

## The Synthesis and Photoalignment Properties of Polymaleimides with Different Photosensitive Groups

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**Abstract.** Two kinds of side chain photopolymers substituted different photosensitive groups of cinnamate and chalcone were synthesized and characterized their optical properties. A good thermal stability of all photopolymers were measured by thermogravimetric analysis (TGA) measurement until 400 °C while the glass transition temperature was observed the slight difference according to the results of differential scanning calorimetry (DSC). The retardation of prepared photoalignment films with different polarized UV exposure energy was evaluated for confirming  $\lambda/4 = 125$  nm at 500 nm. We studied the effect of the chemical structure of polymers and found that the thermal stability and the photosensitivity are very much dependent on the chemical structure of side chain. These results indicated that the thermal stability and the photosensitivity deeply depended on their chemical structure but the retardation is not related to chemical structure of photopolymers.

**Keywords:** Cinnamate, Chalcone, Thermal stability, Photoalignment, Retardation.

### 1. Introduction

In liquid crystal display (LCD) device, the alignment of the liquid crystal (LC) molecules plays the important role to characterize the image quality of LCD. The rubbing process of conventional technique cannot reflect essential demands for improvement of alignment quality since the rubbing process has many problems for LCD such as generation of electrostatic charge and dust. Therefore, many methods for alignment of liquid crystal molecules are developed to replace rubbing methods. Photoalignment process is well known as one of alternative to rubbing method and is investigated as one of promising candidates that solve the generation of electrostatic charge and dust followed by the rubbing method. Photoalignment process consists of photochemical reactions such as photoisomerization, photodimerization (photocrosslinking) and photodecomposition. In general, photodimerization of photosensitive groups in the photopolymer was used to obtain a stable alignment of low molecular weight LC molecules. Additionally, photodimerization occurs by the exposure of relatively longer wavelength of the UV light to avoid partial degradation of photopolymer films by the irradiation of the UV light. The photopolymer with dimerized moiety of cinnamoyl group have been many examined as a photoalignment material. Upon irradiation cinnamate undergo simultaneously photoinduced cis-trans (E/Z) isomerization establishing a consistent state between both isomers and bimolecular  $[2\pi + 2\pi]$  photocycloaddition to form a cyclobutane dimer. The ratio of both reaction depends on the concentration of the photochromic moiety and effects of polymer matrix density. Various groups have exhibited that the irradiation of polymer films with cinnamate group by linearly polarized UV light generates anisotropy, mostly caused by the angular-selective photocycloaddition of the cis (E) isomer. For all that, there is a controversy opinion whether the aligning properties at the interface are mainly induced by the photocycloaddition products or by the photoisomerization. Photoalignment of the nematic liquid crystals (NLC) by using a poly (vinyl) cinnamate and other flexible photopolymer surfaces such as poly methyl methacrylate and poly siloxane has been studied by many researchers. However, the

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poor thermal stability of acrylate materials in backbone structure of photopolymer have not satisfactory to obtain a good liquid crystal aligning properties. In the other hand, the chalconyl group is recognized to be a good photosensitive group and exhibits only photodimerization between the carbon double bonds in chalcone moieties different from the cinnamate group. The photoreaction chalconyl groups take place by irradiation with relatively longer wavelength UV light than that of the cinnamoyl group. Photosensitive polymers with chalcone groups have been examined for photoalignment film. According to the works, good LC alignment was observed for the LC cell using the polymer film with chalcone moiety compared to the cinnamate polymer film when the deep UV light was cut-off. This result indicated that the chalconyl moiety is good photosensitive group. Accordingly, alignment behavior of LC molecules would be simply enhanced by the liquid crystalline polymer surface where mesogenic groups having similar chemical structure to that of the LC molecules existed.

In this study, we prepared the two kinds of photopolymer with the different photosensitive group of cinnamate and chalconyl groups for high thermal stability and superior photoalignment of liquid crystals. We also investigated the photo-alignment properties, thermal stability and influence of photosensitive group for photoinduced films using the low linearly polarized UV-curing energy method for the application to retarder films.

## 2. Experimental

### 2.1. Synthesis of Poly(Succinimide Butyl Methoxy Cinnamate) (PMC3-E2)

This final compound was synthesized from the esterification reaction. In a 250 mL round-bottomed flask, the PM (1.0 g), C3-E2 (2.4 g) were dissolved in dry tetrahydrofuran (THF) 40 mL and under stirring DCC (4.5 g) / DMAP (1.1 g) (dissolved in 60 mL dry THF) was added. The mixture solution was stirred 48 h at room temperature under a nitrogen atmosphere. After reaction, removal of the precipitate by filtering, and then solution layer removed by rotary evaporator. The crude product was precipitated at ethyl alcohol, which was filtered. The white product was dried in vacuum at 60 °C for 24 hr. Yield 75 %. <sup>1</sup>H-NMR : aromatic ring peaks (7.24, 7.38, 7.68 ppm), C=C peaks (7.59, 6.58 ppm), alkyl spacer peaks (4.30, 3.33 ppm).

Similarly the PM4Ch was synthesized. The yellow-white product was obtained to yield 82 %. The proton peaks in the PM4Ch was confirmed that the carboxyl acid peak not showed in 13 ppm whereas exhibited the Ar-CH and -CH<sub>2</sub>=CH<sub>2</sub>- peaks induced chalcone in 8.3-7.2 ppm, CH<sub>2</sub>-COO- peak due to alkyl spacer in 4.3-4.1 ppm, respectively.

### 2.2. Alignment Layer Coating

The PMC3-E2 was solved in toluene/methyl ethyl ketone (MEK) (7:3 weight ratios). The concentration of the PMC3-E2 in the toluene/MEK mixture solution was adjusted 1 wt %. Thin film of the PMC3-E2 was prepared on a glass substrate by spin-coating method (800 rpm, 10 s). The PMC3-E2 thin film was dried at 100 °C for 1 min in a chamber. After dry, LPUV was exposure on PMC3-E2 film. The thickness of the fabricated PMC3-E2 thin films was about 100 nm. PMC4Ch also fabricated similar to method.

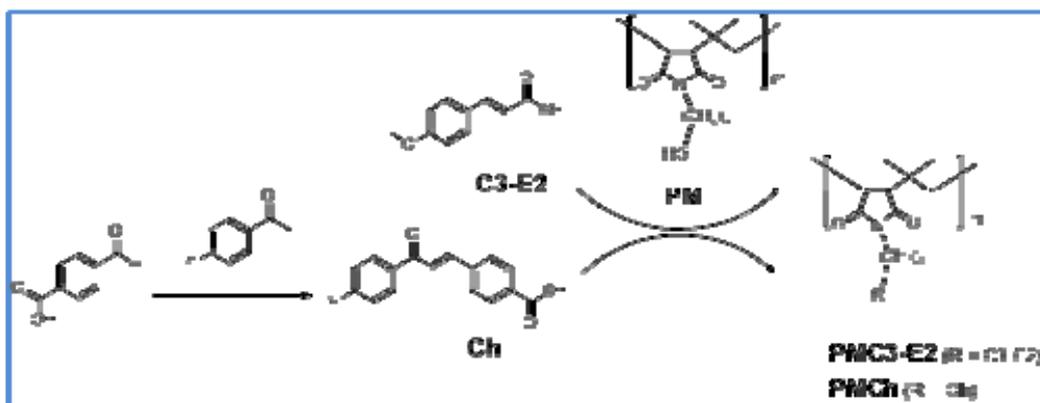


Fig. 1: Synthetic scheme of the photosensitive polymaleimides.

### 3. Results and Discussion

The DSC curves of the polymaleimides are given in Fig. 2. All the polymaleimides show the thermal behavior of a typical amorphous polymer. The DSC traces of all polymaleimides only exhibits 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. The  $T_g$  of PMC3-E2 is lower than the corresponding value of PM4Ch. This result can be suggested to the rigidity due to benzene ring and strong interaction between the chalcone side groups with the polar fluorine, which increases the packing density of the polymeric chains and decrease the free volume in the solid state. This assignment of the phase transition temperature of PM4Ch and PMC3-E2 were supported by optical microscopic observation.

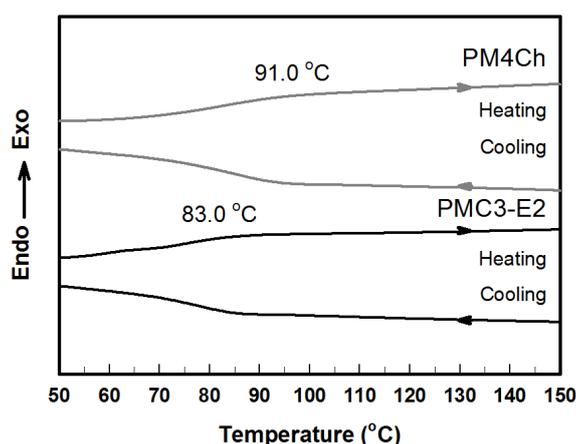


Fig. 2: DSC thermograms of PM4Ch and PMC3-E2 from the second heating and first cooling scan (10 °C /min).

Fig. 3 shows the UV-vis absorption spectra of the polymaleimides before irradiation and after being exposed to UV light with the different irradiation times. Both trans-cis isomerization and dimerization of chalcone are expected upon exposure of the PM4Ch to UV irradiation. The isomerization occurs through a rotation mechanism from the trans to the cis form when the UV light has excited the  $\pi$ -electron of the C=C. The dimerization is a bimolecular, result in crosslinking of the polymer with formation of cyclobutane rings through a [2+2] cycloaddition of the C=C. PM4Ch shows an absorption maximum 306 nm which is attributed to the transition through the chalcone system for the trans-isomer. The intensity of this absorption decreases fast upon exposure to UV light which indicates the disturbance of conjugation, either due to dimerization or trans-cis isomerization. At that same time, an increase of absorption is exhibited at 243 nm attributed to the photochemical product. For exposure does less than 70 mJ/cm<sup>2</sup>, there is an isosbestic point at 268 nm for both polymers which indicates an equilibrium between two species demonstrating that only one process occurs exclusively and only one photochemical product is formed. Further photoirradiation results in deviations from the isosbestic points which reveal the formation of more than one product and the speed of conversion slowly down. The peaks of both photochemical products, the cis-isomer and the dimer, are overlapping each other. In the other hand, the PMC3-E2 films strongly absorb UV light over the range of 250~340 nm. A strong broad band is centered at 293 nm. This band is extensively overlapped with the other two bands discerned as shoulder peaks. The intensities of all these absorption bands apparently decrease as the exposure does increases. These absorption bands could not be resolved quantitatively because of their large overlaps. To resolve these overlapped bands, we are processing a 2D mapping technique to the UV spectra. In case of both photopolymers, after UV irradiation, all the absorbance at dramatically decreases as the exposure does increases, which is caused by the [2+2] photocycloaddition reaction between the photosensitive groups. Furthermore, the products no changes in the spectra of 200 and 500 mJ/cm<sup>2</sup> exposure which indicate that the products are stable. This result suggested that the PMC3-E2 exhibited the more sensitive photoalignment property compared to PM4Ch. The retardation with the directly polarized UV exposure of 90° on the photoalignment polymer film surface as a function of UV exposure energy is shown in Fig. 4. All samples are shown that the retardation mostly was about 121 ~ 124 nm by polarized UV exposure energy 50 mJ on the photo-aligned samples film surface. The retardation almost slightly increases with increasing exposure energy until 200 mJ. When the exposure energy was over 150 mJ, the retardation

tended to uniform. We also represented together the retardation of Rolic company for comparison. This result indicated that retardation rely on the photo-alignment of photopolymer by the polarized UV exposure energy but not depends on the chemical structure of photopolymers.

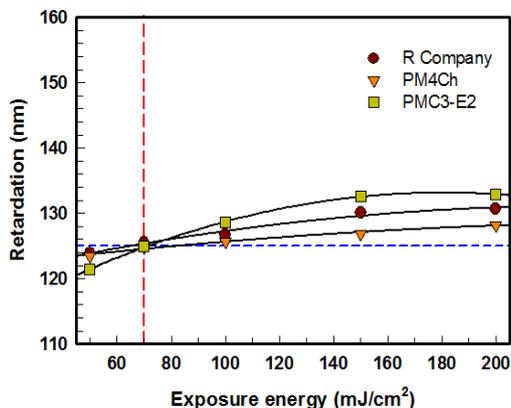


Fig. 4: Dependence of the retardation on UV exposure energy for photopolymers.

The converted percent value of difference between the maximum and minimum of optical transmittance with white mode when photoalignment films were placed between the cross polarizer of 45° is represented in the Fig. 5. All photopolymers shows the high optical transmittance uniformity over 90 %. In particular, PMC3-E2 exhibited high optical transmittance uniformity similar to standard sample of Rolic company. This result suggested that PMC3-E2 films possess excellent ability to induce alignment of LC molecules. We also plotted together the result of Rolic company.

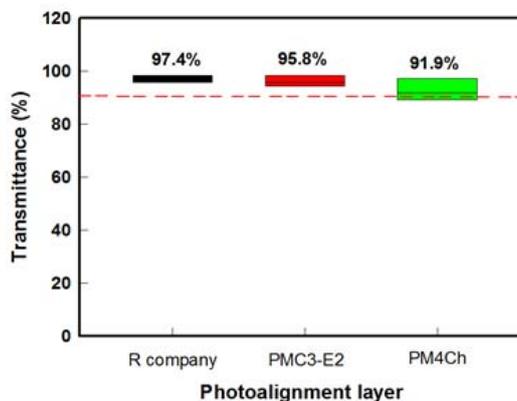


Fig. 5: The optical transmittance uniformity of different photopolymers.

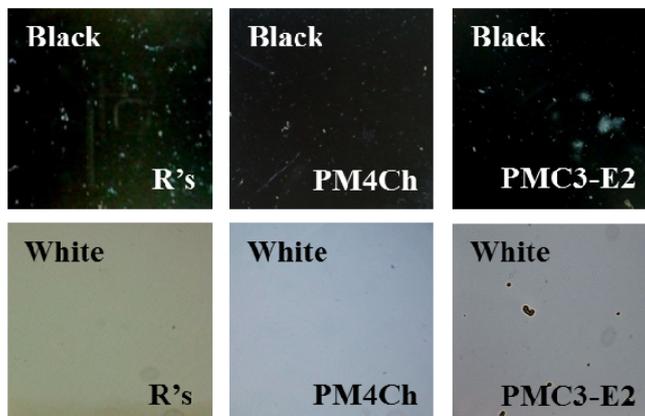


Fig. 6: Polarizing optical micrographs of LC cells with the polymaleimide alignment layers after 50 mJ/cm<sup>2</sup> LPUV exposure.

Fig. 6 shows the micrographs of LC cells using the photosensitive polymaleimides as photoalignment layers. For the observation, the LC cells were placed between the crossed polarizer. The vision is dark when the polarization direction of the LPUV is parallel to the polarizer and is white when changing the cells to  $\pm 45^\circ$ . This result indicates that the cells show significant birefringence and LC molecules in the cells possess a homogenous alignment. Microscopic observation confirmed that the PM4Ch and PMC3-E2 films possess excellent ability to induce LC molecules alignment.

#### 4. Conclusion

In conclusion, we synthesized the two type of photopolymer with the different photosensitive group of cinnamate and chalconyl groups for high thermal stability and superior photoalignment of liquid crystals. The polymaleimides show high thermal stability and good solubility in polar organic solvent. All the polymaleimides commonly can undergo photodimerization reactions and the strong stability to induce homogeneous alignment of LC molecules upon the low polarized UV exposure energy. The retardation of the alignment layers mainly depend on the polarized UV exposure energy rather than chemical structure of photopolymers. These results indicated that the photodimerization contributes to the improvement of enhancement of LC photoalignment as well as thermal stability and the photosensitivity deeply depended on theirs chemical structure but the retardation is not related to chemical structure of photopolymers.

#### 5. References

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