Surface Wettability Controllable Polyimides Having Natural Product Skeletons by UV Light Irradiation

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Abstract: Novel diamine monomers having hydrophobic groups were synthesized from natural products such as ferulic acid, cholesterol and γ-oryzanol. The novel polyimides and copolyimides were synthesized from 3,4'-ODPA as a dianhydride, above diamines having natural product skeleton, and DDE as a diamine co-monomer by two step polymerization systems. The thin films of obtained polyimides were irradiated by UV light (λmax; 254 nm), and the contact angles for the water decreased from 90- 110° (hydrophobicity) to minimum 35° (hydrophilicity) in proportion to irradiated UV light energy. The tendency in this wettability change is larger in the case of polyimides based on a γ-oryzanol skeleton than in the case of polyimides based on a ferulic acid and cholesterol skeleton. From the result of surface analyses (ATR, XPS, AFM), it is recognized that the hydrophobic alkyl groups on the polyimide surface decrease and the hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface.

Keywords: Polyimide / γ-Oryzanol / Feruic acid / Cholesterol / UV irradiation / 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, 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 [(3)-(9)]. 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 [(10)], the surface energy controlled ink-jet printing with UV irradiation [(11)], have been investigated to obtain the fine patterning. Recently, the authors also have investigated the surface wettability control of polyimides bearing long-chain alkyl groups by UV light irradiation [(8), (12)-(16)]. The basic concept of these surface wettability controllable polyimides is shown in Figure 1. In this paper, we report the synthesis and properties of the novel surface wettability controllable polyimides based on natural product skeletons. The features of our research have been to introduce the functional diamine monomer segments having hydrophobic units and photo reactive units into the polyimide backbone. However, it is disadvantageous that the synthesis of these diamine monomers required 6-8 step reactions, and that the yields of some reactions are low. For such reason, we select three natural product skeletons, the first one is ferulic acid that have a photo reactive cinnamic acid group and a reactive phenolic OH group and a COOH group, the second one is cholesterol that have a hydrophobic cholesterol unit, the third one is γ-oryzanol that have a ferulic acid unit and a hydrophobic cholesterol unit (Figure 2). The use of inexpensive natural products is related to the merit of the synthesis cost reduction as well as the simplification of experimental procedure.

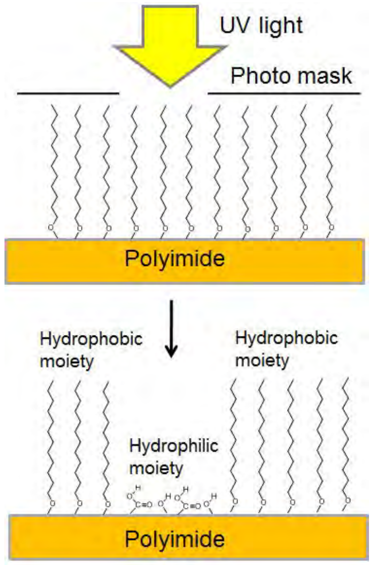


Figure 1. Conceptual scheme of wettability control of the polyimide surface by UV light irradiation.

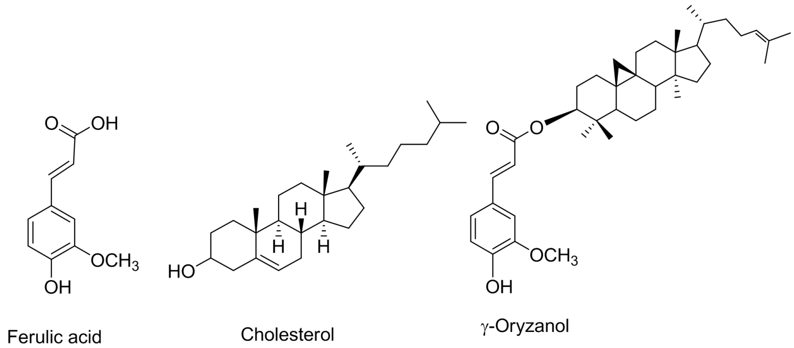
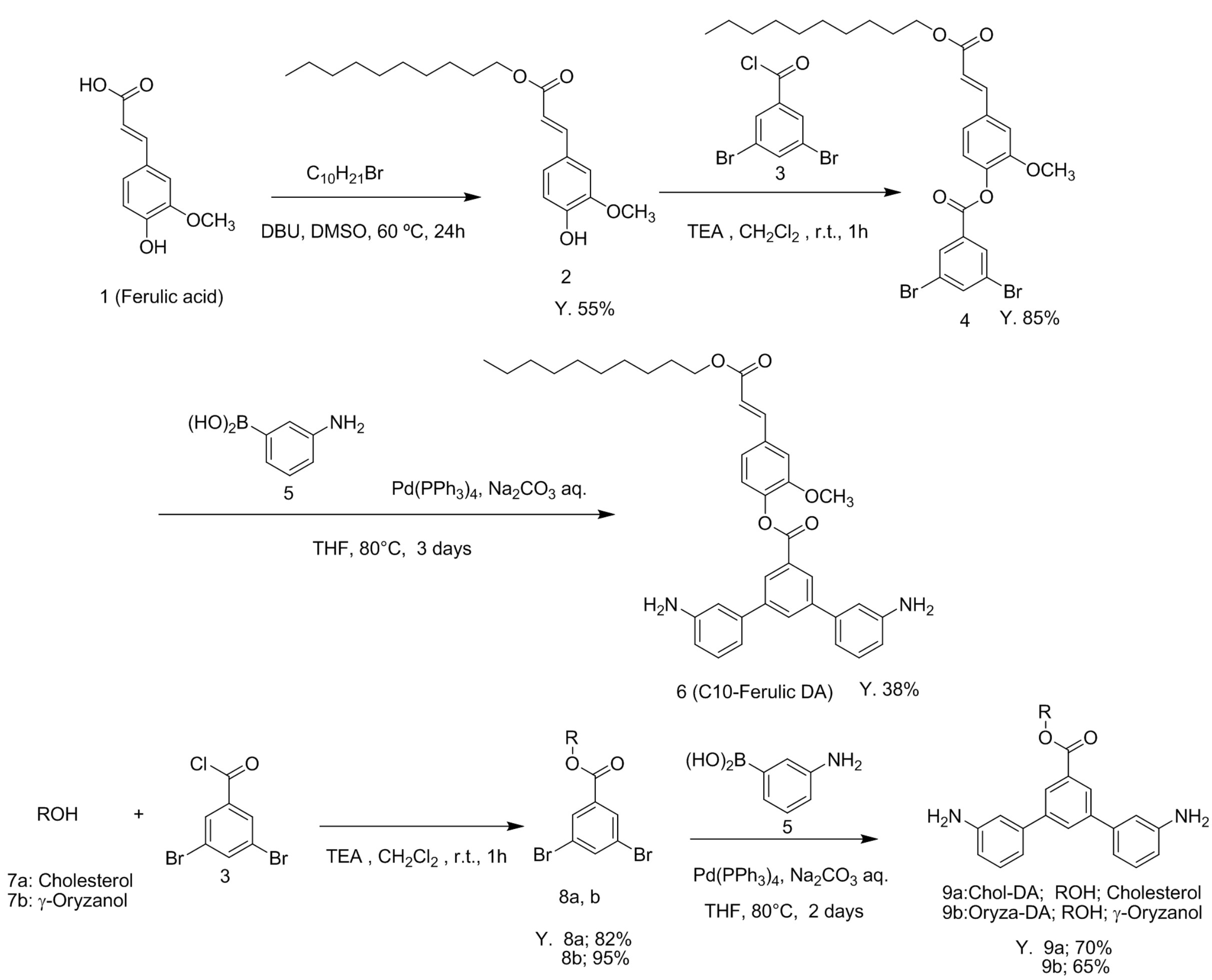


Figure 2. Chemical structures of natural products.

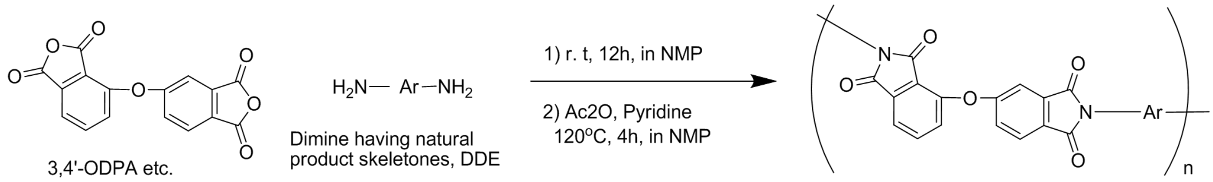
2. Results and Discussion

2.1 Synthesis of polyimides having natural product skeletons

Novel diamine monomers having natural product skeleton were easily synthesized *via* two or three step reactions. It is considered that the simplification of synthetic methods is a large merit. C_{10}-Ferulic-DA [4-((E)-2-((decyloxy) carbonyl)vinyl)-2-methoxyphenyl 3,5-di(3-aminophenyl) benzoate] was synthesized *via* three step reactions from ferulic acid as a starting material (Scheme 1). Chol-DA [Cholesteryl3,5-bis(3-aminophenyl)benzoate] and Oryza-DA [4-((E)-2-((cycloartenoxy) carbonyl)vinyl)-2-methoxyphenyl 3,5-di(3-aminophenyl) benzoate] were synthesized *via* two step reactions from cholesterol or γ-oryzanol as a starting material (Scheme 1). The polyimides were synthesized from 3,4'-ODPA, as a tetracarboxycilic dianhydride, novel diamine monomers, and DDE as a diamine co-monomer (Scheme 2). Two step polymerization systems including poly(amic acid)s synthesis and chemical imidization were performed. The poly(amic acid)s were obtained by reacting the mixture of diamines with an equimolar amount of tetracarboxylic dianhydride at room temperature for 12 h under an argon 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 following the methods previously reported [(3)-(9), (12)-(16)].



Scheme 1. Synthesis of novel diamine monomers having natural product skeleton



Scheme 2. Synthesis of polyimides having natural product skeletons

3.2. General properties of polyimides

The obtained polyimides showed the good solubility in polymerization solvent, NMP. The molecular weights of polyimides were measured by SEC (Mn; 4400~47600, in NMP/10mM LiBr calibrated with standard polystyrenes), and the all polyimides showed the good film forming ability. However, the films obtained from the homo-polyimide based on 3,4'-ODPA/Oryza-DA became brittle. The thermal properties of these polyimides were estimated by glass transition temperatures (Tg; 157~263 ^{o}C) and thermal degradation temperatures (Td_{10}; 338~561 ^{o}C in air, 363~567 ^{o}C under nitrogen), thus, it was recognized that these polyimides showed the good thermal stability. When the concentration of C_{10}-Ferulic-DA or Oryza-DA are low, both the thermal properties and the molecular weights are improved because of the reduction of aliphatic segments and the increment of high reactive fully aromatic diamine monomer, DDE.

Table 1. General properties of polyimides having natural product skeletons.

Monomer[a]						Td_{10}[d]	
Diamine		Molecular Weight[b]			Tg[c]	Air	N_2
mol%		Mn	Mw	Mw/Mn	°C	°C	°C
C_{10}-Ferulic-DA	DDE						
0	100	39100	75400	1.9	ND[e]	597	596
10	90	25800	75100	2.9	164	510	549
20	75	19500	51000	2.6	167	460	494
50	50	22200	49200	2.2	166	390	420
100	0	9900	34800	3.5	157	418	405
Chol-DA	DDE						
0	100	39100	75400	1.9	ND[e]	597	596
10	90	10100	28300	2.8	234	561	567
25	75	11300	24000	2.1	242	370	372
50	50	26000	62000	2.4	231	432	371
75	25	5300	10300	1.9	236	421	341
100	0	4400	7200	1.6	201	425	344
Oryza-DA	DDE						
0	100	39100	75400	1.9	ND[e]	597	596
10	90	33900	78900	2.3	263	538	546
25	75	22700	51400	2.3	230	400	394
50	50	15900	46800	2.9	196	343	376
75	25	47600	186600	3.9	ND[e]	338	371
100	0	10100	33200	3.3	189	349	363

[a]Equimolar amount of 3,4'-ODPA was used to the total amount of diamines. [b]Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard.[c]Measured by DSC at a heating rate of 20℃/min in N_2 on second heating. [d]10% weight loss temperature, measured by TGA at a heating rate of 10℃/min. [e]Not Detectable.

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

The polyimide thin films were irradiated by UV light (254 nm, 0, 2, 4, 6, 8 J), then the contact angles for the water were measured. Figure 1-3 show UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/ C_{10}-Ferulic-DA /DDE polyimides and copolyimides (Figure 1), 3,4'-ODPA/Chol-DA /DDE polyimides and copolyimides (Figure 2), 3,4'-ODPA/Oryza-DA /DDE polyimides and copolyimides (Figure 3) respectively. The water contact angle of polyimide films based on 3,4'-ODPA/DDE polyimides before UV irradiation is around 80°, while the contact angles of polyimides containing C_{10}-Ferulic-DA, Chol-DA, Oryza-DA are 90-110°. This high hydrophobicity is due to the hydrophobic property of a decyl group or a cholesterol unit, and the hydrophobicity is larger in polyimides containing Chol-DA or Oryza-DA unit. The above high water contact angles of polyimides bearing hydrophobic groups decreased in proportion to irradiated UV light energy. The changes of wettability by UV irradiation are larger in the case of polyimides containing an Oryza-DA unit, especially, the contact angles of 3,4'-ODPA/ Oryza-DA/DDE (100/10/90 mol%) drastically decreased from 90.5° (0 J) to 34.5° (8 J). It can be speculated that a photo reactive cinnamic acid skeleton and a cholesterol unit included in Oryza-DA effectively contribute. The changes of wettability by UV irradiation in polyimides based on C_{10}-Ferulic acid seem not to be depended on the mol% of C_{10}-Ferulic-DA, while those based on Chol-DA or Oryza-DA seem to be depended on the mol% of Chol-DA or Oryza-DA. The changes of wettability by UV irradiation were larger in the case of copolyimides containing smaller amounts of cholesterol or oryzanol unit. It can be presumed that this phenomena is based on the "concentration effect" [15] that the larger amounts of hydrophobic groups cover the top surface of polyimides even if the hydrophilic groups were formed on the surface of polyimides by UV irradiation.

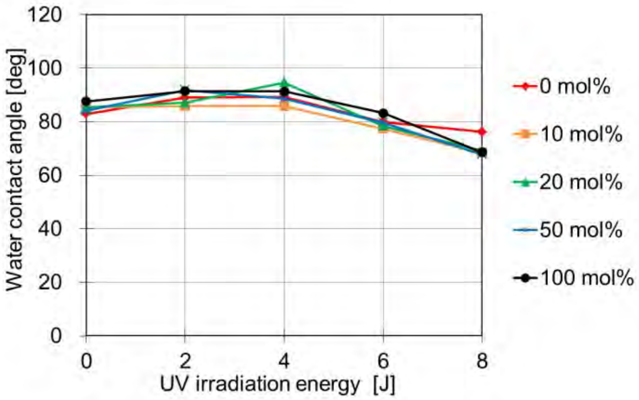


Figure 1. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/ C_{10}-Ferulic-DA /DDE.

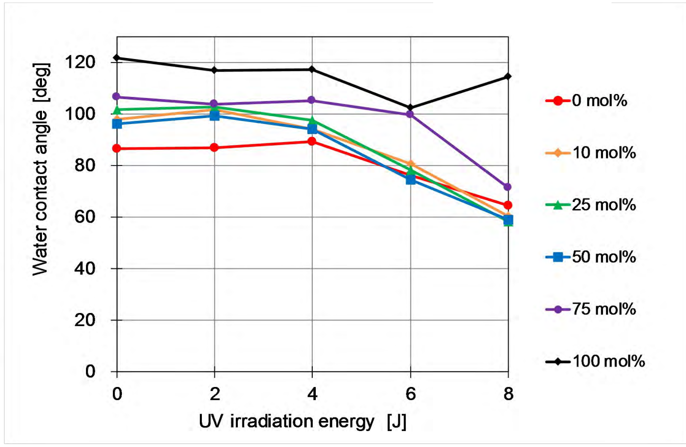


Figure 2. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/ Chol-DA /DDE.

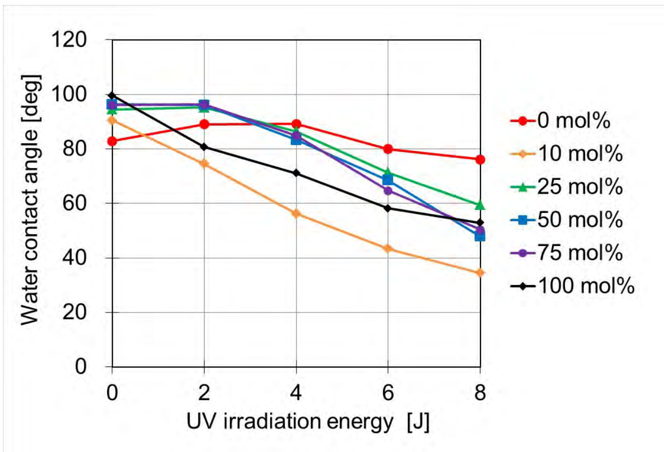


Figure 3. UV irradiation energy dependence of water contact angles of polyimide films based on 3,4'-ODPA/

The surface analyses 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 occurred. The absorption of OH groups around 3300 cm^{-1} increase, the absorption of alkyl groups around 2900 cm^{-1} decrease with the irradiation of UV light (Figure 4).

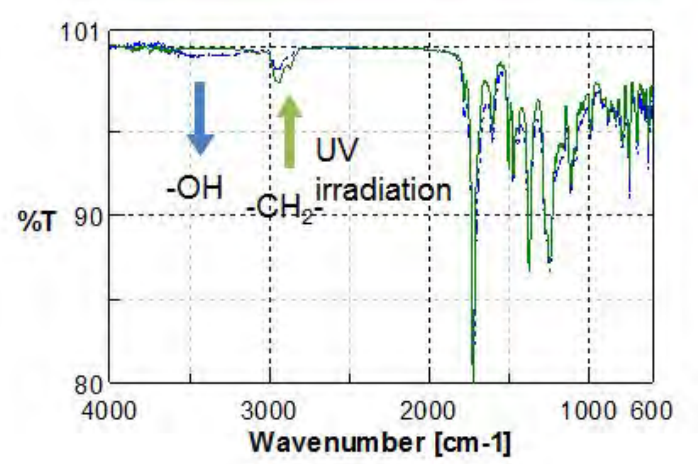


Figure 4. ATR spectrum of polyimides based on 3,4'-ODPA/Oryza-DA/DDE (100/75/25 mol%) before and after UV irradiation

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, the above ATR analysis does not reflect the chemical composition of the film top surface. The intensive surface analyses were examined using XPS and AFM. Table 2 shows the surface elemental analysis of polyimide based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%) by XPS. It is observed that carbon (%) decrease and oxygen (%) increase after UV light irradiation, meaning that hydroxyl groups and carboxyl groups generate 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 increase after UV light irradiation (Figure 5).

Table 2. Surface elemental analysis of polyimide based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%) by XPS

Radiation Energy[a] (J)	Contact Angle[b] (°)	Elemental Analysis based on XPS[c]					
		C (%)		O (%)		N (%)	
		Theo.	Obsd.	Theo.	Obsd.	Theo.	Obsd.
0	90.5	75.0	79.9	19.7	19.4	5.4	0.8
8	34.5	75.0	64.6	19.7	31.8	5.4	3.6

[a] UV light irradiation (254 nm, 0-8 J)at 25 ℃ . [b] Water contact angles (deg) using contact angle meter (Excimer inc.,SImage). [c] XPS measurements were carr ied out on an XPS -APEX (Physical Electronics Co. Ltd.) with an Al Kα X-ray source (200 W). Chamber pressure; 10^{-9} - 10^{-10} Pa; take off angles; 45°.

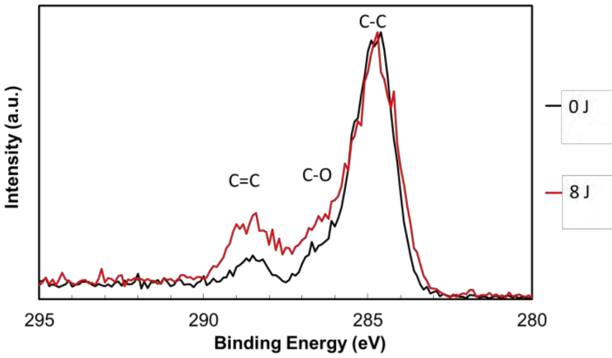


Figure 5. XPS narrow scans of C_{1s} of polyimide films based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%).

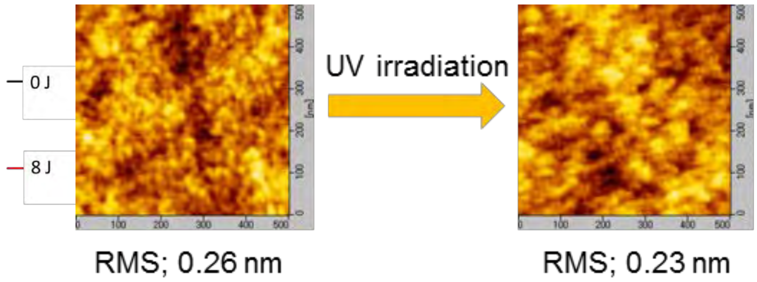


Figure 6. AFM images of polyimide based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%).

The surface nm size micro roughnesses probably based on bulky hydrophobic groups were observed by AFM analysis (Figure 6). However, the changes of these micro roughnesses after UV light irradiation were not recognized. Thus, it is considered that the changes of surface wettability of polyimides are occurred mainly by the changes of chemical structures of polyimide on top surface. It is speculated that the complicated photo-induced reactions such as auto-oxidation, cleavage of ester groups, cleavage of double bond, ozonolysis of double bond and cleavage of cholesterol unit occur on the surface of polyimides on the course of UV light irradiation.

Finally, a simple patterning test at laboratory scale was tried (Figure 7). The polyimide film based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%) was irradiated by UV light (254 nm, 8 J) through a hand-made photo mask, and it was observed that only the UV irradiation part got wet in the water and that the UV non-irradiation part did not get wet in the water. Consequently, it is considered that the novel polyimides developed in this study can be applied for the patterning in printed electronics.

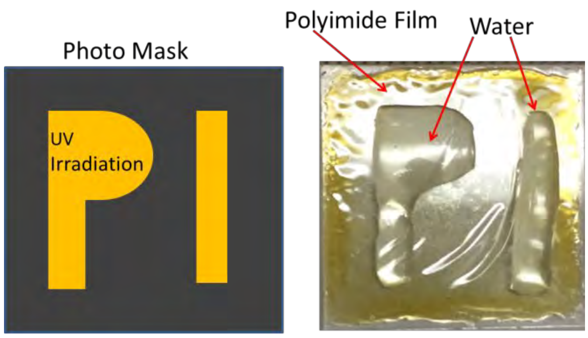


Figure 7. Patterning test at laboratory scale using polyimide film based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%).

3. Conclusions

The novel diamine monomers for surface wttability controllable polyimides were successfully synthesized from natural products such as ferulic acid, cholesterol and γ-oryzanol. The drastic simplification of the synthetic route was accomplished by using natural chemical compounds. The thin films of obtained polyimides were irradiated by UV light (λmax; 254 nm), and the contact angles for the water decreased from 90-100° (hydrophobicity) to minimum 35° (hydrophilicity) in proportion to irradiated UV light energy. Polyimides based on 3,4'-ODPA/Oryza-DA/DDE (100/10/90 mol%) showed the most drastic wettability change, and the laboratory patterning test using this polyimide film indicated the applicability for printed electronics. From the result of surface analysis (ATR, XPS, AFM), it is recognized that the hydrophobic alkyl groups on the polyimide surface decrease and the hydrophilic groups such as hydroxyl groups and carboxyl groups generate on their surface.

The elucidation of mechanism of the photo reactions, the addition of photo acid generator, the variation of hydrophobic groups, the polymer blends with conventional polyimides, the development of the applicable polyimides in UV (365nm) irradiation are now under investigation.

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