

Surface Wettability Control of Polyimide Surface by Photo-irradiation

Yusuke TSUDA

*Kurume Institute of Technology,
2228-66 Kamitsu-machi, Kurume, Fukuoka 830-0052, Japan*

Abstract: The soluble polyimides were synthesized from tetracarboxylic dianhydrides such as 3,4'-oxydiphthalic anhydride (3,4'-ODPA) and diamine monomers having various photoreactive groups, which are photo-oxidative groups, photoreaction groups based on photoresist technology, and photochromic groups. The thin films of obtained polyimides were irradiated by UV light (λ max; 254 nm or 365 nm), and the contact angles for the water decreased from near 100° (hydrophobicity) to minimum 20° (hydrophilicity) in proportion to irradiated UV light energy. The reversible wettability changes of the polyimides having photochromic groups by UV-Vis light irradiation were also investigated. Various surface analysis such as ATR, solid state refractive UV, XPS support above surface wettability changes of the polyimides.

1. Introduction

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 [1], the surface energy controlled ink-jet printing with UV irradiation [2], 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 [3-19]. Our research concept to obtain surface wettability controllable polyimide by photo-irradiation is classified into three categories; (a) photo-oxidation, (b) photoreaction based on photoresist technology, and (c) photochromism (Figure 1). In the cases of (a) and (b), 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 photochromic group such as azobenzene group on their side-chain by UV-Vis (ultraviolet-visible) light irradiation [17, 19]. In this review paper, the authors summarize our recent results with some new results.

2. Experimental

Surface wettability controllable polyimides having various photoreactive groups were synthesized from commercialized tetracarboxylic dianhydride and novel functional diamine monomers synthesized in our laboratory. In the case that the synthesis of diamine monomer was difficult, the polymer reaction method, in other word, post-functional method was performed [17, 19]. Most of experimental techniques containing synthesis of monomers and polymers,

polymer reaction, measurements, characterization, surface properties and analyses were described in our previous papers [3-19].

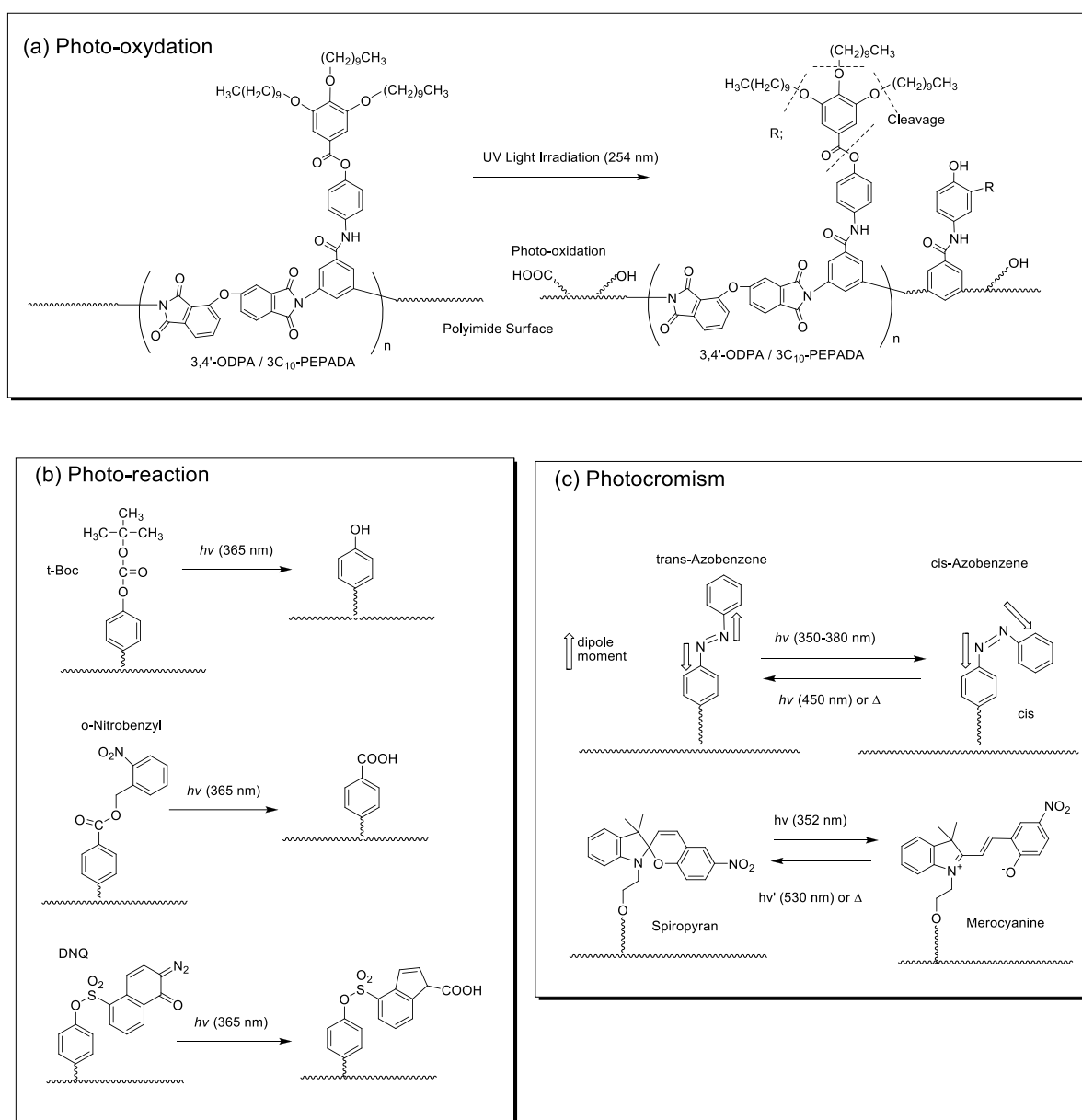


Figure 1. Conceptual scheme of wettability control of the polyimide surface by photo-irradiation.

3. Results and Discussion

3.1. General Properties of Polyimides

The molecular weights of obtained polyimides were measured by SEC (M_n ; 3500~50000, in NMP/10mM LiBr calibrated with polystyrenes), and all polyimides showed the good film forming ability. The thermal properties of these polyimides were estimated by glass transition temperatures (T_g ; 200~250 °C) and thermal

degradation temperatures (Td_{10} ; 400~450 °C), and these polyimides showed the good thermal stability for heat resistance polymers. In case that 3,4'-ODPA was selected as a tetracarboxylic dianhydride, the high molecular weights and the good solubility were observed. Therefore, 3,4'-ODPA is generally used as a standard tetracarboxylic dianhydride.

3.2. Surface Wettability Controllable Polyimides Based on Photo-oxidation

Following experiments are described as a representative example. The thin films based on the polyimides having long-chain alkyl groups were irradiated by UV light (λ_{max} ; 254 nm, 0, 2, 4, 8 J/cm²), then the contact angles for the water were measured. Figure 2 shows UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/DDE (4,4'-diaminodiphenyl ether), 3,4'-ODPA/3C₁₀-PEPEDA, 3,4'-ODPA/3C₁₀-PEPADA, 3,4'-ODPA/3C₁₀-PAPADA, respectively. The high water contact angles of polyimides bearing long-chain alkyl groups decreased from near 100° (hydrophobicity) to the minimum value, 20° (hydrophilicity) in proportion to irradiated UV light energy.

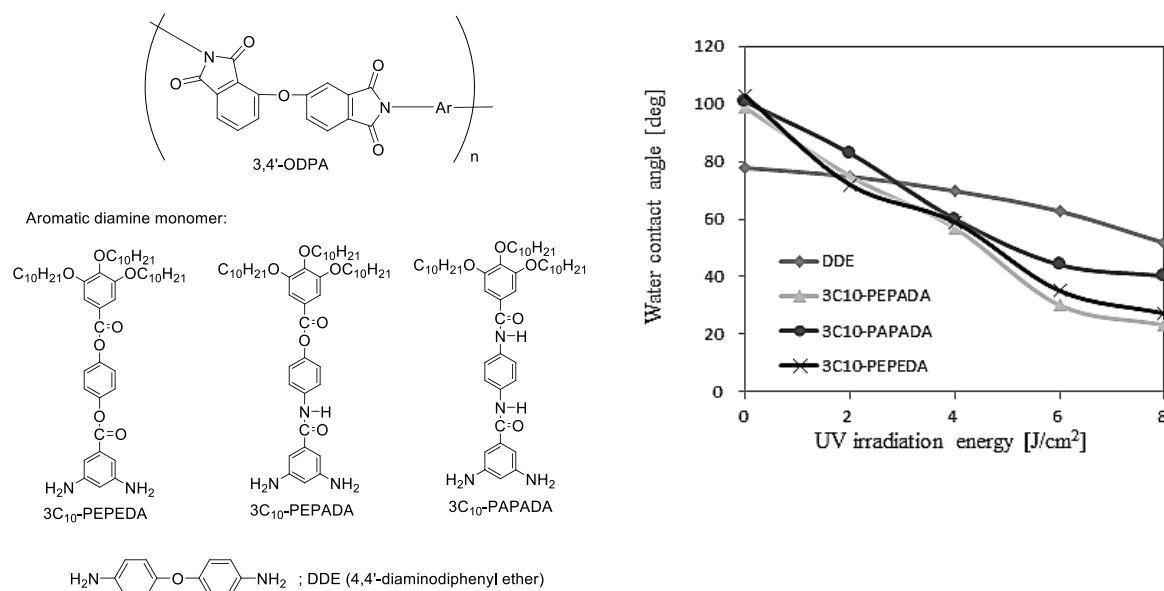


Figure 2. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA and diamines having long-chain alkyl groups.

It is considered that these changes of wettability of polyimides are mainly based on the photo-oxidation, photo-degradation, and scission of long-chain alkyl groups and specific functional groups such as ester group, and that the generation of the hydrophilic functional groups such as COOH and OH groups probably occurred. Although the water contact angles decreased after UV light irradiation, the degrees of changes depended on the structure of diamine components. In these cases, the water contact angles based on 3,4'-ODPA/3C₁₀-PEPEDA polyimide and 3,4'-ODPA/3C₁₀-PEPADA polyimide containing long-chain alkyl groups via phenyl ester (PE) linkages the most greatly decreased from near

100° to near 20°. It is speculated that phenyl ester linkage possibly cause photoreaction such as photo-Fries reaction and generate hydroxyl groups. As the water contact angles based on 3,4'-ODPA/DDE without long-chain alkyl groups also gradually decreased by UV light irradiation, it is imagined that the polyimide back-bones partly oxidized by UV irradiation process. Consequently, it is speculated that the complicated photo-induced reactions such as auto-oxidation, cleavage of ester groups, Fries rearrangement, etc. occur on the surface of polyimides on the course of UV light irradiation process (Figure 1).

3.3. Surface Wettability Controllable Polyimides Based on Photoreactive Groups

In the previous section (3.2), 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 changes 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 focused on tert-butoxycarbonyl (t-Boc) group, *o*-nitrobenzyl (*o*-NO₂Bn) group, and diazonaphthoquinone (DNQ) group that are the components generally used in photoresist technology.

Following experiments are described as a representative example. The thin films based on the polyimides having photoreactive groups were irradiated by UV light (λ max; 365 nm, 0, 5, 10, 15, 20 J/cm²), then the contact angles for the water were measured. Does of 5 J/cm² correspond 1 min UV irradiation in our experimental condition. Figure 3 shows UV light irradiation energy dependence for water contact angles of polyimide films based on HAB-DNQ PI, HAB-DNQ/ADBA-14 (50/50) PI, t-Boc EDA PI, *o*-nitrobenzyl PI, respectively. 3,5-Diamino-N-tetradecylbenzamide (ADBA-14) [14] was introduced to enhance the initial hydrophobicity as a diamine co-monomer. The water contact angles of initial polyimide films before UV irradiation were around 75-90°. These hydrophobicity are probably due to the hydrophobic property of side chain substitute groups (DNQ, t-Boc, *o*-nitrobenzyl, long-chain alkyl group). These high water contact angles of polyimides having hydrophobic groups decreased to around 52-72° in proportion to irradiated UV light energy.

In the case of t-Boc EDA PI, it is speculated that the typical photo de-protection reaction of t-Boc group occurs on the course of UV light irradiation shown in Figure 1. It is speculated that the photo de-protection reaction has also similarly occurred in the case of *o*-nitrobenzyl PI as shown in Figure 1. It is confirmed that the introduction of DNQ component into polyimide side-chain is also effective for the surface wettability control of the polyimide surface by UV light irradiation (λ max; 365 nm). As the initial water contact angle of HAB-DNQ PI was around 75° showing the relatively lower value in comparison with t-Boc EDA PI and *o*-nitrobenzyl PI, long-chain alkyl group was introduced to HAB-DNQ PI by copolymerization with ADBA-14 to enhance the initial water contact angle. Thus, the water contact angle of HAB-DNQ / ADBA-14 (50/50) PI changed from 83° to 51° by UV light irradiation (λ max; 365

nm, 20 J/cm²). It is speculated that DNQ component changed to indene carboxylic acid component by photo-induced Wolff rearrangement. This photoreaction is the polarity transformation that is genelary used in the field of the photoresist technology.

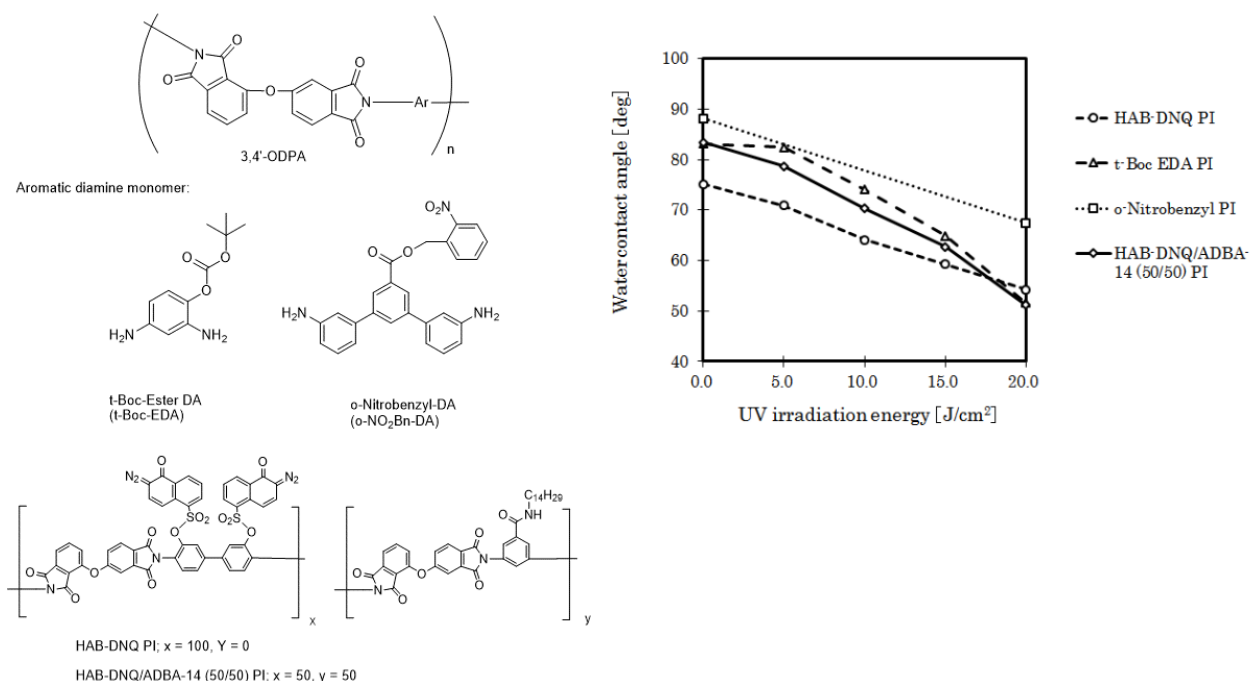


Figure 3. UV irradiation energy dependence of water contact angles of polyimide films based on various photoreactive groups (λ max; 365 nm).

3.4. Reversible Surface Wettability Controllable Polyimides Based on Photochromic Groups

Above wettability changes of polyimide surface mentioned in section 3.2 and 3.3 are irreversible changed from the hydrophobicity to the hydrophilicity by UV light irradiation. The author has recently investigated reversible control of surface wettability of polyimides having azobenzene group or spiropyran group on their side-chain by UV-Vis light irradiation [17, 19]. The thin films of obtained polyimide based on 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) and Azo-DA was irradiated by UV light (λ max; 365 nm), and the contact angle for the water decreased from near 102° to 88°, and the contact angle recovered from 88° to 96° by Vis light irradiation (Figure 4). It is speculated that these reversible wettability changes are based on the polarity changes of azobenzene photo-isomerization. Cis-azobenzene is more polar than trans (E)-azobenzene unit, so cis (Z)-azobenzene is more hydrophilic than trans-azobenzene unit (Figure 1). Although the reversible wettability changes of polyimide based on 3,4'-ODPA/Azo-DA was also observed, the degree of wettability changes was small. Further investigations have been carried out to clarify these phenomena and enhance the wettability changes.

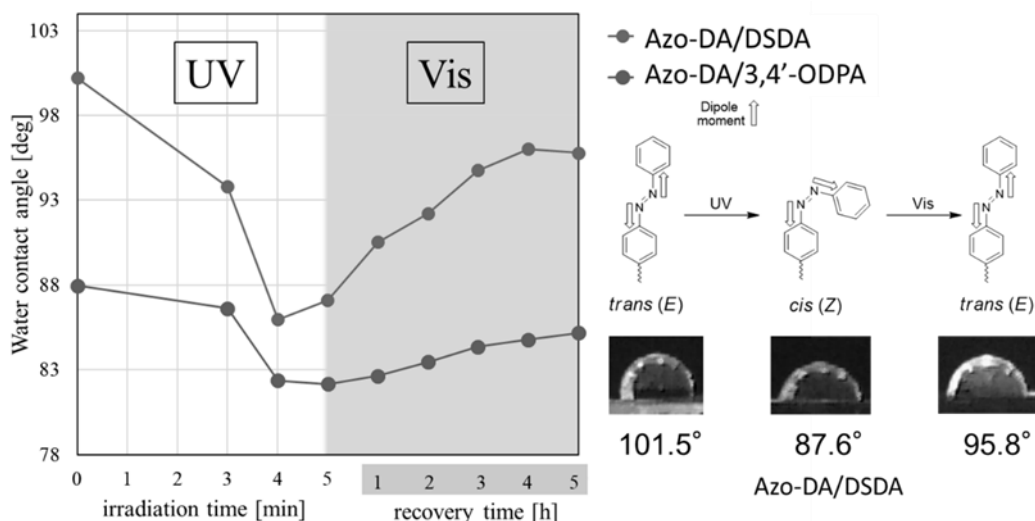


Figure 4. Reversible control of surface wettability of polyimides based on Azo-DA by UV-Vis light irradiation.

Reversible surface wettability controllable polyimides based on spiropyran group have been also investigated, and the similar reversible wettability changes have been observed [19]. 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 (Figure 5). 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 ten times (Figure 6). These wettability changes were about 8°, not enough value for the application. Recently, the introduction of dinitro-spiropyran group has investigated, and the improved wettability changes, about 37° were achieved (Figure 7). The detailed results will be reported in the future paper.

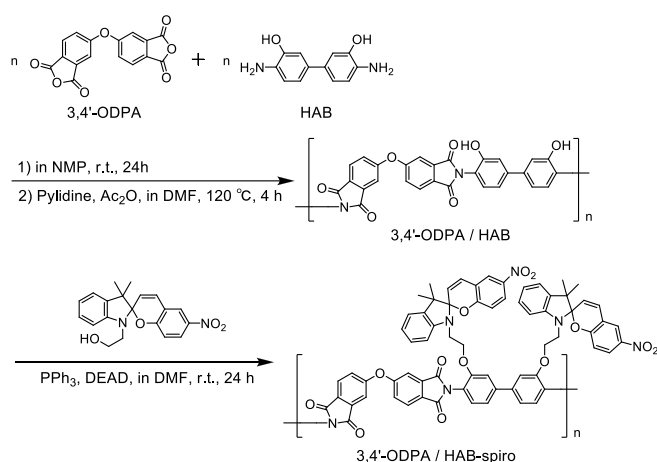


Figure 5. Synthesis of polyimide having spiropyran groups.

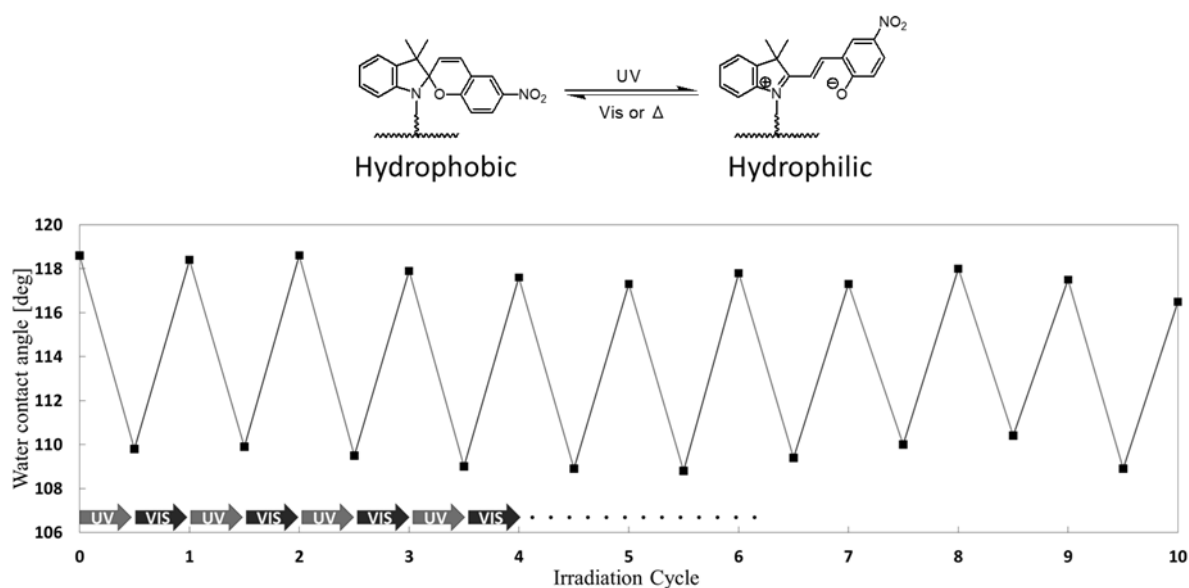


Figure 6. Water contact angle change of polyimide (3,4'-ODPA/HAB-spiro) film by repeated irradiation of UV -Vis light.

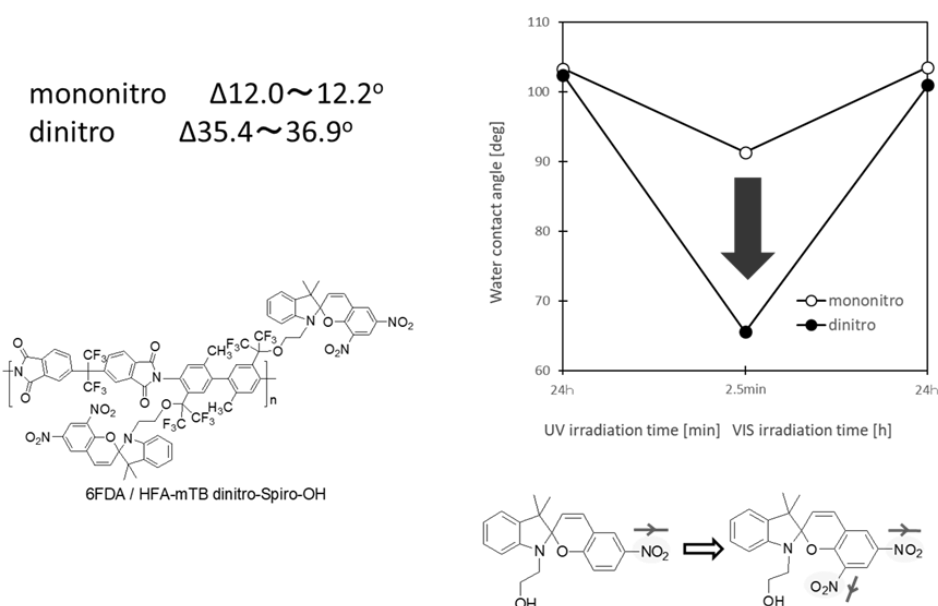


Figure 7. Reversible control of surface wettability of polyimides based on dinitro-spiropyrene by UV-Vis light irradiation.

3.5. Surface Analysis Experiments

The surface analysis of the polyimide films were performed by ATR, XPS, SFM (AFM). ATR measurements of the polyimide surfaces after UV light irradiation support the assumption that the generation of the hydrophilic functional groups such as COOH and OH groups occurred. The surface nm size micro roughness probably based on long-chain alkyl groups was observed by SFM analysis of the polyimides having long-chain alkyl groups. However, the changes of

these micro roughness after UV light irradiation were not recognized. Thus, the change of surface wettability of these polyimides is mainly occurred by the changes of chemical structures of polyimide surface. Solid state surface reflected UV-Vis analysis is the strong tool for the photo-isomerization analysis for the reversible surface wettability controllable polyimides. These results were described in detail in our previous papers [3-19].

4. Conclusions

The thin films of polyimides having various functional groups were irradiated by UV light, and the contact angles for the water decreased from near 100° (hydrophobicity) to minimum value, 20° (hydrophilicity) in proportion to irradiated UV light energy. The utilization of photoresist technics using photoreactive groups such as t-Boc group, *o*-nitrobenzyl group, DNQ group was successfully investigated, and the effective photo-irradiation process was achieved. These methods are expected to be applied in the field of printed electronics. The reversible wettability changes of the polyimides having photochromic groups such as azobenzene and spiropyran by UV-Vis light irradiation were also confirmed, and the further improvement and the application of the reversible wettability changes has been searched.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number 16K05924. This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices” (Dr. Atsushi Takahara of Kyushu University). Financial supports from RICOH Co., Ltd. is gratefully acknowledged. The author thanks Shanghai Research Institute of Synthetic Resins for providing 3,4'-ODPA.

References

- [1] C. Kim, M. Nogi, K. Suganuma, and Y. Yamamoto, *ACS Appl. Mater. Interfaces*, **4** (2012) 2168.
- [2] K. Suzuki, K. Yutani, M. Nakashima, A. Onodera, S. Mizukami, M. Kato, T. Tano, H. Tomono, M. Yanagisawa, and K. Kameyama, *Journal of the Imaging Society of Japan*, **50** (2011) 142.
- [3] Y. Tsuda, Y. Hashimoto, and T. Matsuda, *Kobunshi Ronbunshu (Japanese)*, **68** (2011) 24.
- [4] Y. Tsuda, *J. Photopolym. Sci. Technol.*, **26** (2013) 345.
- [5] Y. Tsuda and Y. Kawashima, *J. Photopolym. Sci. Technol.* **27** (2014) 161.
- [6] Y. Tsuda and S. Kawabata, *J. Photopolym. Sci. Technol.*, **27** (2014) 277.
- [7] Y. Tsuda, R. Nakamura, S. Osajima, and T. Matsuda, *High Perform. Polym.*, **27** (2015) 46.
- [8] Y. Tsuda and R. Shiki, *J. Photopolym. Sci. Technol.*, **28** (2015) 191.
- [9] Y. Tsuda, M. Tahira, N. Shinohara, and D. Sakata, *J. Photopolym. Sci. Technol.*, **28** (2015) 191.
- [10] Y. Tsuda and D. Sakata, *J. Photopolym. Sci. Technol.*, **29** (2016) 283.
- [11] Y. Tsuda and R. Shiki, *J. Photopolym. Sci. Technol.*, **29** (2016) 265.
- [12] Y. Tsuda, *J. Photopolym. Sci. Technol.*, **29** (2016) 383.
- [13] Y. Tsuda, *Kobunshi Ronbunshu (Japanese)*, **74** (2017) 10.
- [14] Y. Tsuda, M. Kojima, T. Matsuda, and J.-M. Oh, *Polym. J.*, **40** (2008) 354.
- [15] Y. Tsuda and S. Kawabata, *J. Photopolym. Sci. Technol.*, **30** (2017) 163.
- [16] Y. Tsuda, *J. Photopolym. Sci. Technol.*, **30** (2017) 217.
- [17] Y. Tsuda and D. Sakata, *J. Photopolym. Sci. Technol.*, **30** (2017) 445.
- [18] Y. Tsuda, T. Koga, T. Shimogawa, R. Shiki, D. Sakata, *J. Photopolym. Sci. Technol.*, **31** (2018), 457.
- [19] Y. Tsuda and T. Shimogawa, *J. Photopolym. Sci. Technol.*, **31** (2018), 587.