Coumarin-Based Polymer Films for Photoalignment of Liquid Crystals

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Introduction

- Orientation of liquid crystals
 - Mechanical rubbing widely practiced for its simplicity
 - Physical damage, dust particles, electrostatic charges
 - Photoalignment, a noncontact method involving polarized UV irradiation of polymer films
 - Photoalignment amenable to patterning for wide viewing angles in LCDs and tunability in electrooptic devices
- Three distinct approaches to photoalignment
 - Anisotropic degradation of polyimide
 - *Cis-trans* isomerization of azobenzene
 - Anisotropic dimerization of cinnamate or coumarin
- Photoalignment demonstrated for
 - Liquid crystal fluids, electrooptic devices
 - Conjugated oligomers and polymers, OLEDs and OFETs
 - Polarized OLEDs, anisotropic field-effect transistors

Chemical Ingredients Serving Photoalignment Polymer Films



Polarized UV-induced cis-trans isomerization



Photoreactive Polymers as Photoalignment Layers





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Schadt, M. et al. Jpn. J. Appl. Phys. 1992, 31, 2155-2164.



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Principle of Photoalignment Based on Dimerization of Coumarin Moieties as Pendants to Polymer Backbones



- Intensity of UV-irradiation absorbed by coumarin monomer proportional to $\cos^2\theta$, where θ is the angle between absorption dipole and polarization axis
- Spontaneous orientation of liquid crystals follows "sergeants-and-soldiers rule"
- Photoalignment behaviors are dictated by progression in dimerization without axis-selective chemical decomposition

Motivation and Objectives

- Quantitative interpretation of LC orientation through kinetic modeling of photodimerization
- Coumarin chosen for illustration
 - Thermal and photochemical stability without isomerization
 - Potential for a wide range of tilt angle
- Specific Aims:
 - To characterize the extent of photodimerization, X, in polymer films enabled by synthesis of coumarin dimers
 - To construct a kinetic model with experimental validation for X as a function of irradiation per unit area, *i.e.* fluence
 - To calculate orientational order parameters for coumarin monomers and dimers,
 S_m and S_d, as functions of X
 - To interpret LC orientation in terms of relative abundance and orientational order of coumarin monomers and dimers as well as the energetics of their interactions with LC molecules

Materials Synthesized for This Study



Absorption Spectra of PMMA Films Doped with Coumarin Monomers and Dimers



- 100-nm-thick PMMA films doped with monomers and dimers I and II at 0.10, 0.20, and 0.33 mole fractions without encountering phase separation
- Mole fractions calculated with unreacted and reacted coumarin moieties as well as methacrylate units
- Molar extinction coefficient, ε= A/IC, where A, I and C are absorbance, exact film thickness, and chromophore concentration in mole fraction
- Monomers preferentially receive UV-irradiation (300 to 320 nm) over dimers, conducive to photodimerization, more so in Monomer II than I
- X monitored by absorbance beyond dimers' absorption cutoff

Absorption Spectra of UV-Irradiated 25-nm-Thick Films of Polymers I and II as a Function of Fluence



- Presence of isobestic points reveals photostability up to 20 J/cm², further supported by FTIR spectroscopy
- Based on the definitions of ϵ for unreacted and reacted coumarin moieties converting at 1:1 molar ratio, presence of isobestic points is readily understood

Polarized Absorbance Profiles of a Dichroic Dye M-137 with Absorption Peak at 643 nm

A 10-mm-thick liquid crystal cell consists of nematic E-7 doped with M-137 at 0.3 wt% on 10-nm-thick Polymer II photoalignment layers



- The arrows indicate the direction of polarized UV-irradiation.
- Orientational order parameter, $S_{lc} = (R-1)/(R+2)$, where dichroic ratio R is absorbance parallel to that perpendicular to M-137 molecule's absorption dipole.

Summary of Characterization Data

Table 1. Mole fraction of coumarin moieties that have dimerized, X, and liquid crystal orientational order parameter, S_{lc} , as functions of fluence ^[a]

	Poly	mer I ^[b]	Po	Polymer II ^[c]		
Film thickness	24 nm		27 nm	10) nm	
Fluence, J/cm ²	X	S_{lc}	X	X	S_{lc}	
0.1 0.2 0.5 1.0 2.0 5.0 10	0.23 0.31 0.40 0.47 	0.74 0.75 0.73 0.72 0.72 0.75	$\begin{array}{c} 0.38 \\ 0.43 \\ 0.52 \\ 0.60 \\ 0.67 \\ 0.74 \\ 0.76 \end{array}$	$\begin{array}{c} 0.37 \\ 0.40 \\ 0.49 \\ 0.60 \\ 0.67 \\ 0.73 \\ 0.75 \end{array}$	0.71 0.70 0.72 ⊥ 0.72 ⊥ 0.75 	
20	0.57	0.78	0.76	0.75	$\perp 0.74$	

[a] Polarized irradiation with 4.8 mW/cm² at 90 °C; presented values for X and S_{lc} both accompanied by an uncertainty \pm 0.02; symbols || and \perp in front of S_{lc} represent a nematic director parallel and perpendicular to the polarization axis of UV-irradiation, respectively. [b] Film insolubility achieved at 0.5 J/cm². [c] Film insolubility achieved at 0.05 J/cm².

Polymer I versus Polymer II

- For the same fluence range, X saturates at 0.57 and 0.75 with Polymers I and II, respectively
 - Much higher absorption coefficient for UV-irradiation in Polymer II than I
 - Dimer I competing with Monomer I to some degree for irradiation energy
- Liquid crystal orientation undergoes crossover on Polymer II but not I because of the difference in attainable *X* and other factors

- Ellipsometry of pristine polymer films revealed a random orientation of coumarin moieties in 3-D
- Distribution of coumarin monomers, each with a radius of unity, represented as a solid sphere with uniform density



Illustration of Orientational Order through Crossover using Polarized Absorption Spectroscopy



UV–Vis absorption dichroism of 10- μ m-thick LC cells of E-7 doped with M-137 on 15-nm-thick Polymer 2 films irradiated at 96 °C to (a) 0.05 J/cm² and (b) 0.2 J/cm²; A_{\parallel} and A_{\perp} represent absorbance parallel and perpendicular, respectively, to the polarization axis of UV-irradiation.



Normalized UV-vis absorption spectra of approximately 100-nmthick films consisting of Monomer and Dimer doped in PMMA films at a mole fraction of 0.050 based on MMA monomer units

Kinetic Modeling of Photodimerization

- Polarization axis of UV-irradiation as common reference for
 - Photodimerization kinetics
 - Orientational order of coumarin monomers and dimers
 - Liquid crystal orientation on photoirradiated polymer films
- Both dipole moments and molecular axes of coumarin monomers and dimers are axisymmetric around the Z-axis, the polarized irradiation direction
- Monomer's and dimer's mole fractions, $X_m(\theta, t)$ and $X_d(\theta, t)$, and the extent of dimerization X(t), where θ is the azimuthal angle with the Z-axis:

$$\frac{dX_{d}}{dt} = -\frac{dX_{m}}{dt} = k \exp(-t/\tau) X_{m} \cos^{2} \theta$$

$$I - X_{d}(\theta, t) = X_{m}(\theta, t) = \exp\left[-A(t)\cos^{2} \theta\right] \qquad A(t) = k\tau \left[1 - \exp(-t/\tau)\right]$$

$$X(t) = \frac{\int_{0}^{\pi} X_{d}(\theta, t) \sin \theta \, d\theta}{\int_{0}^{\pi} \sin \theta \, d\theta} = 1 - \sqrt{\frac{\pi}{4A(t)}} \exp\left[\sqrt{A(t)}\right] \dots (3)$$

- Factor exp $(-t/\tau)$ introduced to account for decaying reaction rate because of the increasing barrier to dimerization as reaction proceeds
- Rate of dimerization proportional to first-order photoexcitation of coumarin monomer
- Solid angle on a sphere with unit radius and axisymmetry with respect to Z-axis, $\sin\theta d\theta$
- $X(\theta, t)$ integrated from $\theta=0$ to π results in X(t) for the entire 3-D space

Experimental Validation of the Kinetic Model



Figure 5. Monomer conversion as a function of fluence at 90 °C: (a) 24-nm-thick Polymer I film, and (b) 10-nm-thick Polymer II film. Filled circles for experimental data; solid, dashed and dotted curves representing, respectively, the best-fit to Equation (3), first-order reaction, $X(t) = 1 - \sqrt{\pi/4 kt} \operatorname{erf}(\sqrt{kt})$ with k=0.0108 and $0.0312 \operatorname{s}^{-1}$ for Polymers I and II, and second-order reaction, $X(t) = 1 - \tan^{-1}(\sqrt{kt})/\sqrt{kt}$ with k=0.0160 and $0.0532 \operatorname{s}^{-1}$ for Polymers I and II

Best fit of experimental data to Eq. (3) represented by solid curves: $k=0.0352 \text{ s}^{-1}$ and $\tau=110 \text{ s}$ for polymer I film, and $k=0.0538 \text{ s}^{-1}$ and $\tau=182 \text{ s}$ for Polymer II film

Calculation of S_m and S_d as Functions of X Using X_m and X_d Prescribed by the Kinetic Model

$$S = (3 < \cos^2 \theta > -1)/2$$

$$< \cos^2 \theta > (t) = \frac{\int_0^{\pi} f(\theta, t) \cos^2 \theta \sin \theta \, d\theta}{\int_0^{\pi} f(\theta, t) \sin \theta \, d\theta}$$

$$S_m(t) = \frac{3}{4A(t)} - \frac{1}{2} - \frac{3 \exp\left[-A(t)\right]}{2\sqrt{\pi A(t)} \exp\left[\sqrt{A(t)}\right]}$$

$$S_{d}(t) = \frac{\left[3 - 2A(t)\right]\sqrt{\pi}\operatorname{erf}\left[\sqrt{A(t)}\right] - 6\sqrt{A(t)}\exp\left[-A(t)\right]}{4A(t)\left\{\sqrt{\pi}\operatorname{erf}\left[\sqrt{A(t)}\right] - 2\sqrt{A(t)}\right\}}$$

in which $f(\theta, t)$ represents $X_m(\theta, t)$ or $X_d(\theta, t)$ as desired.

Kinetic modeling on pp. 15 and 17 is generic with application to Polymers I and II using the k and τ values presented on p.16

Profiles of S_m and S_d



- With fitted k and τ values, X and A are related through real time t.
- Open circles for discontinuity; filled circles for termini of photodimerization as *t* approaches infinity, *X*=0.55 and 0.72 for Polymers I and II, respectively.
- Perfect order: *S*=1, parallel; *S*= –0.5, perpendicular to director; *S*=0, random.
- Algebraic signs of S_m and S_d: coumarin monomers and dimers oriented largely perpendicular and parallel to polarization axis, respectively.

Quantifying Orientation of Coumarin Dimers and Monomers in 3-D as UV-Induced Photodimerization Proceeds



Macromolecules 2006, 39, 3817-3823

Interpretation of Crossover in LC Orientation

- Two limiting cases
 - − As $X \rightarrow 0$, $S_d = 0.4$ and $|S_m| = 0.0$, parallel despite $X_m >> X_d$
 - − As $X \rightarrow 1$, $|S_m| = 0.5$ and $S_d = 0.0$, perpendicular despite $X_d >> X_m$
 - Predominant role of orienting species' order parameter
- Transition from parallel to perpendicular LC orientation
 - Competition between coumarin dimers and monomers to orient liquid crystal molecules
- Three contributing factors
 - Energetics of molecular interaction with liquid crystals
 - Ichimura *et al.* (1999) and Kelly *et al.* (2001): because of planar structure and extended conjugation, coumarin monomers more favorable than dimers
 - Relative abundance and orientational order
 - Unreacted and reacted coumarin moieties on a 1:1 basis
 - Both quantified as functions of X by the kinetic model
 - Observed crossover behaviors to appraise relative importance of the three contributing factors

Interpretation of Crossover Behaviors on Polymers I and II



- Coumarin dimers and monomers motivating LC orientation
- Polymer I, no crossover up to X = 0.57
 - Coumarin dimer : monomer = 57 : 43
 - $S_d = 0.24$ and $|S_m| = 0.33$, and dimers energetically less favored
 - Relative abundance of dimers dictates LC orientation where $S_d \approx |S_m|$
- Polymer II, crossover at X = 0.67
 - $|S_m| = 0.40$ and $S_d = 0.19$, monomers energetically favored
 - Coumarin monomer : dimer = 33 : 67
 - Predominant role of monomers' order parameter beyond crossover, as in two limiting cases where the minor species dictates LC orientation

Conclusions

- A kinetic model constructed for description of orientational order of coumarin monomers and dimers in polymer films
- Kinetic model used for interpretation of LC orientation in terms of relative abundance and orientational order of motivating species, coumarin monomers and dimers in polymer film
- LC orientation on Polymer I remained parallel up to X=0.57 mainly because of dimers' numerical superiority with S_d ≈ |S_m|
- For the same fluence range, dimerization of coumarin proceeded to X=0.75 in Polymer II because of higher absorbance without dimers' competition for irradiation
- LC orientation on Polymer II underwent crossover at X=0.67, a critical point where coumarin monomers were sufficiently better ordered than dimers
- In the limiting cases of X→0 and X→1, motivating species in extreme minority dictate LC orientation because of their superior orientational order

Room-Temperature Processing of π -Conjugated Oligomers into Uniaxially Oriented Monodomain Films



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Materials Used Herein



Polymer 1: *G* 68°C *I*

PF2T: *G*+*K* 109°C, 129°C *K* 274°C *N* 320°C *I*

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

Preparation of Photoalignment Films



Macromolecules 2006, 39, 6983-6989

Spectra-Physics 9700 series illumination system

Preparation of Oligomer Films



Chem. Mater. 2003, 15, 542

Solvent Vapor Annealing Apparatus



- *Pr*: Relative vapor pressure, ratio of solvent partial pressure to solvent vapor pressure at room temperature (determined by volumetric flow rates of A and B)
- *Purge time*: Time required for the equilibration chamber to reach targeted *Pr* values (predetermined at 25 min)
- *Exposure time*: Time for an oligomer film to be equilibrated with solvent vapor (to be determined for each oligomer sample)

Characterization of Orientational Order Parameter, S





90-nm-thick **OF** films on 10-nm-thick **Polymer 1** photoalignment layers annealed with chloroform vapor at Pr=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 monodomain glassy-nematic film with S=0.74. The monodomain glassy-nematic film was further characterized by atomic force microscopy for phase contrast in (c), and its noncrystalline morphology by electron diffraction in (d).

S as Functions of Pr and Exposure Time





OF annealed with chloroform vapor



OF film dewets at Pr = 0.95

OF2T annealed with chloroform vapor



OF2T film dewets at *Pr*=1.00

Comparison with Conventional Thermal Annealing on Rubbed PI



Driving Force for Solvent Vapor Annealing



Solvent Vapor Annealing on Photoalignment versus Rubbed PI Layers

		Molecular weight (g/mol)	Alignment layer	Pr	Asymptotic <i>S</i> , Exposure time
London July	OF2T	1,769	photoalignment Rubbed PI	0.95 0.95	$0.82, 6 \min$ $0.82, \le 5s$
2020202020202020	∫ ◯ OF	1,853	photoalignment Rubbed PI	0.90 0.90	0.74, 8 min 0.74, 10 s
(PF2T	36,200	photoalignment Rubbed PI	1.00 1.00	0.00, 14 h 0.00, 8 h

Conclusions

- Room-temperature process to achieve uniaxially oriented monodomain oligomer films on photoalignment layer
- Orientational order parameter values identical to those obtained by thermal annealing on rubbed polyimide
- Applicability to plastic substrates demonstrated with CR-39
- Lyotropic liquid crystal mesomorphism as the driving force behind solvent vapor annealing