The novel polyimide having spiropyran groups on their side chain was synthesized, and the thin films of the polyimide on glass substrates were prepared. It was confirmed that the surface wettability of these films were changed from around 76° to around 67° by UV (365 nm) light irradiation, and the surface wettability were reversibly changed from 67° to 76° by Vis (visible) light irradiation. These wettability changes were photo-cyclized three times. The UV-Vis spectroscopy analysis indicates that the photo-induced isomerization of the spiropyran group leads to reversible changes on the surface of the polyimide films.

Keywords: Polyimide, Spiropyran, UV-Vis light irradiation, Reversible control, Surface wettability

1. Introduction

Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications [1,2]. Our research group has systematically investigated the synthesis and characterization of soluble polyimides based on aromatic diamines bearing long-chain alkyl groups, and the results from this research were described in the review papers [3,4].

Recently, the printed electronics technology, by which the conductive lines (circuit) can be printed onto the plastic substrate, has been investigated. Polyimide films are the most promising plastics for use in printed electronics because of their high thermal stability. Various approaches such as the use of repellent pore-structured polyimide films [5], the surface energy controlled ink-jet printing with UV irradiation [6], have been investigated to obtain the fine patterning. The authors have investigated the surface wettability control of polyimides having various functional groups such as long-chain alkyl groups, t-Boc group, etc. by UV light irradiation [7-19]. These wettability changes are irreversible from the hydrophobicity to the hydrophilicity by UV light irradiation. The authors have also investigated reversible control of surface wettability of polyimides having azobenzene group on their side-chain by UV-Vis (ultraviolet-visible) light irradiation [20]. In this paper, the authors report that the reversible wettability change of the polyimide having spiropyran groups by UV-Vis light irradiation. This concept is based on the fact that spiropyran-merocyanine photoisomerization showing in Fig. 1. The similar reversible wettability changes of polymer surface based on spiropyran have been previously reported [21-23].

Fig. 1. Photoisomerization of spiropyran.
2. Experimental
2.1. Materials
3,4’-Oxydiphthalic anhydride (3,4’-ODPA; a-ODPA) from Shanghai Research Institute of Synthetic Resins and 3,3’-dihydroxy-4,4’-diaminobiphenyl (HAB) from Tokyo Chemical Industry Co., Ltd. (TCI) were used after drying in a vacuum oven. Ultra-pure grade of N-methyl-2-pyrrolidone (NMP) was purchased from Kanto Chemical Co., Inc. and used as received. Other reagents were purchased from TCI or Wako Pure Chemical Industries (Wako) and used as received.

2.2. Synthesis of novel polyimide having spiropyran groups on their side chain
Polyimide having spiropyran groups on their side chain (3,4’-ODPA/HAB-spiro) was synthesized by introducing spiropyran by Mitsunobu reaction into the polyimide containing phenolic hydroxyl groups (3,4’-ODPA/HAB; base-polyimide) (Scheme 1).

![Scheme 1. Synthesis of polyimide having spiropyran groups.](image)

The base-polyimide was synthesized from 3,4’-ODPA, as a tetracarboxyclic dianhydride and HAB as a diamine monomer (Scheme 1). Two step polymerization systems including poly(amic acid) synthesis and chemical imidization were performed. The poly(amic acid) was obtained by reacting the mixture of diamines with an equimolar amount of tetracarboxylic dianhydride at room temperature for 12 h under an argon atmosphere. The polyimide was obtained by chemical imidization at 120 °C in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent. $^1$H-NMR (500 MHz, DMSO-d$_6$) δ (ppm): 10.13 (d, 2H, OH), 8.06-8.01 (broad peak, 2H), 7.82-7.74 (broad peak, 4H), 7.67-7.58 (broad peak, 6H, Ha, Hb, Hc, Hd, He, Hf).

3,4’-ODPA/HAB (0.100 g, 0.204 mmol), 1-(2-hydroxyethyl)-3,3-dimethylindolino-6’-nitrobenzopyrylospiran (0.287 g, 0.815 mmol) and triphenylphosphine (0.321 g, 1.223 mmol) were dissolved in 10 mL of dry DMF. After cooling the solution to 0 °C, diethyl azodicarboxylate (DEAD, 40% in toluene, 0.56 mL, 1.223 mmol) was slowly added and the mixture was stirred at room temperature for 24 h. The reaction solution was slowly added to 50 mL of methanol, and the precipitated polyimide was collected. $^1$H-NMR (500 MHz, DMSO-d$_6$) δ (ppm): 8.10-6.58 (broad peak, 28H, ArH), 5.79-5.71 (broad peak, 2H, ArH), 4.43-4.18 (broad peak, 4H, -N-CH$_2$-C$_6$H$_2$-O-), 3.46 (broad peak, 4H, -N-C$_6$H$_2$-CH$_2$-O-), 1.23-1.04 (broad peak, 12H, CH$_3$).

2.3. Measurements
$^1$H NMR spectra were measured on a JEOL JNM-AL500 FT NMR in DMSO-d$_6$ with tetramethylsilane (TMS) as an internal reference. Size exclusion chromatography (SEC) measurements were performed in NMP containing 10 mM LiBr at 40 °C with a TOSOH HLC-8020 equipped with a TSK-GEL ALPHA-M using a series of polystyrenes as standard. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in air or under nitrogen (50 mL/min), and 10% weight loss temperatures (T$_{d10}$) were calculated from the second heating scan after cooling from 250 °C. Differential scanning calorimeter (DSC) traces were measured on a Shimadzu DSC-60 under nitrogen and glass transition temperatures (T$_g$) were read at the midpoint of the heat capacity jump from the second heating scan.
Polyimide thin-films were obtained as follows: 3.0 wt % polyimide solution in NMP were cast on glass substrates and the solution were slowly evaporated by heating at approximately 100-120 °C until the films were dried, then the films were dried in a vacuum oven at 100 °C for 3 h. Water contact angles were measured by Slimage mini (Excimer, Inc., Japan). UV light irradiation were performed.
using UV lamp unit LC-L1V3 (λ max; 365 nm, 100 mW/cm², Hamamatsu Photonics. Inc., Japan) at the 50 mm irradiation distance between lamp and sample and Vis light irradiation were performed using LED lamp unit (λ max; 465, 560 nm, Nichia Chemical. Inc., Japan) at the 150 mm irradiation distance between lamp and sample. IR (ATR) measurements were performed by JASCO FT/IR-470 with ATR PRO450-S (Ge prism). Solid state surface reflected UV-Vis measurements were performed by JASCO V-670 double-beam spectrophotometer with integrating sphere.

3. Results and discussion

3.1. Synthesis of polyimide having spiropyran groups

As a result of the 1H-NMR measurement of the synthetic polyimide, the introduction of spiropyran into the polyimide was confirmed by the increase of aromatic peak and appearance of the methylene group and the methyl group peak based on spiropyran unit. In addition, the conversion in Mitsunobu reaction was estimated to be nearly 100%, because the peak of phenolic hydroxyl groups based on HAB disappeared in the spectrum of 3,4’-ODPA/HAB-spiro (Fig. 2).

![Phenolic OH](image)

Fig. 2. 1H-NMR spectra of polyimides; (a) 3,4’-ODPA/HAB, (b) 3,4’-ODPA/HAB-spiro.

3.2. General Properties of Polyimides

The obtained polyimides showed the good solubility in polymerization solvent, NMP. The molecular weights of obtained polyimides were measured by SEC (Mn; 32500~40800, in NMP/10 mM LiBr calibrated with standard polystyrenes) (Table 1). Although these molecular weights were relatively low in comparison with general polyimides, the obtained polyimides showed the good film forming ability.

The thermal properties of these polyimides were estimated by thermal degradation temperatures (Td10; 384~400 °C in air, 385~403 °C under nitrogen) and glass transition temperatures (Tg; 238 °C), and it is recognized these polyimides can be ranked as heat resistant polymers (Table 1). These data suggested that the heat resistance was lowered by the introduction of spiropyran units.

| Polyimide            | Molecular Weight | Td10 (℃) | Tg (℃) |
|----------------------|------------------|----------|--------|
| 3,4’-ODPA/HAB        | 32500            | 400      | 269    |
| 3,4’-ODPA/HAB-spiro  | 40800            | 384      | 238    |

* Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. * Determined by TGA at a heating rate of 10 °C/min. * Measured by DSC at a heating rate of 20 °C/min in N2 on second heating.

3.3. Reversible surface wettability control by UV-Vis light irradiation on polyimide thin films and surface analysis

The polyimide thin films were irradiated by UV light (365 nm), then the contact angles for the water were measured. The water contact angles of the polyimide (3,4’-ODPA/HAB-spiro) decreased with UV light irradiation time (Fig. 3). The contact angle after UV light irradiation for 2.5 minutes decreased from 76° to 67°, this value (67°) almost completely recovered to the initial value (76 °) by subsequent irradiation of Vis light. On the other hand, the contact angle of the polyimide film irradiated with UV light for 5 minutes or more did not recover completely even after irradiation with Vis light. These incomplete reversible changes are probably due to the irreversible formation of hydroxyl groups occur on the surface by UV irradiation for 5 minutes or more. This speculation was based on the fact that hydroxyl groups irreversibly generated probably due to scission, cleavage, or photo-oxidation of the spiropyran unit by strong UV irradiation to the polyimide film surface, while hydroxyl groups did not generate by mild UV irradiation (2.5 minutes, 100 mW/cm²). The ATR spectra supporting above speculation are shown in Fig. 4. The absorption of hydroxyl groups (around 3250 cm⁻¹) increased in the ATR spectra of the film after strong UV light irradiation, while this absorption did not increase after mild UV light irradiation. Therefore, it is considered that the complete reversible change of the surface wettability is only possible by mild UV light irradiation for 2.5 minutes. It is also considered that these reversible wettability changes are based
on the polarity change of spiropyran-merocyanine photoisomerization as showing in Fig. 1.

The water contact angles on polyimide films repeatedly irradiated UV and Vis light under the condition for enabling reversible change were measured (Fig. 5). Consequently, the reversible wettability change in 3 cycles were possible, in other words, these reversible changes were photo-cyclized three times.

Solid state surface reflected UV-Vis measurements were carried out on the polyimide films that repeatedly irradiated UV and Vis light (Fig. 6). These measurements are performed based on the feature that the merocyanine structure after UV light irradiation has absorption in the visible region (>500 nm), and then absorption in the visible region decreases after Vis light irradiation. As shown in Fig. 6, the estimated spectral changes by the photoirradiation were confirmed, and these changes were observed repeatedly. Above data suggests that photoisomerization of the spiropyran shown in Fig. 1 occurs on the polyimide film.

The color of polyimide films before and after UV light irradiation and after Vis light irradiation is shown in Fig. 7. The color of the polyimide film changed from original pale brown color to purple...
color by UV light irradiation and then returned to pale brown color by Vis light irradiation. Consequently, the photoisomerization of spiropyran can be also confirmed from the color change of the film. In addition, the reversible change of such color and UV-Vis spectra have been recognized even in the case in which the reversible wettability change is imperfect by strong UV light irradiation (5 minutes or more). Therefore, it is speculated that these wettability changes described in this paper are only affected by the nature of top surface of polyimide films.

![UV Vis](image)

**Fig. 7.** The color of polyimide films (3,4’-ODPA/HAB-spiro) before and after UV light irradiation, and after Vis light irradiation.

4. **Conclusion**

The novel polyimide having spiropyran groups on their side chain was successfully synthesized by introducing spiropyran groups by Mitsunobu reaction into the polyimide containing phenolic hydroxyl groups. It was confirmed that the surface wettability of these films were changed from around 76° to around 67° by UV light irradiation, and the surface wettability were reversibly changed from 67° to 76° by Vis light irradiation. These wettability changes were photo-cyclized three times. The UV-Vis spectroscopy analysis indicates that the photo-induced isomerization of the spiropyran group leads to a reversible change on the surface of the polyimide films. Although this research presents the novel functional polyimide, the degree of wettability changes are not sufficient. The further research such as the modification of polyimide structure having spiropyran groups, the introduction of alkyl spacers between spiropyran group and polymer backbone, and intensive surface analytical experiments have been investigated to enhance the wettability change.

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