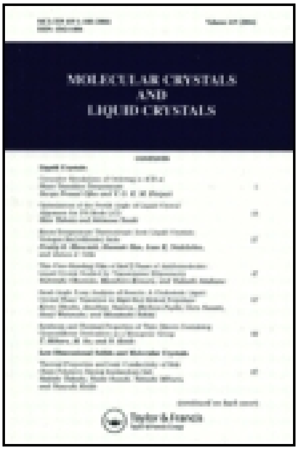

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoalignment of Low-Molecular Liquid Crystals on Photo-Crosslinkable Copolymer Liquid Crystalline Film Comprising Photoreactive and Photoinactive Side Groups

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To cite this article: Nobuhiro Kawatsuki, Katsuya Matsuyoshi & Tohei Yamamoto (2000): Photoalignment of Low-Molecular Liquid Crystals on Photo-Crosslinkable Copolymer Liquid Crystalline Film Comprising Photoreactive and Photoinactive Side Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 338:1, 35-46

To link to this article: http://dx.doi.org/10.1080/10587250008024418

Mol. Cryst. Liq. Cryst., Vol. 338, pp. 35-46
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Photoalignment of Low-Molecular Liquid Crystals on Photo-Crosslinkable Copolymer Liquid Crystalline Film Comprising Photoreactive and Photoinactive Side Groups

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(Received November 18, 1998; In final form March 26, 1999)

We present photoalignment behaviors of low-molecular liquid crystals (LMLCs) on a photo-crosslinkable side-chain copolymer liquid crystal (CPLC) containing a 4-(2-cinnamoyloxyethoxy)biphenyl group and a 4-cyanobiphenyl group by use of linearly polarized (LP) UV irradiation. The LMLC aligned homeotropically on the photoreacted film in the initial state of the photoreaction and the alignment direction changed homogeneously on further irradiation. The direction of the homogeneous alignment can be controlled to be parallel or perpendicular to the electric vector of the LP-UV light, by changing the irradiation temperature or the degree of the photoreaction. These alignment behaviors are explained by the interaction between the LMLCs and the photoreacted CPLC film.

Keywords: Photoalignment; Polymer liquid crystals; Photoreactive polymer; Cinnamic acid; LCD

INTRODUCTION

A photoalignment technique using a linearly polarized (LP) light offers a new way for a liquid crystalline display (LCD) industry to realize a low-molecular-weight liquid crystal (LMLC) alignment without a mechanical rubbing process. Several kinds of materials containing an azobenzene group or a cinnamic

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ester group for the photoalignment process have been developed so far.[1–7] Photoreactive polyimide films have been also investigated for the photoalignment layer.[8–10]

Recently, we reported a photo-crosslinkable polymer liquid crystal (PLC) comprising a cinnamoyloxyalkyloxybiphenyl group for photoalignment material.[5,6] This PLC showed a nematic phase and could regulate the homogeneous LMLC alignment control in both parallel and perpendicular directions to the electric vector (E) of the incident LP-UV light, depending on the degree of photoreaction. Our previous studies suggest that the LMLC alignment direction can be controlled by the photo-crosslinked mesogenic group. Very recently, a homeotropic LMLC alignment was found on the PLC film in the beginning state of the photoreaction when it was irradiated at room temperature.[11] We have also studied a photoinduced alignment of the mesogenic group of a copolymer LC (CPLC) comprising photoreactive and photoinactive mesogenic groups, which exhibits smectic or nematic phases.[12,13] It was clarified that the type of the photoreaction plays an important role for this photoinduced alignment of the mesogenic groups.[12]

The purpose of this paper is to describe an LMLC alignment behavior on the photoreactive CPLC comprising a photoactive 4-(2-cinnamoyloxyethoxy)biphenyl group and a photoinactive 4-cyanobiphenyl group, which shows a smectic phase. The effect of the LP-UV irradiation temperature on the alignment behavior was investigated. It was found that the irradiation temperature is a crucial part for the LMLC alignment direction as well as the photoinduced alignment of the CPLC film.

EXPERIMENTAL

Photoreactive copolymer LC

The chemical structure of the CPLC used in this study is shown in figure 1. The copolymer was synthesized from 4′-(2-cinnamoyloxyethoxy)-4-(6-methacryloxyhexyl)biphenyl (2CiBM6) and 4′-cyano-4-(6-methacryloxyhexyl)biphenyl (CNBM6) according to ref. 12. The number-average molecular weight was 44300 g/mol and the weight-average molecular weight was 108600 g/mol. The composition of the copolymer was estimated by means of ^{1}H-nmr spectroscopy to n = 67 mol-%. This copolymer shows a glass transition at 52 °C and exhibits a smectic phase between 52 °C and 102 °C.

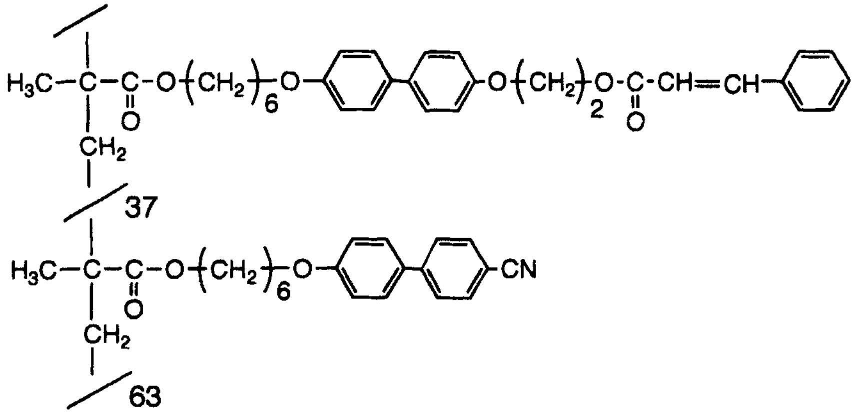


FIGURE 1 Chemical structure of the CPLC used in this study

Preparation of CPLC film and LP-UV irradiation

A thin film was prepared by a spin-coating method from a methylene chloride solution on a quartz substrate. The film thickness was controlled to be 100 nm and the resultant film showed no-optical anisotropy after spin-coating. An LP-UV irradiation was carried out using a high pressure Hg-UV lamp with glan-taylor polarizing prisms and a cut filter under 290 nm. The irradiation temperature was at room temperature (r.t.), at 90 °C (smectic phase), at 100 °C (near T_i) or at 120 °C (isotropic phase). The intensity was 170 mW/cm^2 at 365 nm.

The dichroic UV-absorption of the CPLC film was monitored by a polarized UV absorption spectrum using a Hitachi U-3000 spectrometer equipped with glan-taylor polarizing prisms. The degree of the photoreaction of the CPLC was determined by the following method: The CPLC was spin-coated on glass substrate and irradiated. Then the film was scraped from the substrate and measured by FT-IR (KBr method) to monitor the decrease of -C=C- bond of the cinnamoyl group at 1639 cm^{-1}.

LMLC cell preparation

To evaluate an LMLC alignment behavior on the CPLC film, a parallel LC cell was fabricated using two LP-UV photoreacted substrates. The cell was filled with a nematic LC mixture (E7: Merck Japan) doped with 0.3 wt% of disperse blue 14 (Aldrich Co.). The cell thickness was controlled to be 12.5 μm using a polyimide spacer film. Utilizing a guest-host effect, the orientational order and its direction can be evaluated from dichroic absorption measurements. Detailed experimental procedure is described in ref. 6.

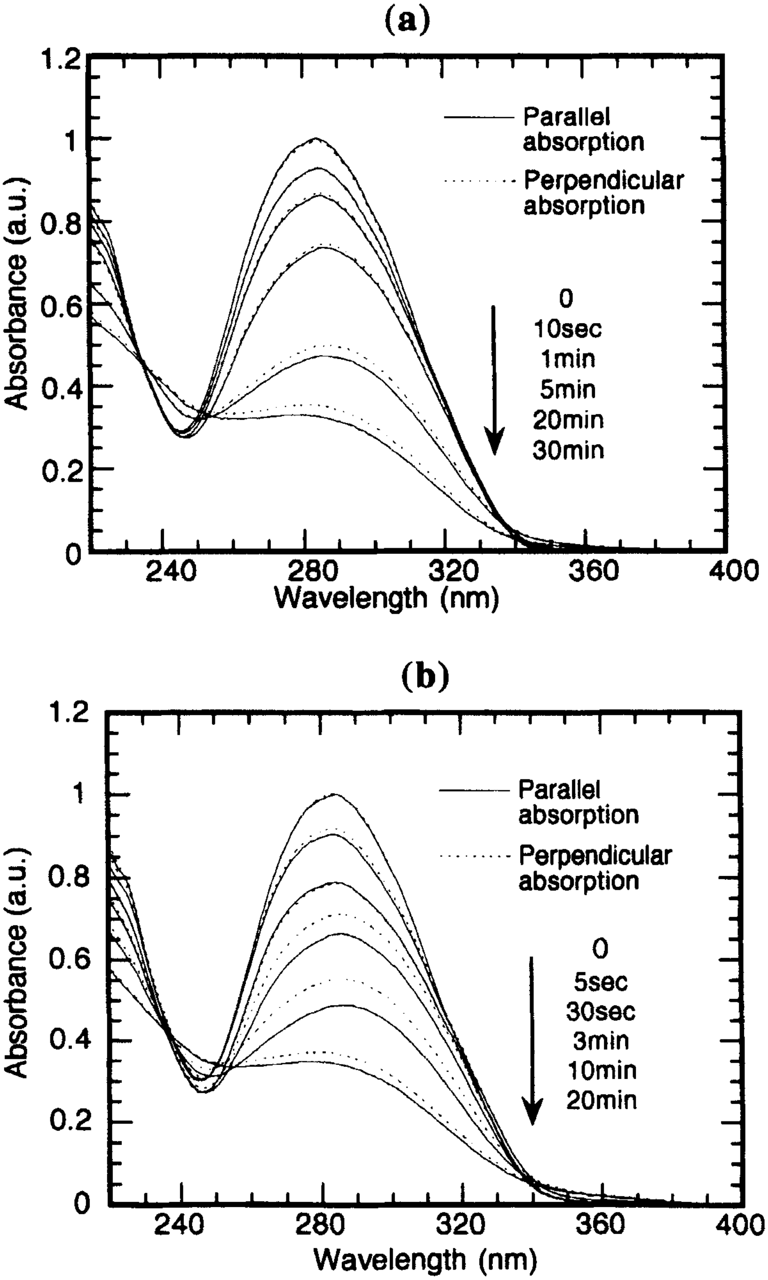
RESULTS AND DISCUSSION

LP-UV photoreaction of CPLC films

Parts a, b, c and d of figures 2 show the change in absorbance of the film photoreacted at r.t., at 90 °C, at 100 °C, and at 120°C, respectively. Because of the photo-crosslinking of the cinnamoyl group, the absorbance decreased after irradiation (except for the 5-sec irradiation of the parallel direction exposed at 100°C) and the irradiated CPLC film became insoluble in ordinary organic solvents. The degree of the photoreaction of the cinnamoyl group as a function of the irradiation time is plotted in figure 3. The photoreaction in the liquid crystalline phase was faster than that at r.t., similar to other homopolymer LCs.[6]

The dichroism ΔA [$= A$(parallel absorption) $- A$(perpendicular absorption)] for the LP-UV irradiated film at each temperature are shown in figures 4a – 4d. For the film irradiated at r.t., ΔA was small and slightly negative as shown in figure 4a. This negative dichroism was caused by the anisotropic photoreaction of the cinnamoyl group.[5,6] It should be noted that the absorbance still decreased (Fig. 2a) and ΔA became large and negative on further irradiation, where most of the cinnamoyl group had reacted (10 – 30 min exposure). This is a consequence of a side-photoreaction for the long irradiation, especially for the mesogenic groups in the parallel direction to **E**.[11]

Figure 4b shows the dichroism of the film irradiated at 90 °C (smectic phase). A negative dichroism was observed even though the degree of the photoreaction was less than 80 %. By considering the insolubilization test of the CPLC film irradiated at various temperatures,[12] we assume that an intramolecular or head-to-head photo-crosslinking reaction will be the major reaction for the photoreaction in the smectic temperature range of the CPLC film. On the other hand, intermolecular one will be a major reaction for the film irradiated at r.t. or near Ti since the time for insolubilization was faster than that in the smectic temperature range. However, further studies should be needed to clarify the chemical evidence for these type of the photoreaction. Based on this presumption, this negative dichroism in the smectic temperature range will be caused by the intramolecular photo-crosslinked group. In addition, the continuous decrease of the absorbance and the shift of the maximum wavelength of the dichroism from 280 nm (cinnamoyl group) to ~ 300 nm (broad: cinnamoyl group and cyanobi-


(a)
Absorbance (a.u.)
1.2
1
0.8
0.6
0.4
0.2
0
240
280
320
360
400
Wavelength (nm)
Parallel absorption
Perpendicular absorption
0
10sec
1min
5min
20min
30min
(b)
Absorbance (a.u.)
1.2
1
0.8
0.6
0.4
0.2
0
240
280
320
360
400
Wavelength (nm)
Parallel absorption
Perpendicular absorption
0
5sec
30sec
3min
10min
20min

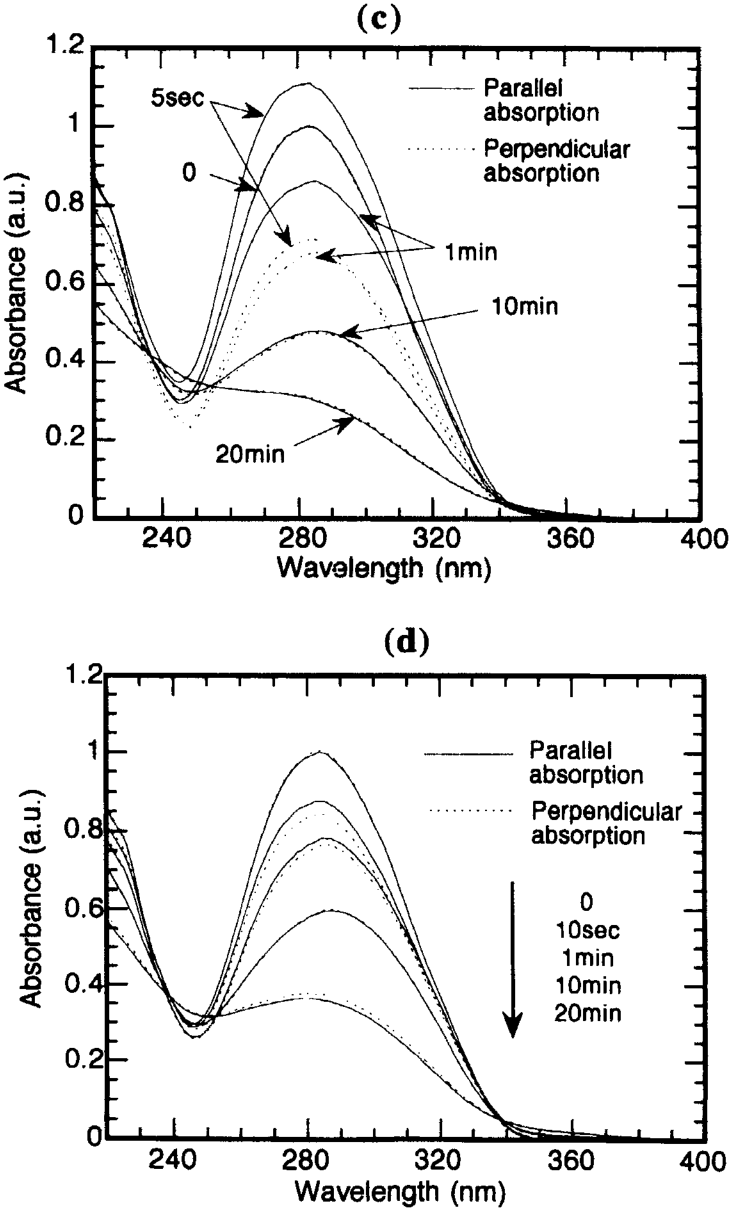


FIGURE 2 Change in absorption spectra of CPLC films: (a) Photoreacted at r.t.; (b) Photoreacted at 90 °C; (c) Photoreacted at 100 °C; (d) Photoreacted at 120 °C; solid line is a parallel absorption and the dotted line is a perpendicular absorption to **E** of LP-UV light

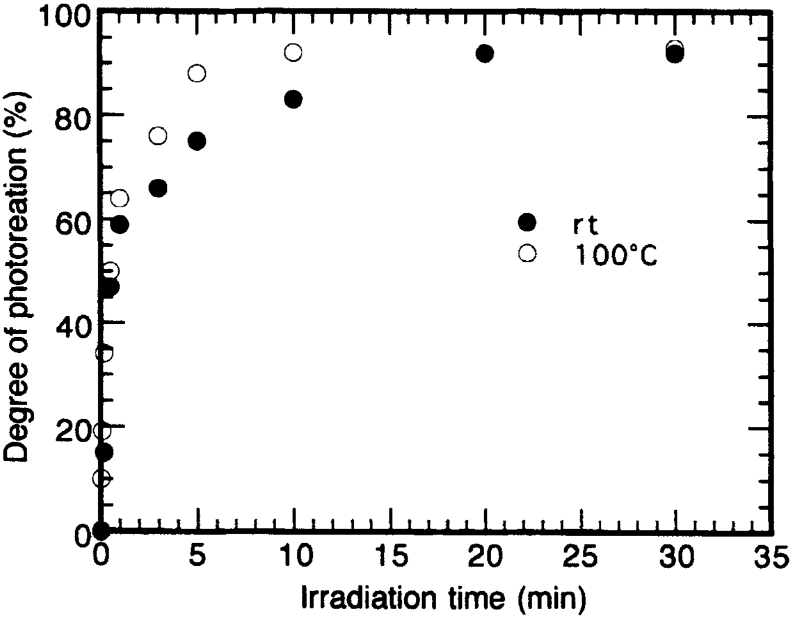
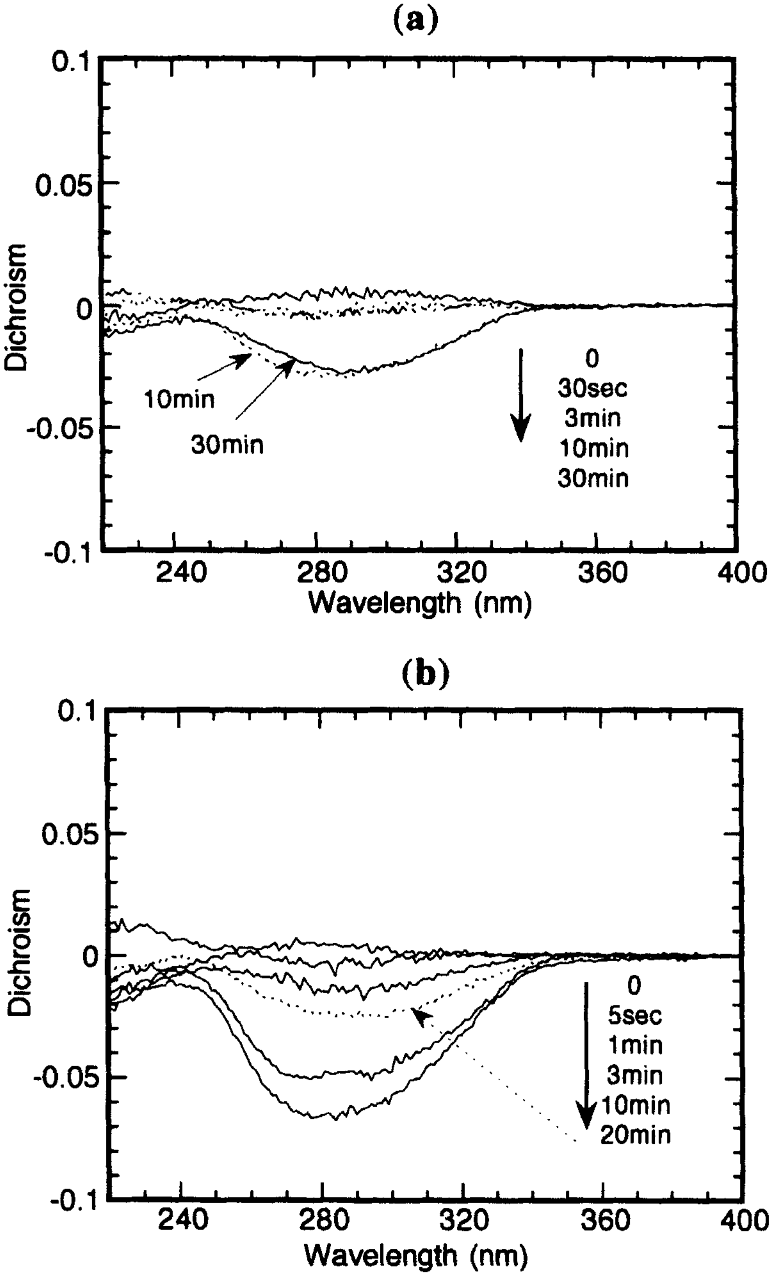


FIGURE 3 Degree of the photoreaction of the cinnamoyl group as a function of the irradiation time: Solid circle is at r.t.; Open circle is at 100 °C

phenyl group) were observed even though most of the cinnamic group had reacted (Fig. 2b). These results are ascribed to the side-photoreaction as described above.

On the other hand, a large positive dichroism was observed when the film was irradiated at 100 °C (just below T_i) as shown in figure 4c. This is attributed to the photoinduced alignment of the non-reacted mesogenic group along the photo-crosslinked mesogenic group during the photoreaction near T_i of the polymer.[12] For the parallel absorption of the film for 2 – 10 sec, the absorbance was larger than the initial one. This also suggests the photoinduced alignment of the mesogenic groups parallel to **E**. In this case, the continuous decrease of the absorbance was observed even though most of the cinnamic group had reacted and the dichroism became nearly zero for more than 10-min irradiation. This is also a consequence of the side-photoreaction.

In the case of the photoreaction at 120 °C, the dichroism was still positive in the initial state of the photoreaction although it was very small as shown in figure 4d. A small amount of the photoinduced alignment will occur near T_i in the isotropic state.


(a)
Dichroism
0.1
0.05
0
-0.05
-0.1
240
280
320
360
400
Wavelength (nm)
10min
30min
0
30sec
3min
10min
30min
(b)
Dichroism
0.1
0.05
0
-0.05
-0.1
240
280
320
360
400
Wavelength (nm)
0
5sec
1min
3min
10min
20min

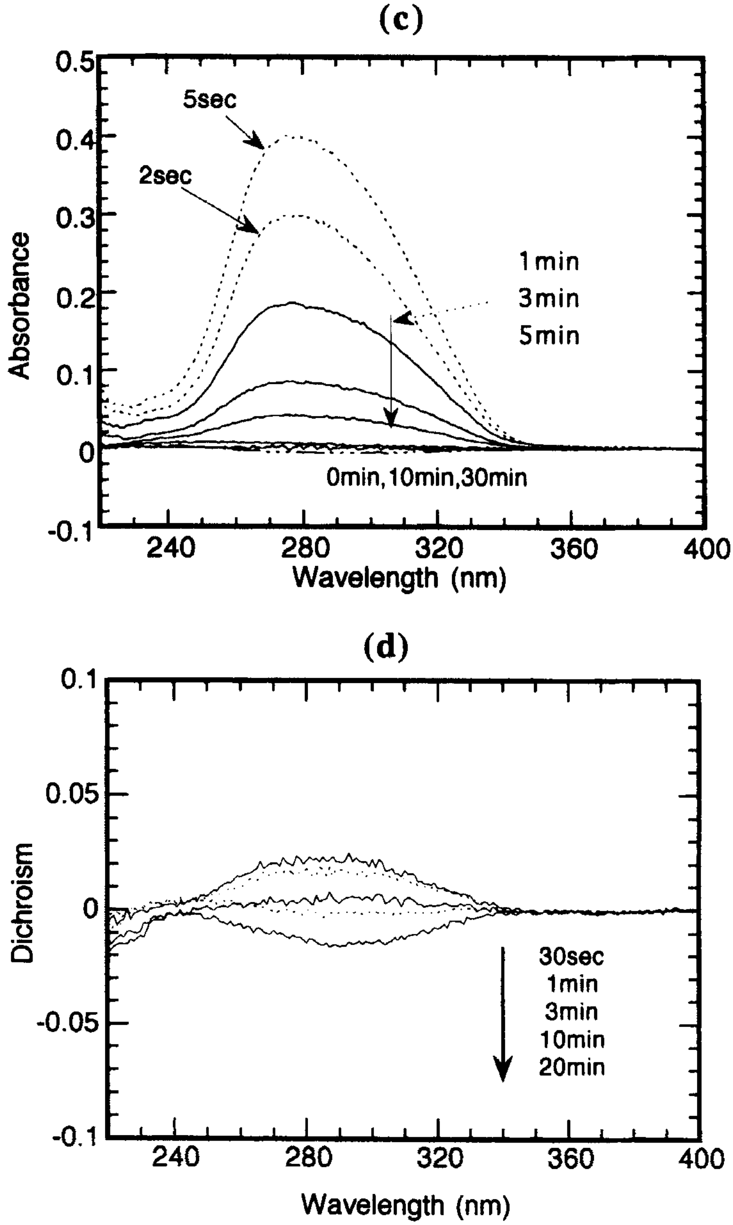


FIGURE 4 Dichroism of the UV-absorption of CPLC films: (a) Photoreacted at r.t.; (b) Photoreacted at 90 °C; (c) Photoreacted at 100 °C; (d) Photoreacted at 120 °C

LMLC alignment behavior on the photoreacted CPLC film

Table I summarizes the LMLC alignment behavior as a function of the irradiation time for each temperature. For the film photoreacted at r.t., both homeotropic and homogeneous alignments were observed. The LMLCs did not align on the non-photoreacted substrate. The homeotropic alignment was available until the degree of photoreaction reached to 75 % and no-defect was detected in the LC-cell on a microscope observation. For the further irradiated films, the LMLC became to align homogeneously and the alignment direction was perpendicular to **E**.

TABLE I Degree of photoreaction and LMLC alignment behavior of the LC-cell

Irradiation time (min)	*Irradiation temperature*						
	r.t.		*90 °C*		*100 °C*		*120 °C*
	DP[a]	*alignment*	*DP*[a]	*alignment*	*DP*[a]	*alignment*	*alignment*
0	0	none	0	none	0	none	none
0.08	-	-	-	-	19	V[b]	-
0.17	15	V[b]	36	⊥[d]	34	V[b]	V[b]
0.5	47	V[b]	50	⊥[d]	50	*[c]	V[b]
1	59	V[b]	58	⊥[d]	64	//[e]	V[b]
3	66	V[b]	70	⊥[d]	76	//[e]	V[b]
5	75	*[c]	88	⊥[d]	88	//[e]	*[c]
10	83	⊥[d]	90	⊥[d]	>92	⊥[d]	⊥[d]
20	>92	⊥[d]	>92	⊥[d]	>92	⊥[d]	⊥[d]
30	>92	⊥[d]	>92	⊥[d]	>92	⊥[d]	⊥[d]

a) Degree of the photoreaction of the cinnamoyl group, mol-%. b) Homeotropic alignment. c) Mixture of homeptropic and homogeneous alignment. d) Homogeneous-perpendicular alignment to E. e) Homogeneous-praralle1 alignment to E.

In the case of the homopolymer p2CiBM6 irradiated at r.t., we reported that the alignment direction changed from homeotropic to homogeneous-parallel to **E** with increasing the irradiation time and the direction of the homogeneous alignment changed to perpendicular to **E** if the side-photoreaction occurred.[11] The homogeneous-parallel alignment is derived from the larger alignment force for the photo-crosslinked mesogenic group in the parallel direction to **E**, than that of the non-photoreacted 2-cinnamoyloxyethoxybiphenyl group.[5,6,11] However, in the case of the CPLC film, we did not observe the homogeneous-parallel alignment even though the type of the photo-crosslinking reaction at r.t. should be the same as p2CiBM6. This will be a consequence that the alignment force for the photo-crosslinked mesogenic group will be smaller than that of the cyanobiphenyl group that is randomly oriented in the film. In addition, the homogeneous-perpendicular alignment is ascribed to the same manner as our previous results using p2CiBM6.[11] Since the side-photoreaction occurred for the longer irradiation as described in the above section, the alignment direction can be determined by the unphotoreacted cyanobiphenyl group, in which the long axis was perpendicular to **E**.

However, the origin for the homeotropic LMLC alignment is not clear at present. In the case of p2CiBM6, we also obtained a homeotropic alignment when the degree of the photoreaction was less than 40%.[11] In addition, the homopolymer of pCNBM6 cannot control the homeotropic LMLC alignment before and after the UV irradiation. Furthermore, if the CPLC film was exposed by isotropic-UV irradiation, the homeotropic alignment can be obtained and the homogenous alignment did not occur. It is expected that the configuration of the mesogenic group might be influenced in the beginning of the photo-crosslinking reaction. Further discussion will be described in a future paper.

The LMLC alignment behavior on the CPLC film irradiated in the smectic temperature range of 90 °C is also summarized in Table I. It was hard to see the homeotropic LMLC alignment, and the homogeneous-perpendicular alignment was observed in the initial state of the photoreaction. In addition, photoinduced alignment of the CPLC film did not occur at 90 °C. By considering the presumed type of the photoreaction, the photo-crosslinked mesogenic group irradiated at 90°C cannot lead the homeotropic LMLC alignment nor homogeneous-parallel alignment. The alignment force of the mesogenic group photo-crosslinked in the smectic temperature range will be smaller than that of the non-photo-crosslinked group, resulting in the homogeneous-perpendicular alignment for the photoreaction in the smectic temperature range.

In contrast to above results, for the film irradiated at 100 °C, the direction of the homogeneous alignment was parallel to **E** and changed to perpendicular on further irradiation. The homeotropic alignment was also achieved in the beginning of the photoreaction. Because of the photoinduced alignment that is parallel to **E** of the CPLC film,[12] the homogeneous-parallel alignment is likely to occur since the interaction between the LMLC and the aligned CPLC film might be large. However, the LMLC aligned homeotropically at first in the initial stage of the photoreaction, where a large positive dichroism of the CPLC film was observed (Fig. 4c). It seems that the intermolecular photo-crosslinking of the photoreactive mesogenic group should be needed for the homeotropic alignment but no-further information has been obtained at present. In addition, the homogeneous-perpendicular alignment for the long irradiation is caused by the same reason as the film irradiated at r.t.

Finally, the alignment behavior on the film irradiated at 120 °C was investigated. In the initial stage of the photoreaction, the homeotropic alignment could be obtained similar to the film irradiated at r.t. or 100 °C. In contrast, the homogeneous-parallel alignment did not occur because the photoinduced alignment was very small.

SUMMARY

We investigated both homeotropic and homogeneous LMLC photoalignment on photoreactive CPLC film. The alignment behavior was strongly dependent on the photoreaction temperature of the CPLC film, where the different type of the photo-crosslinking reaction might occur. Further studies for the origin of the homeotropic alignment and for the effect of the difference of the chemical structure of the LMLCs on the alignment behavior are still under way.

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