Surface Wettability Control of Polyimides Containing Perfluoroalkyl Group by Photo-irradiation

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The novel polyimides containing perfluoroalkyl group on their side chain were synthesized using the novel diamine monomers containing perfluoroalkyl group. The films of obtained polyimides on glass substrates were prepared and the surface wettability of these films were measured before and after UV (ultraviolet) light irradiation (254 nm). The water contact angles of these polyimide films were changed from about 113° to 56° by UV light irradiation. The novel polyimides containing both perfluoroalkyl group and spiropyran group was synthesized by introducing spiropyran group by Mitsunobu reaction with base polyimide containing phenolic OH group. The surface wettability of the polyimide film containing the spiropyran group changes from about 114° to about 104° by irradiation of UV light (365 nm), and reversibly changes from about 104° to about 114° by irradiation of Vis (visible) light.

Keyword: Polyimide, Perfluoroalkyl group, Spiropyran, 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]. Our research group has systematically investigated the synthesis and characterization of soluble polyimides based on aromatic diamines bearing long-chain alkyl group, 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 (ultraviolet) light irradiation [6], have been investigated to obtain the fine patterning. The authors have investigated the surface wettability control of polyimides containing various functional group such as long-chain alkyl group, t-Boc group, etc. by UV light irradiation [7-19].

In this paper, the authors have investigated the use of perfluoroalkyl group as a substitution of the long-chain alkyl group to enhance the initial hydrophobicity before UV light irradiation, and expect the improvement in the difference of wettability before and after UV light irradiation. The authors have recently investigated reversible control of surface wettability of polyimides containing spiropyran group on their side-chain by UV-Vis (ultraviolet-visible) light irradiation [20-23]. The authors also report the reversible wettability change of the polyimides containing both perfluoroalkyl group and spiropyran group by UV-Vis light irradiation.

2. Experimental

2.1. Materials

4,4’-(Hexafluoroisopropyliden)diphtalic anhydride (6FDA) from Central Glass Co., Ltd. 3,4’-Oxydiphthalic anhydride (3,4’-ODPA; a-ODPA) from Shanghai Research Institute of Synthetic Resins, 2,2’-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (F-HAB from Tokyo Chemical
Industry Co., Ltd., TCI), and 4,4’-diaminodiphenyl ether (DDE) from Seika Corporation were used after drying in a vacuum oven. 1H,1H,2H,2H-tridecafluoro-1-n-octanol from TCI and 1H,1H,2H,2H-perfluoro-1-decanol from Fluorochem Ltd. were used as received. 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 FUJIFILM Wako Pure Chemical Corporation and used as received.

2.2. Synthesis of novel diamine monomers containing perfluoroalkyl group

1H,1H,2H,2H-tridecafluoro-1-n-octanoyl 3,5-di(3-aminophenyl)benzoate (C₈-F-DA) and 1H,1H,2H,2H-perfluoro-1-n-decanoyl 3,5-di(3-aminophenyl)benzoate (C₈-F-DA) were synthesized by two step reactions from the corresponding perfluoroalcohol as a starting material via esterification with 3,5-dibromobenzoic acid using DCC/DMAP, then Suzuki coupling reaction with 3-aminophenylboronic acid (Scheme 1). These synthetic procedures are described in the previous literature [14].

2.3. Synthesis of novel polyimides containing perfluoroalkyl group

The polyimides were synthesized from 6FDA, as a tetracarboxylic dianhydride. Two step polymerization systems including poly(amic acid) synthesis and chemical imidization were performed (Scheme 2). The poly(amic acid)s were obtained by reacting the mixture of diamines with an equimolar amount of tetracarboxylic dianhydride at room temperature (r. t.) for 12 h under an argon atmosphere. The polyimides were obtained by chemical imidization at r. t. in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent for 24 h. The experimental details have been described in the previous paper [23]. In the case of polyimides based on 3,4’-ODPA, the imidization condition was the standard condition investigated in our laboratory; 120 °C, 4 h [7-22].

2.4. Synthesis of novel polyimides containing perfluoroalkyl group and spiropyran group on their side chain

Novel polyimides containing perfluoroalkyl group and spiropyran group on their side chain (6FDA/C₈-F-DA/F-HAB-spiro) was synthesized by introducing spiropyran group by Mitsunobu reaction into the polyimide copolymer containing phenolic hydroxyl groups [6FDA/ C₈-F-DA (50 mol%) / F-HAB (50 mol%); base-polyimide (Scheme 3). The experimental details of above polymer reaction have been described in our previous papers [22,23].
Scheme 3. Synthesis of polyimide containing perfluoroalkyl group and spiropyran group.

2.5. Measurements
The detailed experimental methods of film preparation, UV-Vis light irradiation, and the measurements have been described in our previous papers [7-23].

3. Results and discussion
3.1. General properties of polyimides
The obtained polyimides containing perfluoroalkyl group showed the good solubility in many solvents, e.g., NMP, DMSO, dichloromethane, chloroform. The molecular weights of obtained polyimides were measured by SEC (Mn: 7300~15200, in CHCl3 calibrated with standard polystyrenes) (Table 1). Although these molecular weights were relatively lower in comparison with general polyimides (e.g., 3,4'-ODPA/DDE in Table 1), the obtained polyimides showed the good film forming ability.

The thermal properties of these polyimides containing perfluoroalkyl group were estimated by thermal degradation temperatures (Td10: 340~391 °C in air, 343~400 °C under nitrogen) and glass transition temperatures (Tg: 220~281 °C), these data indicated that the heat resistant properties of obtained polyimides are relatively lower than the conventional polyimides, however, it is recognized these polyimides can be still ranked as heat resistant polymers (Table 1).

3.2. Irreversible surface wettability control by UV light irradiation on polyimide thin films containing perfluoroalkyl group

The polyimide thin films based on 6FDA/C8-F-DA, 6FDA/C6-F-DA, 3,4'-ODPA/C8-F-DA, and 3,4'-ODPA/DDE were irradiated by UV light (254 nm, 0, 2, 4, 8 J/cm2), then the contact angles for the water were measured. Figure 1 shows UV light irradiation energy dependence of water contact angles of these polyimide films. The high water contact angles of polyimides containing perfluoroalkyl group decreased from 103°- 113° (hydrophobicity) to 40°- 56° (hydrophilicity) in proportion to irradiated UV light energy. It is considered that these changes of wettability of polyimides are mainly based on the photo-degradation of perfluoroalkyl group and that the generation of the hydrophilic functional group such as COOH group probably appeared on the surface of polyimide films.

Table 1. General properties of polyimides.

| Polyimide | Mn  | Mw  | Mn/Mw | Td10b | Tg  |
|-----------|-----|-----|-------|-------|-----|
| 6FDA/C6-F-DA | 9800 | 36300 | 3.7   | 359  | 364 | 238 |
| 6FDA/C8-F-DA | 7100 | 36400 | 3.2   | 391  | 400 | 242 |
| 3,4'-ODPA/C6-F-DA | 6900 | 35300 | 3.3   | 339  | 341 | 220 |
| 3,4'-ODPA/DDE | 37900 | 71700 | 1.9   | 542  | 520 | 280 |

* Determined by SEC in CHCl3 calibrated with a series of polystyrenes as a standard. **10% Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. ***Measured by DSC at a heating rate of 20 °C /min in N2 on second heating. ****Determined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard. N. D.; Not determined.

![Fig. 1. UV light irradiation energy dependence of water contact angles of polyimide films based on 6FDA/C8-F-DA, 6FDA/C6-F-DA, 3,4'-ODPA/C8-F-DA, and 3,4'-ODPA/DDE.](image-url)
surface of polyimide films (Fig. 2). The increase of OH group absorption around 3200 cm\(^{-1}\) after UV light irradiation was recognized by ATR measurements. The water contact angles of polyimides without perfluoroalkyl groups (3,4’-ODPA/DDE) somewhat decreased from 86° to about 65° in proportion to irradiated UV light energy.

It is speculated that the photo-oxidation occurs on the surface of regular polyimide without functional group by UV light irradiation (254 nm). The initial water contact angles of these polyimides before UV light irradiation increased in proportion to the content of the fluorine atom; 113° (6FDA/C\(_8\)-F-DA) > 109° (6FDA/C\(_6\)-F-DA) > 103° (3,4’-ODPA/C\(_6\)-F-DA) > 86° (3,4’-ODPA/DDE). These differences are of course due to the hydrophobic nature of trifluoromethyl group and perfluoroalkyl group. According to our previous research, the maximum initial water contact angle of polyimide containing long-chain alkyl group are about 90° - 100°, and the water contact angles after UV light irradiation (254 nm, 8 J/cm\(^2\)) are about 40° - 60°. Therefore, the method by this study seems to be effective as a technique for raising the initial contact angle, and for the improvement in the difference of wettability before and after UV light irradiation.

3.3. Reversible surface wettability control by UV-Vis light irradiation on polyimide thin films containing perfluoroalkyl group and spiropyran group and surface analysis

The polyimide thin films based on 6FDA/C\(_8\)-F-DA/F-HAB-spiro were irradiated by UV light (365 nm), then the contact angles for the water were measured. The water contact angles after UV light irradiation for 2.5 minutes decreased in about 10° (117°→107°), and almost completely recovered to the initial value by subsequent irradiation of Vis light irradiation for 15 hours. It is considered that these reversible wettability changes are based on the polarity change of spiropyran-merocyanine photoisomerization as showing in Fig. 3.

Solid state surface reflected UV-Vis measurements were carried out on the polyimide films that irradiated UV and Vis light (Fig. 4). These measurements are performed based on the feature that the merocyanine structure after UV light irradiation has absorption in the visible region.
 (>500 nm), and then absorption in the visible region decreases after Vis light irradiation. As shown in Fig. 3, the estimated spectral changes by the photoirradiation were confirmed. Above data suggests that photoisomerization of the spiropyran shown in Fig. 3 occurs on the polyimide film. However, the change in contact angle was about 10° by UV-Vis light irradiation, which was the same values as previously reported [22,23]. Presently, it is recognized that the introduction of perfluoroalkyl group in the polyimide containing spiropyran group is not effective.

4. Conclusion
The novel polyimides containing perfluoroalkyl group on their side chain, and the novel polyimides containing both perfluoroalkyl group and spiropyran group were successfully synthesized. The former polyimides can be used for the irreversible surface wettability control by UV light irradiation (254 nm), the initial water contact angles before UV light irradiation raised by the introduction of perfluoroalkyl group, consequently the improvement in the difference of wettability before and after UV light irradiation was recognized. The surface wettability of the later polyimide was reversibly controlled by UV-Vis light irradiation. However, the change in contact angle was only about 10° by UV-Vis light irradiation. The further research such as the modification of polyimide structure having spiropyran group, the modification of spiropyran structure, the introduction of alkyl spacers between spiropyran group and polymer backbone, and intensive surface analytical experiments have been investigated to enhance the wettability change by UV-Vis light irradiation. The cycle UV-Vis light irradiation experiments to polyimide films will be also performed in the future.

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