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Liquid Crystal Photoalignment by a Polymaleimide Having a Photoreactive 2-Styrylpyridine Derivative as a *N*-Substituent

Jin Woo Kim, Kyungun Min, and Woo-Sik Kim*

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

Seung Hun Jeon

Dongjin Semichem Co. Ltd., Gyeonggi-do 445-931, Korea

Won Suk Chang

Materials Research Lab., Samsung Electronics Co. Ltd., Gyeonggi-do 446-712, Korea

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Introduction

The photoalignment of photosensitive polymers has attracted considerable interest with a view toward overcoming disadvantages such as the generation of dust, electrostatic problems, and a poor control of rubbing strength of the conventional method using rubbed polymer films for making liquid crystal (LC) display devices because the shortcomings can be eliminated by the photoalignment of photoreactive polymers which occurs through the anisotropic photochemical reaction.[1-10]

In previous studies on the photoalignment of photosensitive polymers using linearly polarized ultraviolet (LPUV) light, polymers with azobenzene moieties as photoisomerizable groups[4], polymers with cinnamoyl group,[11-15] styrylpyridine moieties[5,16,17] and coumarin moieties[1,18,19] as photocyclodimerizable groups, and deep UV light degradable polymers[20,21] have been mainly studied. Among these photosensitive polymers, polyimides with cinnamoyl group[14] or styrylpyridine moieties[5,17] in the side groups were reported to have thermal stability, thin film formation, and low energy LC photoalignment, etc. However, the structure and preparation of the backbone polymers are complex when compared to polymaleimides, and the photosensitive polyimides showed perpendicular LC photoalignment to LPUV light irradiation.[5,14,17]

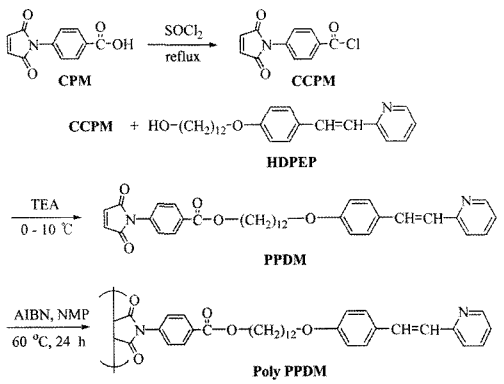
Polymaleimides have excellent thermal stability. Moreover, it was reported that polymaleimides with long alkyl groups on the nitrogen atom have a tough and thin film formation property.[22,23] In addition, styrylpyridines have a high photosensitivity and good thermal properties.[24] Therefore, in the present work, a polymaleimide with a 2-styrylpyridine moiety as a photosensitive group and dodecylene group as a flexible spacer in the same side chain bonded to the nitrogen atom was synthesized and its properties including LC photoalignment behaviors were studied.

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

Experimental

Materials. 2-Picoline (Aldrich, 98%), 4-hydroxybenzaldehyde (Aldrich, 98%), 12-bromo-1-dodecanol (Aldrich, 99%), maleic anhydride (Aldrich, 99%), 4-aminobenzoic acid (Aldrich, 99%), and thionyl chloride (Aldrich, 99%) were used as received. Ethyl acetate and acetone of reagent grade were fractionally distilled. *N,N*-Dimethylformamide (DMF) of reagent grade was distilled in the presence of barium oxide under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) of reagent grade was recrystallized from methanol. 1-Methyl-2-pyrrolidone (NMP) of reagent grade was distilled in the presence of phosphorus pentoxide under reduced pressure. All other reagents were used as received.

Synthesis of the Monomer. The synthesis of a maleimide, *N*-[4-{12-(4-(2-(2-pyridyl) ethenyl) phenyloxy) dodecyloxycarbonyl} phenyl] maleimide (PPDM) (Scheme I) is as follows. First, 2-{2-(4-hydroxyphenyl) ethenyl} pyridine (HPEP) was synthesized by the reaction of 4-hydroxybenzaldehyde with 2-picoline according to the literature.[25] Next, 2-[2-{4-(12-hydroxydodecyloxy) phenyl} ethenyl] pyridine (HDPEP) was prepared by the reaction of HPEP with 12-bromo-1-dodecanol according to our previous study.[26] *N*-(4-Carboxyphenyl) maleimide (CPM) was synthesized from maleic anhydride and 4-aminobenzoic acid according to the literature.[27,28] *N*-(4-Chlorocarboxyphenyl) maleimide (CCPM) was prepared by the reaction of CPM with thionyl chloride to literature.[28] Finally, for the synthesis of the monomer PPDM, HDPEP (3.8 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) were dissolved in 100 mL of dichloromethane. To the solution was added dichloromethane (50 mL) solution of CCPM



Scheme I. Synthesis of polyPPDM.

(2.4 g, 0.01 mol) dropwise at 5-10 °C for 1 h, stirred at this temperature for 5 h, and washed with distilled water. The solvent in the mixture was evaporated. The crude product was purified by column chromatography over silica gel using chloroform-ethyl acetate (v/v=2/1) mixture as the eluent. The yield was 3.59 g (62%). mp: 105-107 °C. ^{1}H NMR (DMSO-d_6, δ in ppm): 1.2-1.5 {16H, -CH_2-CH_2-($\underline{CH_2}$)$_8$-CH_2-CH_2-}, 1.6-1.8 {4H, -CH_2-$\underline{CH_2}$-(CH_2)$_8$-$\underline{CH_2}$-CH_2-}, 4.0 (2H, -CH_2-O-), 4.2 (2H, -$COOCH_2$-), 6.8-8.2 (15H, benzene, pyridine, and -CH=CH-), 8.6 (1H, pyridine). IR (KBr, cm^{-1}): 1710 (CO),[29,30] 1585 (C=C of styrylpyridine),[31] 1380 (C-N).[29] Mass spectroscopy (70 eV): m/z=580 (M^+). UV (1,2-dichloroethane): ε=28,300 ($L \cdot mol^{-1} \cdot cm^{-1}$) ($\lambda_{max}$ = 330 nm).

Polymerization. The synthesis of polyPPDM was conducted by radical polymerization as outlined in Scheme I. In a typical polymerization, 0.29 g of PPDM was dissolved in 4 mL of NMP in the presence of 1% of AIBN with respect to the monomer. The mixture was introduced into a Pyrex glass ampoule, subjected to freeze-pumping thaw cycles and sealed under vacuum. The solution was kept for 24 h at 60 °C. The polymerization mixture was slowly poured into 100 mL of acetone. The precipitate was dissolved in NMP and again poured into acetone. The precipitated polymer was dried under vacuum at ambient temperature. The yield was 71%.

Measurements. IR spectra were recorded on a Jasco-IR810 spectrometer. ^{1}H NMR and mass spectra were measured with a Bruker Avance Digital 400FT-NMR spectrometer and with a Hewlet Packard 5985A GC/MA/DS spectrometer, respectively. Ultraviolet (UV) spectra were measured with a Shimadzu Model 2401 spectrometer. The differential scanning calorimetry (DSC) and the 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 micrographs were measured with a ZEISS AXILAB polarized microscope. The average molecular weights of the polymers were measured in tetrahydrofuran (THF) with a Waters Alliance V2000 gel-permeation chromatograph (GPC), using monodisperse polystyrenes as standard polymers. The intrinsic viscosity of the polymer was measured in chloroform at 25 °C with an Ubbelohde viscometer.

In order to examine the photoreactivity and the photoalignment of the polymer, its chloroform solutions (2%) were coated on quartz plates using a spin coater, dried at room temperature and irradiated with a high pressure mercury lamp without using cutoff filter by using a polarizer or not. The films were transparent. The thickness was 3 μm on average. To examine the ability of the polymer to align a LC, cells of the polymer film were assembled according to the literature[5] and filled with 4-pentyl-4′-cyanodiphenyl (Aldrich) as the LC containing 1% of dichroic dye (Disperse Blue 1, Aldrich). The absorbances of the dye in the cell at 607 nm as a function of rotational angle were measured by anisotropic spectroscopy for both polar diagram and order parameter(s) of the LC. The order parameters were evaluated by the definition {$S=(A_{//} - A_{\perp}) /(A_{//} +2A_{\perp})$} where $A_{//}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to LPUV light irradiation.[32]

Results and Discussion

Scheme I shows the chemical structure of the monomer PPDM. The dodecylene group-containing styrylpyridine moiety in the maleimide was introduced through the reaction of CCPM with HDPEP. The results of ^{1}H NMR, IR, mass, and UV spectra of the monomer are shown in the Experimental Section.

The radical polymerization of the monomer shown in Scheme I resulted in a good yield (71%) of polyPPDM. The number-average molecular weight and the polydispersity of the polymer were measured to be 51,000 and 2.2, respectively. Its intrinsic viscosity in chloroform at 25 °C was measured to be 0.58 (dL/g). These results mean that this polymer has a considerably high molecular weight. This fact can be attributed to a low termination rate of the propagating polymer radical with the long side chain.[23] The polymer was soluble in various organic solvents such as chloroform, dichloromethane, DMF, and THF. When the polymer was spin coated on a glass plate from the chloroform solution, the film was formed.

The TGA curve of polyPPDM showed the initial decomposition temperature of 340 °C, indicating a considerably thermostable polymer. For reference, a polyimide with a 2-styrylpyridine moiety gave the decomposition temperature at 350 °C.[17] The DSC thermogram of polyPPDM did not show the melting point and the glass transition temperature, which indicates that the polymer has an amorphous structure.

The UV transmittance spectra of polyPPDM film heated at various temperatures are shown in Figure 1. In this figure, at room temperature without UV light irradiation the polymer gave a transmittance of 90% at longer wavelengths than

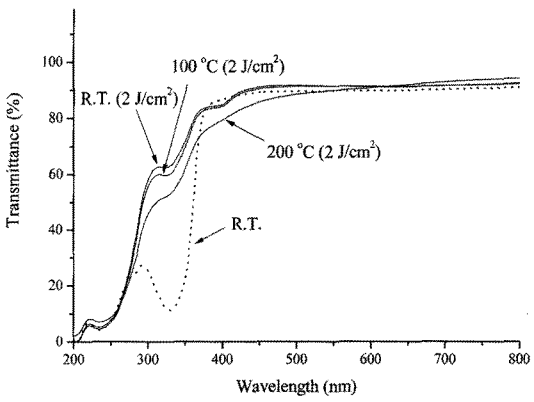


Figure 1. Transmittance spectra of polyPPDM.

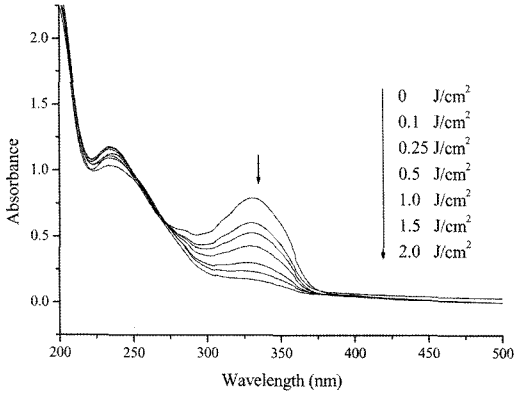


Figure 2. UV spectra of polyPPDM film exposed to unpolarized UV light at exposure doses.

430 nm and that of 12% around 330 nm owing to the absorption band of the carbon-carbon double bond in the 2-styrylpyridine unit. Moreover, the polymer maintained a transmittance of 90% even at 100 °C at an exposure dose of 2 J/cm^2.

The UV absorption spectra of polyPPDM film irradiated at various exposure doses are given in Figure 2. The absorbance at 330 nm decreased rapidly with an increase in the exposure dose up to 1 J/cm^2 and then decreased slowly, which can be a characteristic photoreaction of polymers having photocyclodimerizable groups. The normalized decreases were evaluated to be 24%, 34%, 46%, 63%, 71%, and 78% at 0.1, 0.25, 0.5, 1.0, 1.5, and 2.0 J/cm^2, which means high photochemical reactions of the 2-styrylpyridine unit in the polymer. And the polymer was mostly photocrosslinked after irradiation of 2 J/cm^2. Therefore, these results suggest that the photosensitive polymer has high optical transparency as well as high thermo-stability.

Figure 3 shows the resulting polar diagram of the LC in the cell fabricated from the polymer film exposed to the LPUV light at 0.5 J/cm^2. The diagram gave an oval shape. In particular, the maximum absorbance in the diagram was given at 0° or 180° when the incident beam was cast in a parallel direction to LPUV light irradiation, which indicates

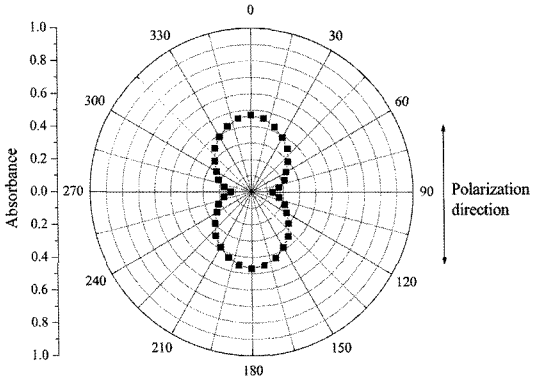


Figure 3. Polar diagram of the LC cell fabricated from polyPPDM film irradiated at an exposure dose of 0.5 J/cm^2 with LPUV light.

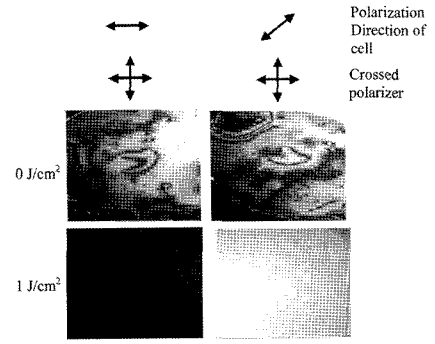


Figure 4. Polarized optical micrographs of the LC cell fabricated from polyPPDM film irradiated with LPUVL.

that the main director of the LC molecules is aligned parallel to the polarization direction.

In order to furthermore confirm the alignment direction of the LC molecules in the cell, polarizing optical micrographs of the cell containing the LC molecules were measured, and are given in Figure 4. As shown in this figure, the two micrographs at the parallel and perpendicular directions showed similar features when the polymer film was not exposed to LPUVL (0 J/cm^2). However, the micrograph at the parallel direction gave black color (opacity) when exposed to LPUVL at 1 J/cm^2, while that at the perpendicular direction displayed light yellow (transparency). This result is attributed to the parallel alignment of the LC molecules. Accordingly, this fact supports the alignment direction of the LC molecules in the polar diagram in Figure 3.

On the other hand, the LC molecules in the cells assembled from photoreactive 2- and 4-styrylpyridine derivatives or cinnamoyl group - containing polyimide films have reported to be aligned perpendicular to the polarization of LPUV light irradiation.[5,14,17] The polymaleimide, polyPPDM, has three aromatic rings in the side group as given in Scheme I. However, the polyimides have four or six aromatic rings in the backbone units whereas only one or two aromatic rings in the side groups.[5,14,17] The LC molecule has two aromatic rings. Considering the π-π interaction of aromatic rings for both the polymaleimide-LC and the polyimides-LC, the LC molecules will interact readily with the side group rather than the backbone unit of the polymaleimide, while those will actively interact with the backbone units of the polyimides rather than the side groups.

To know the maximum alignment of the LC in the polymaleimide film cell with exposure doses of the LPUV light, the orientation order parameter(S)s of the LC were measured with exposure doses and are demonstrated in Figure 5. The positive values of S mean that the LC alignment is parallel to the polarization direction of the LPUV light as explained in the polar diagram of Figure 3. The values showed approximately 0.40 above 0.05 J/cm^2. In particular, it is worthwhile to note that the exposure dose for the polyPPDM film is comparable with that for a polyimide film

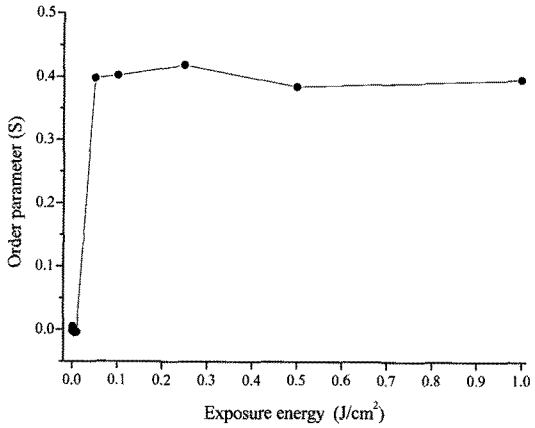


Figure 5. Order parameters (S) of the LC cell fabricated from polyPPDM film with respective exposure doses.

with cinnamoyl group (S=0.42 for 0.05 J/cm^2)[14] or a polymethacrylate film with a 2-styrylpyridine moiety (S=0.35 for 0.06 J/cm^2)[32] reported as a small exposure energy, which could be attributed to the π-π interaction between the polymer films and the LC molecules. Therefore, with properties of good solubility, high thermal stability, high photosensitivity, and excellent optical transparency, this result suggests that this polymaleimide can be a photoalignment material for LC display devices.

Conclusions

A high molecular weight polymaleimide with 2-styrylpyridine unit as a photosensitive group and dodecylene group as a flexible spacer in the side group bonded to the nitrogen atom was synthesized. The polymer was soluble in organic solvents such as chloroform, dichloromethane, DMF, and THF, and its thin film was formed by solution casting. The polymer showed high thermal stability, high photosensitivity, and excellent optical transparency. The polar diagram of the LC molecules in the polymer film cell demonstrated parallel alignment to the polarization direction of LPUV light irradiation. The alignment direction was explained with the aromatic π-π interaction between the side group of the polymer and the LC. The LC in the film cell gave rise to the maximum order parameter of 0.40 at a small exposure dose of 0.05 J/cm^2. Therefore, this polymer will be applicable to birefringent materials for LC display devices.

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