

Preparation and Properties of a Positive, Auto-Photosensitive Polyimide Containing Cyclobutane and Benzophenone Groups

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Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. They are used as encapsulants, insulators and flexible substrates for printed circuits in the electronic industry. Recently, the use of photosensitive polyimides as polymer materials for electronic applications has become increasingly important because the number of steps required to pattern polyimide films is greatly reduced by directly photopatterning photosensitive polyimides, offering a significant cost savings and yielding advantage over wet or dry etching of polyimide.¹⁻³

Most of the reported photosensitive polyimides are negative type. The negative photosensitive polyimides have several drawbacks such as poor shelf life, shrinkage during curing, long exposure time, swelling, and inconsistent photospeed. In general, the resolution for positive features is better than for negative features. On the other hand, only a few cases of positive photosensitive polyimides which can be made soluble by UV irradiation have been reported. Khanna *et al.*⁴ developed hydroxypolyimide precursors containing hexafluoroisopropylidene linking group. The polymers formulated with *o*-naphthoquinonediazide (NQD) showed the properties similar to cresol-novolak resin and NQD. Omoto *et al.*^{5,6} developed fluorinated photosensitive polyimides that linked NQD in the side chain and another polyimide using the chemical amplification process.

Irradiation of maleimide derivatives with 300 nm UV light produces cyclobutane dimers, and photolysis of this photodimers with 254 nm UV light results in original maleimide derivatives by cycloreversion process.⁷ In the previous studies at this laboratory, we reported the positive type photosensitive polyimides having cyclobutane ring structure.^{8,9} The present paper deals with the preparation and properties of photosensitive polyimide containing cyclobutane and benzophenone groups in the main chain. It is expected that the photosensitivity of polyimides would be increased by introducing photosensitizing groups in the polymer chain.

Experimental

Maleic anhydride cyclobutane dimer (MACD) was obtained by irradiation of maleic anhydride with 300 nm UV light in CHCl₃. The polyimide, PI-2~PI-4 were prepared by the reported procedure.⁸ UV spectra were obtained with a Pharmacia Ultraspec III spectrophotometer. FT-IR spectra were recorded on a Mattson Polaris TM infrared spec-

trophotometer. ¹H NMR spectra were taken on a Bruker 300 MHz ASX-32 FT-NMR spectrometer. DSC measurement were carried out under N₂ atmosphere with NETZSCH-Geratebgu GmbH thermal analyser. Thermal stability was examined on a Perkin-Elmer model 7 TGA at a heating rate of 20 °C/min under nitrogen atmosphere. Irradiations are carried out in a Rayonet photochemical reactor (The New Southern California Company model RPR-208) equipped with 254 or 300 nm fluorescent lamps. Intrinsic viscosity was measured with an Ostwald viscometer (size 25, No. 244) immersed in a constant temperature bath at 25 °C.

Preparation of polyamic acid (PA-5). 4,4'-Diaminobenzophenone (1.06 g, 5 mmol) and MACD (0.98 g, 5 mmol) were dissolved in 12 mL of dimethylacetamide (DMAc). The mixture was stirred in the ice bath for 1 hour and then at room temperature. After 20 hours, the reaction mixture was precipitated in 100 mL of methanol and reprecipitated in water to give 1.88 g (92 wt%) of white powder. IR (KBr pellet, cm⁻¹): 3318, 3102, 1651, 1593, 1529, 1312, 1175; ¹H NMR (300 MHz, DMSO-d₆): 3.7-3.9 (4H), 7.5-7.7 (8H), 10.6 (2H).

Preparation of polyimide (PI-1). Polyimide, PI-1 was prepared by thermal imidation of polyamic acid, PA-1.5 Wt% of PA-1 in DMAc was coated on the glass plate and heated at 100 °C for 2 hours, 150 °C for 2 hours, 200 °C for 2 hours, 250 °C for 1 hour, and 300 °C for 1 hour stepwise. IR (KBr pellet, cm⁻¹): 1777, 1721, 1603, 1371, 1277, 1174, 931.

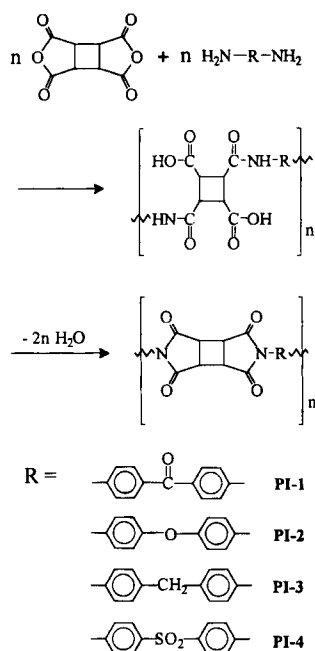
Spectral measurement. PA-1 (5 wt%) in DMAc was coated on the quartz plate and imidized thermally by the above procedure. UV absorption spectral changes were observed with varying irradiation time.

PA-1 (5 wt%) in DMAc was coated on the KBr pellet and imidized thermally by the above procedure. IR absorption spectra were measured after irradiation with 254 nm UV light for 3 hours.

Measurement of dissolved fraction. PA-1 (5 wt%) in DMAc was coated on the quartz plate and imidized thermally. The film on a quartz plate was irradiated with 254 nm UV light. The quartz plate was dipped in DMAc solution for 1 min and then washed with water for 10 seconds. Dissolved fraction of the films after irradiation were determined from the difference between absorbance at the isobestic point of UV spectra before and after dipping the quartz plate in the developing solvent.

Results and Discussion

Preparation and properties. Polyamic acid PA-1 was prepared by the reaction of MACD with 4,4'-di-



Scheme 1. Synthetic route for the preparation of polyimides containing cyclobutane groups.

aminobenzophenone in DMAc at room temperature and polyimide PI-1 was obtained by thermal imidation of PA-1 as shown in Scheme 1. The structure was characterized by IR and NMR analyses. The IR spectrum of PA-1 shows that the absorption band of carboxylic acid group appears at 3,500–2,500 cm^{-1} , amide I band appears at 1690–1600 cm^{-1} , amide II band at 1,530 cm^{-1} , and amide III band at 1,408 cm^{-1} . The NMR spectrum of PA-1 measured in $\text{DMSO}-d_6$ shows that the absorption peak of cyclobutane groups appeared at 3.7–3.9 ppm and that of phenyl groups of benzophenone moiety appeared at 7.5–7.7 ppm. The absorption peak of amide groups appeared at 10.6 ppm. PA-1 is insoluble in non-polar organic solvents but fairly soluble in polar aprotic solvents such as DMAc or N-methyl-2-pyrrolidone (NMP). Intrinsic viscosity measured in NMP was 1.08 dL/g which shows relatively high viscosity.

IR spectrum of PI-1 shows an absorption band of imide carbonyl group appears at 1,777 and 1,721 cm^{-1} and that of C-N bond appears at 1,371 cm^{-1} . The absorption bands of carboxylic acid and amide groups are disappeared. PI-1 is insoluble in most organic solvents. Figure 1 shows DSC and TGA thermograms of PI-1. TGA analysis shows that PI-1 begins to decompose at 425 $^{\circ}\text{C}$ and 50% weight loss was observed at 600 $^{\circ}\text{C}$ which shows relatively high thermal stability. DSC analysis shows that the endothermic peak appeared at 127 $^{\circ}\text{C}$ at the first run completely disappeared at the second run. The result indicates that this endothermic peak is due to the imidation of the partially unimidized fraction of the polyimide. T_g or T_m was not observed. X-ray diffraction analysis was carried out in order to find out crystallinity of PI-1. Broad absorption band with maximum peak intensity at $2\theta=17^{\circ}$ was observed. This result indicates that PI-1 is amorphorous.

Photochemical reaction. To understand the photochemical reaction of PI-1, UV and IR absorption spectral

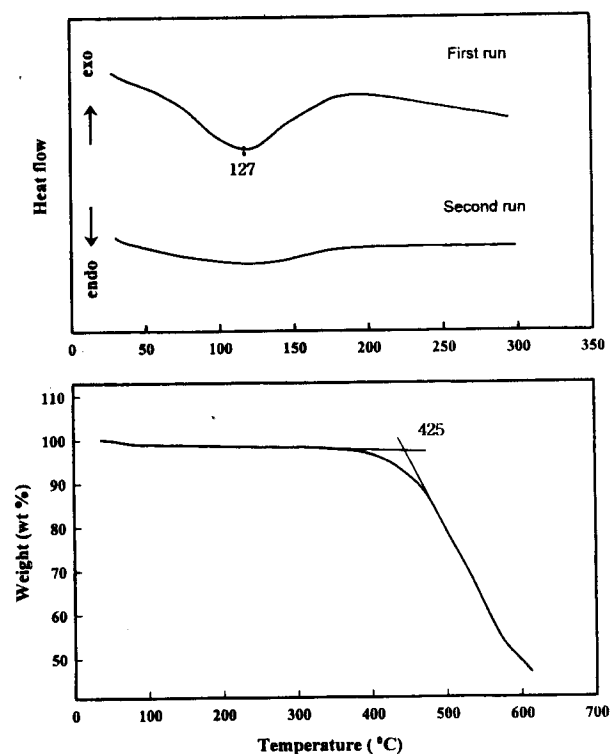


Figure 1. DSC and TGA thermograms of PI-1.

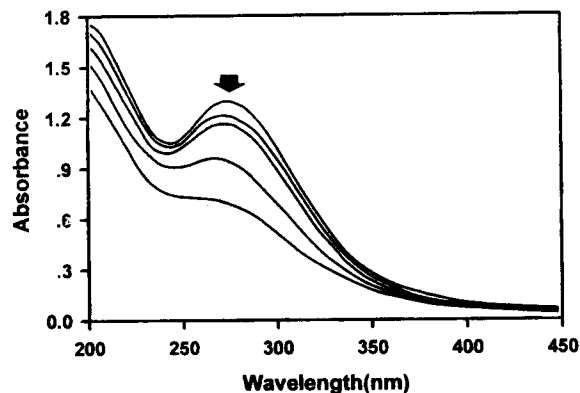


Figure 2. UV absorption spectral changes of PI-1 in CH_3CN upon irradiation with 254 nm light for 0, 10, 20, 30, 60 min (with top to bottom with an arrow).

changes upon irradiation with 254 nm were studied. Figure 2 shows UV absorption spectral changes of PI-1 film upon irradiating with 254 nm UV light. The absorption band which has a maximum wavelength at 276 nm is gradually decreased with irradiation. Neither an isosbestic point nor increase in absorption band of maleimide was observed from this polyimide. This may be due to the large absorption decrease, caused by the photoreduction of benzophenone moiety, which mitigates the absorption increase of maleimide groups produced by photodecomposition of cyclobutane groups.

To understand photochemical reaction of PI-1 upon irradiation, IR spectral changes of PI-1 films cast on KBr pellet before and after photolysis were studied. Figure 3 shows the difference IR spectrum of PI-1 between before and after

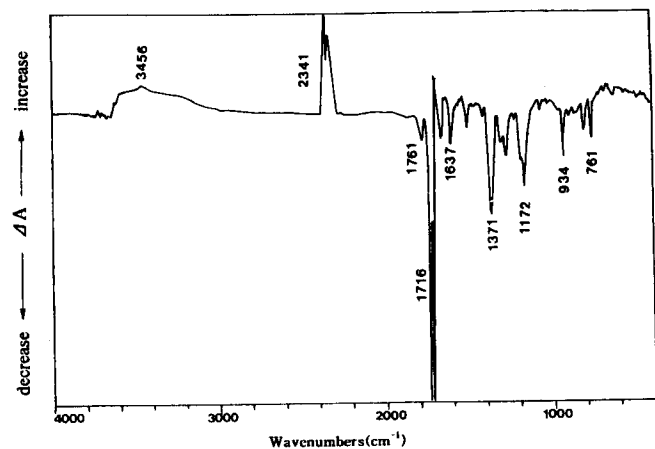


Figure 3. Difference IR spectrum of PI-1 between before and after irradiation with 254 nm light for 3 hours.

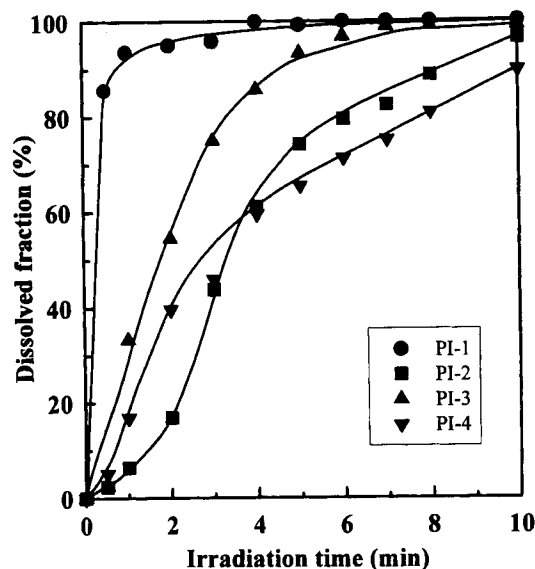


Figure 4. Plot of dissolved fraction as a function of irradiation time for photolysis of polyimide films with 254 nm UV light.

irradiation for 3 hours. The increase in the absorption band around $3,500\text{--}3,200\text{ cm}^{-1}$ indicates the formation of hydroxyl groups. The decrease of absorption bands at $1,761$ and $1,716\text{ cm}^{-1}$ indicates the photodecomposition of imide groups. The decrease of absorption band at 761 cm^{-1} is due to the photosplitting of cyclobutane groups. This result implies that both photosplitting of cyclobutane groups and photooxidation of imide groups take place during the photolysis of PI-1 as reported by Hoyle *et al.*^{10,11}

Dissolution changes. The dissolution changes of polyimides upon irradiation with 254 nm UV light were studied. The polyimides are insoluble in any organic solvents even in very polar solvents such as DMAc or NMP before irradiation, but they become soluble in THF or DMAc upon irradiation. Figure 4 shows the dissolved fraction of polyimide films with time of irradiation. About 90% of PI-1 film was dissolved after 1 min of irradiation and completely dissolved after 4 min of irradiation. The relative dissolution rate of polyimide films decreased in the order of PI-1>PI-3>PI-2>PI-4. The PI-1 which has benzophenone moiety in the polymer chain is the most photosensitive as compared to the other polyimides. This can be explained by the internal energy transfer from benzophenone groups to the cyclobutane or imide groups, leading to more efficient photosplitting of cyclobutane rings or photooxidation of imide bonds.

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