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Control on β conformation of poly(9,9-di-n-octylfluorene) via solvent annealing*

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Films of poly(9,9-dioctylfluorene) (PFO) are of great importance in fabricating light emitting diodes. In practice, the β-phase of PFO is expected due to its high efficiency in the transport of charge carrier. To promote the formation of β-phase, PFO films are immersed and annealed in the mixture of solvent/nonsolvent. The effects of temperature, solvent/nonsolvent ratio, and annealing time are examined systematically. It is found that the fraction of β-phase can be highly improved by increasing the ratio of solvent/nonsolvent. The reconfiguration of PFO molecules for β-phase in annealing is generally finished in 10 min. The finding in this study demonstrates that solvent-assisted annealing offers a fast and economic approach for mass annealing.

Keywords: organic crystal, conjugated polymer, solvent annealing

PACS: 61.82.Pv, 61.82.Rx, 81.40.Ef **DOI:** 10.1088/1674-1056/28/7/076101

1. Introduction

Conjugated polymers are emerging as promising materials for fabricating elastic and flexible electronic and photonic devices.[1] Among them, poly(9,9-dioctylfluorene) (PFO) as a blue-light-emitting polymer has been extensively studied due to its excellent charge transport properties and highly efficient photoluminescence. Optoelectronic devices based on PFO have a wide range of potential applications in organic light-emitter diodes (OLEDs),[2] lasers,[3] solar cells,[4] and field effect transistors.[5] In these applications, the molecular conformation of PFO plays a critical role in determining the performance of the devices. There are two distinct conformations of PFO in films, namely: α-phase and β-phase. In the β-phase, the polymer chains adopt an extended coplanar conformation which allows a high charge-carrier mobility[6] and a high efficiency in photoluminescence.[7–9] For applications such as light emitting diodes and electrically pumped organic lasers, the high charge-carrier mobility is critical.[10] Therefore, improving the fraction of the β-phase in PFO products is of particular interest in fabricating organic semiconductors.[8]

The most widely used methods in preparing thin polymer films are spin-coating, vapor deposition, and solvent evaporation. In these methods, the conformation of the polymer chains in the products is generally arrested in the amorphous glass state because of the fast dynamics. To improve the crystallinity, films are often processed by post-annealing. In the case of PFO, strategies including substrate thermal annealing[11] and solvent vapor treatment[12] have been exploited. Nevertheless, the efficiency of these approaches is limited.[13,14] PFO films with high crystallinity are still a big challenge in practice.

Recently, solvent-assisted annealing has been exploited, in which the PFO film is immersed in the mixture of solvent/nonsolvent vapor for annealing.[15] In this case, the annealing time is as long as tens of hours. Alternatively, Lu immersed the pristine PFO film in a mixture of solvent/nonsolvent solution.[16] The dynamic reconfiguration processes of polymer toward β-phase were highly accelerated via the so called self-dopant[17] mechanism. However, in their study, the effect of solvent/nonsolvent ratio and the temperature of annealing were not addressed. This greatly impeded its practical application.

In this study, PFO films are processed with solvent-assisted annealing. The effects of the volume ratio of solvent/nonsolvent, temperature, and annealing time on the fraction of β-phase are systematically studied. We find that an optimal ratio of solvent/nonsolvent exists in promoting the formation of β-phase, the result of solvent-assisted annealing is not sensitive to the temperature, and the typical time scale of the dynamic process of β-phase formation is around 10 min. The microscopic mechanism underlying these observations is addressed.

2. Experimental details

2.1. Materials

The PFO (ADS129BE) was purchased from American dye source company and used as received.

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2.2. Preparation of the pristine PFO films

The PFO powder was dissolved in toluene and maintained at 60 °C overnight for sufficient dissolution. The solution was then filtered with 0.25 μm polytetrafluoroethylene filters. The PFO solution of concentration 10 mg/ml was spin-coated on indium tin oxide (ITO) substrates to obtain the pristine PFO films.

2.3. Preparation of the β-phase PFO films

The pristine PFO films were immersed into the mixture of toluene (solvent) and ethanol (nonsolvent) for annealing. The annealing processes were conducted at three different temperatures: 30 °C, 40 °C, and 50 °C. To quantify the effect of the temperature, the samples and the annealing solution were heated to the annealing temperature separately. The pristine PFO film was then immersed in the solution mixture to prevent the occurrence of a temperature-gradient-induced crystallization.

2.4. Characterization

The morphologies of the PFO films were first visualized by atomic force microscope (AFM, MFP-3D-SA, Asylum Research) in the tapping mode on Pt-coated Si cantilevers (0.2 $N{\cdot}m^{-1}$ force constant from Nanosensors). UV absorption spectra (UV–vis–near IR spectrometer Lambda 19, Perkin-Elmer) were used to study the absorption behavior of the annealed PFO films. Photoluminescence spectroscopy (PL spectrum, spectrofluorometer FluoroMAX-3, Jobin Yvon) was used to study the emission property.

3. Results and discussion

To examine the effect of the ratio of solvent/nonsolvent and the temperature, PFO films on ITO substrates were processed in the mixture of toluene (solvent)/ethanol (nonsolvent) with different mixing ratios (R) at different temperatures (T) for different processing time (t).

The morphologies of the products after annealing were first investigated by AFM. Figure 1 shows that given the same ratios of toluene/ethanol, the final morphologies of the films annealed at different temperatures do not exhibit significant difference in the size of crystalline domains. In the tapping mode, the bright domains of AFM represent the raised parts, while the dark domains represent the concave parts.

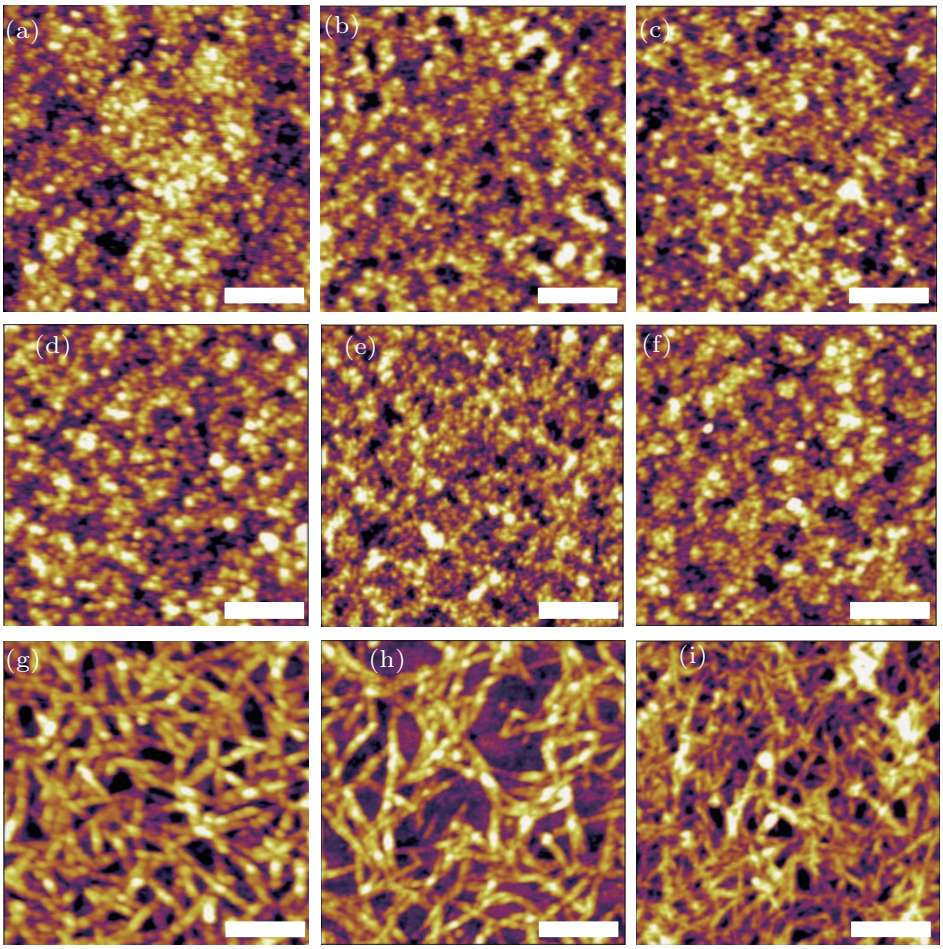


Fig. 1. The AFM images of self-dopant PFO films immersed into the solutions of different ratios of solvent/nonsolvent ((a)–(c) 0.5 : 1, (d)–(f) 1 : 1, (g)–(i) 2 : 1) at different temperatures ((a), (d), (g) 30 °C; (b), (e), (h) 40 °C; (c), (f), (i) 50 °C). The scale bars are 500 nm.

At the ratios of 0.5 : 1 (Figs. 1(a)–1(c)) and 1 : 1 (Figs. 1(d)–1(f)), the morphologies are characterized by small crystalline domains, which suggests that reconfiguration of PFO molecules occurs locally. In contrast, as the ratio goes up to 2 : 1 (Figs. 1(g)–1(i)), the structure of the films is dominated by fibrous crystals. It follows that the β conformation in the film is highly promoted.[19] Nevertheless, as the ratio increases beyond 2 : 1, the dissolution of PFO films becomes significant. The understanding is that the good solvent in the mixture can facilitate the reconfiguration of PFO molecules but also tends to dissolve the film. Consequently, there is an optimal ratio for toluene/ethanol, which can effectively improve the mobility of PFO molecules without dissolving the films.

To quantify the fraction of β-phase in the final products, the UV–vis absorption spectra of the resulting films are investigated, and the fraction of β-phase is estimated according to Lamber–beer's law[18]

$$\beta\% = \frac{A_\beta \times \varepsilon_\alpha}{A_\beta \times \varepsilon_\alpha + A_\alpha \times \varepsilon_\beta}, \tag{1}$$

where A_α and A_β (obtained from experiments) are the absorbencies of α phase and β phase, and ε_α and ε_β are the absorption coefficients of α phase and β phase, respectively. For PFO, $\varepsilon_\beta/\varepsilon_\alpha = 1.08$.[18] In experiments, the peak heights of the α phase and the β phase in the UV–vis absorption spectra correspond to A_α and A_β, respectively. In the previous studies, the highest fraction of β-phase achieved was 1.32%.[16] In our studies, the fraction of β-phase in the film annealed at solvent/nonsolvent ratio 2 : 1 can be as high as 30%. Figure 2 shows the fraction of β-phase in the films annealed at different temperatures with different toluene/ethanol ratios. At all temperatures, the fraction of β-phase in the film increases linearly with the increase of the volume fraction of toluene. It follows that the reconfiguration processes of PFO molecules are not strongly dependent on the temperature in the presence of a good solvent, and therefore the annealing processes can be conducted at room temperature.

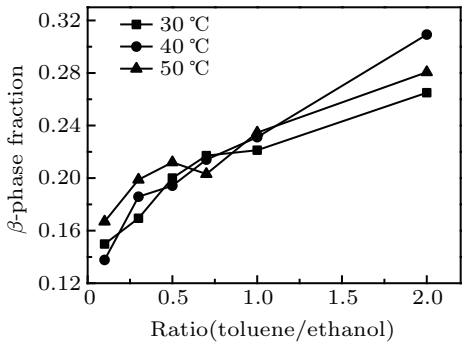


Fig. 2. The β-phase fraction for different temperatures and different solvent/nonsolvent ratios.

To examine the effect of processing time, the PFO films were processed at 50 °C with a solvent/nonsolvent ratio of 2 : 1 for different time. Figure 3(a) shows the AFM image of the PFO films before annealing. As shown in the image, the surface of the pristine film is essentially smooth and crystalline domains are absent. Figures 3(a) and 3(c) show the AFM images of the PFO films annealed for 1 min and 10 min, respectively. Clearly, fibrous crystalline domains emerge after 1 min annealing, and a longer annealing time does not improve the crystallinity significantly. Consistently, the measured β-phase fractions in the films annealed for different time (Fig. 3(d)) show that a significant increasing of β-phase fraction occurs in the first minute, while a longer processing time (10 min) leads to a small further increase. Beyond 10 min, no significant increase is observed, even when the processing time is as long as 1 h. It follows that 10 min is enough for the reconfiguration of PFO molecules in the presence of a good solvent.

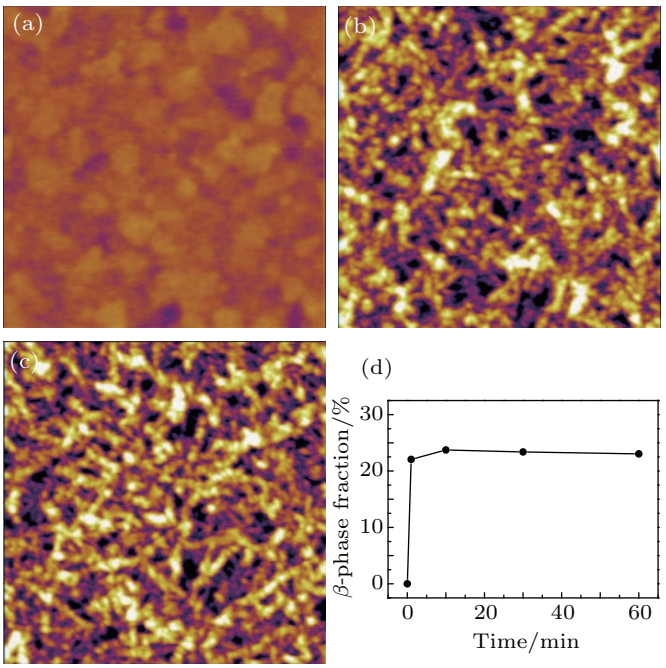


Fig. 3. The effect of annealing time on the β-phase fraction. (a) The AFM height image of the pristine PFO film. The AFM height images of the PFO film after immersion into the solvent/nonsolvent for (b) 1 min and (c) 10 min. (d) The β-phase fractions determined by UV–vis absorption spectra.

To verify the crystalline component of the fibrous structure, the PL spectrum of the PFO films was investigated. Figure 4 show the spectra of the PFO films before and after the annealing. In the pristine film, the spectrum peaks at $\lambda = 422$ nm (0–0 band). After annealing, two main peaks emerge at 439 nm (0–0 band) and 467 nm (0–1 band); a subpeak emerges at 496 nm (0–2 band).[20] The amorphous configuration of PFO is characterized by the peak absorption at 422 nm, while the β-phase is characterized by the absorption peak at 439 nm. Figure 4 reveals that the pristine film is dominated by amorphous configuration while in the annealed film, the fraction of β-phase becomes significant.

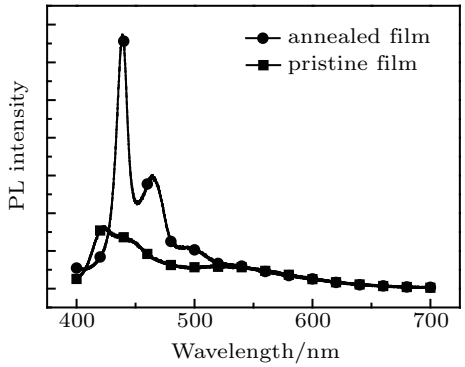


Fig. 4. The PL spectra of the pristine PFO film and the film immersion into the mixed solvent/nonsolvent (volume ratio = 2 : 1) for 10 min at the temperature of 50 °C.

4. Conclusion and perspectives

We suggest that the β-phase formation in the solvent-assisted annealing arises from the local reconfiguration of PFO macromolecular chains, which is facilitated by the presence of a good solvent. The good-solvent molecules diffuse into the PFO molecular mesh in the film and facilitate the relaxation of local molecular configurations. Due to the presence of the poor solvent molecules, the PFO chains cannot be completely dissolved but can relax to a lower free-energy state via local reconfiguration, giving rise to small crystalline domains.[19] The average size and number of the crystalline domains are determined by the number fraction of good-solvent molecules. Increasing the concentration of good solvent in the mixture leads to more and larger crystalline domains, which eventually interconnect to fibrous structures.

In summary, the β component in PFO films can be highly improved by the solvent-assisted annealing process. The annealing temperature does not impact the final results significantly. By contrast, the ratio of solvent/nonsolvent is critical and an optimal value exists to promote the formation of β component without dissolving the film. The annealing process can be accomplished within minutes. Compared with previous studies, our results clarify the effect of temperature, ratio of solvent/nonsolvent, and annealing time. These results offer a general guideline for practical applications of solvent-assisted annealing.

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