

Factors Affecting Photoalignment of Liquid Crystals Induced by Polymethacrylates with Coumarin Side Chains

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It was confirmed that 313 nm light irradiation of thin films of polymethacrylates with coumarin side chains results in photodimerization without any side reaction. When the light was linearly polarized, the dichroism of coumarin chromophores was generated after prolonged irradiation as a result of axis-selective photodimerization. It was found that the photoalignment of liquid crystals was critically influenced by the polymer structure and the nature of liquid crystals when cells were assembled by using substrate plates covered with photoirradiated polymer thin films. The photoalignment direction was parallel to the electric vector of linearly polarized 313 nm light when polymethacrylates with coumarin moieties through ethylene and hexamethylene spacers were used. In contrast, a polymethacrylate having coumarin side chains without spacer induced the reversion of photoalignment. In this case, the parallel orientation at the early stage of polarized light irradiation was reversed into perpendicular orientation. This orientational reversion of the photoalignment was interpreted in terms of the balance between molecular interactions of liquid-crystal molecules with photogenerated cycloadduct(s) and those with unreacted coumarin moieties.

Introduction

The photoinduced control of orientational direction of nematic liquid crystals (LCs) has been attracting increasing interest¹ because of the practical applicability to produce rubbing-free LC films that are key materials in the fabrication of LC display devices.^{2,3} The working principle of the photoalignment control is based on photochemically induced structural as well as orientational alteration of molecules or residues localized at uppermost surfaces of substrate plates, which are termed as command surfaces.¹ Command surfaces have been provided by appropriate combinations of molecular or polymeric films with suitable photoactive molecules. Whereas molecular films incorporating photoreactive moieties have been employed so far to achieve photoalignment control, more extensive studies have been carried out on thin films of polymers having photoreactive units probably because of the good availability of thin films by the spin-coating technique.

In respect to photoreactive units leading to azimuthal LC alignment by linearly polarized light irradiation, three classes of photochemistry have been investigated.

The first involves the photochromic reaction of azobenzenes,^{4–8} spiropyrans,⁹ and stilbenes.¹⁰ The second class displays [2+2] photodimerization of cinnamates,^{11–13} benzylidenephthalimides,¹⁴ benzylideneacetophenones (chalcones),¹⁵ diphenylacetylenes,¹⁶ and coumarins.² The last is the photolysis of imide groups of polyimides¹⁷ while no systematic studies have not yet been done on the working mechanism of this type of photoaligning polymer films from a photochemical viewpoint. The irradiation of thin films of polymers bearing these types of photoreactive units with linearly polarized light gives

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rise to homogeneous alignment so that this technique provides a promising way to prepare LC aligning films in a photochemical manner. One of the requirements to be fulfilled in the application to rubbing-free LC aligning films for LC display devices is the prominent stability of photoaligned states toward external stimulation such as heat. In this context, the last two have been intensively studied from a practical viewpoint, since it has been anticipated that irreversible photochemistry is preferably applicable to LC aligning films. For instance, [2+2] photodimerization of C=C double bonds introduced to polymer chains results in the cross-linkage to form network structures that may suppress the molecular mobility of photoaligned residues which determine the orientation of LCs, leading to the thermal stability of photoinduced LC alignment.¹³ In this respect, it is of significance to reveal the relationship between photochemical behavior and the ability of polymers with photodimerizable side chains to control LC alignment. The photodimerizable moieties studied so far for LC photoalignment are mentioned above and can be classified into two categories. Cinnamates,^{11–13} benzylidenephthalimidines,¹⁴ and benzylideneacetophenones¹⁵ undergo both photodimerization and reversible *E/Z* photoisomerization, whereas coumarins and diphenylacetylenes exhibit no photoisomerization.

It has been reported that slantwise irradiation of a thin film of a polymer with coumarin side chains with linearly polarized UV light generates pretilt angles with homogeneous alignment so that this procedure is applicable to fabricate high-quality LC display devices.² When compared to polymers with cinnamate side chains, no detailed study has been achieved so far on coumarin polymers to elucidate the working mechanism of LC photoalignment. Our motivation to deal with the linearly-polarized-light photochemistry of coumarin polymers stemmed from literature results indicating that the LC alignment direction induced by a film of a coumarin polymer is parallel to an electric vector of polarized UV light. In contrast, a perpendicular orientation of LC molecules is commonly generated in the case of polymers with other photoreactive moieties.^{4–14} We report here that the dichroism of thin films of polymers with coumarin side chains is in fact generated and that the photoalignment behavior of the LC is critically dependent on the length of a spacer between a coumarin moiety and a polymer main chain.

Experimental Section

Materials. 7-Hydroxycoumarin, ethylene carbonate, 6-chlorohexanol-1, and methacryloyl chloride were purchased from Tokyo Kasei Co., Ltd. and used without further purification. Nematic liquid crystals were donated by Lodic, Co., Ltd. Chemical structures of the materials used in this study are shown in Figure 1.

7-Methacryloyloxy coumarin. To a solution of 3.0 g of 7-hydroxycoumarin in 20 mL of pyridine was added a THF solution of 3.0 g of methacryloyl chloride, and the solution was stirred at room temperature for 1 h. The reaction mixture was poured into 300 mL of water, followed by collection of a white precipitate which was recrystallized from ethanol to give colorless plates (mp 146–147 °C) in a 69% yield. Anal. Calcd for C₁₃H₁₀O₄: C, 67.82; H, 4.35. Found: C, 67.55; H, 4.45. ¹H NMR (*d*₆-DMSO) δ (ppm): 2.02 (s, 3H, CH₃), 5.95 (s, 1H, ethylene), 6.32 (s, 1H, ethylene), 6.49 (d, 1H, *J* = 9.58, enone), 7.22 (d, 1H, *J* = 8.42, aromatic), 7.35 (s, 1H, aromatic), 7.79 (d, 1H, *J* = 8.40, aromatic), 8.09 (d, 1H, *J* = 9.58, enone).

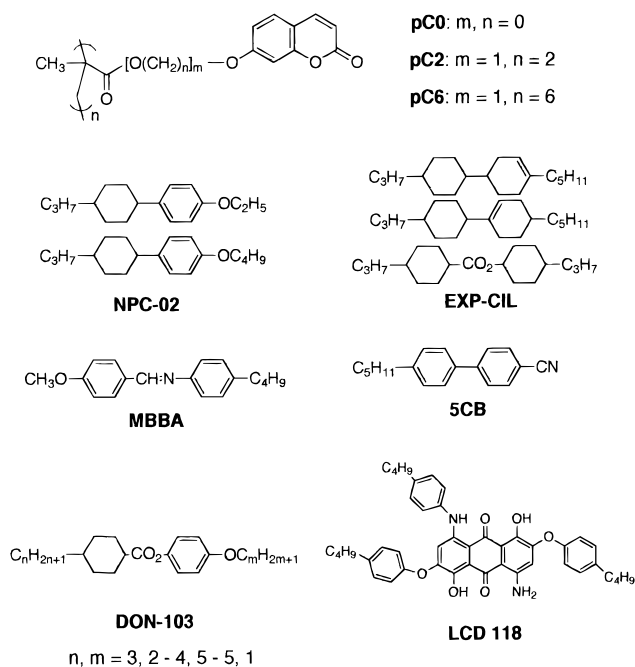


Figure 1. Chemical structures of the coumarin polymers, liquid crystals, and the dichroic dye.

7-(2-Hydroxyethoxy)coumarin. A mixture of 5.0 g of 7-hydroxycoumarin, 5.0 g of ethylene carbonate, and 2.0 g of potassium carbonate in 50 mL of *N,N*-dimethylacetamide was heated under reflux for 5 h and treated with ether and water after cooling. The organic layer was washed with ether thoroughly and dried over magnesium sulfate, followed by the removal of the solvent. A residual solid was recrystallized from ethanol to give prisms (mp 90–91 °C) in a 69% yield. Anal. Calcd for C₁₁H₁₀O₄: C, 64.08; H, 4.85. Found: C, 64.01; H, 4.91. ¹H NMR (*d*₆-DMSO) δ (ppm): 3.71 (q, 2H, CH₂O), 4.10 (t, 2H, CH₂OAr), 4.92 (t, 1H, OH), 6.28 (d, 1H, *J* = 9.58, enone), 6.92–6.98 (m, 2H, coumarin), 7.62 (d, 1H, *J* = 8.22, aromatic), 7.98 (d, 1H, *J* = 9.58, enone).

7-(2-Methacryloyloxyethoxy)coumarin. To a mixture of 1.0 g of 7-(2-hydroxyethoxy)coumarin and 1.0 g of triethylamine in 30 mL of benzene was added 1.0 g of methacryloyl chloride dropwise. After being stirred for 1 h at room temperature and after the addition of 100 mL of ether, the reaction mixture was washed with an aqueous solution of NaCl, followed by drying over magnesium sulfate and the removal of the solvent to give a solid. The crude product was recrystallized from ethanol to afford colorless powdery crystals (mp 131.5–133 °C) in a 67% yield. Anal. Calcd for C₁₅H₁₄O₅: C, 65.69; H, 5.11. Found: C, 65.21; H, 5.12. ¹H NMR (CDCl₃) δ (ppm): 1.96 (s, 3H, CH₃), 4.28 (t, 2H, CH₂OR), 4.53 (t, 2H, CH₂OAr), 5.60 (s, 1H, ethylene), 6.15 (s, 1H, ethylene), 6.27 (d, 1H, *J* = 9.58, enone), 6.8–6.9 (m, 2H, coumarin 6 and 8, aromatic), 7.38 (d, 1H, *J* = 8.02, aromatic), 7.64 (d, 1H, *J* = 9.38, enone).

7-(6-Hydroxyhexyloxy)coumarin. A solution of 5.0 g of 7-hydroxycoumarin, 7.0 g of 6-chlorohexanol-1, and a catalytic amount of potassium iodide in 50 mL of 2-butanone was heated at reflux in the presence of 2.0 g of potassium carbonate for 30 h. After filtration and removal of the solvent, a residual yellowish liquid was dissolved in ethyl acetate, and the solution was washed with an aqueous NaCl solution, followed by drying over magnesium sulfate and removal of the solvent to give a colorless liquid in a 69% yield. The crude product was purified with chromatography on silica gel using a 4:6 v/v mixture of hexane and ethyl acetate. Anal. Calcd for C₁₅H₁₇O₄: C, 68.97; H, 6.51. Found: C, 67.54; H, 6.88. ¹H NMR (CDCl₃) δ (ppm): 1.2–1.9 (m, 10H, CH₂), 3.69 (t, 2H, CH₂OR), 3.98 (t, 2H, CH₂-OPh), 6.23 (d, 1H, *J* = 9.38, enone), 6.79–6.84 (m, 2H, aromatic), 7.36 (d, 1H, *J* = 8.02, aromatic), 7.64 (d, 1H, *J* = 9.38, enone).

7-(6-Methacryloyloxyhexyloxy)coumarin. 2.0 g of 7-(6-hydroxy)hexyloxy coumarin was treated with methacryloyl chloride in the same manner as above to give a colorless liquid in a 72% yield, which was purified by column chromatography on silica gel using a 6:4 v/v mixture of hexane and ethyl acetate. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.06; H, 6.67. Found: C, 68.65; H, 6.63. 1H NMR ($CDCl_3$) δ (ppm): 1.2–1.9 (m, 9H, CH_2), 2.00 (s, 3H, CH_3), 4.02 (t, 2H, CH_2OR), 4.17 (t, 2H, CH_2-OPh), 5.55 (s, 1H, ethylene), 6.09 (s, 1H, ethylene), 6.24 (d, 1H, $J = 9.58$, enone), 6.79–6.84 (m, 2H, aromatic), 7.36 (d, 1H, $J = 8.02$, aromatic), 7.63 (d, 1H, $J = 9.38$, enone).

Polymerization. A coumarin monomer (1.00 g) and 10 mg of AIBN were dissolved in 10 mL of DMF, and the solution was placed in a tube and degassed with repeated freeze and thaw cycles. The sealed tube was heated at 60 °C for 10 h. The viscous solution was poured into methanol to separate a polymer which was purified by reprecipitation from methanol and dried in vacuo at 80 °C for 4 h.

Physical Measurements. Spectral measurements of 1H NMR, UV-vis, and FT-IR were performed by using a Bruker AC200, an HP 8452A spectrometer, and a Bio-Rad FTS 6000 spectrometer, respectively. DSC measurements were made on coumarin polymers using a DSC 22C (Seiko instruments) at a scanning speed of 10 °C min^{-1} while molecular weights of polymers dissolved in chloroform were determined by GPC with polystyrene as a standard. The melting behavior of the polymers was observed using a polarized microscope (OLYMPUS BH-2) with a hot stage (Mettler FP800 thermosystem) at a rate of 10 °C min^{-1} . FT-IR spectra of polymer films spin cast on a CaF_2 plate were taken in transmission mode at 2 cm^{-1} resolution. Film thickness was calculated from absorbances of those films, which is around 80 nm.

Photoirradiation. Light from a high-pressure mercury lamp (Ushio Electronic Co. USH-500D) was passed through a glass filter (UVD-35) and a solution filter ($K_2CrO_4/1$ wt % aqueous NaOH) to isolate the 313 nm line. A Glan-Taylor type polarizer was used for linearly polarized light irradiation. Films of the coumarin polymers were spin cast from a chloroform solution on fused silica plates at 2000 rpm for 20 s to adjust film thickness of 70–80 nm and were subjected to photoirradiation.

Determination of LC Photoalignment. A hybrid LC cell was assembled by sandwiching nematic liquid crystals between a glass plate spin coated with a coumarin polymer and a plate coated with lecithin for homeotropic alignment. Photoirradiation of polymer films were performed before or after LC cell fabrication. The LC was filled into a cell in its isotropic state by a capillary action. In-plane LC alignment was checked by observation of LC textures with the polarized microscope. The level of the LC photoalignment was determined by measuring the transmitted light intensity of a linearly polarized He-Ne laser beam through the cell as a function of the cell rotation angle. The direction of LC alignment was determined by monitoring polarized absorbances of a dichroic dye (LCD 118) dissolved in the LC.

Results and Discussion

Synthesis of Coumarin Polymers. Though Schadt and co-workers reported a novel way to generate pretilt angles of LC by slantwise irradiation of a thin film of a polymer with coumarin side chains with linearly polarized UV light, no discrete information concerning the polymer structure was available from their paper.² In this work, three polymethacrylates substituted with coumarin moieties through a spacer with variant length (pC0, pC2, and pC6 in Figure 1) were prepared by the radical polymerization of the corresponding monomers. Some properties of the polymers are summarized in Table 1. While pC2 and pC6 show glass-transition temperatures (T_g) at 80 or 140 °C, respectively, no clear T_g was observed for pC0 though the latter polymer

Table 1. Properties of Polymers Containing Coumarin Units

polymer	M_w	M_w/M_n	T_g (°C)	T_m (°C) ^a
pC0	33 000	3.5		200
pC2	22 000	3.5	79	
pC6	68 000	3.1	140	

^a The temperature of an endothermic peak.

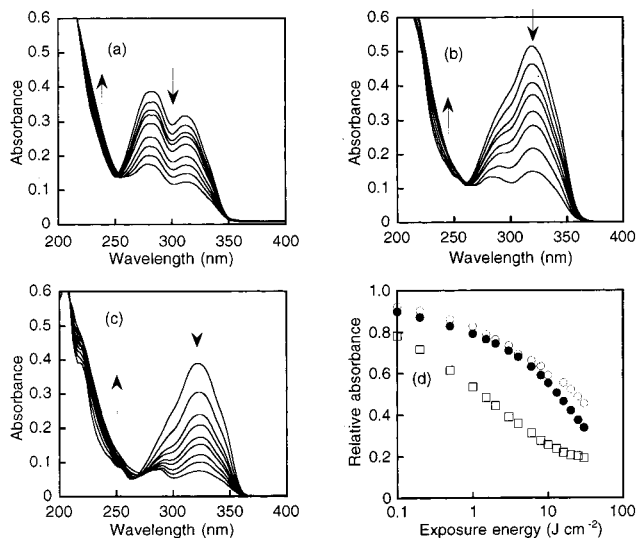


Figure 2. UV absorption spectral changes of (a) pC0, (b) pC2, and (c) pC6 film upon irradiation with 313 nm light. Changes of relative absorbances change of pC0 (○), pC2 (●), and pC6 (□) film at the peak position upon irradiation with 313 nm light are summarized in (d).

exhibited endothermic peaks at 200 °C and at about 360 °C. The endothermic peak at 360 °C may be attributable to the decomposition. On the other hand, the peak at 200 °C was observed reproducibly. Microscopic observation revealed that pC0 melts in the range of 200–220 °C and becomes a fluid completely at 250 °C. X-ray diffraction analysis of the polymer showed an amorphous material.

Photochemistry of Coumarins in Polymer Solids. UV-vis spectral changes of thin films of the coumarin polymers upon UV irradiation are given in Figure 2. Before photoirradiation, only a single peak appears at 320 nm for pC2 and pC6, while pC0 has two peaks at 280 and 310 nm. The red-shifted absorption band of pC2 and pC6 is evidently due to the conjugation of the electron-donating ether oxygen atom with the aromatic system of coumarin, whereas pC0 has an ester oxygen next to the aromatic system. No alteration of absorption spectra of films of all of the polymers was observed even after heating at 100 °C for 4 h, indicating that neither aggregation nor the reorientation of the coumarin moieties is induced upon heat treatment. Irradiation with 313 nm light resulted in the decrease in absorbances at λ_{max} for all of the polymers, whereas a slight increase in absorbances at wavelengths shorter than 250 nm was observed, being in line with the [2+2] cycloaddition at the C=C bond of coumarin moieties to give a benzenoid absorption band. The rate of the disappearance of the absorption band(s) at the early stage of the photolysis was influenced by the chemical structure of the polymers, as illustrated in Figure 2d, and is in the following order: pC6 \gg pC2 > pC0. These results reflect that a longer spacer ensures mobility of

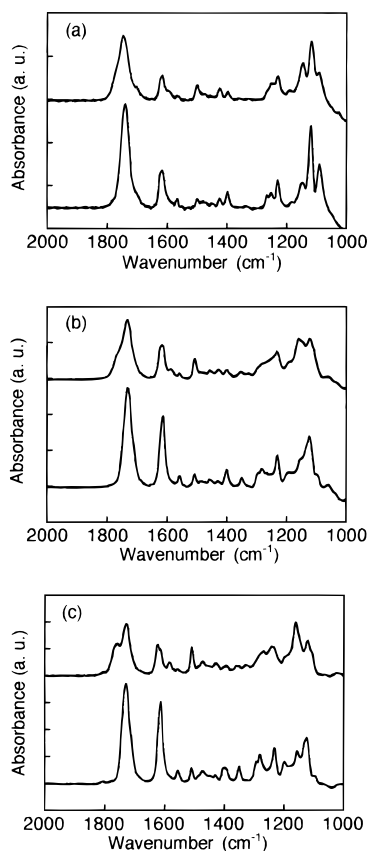


Figure 3. FT-IR spectra of films of (a) pC0, (b) pC2, and (c) pC6 before (upper curves) and after (lower curves) irradiation with 313 nm light of a 15 J cm^{-2} exposure dose.

coumarin units in polymer solids so that the site-specific dimerization takes place. The photochemical conversion of pC6 was leveled off at an exposure dose of about 20 J cm^{-2} while a gradual decrease in absorbances was observed for pC0 and pC2 even after irradiation of exposure doses of more than 30 J cm^{-2} .

To confirm the uniformity of photochemical reaction, spectral analysis by means of an ED (extinction difference) diagram was performed. All polymer films display linear diagrams, indicating that the photochemistry involves a single reaction, that is, the cyclobutane formation.

Further information concerning the photochemistry of coumarin polymers was obtained by FT-IR measurements. Figure 3 shows the FT-IR spectra of pC0, pC2, and pC6 before and after photoirradiation with 313 nm light and an exposure dose of 15 J cm^{-2} . The assignment of representative peaks are summarized in Table 2.¹⁹ The absorption due to C=O stretching of both the C=O bonds of the coumarin and polymethacrylate chains are not separated before photoirradiation. Photoirradiation resulted in a shift of the C=O peak in pC0 from 1738 to 1745 cm^{-1} , implying the disappearance of enone conjugation. Contrary to this, no shift of the peaks at 1732 and 1729 cm^{-1} for the C=O bands of pC2 or pC6, respectively, was observed after photoirradiation, although the bands became broader, suggesting the

Table 2. Assignment of Peaks in the FT-IR Spectra of Films of the Coumarin Polymers

frequency (cm^{-1}) of			assignment ^a
pC0	pC2	pC6	
1739	1732	1729	C=O stretching
1617	1613	1613	ring C=C stretching
1566	1557	1556	cis C=C stretching
1500	1507	1509	ring C=C stretching
1425	1457	1473	CH ₂ scissor
1398	1401	1401	cis C=C stretching
1266	1281	1280	C(C=O)-O asym. stretching
1230	1230	1232	=C-O-C asym. stretching
1147	1127	1123	C(C=O)-O sym. stretching
1091	1062		=C-O-C sym. stretching

^a The sym and asym abbreviate symmetric and asymmetric.

modification of the enone conjugation due to dimerization. A photoirradiated film of pC6 showed a new band at 1756 cm^{-1} , revealing that the dimerization takes place efficiently, consistent with the results obtained by UV-vis spectral analysis. It was reported that a spectral shift of the C=O stretching band of a coumarin moiety incorporated in a self-assembled monolayer arises from the difference in the isomerism of cyclobutane adducts.²⁰ According to the literature, the shift to higher wavenumbers is due to the formation of a *head-to-head* dimer while the peak shift to lower wavenumbers is attributed to the formation of a *head-to-tail* isomer. Since the polymers in the present work possess two kinds of C=O bonds derived from the coumarin and the ester units of polymethacrylate chains, and the rates of reaction are different, the nature of the observed peak shift after photoirradiation is rather difficult to identify. However, it can be rationalized that the difference in the extent of the peak shift among the polymers reflects the difference in the geometrical isomerism of cyclobutane derivatives in films of pC0 and pC2 and pC6.

Absorbances of the peak centered at around 1400 cm^{-1} due to the C=C bond decreased upon photoirradiation for each polymer, indicating the photodimerization of coumarins. The peak around 1500 cm^{-1} for each film increased by photoirradiation, and the peaks around 1150 and 1250 cm^{-1} became broader. This behavior is considered to also be caused by the formation of cyclobutane. IR spectrum data of 3,4-dihydrocoumarin shows peaks at 1500 , 1137 , and 1233 cm^{-1} , respectively. The last two peaks appear at higher wavenumbers than those of coumarin so that the peak broadening may be due to the overlap of those of coumarin and dimerized products.^{19b} The formation of cyclobutane(s) results in the increase of a peak intensity at around 3000 cm^{-1} because of aliphatic C-H. However, absorbance at this region was so weak that no discussion can be made on the disappearance of the C=C bond. From these results, it is reasonably concluded that the coumarins tethered to polymethacrylate main chains dimerize upon photoirradiation for all polymers.

The photodimerization of coumarins has been well-studied in solutions,²¹⁻²³ in crystals,²⁴ in self-assembled

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monolayers,²⁰ and in polymer films.²⁵ Possible cyclobutane isomers are *syn-head-to-head*, *syn-head-to-tail*, *anti-head-to-head*, and *anti-head-to-tail*. The photodimer distribution in solution photochemistry depends on the nature and the position of substituent(s) and the polarity of the solvent. For example, 7-acetoxycoumarin and 7-methoxycoumarin, which are only different in a substituent, produce *syn-head-to-head* and *syn-head-to-tail* products, respectively, either in crystal or in solution. In connection with the elucidation of photoalignment mechanism, the identification of the isomerism of coumarin cycloadducts in polymer films should give essential information. However, no structural analysis of the cycloadducts have not yet been carried out because of the difficulty in the elucidation of the isomerism of the cyclobutane cross-linkage in polymer solids.

Photodichroism. Though it was reported that linearly-polarized-light irradiation of thin films of coumarin polymers generates homogeneous LC alignment with pretilt angles, no information was available concerning the optical anisotropy of photoirradiated films.² This situation led us to determine photoinduced dichroism of the polymers with coumarin side chains that were exposed to linearly polarized 313 nm light. Dichroism determination of films was achieved by measurements solely of polarized UV absorption spectra since significant dichroism was essentially not detected by FT-IR measurements owing to the weak band at 1400 cm⁻¹ because of the C=C bond. Figure 4 shows absorbances at λ_{\max} in parallel with (A_{\parallel}) and perpendicular to (A_{\perp}) the electric vector of polarized 313 nm light as a function of exposure doses. The decrease of A_{\parallel} occurs slightly faster than that of A_{\perp} for each polymer film, suggesting that linearly polarized light induces angular selective photodimerization. But the absorbance difference ($\Delta = A_{\perp} - A_{\parallel}$) is quite minute. Even at exposure doses of several 10 J cm⁻², Δ values were only around 0.01, 0.02, and 0.003 for pC0, pC2, and pC6, respectively.

As discussed in our previous papers, the photogeneration of optical anisotropy of azobenzene polymers consists of two processes including axis-selective photochemical transformation and photoinduced molecular reorientation. The former process involves the axis-selective bleaching of the chromophores in such a way that the molecular axis of the original chromophores is not modified. On the other hand, the latter is based on the repetition of molecular structural changes owing to the reversibility of photochemical transformation. We have so far determined dichroic ratios, defined as $DR = (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$, of polymethacrylates having photoisomerizable moieties including azobenzenes,⁴⁻⁸ cinnamates,¹³ and benzylidenephthalimides.¹⁴ They are all *E/Z*-photoisomerizable, while the latter two having C=C bonds display the simultaneous occurrence of [2+2] photocycloaddition. Our detailed study on the photochemical conversion of cinnamate moieties in polymer films confirmed their photodimerization accompanied by *E/Z*-photoisomerization in polymer films,

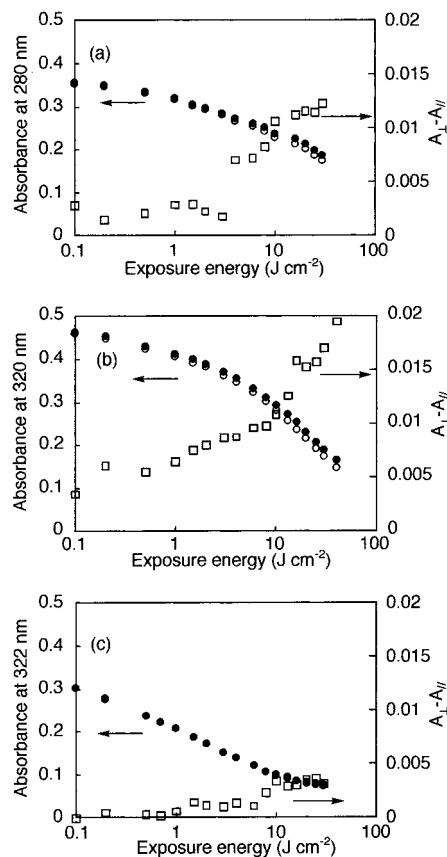


Figure 4. Absorbances in (a) pC0, (b) pC2, and (c) pC6 film, respectively, at λ_{\max} perpendicular to (A_{\perp}) (●) and in parallel with (A_{\parallel}) (○) the electric vector of linearly polarized 313 nm and the differences between both of them (□) as a function of exposure doses of linearly polarized 313 nm light.

though the ratio of both photoreactions is critically dependent on the molecular structure of cinnamate polymers. Contrary to this, the predominant photochemistry of polymers with benzylidenephthalimide side chains is *E/Z*-photoisomerization even in polymer solids, whereas the photo-cross-linking due to photodimerization takes place in fact upon prolonged photoirradiation with lower quantum efficiencies.¹⁴

According to our reports, DR values of amorphous polymers with azobenzenes, cinnamates, and benzylidenephthalimides are approximately 0.10, 0.02–0.04, and 0.05, respectively. On the other hand, DR values for pC0, pC2, and pC6 were calculated to be 0.03, 0.05, and 0.015, respectively. The lower DR values of cinnamate polymers may stem from the contribution of the irreversible process because of photodimerization which does not bring about molecular reorientation. The observation that the DR value of pC0 is not far from those of cinnamate polymers is reasonably interpreted by the participation of [2+2] dimerization in the photogeneration of dichroism. pC6 with spacer units show DR values smaller than that of pC2 or pC0. This feature is supposed to arise from the efficient mobility of coumarin units because of the relatively longer spacer.

Photocontrol of LC Alignment. M. Schadt et al. reported that the control of in-plane LC alignment has been achieved by irradiation of polymethacrylates with coumarin moieties in its side chains with linearly polarized light.² The direction of LC alignment is parallel to the electric vector of the light. We have so

(24) (a) Ramasubbu, N.; Granaguru, K.; Venkatesan, K.; Ramamurthy, V. *Can. J. Chem.* **1982**, *60*, 2159. (b) Granaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1985**, *50*, 13.

(25) (a) Chen, Y.; Wu, J. D. *J. Polym. Sci. A* **1994**, *32*, 1867. (b) Chen, Y.; Chou, C. F. *J. Polym. Sci. A* **1995**, *33*, 2705. (c) Chen, Y.; Hong, R. T. *J. Polym. Sci. A* **1997**, *35*, 2999.

far observed that the orientational direction of LC molecules caused by linearly polarized light irradiation of polymers with photoreactive side chains including azobenzenes,^{4–8} cinnamates,¹³ and benzylidenephthalimides¹⁴ is perpendicular to the electric vector of actinic polarized light. In this respect, it is of great significance to obtain further information about the relationship between the direction of LC photoalignment and the nature of coumarin polymers since the Schadt's paper did not specify the molecular structure of their polymers.

When azobenzenes are employed as photoreactive molecules (command molecules), the photocontrol of azimuthal LC alignment can be performed either before or after the fabrication of LC cells, though it has been commonly observed that more than 1 order of magnitude of greater exposure energies are required when the photoirradiation leading to LC photoalignment is carried out after the assembly of LC cells. It followed that, at first, a hybrid cell filled with a nematic LC, NPC-02, was assembled using a substrate plate spin cast with a coumarin polymer and a plate treated with lecithin for homeotropic alignment, followed by subsequent irradiation with polarized 313 nm light. It was found that no homogeneous alignment is generated at room temperature even after prolonged irradiation of cells modified with thin films of every coumarin polymer. Taking into account our previous observation that the LC photoalignment is enhanced considerably by heating LC cells at temperatures above the transition temperature between nematic and isotropic phases (T_{NI}),²⁶ polarized light irradiation was made under the heating of a cell at 40 °C above T_{NI} . Homogeneous alignment was generated at exposure energies of more than 5 J cm⁻² when a pC2 film was employed, whereas no alignment photocontrol was attained for a cell, the surface of which was spin cast with a pC0 film, even though exposure doses were more than 20 J cm⁻². It is very likely that the photodimerization is markedly retarded here by the presence of LC molecules that may penetrate into a polymer film, leading to the suppression of the bimolecular photoreaction.

Subsequently, the photocontrollability of LC alignment by coumarin polymers was determined by UV irradiation with linearly polarized light before cell assembly. A thin film of a coumarin polymer (pC0, pC2, or pC6) on a substrate plate was exposed to polarized 313 nm light, followed by the fabrication of LC hybrid cells using the plate and a plate treated with lecithin. Photoinduced azimuthal alignment was evaluated by measuring transmitted light intensity of a polarized He–Ne laser beam as a probe light passed through a cell as a function of the rotational angle of the cell. As shown in Figure 5, the azimuthal orientation of LC layers was generated, even though exposure doses of polarized 313 nm light were amazingly low. Exposure doses of about 50 mJ cm⁻² were required for the generation of homogeneous alignment by a pC0 film, whereas a pC2 film and a pC6 film brought about homogeneous alignment at exposure doses of 5 mJ cm⁻². This behavior is quite similar to that of polymethacrylates with cinnamate side chains.¹³ Though the reaction

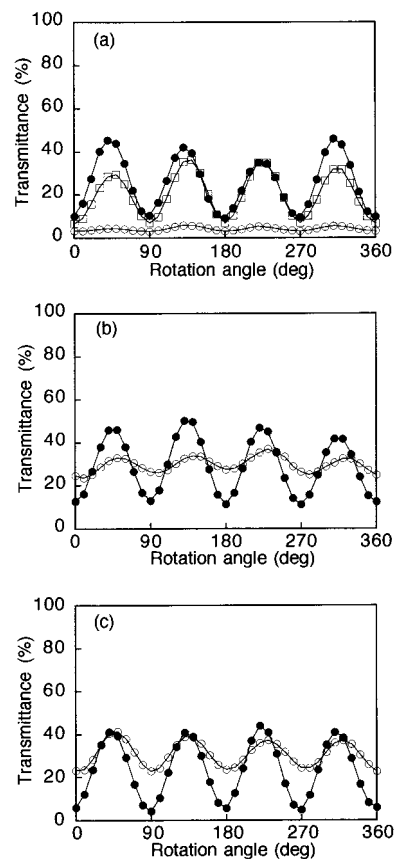


Figure 5. The transmitted intensity of a linearly polarized He–Ne laser beam passed through an LC cell fabricated with films of (a) pC0, (b) pC2, and (c) pC6, respectively, and an analyzer at a crossed position as a function of rotation angles of the LC cells. Exposure doses were 10 mJ cm⁻² (○), 50 mJ cm⁻² (●), and 100 mJ cm⁻² (□) for pC0, respectively, and 5 mJ cm⁻² (○) and 10 mJ cm⁻² (●) for pC2 and pC6.

rate of pC6 is much faster than that of pC2, the dichroism of pC6 is so small that the required energies are almost identical for both polymer films. It should be noted that essentially no observable dichroism was induced at such low exposure doses, as seen in Figure 4. The results indicate that homogeneous alignment is generated, even though photoinduced optical anisotropy of polymer films is negligibly small.

Reversion of Photoalignment Direction. The direction of LC alignment was determined by monitoring the dichroism of a dichroic dye (LCD 118) dissolved in NPC-02. Thin films of the coumarin polymers were exposed to linearly polarized 313 nm light and used for LC cell assembly. Representative results are shown in Figure 6. Both pC2 and pC6 films gave the alignment direction parallel to the electric vector of polarized 313 nm light at any exposure dose. Contrary to this situation, the orientational direction was reversed from parallel to perpendicular alignment, when a film of pC0 was used. Figure 7 shows the order parameter S as a function of exposure doses. S is defined as follows:

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}) \quad (1)$$

where A_{\parallel} and A_{\perp} are absorbances of the dye monitored by polarized light with the electric vector parallel to and perpendicular to the electric vector of the 313 nm light. It was confirmed that the photoalignment direction is

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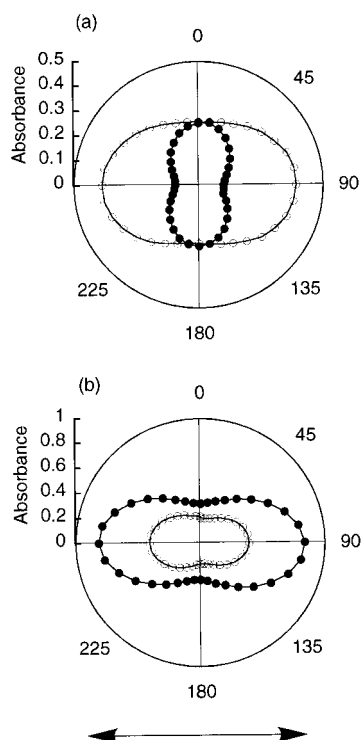


Figure 6. Circular diagrams of absorbances of the dichroic dye (LCD 118) dissolved in NPC-02 (1 wt %) in an LC cell fabricated by using films of (a) pC0 and (b) pC2 after irradiation with linearly polarized 313 nm light at exposure doses of 1 J cm^{-2} (○) and 10 J cm^{-2} (●). The arrow indicates the electric vector of the 313 nm light.

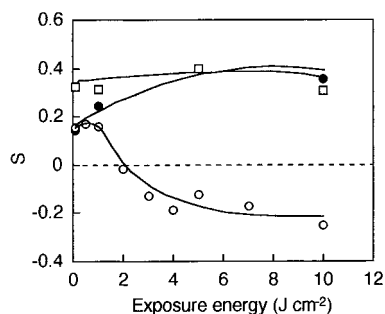


Figure 7. Changes of order parameter (S) of the dichroic dye dissolved in NPC-02 upon irradiation of films of pC0 (○), pC2 (●), and pC6 (□) with linearly polarized 313 nm light as a function of exposure doses.

parallel for pC2 and pC6 and not altered during linearly polarized light irradiation. In the case of pC0, the director of LC was parallel to the electric vector of the light when exposure doses were less than about 2 J cm^{-2} . Subsequently, the homogeneous alignment disappeared. Further photoirradiation resulted in the reversion of the photoalignment to give perpendicular orientation.

The reversion of the LC director during linearly polarized light irradiation has been reported for polymers with cinnamate side chains. Kawatsuki et al. used thin films of liquid-crystalline polymethacrylates with cinnamates side chains as command layers and described that the director of an LC varies from parallel to perpendicular orientation upon linearly polarized light irradiation.²⁷ They demonstrated furthermore that their polymers display the director reversion by anneal-

ing at temperatures above T_{NI} while no reversion is observed without the annealing. On the basis of these results, they suggested that two kinds of moieties play a role in determining the photoalignment direction: mesogenic biphenyl units leading to the parallel orientation and photodimerized products derived from cinnamates for the perpendicular alignment. On the other hand, Reznikov et al. concluded that parallel alignment results from photoproducts of cinnamates attached to polymer chains while perpendicular alignment is determined by E/Z -photoisomerization of cinnamates.²⁸ In relation to this, we observed recently that the orientational direction of LC photoalignment is critically influenced by a spacer length when diphenylacetylene (DPA) is attached to polymethacrylate main chains, though no orientational reversion was generated during linearly polarized light irradiation.¹⁶ Note here that DPA is photodimerizable, but not E/Z -photoisomerizable, just in the case of coumarin. Perpendicular alignment was obtained when DPA units are attached to polymethacrylate main chains without spacers, whereas the introduction of a tetramethylene spacer between the backbone polymer and DPA resulted in parallel alignment. We assumed that the perpendicular alignment originates from remaining DPA moieties while the parallel alignment is determined by photoproduct(s).

Concerning the photoalignment mechanism, Schadt et al. suggested three possibilities: the LC alignment caused by their coumarin polymer(s) may be owing to anisotropic van der Waals interactions of the rigid cores of the anisotropically cross-linked photoproducts, anisotropic steric interactions with their partially aligned hydrocarbon polymer chains, or anisotropically depleted prepolymer molecules.² The second possibility can be excluded for pC6 films since the long hexamethylene spacer decouples the interaction between the coumarin and a polymer main chain. It follows that it is very likely that the parallel alignment results from axis-selectively dimerized photoproduct(s), taking notice of the observation that homogeneous alignment emerges even at very low exposure doses, as stated above.

Concerning the mechanism of the alignment reversion induced by pC0 films, the effect of annealing was studied by preparing three types of films: an as-cast film, films annealed at 100°C for 1 h, and films at 250°C for 4 h, respectively. Every film generated the parallel alignment of LC by irradiation with polarized 313 nm light at a 1 J cm^{-2} exposure dose and displayed the alignment reversion into perpendicular orientation upon the polarized irradiation at an exposure dose of 7 J cm^{-2} . This observation eliminates the possibility that the reversion is not related to the conformations of the polymer before photoirradiation.

The reversion behavior of LC photoalignment induced by pC0 films was influenced by the nature of LCs including 4-pentyl-4'-cyanobiphenyl (5CB), EXP-CIL, DON-103, and N -(4-methoxybenzylidene)-4-butylaniline (MBBA) (Figure 1). The optical and transition characteristics are summarized in Table 3. 5CB showed homogeneous alignment on a pC0 film after polarized

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(28) (a) Reznikov, Y. *Proc. Rad. Tech. Asia '97* **1997**, 104. (b) Private communication.

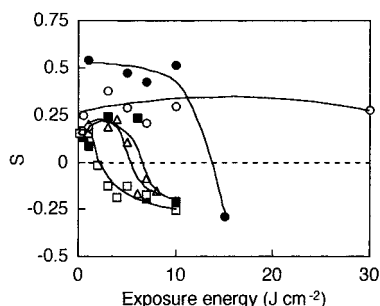


Figure 8. Changes of order parameter (S) of the dichroic dye dissolved in NPC-02 (\square), EXP-CIL (Δ), MBBA (\square), DON-103 (\bullet) and 5CB (\circ) upon irradiation of films of pC0 with linearly polarized 313 nm light as a function of exposure doses.

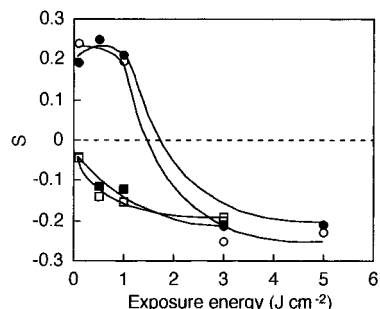


Figure 9. Changes of the order parameter (S) of the dichroic dye dissolved in NPC-02 upon irradiation of films of pC0 with linearly polarized 313 nm light as a function of exposure doses after nonpolarized light irradiation of exposure doses of 0 mJ cm^{-2} (\bullet), 100 mJ cm^{-2} (\circ), 500 mJ cm^{-2} (\square), and 1000 mJ cm^{-2} (\blacksquare).

Table 3. Dielectric Constants of Liquid Crystals Used in This Study

LC	T_{NI} ($^{\circ}\text{C}$)	ϵ_{\parallel}	ϵ_{\perp}	$\Delta\epsilon$
NPC-02	35.0	2.6	2.7	-0.1
EXP-CIL	31.8	3.2	3.1	0.1
MBBA	47	4.7	5.2	-0.5
DON-103	73	3.3	4.7	-1.4
5CB	35	17.9	6.9	11.0

light irradiation of a 50 mJ cm^{-2} dose and displayed no alignment reversion even though exposure energies got to 30 J cm^{-2} . In contrast to this, the director of DON-103, EXP-CIL, and MBBA was switched from parallel to perpendicular orientation upon prolonged polarized light irradiation, while exposure doses required for the alignment reversion were dependent on the nature of LCs (Figure 8). Note that the dielectricity of EXP-CIL is positive while that of MBBA is negative. Both LCs displayed behavior similar to the alignment reversion. Roughly speaking, the higher the dielectric constant of LC, the larger the critical energies for the photoalignment reversion, being irrespective of the dielectric anisotropy of LCs. From these results, it seems to be that the reversion of photoalignment is brought about for LCs with low dielectric constants (Table 3).

To obtain further insight into the photoalignment reversion of the LC, NPC-02, induced by pC0 films, irradiation with *nonpolarized* 313 nm light of various exposure doses was performed before *linearly polarized light* irradiation, leading to the generation of homogeneous alignment. The results are shown in Figure 9. Very interestingly, it was found that no reversion of the photoalignment occurs after nonpolarized light irradiation of critical exposure doses for the first photocuring.

The reversion induced by the linearly polarized light was observed when exposure doses of nonpolarized light are 100 mJ cm^{-2} or less. On the contrary, linearly polarized light irradiation of a pC0 film resulted in only perpendicular alignment when exposure doses of the nonpolarized light were 500 mJ cm^{-2} or more. This observation suggests that the parallel photoalignment is determined by the photochemistry of coumarin residues at the early stage of linearly polarized light irradiation. It is very likely that coumarin moieties orient in a random fashion in a polymer film so that the rate and the product distribution of the photodimerization are crucially dependent on exposure doses. At the early stage of nonpolarized photoirradiation of a pC0 film, the photodimerization takes place predominantly for couples of coumarin residues which are arranged in such a way that the C=C bonds of the moieties are close to each other. In the case of linearly polarized 313 nm light irradiation, coumarin chromophores with a transition moment parallel to the electric vector of the light dimerize favorably to give cycloadduct(s). Though no information is available at the present concerning the geometry of the cycloadduct(s), it is safe to claim at least that the "averaged" plane of the benzene ring systems of the cycloadducts is in line with the coumarin precursors. This means that the parallel photoalignment of LC is triggered by the orientational direction of photocycloadducts. On the other hand, when a pC0 film is subjected to nonpolarized light irradiation in advance, the coumarin residues having the commanding ability to generate the parallel photoalignment dimerize isotropically so that no parallel alignment emerges any longer. Note here that the critical exposure energy of 500 mJ cm^{-2} brings about the extent of the photodimerization of far less than 10%, as seen in Figure 2.

The reversion of the photoalignment can be consequently interpreted as follows. At the early stage of linearly polarized light irradiation, the axis-selective photodimerization leads to the formation of cyclobutane adduct(s) which determine the parallel orientation of LC molecules since the orientational direction of the benzenoid rings of the cyclobutane(s) should be in line with that of the planar coumarin moiety as a result of axis-selective photodimerization. As the polarized photochemistry proceeds, the level of remaining coumarin units with a molecular axis perpendicular to the electric vector of the light exceeds that parallel to the electric vector. It is worthy to mention here that the molecular orientation of both the cycloadducts and remaining coumarin rings is efficiently fixed, owing to the rigid molecular structure of pC0 in which the chromophores are attached directly to polymer main chains. It follows that the photoalignment reversion may be reasonably interpreted in terms of the difference in the strength of molecular interactions of two kinds of residues, the coumarins and photocycloadduct(s), with LC molecules. It can be assumed that the molecular interaction of the coumarin with LC is stronger than that of the cycloadduct(s), taking into account the difference in their molecular shapes; the coumarin bears high planarity that may give birth to effective interactions between the chromophore with LC molecules. This assumption allows us to claim that the overall molecular interactions of the remaining coumarin units with LC molecules

wins over those of cyclobutane adduct(s) at critical exposure doses to result in the reversion of alignment from the parallel to perpendicular orientation. Note that the photoinduced optical anisotropy of a pC0 film increases at exposure doses of more than a few J cm^{-1} , as seen in Figure 4a. The fact that the reversion does not take place for pC2 and pC6 may be ascribable to the effect of the spacers. Being different from pC0, coumarin units of these polymers may suffer from the thermal relaxation of the orientation because of the presence of the spacers to reduce the level of photoinduced optical anisotropy. In fact, as stated above, DR values of the coumarin polymers after prolonged polarized photoirradiation are in the following order: pC0 \cong pC2 > pC6.

Conclusion

It was confirmed that coumarins attached to polymethacrylate main chains undergo photodimerization in films without the occurrence of any side reaction. The disappearance of the chromophores was influenced by the length of a spacer. The longer the spacer between the chromophore and a polymer main chain, the faster the rate of photodimerization. When 313 nm light was linearly polarized, the disappearance of the coumarin chromophores occurred axis-selectively so that A_{\perp} of the remaining coumarins is larger than A_{\parallel} , leading to the emergence of dichroism of polymer films. Dichroic ratios upon prolonged polarized light irradiation were also dependent on the spacer length and in the following order: pC0 \cong pC2 > pC6. This result arises from the level of molecular mobility of the coumarin residues; the longer spacer reduces the dichroic ratio because the interactions between the chromophores and backbone

polymers are decoupled by the efficient length of the spacer to lead to the enhanced orientational relaxation of remaining coumarins.

Homogeneous alignment by irradiation of films of the coumarin polymers with linearly polarized 313 nm light was not generated when the irradiation was carried out after the cell assembly, unless the prolonged irradiation of a pC2 film was done at temperatures above the T_{NI} of LC. No photoalignment was observed for a pC0 film under the same conditions, indicating that axis-selective photodimerization is suppressed by the presence of LC molecules at the uppermost surface of these films. Contrary to this, homogeneous alignment was induced when the cell assembly was achieved after the irradiation of films of the coumarin polymers with the linearly polarized light. It was found that the direction of LC alignment is influenced by the spacer length. Whereas the photoinduced LC director was parallel to the electric vector of the polarized light for films of pC2 and pC6, respectively, quite different behavior was observed for a film of pC0. The orientational direction of LC alignment was parallel to the electric vector of the light at the early stage of photoirradiation, followed by the deterioration of the photoalignment in the middle of photoirradiation and finally by the reversion to the perpendicular orientation upon prolonged irradiation. On the basis of the photochemical behavior of the films of the coumarin polymers, it was concluded that parallel photoalignment is determined by cyclobutane adduct(s) formed by the axis-selective photodimerization. On the other hand, the perpendicular orientation arises from the interaction between the remaining coumarin residues and LC molecules.

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