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Molecular Orientation of Liquid Crystal on Polymer Blends of Coumarin and Naphthalenic Polyimide

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Summary

Photo-induced liquid crystal alignment layers were prepared by blending polyimides and photoreactive polymers followed by polarized UV irradiation. Polyimides are selected for the purpose of improving the thermal stability of the molecular orientation of the photoreactive groups. The thermal stability of the LC alignment layer was enhanced regardless of the type of the polyimide while the direction of LC orientation was dependent on the type of polyimide. The photoreactivity of the polyimide governs the LC orientation in the blend alignment layers.

Introduction

In the manufacture of liquid crystal displays (LCDs), it is essential to align liquid crystal molecules in a specific orientation. The substrate employed for this purpose is called a liquid crystal alignment layer and one directional rubbing of the film surface is generally adopted to acquire the characteristics [1,2]. While the rubbing process offers the advantage of requiring a simple manufacturing apparatus, a static charge is generated, which could lead to dust contamination and lowered process yield. In response, the photoalignment of LC molecules induced by polarized UV irradiation on a photopolymer, i.e., a non-rubbing method has been the subject of extensive research in efforts to overcome the problems associated with the rubbing process [3-5]. The capability of liquid crystal alignment depends strongly on the structure of the photopolymers and the anisotropic intermolecular interactions of oriented photopolymers produced by UV exposure with liquid crystals. In line with this, many studies have been conducted toward the development of polymers with anisotropically photodimerizable moieties, such as cinnamate and coumarin, for the application of the LC alignment materials [6-10]. While the photoalignment layers made from cinnamate and coumarin show good LC alignment, poor thermal stability of LC alignment was reported in previous works [11-13]. In order to achieve improved thermal stability of LC molecules on the surface of photoreactive polymers, stable orientation of the photodimers under high temperature is required. In previous works, we focused on blend systems in efforts to obtain a thermally stable alignment layer [14,15]. Recently, we suggested that polyimides could affect the LC orientation via photoreactivity [16].

In this work, we adopted two different polyimides (6FDA-ODA and NTDA-ODA) that have different photoreactivity according to a change of diamine or dianhydride compared to previous work for the investigation of the effects of structural changes of polyimides on the thermal stability and LC alignment property.

Experimental Part

Materials

Methacryloyl chloride, 7-hydroxycoumarin, 2,2′-azobisisobutyronitrile (AIBN), 4,4’-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 4,4’-oxydianiline (ODA) were reagent grade from Aldrich and used as supplied. N-methyl-2-pyrollidone (NMP) was purified by vacuum distillation and stored under nitrogen.

Synthesis of a photopolymer based on coumarin and a polyimide

Methacryloyl chloride was added to a pyridine solution of 7-hydroxycoumarin and the solution was stirred at room temperature for 1 hr. The mixture was poured into water and the precipitate was filtered and dried under vacuum at room temperature. This monomer and AIBN were dissolved in N,N-dimethylformamide (DMF) and the solution was heated at 60°C for 10 hr under a nitrogen atmosphere. The viscous solution was poured into methanol to separate the polymer which was subsequently purified by reprecipitation from methanol and dried under vacuum at 80°C. Figure 1(a) shows the chemical structure of PMA-g-coumarin.

For the polyimide synthesis, the requisite diamine was dissolved in NMP in a nitrogen-purged flask and an equimolar amount of dianhydride was added. The concentration of the reaction mixture was 10 wt%. The mixture was stirred at room temperature. After a viscous solution was prepared, the reaction temperature was elevated to 180°C and a catalytic amount of isoquinoline was added to the mixture in order to accelerate the conversion of the amic acid group to the imide group. The reaction proceeded for 12 hr under a nitrogen atmosphere. After completion of the imidization reaction, the resulting solution was poured into deionized water. The precipitate was filtered and dried under vacuum at 80°C. We used two different polyimides, which were 4,4’-(hexafluoro-isopropylidene) diphthalic anhydride-4,4’-oxydianiline (6FDA-ODA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride-4,4’-oxydianiline (NTDA-ODA). Figures 1(b) and (c) shows the chemical structure of the polyimides, respectively.

Preparation of alignment layers

2wt% NMP solutions of PMA-g-coumarin and polyimide were prepared in a fixed weight ratio (7/3) and spin-coated onto a glass substrate at 1800 rpm. The cast was prebaked at 60°C for 30 min and then thermally cured at 200°C for 1 hr. After annealing, polarized UV light was irradiated on the thin polymer blend film to induce

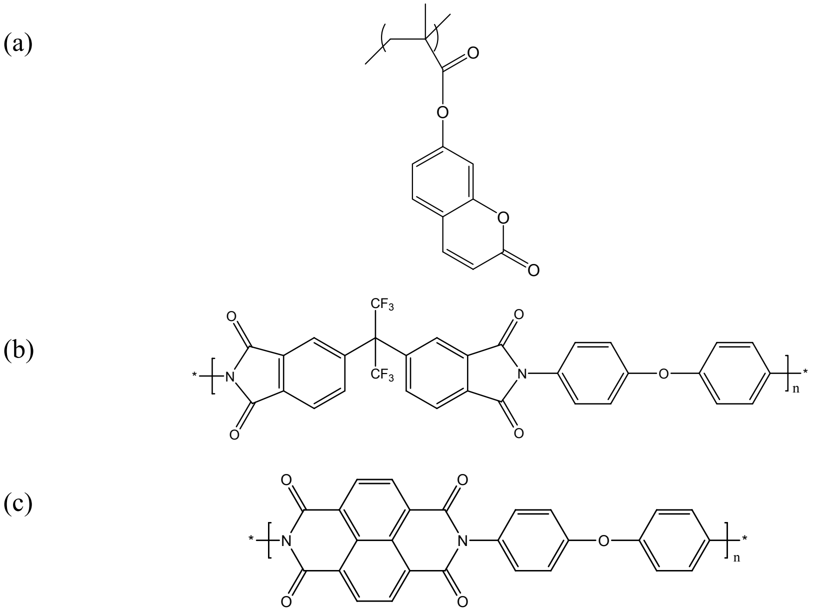

Figure 1. Chemical structure of polymers : (a) PMA-g-coumarin, (b) 6FDA-ODA and (c) NTDA-ODA

a photoreaction. Polarized UV light used was obtained by passing light from a 300W high-pressure mercury arc (Oriel) through a UV linear dichroic polarizer (27320, Oriel) and a UV filter 59800 (Oriel). UV filter 59610 (Oriel) was used to modify the wavelength band of polarized UV. The intensity of the irradiated UV light was measured using a UV detector (UIT-150, Ushio), yielding a value of 4mWcm^{-2}.

Preparation of LC cells

A homogeneously aligned LC cell was constructed by sandwiching nematic LCs (E7, Merck) between a pair of glass substrates coated with a thin film of alignment materials. The thickness of the LC layer was adjusted by using styrene beads of 8 μm diameter. E7 liquid crystals were injected into the cell via capillary action in the isotropic phase. The director of the nematic LCs in the LC cell was determined from the dichroic absorption of a dichroic dye (disperse blue 14) included in the nematic LCs. A small amount of the dichroic dye shows strong absorption at 653 nm. From the angular dependency of the absorbance at 653 nm in the polarized UV spectra of the LC cell, the distribution of the LC director could be determined. UV spectra were recorded with a UV-visible spectrophotometer (UV-1601, Shimadzu).

Results and Discussions

The direction of LC orientation is affected by the alignment materials. Basically, a PMA-g-coumarin, a photopolymer, is utilized for the alignment of LCs via UV irradiation and polyimide is applied for thermal stability. However, the polyimide may be influenced by the UV irradiation, depending on its chemical structure. It is thus important to investigate the photoreactivity of the polyimide, since the photoreactivity of the base material might affect the LC alignment property. We investigated the photoreactivity of 6FDA-ODA, and NTDA-ODA respectively, using a UV spectrophotometer. Figure 2 shows the UV absorbance spectra of the polymer components before UV irradiation and after 60 min UV irradiation. In the case of 6FDA-ODA, we observed that the absorption peaks are in a range of 200 nm to 300 nm and the intensity of the peaks decreased after UV irradiation. The reduction in the intensity of the peaks after UV irradiation was remarkable, thus indicating anisotropic decomposition of 6FDA-ODA. This is attributed to the high photoreactivity of 6FDA-ODA. NTDA-ODA also showed absorption peaks in a range of 200 nm to 300 nm, but the decrease in the peak intensity of the peaks was almost negligible. This indicates that there is no anisotropic decomposition of NTDA-ODA due to its low photoreactivity.

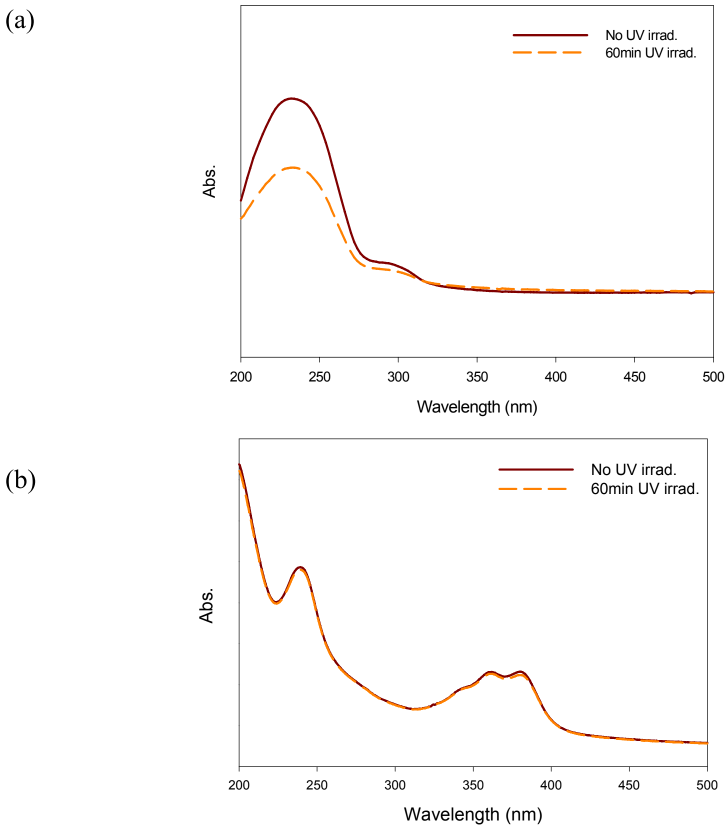

Figure 2. UV absorption spectroscopy of (a) 6FDA-ODA and (b) NTDA-ODA before and after 60 min UV irradiation

In order to investigate the effect of the polyimide (6FDA-ODA and NTDA-ODA) on the enhancement of the alignment layer, thermal treatment was applied and the alignment properties were measured. First, thermal treatment was applied to pristine

PMA-g-coumarin. Figure 3 shows a polar plot of the LC orientation on the alignment layers of PMA-g-coumarin as a function of thermal treatment temperature. When the LC cell was not thermally treated (65°C), alignment of the LCs was clearly observed and the direction of LC orientation was parallel to the polarization direction of the UV source [17]. However, disruption of LC alignment occurred when temperature higher than the glass transition temperature of PMA-g-coumarin (120°C) was applied. The disorder of LC orientation induced by thermal treatment was severe when the temperature was further raised (150°C → 200°C), leading to complete disruption of alignment.

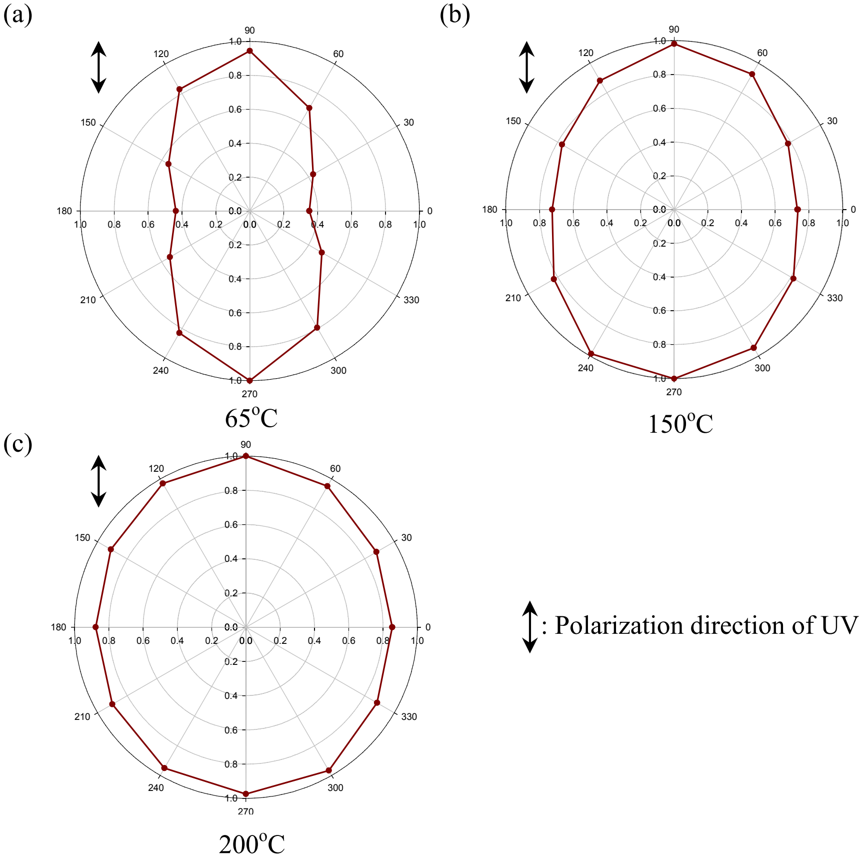

Figure 3. Polar plot of LC orientation on the alignment layer of PMA-g-coumarin as function of thermal treatment temperature of (a) 65°C, (b) 150°C, and (c) 200°C

The same heat treatment was applied to an alignment layer based on a blend of PMA-g-coumarin and 6FDA-ODA or NTDA-ODA. Figure 4 shows the results of heat treatment of the blend alignment layer of PMA-g-coumarin and 6FDA-ODA. In contrast with the LC alignment on the pristine PMA-g-coumarin layer, the LC orientation was maintained after thermal treatment, even at 200°C. However, the direction of LC orientation in the blend alignment layer was different from that of PMA-g-coumarin, i.e., perpendicular to the polarization direction of the UV source. This could be attributable to anisotropic decomposition of 6FDA-ODA due to its higher photoreactivity. Generally, the polyimide alignment layer aligns the LCs perpendicular to the polarization direction of the UV source. The LC orientation was affected by the anisotropic distribution of the 6FDA-ODA chain. Therefore, the reversion of photoalignment from parallel to perpendicular orientation relative to the polarization direction of the UV source is observed for the blend alignment layer.

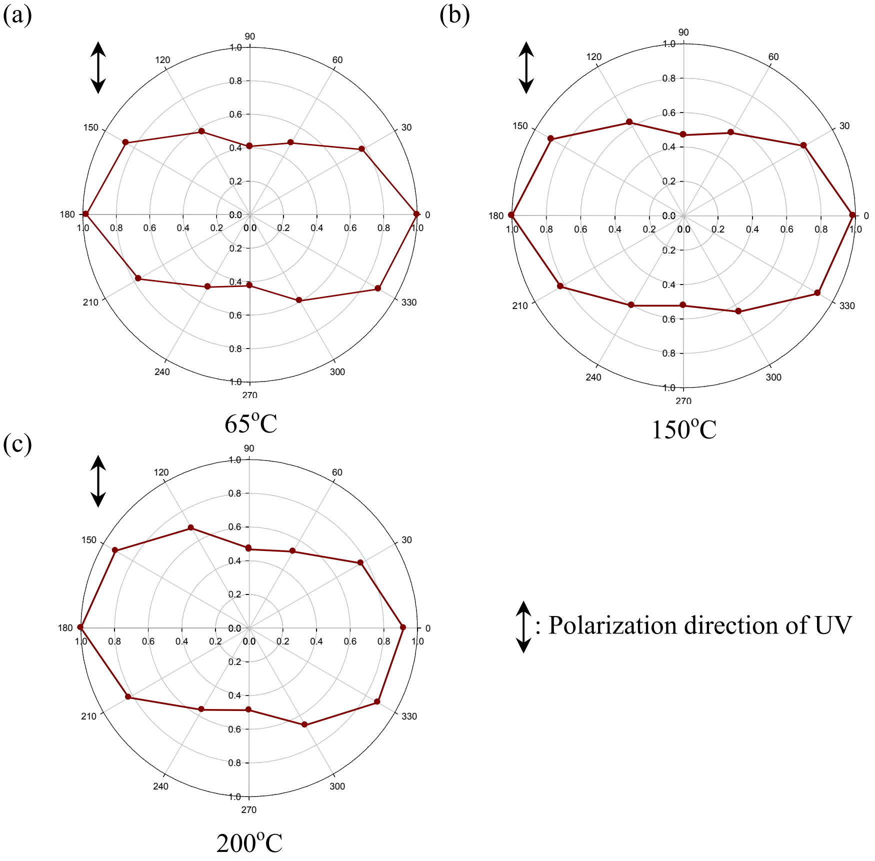

Figure 4. Polar plot of LC orientation on the blend alignment layer of PMA-g-coumarin and 6FDA-ODA as function of thermal treatment temperature of (a) 65°C, (b) 150°C, and (c) 200°C

In the case of the blend alignment layer of PMA-g-coumarin and NTDA-ODA, the LC orientation was stable after thermal treatment and the direction of LC orientation was not changed by the thermal treatment or UV irradiation, as shown in Figure 5. This indicates that there is no anisotropic decomposition of NTDA-ODA due to its low photoreactivity. The anisotropic distribution of coumarin side chains becomes dominant, since NTDA-ODA is not photoreactive.

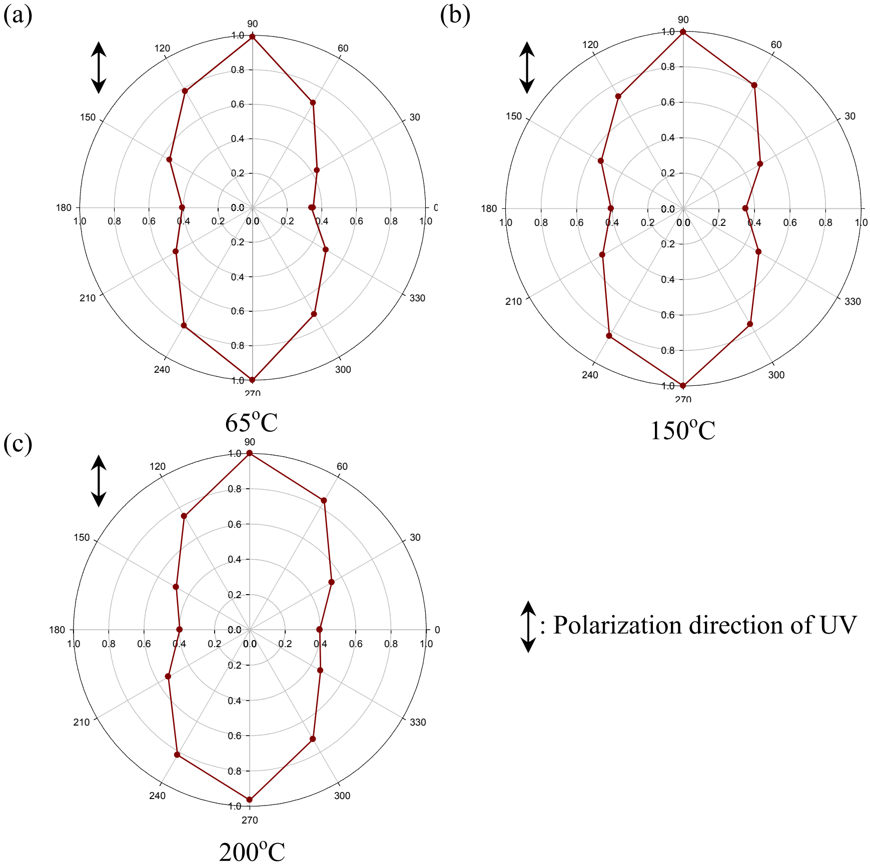

Figure 5. Polar plot of LC orientation on the blend alignment layer of PMA-g-coumarin and NTDA-ODA as function of thermal treatment temperature of (a) 65°C, (b) 150°C, and (c) 200°C

Therefore, NTDA-ODA could maintain the LC alignment properties of PMA-g-coumarin and had no effect on the direction of LC orientation on the blend alignment layers except for enhancing thermal stability. Because of the absence of photoreactivity in the case of NTDA-ODA, the blend alignment layer of PMA-g-coumarin and NTDA-ODA could sustain the LC orientation parallel to the polarization direction of the UV source. From these results, it is concluded that incorporation of a polyimide enhances the thermal stability of the photo-induced alignment layer. However, from the view point of the direction of LC orientation, the choice of polyimide is of major importance.

Conclusions

We have introduced polyimides into a coumarin-based photopolymer in order to improve the thermal stability of the LC alignment layer and investigated the effects of the photoreactivity of the polyimide on the LC orientation in blend alignment layers.

For blend alignment layers of PMA-g-coumarin and polyimides, the thermal stability of the LC orientation was enhanced by incorporation of the polyimide. Based on the findings of previous works with different diamine or dianhydride structure in polyimides as well as the present work, it is clear that photoreactivity is an important factor related to the LC orientation of a photo-induced alignment layer based on blend systems, compared with structural modifications of polyimides. Assessment of the photoreactivity via the UV spectrum of the polyimide provides a criterion for change of the LC orientation.

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