

Thermal reaction of cinnamate oligomers and their effect on the orientational stability of liquid crystals

Hyundae Hah, Shi-Joon Sung and Jung-Ki Park

Dept. of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-ku, Taejeon, 305-701
Phone: +82-42-869-3965, E-mail: hyundaehah@kaist.ac.kr

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Abstract

Cinnamate groups are well-known for a dimerization reaction upon exposure to ultraviolet irradiation and a thermal reaction after being heated. In this study, to verify the thermal reaction of the cinnamate group in detail, we investigated the thermal crosslinking of cinnamate oligomers. The thermal reaction of cinnamate oligomers of low molecular weight is induced more readily by thermal energy compared with that of cinnamate polymers. The orientation of the liquid crystal depended on the length of the spacers in the cinnamate oligomers.

1. Introduction

The surface alignment of liquid crystal (LC) molecules is of great importance in the fabrication of liquid crystal displays (LCDs). The photoalignment of LC molecules induced by 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.¹⁻²⁾ In line with this, many studies have been carried out on the development of polymers with anisotropically photodimerizable moieties, such as cinnamate and coumarin, leading to the alignment of LC molecules for LCDs.³⁻⁷⁾ In order to achieve the thermal stability of LC molecules on the surface of photoreactive polymers, the stable orientation of photodimers with temperature is required. In fact, however, the practical applications of photoreactive polymers are quite restricted due to the significant thermal relaxation of the photoreactive polymers at high temperatures.⁸⁻⁹⁾ In order to enhance the thermal stability of photodimers, various methods have been attempted, such as the grafting of photodimerizable side groups onto a rigid polyimide backbone¹⁰⁾, and preparing photoreactive liquid crystalline polymers.¹¹⁾ In this work, we investigated the thermal stability of LC orientations based on the

thermal crosslinking reactions of photodimerizable oligomeric compounds with different lengths of flexible spacers between the two cinnamoyl end groups and the effect of the length of the flexible spacer of oligomers on the orientation of the LCs.

2. Experimental

Five oligomers having flexible spacers of different lengths were prepared to elucidate the photoreaction and the thermal reaction of cinnamoyl groups and the surface orientation of the LCs. 1,6-hexanediyl dicinnamoyl ether (2Ci-HD), 1,8-octanediyl dicinnamoyl ether (2Ci-OD), 1,10-decanediyl dicinnamoyl ether (2Ci-DD), and 1,12-dodecanediyl dicinnamoyl ether (2Ci-DDD) were synthesized by the reaction of 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, and cinnamoyl chloride, respectively. 1,20-eicosanediol dicinnamoyl ether (2Ci-ED) was synthesized by reacting eicosanedioic acid and cinnamoyl alcohol with thionyl chloride. The synthetic scheme for 2Ci-DD is typical and is described in Fig. 1.

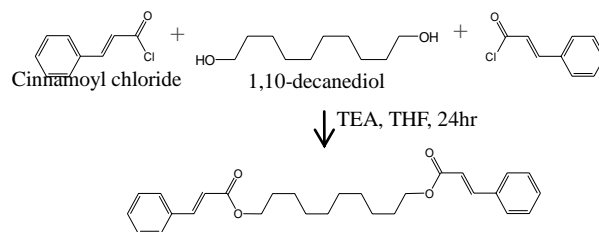


Fig. 1. Synthesis of 1,10-decanediyl dicinnamoyl ether (2Ci-DD)

A 2 wt % solution of cinnamate oligomer in cyclohexanone was spin-coated onto the substrate at 1800 rpm, and the cast was baked at 60°C for 1 h. Photoreaction of the cinnamate oligomer was induced by irradiating polarized UV onto the oligomer film.

Polarized UV light was obtained by passing the light from a 300 W high-pressure mercury arc (Oriel) through a UV linear dichroic polarizer (27320, Oriel) and UV filter (59800 Oriel). Spectral measurements in the UV-visible range were performed using a Shimadzu UV-1601. A homogeneously aligned LC cell was constructed by sandwiching nematic LCs (E7) between a pair of UV-irradiated glass substrates coated with cinnamate oligomer.

3. Results and discussion

(1 line spacing)

To elucidate the effect of cinnamate oligomers with flexible spacers on the photo- and thermal reactions in comparison with the cinnamate polymer, we investigated the photodimerization reactions and the thermal crosslinking reactions of cinnamate oligomers. First, we investigated the photochemical reactions of three representative cinnamate oligomers which have 6, 10, and 20 methylene group as spacers by observing the changes in UV absorbance of the cinnamoyl groups with UV irradiation.

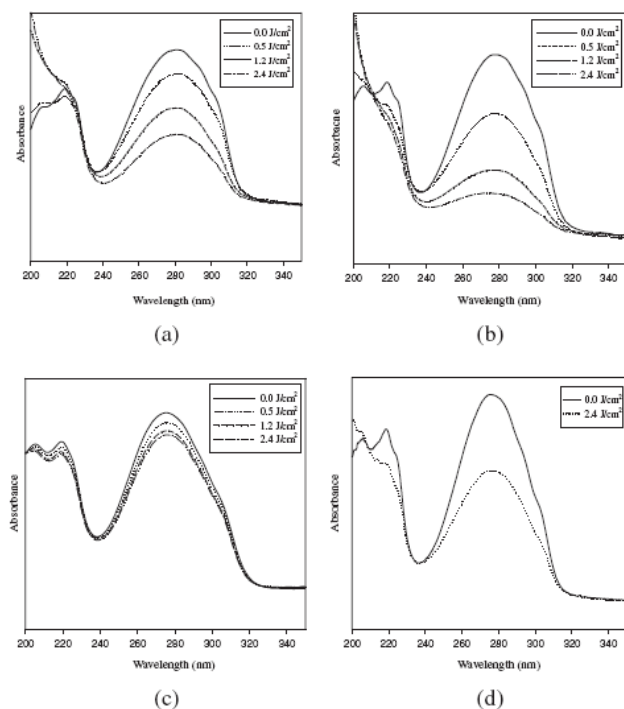


Fig. 2 UV absorption of (a) 2Ci-HD, (b) 2Ci-DD, (c) 2Ci-ED, and (d) PEVCi after UV irradiation.

Figure 2(a) shows the change in the UV absorption spectra of 2Ci-HD with UV irradiation. Irradiation of 2Ci-HD with UV light shows a decrease in the absorption peak intensity of the cinnamate moieties at 284 nm corresponding to the $-C=C-$ bond of the cinnamoyl group, which is attributed to the

photodimerization reaction of the cinnamate moieties. 2Ci-DD shows a more significant decrease in the intensity of the $-C=C-$ absorption peak with irradiation as shown in Fig. 2(b). Figure 2(c) shows that, in the case of 2Ci-ED, there is only a slight decrease in the intensity of the $-C=C-$ absorption peak with irradiation. This seems to be due to the random placement of cinnamate groups with long flexible spacers between the cinnamate groups. For comparison with cinnamate polymers, the degree of photoreaction of 2Ci-DD is compared with that of a cinnamate polymer (PEVCi) evaluated in the previous study as shown in Fig. 2(d). The greater chain flexibility of 2Ci-DD makes the double bond of the cinnamate moieties react more efficiently.

Second, we induced the thermal reactions of the three representative cinnamate oligomers having 6, 10, and 20 spacers and observed the changes in UV absorbance of the cinnamoyl groups with heating as shown in Figs. 3(a), 3(b), and 3(c), respectively. We induced thermal crosslinking reactions of the photoreacted cinnamate oligomers by heating the oligomers film to 200 °C. The degree of reaction was monitored by checking the UV absorption intensity of the $-C=C-$ bond of the cinnamoyl group. Heating 2Ci-HD caused a decrease in the absorbance of the cinnamate groups at 284 nm, and this indicates that the carbon-carbon double bond of the cinnamate side groups is reacted by thermal energy. The 2Ci-DD showed an enhancement of the thermal reaction of the cinnamate groups due to the presence of a more flexible spacer. The chain flexibility of 2Ci-DD makes the double bond of the unreacted cinnamate moieties react more efficiently than that of 2Ci-HD. In the case of 2Ci-ED, only a slight decrease in the intensity of the $-C=C-$ absorption peak is observed with heating. This seems to be due to the random placement of cinnamate groups with long flexible spacers. The degree of thermal crosslinking of the cinnamate groups of 2Ci-DD is higher than that in the cinnamate polymer [Fig. 3(d)] reported in our previous study. Heating the cinnamate oligomer film with polarized UV irradiation could induce a thermal crosslinking reaction of the unreacted cinnamate side groups, and this could fix the anisotropic distribution of the photodimers of cinnamate groups. Contrary to conventional knowledge that the flexible oligomers of low molecular weight are not suitable in terms of the thermal stability, 2Ci-DD was advantageous for the thermal molecular orientational stability due to the post-thermal crosslinking compared with the cinnamate polymers. After UV irradiation and

subsequent thermal reaction, the T_g of 2Ci-DD was increased to 145 °C.

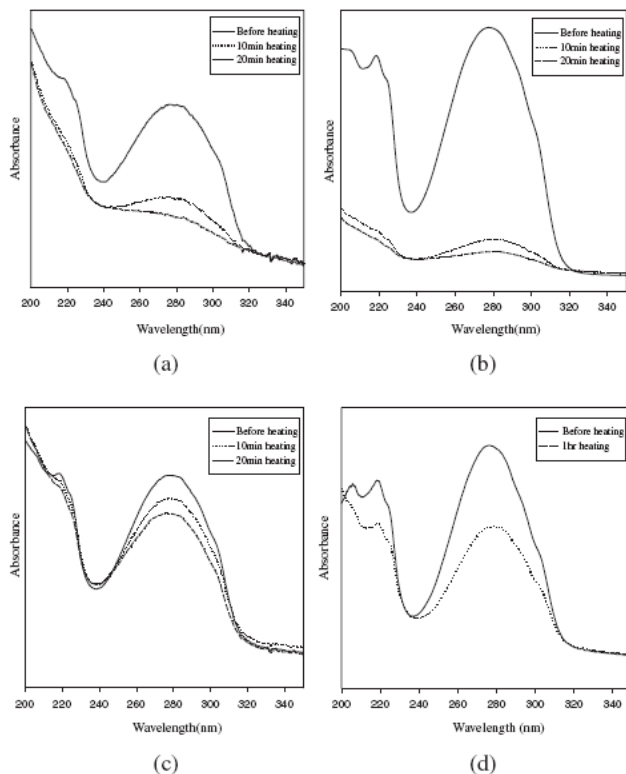


Fig.3 UV absorption of (a) 2Ci-HD, (b) 2Ci-DD, (c) 2Ci-ED, and (d) PEVCi after heating.

To investigate the effect of the thermal crosslinking reaction on the LC orientation, we prepared LC cells using films of 2Ci-HD and 2Ci-OD with 6 and 8 methylene groups as spacers between cinnamate groups with polarized UV irradiation of 2.4 J/cm² to check the liquid crystal orientation on the surface of the irradiated film. It shows that the LCs orient in a direction perpendicular to the polarization direction of UV light. For 2Ci-DD and 2Ci-DDD with 10 and 12 methylene groups between cinnamate groups, the liquid crystal orientation on the film was checked under the same conditions as previously taken. It is found that the LC molecules orient in the direction parallel to the polarization direction of UV light. For 2Ci-ED, which has 20 methylene groups between cinnamate groups, no distinct orientation of LCs on 2Ci-ED was observed. This may be due to the random placement of the cinnamate groups with long, flexible spacers between the cinnamate groups. The directions of LC orientation for the five photoreactive oligomers with different length spacers between the two cinnamoyl groups at the chain ends are summarized in Table I.

	2Ci-HD	2Ci-OD	2Ci-DD	2Ci-DDD	2Ci-ED
Direction of LC	Perpendicular	Perpendicular	Parallel	Parallel	No

Table I. Direction of LC orientation of photoreactive oligomers with respect to the polarization direction of UV light.

It is concluded that the length of the spacer group between the cinnamate units has a significant influence on the orientation of LCs. The detailed mechanism of the dependence of LC orientation on the flexible spacer length requires further study.

4. Summary

In summary, we have demonstrated that photoreactive cinnamate oligomers could also react as a result of thermal energy. Cinnamate oligomers could induce the photo- and thermal reactions of the cinnamate groups more readily than the cinnamate polymers leading to a higher thermal stability of LC molecules. This may be attributed to the higher mobility of the photodimerized product based on cinnamate oligomers. The orientation of LCs could be changed from perpendicular to parallel with respect to the direction of UV polarization by simply changing the spacer length of the oligomers.

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. Schadt, K. Schmitt, V. Koznikov and V. Chigrinov, *Jpn. J. Appl. Phys.* **7** (1992) 2155.
- 4) M. Schadt, H. Seiberle and A. Schuster, *Nature (London)* **381** (1996) 212.
- 5) B. Sapich, J. Stumpe, T. Krawinkel and H. R. Kricheldorf, *Macromolecules* **34** (2001) 5694
- 6) P. O. Jackson and M. O'Neill: *Chem. Mater.* **13** (2001) 694.
- 7) M. Obi, S. Morino, K. Ichimura, *Chem. Mater.* **11** (1999) 656.
- 8) N. Kawatsuki, T. Kawakami, T. Yamamoto. *Adv. Mater.* **13** (2001) 1337.
- 9) N. Kawatsuki, K. Matsuyoshi, M. Hayashi, H. Takatsuka, T. Yamamoto. *Chem. Mater.* **12** (2000) 1549.
- 10) H. T. Kim, J. W. Lee, S. J. Sung, J. K. Park, *Mol. Cryst. Liq. Cryst.* **338** (2000) 99.
- 11) L. Oriol, M. Pinol, J. L. Serrano, R. M. Tejedor. *J. Photochem. Photobiol. A* **37** (2003) 45.