

High Out-of-Plane Alignment of Liquid Crystalline Methacrylate Copolymer Bearing Photoreactive 4-Styrylpyridine Moiety

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Abstract: This paper describes the out-of-plane order of a liquid crystalline (LC) methacrylate copolymer (**3**) comprised of a methacrylate (**1**) with a 4-styrylpyridine moiety as the photo-cyclodimerizable group and a benzoate moiety as the mesogenic group in the side chain, and another methacrylate (**2**) with a 4-(4-methoxyphenyl)benzoate moiety as the mesogenic group. The composition of **1** and **2** units in **3** was estimated to have a molar ratio of 54.2:45.8 by ^1H NMR spectroscopy. The X-ray diffraction study revealed that the copolymer forms a partial bilayer smectic structure. The copolymer gave rise to a high out-of-plane order parameter of about 0.74 in a wide LC temperature range of 110~160 °C after linearly polarized, UV light irradiation and subsequent annealing. Moreover, the external reflection IR analysis indicated that excess UV-light irradiation makes the out-of-plane LC structure of the copolymer appear in a higher and wider temperature range.

Keywords: out-of-plane alignment, liquid crystal, methacrylate copolymer, 4-styrylpyridine, UV irradiation, annealing.

Introduction

The molecular alignment of liquid-crystalline (LC) polymers with photosensitive groups is today of great interest for liquid crystal display devices because the LC polymers can be aligned by anisotropic photoreactions and thermal treatment.¹⁻⁷ In particular, photoisomerizable azo groups- or photocyclodimerizable cinnamoyl groups-containing LC polymers were mainly studied on photoalignments or thermal alignments. The research interests have been focused on not only the structural effects such as flexible spacer length,⁸⁻¹¹ copolymer composition,^{3,7,10,12} and comonomer units,^{8,11,13} on the orientational order and directions, *i.e.* in plane or out-of-plane, but also the processing effects such as UV light exposure intensity,^{9,12,14} LC temperature,^{10,12,14,15} heating rate,⁹ etc. These factors contributed to the changes of the orientational order and directions.

Photosensitive LC copolymers comprising comonomer units with mesogenic groups are important for the alignment order and directions as described above. Previously, we have synthesized LC polymethacrylates with 2- or 4-styrylpyridine moiety as a photocyclodimerizable group and benzoate unit as a mesogenic group in the side chain. The 4-styrylpyridine unit-containing polymer showed high homeotropic alignment in an out-of-plane direction, whereas the 2-styrylpyridine unit-containing polymer gave an in-plane alignment. The role of 4-styrylpyridine structure for out-

of-plane alignment of the polymer was discussed in detail.¹⁶

Considering alignment behaviors with these structural factors, other photosensitive LC polymers with high out-of-plane alignment ability could be LC copolymers of 4-styrylpyridine group-containing monomers and mesogenic group-containing monomers. The copolymers are more convenient for storage compared to the LC homopolymer with 4-styrylpyridine moiety described above because of less amount of the photosensitive group in the former polymer.

In this work, for exploring structural characteristics of high out-of-plane alignment LC copolymer with importance of the isomer, a LC copolymer from a methacrylate with 4-styrylpyridine unit as the photosensitive group and a methacrylate with 4-(4-methoxyphenyl)benzoate unit as a mesogenic group was prepared and its properties including alignment behaviors were studied.

Experimental

Materials. A monomer with a 4-styrylpyridine unit, 6-[4-{2-(4-pyridyl)ethenyl}phenoxy carbonyl]phenoxy]hexylmethacrylate (**1**) was synthesized from 4-picoline, 4-hydroxybenzaldehyde, 4-hydroxy benzoic acid, 6-bromo-1-hexanol, and methacrylic acid in the same method as reported previously.¹⁶ Another comonomer with a mesogenic 4-methoxyphenyl benzoate unit, 6-[4-(4-methoxyphenyl)oxycarbonyl]phenoxy]hexylmethacrylate (**2**) was prepared from 4-methoxyphenol, 6-bromo-1-hexanol, 4-hydroxybenzoic acid, and

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methacrylic acid according to the literature.^{17,18} The 2,2'-azobisisobutyronitrile (Junsei, 98%) (AIBN) was recrystallized from methanol and used as an initiator for the polymerization. As a solvent for the polymerization, *N*-methyl-2-pyrrolidone (Junsei, 99%) (NMP) was distilled under reduced pressure in the presence of phosphorus peroxide. All other reagents were used as received.

Polymerization. An AIBN solution (10 mg, 61 μ mol) was added to a mixture solution of **1** (1 g, 2.1 mmol) and **2** (0.87 g, 2.1 mmol) in NMP (6 mL) and then sealed under vacuum. After the polymerization for 24 h at 57.5 °C, the mixture was poured into a large excess of methanol to precipitate a white solid product. The product was filtered with a sintered glass (G3) and dried under reduced pressure to give a polymer **3** in a yield of 66%.

Measurements. The number- and weight-average molecular weights (M_n and M_w , respectively) of the copolymer were measured in tetrahydrofuran (THF) with a Waters Alliance V2000 gel permeation chromatograph (GPC) using monodisperse polystyrenes as the standard polymers. The ¹H NMR spectrum of the copolymer was measured in CDCl₃ solution at ambient temperature using a Bruker Avance Digital 400 FT-NMR spectrometer. Its UV-visible spectra were measured using a Shimadzu Model 2401 spectrophotometer. Its differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted with a Dupont 2000 differential scanning calorimeter and a Dupont 2100 thermal gravimetric analyzer, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min. Polarizing optical microscopy (POM) investigation of the copolymer was performed with a Zeiss AX1 LAB POM instrument. Its X-ray measurement was carried out using a Rigaku RAD-RS with a copper anode and a nickel filter.

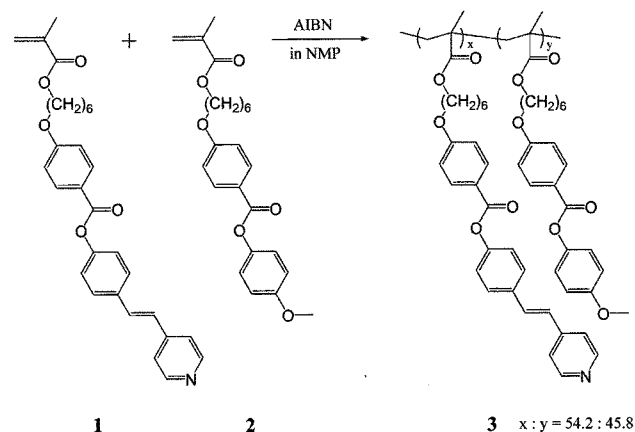
In order to examine the alignment of the copolymer, 2 wt% polymer solutions in chloroform were coated on quartz plates using a spin coater and dried at ambient temperature. The films were transparent. Their thickness was 3 μ m on average. Polarized UV spectra of the films irradiated by LPUV light from a high pressure mercury lamp were measured before and after annealing. Its out-of-plane alignment was estimated by out-of-plane order parameter [$sh=1-(A_{\text{annealed}}/A_{\text{irradiated}})$],¹² where $A_{\text{irradiated}}$ and A_{annealed} are the average values of A_{\parallel} and A_{\perp} from the LPUV light irradiated film and the annealed one after irradiation, respectively. These A_{\parallel} and A_{\perp} mean absorbances parallel and perpendicular to LPUV light irradiation.

For the external reflection FTIR analysis of the copolymer, its 2 wt% solution in chloroform was spin-coated on gold-coated silicon wafer (10 mm \times 10 mm). The film was exposed to LPUV light of 2.5 J/cm². The spectra were obtained with polarized radiation at an angle of the incidence of 82° at different temperatures using a Bomem DA8 FTIR spectrometer.

Results and Discussion

Scheme I shows the chemical structures of the two comonomers, **1** and **2**, and copolymer **3**. The radical copolymerization of **1** and **2** in the same molar ratio using AIBN as an initiator provided copolymer **3** in a high yield of 66%. The copolymer **3** was a white solid, which was soluble in THF, chloroform, dichloroethane, etc. Although both the comonomers **1** and **2** have bulky side groups, **3** showed relatively high weight-average molecular weights of 55,000 ($M_w/M_n=2.3$).

Figure 1 shows the ¹H NMR spectrum of **3**. The peak at 8.55 ppm is assigned to the pyridine hydrogens (*a*), and peaks at 3.95 and 3.8 ppm are assigned to the hydrogens *c+d* and *b*, respectively. The peaks at 6.9~8.1 ppm are attributed to the hydrogens of the benzene rings. The peaks at 0.9~1.9 ppm are due to the hydrogens of both the methylene groups in the main chain as well as in the side chains and the α -methyl group except the hydrogens *c+d*. The



Scheme I. Structures of monomers, **1** and **2**, and copolymer **3**.

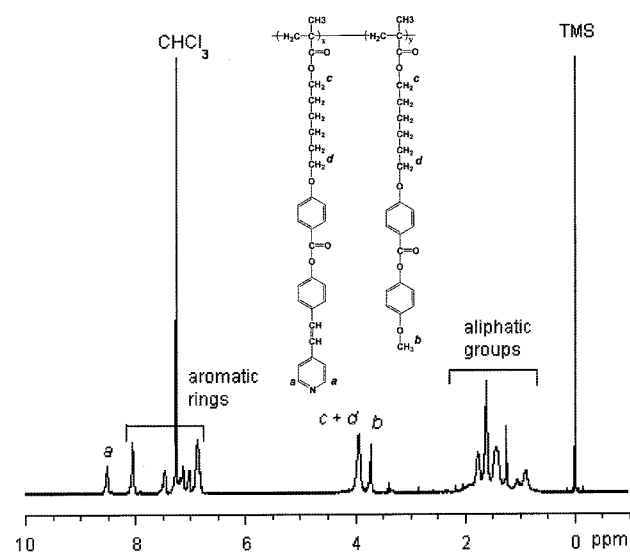


Figure 1. ¹H NMR spectrum of **3** in CDCl₃.

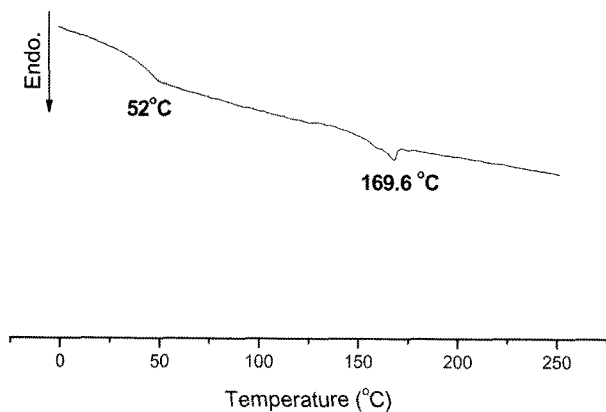


Figure 2. DSC thermogram of **3** under a nitrogen atmosphere at a heating rate of 10 °C/min.

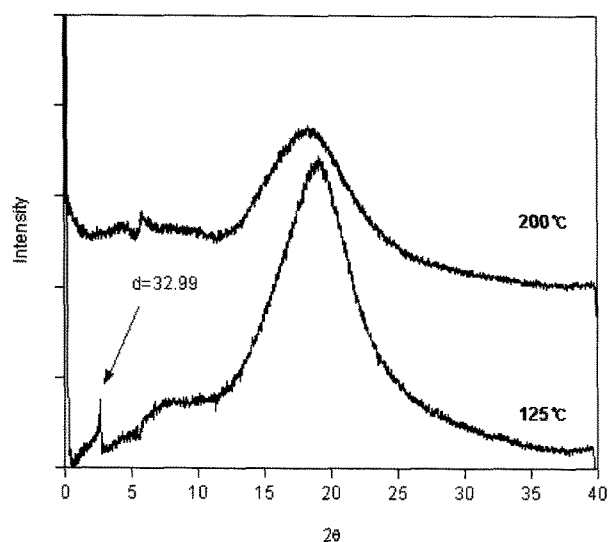


Figure 3. Temperature-dependent X-ray diffraction patterns of **3**.

composition of **1** and **2** units in **3** was estimated to be 54.2:45.8 in molar ratio from the area ratio of the peaks *a* and *b*.

Figure 2 shows the DSC thermogram of **3**. It gave two transition endothermic peaks at 52 and 169.6 °C. The TGA curve of **3** displayed 5% weight loss at 345 °C. These results mean that the bulky side chains of **1** and **2** units contribute to thermal stability.

Figure 3 shows the x-ray diffraction pattern of the copolymer. It gave a reflection peak with the layer period of 32.99 Å in a small angle region. The side chain of unit **1** in the copolymer is longer than that of unit **2**, and the length for that of the former unit was calculated to be 27.85 Å. Therefore, this result indicates that the copolymer forms a smectic structure with a partial bilayer spacing.¹⁶ In addition, the POM photograph of the copolymer revealed a characteristic birefringent texture at 165 °C.

Figure 4 displays the UV spectra of the copolymer film exposed to UV light with various exposure doses. The absor-

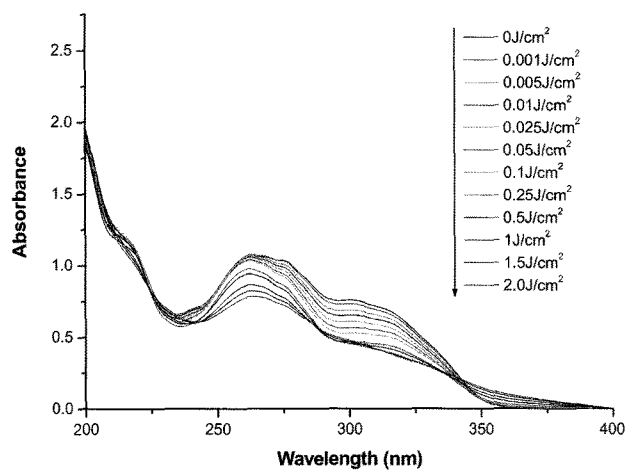


Figure 4. UV spectra of **3** in film with exposure doses.

bances of the film around both 300 and 260 nm decreased with an increase in the exposure dose. The decrease of the former band is attributed to the photocyclodimerization of the carbon-carbon double bond between the benzene and pyridine rings in the 4-styrylpyridine unit¹⁹⁻²¹ and that of the latter band is due to the Fries photorearrangement of the benzoate group in the units **1** and **2**.²² In addition, the slight increase in absorption of more than 350 nm with exposure doses is also probably due to the Fries reaction. This increase in absorption band may influence the decrease at 300 nm. Accordingly, the absorption decrease due to the photoreaction of 4-styrylpyridine moiety should be actually larger than those shown in Figure 4.

In order to investigate photo- and thermo-alignments of **3**, the film was treated with LPUV light irradiation at room temperature and subsequent annealing at the LC temperature of 160 °C. Figure 5 shows the change in polarized UV

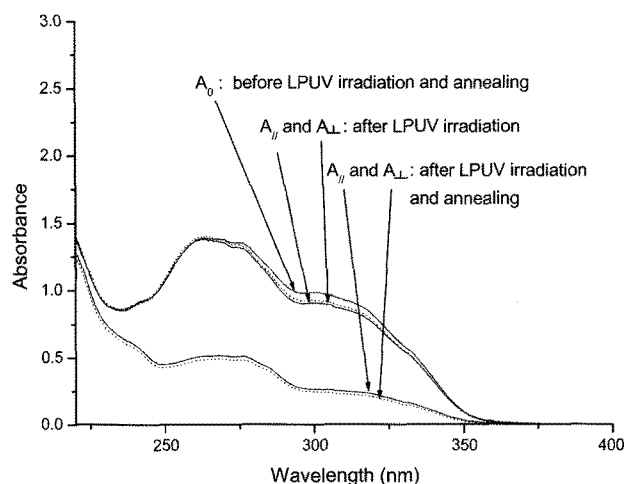


Figure 5. UV spectra of **3** in film annealed at 160 °C for 10 min after linearly polarized UV irradiation at 0.001 J/cm². A_{\parallel} (—) and A_{\perp} (---) are absorbances parallel and perpendicular to the LPUV light irradiation.

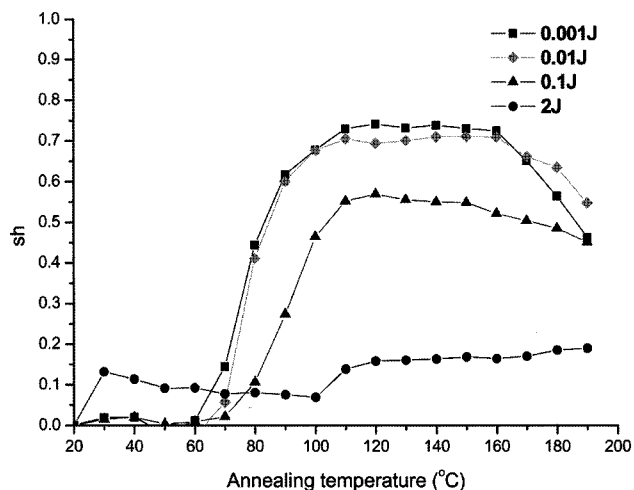


Figure 6. Out-of-plane order parameters (*sh*) at 300 nm of **3** in film annealed at different temperatures for 10 min after linearly polarized UV irradiation at various exposure doses.

absorption spectra of **3**. The absorbances at 300 and 260 nm after the LPUV light irradiation at 0.001 J/cm² decreased owing to the photoreactions of both the 4-styrylpyridine unit and the benzoate group. In particular, both the A_{\parallel} and A_{\perp} at the wavelengths after subsequent annealing at 160 °C for 10 min largely decreased, and the values of A_{\parallel}/A_{\perp} were near 1.0. This indicates that an amount of the unreacted 4-styrylpyridine groups in unit **1** together with the benzoate group in units **1** and **2** aligns to an out-of-plane direction at the LC temperature.^{11,14} The out-of-plane alignment might be due to a smectic structure A with a partial bilayer spacing.²³

Figure 6 shows the change of out-of-plane order parameters for the copolymer at 300 nm as functions of exposure doses and annealing temperatures. In the range between 0.001 and 2 J/cm² for all temperatures, the *sh* values were plus, which means that the unphotoreacted 4-styrylpyridine units align to an out-of-plane direction at the LC temperatures. In particular, at the exposure dose of 0.001 J/cm² in the LC temperature between 110 and 160 °C, the values reached approximately 0.74. This value was almost similar to that of a homopolymer from **1**.¹⁶ However, the solubility of this copolymer for organic solvents was better than that of the homopolymer.¹⁶ Moreover, the copolymer has less amount of the photoreactive group compared to the homopolymer. In these viewpoints, the former polymer is more convenient for applications than the latter polymer. This high value is presumably attributed to the dipole-dipole interactive cooperation of the phenyl benzoate moieties in units **1** and **2** of the copolymer. The decrease in absorption around 260 nm well supports this idea. On the other hand, the parameter significantly decreased with an increase in the exposure dose between 0.1 and 1 J/cm² in the LC temperature range of 110 and 160 °C. This may be a consequence of the excess photocrosslinked 4-styrylpyridine units in the **3**

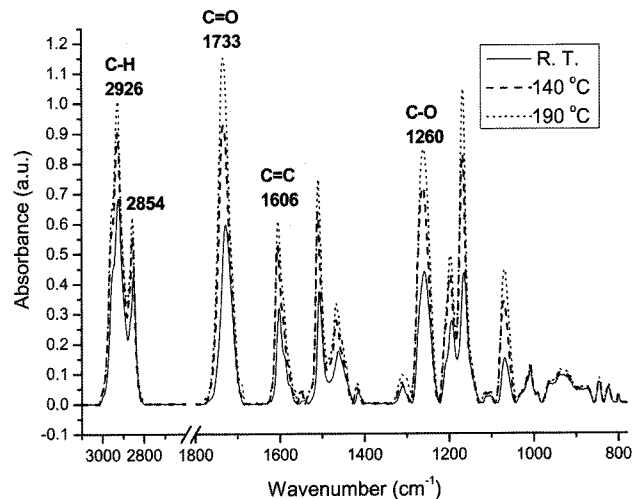


Figure 7. External reflection FTIR spectra of **3** in film with polarized radiation at the incidence angle 82° at different temperatures after UV irradiation of 2.5 J/cm².

film because they will not align the unreacted 4-styrylpyridine units to an out-of-plane direction. The decrease of *sh* values between 160 and 190 °C around the isotropic temperature became gradually smaller with an increase in the exposure dose from 0.001 to 0.1 J/cm². In the case of 2 J/cm², the *sh* values were small as compared to other cases, but increased exclusively around the isotropic temperature.

To further confirm this phenomenon, the temperature-variable polarized IR absorption spectra of the copolymer was measured in external reflection mode. Figure 7 shows the changes in IR spectra of the copolymer with annealing temperatures. The main peaks are assigned to stretching vibrations of the side chains in units **1** and **2**. That is, the peaks at 2926, 1733, 1606, and 1260 cm⁻¹ correspond to C-H stretching, C=O stretching, C=C stretching, and C-O stretching, respectively. The peak intensity increases with increase in temperature from room temperature to 190 °C. This result agrees with the fact that the *sh* value increases with the increase in temperature at the exposure dose of 2 J/cm². This unique behavior can be explained by the idea that the unreacted 4-styrylpyridine units, although they are locked by the excess photocrosslinked side chains, may be highly ordered in an out-of-plane direction owing to the thermal motion if sufficiently annealed at a high temperature.¹⁹ This means that the excess photocrosslinked structure makes the LC temperature shift to a higher and wider temperature.

Conclusions

Photocrosslinkable methacrylate copolymer, **3**, was prepared by the radical copolymerization of **1** and **2** monomers. The copolymer was soluble in such solvent as THF, chloroform, etc. The M_w and polydispersity were 55,000 and 2.3,

respectively. The composition of **1** and **2** units in the copolymer was found to be 54.2:45.8 in the molar ratio. The copolymer **3** was observed to be a partial bilayer smectic structure. Its out-of-plane order parameter was estimated to be about 0.74 in the temperature range of 110–160 °C at the exposure dose of 0.001 J/cm², which means that the copolymer has a high out-of-plane ordering ability in the wide LC temperature range. When excess photoreacted, this copolymer exhibited a higher and wider LC temperature.

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