

Effect of Plasticization of Poly(Vinyl Cinnamate) on Liquid Crystal Orientation Stability

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Abstract

A cinnamate group is a well-known compound group used in the dimerization reaction by ultraviolet irradiation, and cinnamate polymers are studied as photoalignment materials. In this study, the radical reaction of cinnamate side groups attached to a flexible polymer backbone is considered feasible using thermal energy. To induce the thermal reaction of cinnamate side groups, we modified the flexibility of poly(vinyl cinnamate) by introducing a plasticizer into the polymers and investigated the thermal reaction behavior of cinnamate side groups. The plasticization of poly(vinyl cinnamate) makes the induction of the thermal reaction of cinnamate side groups easier than that of unmodified poly(vinyl cinnamate). The thermal reaction of cinnamate side groups is closely related to the enhancement of the thermal stability of the liquid crystal orientation of polymer films with polarized UV irradiation.

1. Introduction

The photoalignment induced by the polarized UV irradiation of a polymer film has been the subject of extensive research since the discovery of the optical control of liquid crystal anchoring nearly a decade ago.^{1,2)} Several photoreactive materials for a photoalignment layer have been investigated.³⁻⁷⁾ Poly(vinyl cinnamate) (PVCi), which is a typical negative photoresist, has been applied to the photoalignment layer by linearly polarized ultraviolet light exposure.⁸⁻¹⁰⁾ PVCi can be photocrosslinked anisotropically by polarized UV irradiation, and the thermal stability of the liquid crystal orientation is closely related to the crosslinking structure. In our previous work, we found that the radical reaction of cinnamate side groups attached to a flexible polymer backbone is induced by thermal energy, and this resulted in the enhancement of the thermal stability of

the liquid crystal orientation.¹¹⁾ We also found that the chain flexibility of a cinnamate polymer is closely related to the thermal reaction of cinnamate side groups, and that the additional crosslinking structure induced by the thermal reaction of cinnamate side groups is an important factor for the fixation of the molecular orientation of cinnamate polymers.

To enhance the stability of the liquid crystal orientation of photoreactive polymers, a systematic study on the relationship between polymer chain flexibility and liquid crystal orientation is required. The polymer chain flexibility was previously conventionally controlled by introducing small compatible molecules, such as a plasticizer.¹²⁾ In this work, to elucidate the relationship between the chain flexibility of cinnamate polymers and the thermal reaction of cinnamate side groups, we intentionally controlled the flexibility of PVCi by introducing ethyl cinnamate as a plasticizer. The effect of the plasticization of PVCi on the thermal reaction of cinnamate side groups was investigated by UV absorption spectroscopy. The relationship between the thermal reaction of cinnamate side groups and the thermal stability of the liquid crystal orientation of PVCi films with polarized UV irradiation was also studied.

2. Experimental

PVCi and ethylene cinnamate were purchased from Sigma-Aldrich. A 2 wt% cyclohexanone solution of polymer was spin-coated onto the substrate at 1800 rpm and the cast was baked at 60 °C for 1 h and the thickness of film was 80 nm. Thermal analysis was performed by using a DSC 2010 (TA Instruments) and the molecular weight of polymers dissolved in THF was determined by GPC with polystyrene as standard. 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 $4\text{mW}/\text{cm}^2$. Thermal reaction of polymer was carried out by placing the polymer film on hot-plate at 200°C . Spectral measurements of FT-IR and UV-vis were performed by using a Bruker TENSOR27 and Shimadzu UV-1601, respectively.

A homogeneously aligned LC cell was constructed by sandwiching nematic LC (E7) between a pair of UV irradiated glass substrates coated with a cinnamate polymers. The cell gap of LC cell was adjusted by using the styrene bead of $8\ \mu\text{m}$ diameter. The director of nematic LC in the LC cell was determined from a dichroic absorption of dichroic dye (disperse blue 14, 0.2 wt%) included in nematic LC. A small amount of the dichroic dye show strong absorption at $653\ \text{nm}$ and from the angular dependency of the absorbance at $653\ \text{nm}$ in the polarized UV spectra of the LC cell, the distribution of LC director could be figured out.

3. Results and discussion

The chemical structures of PVCi and ethyl cinnamate used in this work are shown in Fig. 1.

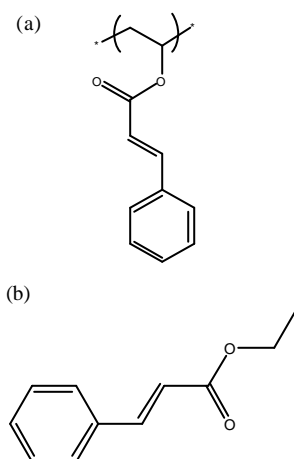


Fig. 1. Chemical structures of (a) PVCi and (b) ethyl cinnamate.

PVCi and ethylene cinnamate were purchased from Sigma-Aldrich. The photochemical reaction of a cinnamate polymer is generally induced by the

reaction of the carbon double bonds of cinnamate side groups with UV irradiation.¹³⁾ However, the carbon double bonds of cinnamate side groups also thermally react with each other, as described in a report on the thermal reaction of cinnamate side groups attached to a flexible polymer backbone.¹¹⁾ To elucidate the effect of the polymer chain flexibility on the thermal reaction of cinnamate side groups, we modified the flexibility of PVCi by introducing ethyl cinnamate as a plasticizer. In polymer applications, the polymer chain flexibility is controlled by introducing small appropriate molecules such as a plasticizer. In our work, we prepared plasticized PVCi films by adding 100 or 200wt% ethyl cinnamate based on the polymer into the cyclohexanone solution of PVCi (EtCi100 and EtCi200). The enhancement of the polymer chain flexibility is generally confirmed by a decrease in the glass transition temperature of a polymer.

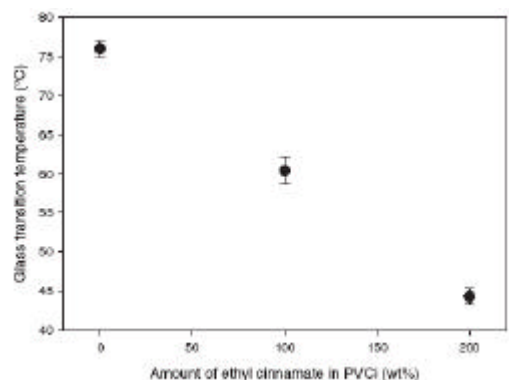


Fig. 2. Glass transition temperature of plasticized PVCi plotted against of ethyl cinnamate.

Figure 2 shows the glass transition temperatures of PVCi, EtCi100, and Et-Ci200. The glass transition temperature of PVCi is about 77°C , and the plasticized PVCi shows a decreased glass transition temperature compared with PVCi. The glass transition temperatures of EtCi100 and EtCi200 are 60°C and 45°C , respectively. As the amount of ethyl cinnamate increases in the plasticized PVCi, the glass transition temperature decreases.

In our previous work, we found that the chain flexibility of cinnamate polymers is closely related to the thermal reaction of cinnamate side groups. To elucidate the effect of the plasticization of cinnamate polymers on the thermal reaction of cinnamate side groups, we investigated the change in the UV absorbance of the plasticized PVCi film with heating (Fig. 3). The heating of PVCi at 200°C shows a

decrease in the absorbance of the cinnamate groups at 280 nm, indicating that the reaction of the carbon double bonds of the cinnamate side groups is induced by thermal energy. The thermal reaction of the cinnamate side groups of PVCi is not as highly significant as that in the flexible cinnamate polymers. However, the plasticization of PVCi shows an enhancement of the thermal reaction of the cinnamate side groups, and the degree of thermal reaction of EtCi200 is higher than that of EtCi100.

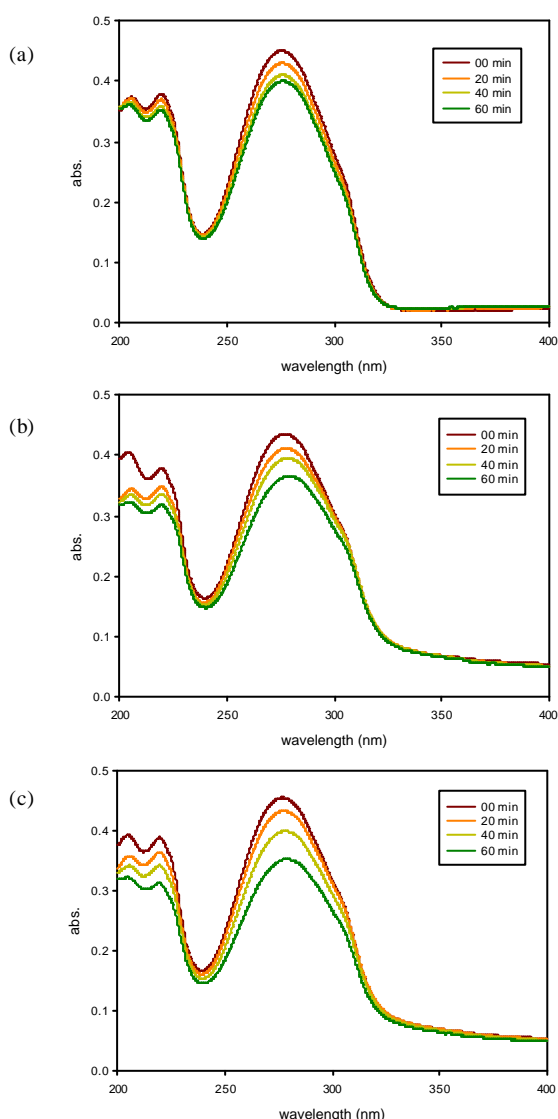


Fig. 3. Change in UV absorbance of plasticized PVCi with heating at 200°C: (a) PVCi, (b) EtCi100, and (c) EtCi200.

From the results of the thermal analysis of the plasticized PVCi, it was found that the degree of the thermal reaction of the cinnamate side groups is closely related to the polymer chain flexibility. The thermal reaction of the cinnamate side groups is different from their photochemical reaction. The photochemical reaction of the cinnamate side groups is photocycloaddition based on the Diels-Alder reaction mechanism, and it is easily induced by the selected absorption of UV energy.¹⁴⁾ However, the thermal reaction of the cinnamate side groups seems to be attributed to the radical reaction mechanism of the carbon double bonds of the cinnamate side groups. Accordingly, the thermal reaction of the cinnamate side groups is affected by the chain flexibility of the cinnamate polymers. The plasticization of PVCi makes the cinnamate side groups more flexible compared with that in case of the pure PVCi, and the degree of the thermal reaction of the plasticized PVCi is enhanced. Moreover, the plasticizer ethyl cinnamate thermally reacts with the existing PVCi. Thus, residual plasticizers are not observed after the thermal reaction is completed. This additional crosslinking reaction induced by the thermal reaction of the cinnamate side groups makes the photodimer align the liquid crystals more stably.¹⁵⁾

To investigate the effect of the chain flexibility of PVCi on the liquid crystal (LC) orientation of the film with polarized UV irradiation, we prepared LC cells using PVCi and plasticized PVCi films with polarized UV irradiations of 0.5 and 2.4 J/cm². Figure 4 shows the order parameter (*S*) of dichroic dye dissolved in LC as a function of heating temperature of the LC cells. *S* is defined as

$$S = (A_{\parallel} - A_{\perp}) / (A_{\text{large}} + 2A_{\text{small}}),$$

where A_{\parallel} and A_{\perp} denote absorbance of the doped dye parallel and perpendicular to the polarization direction of irradiated UV light respectively, while A_{large} is taken to be the larger of A_{\parallel} and A_{\perp} , while A_{small} is taken to be the smaller.¹⁶⁾ The order parameters of LC for all the polymers are negative due to the perpendicular liquid crystal orientation of PVCi to the polarization direction of UV. Due to the higher photoreaction of the cinnamate side groups, the order parameter of the 2.4 J/cm² UV irradiation is larger than that of the 0.5 J/cm² UV irradiation. Before the heating of the LC cells, the order parameter of PVCi is similar to that of the plasticized PVCi.

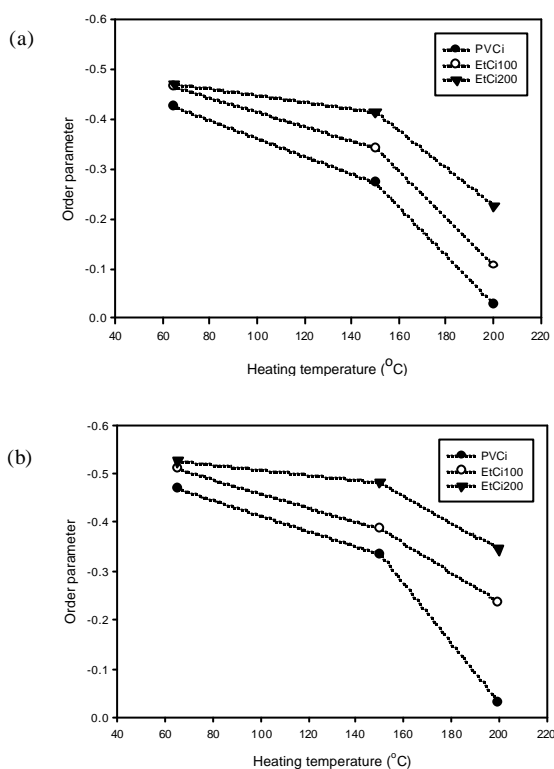


Fig. 4. Changes in order parameter (S) of dichroic dye dissolved in LC filled in cells prepared using PVCi (?), EtCi100 (?), and EtCi100 (?) as a function of heating temperature of LC cells with UV irradiation with (a) 0.5 J/cm² and (b) 2.4 J/cm².

However, the order parameter of PVCi decreases to near zero after the heating of the LC cells at 200°C. This is caused by the randomization of the photodimers due to the thermal relaxation of the polymer chains.¹⁷⁾ The order parameter of the plasticized PVCi is similar to that of PVCi, regardless of the amount of the plasticizer. However, the degree of the decrease in the order parameter of the plasticized PVCi induced by the heating of LC cells is smaller than that of PVCi, and EtCi200 shows an order parameter larger than EtCi100. EtCi200 with the 2.4 J/cm² UV irradiation shows a stable liquid crystal orientation despite the thermal treatment at 200°C. From these results, the chain flexibility of the cinnamate polymer is considered to affect the stability of the liquid crystal orientation of the film. Compared with that in the case of the pure PVCi, the reaction of the cinnamate side groups of the plasticized PVCi is induced more easily by thermal energy. Therefore, the heating of the plasticized PVCi film with polarized

UV irradiation induces the thermal crosslinking reaction of the unreacted cinnamate side groups, and this defines the anisotropic distribution of the photodimers of the cinnamate side groups. In contrast to the conventional knowledge that a flexible polymer is not suitable for the thermal stability of polymers, the plasticized PVCi is considered advantageous for the photoinduced molecular orientation due to the post-thermal crosslinking.

4. Conclusion

The thermal reaction of the cinnamate side groups of PVCi is closely related to the plasticization of PVCi. The enhancement of the chain flexibility of PVCi by introducing ethyl cinnamate as a plasticizer is confirmed by measuring the glass transition temperature of the polymers. The increased chain flexibility of the plasticized PVCi makes the introduction of the thermal reaction of the cinnamate side groups easier than that of the pure PVCi. The cinnamate side groups of the plasticized PVCi are crosslinked by heating, and this thermal crosslinking makes the molecular orientation of PVCi more stable.

5. References

- [1] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki: *Langmuir* 4 (1988) 1214.
- [2] W. M. Gibbons, P. J. Shannon, S. T. Sun and B. J. Swetlin: *Nature* 351 (1991) 49.
- [3] M. Obi, S. Morino and K. Ichimura: *Macromol. Rapid Commun.* 19 (1998) 643.
- [4] P. O. Jackson and M. O'Neil: *Chem. Mater.* 13 (2001) 694.
- [5] D. H. Suh, K. Kudo and K. Ichimura: *Macromol. Chem. Phys.* 199 (1998) 375.
- [6] Y. Makita, T. Natsui, S. Kimura, S. Nataka, M. Kimura, Y. Matsuki and J. Takeuchi: *J. Photopolym. Sci. Technol.* 11 (1998) 187.
- [7] M. Obi, S. Mirono and K. Ichimura: *Chem. Mater.* 11 (1999) 656.
- [8] M. Schadt, K. Schmitt, V. Koznikov and V. Chigrinov: *Jpn. J. Appl. Phys.* 7 (1992) 2155.
- [9] X. T. Li, D. H. Pei, S. Kobayashi and Y. Iimura: *Jpn. J. Appl. Phys.* 36 (1997) L432.
- [10] M. Obi, S. Morino and K. Ichimura: *Jpn. J. Appl. Phys.* (1999) 38 L145.
- [11] S. J. Sung, K. Y. Cho, J. H. Yoo, W. S. Kim, H.

S. Chang, I. Cho and J. K. Park: Chem. Phys. Lett. 394 (2004) 243.

[12] J. C. Salamone: Polymeric Materials Encyclopedia (CRC Press, Boca Raton, 1996) Vol. 7, p. 5301.

[13] N. Kawatsuki, H. Ono, H. Takatsuka, T. Yamamoto and O. Sangen: Macromolecules 30 (1997) 6680.

[14] D. Harris: Organic Chemistry, ed. J. McMurry (Brooks/Cole, Belmont, 2004) 6th ed., Chap. 14, p. 474.

[15] S. J. Sung, K. Y. Cho, H. Hah, J. Lee, H. K. Shim and J. K. Park: submitted to Polymer.

[16] N. Kawatsuki, K. Goto, T. Kawakami and T. Yamamoto: Macromolecules 35 (2002) 706.

[17] H. T. Kim, J. W. Lee, S. J. Sung and J. K. Park: Mol. Cryst. & Liq. Cryst. 338 (2000) 99.