Influence of the Casting Solvent on the Thermotropic Alignment of Thin Liquid Crystalline Polyfluorene Copolymer Films

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ABSTRACT: The morphology of a conjugated polymer thin film determines how it will behave as an active layer in optoelectronic devices. The liquid crystalline phase present in some conjugated polymers offers a unique way of controlling the film morphology. For example, films in which the chains are aligned in a single direction can be fabricated by processing films on a templating layer and annealing them above the liquid crystalline melting point of the polymer. However, the ability to align to a templating layer will be influenced by the character of the as-cast film. This effect was examined by casting poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) films from a range of both aromatic and chlorinated solvents on top of rubbed polyimide layers and aligning via the thermotropic melt. Measurements of the dichroic ratio as a function of annealing time revealed that films cast from high boiling point aromatic solvents like isodurene (ISO) and *o*-xylene (OXY) aligned well with a maximum dichroic ratio over 10. Films cast from toluene (TOL), a lower boiling aromatic solvent, exhibited a lower $D_{\max}$ of only around 5, while the films cast from chloroform (CHL) and tetrachloroethane (TCE), both chlorinated solvents, exhibited very low dichroic ratios. The best alignment ($D_{\max} = 15$) was achieved when a F8BT film was annealed while still “wet”, which proves that a plasticizer (in this case ISO molecules) can improve the mobility of the polymer chains as they initially align to the rubbed surface. However, it is unclear whether a plasticizing effect (from residual solvent) is responsible for the differences in the alignment observed in films that were dried before annealing, as $D_{\max}$ for these samples did not directly correlate to the volatility of the solvent. Ellipsometric measurements showed that all the films that aligned well exhibited a much more dramatic densification upon annealing than those that did not align well. Since all the well-aligned films were cast from aromatic solvents, we believe that aromatic interactions between polymer and solvent is critical in spinning a film that will align well. These results will guide future efforts into improving molecular orientation of liquid crystalline polyfluorene films.

Introduction

Processing techniques that facilitate a higher degree of macroscopic order in conjugated polymer films are desirable to improve the viability of conjugated polymers for both display[1] and transistor applications.[2] The thermotropic liquid crystalline phase exhibited by some polyfluorene thin films has been used as a potential way to fabricate light-emitting diodes with high polarization ratios[3−5] and increase the mobility of charges in polymer transistors.[6] The influence of many different factors on the macroscopic order achievable in liquid crystalline conjugated polymer films has already been investigated. Grell et al. showed that a polyfluorene polymer with a branched side chain was more conducive to ordering than a polymer with a straight side chain due to an effective increase in the axial ratio of the mesogen and a possible reduction of the polymer viscosity in the melt.[7,8] In a recent study of a polyfluorene copolymer of three different chain lengths, we showed that the viscosity of the polymer is a paramount consideration when considering both the achievable macroscopic order and alignment times.[9] Low molecular weight polymers align both quicker and to higher degree than their higher molecular weight counterparts.

The molecular architecture and length of the polymer chain are the most critical factors in determining how molecules will move and order in the solid state. However, when a film is cast from solution, the choice of casting solvent will affect its initial morphology and thus could influence the ability of molecules to order in the solid state. Both the boiling point and the polarity of the casting solvent can affect the morphology of the film. Polymer molecules will adapt different conformations in solvents of varying polarity. In a good solvent the polymer molecule will have an extended conformation, and in a bad solvent the polymer is more likely to fold up upon itself.[10] Researchers have recently noticed that the conformational differences in solution will be carried into the spin-casted films. Nguyen et al. used light scattering to show that the hydrodynamic radius of a common PPV-based polymer (MEH−PPV) is twice as large in a chlorobenzene solution as it is in tetrahydrofuran.[11] Since the polymer adopted a more extended conformation in chlorobenzene, it was reasoned that it is a better solvent for MEH−PPV. Spectroscopic results showed that the polymer had a greater tendency to aggregate in solution when the polymer was in its most extended conformation. Evidence of interchain interactions was also found in films cast from the “aggregated” solution, and it was believed that these interactions were further promoted by the high boiling point of the solvent that allowed the film to dry slowly.[11] Yang et al. also observed a solvent-dependent film morphology.[12] They used X-ray diffraction results to show that the crystallinity of MEH−PPV films was dependent on the solvent used to drop-cast the film. Finally, the composition of the spin-casted film could vary with casting solvent. Frank et al. showed a large amount of residual solvent can be left in a spin-casted film.[13] This behavior would likely be highly dependent on the volatility of the solvent and specific solvent−polymer interactions. Re-

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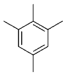
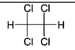
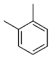
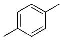
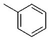
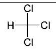
Table 1. Chemical Structure, Boiling Point, Estimated Cohesion Parameter, and the Estimated Polar Component of the Cohesion Parameter for the Solvents Used in This Study

Solvent	Structure	Boiling Point (°C)	Hoy's Cohesion Parameter[a] δ_t ($\mathrm{Mpa}^{1/2}$)	Polar Component[b] δ_p($\mathrm{Mpa}^{1/2}$)
Isodurene (ISO)		198	18.9	3.3
Tetrachloroethane (TCE)		147	23.8	14.5
o-Xylene (OXY)		144	20.3 (18.5)	3.3
p-Xylene (PXY)		138	20.9 (18.1)	3.8
Toluene (TOL)		110	21.1 (18.3)	4.9
Chloroform (CHL)		61	26.0 (18.7)	18.2

[a] Hoy's cohesion parameters were calculated using the group molar method explained in section 6.2 of ref 17. The group contributions are shown in Table 7 (Chapter 6) in the reference. Empirical values for the total cohesion parameter are given for selected solvents in parentheses.[17] [b] The polar component was calculated using Hoy's group contribution eq 34 (Chapter 6) in ref 17. The group contributions are shown in Table 7 of that chapter, and the δ_t used was the one calculated above.

gardless of why it stays in the film, it is expected that residual solvent will affect the mobility of the polymer molecules during the initial templating stage.

Recent studies have already shown the morphology of polyfluorene thin films are also affected by the solvent from which they are cast. Grell et al. showed that a second phase associated with a more extended chain conformation will be formed when poly(9,9-dioctylfluorene) (F8 or PFO) films are cast or exposed to "moderately poor" solvents.[14] Here we will examine how the initial morphology of spin-casted F8BT films can be influenced by the casting solvent and, more importantly, how the initial morphology affects the polymer when it is aligned in the thermotropic melt to an alignment layer.

Experimental Section

Poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) was obtained from Cambridge Display Technology and was used without further purification. The polystyrene equivalent molecular weight of the polymer was determined by gel permeation chromatography. The number-average was determined to be 110 000, and the peak average molecular weight was 240 000. Six solvents representing a wide polarity and volatility range were selected as casting solvents for F8BT films. Five of the solvents [tetrachloroethane (TCE), *p*-xylene (PXY), *o*-xylene (OXY), toluene (TOL), and chloroform (CHL)] were purchased from Aldrich Chemicals in a highly pure form (>95%) and thus were used directly as received. A high-purity isodurene (ISO) was obtained through collaboration with Cambridge Display Technology. Selected properties of each solvent are shown in Table 1. The cohesion parameter is a measure of the attractive interactions between molecules in the liquid phase. There have been many techniques used to determine the cohesion parameters of liquids; however, a table including all the solvents listed above was not found. Therefore, to gather comparative quantities for the cohesion parameter of these solvents, a group contribution method was used to calculate their values.[15] The Hoy cohesion parameter (δ_t) takes into account all interactions between molecules (dispersive, polar, and hydrogen bonding).[15] The polar component (δ_p) of the total cohesion parameter was estimated using Hoy's methods.

It was important that films cast from each solvent were of similar thickness; therefore, the solution concentration was varied from 8 to 17 g/L to ensure that when cast with a 2000 rpm spin speed the film thickness was near 90 nm. All the solutions (except the chloroform solutions) were heated to 80 °C to ensure the F8BT was completely dissolved. Solutions were always reheated to 80 °C before films were cast.

Templating layers were prepared following the techniques established in the literature.[8] A Merck Liquicoat ZL1 2650 polyimide solution (30 g/L) was prepared and spin-casted at 2000 rpm on a cleaned soda-lime glass slide. The film was dried at 90 °C for 10 min before being cured at 310 °C for 4 h under vacuum. After curing the film thickness was 100 nm. The substrates with the PI layer were cleaned again in acetone and 2-propanol prior to rubbing. Large (3 in. by 1 in.) substrates were rubbed with a commercial machine equipped with a rayon cloth and then cut into 12 approximately 1 cm by 1 cm squares. Only samples that were prepared from the same initial substrate were compared directly.

A Hewlet-Packard HP8453 UV−vis spectrometer equipped with a calcite cube polarizer was used to measure the dichroic ratio. Spectra of the aligned films were taken with the polarizer oriented parallel and perpendicular to the rubbing direction. The absorption at the peak of these spectra was divided by each other to give the dichroic ratio. For dichroic ratios up to 15, the error due to scattering effects and baselines corrections was no greater than 10%. These effects become more important when the absorption is smaller; thus, there is less confidence in dichroic ratios above 15.

Changes in the morphology or amount of residual solvent in the F8BT films cast from the different solvents was studied with a M-2000 J.A. Woollam spectroscopic ellipsometer. For these measurements films were cast on silicon substrates that were supplied with only the native oxide layer. For every measurement, a spectroscopic scan was taken at three angles of incidence (60°, 65°, and 70°). The thickness and refractive index were extracted from the data by determining the values that best fit the ellipsometric parameters (Δ and Ψ). Only the long wavelengths (550−900 nm) were used in the fitting process to avoid the effect of optical absorption. To aid the fitting process, the change in the refractive index of the polymer film as a function of wavelength was confined to the Cauchy relationship. Since the oxide layer was so thin, its effect on the optical properties of the silicon substrate was ignored when determining the best fits to the ellipsometric data.

Results

Polymer Aggregation. Table 1 shows how the cohesion parameter varies for the solvents selected for this study. Poor solubility of the polymer in a solvent can induce aggregation of the polymer molecules that is subsequently transferred to the film upon casting. Aggregation will change the electronic structure of the ground state of the polymer and thus can be detected by changes in the absorption spectrum. Therefore, an absorption spectrum was taken of a film cast from each solvent on a templating PI layer. The spectra in Figure 1 show two peaks associated with the two separate electronic transitions in F8BT. The broad longer wavelength peak centered near 465 nm was used to measure the dichroic ratio throughout this study, and the fact that the ratio is usually substantial indicates that this transition is polarized along the chain. The peak near

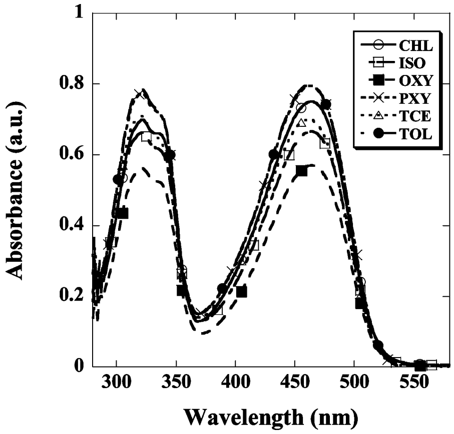


Figure 1. Absorption spectra of 90 nm thick F8BT films cast from different solvents onto a rubbed polyimide layer. These spectra were taken immediately after the film was cast.

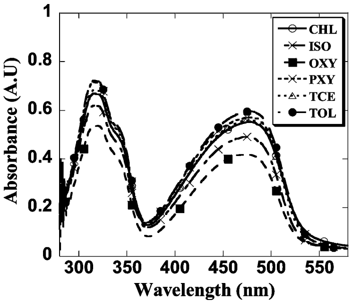


Figure 2. Absorption spectra the same F8BT films shown in Figure 1. These spectra were taken after the films were annealed at 282 °C for 1 min.

320 nm always exhibits a lower dichroic ratio, which is indicative of the transition not being as highly polarized along the chain. This suggests that this absorption band is formed between a delocalized and localized state.[16] The lower wavelength peak also exhibits a shoulder around 340 nm. This is most likely associated with another excited state and is currently under further investigation. Figure 1 clearly shows that the spectrum of F8BT does not change when it is cast from the different solvents. This suggests that there is no solvent-induced change in the aggregation behavior of F8BT films when they are cast from the solvents selected for this study. This does not discount solvent-induced changes to excited-state structures (or excimers), which could be more sensitive to subtle morphological changes in the polymer.

Another absorption spectrum was taken of the films after they were annealed for 1 min, and these spectra are shown in Figure 2. A few subtle changes are observed when these spectra are compared to those of the as-spun films. The peak at 320 nm is much more pronounced in the annealed films, and the shoulder at 340 nm is weaker. Also, the higher wavelength peak has been slightly red-shifted (now about 475 nm) in all the films. This can be attributed to the higher dielectric constant and longer effective conjugation length in the F8BT films that became more dense during the annealing process.

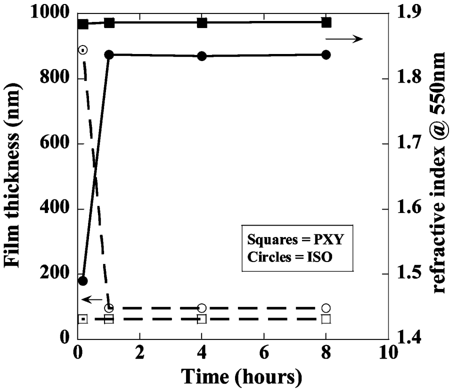


Figure 3. Change in the thickness and refractive index of F8BT films as a function of time after spin-casting as determined by ellipsometry. The *y* error bars (determined by the quality of the fit of the model to the ellipsometric parameters) are smaller than the size of each point. The squares are indicative of films cast from PXY, and the circles are cast from ISO. Filled shapes are refractive index values, and open shapes are thickness values. Lines were added to act as a guide.

Densification of F8BT Films after Casting. Solvent will be left in polymer films after spin-casting.[13] The amount of solvent left will be a function of the casting solvent and the processing conditions used to cast the film. These differences were examined by monitoring the density of as-cast F8BT films using ellipsometry. Before the data are presented, it should be noted that the measurements here assume that the refractive index of the film is isotropic. It is known that the refractive index in the plane of a spin-casted conjugated polymer film is much larger than the out-of-plane index, and precise measurements of the film thickness require the use of an anisotropic model.[18] However, modeling an anisotropic index requires transmission data[18] that could not be obtained with films cast on silicon, as they were for this study. Using an isotropic model for an anisotropic film will yield a value for the film thickness that is too thin.[19] However, since the data for this study are meant primarily for a relative comparison between films cast from different solvents, an isotropic model was used despite its limitations.

By continuously monitoring the thickness and the refractive index of the film after casting, the ellipsometer should be sensitive to any solvent left in the film that evaporates away over time. The films cast from ISO were visibly “wet” after casting and slowly dry as they age. A F8BT film was cast from ISO on a silicon wafer and placed on the sample stage of the ellipsometer. The first ellipsometric measurement was taken 10 min after the film was cast. The film was left on the sample stage, and ellispometric measurements were taken intermittently over an 8 h span. For comparison purposes, a similar test was performed with a film cast from PXY. The results are shown in Figure 3. The ISO film started with a film thickness close to 900 nm and a refractive index of 1.49. After 1 h the film had shrunk to 95 nm thick with a refractive index of 1.84. The 90% reduction in the film thickness and increase in the index (and therefore the density of the film) confirms the presence of solvent in the cast film, the majority of which evaporates away within the first hour of aging. In contrast, the PXY film exhibited an initial thickness of 62 nm and a refractive index of 1.88, both of which did not change in the subsequent measurements throughout the 8 h span. Therefore, the F8BT films cast from ISO using the processing conditions in this study will produce films that are “wet” immediately after casting but that dry within an hour. The ellipsometer was not sensitive to any changes in the film morphology which occur in F8BT films cast from PXY that are aged at room temperature.

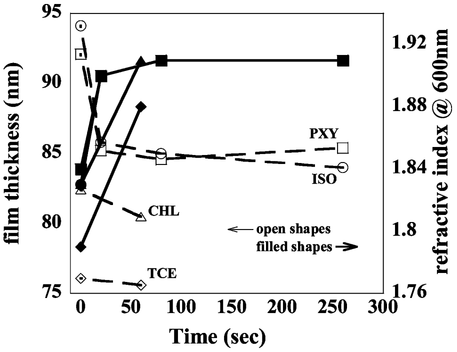


Figure 4. Change in the thickness and refractive index of F8BT films as a function of annealing time at 282 °C as determined by ellipsometry. The *y* error bars (determined by the quality of the fit to the ellipsometric parameters) are smaller than the size of each point. The squares are indicative of films cast from PXY, circles are films cast from ISO, and the triangles are films cast from CHL. Filled shapes are refractive index values, and open shapes are thickness values. Because of the complication of annealing in a controlled atmosphere environment, the as-cast film was a different film from the film that was subsequently annealed. The whole process is explained in more detail in the text.

The ellipsometric results in Figure 3 showed that no change in the refractive index or thickness of the PXY film occurred after the film was cast. However, small amounts of residual solvent can be entrapped in the glassy polymer as the film forms. The increase in the molecular mobility that occurs in the molten polymer should allow any entrapped solvent to escape. Therefore, the thickness and refractive index of F8BT films were monitored as a function of time in the molten phase using the ellipsometer. This study was complicated by the fact that the films needed to be annealed in a controlled atmosphere environment to limit the effect of oxidation. Therefore, films were annealed at 282 °C (which is 10 °C higher than the melting point for this polymer) for a short period of time in the glovebox, quenched to room temperature, and brought out of the glovebox to be tested, and then the process was repeated. However, to bring a sample into the glovebox, it is passed through a vacuum chamber (which is pumped down to about 75 mTorr), which could affect the concentration of entrapped solvent. Thus, for this study two films were needed: One was cast outside the glovebox and tested prior to annealing. The other was cast in the glovebox and used for the subsequent annealing study. It is important to note that all films were allowed to age for 1 h before testing or annealing to ensure they all started in the "dry" state seen in Figure 3.

Figure 4 shows the change in the refractive index and thickness of the PXY and ISO films as a function of annealing time. The most dramatic change in both parameters happens within the first 20 s of annealing. During that time there was a 9% reduction in the measured thickness of the ISO film and an 8% reduction in the measured thickness of the PXY film. Supplementary experiments showed that this densification cannot be attributed to the differences in the environment from which each film was cast. Compared to the initial 20 s annealing step, little change in the film thickness of either film was observed for the additional annealing times. In both cases the reduction in the film thickness had a corresponding increase in the refractive index, which suggests a much denser film. As mentioned above, the change in the measured refractive index cannot be exclusively attributed to densification of the film, as there is probably a significant contribution due to the change in the anisotropy induced by the formation of the liquid crystalline phase. It is, however, interesting to note that the refractive index of each film is approximately the same after annealing, which suggests the molecular packing and ordering reaches the equilibrium configuration regardless of solvent. However, the most important observation from Figure 4 is that ellipsometry is sensitive to changes that occur in the film morphology or composition when it is annealed. It also shows that most of these changes happen within the first minute of annealing.

Table 2. Comparison of the Thickness and Refractive Index of F8BT Films in the As-Cast State and after Annealing for 1 min at 282 °C[a]

solvent	thickness, nm (as-cast)	n_{600} (as-cast)	thickness, nm (annealed)	n_{600} (annealed)	% thickness reduction
ISO	118.7 ± 0.1	1.87	106.0 ± 0.3	1.97	10.7
PXY	92.3 ± 0.1	1.84	87.0 ± 0.1	1.91	6.7
OXY	88.6 ± 0.1	1.80	71.5 ± 0.1	1.86	19.3
TOL	109.1 ± 0.1	1.87	95.5 ± 0.1	1.93	12.5
TCE	76.1 ± 0.1	1.79	75.6 ± 0.1	1.88	0.6
CHL	82.4 ± 0.1	1.83	80.5 ± 0.1	1.90	2.3

[a] Both properties were determined using ellipsometry, and the error bars were determined by the quality of the fit of the model to the ellipsometric data. The ISO and PXY films are different films from the ones tested for Figure 3.

Also included in Figure 4 is the result from a similar study performed with a F8BT film cast from TCE and CHL. Since it was established that most of the changes in the thin film morphology occurs within the first minute of annealing, these films were annealed at 282 °C for only 1 min, and no subsequent annealing was performed. The index change in the TCE and CHL films is similar to that observed in the ISO and PXY films, but the change in the thickness is noticeably smaller. Films were cast from all seven of the selected solvents and tested using the same method as used for the two chlorinated solvents. Table 2 shows the thickness and refractive index of both the as cast and annealed films. Assuming that all the films that have been annealed at 282 °C reach an equilibrium morphology or density, the changes in the refractive index observed in the annealed films are probably thickness induced. This is supported by the fact that the refractive index of the annealed films correlates well with the thickness variation between samples. The morphology of the films (and orientation of polymer molecules) can change with film thickness,[19] and it is clear that the refractive index is sensitive to those changes. Therefore, the changes in the measured index cannot be independently associated with changes in the density of the as-spun films. However, the reduction in the measured thickness of different films does not correlate with film thickness. All the films cast from solvents with an aromatic group in the chemical structure (TOL, ISO, PXY, and OXY) showed at least a 6% reduction in the film thickness after annealing. The two chlorinated solvents (CHL and TCE) showed very little change in the film thickness after annealing.

The difference in the thickness reduction between the films can be attributed to either a less dense initial state or a more dense final state in the films cast from aromatic solvents. All the annealed films exhibited a similar pattern of birefringence when viewed in an optical microscope equipped with crossed polarizers, which suggests that they all had the same densely packed morphology after being cooled from the liquid crystalline melt. Therefore, we believe the difference in the thickness reduction for the films cast from the various solvents is due to less dense initial state in those cast from the aromatic solvents. This could be associated with entrapped solvent or conformational differences, yielding a less dense initial morphology.

Alignment Properties for Films Cast from Different Solvents. The ellipsometry results showed that the there are morphological differences in F8BT films cast from six different solvents. The effect of these differences on the alignment properties of F8BT was studied by monitoring the alignment kinetics. A method similar to the one previously reported for F8BT films of different molecular weights was used.[9] A slight variation was that the study was done once with the films cast in the glovebox and once with the films cast outside the glovebox. The films cast outside the glovebox were placed in a vacuum port (75 mTorr) for about 1 min prior the first annealing step, which could affect the concentration of residual solvent. Both sets of films were placed on a hot stage set at 282 °C for a finite time, quenched to room temperature on a metal surface, and brought out of the glovebox to measure the dichroic ratio, and then the process was repeated with another annealing step. For the set of the films cast in the glovebox, one film cast from ISO was annealed immediately after spinning, and another was dried for 1 h before being annealed.

The dichroic ratio as a function of annealing time was plotted for each set of films and is shown in Figure 5. The data were fit using eq 1, and the alignment times and maximum dichroic ratios are shown in Table 3. There are differences between the two sets of films which shows that the vacuum step does influence the alignment process. Those differences will the discussed in more detail below. However, it is important to note some similarities between the two set of films. All the films cast from TCE and CHL did not align well. The dichroic ratios for these films were still slowly increasing after annealing for close to 3 h. Since the fit assumes saturation of the dichroic ratio, the τ obtained from the fits for these films would be too short; thus, they are not reported in Table 3. The films cast from ISO exhibited the highest dichroic ratios and aligned the fastest in both studies. The films cast from OXY and PXY both aligned to a saturated dichroic ratio, while the films cast from TOL aligned better than those cast from chlorinated solvents but not as well as from the other aromatic solvents.

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

One obvious anomaly between the two set of films is the alignment behavior of both ISO films. The ISO films that were cast in the glovebox aligned 5 times quicker than one cast in the fume hood, and the maximum dichroic ratio was also significantly higher. The $D_{\max}$ was highest for the film first annealed when wet. This confirms that residual solvent does play a role in improving the dichroic ratio in the ISO films. Table 3 shows that the change was not as dramatic for the other films, but slightly faster alignment times and higher dichroic ratios are mostly observed from the films that were not exposed to the vacuum. This suggests that residual solvent is aiding the alignment process for all the films to some degree.

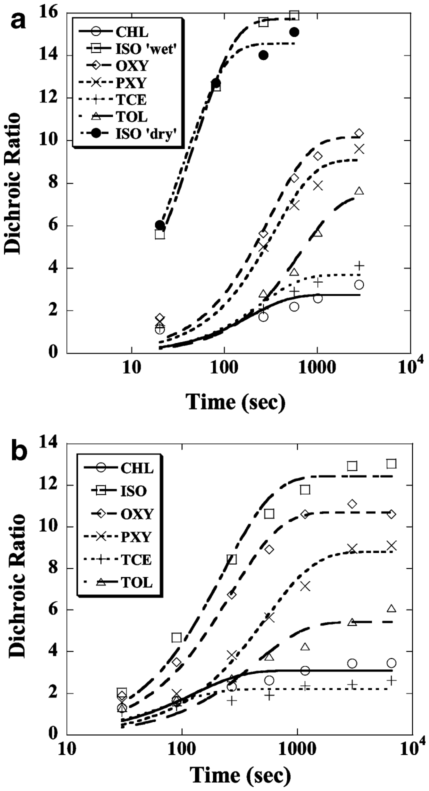


Figure 5. Dichroic ratio plotted as a function of annealing time for F8BT films cast from different solvents and aligned at 282 °C. The films were initially cast in glovebox (a) or in the fume hood and exposed to vacuum prior to annealing (b). The "wet" ISO film is indicative of film annealed 10 min after casting, and the dry film was annealed over an hour after casting (a "wet" film was only tested with those cast in the glovebox). The data were fit to eq 1, and the lines represent the result of the fit.

Table 3. Maximum Dichroic Ratio and Alignment Times for F8BT Films Cast from Different Solvents in the Glovebox and Fume Hood[a]

	glovebox		fume hood	
solvent	$D_{\max}$	τ (s)	$D_{\max}$	τ (s)
CHL	2.8 ± 0.3		3.1 ± 0.2	
ISO(dry)	14.6 ± 0.4	38 ± 4	12.4 ± 0.4	230 ± 28
OXY	10.2 ± 0.4	309 ± 45	10.7 ± 0.3	264 ± 28
PXY	9.1 ± 0.4	345 ± 60	8.8 ± 0.5	526 ± 91
TCE	3.7 ± 0.4		2.2 ± 0.2	
TOL	7.5 ± 0.7	650 ± 177	5.4 ± 0.5	
ISO(wet)	15.7 ± 0.2	48 ± 2		

[a] The quantities were determined by fitting the curves seen in Figure 5a,b to eq 1. The error bars were determined by the quality of the fit.

Another important observation from comparing the two sets of data is the large increase in the dichroic ratio of ISO film in the initial stages of annealing. The ISO film cast in the glovebox exhibited a dichroic ratio of over 5 after only 20 s, while the ISO film brought into the glovebox through a vacuum port exhibited a dichroic ratio near 2. This coupled with the ellispometry results showing that the densification of the film occurs within the first minute of annealing suggests that this minute is the most critical to the alignment process.

Figure 5 shows that films cast from only three solvents (PXY, OXY, and ISO) aligned well. However, it was discovered that even films cast from these solvents did not align well, if after casting they were allowed to sit (or for the purpose of this study: age)

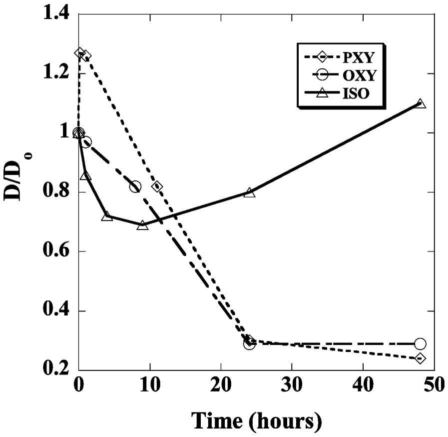


Figure 6. Dichroic ratio (D) as a function of aging time for F8BT films cast from three different solvents. Multiple films were cast on rubbed polyimide layers from the same initial substrate and aged a finite time before being aligned at 282 °C. One film was annealed immediately, and its dichroic ratio is D_0. The PXY films were 40 nm thick and annealed for 14 min, the OXY were 90 nm thick and annealed for 10 min, and the ISO films were 90 nm thick and annealed for 5 min. The lines are there only as a guide.

before being annealed into the thermotropic phase. To quantify this effect, multiple films were cast from each solvent onto rubbed polyimide layers that were all from the same initial substrate. One film cast from each solvent was immediately brought into the glovebox and annealed at 282 °C for at least as long as it took to reach a saturated dichroic ratio in Figure 1. After a finite aging time the same annealing process was performed for another film. This was continued to obtain data for aging times as long as 2 days. The dichroic ratio as a function of aging time for the three casting solvents is seen in Figure 6. The slight increase in the dichroic ratio of the PXY film over the first hour of aging can be attributed to the error intrinsic to measuring high dichroic ratios (around 10% for these films) and small variations in the templating ability of the polyimide layers. However, the film aged for 9 h had a significantly lower dichroic ratio than the initial film, and after a full day of aging the dichroic ratio was only about 20% of its initial value. A similar behavior is observed in the films cast from OXY. The films cast from ISO showed a small decrease in the dichroic ratio at short aging times, but the fact that large dichrioc ratios are again observed after aging for 2 days would suggest that the initial decline is insignificant.

The reduction of the dichroic ratio with aging time is an important observation from the prospective of consistently obtaining well-aligned films. In an attempt to understand this effect, we took optical micrographs under crossed polarizers of the aged films. These confirmed that no matter how long the film was aged it became birefringent after being annealed to 282 °C. So the aging effect cannot be attributed to an inability to form the liquid crystalline phase. Other possible explanations include residual solvent escaping from the film, a loss in the templating ability of the rubbed PI, or some delamination of the dry F8BT film from the rubbed surface; however, none of these can be confirmed. Regardless of the mechanism, the observation of films not aligning when they are left for more than hour after casting before annealing needs to be accounted for when studying liquid crystalline alignment in thin polymer films.

Discussion

It is instructive to compare the alignment properties seen in Table 3 to the physical properties of the casting solvents listed in Table 1. The weakest alignment was observed in the CHL and TCE films. Table 1 shows that these two chlorinated solvents differ from the rest in two significant ways. First, they have the largest cohesion parameters, mainly due to a large polar contribution. Second, they are the only two that lack a conjugated ring within the structure. The four other films were cast from solvents that had similar cohesion parameters. The $D_{\max}$ for these films scaled with the boiling point of the casting solvent.

It is apparent from comparing Table 2 to the alignment results seen in Table 3 that the density of the starting state is critical to the alignment process. All the films that exhibited a significant reduction in the film thickness after annealing went on to align relatively well. The most obvious difference between the solvents from which F8BT aligned (ISO, PXY, OXY, and TOL) and those that in which it did not (TCE and CHL) is the presence of an aromatic group. This is especially true for the TCE compared to OXY, which have an almost identical boiling point. Specific interactions between aromatic groups are currently being investigated due to their importance in molecular recognition processes.[20] The aromatic ring has been described as a positively charged σ-framework sandwiched between two negatively charged π-electron clouds. The size of the negatively charged electron cloud will be affected by the substituents added to the aromatic ring. Electrostatic considerations make a stacked interaction unfavorable, and the two rings would prefer to be positioned offset to one another or in an edge-to-face orientation.[20] However, the π-electron surface is nonpolar; thus, the stacked morphology could become more favorable in the presence of a polar solvent.[20] Thus, two potential mechanisms for a solvent-induced change in the initial morphology can be envisioned. The first is a specific interaction that can occur between the aromatic groups in the polymer and the solvent. This could explain a large amount of entrapped solvent in the polymer films that subsequently escapes when annealed. The second potential mechanism is that more polar chlorinated solvents promote the formation of stacked aromatic interactions between F8BT molecules (or that the aromatic solvents prevent them). This would induce a more densely packed initial morphology that is more difficult to align.

Figure 5 also showed that the ISO films which were not exposed to vacuum prior to annealing aligned much quicker and to a higher degree than those which had been placed in the vacuum port. The results from the ellipsometer showed that a significant amount of solvent is left in the ISO film after spinning. Any small solvent molecules left in the film would act as a plasticizer for F8BT, reducing the effective viscosity of the film and thus allowing for easier alignment of the molecules. This could be used as a viable way to improve the alignment of liquid crystalline polymers to templating surfaces.

Conclusions

The highest degree of macroscopic order was observed in films that were cast from an aromatic solvent and annealed while still “wet”. This can be attributed to the plasticizing effect of solvent molecules during the reorientation process. The macroscopic order induced in films that were allowed to dry did not directly correlate with the boiling point of the solvent and was especially poor in films cast from chlorinated solvents. This is best illustrated by the difference between the films cast from the aromatic solvent OXY ($D_{\max} = 10.2$) and the chlorinated solvent TCE ($D_{\max} = 3.7$), which have the same boiling point. Ellipsometric results showed that all the films cast from aromatic solvents showed a dramatic densification upon annealing that did occur in the films cast from chlorinated solvents. This is potentially due to a looser initial morphology in films cast from aromatic solvents which is facilitated by the presence of aromatic interactions between the solvent and polymer.

The macroscopic order achievable by melting a conjugated polymer film into a thermotropic liquid crystalline phase on a templating substrate is dependent on the solvent from which the film was initially cast. By careful selection of casting solvent higher degrees of order can be obtained. This could lead to polymer light-emitting devices with higher polarization ratios, making them a more attractive option for applications like polarized backlights in liquid crystal displays. Also, the higher degree of macroscopic order will improve the intrachain transport of charges, which will increase the mobilities of charges in polymer semiconductors currently used for transistor applications.

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