

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Positive Photoreactive Polyimides. II. Preparation and Characterization of Polyimide Precursors Containing α -(2-Nitrophenyl)ethyl Ester Side Chains

Shigeru Kubota^a; Toshimoto Moriwaki^a; Torahiko Ando^a; Akira Fukami^a

^a Polymer Engineering Department, Materials and Electronic Devices Laboratory Mitsubishi Electric Corporation, Amagasaki, Japan

To cite this Article Kubota, Shigeru , Moriwaki, Toshimoto , Ando, Torahiko and Fukami, Akira(1987) 'Positive Photoreactive Polyimides. II. Preparation and Characterization of Polyimide Precursors Containing α -(2-Nitrophenyl)ethyl Ester Side Chains', Journal of Macromolecular Science, Part A, 24: 12, 1407 – 1422

To link to this Article: DOI: 10.1080/00222338708078150

URL: <http://dx.doi.org/10.1080/00222338708078150>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POSITIVE PHOTOREACTIVE POLYIMIDES. II. PREPARATION AND CHARACTERIZATION OF POLYIMIDE PRECURSORS CONTAINING α -(2-NITROPHENYL)ETHYL ESTER SIDE CHAINS

SHIGERU KUBOTA, TOSHIMOTO MORIWAKI, TORAHIKO ANDO,
and AKIRA FUKAMI

Polymer Engineering Department
Materials and Electronic Devices Laboratory
Mitsubishi Electric Corporation
8-1-1 Tsukaguchi-honmachi Amagasaki, 661, Japan

ABSTRACT

The monomers were derived from pyromellitic dianhydride and α -(2-nitrophenyl)ethanol, which was prepared by selective reduction of 2-nitroacetophenone. Polyimide precursors were synthesized by an interfacial polycondensation technique. Their thermal properties in nitrogen were studied by dynamic thermogravimetry. The photorearrangement of 2-nitrobenzyl ester having a methyl group at the α -position compared to that of the unsubstituted ester was investigated by infrared spectrophotometry. The polymers obtained in this study gave a high proportion of photorearrangement to show high sensitivity. The exposed areas dissolved in 2% aqueous KOH, forming high resolution patterns because they did not swell during the developing process.

INTRODUCTION

Polyimides have found applications in the microelectronics industry because of excellent electrical properties and high thermal stability [1]. In a

previous study [2] we tried to prepare a positive photoreactive polyimide and showed that this purpose is achieved when the 2-nitrobenzyl group is introduced into the side chain of a polyamic acid through an ester linkage. However, as the imaging characteristics are investigated, it has become apparent that there is a limit to the film thickness that can be exposed and developed. This system, therefore, is of low sensitivity for practical purposes.

It was reported that substitution at the α -position of the 2-nitrobenzyl group increased the conversion for the photorearrangement of this ester [3]. Further, Reichmanis and coworkers prepared a series of 2-nitrobenzyl cholates which had substituent groups in the alcohol portion, and they reported that the derivative with methyl groups in the α -position showed a high quantum yield [4].

The object of this article is to improve the sensitivity of the reported polymer [2]. The monomer's synthesis (from α -(2-nitrophenyl)ethanol) and polymerization are described. Moreover, we discuss the characterization of the polyimides prepared.

EXPERIMENTAL

Solvents and Reagents

Pyromellitic dianhydride (PMDA) was obtained from commercial sources and purified by recrystallization from acetic anhydride.

4,4'-Diaminodicyclohexylmethane (MCH) was purified by distillation under reduce pressure. 4,4'-Diaminodiphenyl ether (ODA) and 4,4'-(di-4-aminophenyl)diphenyl sulfone (PAS) were purified by recrystallization from toluene.

1,2-Dichloroethane and toluene were distilled at atmospheric pressure.

2-Nitroacetophenone (NA), methanol, tetrahydrofuran (THF), sodium borohydride, diethyl ether, acetic acid, thionyl chloride, sodium carbonate, *m*-cresol, and *N*-methyl-2-pyrrolidone (NMP) were obtained from commercial sources and used without purification

Materials

α -(2-Nitrophenyl)ethanol (NPE) was prepared by selective reduction of 2-nitroacetophenone [5]. Sodium borohydride (6.0 g, 0.158 mol) was gradually added as a solid to a solution of 25.0 g (0.152 mol) of 2-nitroacetophenone in 200 mL of methanol at room temperature. Cooling was used to

moderate the reactions and to maintain the temperature in the range from 25 to 30°C. After the addition was complete, the resulting solution was stirred for 2 h at room temperature. Most of the solvent (methanol) was evaporated *in vacuo*. The residue was poured into 200 mL of a saturated aqueous solution of sodium chloride, and the crude product was extracted with four 150-mL portions of diethyl ether. After the solution was dried over anhydrous magnesium sulfate, and diethyl ether was removed by evaporating, the fraction boiling in the range 113-114°C at 1.5 torr was collected as a pale yellow oil. Yield 88.0%; bp 125-126°C/3 torr, 117-118°C/2 torr, 113-114°C/1.5 torr.

Analysis. Calculated for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38%. Found: C, 57.66; H, 5.33; N, 8.41%.

Pyromellitic acid di(α -(2-nitrophenyl)ethyl)ester (NPEPA) was prepared from the reaction of PMDA with NPE in acetic acid. A solution of PMDA (21.8 g, 0.1 mol) and NPE (40.0 g, 0.24 mol) in 350 mL acetic acid was made to react at reflux temperature for 24 h. Acetic acid was removed by evaporating at reduced pressure to yield a white solid. The solid was washed with toluene, filtered, and dried *in vacuo* for 16 h. Yield 56%, mp 212°C.

Analysis. Calculated for $C_{20}H_{20}O_{12}N_2$: C, 56.53; H, 3.65; N, 5.07%. Found: C, 56.74; H, 3.55; N, 5.25%.

Pyromellitic acid dichloride di(α -(2-nitrophenyl)ethyl)ester (NPEPC) was prepared as follows. A mixture of NPEPA (10 g) in thionyl chloride (150 g) with a few drops of *N,N'*-dimethylformamide as a catalyst was refluxed for 2 h to give a clear solution. After the reaction, thionyl chloride was removed by evaporating at reduced pressure to give a brown oil which was dissolved in 50 mL dried toluene with heating. NPEPC was recovered as crystals from the solution on standing for a few days at room temperature. Yield 50.0%, mp 189°C.

Analysis. Calculated for $C_{26}H_{18}O_{10}N_2Cl_2$: C, 52.99; H, 3.08; N, 4.75%. Found: C, 53.14; H, 3.05; N, 4.93%.

Polymerization

Polyimide precursors were synthesized by an interfacial polycondensation technique, as previously reported [2]. A typical polymerization was carried out by the following method.

MCH (1.05 g, 5 mmol) in 100 mL THF was mixed with sodium carbonate (1.06 g, 10 mmol) in 150 mL distilled water, and the resulting solution was cooled in an ice bath. As the blender rotor was raised to a high speed, a solu-

tion of 2.947 g (5 mmol) of NPEPC in 300 mL 1,2-dichloroethane was added. The mixture was stirred for 15 min at ice-bath temperature and then for 30 min at room temperature. After the polymerization the reaction suspension was poured into 500 mL methanol, and the polymer was washed several times with water and finally with methanol. The polymer was collected by filtration and dried in a vacuum oven for about 16 h at room temperature. The yield was 3.56 g (98%).

The intrinsic viscosities of the obtained polymers were measured at 30°C in *m*-cresol with an Ubbelohde suspended-level viscometer. The results of the polymer synthesis are summarized in Table 1.

Measurements

Thermogravimetric analyses (TGA), differential temperature analyses (DTA), and IR and UV spectra were measured by the previously reported method [2].

Lithographic Evaluation

Polymer Coating. The polymers in NMP (12% solid) were spin-coated on silicon wafer substrates which had been treated with 0.2% γ -aminopropyltrimethoxysilane solution in isopropanol to increase the adhesion force. The coating films were prebaked at 70°C for 30 min. The spun-on coating thickness and the step heights after development were measured with an Alpha Step-100 profilometer.

Exposure. The coating film was exposed with a 500-W Xe-Hg high pressure lamp (Ushio Electric Inc.) through a chromium mask on a quartz substrate in contact.

Development. The irradiated films were developed by immersion development with 2% aqueous KOH at 22–24°C. They were washed with a large excess of water after development.

RESULTS AND DISCUSSION

Synthesis

It is considered that the introduction of substituent groups into the 2-nitrobenzyl group facilitates the photorearrangement of the 2-nitrobenzyl ester. Introducing the methyl group into the α -position of 2-nitrobenzyl group gives a

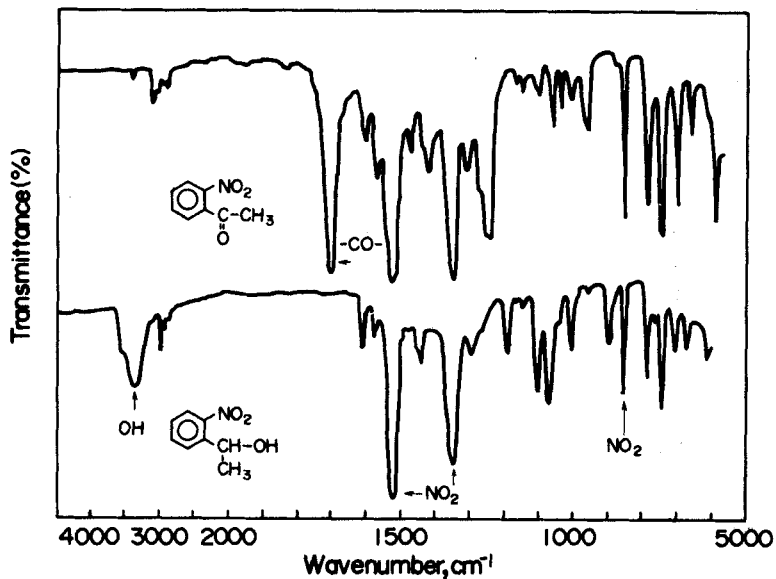


FIG. 1. IR spectra of 2-nitroacetophenone and its reduced product.

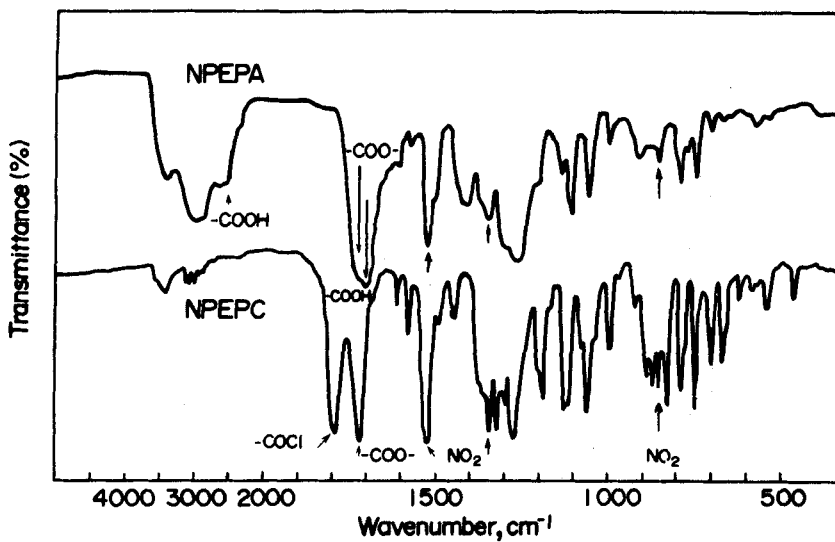


FIG. 2. IR spectra of monomeric materials.

TABLE 1. Characteristics of Prepolymers

Polymer	Dichloride	Diamine	Yield, %	$[\eta]^a$	Thermal analysis ^b	
					EPT, ^c °C	IDT, ^d °C
H	NPEPC	MCH	98	0.70	274	190
B ^e	NBPC	MCH	97	0.65	259	168
I	NPEPC	ODA	97	1.08	249	186
K	NPEPC	<i>p</i> -DADS	99	0.86	237	198

^aMeasured in *m*-cresol at 30°C.

^bDetermined in nitrogen at 10°C/min heating rate.

^cEndothermic peak temperature by DTA.

^dInitial decomposition temperature by TGA.

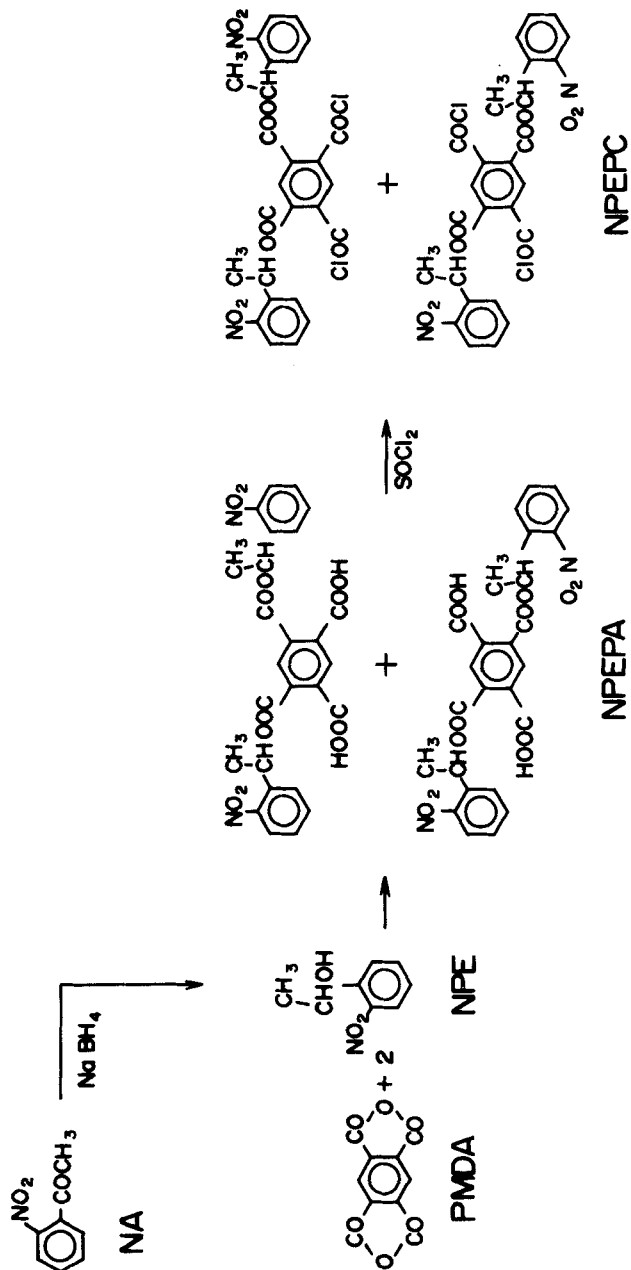
^ePolymer B was prepared from pyromellitic acid dichloride di(2-nitrobenzyl) ester (reported in Ref. 2).

high quantum yield for the photoreaction [4]. In this study we tried to prepare a positive photoreactive polyimide having higher sensitivity than a previously reported polyimide [2] on the basis of the above data.

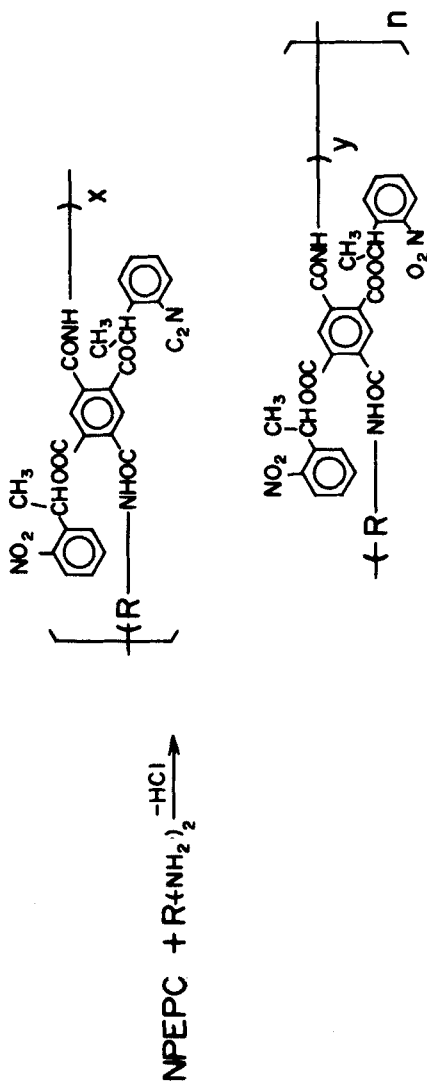
There are two methods for synthesis of 2-nitrobenzyl alcohol with a methyl group in the α -position: one is a nucleophilic addition reaction between acetaldehyde and arylmagnesium halides (Grignard reagents), and the other is a selective reduction of 2-nitroacetophenone by metal hydride. The former is very sensitive and must be protected carefully from the atmosphere (oxygen, carbon dioxide, water vapor, etc.), while the latter does not require the reaction environment to be as strictly controlled. Therefore, we attempted to prepare the alcohol by the latter method.

When sodium borohydride was used in the method described in the Experimental section, the alcohol was obtained in high yield. Figure 1 presents the IR spectra of the alcohol and the ketone. The carbonyl absorption at 1700 cm^{-1} in 2-nitroacetophenone disappears completely, the new band at 3350 cm^{-1} , attributed to the alcohol, appears after the reduction, and the nitro absorption at 1520, 1340, and 860 cm^{-1} remains unaltered before and after the reaction. This indicates that the materials are reduced with very high selectivity in this system.

The synthesis of the monomers and subsequent polymerization are described in Schemes 1 and 2. Figure 2 shows that NPEPA exhibits the IR band charac-



SCHEME 1. Synthesis of monomeric materials.



SCHEME 2. Synthesis of polymers.

teristic of carboxylic acid at 2500 and 1700 cm^{-1} , the ester linkage at 1720 cm^{-1} as a shoulder, and the nitro group at 1520 , 1340 , and 860 cm^{-1} . In the IR spectrum of NPEPC, the 2500 cm^{-1} acid absorption disappears, and a carbonyl absorption at 1790 cm^{-1} , due to acid chloride, appears, while the absorptions of the ester linkage and the nitro group remain unaltered. Acid and acid chloride derivatives described in the preceding paper [2] had melting points of 186 and 168°C , respectively. The derivatives obtained in this study have higher melting points, 212 and 189°C , respectively. The monomers are mixtures of two isomers, as shown in Scheme 1, similar to those reported in the preceding paper. They were used for further synthesis without separation.

The polymerizations were carried out according to Scheme 2. Polymer characteristics are summarized in Table 1. Polymers were recovered in good yield. In Fig. 3, typical IR spectra of a thin film of Polymer H are shown and compared with that of the polymer reported previously (Polymer B) [2]. The characteristic absorptions for ester linkage at 1720 cm^{-1} , amide linkage at

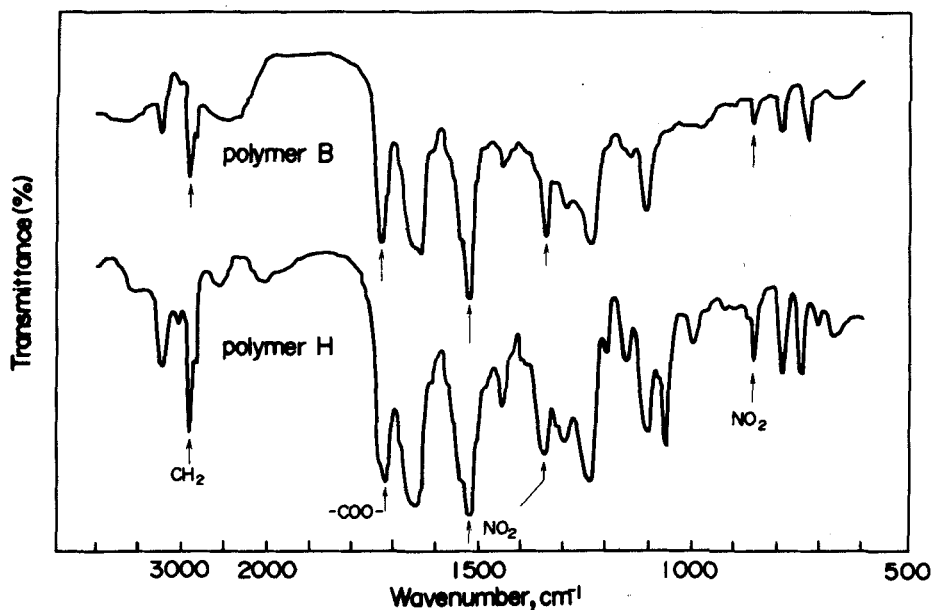


FIG. 3. IR spectra of Polymers B and H.

1650 cm^{-1} , and nitro group at 1520 , 1340 , and 860 cm^{-1} are present in both spectra. It is also possible to prepare a polyimide precursor from NPEPC.

Thermal Analysis

TGA was performed in a stream of nitrogen (50 mL/min) at a heating rate of 10°C/min on the polymer powder (5 mg) (Fig. 4 and Table 1). All the polymers exhibited a pronounced weight loss in two stages, similar to the polymer reported previously. The first weight loss in Fig. 4 is due to the imidization [2], and this value is in near agreement with the values calculated for the elimination of alcohols (Polymer H 45.99% , I 46.67% , K 35.22%).

In the preceding paper [2] the initial decomposition temperature (IDT) of Polymer B obtained from MCH was 168°C , and the endothermic peak temperature (EPT) by DTA was 259°C , the temperatures at which the imidization rate has its maximum value. Those of Polymer H, obtained in this study, are higher, 190 and 274°C (Table 1). The same results are also obtained for polymers prepared from aromatic diamines. This indicates that these temperatures

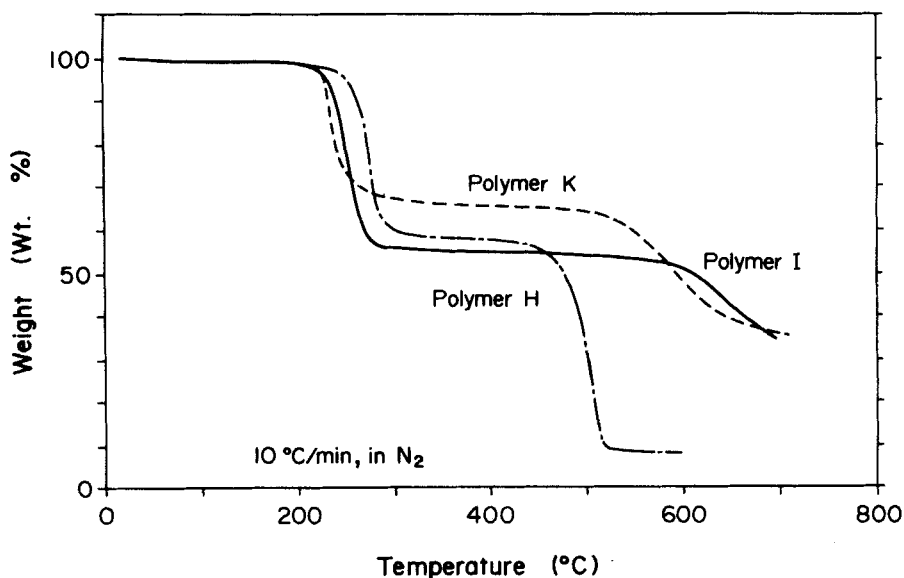


FIG. 4. TGA curves for polyimide precursors.

will rise with increasing molecular weight of the alcohols released by heating, and this agrees with the experimental results already reported [6].

The second weight loss in Fig. 4 is attributed to the thermal degradation of the polyimide main chain. Noticeable weight loss is observed in the range 450-500°C for Polymer H, 500-600°C for Polymer K, and 550-650°C for Polymer I. Polymers K and I are wholly aromatic polyimides and show a high char yield. In addition, Polymer I shows better thermal stability because it has a higher imide content in the repeating units than Polymer K, and is free of the aryl sulfone linkage, which is less stable on heating than aryl ether [7].

Photochemical Study

As described in the preceding paper [2], 2-nitrobenzyl ester groups introduced in the side chain of the polyamic acid undergo scission of an ester linkage based on intramolecular photorearrangement by UV irradiation. This reaction was confirmed by evaluating the changes in the IR absorption spectra of the polymer upon UV irradiation. In order to compare the photorearrangement conversion of 2-nitrobenzyl ester having a methyl group at the α -position to that of an unsubstituted ester, the changes in the IR nitro [8] and ester absorbance upon UV irradiation were determined. The absorbance at 1530 cm^{-1} (nitro group) and at 1730 cm^{-1} (ester linkage) were used, and these ratios were calculated with reference to the absorbance of the alicyclic methylene group at 2830 cm^{-1} , which remains unaltered on UV irradiation (Fig. 5). There is a marked decrease in the intensity of the nitro group and the ester linkage on UV irradiation. As shown in Fig. 5, the decrease of these intensities for Polymer H (having a methyl group at the α -position) is greater than that for Polymer B (having no substituted group). This means that the characteristic rearrangement in the 2-nitrobenzyl ester occurs more readily in Polymer H than in Polymer B. It is considered that the difference in the proportion reacted will influence the sensitivity of these polymers.

In order to compare the sensitivity, the development characteristic curves for Polymers B and H were measured. As is clear from Fig. 6, Polymer H is able to be exposed and developed to a greater depth than Polymer B for the same exposure time. The UV absorption spectra for the polymers are shown in Fig. 7. The absorption peak due to the 2-nitrobenzyl group (a discernible shoulder in the vicinity of 250-260 nm) is not shifted in Polymer H and has about the same intensity. Therefore, the sensitivity in this system is affected by the increase in the conversion caused by introducing the substituent groups into the α -position of the 2-nitrobenzyl ester group.

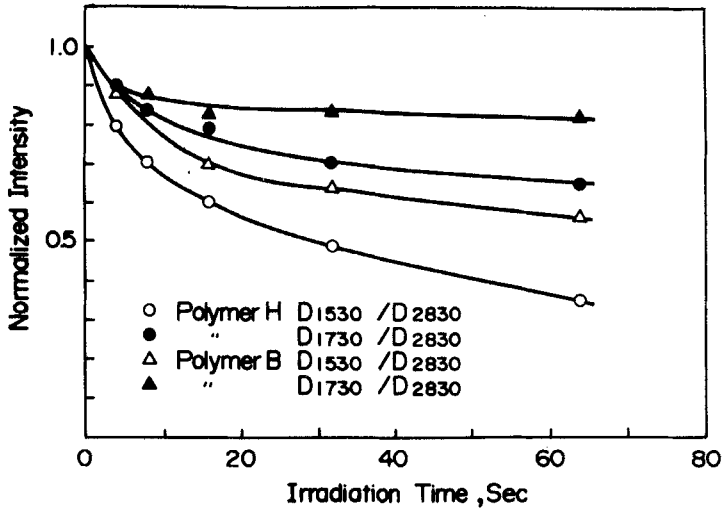


FIG. 5. Change in IR absorption for nitro group and ester linkage upon irradiation of $2\ \mu\text{m}$ polymer film, cast on germanium plates and prebaked at 70°C for 30 min, normalized to the initial absorbance ratio.

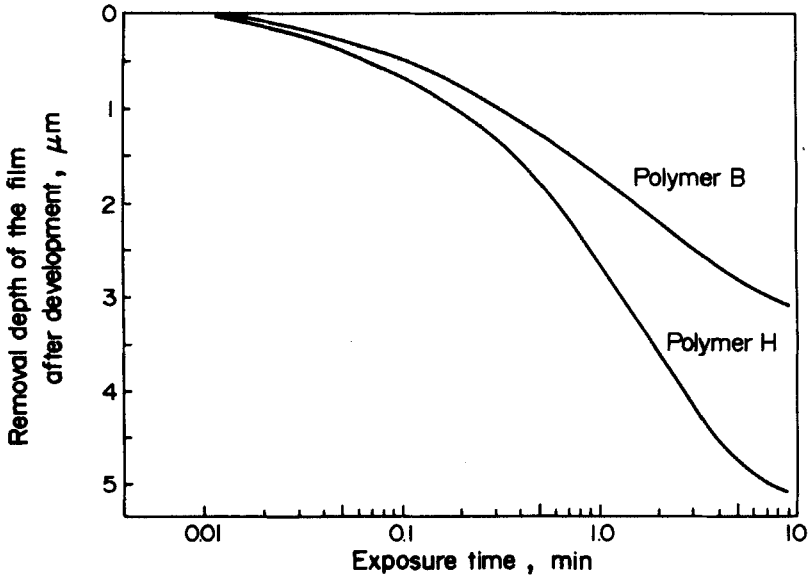


FIG. 6. Exposure characteristics of polymers B and H.

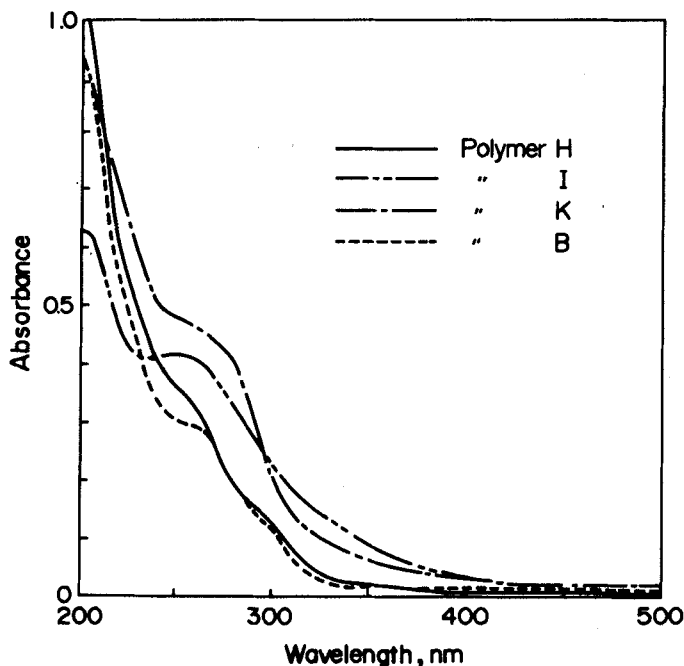


FIG. 7. The UV spectra of polyimide precursors. Film thickness: Polymers H and B, $0.12 \mu\text{m}$; I, $0.060 \mu\text{m}$; K, $0.062 \mu\text{m}$.

Lithographic Performance

The characteristic curves for the polymers obtained were determined in order to evaluate the film thicknesses exposed and developed. Figure 8 shows that the sensitivity of the polymer obtained from the aliphatic diamine was slightly higher than that from the aromatic diamine, as described in the preceding study [2] (comparison between Polymers H and I). There was also a marked difference in sensitivity between Polymers I and K, i.e., Polymer I is exposed and developed more deeply than Polymer K when these polymers are irradiated with the same dose. For these reasons it is considered that they differ from one another in carboxylic acid concentration. Polymer K is synthesized from a long-chain diamine and has longer segments in the repeating unit than Polymer I. Although these polymers are irradiated with the same dose to form the same number of moles of carboxylic acid, the carboxylic

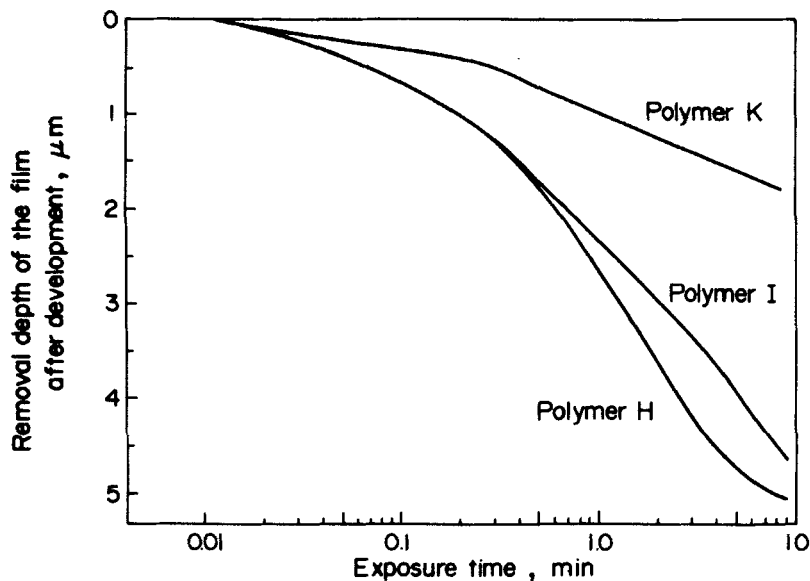


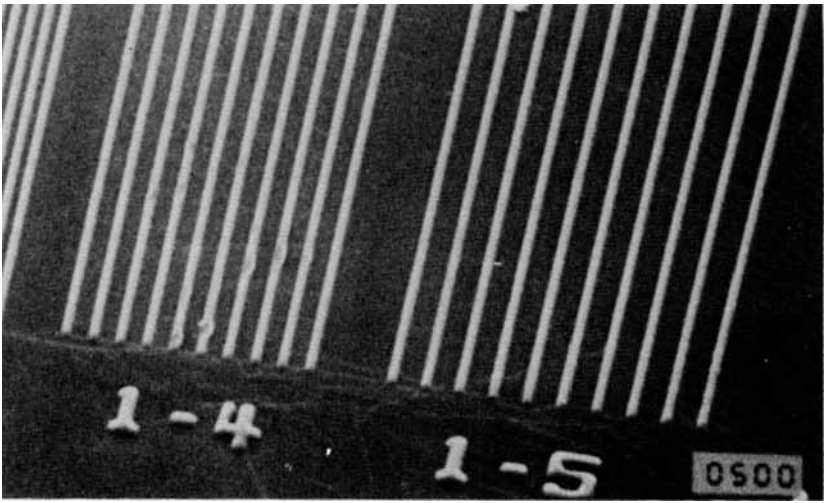
FIG. 8. Exposure characteristics of Polymers H, I, and K. Exposure with unfiltered UV light from a 500-W high-pressure Hg-Xe lamp; development with 2% aqueous KOH.

acid concentration for the molecular length differs in these polymers, and this influences their solubilities in alkali solution. Thus, Polymer I has a high carboxylic acid concentration and better solubility, and hence, higher sensitivity than Polymer K.

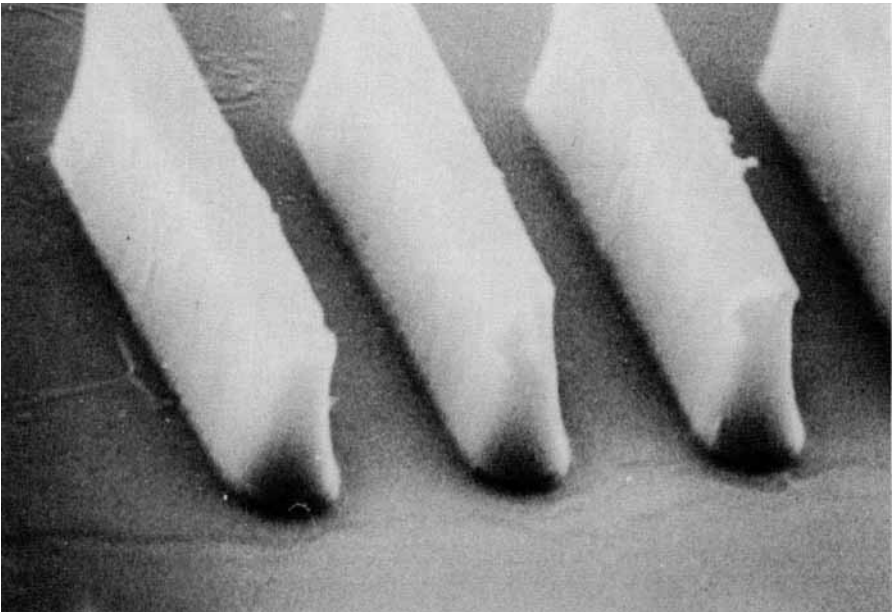
Figure 9 shows scanning electron micrographs of typical positive tone which can be obtained using 2% aqueous KOH developer. Resolution is good, as shown in photograph (A), of the pattern produced by using a photomask havein 1 μm lines (film thickness about 1 μm). Further, it is possible to image high-aspect-ratio geometries (Photograph B). High resolution is obtained in this system because there is no swelling during the developing process.

(opposite page)

FIG. 9. Scanning electron micrographs of typical positive tone. (A) 1 μm lines in 1 μm layer thickness; (B) 2 μm lines in 4 μm thickness.



(A)



(B)

REFERENCES

- [1] *Proceedings of 2nd International Conference on Polyimides, Synthesis, Characterization and Application*, Mid-Hudson Section, Society of Plastics Engineers, New York, 1985.
- [2] S. Kubota, T. Moriwaki, T. Ando, and A. Fukami, *J. Appl. Polym. Sci.*, In Press.
- [3] J. A. Barltrop, P. J. Plant, and P. Schofield, *Chem. Commun.*, p. 822 (1966).
- [4] E. Reichmanis, R. Gooden, C. W. Wilkins Jr., and H. Schonhorn, *J. Polym. Sci., Polym. Chem. Ed.*, *21*, 1075 (1983).
- [5] S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, *71*, 122 (1949).
- [6] S. Nishizaki and T. Moriwaki, *Kogyo Kagaku Zasshi*, *73*, 1873 (1970).
- [7] N. A. Adrova, M. I. Bessonov, L. A. Laivs, and A. P. Rudakov, *Polyimides: A New Class of Heat-Resistant Polymers*, Israel Program for Scientific Translations, Jerusalem, 1969, p. 54.
- [8] J. N. Pitts Jr., J. K. S. Wan, and E. A. Schuck, *J. Am. Chem. Soc.*, *86*, 3606 (1964).

Received March 7, 1987

Revision received April 14, 1987