Alignment of Photo-Cross-Linkable Copolymer Liquid Crystals Induced by Linearly Polarized Ultraviolet Irradiation and Thermal Treatment: Effect of Copolymerization Ratio. 2[1]

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Received October 21, 1999; Revised Manuscript Received January 11, 2000

ABSTRACT: Linearly polarized (LP) ultraviolet (UV) photoirradiation of methacrylate copolymer liquid crystal films comprising a photo-cross-linkable 4-(2-cinnamoyloxyethoxy)biphenyl side group and a photoinactive 4-cyanobiphenyl group with various copolymer composition has been carried out to induce an optical anisotropy. The effect of the copolymerization ratio on the orientational behavior of the film was investigated by means of UV and FT-IR polarization spectroscopy. For all copolymer films, the orientation of the mesogenic groups was generated with the direction parallel to the electric vector of LP-UV light after annealing the irradiated film near clearing temperature of the copolymer. The maximum optical anisotropy was obtained when the photo-cross-linked side group in the whole mesogenic groups was 4−14 mol %, depending on the copolymer composition. It was suggested that the alignment ability of the cyanobiphenyl group was larger than that of another group.

Introduction

Linearly polarized (LP) light irradiation is one of the most conventional techniques to induce molecular alignment in photoreactive polymer films.[2−8] Some kinds of materials for the photomanipulation of mesogenic groups of the polymer film have been reported including azobenzene polymers[9−17] and photo-cross-linkable polymers[1,18−25] by the use of LP light. For the azobenzene polymer system, which is widely studied, photoreversible alignment control can be realized due to the *E*/*Z* photoisomerization of the azo-chromophore. There are some studies for the photoinduced optical anisotropy using photo-cross-linkable polymer systems. However, the photoinduced optical anisotropy of a poly(vinyl cinnamate) derivatives is derived by an anisotropic photo-cross-linking of the cinnamate group.[18,19] The *E*/*Z* photoisomerization of polymethacrylate films comprising cinnamate side groups was also demonstrated.[24]

We have reported that an LP ultraviolet (LP-UV) irradiation could induce the alignment of mesogenic groups in photo-cross-linkable methacrylate copolymer liquid crystal (CPLC) films comprising a photoreactive cinnamoyloxyalkyloxybiphenyl group and a photoinactive cyanobiphenyl side group.[1,21−23,26] The photocrosslinked mesogenic group with a direction parallel to the electric vector (**E**) of the LP-UV light aligned the nonphotoreacted group and the cyanobiphenyl group along the photo-cross-linked mesogenic direction. Three-dimensional alignment of the mesogenic groups can be feasible by the use of slantwise exposure because the aligned direction is parallel to **E**.[26] In our previous study, we studied the effect of the irradiation temperature and the thermotropic nature of the CPLC on the alignment behavior and clarified that the reacted direction of the photo-cross-linked mesogenic group played an important role for the alignment behavior.[1] However, we did not fully explore the effect of the copolymer composition on the orientational order of each mesogenic side group.

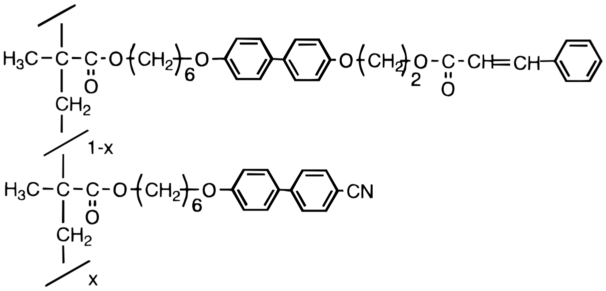

Figure 1. Chemical structure of the CPLCs used in this study.

This paper describes further investigation of the effect of the copolymerization ratio on the alignment behavior of CPLC films. We newly synthesized copolymers having the same side groups with various copolymer composition and studied the orientational order of each mesogenic groups separately by FT-IR polarization spectroscopy. To obtain an effective alignment of the mesogenic groups, a higher degree of photoreaction is required for the CPLC with higher composition of cyanobiphenyl group. The orientational order of the cyanobiphenyl group is larger than that of the cinnamoyloxyalkyloxybiphenyl group in all cases.

Experimental Section

Materials. Figure 1 shows the chemical structure of a photo-cross-linkable CPLC used in this study. Methacrylate monomers comprising a 6-[4′-(2″-cinnamoyloxylethoxy)biphenyl-4-yloxy]hexyl (CiB) side group and a 6-(4′-cyanobiphenyl-4-yloxy)hexyl (CNB) side group and their copolymers were synthesized and characterized according to the literature.[27,28] The two monomers were randomly polymerized by the radical solution polymerization. Table 1 summarizes the copolymer compositions and molecular weights of CPLCs.

LP−UV Photoreaction of CPLC Films. A thin film of CPLC was prepared by spin-coating a methylene chloride solution (~5 w/w %) of polymers onto a quartz or CaF_2

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10.1021/ma991758+ CCC: $19.00

Table 1. Composition, Molecular Weight, and Thermal Properties of Synthesized CPLCs 1a–1d

		molecular weight[b]		thermal property[c]				
	X^a	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	T_g (°C)	phase	T_i (°C)	ΔH (kJ/mol)	ΔH (J/(mol K))
1a	20	100.1	3.1	42	N	75	1.4	4.0
1b	53	81.3	2.5	47	S	95	2.3	6.2
1c	71	62.0	3.2	46	S	101	2.2	6.0
1d	92	63.2	3.0	49	S	111	2.5	6.6

[a] Composition of CNB Side group. Determined by ^{1}H NMR. [b] Determined by GPC using polystyrene standard. [c] Determined by polarization optical microscopy and DSC. T_g = glass transition, T_i = clearing point, N = nematic, S = smectic A or C. It was difficult to determine the type of smectic phase.

Table 2. Spectroscopic Data of CPLCs 1a–1d

	solution/nm[a]		film/nm[b]
	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}
1a	275	(3.6)	274
1b	280	(3.5)	278
1c	284	(3.1)	285
1d	292	(3.1)	292

[a] In methylene chloride. [b] On quartz substrate.

substrate. There was no special pretreatment on the substrate. Film thickness was controlled to be 0.3–0.5 μm. The spin-coated film was transparent and showed no optical anisotropy. The spin-coated film was stored for several days for complete removal of the solvent. The LP-UV irradiation was carried out at room temperature by a 250 W high-pressure Hg–UV lamp passed through Glan-Taylor polarizing prisms with a cutoff filter under 290 nm. The light intensity was 50 mW/cm^2 at 365 nm. After irradiation, the film was heated to an elevated temperature to induce the optical anisotropy.

Characterization. The same analytical equipment and technique previously reported were used for the characterization in this study.[1]

Orientational Order of CPLC Films. The macroscopic orientational order of the film was evaluated by UV polarization spectroscopy using a dichroic ratio (DR = $(A_\parallel - A_\perp)/(A_\parallel + A_\perp)$), where $A_\parallel$ and $A_\perp$ are the absorbances parallel and perpendicular to **E**, respectively. A wavelength of an absorption maximum of the film before UV exposure was used to calculate the DR value. Furthermore, the orientational order of each mesogenic group was determined by the specific absorption of the mesogenic group in FT-IR polarization spectra.

Results and Discussion

Thermal and Spectroscopic Properties and Photoreaction of CPLC Films. The thermal properties of the synthesized CPLC's are summarized in Table 1. All synthesized copolymers exhibited an LC phase, and the clearing temperature (T_i) increased with increasing amount of the CNB group. Copolymer **1a** exhibited a nematic phase, and the other copolymers showed smectic behavior. Table 2 summarizes the spectroscopic data of the CPLC films and solutions. The wavelength of the maximum absorption shifted to longer wavelengths with increasing amount of the CNB group. Since there is no significant difference in the UV spectrum between the solution and the film, the mesogenic groups do not aggregate in the as-coated film.

When the as-coated film was irradiated by UV light, it became insoluble due to [2 + 2] photocycloaddition reaction as previously reported.[27] Figure 2 plots the intensity of the cinnamoyl –C=C– vibration in the FT-IR spectrum as a function of the irradiation time of the LP-UV light. It seems that the photoreaction was slightly slower by increasing the content of the CNB group in the copolymer. The concentration of the photo-cross-linkable CiB group might influence the rate of the photoreaction of the films.

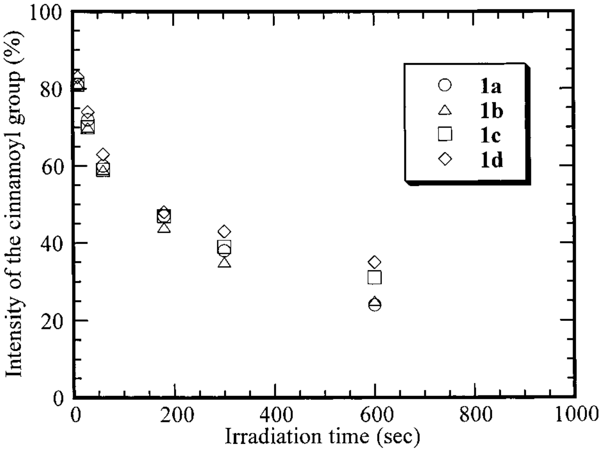

Figure 2. Photoreaction of the cinnamoyl group as a function of the irradiation time. The ν(C=C) vibration at 1639 cm^{-1} was used to monitor the reaction.

Alignment Behavior of CPLC Films. We had already reported that the alignment of mesogenic groups in a methacrylate copolymer comprising CiB side groups was induced by the LP-UV irradiation at room temperature, followed by heating.[23,26] It had been clarified that the nonphotoreacted CiB groups and photoinactive CNB groups could align along the photo-cross-linked mesogenic groups that were parallel to **E** of the LP-UV light. It can be expected that the orientational behavior may depend on the copolymer composition and the annealing temperature. To investigate the effect of the annealing temperature of the CPLC film after LP-UV irradiation, UV polarization spectra were measured after annealing the films at various temperatures. Figure 3a–d shows the results. For all copolymer films, the maximum DR was obtained when the LP-UV-irradiated film was annealed near T_i of the copolymer, and the DR value decreased when it was heated above T_i. Furthermore, the magnitude of the DR value was dependent on the copolymerization ratio and the degree of the photoreaction. The DR of the **1c** film was larger than that of others, and the DR of **1a** film was much smaller. These differences arise from the different mobility among the CiB groups, CNB groups, and photo-cross-linked CiB groups at the elevated temperature after LP-UV irradiation. Further results will be discussed in the following section.

In addition, the effective annealing temperature was not influenced by the exposure time for all CPLC films, although the thermal properties of the films might change after UV exposure due to the photo-cross-linking. By the use of polarization optical microscopy, it was observed that, if the degree of the photoreaction was less than 70%, the optical anisotropy appeared and increased with increasing the film temperature, and it disappeared above the temperature of T_i ± 2 °C. This result suggests that the nonphotoreacted mesogenic groups can be mobile under heating, and the film shows the mesophase below T_i even after the photo-cross-linking.

Effect of the Degree of Photoreaction. Since the alignment of the CPLC films is induced by the mobilization of the mesogenic groups under heating, the cross-

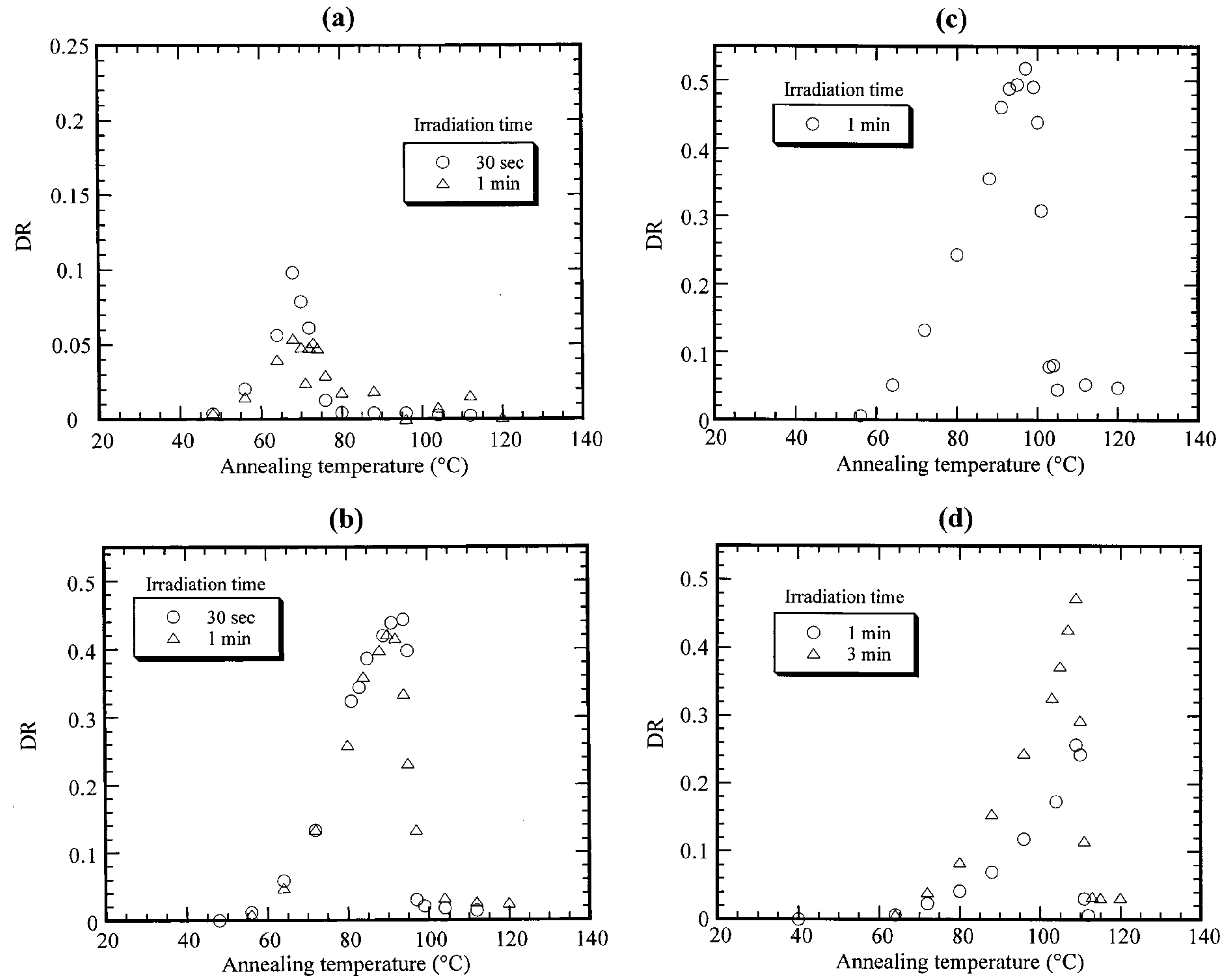

Figure 3. Thermally induced DR of the LP-UV-irradiated CPLC film as a function of the annealing temperature. Annealing time was 30 min for all films. The DR was calculated at 274 nm for **1a**, 278 nm for **1b**, 285 nm for **1c**, and 292 nm for **1d**. (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**.

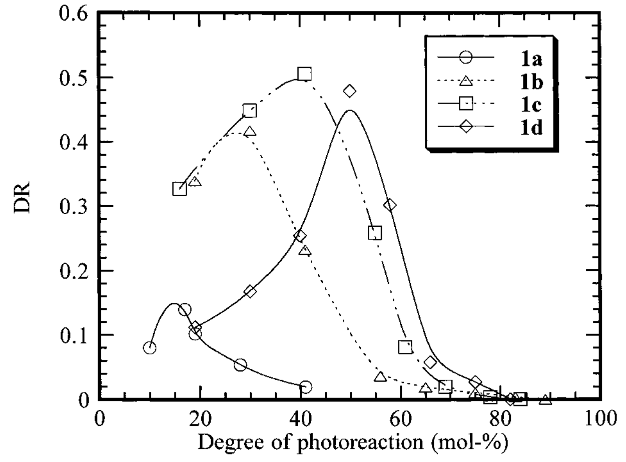

Figure 4. DR value of each polymer film as a function of the degree of the photoreaction. Annealing temperature: 69 °C for **1a**, 94 °C for **1b**, 97 °C for **1c**, and 109 °C for **1d**. Annealing time was 30 min for all films.

linking density may affect the orientational order of the films. As shown in Figure 4, the DR of each copolymer film was dependent on the degree of the photoreaction. The required degree of the photoreaction for the maximum DR of each CPLC film increased by increasing the amount of the CNB group. In the case of **1d** film, a maximum DR of 0.48 was obtained when 50% of the cinnamoyl group had reacted, and the DR value decreased quickly when the degree of the photoreaction was more than 50%. This is a consequence of the increase of the photo-cross-linked CiB side group in the

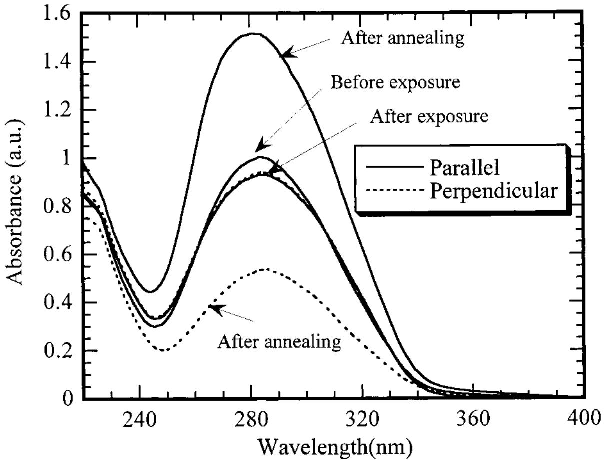

Figure 5. UV Polarization spectrum of **1c** film before and after LP-UV irradiation and heating. Irradiation time was 60 s. Annealing temperature was 97 °C.

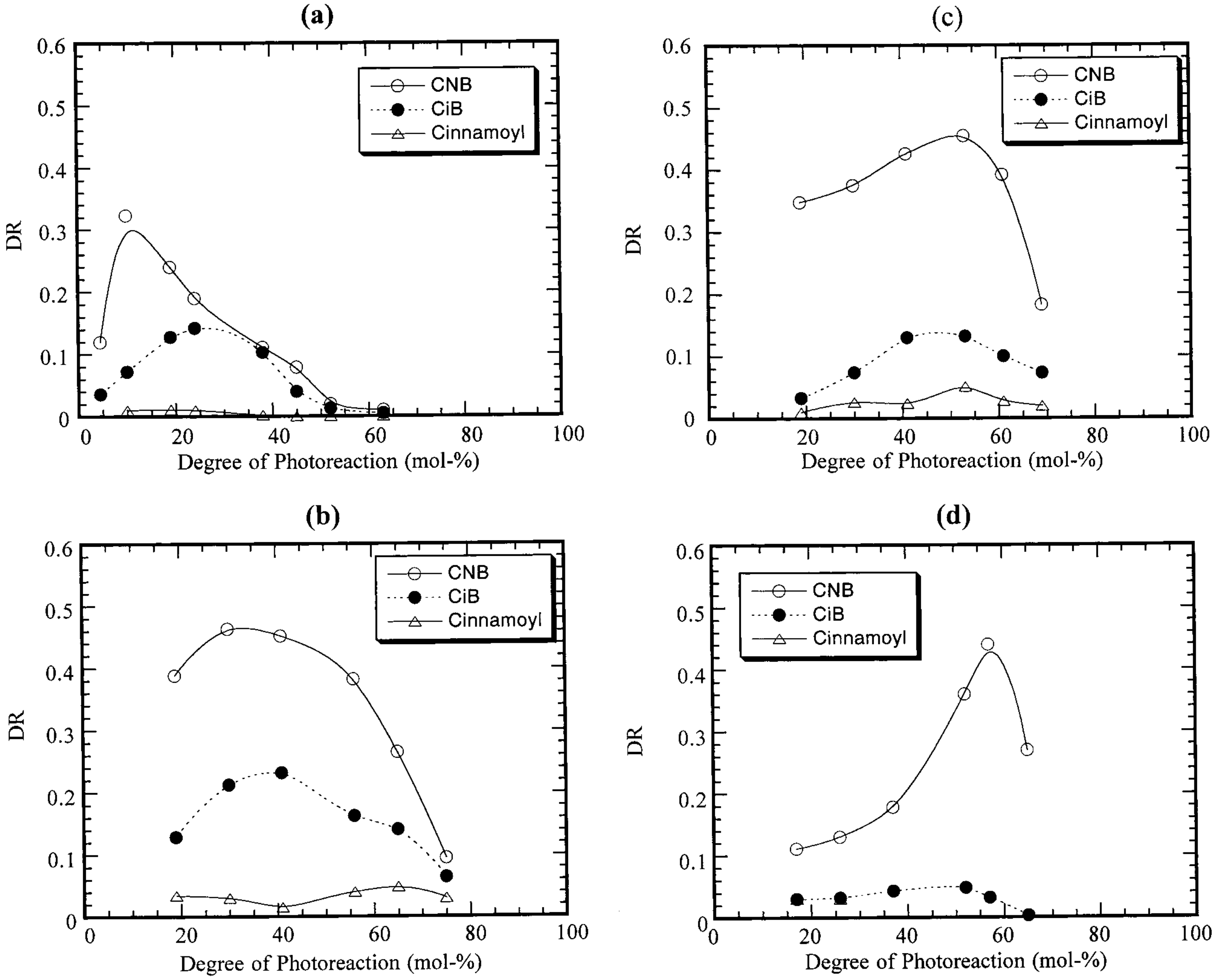

Figure 6. DR values of CNB, phenoxy group in CiB, and cinnamoyl groups estimated by FT-IR polarization spectroscopy as a function of the degree of the photoreaction. (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**.

direction perpendicular to **E**. For **1b** and **1c** films, maximum DR values were 0.42 and 0.51 when the degree of the photoreaction was 30% for **1b** and 41% for **1c**, respectively. In these cases, the ratio of the photo-cross-linked CiB group in the whole mesogenic groups was about 14% for **1b**, 12% for **1c**, and 4% for **1d**. It is worth mentioning that a DR value of 0.3 was obtained in these films even when the degree of the photoreaction was 20%, where the ratio of the photo-cross-linked CiB group in the whole mesogenic groups was less than 10%. Therefore, a small amount of photo-cross-linked CiB group in the film could regulate the orientation of other mesogenic groups, while large amounts of cross-linked group will prevent the orientation.

On the other hand, the DR of **1a** film was very small compared to the other films. The maximum DR was 0.14 when the degree of the photoreaction was 18%, and the ratio of the photo-cross-linked CiB group in the whole mesogenic groups was 14%. This result suggests that the alignment ability of the nonphotoreacted CiB group along the photo-cross-linked CiB direction will be smaller than that of the CNB group.

However, it will be difficult to estimate the orientational order of the CiB group and the CNB group separately by the UV spectrum since the DR exhibits the orientational order at a certain wavelength of the film. For example, Figure 5 shows the change in the UV polarization spectrum of **1c** film before and after LP-UV irradiation followed by heating. After annealing, the absorption in the direction parallel to **E** was increased and that in the perpendicular direction decreased in the whole UV spectrum range. This means that both mobile CiB and CNB groups could align along the **E** direction. It should be noted that the absorption maximum with parallel polarization shifted to shorter wavelengths and that with perpendicular polarization shifted to longer wavelengths after annealing as summarized in Table 3. This result suggests that the biphenyl group in the CiB group aligned more effectively than the cinnamoyl group because the absorption of the biphenyl group was located at 260 nm.

FT-IR Polarization Measurements. To observe the orientational order of each mesogenic group separately, FT-IR polarization measurements of the films were performed. Since the absorptions of the cyano stretching and cinnamoyl −C=C− stretching appear at 2225 and 1639 cm^{-1}, respectively, the DR of the CNB group and the cinnamoyl group can be determined using these wavenumbers. Although the absorption of the phenoxy antisymmetric stretching appeared at 1248 cm^{-1}, it is a combined absorption of phenoxy in CNB and CiB groups. Therefore, the DR of the phenoxy group in the CiB group can be estimated by $\mathrm{DR}_{(\mathrm{CiB})} = (\mathrm{DR}_{(1248)} - x\mathrm{DR}_{(\mathrm{CNB})})/2(1 - x)$, where $\mathrm{DR}_{(1248)}$ and $\mathrm{DR}_{(\mathrm{CNB})}$ are the

Table 3. Wavelength (nm) of the Maximum Absorption of the Oriented CPLC Films[a]

	before irradiation	after annealing[b]	
		parallel	perpendicular
1a	274	271	277
1b	278	274	285
1c	285	281	286
1d	292	289	292

[a] Degree of the photoreaction was between 20% and 50%. [b] Annealing condition was the same as Figure 4.

DR values at 1248 and 2225 cm^{-1}, respectively, and x is the fraction of CNB groups in the CPLC. Plots a−d of Figure 6 exhibit the DR values of each side group as a function of the degree of photoreaction of the cinnamoyl group. In all cases, the DR of the CN vibration was larger than that of other groups, and the DR of the cinnamoyl groups was very small. There are two reasons for this small DR value of the CiB group compared to that of the CNB group. (1) The CiB groups photo-cross-linked in the direction perpendicular to **E** could not align parallel to **E** under heating. (2) Because the cinnamoyl group hardly aligned along the cross-linked direction as shown in Figure 6 and the photo-cross-linked CiB group could not be mobile, the orientation of the phenoxy group in the non-photo-cross-linked CiB group should be restricted. This result is consistent with the shift of the absorption observed in the UV polarization spectrum as summarized in Table 3. In addition, the required degree of the photoreaction to obtain a maximum DR of the mesogenic groups was dependent on the copolymer composition, and its tendency was similar to that obtained by the UV polarization spectrum. In the case of **1a** film, the DR of the CNB group was more than 0.3 when the degree of the photoreaction was 10%, while the DR of the CiB group was less than 0.1. The required degree of the photoreaction for the maximum DR of the CiB group shifted toward higher degrees of the photoreaction (∼30%). This result suggests that the orientational ability of the CNB group might be larger than that of the CiB group. A similar tendency was observed for the **1b** film. For the **1c** and **1d** films, the difference of the orientational order between the CNB group and the CiB group was much higher than that of the other specimens. Since a larger amount of the cross-linked CiB group is required to obtain a maximum DR with increasing the numbers of CNB groups in the copolymer as seen in Figure 4, the orientation of nonphotoreacted CiB group became difficult.

Conclusion

Photo-cross-linkable methacrylate copolymers comprising a CiB group and a CNB group were synthesized, and LP-UV irradiation and thermal treatment induced the alignment of the mesogenic groups. To obtain a high optical anisotropy of the film, the effective amount of the photo-cross-linked CiB group in the whole mesogenic groups was 4%−14%, and the effective annealing temperature was just below T_i of the copolymer. The FT-IR polarization study suggested that the alignment ability of the CNB group was larger than that of the CiB group.

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MA991758+