

SHORT COMMUNICATIONS

Synthesis and Characterization of a Photo-Crosslinkable Side-Chain Liquid-Crystalline Polymer

Woo-Sik KIM,[†] Jae-Won LEE, Young-Woo KWAK,* Jae-Keun LEE,* Yong-Tae PARK,* and Soo-Dong YOH**

Department of Polymer Science, Kyungpook National University, Taegu 702–701, Korea

**Department of Chemistry, Kyungpook National University, Taegu 702–701, Korea*

***Department of Chemistry Education, Kyungpook National University, Taegu 702–701, Korea*

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Side-chain liquid-crystalline polymers (SLCPs) have attracted considerable attention because of their potential applications to opto-electron devices.^{1–3} Among them, some photo-crosslinkable SLCPs which can lock in their aligned structure were recently reported.^{3–7} For example, liquid-crystalline polymethacrylates^{3,4} and polysiloxanes⁵ with cinnamoyl group as a photo-crosslinkable center were synthesized and the photo-crosslinked polymers showed thermal stability of the mesophase. Also, liquid-crystalline polymethacrylates with 3-methyl-2-butenyl group as a photo-crosslinkable center were synthesized and the photo-crosslinked polymers exhibited thermally stable orientation.⁶ In addition, SLCPs with both bis(benzylidene)cyclohexanone unit as a photo-reactive center and cholesterol unit as a monitor of the mesophase were prepared and their cholesteric supramolecular order was found to remain even after photo-crosslinking.⁷

The purpose of this study was to synthesize a new photo-crosslinkable SLCP which can lock in its liquid-crystalline structure. It is known that polystyrylpyridines have not only good thermal properties⁸ but also high photo-sensitivity in their cyclodimerization like cinnamoyl group.^{9,10} Therefore, this paper deals with the synthesis and characterization of a photo-crosslinkable liquid crystalline polymethacrylate with both biphenyl unit as a mesogen and styryl-2-pyridine unit as a photo-sensitive center in the same side-chain.

EXPERIMENTAL

Materials

2-Picoline, 4-hydroxybenzaldehyde, 1,6-dibromohexane, and 4,4'-biphenol were purchased from Aldrich Chemical Co. and used as received. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Acetone of reagent grade was distilled in the presence of calcium sulfate. All other reagents were used as received.

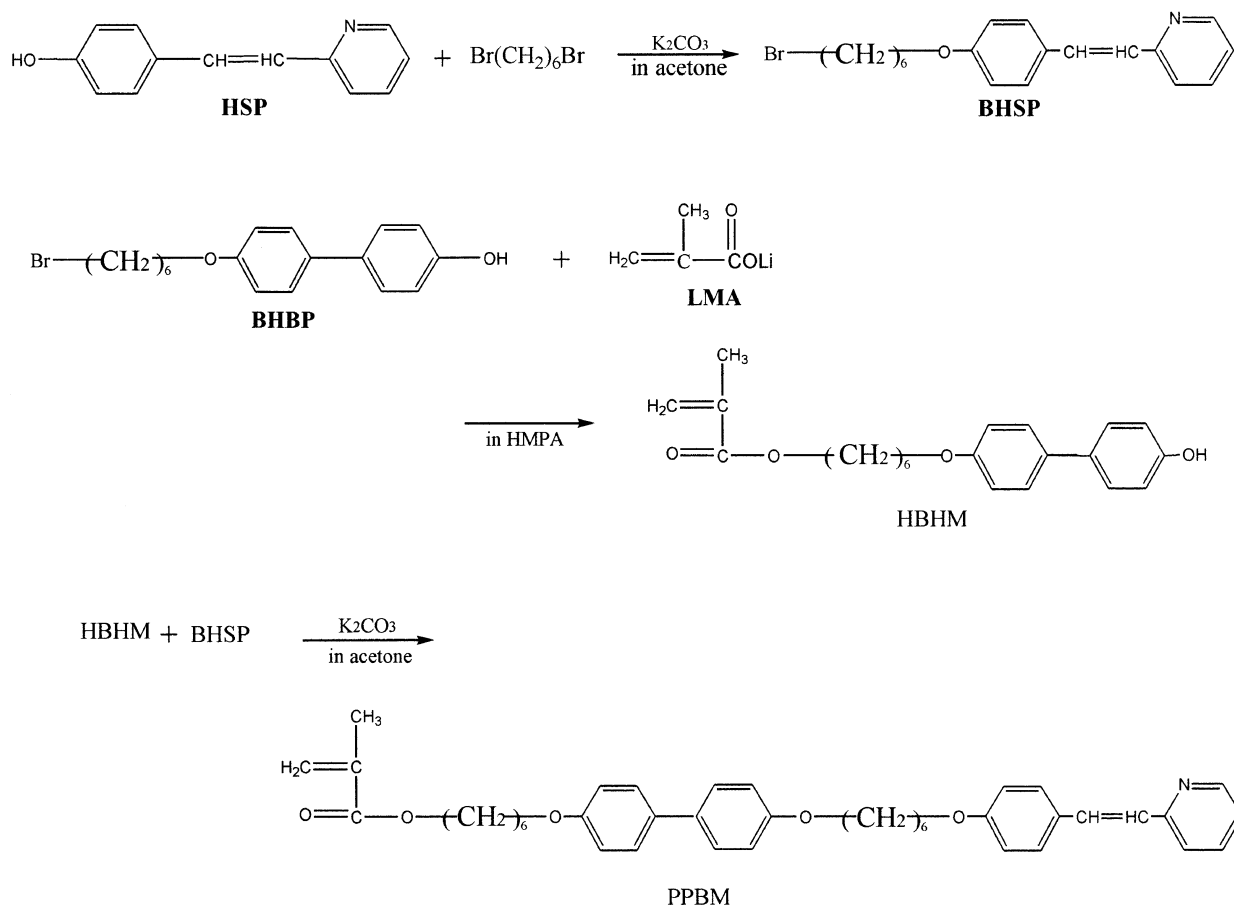
Synthesis of 6-[4-(6-{4-[2-(2-Pyridyl)ethenyl] phenoxy} hexyloxy) biphenyl-4'-yloxy] hexylmethacrylate (PPBM)

The monomer PPBM was synthesized by the following reactions :

2-(4-Hydroxystyryl)pyridine (HSP) was synthesized from 2-picoline and 4-hydroxybenzaldehyde according to the literature.¹¹ The melting point was 218–220°C (219–220°C¹¹).

For the synthesis of 6-{4-[2-(2-pyridyl)ethenyl]phenoxy}hexylbromide (BHSP), HSP (2.4 g, 0.012 mol) and potassium carbonate (6.6 g, 0.048 mol) were added to acetone of 200 mL. The mixture was refluxed with stirring for 1 h and 1,6-dibromohexane (14.6 g, 0.06 mol) was slowly added to the solution. The mixture was stirred at the refluxing temperature for 24 h and filtered to remove the formed potassium bromide. The filtrate was concentrated and poured into an excess of *n*-hexane to precipitate the product. The precipitated product was filtered and recrystallized from acetone-ethanol (3/2, v/v). The yield of BHSP was 2.7 g (63%) with the melting point of 72–73°C. IR (KBr, cm⁻¹): 1578 (–CH=CH–). ¹H

[†]To whom correspondence should be addressed.



NMR (CD_3SOCD_3 , δ): 1.5 (4H, $\text{Br}-\text{CH}_2-\text{CH}_2\text{HCH}_2-\text{CH}_2-$), 1.7 (2H, $\text{Br}-\text{CH}_2-\text{CH}_2$), 1.8 (2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.6 (2H, $\text{Br}-\text{CH}_2-$), 4.0 (2H, $-\text{CH}_2\text{O}-$), 6.9–7.7 (7H, benzene and pyridine rings), 7.6 (2H, $-\text{CH}=\text{CH}-$),

8.5 (1H,).

4-(6-Bromohexyloxy)biphenyl-4'-ol (BHBP) was synthesized from 4,4'-biphenol and 1,6-dibromohexane according to the literature.⁴ The melting point was 122–125°C (122–126°C⁴). Lithium methacrylate (LMA) was prepared from methacrylic acid and lithium hydroxide.¹²


For the synthesis of 6-(4-(6-hydroxybiphenyl-4'-yloxy)hexyl)hexylmethacrylate (HBHM), BHBP (2.9 g, 0.008 mol) and LMA (1.5 g, 0.016 mol) were added to hexamethyl phosphoramide (HMPA) of 30 mL. The mixture was heated at 40°C with stirring for 48 h and was poured into a large excess of distilled water to precipitate the product. The precipitated product was filtered and dried under vacuum at room temperature. The crude product was purified by column chromatography over silica using cyclohexane-ethyl acetate (7/3, v/v). The yield of HBHM was 1.7 g (57%) with the melting point of 47–48°C.

IR (KBr, cm^{-1}): 1633 (vinyl). ¹H NMR (CD_3-

CCD_3 , δ): 1.5 (4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.7–1.8 (4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.9 (3H, CH_3), 4.1–4.2 (4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 5.6 (1H, CH_2- of vinyl), 6.1 (1H, $-\text{CH}_2-$ of vinyl), 6.9–7.0 (4H, biphenyl), 7.4–7.6 (4H, biphenyl), 8.3 (1H, OH).

For the synthesis of 6-[4-(6-{4-[2-(2-pyridyl)ethenyl]phenyloxy}hexyloxy)biphenyl-4'-yloxy]hexylmethacrylate (PPBM), HBHM (1.5 g, 0.0041 mol), potassium carbonate (1 g, 0.0072 mol), and a trace of hydroquinone as a polymerization inhibitor were added to acetone of 70 mL and heated at 60°C with stirring for 1 h. To the mixture was added BHSP (1.8 g, 0.005 mol) and refluxed with stirring at the same temperature for 24 h. During the reaction, the product was precipitated from the solution. The precipitate was filtered, washed with acetone and distilled water, and dried under vacuum at room temperature. The crude product was purified by column chromatography over silica using benzene-ethyl acetate (7/3, v/v). The yield of PPBM was 1.4 g (53%) with the melting point of 150–152°C.

IR (KBr cm^{-1}): 1584 ($-\text{CH}=\text{CH}-$), 1634 (vinyl). ¹H NMR (CDCl_3 , δ): 1.6 (8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.7–1.8 (8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

CH₂-CH₂-), 1.9 (3H, CH₃), 4.0 (6H, -CH₂-CH₂-CH₂-CH₂-), 4.1 (2H, -COCH₂-), 5.6 (1H, CH₂- of vinyl), 6.1 (1H, -CH₂- of vinyl), 6.9-7.7 (17H, benzene and pyridine rings and -CH=CH-), 8.6 (1H, ). Mass spectrometry (70 eV) : m/z 633 (M⁺).

Preparation of PolyPPBM

In a 30 mL ampoule were placed PPBM (1 g, 1.58 mmol), 1-methyl-2-pyrrolidone of 15 mL, and 1 mol% of AIBN with respect to the monomer. The monomer in the sealed ampoule was polymerized at 60°C for 24 h. The reaction mixture was poured slowly dropwise into an excess of 1,2-dichloroethane to precipitate the polymer. The precipitated polymer was filtered and dried under vacuum at room temperature. The yield was 0.64 g (64%).

Measurements

IR spectra were recorded on a JASCO-IR 810 spectrometer by KBr method. UV spectra were measured with a Shimadzu Model 2401 spectrophotometer. ¹H NMR and mass spectra were measured with a Bruker Advanced Digital 400 FT-NMR spectrometer and with a Hewlett Packard 5985A GC/MA/DS spectrometer, respectively. The initial thermal decomposition temperature of the polymer was measured in a nitrogen atmosphere at a heating rate of 20°C min⁻¹ with a Dupont 2100 thermal gravimetric analyzer (TGA). Thermal transition temperatures were obtained in a nitrogen atmosphere at a heating rate of 5°C min⁻¹ with a Dupont 2000 differential scanning calorimeter (DSC). Microscopic investigations were carried out with a polarizing light microscope (Zeiss A×10 LAB). X-Ray studies were performed with a Rigaku RAD-RS (Cu anode and Ni filter). The intrinsic viscosity of the polymer was measured in hexafluoro-2-propanol at 25°C with a Ubbelohde viscometer. A high pressure mercury lamp was used as the light source for the investigation of the photo-reaction of the polymer.

In order to examine the alignment of mesogen groups in the polymer after photo-crosslinking, its hexafluoro-2-propanol solutions were coated on rubbed polyimide thin films supported on slide glasses and dried. One of the coated samples was irradiated at the liquid-crystalline forming temperature with the same high pressure mercury lamp described above. The transmittances of the irradiated sample and the sample without irradiation were evaluated by monitoring the intensity of a linearly polarized He-Ne laser beam at 632.8 nm.⁶

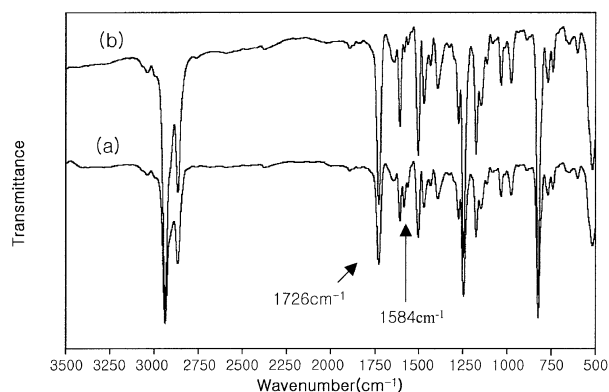


Figure 1. IR spectra of polyPPBM before irradiation (a) and after 10 min irradiation (b).

RESULTS AND DISCUSSION

PPBM was identified by NMR, IR, and mass spectroscopies. Its molar absorptivity at 393 nm was determined to be 21800 in 1,1,2,2-tetrachloroethane (TCE). Even though the NMR spectrum of polyPPBM was broad, it was confirmed that the two peaks of hydrogens of the vinyl group disappeared. The IR spectrum of the polymer evidently showed the peak of ethenyl group of the styrylpyridine unit at 1584 cm⁻¹ and the peak of carbonyl of the ester group at 1726 cm⁻¹. The polymer was soluble in hexafluoro-2-propanol, trifluoroacetic acid, and TCE. The intrinsic viscosity of the polymer was 0.18.

IR spectra of the polymer before irradiation (a) and after irradiation for 10 min (b) are given in Figure 1. The intensity of spectrum (b) at 1584 cm⁻¹ decreased compared with that of spectrum (a). This decrease can be attributed to the photo-cyclodimerization of ethenyl of the styrylpyridine group in the polymer.⁸⁻¹⁰ The extent of the decrease was calculated as 67% by using the ratio of the area at 1584 cm⁻¹ to that at 1726 cm⁻¹. Accordingly, the polymer was found to be high photosensitivity than SLCPs with cinnamoyl group^{3,5} and 3-methyl-2-butenyl group,⁶ respectively.

The initial thermal decomposition temperature of the polymer was known to be around 400°C from its TGA thermogram. DSC thermograms of the monomer and the polymer are shown in Figure 2. The monomer showed two endothermic peaks around 156°C and 173°C and the polymer displayed three endothermic peaks around 165°C, 179°C, and 210°C. From these results, it was assumed that they formed a liquid-crystalline structure. From polarized optical microscopy observations, the monomer melted around 156°C and showed isotropic state around 173°C and the polymer exhibited a mesophase structure around 179°C and became isotropic state around 210°C. However,

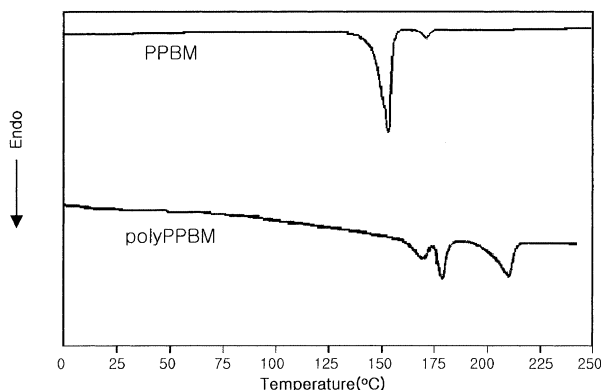


Figure 2. DSC thermograms of PPBM and polyPPBM.

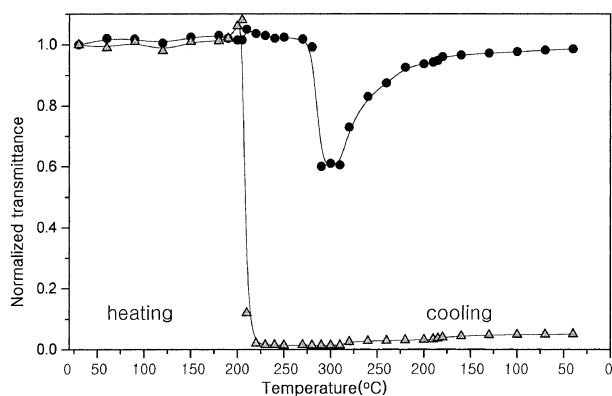


Figure 3. Temperature dependence of the normalized transmittance for the oriented polyPPBM: (Δ) before irradiation; (\bullet) after 10 min irradiation at 185°C.

it was difficult to identify what the liquid-crystalline structures of the monomer and the polymer were from the microscopic investigation. Therefore, their diffraction peaks were obtained on the temperature-controlled X-Ray measurements. As the results, the liquid-crystalline structure of the monomer corresponded to a smectic structure with a layer period of 37Å in the range of 156°C to 173°C and that of the polymer corresponded to a smectic structure with a layer period of 42Å in the range of 179°C to 210°C.

The normalized transmittances of the sample without irradiation (a) and the 10 min irradiated sample (b) are plotted against the temperatures in Figure 3. The transmittances of the sample (a) above the isotropic temperature rapidly became zero and scarcely recovered after cooling to room temperature. On the other hand, for the 10 min irradiated sample (b), the transmittances did not decrease up to 275°C. Moreover, the values after cooling recovered to almost their original level from 200°C to room temperature, even though they decreased to 0.6 around 300°C. The changes of transmittances of the polymer with the temperatures after photo-crosslinking were similar to those of polymers having cinnamoyl group³ or 3-methyl-2-butenyl

group⁶ as the photo-sensitive center. IR investigation for the polymer after 10 min irradiation showed that the decrease of the intensity of the ethenyl group was 67% as described above. Therefore, these results indicate that the crosslinked side-chains of the polymer cause the re-alignment of the uncrosslinked side-chains of the polymer after cooling and contribute to thermally stable orientation of the polymer.⁴

In conclusion, a new polymethacrylate with both biphenyl unit as a mesogen and styryl-2-pyridine unit as a photosensitive center in the same pendant group was synthesized. The polymer showed a smectic liquid-crystalline structure. The polymer gave rise to high photo-sensitivity and could be photo-crosslinked without change in the alignment. The photo-crosslinked polymer exhibited a stable alignment up to 275°C.

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REFERENCES

1. H. Ringsdorf, H. W. Schmidt, and A. Schneller, *Macromol. Chem. Rapid Commun.*, **3**, 745 (1982).
2. C. H. Legge, M. J. Witcombe, A. Gilbert, and G. R. Mitchell, *J. Matter. Chem.*, **1**, 303 (1991).
3. N. Kawatsuki, H. Takatsuka, T. Yamamoto, and O. Sengen, *Macromol. Rapid Commun.*, **17**, 703 (1996).
4. N. Kawatsuki, S. Sakashita, K. Takatani, T. Yamamoto, and O. Sengen, *Macromol. Chem. Phys.*, **197**, 1919 (1996).
5. L. C. Chien and L. G. Cada, *Macromolecules*, **27**, 3721 (1994).
6. N. Kawatsuki, K. Takatani, T. Yamamoto, and O. Sengen, *Macromol. Chem. Phys.*, **198**, 2853 (1997).
7. Gangadhara and K. Kishore, *Macromolecules*, **28**, 806 (1995).
8. M. Y. Li, E. M. Pearce, and A. Reiser, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2517 (1988).
9. K. Ichimura, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1411 (1982).
10. K. Ichimura and S. Watanabe, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1419 (1982).
11. D. Papa, E. Schwenk, and E. Klingsberg, *J. Am. Chem. Soc.*, **73**, 253 (1951).
12. M. Tabrizian, C. Bunel, and J. P. Vairon, *Makromol. Chem.*, **194**, 6890 (1993).