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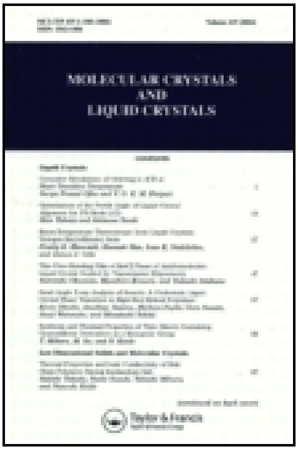

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Alignment of Photo-Cross-Linkable Copolymer Liquid Crystals Induced by Linearly Polarized UV Irradiation and Thermal Treatment

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Alignment of Photo-Cross-Linkable Copolymer Liquid Crystals Induced by Linearly Polarized UV Irradiation and Thermal Treatment

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This paper describes the photoinduced thermal orientation of the photo-cross-linkable methacrylate copolymer liquid crystal (CPLC) film comprising a photoreactive 6-[4-(2-cinnamoyloxyethoxy)biphenyloxy]hexyl side group and a photoinactive n-(4-cyanobiphenyloxy)alkyl (nCB, n=5, 6, 9, 10) side group by the use of linearly polarized ultraviolet (LPUV) light irradiation followed by annealing. The orientational behavior of the mesogenic groups was greatly dependent on the number of the spacer length **n** and a heating condition. When the **n** was 6 or 10, the in-plane alignment of the mesogenic groups was the major component, while the out-of-plane alignment was prevalent when the **n** was 5 or 9. In addition, the orientational behavior was also affected for **1b** and **1c** (n=5, 9) by the heating rate after the LPUV light irradiation at room temperature.

Keywords: polymer liquid crystal; polarized UV light; photoorientation; photo-cross-linking; photoalignment

INTRODUCTION

Linearly polarized light irradiation can induce the optical anisotropy of the photoreactive polymer films, such as azobenzene-containing polymers [1-3], and photo-cross-linkable polymers. [4-7] Cooperative

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photo-orientation of the photoinactive mesogenic group could be induced for the copolymer liquid crystals comprising a photoreactive side group and a photoinactive side group, and many studies for the copolymers with azobenzene side groups had been reported. [8]

We have been focusing on the photoinduced thermal orientation of photo-cross-linkable methacylate copolymer liquid crystals (CPLCs) comprising a 6-[4-(2-cinnamoyloxyethoxy)biphenyloxy]hexyl (6CiB) side group and a photoinactive 6-(4-cyanobiphenyloxy)hexyl (6CB) side group. [5-7] The 6CB and the nonphotoreacted mesogenic side groups aligned thermally along the photo-cross-linked 6CiB group in a direction parallel to the electric vector (E) of the incident LPUV light irradiation. [6,7]

In this paper, to study a further insight for the photoinduced thermal orientation behavior of our CPLC series, a photo-cross-linkable CPLC comprising the 6CiB side group and a n-(4-cyanobiphenyloxy)alkyl (nCB, n=5, 6, 9, 10) side group was synthesized, and we investigated the effect of the length of the spacer of the photoinactive mesogenic group on the orientation of the film. The photoinduced thermal orientation of the CPLC films was generated by the use of the LPUV light. We found that the orientational direction of the mesogenic groups was greatly dependent on the spacer length as well as the heating condition after the LPUV light.

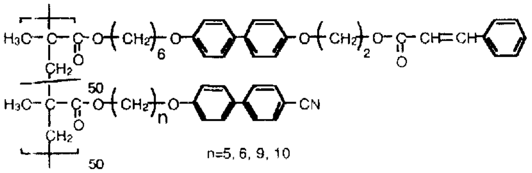

FIGURE 1 Chemical structure of the photo-cross-linkable CPLCs **1a-1d**

EXPERIMENTAL

Materials

Figure 1 shows the chemical structure of a CPLC **1a-1d** used in this study. Methacrylate monomers and their copolymers were synthesized according to the literature. [6] Table summarizes thermal property and spectroscopic data of the CPLCs.

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Table Thermal property and spectroscopic data of CPLCs

	n	Transition (°C)	λmax (nm) on quartz
1a	5	G 72 LC 97 I	279
1b	6	G 47 LC 89 I	279
1c	9	G 88 LC 104 I	278
1d	10	G 71 LC 93 I	282

LPUV Photoreaction and characterization

The polymer was spin-coated on a quartz or a CaF_2 substrate from a methylene chloride solution, resulting in a 300~500 nm-thick film. The film was irradiated by LPUV light at 30 °C with an intensity of 50 mW/cm^2 at 365 nm. After irradiation, the film was heated to (Ti-2) °C of the polymer film, quickly. In some cases, the heating rate was controlled to be 90°C/min or 1°C/min. The macroscopic orientational order of the film was evaluated by UV polarization spectroscopy using a dichroic ratio (DR= $(A_{//}-A_{\perp})/(A_{//}+A_{\perp})$), where $A_{//}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to electric vector (**E**) of the LPUV light, respectively.

RESULTS AND DISCUSSION

LPUV Photoreaction and Thermally Induced Optical Anisotropy of the Film

For all polymers, a small negative optical anisotropy of the film was generated after the LPUV light irradiation at 30 °C because of the angular-selective photo-cross-linking of the cinnamoyl group. [5] In our previous study using the methacrylate CPLC comprising 6CiB and 6CB side groups (CPLC **1b**), an annealing the LPUV-irradiated film at the elevated temperature induced the positive optical anisotropy. [6,7] In this case, the absorbance of parallel direction $A_{//}$ increased, while that of perpendicular $A_{\perp}$ decreased. Parts a – d of Figure 2 show the change in absorbance for both $A_{//}$ and $A_{\perp}$ at λ_{max} as a function of the irradiation time. The irradiated polymer film was annealed at the elevated temperature quickly, kept for 10 min and cooled quickly for all cases. After irradiation, the absorbance decreased for all polymers due to [2+2] photocycloaddtion reaction of the cinnamate group with very small dichroism. After annealing, for **1b** and **1d**, $A_{//}$ increased while $A_{\perp}$

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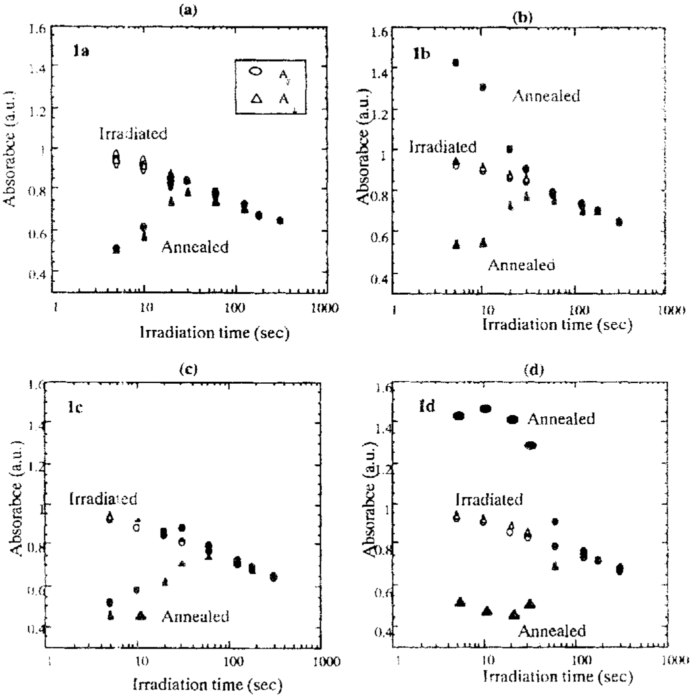

FIGURE 2 Absorbance at absorption maximum of CPLC film as a function of irradiation time. (a) **1a** (b) **1b** (c) **1c** (d) **1d**

decreased as shown in Figure 2(a) and (d). This exhibited the positive optical anisotropy was caused by the in-plane alignment of the mesogenic groups in a direction parallel to **E**. [6,7] This anisotropy decreased when the irradiation time was 100 sec and more, where the degree of the photoreaction was 60% and more. This is due to the immobilization of the mesogenic groups because of the highly cross-linked structure. On the other hand, for **1a** and **1c**, the induced anisotropy was very small and both absorption of $A_{//}$ and $A_\perp$ decreased after annealing as shown in Figure 2(b) and (c). For the FT-IR spectroscopy observation, the IR-absorbance of the mesogenic groups was also decreased after annealing for **1a** and **1c**. These results suggest that the decrease of the absorption may be caused by the out-of-plane alignment of the mesogenic groups.

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Effect of the Heating Rate

To compare the effect of the heating rate on the orientational behavior of the **1a** film, two kinds of heating rates of both 1°C/min and 90° C/min was carried out after the LPUV light irradiation. Parts a and b of Figure 3 show the polarization UV spectra of the **1a** film before and after the LPUV light irradiation for 5 sec, and after heating with different heating rates.

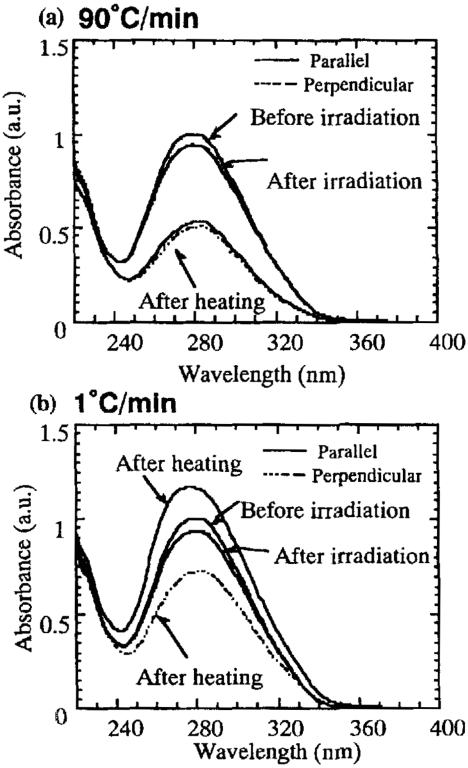

FIGURE 3 Absorption spectra of CPLC **1a** exposed to LPUV light for 5 sec.
(a) Heating rate ; 90 °C/min, (b) Heating rate ; 1 °C/min.

When the heating rate was 90 °C/min, the strong decrease of the absorption was observed. The induced DR value was less than 0.13. It

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was confirmed that the induced optical anisotropy did not change if the annealing time was 10 min and more. Since no-shift of the wavelength of the absorption maximum was observed after annealing, we assume that the decrease of the absorbance is due to the out-of-plane alignment of the mesogenic groups and is not due to the aggregation of the mesogenic groups. In contrast, when the irradiated **1a** film was heated slowly (1 °C/min), the positive optical anisotropy was generated as shown in Figure 3(b), as is the case for **1b** and **1d**. The intensities of $A_{//}$ increased and $A_{\perp}$ decreased compared to that before heating, and the average absorbance $Aav=(A_{//}+A_{\perp})/2$ was larger than that before heating. This is a consequence of the in-plane alignment of the mesogenic groups with the direction parallel to **E** of the incident LPUV light. However, the induced DR value was smaller than that for the **1b** film. [7]

Three Dimensional UV Spectroscopy of the Film

To investigate the three-dimensional information for the alignment of the mesogenic groups, we measured the polarization UV spectrum with rotating the incident *p*- and *s*-polarized monitoring lights, where the polarization plane of the actinic LPUV light was parallel to that of *p*-polarized monitoring light. Parts a and b of Figure 4 plot absorbances at 279 nm of the film, that was irradiated for 5 sec, and heated with 90 °C/min and 1 °C/min, respectively. After irradiation, the absorbances for both polarizations were similar regardless of the incident angle of the monitoring lights. After annealing, in the case of the heating rate of 1 °C/min, the absorption of *p*-polarized monitoring beam increased and showed a maximum value when the angle of the monitoring light was 0 °, while the absorption of *s*-polarized beam decreased and exhibited no maximum nor minimum. This means that mesogenic groups aligned uniaxially with the direction parallel to **E** of the LPUV light.

On the other hand, for the heating rate of 90 °C/min, the absorption decreased and the absorbance of *p*-polarized monitoring beam showed a minimum when the angle of the monitoring light was 0°. The absorbance of *s*-polarized beam exhibited neither maximum nor minimum, and smaller than that heated with 1 °C/min. This is a consequence of the out-of-plane alignment of the mesogenic groups. Note that the absorbance of *p*-polarized monitoring light at 0° was larger than that of *s*-polarized monitoring light. This small difference will result from the partial orientation of the mesogenic groups parallel to **E**.

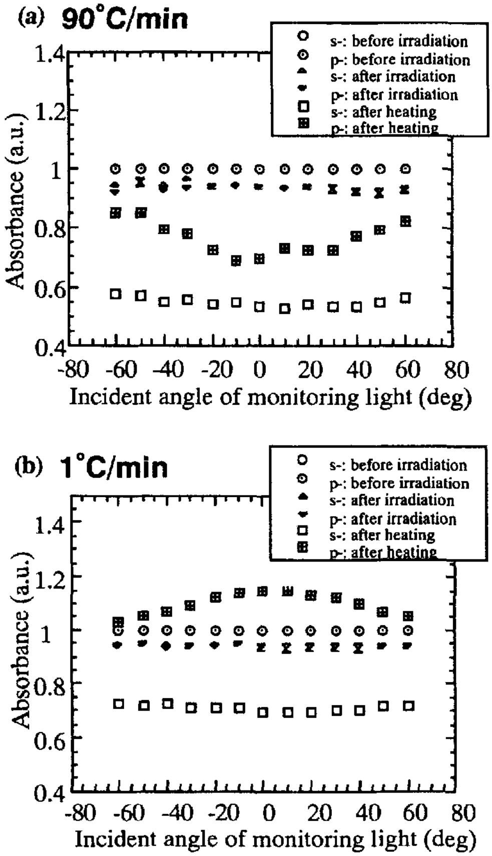

FIGURE 4 Absorbances at 279 nm of **1a** film irradiated for 5 sec as a function of incident angle of *p*- and *s*-polarized monitoring lights. (a) Heating rate ; 90 °C/min, (b) Heating rate ; 1°C/min.

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SUMMARY

The photo-cross-linkable methacrylate CPLCs comprising a 6CiB side group and a n-(4-cyanobiphenyloxy)alkyl (nCB) side group was synthesized. We investigated the photo-induced thermal orientation of the CPLC film by the use of the LPUV light followed by annealing. The orientational direction of the mesogenic groups was greatly dependent on the heating condition after the LPUV light exposure for the CPLC having the 5CB side group. When the heating rate was 1 °C/min, the in-plane alignment of the mesogenic groups was the major part in the direction parallel to the electric vector of the incident LPUV light. On the other hand, the out-of-plane alignment of the mesogenic side groups was major when the heating rate after the LP-UV light exposure was 90 °C/min. Further study for the effect of the heating rate condition and the length of the spacer of the CB side group on the orientational behavior will be reported in a forthcoming paper.

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