

# Study on the relationship between phthalic and naphthalenic polyimide structures and the photo-induced molecular orientation of liquid crystals on polyimides

Ki-Yun Cho, Shi-Joon Sung, Hyundai Hah, and Jung-Ki Park

Dept. of Chem. and Biomolecular Eng., Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea  
Phone : +82-42-869-3965 , E-mail : jungpark@kaist.ac.kr

## Abstract

Polarized ultraviolet irradiation techniques have been developed recently to produce alignment of liquid crystals (LC). Because of the excellent thermal stability and the alignment ability of polyimides, polyimides has attracted considerable research interest for the photoinduced alignment layer. Hasegawa and Taira confirmed homogeneous alignment of LC by the decomposition of a polyimide induced by linearly ultra-violet polarized light. It was reported that ultraviolet visible absorption spectra of a polyimide alignment film showed a remarkable change upon irradiation. In this study, we synthesized phthalic polyimide and a naphthalenic polyimide in order to investigate the effect of the polyimide structure. Some difference in terms of the photo-induced molecular orientation of liquid crystals were observed with the polyimide structure.

## 1. Introduction

The excellent mechanical, thermal and optical stability of polyimide thin films result in their widespread use as liquid crystal alignment layers in commercial LCD. The alignment direction and pretilt angle are chosen by rubbing the alignment layer but this process can generate dust and static electricity which affects the yield of active matrix liquid crystal displays. Furthermore, rubbing cannot provide the microscopic variations in director orientation required for multi-domain displays which give wide viewing angles. The anisotropic crosslinking of polymers with cinnamate or coumarin sidechains on illumination with linearly polarised UV light was firstly explored as a non-contact alignment technology. More recently it was found that prolonged exposure of polyimides to linearly polarised light from a UV lamp can also achieve liquid crystal orientation. The alignment results from the anisotropic decomposition of the polyimide chains along the polarisation direction of

the incident light. In this study, we have studied the relationship between phthalic and naphthalenic polyimide structures and the photo-induced molecular orientation of liquid crystals on polyimides.

## 2. Experimental

### Material

4,4'-(hexafluoro-isopropylidene) diphtalic anhydride (6FDA), pyromellitic dianhydride (PMDA), 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

In each case, 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.

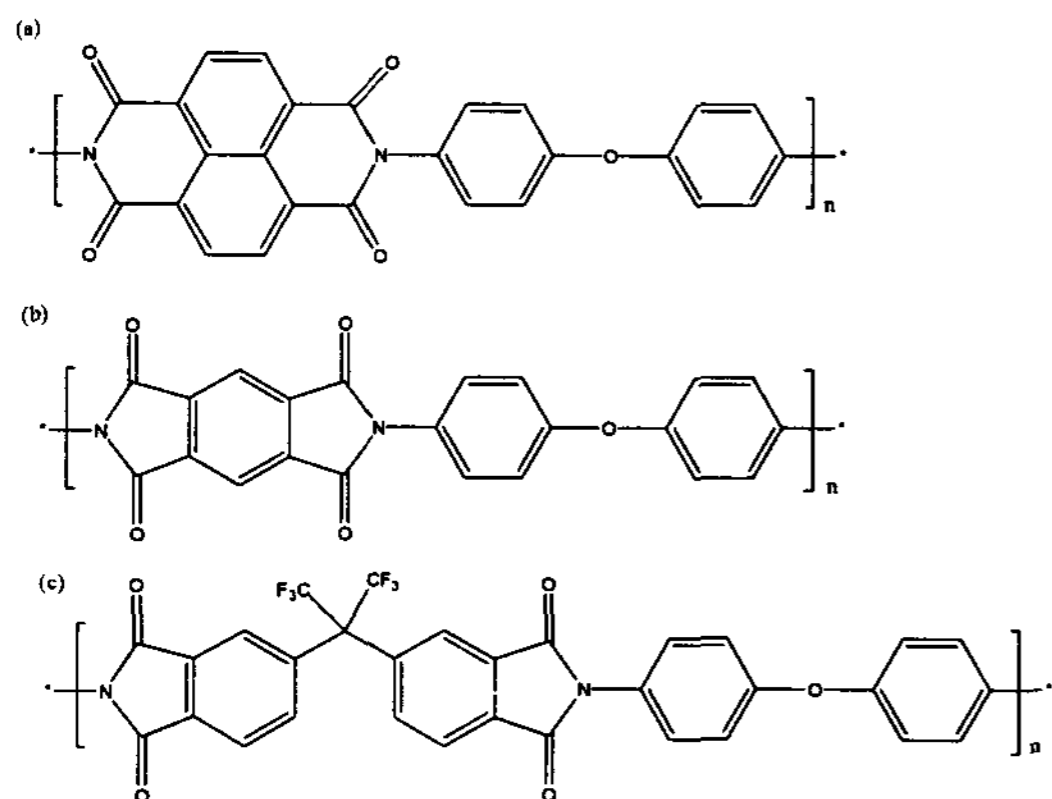
A 2wt% NMP solution of the polyamic acid was spin-coated onto the glass substrate at 1800rpm and the cast was prebaked at 60°C for 30 min. Thermal imidization of the cast was then conducted at a given temperature for 1hr.

We used three different polyimides such as 4,4'-(hexafluoro-isopropylidene) diphtalic anhydride-4,4'-oxydianiline (6FDA-ODA), pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride-4,4'-oxydianiline (NTDA-ODA). Figure 1 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

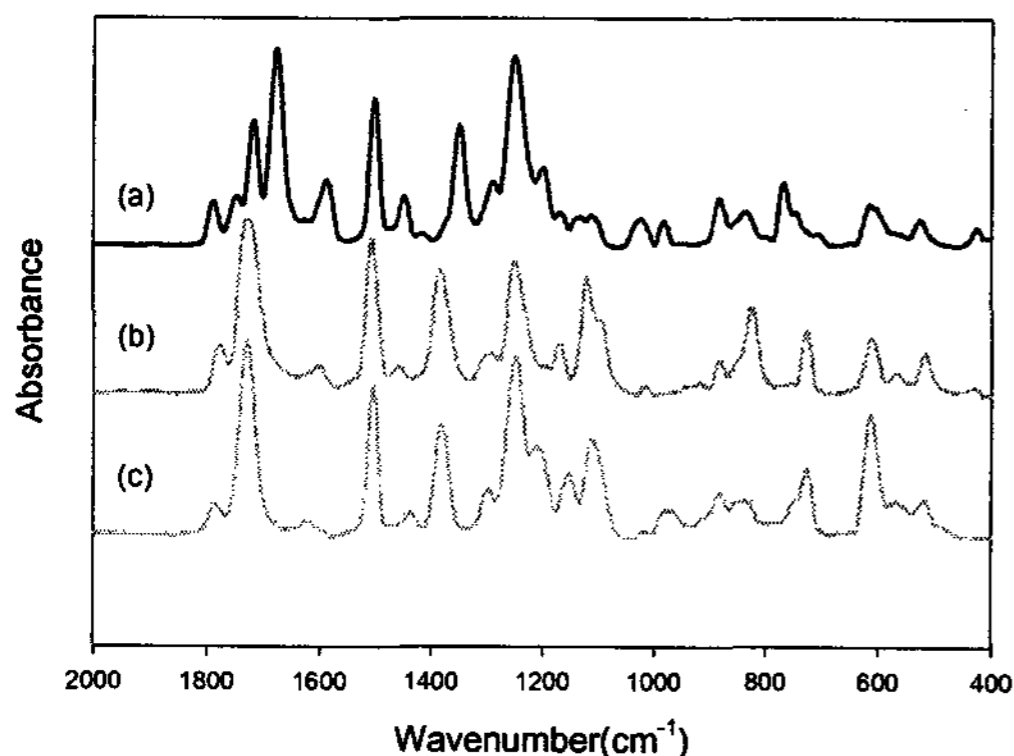
from a 300W high-pressure mercury arc (Oriol) through UV linear dichroic polarizer (27320, Oriol) and UV filter 59800 (Oriol). The intensity of irradiated UV light measured with a UV detector (UIT-150, Ushio) was  $4\text{mW}/\text{cm}^2$ .



**Figure 1. Chemical structure of polyimides : (a) NTDA-ODA, (b) PMDA-ODA and (c) 6FDA-ODA**

### 3. Results and discussion

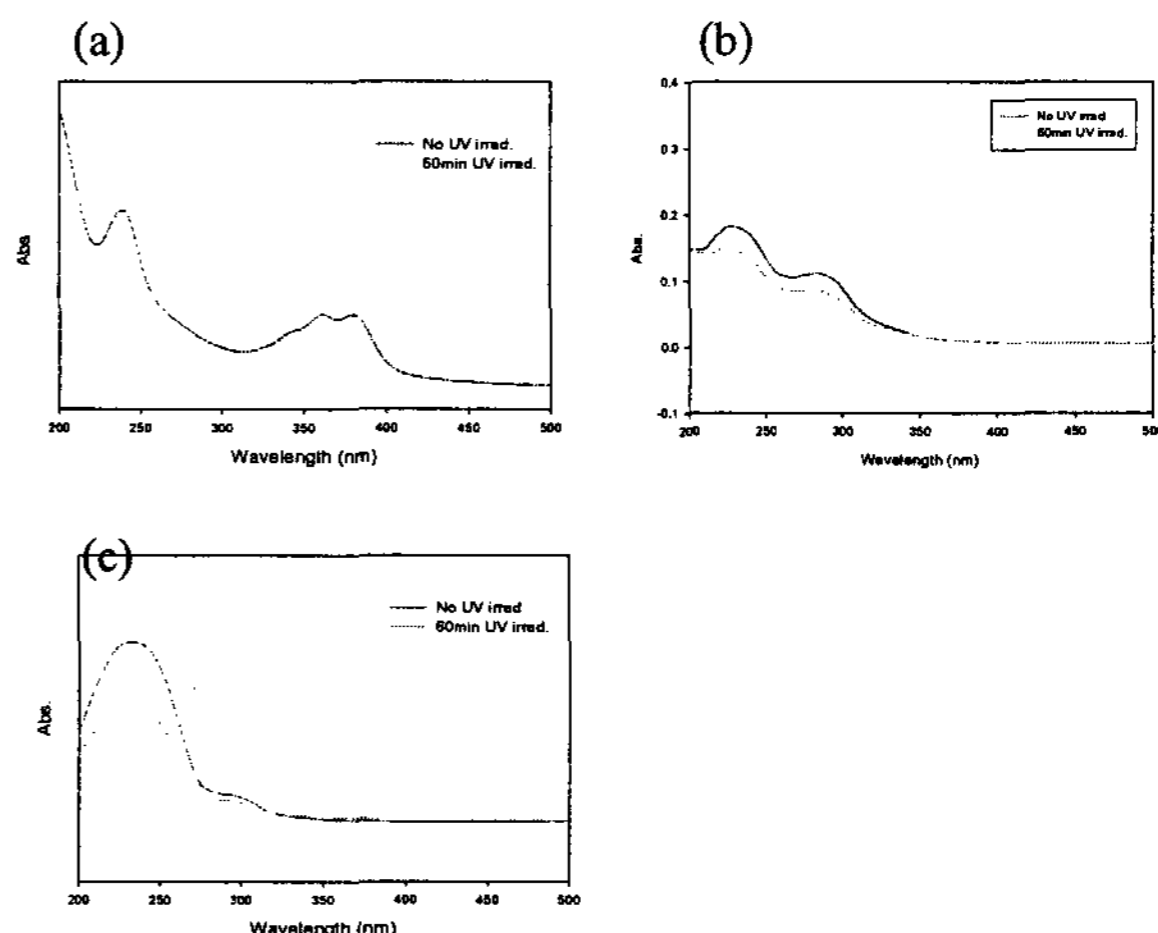
Figure 2 show the FT-IR spectra in the range  $400\text{-}2000\text{ cm}^{-1}$  of polyimides. The symmetric C=O stretching, the asymmetric C=O stretching, and C-N stretching vibration bands for the imide group are



**Figure 2. FT-IR spectra of polyimides : (a) NTDA-ODA, (b) PMDA-ODA and (c) 6FDA-ODA**

found at  $1780\text{cm}^{-1}$ ,  $1720\text{cm}^{-1}$  and  $1380\text{cm}^{-1}$  respectively in phthalic polyimide. However, the C-N stretching vibration bands for imide group in naphthalenic polyimide is found at  $1345\text{cm}^{-1}$ .

Figure 3 shows the changes of the UV spectra of the polyimides layers during their exposure to polarized UV. After UV irradiation, the naphthalenic polyimide is not changed. However, the phthalic polyimides is some changed. The naphthalenic polyimide was more stable at UV exposure than the phthalic polyimide.



**Figure 3. UV spectra of polyimides : (a) NTDA-ODA, (b) PMDA-ODA and (c) 6FDA-ODA**

### 4. Conclusion

The imide ring structure of polyimides was related with the photoreaction. The phthalic polyimide stability was inferior to the naphthalenic polyimide in the UV polarisation. This UV stability could be explained by the structure stability of the electron density.

### 5. References

- [1] M. Schadt, K. Schmitt, V. Kozinkov, V. G. Chigrinov, *Jpn. J. Appl. Phys.*, 31, 2135 (1992)
- [2] M. Schadt, H. Seiberle, A. Schuster, S. M. Kelly, *Jpn. J. Appl. Phys.*, 34, 3240 (1995)
- [3] M. Schadt, H. Seiberle, A. Schuster, *Nature*, 381, 212 (1996)
- [4] K. Ichimura, Y. Akita, H. Akiyama, K. Kudo, Y. Hayashi, *Macromolecules*, 30, 903 (1997)
- [5] M. Hasegawa, Y. Taira, *J. Photopolym. Sci. Tech.*, 8, 241 (1995)
- [6] J. L. West, X. Wang, Y. Ji, J. R. Kelly, *SID 95 Digest*, 703 (1995)