Polymeric morphologies and fluorescence of poly(p-phenylene) films by self-assembly

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ABSTRACT

Polymer morphologies in thin films strongly depend on the state of the solution and the film processing conditions, which lead to significant impacts on the optoelectronic properties. In this work, the morphologies of poly(p-phenylene) films are investigated by concentration-dependent fluorescence spectroscopy and scanning electron microscopy combined with the contact angle tests. We find that the well-defined nanowires of the hairy-rod conjugated polymer can be self-assembled in different good solvent vapor atmospheres from the dilute solutions. The driving force of aggregation would be the side-chain entanglement and the intermolecular π–π interactions, which are sensitive to concentration. Moreover, the optical properties are strongly affected by the polymer concentration, which is the main factor to form different conformations and aggregations of polymers. These results are valuable for the intrinsic properties of poly(p-phenylene) and the potential application in optoelectronic devices.

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1. Introduction

In recent years, the conjugated polymers have attracted more and more attention to applications in polymer light-emitting diodes, polymer solar cells, and field effect transistors [1–3], not only due to their unusual electrical, magnetical, and optical properties [4,5], but also being light-weight, low-cost, and flexible, and exhibit irreplaceable advantage over their traditional inorganic counterparts. One of the biggest advantages of conjugated polymers is their solution-processability, which can be achieved by attaching flexible aliphatic side-chains to stiff conjugated backbones [6]. This kind of polymer is usually called hairy-rod polymer [7,8].

As the solubility improved, the introduction of side-chains can also lead to the conformational change of conjugated backbones [9–11], which has an important influence on the electronic structure of conjugated materials. Because the steric repulsion between the side-chains causes a marked torsion in the conjugated chain disrupted π-electron overlap, the results can result in the decreasing of effective conjugation length and a corresponding blue shift of the emission, which were suggested by the experimental measurements and the theoretical calculations [12,13]. The relationship between the conformations of conjugated backbones and electronic structures is a fundamental feature of conjugated polymers. Furthermore, it is well-known that optoelectronic properties are dependant on not only the nature of isolated polymers, but also the intermolecular effects, which are governed by the nature of the chain packing and the aggregation morphology in solid state [14]. For example, the solvatochromism, as commonly observed in poly(3-alkylthiophenes) solutions and films, were explained in terms of intrachain and interchain mechanisms, attributing to the conformational transition of conjugated backbones and the formation of foliated aggregates [15–17]. The long-wave emission of polyfluorenes has attracted much attention due to the reduced color purity for the famous blue emitting luminescent material [18]. Besides explained as resulting from oxidative (keto) defects formed along the polymer backbones, the obvious low energy emission was attributed to interchain interactions such as aggregates and excimers [19]. And the more coplanar conformations of polyfluorenes named as β type can also result in the red-shift of the emission due to the additional local conjugation order state [20]. Consequently, the polymer morphology in thin film strongly depends on the state of the solution and

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the film processing conditions, leading to important impacts on the optoelectronic properties, i.e., the solid-state luminescence and the charge mobility properties [21–23].

Therefore, considerable attention has been drawn to modulate the morphologies of polymer films via many useful processing methods, such as slow growth, thermal annealing and the use of additives and mixing solvents, which have been successfully employed to promote the formation of nano-scale phase separation with appropriate aggregation size as well as the ordered interchain packing of polymers [24–26]. Especially, solvents have a strong influence on the rigid backbones and flexible side-chains of hairy-rod polymers to form various conformations and aggregates [27,28] with π–π stacking of conjugated backbone and entanglement of side-chain substitutions as the main driving force [29–31]. Therefore, the various polymer morphologies can be formed from the polymer solutions and further affect the optical properties of the polymer films.

Phenylene-based polymers are one of the most important classes of conjugated polymers, and have been the subject of extensive research. In particular, poly(p-phenylene) (PPP) has the most simple structures with the repeating phenylene units at the 1,4 positions, displaying good solubility and thermal stability. The emission in the near-ultraviolet region [32,33] is attributed to the torsion of the polymer backbones induced by the flexile side chains, which modified by introducing different mesogens such as light-emitting chromophores and chiral groups [34], also can tailor the substituted PPP show excellent luminescence and photoconductivity.

In our previous study, the hairy-rod polymer, poly(2,5-dioctyloxy-p-phenylene) (PP8P) has been chosen as the model representative to investigate the relationship between conformations and photophysical properties in dilute solutions and the self-assembly behaviors from the solutions under the nonsolvent vapor atmospheres [35,36]. This encouraged us to extend our investigations to investigate the aggregation morphologies of PP8P in the self-assembled films with the role in optical properties. The aggregation behaviors in the good solvent vapor atmospheres and the optical properties are demonstrated as the function of concentrations. The driving force of polymeric aggregation and the relationship between polymeric morphologies and optical properties are discussed.

2. Experimental section

2.1. Materials

Analytical grade toluene (Tol), chlorobenzene (CB), chloroform (CHCl$_3$), and tetrahydrofuran (THF) were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(2,5-dioctyloxy-p-phenylene)s (PP8P) was synthesized by the solid-state oxidative coupling polymerization using FeCl$_3$ as the oxidative catalyst [37]. The number-average molecular weight (Mn) is 7×10^3 with a dispersity of 2.7 determined by gel permeation chromatography (GPC).

2.2. Film formation

All of the self-assembly processes were performed at ambient temperature in a cap-sealed glass vessel, where 3 mL of solvent was added to generate a saturated vapor atmosphere. The glass substrates were positioned above the liquid level after cleaned by detergents, demineralized water, ethanol and acetone successively, and then dried in an oven at 50 °C. The contact angle between H$_2$O and the glass was 35.6°. The PP8P samples were dissolved in Tol, CB, CHCl$_3$ and THF respectively for the preparation of solution with different concentrations (0.5, 1, 5, 10, and 15 mg mL^{-1}). A typical

self-assembly process was carried out by casting 5 μL PP8P solution with the desired concentration onto a glass substrate by a microsyringe. After complete evaporation of the solution, a thin film remained on the substrate. The process of the film formation in the solvent vapor atmosphere is shown in Scheme 1.

In order to understand the difference between spin-coated films and self-assembled films, the thin films were prepared by spin-coating polymer solutions on glass plates. The solvent-annealing process was performed at ambient temperature in a cap-sealed glass vessel, where 3 mL of solvent was added to generate a saturated vapor atmosphere. The solvent-annealed films were removed from the solvent vapor-filled chamber after 24 h.

2.3. Instrumentation

The relative molecular weight and molecular weight distributions were determined by GPC using a Waters GPC 1515 with THF as the eluent and polystyrene standards as the references. Scanning electron microscopy (SEM) images were obtained by a Hitachi S4800 scanning electron microscope. The contact angles were measured on an SL200B Contract-angle System at room temperature. The contact angle values are averages of three independent measurements. UV–vis spectra of the samples were recorded on a double-beam Perkin-Elmer Lampda850 UV–vis spectrometer. Fluorescence (PL) spectra of the polymer films on glass were measured on a PE-LS55 fluorescence spectrophotometer.

3. Results and discussion

3.1. Micro/nanostructures and morphologies of the films

In our experiment, the PP8P films on the glass substrates were cast from the solutions with different concentrations ranged from 0.5 to 15 mg mL^{-1}. We created a static solvent vapor atmosphere, in which the PP8P films were assembled, as shown in Scheme 1. The polymer sub-micron level patterns were observed by SEM as shown in Fig. 1. SEM images revealed that there were typical 1D nanowires self-assembled from the PP8P solution with the concentration of 0.5 mg mL^{-1} in the solvent vapor atmospheres. Obviously, the solvent quality can affect on the sizes of the polymeric nanowires, whose diameter distribution was shown in Fig. 2. The nanowires self-assembled from the aromatic solvents had broader width of 340 nm (from Tol, in Fig. 2a) and 470 nm
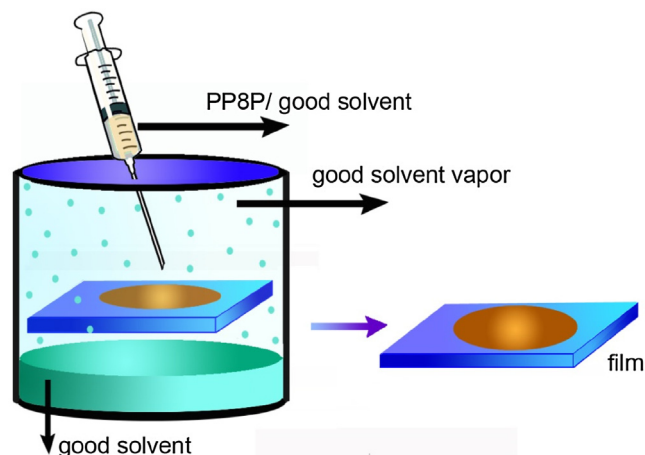
Scheme 1. Self-assembly process of the PP8P film in a good solvent vapor atmosphere.