

## Enhancement of Molecular Orientation of Liquid Crystal on Photoreactive Polymers by using Non-Photoreactive Naphthalenic Polyimide

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### Abstract

*Polyimides are blended with photoreactive polymers in order to improve the thermal stability of molecular orientation of photoreactive groups induced by polarized UV irradiation. The polyimide/photopolymer blends can be applied for the photo-induced liquid crystal alignment layers. However, the polyimides are also decomposed by UV irradiation and this may have the negative effect on the orientation of liquid crystals. In order to elucidate the influence of polyimide on the molecular orientation of liquid crystal, non-photoreactive naphthalenic polyimide (1,4,5,8-naphthalene tetracarboxylic dianhydride) was selected for the blend alignment layers. We prepared the blends of photo-reactive coumarin polymers and naphthalenic polyimide, and investigated the orientation of liquid crystals. Thermal stability of the orientation of liquid crystals was enhanced due to the thermally stable polyimide. However, there was no other side-effect of polyimide on the orientation of liquid crystals and this might be attributed to the non-photo-reactivity of naphthalenic polyimide.*

### 1. Introduction

In order to align liquid crystal(LC) molecules, the process of rubbing the surface of polyimide film is usually adopted in manufacturing liquid crystal display(LCD). However, this process has the problems such as generation of static charge, dust, or scratches caused by rubbing. Therefore the establishment of a rubbing-free method is an important target due to its possibility of overcoming the problems in rubbing process. LC alignment using ultraviolet(UV) exposure is a promising candidate for non-rubbing method.<sup>1</sup> The photo-alignment layers made from photoreactive polymers such as polyvinylcinnamate<sup>2</sup> and coumarin<sup>3</sup> show good LC

alignment, but the thermal stability of LC alignment is poor. In order to enhance the thermal stability of alignment layer, we previously reported using polyimide to enhance the thermal stability of alignment layers of polyvinylcinnamate.<sup>4</sup>

In this work we adopted the polyimide to coumarin based photopolymer. We blended two different polyimide with coumarin based photopolymer.. We investigated the effect of polyimide on the liquid crystal alignment properties. Here we report the enhancement of thermal stability of LC alignment on blend alignment layer. We also compared the degree of photoreaction of polyimides and coumarin based photopolymer and related the difference to the direction of LC alignment on blend alignment layers.

### 2. Experimental

#### Material

Methacryloyl chloride, 7-hydroxycoumarin, 2,2'-azobisisobutyronitrile (AIBN), 4,4'-(hexafluoroisopropylidene) 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-pyrrolidone (NMP) were purified by vacuum distillation and stored under nitrogen.

#### Synthesis

Methacryloyl chloride was added to a pyridine solution of 7-hydroxycoumarin and the solution was stirred at room temperature for 1 h. The mixture was poured into water and the precipitate was filtered and dried in 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 h under nitrogen atmosphere. The viscous solution was poured into methanol to separate a polymer which was purified by reprecipitation from methanol and dried in

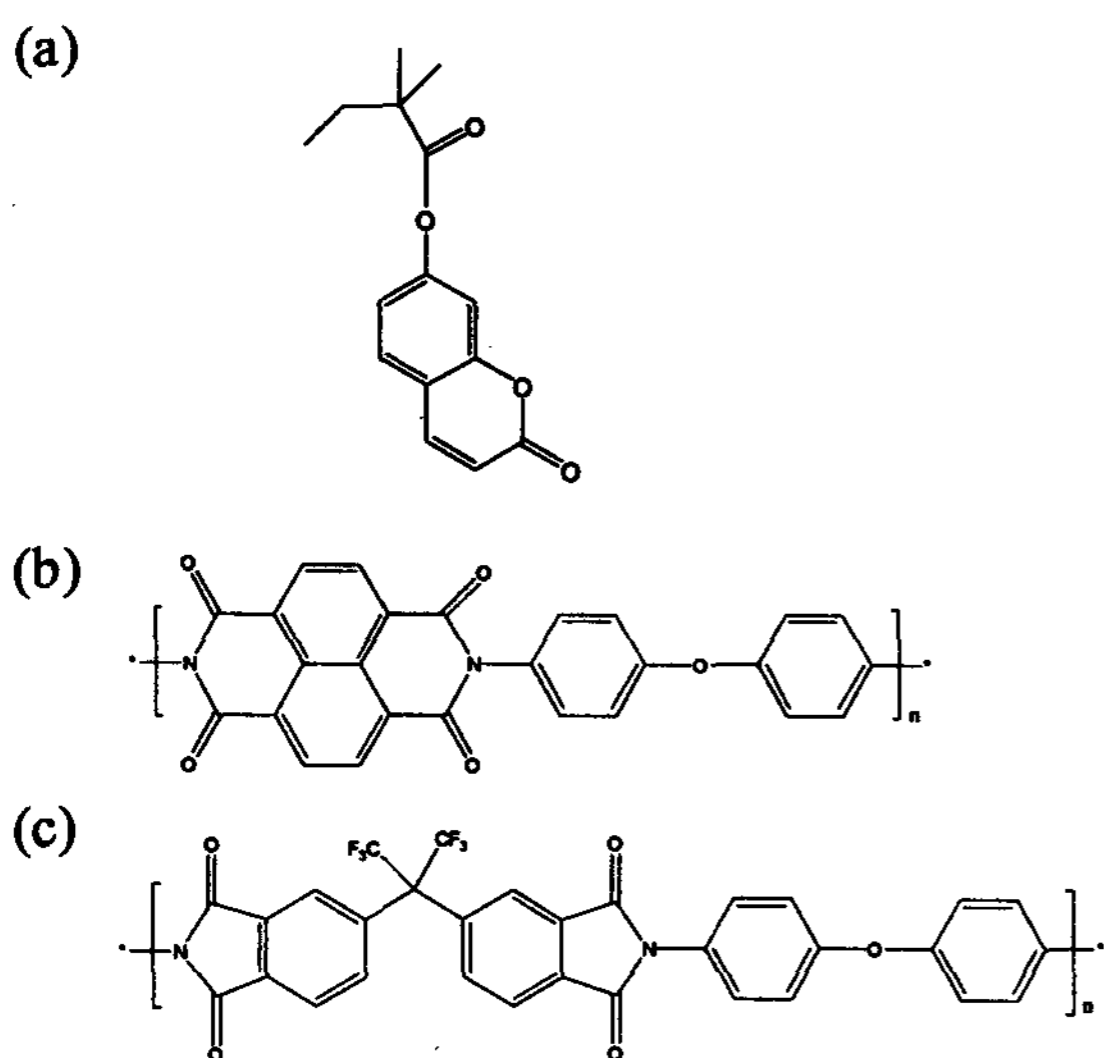
vacuum at 80°C. Figure 1(a) shows the chemical structures of PMA-g-coumarin.

In the case of polyimide synthesis, the requisite diamine was dissolved in NMP in a nitrogen-purged flask and an equimolar amount of the dianhydride was added. The reaction mixture contained 10 wt% solids and stirred at room temperature for 12h. The polyamic acid solution was poured onto deionized water. The precipitate was filtered and dried *in vacuo* at 80 °C.

We used two different polyimides such as 4,4'-(hexafluoro-isopropylidene) diphthalic anhydride-4,4'-oxydianiline (6FDA-ODA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride-4,4'-oxydianiline (NTDA-ODA). Figure 1(b), (c) shows the chemical structure of polyimides.

#### Photo-reaction

Photo-reaction of polymer was carried out by irradiating polarized UV onto the polymer film. Polarized UV light was obtained by passing the light from a 300W high-pressure mercury arc (Oriel) through UV linear dichroic polarizer (27320, Oriel) and UV filter 59800 (Oriel). The intensity of irradiated UV light measured with a UV detector (UIT-150, Ushio) was 4mW/cm<sup>2</sup>.



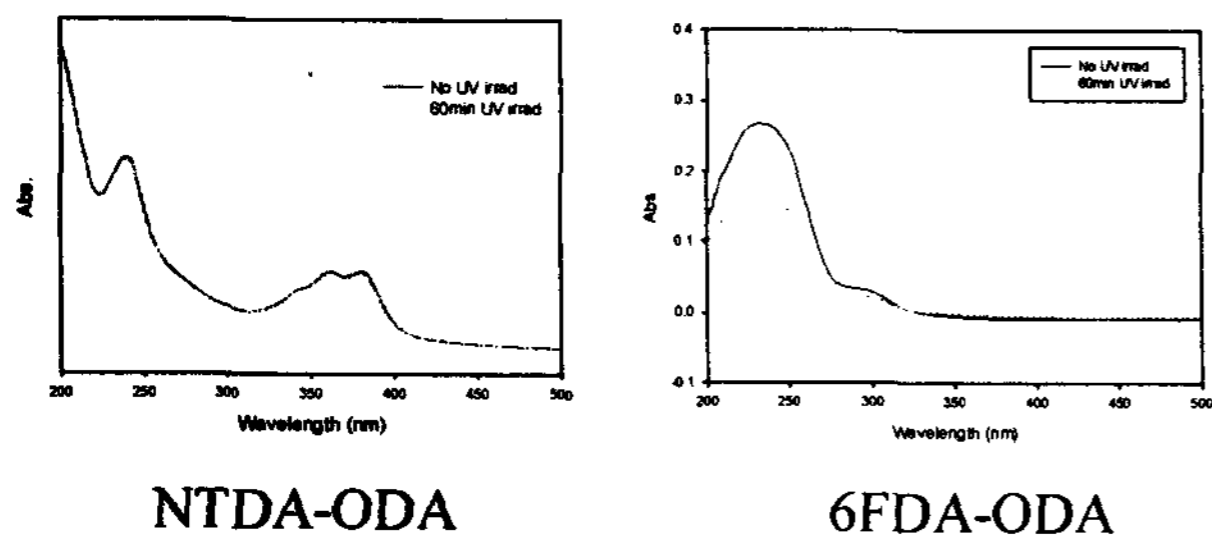
**Figure 1. Chemical structure of polymers :**  
**(a) PMA-g-coumarin, (b) NTDA-ODA, and**  
**(c) 6FDA-ODA**

2wt% NMP solutions of PMA-g-coumarin and polyimide were mixed in fixed weight ratio (10/0, 7/3) and spin-coated onto the glass substrate at 1800 rpm. The cast was prebaked at 60°C for 30min and the thermal curing of the cast was then conducted at 200°C for 1 hour. After annealing, the photoreaction of coumarin and polyimide was carried out by irradiating polarized UV light onto the polymer thin film. Polarized UV light 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) for light irradiation onto polymer thin film. The intensity of the irradiated UV light measured using a UV detector (UIT-150, Ushio) was 4mWcm<sup>-2</sup>.

A homogeneously aligned LC cell was constructed by sandwiching nematic LC (E7) between a pair of glass substrate coated with a thin film of alignment materials. The thickness of LC layer was adjusted by using the styrene bead of 8 μm diameter for measuring the order parameter and by using the adhesion tapes of 50 μm thickness for pretilt angle measurement. E7 liquid crystal was injected into the cell via capillary action in the isotropic phase. The director of nematic LC in the LC cell was determined from a dichroic absorption of dichroic dye (disperse blue 14) included in nematic LC. 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 LC director could be figured out.

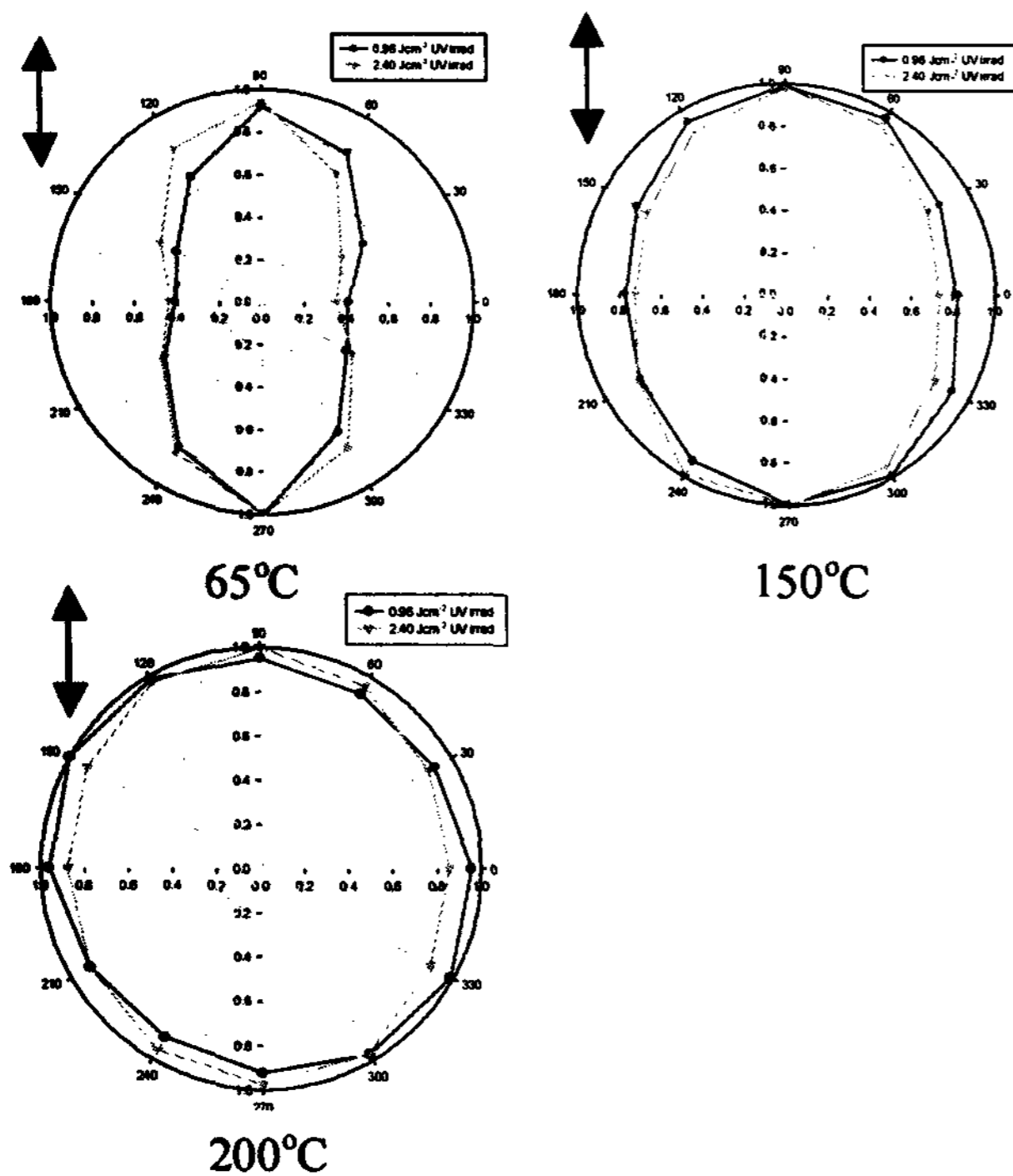
### 3. Results and discussion

We investigated the photoreactivity of 6FDA-DBA, and PMDA-ODA by using the UV spectrophotometer. Figure 2 shows the UV absorbance spectra of the polymer components of the blend alignment layers before UV irradiation and after 60 min UV irradiation. NTDA-ODA also shows the absorption peaks in the range from 200 nm to 300 nm, but the intensity decrease of the absorption peaks was negligible. In the case of 6FDA-ODA, we observed that the absorption peaks are in the range from 200 nm to 300 nm and decreased by UV irradiation. From these UV absorption spectra it is considered that the photoreactivity of 6FDA-ODA is higher than that of NTDA-ODA.



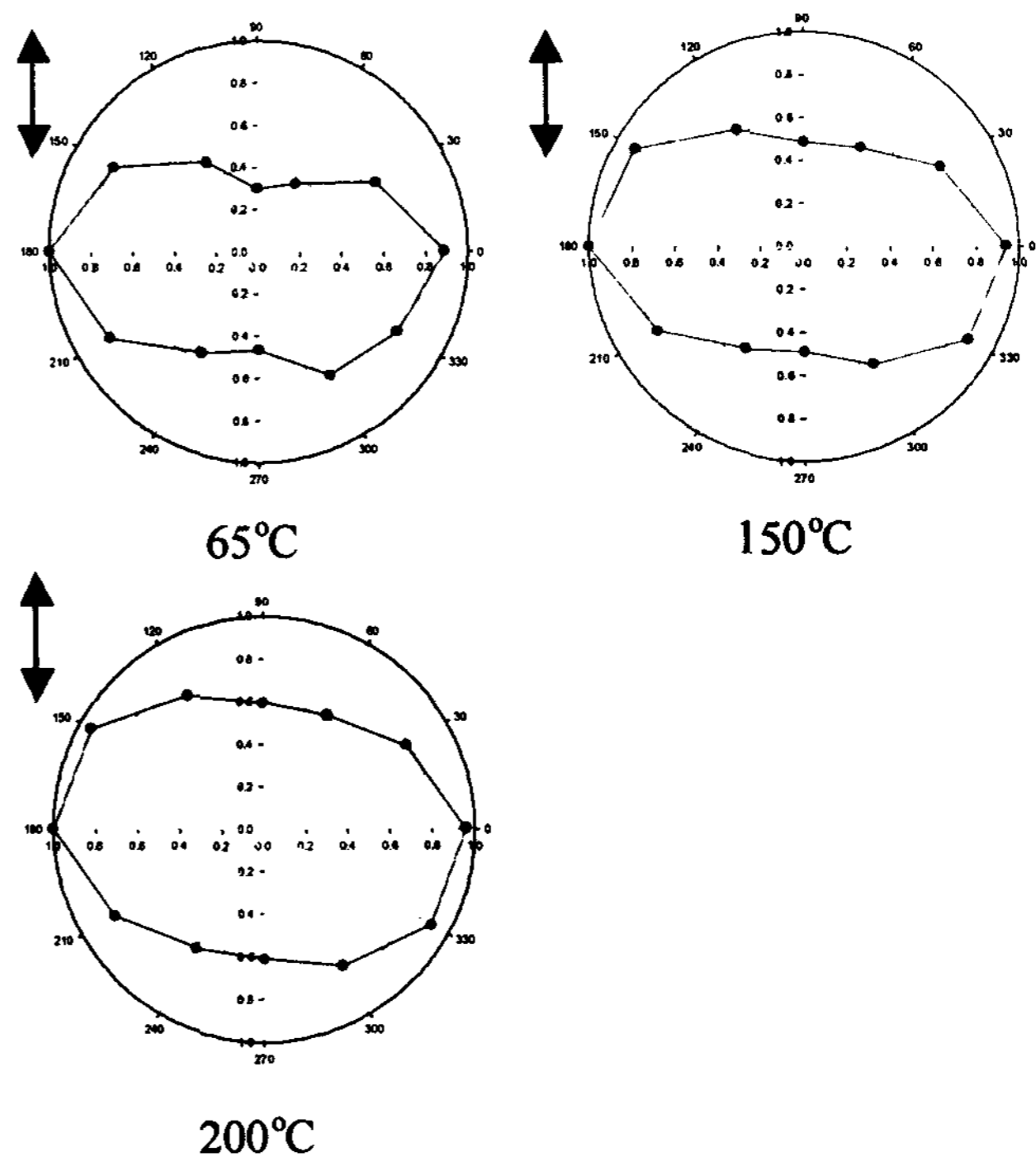
**Figure 2. UV absorption spectroscopy of NTDA-ODA and 6FDA-ODA before and after 60 min UV irradiation**

Figure 2 shows the polar plot of LC orientation on the alignment layers of PMA-g-coumarin as a function of thermal treatment temperature. The irradiation energy of the polarized UV was varied;  $0.5 \text{ J/cm}^2$  and  $2.4 \text{ J/cm}^2$ . When the LC cell was not thermally treated ( $65^\circ\text{C}$ ), the LC alignment was good and the direction of LC orientation was parallel to the polarization direction of UV source.



**Figure 3. Polar plot of LC orientation on the alignment layer of PMA-g-coumarin as a function of thermal treatment temperature.**

In the case of the blend alignment layer of PMA-g-coumarin and 6FDA-ODA, the LC orientation was maintained after the thermal treatment at  $200^\circ\text{C}$  (Figure 4). However, the direction of LC orientation was different from that of PMA-g-coumarin. The direction of LC orientation was perpendicular to the polarization direction of UV source. However, as the LC cell was thermally treated at  $150^\circ\text{C}$  and  $200^\circ\text{C}$ . The thermal treatment of LC cell randomizes the photodimer of coumarin side chains due to the low thermal stability of PMA-g-coumarin. However, 6FDA-ODA polyimide is well known to be thermally stable over  $200^\circ\text{C}$ . Thus, the LC orientation was affected by the anisotropic distribution of 6FDA-ODA chain. Generally the LC alignment layer of polyimide aligns LC perpendicular to the polarization direction of UV source. Therefore, the LC alignment direction on the blend alignment layer after thermal treatment was perpendicular to the polarization direction of UV source.

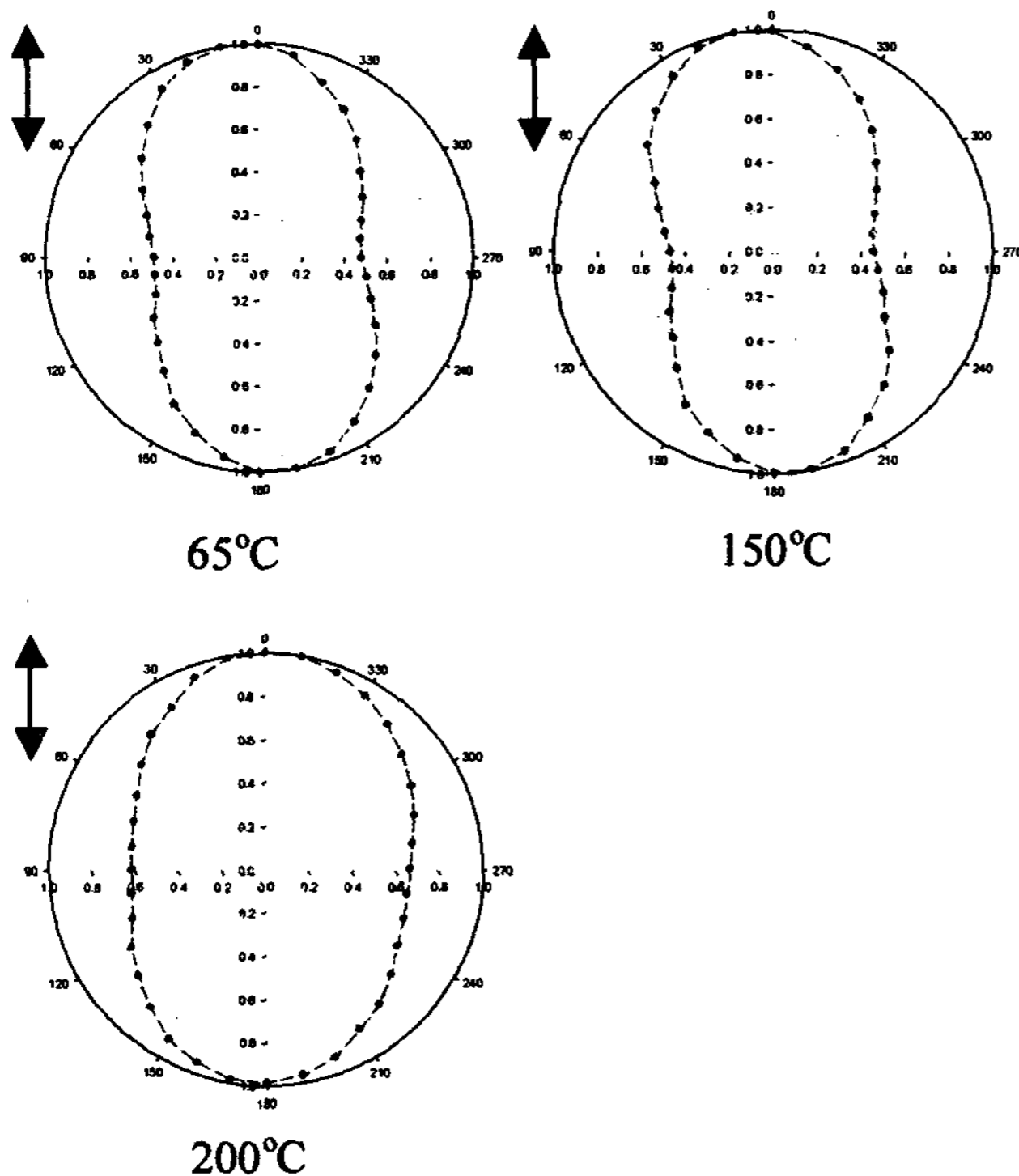


**Figure 4. Polar plot of LC orientation on the blend alignment layer of PMA-g-coumarin and 6FDA-ODA as a function of thermal treatment temperature for 10 min.**

However, in the case of NTDA-ODA, the photodimerization reaction of coumarin side chains becomes dominant since NTDA-ODA is not photoreactive (Figure 5). Therefore, NTDA-ODA could maintain the LC alignment properties of PMA-g-coumarin in the process of thermal treatment and had no effect on the direction of LC orientation on the blend alignment layers. Because of the non-photoreactivity of NTDA-ODA, the blend alignment layer of PMA-g-coumarin and NTDA-ODA could sustain the parallel LC orientation to the polarization direction to UV source in spite of the thermal treatment. In the blend alignment layer of PMA-g-coumarin and polyimide, the photoreactivity of polyimide is considered importantly for the determination of the direction of LC orientation after thermal treatment.

#### 4. Conclusion

For the blend alignment layers of PMA-g-coumarin and polyimide, the thermal stability of LC orientation was enhanced by polyimide. However, the direction of LC orientation was affected by the photoreactivity of polyimides. In the case of the blend alignment layer of PMA-g-coumarin and 6FDA-ODA, the direction of LC orientation was perpendicular direction to the polarization direction of UV source. This phenomenon might be attributed to the anisotropic decomposition of 6FDA-ODA due to the higher photoreactivity of 6FDA-ODA. However, the direction of LC orientation was not changed when the NTDA-ODA without photoreactivity was employed for the blend alignment layer.



**Figure 5. Polar plot of LC orientation on the blend alignment layer of PMA-g-coumarin and NTDA-ODA as a function of thermal treatment temperature for 10min.**

#### 5. References

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