Synthesis and Photodegradation of Positive Working Polyimides Derived from 2-Nitro-*p*-xylyleneoxyamine

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Two kind of diamines, 2-nitro-*p*-xylyleneoxyamine (**5a**) and *p*-xylyleneoxyamine (**5b**) were synthesized and used as monomers together with various tetracarboxylic dianhydrides to prepare the main-chain photodegradative polyimides which exhibited a positive working image upon light irradiation. The photosensitivities of the polyimides and the viscosities of their precursors on irradiation indicated that the nitro group substituted at the ortho position of the benzene ring of the diamine moiety improved the photolytic decomposability of polymers by at least 1−2 orders of magnitude compared with the hydrogen at the same position. Furthermore, much higher sensitivity was attained by using polyimide films such as 6FDA−**5a** (polycondensate of 2,2-bis(3,4-dicarboxypheny)hexafluoropropane dianhydride and **5a**) and BHTCA−**5a** (polycondensate of bicyclo[2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride and **5a**), which contained either a bulky trifluoromethyl (−CF_3) substituent or a polyalicyclic structure along the polymer backbone. The higher photosensitivities of 6FDA−**5a** and BHTCA−**5a** (95 and 85 mJ/cm^2, respectively) might be explained by the greater solubilities of the segments decomposed from these polyimides in development solvent. Therefore, a discussion on the photochemical behavior of polyimides studied was presented.

Introduction

Due to the unique combination of low dielectric constant, high thermal stability, and excellent mechanical properties, polyimides are becoming more and more important in the field of polymeric photoresists for microelectronic applications. In recent years, many research efforts have been concentrated on attempts to prepare photosensitive polyimides and their precursors. Photopositive polyimides are much more desirable in lithography because they offer many advantages including simplicity of the patterning process, better suited shapes, and lower shrinkage of the pattern profiles for multilayer systems, as well as developers less harmful to the environment.[1] However, such positive working polyimides are still limited.

Several photopositive polyimides have been reported. Crivello and co-workers succeeded in the synthesis of the first positive polyimides bearing diarylsulfide linkages in the main chain, which showed photosensitivity after phenylation with diphenyl iodonium salts.[2] An intrinsically deep-UV sensitive polyimide containing a cyclobutane ring was reported by Moor et al.[3] Other positive polyimide systems were derived either from hydropolyimides (by substitution of the ortho hydrogen of the amine comonomer with a hydroxyl group)[4] or from fluorine hydropolyimides with a protection group in the presence of photosensitive components and photoacid generators, respectively.[5,6]

We have reported several types of soluble polyimides with a polyalicyclic unit in polymer backbones.[7−10] Photolysis on light irradiation of *N*-oxysuccinimide derivatives and *N*-oxymaleimide derivatives which contain an >N−O−R structure was also studied in our laboratory. The results showed an acceleration in cleavage of the O−R bond induced by substitution of the phenyl hydrogen of R with a nitro group. On the other hand, polymers containing *o*-nitrobenzyl esters and ethers were known as deep-UV positive resists.[11] Hence, it appears worthwhile to attempt to incorporate the above-mentioned >N−O−R moiety and a polyalicyclic unit or other bulky substituent into the backbone of the polyimide and to elucidate the resulting polymer as a photoresist with both potential positive and processable characteristics.

In the present paper, we describe the synthesis and characterization of two diamines, 2-nitro-*p*-xylyleneoxyamine (**5a**) and *p*-xylyleneoxyamine (**5b**), as well as the preparation of the main-chain degradative polyimides obtained from both of the two diamines and various tetracarboxylic dianhydrides. Particularly, we focus attention on the investigation of the photodecom-

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posite properties of the polyimides from **5a** such as viscosity on irradiation, photosensitivity and spectroscopic alteration in comparison with those of the polyimides from **5b**.

Experimental Section

Materials and Measurements. All solvents and the chemicals such as hydroxylammonium chloride and *p*-xylylene chloride were obtained from commercial sources and used as received. *N*,*N*-Dimethylacetamide (DMAc) used for the polycondensation medium was dried over CaH_2 and then fractionally distilled under reduced pressure. The aromatic dianhydrides such as 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, from Daisel Chemical) and 4,4′-oxydiphthalic anhydride (ODPA, from Chriskev) were used after vacuum-drying at 130 °C for 5 h, while 2,2-bis(3,4-dicarboxypheny)hexafluoropropane dianhydride (6FDA, from Hoechst) was of reagent grade and was used without further purification. The polyalicyclic dianhydride, bicyclo[2.2.1]heptane-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (BHTCA), was synthesized according to our previously reported procedure.[8]

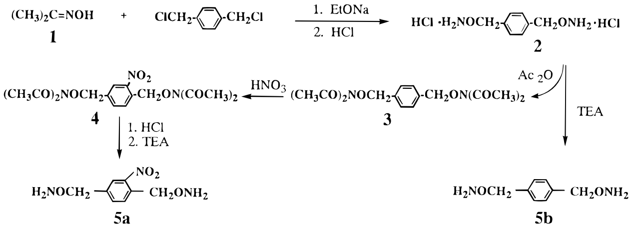
Infrared spectra were recorded using a JASCO VALOR-III Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-EX 400WB spectrometer operating at 400 and 100 MHz, respectively. The proton signals in part of the ^1H NMR spectra were assigned in H,H−COSY and H,C−COSY spectra. Thermal analyses were performed on a Seiko SSC 5200-TG/DTA 220 instrument at a heating rate of 10 °C/min in nitrogen atmosphere for thermogravimetric analysis (TGA) and a Seiko SSC 5200-TMA/SS 100 instrument with a constant load of 10 g (stress; 0.125 MPa) at a heating rate of 10 °C/min in air for determination of glass transition temperature.

Preparation of *p*-Xylyleneoxyamine Acetylate (3). Acetone oxime (**1**, 58.4 g, 0.8 mol), which was obtained from the reaction of acetone with hydroxylammonium chloride in the presence of Na_2CO_3, and *p*-xylylene chloride (70.0 g, 0.4 mol) were dissolved in ethanol (600 mL) containing sodium ethoxide (0.8 mol) and heated under reflux for 4 h. After concentration of the solution and hydrolysis with HCl acid (aq), *p*-xylyleneoxyamine dihydrochloride (**2**) was isolated by removal of the solvent under reduced pressure, washed with ethanol, and dried. Acetic anhydride (230 mL) was then added dropwise to **2** which had been neutralized with triethylamine (2.0 mol) in DMAc (800 mL). The reaction mixture was heated at 110 °C for 1 h, cooled, and then poured into ice water, and the white precipitates were collected by filtration. A final recrystallization from acetonitrile gave 87.5 g (65% yield overall) of **3**: mp 186−188 °C. Anal. Calcd for $C_{16}H_{20}O_6N_2$: C, 57.13; H, 6.01; N, 8.33. Found: C, 57.10; H, 5.96; N, 8.51.

Preparation of 2-Nitro-*p*-xylyleneoxyamine Acetylate (4). In an ice bath, 61% nitric acid (200 mL) was added to **3** (26.8 g, 0.08 mol) in acetic anhydride (800 mL). After a catalytic amount of sulfuric acid was dropped in, the mixture was stirred for 10 h at room temperature and then poured into ice water, and a yellow precipitate formed which was washed with cooled water and ethanol. The crude product was recrystallized from ethanol to give pure **4** (23.2 g, 76% yield): mp 144−145 °C; ^1H NMR ($CDCl_3$) 8.23 (1H, d, $J_{3,5} = 2$, H-3), 7.97 (1H, d, $J_{6,5} = 8$, H-6), 7.85 (1H, dd, $J_{5,3} = 2$, $J_{5,6} = 8$, H-5), 5.37 (2H, s, CH_2 (attached to C-4)), 5.05 (2H, s, CH_2 (attached to C-1)), 2.45 (12H, CH_3); ^{13}C NMR ($CDCl_3$) 169.8 (C=O), 147.5 (C-2), 135.9 (C-4), 134.3 (C-1), 130.6 (C-5), 130.3 (C-6), 125.2 (C-3), 76.3 (CH_2, C-1 side), 73.6 (CH_2, C-4 side), 24.8 (CH_3). Anal. Calcd for $C_{16}H_{19}O_8N_3$: C, 50.39; H, 5.03; N, 11.02. Found: C, 50.37; H, 4.89; N, 11.29.

Synthesis of 2-Nitro-*p*-xylyleneoxyamine (5a). The acetylate **4** (3.8 g, 0.01 mol) in 5% HCl acid (aq) (500 mL) was heated at 90 °C until **4** was dissolved completely, then cooled, and allowed to continue for 2 h at room temperature. A solid was obtained by the concentration of the reaction mixture under reduced pressure and washed with ether and dried. The solid was then neutralized in H_2O (35 mL) with triethylamine (0.06 mol) for 6 h at room temperature, and the solution was extracted twice with CH_2Cl_2. After removal of the solvent on a rotary evaporator and drying overnight at 65 °C under reduced pressure, a yellow liquid (**5a**, 1.51 g) was obtained in 71% overall yield: IR (neat) 3317, 3245, 1589, 1529, 1346 cm^{-1}; ^1H NMR ($CDCl_3$) 8.03 (1H, d, $J_{3,5} = 2$, H-3), 7.65 (1H, d, $J_{6,5} =$ 8, H-6), 7.62 (1H, dd, $J_{5,3} = 2$, $J_{5,6} = 8$, H-5), 5.54 (4H, br s, NH_2), 5.06 (2H, s, CH_2 (attached to C-4)), 4.74 (2H, s, CH_2 (attached to C-1)); ^{13}C NMR ($CDCl_3$) 148.1 (C-2), 138.9 (C-4), 133.6 (C-1), 132.9 (C-5), 129.4 (C-6), 124.3 (C-3), 76.2 (CH_2, C-1 side), 74.2 (CH_2, C-4 side). Anal. Calcd for $C_8H_{11}O_4N_3$: C, 45.06; H, 5.21; N, 19.71. Found: C, 45.20; H, 5.17; N, 19.50.

Scheme 1



Synthesis of *p*-Xylyleneoxyamine (5b). As described above for the monomer **5a**, **5b** was prepared from the neutralization of **2** and purified by sublimation under reduced pressure. The total yield was 41%: mp 52−53 °C; IR (KBr) 3310, 3248, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 7.36 (4H, s, Ph), 5.40 (4H, br s, NH_2), 4.69 (4H, s, CH_2); ^{13}C NMR ($CDCl_3$) 137.42 (C-1), 128.69 (C-2), 77.84 (CH_2).

Poly(amic acid) and Polyimide. In a 30-mL three-necked flask equipped with a magnetic stirrer and a nitrogen inlet were placed dianhydride (2 mmol), dried DMAc (6 mL), and diamine (**5a** or **5b**) (2 mmol). The reaction was allowed to proceed under nitrogen for 2 days at ambient temperature. The resulting viscous mixture was poured into H_2O and the precipitate formed was dried in vacuum for 12 h at room temperature and 6 h at 80 °C. The poly(amic acid) was obtained in 70−85% yield. The polyimide film was prepared from the poly(amic acid) solution by casting on a cover glass followed by heating in vacuo at 50 °C for 1 h and then at 80 and 170 °C for 2 h, respectively.

Film Photolysis. The 1 μm polyimide film on the cover glass was irradiated with a high-pressure 500 W xenon lamp. The intensity on the exposed surface was 1.5−2.5 mW/cm^2 in the range 240−270 nm, measured with an ORC M-02 UV light measuring meter. The exposed film was developed for 4 min in the 2:3 mixed solvent of 2-butanone and 2-propanol, which does not dissolve the unirradiated film part. The film thickness was determined with a Dektak ^{3}ST Surface Profiler (Veeco Sloan Technology Co.). All the polyimide films possessed similar thicknesses. The photosensitivity ($D^{0.5}$) was obtained in terms of an exposure dose at which the film thickness was reduced by 50% of the initial thickness.

In the case of infrared spectra measured after photolyses, the polyimide film spin-coated on a silicon wafer was exposed to the above Xe lamp at the same light intensity. The silicon wafer was fixed in the IR sample holder during photolyses so that the IR measurements were taken at the same point or area for each exposure.

Inherent Viscosity. Inherent viscosity was measured with an Ostwald viscometer in DMAc solution at a concentration of 0.5 g/dL at 30 °C. The effect of light irradiation on the inherent viscosity of poly(amic acid) was also examined. The polymer solution was placed in a quartz cell and purged with an inert gas such as nitrogen prior to irradiation, then exposed to the light from a Xe lamp at specified time intervals and transferred to the viscometer for determination.

Results and Discussion

Synthesis of Polyimides. To assess the effect of a nitro group substituted on the benzene ring of the diamine moiety on the photolysis of the polyimide, two diamines **5a** and **5b** were synthesized using *p*-xylylene chloride as the starting material according to the route

Scheme 2

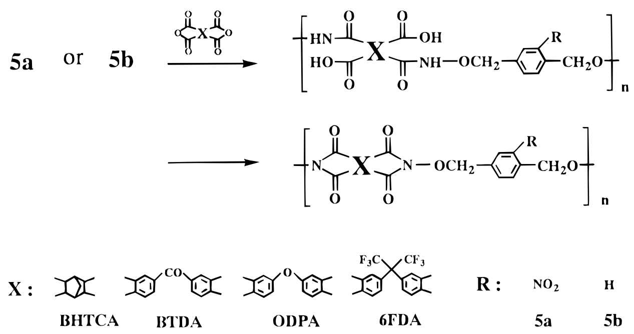


Table 1. Properties of Polymers

diamine	dianhydride	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_5[c] (°C)	$D^{0.5}$ [d] (mJ/cm^2)
5a	BHTCA	0.39	137	292	85
5a	BTDA	0.67	134	290	1.0×10^3
5a	ODPA	0.47	118	295	1.9×10^3
5a	6FDA	0.37	131	305	95
5b	BHTCA	0.34	150	301	1.7×10^3
5b	BTDA	0.69	158	304	$>1.0 \times 10^4$
5b	ODPA	0.60	134	305	$>1.0 \times 10^4$

[a] Poly(amic acid)s; measured in DMAc at a concentration of 0.5 g/dL at 30 °C. [b] Glass transition temperature determined by TMA (10 °C/min in air). [c] Temperature for 5% weight loss and measured by TGA (10 °C/min in N_2). [d] Photosensitivity, the dose at 50% initial film thickness loss with irradiation of a xenon lamp.

illustrated in Scheme 1. It is noted that **5a** could be prepared by neither the nitration of *p*-xylylene acetone oxime nor the reaction between 2-nitroxylylene chloride and acetone oxime in the presence of sodium ethoxide.

The polymerization of **5a** and **5b** with four kinds of dianhydrides (BHTCA, BTDA, ODPA, and 6FDA) was then conducted, and the resulting poly(amic acid)s were converted into polyimides by a curing cycle as described previously (Scheme 2). IR spectra of the polyimides confirmed the complete imidization, in which the imide carbonyl absorption at 1787 and 1735 cm^{-1} and the disappearance of the N–H and O–H bands at ca. 3300 cm^{-1} were observed. Properties of the polymers prepared here are partially listed in Table 1. Worthy of mention is that all the polyimides were soluble in polar aprotic solvents such as DMAc, and especially BHTCA-**5a** and 6FDA-**5a** showed higher solubility than others.[12]

Inherent Viscosity on Irradiation. The photochemical degradation of poly(amic acid) from BHTCA and **5a** (PA BHTCA-**5a**) was investigated in DMAc solution using a Xe lamp. The poly(amic acid) based on BHTCA and **5b** (PA BHTCA-**5b**) was also measured in an identical manner for comparison. Figure 1 shows the plot of the ratio of the inherent viscosity at irradiation time *t* (η_t) to that at irradiation time $t = 0$ (initial inherent viscosity, η_0). The viscosity decrease with irradiation time for both polymers was readily apparent, indicating the main-chain scission of poly(amic acid)s leading to the decrease in molecular weights. In addition, the viscosity decrease of 28% in the first 1-h exposure for PA BHTCA–**5a** was greater than that for PA BHTCA–**5b**, the latter tended toward gradual reduction during 4-h irradiation. This result suggests that the nitro group substituted at the benzene ring enhanced the photolytic decomposability of the poly(amic acid).

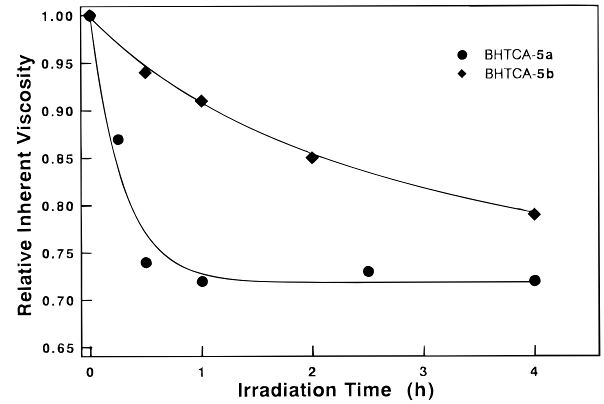


Figure 1. Relative inherent viscosity η_t/η_0 versus irradiation time for poly(amic acid).

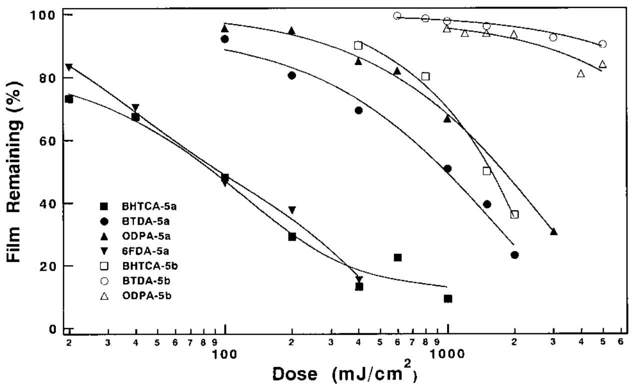


Figure 2. Characteristic curves for polyimides exposed to the light from Xe lamp.

Photosensitivity. The photosensitivity ($D^{0.5}$) of the polymer was evaluated by its characteristic exposure curve, the plot of the ratio of the remaining film thickness to the initial film thickness after development at each exposure energy. Figure 2 shows the characteristic curves of polyimides from **5a** and **5b**, which present positive working photoreactive materials. Furthermore, the polyimides with **5a** were much more sensitive than those with **5b** for utilization of the same dianhydride. When exposed up to 1.0×10^3 mJ/cm^2, for example, approximately 50% of the initial film thickness was removed from the polyimide BTDA–**5a**, while only 3% was removed from BTDA–**5b**. This result is identical with that obtained from the varying viscosities in Figure 1, demonstrating the acceleration in photodegradation of the polyimide chains due to the nitro group on the benzene ring.

In addition, the polyimides made from **5a** and **5b** exhibited optical transparency, i.e., the transmittances of all the polyimide films at 300 nm were over 85% in the UV–visible spectra. No apparent differences in transmittances were observed for all of the films in the range 250–700 nm.

The photosensitivity values of polyimides obtained from the characteristic curves are also summarized in Table 1. It is noted that even though the polyimides were composed of the same diamine, there was a much larger difference in sensitivities. Much higher sensitivity compared to other polyimides was observed in polyimides such as 6FDA–**5a** and BHTCA–**5a**, which contained either a bulky trifluoromethyl (–CF_3) substituent or a polyalicyclic structure along the polymer backbone. We know, based on our previous reports and

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(12) Feng, K.; Matsumoto, T.; Kurosaki, T. *J. Photopolym. Sci. Technol.* **1996**, *9*, 347.

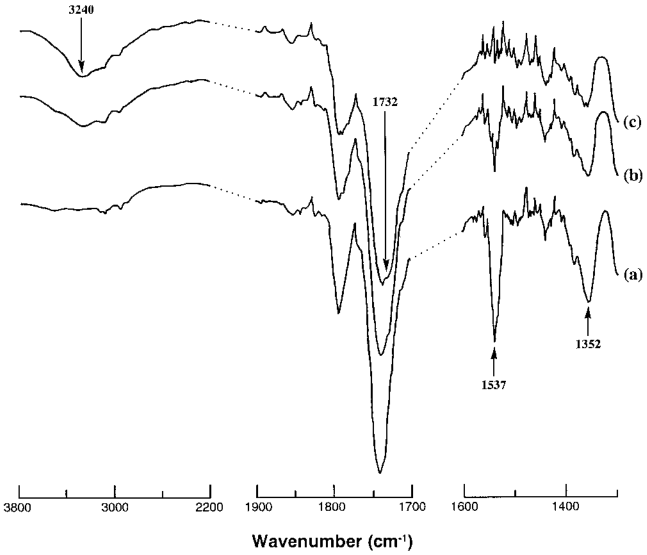

Figure 3. FTIR spectra of polyimide based on 6FDA and **5a** in exposure dose of (a) 0, (b) 400, and (c) 2000 mJ/cm^2.

the literature,[9–10,13] that the introduction of a bulky substituent or a polyalicyclic structure into the polyimides inhibits polymer–polymer interaction by enlarging the distances between polymer chains and leads to an increase in solubility. Because the photosensitivity obtained from the characteristic curve is expressed by the solubility of the segments which result from the photochemical decomposition of the polymer chains, the difference in photosensitivity of the polyimides may come from the different solubility of the segments. Hence, it is considered that the segments containing a bulky substituent or a polyalicylic structure moiety are more soluble in comparison to other polymer segments so that their parent polyimides exhibit higher sensitivity.

Photochemistry. According to the results shown above that the nitro group of the diamine moiety results in an increase in the photosensitivity of the polyimide film, we estimated that the changes in the nitro group might be involved in the photocomposition of the polymer chains. It was also expected that detectable changes in the nitro group occurring during irradiation should readily appear in FTIR, attributed to its strong and divided absorption band in the spectrum.

Figure 3 is an example of a polyimide from 6FDA and **5a**. Some apparent changes were exhibited by comparison of the spectra of the polyimide films before and after photolysis on irradiation. At the same time as the rapid decrease in nitro group absorptions at 1537 and 1352 cm^{-1}, new vibrational absorptions such as an OH stretching band at 3240 cm^{-1}, and an aldehyde carbonyl stretching band at 1732 cm^{-1} appeared more and more obviously in the spectra with the increase in exposure time. This indicated that the nitro group substituted at the ortho position of the benzene ring of the diamine moiety was involved in the main-chain scission of the polymers, and the alcohol and aldehyde as primary photoproducts might be generated in the photolysis process.

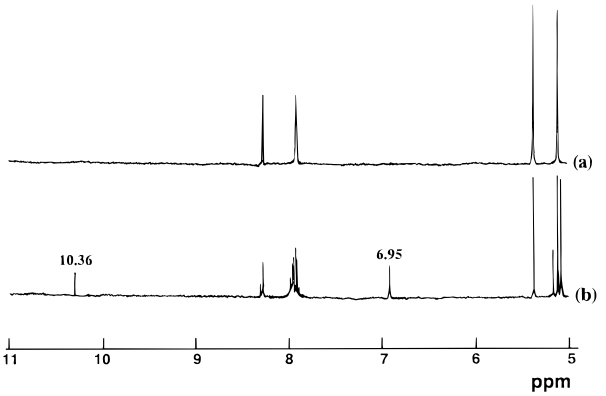

Figure 4. ^{1}H NMR spectra of model compound 2-nitro-*p*-xylyleneoxyamine acetylate (**4**): (a) before and (b) after irradiation for 1 min in deuterated methanol.

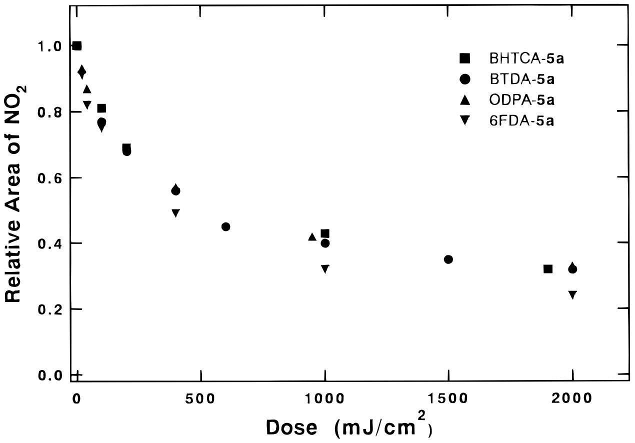

Figure 5. Normalized area of nitro group absorption at 1537 cm^{-1} in FTIR spectra of polyimide films as a function of exposure energy.

In addition, the evidence for the formation of aldehyde was also obtained from the ^{1}H NMR spectrum of model compound **4** after photolysis. Deuterated methanol was selected as the solvent for ^{1}H NMR measurements in order to reduce the disturbance from solvent photolysis, though compound **4** had limited solubility in it. The measurement was carried out after compound **4** in an ordinary NMR tube was irradiated with a Xe lamp. The results are given in Figure 4, in which the signal of a chemical shift of 10.36 ppm was assigned as the proton from the aldehyde. This assignment seems reasonable when compared to the result from 2-nitrobenzaldehyde whose chemical shift for the aldehyde proton was 10.30 ppm. Another signal at 6.95 ppm in Figure 4 probably came from the alcohol (>N–O–H). However, both of the two signals disappeared after longer irradiation, indicating the instability of the two photoproducts in this circumstance.

To provide a quantitative description for the loss of nitro group absorption shown in FTIR, the area of the NO_2 stretching band with a peak maximum at 1537 cm^{-1} was measured as a function of photolysis energy as illustrated in Figure 5. The relative area of NO_2 in Figure 5, which is the ratio of the NO_2 area at the irradiation dose to its initial area at dose = 0, exhibited almost the same decrease trend for all of the polyimides derived from **5a**. Because the photolysis for IR determination and that for photosensitivity proceeded under identical irradiation circumstances, after comparison of these two experimental results, it was known that the varying photosensitivities of the polyimides from **5a** were independent of the elimination rate of the nitro

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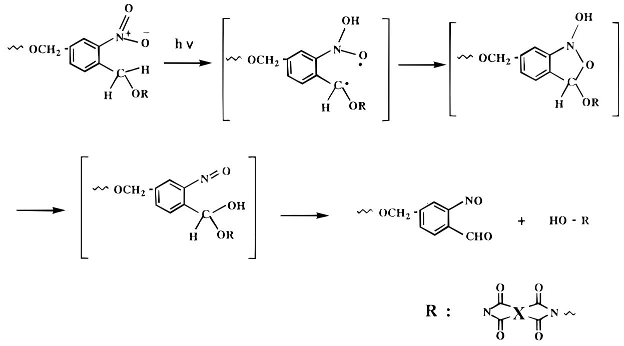
(13) Omote, T.; Yamaoka, T.; Koseki, K. *J. Appl. Polym. Sci.* **1989**, *38*, 38, 389.

Scheme 3



group, although the photoreaction was induced from the H-abstraction by the nitro group. The difference in photosensitivity was due to the different solubility of the decomposed polymer segments, as indicated already.

On the basis of the results from FTIR and ^{1}H NMR, a primary mechanism for the photodecomposition of polyimide from **5a** was proposed as shown in Scheme 3. The photochemical reaction was considered to proceed via abstraction of a benzylic hydrogen atom by a nitro group oxygen. Subsequent rearrangement and cleavage generated the segments and ended in *o*-nitrosobenzaldehyde and alcohol, which might be soluble in the development solvents if their molecular weights were low enough.

If the polyimides were based on **5b**, they showed slower reduction in inherent viscosity on irradiation and a reduced photosensitivity ($D^{0.5}$) in characteristic curves, as indicated in Figures 1 and 2. In our previous studies, *N*-oxymaleimide−styrene copolymers containing the >N−O−R structure were used for photolysis on light irradiation. The evidence for the cleavage of the N−O bond was obtained with IR spectroscopy when the phenyl hydrogen of R above was substituted without any group. Hence, in addition to the mechanism shown in Scheme 3, it is believed that another mechanism leading to the main chain scission included the cleavage of the N−O bond, though its decomposition rate was relatively low.

Concluding Remarks

In this paper, we have succeeded in the preparation of several intrinsically photopositive polyimides derived from diamine **5a** or **5b**, which contain an >N−O−R structure along the polymer backbones, and have shown the effect of the nitro group of the diamine moiety on the photolysis of the polyimides. The nitro group substituted at the ortho position of the benzene ring greatly enhanced the photodegradation of the polymer chains. This is because the decomposition included not only the breaking of the N−O bond but also the fast cleavage of the O−R bond starting with the abstraction of a benzylic hydrogen atom by a nitro group oxygen. Furthermore, it was also observed that the polyimides containing a bulky trifluoromethyl substituent or a polyalicyclic structure displayed much higher photosensitivity, for example, 95 and 85 mJ/cm^2 for 6FDA−**5a** and BHTCA−**5a** films.

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