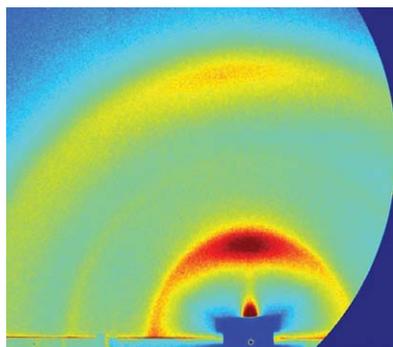


POLYMER ALIGNMENT

Alignment layers can be used to fabricate ordered polymer films for applications in electronics such as polarized organic light-emitting diodes, anisotropic field-effect transistors, and polarization-sensitive photodiodes. Traditionally, rubbed polyimide films have been used to create such alignment, but this method requires high-temperature baking and rubbing in addition to thermal annealing, causing mechanical damage, dust generation and incompatibility with plastic substrates. On page 725 of this issue, Shaw Chen and colleagues introduce a room-temperature processing technique. A coumarin-based polymer was irradiated to create the alignment layer, on which a conjugated oligomer film was solution cast for solvent-vapor annealing to create a monodomain oriented active layer. The researchers achieved orientational order parameter values identical to those on traditional rubbed polyimide layers using the new, low-temperature technique.



SOLAR CELLS

Adding small amounts of alkane dithiols to the processing solution has been shown to increase the efficiency of some polymer/fullerene solar cells, but the mechanism underlying the improvements has been difficult to elucidate. On page 717 of this issue, Tiziano Agostinelli and colleagues study the effects of 1,8-octanedithiol (ODT) on the microstructure of a small bandgap polymer blended with a fullerene derivative. They find that enhanced crystallization and an improved percolating fullerene network are achieved, leading to improvements in the devices' efficiency. However, the bimolecular recombination rate also increases upon addition of ODT, limiting the power conversion efficiency to values below those expected from the energy levels of the polymer. Spectroscopic ellipsometry measurements allow them to offer some explanations for this behavior.

Coming soon Look for these important papers in upcoming issues of Polymer Physics

Ellis S. Kempner

Direct Effects of Ionizing Radiation on Macromolecules

DOI: 10.1002/polb.22250

Chloé Chevigny, Nicolas Jouault, Florent Dalmas, François Boué and Jacques Jestin

Tuning the Mechanical Properties in Model Nanocomposites: Influence of the Polymer-Filler Interfacial Interactions

DOI: 10.1002/polb.22246

Russell J. Stewart, Todd C. Ransom, and Vladimir Hlady

Natural Underwater Adhesives

DOI: 10.1002/polb.22256

All our articles are available online in advance of print. The articles listed here have been judged by either the referees or the editor to be very important, and were immediately copyedited, proofread and published online. As long as there is no page number available, online manuscripts should be cited in the following manner: Authors, *J. Polym. Sci. Part B: Polym. Phys.*, online publication date, DOI

Room-Temperature Processing of π -Conjugated Oligomers into Uniaxially Oriented Monodomain Films on Coumarin-Based Photoalignment Layers

Simon K.-H. Wei,¹ Lichang Zeng,¹ Kenneth L. Marshall,² Shaw H. Chen^{1,2}

¹Department of Chemical Engineering, University of Rochester, Rochester, New York 14627-0166

²Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623-1212

Correspondence to: S. H. Chen (E-mail: shch@lle.rochester.edu)

Received 14 December 2010; revised 18 February 2011; accepted 18 February 2011; published online 21 March 2011

DOI: 10.1002/polb.22235

ABSTRACT: Photoalignment layers comprising **Polymer 1** were prepared using linearly polarized UV-irradiation for chloroform-vapor annealing of π -conjugated oligomer films, both processes conducted at room temperature. The resultant uniaxially oriented monodomain films exhibited $S = 0.74$ (at $P_r = 0.90$) and 0.82 (at $P_r = 0.95$) in **OF** and **OF2T** films, respectively, apparently limited by film dewetting in comparison to $S = 0.82 \pm 0.01$ from thermal annealing on rubbed polyimide alignment and **Polymer 1** photoalignment layers. The time to arrive at maximum S values varied from 5–10 s to 6–8 min on rubbed polyimide alignment layers and **Polymer 1** photoalignment layer, respectively, because of favorable π - π interactions

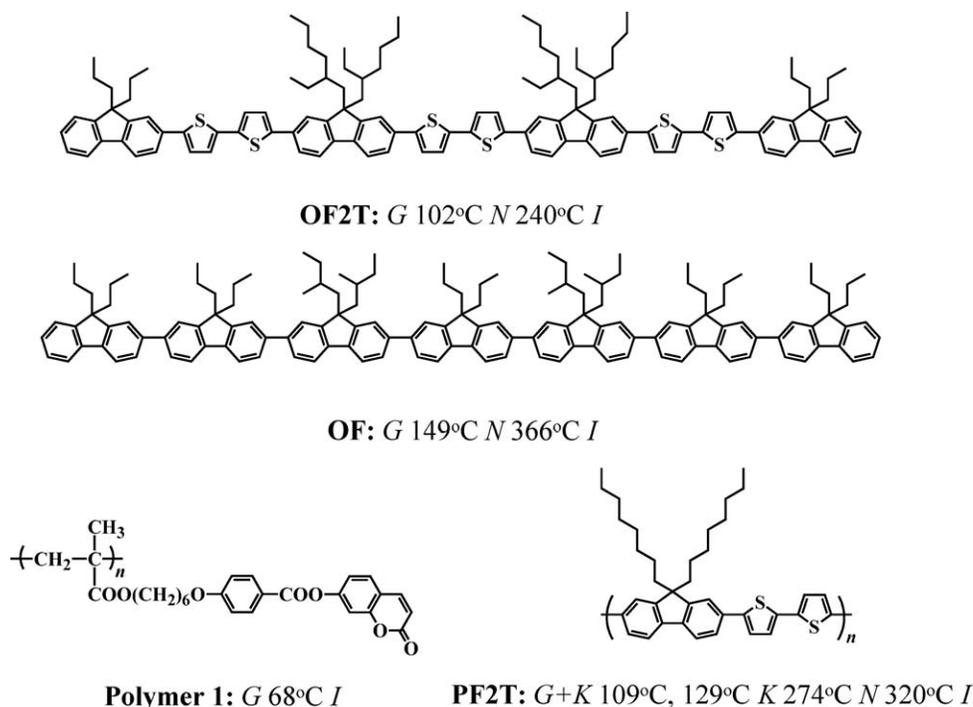
enhanced by rubbing. In contrast, **PF2T** could not be oriented on either type of alignment layers after annealing under saturated chloroform vapor up to 14 h. Annealing of an **OF2T** film under saturated chlorobenzene vapor at room temperature permitted lyotropic nematic mesomorphism to be observed in situ, which is equivalent to thermotropic nematic mesomorphism as the driving force behind thermal annealing. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 49: 725–731, 2011

KEYWORDS: annealing; conjugated oligomers; oligomers; orientation; oriented films; vapor annealing

INTRODUCTION Polymers and monodisperse oligomers with an extended π -conjugation in amorphous, crystalline, and liquid crystalline morphologies have found numerous potential applications to electronics and photonics,^{1–7} most notably in light-emitting diodes, field-effect transistors, and photovoltaic devices. Uniaxial orientation of conjugated backbones enables polarized light emission as energy-efficient backlights for liquid crystal displays,⁸ anisotropic charge transport to suppress crosstalk in logic circuit and pixel switching elements,⁹ and polarization-sensitive photodiodes for sensing applications.^{10–12} Monodomain glassy-nematic films have been accomplished with poly(flourene)s,^{13,14} poly(flourene-co-bithiophene)s,¹⁵ and monodisperse oligo(flourene)s,^{16–20} and oligo(flourene-co-bithiophene)s²¹ films through thermal annealing above their glass-transition temperatures on rubbed polyimide, PEDOT:PSS, and poly(*p*-phenylenevinylene) alignment layers with subsequent cooling to room temperature. To overcome the problems arising from rubbing, e.g., mechanical damage and the generation of dust and electrostatic charges, photoalignment induced by polarized UV-irradiation has emerged as an attractive alternative. Three distinct material approaches have been demonstrated: axis-selective degradation of polyimides,^{22–26} cis–trans isomerization of azobenzenes,^{27–29} and cycloaddition of cinnamates,^{30–34} or coumarins.^{35–42} Orientational order parameter values emulating those on rubbed polymer alignment layers

have been realized via thermal annealing of films comprising π -conjugated polymers^{43,44} and oligomers^{39,40} on photoalignment layers.

In a recent article,²¹ we have reported the first demonstration of chlorobenzene-vapor annealing at room temperature of oligo(flourene-co-bithiophene) films on rubbed polyimide alignment layers. The resultant monodomain glassy-nematic films, referred to hereafter as uniaxially oriented monodomain films, were as well ordered as those from thermal annealing at 110 to 120 °C, i.e., 10 °C above glass-transition temperatures. Nonetheless, the preparation of polyimide alignment layers involved high-temperature baking. To pave the way for plastic electronics, it is highly desirable to develop room-temperature processing of oriented films, including the preparation of alignment layers. This study was motivated to develop a new process in which both the preparation of photoalignment layer and solvent-vapor annealing are conducted at room temperature. A coumarin-containing polymer was chosen for its superior thermal and photochemical stability without complication from photo-induced isomerization.^{31,35} Specific objectives are identified as follows: (i) solvent-vapor annealing of conjugated oligomers into uniaxially oriented monodomain films; (ii) elucidation of how vapor absorption affects the vapor annealing process; (iii) lyotropic nematic mesomorphism as the driving force for solvent-vapor annealing; (iv) effectiveness of



Symbols *G* for glass transition, *N* for nematic mesomorphism, *I* for isotropic liquid, and *K* for crystallization or crystalline melting

CHART 1 π -Conjugated Oligomers and Coumarin-Based Polymer 1 for Photoalignment under Present Investigation.

solvent-vapor annealing on photoalignment layers versus rubbed polyimide alignment layers, and that of solvent-vapor annealing versus thermal annealing on rubbed polyimide alignment layers; and (v) demonstration of uniaxially oriented monodomain films on plastic substrates.

EXPERIMENTAL

Materials

The molecular structures of all materials used in this study are depicted in Chart 1. The synthesis and properties of **OF**, **OF2T**, and **Polymer 1** have been reported previously;^{16,21,39} **Polymer 1** was characterized to have a number average molecular weight of 8,960 g mol⁻¹ and a polydispersity index of 4.6. The polymer analog of **OF2T** and **PF2T** with a number-average molecular weight of 36,200 g mol⁻¹ and a polydispersity index of 3.1, was used as received from American Dye Source (Quebec, Canada); its thermotropic properties have been reported earlier.²¹ The differential scanning calorimetry (DSC) data accompanying the molecular structures in Chart 1 were collected from 20 °C min⁻¹ heating scans of samples that had been preheated to isotropic liquids and then quenched at -100 °C min⁻¹ to -30 °C using a DSC-7 (Perkin-Elmer). The nature of the phase transition was characterized by hot-stage polarizing optical microscopy (DMLM, Leca; FP90 central processor and FP82 host stage, Mettler Toledo), which was also used to observe vapor annealing of an **OF** film under saturated chlorobenzene in a sealed element at room temperature.

Preparation and Characterization of Polymer 1

Photoalignment and Rubbed Polyimide Alignment Layers

Photoalignment layers were prepared by spin casting a 0.1-wt % solution of **Polymer 1** in chloroform at 4000 rpm on optically flat fused silica substrates (25.4-mm diameter \times 3.0-mm thickness, EscoProducts) transparent to 200 nm, producing photoalignment layers with a thickness of 10 nm determined by variable angle spectroscopic ellipsometry (V-VASE, Woollam). After vacuum drying at room temperature for 3 h, the **Polymer 1** films were irradiated at room temperature under an argon atmosphere using a 500 W Hg-Xe lamp (model 66142, Oriel) equipped with optical filters (model 87031, Oriel and model XUVB280, Asahi), allowing transmission from 300 to 330 nm. The transmitted light was linearly polarized using a polarizing beam splitter (HPB-308 nm, Lambda Research Optics). The irradiation intensity was monitored by a UVX digital radiometer coupled with a UVX-31 sensor (UVP). The extent of coumarin dimerization, *X*, was determined by the diminishing absorbance of coumarin monomers at 310 nm with UV-vis-NIR spectrophotometry (Lambda 900, Perkin-Elmer). The insolubility of irradiated films was ascertained by UV-vis absorption spectroscopy after submerging in liquid chloroform for 2 min. Polyamic acid solution in 2-butoxyethanol (Sunever grade 610 polyimide varnish, Nissan) was diluted with a mixed solvent, 2-ethoxyethanol:2-butoxyethanol at a 4:1 volume ratio, for the preparation of 15-nm-thick films by spin coating on fused silica substrates, followed by soft-baking at 80 °C for 10 min, hard

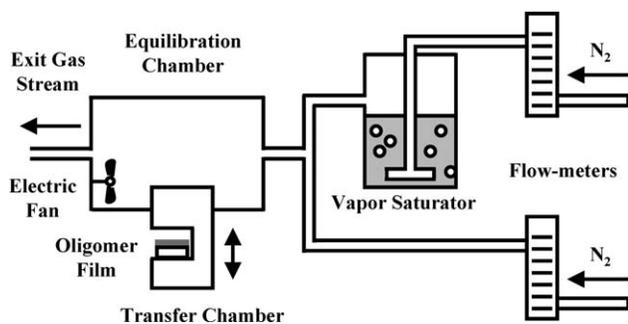


FIGURE 1 A schematic diagram of the apparatus for solvent-vapor annealing under controlled partial pressure.

curing at 250 °C for 1 h, and uniaxial rubbing with a velvet fabric for use as an alignment layer.

Preparation and Characterization of Oriented π -Conjugated Oligomer Films

Conjugated oligomer films were prepared by spin coating from 1.0-wt % chloroform solutions at 2000 rpm onto substrates containing either **Polymer 1** or polyimide alignment layers. The spin-cast films were dried under vacuum at room temperature for 3 h, before solvent-vapor annealing using the apparatus shown in Figure 1. Defined as the solvent partial pressure over its vapor pressure (P_s) at room temperature, the relative vapor pressure (P_r) in the equilibration chamber was controlled by mixing a vapor-saturated nitrogen gas stream with a pure nitrogen stream at varying ratios of volumetric flow rates regulated by flow meters (R-03227-12 150 mm flow-meter, Cole-Parmer). After allowing for sufficient purge time through the equilibration chamber, the oligomer films on **Polymer 1** photoalignment layers and rubbed polyimide alignment layers were loaded into the equilibration chamber to start solvent-vapor annealing at room temperature for predetermined durations and then vacuum-dried at room temperature for 3 h. Thermal annealing of conjugated oligomer films on rubbed PI alignment layers was performed under an argon atmosphere at 10 °C above the conjugated oligomers' glass-transition temperatures for varying annealing times. The dried films were characterized for their thickness using a white light optical profilometer (Zygo NewView 5000).

Absorption dichroism of the oriented conjugated oligomer films was characterized using a Lambda 900 UV-vis-NIR spectrophotometer equipped with linear polarizers (HNP'B, Polaroid) for the calculation of orientational order parameter, $S = (R - 1)/(R + 2)$, in which the dichroic ratio R represents the absorbance parallel divided by that perpendicular to the direction of linearly polarized UV-irradiation of **Polymer 1** photoalignment layer or the rubbing direction on polyimide alignment layer. Micrographs of the oriented films were taken with a digital camera (MicroPix C-1024) mounted on a polarizing optical microscope (Leitz Orthoplan-Pol). The phase and topography images of the oriented films were recorded on a Nanoscope III atomic force microscope (AFM, Digital Instrument) in tapping mode with a NT-

MDT NSG01 cantilever at a scan rate of 1 Hz under ambient condition. Films for electron diffraction were prepared under the same conditions except on sodium chloride substrates (International Crystal Laboratories) and then floated off in a trough filled with deionized water for mounting onto copper grids. Electron diffraction patterns were collected on a transmission electron microscope (FEI Tecnai F20). For a demonstration of solvent-vapor annealing on a plastic substrate, **OF** films were prepared and characterized on poly(allyl diglycol carbonate) substrate (CR-39, 25.4 × 25.4 × 1.5 mm³ thickness) with a UV absorption cutoff at 380 nm (track analysis systems, TASTRAK) following the same procedures as described above for fused silica substrate. The solvent and UV resistance of the CR-39 substrates were demonstrated by UV-vis absorption spectroscopy after submerging in liquid chloroform for 2 min and UV irradiation to a fluence of 1.0 J cm⁻².

RESULTS AND DISCUSSION

Approximately 90-nm-thick **OF** films were prepared by spin coating on fused silica substrates containing 10-nm-thick **Polymer 1** photoalignment layers, which had been irradiated with 1.0 J cm⁻² to $X = 0.31$ using linearly polarized light between 300 and 330 nm, followed by vacuum drying at room temperature for 3 h. In principle, a good solvent for the conjugated oligomer and one that is also relatively volatile at room temperature would be effective for solvent-vapor annealing. As a good solvent for **OF** and with $P_s = 170$ mmHg at 22 °C, chloroform was tested for vapor annealing of **OF** films with 25-min purge by flushing two incoming gas streams through the equilibration chamber as shown in Figure 1. The S values are plotted as a function of exposure time in Figure 2 for films dried *in vacuo* after vapor annealing at $P_r = 0.75$ to 0.90. Doubling the purge time resulted in essentially the same S profiles shown in Figure 2, thereby justifying 25 min as sufficient for the equilibration chamber

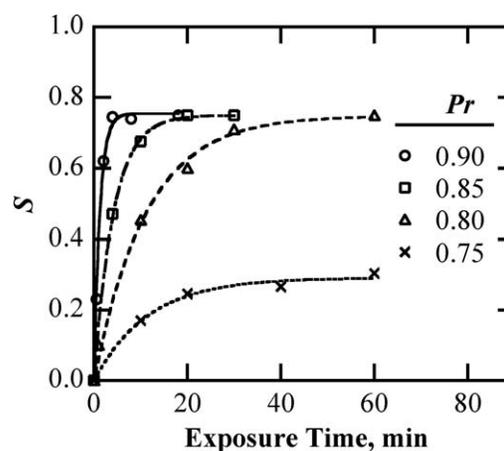


FIGURE 2 S of 90-nm-thick spin-cast **OF** films on 10-nm-thick **Polymer1** photoalignment layers with $X = 0.31$ as a function of exposure time to chloroform vapor at specified P_r values preceded by 25-min purge. The data points are accompanied by an error of ± 0.03 overall.

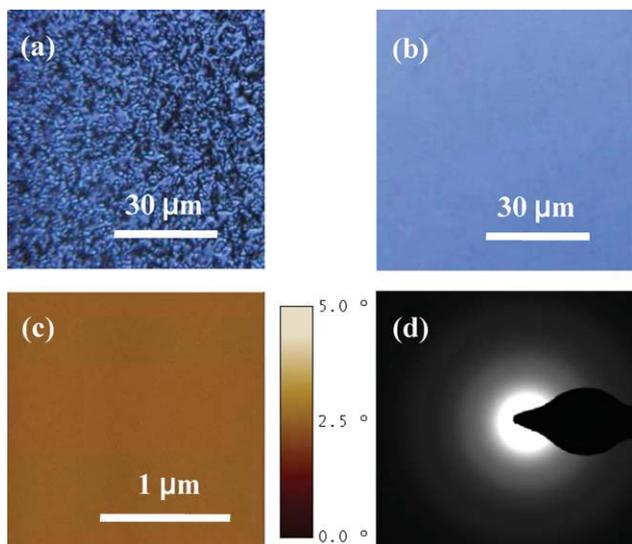


FIGURE 3 Polarizing optical micrographs of 90-nm-thick **OF** films on 10-nm-thick **Polymer 1** photoalignment layers at $X = 0.31$ annealed with chloroform vapor at $P_r = 0.90$ followed by vacuum drying, both conducted at room temperature. (a) 1/2-min exposure to yield polydomain glassy-nematic film with $S = 0.23$, and (b) 8-min exposure to yield uniaxially oriented monodomain film with $S = 0.74$. The uniaxially oriented monodomain film was further characterized by atomic force microscopy for phase contrast in (c), and its noncrystalline morphology by electron diffraction in (d).

to reach the intended P_r values. The curves through data points represent the least-squares fit to yield asymptotic S values at long exposure times. The **OF** film was found to be dewetted at $P_r = 0.95$, which limited solvent-vapor annealing to an asymptotic S value of 0.74 at $P_r = 0.90$. The S profiles presented in Figure 2 indicate that the time to reach the asymptotic S value increases with a decreasing P_r value, suggesting a fast absorption equilibrium of the **OF** film with ambient chloroform vapor relative to the time for **OF** molecules to orient themselves with the underlying photoalignment layer. This observation is consistent with time for the **OF** film on an impermeable substrate to reach equilibrium with chloroform vapor, $\tau \sim 4d^2/D_{12}$, where d and D_{12} denote the **OF** film thickness and the diffusivity of chloroform (subscript 1) in the **OF** film (subscript 2), respectively.⁴⁵ Given that $d = 90$ nm encountered herein and that $D_{12} \geq 10^{-10}$ $\text{cm}^2 \text{s}^{-1}$ at room temperature,⁴⁶ τ is estimated on the order of seconds or less, which is orders of magnitude shorter than the solvent-vapor annealing time.

The last two data points for $P_r = 0.90$ and 0.85 and the last data point for $P_r = 0.80$ at the longest exposure times presented in Figure 2 correspond to uniaxially oriented monodomain films, and the rest to polydomain films. The polydomain and monodomain characteristics of glassy-nematic films are illustrated by the polarizing optical micrographs shown in Figure 3. A polydomain glassy-nematic film is readily identifiable with threaded textures as shown in Figure 3(a), whereas a uniaxially oriented monodomain film

across the 2-cm-diameter fused silica substrate is characterized by the absence of threaded textures, Figure 3(b), and the compositional and morphological uniformity revealed by the AFM phase image shown in Figure 3(c). Moreover, a root-mean-square roughness of 0.35 nm resulted from the AFM topography image. That the vapor-annealed film is noncrystalline is verified by the electron diffraction pattern shown in Figure 3(d). In principle, room-temperature processing of oriented π -conjugated oligomer films should be applicable to plastic substrates. Indeed, chloroform-vapor annealing at $P_r = 0.90$ of an **OF** film on a CR-39 substrate coated with a **Polymer 1** photoalignment layer irradiated with 1.0 J cm^{-2} to $X = 0.30$ produced a uniaxially oriented monodomain film with $S = 0.75$, the same value as that on a fused silica substrate within experimental error.

In addition to **OF**, **OF2T** films were tested for annealing by chloroform vapor. The results presented in Figure 4 in comparison to those in Figure 2 reveal a delayed arrival at asymptotic S values by **OF2T** compared to **OF** films at the same P_r values. Under the condition of fast absorption equilibrium, **OF** films must have been more absorptive of chloroform vapor than **OF2T** films at the same P_r , which also appeared to be responsible for the **OF** film to undergo film dewetting at a lower P_r value than **OF2T**, 0.95 versus 1.00. As a result, a higher asymptotic S value of 0.82 was achieved at $P_r = 0.95$ in **OF2T** film than 0.74 at $P_r = 0.90$ in **OF** film. Recall that thermal annealing of these two films on rubbed polyimide alignment layers produced essentially the same S value, 0.83 for **OF**¹⁶ and 0.82 for **OF2T**²¹ annealed at 160 and 115 °C, respectively, despite the difference in their molecular structures. Thermal annealing of **OF** and **OF2T** films on **Polymer 1** photoalignment layers at 185 and 155 °C also

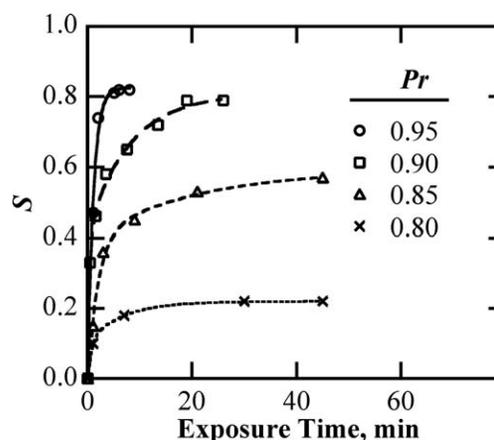


FIGURE 4 S of 90-nm-thick **OF2T** films on 10-nm-thick **Polymer 1** photoalignment layers with $X = 0.31$ as a function of exposure time to chloroform vapor at specified P_r values followed by vacuum drying at room temperature for 3 h. At $P_r = 1.00$ over 1/2 and 1 min exposure, $S = 0.28$ and 0.00 (dewetting), respectively. The reported S values are accompanied by an experimental error of ± 0.02 overall. The last two data points at $P_r = 0.95$ correspond to uniaxially oriented monodomain films, and the rest to polydomain glassy-nematic films.

TABLE 1 S Values of **OF2T**, **OF**, and **PF2T** Films after Annealing with Chloroform Vapor at 22 °C on **Polymer 1** and Rubbed Polyimide Alignment Layers

	Alignment Layer ^{a,b}	Asymptotic S , Exposure Time
OF2T ^c	Polymer 1	0.82, ^d 6 min
	rubbed PI	0.82, ^d \leq 5 s
OF ^e	Polymer 1	0.74, ^f 8 min
	rubbed PI	0.74, ^f 10 s
PF2T ^g	Polymer 1	0.00, ^h 14 h
	rubbed PI	0.00, ^h 8 h

^a $X = 0.31$, 10-nm-thick **Polymer 1** photoalignment layers.

^b 15-nm-thick rubbed polyimide alignment layers.

^c 90-nm-thick **OF2T** films on **Polymer 1** photoalignment and rubbed polyimide alignment layers.

^d $P_r = 0.95$, film dewetting at $P_r = 1.00$.

^e 90-nm-thick films **OF** on **Polymer 1** photoalignment and rubbed polyimide alignment layers.

^f $P_r = 0.90$, film dewetting at $P_r = 0.95$.

^g 55-nm-thick **PF2T** films on **Polymer 1** photoalignment and rubbed polyimide alignment layers.

^h $P_r = 1.00$ without film dewetting.

produced $S = 0.82 \pm 0.01$. It is concluded (i) that solvent-vapor annealing on **Polymer 1** photoalignment layer at room temperature could achieve the same S value as conventional thermal annealing on rubbed polyimide alignment layer, and (ii) that the highest S values achieved in **OF2T** and **OF** films with chloroform-vapor annealing are determined largely by maximum solvent contents without encountering dewetting.

The results from solvent-vapor annealing of **OF**, **OF2T**, and **PF2T** films on **Polymer 1** and rubbed polyimide alignment layers are summarized in Table 1. Regardless of the underlying alignment layers, the same maximum S values—namely, 0.82 and 0.74 for **OF2T** and **OF**, respectively—resulted from annealing with chloroform vapor at room temperature. The

time to achieve asymptotic S values, however, increased from 5 to 10 s on rubbed polyimide alignment layers to 6–8 min on **Polymer 1** photoalignment layers. The difference in time scale can be interpreted as polyimide alignment layer offering π – π electronic interactions with **OF2T** and **OF** molecules. Along the rubbing direction, grooves were generated and polyimide backbones were reoriented on the alignment layer surface, both conducive to uniaxial orientation of overlying nematic liquid crystal molecules thanks to the enhanced π – π interactions.^{47,48} These two factors are absent on the **Polymer 1** photoalignment layer without rubbing, where liquid crystal orientation is dictated by coumarin dimers through molecular interactions of dispersive and steric origins at the early stage of photodimerization before cross-over,³⁸ e.g., $X = 0.31$ as implemented in this study.

Although polydomain glassy-nematic films were shown to result from vacuum drying after chloroform vapor annealing [e.g., Fig. 3(a)], it would be informative to observe the evolution of mesomorphism during the annealing process. As noted above, both **OF** and **OF2T** films lost their physical integrity to dewetting by chloroform vapor at $P_r \leq 1.00$. In principle, a solvent less volatile than chloroform is desired for *in situ* observation at $P_r = 1.00$. Having a low vapor pressure, chlorobenzene was selected for annealing an **OF2T** film under its saturated vapor, $P_s = 10$ mmHg at 22 °C. The low chlorobenzene content in the **OF2T** film is the reason for the long 40 min annealing time to asymptotic S value, as shown in Figure 5(a). The low chlorobenzene content during vapor annealing of **OF2T** films is also responsible for the modest asymptotic $S = 0.56$ in the thoroughly dried film, inferior to 0.82 achieved with chloroform. The polarizing optical micrograph is shown in Figure 5(b) for *in situ* observation of an **OF2T** film after exposure to saturated chlorobenzene vapor for 40 min, indicating lyotropic nematic mesomorphism as the driving force behind solvent-vapor annealing of a solid film at room temperature well below its glass-transition temperature at 102 °C.

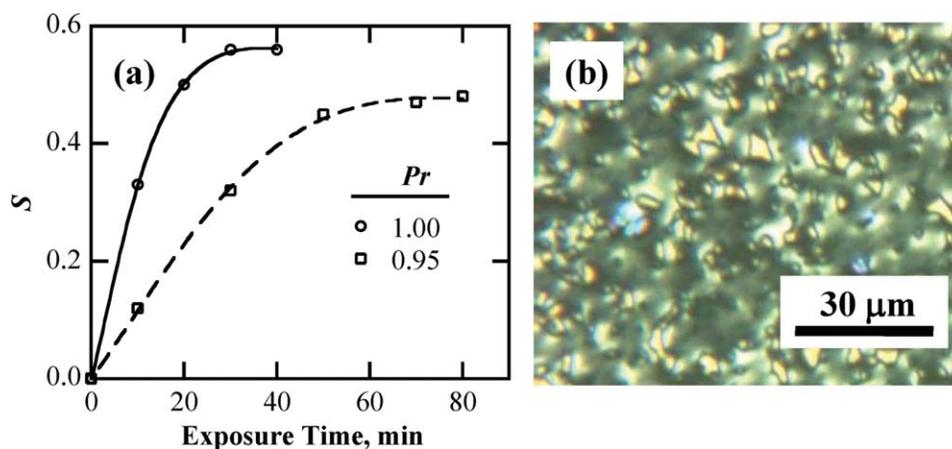


FIGURE 5 90-nm-thick **OF2T** films on 10-nm-thick **Polymer 1** photoalignment layers with $X = 0.31$: (a) S of polydomain glassy-nematic films as a function of exposure time to chlorobenzene vapor at specified P_r values followed by vacuum drying at room temperature for 3 h; (b) *In situ* polarizing optical micrograph of lyotropic nematic mesomorphism upon exposure to saturated chlorobenzene vapor for 40 min.

The chlorobenzene content in **OF2T** film, however, can be substantially increased by spin coating from a chlorobenzene solution under its own vapor at a predetermined P_r value to slow down solvent evaporation. As an expedient approach, quasi-solvent annealing was performed by spin coating in air from a chlorobenzene solution onto rubbed polyimide alignment layer before subjecting the relatively wet film to saturated chlorobenzene vapor to obtain $S = 0.82$.²¹ This value is identical to that observed in an **OF2T** film spin-cast from chloroform on rubbed polyimide alignment layer, dried and then exposed to chloroform vapor at $P_r = 0.95$ (see Table 1). The same observations should apply to the **Polymer 1** photoalignment layer, although the annealing time is expected to be longer than that on the rubbed alignment layer following the trend in time scale established in Table 1.

CONCLUSIONS

This article reports the first demonstration of uniaxial orientation of π -conjugated oligomers into macroscopic scale uniaxially oriented monodomain films on coumarin-containing photoalignment layers through room-temperature processing. Spin-cast films of π -conjugated oligomers, **OF**, and **OF2T**, on **Polymer 1** photoalignment layers were annealed at room temperature with chloroform vapor diluted by nitrogen gas to varying extents to prevent film dewetting. In place of **Polymer 1** photoalignment layers prepared at room temperature, rubbed polyimide alignment layers that had been cured at 250 °C were also used for chloroform-vapor annealing of **OF** and **OF2T** films for a comparison of maximum attainable S values in the resultant glassy-nematic films. In addition, saturated chlorobenzene vapor and a CR-39 substrate were used to unravel the driving force behind solvent-vapor annealing and to demonstrate its feasibility on plastic substrates, respectively. Key observations are recapitulated as follows:

1. As validated by polarizing optical microscopy, AFM, and electron diffraction, chloroform-vapor annealing yielded uniaxially oriented monodomain **OF** and **OF2T** films on **Polymer 1** photoalignment layers with S values of 0.74 (at $P_r = 0.90$) and 0.82 (at $P_r = 0.95$), respectively. Compared to $S = 0.82 \pm 0.01$ for **OF** and **OF2T** films with thermal annealing on both rubbed polyimide alignment layers and **Polymer 1** photoalignment layers, solvent-vapor annealing is limited by film dewetting above a threshold partial pressure of chloroform.
2. Chloroform-vapor annealing at room temperature of **OF** and **OF2T** films on rubbed polyimide alignment layers was performed to further assess the potential of **Polymer 1** photoalignment layers. Maximum S values were found to be independent of the underlying alignment layers. Because of rubbing-induced grooves and reorientation of the polyimide backbone, both conducive to π - π interactions of conjugated oligomers with the rubbed polyimide alignment layer, the orientation of conjugated oligomers on rubbed polyimide alignment layers proceeded much faster than on **Polymer 1** photoalignment layers. In contrast, **PF2T** was not amenable to solvent-vapor annealing on either alignment layer even under saturated chloroform vapor.

3. With a much lower vapor pressure than chloroform at room temperature, saturated chlorobenzene vapor facilitated *in situ* observation of lyotropic nematic mesomorphism during the solvent-vapor annealing, equivalent to thermotropic nematic mesomorphism behind thermal annealing above **OF**'s and **OF2T**'s glass-transition temperatures.
4. A uniaxially oriented monodomain **OF** film was demonstrated with $S = 0.75$ through chloroform-vapor annealing at $P_r = 0.90$ on CR-39, a plastic substrate, coated with **Polymer 1** photoalignment layer prepared at room temperature, as opposed to polyimide alignment layers requiring high-temperature processing.

ACKNOWLEDGMENTS

The authors are grateful for the financial support by the New York State Energy Research and Development Authority. Additional funding was provided by the Department of Energy Office of Inertial Confinement Fusion under Cooperative Agreement No. DE-FC52-08NA28302 with Laboratory for Laser Energetics at the University of Rochester. The support of DOE does not constitute an endorsement of DOE of views expressed in this article.

REFERENCES AND NOTES

- 1 Müllen, K.; Scherf, U. *Organic Light Emitting Devices: Synthesis, Properties and Applications*; Wiley-VCH: Weinheim, Germany, **2006**.
- 2 Klauk, H. *Organic Electronics: Materials, Manufacturing and Applications*; Wiley-VCH: Weinheim, Germany, **2006**.
- 3 Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem. Int. Ed.* **2008**, *47*, 4070–4098.
- 4 Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091.
- 5 Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868–5923.
- 6 Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323–1338.
- 7 Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3–24.
- 8 Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, *11*, 895–905.
- 9 Chou, W.-Y.; Cheng, H.-L. *Adv. Funct. Mater.* **2004**, *14*, 811–815.
- 10 Zen, A.; Neher, D.; Bauer, C.; Asawapirom, U.; Scherf, U.; Hagen, R.; Kostromine, S.; Mahrt, R. F. *Appl. Phys. Lett.* **2002**, *80*, 4699–4701.
- 11 Tanaka, H.; Yasuda, T.; Fujita, K.; Tsutsui, T. *Adv. Mater.* **2006**, *18*, 2230–2233.
- 12 Nishizawa, T.; Lim, H. K.; Tajima, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2009**, *131*, 2464–2465.
- 13 Whitehead, K. S.; Grell, M.; Bradley, D. D. C.; Jandke, M.; Strohriegel, P. *Appl. Phys. Lett.* **2000**, *76*, 2946–2948.
- 14 Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565–570.
- 15 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*, 406–408.
- 16 Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542–549.

- 17 Geng, Y.; Chen, A. C. A.; Ou, J. J.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Chem. Mater.* **2003**, *15*, 4352–4360.
- 18 Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2003**, *15*, 1176–1180.
- 19 Chen, A. C. A.; Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K. P.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2004**, *16*, 783–788.
- 20 Yasuda, T.; Fujita, K.; Tsutsui, T.; Geng, Y.; Culligan, S. W.; Chen, S. H. *Chem. Mater.* **2005**, *17*, 264–268.
- 21 Zeng, L. C.; Yan, F.; Wei, S. K.-H.; Culligan, S. W.; Chen, S. H. *Adv. Funct. Mater.* **2009**, *19*, 1978–1986.
- 22 Lu, J.; Deshpande, S. V.; Gulari, E.; Kanicki, J.; Warren, W. L. *J. Appl. Phys.* **1996**, *80*, 5028–5034.
- 23 Kim, J.-H.; Kumar, S.; Lee, S.-D. *Phys. Rev. E* **1998**, *57*, 5644–5650.
- 24 Newsome, C. J.; O'Neill, M. *J. Appl. Phys.* **2002**, *92*, 1752–1756.
- 25 Xu, C.; Shiono, T.; Ikeda, T.; Wang, Y.; Takeuchi, Y. *J. Mater. Chem.* **2003**, *13*, 669–671.
- 26 Zhong, Z.-X.; Li, X.; Lee, S. H.; Lee, M.-H. *Appl. Phys. Lett.* **2004**, *85*, 2520–2522.
- 27 Gibbons, W. M.; Shannon, P. J.; Sun, S.-T.; Swetlin, B. J. *Nature* **1991**, *351*, 49–50.
- 28 Furumi, S.; Ichimura, K. *Adv. Funct. Mater.* **2004**, *14*, 247–254.
- 29 Sakamoto, K.; Miki, K.; Miki, M.; Sakaguchi, K.; Hijikata, Y.; Chikamatsu, M.; Azumi, R. *J. Appl. Phys.* **2010**, *107*, 113108-1–113108-9.
- 30 Schadt, M.; Schmitt, K.; Kozinkov, V.; Chigrinov, V. *Jpn. J. Appl. Phys.* **1992**, *31*, 2155–2164.
- 31 Ichimura, K.; Akita, Y.; Akiyama, H.; Kudo, K.; Hayashi, Y. *Macromolecules* **1997**, *30*, 903–911.
- 32 Kawatsuki, N.; Goto, K.; Kawakami, T.; Yamamoto, T. *Macromolecules* **2001**, *35*, 706–713.
- 33 Shenoy, D.; Beresnev, L.; Holt, D.; Shashidhar, R. *Appl. Phys. Lett.* **2002**, *80*, 1538–1540.
- 34 Kawatsuki, N.; Yamashita, A.; Kondo, M.; Matsumoto, T.; Shioda, T.; Emoto, A.; Ono, H. *Polymer* **2010**, *51*, 2849–2856.
- 35 Schadt, M.; Seiberle, H.; Schuster, A. *Nature* **1996**, *381*, 212–215.
- 36 Obi, M.; Morino, S.; Ichimura, K. *Chem. Mater.* **1999**, *11*, 656–664.
- 37 Jackson, P. O.; O'Neill, M.; Duffy, W. L.; Hindmarsh, P.; Kelly, S. M.; Owen, G. J. *Chem. Mater.* **2001**, *13*, 694–703.
- 38 Kim, C.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Macromolecules* **2006**, *39*, 3817–3823.
- 39 Trajkovska, A.; Kim, C.; Marshall, K. L.; Mourey, T. H.; Chen, S. H. *Macromolecules* **2006**, *39*, 6983–6989.
- 40 Kim, C.; Wallace, J. U.; Trajkovska, A.; Ou, J. J.; Chen, S. H. *Macromolecules* **2007**, *40*, 8924–8929.
- 41 Kim, C.; Wallace, J. U.; Chen, S. H.; Merkel, P. B. *Macromolecules* **2008**, *41*, 3075–3080.
- 42 Droge, S.; O'Neill, M.; Lobbert, A.; Kitney, S. P.; Kelly, S. M.; Wei, P.; Dong, D. W. *J. Mater. Chem.* **2009**, *19*, 274–279.
- 43 Sainova, D.; Zen, A.; Nothofer, H.-G.; Asawapirom, U.; Scherf, U.; Hagen, R.; Bieringer, T.; Kostromine, S.; Neher, D. *Adv. Funct. Mater.* **2002**, *12*, 49–57.
- 44 Fujiwara, T.; Locklin, J.; Bao, Z. *Appl. Phys. Lett.* **2007**, *90*, 232108.
- 45 Welty, J. R.; Wicks, C. E.; Rorrer, G.; Wilson, R. E. *Fundamentals of Momentum, Heat, and Mass Transfer*, 4th ed.; Wiley: New York, **2001**; p 541.
- 46 (a) Chang, M.-J.; Liao, Y.-H.; Myerson, A. S.; Kwei, T. K. *J. Appl. Polym. Sci.* **1996**, *62*, 1427–1436; (b) Gupper, A.; Kazarian, S. G. *Macromolecules* **2005**, *38*, 2327–2332.
- 47 Stohr, J.; Samant, M. G.; Cossy-Favre, A.; Diaz, J.; Momoi, Y.; Odahara, S.; Nagata, T. *Macromolecules* **1998**, *31*, 1942–1946.
- 48 Lee, S. W.; Chae, B.; Lee, B.; Choi, W.; Kim, S. B.; Kim, S. I.; Park, S.-M.; Jung, J. C.; Lee, K. H.; Ree, M. *Chem. Mater.* **2003**, *15*, 3105–3112.