

Synthesis of Side Chain Chalcone Polymers and Their Photoalignment Capability for Film Patterned Retarder

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Abstract. We synthesized two kinds of photocrosslinkable side chain photopolymer with a chalcone group in the side chain. Two photopolymers have the different alkyl spacer length introduced between main chain and chalconyl moiety. The thermal stability of these photopolymer measured by differential scanning calorimetry and the thermogravimetric analysis measurement. 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 length of alkyl spacer in side chain chalcone polymers and found that the thermal stability and the photoalignment properties are very much dependent on the alkyl chain spacer. This result indicated the photodimerization contributes to the enhancement of LC photoalignment.

Keywords: Chalcone, Liquid crystals, Thermal stability, Photodimerization, UV exposure energy

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 the non-contact alignment method for LC unlike rubbing method and is investigated as one of promising candidates that solve the generation of electrostatic charge and dust during the rubbing method. Despite of many advantages, photoalignment method has been the major problem due to the worse image sticking and reliability than that using 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+2] photocycloaddition to form a cyclobutane dimer. The ratio of both reactions 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. 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

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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 photopolymer with imide linkage and chalconyl groups for high thermal stability and superior photoalignment of liquid crystals. We investigated the photoalignment properties and thermal stability of photoinduced films using the low linearly polarized UV-curing energy method for the application to film patterned retarder.

2. Experimental

2.1. Sample Synthesis

Photopolymers were prepared according to the route of Fig 1.

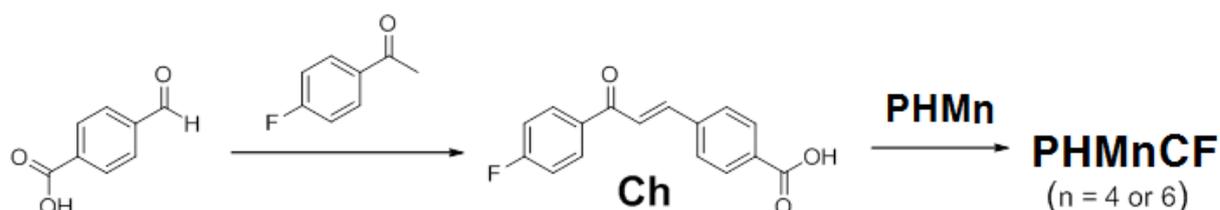


Fig. 1: Synthetic route of PHMn.

2.1.1. Synthesis of Poly (Hydroxyalkylmaleimide) (PHMn, n=4, 6).

Set up 100 mL 3-neck round bottom flask, Dean stark and condenser. Dissolve 1.54 g of poly(maleic anhydride) in 12.6 mL NMP and 2.9 mL toluene, stir 1h under N₂ atmosphere. Add 1.29 g 6-amino hexanol (or 4-amino butanol) in N-methyl-2-pyrrolidone (NMP) and then stir at room temperature for 24 hr under N₂ atmosphere. The NMP and toluene solution refluxed at 200 °C for 12 hr on a Dean-Stark condenser equipped. After cooling the mixture to room temperature, the liquid is decanted away from the precipitate and the precipitate was washed with water. The solid is filtered and dried overnight under reduce pressure. Poly(hydroxybutylmaleimide) (PHM4) and Poly(hydroxyhexylmaleimide) (PHM6) as products was afford each (78% yield, mp 117 °C) and (80 % yield, mp 145 °C) as white solid. FT-IR (KBr, cm⁻¹): 1782(imide C=O). 1713(imide, C=C)

2.1.2. Synthesis of 4-carboxy-4' -Fluorochalcone (CF).

Set up 100 mL round bottom flask under N₂ atmosphere. Terephthalaldehydic acid (1.54 g) and sulfuric acid (3.46 g) was dissolved in 20 mL acetic acid. Add 4' -fluoroacetophenone in 20 mL acetic acid. The solution was reacted at 140 °C for 2 hr. The solution was diluted with 500 mL water and neutralized by dropwise addition of sodium hydroxide solution. The precipitate was filtrated using Büchner funnel, removed the filterate, and collected the solid. The solid cake was recrystallized from n-hexane and ethyl acetate (4:1, volume ratio). Dry in vacuum oven overnight. 4-carboxy-4' -fluorochalcone was dried in vaccum oven over 24 hr and afforded 4.99 g (18.5 mmol, yield 93 %, mp 263 °C) as yellow green solid. FT-IR (KBr, cm⁻¹): 3384 (OH), 1653(C=O), 1601 (chalcone C=C, Ar C=C), 1569, 1507(Ar C=C), 983 (C-H).

2.1.3. Synthesis of Polymaleimide with Chalcone Moiety (PHMnCF, n=4, 6).

A dry, 250 mL, 1-necked flask equipped is charged with poly(hydroxyalkylmaleimide) (PMn, 0.5 g), 4-carboxy-4'-fluoro chalcone (Ch, 1.2 g), and tetrahydrofuran(THF) 100 mL. The solution of dicyclohexylcarbodiimide (DCC, 2.29g) and 4-dimethylaminopyridine (DMAP, 0.68 g) in THF 20 mL mixed the PM and Ch solution stirred at room temperature for 48 hr. To remove dicyclohexyl urea as impurity, the solution was filtered. The method to remove the impurity is concentrated the solution, added methylene chloride and acetone, and re-filtered. And the liquid is decanted away from the precipitate, and the

precipitate was washed with iso-propyl alcohol. The solid is dried overnight on vacuum dry oven. The products were to afford PHM4CF (75 % yield, mp 138 °C) and PHM6CF (82 % yield, mp 132 °C) as white yellow solid. FT-IR (KBr, cm⁻¹): 1772(imide C=O), 1692(imide, C=C).

3. Result and Discussion

All The ¹H-NMR spectra of are shown in Fig.2. The proton peaks in the series of PHMnCF was confirmed that the carboxyl acid peak not showed in 13 ppm whereas exhibited the Ar-CH and -CH₂=CH₂- peaks induced Chalcone in 8.3-7.2 ppm, CH₂-COO- peak due to alkyl spacer in 4.3-4.1 ppm, respectively.

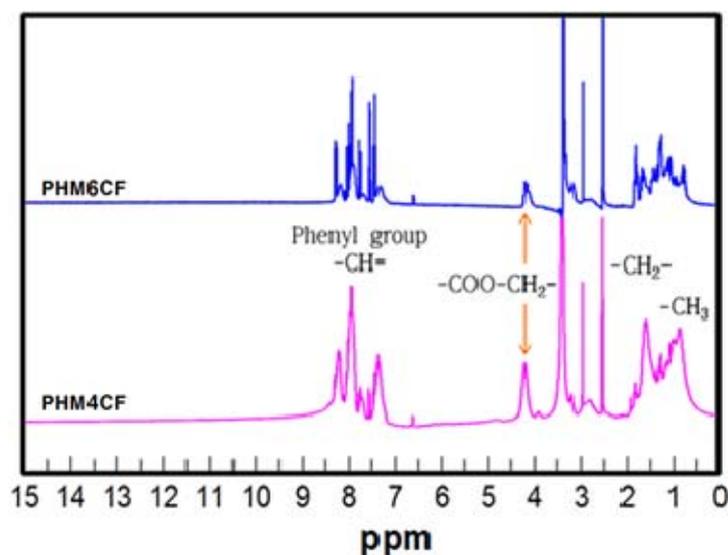


Fig. 2: ¹H-NMR spectra of PHM4CF.

Thermal stability of the photopolymers was investigated by thermogravimetric analysis (TGA) measurement. Fig. 3 exhibits the TGA curves of the photopolymers. TGA measurement revealed that the synthesized photopolymers have satisfactory thermal stabilities until 380 °C. The thermal stability of the photopolymers sensitively depends on the spacer length of PHMnCF. PHM4CF shows the more thermal stability than PHM6CF. The decomposition of the polymers was almost completed around 480 °C, after that no weight loss was observed.

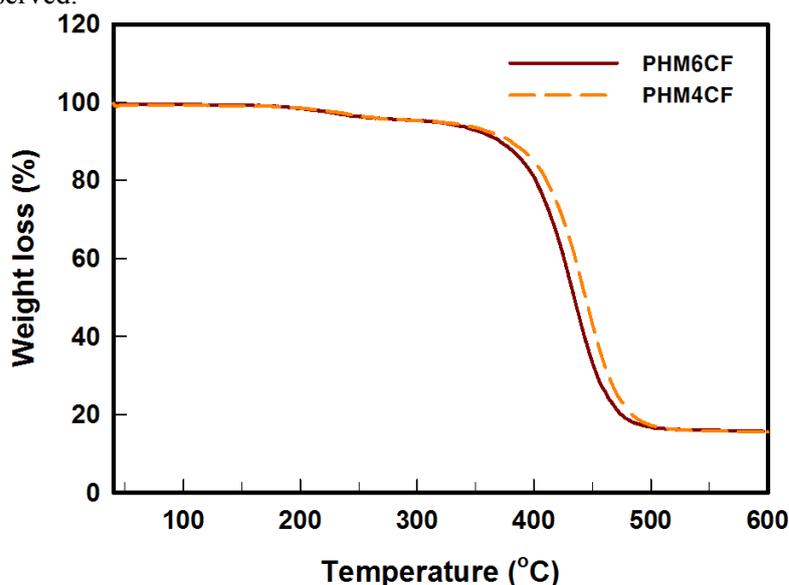


Fig. 3: TGA thermograms of PHMnCF (20°C/min).

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. Similar to TGA result, PHM4CF exhibits the higher glass transition temperature than PHM6CF. This assignment of the phase transition temperature of PHM4CF and PHM6CF was confirmed by optical microscopic observation.

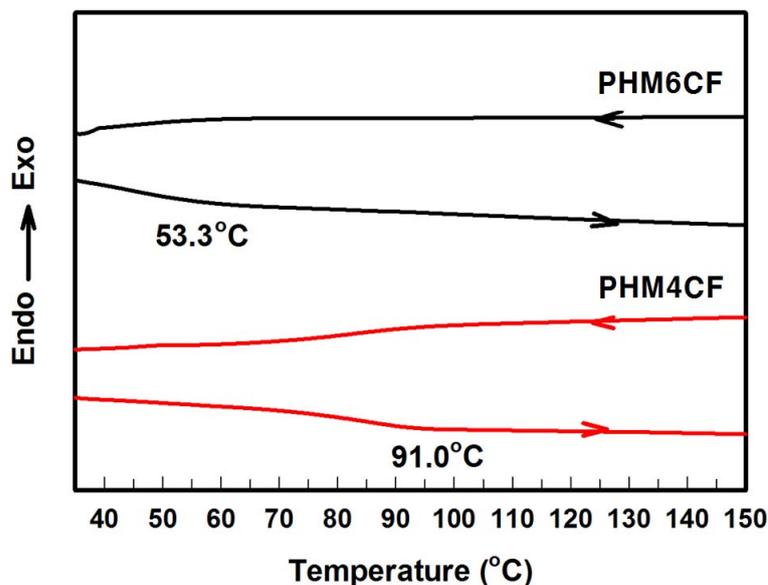


Fig. 4: DSC thermograms of PHMnCF (10°C/min).

Both trans-cis isomerization and dimerization of chalcone are expected upon exposure of the PM4Ch to UV irradiation as illustrated in Fig. 2. The isomerization occurs through a rotation mechanism from the trans to the cis form when the UV light has excited the π -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. PHM4CF 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/cm², 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. After exposure 500 mJ/cm² there are no changes in the spectra which indicate that the products are stable.

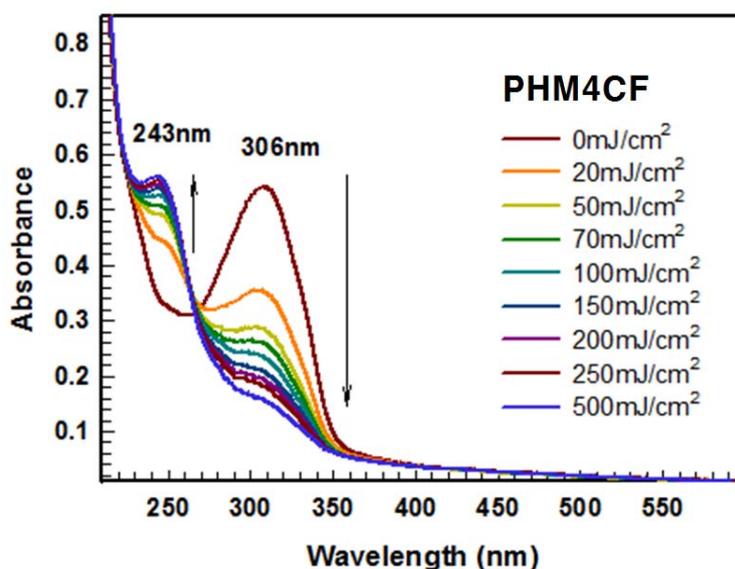


Fig. 5: Absorption spectral changes of PHM4CF in film irradiated with unpolarized UV light.

4. Summary

In this paper, we synthesized the two type photopolymers with different alkyl spacer length via imide linkage and chalconyl groups for high thermal stability and superior photoalignment of liquid crystals and investigated their thermal stability and retardation by using the polarized UV exposure energy on the photopolymers. The thermal stability of photopolymers was confirmed by the glass transition temperature of 53-91 °C, decomposition temperature of 380-395 °C, respectively. In the other hand,

Furthermore, photodimerization is affected to the improvement of the thermal stability of LC photoalignment because of the suppressive effect of the cross-linked structure on the randomization of photochemically oriented chromophoric residues.

5. References

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