Highly Polarized Blue Luminescence from the Oriented Poly(9,9-dioctylfluorene)/Polyethylene Blending Films

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Introduction. In the past decade, many researches have focused on the electroluminescent (EL) properties of conjugated polymers because of their potential application as an emitting layer in EL devices. It has been found that the uniaxially oriented conjugated polymers can emit polarized light, which is useful as the backlight for conventional liquid crystal displays (LCDs). Plentiful devices based on EL properties of the polarized luminescent polymer films have been widely developed. However, the polarized photoluminescence (PL) properties of the oriented conjugated polymers have been little exploited in application. In fact, isotropic luminescent films were previously used to enhance the visual performance of LCDs, especially with respect to brightness.[1] An anisotropic luminescent film can combine polarization of light and bright colors and it can replace the polarizer (analyzer) and the color filter used in current LCDs.[2] Therefore, using a PL polarizer can efficiently increase the brightness and power efficiency of PL LCDs. Many methods have been used to orient conjugated luminescent polymers, such as the Langmuir−Blodgett(LB) technique,[3,4] mechanical treatment of conjugated polymer films,[5,6] liquid-crystalline self-organization,[7] and alignment on specific substrates.[8,9] However, the degree of orientation (or the dichroic ratio) obtained with these methods is usually modest, typically below 25 in PL, which limits the device performances with respect to resolution and contrast.

The tensile deformation of host−guest systems is a different promising technique, which has been used to orient green-light-emitting conjugated polymers in a thermoplastic polymer matrix. Haggler et al.[10,11] have adopted this method to align (poly(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene)) (MEH−PPV) in PE films and found a PL dichroic ratio in excess of 60 when exciting with linear polarized light. Weder et al.[12,13] have used a similar technique to orient poly(*p*-phenyleneethynylene) (PPE) and the PL dichroic ratio was 72 when exciting with unpolarized light. In a further development of this approach, Montali et al.[14−16] have added an isotropic sensitizer, which is not aligned sufficiently during the drawing, into the polarized luminescent film. The sensitizer can absorb all excited light and efficiently transfer the energy to the oriented conjugated polymers, and this thus results in the improved power efficiency.

However, as yet a highly polarized PL blue-light polarizer has not been obtained. Poly(9,9-dioctylfluorene) (PFO) has emerged as an attractive blue-light-emitting material for light-emitting diodes owing to its pure blue emission, efficient electroluminescence coupled with a high charge-carrier mobility, and good processability. In recent years, many researches on polarized blue emission materials have been reported.[6,8,17−24] Miller et al.[24] have studied the orientation of PFO using a tensile deformation technique; a dichroism of 7:1 in PL and absorbance has been obtained at a high drawing ratio ($\lambda = 50$). Whitehead et al.[8] have studied PFO aligned on an alignment layer of segmented poly(*p*-phenylenevinylene)(PPV), and a polarization ratio of about 25 in EL and 10 in PL have been obtained. Misaki et al.[6] have investigated the orientation of PFO by friction-transfer and subsequent thermal treatment technique, reaching the dichroic ratio of 25 in PL and 10 in absorbance, which is the highest polarization ratio in PL for PFO reported. However, the application of a PL polarizer requires a higher polarization ratio, depending on application fields. To achieve high polarization ratio device is still a challenge in this area.

In this work, tensile deformation technique was used to prepare the oriented blending films of PFO and ultrahigh molecular weight polyethylene (U-PE). The influences of the molecular weight of PFO, the composition of the blends, the drawing ratio of blending films, and the excitation with polarized or unpolarized light on the dichroic ratio of the blending films were investigated, reaching a very highly dichroic ratio of 58. Additionally, the photophysical properties of PFO in such special environment conformed clearly that the variation of the dispersion of the PFO chains in the film was from initial crystal state to the fragment of PFO crystal and to the final molecular dispersion in the U-PE matrix with increasing drawing ratio.

Results and Discussion. The absorption spectra of the 1% L-PFO/U-PE films with a drawing ratio of 70 are shown in Figure 1a. In the parallel polarization, the maximum absorption peak is located at 396 nm, which is associated with delocalized $\pi-\pi^*$ transitions on fluorene backbones. In the perpendicular polarization, however, the peak is sufficiently suppressed. Thus, the film shows very strong dichroism ($DR_A = 24$) as shown in the absorption spectra, which is well in excess of the results reported about oriented PFO, indicating that polymer backbones in the film are highly aligned parallel to the drawing direction. The macroscopic order parameter is calculated from the absorption spectra using the relation $S = (DR_A - 1)/(DR_A + 1)$,[25] and it turns out to be $S = 0.92$, indicating a very high degree of the orientation.

Figure 1b shows the polarized PL spectra of the same sample in Figure 1a. The PL spectrum of the parallel polarization shows a well-marked vibronic structure with peaks at 430 and 455 nm, and a shoulder at 488 nm. On the other hand, in the spectrum of the perpendicular polarization, these peaks are sufficiently suppressed. The peaks of the perpendicular spectrum are red shifted 3 nm with respect to those of the parallel spectrum and the spectrum loses the well-resolved features, which is responsible for the residuals of nonoriented materials in the film.[11] The dichroic ratio

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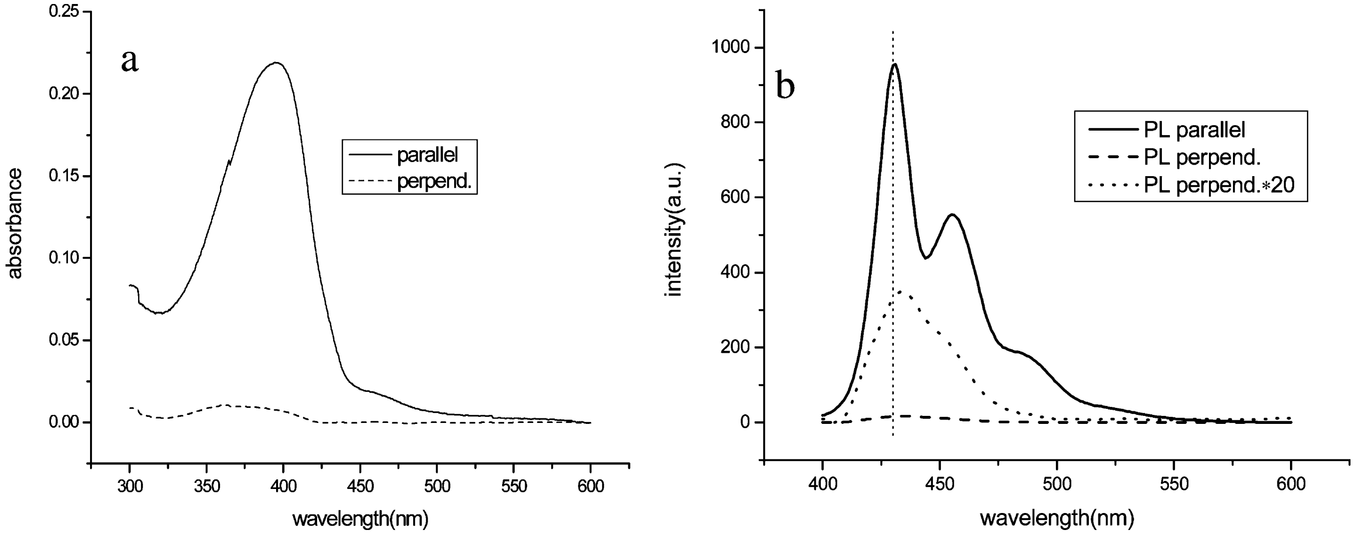

Figure 1. Polarized absorption spectra (a) and polarized PL spectra (b) of the 1% L-PFO/U-PE blending film (the drawing ratio is 70).

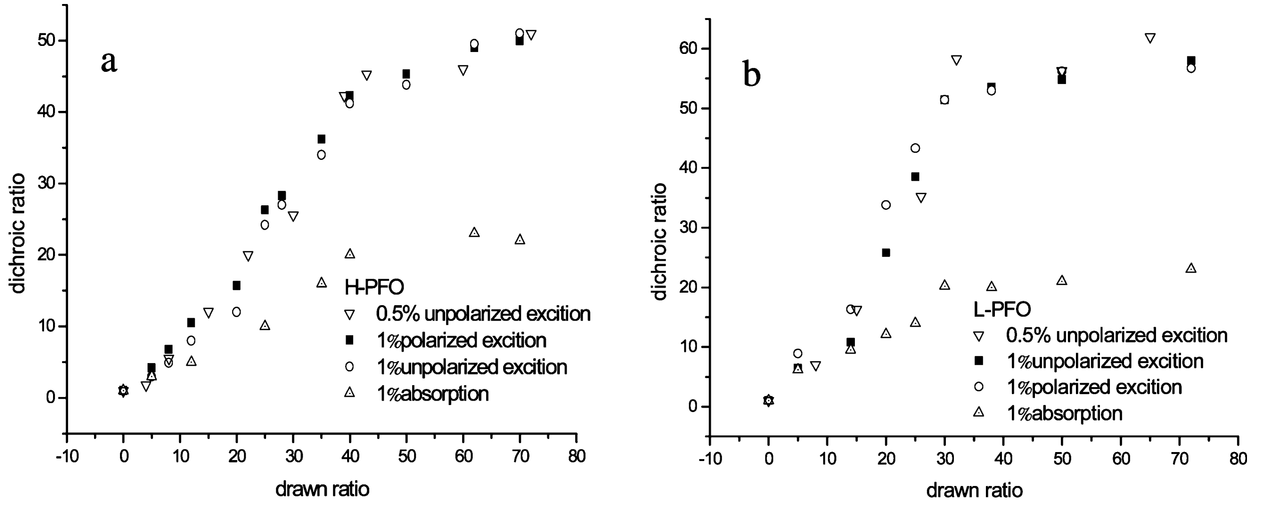

Figure 2. PL and absorption dichroic ratios as a function of drawing ratio for the H-PFO/U-PE blending films (a) and L-PFO/U-PE blending films (b) with 1−0.5% PFO, excitated with parallel polarized light or unpolzrized light.

is 58:1 for the peak at 430 nm. It is the highest polarization obtained for PFOs up to now.

The influences of the drawing ratio, molecular weight of PFO, the composition of the blends, and the kind of the excited light on the dichroism of H-PFO/U-PE and L-PFO/U-PE blending films are summarized in Figure 2, parts a and b, respectively. It is apparent that a higher drawing ratio is necessary to obtain a higher dichroic ratio. The significant influences of the drawing ratio on the dichroism in all systems under investigation are characterized by an initial linear increase of the dichroic ratio, with a tendency to level off at the drawing ratio beyond some value. Comparing the dichroic ratio of the blends based on PFO with $\overline{M_n}$ of 45000 and 9000, it can be easily found that the molecular weight of PFO has a remarkable influence on the orientation of the PFO chains. With increasing the drawing ratio, the dichroic ratio of the L-PFO/U-PE blending film increases faster than that of the H-PFO/U-PE film. In the former, the dichroic ratio is up to platform when the drawing ratio is above 30, and a high dichroic ratio is obtained ($DR_E = 52$) at the inflection in the curve of dichroic ratio−drawn ratio in Figure 2b. In the latter one, the dichroic ratio is only 41 when the drawing ratio is 40, which is the inflection of the curve in Figure 2a. Further drawing the samples to the drawing ratio of 70, the higher dichroic ratio with DR_E of 58 for the L-PFO/U-PE blending film or 51 for the H-PFO/U-PE blending film is obtained. It suggests that the L-PFO exhibits higher orientation and the L-PFO/U-PE blending drawn film shows a better dichroism. This may be due to easier phase-separation and a stronger interchain force of H-PFO than those of L-PFO in the PE matrix. The molecular weight of PFO is higher, the interaction force between the PFO chains is bigger, and it is more difficult for the PFO chains to be detached during the drawing. Therefore, it is more difficult to orient H-PFO compared with the L-PFO.

The orientation of PFO in the drawing films is not influenced by the blending composition in the concentration range of 1−0.5% (w/w). Miller et al.[24] have reported that the dichroic ratio of PFO/U-PE blending films with the concentration of 15% was very low, only 7 in PL and in absorbance. This may be due to the depolarization of the emission in the high concentration of PFO.[26]

It is found that the dichroic ratio obtained by exciting with the unpolarized light is lower than those obtained

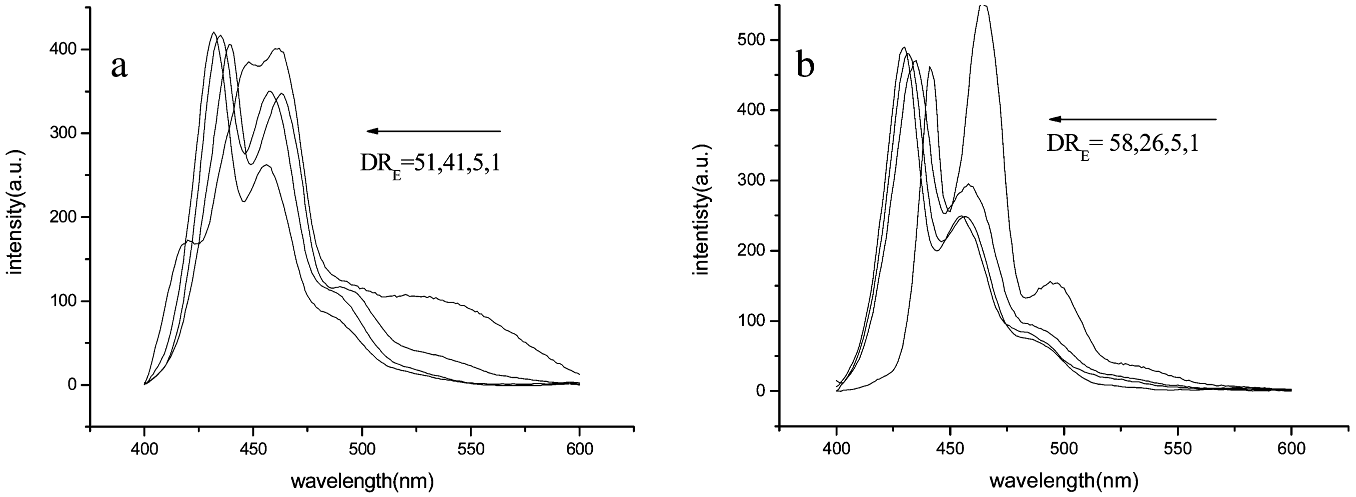

Figure 3. PL spectra of 1% H-PFO/U-PE blending films (a) and 1% L-PFO/U-PE blending films (b) with different dichroic ratios.

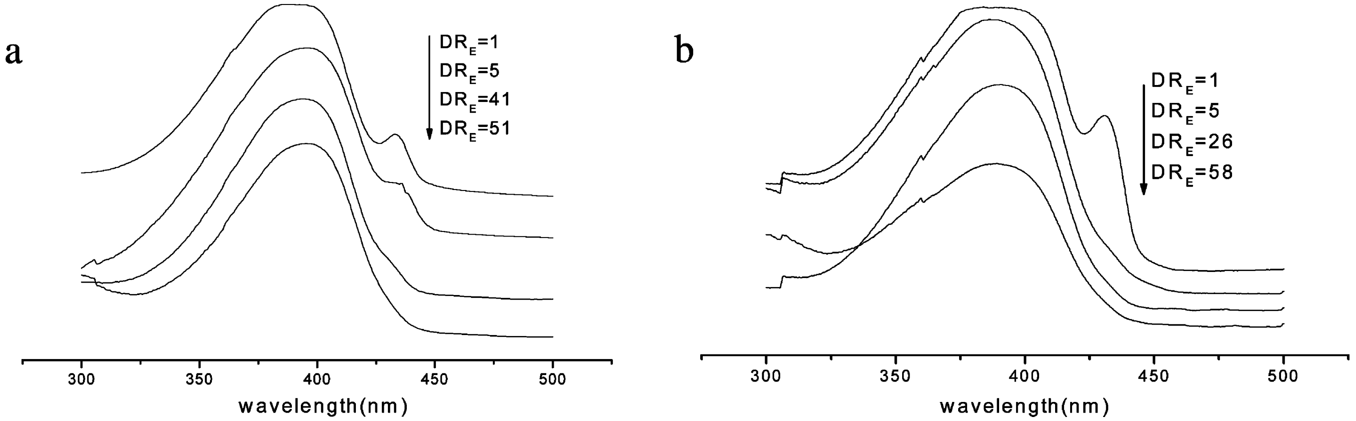

Figure 4. Absorption spectra of 1% H-PFO/U-PE blending films (a) and 1% L-PFO/U-PE blending films (b) with different dichroic ratios.

with the polarized light at the low drawing ratio. At high drawing ratio, the dichroic ratios are comparable for the two excitations. The dichroic ratio is defined as the intensity ratio of the parallel polarization and the perpendicular polarization. At low drawing ratios, there exist many nonoriented PFO chains in the blending film, which can increase the intensity of parallel and perpendicular spectra at the same time when exciting with unpolarized light. Therefore, the lower dichroic ratio is obtained. When exciting is performed with polarized light, the influences of the nonoriented PFO chains are greatly suppressed because the absorption of the PL films is also anisotropic,[16] so a higher dichroic ratio is obtained. The nonoriented PFO chains become very few at high drawing ratio, the contribution of the nonoriented chains on the spectra can be ignored, which results in identical dichroic ratio for the two excitations at high drawing ratio. It is noted that the dichroism in PL is higher than that in absorption, which might be consistent with the migration of excitons to the lowest energy, most highly oriented segments of the polymer before emission occurred.[8]

The variation of PL photophysical properties of the PFO/U-PF blending films with the dichroic ratio is presented in Figure 3. The shape and the location of the peak in the spectrum of the PFO/U-PE drawing film are different from those of the undrawing films. In the H-PFO /U-PE blending films (Figure 3a), the spectrum of the sample without drawing shows relatively broad and only poorly resolved peaks at 420, 448, and 463 nm, similar to the spectrum of the pure PFO powder, which implies that the PFO molecules aggregate, evidently due to the phase separation between U-PE and PFO. An additional emission peak at 535 nm appears, which is an aggregate peak, i.e., a g-band, attributable to interchain/intersegment interactions of fluorenone (or fluorenone-based excimers),[27] which may be produced during the preparation of the films. The interactions occur easily due to the phase separation between PFO and U-PE. After drawing, the spectra with well-resolved peaks are obtained. And the peaks are blue shifted with increasing the drawing ratio. The peaks shift from 448 to 431 nm and from 463 to 456 nm when the dichroic ratio of the film goes from 1 to 51, respectively. The spectra characteristics of the films with high dichroic ratio (i.e., high drawing ratio) are similar to that of the dilute solution of PFO/THF. Furthermore, the g-band at 535 nm disappears after drawing even though this takes place at the low drawing ratio. In the drawing films, PFO chains are forced to disperse in the U-PE matrix and the chains are extended. The interchain/intersegment interactions are held back. Therefore, the g-band disappears in the drawn films.

The spectrum variations of the L-PFO/U-PE blending samples with the dichroic ratio are shown in Figure 3b. It is clear that the photophysical properties of the L-PFO/U-PE blending film without drawing are different from those of the H-PFO/U-PE blending film without drawing. In the former, the well-resolved peaks at 442, 465, and 496 nm are sharper and the g-band centered

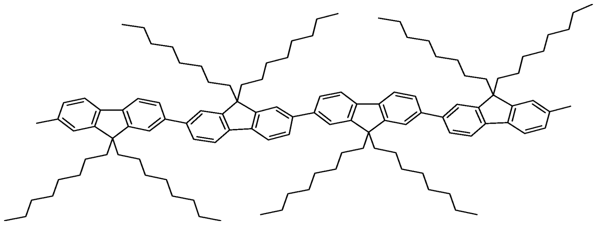

Figure 5. Fully extended PFO chain segment, adopting the "planar zigzag" or 2_1 helix conformation.

at 535 nm is weaker. These suggest that the L-PFO chains in the blending film are dispersed more efficiently than H-PFO chains.

It is also noted that the absorption spectra of the blending films are varied with the dichroic ratio. Figure 4 shows the absorption spectra of the blending films with different dichroic ratios. The maximum absorption peak is at 396 nm for the blending films. However, an additional absorption peak at 432 nm is observed in the blending film without drawing. From Figure 4, it can seen that the additional peak has well-resolved structure in the blending films without drawing ($DR_E = 1$). And the additional peak becomes shoulder and then disappears with increasing the dichroic ratio. In the H-PFO/U-PE blending film (Figure 4a), a "strong" shoulder is observed at the dichroic ratio of 5. And the shoulder disappears totally when the dichroic ratio is beyond 41. The value is corresponding to the inflection of the curve of the drawing ratio−the dichroic ratio in Figure 2a. In the L-PFO/U-PE blending film (Figure 4b), a "weak" shoulder is observed at the dichroic ratio of 5 and disappears when the dichroic ratio is beyond 26.

The additional peak (or shoulder) in the absorption spectrum of PFO is always observed in the crystalline samples of PFO, and the shoulder is regarded as a "precursor" of a fully developed additional peak.[28] Therefore, it is believed that the additional peak (or shoulder) is related to the crystal of PFO.[8,19,20,28] The PFO chains in the crystal samples adopt an extended conformation, which can be described as "planar zigzag" or 2_1 helix structure as shown in Figure 5. Therefore, the variations of the photophysical properties, where the emission spectra are blue shifted and the additional peaks in the absorbance spectra gradually disappear with increasing the dichroic ratio, reflect the different physical states of the PFO chains in the U-PE matrix. From the variations of the photophysical properties of the films with different dichroic ratios, the process of dispersion of the PFO chains in the U-PE matrix can be assumed in Figure 6. First, the PFO chains are easily aggregated to form crystal due to no thermodynamic compatibility of PFO with U-PE during the geletation of the PFO/U-PE/xylene solution (Figure 6a). The PFO chains in the crystal adopt an extended conformation. Then, the crystal of PFO is fragmented (Figure 6b) after drawing. This may be more easily taken place at the points of fluorenone defects,[27] which destroys the fluorenone-based excimers and results in rapid disappearance of the g-band in the PL spectra of the drawing films. The fragments of the crystal are oriented along the drawing direction and the amount of the fragments is increased with increasing the drawing ratio, leading to increasing linearly the dichroic ratio. Subsequently, the PFO chains in the fragments are detached and molecularly dispersed in a U-PE matrix with the macroscopic orientation along the drawing direction under the higher drawing ratio (Figure 6c). Finally, the PFO chains are fully oriented along the drawing direction (Figure 6d), and the dichroic ratio of the blending film is unchanged during further drawing.

Conclusions. The highly oriented blue-light-emitting blending films based on the PFO and U-PE are prepared using the tensile deformation technique, resulting in

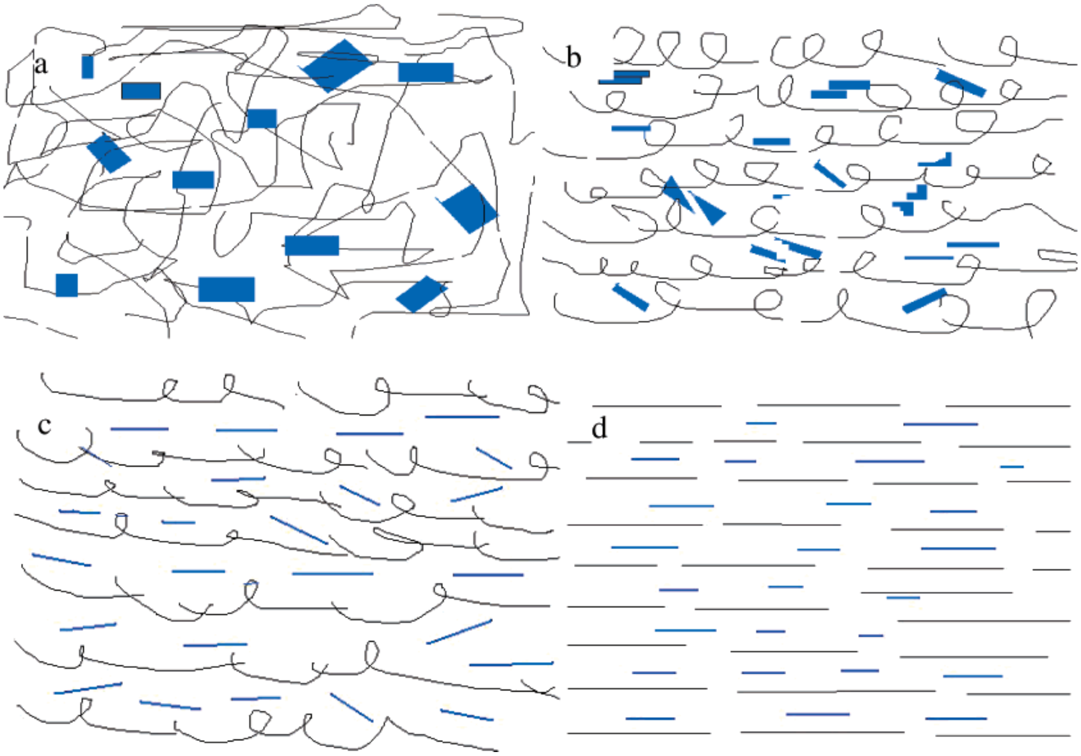

Figure 6. Sketch of the dispersion of PFO chains in the U-PE matrix, (a) the crystal of PFO in the blending film without drawing, (b) the fragment of crystal in the blending film during drawing, (c) the PFO chains dispersed in U-PE matrix, (d) the full orientation of PFO chains in the U-PE matrix with high drawing ratio.

highly polarized photoluminescence and absorbance. The maximum dichroic ratio of 58 in PL and 24 in absorbance, which is the maximum polarization reported on PFO materials up to now, is obtained when using low molecular weight PFO at a concentration range of 1−0.5%. A higher dichroic ratio is obtained when exciting with parallel polarized light at the low drawing ratio, and the dichroisms are comparable for the two excitations at high drawing ratio. The photophysical properties of the PFO/U-PE blending films are varied with the drawing ratio, which reflects the physical state of the PFO chains in the U-PE matrix. It is suggested that the variation of the dispersion of the PFO chains in the film is from the initial crystal state to the fragment of PFO crystal and to the final molecular dispersion in the U-PE matrix with increasing drawing ratio.

Experimental Section. PFO was synthesized by using the Suzuki coupling route.[29] The typical polystyrene equivalent number-average molecular weight of the PFO was 45000 (H-PFO) and 9000(L-PFO), as determined by gel permeation chromatography (GPC). U-PE was purchased from Beijing Chemical(M-II, $\overline{M_\eta}$ = 2000000−3000000).

A 1.0 g sample of U-PE was dissolved into 100 g of xylene in a hot oil bath kept at 135 °C for half an hour. Then the desired amount of the PFO/xylene solution was added into the boiling solution and allowed to equilibrate for 10 min. Finally, the hot U-PE/PFO/xylene solution was poured into a Petri dish, where it formed a gel upon cooling, and was dried under ambient conditions for 2 days. All resulting blending films had a homogeneous thickness of about 60 μm. The resulting PFO/U-PE films were mounted on a self-made clamp, heated in a vacuum stove at temperatures of 90−100 °C for 15 min, and then drawn at that temperature. The drawing ratio was defined as a ratio between the length of the film after and before drawing.

The anisotropic photophysical behaviors of the drawn films were studied by UV−vis absorption and steady-state PL spectroscopy. The polarized absorption spectra were recorded with a UV−visible spectrophotometer (Shimadzu, UV-1601PC), fitted with a Glan-Thomson polarizer on a rotational stage just before the sample. All absorption spectra were corrected for background with pure U-PE films of the comparable drawing ratio and thickness. The polarized PL spectra were recorded with a fluorescence photometer (Varian, Cary Eclipse, FLR025), using a Glan-Thomson polarizer on the detector side. For excitation with the polarized light, a Glan-Thomson polarizer was fitted before the sample with polarization parallel to drawing direction. And for excitation with unpolarized light, a depolarizer was used to eliminate the polarization of the photometer. For the photophysical experiments, the blending films were sandwiched between two quartz slides, applying silicon oil in order to minimize light scattering at the film surfaces. The dichroic ratio for emission (DR_E) and absorption (DR_A) was defined as the ratio between the respective spectra measured with polarization parallel and perpendicular to the drawing direction. These values were calculated from the region of maximum spectral intensity.

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