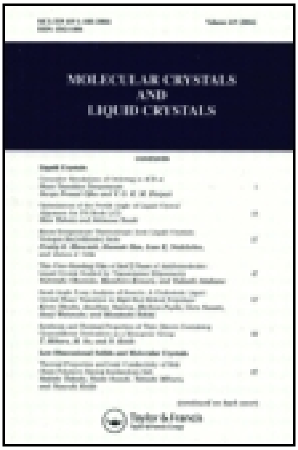

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Photoalignment Control of Liquid Crystals on Photo-Cross-Linkable Methacrylate Copolymer Films Comprising 4-(4′-Methoxycinnamoyloxy)Biphenyl Side-Group

Nobuhiro Kawatsuki [a] , Tetsuro Kawakami [a] & Tohei Yamamoto [a]

[a] Department of Applied Chemistry, Himeji Institute of Technology, 2167, Shosha Himeji, 671-2201, Japan

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Photoalignment Control of Liquid Crystals on Photo-Cross-Linkable Methacrylate Copolymer Films Comprising 4-(4′-Methoxycinnamoyloxy)Biphenyl Side-Group

NOBUHIRO KAWATSUKI*, TETSURO KAWAKAMI and
TOHEI YAMAMOTO

Department of Applied Chemistry, Himeji Institute of Technology,
2167 Shosha Himeji, 671-2201 Japan

We describe a photoalignment control of liquid crystal (LC) on photo-cross-linkable polymer films using a slantwise nonpolarized ultraviolet (NP-UV) light irradiation. A polymer having a photoreactive mesogenic 6-[4-(4′-methoxycinnamoyloxy)biphenyloxy]hexyl side-group and its copolymer with methacrylate derivatives comprising photoinactive side-groups were synthesized and used for the LC alignment layer. The LC aligned homogeneously or homeotropically with tilt angles, and the alignment behavior was dependent on the type of the (co)polymers and LCs.

Keywords: photoalignment; tilt angle; photo-cross-linking; nematic liquid crystal; LCD

INTRODUCTION

Photoalignment of liquid crystal (LC) has become very attractive because of its potential advantage compared to a mechanical rubbing process for the fabrication of LC display devices. [1] Several kinds of photoreactive materials for the photoalignment layer have been investigated, including photo-cross-linkable polymers, [1-5] photo-

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* Corresponding author, e-mail: kawatuki@chem.eng.himeji-tech.ac.jp

isomerizable polymers [6-8] and photodegradable polymers. [9-11] A linearly polarized (LP) light irradiation induces an optical anisotropy of the film based on an angular-selective photoreaction, and LC can align on these polymer films.

Recently, a new technique for the LC photoalignment has been proposed by the use of a nonpolarized (NP) light exposure. [12,13] A slantwise NP-light irradiation to the azobenzene-containing polymer film aligns the LC on the resultant film with a direction parallel to the incident light propagation. This technique is based on a direction-selective *trans-cis-trans* photoisomerization of the azobenzene group. [12] Kobayashi et al reported the direction-selective photoreaction of the polyimide derivatives for the LC alignment layer. [14,15] We have also studied the direction-selective photo-cross-linking of a methacrylate polymer film comprising a photo-cross-linkable cinnamoyloxybiphenyl side group or a cinnamoyloxyethoxybiphenyl side-group by the use of slantwise NP-ultraviolet (UV) light exposure. [16,17] Since the LC aligned along the nonphotoreacted side-group, a control of the tilt angle of the homogeneous LC alignment could be feasible by adjusting the irradiation angle. [16] However, the photoreactivity of the mesogenic side-group was low because the absorption band of the biphenyl group was close to that of the cinnamoyl group.

In this paper, to improve the photoreactivity of the side-group and a controllability of the tilt angle of the LC, we synthesized a methacrylate polymer comprising a photoreactive mesogenic 6-[4-(4'-methoxycinnamoyloxy)biphenyloxy]hexyl side-group and its copolymer with methacrylate derivatives comprising photoinactive side-group. The slantwise NP-UV photoreaction was performed on the synthesized copolymer films, and the effects of the type of the (co)polymer and the LC on the alignment behavior were studied.

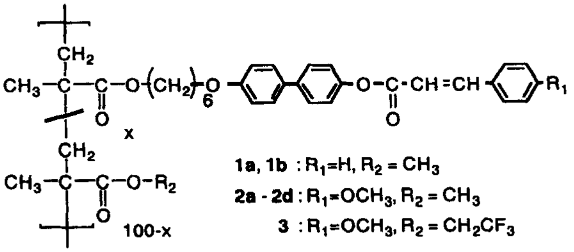

FIGURE 1 Chemical structure of the photo-cross-linkable copolymer

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and 2, 2, 2-trifluoroethyl methacrylate were used after distillation to remove an inhibitor. *6-[4-(4'-Methoxycinnamoyloxy)biphenyloxy]hexyl methacrylate* was synthesized from 4-methoxycinnamoyl chloride and 4-hydroxy-4'-(6-methacryloyloxyhexyl)biphenyl, and its chemical structure was confirmed by ^{1}H-nmr and FT-IR. All (co)polymers were synthesized by a radical solution polymerization in THF.

Photoreaction and LC Alignment

The polymer was spin-coated on a quartz substrate from methylene chloride solution, resulting in a 50 nm-thick film. The film was irradiated obliquely by a NP-UV light with an intensity of 150 mW/cm^2 at 313 nm. After irradiation, the induced optical anisotropy of the film was evaluated by a polarization UV absorption spectrum. The degree of the photo-cross-linking reaction was measured by FT-IR spectroscopy by using a cinnamoyl absorption at 1639 cm^{-1}. After the NP-UV irradiation, we fabricated an anti-parallel LC cell using two substrates. The cell gap was 12.5 μm and the LC was injected at its clearing point. The nematic LC of E7, ZLI-2061, ZLI-4801-100, ZLI-4318, ZLI-4792 (Merck Japan) and MBBA were used for the alignment behavior. The homogeneous LC alignment direction was determined by a polarization UV absorption spectrum and the pretilt angle of the LC was measured by a crystal-rotation method.

RESULTS AND DISCUSSION

Thermal and Spectroscopic Properties, and Photoreaction of the Synthesized Polymer Films

Composition, thermal properties and spectroscopic data of synthesized copolymers are summarized in Table I. The wavelength of the maximum absorbance of the film state was shorter than that in solution if the polymer exhibited liquid crystalline phase. This blue shift is a consequence of head-to-head aggregation of the mesogenic group in the solid state. [18] However, the spectrum of **2d** film was similar to that in solution since it did not exhibit the LC behavior.

TABLE I Composition, thermal properties and spectroscopic data of copolymers

	Composition $^{a)}$			Transitions °C $^{b)}$				λ_{max} $^{c)}$	
	R_1	R_2	x	Tg	Tm	Tsn	Ti	Solution	Film
1a	H	-	100	-	144	157	219	282	272
1b	H	CH_3	55	-	99	-	144	283	275
2a	OCH_3	-	100	-	106	-	>300	313	295
2b	OCH_3	CH_3	49	81	-	214	230	314	293
2c	OCH_3	CH_3	28	91	-		172	315	298
2d	OCH_3	CH_3	10	102	-		-	314	314
3	OCH_3	CH_2CF_3	51	-	98	-	233	314	287

a) Determined by 1H-nmr, b) Determined by DSC, Tg; glass transition, Tm; melting point, Tsn; smecti-nematic transition, Ti; clearing point. c) methylene chloride solution, thin film on quartz.

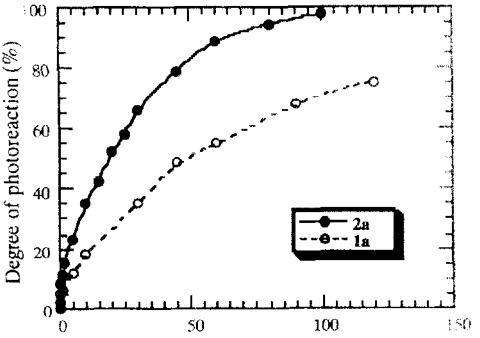

FIGURE 2 Degree of the photoreaction of the cinnamoyl group as a function of the irradiation time

After the UV irradiation, films became insoluble in ordinary solvents due to [2+2] photocycloaddition reaction of the cinnamoyl group. Figure 2 plots the degree of the photo-cross-linking of polymer films **1a** and **2a** as a function of the irradiation time. The rate of the photoreaction of the polymer with a methoxy-group (**2a**) was faster than that without it (**1a**). This is because of the effective absorption at 313 nm of the UV light source for **2** series compared to that of **1** series. Other copolymers showed the similar results.

Optical Anisotropy of NP-UV Irradiated Films

When the NP-UV light obliquely irradiated the film, a slantwise

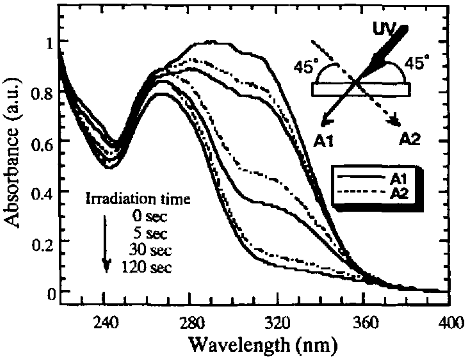

FIGURE 3 Absorption spectrum of **2b** film before and after slantwise NP-UV exposure. A1 and A2 mean the measurement light beam.

optical anisotropy of the film was induced by the direction-selective photo-cross-linking reaction. After the slantwise NP-UV light exposure, the absorption of the film was dependent on the direction of prove beam propagation as shown in Figure 3. It exhibits that the degree of the photo-cross-linking reaction of the mesogenic group with the direction parallel to the UV light propagation is smaller than that in the opposite direction. To confirm the inclination angle of the photoreacted plane, the absorbance of the irradiated film was measured with rotating the film. Figure 4 plots the absorbance of polymer films at 278 nm as a function of angle of *p*- and *s*-polarized monitoring lights. The films were irradiated with nonpolarized UV light for 30 sec

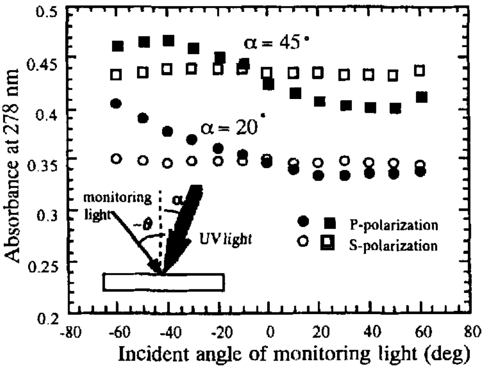

FIGURE 4 Absorbance of the obliquely NP-UV irradiated **2b** film as a function of the angle of the monitoring light beam.

at incident angles of 20° and 45°. The absorbance of *p*-polarized monitoring beam showed a minimum value when the angle of the monitoring light was consistent with the incident angle of the UV light, while the absorbance of *s*-polarized beam exhibited no maximum nor minimum. This means that the mesogenic groups in the perpendicular plane against the direction of the NP-UV light propagation preferentially photo-cross-linked. In other words, the mesogenic group with the direction parallel to the light propagation uniaxially remained.

LC Alignment Behavior

To evaluate the LC alignment, an anti-parallel nematic LC cell was fabricated by using two NP-UV irradiated substrates. We had reported that the LC aligned with tilt angles on the polymer **1a** film irradiated by a slantwise NP-UV light. [16] The polymers comprising the 4-(4'-methoxycinnamoyloxy)biphenyl side-group (**2** and **3** series) could also align the LC homogeneously. Since the photoreaction-efficiency of these copolymers was superior to that of **1** series as described in the above section, the less exposure doses were required for the homogeneous LC alignment on the copolymers **2a**, **2b**, **2c** and **3** films compared with the **1a** and **1b** films. However, in the case of the copolymer **2d**, the uniformity of the LC alignment was poor. This is due to the small interaction between the film and the LC because the amount of the mesogenic group in the copolymer **2d** was low. In addition, the LC did not align on polymer films before irradiation.

Figure 5 plots the tilt angle of the LC (E7) as a function of the

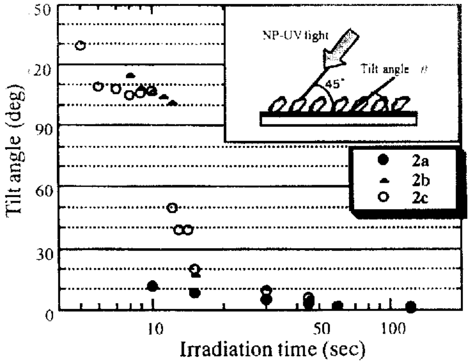

FIGURE 5 Tilt angle of the nematic LC (E7) on various polymer-films as a function of the irradiation time.

exposure time. The irradiation angle was 45°. In the case of the homopolymer **2a** film, the homogeneous LC alignment with tilt angles was obtained, and the inclined direction of the LC was parallel to the direction of the incident NP-UV light propagation because the direction of non photo-cross-linked mesogenic group determines the LC alignment direction. [16] For the copolymers **2b** and **2c**, on the other hand, the LC aligned homeotropically with an inclination at the opposite side of the NP-UV light propagation (θ>90°) in the beginning of the photoreaction. The alignment direction changed to be homogeneous with a tilt angle (θ<90°) with increasing the exposure doses. Figure 5 exhibits that the tilt angle of the LC alignment suddenly changed to be small when the irradiation time was 15 sec and more, and the tilt angle of the homogeneous LC alignment decreased with increasing the irradiation time for all cases. In addition, the tilt angle was larger for the copolymer containing larger composition of MMA comonomer. This will be a consequence of the lower surface energy and a steric interaction between the LC and the methyl side-group. [14] The LC alignment became disordered when the irradiation time was 180 sec and more, where the degree of the photoreaction was 95 % and more. Similar tilt angles were observed for copolymers **1** series if both the MMA composition and the degree of the photoreaction were similar to copolymer **2** series.

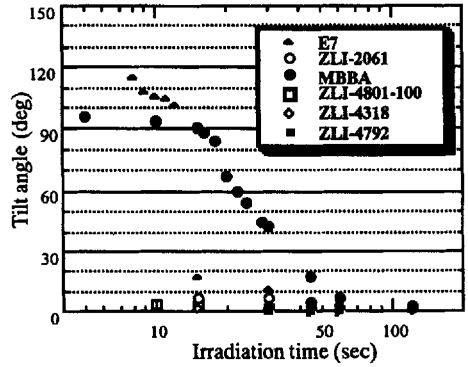

FIGURE 6 Tilt angle of the various nematic LCs on **2b** film as a function of the irradiation time.

Furthermore, the tilt angle was dependent on the type of nematic LC molecules as shown in Figure 6. The inclined homeotropic LC alignment was not obtained for ZLI-2061, ZLI-4801-100, ZLI-4318 and ZLI-4792 on the **2b** film, and their tilt angle was smaller than that of E7. The inclined homeotropic alignment was achieved for E7 and MBBA. The tilt angle of the homogeneous alignment of ZLI-4801-100 was around 1~5°, and that of ZLI-4792 and ZLI-4318 was less than 2°. It was interesting that the inclined direction of MBBA changed from $\theta > 90°$ to $\theta < 90°$ with increasing the exposure doses. The change of the direction of the inclined homeotropic LC alignment was also observed on a photoreactive polyimide film. [14] In addition, the LC alignment direction was not dependent on the dielectric anisotropy $\Delta\varepsilon$ of the LC (positive $\Delta\varepsilon$ for E7, ZLI-2061, ZLI-4801-100 and ZLI-4792, and negative $\Delta\varepsilon$ for MBBA and ZLI-4318). This indicates that the chemical structure of the LC may play an important role for the alignment behavior.

Finally, we investigated the LC alignment behavior on the copolymer containing fluorine atom (**3**). Figure 7 plots the tilt angle of various LCs on the **3** film as a function of the exposure time. For all LCs, the tilt angle was slightly larger than that on the **2b** film. The inclined homeotropic LC alignment of E7 was obtained although the LC tilted with the same direction of the incident UV light propagation. The larger tilt angle on the **3** film will be caused by lower surface energy due to the fluorine atom.

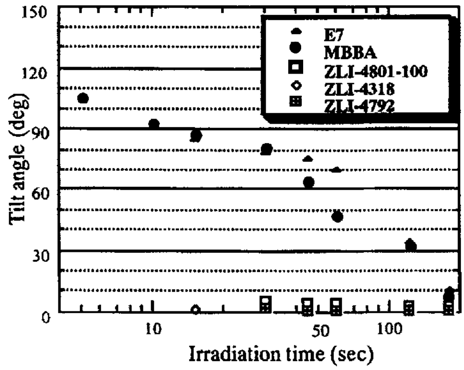

FIGURE 7 Tilt angle of the various nematic LCs on **3** film as a function of the irradiation time.

SUMMARY

The photoreactivity of the photo-cross-linkable methacrylate copolymer for the LC alignment layer was improved by introducing the *p*-methoxycinnamoyl group at the end of the side-group. The uniform LC alignment on the copolymer films could be achieved after the irradiation of the slantwise NP-UV light exposure. The LC aligned homogeneously with inclination, and the inclined direction was dependent on the type of the copolymers and the LC. The inclined homeotropic alignment was achieved for E7 and MBBA. The copolymerization of methacrylate with an alkyl group or a fluorine-containing group increased the tilt angle of the LC. The exposure doses also control the tilt angle of the LC.

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