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UNIAXIAL ALIGNMENT OF POLY(3-HEXYLTHIOPHENE) NANOFIBERS BY ZONE-CASTING APPROACH*

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Abstract The preparation of large area coverage of films with uniaxially aligned poly(3-hexylthiophene) (P3HT) nanofibers by using zone-casting approach is reported. The length and the orientation of the nanofibers are defined by the solubility of the solvent, the P3HT molecular weight and the substrate temperature. The length of the oriented nanofibers could be increased from 1 μm to more than 10 μm by adding poor solvent into the P3HT solution. It is found that for P3HT of relatively low molecular weight, a solvent with relatively low solubility has to be chosen to get the oriented film. While for the high molecular weight P3HT, the solvent with a relatively high solubility has to be used. The well-aligned film could be obtained because of the solute concentration gradient in the region where the critical concentration is reached during the zone-casting process. Particularly, the solvent evaporation rate and crystallization rate must be chosen properly to satisfy the stationary conditions above, which were controlled by an appropriate choice of solvent and substrate temperature. The film prepared by zone-casting approach had microcrystalline P3HT domains with more inter-chain order than spin-coating film. Meanwhile, the P3HT π-π stacking direction was parallel to the alignment direction of the nanofibers.

Keywords: Conjugated polymer; Zone-casting; Uniaxial alignment.

INTRODUCTION

Regioregular poly(3-hexylthiophene) (P3HT) has great attracting interest for applications in polymer field effect transistors (OFETs) and solar cells, because it has good electrical properties[1], chemical stability and easy processability[2]. Recently, researchers have shown that the charge-carrier transport property critically depends on the crystallinity of P3HT because charge carriers in P3HT films mainly transfer through the coplanar plane along the π-π stacking direction and the polythiophene main-chain direction[3, 4]. As a result, the film with high crystallinity would exhibit high field-effect mobility[5, 6]. Besides that, it is well known that the presence of a grain-boundary consisting of interfaces and amorphous regions between adjacent crystalline regions is a major limiting factor for charge transport in thin films of conjugated polymers[7, 8]. In isotropic P3HT films, many grain boundaries are present along the charge-transport path because of the disordered alignment of P3HT crystals, which would hinder the carrier transport in a certain direction. To increase the mobility of carriers, one can align P3HT crystals along the carrier transport direction to reduce the quantity of grain boundaries.

At present, various methods have been applied to fabricate the oriented crystals, such as using the orienting surface as the role of the substrate for directional solidification[9–13], employing the shearing force[14, 15],

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fabricating the anisotropic films due to the liquid crystal property of conjugated polymers[16–18], and so on.

Zone-casting[19–21] approach has recently been proposed as a simple approach to make the oriented film or long-range ordered thin films due to the solute concentration gradient. With this approach, dodecyl-substituted hexa-peri-hexabenzocoronenes (HBC) formed columnar structures aligned uniaxially in the casting direction with a long-range order[19]. The pronounced columnar orientation and the appearance of the characteristic intracolumnar correlation can be regarded as consequences of the intrinsic property of discotic molecules, leading to improved charge carrier migration due to enhanced overlaps of the π-orbitals. The zone-casting approach was also used to achieve large-scale alignment of nanoscale domains of the phase separated diblock copolymer[22]. Oriented block copolymer films were converted into carbon films with well-defined long-range ordered texture for the synthesis of nanostructured carbon by applying this recently developed approach.

In this study, we reported on the preparation of P3HT films with a large area coverage of uniaxially aligned nanofibers from solution by using the zone-casting approach. In the film, the P3HT π-π stacking direction is parallel to the alignment direction of the nanofibers. We showed that the length and the orientation of the nanofibers were defined by the solubility of the solvent, the P3HT molecular weight and the substrate temperature. We also found that the P3HT film prepared by the zone-casting approach had microcrystalline domains with more inter-chain order than the spin-coating film.

EXPERIMENTAL

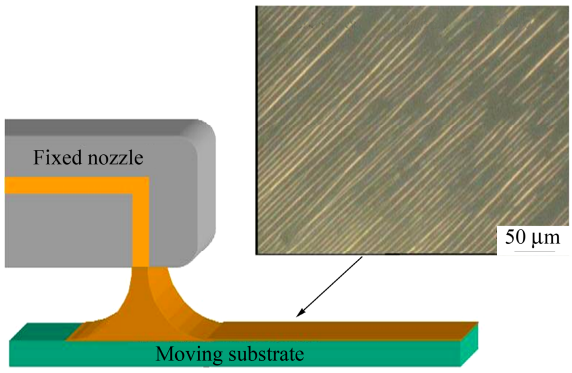
Materials

The regioregular P3HT (98.5% head-to-tail, M_w = 87 kDa) was from Sigma-Aldrich Co and P3HT with the moderate molecular weight (M_w = 30–40 kDa, 68 kDa) was purchased from Nichem Fine Technology Co. Ltd., Taiwan. The solvents, toluene, xylene and chlorobenzene were purchased from Beijing Chemical Plant and used as received. The glasses were cleaned in a piranha solution (70/30 *V*/*V* of concentrated H_2SO_4 and 30% H_2O_2) at 90 °C for 20 min, thoroughly rinsed with deionized water, and finally blown dried in nitrogen.

Sample Preparation

P3HT was dissolved in the solvent with a concentration of 1 mg/mL. The P3HT solution was placed at an elevated temperature of 80 °C for complete dissolution. After cooling to room temperature, the solutions were placed in a dark and vibrationless environment over two days at room temperature to obtain homogeneous samples.

Zone-casting[19–21] process is schematically presented in Scheme 1, showing the deposition of P3HT from the solution on a moving substrate. The P3HT film was prepared by zone-casting solutions onto pre-cleaned glass with a solution supply rate of 10 μL/s and a substrate velocity of 50 μm/s at 20 and 30 °C on a self-made device. The solution was continuously supplied to the evaporation zone by a flat nozzle. The solvent evaporated from the meniscus zone and the solute was deposited on the moving substrate. Particularly, the solvent



Scheme 1 Schematic illustration of the zone-casting process

evaporation rate and crystallization rate must be chosen properly to obtain stationary conditions. Then, the well oriented P3HT films can be obtained because of the solute concentration gradient in the region where the critical concentration is reached. In our work the solvent evaporation rate and crystallization rate were controlled by an appropriate choice of solvent and substrate temperature[23].

The spin-coating P3HT films were prepared by spin-coating solutions onto precleaned glass at 3000 revolutions per minute for 30 s using a commercial spin-coater (KW-4A, Chemat Technology Inc). The residual solvents were removed by vacuum-drying.

Characterization

The surface morphology was characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). A commercial AFM operated in tapping mode (SPA300HV with a SPI3800N Probe Station, Seiko Instruments Inc., Japan) equipped with a silicon cantilever (nominal spring constant 2 N/m and resonant frequency *ca*. 70 kHz, Olympus, Japan) was used to investigate the morphological features of the samples.

The TEM characterization was performed on a TEM (JEOL JEM-1011) under 100 kV. Thin films were first floated on deionized water, and then transferred onto copper grids. The samples were dried at room temperature for 24 h before TEM experiments.

The grazing incidence X-ray diffraction (GIXD) profiles were obtained by using a Bruker D8 Discover Reflector with X-ray generation power of 40 kV tube voltages and 40 mA tube current. The measurements were obtained in a scanning interval of 2θ between 4° and 30°. To increase GIXD peak intensity for investigating the crystallinity and orientation prevailing throughout the film, an incident angle (α = 0.2°) slightly above the critical angle (α_c = 0.18°) was employed.

UV-Vis absorption spectra were acquired on a Lambda 750 spectrometer (Perkin-Elmer, Wellesley, MA) with a 5.0 nm slit width.

The orientation of the P3HT films was proven by cross-polarized optical microscopy and polarized UV-Vis absorption spectroscopy. Cross-polarized optical microscopy (Carl Zeiss A1m microscope) was used to record the brightness of the films at different angles. Polarized UV-Vis absorption spectroscopy was also recorded with a Lambda 750 spectrometer equipped with a green prism. The dichroic ratio D can be calculated using the following equation:

$$D = A_p/A_o \quad (1)$$

A_p and A_o are the maximum absorption intensities for light polarized parallel and orthogonal to the polymer chain orientation, respectively. The dichroic ratio D quantifies the degree of alignment by comparing the absorption polarized parallel and perpendicular to the polymer chains. When D value is larger, the anisotropic alignment is better.

RESULTS

In our experiments, the oriented P3HT film was prepared by zone-casting approach. During the film-formation process, two intrinsic parameters should be controlled to form the oriented film: (1) the aggregations which were defined by the solubility of the solvent and the P3HT molecular weight, (2) the evaporation rate of the solvent. To illustrate the effects of the two intrinsic parameters, two extra experiments were performed: (1) film fabrication with different solvents and P3HTs of different molecular weights, (2) film fabrication at different substrate temperatures.

In the following text, the co-effect of the solvent, the P3HT molecular weight and the effect of the substrate temperature on the orientation degree, the molecular orientation and the degree of inter-chain order of the aligned P3HT nanofibers will be illustrated in turn. Then, the mechanism for the formation of an anisotropic film will be discussed in detail.

Co-effect of the Solvent and the P3HT Molecular Weight on the Aligned Nanofibers

The solubility of the solvent and the molecular weight have influences on the orientation of P3HT nanofibers

prepared using the zone-casting approach. For different molecular weight P3HTs, different kinds of solvent mixtures should be used to obtain the oriented P3HT film. In the experiment, it was found that with the decrease of the P3HT molecular weight, the solvent with a lower solubility had to be used.

Table 1 shows the boiling point and the solubility parameter of the solvents. The boiling point of chlorobenzene and mesitylene are higher than that of toluene. For the solubility, chlorobenzene is better than toluene, and mesitylene is worse than toluene. To make oriented films of 87k-P3HT, three solvents were used: toluene, toluene-chlorobenzene 2:1 mixture and toluene:mesitylene 6:1 mixture. As shown in Fig. 1, the oriented nanofibers were 5 μm long in the zone-casting film from toluene. However, because contact line of the solution moved in a repetitive stick-slip motion, the film was not a continuous layer. On the contrary, the films cast from mixture made of toluene and solvent with the high boiling point were all continuous. The length of the nanofibers in the film cast from chlorbenzene-toluene mixture was about 1 μm, much shorter than that cast from toluene. The length of the nanofibers cast from mesitylene-toluene mixture is more than 10 μm, much longer than that under other conditions.

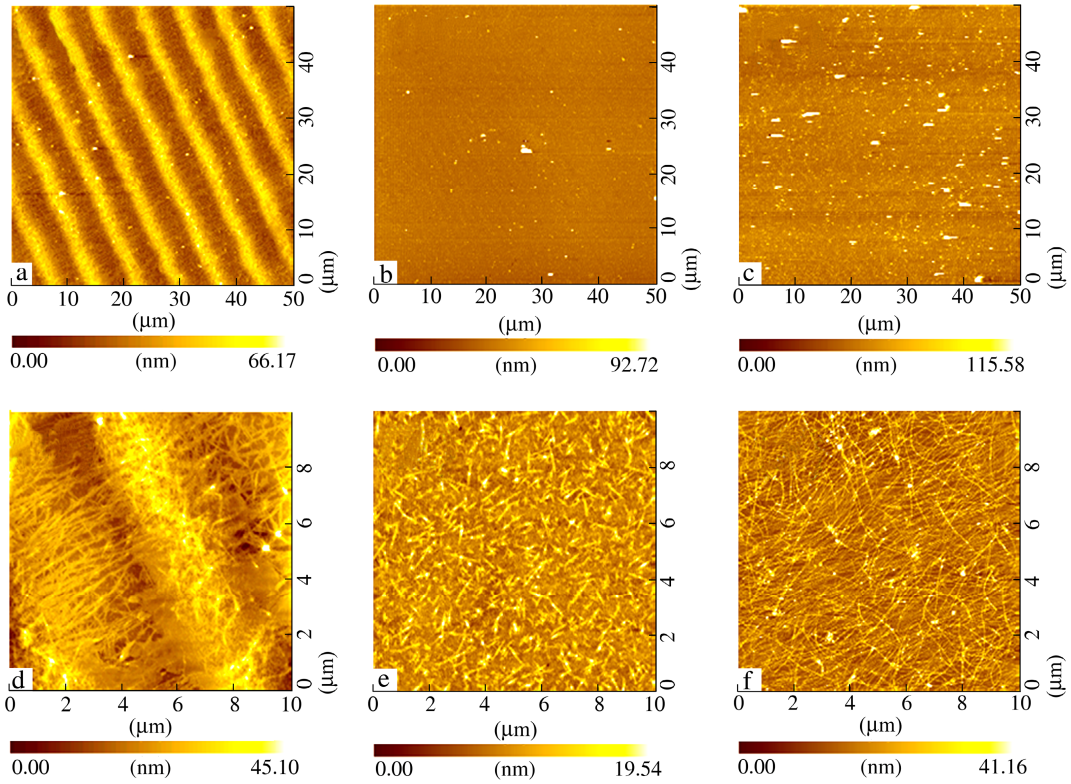


Fig. 1 AFM images (50 μm × 50 μm) of the 87k-P3HT films zone-cast from solutions in different solvents: (a) toluene, (b) chlorbenzene:toluene 1:2 and (c) mesitylene:toluene 1:6; AFM images (5 μm × 5 μm) of the 87k-P3HT films zone-cast from solutions in (d) toluene, (e) chlorbenzene:toluene 1:2 and (f) mesitylene:toluene 1:6

Table 1. The boiling temperature and the solubility parameter of the solvents and P3HT

Specimen	Toluene	Chlorobenzene	Mesitylene	Xylene	P3HT
T_b (°C)	110	132	164	138–144	
δ(cal/cm^3)$^{1/2}$	8.9	9.5	8.8	8.8	9.5

The morphology of the 87k-P3HT zone-casting film was investigated using cross-polarized optical microscopy, AFM and TEM (Fig. 2). Under cross-polarized light, when the sample was rotated from 0º to 90º with respect to the direction of polarized light, the film presented a bright-dark-bright variation, which implies

that the P3HT nanofibers in these regions align parallel and then result in optical anisotropy. The AFM height images in Fig. 2(b) show the oriented P3HT nanofibers, which contribute to the optical anisotropy observed under cross-polarized optical microscope. The electron diffraction result of the film can also prove the oriented structure. In Fig. 2(c), a misorientation of *ca*. 20 degree to the fiber axis can be derived from the width of the reflection arcs arising from the *ca*. 0.38 nm π-π stacking distance of the P3HT molecules. Polarized UV-Vis absorption spectroscopy was also performed to calculate the orientation degree of the film quantitatively (Fig. 2d). The 87k-P3HT zone-casting film prepared from toluene:mesitylene 6:1 mixture had the best orientation with a dichroic ratio (*D*) of 1.73 according to Eq. (1). This result is corresponded to the result obtained from the cross-polarized optical microscopy.

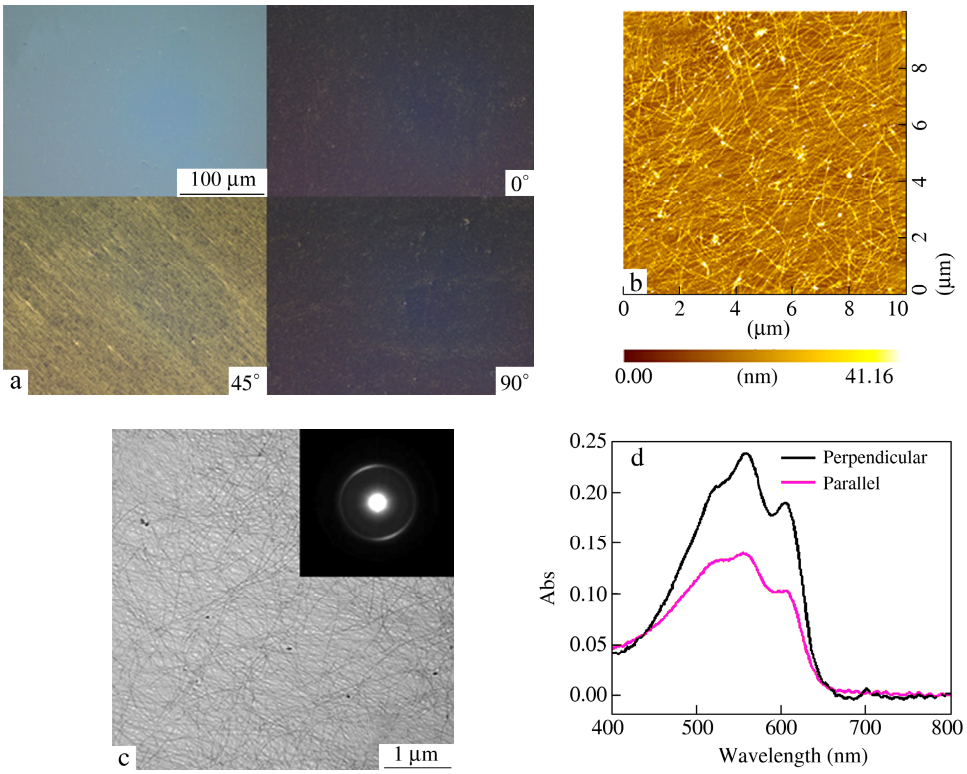


Fig. 2 The orientation of the P3HT films made by zone-casting approach: (a) Optical images and images under cross-polarized optical microscope recorded over the same area at different angles (0°, 45°, and 90°) between cross-polarized light and the nanofiber orientation; (b) AFM height image of the anisotropic films; (c) TEM image of the anisotropic film and its corresponding SAED pattern and (d) UV-Vis absorption spectra using cross-polarized light parallel and perpendicular to the direction of the aligned P3HT nanofibers (The oriented film was prepared by zone-casting approach of 87k-P3HT using mesitylene:toluene 1:6 mixture at 30 °C.)

The UV-Visible absorption spectra of spin-coating and zone-casting P3HT films confirm the changes in the degree of inter-chain order in P3HT microcrystalline domains (Fig. 3a). The red-shift of the absorption peak indicates that P3HT has an increased conjugation length because of its higher degree of inter-chain order in microcrystalline domains and good self-organization ability of P3HT. The band at *ca*. 600 nm is indeed correlated with the degree of inter-chain order in microcrystalline domains of P3HT, as recently reported[24, 25]. We can find that the band at *ca.* 600 nm for the 87k-P3HT film zone-cast from mesitylene-toluene mixture is much stronger than that for the 87k-P3HT spin-coating film. It means the zone-casting approach can get a high degree of inter-chain order in microcrystalline domains of P3HT. We can also find that the nanofibers are very disordered in the spin-coating film in Fig. 3(b). The length and the density of the nanofibers in the zone-casting film are higher than those in the spin-coating film as shown in Fig. 3(c).

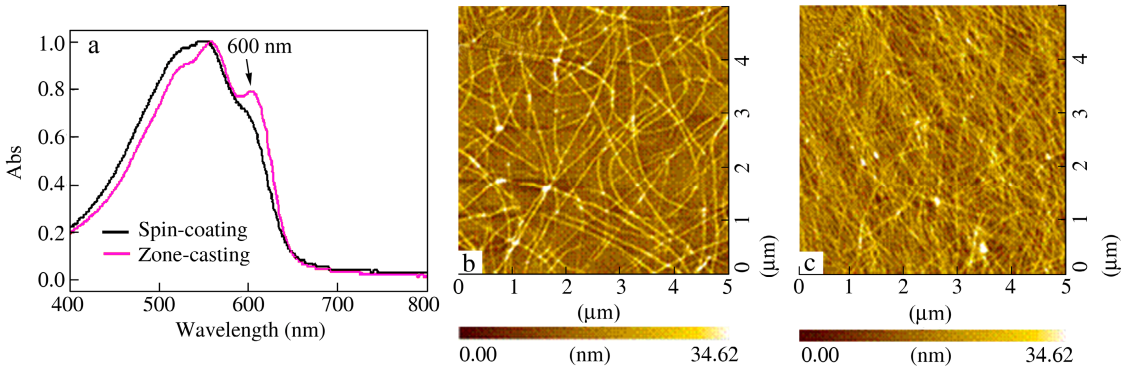


Fig. 3 Comparison of the zone-casting and the spin-coating films: (a) UV-Vis absorption spectra of the 87k-P3HT films; AFM images of the 87k-P3HT films prepared from solutions in mesitylene-toluene mixture by (b) spin-coating and (c) zone-casting

However, for the 68k-P3HT and 30k-40k-P3HT, using the toluene:mesitylene 6:1 mixture we cannot get the oriented film. In Fig. 4, the zone-casting film from solution in toluene:mesitylene 6:1 mixture was disordered for the 68k-P3HT. To prepare the oriented P3HT film, the toluene:xylene 1:1 mixture with a lower solubility than toluene:mesitylene 6:1 mixture was used as solvent. By using the toluene-xylene 1:1 mixture, the nanofibers oriented along the zone-casting direction could be obtained in the 68k-P3HT film like the 87k-P3HT film zone-cast from solution in the toluene:mesitylene 6:1 mixture. However, the nanofibers in the film would grow randomly if the solubility of solvent is much too low, such as the pure xylene. The dichroic ratio *D* of the 68k-P3HT film zone-cast from solution in toluene-xylene 1:1 mixture is 1.83, and that of the 68k-P3HT films zone-cast from solutions in the other solvents is *ca* 1.00. The well-defined diffraction arcs pattern and the optical anisotropy under crossed polar light can demonstrate the formation of the high degree orientation of the zone-casting film. For 68k-P3HT, the phenomenon can only be found in the films cast from solution in the toluene:xylene 1:1 mixture.

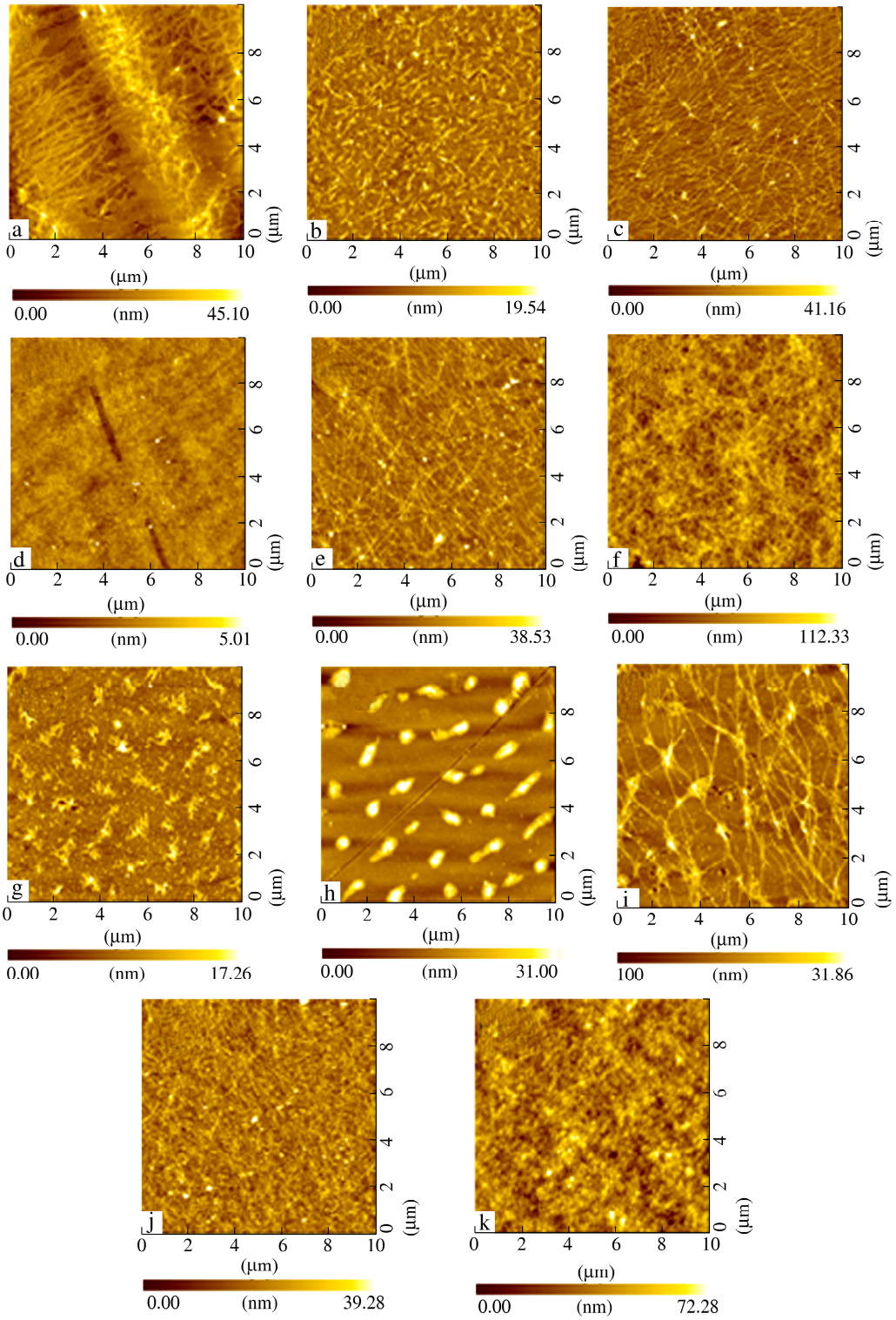
For the 30k-40k-P3HT, zone-casting film from the solution in pure toluene was not continuous. The nanofibers would aggregate into conglobations and disperse in the whole film. When the solubility became lower, such as the toluene:mesitylene 6:1 mixture, the P3HT nanofibers congeries became larger but did not connect with each other. When the toluene:xylene 1:1 mixture was used, the long nanofibers which oriented to the zone-casting direction would connect the congeries together. When toluene:xylene 1:2 mixture was used, the longer nanofibers oriented to the zone-casting direction could be obtained in the film like the 87k-P3HT film zone-cast from solution in the toluene:mesitylene 6:1 mixture. When the pure xylene was used, the nanofibers in the zone-casting film would grow randomly as in the case of 68k-P3HT. The dichroic ratio *D* of the film zone-cast from solution in toluene-xylene 1:2 mixture is 1.79, and the dichroic ratio *D* of the films zone-cast from solution in the other solvent is *ca* 1.00. The diffraction arcs and the optical anisotropy under crossed polar light could also be found in the 30k-40k-P3HT films cast from solution in the toluene:xylene 1:2 mixture, like the 87k-P3HT films cast from solution in the toluene:mesitylene 6:1 mixture.

Effect of the Substrate Temperature on the Aligned P3HT Nanofibers

Three 87k-P3HT films cast from solutions in mesitylene-toluene mixture were prepared on the substrate at different substrate temperatures. To confirm the oriented structure of the film, the morphology of the samples was observed using a cross-polarized optical microscope. By rotating the sample, the images were recorded at different angles (0º, 45º and 90º) between cross-polarized light and the nanofiber orientation as shown in Fig. 5(A). Under cross-polarized incident light, the brightness of the images changed from minimum to maximum and then to minimum when the polarized direction changed from a parallel to perpendicular orientation with respect to the nanofiber orientation. The brightness variation indicates that the P3HT crystals must be aligned parallel. In Fig. 5(A), the brightness variation could be found at 20 and 30 °C both. The

brightness variation at 30 °C is more marked than at 20 °C. However, with a higher substrate temperature, 40 °C, the stick-slip motion came again making the film not continuous, and the brightness variation could not be found.

(A)



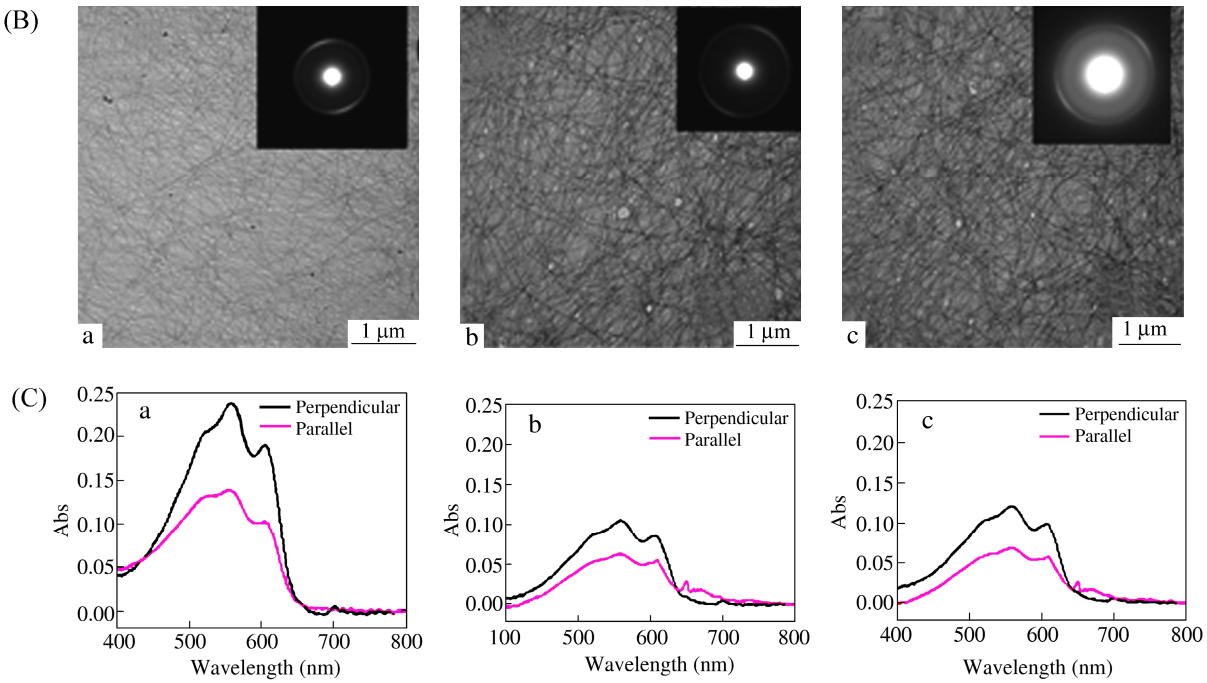


Fig. 4 The P3HT films with different molecular weights zone-cast from solutions of different solvents: (A) AFM images of 87k-P3HT: (a) toluene, (b) chlorbenzene:toluene 1:2 and (c) mesitylene:toluene 1:6; AFM images of 68k-P3HT: (d) mesitylene:toluene 1:6, (e) toluene:xylene 1:1 and (f) xylene; AFM images of 30k-40k-P3HT: (g) toluene, (h) mesitylene:toluene 1:6, (i) toluene:xylene 1:1, (j) toluene:xylene 1:2 and (k) xylene; (B) TEM images and corresponding SAED patterns of the zone-casting films: (a) 87k-P3HT from mesitylene:toluene 1:6, (b) 68k-P3HT from toluene:xylene 1:1 and (c) 30k-40k-P3HT from toluene:xylene 1:2; (C) UV-Vis absorption spectra using cross-polarized light parallel and perpendicular to the direction of the aligned P3HT nanofibers: (a) 87k-P3HT from mesitylene:toluene 1:6, (b) 68k-P3HT from toluene:xylene 1:1 and (c) 30k-40k-P3HT from toluene:xylene 1:2

For 87k-P3HT, the *D* values of films zone-cast at 20, 30 and 40 °C are 1.53, 1.73 and 1.08, respectively. This result corresponds to the result from the cross-polarized optical microscopy. It is found that a suitable substrate temperature should be chosen (in our study, the substrate temperature is 30 °C) to get the best oriented film.

The Molecular Orientation and the Degree of Inter-chain Order of the Aligned P3HT Nanofibers

In order to investigate the molecular orientation of the P3HT molecules in the films, the 87k-P3HT film cast from solution in toluene:mesitylene 6:1 mixture was examined by using the GIXD. In the case of the pure P3HT sample, the intensities of the (100) reflection arising from the lamellar layer structure and the (010) reflection arising from π-π interchain stacking are strong, which indicates that the pure P3HT film contains a mixture of standing and lying (edge-on and face-on) polymer backbone chains[11]. Figure 6 shows the out-of-plane XRD profiles of the P3HT films. Here, the (100) reflection is very strong, and the (010) reflection is negligible. We can conclude that the thiophene ring plane of crystalline P3HT is oriented preferentially normal to substrate (edge-on orientation) in the films cast from solution in mesitylene-toluene mixture. It seems that an edge-on orientation prevails for P3HT molecules in the zone-casting films.

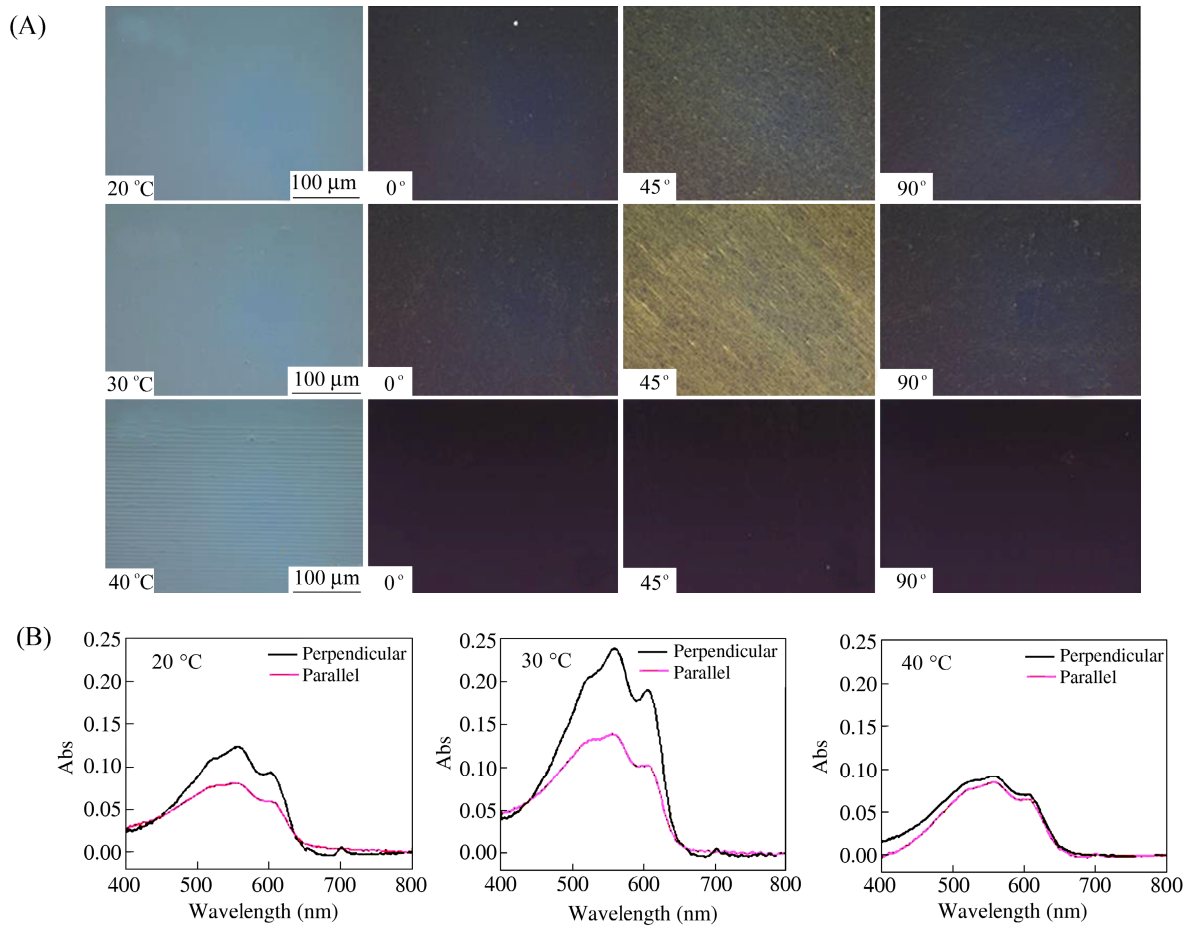


Fig. 5 The optical anisotropy of 87k-P3HT films prepared at different zone-casting substrate temperatures: (A) optical images recorded over the same area using cross-polarized optical microscopy at different angles (0°, 45°, and 90°) between cross-polarized light and the nanofiber orientation; (B) UV-Vis absorption spectra using cross-polarized light parallel and perpendicular to the direction of the aligned P3HT nanofibers

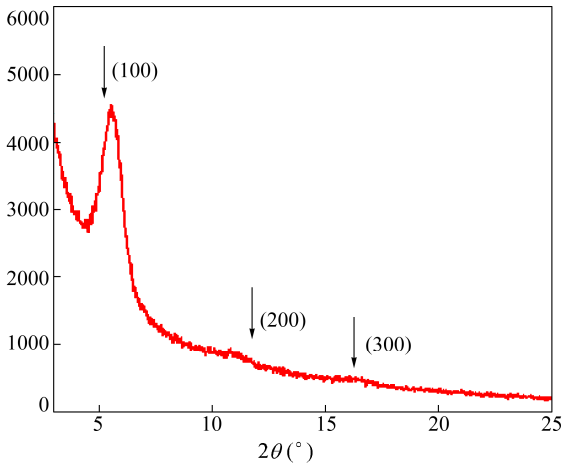


Fig. 6 Out-of-plane grazing-incidence X-ray diffraction profile of the 87k-P3HT film zone-cast from solution in mesitylene-toluene mixture at 30 °C

DISCUSSIONS

AFM measurement shows clear morphological differences among films prepared using different solvents and P3HTs of different molecular weights. In our opinion, the aggregations which are influenced by the solubility of the solvent and the molecular weight are the most important factor to achieve the uniaxially alignment of the P3HT nanofibers.

Figure 7(a) shows the UV-Visible absorption spectra of the solutions of the 87k-P3HT in different solvents. We observed obvious absorption bands at *ca.* 600 nm (these signals are typical of highly ordered P3HT chains)[26, 27], in the toluene:mesitylene 6:1 mixture. However, we couldn't find the absorption bands at *ca*. 600 nm in other solvents. It is considered that in different solvents, P3HT has different solubility and different aggregation behavior. In the poor solvent, the P3HT backbones self-assembled into aggregations because of the π-π interaction. During the evaporation processes, the aggregations were aligned along the π-π interaction orientation. It is inclined to get the longer P3HT nanofibers. The P3HT backbones extended better in the good solvent and adopt a random-coil conformation because of a good solubility. Meanwhile, the π-π interaction was worse than that in the poor solvent, resulting in that the nanofibers cast from solutions in good solvent were not as long as that cast from solutions in the poor solvent.

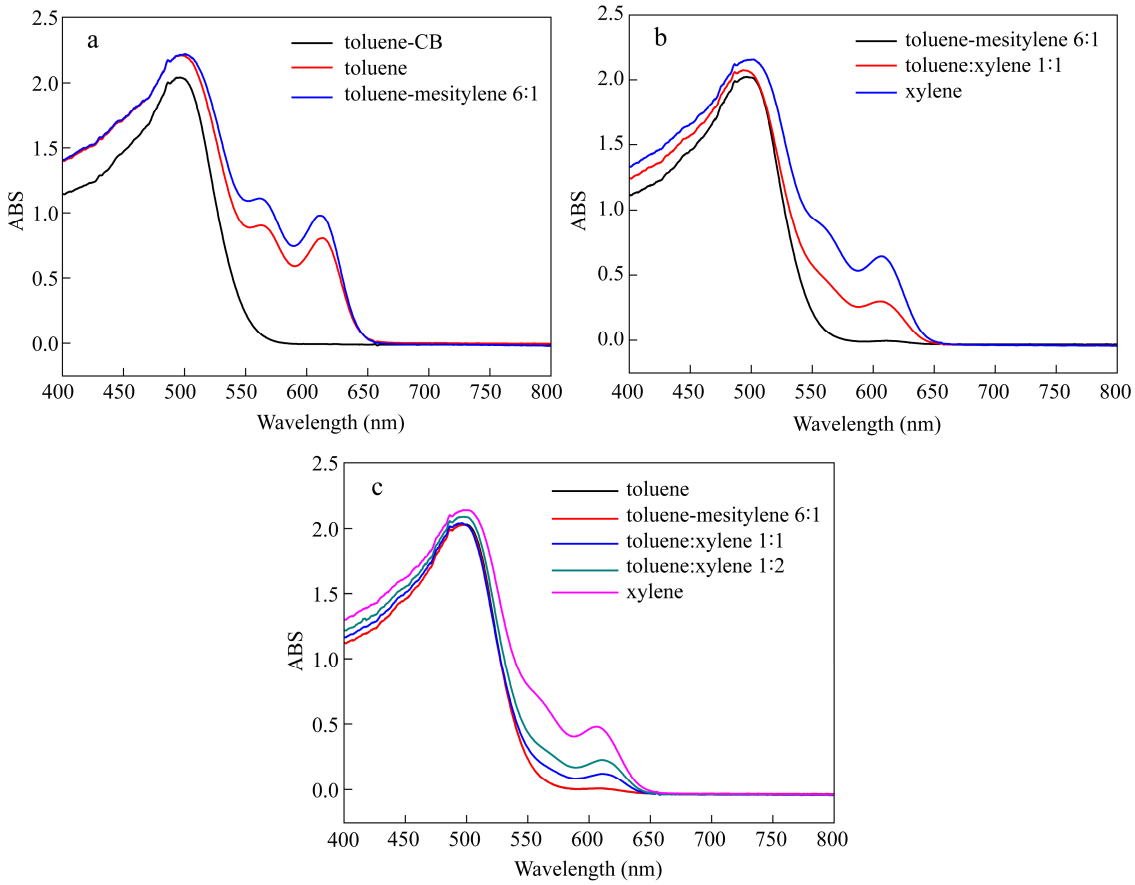


Fig. 7 UV-Vis absorption spectra of the P3HT samples in solutions of different solvents: (a) 87k-P3HT, (b) 68k-P3HT and (c) 30k-40k-P3HT

In the same solvent, such as toluene:mesitylene 6:1 mixture, P3HT with different molecular weights has different morphology. Uniaxial orientated nanofibers were found in the 87k-P3HT film. However, only disordered structures were found in the 68k-P3HT film and some island structures were found in the 30k-40k-

P3HT film. It is attributed to that the backbones of the P3HT with a low molecular weight extended better than those of the P3HT with a high molecular weight in the same solvent. Thus, the π-π interaction of P3HT with a low molecular weight was not strong enough to get a highly ordered P3HT aggregation. In Fig. 7(b) and Fig. 7(c), we could not find the absorption bands at *ca*. 600 nm for 68k-P3HT and 30k-40k-P3HT in the toluene:mesitylene 6:1 mixture.

To get the oriented film, we used the toluene:mesitylene 6:1 mixture for 87k-P3HT, toluene:xylene 1:1 mixture for 68k-P3HT, and toluene:xylene 1:2 mixture for 30k-40k-P3HT as solvents. It is found that with the decrease of the P3HT molecular weight, to get the film with oriented nanofbires, the solvent with a corresponding low solubility must be used. However, the aggregations in the solution are too severe and the solute precipitated disorderly in the meniscus zone if the solubility is too low such as the pure xylene. The nanofbires in the zone-casting film will not be oriented very well.

The red shift of the absorption peak at *ca*. 550 nm indicates that P3HT has an increased conjugation length arising from its higher crystalline order, and the band at *ca*. 600 nm is indeed correlated with the degree of inter-chain order in microcrystalline domains of P3HT. The length and the density of the nanofibers of the zone-casting film are much higher than those of the spin-coating film. It might be estimated that the P3HT nanofibers consist of π-π stacked P3HT chains with a limited conjugation length, while the longer nanofibers may comprise P3HT chains with a more extended conjugation length, which may be due to intermolecular rod-to-rod associations[28, 29]. The evaporation of solvent in the zone-casting approach is similar to the naturally evaporation. However, the evaporation in the spin-coating is very fast. Thus, zone-casting approach can provide more solidify time than spin-coating approach. The fast evaporation of the P3HT solution leads to the inhibition of the 1D self-assembly governed by π-π stacking leading the P3HT chains not to self-assemble sufficiently. The slow evaporation of the P3HT solution provides the P3HT chains enough time to self-organize during solidification[7, 30] which allows more P3HT backbones having much more time to close to other P3HT backbones to get closer and crystallize by π-π interaction. Meanwhile, the inter-chain order in microcrystalline domains is enhanced.

In our experiments, we found that the films zone-cast at different substrate temperatures had different morphologies and orientation degrees. It is perhaps because the evaporation rate is decided by the substrate temperature. There is a competitive relation between the evaporation and the crystallization in the meniscus zone. The crystallization leads the P3HT to separate from the solution in the meniscus zone. The solvent evaporation and the moving of the substrate supply the “space” for alignment of P3HT nanofibers. If the substrate temperature is too low, the evaporation rate of the solvent is slower than the crystallization rate of the P3HT. With a slow evaporation, there is no enough space for crystallization, and the space cannot accmmodate all of the nanofibers which are precipitated in the meniscus zone from the solvent. Thus, the orientation order will be declined. If the substrate temperature is too high, the evaporation rate of solvents is much faster than the crystallization rate of P3HT. With a fast evaporation, too much space is given to the crystallization and there is no adequate solidification of P3HT molecules from the solution in time. Thus, the film will not be continuous. In our experiments, 30 °C was a suitable substrate temperature to get the oriented nanofibers. In this condition, an appropriate space was given to the crystallization and the well-aligned P3HT films could be obtained because of the solute concentration gradient in the region where the critical concentration is obtained. Meanwhile, the evaporation rate matches the crystallization rate at this substrate temperature leading to a well-aligned continuous P3HT film by zone-casting approach[23].

CONCLUSIONS

In summary, the well-aligned nanofibers of P3HT in films prepared by zone-casting approach could be attributed to two intrinsic parameters: (1) the aggregations which were determined by the solubility of the solvent and the P3HT molecular weight, (2) the evaporation rate of the solvent. Adding the poor solvent into the solution to promote self-assembly of the P3HT into highly ordered aggregation can increase the length of the oriented

nanofibers from 1 μm to more than 10 μm. With the decrease of the P3HT molecular weight, the solvent with lower solubility should be used to get the oriented film. When the evaporation speed matches the crystallization rate, the nanofibers are aligned better.

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