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The broken out and confinement phase separation structure evolution with the solution aggregation and relative crystallization degree in P3HT/N2200

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ABSTRACT

The phase separation structure evolution process, i.e. confinement and broke out phenomenon in crystallization/crystallization poly (3-hexylthiophene) (P3HT) and poly [[*N*,*N*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]- alt-5, 5′-(2,2′-bithiophene)] (N2200) blends were controlled by the polymer solution aggregation behavior and relative crystallization degree of each component. In this study, two different molecular weight of P3HT, Mw = 6 kDa and Mw = 55 kDa were selected and blend with N2200 as the model systems. Different molecular weight of P3HT had different crystalline ability in blend films. A similar phase separation of both two polymer blends could form in good solvent chloroform (CF). Marginal solvents and thermal annealing were employed to change the polymer solution aggregation behavior and relative crystallization degree of the two components. On one hand, when p-xylene (pX) was added as the co-solvent to increase the aggregation of P3HT molecules, for P3HT (Mw = 6 kDa)/N2200, the P3HT phase broke the restriction of N2200 phase while there was almost unchanged in P3HT (Mw = 55 kDa)/N2200. On the other hand, during thermal annealing, the P3HT molecule had a stronger molecular moving ability in P3HT (Mw = 6 kDa)/N2200 than that in P3HT (Mw = 55 kDa)/N2200 (the relative crystallization degree of these two polymers in P3HT (Mw = 6 kDa)/N2200 and P3HT (Mw = 55 kDa)/N2200 are 142 and 3, respectively). The pristine phase separation of P3HT (Mw = 6 kDa)/N2200 was destroyed effectively due to the unmatched crystallization degree of the two components and large sized fibrous phase separation was formed during thermal annealing. However, the pristine phase separation was almost unchanged in P3HT (Mw = 55 kDa)/N2200, and the P3HT molecule could partly ordered arrangement, which probably come from the almost matched crystallization degree of these two polymers. The results indicate that it is the Gibbs free energy that controls the phase separation in different relative crystallization degree. And different chain entanglements behavior was likely to be the main source of the morphological stability.

1. Introduction

Considerable attention has been paid to phase separation morphology control on conjugated polymer blends in order to meet the organic optoelectronic functional devices such as organic solar cells, organic thin film transistor and so on [1–7]. Owing to their low entropy of mixing, conjugated polymer blends tend to phase separation into relatively pure phase of the two components which is negative to organic electronic devices [8]. There are two different

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phase separation mechanisms for polymer blend: one is nucleation and growth phase separation and the other is spinodal decomposition [9–11]. In most miscible blend systems, the typical “bicontinuous” and “island” phase separation formed because of spinodal decomposition [12,13]. While for some immiscible blends, a large sized phase separation will appear because of the nucleation and growth mechanism [14].

According of the crystallization behavior, the polymer blend system can be divided into three types: amorphous/amorphous polymer blend system, crystallization/amorphous polymer blend system, crystallization/crystallization polymer blend system [15–17]. For all the three polymer blend types, it is more interesting and difficult to study the crystallization morphology and crystallization behaviors of crystallization/crystallization polymer blends than amorphous/amorphous and crystallization/amorphous systems because both of the components crystallize separately or simultaneously, providing various possibilities for a better study and a better understanding of crystalline polymer blends [10,18–21]. For polymers, with strong covalent bonding extending linearly over enormous distances along polymer chains, the effect of local mismatch is propagated through the crystal, creating a large increase in the internal energy of the crystal [22]. In general, it is possible that the phase separation process is coupled with other ordering process such as crystallization. Until now, the renowned Flory-Huggins theory plays a central role in our understanding of the thermodynamics of polymer-solvent and polymer-polymer mixing and de-mixing [9,23,24]. The Gibbs free energy derived from this theory has been applied to wide variety of systems in which at least one of the components is polymer. The overwhelming use of the Flory-Huggins theory as a starting point for the theoretical interpretation or analysing of phase behavior is mainly due to its simplicity and the phase diagrams can be constructed easily based on this theory. Its usage is, consequently, made in various contexts which may be classified into three general categories. In the first category, the original expression of the Gibbs free energy of mixing $\triangle G$, or the version extended in obvious ways to cover ternary systems is employed in order to obtain qualitative insight at the expense of quantitative accuracy of the calculated phase diagrams. The binary interaction parameters between the components are assumed to be independent of both composition and molecular weight, and are treated only as function of temperature [25,26]. Another important phase separation theory for crystallization/crystallization polymer blend systems is the crystallization half-time ($t_{1/2}$), defined as the time when the relative crystallinity reached at 50%. It is an important measure of overall kinetics which is interesting that the values of $t_{1/2}$ first increased and then decreased with the increase of viscoelastic phase separation (VPS) time. The overall crystallization kinetics obtained by DSC is statistical averaged for the whole sample, including both crystal nucleation and growth rate [27–30].

Fortunately, it is possible to adjusting the microstructure by controlling the kinetics and thermodynamics of crystallization/crystallization film formation such as changing chain structure [31], choosing different solvents [32], adjusting polymer molecular weights and blend ratios [33], and so on. Han et al. [27] reported the interplay between viscoelastic phase separation (VPS) and crystallization in a dynamically asymmetric crystalline/crystalline polymer blend system of poly (butylenes succinate) (PBS)/poly (ethyleneoxide) (PEO). The dynamic asymmetry came from the large molecular weight difference between the slow relaxing PEO and the fast relaxing PBS molecules. It was found that both the crystal nucleation and growth of PBS were strongly influenced by the existence and relaxation of the entangled PEO network, even though PEO was the minor component. Wanli Ma et al. [34] synthesized a series of donor-acceptor type polymer acceptors which have different building blocks and side-chains. They think that the improved device performance may be attributed to the resemble crystallinity of the donor/acceptor polymers, which can lead to the optimal phase separation morphology balancing both charge transfer and transport. Ergang Wang et al. [35] also found the similar phenomenon. They synthesized a series of NDI-bithiophene-thiophene random polymers with the intension to fine-tune the crystallinity and nanostructures of the resulting donor:acceptor blends. Upon varying the content of thiophene units, this simple strategy gradually reduces the crystallinity and largely improves the solubility and thus molecular weights of the random polymers. The polymer PNDI-T10 shows optimal miscibility with the donor PTB7-Th and balanced hole and electron mobility in the blend, which leads to the best performance with a high PCE of 7.6% and a decent FF of 0.71 for the solar cells with a device area of 16 mm^2. In our previous work [36], we also demonstrated that the crystallization and orientation of P3HT molecular played an important role in forming the interpenetrating network phase separation.

In this work, the phase separation evolution process in crystallization/crystallization P3HT/N2200 polymer blend system was investigated by thermal annealing and using co-solvent. We chose two different molecular weight P3HT as one of the polymer blend system components. P3HT with different molecular weight had different crystalline ability in blend films. In P3HT (Mw = 55 kDa)/N2200 polymer blend system, the relative crystallization degree of these two polymer was almost matched, the P3HT molecule could only partly ordered arrangement when thermal annealing or using co-solvent. The pristine interpenetrating network phase separation was almost unchanged during those process. In P3HT (Mw = 6 kDa)/N2200 polymer blend system, the crystallization ratio of these two polymer was unmatched, the P3HT molecule had a strong molecular move ability when thermal annealing or using co-solvent. The pristine interpenetrating network phase separation was destroyed effectively and the nanorod phase separation formed during those processes.

2. Experimental section

2.1. Materials

P3HT with a weight-average molecular weight of 55 kDa (PDI = 2.2) was purchased from Solarmer Materials. P3HT with a weight-average molecular weight of 6 kDa (PDI = 1.5) was synthesized in our laboratory. N2200 with a weight-average molecular of 84 kDa (PDI = 3.1) was purchased from Polyera Corporation, respectively. The blends were prepared by solution-casting using chloroform (CF) as solvent which was purchased from Beijing Chemical Reagent Co. Ltd., China. The solvent was used without a further purification.

2.2. Sample preparation

The two conjugated polymers were dissolved in CF with the weight ratio of 1:1. The total concentration of the blend system was 10 $mg\ mL^{-1}$. After the solvent dissolved completely, the samples were spin-coated at glass wafer with the dimensions of 1.5 × 1.5 cm. Prior to spin-coating, the wafers were obtained by sonication in acetone for 30 min, sonication in ethanol for 30 min, cleaning with a 70/30 v/v solution of 98% H_2SO_4/30% H_2O_2 (piraha solution) between 90 and 110 °C for 30 min and sonication in deionized water for 30 min and thoroughly rinsed. The substrates were subsequently dried in a flow of nitrogen. The condition of spin-coating was 1200 rpm for 30 s in the air which kept the thickness of films to about 150 nm.