Surface Wettability Controllable Polyimides Bearing Long-chain Alkyl Groups by UV Light Irradiation

Yusuke Tsuda* and Syouma Kawabata

Department of Biochemistry & Applied Chemistry
Kurume National College of Technology,
Komorino 1-1-1, Kurume, Fukuoka 830-8555, Japan
* tsuda@kurume-nct.ac.jp

The novel aromatic diamine monomer, 4-(3,5-diaminobenzoyl)phenyl 3,4,5-tris(decyloxy)benzoate (3C₁₀-PEBPDA) having three long-chain alkyl groups connected by phenylester and benzophenone linkages was synthesized *via* six step reactions from gallic acid methyl ester. The novel polyimides and copolyimides were synthesized from 3,4'-oxydiphthalic anhydride (3,4'-ODPA) as a dianhydride, 3C₁₀-PEBPDA, and 4,4'-diaminodiphenylether (DDE) as a diamine co-monomer by two step polymerization systems. The thin films of obtained polyimides were irradiated by UV light (λ_{max} ; 254 nm), and the contact angles for the water decreased from near 100° (hydrophobicity) to near 50° (hydrophilicity) in proportion to irradiated UV light energy. Furthermore, it was observed that the incorporation ratios of 3C₁₀-PEBPDA in copolyimides affected the changes of surface wettability by UV light irradiation. From the result of various analytical experiments, it is recognized that the hydrophobic long-chain alkyl groups on the polyimide surface decrease and the hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface, and that oxygen in an air affect the generation of these hydrophilic groups.

Keywords: Polyimide, Long-chain alkyl group, UV light irradiation, Surface wettability, Printed electronics

1. Introduction

Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications [1,2]. 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 [3], the surface energy controlled ink-jet printing with UV irradiation [4], 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 [5-15]. The incorporation of long-chain alkyl groups in polyimide backbones has been performed by using the various diamine monomers having long-chain alkyl groups. From the results of various analytical experiments, it is recognized that the hydrophobic groups such as long-chain alkyl groups on the polyimide surface are cleaved or oxidized and the hydrophilic groups such as carboxyl groups and hydroxyl groups generate on their surface by UV light irradiation. The library of these diamine monomers contains 4-[3,5-Bis(3-aminophenyl)phenyl] carbonylamino]phenyl 3,4,5-tris(n-dodecyloxy)benzyloxy benzoate (12G1-AG-Terphenyldiamine) [5], 4-[3,5-Bis(3-aminophenyl)benzophenone]phenyl 3,4,5-tris(decyloxy)benzoate (TerKetone) [7], 4-

(3,5-diaminophenyl carboxy) phenyl 3,4,5-tris(decyloxy) benzoate (3C₁₀-PEPEDA; phenyl ester phenyl ester diamine) and 4-(3,5-diaminophenyl carboxy) phenyl 3,4,5-tris(dodecyloxy) benzoate (3C₁₂-PEPEDA; phenyl ester phenyl ester diamine) [6,9], 4-(3,5-diaminobenzamide)phenyl 3,4,5-tris(decyloxy)benzoate (3C₁₀-PEPADA; phenyl ester phenyl amide diamine) [6,9], and 3,4,5-tris(decyloxy)-N-(4-(3,5-diaminobenzamide)phenyl)benzamide (3C₁₀-PAPADA; phenyl amide phenyl amide diamine) [6] (Fig. 1).

Fig. 1. Diamine monomers having long-chain alkyl groups previously reported.

In this paper, we report the synthesis and properties of the novel polyimides and copolyimides having long-chain alkyl groups based on a novel diamine monomer, 4-(3,5-diaminobenzoyl)phenyl 3,4,5-tris(decyloxy) benzoate (3C₁₀-PEBPDA; 3C₁₀-phenylester benzophenone diamine) having three decyl groups (3C₁₀) connected by phenylester and benzophenone linkages synthesized *via* several step reactions from gallic acid methyl ester. The characteristic feature of 3C₁₀-PEBPDA is that this diamine monomer contains both phenyl ester and benzophenone linkages. According to our previous researches, the phenyl ester linkage group seem to enhance the wettability change by UV light irradiation [6,

9], and the benzophenone linkage seem to play a characteristic roll in the wettability change by UV light irradiation [7]. Although the similar researches have been reported from our laboratory, this paper features the detailed explanation of synthetic procedures and properties of the functional polyimides, also describes some analytical experimental results for explaining the mechanism of these surface wettability changes.

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 3C₁₀-PEBPDA

3C₁₀-PEBPDA having three long-chain alkyl groups connected by phenylester and benzophenone linkages was synthesized *via* six step reactions from gallic acid methyl ester as a starting material (Fig. 2). 3,5-Dinitro-4-hydroxybenzophenone (**1**) were synthesized from 3,5-dinitrobenzoyl chloride and anisole by Friedel-Crafts acylation reaction using aluminum chloride as a catalyst, followed by demethylation using hydrogen bromide as the same manner previously reported [16]. 3,4,5-Tris(decyloxy) benzoic acid (**2**) were synthesized from gallic acid methyl ester followed by Williamson etherification reaction using decylbromide, then hydrolysis reaction in potassium hydroxide solution as the same manner described in previous literatures [17, 18].

Synthesis of 4-(3,5-dinitrobenzoyl)phenyl 3,4,5-tris(decyloxy)benzoate (**3**): 3,5-dinitro-4'-methoxybenzophenone (**1**, 1.00 g, 3.47 mmol) and 3,4,5-tris(decyloxy) benzoic acid (**2**, 2.03g, 3.43 mmol) were dissolve in 65 ml of dry dichloromethane. After adding *N,N*-dicyclohexylcarbodiimide (DCC, 1.43 g, 6.94 mmol) and a catalytic amount of *N,N*-dimethyl-4-aminopyridine (DMAP) while stirring, the reaction was continued for 24 h at 50 °C. Completion of the reaction was

monitored by thin layer chromatography (TLC, MERCK Silica gel F254, dichloromethane, $R_f = 0.88$). 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 evaporated, then, the residue was washed with hot methanol. Yield, 89%. Mp 56.0 °C; ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.86-0.90 (t, 9H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.27-1.37 (m, 36H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.46-1.51 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.73-1.88 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 4.04-4.09 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 7.41 (s, 2H, Ha), 7.45 (d, 2H, Hb, $J = 8.7$ Hz), 7.93 (d, 2H, Hc, $J = 8.8$ Hz), 8.96 (d, 2H, Hd, $J = 2.0$ Hz), 9.27 (t, 1H, He, $J = 2.0$ Hz) ppm (Fig. 4); IR (ATR): 2920 and 2850 (C-H), 1730 and 1670 (C=O), 1540 and 1340 (NO₂), 1190 (-O-) cm⁻¹. Anal. Calcd for C₅₀H₇₂N₂O₁₀: C, 69.74%; H, 8.43%; N, 3.25%. Found: C, 69.50%; H, 8.48%; N, 3.02%.

Fig. 2. Synthesis of 3C₁₀-PEBPDA.

Synthesis of 4-(3,5-diaminobenzoyl)phenyl 3,4,5-tris(decyloxy)benzoate (**4**, 3C₁₀-PEBPDA): a mixture of 4-(3,5-dinitrobenzoyl)phenyl 3,4,5-tris(decyloxy)benzoate (**3**, 1.00 g, 1.16 mmol) and 10% palladium on carbon (Pd/C, 0.12 g) in a mixture of tetrahydrofuran

(THF; 5 mL) and ethanol (20 mL) was stirred at 50 °C for 4 h using the apparatus attached with a balloon filled with hydrogen gas. Completion of the reaction was monitored by thin layer chromatography (TLC, MERCK Silica gel F254, ethyl acetate / hexane = 1: 1, $R_f = 0.58$). The Pd/C was filtered off and the solvent were evaporated. The residue was subjected to a column chromatograph (Wako SiO₂ C-300, ethyl acetate/ hexane = 1: 1). The second fraction was collected and recrystallized from methanol. Yield, 22%. Mp 77.0 °C; ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.86-0.90 (m, 9H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.27-1.34 (m, 36H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.45-1.53 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 1.73-1.87 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 3.72 (broad s, 4H, -NH₂), 4.04-4.09 (m, 6H, -OCH₂CH₂CH₂(CH₂)₆CH₃), 6.23 (t, 1H, Ha, $J = 2.0$ Hz), 6.51 (d, 2H, Hb, $J = 2.0$ Hz), 7.29 (d, 2H, Hc, $J = 8.5$ Hz), 7.41 (s, 2H, Hd), 7.91 (d, 2H, He, $J = 8.5$ Hz) ppm (Fig. 4); IR (ATR): 3380 (NH₂), 2920 and 2850 (C-H), 1730 and 1660 (C=O), 1190 (-O-) cm⁻¹. Anal. Calcd for C₅₀H₇₆N₂O₆: C, 74.96%; H, 9.56%; N, 3.50%. Found: C, 74.66%; H, 9.46%; N, 3.47%.

2.3. Synthesis of Polyimides Having 3C₁₀-PEBPDA

Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed (Fig. 3). The poly(amic acid)s were obtained by reacting the mixture of diamines with an equimolar amount of 3,4'-ODPA at room temperature for 12 h under a nitrogen 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. The experimental details are described in the previous papers [5-15].

2.4. Measurements

¹H NMR spectra were measured on a JEOL JNM-AL400 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. Number average molecular weights (M_n), weight average

Fig. 3. Chemical structures of polyimides based on 3,4'-ODPA/3C₁₀-PEBPDA and DSDA/3C₁₀-PEBPDA.

molecular weights (M_w), and polydispersities (M_w/M_n) were determined by TOSOH Multi Station GPC-8020 calibrated with a series of polystyrenes as a standard. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in air or under nitrogen (50 mL/min) at a heating rate of 10 °C/min using ca. 5 mg of a dry powder sample, and initial decomposition temperatures (T_{d0}), 5% weight loss temperatures (T_{d5}), and 10% weight loss temperatures (T_{d10}) were calculated from the second heating scan after cooling from 250 °C to 800 °C. Differential scanning calorimeter (DSC) traces were measured on a Shimadzu DSC-60 under nitrogen at a heating rate of 10 °C/min 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: 1.0-5.0 wt% polyimide solution in NMP were cast on glass substrates and the solution were slowly evaporated by heating at approximately 100-120 °C until the films were dried, then the films were 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 UV lamp unit E50-254-270U-1 (λ_{max} ; 254 nm, 6.0 mW/cm², Excimer. Inc., Japan) and a cool plate NCP-2215 (NISSIN Laboratory equipment, Japan) adjusted at 25 °C that was used to avoid the effect of the heat that arose in UV light 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 K α X-ray source (150 W). Chamber pressure; 10⁻⁹-10⁻¹⁰ Pa; take off angles; 15°, 30°, 45°. SFM (SII Nanotechnology Inc., SPA 400) was operated in a dynamic force microscopic (DFM) mode.

3. Results and discussion

3.1. Synthesis of 3C₁₀-PEBPDA

The synthetic strategy for 3C₁₀-PEBPDA includes several key points as follows. As the building block containing long-chain alkyl groups, we select gallic acid substituted by long-chain alkyloxy groups that are expected to show the high hydrophobicity due to multiple long-chain alkyl groups. The alkyl chain length is fixed as decyl group (C₁₀), because it is concluded that decyl group is the effective chain length for the generation of hydrophobicity and the improvement of solubility of polyimides according to our previous research [19]. As the connecting group of gallic acid having long-chain alkyl groups and an aromatic diamine, we select the combination of phenyl ester (phenyl benzoate) group and benzophenone group. Because, phenyl ester (phenyl benzoate) group has the possibility to cause the photo reactions such as photo-Fries rearrangement and generate hydroxy groups, and benzophenone is the representative photosensitizer. The synthesis of 3C₁₀-PEBPDA was performed by a condensation of two building blocks (compounds **1** and **2**) using DCC/DMAP followed by a catalytic hydrogenation using Pd/C (palladium on carbon). Although various hydrogenation catalysts such as Os/C (osmium activated carbon) and Pd/Fib (palladium-fibroin) and the various reaction conditions were tried, the yields of these experiments were as low as 22%. The improvement on the yield will be desired in future.

3.2. Synthesis of polyimides and copolyimides based on 3C₁₀-PEBPDA

The synthetic route of the polyimides and copolyimides based on 3C₁₀-PEBPDA is illustrated in Fig. 3. Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed. These are the optimized synthetic conditions previously developed for

the synthesis of soluble polyimides in our laboratory [3-15,19,20]. If the polyimides were insoluble in the polymerization solvent, NMP, gelation or precipitation happened in the course of imidization process. 3,4'-ODPA (a-ODPA; asymmetric ODPa) known as an aromatic tetracarboxylic dianhydride monomer suitable for soluble polyimides [21] was used. DDE, that is a high reactive and common aromatic diamine, was used as a diamine co-monomer.

Experimental results of the synthesis of polyimides and copolyimides based on 3C₁₀-PEBPDA are summarized in Table 1. All of polyimides and copolyimides were soluble in polymerization solvent, NMP without any problem. As these polyimides were also soluble in CHCl₃, the incorporation of 3C₁₀-PEBPDA units in polymer backbones were directly observed by ¹H NMR measurements using CDCl₃ as a NMR solvent (*ca.* 1 wt%, NMR). These molecular weights of obtained polyimides were evaluated by means of SEC measurements (Table 1). The number average molecular weights (*M_n*) and weight average molecular weights (*M_w*) determined by SEC measurements were in the range of 4200 to 39100 (*M_n*), 6500 to 75400 (*M_w*) respectively. These values indicated that the molecular weights of these polyimides are considered medium or rather lower values for polyimides, however, all polyimides show the good film formation ability. The molecular weights were increased with the amounts of DDE that is a high reactive diamine in comparison with 3C₁₀-PEBPDA that is a steric hindered and low reactive *m*-substituted diamine. The *M_n* and *M_w* of homopolyimide based on 3,4'-ODPA/3C₁₀-PEBPDA seem to be very low for the polymers having film forming ability. It can be imagined that the polymer structure became more spherical due to the attachment of multiple long chain alkyl groups, so apparent molecular weights observed by SEC measurements seem to decrease, as describing in our previous literature [7].

3.3. Thermal properties of polyimides based on 3C₁₀-PEBPDA

The glass transition temperatures (*T_g*) of these polyimides were determined by DSC measurements and the thermal stabilities were evaluated by 0 wt% weight-loss temperatures

Table 1. Polyimides and copolyimides based on 3C₁₀-PEBPDA.

Monomer			Polyimide				
Dianhydride	Diamine		Solubility		Molecular Weight ^a		
	mol%		NMP	CHCl ₃	<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
3,4'-ODPA	3C ₁₀ -PEBPDA	DDE					
100	100	0	soluble	soluble	4200	6500	1.6
100	75	25	soluble	soluble	5500	9800	1.8
100	50	50	soluble	soluble	9600	21900	1.8
100	25	75	soluble	soluble	18800	53500	2.8
100	10	90	soluble	soluble	18400	49900	2.7
100	0	100	soluble	soluble	39100	75400	1.9

^a Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrene as a standard.

(*T_{d0}*, degradation onsets), 5 wt% weight-loss temperatures (*T_{d5}*), and 10 wt% weight-loss temperatures (*T_{d10}*) in TGA measurements. All data are summarized in Table 2. *T_g* values obtained by DSC were in the range of 193–200 °C, meaning that the glass transition temperatures lower from 274 °C by the introduction of 3C₁₀-PEBPDA. It is speculated that the flexible long-chain alkyl groups in 3C₁₀-PEBPDA lower the glass transition temperatures. The thermal stabilities of obtained soluble polyimides were evaluated in air and under nitrogen atmospheres using *T_{d0}* (degradation onset), *T_{d5}* and *T_{d10}* for comparison. *T_{d0}* of polyimides based on polyimides and copolyimides based on 3C₁₀-PEBPDA were in the range of 312–382 °C in air and 346–407 °C under nitrogen, *T_{d5}* of these polyimides were in the range of 387–437 °C in air and 394–448 °C under nitrogen, and *T_{d10}* of these polyimides were in the range of 403–536 °C in air and 409–531 °C under nitrogen. These values show the regular values that were observed in soluble polyimides based on long-chain alkyl groups studied in our laboratory (*ca.* 350–500 °C) [3-7,19,20]. As the incorporation of DDE resulted in a reduction of aliphatic components of the polyimides, 0%, 5% and 10% weight-loss temperatures of these polyimides tended to increase by the increment of the DDE component. In most cases, *T_d* values in air were lower than *T_d* values under nitrogen following the general fact that oxidative degradation proceeds rapidly in air than under nitrogen. Consequently, above degradation temperatures are 100–200 °C lower than the conventional fully aromatic polyimides, however, obtained polyimides based on 3C₁₀-PEBPDA still can be ranked as heat resistant polymers.

Table 2. Thermal properties of polyimides and copolyimides based on 3C₁₀-PEBPDA.

Monomer			Polyimide					
Dianhydride	Diamine		T _g ^a	Td ₀ ^b		Td ₅ ^c	Td ₁₀ ^d	
mol%	mol%		°C	Air °C	N ₂ °C	Air °C	Air °C	N ₂ °C
3,4'-ODPA	3C ₁₀ -PEBPDA	DDE						
100	100	0	193	328	346	387	403	409
100	75	25	196	312	368	393	418	420
100	50	50	200	344	376	416	428	426
100	25	75	199	338	367	383	426	441
100	10	90	193	382	407	437	536	531
100	0	100	274	557	554	581	595	596

^a Measured by DSC at a heating rate of 10 °C /min in N₂ on second heating. ^b 0% Weight loss temperature (degradation onset), measured by TGA at a heating rate of 10 °C /min. ^c 5% Weight loss temperature, measured by TGA at a heating rate of 10 °C /min. ^d 10% Weight loss temperature, measured by TGA at a heating rate of 10 °C /min.

3.4. Surface wettability control of polyimides based on 3C₁₀-PEBPDA by UV light irradiation

The polyimide thin films were irradiated by UV light (λ_{max} ; 254 nm, 0, 2, 4, 6, 8 J), then the contact angles for the water were measured. Fig. 4 shows UV light irradiation energy dependence of water contact angles of polyimide films based on 3C₁₀-PEBPDA. The water contact angle of polyimide films based on 3,4'-ODPA/DDE polyimides before UV irradiation is 89.4 deg, while, those of 3,4'-ODPA/3C₁₀-PEBPDA/DDE copolyimides are around 100°. This high hydrophobicity is certainly due to the hydrophobic property of multiple long-chain alkyl groups. These high water contact angles of polyimides bearing long-chain alkyl groups decreased from around 100° (hydrophobicity) to the minimum value; 50.9 deg (hydrophilicity) in proportion to irradiated UV light energy. It is considered that these changes of surface wettability of polyimides are mainly based on the photo-degradation or scission of long-chain alkyl groups and specific functional groups such as an ester group, and that the generation of the hydrophilic functional groups such as COOH and OH groups probably occurs. It is interesting that the changes of contact angles by UV light irradiation are larger in the case of copolyimides containing smaller amounts of 3C₁₀-PEBPDA (3C₁₀-PEBPDA; 25 mol%, 10 mol%). On the other hand, the water contact angle of 3,4'-ODPA /DDE polyimide also somewhat decreases after UV light irradiation, therefore, the generation of hydrophilic groups

on polymer main chains possibly occurs to some extent. Consequently, it can be imagined that the hydrophobicity is maintained by a large amounts of long-chain alkyl groups cover the top surface of polyimides, even if the hydrophilic groups are formed on the surface of polyimides by UV light irradiation, in the case that the concentration of the long-chain alkyl groups is larger (3C₁₀-PEBPDA; 100 mol%, 75 mol%, 50 mol%). The authors named this speculation as “the concentration effect” that was described in detail in the previous literature [7].

Fig. 4. UV light irradiation energy dependence of water contact angles of polyimide films.

3.5. Surface analysis

The surface analysis of the polyimide films were performed by ATR, XPS, and AFM. 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 occur. The absorption of OH groups around 3600 cm⁻¹ appeared, the absorption of alkyl groups around 2900 cm⁻¹ decreased, and the absorption of ether groups around 1200 cm⁻¹ decreased by UV light irradiation (Fig. 5). In the case of ATR

Fig. 5. ATR spectra of polyimide based on 3,4'-ODPA/ 3C₁₀-PEBPDA (100/100) before and after UV light irradiation. ATR: attenuated total reflectance.

measurements, the penetration depth of a beam of infrared light into the sample is typically between 0.5 and 2 μm . Therefore, the above ATR analysis does not reflect the chemical composition of the film top surface.

The intensive surface analyses were examined using XPS analysis that give the information of each elements at the region of the single nm depth from the film top surface before/after UV light irradiation. The atomic percent data of the polyimide surface based on the XPS measurements under the standard take-off angle (45 deg) are summarized in Table 3, using polyimide films containing different amounts of 3C₁₀-PEBPDA (0 mol%, 10 mol%, 100 mol%). The observed atomic percent of C, O, N were calculated based on the peaks of C_{1s}, O_{1s}, and N_{1s} respectively. In all cases, the atomic percent of C were decreased and the atomic percent of O were increased after UV light irradiation, meaning that C-C bond based on alkyl groups decreased and C=O and C-O bond based on carboxyl groups and hydroxyl groups increased. However, these tendency was similar in both polyimides containing 3C₁₀-PEBPDA (10 mol%, 100 mol%) and it is difficult to explain why the lowering degree of the contact angle after UV light irradiation of the polyimide containing 10 mol% of 3C₁₀-PEBPDA is larger than those of the polyimide containing 100 mol% of 3C₁₀-PEBPDA. In order to clarify this phenomena, the characterization of XPS narrow scans of C_{1s} under the different take-off angles (45-30-15 deg) were performed (Fig. 6). The information of the more top surface are obtained in the lower take-off angles (15 deg). Consequently, it was observed that the peaks based on C-O and C=O appears in the case of the polyimide containing 10 mol% of 3C₁₀-PEBPDA after UV light irradiation on the film top surface (take-off angle; 15 deg), while those peaks in the case of the polyimide containing 100 mol% of 3C₁₀-PEBPDA were not observed. On the other hand, it was observed C-O and C=O bonds at the deeper region from the top surface (the take-off angle; 30 deg, 45 deg) after UV light irradiation in the case of both polyimides containing 100 mol% of 3C₁₀-PEBPDA and containing 10 mol% of 3C₁₀-PEBPDA. It can be presumed that the larger amounts of long-chain alkyl groups of 3C₁₀-PEBPDA cover the top surface of polyimide films after UV light irradiation, even though the carboxyl and hydroxyl groups partly generate.

The nm size micro roughnesses of film top surface was analyzed by AFM (DFM mode) (Fig. 7).

Table 3. Atomic percent of polyimide surface based on XPS measurements.

Polyimide Sample	Radiation Contact		Atomic percent based on XPS ^c					
	Energy ^a (J)	Angle ^b (deg)	C (%)		O (%)		N (%)	
			Theo.	Obsd.	Theo.	Obsd.	Theo.	Obsd.
3,4'-ODPA / 3C ₁₀ -PEBPDA / DDE (100/100/0)	0	100.8	79.5	77.8	17.7	18.4	2.8	3.8
	8	88.9	79.5	68.7	17.7	27.8	2.8	3.5
3,4'-ODPA / 3C ₁₀ -PEBPDA / DDE (100/10/90)	0	103.5	74.3	82.7	20.2	15.2	5.5	2.1
	8	50.9	74.3	71	20.2	23.4	5.5	5.6
3,4'-ODPA / 3C ₁₀ -PEBPDA / DDE (100/0/100)	0	89.4	73.6	77.2	20.9	18.7	6.1	4.1
	8	81.3	73.6	72.6	20.9	27.3	6.1	0.1

^a UV light irradiation (λ_{max} ; 254 nm, 0-8 J). ^b Water contact angles (deg) using contact angle meter (Excimer inc., SImage). ^c 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°.

Fig. 6. XPS narrow scan of C_{1s} of polyimides based on 3,4'-ODPA/3C₁₀-PEBPDA/DDE before and after UV light irradiation (Take-off angles; 45 deg, 30 deg, 15 deg).

It was observed that RMS (root mean square) values that indicated the micro roughness of film surface were slightly increased with the amounts of 3C₁₀-PEBPDA segments before UV light irradiation, meaning that the existence of long-chain alkyl groups somewhat affect the surface roughness. After UV light irradiation, these micro roughness somewhat increased probably because of the film roughening by the UV light irradiation, and seem not to be correlated with the changes of surface wettability. Thus, it can be concluded that the changes of surface wettability of polyimide films are occurred mainly by the changes of chemical structures in polyimide surface.

3.5. Elucidation of the mechanism of the wettability change

Finally, the following experimental were carried out to elucidate the mechanism of the wettability change of polyimides by UV light irradiation. Firstly, UV light irradiation to the polyimide;

Fig. 7. AFM images of the polyimides based on 3,4'-ODPA/3C₁₀-PEBPDA/DDE before and after UV light irradiation.

3,4'-ODPA/3C₁₀-PEBPDA (100/100) in dichloromethane (0.05 mmol unit/L), that is UV transparent solution, was performed to analyze the photo-degradation products. After the UV light irradiation (8 J) to the polyimide solution in quartz cell, the solution was poured in a large amounts of methanol and ¹H NMR spectra of the precipitated polyimide (methanol insoluble parts) and the methanol soluble parts were measured and compared with ¹H NMR spectra of the original polyimide before UV light irradiation (Fig. 8). Consequently, the similar peaks appeared in ¹H NMR spectra of the original polyimide and the precipitated polyimide, while large aliphatic proton peaks and very small aromatic peaks appeared in ¹H NMR spectra of methanol soluble parts. Although photoreaction in the solution and photoreaction of the solid surface cannot be completely the same, it is confirmed that the scission of the long-chain alkyl groups occur in the photo-irradiation process.

Secondly, the effect of atmospheres in the course of UV irradiation were investigated using the quartz cell with the seal cap in which the oxygen or argon

Fig. 8. ¹H NMR spectra in UV light irradiation experiment using polyimide solution (3,4'-ODPA/DDE homopolyimide in dichloromethane solution; 0.05 mmol unit/L, UV light irradiation energy; 8 J).

gas and polyimide film on glass substrates were enclosed (Fig. 9). In argon atmosphere, the water contact angle of the polyimide containing 10 mol% of 3C₁₀-PEBPDA slightly reduced from 95 deg to 87 deg by UV light irradiation, while those of the polyimide containing 100 mol% of 3C₁₀-PEBPDA are the quite same; 103 deg. In air or oxygen atmosphere, the water contact angle of the polyimide containing 10 mol% of 3C₁₀-PEBPDA largely decreased from 95 deg to 50-55 deg by UV

Fig. 9. Effect of atmospheres (argon, air, oxygen) on the course of UV light irradiation to the change of surface wettability.

light irradiation, while those of the polyimide containing 100 mol% of 3C₁₀-PEBPDA considerably decreased from 103 deg to 82-85 deg. From these results, it is convinced that the changes of surface wettability mainly occurs by the photo-oxidation and eventually hydroxyl groups and carboxyl groups generate on the polyimide surface. It is interesting that the margins of the decrease of contact angles after UV light irradiation in air or oxygen atmosphere are larger in the case of the polyimide containing 10 mol% of 3C₁₀-PEBPDA than in the case of the polyimide containing 100 mol%. It is again speculated that a large amounts of long-chain alkyl groups cover the polyimide surface even after UV light irradiation in the case of the polyimide containing 100 mol%.

4. Conclusion

The thin films of polyimides bearing three long-chain alkyl groups were irradiated by UV light, and the contact angles for the water decreased from near 100° (hydrophobicity) to near 50° (hydrophilicity) in proportion to irradiated UV light energy. From the result of surface analysis, it is recognized that the hydrophobic long-chain alkyl groups on the polyimide surface decrease and the hydrophilic groups generate on their surface mainly by the scission of long-chain alkyl groups and the photo oxidation. The changes of surface wettability by UV light irradiation were larger in the case of copolyimides containing smaller amounts of long-chain alkyl groups (3C₁₀-PEBPDA; 25 mol%, 10 mol%). It can be presumed that this phenomena is based on “the concentration effect” that the larger amounts of long-chain alkyl groups cover the top surface of polyimides even though the hydrophilic groups generate on their surface by UV light irradiation and XPS analysis supports this effect. Practically, the reduction of the amounts of special monomer, 3C₁₀-PEBPDA is the great merit. Although these results contain the similar ones previously reported by our laboratory, the mechanism of the surface wettability changes is considerably clarified in this paper.

The fine-tuning of dimaine monomer structures, the addition of photo acid generator, the variation of hydrophobic groups, the reversible changes of surface wettability by UV light irradiation are now under

investigation.

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