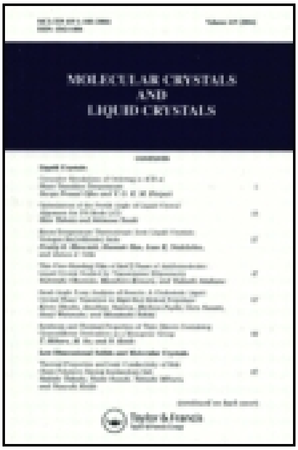

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Synthesis and Photodegradation of a Polyimide Having N-Carbonyloxyimide Moieties in the Main Chain

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Synthesis and Photodegradation of a Polyimide Having *N*-Carbonyloxyimide Moieties in the Main Chain

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A new positive-type photosensitive polyimide containing simultaneously *N*-carbonyloxyimide groups and cyclobutane rings in the main chain was prepared, and its photodegradation behavior was investigated by FT-IR, ^{1}H NMR, and GC-MS spectroscopy. The polyimide underwent a photo-induced decomposition through the cleavage of N-O bond as well as cyclobutane ring, affording maleimide as a photoproduct. The polyimide exhibited enhanced photosensitivity compared to conventional cyclobutane-containing polyimides.

Keywords: photosensitive polyimide; *N*-carbonyloxyimide; cyclobutane

INTRODUCTION

A number of photosensitive polyimides and their precursors have been reported, and most of them are negative-type photoresists. Few reports on positive-working photosensitive polyimides or the precursors have appeared in spite of practical advantages in their fabrication [1]. A typical positive-type polyimide contains cyclobutane rings in the main chain, which are cleaved by photoirradiation with UV light [1-3].

The authors previously reported the photodegradation behavior of a cyclobutane-containing polyimide to which imidosulfonate groups were incorporated to enhance its photosensitivity [4]. In this work a novel positive-type photosensitive polyimide containing simultaneously *N*-carbonyloxyimide groups and cyclobutane rings in the main chain was newly prepared, and its photodegradation behavior was investigated and compared with that of the previous imidosulfonate-type polyimide

EXPERIMENTAL

N,N'-Dihydroxycyclobutanetetracarboxylic diimide (DHCD) was prepared by a method previously reported [5]. The polyimide was prepared by reacting DHCD with 2,6-naphthalenedicarboxylic acid in the presence of dicyclohexylcarbodiimide (DCC) [6] at room temperature. Inherent viscosity of the polymer was measured to be 0.27 dL/g at a concentration of 0.20 g/dL in *N,N*-dimethylformamide (DMF) at 30 °C. A 10 wt% solution of the polymer in DMF was applied onto NaCl or silicon wafers. Photoirradiation of the polyimide films was conducted with an exposure system of Spectra Energy Co. equipped with a 500 W high-pressure mercury lamp in conjunction with a narrow band pass filter for 254 nm. IR spectra were recorded on a Genisis FT-IR spectrophotometer (Mattson Instrument Co.). The photolysis product was extracted from the irradiated polyimide film with tetrahydrofuran and analyzed with a Hewlett Packard HP 5890II GC-MS. ^{1}H NMR spectra were taken on a Varian Gemini 300-MHz spectrometer in dimethyl-d_6 sulfoxide using tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

The polyimide (Figure 1) was derived from DHCD and 2,6-naphthalenedicarboxylic acid in 1:1 molar ratio by use of DCC and a mixed solvent of DMF and dimethyl sulfoxide (DMSO). The polymer structure was characterized by ^{1}H NMR and FT-IR spectra. The polyimide is soluble in DMF, DMSO, *N,N*-dimethylacetamide and have a good film-forming property.

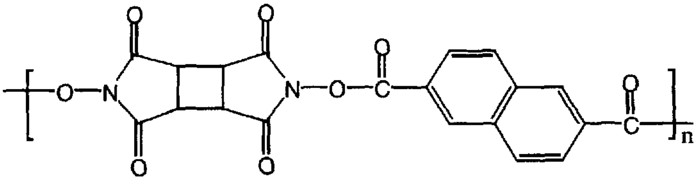

FIGURE 1 The photosensitive polyimide in this study.

When the polyimide film was irradiated with 254-nm light, the absorption at 1642 cm^{-1} representing the N-O stretching vibration decreased in its FT-IR spectral analysis, implying photocleavage of the N-O bond. Increase in absorption at 668 cm^{-1} was also observed, which is probably due to the photosplitting of cyclobutane ring to afford maleimide derivatives. Increase in absorption around 3250 cm^{-1} is attributable to the formation of imide structure.

In analysis of the photolysis mixture, several peaks were detected in the gas chromatograph, and a peak with the same retention time as that of authentic maleimide was observed. The mass spectrometry of the peak revealed a molecular ionic mass peak of maleimide (M/Z 97), indicating the generation of maleimide upon irradiation of the polyimide. The ^{1}H NMR spectrum of the photoproduct also showed a singlet peak at 6.87 ppm (solvent: DMSO-d_6), which corresponds to maleimide. It is concluded from these results that the photodegradation of the polyimide results from the cleavage of N-O bond and cyclobutane ring. This photodegradation behavior is quite similar to that of imidosulfonate-containing polyimide previously reported [4].

The polyimide used here exhibited higher photosensitivity than conventional cyclobutane-containing polyimides [3].

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