Photoinduced Alignment of Photo-Cross-Linkable Side-Chain Liquid Crystalline Copolymers Comprising Cinnamoylethoxybiphenyl and Cyanobiphenyl Groups

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ABSTRACT: Photo-cross-linkable side-chain liquid crystalline copolymers comprising a photoreactive 4-(2-cinnamoylethoxy)biphenyl side group and a photoinactive 4-cyanobiphenyl group were synthesized, and thin films of them were irradiated by linearly polarized (LP)-UV light, inducing an alignment of both mesogenic groups with the direction parallel to the electric vector (**E**) of the incident LP-UV light. The effects of copolymer composition and irradiation temperature on the photoinduced alignment behavior have been investigated in detail. For nematic copolymers, an induced anisotropy increased with increasing the LP-UV irradiation temperature and decreased above the clearing temperature (T_i) of the film. On the other hand, for smectic copolymer films, the photoinduced alignment was only observed when they were exposed at the temperature just around T_i. For the smectic copolymers irradiated in their smectic temperature range, intramolecular photoreaction was the major reaction. In contrast, intermolecular photoreaction became the major reaction around T_i as well as the nematic copolymers since the mobility of the mesogenic group became large. We conclude that the intermolecular photo-cross-linked mesogenic group can control the alignment of nonphotoreacted and photoinactive mesogenic groups along to the **E** direction, whereas the intramolecular photoreacted group cannot control the alignment of the other mesogenic groups.

Introduction

The manipulation of the molecular alignment of polymer system is of great interest. Several kinds of materials based on anisotropic photoisomerization or photo-cross-linking reaction have been studied by linearly polarized (LP) light. One is focused on photoreorientation of azobenzene-containing liquid crystalline polymers[1−9] and amorphous polymers.[10−15] These materials are based on *E*/*Z* photoisomerization of azo side units and can be applicable for optical memory devices because they are reversible systems. It is known that the alignment direction of the azobenzene group is perpendicular to the electric vector (**E**) of the incident LP light. Photoinduced alignment of the azobenzene-containing polymers can also be achieved by using copolymers with a photoinactive mesogenic group.[2−9,11] In addition, the effect of the irradiation energy and the temperature on the alignment efficiency have been widely studied.[2,5,16,17]

Another system is based on the anisotropic photoreaction of poly(vinyl cinnamate) (PVCi) derivatives.[18−26] These materials are mainly studied for the alignment layer for low-molecular-weight liquid crystals (LMW-LCs) of LC display devices.[19−26] For the PVCi films, the optical anisotropy is induced by LP-UV irradiation through the anisotropic [2 + 2] photocycloaddition reaction and the induced slow optical axis is perpendicular to **E** of the LP-UV light.[18] The mechanism of the photoinduced optical anisotropy for PVCi derivatives has been studied in detail.[22−24] In addition, to generate a pretilt angle of the slow axis of the PVCi film, the method of double exposure and slanted irradiation is proposed.[23,24]

Recently, we have investigated the photoinduced alignment of a photo-cross-linkable side-chain liquid crystalline (SLC) polymer film comprising a mesogenic cinnamoylalklyloxybiphenyl group.[27−29] This SLC polymer is also used for the alignment layer for LMW-LCs.[27] In the case of our polymer system, when the film is irradiated in the LC temperature range of the polymer, the alignment of the mesogenic group can be induced with the direction parallel to **E** of the LP-UV light.[28] A large optical anisotropy could be obtained by a copolymer with a photoinactive mesogenic group.[29] However, we did not examine the effects of the copolymer composition and the irradiation temperature on the photoinduced alignment behavior. The purpose of this paper is to investigate these effects on the photoinduced alignment behavior of our SLC copolymer comprising a photoreactive 4-(2-cinnamoylethoxy)biphenyl side group and a photoinactive 4-cyanobiphenyl group. Another purpose is to clarify the origin of the alignment force for the photoinduced alignment of the mesogenic group. Several compositions of copolymers were synthesized, and the copolymers showed nematic or smectic phases. The photoinduced anisotropy was monitored by polarized UV and FT-IR spectroscopy. A great temperature dependence for the photoinduced anisotropy was observed in the case of the smectic copolymer films.

Experimental Section

Materials. Figure 1 shows the chemical structure of photo-cross-linkable SLC copolymers used in this study. Monomers 6-[(4′-(2″-cinnamoylethoxy)biphenyl-4-yl)oxy]hexyl methacrylate and 6-((4′-cyanobiphenyl-4-yl)oxy)hexyl methacrylate were synthesized according to the literature.[30,31] Copolymerization was performed in THF with 2 mol % AIBN as an initiator at 54 °C for 1 day. The concentration of monomers was 10 w/v % and the copolymer composition was controlled by changing

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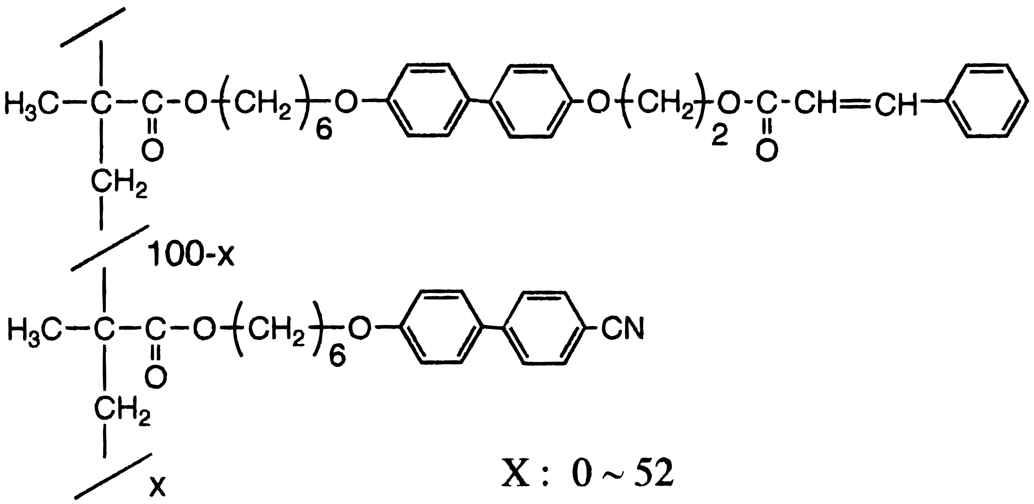

Figure 1. Chemical structure of photo-cross-linkable liquid crystalline copolymer **1**. *x* is the composition of comonomer comprising a cyanobiphenyl group.

the monomer feed ratio. The polymerization was stopped by dripping the solution into diethyl ether to precipitate the polymer. After two additional precipitations from dichloromethane solution into diethyl ether, the polymer was dried at 25 °C in a vacuum for 48 h. Copolymer composition was determined by ^{1}H-NMR spectroscopy using each monomer unit signal.

Characterization. The molecular weight was measured by gel permeation chromatography (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, THF) calibrated with polystyrene standards. Thermal properties were examined on a polarizing optical microscope (Olympus BHA-P) equipped with a Linkam TH600PM heating and cooling stage and differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 K/min. Polarized FT-IR spectra were recorded with a JASCO FT/IR-410 system attached with a wire-grid polarizer. Polarized UV−vis spectra were measured with a Hitachi U-3000 spectrometer equipped with glan-taylar polarizing prisms and JASCO TC-250 temperature control systems.

LP-UV Photoreaction of SLC Copolymers. A thin film of the SLC copolymer was prepared by spin-coating a methylene chloride solution (~5 w/w %) of polymers onto quartz or the CaF_2 substrate. There was no special treatment on the substrate. The film thickness was controlled to be 0.2−0.6 μm on the quartz substrate and 1.2 μm on CaF_2 for FT-IR measurement. The spin-coated film was transparent and showed no optical anisotropy. The film was set on a Linkam TH600PM heating stage and irradiated by a 250 W high-pressure Hg−UV lamp passed through glan-taylar polarizing prisms with a cutoff filter under 290 nm. The light intensity was 150 mW/cm^2 at 365 nm. Because the film was thin enough, there was little scattering even if it was heated in the LC temperature range of the polymer.[32] After irradiation, the film was cooled quickly to room temperature. The optical anisotropy of the film was measured by polarizing microscopy and polarized UV and FT-IR spectra at room temperature. The degree of the photoreaction of the copolymer was determined by monitoring the decreasing of −C=C− bond of the cinnamoyl group at 1639 cm^{-1} by FT-IR.

Gel Point Determination. The spin-coated film (thickness, 0.2−0.3 μm) was exposed to UV light with the energy of 65 mW/cm^2 at various temperatures. After irradiation, the film was treated in chloroform for 1 min, rinsed in 2-propanol for 1 min, and dried. The resultant film thickness was measured on the basis of a stylus contact method (Taylor Hobson Taly step).

Results and Discussion

Table 1. Thermal Properties and Molecular Weights of Synthesized SLC Copolymers

		phase transition (°C)^b			ΔH	ΔS	10^{-3}	M_w/
polymer	x^a	T_g	phase	T_i	(kJ/mol)	[J/(mol·K)]	$M_w{}^c$	M_n
1a	0	47	N	75	1.3	3.7	130	2.8
1b	18	42	N	77	1.4	4.0	101	3.1
1c	36	43	S	85	2.9	8.1	96	2.2
1d	52	46	S	94	2.6	7.1	123	3.2

[a] Composition of the cyanobiphenyl group. Copolymer composition determined by ^{1}H-NMR. [b] Determined by DSC and polarizing microscope observation: N, nematic; S, smectic. [c] M_w, weight average molecular weight; M_n, number average molecular weight. Determined by GPC with PSt standards.

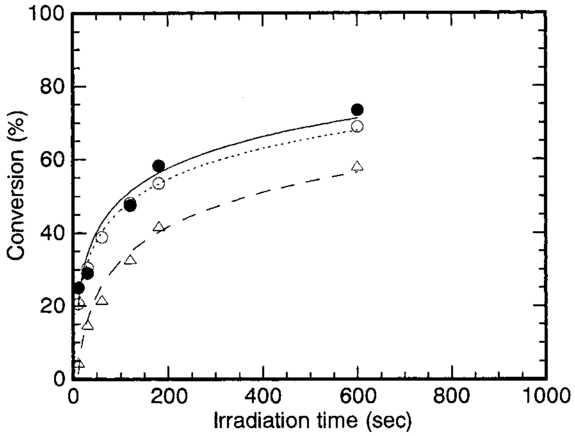

Figure 2. Progress of the photoreaction of the cinnamoyl group at various irradiation temperatures for **1d** film: (○) at 91 °C; (●) at 80 °C; (△) at room temperature.

Characterization of Copolymers. The composition, molecular weights, and thermal properties of synthesized copolymers are summarized in Table 1. Copolymers containing more than 36% of cyanobiphenyl side group showed a smectic phase and others nematic phase. All copolymers exhibited a glass transition (T_g) around 42−47 °C, while the clearing temperature (T_i) increased with increasing composition of the cyanobiphenyl group.

After UV irradiation, all copolymers became insoluble in ordinary organic solvents such as chloroform, toluene, and THF because of the [2 + 2] photocycloaddition reaction of the cinnamoyl group. Figure 2 shows the progress of the photoreaction of the cinnamoyl group at various irradiation temperatures for a **1d** film. It shows that the reaction is faster in the LC temperature

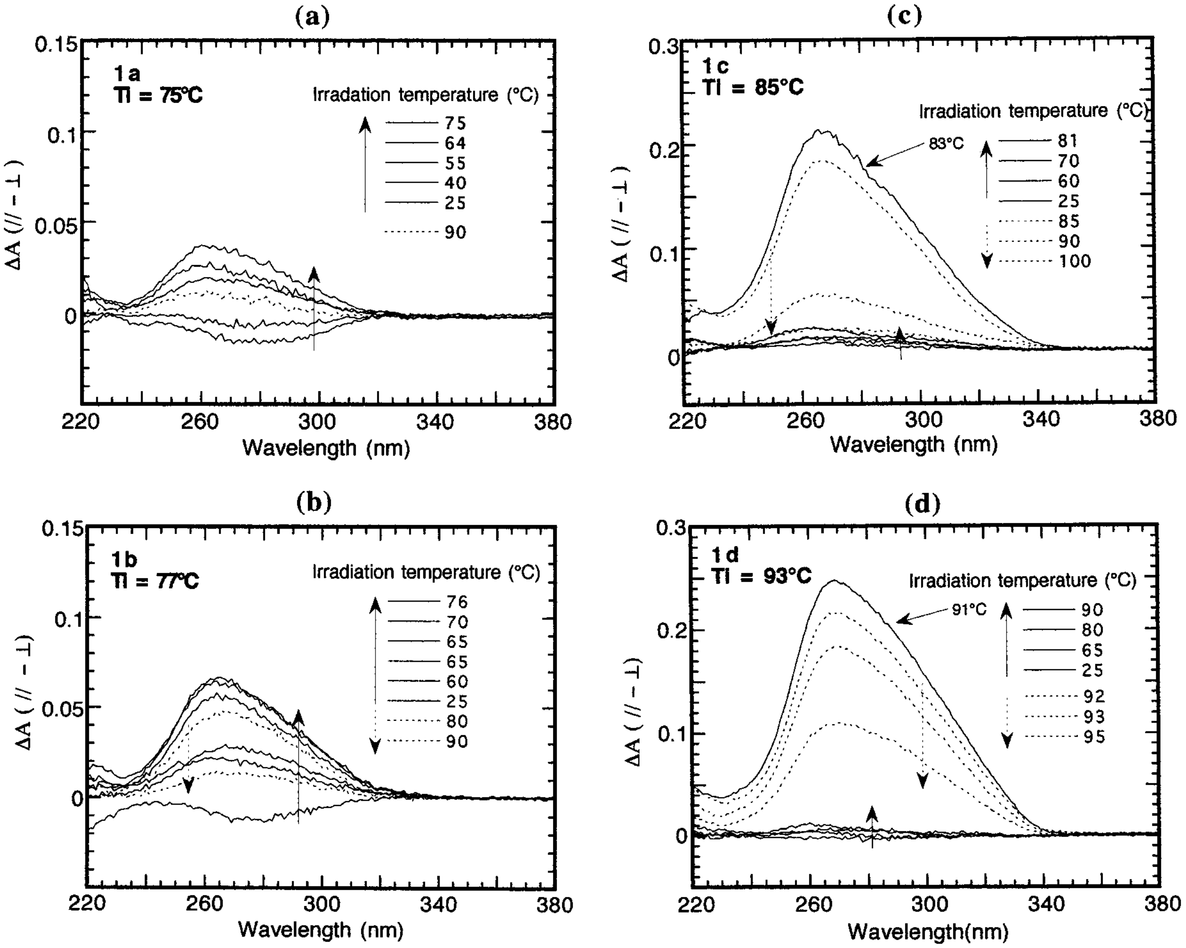

Figure 3. Dichroism Δ*A* of the UV absorption of copolymer film irradiated by LP-UV light at various temperatures: (a) **1a**; (b) **1b**; (c) **1c**; (d) **1d**. The irradiation time was 10 s for all films. The film thickness was 0.2−0.4 μm. The absorbance maxima before LP-UV irradiation were normalized to be one.

range of the copolymer than that at room temperature. Other copolymers showed similar tendencies.

Effect of Irradiation Temperature on Alignment Behavior of the Copolymers. If the irradiated film exhibits a birefringence, the difference of the UV absorption spectrum between the parallel and perpendicular direction to **E** of the LP-UV light should be observed. Therefore, we conventionally evaluated the optical anisotropy by the dichroism ($\Delta A = A_{\parallel} - A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ denote parallel and perpendicular absorption of the UV spectrum, respectively) of the irradiated film. Figure 3 shows Δ*A* of the copolymers **1a**−**1d** irradiated at various temperatures, where the absorbance maximum before LP-UV irradiation is normalized to be one. In the case of the homopolymer **1a** film, Δ*A* was negative and small when the film was irradiated below T_g, while Δ*A* became positive and increased when the irradiation temperature was above T_g and decreased above T_i. Positive Δ*A* is caused from the photoinduced alignment of the nonphotoreacted mesogenic group along the photo-cross-linked mesogens, in which the direction is parallel to **E** of LP-UV light.[28] A similar behavior was observed for the **1b** film, and the maximum Δ*A* of the **1b** film, was larger than that of the **1a** film. These temperature dependencies of the photoinduced alignment had been also observed in the azobenzene-containing polymer films.[5,9,16,17]

On the other hand, a great temperature dependence was observed for the smectic copolymers **1c** and **1d**. As shown in Figure 3c,d, the induced optical anisotropy was scarcely observed for these films below T_g. Furthermore, even if the film was irradiated in their smectic temperature range, optical anisotropy was not detected. However, a very large positive Δ*A* appeared when the photoreaction temperature was near T_i of the copolymer film. It is very interesting that this photoinduced anisotropy is very sensitive to the irradiation temperature. For example, a large Δ*A* was observed at 91 °C for the **1d** film, whereas no Δ*A* was detected at 90 °C. Above T_i, Δ*A* decreased as well as the nematic copolymers. The **1c** film exhibited similar phenomena. This temperature dependence might be caused from a different type of photoreaction at each temperature that will be discussed in another section. For all copolymer films, the maximum Δ*A* was obtained when the film temperature was 1−3 °C below T_i of the copolymers.

Table 2 summarizes the induced birefringence (dN) of the copolymers after the 10-s irradiation near T_i of

Table 2. Photoinduced Birefringence and Order Parameter of Copolymer Films

polymer	1a	1b	1c	1d
T^a	72	74	83	91
DP^b	25	21	22	22
dN^c	~0.01	0.03	0.06	0.07
$S_{CN}{}^d$		0.09	0.23	0.28
$S_{O-Ph}{}^e$	0.03	0.06	0.19	0.24

[a] Reaction temperature, °C. [b] Degree of photoreaction, mol %. Irradiation time was 10 s. [c] At 632.8 nm. [d] Order parameter of CN vibration. [e] Order parameter of Ph−O− vibration.

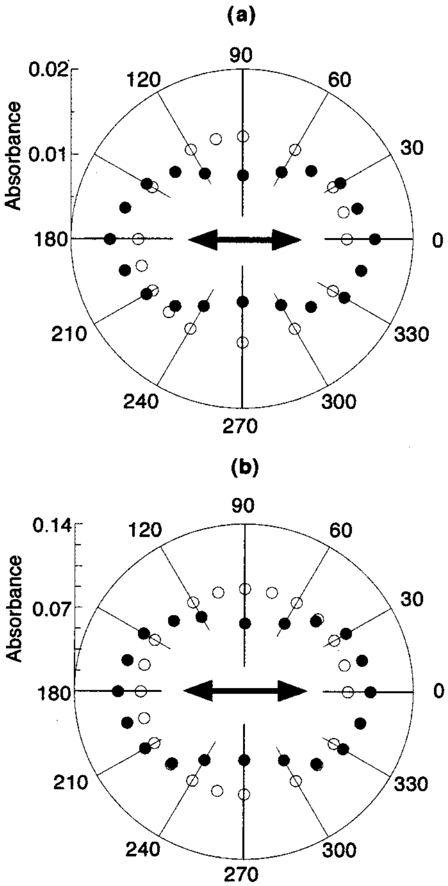

Figure 4. Angular-dependent absorbance of the **1d** film at (a) 2225 cm^{-1} and (b) 1248 cm^{-1} with FT-IR: (○) before irradiation; (●) after irradiation for 10 s at 91 °C. The arrows correspond to the **E** direction of LP-UV light.

the film. The dN value increased with increasing cyanobiphenyl composition, and it was larger for the smectic copolymers than for the nematic one. Since the degree of the photoreaction was similar for all copolymers in the range 21–25%, the cross-linking density should be smaller with increasing composition of cyanobiphenyl group. The induced dN would depend on the mobility of the nonphotoreacted group and the cyanobiphenyl group during the LP-UV photoreaction. Therefore, the larger dN for the copolymers containing a cyanobiphenyl group, especially for **1c** and **1d**, may be caused from the lower cross-linking density and a large alignment ability of the cyanobiphenyl mesogen along the photo-cross-linked direction (**E** direction).

Orientational Order of the Mesogenic Groups. The orientational order of the cyanobiphenyl group could be determined by estimating the intensity of the CN vibration at 2225 cm^{-1}. For example, Figure 4a shows an angular-dependent absorbance of the CN group for the **1d** film before and after irradiation. Before irradiation, the absorbance did not change with the direction of the polarized measurement beam. After irradiation, the absorbance reached the maximum when the direction of polarization of the measurement beam and the irradiated LP-UV light beam was parallel and reached a minimum when the direction of polarization of the measurement beam was perpendicular to the **E** direction. This indicates that the orientation of the CN group was parallel to **E** of the LP-UV light. The calculated order parameter ($S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$) was 0.28. The order parameter of the biphenyl group

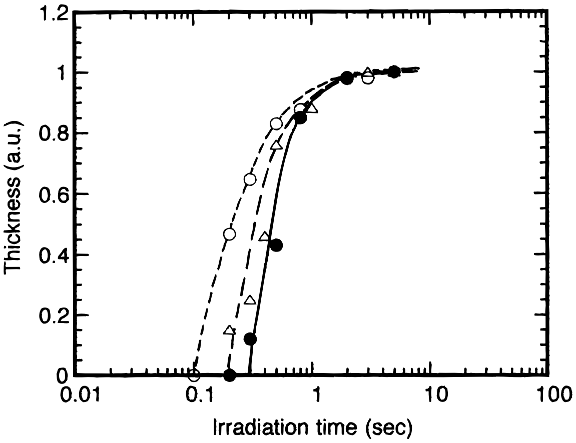

Figure 5. Insolubilization of **1d** film upon irradiation: (○) at 91 °C; (●) at 80 °C; (△) at room temperature.

can be estimated by the absorbance of the Ph–O–alkyl group at 1248 cm^{-1}. Since the angular-dependent absorbance at 1248 cm^{-1} (Figure 4b) exhibits a behavior similar to that of the CN absorbance, the direction of the biphenyl group is also parallel to **E**. The calculated order parameter of the Ph–O–alkyl group was 0.24 and somewhat smaller than that of the CN group. However, because the absorbance at 1248 cm^{-1} is a superposed absorbance of both the phenyl ether vibrations of cyanobiphenyl group and the photoreactive mesogenic group, it will be difficult to determine the orientational order of both mesogenic groups independently. The order parameter of other copolymers is also summarized in Table 2. It was clear that the order parameter was correlated to dN and the order parameter of Ph–O–alkyl group was smaller than that of the CN group in all cases.

Photoinsolubilization and Type of the Photoreaction at Different Temperatures. It is known that the photoinsolubilization having a cinnamoyl group is caused by the [2 + 2] photocycloaddition to form intermolecular cross-linkages. Since the progress of the photoreaction of the **1d** film at 80 °C was similar to that at 91 °C, as shown in Figure 2, we can compare the intermolecular and intramolecular photo-cross-linking reactions by measuring the time required for gelation (T_{gel}) at both irradiation temperatures. Figure 5 plots the normalized film thickness as a function of the irradiation time. It shows that T_{gel} at 80 °C is 2–3 times longer than that at 91 °C. This indicates that the intermolecular photo-cross-linking is the major reaction at 91 °C, while the intramolecular photoreaction occurs when irradiated at 80 °C. The smectic character of the copolymers **1c** and **1d** may be attributed to the cyanobiphenyl group, since the homopolymer of poly(6-((4′-cyanobiphenyl-4-yl)oxy)hexyl methacrylate) exhibits a smectic phase.[33] If the cyanobiphenyl group has a layered structure at the smectic temperature range of the copolymer film, the formation of the cinnamoylethoxybiphenyl group should be overlayered, as illustrated in Figure 6a. In this case, intramolecular or head-to-head photoreaction is only accepted (Figure 6b). On the other hand, the intermolecular photoreaction, which is illustrated as a dotted square in Figure 6d, can occur just below T_{i} because of the increased mobility of the mesogenic groups. These different types of photoreaction will affect the great temperature dependence of the alignment behavior of the mesogenic groups.

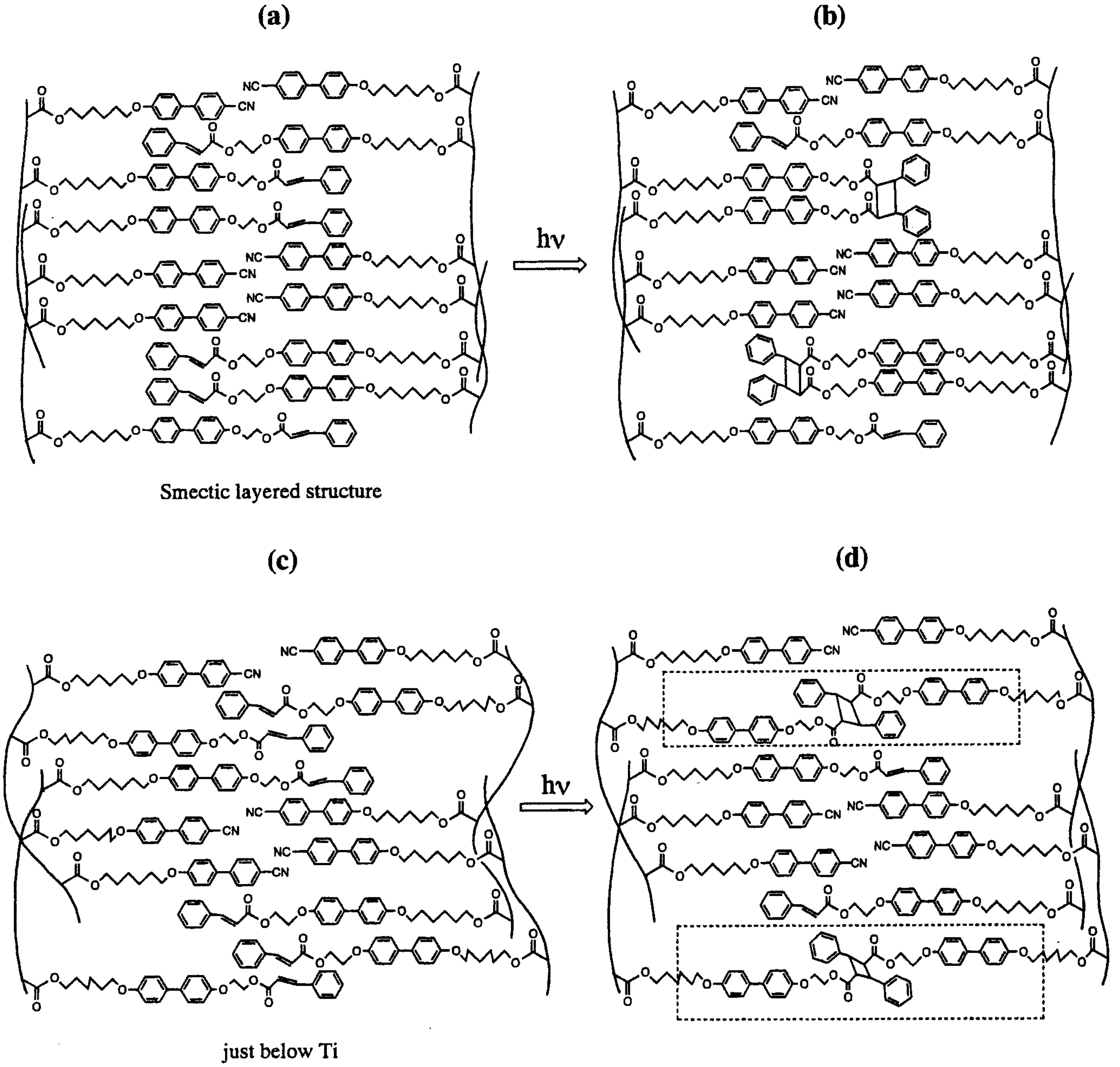

Figure 6. Schematic illustration of a photoreaction of **1d** film: (a) in the layered structure of the smectic phase; (b) photoreaction in the smectic phase; (c) at just below T_i; (d) photoreaction of (c) state.

In addition, T_{gel} irradiated at room temperature was slightly faster than that at 80 °C (Figure 5). The mesogenic group could align randomly before irradiation since the as-coated film was transparent and amorphous in nature. Taking into account that the photoreaction of the cinnamoyl group irradiated at room temperature was slower than that at the LC temperature range of the film, as plotted in Figure 2, the intermolecular photo-cross-linking will also be the major reaction at room temperature.

Photoinduced Alignment Mechanism. We had reported that the photoinduced alignment of the homopolymer **1a** film can be achieved by heating the film that was LP-UV-irradiated at room temperature.[28] When the nonphotoreacted mesogenic groups became mobile by heating, they could align along to the photo-cross-linked mesogenic group. This alignment behavior for the smectic copolymers after irradiation was also evaluated by measuring the ΔA as a function of the film temperature. We prepared three kinds of **1d** films for this experiment: (sample A) irradiated at room temperature using an as-coated film, (sample B) irradiated at 80 °C, which was the smectic temperature of **1d**, and (sample C) irradiated at room temperature using a film that was heated at 80 °C and quenched.[34] The results are shown in Figure 7. After irradiation, all samples showed no optical anisotropy. For sample A, ΔA was not observed below 40 °C after irradiation, while small positive ΔA appeared when it was heated at 50 °C, as exhibited in Figure 7a. The ΔA increased with increasing film temperature, indicating that the alignment of the nonphotoreacted and photoinactive mesogenic groups along **E** occurred on heating. In other words, the mesogenic groups aligned along the photo-cross-linked mesogenic group when they became mobile. In addition, this thermally induced ΔA was maintained after the film was cooled to room temperature. Other as-coated smectic copolymer film (**1c**) irradiated at room temperature exhibited similar results on heating.

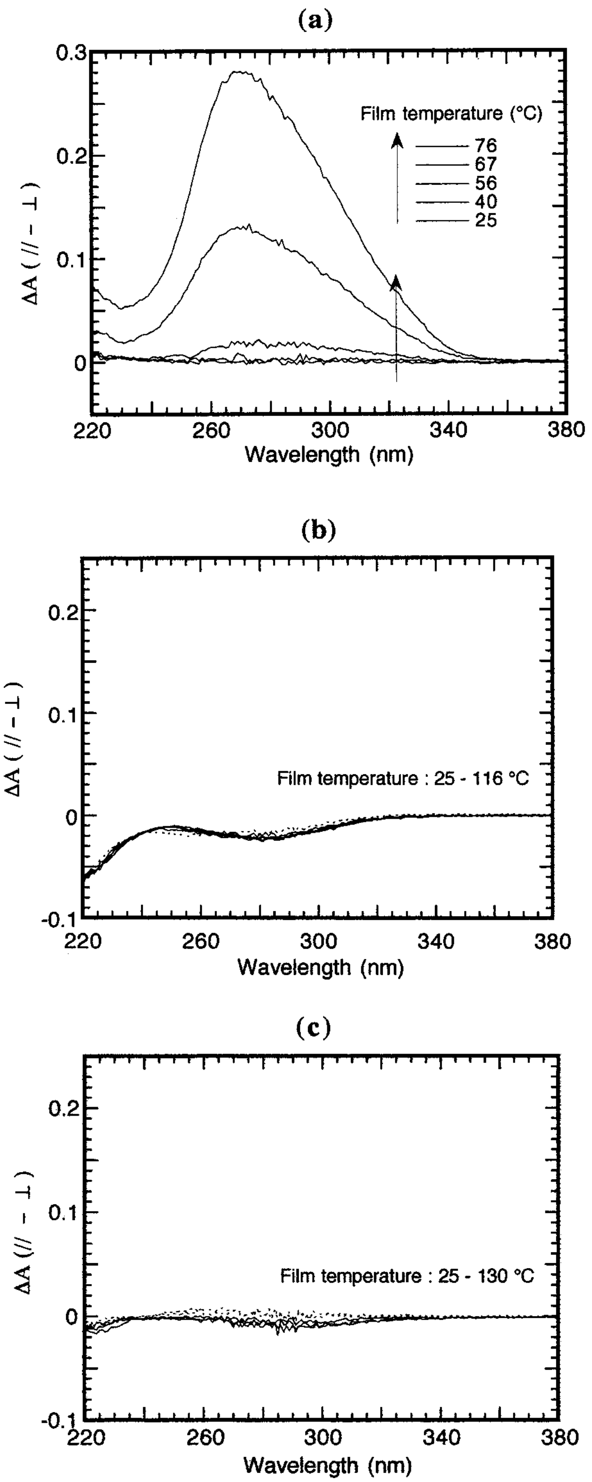

Figure 7. Change in dichroism ΔA for the LP-UV irradiated **1d** film during the heat treatment: (a) sample A; (b) sample B; (c) sample C. The irradiation time was 10 s.

On the other hand, no dichroism was observed after heating sample B and sample C, as shown in Figure 7b,c. These results suggest that the type of photo-cross-linking will play an important role for the photoinduced alignment of the mesogenic group. For sample A, the photoreactive mesogenic group could photo-cross-link intermolecularly due to the no-layered structure, as shown in Figure 6c,d (dotted square). This intermolecular photo-cross-linked mesogenic group will act as the alignment force for the orientation of the nonphotoreacted mesogen and photoinactive groups along the **E** direction when these mesogenic groups became mobile upon heating. In contrast, samples B and C should exhibit smectic layer structure, as shown in Figure 6a before irradiation, and the photoreactive mesogenic group photo-cross-linked intramolecularly (Figure 6b). The intramolecular or head-to-head photoreacted mesogenic group may not control the alignment even though the other mesogenic group became mobile. Therefore the optical anisotropy of the **1c** and **1d** films was only observed when the film was irradiated near T_i, where the smectic layered structure could be disturbed and the main photoreaction was intermolecular photo-cross-linking. In the case of the nematic **1a** and **1b** films, photoinduced anisotropy was observed in the nematic LC temperature range of the polymer since the film cannot compose a layered structure.

Conclusion

We synthesized photo-cross-linkable side-chain liquid crystalline copolymers comprising a photoreactive 4-(2-cinnamoylethoxy)biphenyl side group and a photoinactive 4-cyanobiphenyl mesogen and prepared the aligned copolymer film with the direction parallel to **E** of the exposed LP-UV light. For the nematic copolymers, the photoinduced anisotropy increased with increasing LP-UV irradiation temperature and decreased above the T_i of the film. On the other hand, the anisotropy was only observed when the film was exposed at the temperature just around T_i for the smectic copolymer films. Optical anisotropy was also obtained when the spin-coated films were irradiated at room temperature followed by heating. For the smectic copolymers irradiated at their smectic temperature, the major reaction was intramolecular or head-to-head photoreaction, which could not control the alignment of the mesogenic groups. In contrast, intermolecular photoreaction became the major reaction near T_i as well as for the nematic copolymers and the photoreaction at room temperature. We clarified that this intermolecular photo-cross-linked mesogenic group can only control the alignment of nonphotoreacted mesogen and photoinactive groups along the **E** direction. Since our photoinduced alignment system is accompanied by the photo-cross-linking of the mesogenic groups, the alignment efficiency might be affected by the irradiation intensity, and the alignment stability can also be anticipated.

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(32) If the film thickness was more than 10 μm, the film became turbid when it was heated in the liquid crystalline temperature range.

(33) Shibaev, V. P.; Platé, N. A. *Pure Appl. Chem.* **1985**, *57*, 1589−1602.

(34) Quenching of the film was performed as follows: A spin-coated film was heated to 80 °C, maintained for 10 min, and quenched rapidly.

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