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Influence of the Molecular Weight on the Thermotropic Alignment of Thin Liquid Crystalline Polyfluorene Copolymer Films

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ABSTRACT: Mechanisms that limit the thermotropic alignment of a liquid crystal semiconducting polymer on a rubbed polyimide film were studied using three different molecular weights of poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT), one of a large class of polyfluorene polymers currently being investigated for use in highly polarized light-emitting diodes and high-performance polymer-based transistors. The molecular weight was found to influence the melting temperature of the polymer, the speed at which the polymer aligns to a rubbed surface, and the ultimate molecular alignment that can be achieved. The alignment of F8BT with the highest molecular weight was severely limited by the viscosity of the polymer, while the films with low and intermediate molecular weights reached a maximum alignment in reasonable processing times. The maximum saturated dichroic ratio ($D_{\max}$) was consistently higher, the largest $D_{\max}$ observed was over 29, in the lowest molecular weight films. Optical microscopy revealed that the lower dichroic ratio could be attributed to an inability of the domains in the higher molecular weight film to reorient to the templating direction; thus, the final film retains a multidomain structure. This has serious implications on the charge transport through these materials since any domain boundaries will adversely affect the charge carrier mobility. Therefore, despite the advantages that higher molecular weights could have on optoelectronic device performance, the long chain lengths will also limit macroscopic liquid crystalline alignment. For F8BT, the maximum molecular weight in which monodomain alignment is still achieved appears to be in the range 62 000−129 000.

Introduction

Conjugated, semiconducting polymers such as polyfluorenes have emerged over the past 10 years as an attractive candidate for many optoelectronic applications.[1] The polyfluorene copolymer used in this study, F8BT, has been of specific interest for photovoltaic[2] and light-emitting applications[3] because it is one of the only polymers in this class that has shown fast electron transport.[4] Researchers have also found that many of the polyfluorenes, including F8BT, melt into a liquid crystal at reasonable processing temperatures. Surface-induced alignment techniques have been used to process thin polyfluorene films into monodomains with high orientation parameters.[5−7] These films have been incorporated into light-emitting devices to produce highly polarized emission potentially suitable for backlighting current liquid crystal displays.[8−11] Recently, we have reported that these alignment procedures can also be used to improve charge transport in a polyfluorene film, thus making it advantageous for polymer transistors.[12]

Current polarization ratios obtained for various polyfluorenes are still too low for backlighting applications. Therefore, many researchers have focused on potential routes to improve the molecular order. Whitehead et al. observed a change in the dichroic ratio of polyfluorenes with different mesogenic backbones.[13,14] Thus, chemical tailoring of the mesogen is one route to improved alignment; however, it will come at the expense of spectral changes. Nothofer et al. found that simply reducing the size of the side chain in polyfluorene derivatives lowered the effective diameter of the mesogen and lead to a higher orientation parameter.[15] Grell et al. showed that a red-shifted peak developed in poly(9,9-dioctylfluorene) after it was thermotropically aligned, cooled to 77 K, and then slowly reheated to room temperature.[16] The red-shifted peak was attributed to chains of extended conjugation, and the dichroic ratio of this absorption peak was about 3 times larger than that of the normal $\pi-\pi^*$ transition. The chains associated with the red-shifted absorption have a more extended, rigid chain conformation, which leads to a higher axial dipole moment and thus larger polarization ratio.

One variable that has yet to be independently studied is the effect of molecular weight on polyfluorene alignment. Liquid crystalline polyfluorenes are wormlike molecules with a persistence length only around 7 nm.[16,17] This is low when compared to polymers used for structural applications that can have a persistence length near 40 nm.[18] The microscopic order parameter is expected to grow with the stiffness of the polymer chain. In the short chain length regime, the persistence length of a polymer liquid crystal will grow with molecular weight, which can be a potential route to improved macroscopic order.[18] Moreover, high molecular weight polymers are viewed as advantageous for emissive devices because the luminescent efficiency is often higher due to a lower concentration of chain ends that can act as quenching centers. However, increasing the molecular weight will influence the ability of a liquid crystal polymer to align to a templating layer. First, the transition into the liquid crystal melt will occur at higher temperatures for longer chains. Second, the viscosity of a polymer melt is highly dependent on molecular weight; thus, changing the chain length will affect the kinetics of alignment. The increasing viscosity at higher molecular weights should increase the time needed for maximum alignment. Finally, the molecular weight of the polymer will affect the equilibrium morphology and domain structure of the liquid crystalline

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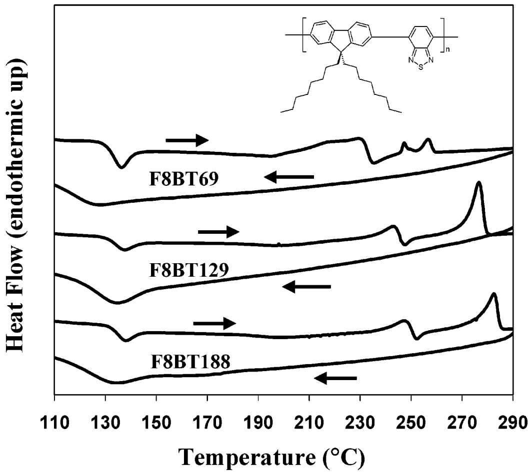


Figure 1. Differential scanning calorimetry of the three different molecular weight F8BT samples. A heating scan (top) taken at 10 °C/min and the cooling scan (bottom) at 50 °C/min. The weights of the samples were 6.8, 6.0, and 5.9 mg for F8BT69, F8BT129, and F8BT188, respectively. The curves have been offset along the *y*-axis for clarity. Also included is the chemical structure of poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT).

Table 1. Physical Properties of F8BT Polymers

	M_n	M_w	PD[a]	T_g (°C)	T_m (°C)
F8BT69	69 000	101 000	1.46	125	258
F8BT129	129 000	220 000	1.71	133	277
F8BT188	188 000	417 000	2.22	135	283

[a] Polydispersity index.

film, and thus the polarization ratio of the potential device. Here we will examine how the molecular weight of F8BT affects the kinetics of thermotropic alignment of a thin film on a rubbed substrate and the mechanisms that limit the macroscopic order in these films.

Experimental Section

F8BT, the chemical structure of which is shown in Figure 1, of three different molecular weights were used as received from Cambridge Display Technology. The polystyrene equivalent molecular weights were determined by gel permeation chromatography (GPC) and are listed in Table 1.

A Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) was used to determine the transition temperatures for the different polymers. There was poor heat contact between the polymer and aluminum when polymer powder was placed directly into the pan. Therefore, the polymers were dissolved in *p*-xylene (30 g/L) and subsequently dropped into aluminum pans. The *p*-xylene was evaporated off at 90 °C. Scans were taken with a 10 °C/min heating and a 50 °C/min cooling rate. An initial heating scan beyond the boiling point of the *p*-xylene (130 °C) was taken for each polymer to ensure all the solvent was gone. Thermal transitions were determined from the subsequent cooling scans or upon reheating.

Additional thermal characterization of F8BT films was accomplished using low-resolution (5×) optical microscopy while heating them with a Linkham hot stage. Birefringence was observed using crossed polarizers. The films, which were slowly spun-cast (200 rpm) from dilute solutions (around 4−10 g/L), were about 120 nm thick and provided good contrast. Samples were viewed in a nitrogen environment to mitigate the effect of degradation at high temperatures. The domain structure of aligned and unaligned thin films (40 nm) was observed using an Olympus BX60 fluorescence microscope equipped with crossed polarizers. The micrographs were taken using the 100× lens.

Monodomain orientation was obtained using established techniques.[8] A Merck Liquicoat ZL1 2650 polyimide solution was prepared and spun-cast at 2000 rpm on a cleaned glass slide. The film was dried at 90 °C for 5 min before being cured at either 310 °C for 4 h under vacuum. Large (3 in. by 1 in.) substrates were passed twice through a commercial rubbing machine with a rayon cloth spinning at 1200 rpm. The substrates were then cut to approximately 1 cm by 1 cm squares, and only samples that were prepared from the same initial substrate were compared directly. Thin F8BT films were then spun-cast on top at 2000 rpm. The higher molecular weight polymers were cast from more dilute solutions to achieve a similar film thickness (around 40 nm). All the F8BT solutions were heated to 60 °C before spinning to mitigate the effects of solution aggregation. Thermotropic alignment was achieved by placing the films on a Linkham hot stage set at least 10 °C above the melting temperature of the polymer in a nitrogen environment. After the annealing step films were quenched back to room temperature to prevent crystallization.

Polymer alignment was studied through the dichroic ratio measurements taken with a Hewlett-Packard 8453 spectrometer. A cube polarizer was placed in the optical path, and separate spectra were taken with polarizer oriented parallel and perpendicular to the rubbing direction. All dichroic ratios were measured at the absorption peak centered around 470 nm. The error associated with the dichroic ratio measurements were calculated assuming that the peaks of the spectra can be determined to within 0.0025 absorption units. The error was less then 10% for all dichroic ratios up to 15; the error increased to around 20% for dichroic ratios above 15 as the baseline shifts due to scattering play a larger role in the ratio.

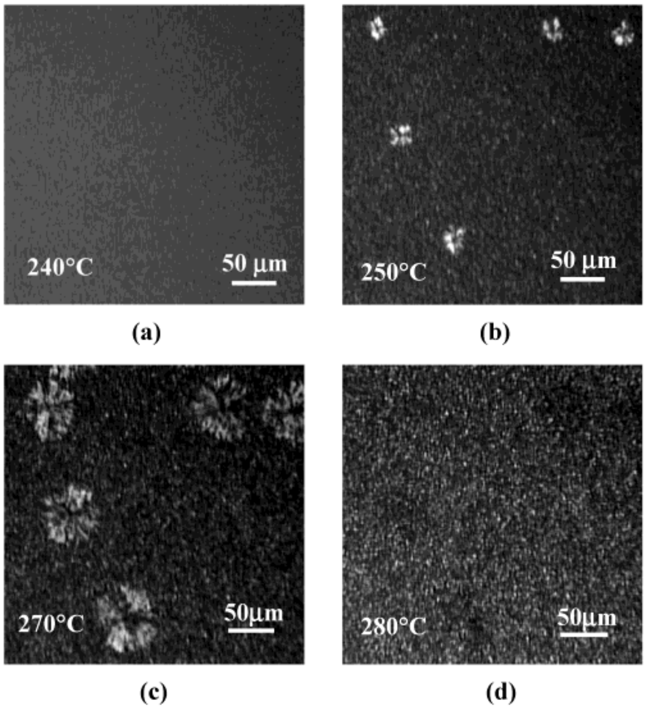
Results and Discussion

Change in the Melting Temperature. The melting temperature of a polymer crystal is satisfied by eq 1

$$T_M = \Delta H/\Delta S \tag{1}$$

where ΔH is the enthalpy difference between the melt and crystal and ΔS is the entropy difference that reflects the greater molecular randomness of the melt.[18] For a rigid monomer unit, like F8BT, ΔS will be relatively independent of chain length as few additional conformational changes arise with lengthening the rigid backbone. ΔH increases with chain length; thus, the melting temperature will increase with molecular weight. However, there is expected to be a limit to this behavior as even the limited conformational changes in a rigid mesogen will contribute enough entropy to prevent the melting temperature from growing indefinitely.[18] Therefore, prior to examining the mechanisms that limit surface alignment, it is important to clearly identify the melting temperature of each polymer. Phase transitions were monitored using DSC scans. The three polymers were initially heated to 300 °C at 10 °C/min, cooled to 50 °C at 50 °C/min, and finally reheated to 320 °C at 10 °C/min.

Figure 1 shows final heating scans for each of the three molecular weight polymers. In all the polymers a feature is observed near 130 °C. A previous study showed that a lower molecular weight F8BT (M_n = 14 500) crystallizes at 130 °C,[14] so the feature might be due to a fractionation and crystallization of a low molecular weight component of our polydisperse polymers. However, we attribute this feature to a transition of the polymer from the glassy to a rubbery state. The fact that the shift in the baseline is exothermic as opposed to the endothermic shift expected at the glass transition suggests that some crystallization may also be occurring when the chains become more mobile.[19] The cooling curves in Figure 1 show that this transition point shifts from 125 °C for F8BT69 to 135 °C for



(a) (b)

(c) (d)

Figure 2. Optical micrographs through crossed polarizers of a F8BT129 film heated to (a) 240, (b) 250, (c) 270, and (d) 280 °C.

F8BT188. A second exothermic feature was observed at 237−245 °C when heating all the polymers. This peak was attributed to the rubbery polymer crystallizing in the solid state. Endothermic peaks indicative of the polymer melting into a liquid crystal were clearly observed above the crystallization temperature for all the polymers. The presence of two peaks in F8BT69 at 247 and 258 °C could be due to fractionation of our highly disperse polymers. Only one endothermic peak was observed in both F8BT129 at 277 °C and F8BT188 at 283 °C. No evidence of crystallization was observed in any of the polymers upon cooling at 50 °C, which indicates that quenching the liquid crystalline melt will result in the polymer being in the glassy state.

Transmission optical microscopy as a function of temperature was also used to examine the phase transitions in the polymer films. The crystalline and liquid crystalline domains that form in a F8BT film as it is heated are expected to be birefringent, so that these morphological changes can be detected using optical microscopy under crossed polarizers. Figure 2 shows selected micrographs of F8BT129 as it was heated from room temperature to 300 °C. Figure 2a shows the film is still isotropic at 240 °C, which adds further evidence that the DSC feature at 130 °C is not crystallization. By 250 °C small birefringent domains begin to form in a still fairly isotropic background. The Maltese cross pattern that is observed in the birefiregent domains (called spherulites) is indicative of polymer crystallization.[20] This agrees with the DSC results that showed a crystallization peak at 245 °C. The micrograph at 270 °C shows the spherulites have grown, so the film is still crystallizing. Figure 2d shows that the spherulites completely disappear by 280 °C and give way to a completely birefringent background. The bright spots in the image are indicative of small liquid crystalline domains in which the orientation of the director is not parallel with either polarizer. This correlates well with the DSC scans that also exhibited an endothermic melting peaks around 277 °C. It is important to note that no residual spherulites were observed when the film was allowed to equilibrate above 280 °C. The film was heated to above 300 °C, and no transition from a nematic liquid crystal to an isotropic liquid was observed. Similar behavior was observed in both the F8BT69 and F8BT188 films heated under cross polarizers, with transition temperatures correlating well with the DSC results. A summary for the thermal characterization results is given in Table 1.

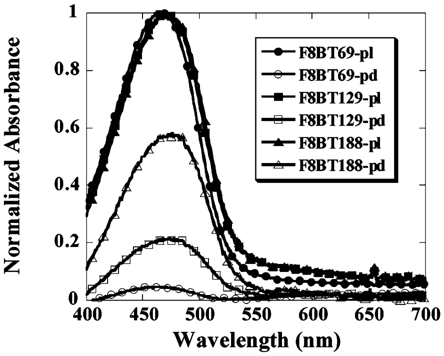


Figure 3. UV−vis absorption of the different molecular weight F8BT films on a rubbed polyimide alignment layer. Orientation was achieved by annealing at least 10 °C above the melting temperature for 1 min. The spectra parallel (par) and perpendicular (perp) to the rubbed direction were normalized to the peak absorption of the parallel spectrum. After annealing all the films do scatter some light, and our setup measures optical absorption in a transmission geometry in which reflected light cannot be measured. Therefore, finite reflection manifests itself as a shift of the baseline, which is small but limits the accuracy with which the dichroic ratio can be determined.

Effect of Viscosity on Surface Alignment. The thermal characterization results were used to guide our study of the molecular weight dependence on the thermotropic alignment of F8BT on a rubbed polyimide substrate. Initially, all three films were annealed for 1 min at temperature at least 10 °C higher than their melting temperature into the liquid crystalline phase. Figure 3 shows the optical absorption parallel and perpendicular to the rubbing direction. The dichroic ratio for each film was determined by dividing the peak value for the two spectra. F8BT69 exhibited a dichroic ratio of 27.8, F8BT129 a ratio of 5.2, and F8BT188 a ratio of 1.8.

The low dichroic ratio after a 1 min annealing exhibited by the higher molecular weight F8BT polymers can partly be attributed to slower alignment kinetics. It is well-known that a polymer melt will become more viscous with increasing molecular weight, especially when chain entanglements limit molecular motion. The effects of viscosity can be determined by looking at the kinetics of orientation for the different F8BT polymers. Figure 4 shows the change in the dichroic ratio for each molecular weight as a function of annealing time. The F8BT69 film reached its maximum value after only 10 min, while the F8BT129 film saturated after a 1 h anneal. Both films exhibited a slight decrease in the dichroic ratio at longer annealing times that is associated with areas of the F8BT films dewetting from the substrate and possible photodegradation. The dichroic ratio of the F8BT188 film was still increasing after a 10 h anneal.

Previous researchers have used an exponential relationship to fit the kinetics of alignment for liquid crystal

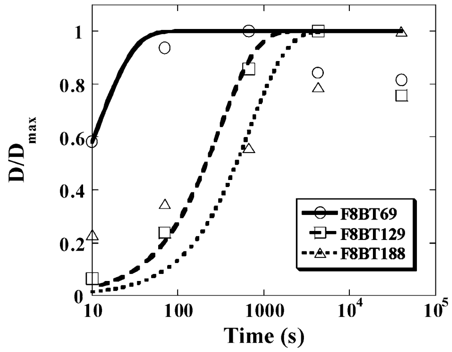


Figure 4. Dichroic ratio of the different molecular weights F8BT as a function of annealing time. The dichroic ratio (D) was determined by dividing the peak absorption parallel to the rubbing direction by the peak absorption perpendicular to it. D_{max} is the maximum dichroic ratio measured over the entire annealing time. The line is a fit of the data to eq 2.

Table 2. Summary of the Fits of the Change in Dichroic Ratio as a Function of Annealing Time to Eq 2 for Different Molecular Weight F8BT

	annealing temp (°C)	D_{max}	τ (s)
F8BT69	268	29.7 ± 4.4	12 ± 4
F8BT129	288	21.8 ± 3.2	306 ± 125
F8BT188	297	5.2 ± 0.5	689 ± 361

polymers in a magnetic field.[21,22] The surface alignment technique used in the present study does not rely on a molecular torque being applied onto each molecule by an externally applied field. However, to get a relative value for the viscous force that is experienced by the mesogen in the different molecular weight films, the data in Figure 4 were fit to a simple exponential relationship:

$$D/D_{max} = 1 - \exp(-t/\tau) \qquad (2)$$

where D is the dichroic ratio and τ is a characteristic time of the process. The fits are shown in Figure 4 and summarized in Table 2. The data for the lower molecular weight polymers fit very convincingly, yielding a τ value of 12 and 306 s for F8BT69 and F8BT129, respectively. The function does not fit the F8BT188 data very well, which can be attributed to the alignment not reaching a maximum in the experimental length scale. Thus, the measured characteristic time of 689 s is certainly too short but at least gives a lower limit estimate.

In a simple model, τ is expected to be directly proportional to the polymer viscosity and inversely proportional to the alignment torque (T):

$$\tau \propto \eta/T \qquad (3)$$

All the films were cast on polyimide alignment layers processed under the identical conditions so it is assumed that the observed changes in τ are due exclusively to a change in the polymer viscosity. We do not have enough data points to determine functional relationship between viscosity and molecular weight and thus make any conclusions about molecular dynamics in thin F8BT films. However, in the future this technique could provide a unique way of monitoring the dynamics of polymer molecules in thin films.

Change in the Maximum Orientation with Molecular Weight. Perhaps the most important observation from the perspective of device performance is the dependence of the maximum dichroic ratio (D_{max}) on molecular weight. Table 2 shows D_{max} for the three polymers. The dichroic ratio in the F8BT188 film was severely limited by viscosity and thus did not saturate even after a 12 h anneal. Also, the saturated dichroic ratio for the F8BT69 was significantly higher than that for the F8BT129 film.

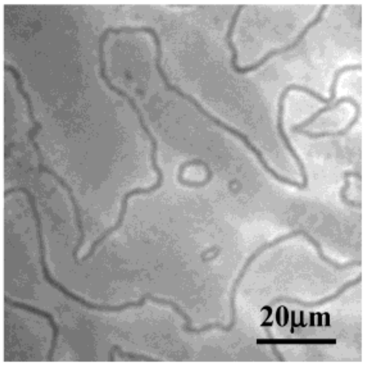


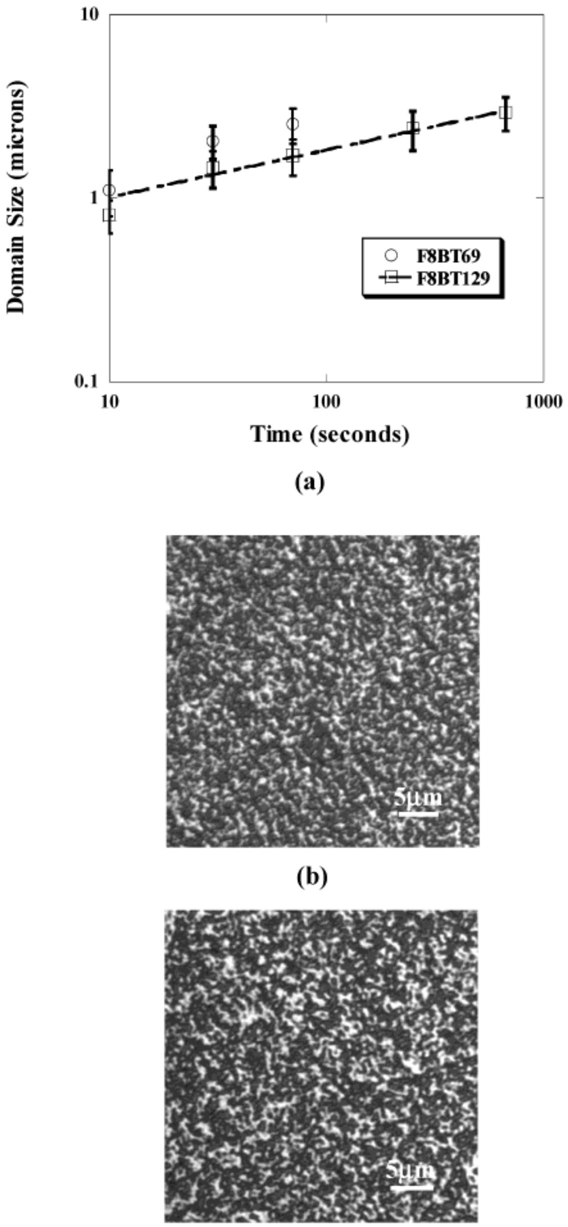
Figure 5. Fluorescence micrographs taken under crossed polarizers for thick film of F8BT69 melted into a liquid crystal and quenched back into a glass. The thick film was spun-cast slowly (200 rpm) from dilute solution (10 g/L) and then slowly heated to 268 °C, which yielded the large domains. The black filaments are indicative of a nematic liquid crystal.

There are many plausible mechanisms that can limit the thermotropic alignment of higher molecular weight liquid crystalline polymers on a rubbed substrate. First, there could be a change in the microscopic order parameter with molecular weight. However, the local order is only expected to increase with molecular weight,[18] which would not explain the observed trend. Second, polymers will form domains upon being melted into the liquid crystalline phase. Any decrease in the domain size with increasing molecular weight would increase the concentration of domain boundaries. This would limit the macroscopic order because in the area of domain boundaries the director is not aligned parallel to the rubbing direction.[23] Third, it has been reported that high molecular weight liquid crystalline films contain disordered, amorphous regions that can limit the macroscopic orientation.[22] Moore and Stupp observed a smaller orientation parameter in the highest of a series of molecular weight polyester copolymers with flexible spacers aligned in a magnetic field. NMR results showed a larger concentration of mobile segments with increasing molecular weight, and thus they postulated that the smaller orientation parameter was due to presence of regions of reduced local order.[22] Last, the lower molecular weight polymer might be more capable of reorienting domains in which the liquid crystalline director is originally not aligned with the preferred direction due to a reduced role of chains sharing domains and entanglements. Anwer and Windle used this “elastic resistance to orientation possibly associated with defects and boundaries” to explain the observed reduction of the orientation parameter with increasing molecular weight of polyester copolymers aligned in a magnetic field.[21]

The nematic liquid crystalline phase is characterized by its domain structure observed in the optical microscope under crossed polarizers. The black filaments associated with a singularity in the molecular alignment between nematic domains[24] are observed in the micrograph of a thick F8BT69 film shown in Figure 5. Even in the absence of an alignment field these liquid crystalline domains are expected to grow to achieve the lowest energy state, a monodomain.[24] Experimentally, it has been shown that the domain growth in polymer liquid crystals saturates before the formation of a monodomain. Domain growth in polymer liquid crystals does follow the expected power law relationship with time (domain size $\sim t^{\gamma}$)[25] with a scaling exponent ranging from 0.25 to 0.37.[26,27]

Domain growth was monitored in F8BT129 and F8BT69 by casting films using the same conditions as used for the films on the rubbed polyimide, except using a plain glass slide with no templating layer as the substrate. These films were annealed at the temperature prescribed in Table 2, and the domain growth was monitored as a function of time using a high-resolution fluorescence microscope equipped with crossed polarizers. An average domain size for each film was determined by measuring the width of 20 spots that show up as light areas in both micrographs. Growth of the domains in the F8BT69 film arrested after only 70 s, while the F8BT129 film took close to 11 min. Figure 6a shows the increase in the domain size prior to saturation as a function of annealing time for F8BT69 and F8BT129. The domain size for the F8BT69 film saturated too quickly to fit, but a power law fit to the F8BT129 data yielded an exponent of 0.25. A similar exponent has been previously observed for the domain coarsening of a liquid crystalline polymer.[27] Optical micrographs of both films after the domain size had saturated is seen in Figure 6b,c. The average domain size in the F8BT129 film was actually slightly larger, 2.9 μm, when compared the F8BT69 film, 2.5 μm. Therefore, a larger saturated domain size is unlikely to account for the larger dichroic ratio observed in the F8BT69 films.

The role of domain growth in aligned films was also monitored using high-resolution optical microscopy, except in this case the F8BT films were again cast on rubbed polyimide layers. Figure 7 shows a series of optical micrographs a F8BT129 film, with the polarizer oriented both parallel and at a 45° angle to the rubbing direction. After 30 s domains are clearly seen, but there is little difference in the images obtained at different orientations, indicating there is very little preferential molecular orientation. After 250 s the domains have definitely grown, and the image taken with the rubbing direction oriented 45° to the polarizer is noticeably brighter, showing that the domains are preferentially oriented along the alignment direction. The last two micrographs (Figure 7c) are of the film after 670 s when both the microstructure reached equilibrium and the dichroic ratio had saturated. Most of the domains appear light when the rubbing direction is oriented 45° to the polarizer, indicating that the molecular orientation within the domain is parallel to the templating direction. However, dark spots are observed in the image. These could be due to either isotropic regions or regions in which the molecular orientation does not follow the rubbing direction. The corresponding image of the film, turned by 45° so the rubbing direction is parallel to the polarizer, reveals that light spots are still observed. This indicates that there are certainly regions in the film in which the molecular orientation is not parallel to the alignment direction. No conclusive evidence was found to completely discount the presence of isotropic regions, but Figure 7c indicates that they are not solely responsible for the reduction in the dichroic ratio for the F8BT129 film.



(a)

(b)

(c)

Figure 6. Domain coarsening in F8BT69 and F8BT129 films cast on a plain glass slide and annealed at 268 and 288 °C, respectively. (a) The domain size (determined by fluorescence micrographs taken under crossed polarizers) as a function of annealing time for both films. The F8BT129 data were fit to domain size $\sim t^{\gamma}$. The actual fluorescence micrographs for the films after the domain size had saturated are also included: (b) the F8BT69 film annealed for 70 s and (c) F8BT129 film annealed for 670 s.

Figure 8 shows a similar series of optical micrographs for a F8BT69 film on a rubbed polyimide substrate. For this film, even after the 10 s there is already a noticeable difference in the number of domains oriented parallel to the alignment direction. After 30 s the domain boundaries are difficult to see in the image of the film oriented 45° to rubbing direction as the light areas are starting to merge. The final two images are taken after 70 s when again both the microstructure had reached equilibrium and dichroic ratio had saturated. No domain boundaries can be seen regardless of the orientation of the film, suggesting that a monodomain has been formed. If a polydomain structure is still present in the

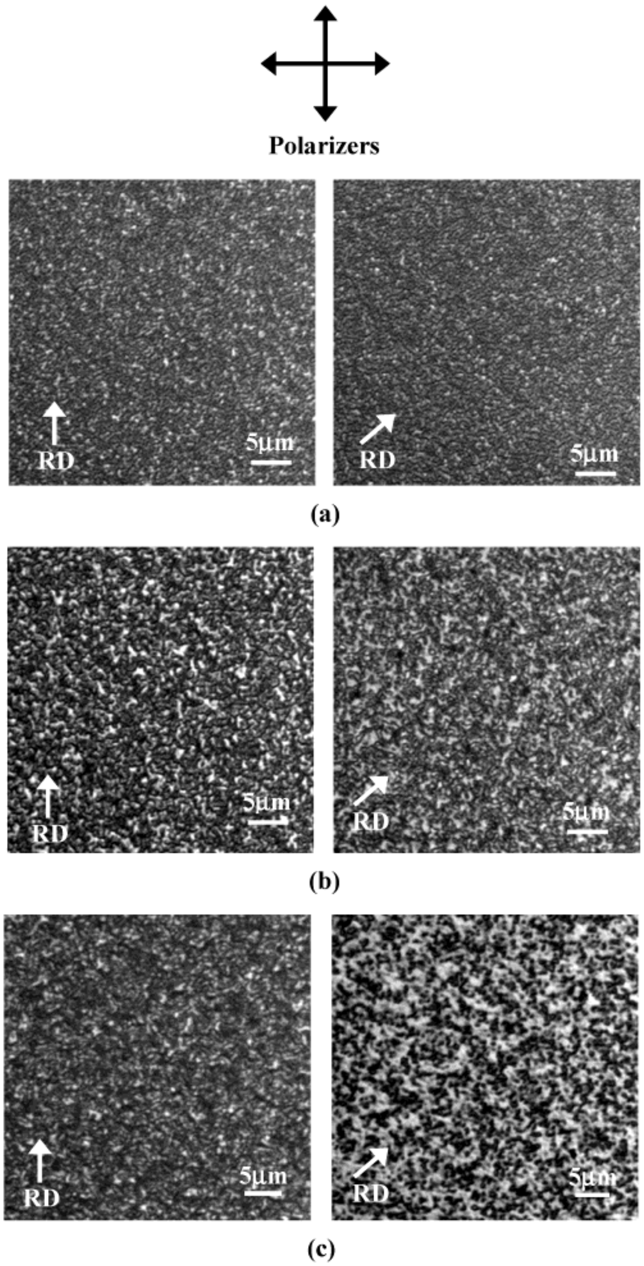


Figure 7. Fluorescence micrographs taken under crossed polarizers for a F8BT129 film cast on a rubbed polyimide substrate. Images were taken with the rubbing direction oriented both parallel and at a 45° angle to the polarizer after annealing at 288 °C for a total of (a) 30, (b) 250, and (c) 670 s. For each heat treatment the films were placed on the hot stage set at the annealing temperature and quenched to room temperature for observation.

aligned F8BT69 film, it cannot be observed in the optical micrographs. This could be due in part to very little contrast between domains because they are all perfectly oriented with the rubbing direction. However, any domain boundaries that are present must be very thin (less than a micron) to be unnoticeable in the micrographs.

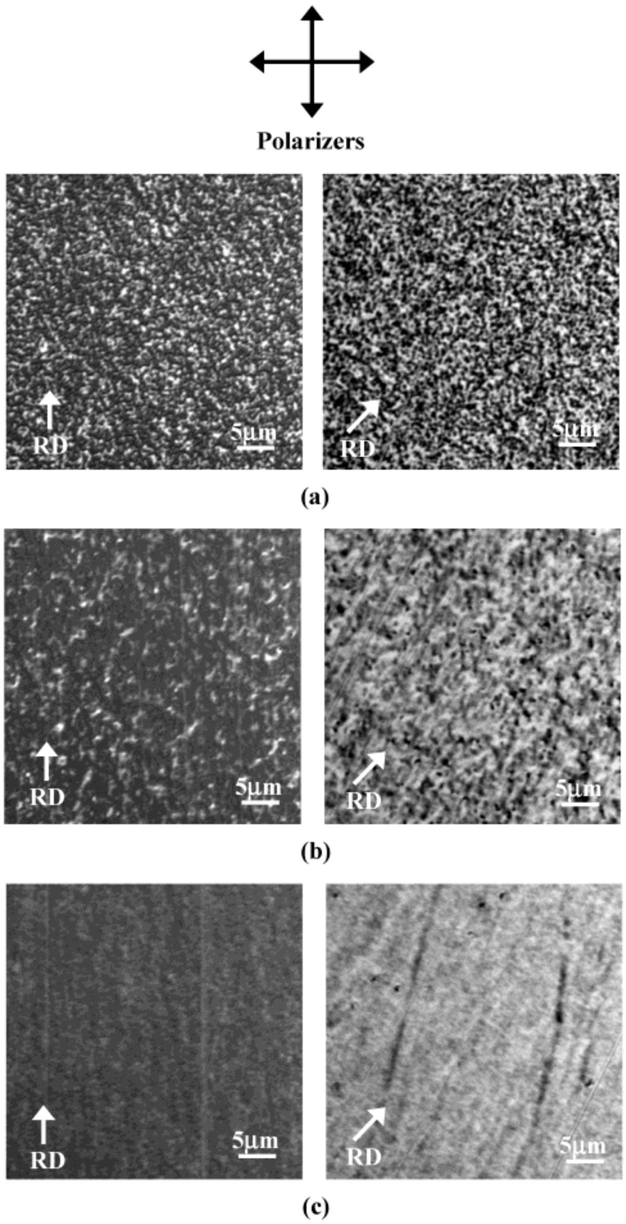


Figure 8. Fluorescence micrographs taken under crossed polarizers for a F8BT69 film cast on a rubbed polyimide substrate. Images were taken with the rubbing direction oriented both parallel and at a 45° angle to the polarizer after annealing at 268 °C for a total of (a) 10, (b) 30, and (c) 70 s. For each heat treatment the films were placed on the hot stage set at the annealing temperature and quenched to room temperature for observation.

In summary, even after accounting for the longer alignment times for F8BT129, the maximum dichroic ratio observed was still lower than its low molecular weight counterpart F8BT69. The lower dichroic ratio could not be justified by any change in the size of unaligned domains between the two polymers, and no evidence was found for isotropic regions existing in the higher molecular weight polymer film. The increase in the dichroic ratio in the F8BT69 film was attributed to the ability of the liquid crystalline director within a domain to reorient to the alignment direction. The aligned F8BT69 film showed no evidence of a domain structure in the optical micrograph, which suggests that domain boundaries were annihilated in favor of a monodomain. In contrast, domains were still observed in the equilibrium microstructure of the aligned F8BT129 film. The reduced ability of domains in the high molecular weight films to reorient to the rubbing direction could be due to a larger number of chains sharing domains and the increase in the number of entanglements in the film.

Conclusion

The thermotropic alignment of high molecular weight liquid crystalline polymers on a rubbed surface is limited by two factors. The first is viscosity, which can prevent films from reaching a saturated dichroic ratio in reasonable processing times. The second mechanism was observed in a slightly lower molecular weight film in which the dichroic ratio did saturate. In this case not all the domains are able reorient to the rubbed direction and aligned film maintained an equilibrium multidomain structure. In contrast, the lowest molecular weight polymer aligned into a mondomain structure and thus exhibited the largest dichroic ratio. The domain structure in conjugated polymer films will be critical for device performance, as it could limit the polarization ratio in polymer light-emitting devices and the charge transport in transistors. This study shows that low molecular weight polymers are needed to obtain a monodomain that is conducive to optoelectronic applications.

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References and Notes

(1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.
(2) Arias, A. C.; Corcoran, N.; Banach, M.; Friend, R. H.; MacKenzie, J. D.; Huck, W. T. S. *Appl. Phys. Lett.* **2002**, *80*, 1695.
(3) Corcoran, N.; Arias, A. C.; Kim, J. S.; MacKenzie, J. D.; Friend, R. H. *Appl. Phys. Lett.* **2003**, *82*, 299.
(4) Campbell, A. J.; Bradley, D. D. C.; Antoniadis, H. *Appl. Phys. Lett.* **2001**, *79*, 2133.
(5) Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, *11*, 895.
(6) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. *Adv. Mater.* **1997**, *9*, 798.
(7) Schartel, B.; Wachtendorf, V.; Grell, M.; Bradley, D. D. C.; Hennecke, M. *Phys. Rev. B* **1999**, *60*, 277.
(8) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H. G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.
(9) Clauswitz, K.-U. W.; Geffarth, F.; Greiner, A.; Lüssem, G.; Wendorff, J. H. *Synth. Met.* **2000**, *111*−*112*, 169.
(10) Miteva, T.; Meisel, A.; Grell, M.; Nothofer, H. G.; Lupo, D.; Yasuda, A.; Knoll, W.; Klopperburg, L.; Bunz, U. H. F.; Scherf, U.; Neher, D. *Synth. Met.* **2000**, *111*−*112*, 173.
(11) Whitehead, K. S.; Grell, M.; Bradley, D. D. C.; Jandke, M.; Strohriegl, P. *Appl. Phys. Lett.* **2000**, *76*, 2946.
(12) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* **2000**, *77*, 406.
(13) Whitehead, K. S.; Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Synth. Met.* **2000**, *111*−*112*, 181.
(14) Grell, M.; Redecker, M.; Whitehead, K. S.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P.; Wu, W. *Liq. Cryst.* **1999**, *26*, 1403.
(15) Nothofer, H.-G.; Meisel, A.; Miteva, T.; Neher, D.; Forster, M.; Oda, M.; Lieser, G.; Sainova, D.; Yasuda, A.; Lupo, D.; Knoll, W.; Scherf, U. *Macromol. Symp.* **2000**, *154*, 139.
(16) Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M. *Acta Polym.* **1998**, *49*, 439.
(17) Fytas, G.; Nothofer, H. G.; Scherf, U.; Vlassopoulos, D.; Meier, G. *Macromolecules* **2002**, *35*, 481.
(18) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, 1992.
(19) Kroschwitz, J. I. *Polymers: Polymer Characterization and Analysis*; Wiley Interscience: New York, 1990.
(20) Strobl, G. *The Physics of Polymers*, 2nd ed.; Springer-Verlag: Berlin, 1997.
(21) Anwer, A.; Windle, A. H. *Polymer* **1991**, *32*, 103.
(22) Moore, J. S.; Stupp, S. I. *Macromolecules* **1987**, *20*, 282.
(23) Anwer, A.; Windle, A. H. *Polymer* **1993**, *34*, 3347.
(24) DeGennes, P. G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: New York, 1993.
(25) Chuang, I.; Turok, N.; Yurke, B. *Phys. Rev. Lett.* **1991**, *66*, 2472.
(26) Shiwaku, T.; Nakai, A.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1990**, *23*, 1590.
(27) Elias, F.; Clarke, S. M.; Peck, R.; Terentjev, E. M. *Macromolecules* **2000**, *33*, 2060.

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