

Surface Wettability Controllable Polyimides Having Photo-reactive Groups by UV Light Irradiation

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Abstract: Novel diamine monomers having tert-butoxycarbonyl (t-Boc) group and *o*-nitrobenzyl (*o*-NO₂Bn) group were synthesized. The novel soluble polyimides and copolyimides were synthesized from 3,4'-oxydiphthalic anhydride (3,4'-ODPA) as a tetracarboxylic dianhydride, above functional diamines by the chemical imidization system. The thin films of obtained polyimides were irradiated by UV light (λ_{max} ; 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 or *o*-NO₂Bn group significantly affect the changes of wettability by UV light irradiation based on the various analyses.

Keywords: Polyimide, t-Boc group, *o*-nitrobenzyl group, UV light irradiation, Surface wettability

1. Introduction

The author's research group has systematically investigated the synthesis, characterization and application of soluble polyimides based on the aromatic diamine monomers having long-chain alkyl groups [1, 2]. Recently, the printed electronics technology, by which the conductive lines (circuit) can be printed onto the plastic substrate such as polyimides, has been investigated [3, 4]. Thus, the surface wettability controllable polyimides bearing long-chain alkyl groups by UV light irradiation to establish the fine patterning method for printed electronics have been investigated in our laboratory [5-11]. The basic concept of these functional polyimides is shown in Figure 1. Until now, the surface wettability control has been carried out by UV light irradiation (λ_{max} ; 254 nm). However, 254 nm UV light 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 light irradiation is worse than the one of 365 nm UV light irradiation that is preferable wavelength in industry. Consequently, the author has

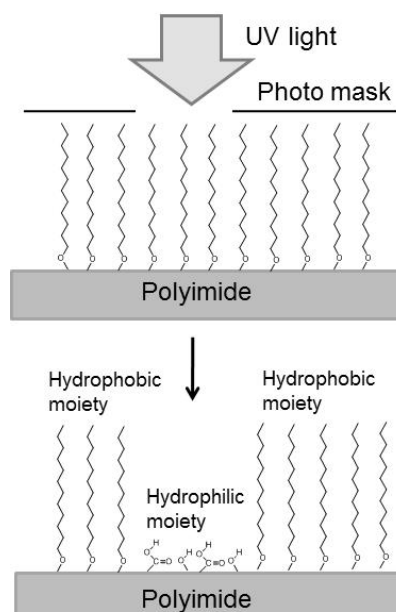


Figure 1. Conceptual scheme of surface wettability controllable polyimides by UV light irradiation

focused on tert-butoxycarbonyl (t-Boc) group and *o*-nitrobenzyl (*o*-NO₂Bn) group that is the protecting group of amino group and/or hydroxyl group and easily deprotected by UV light irradiation (365 nm) [12-13].

2. Experimental

2.1 Materials

3,4'-Oxydiphthalic anhydride (3,4'-ODPA; a-ODPA) was kindly supplied from Shanghai Research Institute of Synthetic Resins, and used after drying in a vacuum oven. CPI-100P was kindly supplied from Sanyo Chemical Industries, Ltd.

2.2. Synthesis of novel polyimides based on diamine monomers having photo-reactive groups

Figure 2 shows the synthetic schemes of polyimides having photo-reactive groups. Novel diamine monomers (t-Boc ADA, t-Boc EDA) having tert-butoxycarbonyl (t-Boc) groups were synthesized from the corresponding dinitro compounds by reductive reaction. The novel polyimides and copolyimides were synthesized from 3,4'-ODPA as a dianhydride, above functional diamines having t-Boc groups, and 3,5-diamino-N-tetradecylbenzamide (ADBA-14) as a diamine co-monomer by one-pot polymerization systems using pyridine as a solvent. Novel diamine monomer (*o*-NO₂Bn-DA) having *o*-nitrobenzyl (*o*-NO₂Bn) group was synthesized from *o*-nitrobenzyl alcohol as a starting material. The polyimides were synthesized from 3,4'-ODPA as a dianhydride, *o*-NO₂Bn-DA, and ADBA-14 as a diamine co-monomer by two steps polymerization systems.

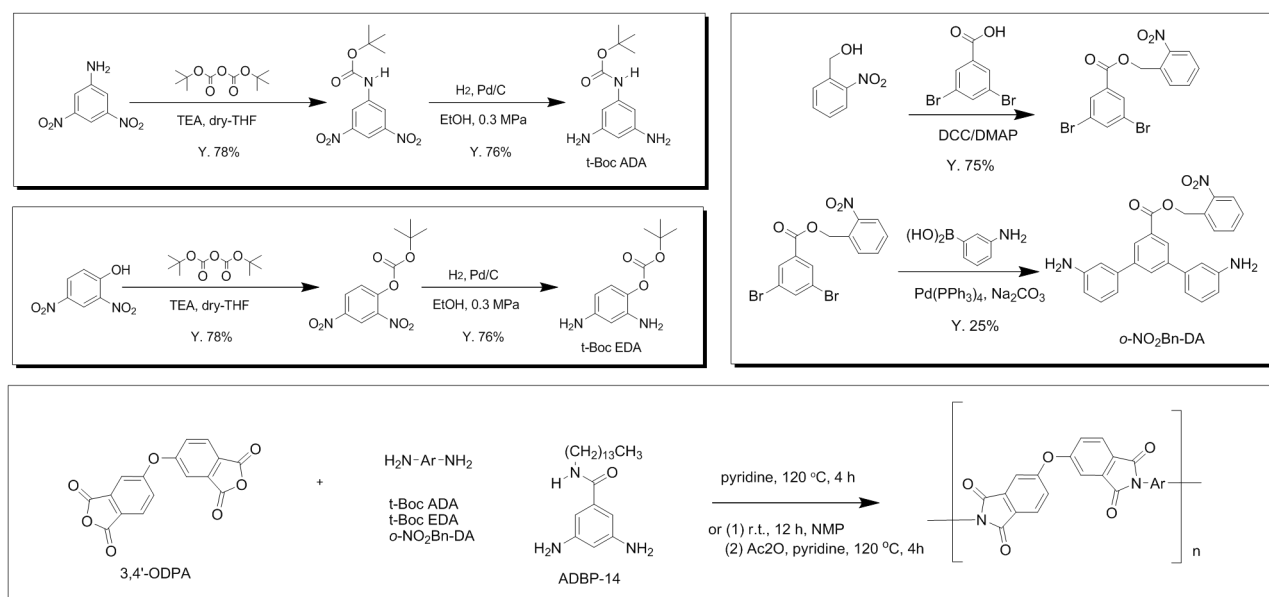


Figure 2. Synthesis of polyimides having photo-reactive groups

2.3. Measurement

Experimental details of measurements were described in the previous literature [5-13].

3. Results and Discussion

3.1. General properties of polyimides

The obtained polyimides and copolyimides showed the good solubility in polymerization solvent, NMP. The molecular weights of obtained polyimides were measured by SEC (M_n; 4100~11200, in

NMP/10mM 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 (T_{d10} ; 348~597°C in air, 392~611 °C under nitrogen) and glass transition temperatures (T_g ; 198~280°C). Thus, it was confirmed that these polyimides showed the good thermal stability.

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 3 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. 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 4, left). This speculation was confirmed by the various analytical experiments described in the next section.

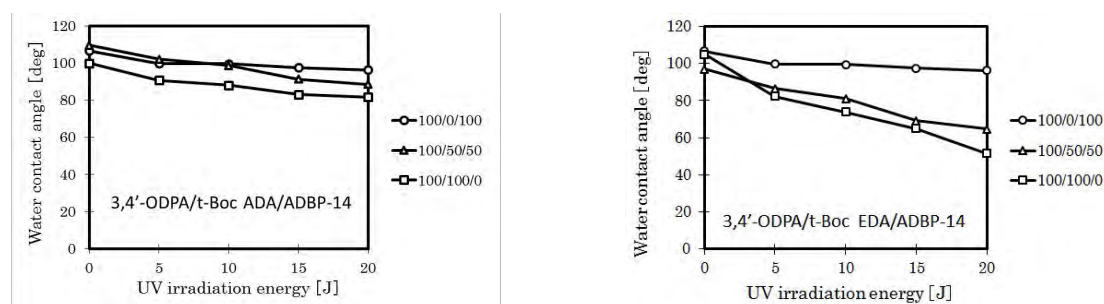


Figure 3. UV irradiation energy dependence of water contact angles of polyimide films based on; 3,4'-ODPA/t-Boc ADA/ADBA-14 (left), 3,4'-ODPA/t-Boc EDA/ADBA-14 (right).

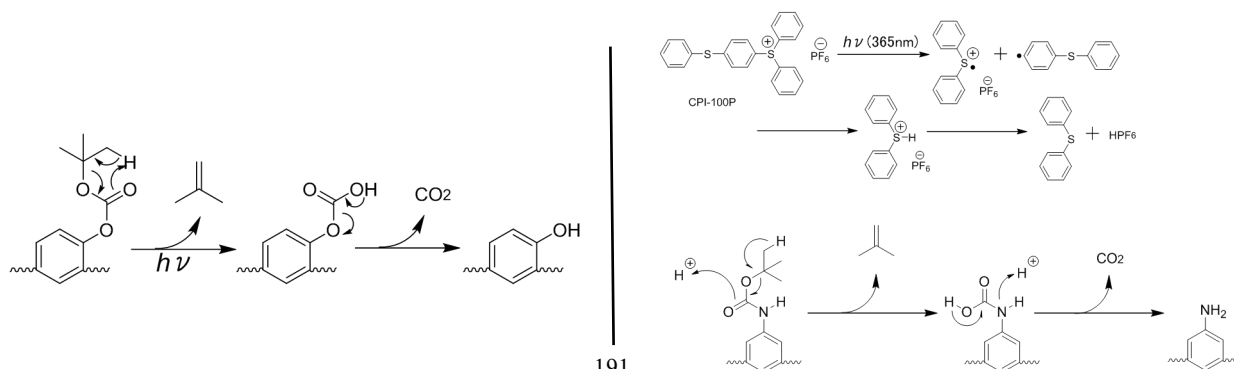


Figure 4. Elucidated reaction mechanism on the polyimide surface containing t-Boc EDA group (left). Elucidated reaction mechanism on the polyimide surface using PAG (CPI-100P) (right).

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 [11]. Figure 5 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 (5J) UV light irradiation. 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 4 (right).

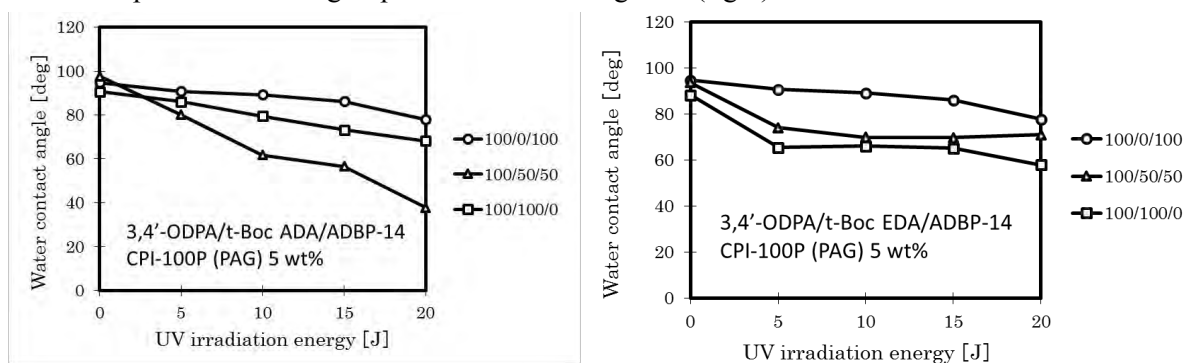


Figure 5. UV irradiation energy dependence of water contact angles of polyimides based on; 3,4'-ODPA/t-Boc ADA/ADBA-14 with CPI-100P (left), 3,4'-ODPA/t-Boc EDA/ADBA-14 with CPI-100P (right).

Figure 6 shows UV light 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 respectively. The initial water contact angles of polyimide films based on 3,4'-ODPA/*o*-NO₂Bn-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*-NO₂Bn-DA decreased from 88° to 59° by UV light irradiation (Figure 6), 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*-NO₂Bn group occurs and hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface (Figure 7). 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 [5-11]. Figure 6 (right) 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%). 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 following the speculated mechanism shown in Figure 7. 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, and 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.

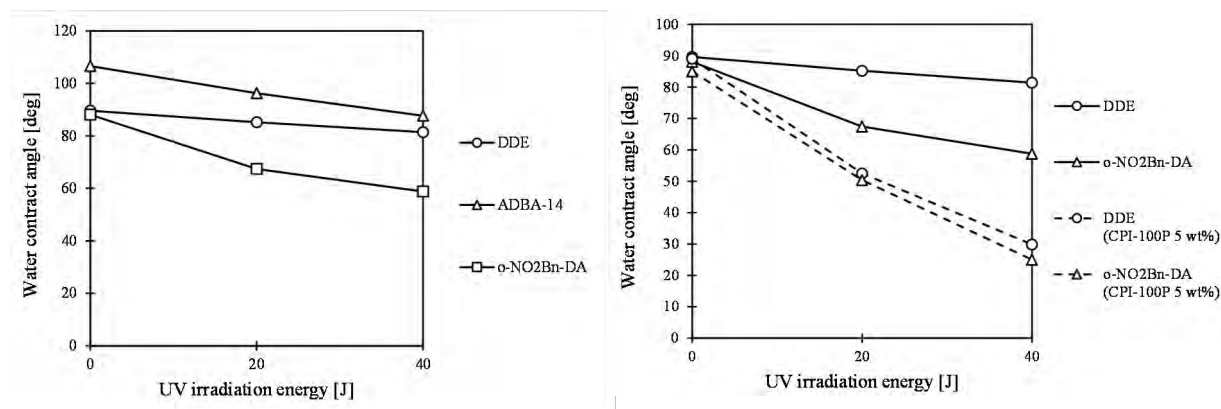


Figure 6. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/*o*-NO₂Bn-DA, 3,4'-ODPA/ADBA-14, 3,4'-ODPA/DDE (left). UV irradiation energy dependence of water contact angles of polyimide films based on; 3,4'-ODPA/DDE and 3,4'-ODPA/*o*-NO₂Bn-DA with or without CPI-100P (5 wt%) (right).

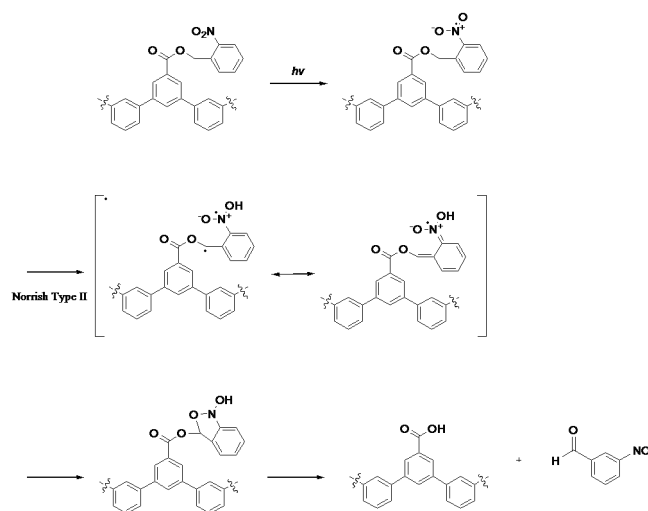


Figure 7. Elucidated reaction mechanism of *o*-NO₂Bn group by UV light irradiation.

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. In this paper, the analytical experiments using the polyimides having t-Boc group are described. In ATR measurements, the absorption of OH groups around 3300 cm⁻¹ increase, and the

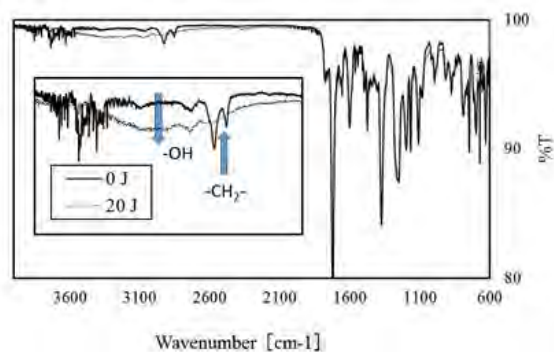


Figure 8. ATR spectrum before/after UV light irradiation (3,4'-ODPA/t-Boc EDA, 0 J; full line, 20 J; broken line).

absorption of alkyl groups around 2900 cm^{-1} decrease with the irradiation of UV light irradiation (Figure 8).

In the case of ATR measurements, the penetration depth of a beam of infrared light into the sample is typically between 0.5 and $2\ \mu\text{m}$. Therefore, above ATR analysis does not reflect the chemical composition of the film top surface. The intensive surface analysis was examined using XPS. From the results of 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 C_{1s} , and the chemical shifts due to C-O and C=O bonds clearly increased after UV light irradiation (Figure 9).

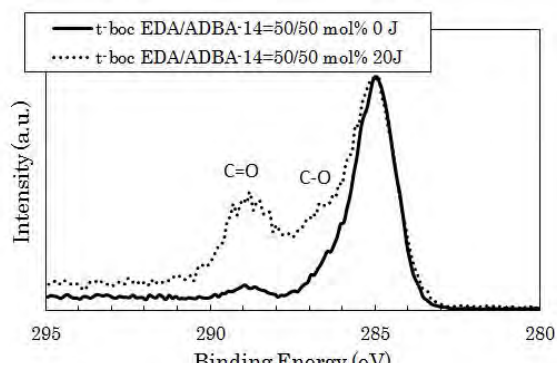


Figure 9. XPS narrow scans of C_{1s} of polyimide films based on 3,4'-ODPA/t-Boc EDA/ADBA-14 (100/50/50 mol%).

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_2Cl_2 . This solution in a quartz cell was irradiated by UV light (365 nm, 5 J) (Figure 10). After UV light irradiation, the generation of the gas was confirmed, when the cell was opened. The polyimide solution was precipitated onto methanol, then ^1H NMR of the polyimide before and after UV light irradiation was measured. From this ^1H 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 (Figure 10).

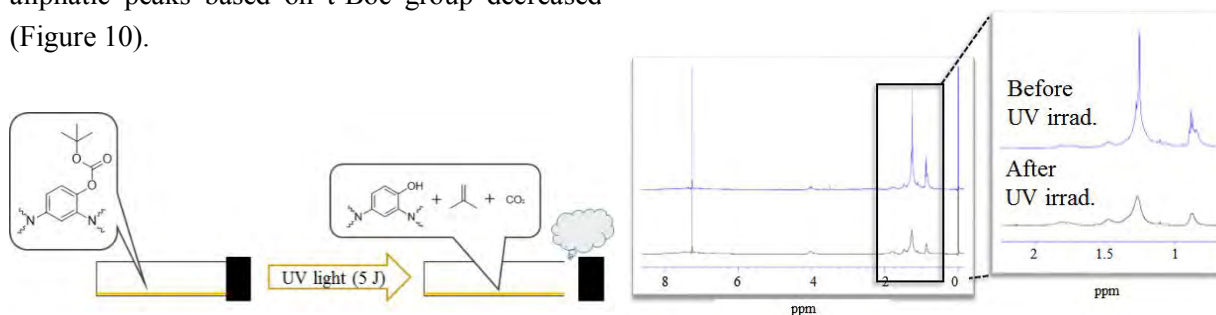


Figure 10. Schematic drawing of photo-degradation experiment in solution and ^1H NMR spectra of polyimide based on 3,4'-ODPA/t-Boc EDA.

4. Conclusion

The novel polyimides bearing t-Boc group or *o*-nitrobenzyl group were successfully synthesized, and it was confirmed that the introduction of t-Boc group or *o*-nitrobenzyl 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, *o*-nitrobenzyl, or long-chain alkyl groups 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 or *o*-nitrobenzyl group play an important role.

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