Reversible Control of Surface Wettability of Polyimides Having Azobenzene Group on Their Side-chain by UV-Vis Light Irradiation

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Novel diamine monomer, 4-(phenylazo) 3,5-di(3-aminophenyl) benzoate (Azo-DA) having azobenzene group was synthesized from 4-(phenylazo)phenol as a starting material. The polyimides were synthesized from 3,4'-oxydiphthalic anhydride (3,4'-ODPA) or 3,3',4,4'-diphenylsulfonetetra carboxylic dianhydride (DSDA) as a dianhydride and Azo-DA by two steps polymerization systems. The thin films of obtained polyimide based on DSDA/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. This reversible control of surface wettability of the polyimide having azobenzene group by UV-Vis light irradiation was analyzed by solid-state surface reflected UV-Vis spectra and XPS measurements. Although the reversible wettability change of polyimide based on 3,4'-ODPA/Azo-DA was also observed, the degree of wettability changes was small.

Keywords: Polyimide, Azobenzene group, 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]. Since conventional aromatic polyimides are insoluble, extensive research has been carried out to improve the solubility of polyimides. 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 also 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 [7-17]. However, these wettability changes are irreversible from the hydrophobicity to the hydrophilicity by UV light irradiation. In this paper, the authors have firstly investigated reversible control of surface wettability of polyimides having azobenzene group on their side-chain by UV-Vis light irradiation. It is previously reported that the reversible *trans-cis* isomerization of azobenzene groups through UV-Vis irradiation

is accompanied by fast and large changes in both geometry dipole moment [18,19], and this fact is expected to affect the reversible wettability change (Fig. 1).

Fig. 1. Schematic representation of *trans* and *cis* states of the azobenzene units through UV-Vis light irradiation.

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 azobenzene group

4-(Phenylazo)phenyl 3,5-di(3-aminophenyl)benzoate (Azo-DA) was synthesized by two step reactions from 4-(phenylazo)phenol as a starting material *via* esterification with 3,5-dibromobenzoic acid using DCC/DMAP, then *via* Suzuki coupling reaction with 3-aminophenylboronic acid (Fig. 2).

4-(Phenylazo)phenyl 3,5-dibromobenzoate (Azo-Br₂)

4-(Phenylazo)phenol (1.0 g, 5.04 mmol) and 3,5-dibromobenzoic acid (1.41 g, 5.04 mmol) were dissolved in 50 mL of dry dichloromethane. After adding *N,N*-dicyclohexylcarbodiimide (DCC) (2.08 g, 10.08 mmol) and a catalytic amount of *N,N*-dimethyl-4-aminopyridine (DMAP) while stirring, the stirring was continued for 3 h at 50 °C.

Fig. 2. Synthesis of Azo-DA.

Completion of the reaction was monitored by TLC (MERCK Silica gel F254, dichloromethane, R_f = 0.83). Precipitated *N,N*-dicyclohexylurea (DCU) was filtered off and the filtrate was evaporated and the residue was subjected to a column chromatograph (Wako SiO₂ C-300, CH₂Cl₂). The first fraction was collected and recrystallized from a mixture of methanol and dichloromethane. Yield, 68 %. Mp. 134.8 °C; ¹H NMR (500 MHz, CDCl₃, δ): 7.38-7.38 (m, 2H, Ha) 7.50 (m, 3H, Hb) 7.92 (s, 1H, Hc) 7.94-7.95 (m, 2H, Hd) 8.01-8.03 (m, 2H, He) 8.29 (s, 2H, Hf) ppm; IR (ATR); 3073 (C-H), 1740 (C=O), 1558 (N=N) cm⁻¹.

4-(Phenylazo)phenyl 3,5-di(3-aminophenyl)benzoate (Azo-DA)

Azo-Br₂ (1.0 g, 2.17 mmol) and 3-aminophenylboronic acid (0.77 g, 5.62 mmol) were dissolved in mixture of 40 mL of deoxidized THF and 13 mL of 1 M sodium carbonate aqueous solution. After adding tetrakis(triphenylphosphine) palladium (0) (0.252 g, 0.217 mmol) while stirring, the stirring was continued for 48 h at 75 °C. This reaction was carried out under argon atmosphere. Completion of the reaction was monitored by TLC (MERCK Silica gel F254, ethyl acetate:hexane = 2:3, R_f = 0.08). Solvents were evaporated and the residue was subjected to a column chromatograph (Wako SiO₂ C-300, ethyl acetate:hexane = 2:3). The second fraction was collected and recrystallized from a mixture of chloroform and hexane. Yield. 30 %. The analytical data of Azo-DA are as follows: Mp 180.5 °C; ¹H NMR (500 MHz, CDCl₃, δ): 3.78 (s, 4H, -NH₂), 6.73(d, 2H, J = 8.0Hz, Ha), 7.00 (s, 2H, Hb), 7.09 (d, 2H, J = 7.5 Hz, Hc), 7.28 (t, 2H, J = 7.75 Hz, Hd), 7.42 (d, 2H,

$J = 8.5$ Hz, He), 7.48 (t, 1H, $J = 3.75$ Hz, Hf), 7.53 (t, 2H, $J = 7.5$ Hz, Hg), 7.92 (d, 2H, $J = 8.0$ Hz, Hh), 8.02 (d, 2H, $J = 8.0$ Hz, Hi), 8.02 (s, 1H, Hj), 8.36 (s, 2H, Hk) ppm; IR (ATR); 3370 (-NH_2), 2925 (C-H), 1720 (C=O) cm^{-1} , 1520 (N=N) cm^{-1} .

2.3. Synthesis of polyimide having azobenzene group on their side chain

The polyimides having azobenzene group on their side chain were synthesized from 3,4'-ODPA or DSDA, as a tetracarboxylic dianhydride and a novel functional diamine monomer, Azo-DA. Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed as a same manner as previously reported [7-17]. The chemical structures of obtained polyimides are shown in Fig. 3.

Fig. 3. Chemical structures of polyimides based on 3,4'-ODPA/Azo-DA and DSDA/Azo-DA.

2.4. Measurements

^1H NMR spectra were measured on a JEOL JNM-AL500 FT NMR in CDCl_3 with tetramethylsilane (TMS) as an internal reference. Size exclusion chromatography (SEC) measurements were performed in NMP containing 10 mM LiBr at 40 $^\circ\text{C}$ 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 $^\circ\text{C}$. 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: 0.5-2.0 wt % polyimide solution in NMP were cast on glass substrates and the solution were slowly evaporated by heating at approximately 100-120 $^\circ\text{C}$ until the films were dried, then the films were dried in a vacuum oven at 100 $^\circ\text{C}$ for 12 h. Water contact angles were measured by SImage mini (Excimer. Inc., Japan). UV light irradiation were performed using UV lamp unit LC-L1V3 (λ max 365 nm, 800 mW/cm^2 , Hamamatsu Photonics. Inc., Japan) at the 15 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 40 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. XPS measurements were carried out on an XPS-APEX (Physical Electronics Co. Ltd.) with an Al K α X-ray source (150 W). Chamber pressure; 10^{-9} - 10^{-10} Pa; take off angles; 45 $^\circ$.

3. Results and discussion

3.1. Synthesis of polyimide having azobenzene group

Since the reductive reaction of aromatic dinitro precursor cannot be used in the diamine synthesis having azobenzene group, Suzuki coupling reaction using 3-aminophenylboronic acid is a strong tool to obtain the aromatic diamine having the functional groups that are reactive with reductive reagents. 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 (M_n ; 11700~20900, 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.

The thermal properties of these polyimides were estimated by thermal degradation temperatures (T_{d10} ; 420~422 $^\circ\text{C}$ in air,

420~427 °C under nitrogen) and glass transition temperatures (T_g ; 250~261 °C), and it is recognized the all polyimides can be ranked as heat resistant polymers (Table 1).

Table 1. General properties of polyimides based on Azo-DA.

Monomer			Polyimide				
Anhydride	Diamine		Molecular Weight ^a			T_d ^b	
	mol %		Mn	Mw	Mw/Mn	°C (in Air)	°C (under N ₂)
3,4'-ODPA	DSDA	Azo-DA					
100	0	100	20900	56700	2.7	420	427
0	100	100	11700	21800	1.9	422	420
							T_g ^c (under N ₂)
							250
							261

^aDetermined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. ^b10% Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. ^cMeasured 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

The polyimide thin films were irradiated by UV light (365 nm, 0, 3, 4, 5 min), then the contact angles for the water were measured (Fig. 4). The water contact angles of the polyimide based on DSDA/Azo-DA decreased from 101.5° to 87.6° by UV light irradiation, while the water contact angle of the polyimide based on 3,4'-ODPA/Azo-DA decreased from 88.0° to 82.2° by UV light irradiation. Then, these thin films irradiated by UV light (5 min) were irradiated by Vis light (1, 2, 3, 4, 5 hr) and the contact angles for the water were measured (Fig. 4). The water contacts of the polyimide based on DSDA/Azo-DA recovered from 87.6° to 95.8° by Vis light irradiation, while the water contact angle of the polyimide based on 3,4'-ODPA/Azo-DA recovered from 82.2° to 85.5° by Vis light irradiation.

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

Thus, reversible control of surface wettability of polyimides based on Azo-DA by UV-Vis light irradiation were observed, and the degree of wettability change was larger in the case of polyimides based on DSDA/Azo-DA than in the case of polyimide based on 3,4'-ODPA/Azo-DA. It is speculated that these reversible wettability changes are based on the polarity changes of azobenzene photoisomerization. *Cis*-azobenzene is more polar than *trans* (*E*)-azobenzene unit so *cis* (*Z*)-azobenzene is more hydrophilic than *trans*-azobenzene unit (Fig. 5).

Fig. 5. The reversible change of the wettability based on the photo-isomerization of the azobenzene.

3.4. Surface analysis

Solid state surface reflected UV-Vis measurements were performed using the polyimide film based on DSDA/Azo-DA (Fig. 6). UV absorption based on azobenzene *cis*-form was observed around 440 nm, and the intensities of this absorption increased by the UV light irradiation time and decreased by Vis light irradiation. These data support that the photo-isomerization of azobenzene unit occurs on the polyimide surface shown in Fig. 5. On the other hand, UV absorption based on azobenzene *trans*-form around 330 nm could not be observed, because the UV absorption of the polyimide back-bone overlaps.

The intensive surface analysis was performed by XPS using the polyimide film based on DSDA/Azo-DA. The elemental analysis values (%) obtained from the wide scans are organized in Table 2. It should be noticed that O% increases from 15.85 % to 20.44 % after the UV light irradiation (365 nm, 5 min). It is speculated that OH groups and COOH groups appears on the polyimide surface. However, this value (20.44 %) showed almost same value

(21.28 %) after Vis light irradiation. The elemental analysis of S (%) decreased by UV light irradiation, and not recover by Vis light irradiation. It is imagined that S=O bonds in DSDA/Azo-DA polyimide surface are decomposed on the course of photo irradiation process. On the other hand, N 1s narrow scan indicate that reversible photo-isomerization occurs based on the reversible changes of N 1s peak binding energy and full width at half maximum (FWHM, calculated by MultiPak software) (Table 2, Fig. 7). The similar analysis of azobenzene analogue was previously reported in detail using X-ray absorption spectroscopy [20].

Fig. 6. Solid state surface reflected UV-Vis measurements using the polyimide film based on DSDA/Azo-DA. Upper; UV light irradiation, Lower; Vis light irradiation.

Table 2. Elemental analysis by XPS wide scan and N 1s peak analysis by XPS N 1s narrow scan using DSDA/Azo-DA polyimide film.

	Elemental analysis by XPS wide scan				N 1s peak analysis	
	C (%)	O (%)	N (%)	S (%)	Binding energy [eV]	FWHM ^a
0J	78.29	15.85	4.77	1.09	400.89	1.4238
UV 5min	73.82	20.44	5.38	0.36	401.09	1.5527
Vis 5h	73.16	21.28	5.43	0.14	400.65	1.3527

a) Full width at half maximum

Concerning on the above analytical results, it can be speculated that the following photochemical reactions are generated in the polyimide surface (Fig. 8). After UV light irradiation, *trans*-azobenzene unit is isomerized to *cis*-azobenzene unit and the photo-oxidation of polyimide partly occurs on the surface. Consequently, the polyimide surface become more

hydrophilic (water contact angle; $101.5^\circ \rightarrow 87.6^\circ$). By the following Vis light irradiation, *cis*-azobenzene unit is isomerized to *trans*-azobenzene unit, however, the oxidized surface remains. Therefore, the reversible wettability change was not enough completed (water contact angle; $87.6^\circ \rightarrow 95.8^\circ$). Although the reversible wettability changes of polyimide based on 3,4'-ODPA/Azo-DA was also observed, the degree of wettability changes was small, and this phenomenon has not been well explained. It is necessary to carry out the many experimental using various polyimides having azobenzene groups to optimize the structure of polyimides.

It is also necessary to optimize the UV-Vis irradiation process, investigate the effect of substitute groups of azobenzene ring [21], and perform the detail surface analysis.

Fig. 7. N 1s peak analysis by XPS narrow scan using DSDA/Azo-DA polyimide film.

Fig. 8. Anticipated photochemical reactions on the surface of polyimides by UV-Vis light irradiation.

4. Conclusion

Novel aromatic diamine monomer (Azo-DA) having azobenzene group and corresponding polyimides were successfully synthesized. The reversible control of surface wettability of polyimide films having azobenzene group by UV-Vis light irradiation was accomplished and analyzed by solid-state surface reflected UV-Vis spectra and XPS measurements. However, the complete reversible changes of surface wettability were not achieved and the cycle photo-isomerization was not examined. The further research focusing on the enhancement of reversible control of wettability and the thorough surface analysis are desired.

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