

Liquid Crystal Photoalignment Behaviors by Photosensitive Polymaleimide with Cinnamate Side Chain

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Abstract. Two kinds of side chain photopolymers containing terminally substituted cinnamoyl ester were synthesized and characterized. The para position in the cinnamoyl group was connected with polymer backbone through 4 numbers of methylene spacers. A good thermal stability of all photopolymers were measured by thermogravimetric analysis (TGA) measurement until 400 °C while the glass transition temperature was observed that higher PMC2 than PMC1 according to the results of differential scanning calorimetry (DSC). The nematic liquid crystal (NLC) pretilt angle generated was about 0.06-1.66 by polarized different UV exposure energy. Especially, the low pretilt angle of the NLC was measured by the longer polarized UV exposure time. This result indicated that the NLC pretilt angle generated sensitively depends on the UV exposure time on the photopolymers.

Keywords: Cinnamate, Liquid crystals, Thermal properties, Photoisomerization, Pretilt angle.

1. Introduction

Recently, there has been increasing needs for various Liquid crystal (LC) devices such as liquid crystal displays (LCD) in practical application. One of the demands is to control precise alignment of the LC molecules. In the most types of LCD, LC molecules are aligned with high precision in directions parallel and perpendicular to the display substrate. This is usually done by a method which has been in use since the discovery of substrate-aligned layers-rubbing. Photoalignment process is well known as one of alternative method to rubbing process and is investigated as one of effective solution that control the generation of electrostatic charge and dust induced the rubbing method. Photoalignment using photoisomerization phenomena controls the LC alignment by a conformational change between cis and trans type azobenzene functional units. The photoisomerization occurred by changing the wavelength or polarization direction of the exposed light can switch the LC alignment reversibly between homeotropic and homogeneous, or change the direction of the homogeneous alignment. In the other hand, cinnamate undergo both reversible E/Z photoisomerization and photodimerization via a (2+2) cycloaddition to form a cyclobutane dimer from two cinnamate groups and was first developed for use as a negative photoresist using isotropic UV light. The photopolymer with dimerized moiety of cinnamoyl group have been many examined as a photoalignment material. A thin film of poly (vinyl) cinnamate and other flexible photopolymer surfaces such as poly methyl methacrylate and poly siloxane, the representative photo-crosslinkable photoresists, provides a photo-active surface for achieving the deliberate alignment of LC with linearly polarized UV (LPUV) irradiation. Despite, these photopolymers suffer from its poor thermal stability in practical application since low thermal stability in backbone structure of photopolymer have not satisfactory to obtain a good liquid crystal aligning properties.

The purpose of this study is to synthesize the new type photopolymer by immidization of backbone and side chain with various cinnamoyl moiety attached to a mesogenic group for high thermal stability, superior

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photoalignment of liquid crystals and control of low pretilt angle for a nematic liquid crystal (NLC), especially for use low UV-curing energy by LPUV system on the photopolymers.

2. Experimental

2.1. Sample Synthesis

2.1.1. Synthesis of Poly (Succinimide Butyl Cinnamate) (PSBC)

In a 250 mL round-bottomed flask, the PMI (1.0 equiv), trans-cinnamic acid (C1, 1.1 equiv) were dissolved in THF (40 ml). The solution was cooled at room temperature, and under stirring dicyclohexylcarbodiimide (DCC, 3.0 equiv) / 4-dimethylaminopyridine (DMAP, 1.5 equiv) (dissolved in 60 mL THF) was added dropwise. The mixture was stirred 48 h at room temperature. Dicyclohexylurea (DCU) as impurity was removed by filtering. The product was precipitated at ethyl alcohol.

2.1.2. Synthesis of Poly (Succinimide Butyl Methoxy Cinnamate) (PSBmC)

In a 250 mL round-bottomed flask, the PMI (1.0 equiv), 4-methoxycinnamic acid (C2, 1.1 equiv) were dissolved in tetrahydrofuran (THF) 40 mL. The solution was cooled at room temperature, and under stirring DCC (3.0 equiv) / DMAP (1.5 equiv) (dissolved in 60 mL THF) was added dropwise. The mixture was stirred 48 h at room temperature. DCU was removed by filtering. The product was precipitated at ethyl alcohol. The synthesis of photopolymers with cinnamate group and precursors is represented in Fig. 1.

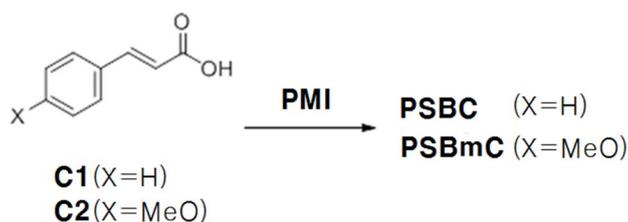


Fig. 1: The route of synthesis PSBC and PSBmC.

2.2. Cell Preparation

2.2.1. Alignment Layer Coating

The PSBC was solved in toluene as the solvent. The concentration of the polymers in the toluene solutions was 1 wt %. Films of the polymer were prepared on a glass substrate by spin-coating of the solutions (800 rpm, 10 s). The PSBC film was dried at 100 °C for 1 min in a chamber. And LPUV was exposure on PSBC film. The thickness of the polymers films was about 100 nm. PSBmC also fabricated similar to method.

2.2.2. LC Cell Assembly

Parallel LC cells were fabricated using the spin-coated PSBC and PSBmC films onto glass substrates. The parallel LC cells were constructed by assembling the spin-coated polymer films together parallel with respect to the LPUV exposure direction using spacers with thicknesses of 4.5 nm. The fabricated LC cells were filled with a NLC ($\Delta n=0.170$). Manufactured LC cells were sealed with epoxy.

3. Result and Discussion

The $^1\text{H-NMR}$ (DMSO-d_6) spectra of are shown in Fig. 2. Synthesis of PSBC is successfully by the proton peaks in the aromatic ring peaks (a = 7.24 ppm, b = 7.38 ppm, c = 7.68 ppm), C=C peaks (d = 7.59 ppm, e = 6.58 ppm), spacer peaks (f = 4.30 ppm, g = 3.33 ppm) confirming. Similar to PSBmC is confirmed by the proton peaks in the aromatic ring peaks (b = 6.93 ppm, c = 7.60 ppm), C=C peaks (d = 7.59 ppm, e = 6.42 ppm), spacer peaks (f = 4.10 ppm, g = 3.38 ppm) methoxy peak (a = 3.76 ppm).

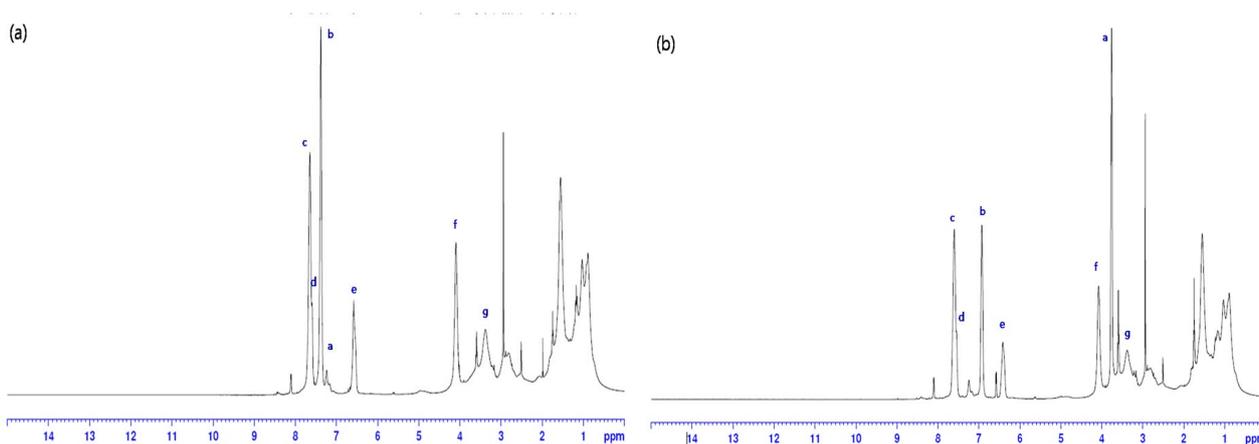


Fig. 2: ¹H-NMR signatures of (a) PSBC and (b) PSBmC.

The TGA curves of all the polymers are shown Fig. 3. The thermal stability of all the polymers was investigated by 5 % weight loss minimum temperature. TGA revealed that the photopolymers were stable up to 240-400 °C. The thermal stability of the photopolymers not depends on the terminal groups. Both -CH₃O and -H substituted photopolymers shows the similar thermal stability. The decomposition of the polymers was almost completed around 480 °C, after that no weight loss was observed.

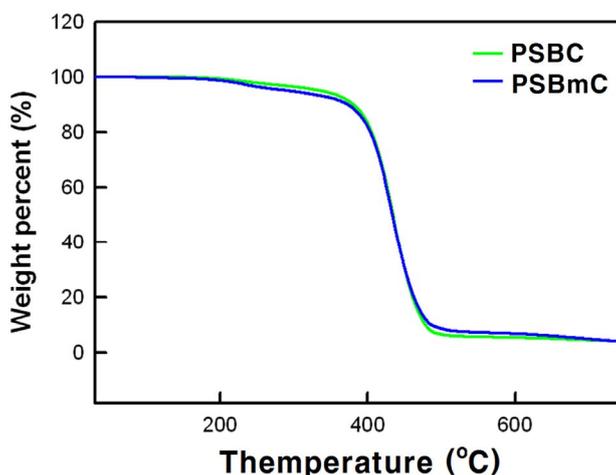


Fig. 3: TGA curves for PSBC and PSBmC.

DSC curves of photopolymer are shown in Fig. 4. The DSC traces of all photopolymers only show a shift baseline corresponding to glass transition temperature (T_g), while no peak was assigned to the others phase transition on the heating and cooling. This assignment of the phase transition temperature of photopolymer was supported by optical microscopic observation.

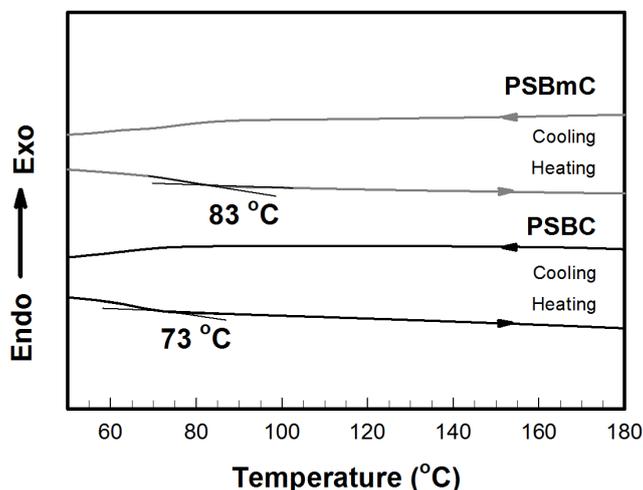


Fig. 4: DSC curves for PSBC and PSBmC.

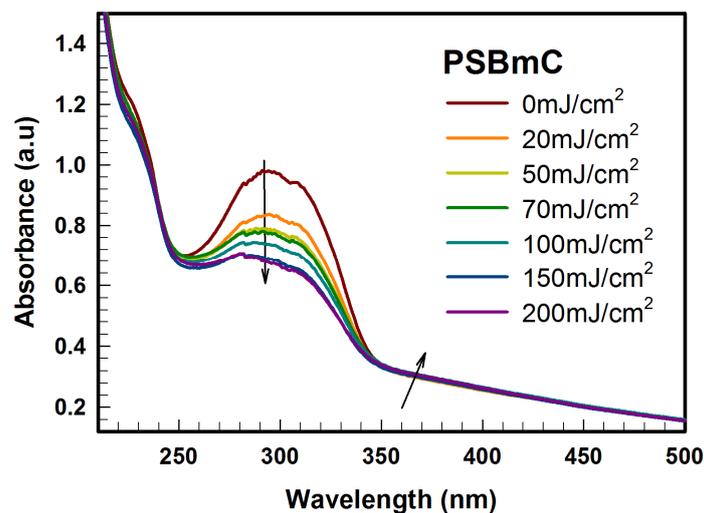


Fig. 5: Absorption spectral changes of PSBmC in film irradiated with unpolarized UV light.

NLC pretilt angles with the directly polarized UV exposure of 90° on the PSBC and PSBmC surface as a function of UV exposure energy are shown in Fig. 6. It is shown that the high pretilt angle of the NLC generated was about 1.66° by polarized UV exposure energy 40 mJ/cm² on the photo-alignment polymer surface. The pretilt angle of the NLC is an immediate sharp decrease with increasing exposure energy until 100 mJ/cm². When the exposure energy was over 100 mJ/cm², the pretilt angle tended to saturate. However, pretilt angle of NLC on the PSBC was measured only over 70 mJ/cm². This result indicated that pretilt angle of NLC rely on the photo-alignment of photopolymer by the polarized UV exposure energy.

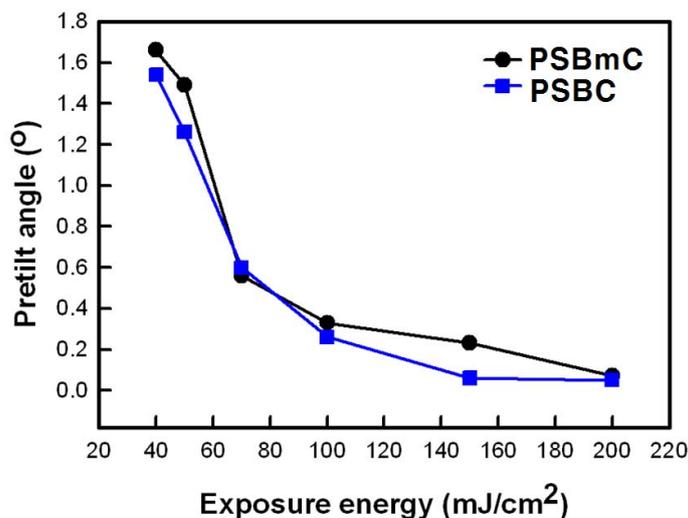


Fig. 6: Change of pretilt angle for PSBC and PSBmC by changed exposure energy.

4. Summary

In conclusion, we synthesized the two type photopolymers with different chemical structure of terminal group and investigated their thermal stability and generation of the NLC pretilt angle using the polarized UV exposure energy on the photopolymers. A good thermal stability of the photopolymers was measured by DSC and TGA measurement. A good thermal stability of photopolymers was measured the glass transition temperature of 65-70 °C, decomposition temperature of 400 °C by DSC and TGA measurement, respectively. The NLC pretilt angle generated strongly depended on the polarized UV exposure energy rather chemical structure of terminal group such as -H and -CH₃O. These results indicated that the thermal stability and the pretilt angle of photopolymers not depends on the theirs chemical structure but alignment of NLC deeply is related to between terminal group and degree of photo-alignment by polarized UV exposure energy on the photopolymers.

5. References

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