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New Soluble and Intrinsically Photosensitive Polyimide: Synthesis and Properties of Poly(amide-*co*-imide) Containing *p*-Phenylenediacryloyl Moiety

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Abstract : A new soluble photosensitive poly(amide-*co*-imide) containing *p*-phenylenediacryloyl moiety was synthesized and its photoreactivity was characterized. The copolymer was synthesized from *p*-phenylenediacryloyl chloride, 4,4-(hexafluoroisopropylidene)diphthalic anhydride and two equivalents of bis(4-aminophenyl) ether in NMP with a subsequent chemical imidization of the resulting poly[amide-*co*-(amic acid)] by acetic anhydride and pyridine. The structure and thermal properties of the polymer were characterized by spectroscopic methods and thermal analyses. The polymer was stable up to 350°C, showed good solubility in polar aprotic solvents, and became insoluble after UV irradiation due to the [2+2] cycloaddition of phenylenediacryloyl moiety. Photoreactivity of the polymer was investigated in solution or as a film with respect to the various exposure conditions by UV/Vis spectroscopy. The photosensitivity was noticeably increased with the irradiation temperature, especially in the presense of photosensitizer. The reason for the increased sensitivity was speculated based on the flexibilization of main chain at elevated temperature. Exposure characteristic curves were obtained from the gel fraction experiments after UV irradiation. The sensitivity and contrast at 160°C were measured to be 293 mJ/cm^2 and 1.64, respectively.

Introduction

Photosensitive polyimide has been widely used in electronic industry as an insulating material for printed circuit boards (PCB), integrated circuits (IC), large-scale integrated circuits (LSI) and multichip module (MCM) due to its high temperature resistance, good mechanical property, chemical resistance, and low dielectric property.[1-6] Compared to the ordinary polyimides functioned as low-dielectric interlayer, photosensitive polyimide also provides an advantage of simple processing method for micro-patterning of polyimide layer, since patterning of ordinary polyimide is achieved by multiple processes including lithography via photoresist polymers. Typically, photosensitive polyimide is prepared from soluble poly(amic acid), where photo-crosslinkable sites are attached to amic acid moiety either through ester linkage or acid-amine salt. For example, Rubner *et al.* have introduced methacrylic group to poly(amic acid) by ester linkage.[7~9] Yoda *et al.* reported a precursor resin prepared by addition of aminoalkyl methacrylate to poly(amic acid) as an acid-base salt.[10] Kataoka *et al.* also reported polyimide precursors containing aromatic azide additives.[11] These negative-working photosensitive polyimide precursors, however, exhibit some disadvantages because the added substance should be completely removed during thermal imidization of precursors and their elimination gives extensive shrinkage of pattern thick-ness as well as deformation of polyimide pattern so called “crowning effect”.[12] The thermal imidization at high temperature can also cause a damage

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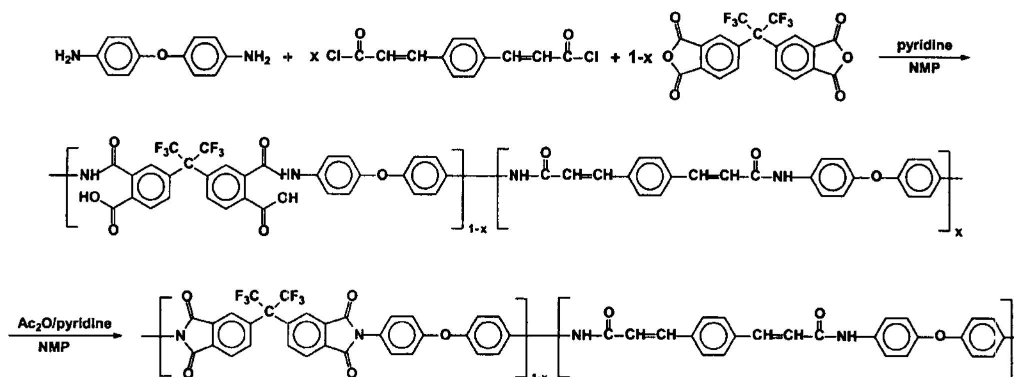

Scheme I. Synthetic scheme of photosensitive poly(amide-*co*-imide) containing *p*-phenylenediacryloyl moiety.

to the other semiconductor materials.[13] Therefore, it is desirable to design a soluble and fully imidized photosensitive polyimide that offer low shrinkage and require no high thermal treatment. There are reported few examples of such intrinsically photosensitive polyimides.[14-16]

There have been considerable amount of studies on phenylenediacrylate-containing polymers, mainly based on photosensitive liquid crystalline polyesters.[17-21] However, the photosensitive polyamide or polyimides containing this moiety has not been found. Recently, we have synthesized successfully a novel photosensitive poly(amide-*co*-imide) containing *p*-phenylenediacryloyl moiety via copolymerization of aromatic dianhydride and *p*-phenylenediacryloyl chloride with aromatic diamine as shown in Scheme I. These new photosensitive poly(amide-*co*-imide) showed intrinsic photosensitivity without any additives, and good processability in solution.

Experimental

Reagents. Terephthalaldehyde and malonic acid were purchased from Aldrich Chem. Co., and used after recrystallization in an appropriate solvent. 4,4'-(hexafluoropropylidene)diphthalic anhydride (6FDA) and bis(4-aminophenyl) ether (ODA) were purified by sublimation under reduced pressure. Solvents were used after appropriate purification procedures. Other chemicals were used as purchased.

Synthesis of *p*-Phenylenediacrylic Acid (PDAC).[21-26] In a round bottom flask, terephthalaldehyde (26 mmol) and malonic acid (94 mmol) were added to 30 mL of pyridine containing small amout of piperidine. The reaction mixture was stirred for 2 h at 45 °C, for 4 h at 80 °C and for 3 h at 110 °C, respectively. The solution was poured into large amount of distilled water and neutralized with HCl to obtain white precipitate. The precipitate was filtered, washed with water, acetic acid and acetone, respectively, and dried in a vacuum oven at room temperature. (Yield = 91%, m.p. > 300 °C)[21] FT-IR (KBr, cm^{-1}): 1677 (carboxylic acid C=O streching), 1622 (phenylene) and 980 (*trans*-vinylene). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.75 (Ph-CH=, 2H), 7.70 (=CH-CO-, 2H), 12.5 (-COOH, 2H).

Synthesis of *p*-Phenylenediacryloyl Chloride (PDACl). 9.2 mmol of PDAC was refluxed with 14 mL of thionyl chloride and a few drop of DMF for 5 h. The remaining thionyl chloride was distilled off with evaporator and the resulting solid was recrystallized in 1,4-dioxane to obtain PDACl as a yellow solid (m.p. = 170°C) with 89% yield.[21]

FT-IR (KBr, cm^{-1}): 1770 (carboxylic C=O streching), 1622 (phenylene) and 980 (*trans*-vinylene). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.72 (Ph-CH=, 2H), 7.80 (=CH-CO-, 2H).

Syntheses of Poly(amide-*co*-imide). As shown in Scheme I, 4 mmol of ODA was dissolved in 20 mL of NMP and 0.3 mL of pyridine under N_2 atmosphere. 2 mmol of PDACl was added and the reaction mixture was stirred at 0°C. After 2 h, 2 mmol of 6FDA was added to the reaction mixture at ambient temperature and the reaction was continued for 24 h under N_2 atmosphere. To the

light yellow and viscous solution, 6 mmol of pyridine and acetic anhydride was added, and the reaction mixture was stirred for 24 h at room temperature. The resulting solution was precipitated into 1 : 1 (v/v) mixture of water and methanol for two times to obtain light yellow powder which was dried in vacuum oven at 60°C for 48 h.

FT-IR (KBr, cm^{-1}): 1780 and 720 (imide C=O), 1650 (amide C=O streching), 1630 (phenylene) and 970 (*trans*-vinylene). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 10.4 (CO-NH-, 1H), 7.1 ~ 8.2 (aromatic Hs, 18H), 6.5 ~ 7.0 (Ph-CH=CH-CO, 2H).

Instrumentations and Measurements. Structural characterizations were performed by using FT-IR spectrometer (Shimazu, 300SE) and ^{1}H-NMR spectrometer (Bruker, 400 MHz). Thermal analyses were performed by differential scanning calorimetry (TA Instruments, DSC 2010) and thermogravimetric analysis (TA Instruments, TGA 2050). UV spectra of polymer solution and film were taken by using photodiode-array UV spectrophotometer (Scinco, UV S-2100). UV irradiation was done by using a portable UV lamp (Spectroline, ENF-240C, 365 nm, filtered, 2 mW) and Xe lamp (Oriel, 450 mW). Polymer samples for the irradiation experiment were prepared by spin-coating a 10 wt% polymer solution in NMP on a slide glass or quartz plate and drying under reduced pressure for 30 min at 60°C prior to the irradiation. Gel fractions of irradiated polymer films were measured by comparing the dried thickness (Tencor, α-step profilometer) of irradiated polymer film after developing in NMP/diglyme (70/30 v/v) for 3 to 15 min at 30°C to the original thickness. The developing for each sample was continued until the unirradiated part was dissolved completely. UV irradiations were performed at various temperatures (25, 100, 130 and 160°C, respectively) and with various exposure dose (from 30 to 300000 mJ/cm^2).

Results and Discussion

Syntheses and Characterization of Poly (amide-*co*-imide). *p*-Phenylenediacryloyl chloride (PDACl) was synthesized according to the literature.[8] Copolymerizations of PDACl with 6FDA and ODA were conducted in NMP as shown in Scheme I. Typically 2 mmol of PDACl was reacted with 4 mmol of ODA in the presence of pyridine at 0°C for 2 h followed by subsequent reaction with 2 mmol of 6FDA. Chemical imidization of poly(amide-*co*-amic acid) was performed *in situ* by the addition of 6 mmol of pyridine/acetic anhydride. The resulting poly(amide-*co*-imide) (6FOD) were soluble in aprotic polar solvents with $[\eta]$ = 0.4 ~ 0.7 dL/g. Light-yellow transparent film was obtained from NMP solution by spin-coating on a glass substrate. Polymer structure was confirmed by FT-IR and ^{1}H-NMR spectroscopy. From FT-IR spectra, absorption peak due to the stretching vibration of amide carbonyl was observed at 1650 cm^{-1} and those of vinylene double bond were found at 1630 and 970 cm^{-1}. Stretching vibrations of imide were found at 1780 and 720 cm^{-1} (carbonyl) and 1368 cm^{-1} (C-N). Absorptions corresponding to carboxylic acid were not observed, which showed the chemical imidization was effectively completed. In ^{1}H-NMR spectra, proton of amide (N-H) was observed at 10.4 ppm and protons of aromatic hydrogens and vinylene hydrogens were found at 7.1 ~ 8.2 and 6.5 ~ 7.0 ppm, respectively. Thermal properties were investigated by DSC and TGA, which showed the polymers are stable up to 300°C showing T_g at about 268°C. From the DSC thermogram, it was found that thermal crosslinking reaction occurred near at 300°C accompanied with strong exothermic reaction (360°C) which corresponds to thermal degradation of polymer as evidenced by TGA thermogram. TGA thermogram showed initial degradation (T_{di}) at 350°C and the temperature at 5% weight loss (T_{d5}) was found to be 400°C.

Photosensitivity in Solution. UV absorption spectroscopy of the films containing 0, 5, 10, 15 wt% of photosensitizer (Micheler's ketone (BDP), or phenanthrenequinone (PAQ)) upon UV irradiation exhibited gradual decrease of absorption peak at c.a. 350 nm which corresponds to the $\pi \rightarrow \pi^*$ transition of double bond in phenylenediacryloyl moiety, indicating [2+2] cycloaddition.[17] Figure 1 shows the absorption intensity change at 350 nm for 6FOD films containing 10 wt% of photosensitizers during the irradiation of 365 or 254 nm UV light compared with that of 6FOD film without photosensitizers. The polymers were more sensitive

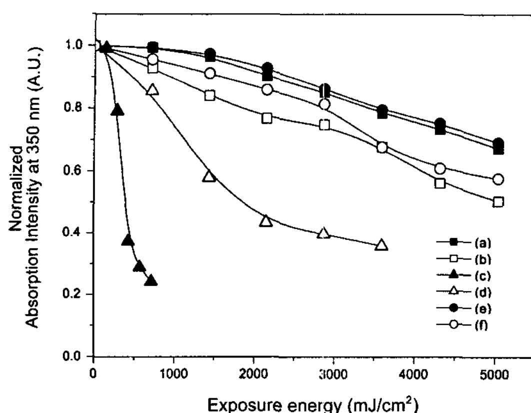

Figure 1. Absorption intensity changes at 350 nm for 6FOD solution in NMP with and without photosensitizer under 365 and 254 nm UV irradiation at room temperature: (a) no sensitizer and 365 nm, (b) no sensitizer and 254 nm, (c) 10 wt% BDP and 365 nm, (d) 10 wt% BDP and 254 nm, (e) 10 wt% PAQ and 365 nm, and (f) 10 wt% PAQ and 254 nm, respectively.

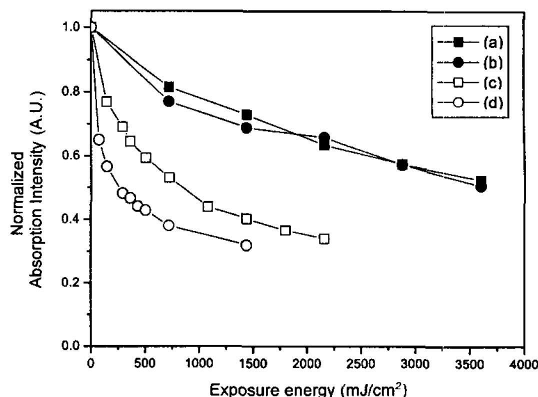

Figure 2. UV absorption intensity change at 350 nm for 6FOD film at various conditions with respect to the UV (365 nm) exposure energy: (a) no BDQ at room temperature, (b) 10 wt% BDQ at room temperature, (c) no BDQ at 160 °C, and (d) 10 wt% BDQ at 160 °C, respectively.

to 365 nm irradiation than to 254 nm. In solution, BDP was more effective, probably because the λ_{max} of BDP (λ_{max} = 355 nm) overlaps with the iraradiated light. The sensitivity toward type and amount of photosensitizer, however, depends on the overlap of absorption ranges between chromophores of 6FOD and sensitizer, which should be understood more precisely by calculating the triplet energy states of each component.[23]

Photosensitivity of Films. To investigate photosensitivity in solid state, 6FOD film was prepared by spin coating of a polymer solution in NMP on glass or quartz substrates and subsequent drying in a vacuum oven at 60°C for 30 min. Figure 2 shows the absorption intensity change at 350 nm for 6FOD films with and without 10 wt% of BDP under the UV exposure of 365 nm at room temperature and 160°C, respectively. In any cases, decrease of absorption intensity was observed. However, the photosensitivity of films measured by the decrease rate of absorption intensity was comparably lower than those in solution. Furthermore, while the photosensitizer affected the photosensitivity in solution, no appreciable difference was observed between films with and without sensitizer at room temperature. This is probably due to the lower degree of freedom of polymer backbone in the solid state than in solution. Therefore, the overall photosensitivity in the solid state was decreased in either case, with or without sensitizer, and as a result, the effect of photosensitizer would become relatively small.

The effect of irradiation temperature was also investigated. Compared to those at room temperature, the photosensitivities at higher temperature were dramatically enhanced. This is attributed to the flexibilization of main chain at high temperature. Although the temperature was far below T_g of the polymer (ca. 268°C), the flexibilization of main chain can be assumed because of the plasticizing effect owing to the residual solvent (c.a. 5 wt% from ^{1}H-NMR) in the film even after the prebake procedure. The 6FOD film containing 10 wt% BDP showed a higher photosensitivity than the film without sensitizer, presumably because BDP acted as a plasticizer as well as a sensitizer.

Characteristic Curves. Exposure characteristic curves of polymer films were obtained from the normalized gel fraction experiments at various exposure temperatures. In Figure 3, the normalized thickness of the residual films was plotted with respect to the exposure energy. The sensitivity was defined as the irradiated energy to cross-link the resist such that the exposed area retained 50% of the original thickness after development. The contrast of the film was defined as the slope of the curve at 50% of the normalized thickness. As in the UV experiments, it was again found that the

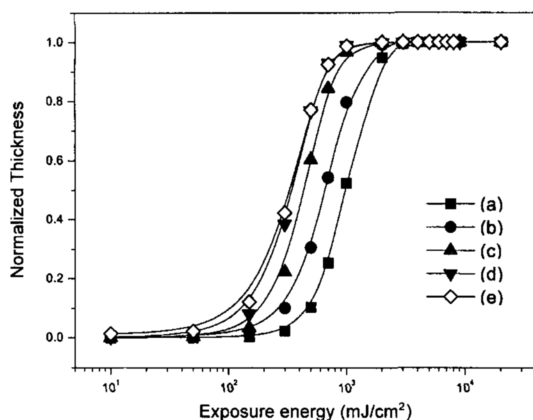

Figure 3. Characteristic curves of 6FOD film exposed with 365 nm UV light at various irradiation temperatures: (a) 25, (b) 100, (c) 130, (d) 160, and (e) 190 °C.

sensitivity increased with the irradiation temperature. The sensitivity and the contrast at 160°C were 293 mJ/cm^2, and 1.64, respectively.

Conclusion

A novel photosensitive poly(amide-*co*-imide) containing *p*-phenylenediacryloyl moiety was synthesized via copolymerization of aromatic dianhydride and *p*-phenylenediacryloyl chloride with aromatic diamine and its photoreactivity was characterized. The polymer was stable up to 350°C, showed good solubility in polar aprotic solvents, and became insoluble after UV irradiation due to the [2+2] cycloaddition of phenylenediacryloyl moiety. Photoreactivity of the polymer was investigated in solution or as a film with respect to the various exposure energy and exposing temperature by UV/Vis spectroscopy. The sensitivity and contrast at 160°C were measured to be 293 mJ/cm^2 and 1.64, respectively.

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References

(1) *Polyimides and Other High-Temperature Polymers,* M. J. M. Abadie, B. Sillion Eds., Elsevier, Amsterdam (1991).
(2) H. Hiramoto, *Mater. Res. Soc. Proc.,* **167**, 87 (1990).
(3) A. Endo and T. Yoda, *J. Electrochem. Soc.,* **132**, 155 (1985).
(4) A. M. Wilson, *Thin Solid Films,* **83**, 145 (1981).
(5) A. Schlitz, *IEEE Trans. on Components, Hybrides, and Manufacturing Technology,* **15**, 226 (1992).
(6) D. Darrow and S. Vilmer-Bagen, *Proceedings of 43rd ECTC,* 544 (1993).
(7) R. Rubner, *Siemens Forsch. Entwickl. Ber.,* **5**, 92 (1976).
(8) R. Rubner, B. Barter, and G. Bald, *Siemens Forsch. Entwickl. Ber.,* **5**, 235(1976).
(9) R. Rubner, H. Ahne, E. Ruhn, and C. Koloddieg, *Photogr. Sci. Eng.,* **23**, 303 (1979).
(10) N. Yoda and H. Hiramoto, *J. Mocromol. Sci., Chem.,* **A21**, 1641 (1984).
(11) E. Kataoka, F. Shoji, I. Takemoto, I. Obara, M. Kojima, H. Yokono, and T. Isogai, in *Polyimides: Synthesis, Characterization, and Applications,* K. L. Mittal Ed., Plenum Press New York, 1984, vol. 2, pp 933.
(12) H. Hiramoto, *Mat. Res. Soc. Symp.,* **169**, 87 (1990).
(13) H. Ahne, R. Leuschner, and R. Rubner, *Polym. Adv. Technol.,* **4**, 217 (1992).
(14) J. Pfeifer and O. Rohde, *Proc. 2nd Int. Conf. Polyimides,* Ellenville, Soc. Plastics Eng., New York, 1985, pp 130.
(15) T. Nakano, *Proc. 2nd Int. Conf. Polyimides, Ellenville,* Soc. Plastics Eng., New York, 1985, pp 163.
(16) H. -R. Lee and Y. -D. Lee, *J. Polym. Sci., Part A, Polym. Chem.,* **27**, 1481 (1988).
(17) P. L. Egerton, J. Trigg, E. M. Hyde, and A. Reiser, *Macromolecules,* **14**, 100 (1984).
(18) L. Chienhui, C. Tehchou, and H. Kehying, *J. Polym. Sci., Part A, Polym. Chem.,* **31**, 1119 (1993).
(19) H. Kehying, L. Chenhui, C. Tehchou, and C. Tsuyao, *J. Polym. Sci., Part A, Polym. Chem.,* **31**, 971 (1993).
(20) H. Tanaka, K. Sasai, T. Sato, and O. Tadatoshi, *Macromolecules,* **21**, 3536 (1988).
(21) P. Ruggli and W. Theiheimer, *Helv. Chem. Acta.,* **24**, 899 (1941).
(22) F. Navarro and J. L. Serrano, *J. Polym. Sci., Part A, Polym. Chem.,* **27**, 3691 (1989).
(23) K. Iwata, T. Hagiwara, and H. Matsuzawa, *J. Polym. Sci., Part A, Polym. Chem. Ed.,* **23**, 2361 (1985).
(24) K. Spiliopoulos and J. Mikroyanndis, *J. Polym. Sci., Part A, Polym. Chem.,* **34**, 2799 (1996).
(25) L. Chenhui, C. Tehchou, and C. Tsuyao, *J. Polym. Sci., Part A, Polym. Chem.,* **31**, 1125 (1993).
(26) T. Nishikubo, T. Iizawa, and Y. Shiozaki, *J. Polym. Sci., Part A, Polym. Chem.,* **30**, 449 (1992).