

Synthesis and Dual Alignment of Liquid Crystalline Polymethacrylate Bearing 4-Styrylpyridine and Biphenylene Moieties

Giseop Kwak, Hyeryun Kim, Min-Woo Kim, Seok-Hee Hyun, and Woo-Sik Kim*

Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea

Received September 3, 2008; Revised November 11, 2008; Accepted November 12, 2008

Introduction

The molecular alignment of liquid-crystalline (LC) polymers with photosensitive groups has been intensively studied in the field of liquid crystal display devices.¹⁻⁸ In practical view, photoisomerizable azobenzene groups- and photodimerizable cinnamoyl groups-containing LC polymers have been mainly studied so far. In these studies, research interests have been focused on such polymeric structures as spacer lengths,⁹⁻¹¹ copolymer compositions,^{2,12-14} and comonomer units.^{1,12,15} These structural factors have contributed to the changes of the orientational order and directions.

In a previous study,⁸ we examined the isomeric structure effect of the photosensitive group on the alignment of the photosensitive styrylpyridine moiety-containing LC polymethacrylates. As a result, the 2-styrylpyridine moiety-containing polymer showed an in-plane alignment after linearly polarized ultra-violet (LPUV) light irradiation and subsequent annealing, whereas the 4-styrylpyridine moiety-containing polymer exhibited a high out-of-plane orientation after the same treatment. That is, the structure of the 4-styrylpyridine group played an important role for the out-of-plane alignment of the polymer.

Meanwhile, a biphenylene unit is a representative mesogenic group for LC polymers. LC polymethacrylates with the biphenyl group linked to a photosensitive cinnamoyl group through alkylene spacers showed different alignment behaviors with dependence on spacer length. Moreover, the orientational order and direction of the cinnamoyl group were significantly affected by the mesogenic group.^{10,16} The 4-styrylpyridine unit is not only a photocyclodimerizable group but also a mesogenic group. In view of alignment changes with these structural factors, in the present work, a LC polymethacrylate bearing not only the 4-styrylpyridine

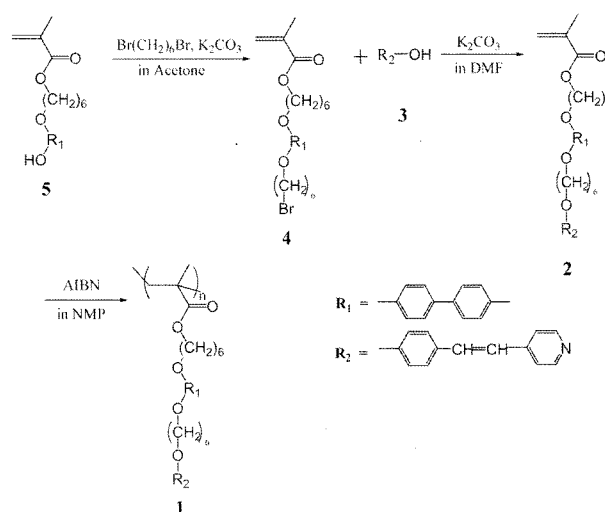
moiety but also biphenyl unit as a mesogenic group and hexylene group as a flexible spacer was synthesized and its properties including alignment behaviors were studied.

Experimental

Materials. 4-Picoline (Aldrich, 99%), 4-hydroxybenzaldehyde (Aldrich, 98%), 1,6-dibromohexane (Aldrich, 96%), 4,4'-biphenol (Aldrich, 97%), and lithium hydroxide (Aldrich, 98%) were used as received. *N,N'*-Dimethylformamide (Aldrich, 99%) (DMF), and 1, 1, 1-trifluoroacetic acid (Aldrich, 99%) (TFA), and 1, 1, 2, 2-tetrachloroethane (Aldrich, 97%) (TCE) were also used as received. Methacrylic acid (Junsei, 99%) was distilled under reduced pressure in the presence of hydroquinone. 2, 2'-Azobisisobutyronitrile (Junsei, 98%) (AIBN) was recrystallized from methanol. Acetone of reagent grade was distilled in the presence of calcium sulfate. *N*-Methyl-2-pyrrolidone (Junsei, 99%) (NMP) was distilled under reduced pressure in the presence of phosphorus pentoxide. All other reagents were used as received.


Monomer and Polymer Syntheses. The syntheses of monomer 6-[4-[6-[4-{2-(4-pyridyl)ethenyl}phenoxy]hexyloxy]biphenyl-4'-yloxy]hexyl methacrylate (**2**) and the corresponding polymer (**1**) are outlined in Scheme I.

First, 6-(4-hydroxybiphenyl-4'-yloxy)hexyl methacrylate (**5**) was prepared according to the literature¹⁷ from 4,4'-biphenol, 1,6-dibromohexane, methacrylic acid, and lithium hydroxide. The melting point of **5** was 47-48 °C (47-48 °C).¹⁷ Also, 4-(4-hydroxystyryl)pyridine (**3**) was synthesized according to the literature¹⁸ from 4-hydroxy benzaldehyde and 4-picoline. The melting point was 272-274 °C (272-275 °C).¹⁸ Next, for the synthesis of 6-{4-(6-bromohexan-



Scheme I. Syntheses of monomer **2**, and the corresponding polymer **1**.

*Corresponding Author. E-mail: wskim@knu.ac.kr

oxy)biphenyl-4'-yloxy}-hexyl methacrylate (**4**), **5** (5.3 g, 15 mmol) together with potassium carbonate (2.1 g, 15 mmol) was added to 100 mL of acetone, and 1,6-dibromohexane (8.5 g, 35 mmol) was slowly dropped to the mixture, which was stirred at 40 °C for 48 h and poured into 1 L of distilled water. The precipitate was filtered and dried under a vacuum, and the crude product was purified by column chromatography on silica gel using an ethyl acetate-cyclohexane (6/4 : v/v) mixture as the eluent, to obtain the intermediate **4** in a yield of 5.0 g (65%). mp : 78-79 °C. IR (KBr, cm⁻¹): 1633 (vinyl). ¹H NMR (CDCl₃, δ in ppm) : 1.5 (8H, -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.7-1.8 (8H, -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.9 (3H, CH₃), 3.5 (2H, -CH₂Br), 4.1 (2H, -COOCH₂-), 4.2 (4H, -)-, 5.5 (1H, CH₂=, vinyl), 6.1 (1H, CH₂=, vinyl), 6.9 (4H, biphenylene), 7.5 (4H, biphenylene).

For the synthesis of **2**, **3** (5.91 g, 30 mmol) and potassium carbonate (12.43 g, 90 mmol) were added to 100 mL of DMF and heated at 45 °C with stirring for 1 h. To the mixture was added **4** (7.8 g, 15 mmol) and maintained with stirring at the same temperature for 48 h. The mixture was poured into a large excess of distilled water to precipitate the product. The precipitated product was filtered and dried under a vacuum at room temperature. The crude product was purified by column chromatography over silica using chloroform as the eluent, to obtain the monomer **2** in a yield of 6.5 g (68%). mp: 162-164 °C. IR (KBr, cm⁻¹): 1590 (-CH=CH-), 1636 (vinyl), 1718 (carbonyl of ester). ¹H NMR (CDCl₃, δ in ppm): 1.6 (8H, -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.7-1.8 (8H, -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.9 (3H, -CH₃), 4.0 (6H, -OCH₂-CH₂-CH₂-CH₂-CH₂-CH₂O- and -OCH₂-), 4.2 (2H, -COOCH₂-), 5.5 (1H, CH₂=, vinyl), 6.1 (1H, CH₂=, vinyl), 6.8-7.5 (16H, benzene, pyridine and -CH=CH-), 8.5 (2H, pyridine). Mass spectrometry (70 eV): m/z = 633 (M⁺). UV (TCE) : ε = 20300 (λ = 393 nm).

For the synthesis of **1**, 1.0 g of **2** was dissolved in 10 mL of purified NMP in the presence of 1 wt% of AIBN to the monomer. The polymerization mixture was introduced into a Pyrex glass ampoule, subjected to freeze pumping thaw cycles and sealed under a vacuum. After the polymerization for 24 h at 57.5 °C, the mixture was poured slowly dropwise into an excess of 1,2-dichloroethane to precipitate the polymer. The precipitate was filtered and dried under a vacuum at ambient temperature. The final polymer product was 0.70 g (70%) in yield.

Measurements. ¹H NMR and mass spectra were measured with a Bruker Avance Digital 400 FT-NMR spectrometer and with a Hewlett Packard 5985A GC/MA/DS spectrometer, respectively. IR and UV absorption spectra were measured with a JASCO-IR 810 spectrophotometer and a Shimadzu Model 2401 spectrophotometer, respectively.

Differential scanning calorimetry (DSC) measurement was performed at a heating rate of 10 °C/min with a Dupont 2000 instrument. Polarizing optical microscopy (POM) investigation was performed with a Zeiss AX1 LAB POM instru-

ment. X-Ray measurement was carried out using a Rigaku RAD-RS with a copper anode and a nickel filter. The intrinsic viscosity of the polymer was measured in TFA at 25 °C with an Ubbelohde viscometer.

In order to examine the photoreaction and the alignment of the polymer, 2 wt% TFA solutions were coated on quartz plates using a spin coater and dried at room temperature. The film thickness was 3.0 μm on average. The films were irradiated by the light of a high pressure mercury lamp without using a cutoff filter. Polarized UV spectra were measured before and after annealing with the UV spectrophotometer described above. The homogeneous alignment of the film was estimated by an in-plane order parameter [$S = (A_{\parallel} - A_{\perp}) / (A_{(large)} + 2A_{(small)})$], where A_{\parallel} and A_{\perp} are the absorbances parallel and perpendicular to the LPUV light irradiation after the annealing of the film irradiated with the LPUV light. $A_{(large)}$ and $A_{(small)}$ are the larger and the smaller of A_{\parallel} and A_{\perp} .¹⁴ The out-of-plane alignment of the film was estimated by an out-of-plane order parameter [$Sh = 1 - (A_{annealed} / A_{irradiated})$], where $A_{irradiated}$ and $A_{annealed}$ are the average absorbances of A_{\parallel} and A_{\perp} from the irradiated film and the annealed one after irradiation, respectively.¹⁴

Results and Discussion

A methacrylate type monomer with 4-styrylpyridine unit as a photosensitive group, biphenylene unit as a mesogenic group, and two hexylene groups as flexible spacers in the side chain was designed by modifying the synthetic route of 2-styrylpyridine unit-containing methacrylate.¹⁷ Scheme I shows the synthetic route of the designed monomer, **2**, and the corresponding polymer, **1**. In place of the reaction of 1,6-dibromohexane with **3** for the absence of the quaternization, the bromide was reacted with **5** to prepare **4**, and then the **2** was obtained in a good yield by the reaction of **4** with **3** in DMF. Also, the radical polymerization of **2** using AIBN gave **1** in a high yield of 70%. The chemical structures of **2** and the intermediate, **4**, were confirmed by IR, ¹H NMR or mass spectroscopy as given in the experimental part. In ¹H NMR spectrum of **1**, two peaks due to the vinyl protons around 5.5 and 6.1 ppm completely disappeared, indicating complete consumption during the polymerization process. The IR spectrum of **1** showed two characteristic absorption peaks of the ethenyl group in the styrylpyridine unit at 1590 cm⁻¹ and carbonyl group in the ester unit at 1719 cm⁻¹. **1** was well dissolved in TFA and TCE. Its intrinsic viscosity in TFA at 25 °C was 0.25 dL/g.

In order to know the photoreactivity of the 4-styrylpyridine group within **1**, we measured the UV absorption spectra of **1** in film with increasing exposure doses (Figure 1). The absorption band due to the styrylpyridine structure around 365 nm decreased with the increasing of exposure doses. The degrees of photoreaction were estimated to be 9, 24, 36, 47, 56, 62, 67 and 70%, respectively at the exposure

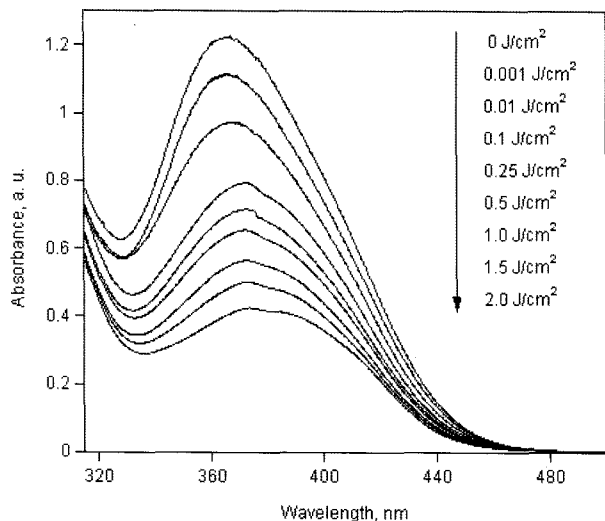


Figure 1. UV spectra of **1** in film exposed to unpolarized UV light at various exposure doses.

doses of 0.001, 0.01, 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 J/cm² according to the normalized absorbances. Simultaneously, the absorption maximum wavelength of the band was slightly shifted to the longer wavelength with the photoreaction, indicating a cyclodimerization of styrylpyridine.⁸

Figure 2 shows the DSC thermogram of **1**. Two endothermic peaks with 3.18 and 0.75 J/g were seen at 197 and 268 °C, respectively. These transition temperatures correspond to its melting point and LC-isotropic transition temperature, respectively, which are higher than those (179 and 210 °C) of the LC polymethacrylate with 2-styrylpyridine unit in the place of the 4-styrylpyridine unit.¹⁷ As shown in Figure 3, **1** exhibited a characteristic birefringent texture at 240 °C. The XRD showed a layer distance-space of 34.48 Å at the same temperature, indicating that the polymer forms a smectic structure.

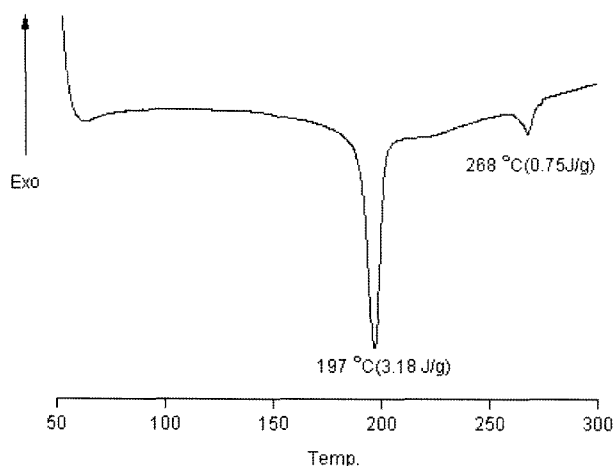


Figure 2. DSC thermogram of **1** under a nitrogen atmosphere at a heating rate of 10 °C/min.

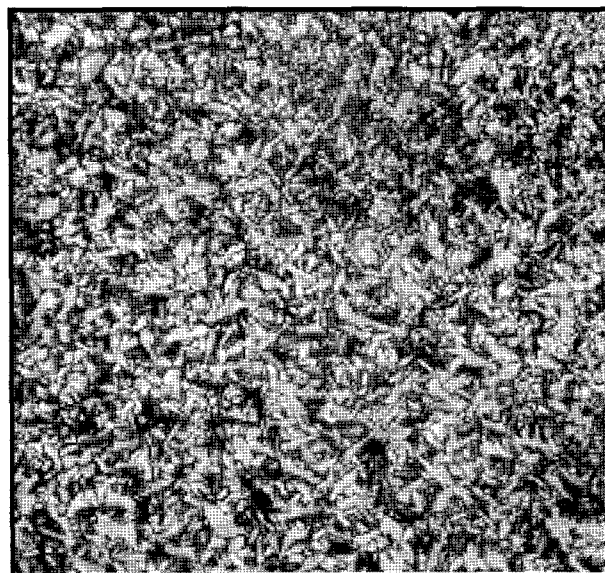


Figure 3. Polarized optical microscope photograph of **1** annealed at 240 °C for 24 h.

In order to examine the photo- and thermo- alignment behavior of **1** in film, we treated the film by LPUV light irradiation at room temperature and subsequent annealing for 10 min at the LC temperature of 250 °C and measured the polarized UV absorption spectra of the film (Figure 4). The absorption maximum wavelength of 365 nm before irradiation was shifted to 350 nm after the subsequent annealing at the LC temperature of 250 °C. This blue shift could be due to H-aggregation of the unreacted 4-styrylpyridine units of **1** with the annealing.^{19,20} Likewise, the **1** showed a weak shoulder around 380 nm after the annealing, the shoulder

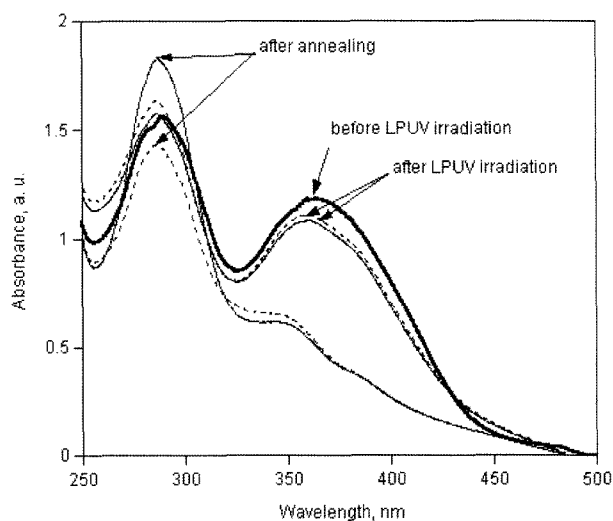


Figure 4. UV polarization spectra of **1** in film before and after LPUV light irradiation of 0.001 J/cm² and subsequent annealing at 250 °C for 10 min. A_{\parallel} (—) and A_{\perp} (---) are absorbances parallel and perpendicular to the LPUV light irradiation, respectively.

could be attributed to the residual of the 4-styrylpyridine units excluded from the H-aggregation. On the other hand, another maximum peak due to the biphenylene group at 280 nm scarcely changed after irradiation and subsequent annealing. This could be due to the fact that the biphenyl group is sufficiently separated from the 4-styrylpyridine group by the hexylene group.

Both the $A_{//}$ and A_{\perp} of 4-styrylpyridine unit at 365 nm after LPUV irradiation at 0.001 J/cm² decreased, where $A_{//}$ and A_{\perp} are the absorbances parallel and perpendicular to LPUV light. However, the $A_{//}$ and A_{\perp} at the 365 nm-wavelength largely decreased after the subsequent annealing at 250 °C for 10 min, and the $A_{//}/A_{\perp}$ ratio was near 1. This result indicates that the unreacted 4-styrylpyridine units align to an out-of-plane direction at the LC temperature.¹⁴ This also well supports the idea that 4-styrylpyridine units exclusively contribute to out-of-plane alignment.⁸ The out-of-plane order parameter (Sh) of **1** was estimated to be 0.54 from the average absorbances of $A_{//}$ and A_{\perp} at 360 nm after the LPUV light irradiation and those of $A_{//}$ and A_{\perp} at 350 nm after the annealing. Accordingly, the 4-styrylpyridine unit of the polymer was found to have high out-of-plane order ability at the LC temperature. On the other hand, the $A_{//}$ at 280 nm of the biphenylene unit gave rise to the largest value after subsequent annealing at 250 °C for 10 min while the A_{\perp} became the smallest value. This result indicates that the alignment of the biphenylene units after the annealing is thermally enhanced in the direction parallel to the LPUV light irradiation. The in-plane order parameter (S) was estimated to be 0.09 from the $A_{//}$ and A_{\perp} at 280 nm after the annealing. Thus, it could be said that the 4-styrylpyridine and biphenylene units have independently different orientation planes, due to the separating role of the flexible spacer of the hexylene group. To our knowledge, such dual alignment phenomenon was found for the first time. Further study will be needed to support the suggestion that the order and directions of the out-of-plane orientation of 4-styrylpyridine units of the polymer can be controlled by the orientational role of the biphenyl group through shorter alkylene spacers.

Conclusions

A new methacrylate monomer, **2** with 4-styrylpyridine unit as a photocyclodimerizable group, biphenylene unit as a mesogenic group, and two hexylene groups as flexible spacers, was synthesized. Radical polymerization of **2** provided the corresponding polymer, **1**. The intrinsic viscosity of **1** in TFA at 25 °C was 0.25 dL/g. The polymer showed a smectic texture with a layer period of 34.48 Å at 240 °C. Also, it was found that the biphenylene unit of the polymer gave

rise to an in-plane alignment after LPUV light irradiation at room temperature and subsequent annealing at the LC temperature of 250 °C while the 4-styrylpyridine unit in the same side chain of the polymer resulted in a high out-of-plane order by the same treatment, being due to the separating ability of the flexible hexylene group between the two mesogenic units.

Acknowledgments. This work was supported by the KOSEF (R05-2001-1-30800-007-2) and KRF (R05-2004-000-11071-0).

References

- (1) K. Anderle, R. Birenheide, M. Eich, and J. H. Wendorff, *Makromol. Chem., Rapid Commun.*, **10**, 477 (1989).
- (2) N. Kawatsuki, C. Suehiro, and T. Yamamoto, *Macromolecules*, **31**, 5984 (1998).
- (3) M. Han, S. Morino, and K. Ichimura, *Chem. Lett.*, 645 (1999).
- (4) Y. Wu, T. Ikeda, and Q. Zhang, *Adv. Mater.*, **11**, 300 (1999).
- (5) R. Penterman, S. I. Klink, H. de Koning, G. Nisato, and D. J. Broer, *Nature*, **417**, 55 (2002).
- (6) S. Nespurek, Y. Zakrevskyy, J. Stumpe, B. Sapich, and A. Kadashchuk, *Macromolecules*, **39**, 690 (2006).
- (7) S. W. Nam, S. H. Kang, and J. Y. Chang, *Macromol. Res.*, **15**, 74 (2007).
- (8) G. Kwak, M. W. Kim, D. H. Park, J. Y. Kong, S. H. Hyun, and W. S. Kim, *J. Polym. Sci. Part A: Polym. Chem.*, **46**, 5371 (2008).
- (9) M. Han and K. Ichimura, *Macromolecules*, **34**, 90 (2001).
- (10) N. Kawatsuki, K. Matsuyoshi, M. Hayashi, H. Takatsuka, and T. Yamamoto, *Chem. Mater.*, **12**, 1549 (2000).
- (11) N. Kawatsuki, M. Hayashi, and T. Yamamoto, *Macromol. Chem. Phys.*, **202**, 3087 (2001).
- (12) N. Kawatsuki, K. Matsuyoshi, and T. Yamamoto, *Macromolecules*, **33**, 1698 (2000).
- (13) J. G. Meier, R. Ruhmann, and J. Stumpe, *Macromolecules*, **33**, 843 (2000).
- (14) N. Kawatsuki, N. Furuso, E. Uchida, and T. Yamamoto, *Macromol. Chem. Phys.*, **203**, 2438 (2002).
- (15) A. Bobrosky, N. Boiko, V. Shibaev, and J. Stumpe, *J. Photoch. Photobio. A*, **163**, 347 (2004).
- (16) N. Kawatsuki, H. Ono, H. Takatsuka, T. Yamamoto, and O. Sengen, *Macromolecules*, **30**, 6680 (1997).
- (17) W. S. Kim, J. W. Lee, Y. W. Kwak, J. K. Lee, Y. T. Park, and S. D. Yoh, *Polym. J.*, **33**, 643 (2001).
- (18) D. Papa, E. Schwenk, and E. Kingsberg, *J. Am. Chem. Soc.*, **73**, 253 (1951).
- (19) R. W. Wata, A. H. Fawcett, T. Gene, J. Haferkorn, R. K. Malcolm, and J. Stumpe, *Macromolecules*, **31**, 4935 (1998).
- (20) J. M. Kuiper and J. B. F. N. Engberts, *Langmuir*, **20**, 1152 (2004).