Surface Wettability Controllable Polyimides Bearing t-Boc Group by UV Light Irradiation

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Novel diamine monomers having tert-butoxycarbonyl (t-Boc) group were synthesized from the corresponding dinitro compounds by reductive reaction. The novel polyimides and copolyimides were synthesized from 3,4'-oxydiphthalic anhydride (3,4'-ODPA) as a tetracarboxylic dianhydride, above functional diamines having t-Boc group, and 3,5-diamino-N-tetradecylbenzamide (ADBA-14) as a diamine co-monomer by one-pot polymerization system using pyridine as a solvent. 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 and XPS, it is recognized that the hydrophobic groups on the polyimide surface decrease and the hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface. Furthermore, it is considered that the cleavage of t-Boc group significantly affect the changes of wettability by UV light irradiation based on the various analyses.

Keyword: polyimide, t-Boc group, UV light irradiation, surface wettability

1. Introduction
Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications [1]. 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 [2-8].

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 [9], the surface energy controlled ink-jet printing with UV irradiation [10], have been investigated to obtain the fine patterning. The authors also have investigated the surface wettability control of polyimides bearing long-chain alkyl groups by UV light irradiation [8, 11-16]. Until now, the authors have been 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 that of 365 nm UV irradiation that is preferable wavelength in industry. Consequently, we have focused on tert-butoxycarbonyl (t-Boc) group that is the protecting group of amino group and hydroxyl group and easily deprotected by UV light irradiation (365 nm) [17, 18]. In this paper, we report the synthesis and properties of the novel surface wettability controllable polyimides bearing t-Boc group.

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. CPI-00P was kindly supplied from Sanyo Chemical Industries, Ltd. Other reagents were purchased from TCI or Wako Pure Chemical Industries (Wako) and used as received.

2.2. Synthesis of novel diamine monomers having t-Boc group

*Tert*-butyl 3,5-diaminophenylcarbamate (t-Boc ADA) and *tert*-butyl 2,4-diaminopenyl carbonate (t-Boc EDA) were synthesized via two step reactions from the corresponding dinitro compounds as starting materials (Scheme 1). The reduction of dinitro precursors were carried out by catalytic hydrogenation using Pd/C as a catalyst.

The analytical data of t-Boc ADA are as follows: Mp 114.4 °C; ¹H NMR (500 MHz, CDCl₃, δ): 1.32 (s, 9H, -O-C(CH₃)₃), 3.02-3.63 (s, 4H, -NH₂), 5.96-5.98 (d, 1H, J=5.48Hz, Ha), 6.05-6.06 (d, 1H, J=1.40Hz, Hb), 6.72 (s, 1H, He) ppm; IR (ATR) : 3370 (-NH₂), 2925 (C-H), 1720 (C=O) cm⁻¹.

The analytical data of t-Boc EDA are as follows: Mp 112.3 °C; ¹H NMR (500 MHz, CDCl₃, δ): 1.32 (s, 9H, -O-C(CH₃)₃), 3.56 (s, 4H, -NH₂), 5.80 ( s, 1H, Ha ), 6.19 ( s, 2H, Hb ), 7.26 ( s, 1H, -NH ) ppm; IR (ATR) : 3370 (-NH₂), 2930 (C-H), 1720 (C=O) cm⁻¹.

2.3. Synthesis of polyimides bearing t-Boc group

The polyimides bearing t-Boc group were synthesized from 3,4′-ODPA, as a tetracarboxylic dianhydride, t-Boc ADA or t-Boc EDA, and 3,5-diamino-N-tetradecylbenzamide (ADBA-14) [4] as a diamine co-monomer (Scheme 2). ADBA-14 was introduced to enhance the initial hydrophobicity. In general, two step polymerization systems including poly(amic acid)s synthesis and chemical imidization in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent were performed in our laboratory. However, it was confirmed that the t-Boc group decomposed under the acidic condition. Therefore, the one-pot polymerization system was performed in the pyridine as a solvent and a base catalyst.

2.4. Measurement

¹H NMR spectra were measured on a JEOL JNM-AL500 FT NMR in CDCl₃ or dimethyl sulfoxide-d₆ 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 (Td10) 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 (Tg) were read at the midpoint of the heat capacity jump from the second heating scan.

Polyimide thin-films were obtained as follows: polyimide solutions in NMP (0.5-2.0 wt%) were casted on glass substrates and the solution were slowly evaporated by heating at approximately 100-120 °C on a hot plate until the films were dried, then the films were thoroughly dried in a vacuum oven at 100 °C for 12 h. Water contact angles were measured by SImage mini (Excimer. Inc., Japan) and UV light irradiation were performed using high-pressure mercury lamp unit (HLR 100T-2, λmax: 365 nm, 170 mW/cm², SEN Light Corp., Japan) on a cool plate NCP-2215 (NISSIN Laboratory equipment, Japan) adjusted at 25°C that was used to neglect the effect of thermal degradation of polyimide films during UV irradiation process. IR (ATR) measurements were performed by JASCO FT/IR-470 with ATR PRO450-S (Ge prism). XPS measurements were carried out on an XPS-APEX (Physical Electronics Co. Ltd.) with an Al Kα X-ray source (150 W). Chamber pressure; 10^-9-10^-10 Pa; take off angles; 45°.

3. Results and Discussion

3.1. 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; 4100~10500, in NMP/10 mM LiBr calibrated with standard polystyrenes). Although these molecular weights were relatively low in comparison with general polyimides, the all of obtained polyimides showed the good film forming ability.

The thermal properties of these polyimides were estimated by thermal degradation temperatures (Td10; 370~552 °C in air, 414~611 °C under nitrogen) and glass transition temperatures (Tg; 198~221 °C). Thus, it was confirmed that these polyimides showed the good thermal stability.

### Table 1. General properties of polyimides based on t-Boc ADA and t-Boc EDA.

| Monomer | Molecular Weight | Td10 | Tg  |
|---------|------------------|------|-----|
| a       | b                | c(Air)| c(N2) |
| t-Boc ADA ADBA-14 | 0 100 6500 9900 1.5 | 431 | 414 | 198 |
| 0 50 8800 17200 2.0 | 370 | 420 | 210 |
| 100 0 10500 32200 3.1 | 552 | 611 | 221 |
| t-Boc EDA ADBA-14 | 0 50 4100 6500 1.3 | 441 | 447 | 205 |
| 100 0 5800 10600 1.5 | 513 | 605 | 214 |

Equimolar amount of 3,4’-ODPA was used to the total amount of diamines. a Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. b Td10 Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. c Tg Measured by DSC at a heating rate of 20 °C/min in a dry nitrogen atmosphere.

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

The thin films based on the synthesized polyimides were irradiated by UV light (365 nm, 0, 5, 10, 15, 20 J), then the contact angles for the water were measured. Does of 5 J correspond 1 min UV irradiation. Figure 1 shows UV light irradiation energy dependence for water contact angles of polyimide films based on 3,4'-ODPA/t-Boc ADA/ADBA-14 polyimides and copolyimides, and 3,4'-ODPA/t-Boc EDA/ADBA-14 polyimides and copolyimides respectively.

Figure 1. UV irradiation energy dependence of water contact angles of polyimide films based on; 3,4'-ODPA/t-Boc ADA/ADBA-14 (upper), 3,4'-ODPA/t-Boc EDA/ADBA-14 (lower).
The water contact angles of initial polyimide films before UV irradiation were around 100°. These high hydrophobicity are probably due to the hydrophobic property of t-Boc group and long-chain alkyl group. These high water contact angles of polyimides having hydrophobic groups decreased in proportion to irradiated UV light energy. The changes of wettability by UV light irradiation are larger in the case of polyimides containing t-Boc EDA group than in the case of polyimides containing t-Boc ADA group. Especially, the contact angles of 3,4'-ODPA/t-Boc EDA (100/100) drastically decreased from near 105° (hydrophobicity) to the minimum value, 60° (hydrophilicity). On the other hand, the water contact angles of polyimide films based on 3,4-ODPA/ADBA-14 slightly decreased by UV light irradiation. Consequently, the introduction of t-Boc group in the polyimide back-bones is effective for the changes of surface wettability from hydrophobicity to hydrophilicity, and the introduction of t-Boc EDA is more effective than the introduction of t-Boc ADA. Therefore, it can be speculated that the generation of hydroxyl groups is occurred by the specific photoreaction such as [3,3] sigmatropic rearrangement on the surface of polyimides containing t-Boc EDA group with the general photo-oxidation (Figure 2). This speculation was confirmed by the various analytical experiments described in the next section.

![Figure 2](image2.png)

Figure 2. Elucidated reaction mechanism on the polyimide surface containing t-Boc EDA group.

Figure 3 shows UV light irradiation energy dependence of water contact angles of polyimide films containing 5 wt% of CPI-100P as a photoacid generator (PAG). By the addition of PAG, the changes of surface wettability of the polyimide were accelerated. Thus, the water contact angle of polyimide containing 3,4'-ODPA/t-Boc EDA (100/100) decreased around 30° by just 1 minute (5 J) UV irradiation at room temperature. This wettability change is good enough for the patterning of water in a simple laboratory test using handmade photomask (Figure 4). Concerning on the reaction mechanism in the case of the addition of PAG, it is speculated that the acid species generated from PAG by UV light irradiation cause the deprotect of t-Boc group as illustrated in Figure 5. Although we have demonstrated the heating in the photo irradiation process made the wettability change somewhat accelerate [16], the heating or post-bake experiment was not examined because the enough wettability changes were recognized even at room temperature. In chemically amplified photo resists, the heating process is necessary to diffuse the acid species in whole polymer film [18]. On the other hand, the photoreaction on the top surface of polymers is important in the case of our study. Consequently, it is considered that the heating is not always necessary for the surface wettability controllable polyimides with PAG. The UV light irradiation process at room temperature is practically useful.

![Figure 3](image3.png)

Figure 3. UV irradiation energy dependence of water contact angles of polyimides based on; 3,4'-ODPA/t-Boc ADA/ADBA-14 with CPI-100P (upper), 3,4'-ODPA/t-Boc EDA/ADBA-14 with CPI-100P (lower).

![Figure 4](image4.png)

Figure 4. Patterning test at laboratory scale using polyimide film based on 3,4'-ODPA/t-Boc EDA.
3.3. Analytical experiments for the elucidation of photoreaction.

The surface analyses of the polyimide films were performed by ATR and XPS. 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, and the absorption of alkyl groups around 2900 cm\(^{-1}\) decrease with the irradiation of UV light irradiation (Figure 6).

![Figure 6](image6.png)

Figure 6. ATR spectrum before/after UV light irradiation. (3,4'-ODPA/t-Boc EDA, 0 J; full line, 20 J; broken line)

In the case of ATR measurements, the penetration depth of a beam of infrared light into the sample is typically between 0.5 and 2 µm. Therefore, above ATR analysis does not reflect the chemical composition of the film top surface. The intensive surface analysis was examined using XPS. Table 2 shows the surface elemental analysis of polyimide based on 3,4'-ODPA/t-Boc EDA/ADBA-14 (100/50/50 mol\%) by XPS. It was observed that carbon (%) decrease and oxygen (%) increase after UV light irradiation, meaning that hydroxyl groups and carboxyl groups generated on the top surface of polyimide films. The generation of hydrophilic groups was also analyzed by XPS narrow scans of C1s, and the chemical shifts due to C-O and C=O bonds clearly increased after UV light irradiation (Figure 7).

![Table 2](image7.png)

Table 2. Surface elemental analysis of polyimide based on 3,4'-ODPA/t-Boc EDA/ADBA-14 (100/50/50 mol\%) by XPS.

![Figure 7](image8.png)

Figure 7. XPS narrow scans of C1s of polyimide films based on 3,4'-ODPA/t-Boc EDA/ADBA-14 (100/50/50 mol\%).

The UV light irradiation for the polyimide solution was carried out in order to confirm the decomposition products by the UV light irradiation. Polyimides based on 3,4'-ODPA/t-Boc EDA(100/100 mol\%) was dissolved in 1 wt\% in CH\(_2\)Cl\(_2\). This solution in a quartz cell was irradiated by UV light (365 nm, 5 J). After UV light irradiation, the generation of the gas was confirmed, when the cell was opened. The polyimide solution was precipitated onto methanol, then \(^1\)H NMR of the polyimide before and after UV light irradiation was measured (Figure 8). From this \(^1\)H NMR spectrum of 3,4'-ODPA/t-Boc EDA polyimide after UV light irradiation, it was observed that the aliphatic peaks based on t-Boc group decreased.
We have investigated the UV irradiation experiments under an argon atmosphere in order to examine the effect of the oxygen in the UV irradiation process. While the water contact angles did not change under an argon atmosphere, the water contact angles decreased in an air according to our previous research [15]. These experiments indicate that the change of surface wettability of polyimide surface is mainly caused by photo-oxidation reaction. From such reason, the UV irradiation experiments using the polyimides containing t-Boc group under an argon atmosphere were performed, and the results are illustrated in Figure 9. Although the contact angles did not change after UV light irradiation in the case of 3,4’-ODPA/t-Boc ADA polyimide, the contact angles deceased in the case of 3,4’-ODPA/t-Boc EDA polyimide even under argon atmosphere. Consequently, it is confirmed that the cleavage of t-Boc group as shown in Figure 2 occurs in the case of 3,4’-ODPA/t-Boc EDA polyimide. It is speculated that the cleavage of t-Boc group may not occur due to the stability of carbamate linkages in t-Boc ADA group in comparison with carbonate linkages in t-Boc EDA group.

In summary, it is considered that the cleavage of t-Boc group play an important role in these surface wettability controllable polyimides by UV light irradiation. It is noteworthy that the cleavage of t-Boc group occurs without PAG.

As UV lamp used in our study is high-pressure mercury lamp and it radiates not only 365 nm light but also various light such as 254 nm light, it can be imagined that the general photo-oxidation reaction occurs on the polyimide surface and the oxidative products cleave t-Boc group. The further experiments using monochromatic light or filtered light is necessary to clarify the photoreaction mechanism. The use of a low molecular weight model compound is also under investigation to clarify the structure of photoreaction products.

4. Conclusion
The novel polyimides bearing t-Boc group were successfully synthesized, and it was confirmed that the introduction of t-Boc group affected the surface wettability control of these polyimides by UV light (365 nm) irradiation. The contact angles of these polyimides for the water decreased from near 90° (hydrophobicity) to minimum 60° (hydrophilicity) in proportion to irradiated UV light energy at room temperature without PAG. These changes are larger in the case of polyimide films based on 3,4’-ODPA/t-Boc EDA containing carbonate linkages. Furthermore, the addition of PAG accelerates the surface wettability changes. From the result of various analytical experiments, it is recognized that hydrophobic t-Boc group and long-chain alkyl group on the polyimide surface decrease and the hydrophilic groups generate on their surface by UV light irradiation, and that the cleavage of t-Boc group play an important role. 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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