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

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Introduction

The author has systematically investigated the synthesis, characterization and application of soluble polyimides based on the aromatic diamine monomers having long-chain alkyl groups. Recently, various printing methods such as an ink-jet print method have been investigated for manufacturing polymeric thin-films, and the surface wettability and their control methods have become important. Thus, the author has presently examined the surface wettability control of these polyimides by UV light irradiation that is a conventional method for microlithography [Figure 1].

Results and Discussion

The soluble polyimides bearing long-chain alkyl groups used for this study were synthesized from novel aromatic diamines having long-chain alkyl groups such as 12G1-AG-Terphenyldiamine, $3C_{10}$-PEPEDA, $3C_{10}$-PEPADA, $3C_{10}$-PAPADA, $3C_{10}$-PEBPDA, and tetracarboxylic dianhydrides such as cyclohexene-DA, DSDA or 3,4'-ODPA, and DDE as a diamine co-monomer [Scheme 1]. Above functional diamine monomers were synthesized in the 5-7 step reactions using advanced synthetic techniques such as protect group methods, Suzuki-coupling reaction, and mild dehydration reaction. Two-step polymerization systems consisting of poly(amic acid)s synthesis and chemical imidization in the presence of pyridine as base catalyst and acetic anhydride as dehydrating agent was performed. The obtained polyimides showed the good solubility in polar organic solvents such as NMP. Although the molecular weights from SEC measurements were not so high (Mn; ~10000, in NMP/10mM LiBr calibrated with polystyrenes), these polyimides showed the good film forming ability. The thermal properties of these polyimides were estimated by glass transition temperatures (Tg; ~250°C) and thermal degradation temperatures (Td_{10}; ~400°C), and these polyimides showed the good thermal stability. The thin films of obtained polyimides were irradiated by UV light (λmax; 254 nm, 2-8 J) , and the contact angles for the water decreased from near 100° (hydrophobicity) to near 20° (hydrophilicity) in proportion to irradiated UV light energy [Figure 2]. From the result of contact angle measurements and the result of the ATR[Figure 3] and XPS [Figure 4] analysis, it is recognized that the hydrophobic long-chain alkyl groups on the polyimide surface decrease and the hydrophilic groups such as a hydroxyl group generate on their surface. The surface nm size roughness probably based on long-chain alky groups was observed by SFM analysis (Fig. 17), however, these micro roughness seemed not to change after UV light irradiation. Thus, the change of surface wettability of polyimides is occurred mainly by the changes of chemical structures of polyimide surface.

Conclusions

In conclusion, the surface wettability of polyimides bearing long-chain alkyl groups can be controlled by UV light irradiation, and these methods are expected to be applied in the field of printed electronics. 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. The fine tuning of dimaine monomer structures, the addition of photoacid generator or photobase generator, the variation of long-chain alkyl groups, the elucidation of mechanism of the photo reactions are now under investigation.

Acknowledgement

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Reference

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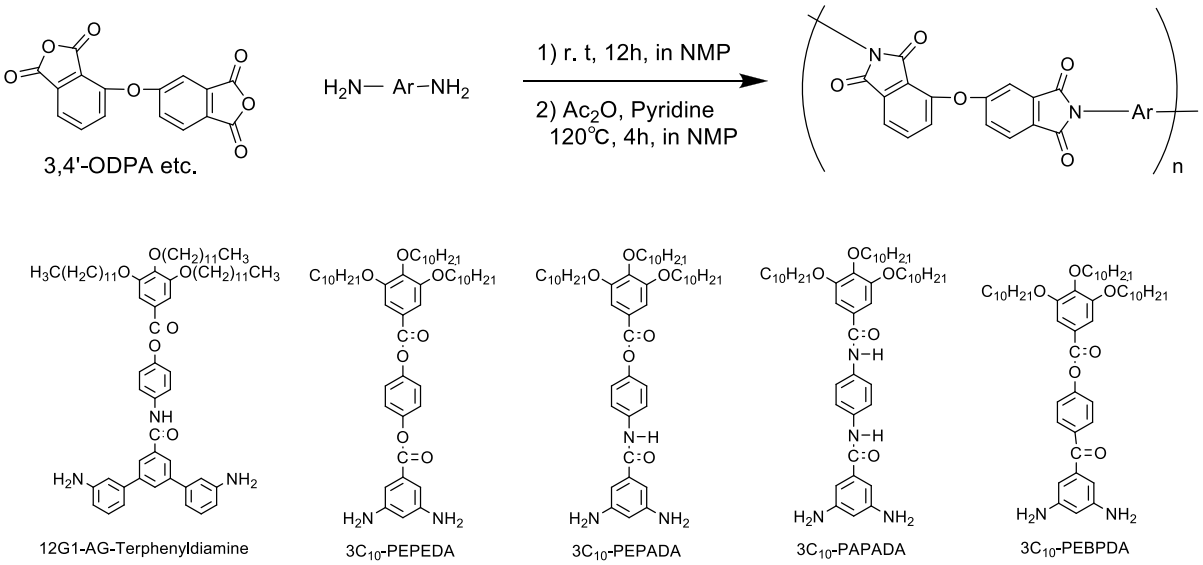

Scheme 1. Synthesis of polyimides bearing long-chain alkyl groups

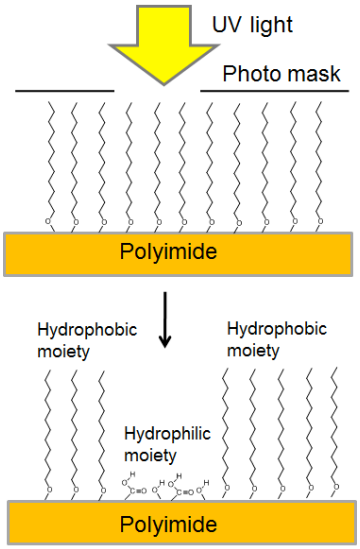

Figure 1. Conceptual scheme of wettability control of the polyimide surface by UV irradiation

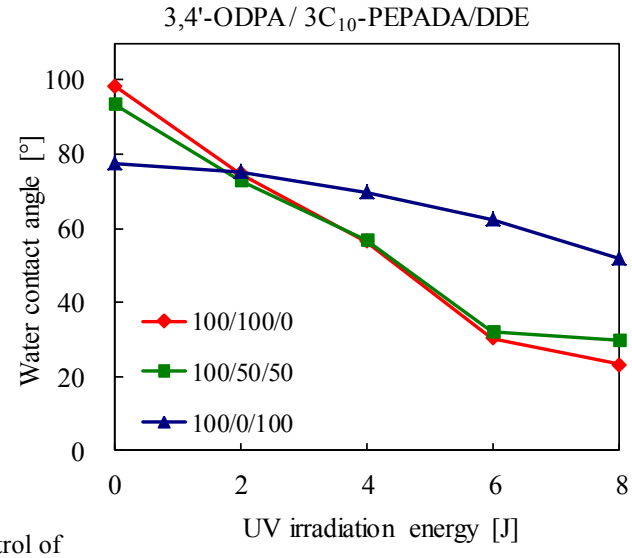

Figure 2. UV irradiation energy dependence of water contact angles of polyimide films

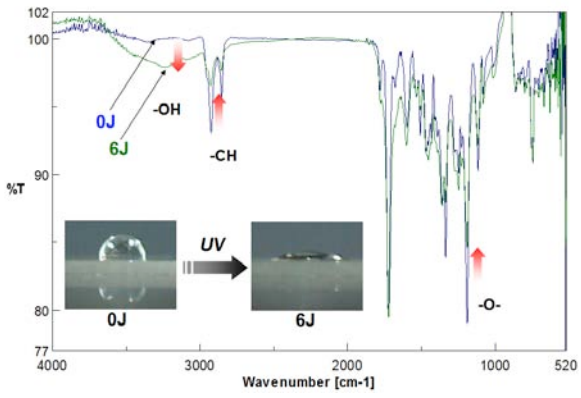

Figure 3. Representative ATR spectrum of polyimides bearing long-chain alkyl groups before and after UV irradiation

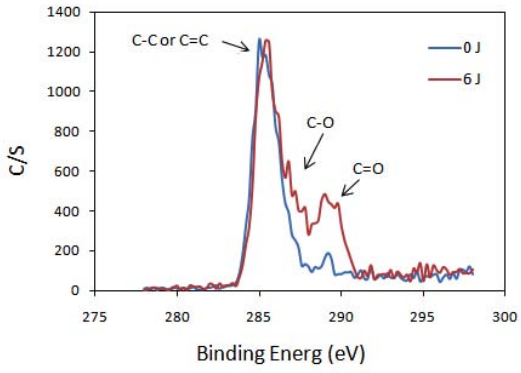

Figure 4. XPS narrow scan of 3,4'-ODPA / $3C_{10}$-PEPADA