

Dimerization Behavior of Cinnamate Group attached to Flexible Polymer Backbone and Its Application to Liquid Crystal Alignment

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Abstract

Cinnamate group is well-known for the dimerization reaction by ultra-violet irradiation and cinnamate polymers are studied for photo-alignment materials. The cinnamate groups of flexible polymer are found to produce LC alignment parallel to polarization direction of ultra-violet light, which is contrary to the LC orientation on conventional cinnamate polymers. The un-reacted cinnamate groups in the flexible polymer are also found to participate in cycloadducts formation by additional thermal reaction that preserves the orientation of cycloadducts, leading to the enhancement of thermal stability of LC alignment.

1. Introduction

Irradiation of thin polymer films containing photo-reactive moieties with linearly polarized ultraviolet (UV) light induces optical anisotropy and has attracted intensive interest from a practical viewpoint due to the alignment of liquid crystals (LCs). Extensive efforts have been concentrated on the development of polymers with photo-dimerizable residues such as cinnamate and coumarin for the application to LC alignment materials for the liquid crystal displays (LCDs). It has been known that LC alignment direction with respect to the electric vector of linearly polarized light is dependent on the nature of photo-reactive moieties and polymer backbone. It has been reported that poly(vinyl cinnamate) (PVCi) aligns LC perpendicular to the electric vector of polarized UV light. However, the reversion of LC alignment direction was also reported for the polymer with cinnamate moieties containing alkyl spacer or having different chemical structures. Besides different chemical structure of cinnamate moieties, the flexibility of polymer might also be related to the photo-dimer orientation and LC alignment. However, in the previous research on photo-induced LC alignment material, there have been no interests on the

flexible polymer backbone due to the requirement of thermal stability of LC alignment.

2. Experimental

PVCi was purchased from Sigma-Aldrich and poly(3-ethylene-alter-1 vinyl cinnamate) (PEVCi) was prepared by ring-opening metathesis polymerization. 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 (Oriental) through UV linear dichroic polarizer (27320, Oriental) and UV filter 59800 (Oriental). The intensity of irradiated UV light measured with a UV detector (UIT-150, Ushio) was 4mW/cm². 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 μm 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 nm and from the angular dependency of the absorbance at 653 nm in the polarized UV spectra of the LC cell, the distribution of LC director could be figured out.

3. Results and discussion

We prepared the flexible cinnamate polymer, poly (3-ethylene-alter-1 vinyl cinnamate) (PEVCI) and investigated the dimerization behavior of cinnamate group and the liquid crystal orientation on this polymer. Figure 1 shows the chemical structure of PVCi and PEVCI. This polymer has flexible ethylene backbone and the glass transition temperature was 15°C.

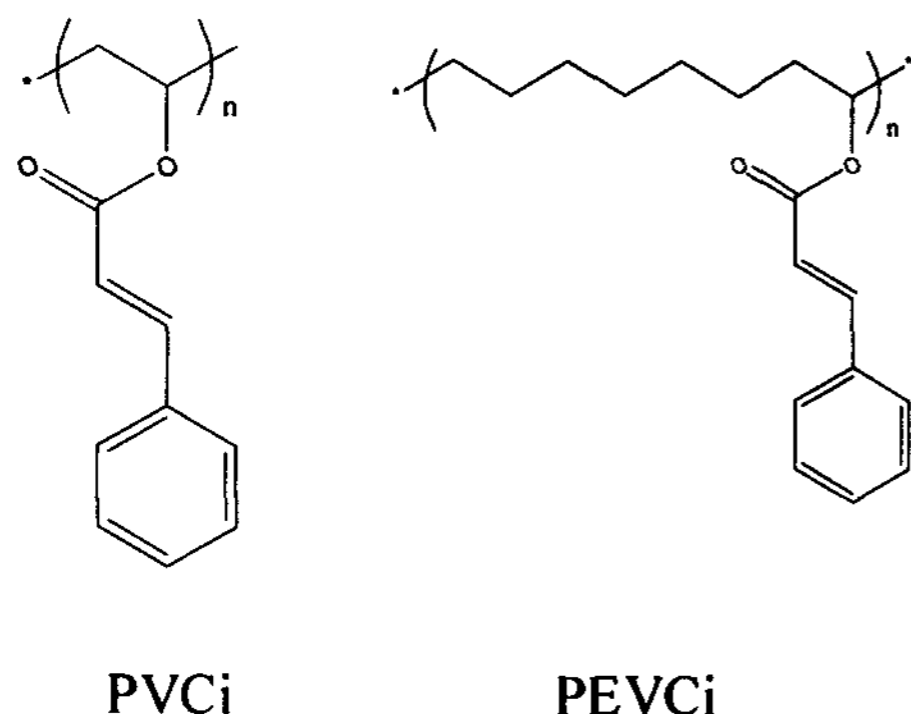


Figure 1. Chemical structure of PVCi and PEVCI

Figure 2 shows a change of polarized UV absorbance with polarized UV light irradiation time. The maximum absorbance peak (λ_{max}), considered to be due to cinnamate group, lies at 280 nm and decreases with increasing UV irradiation time. This means that cinnamate groups attached to PEVCI polymer react each other and form photo-dimer of cinnamate. Before UV irradiation, parallel and perpendicular UV absorbance was identical. However, after UV irradiation, parallel UV absorbance shows further decrease than perpendicular UV absorbance and the difference of UV absorbance increases with UV irradiation time. Cinnamate moieties parallel to the polarization direction of UV could participate in photo-dimerization reaction more easily compared with cinnamate moieties perpendicular to the polarization direction and the decrease of maximum peak of parallel UV absorbance was larger than that of perpendicular UV absorbance. From this result, we could conclude that cinnamate moiety regularly separated in ethylene backbone shows same photo-chemical reaction with other cinnamate containing polymers and PEVCI could be applied to photo-alignment materials.

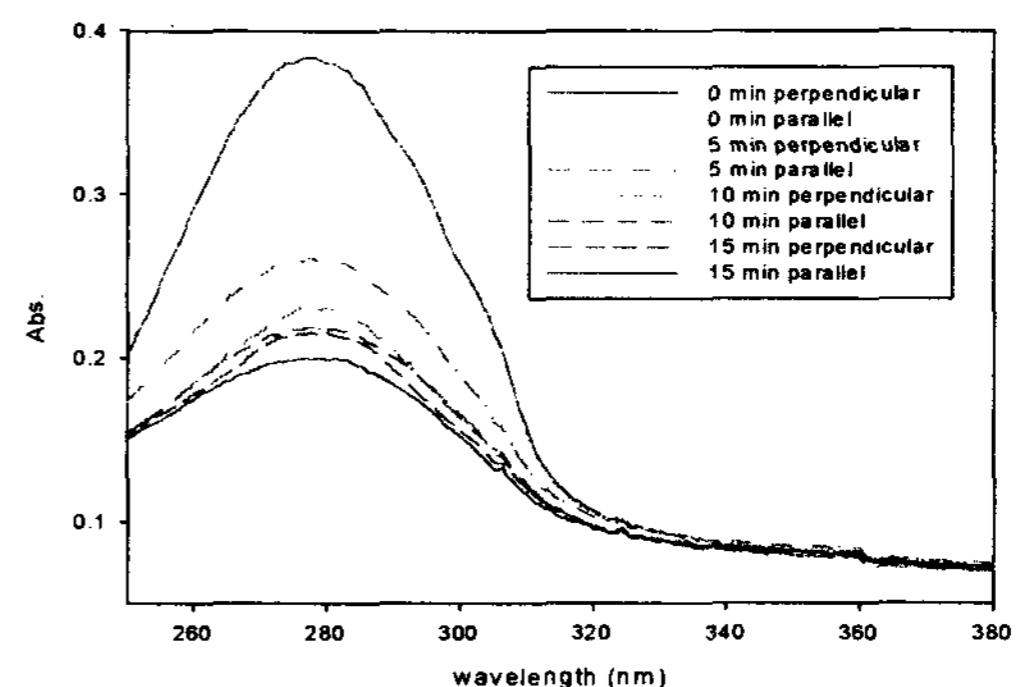


Figure 2. Polarized UV spectra of EVC polymer films irradiated with polarized UV light.

In order to examine the possibility of PEVCI for LC photo-alignment materials, we prepared LC cells and investigated LC alignment properties of PEVCI polymers. In this study, we also prepared LC cell using PVCi in order to reveal effect of chemical structure of cinnamate moiety in polymers on LC alignment properties. Figure 3 shows the polar plot of LC alignment on PVCi and PEVCI polymers with UV irradiation energy. The direction of LC alignment was determined by monitoring the dichroism of a dichroic dye (disperse blue) dissolved in E7. The irradiation energy is 0.48, 1.20, 2.40 Jcm⁻².

It is generally known that the cinnamate containing polymers generate perpendicular LC alignment to the polarization direction and we also confirmed the perpendicular LC alignment of PVCi (Figure 3 (a)). However, PEVCI polymer prepared in this work shows parallel LC alignment to polarization direction of UV and this is first report of parallel LC alignment of cinnamate polymers. The difference of chemical structure of PEVCI and PVCi is the spacing of cinnamate moiety in ethylene backbone polymer and this might be attributed to the parallel LC alignment direction to of PEVCI compared with PVCi. As shown in Figure 2, we found that cinnamate moiety of PEVCI aligned parallel to polarization direction of UV participates in photo-dimerization reaction more easily than perpendicularly aligned cinnamate moiety, and this phenomenon was the same as PVCi homopolymer. However, the LC alignment direction on PEVCI was the exact opposite to PVCi and this means that the orientation of photo-dimer of

cinnamate might be aligned parallel to the polarization direction of UV. The reason for the unique parallel LC alignment on PEVCi will be investigated in future work.

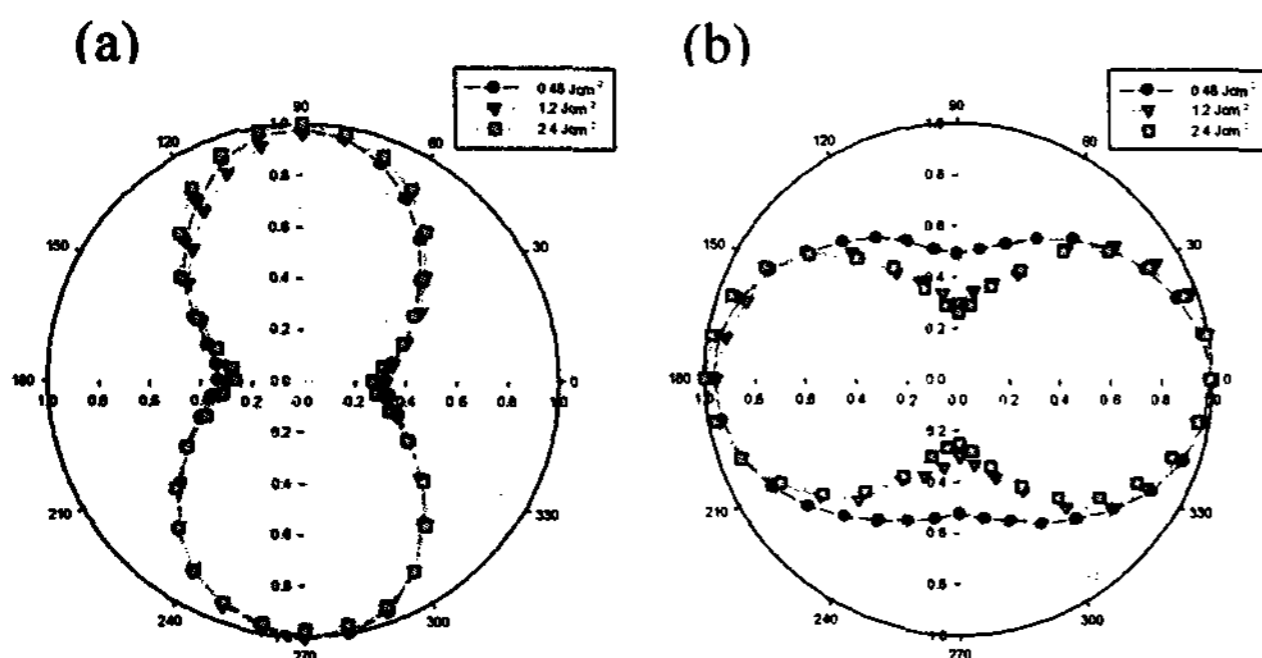


Figure 3. Circular diagrams of absorbance of the dichroic dye (disperse blue) dissolved in E7 (0.1 wt %) in an LC cell fabricated by using films of (a) PVCi and (b) EVC polymer after irradiation with linearly polarized UV irradiation of 0.24, 0.72, 1.2, and 2.4 Jcm⁻². The arrow indicates the direction of polarization of UV light.

Polymers containing cinnamate moiety are representative photo-alignment materials due to high photo-reactivity. However, LC alignment direction is perpendicular to the polarization direction of UV and so the pretilt angle of LC on cinnamate polymers are almost zero, that is the great weakness of cinnamate polymers. It is well known that pretilt angle generation is facile in the case of LC alignment parallel to the polarization direction. From the foregoing result of LC alignment for PEVCi, we verified that PEVCi polymer aligns LC parallel to the polarization direction of UV and we respected that the pretilt angle generation of PEVCi would be easier than PVCi. We irradiated polarized UV on alignment layers obliquely to the substrate and fabricated LC cell using PVCi and PEVCi. Pretilt angle of LC on PVCi shows almost zero regardless of UV irradiation energy and this result is consistent with reported pretilt angle for PVCi. In contrast to PVCi, pretilt angle of LC on PEVCi was above 1° and increased with increasing UV irradiation time. Pretilt angle of 3.1° for PEVCi polymer is the highest value compared with reported pretilt angle of other cinnamate polymers. The high

pretilt angle of LC on NVC might be attributed to the parallel LC alignment to polarization direction of UV.

The other weak point of LC alignment layers based on PVCi is low thermal stability of LC alignment, that is related with low glass transition temperature of PVCi (77°C). The thermal motion of main chain may randomize the anisotropic distribution of the dimer of un-reacted cinnamate moieties and so the glass transition temperature of cinnamate polymer would be important factor for determining thermal stability of LC alignment. However, in the case of PEVCi, glass transition temperature of alignment material is not related with the thermal stability of LC alignment. Glass transition temperature of PEVCi is 16°C and this value is much lower than that of PVCi. If we estimate the thermal stability of LC alignment on PEVCi by comparing glass transition temperature, we could expect that LC alignment on PEVCi shows poor thermal stability.

However, in contrast to our expectation, thermal treatment on LC alignment on PEVCi shows very interesting results. Figure 4 shows the polar plot of LC alignment on PVCi and PEVCi as a function of thermal treatment temperature (65, 150, and 200°C). LC alignment on PVCi was considerably disturbed by thermal treatment above 150°C and this result is consistent with general phenomenon of PVCi. On the contrary, the thermal treatment up to 200°C has no effect on LC alignment on PEVCi and this result is contradictory to the low glass transition temperature of PEVCi. In the case of PEVCi, the chain mobility of backbone has little effect on the relaxation of photo-dimer or un-reacted cinnamate, but detailed researches on the thermal stability of LC alignment on PEVCi are underway.

In spite of similar chemical structure with PVCi, PEVCi shows very unique LC alignment properties compared with PVCi homopolymer. There are two possible factors corresponding to the interesting phenomenon of PEVCi. First, cinnamate moieties of PEVCi are attached to the ethylene backbone with regular spacing, and the ethylene backbone is much flexible than PVCi homopolymer. Further studies on the interesting LC alignment properties of PEVCi are in progress.

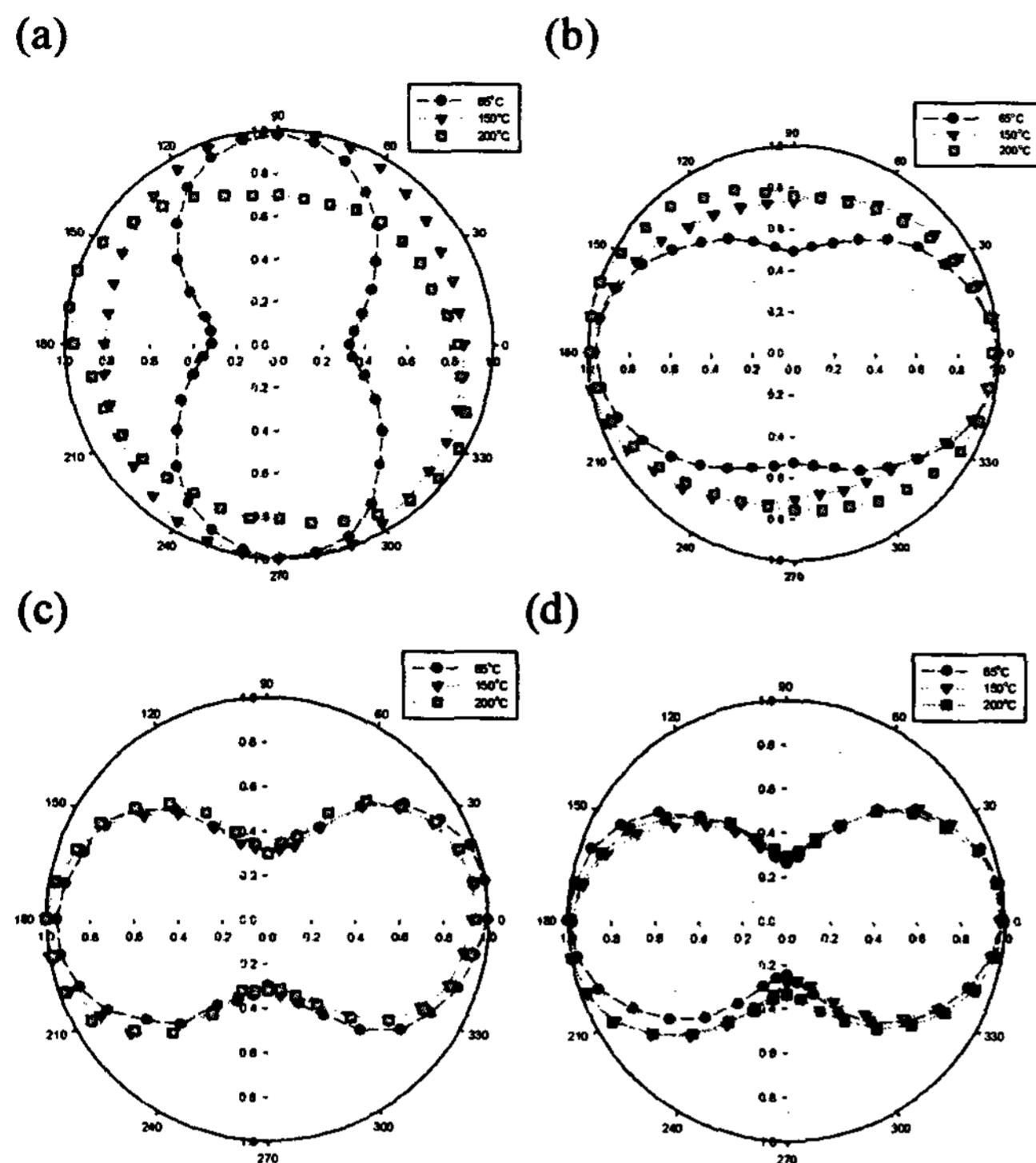


Figure 4. Circular diagrams of absorbance of the dichroic dye (disperse blue) dissolved in E7 (0.1 wt %) in an LC cell fabricated by using films of cinnamate polymers with various UV irradiation energy, (a) PVCi 2.4 Jcm^{-2} , (b) PEVCI 0.48 Jcm^{-2} , (c) PEVCI 1.2 Jcm^{-2} , (d) PEVCI 2.4 Jcm^{-2} , as a function of thermal treatment temperature (65, 150, 200°C).

4. Conclusion

A novel sequence-controlled copolymer of ethylene and vinyl cinnamate (PEVCI) was sensitive towards UV irradiation and aligns LC with polarized UV irradiation. Alignment direction of LC of PEVCI is parallel to the polarization direction of polarized UV and this is contrary to the conventional cinnamate polymers. Due to the peculiar parallel LC alignment

of PEVCI, pretilt angle of LC on PEVCI is $1.3\text{-}2.6^\circ$, which is the considerably higher value compared with other cinnamate polymers. Glass transition temperature of PEVCI polymer is very low due to the flexible ethylene backbone, but LC alignment on PEVCI was maintained stably in spite of thermal treatment at 200°C . Unique LC alignment properties of PEVCI might be related with the cinnamate moieties with regular spacing and flexible backbone of PEVCI.

5. References

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