtained in 80 vol% and pure CHCl$_3$ because the POM images of these clear samples were similar; we do not present them herein. We suspected that the small crystallites that existed in the 60 vol% CHCl$_3$ gel solution would have provided “loose” main chain aggregates, with small domain sizes and low degrees of crystallinity, in the films formed after drying. We also expected the enthalpy of the main chain melting point of the P3HT film gel-casted from 60 vol% CHCl$_3$ to be lower than those obtained from 20 to 40 vol% CHCl$_3$ because of its smaller crystallite sizes. Such small domains contain many boundaries that act as barriers for electron transfer and also lower the degree of carrier transport in P3HT film [26]. We expected lower melting enthalpies and melting temperatures for the P3HT films cast from the 80 and 100 vol% CHCl$_3$ solutions because P3HT polymers exist in random-coil states in high-CHCl$_3$-ratio solutions and because the rapid rates of evaporation of these solutions would result in low-density packing structures [5].

3.2. UV–Vis spectroscopy data

We recorded UV–Vis absorption spectra to explore the conformational transformations and π–π stacking of P3HT in the CHCl$_3$/p-xylene cosolvent. It has been demonstrated previously that the conformations of P3HT chains can be resolved using UV–Vis spectroscopy [34–36]. Fig. 3 displays the absorption spectra of P3HT in CHCl$_3$/p-xylene mixed solvents of various proportions after being aged for 36 h at ambient temperature to allow further main chain aggregation and interchain π–π packing. The freshly made solution displayed an orange color and a single absorption peak at a value of $\lambda_{\text{max}}$ of 451 nm, indicating that P3HT existed in a coil disorder state. The absorption peak at 451 nm in the 80 vol% CHCl$_3$ mixed solution shifted to 455 nm after aging for 36 h. An additional weak absorption peak appeared near 605 nm; this signal, which is associated with interchain π–π stacking and hopping effects between interdigitated backbones [37], revealed the stable
p-xylene, allowing control over the degree of crystallinity in the resulting P3HT film. We anticipate that our results will benefit the development of semi-rigid polymers, particularly those based on P3HT, for use in controlling the aggregation behavior within gel-cast films.

Acknowledgments

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References