Surface Wettability Controllable Polyimide Bearing o-Nitrobenzyl Group by UV Light Irradiation

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Novel diamine monomer (o-NO₂Bn-DA), having o-nitrobenzyl (o-NO₂Bn) group was synthesized from o-nitrobenzylalcohol as a starting material. The polyimides were synthesized from 3,4’-oxydiphthalic anhydride (3,4’-ODPA) as a dianhydride and o-NO₂Bn-DA by two steps polymerization systems. The thin films of obtained polyimides were irradiated by UV light (λmax; 365 nm), and the contact angles for the water decreased from near 90° (hydrophobicity) to minimum 60° (hydrophilicity) in proportion to irradiated UV light energy. The addition of photoacid generator (PAG) accelerated these changes of wettability. From the result of surface analyses such as ATR, it is recognized that the hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface. Consequently, it is considered that the photoreaction of o-NO₂Bn group significantly affects the changes of wettability by UV light irradiation.

Keyword: polyimide, o-nitrobenzyl group, UV light irradiation, surface wettability

1. Introduction
Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications [1,2]. Since conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly(amic acid) precursors, and then either thermally or chemically imidized. Extensive research has been carried out to improve the solubility of polyimides, and our research group has systematically investigated the synthesis and characterization of soluble polyimides based on aromatic diamines having long-chain alkyl groups [3-9].

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 [10], the surface energy controlled ink-jet printing with UV irradiation [11], have been investigated to obtain the fine patterning. Recently, the authors also have investigated the surface wettability control of polyimides bearing long-chain alkyl groups by UV light irradiation [8,12-17]. In this paper, we report the synthesis and properties of the novel surface wettability controllable polyimides based on o-nitrobenzyl (o-NO₂Bn) group. The features of our research have been to introduce the functional diamine monomer segments having hydrophobic units and photo reactive units into the polyimide backbone. Until now, the authors have mainly investigated the surface wettability control by UV irradiation (λmax; 254 nm). However, 254 nm UV is powerful, and many organic compounds are easily decomposed by photo-oxidation. In fact,
the wettability change of the polyimides developed in our laboratory seems to be caused mainly by the photo-oxidation reactions. In addition, the energy efficiency of 254 nm UV irradiation is worse than the one of 365 nm UV irradiation that is preferable wavelength in industry. Consequently, we have focused on o-NO₂Bn group that is the protecting group of phenolic hydroxyl group and easily deprotected by UV light irradiation at 365 nm [18,19].

2. Experimental

2.1. Materials

3,4'-Oxydiphthalic anhydride (3,4'-ODPA; a-ODPA) from Shanghai Research Institute of Synthetic Resins was 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 diamine monomer having o-NO₂Bn group

o-Nitrobenzyl 3,5-di(3-aminophenyl) benzoate (o-NO₂Bn-DA) was synthesized by two step reactions from o-nitrobenzyl alcohol as a starting material via esterification with 3,5-dibromobenzoic acid using DCC/DMAP, then Suzuki coupling reaction with 3-aminophenylboronic acid (Scheme 1). These synthetic procedures are described in the previous literature [9].

Scheme 1. Synthesis of o-NO₂Bn-DA

The analytical data of o-NO₂Bn-DA are as follows: Mp 151.79 °C; ¹H NMR (500 MHz, CDCl₃, δ): 3.80 (s, 4H, -NH₂), 5.84 (s, 2H, H₆), 6.74 (d, 2H, J = 8 Hz, H₂), 6.90 (s, 2H, H₁₀), 7.07 (d, 2H, J = 7.4 Hz, H₅), 7.29 (t, 2H, J = 8.2 Hz, H₁), 7.53 (t, 1H, J = 6.7 Hz, H₃), 7.65 – 7.69 (m, 2H, H₁), 7.98 (s, 1H, H₇), 8.16 (d, 1H, J = 8.2 Hz, H₉), 8.25 (s, 2H, H₇) ppm; IR (ATR): 3370 (-NH₂), 2925 (C-H), 1720 (C=O) cm⁻¹, 1520 (NO₂) cm⁻¹.

2.3. Synthesis of polyimide bearing o-NO₂Bn group

The polyimides bearing o-NO₂Bn group were synthesized from 3,4'-ODPA, as a tetracarboxylic dianhydride and a novel functional diamine monomer, o-NO₂Bn-DA. 3,5-Diamino-N-tetradeacylbenzamide (ADBA-14) [5] having a long-chain alkyl group and conventional diamine monomer; 4,4’-diaminodiphenylether (DDE) were used as a reference (Scheme 2). Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed. The poly(amic acid)s were 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 polyimides were obtained by chemical imidization at 120 °C in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent [3-9,12-17].

Scheme 2. Synthesis of polyimides based on 3,4'-ODPA/o-NO₂Bn-DA (DDE, ADBA-14)
2.4. Measurement

$^1$H NMR spectra were measured on a JEOL JNM-AL500 FT NMR in CDCl$_3$ or dimethyl sulfoxide-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 $T_g$ transition temperatures ($T_d$) were measured by DSC at a heating rate of 20 °C/min. The thermal properties of these polyimides were estimated by thermal degradation temperatures ($T_{d10}$; 348–597 °C in air, 392–596 °C under nitrogen) and glass transition temperatures ($T_g$; 198–280 °C). Although the introduction of the functional monomer, $o$-$NO_2$Bn-DA or ADBA-14 lowered the thermal stability, it is recognized that all polyimides still can be ranked as heat resistant polymers.

3. Results and Discussion

3.1. Synthesis of polyimide having $o$-$NO_2$Bn group

Since the reductive reaction of dinitro precursor cannot be used in the diamine synthesis having $o$-$NO_2$Bn group, Suzuki coupling reaction is an effective technique. However, it was a problem that the yield of Suzuki coupling reaction was as low as 25% in the synthesis of $o$-$NO_2$Bn-DA, and future improvement is desired. All polyimides were successfully synthesized without any problems.

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; 6500–11200, in NMP/10 mM LiBr calibrated with standard polystyrenes) (Table 1). Although these molecular weights were relatively low in comparison with general polyimides, the all of obtained polyimides showed the good film forming ability.

Table 1. General properties of polyimides based on $o$-$NO_2$Bn-DA (ADBA-14, DDE).

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Diamine</th>
<th>Molecular Weight</th>
<th>$T_{d10}$</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3,4'$-ODPA</td>
<td>$o$-$NO_2$Bn-DA</td>
<td>ADBA-14</td>
<td>DDE</td>
<td>in Air (under N$_2$)</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>6500</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>39100</td>
</tr>
</tbody>
</table>

* Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. #10% Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. $^a$ Measured by DSC at a heating rate of 20 °C/min in N$_2$ on second heating.

The thermal properties of these polyimides were estimated by thermal degradation temperatures ($T_{d10}$; 348–597 °C in air, 392–596 °C under nitrogen) and glass transition temperatures ($T_g$; 198–280 °C). Although the introduction of the functional monomer, $o$-$NO_2$Bn-DA or ADBA-14 lowered the thermal stability, it is recognized that all polyimides still can be ranked as heat resistant polymers.

3.3. Surface wettability control by UV light irradiation on polyimide thin films

The polyimide thin films were irradiated by UV light (365 nm, 0, 20, 40 J; 6 J ≈ 60 sec), then the contact angles for the water were measured.

Figure 1 shows UV light irradiation energy dependence of water contact angles of polyimide films based on $3,4'$-ODPA/$o$-$NO_2$Bn-DA, $3,4'$-ODPA/ ADBA-14, $3,4'$-ODPA/DDE respectively. The initial water contact angles of polyimide films based on $3,4'$-ODPA/$o$-$NO_2$Bn-DA and $3,4'$-ODPA/DDE before UV light irradiation show the similar value, around 90°. The water contact angles of the polyimide based on $3,4'$-ODPA/$o$-$NO_2$Bn-DA decreased from 88.1° to 58.8° by UV light irradiation (Figure 2), while the water contact angle of the polyimide based on $3,4'$-ODPA/DDE showed the similar value even after UV light irradiation. It is speculated that the typical photoreaction of $o$-$NO_2$Bn group occurs and hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface (Figure 3). The initial water contact angle of $3,4'$-ODPA/ADBA-14 based polyimide was as
high as 105° due to the hydrophobic nature of long-chain alkyl group, and somewhat decreased by UV light irradiation. This change is probably due to the photo-oxidation reaction generally observed in the case of polyimides bearing long-chain alkyl groups [8,12-17].

Figure 1. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/o-NO2Bn-DA, 3,4'-ODPA/ADBA-14, 3,4'-ODPA/DDE.

![Figure 1](image1.jpg)

Figure 2. Water contact angle change of 3,4'-ODPA/o-NO2Bn-DA by UV light irradiation.

![Figure 2](image2.jpg)

Figure 3. Elucidated reaction mechanism of o-NO2Bn group by UV light irradiation.

3.4. Effect of Photoacid Generator

The effect of the addition of photoacid generator (PAG) has been examined to accelerate the surface wettability changes and speculate the photo reaction mechanism, and it was confirmed that the addition of PAG (5-10 wt%) was effective for the acceleration of surface wettability changes from hydrophobicity to hydrophilicity [17]. Figure 4 shows the changes of water contact angles of the polyimide films based on 3,4'-ODPA/DDE and 3,4'-ODPA/o-NO2Bn-DA with or without PAG (CPI-100P; 5 wt%).

![Figure 4](image3.jpg)

By the addition of the PAG, the water contact angle of 3,4'-ODPA/o-NO2Bn-DA extremely decreased from near 90° to minimum 25° in proportion to irradiated UV light energy. This result indicated that PAG accelerated the cleavage of o-NO2Bn and the generation of hydrophilic groups. However, the water contact angle of 3,4'-ODPA/DDE polyimide non-containing o-NO2Bn group also decreased as the same level as the polyimide containing o-NO2Bn group. However, it was observed that the surface of a film deteriorated after UV light irradiation in case of 3,4'-ODPA/DDE polyimide with PAG. Therefore, it can be speculated that the acid species generated by PAG cleave not only side-chain o-NO2Bn group but also polyimide main chain in some degree (Figure 5).

3.5. Surface Analysis

The surface analyses of the polyimide films were performed by ATR. ATR measurements of the polyimide surface after UV light irradiation support the assumption that the generation of the hydrophilic functional groups such as COOH and OH groups occurred. The absorption of OH groups around 3300 cm\(^{-1}\) increase, the absorption of nitro group around 1520 cm\(^{-1}\) decrease with the irradiation of UV light (\(\lambda_{max}; 365\) nm) (Figure 6).
4. Conclusion

The novel diamine monomer for surface wettability controllable polyimides having \( o\)-\( NO_2Bn \) group and the corresponding polyimides were successfully synthesized. The thin films of obtained polyimides were irradiated by UV light (\( \lambda_{\text{max}}; 365 \text{ nm} \)), and the contact angles for the water decreased from near 90° (hydrophobicity) to minimum 60° (hydrophilicity) in proportion to irradiated UV light energy. Furthermore, the addition of the PAG accelerated the surface wettability change and the contact angles for the water eventually decreased as low as 25°. The introduction of \( o\)-\( NO_2Bn \) group is the effective method for the improvement of surface wettability control of polyimides by UV light irradiation. From the result of surface analysis (ATR), it is recognized that the nitro group on the polyimide surface decrease and the hydrophilic groups generate on their surface. It is indicated that this change is mainly caused by the photo reaction of the molecular units having \( o\)-\( NO_2Bn \) group. Consequently, it is considered that the novel polyimides developed in this study can be applied in the field of printed electronics.

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