Macromol. Symp. ***154,*** *83–93 (2000)*

Anisotropic Photo-polymerization and Fluorescence Study Of Discotic Materials

Milind M. Sonpatki, Tatiana Sergan, Jack Kelly, and L.C. Chien*

Liquid Crystal Institute, Chemical Physics Interdisciplinary Programs and
NSF ALCOM Center, Kent State University, Kent, Ohio 44242, USA

SUMMARY: The discotic films were prepared by coating the solution of liquid crystalline discotic monomer and initiator onto rubbed polyimide as alignment substrate. Liquid crystalline orientation in films was freezed-in by photo-polymerization (UV light) in nematic melt. Thickness and chemical constituents of polyimide was varied so as to obtain planar or homeotropic alignment. Photo-polymerization was studied with respect to isothermal DSC, PM, high temperature IR and solubility behavior of polymerized films. Further, the alignment of discotic films was studied by polarized fluorescence. Order parameter values were compared for planar, homeotropic and for films without any alignment substrate. Higher values were obtained for planar films formed on polyimide layer than formed solely on glass surface.

Introduction

Good gray-level and contrast performance at wide viewing angles is a critical demand for direct view liquid crystal diplays (LCD). One way to achieve this is to use compensation film with opposite birefringence to that of LCD which cancels the viewing angle dependence of the retardation of liquid crystals. The goal of phase compensation is to minimize the light leakage of a LCD panel over a wide range of viewing angle by means of a compensation films. Wu[1] had reported theory of phase compensation for normally white and normally black twisted nematic (TN) cell. Further he had also reported expression for phase retardation analysis of homeotropic cell at oblique angle as[2]:

$$\Delta\Phi = \delta(\theta, \lambda) = 2\pi\,(d\Delta n)_{eff} / \lambda$$

where θ = incident angle of light in the LC medium, λ is the wavelength, and

$$(d\Delta n)_{eff} = (d/\cos\theta)\,\{[n_e n_o/(n_e^2\cos^2\theta + n_o^2\sin^2\theta)^{1/2}] - n_o\}$$

when θ is small, $$(d\Delta n)_{eff} \sim d\Delta n[1-(3\Delta n/2n_e)]\theta^2$$

Above equation reveal that film thickness, d, magnitude and sign of Δn and n_e all play important role in determining the phase retardation of LC cell.

Most liquid crystals employed in diplay applications are positively birefringent, hence, compensation films with negative birefringence is needed. Number of approaches have

CCC 1022-1360/00/$ 17.50+.50/0

been reported in literature for fabricating such compensation films. Nitto Denko, Japan have reported biaxial stretching of positively birefringence polymeric films made up of poly(vinyl alcohol), poly(carbonate) and poly(sulfone) to give negative birefringence with normal optic axis.[3] Bowing resulted during stretching is the major problem in this method. Researchers from University of Akron and Hughes Research Laboratory have reported spin coating of a polymer solution such as rigid aromatic poly(imides) so as to form negative birefringent films with normal optic axis.[4,5] Uniform film with oblique optic axis is difficult to obtain by this technique. Nippon petroleum chemical have used cholesteric side-chain liquid crystalline polyester with pitch less than the wavelength of light.[6] Due to this film becomes negatively birefringent but with optic axis normal to the plane. It is difficult to obtain oblique optic axis by this approach since the spiral axis corresponds to the optic axis. All these approaches lead to compensation films which improves viewing angle only in horizontal direction. Oblique optic axis is desired for improving viewing angle over wide range. First approach for getting films with oblique optic axis is by Rockwell.[7,8] They utilized the stacks of alternating thin layers of SiO_2 and TiO_2 taking advantage of their different refractive indices. However, method is complicated as formation of each layer requires deposition by the evaporation on a substrate film. Discotic liquid crystals can have negative birefringence relatively easily because of their disc-like shape and are expected to be easy to control the angle of the optical axis, which will allow facile designing of optical compensation films.

Recently Fuji Film Corporation has introduced such films using discotic liquid crystals having splayed director configuration.[9] Although viewing angle in both horizontal and vertical direction is improved as compared to other negative compensators, their performance still lie far from ideal behavior. In our work we found the way to obtain the desirable configuration, changing the optic axis oriented from planar to homeotropic, for discotic-based retardation films. Although number of references could be found on synthesis of discotic nematic liquid crystals,[10-12] very little work exists on controlling their alignment and fabrication of films.[9,13,14] Techniques usually used for aligning liquid crystal molecules on surface of substrate are oblique evaporation of SiO, unidirectional rubbing of suitable coated substrate and photo-alignment using ultraviolet light.

In this investigation we report fabrication of films on various rubbed polyimide substrate as well as photo-alignment of discotic liquid crystal molecule via cationic ring opening polymerization of epoxide based discotic compound. Photo-polymerization is studied by solubility, infrared spectroscopy (IR), differential scanning calorimetry (DSC) and polarizing optical microscope (POM). Further, the alignment of polymerized discotic films was evaluated by polarized fluorescence.

Experimental

Materials preparation: Hexahydroxy triphenylene and the epoxy monomer was synthesied as per the standard procedure.[15] Films were fabricated by employing 10-20 weight % solution of epoxy monomer and photo-initiator Irgacure 261 (Ciba-Gigy) (0.5 to 7.0 weight percent of monomer) in solvent (chlorinated, polar or nonpolar) on various rubbed substrates by rolling technique as well as by spin coating. Films were dried by gradual evaporation of the solvent. Polymerization was achieved in solid as well as in melt (100-130°C) under UV irradiation (intensity= 18 mw/cm^2) with exposure time 200 sec to 30 minute. (scheme 1).

Methods of characterization: IR spectra of thin film on NaCl plate formed from solution of monomer and photoinitiator in dichloromethane was recorded on a Nicolet Magna-IR 550 spectrometer before and after UV irradiation (intensity= 18 mw/cm^2). Photo-initiated polymerization experiments were carried out using Perkin Elmer DSC7 system coupled with UV light (intensity= 4 mw/cm^2). Isothermal measurements were done under N_2 atmosphere with 30-minute UV exposure time using samples (in form of films weighing from 1.0-1.5 mg) with photoinitiator. The anisotropic textures of liquid crystalline monomer and polymer were analyzed by Nikon polarizing microscope equipped with Mettler FP52 hot stage and Mettler FP5 heating controller. Polarized fluorescence spectra of polymerized films, casted on alignment substrate, were measured using Fluorolog-3 (model 3FL-11) flurometer. Polarized fluorescence was studied by placing two polarizers: one in excitation path and other in emission path. The parallel and perpendicular spectra were recorded by aligning the polarizer in emission path parallel and perpendicular to the rubbing direction of the film. The excitation wavelength was 349 nm.

Results and discussion

Monomer selection: Discotic liquid crystals tend to form columnar phase, forming non-uniform and multi-domain structure, which is undesirable for optical films. Liquid crystals with discotic nematic phase are preferable. In addition as these films has to be coated on polymer substrates, their melting temperature should be below the glass transition of polymer substrate. Further, for operation of LCD at room temperature, discotic nematic structure should be fixed. In present study, the compound synthesized has long aliphatic chain terminated with epoxide group attached as a side chains to triphenylene central core. This compound melts at103°C and shows isotropization at 172°C. DSC thermogram of this compound is represented in figure 1. Polarizing microscopy indicates distinct nematic phase as shown in figure 2.

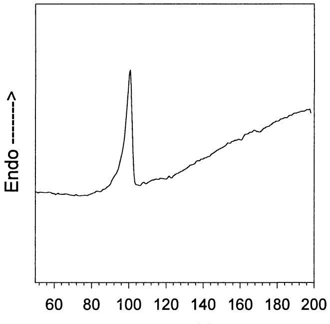


Fig 1: DSC thermogram of monomer

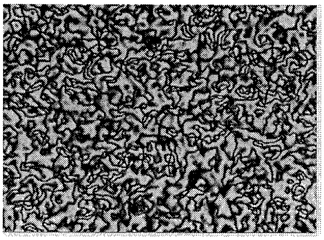
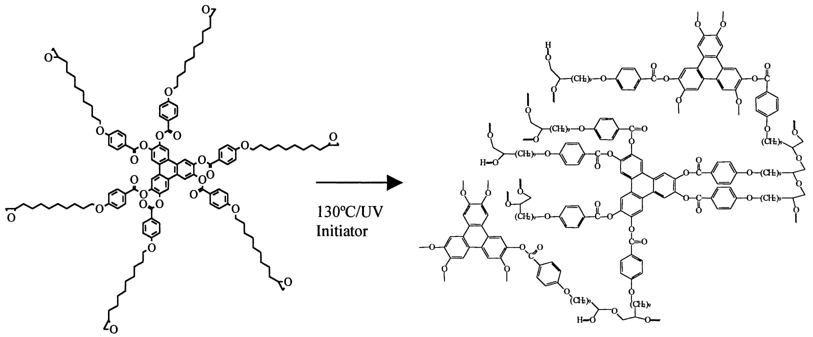


Fig 2: Nematic texture of monomer

Nematic state of this compound can be fixed by virtue of polymerization of epoxide groups.[16] Epoxides are Lewis bases and therefore their ring opening by cationic species e.g by Lewis acids is easy. Another advantage is that cationic polymerization is not affected by molecular oxygen. This makes easy film handling for fabrication and polymerization.

Film fabrication and its polymerization: Monomer is found to be soluble in variety of chlorinated solvents, polar and non-polar solvents allowing their coating on wide variety of substrates without destruction of substrate viz. rubbed glass, treated glasses, rubbed alignment layer: poly(vinyl) alcohol, poly(diallyl dimethyl) ammonium chloride and various kind of polyimide. Alignment of molecules on this substrates were found to depend on various factors such as nature and thickness of substrate, rubbing speed and pressure, coating technique i.e rolling technique and spin coating. In addition, amount of photo-initiator used and temperature employed for polymerization also plays vital role in retaining or fixation of alignment. Although, high photo-initiator concentration and temperature would increase the rate of polymerization, we observed that earlier formed planar orientation gets transformed into the homeotropic arrangement when high amount of initiator is used. Best results in terms film uniformity and planar alignment were obtained using polyimide 7511 and fluorinated polyimide. Monomer polymerization is represented in scheme 1.

It can be seen that polymerization can occur intra-molecularly i.e between adjacent epoxide units of same molecule or inter-molecularly between different monomer molecules. It is also observed that film after polymerization become insoluble in all solvents in which monomer is soluble. Such drastic change in solubility suggests that significant intra-molecularly polymerized chains must be present in addition to inter-molecularly polymerized chains. Moreover, after polymerization, both the POM and DSC studies revealed that the film did not exhibit a change in phase transition and the optical texture till 300°C.



Scheme 1: Photopolymerization of epoxy discotic monomer

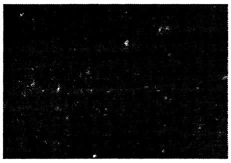


Fig. 3a: Texture of planar film

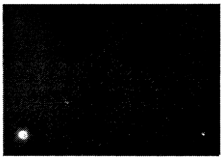


Fig. 3b: Texture of homeotropic film

Figures 3a and 3b are the photomicrographs for planar and homeotropic alignment observed under optical microscopy under crossed polarizer, respectively. Their molecular arrangements were illustrated in figures 4a and 4b. For planar film, optic axis of discs lie parallel to the alignment substrate, whereas for homeotropic film discs lie flat with their optic axis perpendicular to alignment substrate. We succeeded in fabricating various films with thickness 0.5 μm and 3 μm.

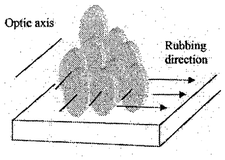


Fig. 4a: Planar arrangement

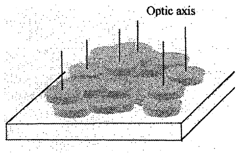


Fig. 4b: Homeotropic arrangement

Photo-polymerization study by infra-red spectroscopy: Photo-polymerization involving ring opening of epoxide groups was monitored by IR spectra as a function of UV dose. Thin film was spin-coated on NaCl plate with 0.5 weight % of photo-initiator and heated to 130°C. No change in IR spectra was detected in solid films and film quench cooled to room temperature after melting. However, after exposing the film to UV irradiation for 200 to 1800 second at 130°C the IR spectra shows new absorption peak between 3300-3500 cm^{-1} due to O-H stretching (Figure 5a). The intensity of which was found to increase with the increase of UV exposure time or with UV dose as shown in plot of absorbance versus UV dose (Figure 5b).

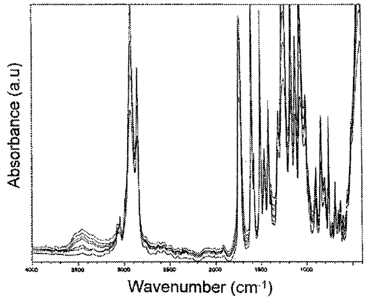


Fig. 5a: Photopolymerization study by IR spectroscopy: (lower to upper): solid film, molten film, uv exposure for 200,600,1000,1400,1800 sec.

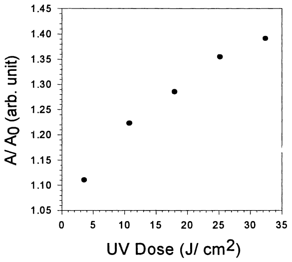


Fig. 5b: Variation in IR absorbance (for O-H peak) with UV dose

The origin of this peak is presumably due to the formation of small number of O-H end-groups after the ring opening of epoxide groups. The rest of the IR spectra, i.e., within 3000- 400 cm^{-1} remains unchanged. Origin of peak at 3300-3500 cm^{-1} is not due to atmospheric moisture was further proved by conducting the experiment with similar weight percent of photo-initiator but at 80°C i.e in solid state. No such peak between 3300-3500 cm^{-1} due to O-H stretching was seen. In addition, the film was found to be soluble just like monomer indicating no polymerization. However, when experiment was conducted at 80°C but with high photo-initiator concentration (7 wt. %), again peak at 3300-3500 cm^{-1} was revealed and film remains insoluble in common organic solvents. This again indicates polymerization. As C-O-C stretching in epoxide overlaps with that of aryl-alkyl C-O-C stretching already present in the molecule and with C-O-C stretching after ring opening of epoxide, it is difficult to assign any change in spectra between 1000-1300 cm^{-1} region.

Photo-polymerization study by DSC: IR spectroscopy study indicates that the ring opening polymerization is dependent both on initiator concentration and temperature. DSC experiments were carried out to support these findings. Thin films from mixture of monomer and initiator in dichloromethane were made by evaporating the solution directly in DSC pans. Kinetic of photo-polymerization was studied using isothermal DSC measurements under UV exposure at different temperature. An exothermic peak was found during the irradiation, indicating a polymerization.

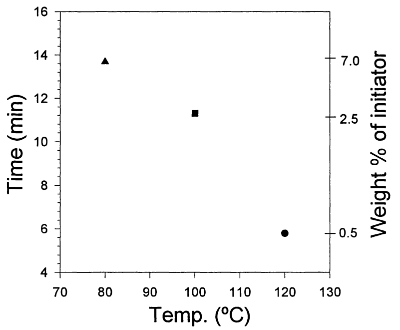


Fig. 6: Photo-polymerization study by DSC: Plot of time and wt.% of initiator Vs temperature.

Figure 6 shows plot of time and weight percent of initiator with respect to temperature. As seen from the plot, for film with 0.5 weight % of initiator exothermic peak appears at 5.8 minute, at polymerization temperature of 120°C, i.e., above the melting temperature of monomer. Decreasing the temperature to 100°C (at crystal to nematic peak maxima of monomer) and simultaneous increasing the initiator concentration to 2.5% an exothermic peak appears at 11.3 minute. At the polymerization condition of 80°C (below the melting of monomer) and 7 wt. % of initiator, the exothermic peak appears at 13.7 minute. Surprisingly, no exothermic peaks were detected when above combinations of temperature and initiator concentration were changed. All these experiments indicate that both temperature and initiator concentration are crucial in polymerization of epoxy compound. Polymerization takes place at a faster rate even though initiator concentration is less when temperature is equal to or higher than 120°C. Increase in the initiator concentration at this temperature makes polymerization very fast. We observed that the polymerization took place before it can be detected in DSC because of the resolution limit. Below 120°C and low initiator concentration (0.5 weight %) low degree of polymerization occurred which were undetectable by the photo-DSC. However, significant polymerization can also be achieved in solid films at 80°C, below melting of monomer, when we increased the initiator concentration to 7 wt%. Furthermore, the polymerized films were found to be insoluble in common organic solvents. Such drastic change in solubility behavior further supports their polymerized nature.

Polarized fluorescence study of polymerized films: Fluorescence behavior as well as polarized photoluminescence for low molar mass as well as rigid rod thermotropic polyesters has been reported in literature.[17-19] However, no polarized fluorescence study is reported on discotic liquid crystalline systems. We conducted polarized fluorescence studies for oriented discotic films on surfaces with homeotropic and planar alignment layers. For the discotic films with alignment layers, dichroic ratio was calculated as $R = E_{II}/E_{\perp}$ and the effective order parameter, S, could be governed by equation 1,

$$S = R\text{-}1/R\text{+}2 \qquad (1)$$

where E_{II} and $E_{\perp}$ are the emission intensities obtained parallel and perpendicular to the rubbing direction of alignment layer, respectively. For discotic films without surface alignment layers, the polarized fluorescence was studied by rotating the emission polarizer at 0° and 90°, with respect to long edge of the glass. For all discotic films, an emission peak was observed at 494 nm with excitation wavelength of 349nm. Representative fluorescence spectra for a discotic film with planar alignment are shown in figure 7.

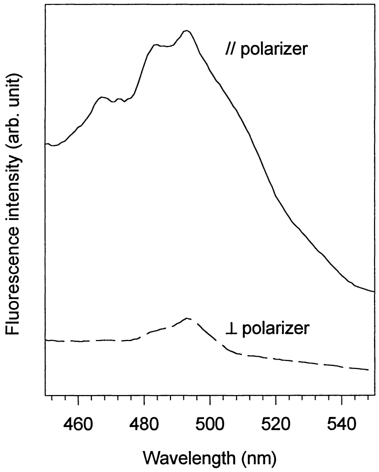


Fig. 7: Linear polarized fluorescence of planar discotic film.

Maximum emission was resulted when polarizer was set parallel to the rubbing direction, whereas, intensity diminishes on setting polarizer to perpendicular position. This indicates that liquid crystalline molecules are oriented along the rubbing direction. Dichroic ratios and order parameter of various discotic films studied are presented in Table 1.

Table 1. Dichroic ratios and order parameter of discotic films.

Sample	Polarized // excitation		Non-polarized excitation	
	R = $E_{II}/E_{\perp}$	S = R-1/ R+2	R = $E_{II}/E_{\perp}$	S = R-1/ R+2
Planar	4.73	0.55	1.64	0.18
Homeotropic.	1.76	0.20	1.37	0.11
Glass	2.23	0.29	1.15	0.05
Linear polarized UV-polymer	2.94	0.39	1.59	0.16

Very low values of order parameter were resulted when experiment was conducted under non-polarized excitation i.e in absence of polarizer in excitation path. Particularly for planar sample order parameter obtained under polarized condition was 0.55 whereas that under non-polarized condition was only 0.18 indicating around three times difference. Comparison made with homeotropic film (s = 0.20) under similar experimental condition also reveals higher order parameter for planar film (s = 0.55). This can be explained by the fact that optic axis of molecules in planar film lies parallel to rubbing direction of alignment substrate leading to maximum absorption and thus the emission. Similarly, film casted solely on rubbed glass and without any alignment layer also shows lower value of order parameter (0.29). In another study we prepared oriented discotic films using similar substrate i.e glass, however, photo-polymerization was conducted in nematic state using linearly polarized UV light. Order parameter obtained for such film was also found to be higher (0.39) than the film where non-polarized UV light was used for polymerization (0.29). This indicates alignment by reorientation of liquid crystalline molecules.

Conclusions

Liquid crystalline discotic films were fabricated after careful selection/ synthesis of monomer and their alignment was suitably controlled by optimizing the substrates, coating technique, rubbing speed/ pressure and polymerization. Progress of ring opening photo-polymerization was followed from IR spectroscopy as appearance of O-H end groups with variation in UV exposure time. Polymerization temperature and photo-initiator concentration was optimized by studying photo-polymerization by DSC. Ordered solid films exhibit distinct fluorescence at 494nm and polarized fluorescence study indicate higher order parameter for planar film as well as for film polymerized by UV linear polarized light.

Acknowledgement

Financial support by Ohio Board of Regent and NSF ALCOM is gratefully acknowledged.

References

1) S.T. Wu, *SID 96 Applications Digest*, p 21 (1996)
2) S.T. Wu, *Mat. Chem. Phys.*, **99**, 111 (1995)
3) H.L. Ong, *Japan Display' 92*, p 247 (1992)
4) F. Li, F.W. Harris, S.Z.D. Cheng, *Polymer*, **37(23)**, 5321 (1996)
5) S.T. Wu, *J. Appl. Phys.*, **76**, 5975 (1994)
6) Y. Takiguchi, *Euro Display' 90*, p 96 (1990)
7) US Pat. 5, 196, 953 (1995), Rockwell
8) US Pat. 5, 504, 603 (1996), Rockwell
9) US Pat., 5,583,679 (1996), Fuji Photo Films, invs.: Y. Ito, Y. Nishiura, K. Kamada, H. Mori, T. Nakamura
10) S Chandrasekhar, *Liq. Cryst.*, **14**, 3 (1993)
11) P. Hindmarsh, M.J. Watson, M. Hird, J.W. Goodby, *J. Mater. Chem.*, **14**, 2111 (1991)
12) H.T Nguyen, H. Gasparoux, C. Destrade, *Mol. Cryst. Liq. Cryst.,* **71**, 111 (1981)
13) T. Yamada, M. Okazaki, Y. Shinagawa, *IDW '96,* p: 348.(1996)
14) C.D Favre-Nicolin, J. Lub, *Macromolecules*, **29**, 6143 (1996)
15) N. Boden, R.C. Borner, R.J. Bushby, A.N. Cammidge, M.V. Jesudason, *Liq. Cryst.*, **15 (6)**, 851 (1993)
16) B. Klingert, M. Riediker, A. Roloff, *Comments Inorg. Chem.*, **7 (3)**, 109 (1988)
17) B.M Conger, J.C Mastrangelo, S.H. Shen, *Macromolecules*, **30**, 4049 (1997)
18) A.P Davey, R.G. Howard, W.J. Blau, *J. Mater. Chem.*, , **7 (3)**, 417 (1997)
19) H.W Huang, K. Horie, T. Yamashita, *J. Polym. Sci., Polym. Phys.*, **33**, 1673 (1995)