Synthesis and Photoalignment of Soluble Polyimides Containing Photoreactive 2-Styrylpyridine Derivatives as Side Groups

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Abstract: We describe the synthesis and characterization of soluble photoreactive polyimides. The precursor of the polyimides was prepared from 4,4'-(2,2,2-trifluoro-1-phenylethylidene)diphthalic anhydride and 3,3'-hydroxy-4,4'-diaminobiphenyl. The photoreactive polyimides (PI-SP6 and PI-SP12) were then prepared by the polymer reaction of the hydroxyl groups in the precursor polymer with 2-[2-4-\(\omega\)-hydroxalkyloxy]phenyl|ethenyl|pyridines as photoreactive 2-styrylpyridine derivatives (alkyl: hexyl and dodecyl). The photoreactive polymers and the precursor polyimide showed their initial decompositions at temperatures of 350 and 480 °C, respectively. These polymers were soluble in various polar organic solvents and their thin films were easily formed by solution casting. The normalized absorbances of the photoreactive polymers in the film state decreased to ca. 74 % at a 2.0 J/cm\(^2\) exposure dose. Transmittances of their films were ca. 90 % at room temperature and ca. 85 % at 200 °C. These results indicate that the polyimides are photoreactive polymers exhibiting good photosensitivity and high optical transparency. The dichroic ratios of PI-SP6 and PI-SP12 were observed to be 0.019 and 0.030 at a 0.1 J/cm\(^2\) exposure dose; these values indicate that the polymers show the effect of alkylene spacer length on the photoalignment. The liquid crystal in the film cells of the polymers was oriented perpendicularly to the electric vector of the linear polarized UV light. These photoalignment results are discussed in light of the differences between the structures of the photoreactive polyimides obtained in this study and those in a previous report.

Keywords: soluble polyimide, 2-styrylpyridine, dichroic ratio, liquid crystal

Introduction

Polyimides (PIs) are widely used as alignment layers of liquid crystals (LC) for LC display devices because of their advantageous properties, such as adhesion, heat resistance, dimensional stability, and insulation [1]. Until now, the only technique adopted in the LC display industry to treat the surfaces of the PI films used as alignment layers is a rubbing process using fabric velvets [2-4]. However, this process has shortcomings, such as electrostatic problems, dust generation, and poor control of rubbing strength and uniformity [5]. In connection with such disadvantages, some photo-induced LC alignment concepts have been reported [6-10]. With these findings, the photoinduced alignment method using PIs as alignment layers has attracted considerable research interest [11]. For instance, it has been reported recently that polyimides [12-16] as UV-degradable polymers provided LC alignment when the polymers underwent anisotropic photochemical reactions. Furthermore, since 2000, Kee and coworkers have studied the photoalignment of polyimides possessing 4-styrylpyridine units [5], cinnamoyl groups [17], and coumarin units [18] as photodimerizable groups in their side groups. Also, we have reported the synthesis and photoalignment of soluble polyimides [19,20] incorporating photoreactive 2- or 4-styrylpyridine units and two trifluoromethyl groups as the side groups. Thus, our polyimides gave rise to photoinduced alignment and very thin films [19,20]. In

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3,3'-Hydroxy-4,4'-diaminobiphenyl (HAB; Tokyo Kasei) was purified by sublimation. N,N'-Dimethylformamide (DMF; Junsei Chemicals) was distilled over phosphorus pentoxide under vacuum. N-Methyl-2-pyrroldione (NMP; Aldrich) was distilled over phosphorus pentoxide under vacuum. Xylene (Duksan Chemicals) was purified by distillation over a sodium wire under vacuum. Acetone (reagent grade) was distilled in the presence of calcium sulfate. Triphenylphosphine (PPh₃; Aldrich) was used as received. Diethylazodicarboxylate (DEAD; 40 wt% solution in toluene; Aldrich) was used after elimination of toluene. All other reagents were used without purification.

Synthesis

Synthesis of Precursor Polyimide (PI-0)

For the synthesis of PI-0 (Scheme 1), according to the previous report [19,20], a mixture containing 10.00 g (22 mmol) of 3FDA, 4.76 g (22 mmol) of HAB, and 150 mL of NMP was stirred at room temperature for 24 h. To the solution of poly(amic acid) of 3FDA-HAB was added 100 mL of dry xylene and then the solution was heated at 160 °C with stirring for 3 h to eliminate the water formed during the imidization. The crude solution was poured slowly into an excess of methanol to precipitate the polymer. A DMF solution of the precipitate was again poured into an excess of methanol and the precipitated solid was filtered out. The separated precipitate was dried under vacuum at room temperature. The yield was 10.47 g (74%).

Synthesis of Photoreactive Polyimides (PI-SP6 and PI-SP12)

For the synthesis (Scheme 1) of photoreactive polyimide PI-SP6, according to the Mitsunobu reaction [24], 1.00 g (1.6 mmol for molar repeating unit) of PI, 1.90 g (6.4 mmol) of SP6, and 2.93 g (11.2 mmol) of PPh₃ were dissolved in 50 mL of DMF; this solution was cooled to 0 °C and 2.04 mL (11.2 mmol) of DEAD was slowly added. The mixture was warmed to 40 °C and stirred for 72 h. The solution was filtered to remove the formed urea, and the filtered solution was slowly poured into an excess of methanol; the precipitated solid was filtered out. The precipitate was dried under vacuum at room temperature. The yield was 1.05 g (72%).

For the synthesis (Scheme 1) of the photoreactive polyimide PI-SP12, 1.00 g (1.22 mmol for molar repeating unit) of PI, 1.85 g (4.84 mmol) of SP12, and 2.44 g (6.44 mmol) of PPh₃ were dissolved in 50 mL of DMF; this solution was cooled to 0 °C and 2.04 mL (11.2 mmol) of DEAD was added slowly. The solution was reacted for 84 h under the same conditions as those described for PI-SP6. The separation and drying conditions for the

Experimental

Materials

2-[2-(4-(ω-Hydroxyalkyloxy)phenyl]ethenyl]pyridines as 2-styrylpyridine derivatives (hexyl: SP6; dodecyl: SP12) were prepared according to the literature [22]. 4, 4’-(2,2,2-Trifluoro-1-phenylethylidene)triphenylenediamide (3FDA) was prepared using a known method [23].

Scheme 1. Synthesis of photoreactive polyimides.

addition, not only do fluorine-containing polyimides have good solubility but also a high transparency [21].

Despite all of these reports, the relationship between the photoalignment ability and the structures of the polyimides remains unknown. Accordingly, it is necessary to obtain fundamental photoalignment data of photosensitive polyimides having various structures. Therefore, in this study, two soluble photoreactive polyimides, without two phenoxy units in the backbone unit but with one phenyl ring in the side chain, compared to the soluble polyimide with a photoreactive 2-styrylpyridine derivative [19] described above, were synthesized, and their properties, including photoalignment ability, were investigated.
PI-SP12 were the same as those for PI-SP6. The yield was 1.17 g (73%).

Measurements

Fourier transform infrared (FTIR) spectra were obtained using a Jasco FT/IR 620 spectrometer. $^1$H-NMR spectra were measured using a Bruker Avance Digital 400 FT-NMR spectrometer, UV spectra were measured using a Shimadzu Model 2401 spectrophotometer. The initial thermal decomposition temperatures of the precursor polyimide (PI-0) and the photoactive polyimides (PI-SP6 and PI-SP12) were measured under a nitrogen atmosphere at a heating rate of 20 °C min$^{-1}$ using a Dupont 2100 thermal gravimetric analyzer (TGA). The thermograms for the glass transition temperatures of the polymers were measured under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$ using a Dupont 2000 differential scanning calorimeter (DSC). The intrinsic viscosities of the polymers were measured in DMF at 25 °C using a Ubbelohde viscometer. A high-pressure mercury lamp was used as the light source for the investigation of the photoalignment of the polymers.

To examine the photoalignment of the photoactive polyimides, trifluoroacetic acid (TFA) solutions (1.5 %) of PI-SP6 and PI-SP12 were coated on quartz plate using a spin coater and then dried at room temperature. The thickness of the films was in the range 30 to 50 μm; they were irradiated with a high-pressure mercury lamp using a polarizer with a cutoff filter under 290 nm. The photoalignment of the polymers was evaluated from the dichroic ratio [DR = ($\lambda_\perp - \lambda_\parallel$)/($\lambda_\perp + \lambda_\parallel$)], where $\lambda_\perp$ and $\lambda_\parallel$ were the absorbances perpendicular and parallel to the linearly polarized UV light (LPUVL) [19].

To evaluate the ability of the photoactive polyimides to align an LC compound, cells of the polymers were assembled according to the literature [5,19] and filled with 4-pentyl-4′-cyanodiphenyl (Aldrich) as the LC compound containing 1 % of a dichroic dye (Disperse Blue1, Aldrich). The absorbance of the dye at 607 nm, as a function of rotational angle, was measured by the LPUVL with a UV spectrophotometer as described above; and polar diagrams were obtained using the absorbances [5,19].

Results and Discussion

Characterization of PI-0, PI-SP6, and PI-SP12

For confirmation of the successful synthesis of the precursor polyimide PI-0 and the photoactive polyimide PI-SP6, the IR spectra are shown in Figures 1(a) and 1(b). As given in Figure 1(a), the band at 1380 cm$^{-1}$ is attributed to the C-N group of the polyimide [25] and the bands at 1778 and 1720 cm$^{-1}$ are due to symmetrical and asymmetrical carbonyl stretchings of the imide group [21,25]. Also, the band at 3450 cm$^{-1}$ corresponds to the two hydroxyl groups in the HAB unit of the polyimide [21,25]. In Figure 1(b), the peak of the two hydroxyl groups of the HAB unit at 3450 cm$^{-1}$ in spectrum of PI-0 disappeared almost completely in the spectrum of PI-SP6 because of the Mitsunobu reaction. The residual small peak at 3450 cm$^{-1}$ in spectrum (b) of the photoactive polyimide can be attributed to moisture in the air, considering the NMR spectra of the precursor polyimide and the photoactive polyimide in Figures 2(a) and 2(b). The band at 1585 cm$^{-1}$ is attributed to the ethenyl group of the 2-styrylpyridine unit in PI-SP6 [19]. The peaks of the carbonyl groups of the imide groups of PI-SP6 at 1778 and 1720 cm$^{-1}$ and the peak of the C-N groups of the imide groups of PI-SP6 at 1380 cm$^{-1}$ were similar to those of PI-0. The IR spectrum of PI-SP12 showed almost the same peaks as that of PI-SP6.
Table 1. Yields and Intrinsic Viscosities of the Precursor Polyimide (PI-0) and the Photoreactive Polyimides (PI-SP6 and PI-SP12)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>Conversion (%)</th>
<th>Intrinsic viscosity (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-0</td>
<td>76</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td>PI-SP6</td>
<td>86</td>
<td>100</td>
<td>0.52</td>
</tr>
<tr>
<td>PI-SP12</td>
<td>79</td>
<td>100</td>
<td>0.47</td>
</tr>
</tbody>
</table>

*Measured using $^1$H NMR spectrometer with DMSO-$d_6$ as the solvent.

*Measured using an Ubbelohde viscometer in DMF at 25°C.

Figure 3. TGA thermograms of precursor polyimide PI-0 (—) and photoreactive polyimides PI-SP6 (---) and PI-SP12 (-----).

NMR spectra of the precursor polyimide PI-0 and photoreactive polyimide PI-SP6 are shown in Figures 2(a) and (b). As given in Figure 2(a), the peak at 10.1 ppm corresponds to the protons of the two hydroxyl groups in the HAB unit and the peaks between 7.2 and 8.0 ppm are assigned to the protons of the aromatic rings in the polyimide because the chemical shifts were the same as those in the spectra of HAB and 3FDA [19,20]. In Figure 2(b), the signal at 10.2 ppm in the spectrum of the precursor polyimide (Figure 2a) disappeared because all of the two hydroxyl groups in the HAB unit reacted with the hydroxyl group of SP6, indicating that the conversion for the reaction of the precursor polymer with SP6 was 100%. The peaks between 6.8 and 8.7 ppm correspond to the protons of the aromatic rings in the backbone and the side chains. The signals between 3.7 and 4.3 ppm are assigned to 9 and 14 hydrogen atoms, and the peaks between 1 and 1.7 ppm are assigned to hydrogens 10−13. Although the NMR spectrum of PI-SP12 is not given here, it was almost the same as that of PI-SP6. However, the area of the peaks of PI-SP12 between 1 and 1.7 ppm was larger than that of PI-SP6 because of the dodecyl group of PI-SP12 and the hexyl group of PI-SP6.

The yields and the intrinsic viscosities of PI-0, PI-SP6, and PI-SP12 are given in Table 1 along with the conversions of the latter two polyimides. As shown in Table 1, the precursor polyimide and the two photoreactive polyimides were synthesized in comparatively good yields (76, 86, and 79%). The conversions of PI-0 to PI-SP6 and PI-SP12 were 100%, as already explained in the discussion of the spectra of the latter two polymers. Accordingly, the polymer reaction of the precursor polyimide with SP6 or SP12 by the Mitsunobu reaction was excellent. Their average molecular weights were not measured because they were not soluble in tetrahydrofuran. Instead, their intrinsic viscosities were measured in DMF and are given in Table 1. The photoreactive polyimides have lower intrinsic viscosities than does the precursor polyimide, even though the former polymers should have high intrinsic viscosities relative to the latter polymer because of the coupling reaction of the latter polymer with SP6 or SP12. This result is similar to those of our previous studies [19,20,26]. The first reason for this result could be the breaking of the backbone of the precursor polymer of the photoreactive polymers with stirring during the polymer reaction [19,20,26]. The second reason could be the structural change (branching formation) of the polymers after the coupling reaction of PI-0 with PI-SP6 or PI-SP12, which would have an influence on the viscosity. In addition, the precursor polymer and the photoreactive polymers were soluble in polar solvents, such as DMF, NMP, dimethyl sulfoxide (DMSO), formic acid, and TFA, and their thin films were easily formed by solution casting. However, the films were not flexible. Comparing this result with the properties of the photoreactive polyimides obtained in our previous study [19], this inflexibility seems to be due to the absence of the two phenoxy groups in the backbone unit and the presence of the phenyl ring, instead of one trifluoromethyl group in the three polymers.

Thermal Properties of Polymers

The TGA thermograms of the precursor polyimide PI-0 and photoreactive polyimides PI-SP6 and PI-SP12 are given in Figure 3. PI-0 showed an initial thermal decomposition temperature at ca. 480 °C. The temperature was 10 °C higher than that of the precursor polymer of the photoreactive polyimides described in the previous reports [19,20]; this result might be attributed to the absence of the two phenoxy groups in the backbone and the presence of the phenyl group in the side chain of PI-0. Also, PI-SP6 and PI-SP12 displayed first decomposition temperatures at ca. 350 °C and second decomposition temperatures at ca. 450 °C, indicating that the 2-styrylpyridine derivative units as the side groups of the photoreactive polymers preferentially decompose at the former temperature and the backbone groups of the photoreactive polymers decompose at the latter tempera-
As shown in these thermograms, the residual weights of PI-0, PI-SP6, and PI-SP12 at 800 °C were ca. 65, 50, and 40 %, respectively. In addition, the DSC thermograms of PI-0, PI-SP6, and PI-SP12 did not exhibit glass transition temperatures or melting points, indicating that the polymers are rigid and amorphous.

Photoreactions of Photoreactive Polyimides
The UV spectra of the PI-SP6 film irradiated with unpolarized UV light at various exposure doses are given in Figure 4(a). As shown, the absorption band at ca. 330 nm decreased upon an increasing the exposure dose because of the photoreactions of the 2-styrylpyridine groups [19,27]. Figure 4(b) illustrates the normalized absorbances of the photoreactive polyimides PI-SP6 and PI-SP12 at various exposure doses. The normalized absorbances decreased upon increasing the UV irradiation energy because of the photochemical reactions of the styrylpyridine groups. The UV absorbances of PI-SP6 and PI-SP12 at an exposure dose of 2.0 J/cm² decreased to ca. 75 %. When the photochemical reactions reached this level, the polymers were mostly photocrosslinked because the 2-styrylpyridine groups in the side chain underwent intermolecular photocyclodimerization [5,19]. The transmittance spectra of the PI-SP6 and PI-SP12 films exposed to UV energy of 2.0 J/cm² and heated at various temperatures are given in Figure 5. The films of the polymers maintained transmittances of ca. 90 % at room temperature and of ca. 85 % at 200 °C at wavelengths higher than 400 nm. These results suggest that the photoreactive polyimides PI-SP6 and PI-SP12 have high optical transparencies [19,20].

Photoalignment of Photoreactive Polymers
Figure 6 shows the DR values of the films of PI-SP6 and PI-SP12 at various LPUV exposure doses at 330 nm. The maximum DR values of PI-SP6 and PI-SP12 were 0.019 and 0.030 at the 0.1 J/cm² exposure dose. Ichimura and coworkers [26] reported that a polymethacrylate with SP12 moieties had a higher DR value than that with SP6 moieties. For the increasing tendency of the DR values with respect to the alkyl spacer length, the DR values of our polymers agree with those of the polymethacrylates. This fact might be attributed to the differences in flexibility between the hexyl and dodecyl groups. Because PI-SP6 and PI-SP12 had positive DR values, as shown in Figure 6, their photoalignment was perpendicular to the electric vector E of the LPUV light. Also, PI-SP6 and PI-SP12 exhibited their maximum DR values even at a small initial exposure dose (0.1 J/cm²) and their DR values decreased upon increasing the exposure above this dose. The former result indicates that a small amount of photocyclodimerization of 2-styrylpyridine units contributes to their photoalignment because the reaction is important in the initial stage. However, the
latter result might be due to an unfavorable photochemical reaction affecting their alignment because these phenomena are related with increasing exposure doses. As mentioned above, the maximum DR value of PI-SP6 in this study was 0.019, whereas that of the photoreactive polyimide with SP6 moieties in the previous report [19] was 0.025. Because the former polyimide does not have the two phenoxy groups in the backbone unit, but has one phenyl ring as the side chain, compared to the latter polyimide [19], there should be a difference in both the flexibility of the backbone unit and the density of the photoreactive group between the two polymers. Accordingly, the difference of the DR values might be attributed to these structural factors.

Figure 7 illustrates polar diagrams of LC cells fabricated from the films of photoreactive polyimide PI-SP6 after irradiation with LPUVL at various exposure doses. The arrow indicates the electric vector of LPUVL.

Figure 6. Dichroic ratios of the films of photoreactive polyimides PI-SP6 (■) and PI-SP12 (○) exposed to LPUVL at various exposure doses. The diagram at 0 J/cm² shows a circle, which means an isotropic structure in all directions. On the other hand, the diagrams at 0.5 and 2 J/cm² show oval shapes. The maximum absorbances in the diagrams were obtained at 90°. The photoreacted polyimide was aligned perpendicularly, as explained above. Therefore, these results indicate that the alignment direction of the LC molecules with the dichroic dye molecules is induced perpendicularly to the LPUVL by that of the photoreacted polyimide PI-SP6. Moreover, PI-SP12 showed the same result. This result is in agreement with that of the photopolyimide described in the previous report [19] with the same SP6 moiety-containing side chain, but the other backbone structure. Accordingly, the side chain structure of the photoreactive polyimides may possibly be more important than the backbone structure for the photoalignment of the LC molecules.

Conclusions

A new, soluble polyimide PI-0 was synthesized from 3FDA and HAB. Photoreactive polyimides PI-SP6 and PI-SP12, with 2-styrylpyridine moieties as photosensitive side chain groups, were prepared using the Mitsunobu reaction. These polymers were soluble in various polar organic solvents and their films were easily formed by solution-casting. The initial decomposition temperatures of these polymers were ca. 350 °C, and they are amorphous materials. Moreover, they showed high residual weights, even at 800 °C. The normalized absorbances of PI-SP6 and PI-SP12 in the film state decreased to ca. 75% at a 2.0 J/cm² exposure dose. The transmittances of the polymer films were ca. 90% at room temperature and ca. 85% after annealing at 200 °C for 30 min. These polymers are photoreactive polyimides with good transparency, good thermal stability, and good solubility. For the photoalignment of photoreactive polyimides, the DR values of PI-SP6 and PI-SP12 were 0.019 and 0.030 at a 0.1 J/cm² LPUVL exposure dose; these values decreased upon increasing the exposure doses above 0.1 J/cm². This result indicates that the photoreactive polyimide films show the effect of the alkyne spacer length on the photoinduced alignment; the intral intercyclodimerization of 2-styrylpyridine units contributes to their photoalignment. In addition, polar diagrams showed that low molecular LCs aligned perpendicularly with the LPUVL.

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