

Photodecomposition of Polyimides Derived from 2-Nitro-*p*-xylyleneoxyamine

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Introduction

Photosensitive polyimides are widely utilized in microelectronics field. In recent years, positive working polyimides are more attractive since 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.

This paper describes the preparation and decomposition of the main-chain photodegradative polyimides which exhibited positive working image upon light irradiation. The polyimides were obtained from the diamines of 2-nitro-*p*-xylyleneoxyamine (**5a**) or *p*-xylyleneoxyamine (**5b**), and various tetracarboxylic dianhydrides. Additionally, much higher photosensitivity was attained when the polyimide was composed of **5a** and a dianhydride containing either bulky trifluoromethyl (-CF₃) substituent or polyalicyclic structure moiety.

Experimental

Materials. The polyalicyclic dianhydride, bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (BHTCA), was synthesized according to our previously reported procedure.¹ The aromatic dianhydrides such as 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and 4,4'-oxydiphthalic anhydride (ODPA) were used after vacuum drying at 130 °C for 5 hr, while 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was of reagent grade and was used without further purification. *N,N*-Dimethylacetamide (DMAc) was dried with over CaH₂ and then fractionally distilled under reduced pressure and stored over 4 Å molecular sieves. Other solvents and reagents were obtained from commercial sources and used as received.

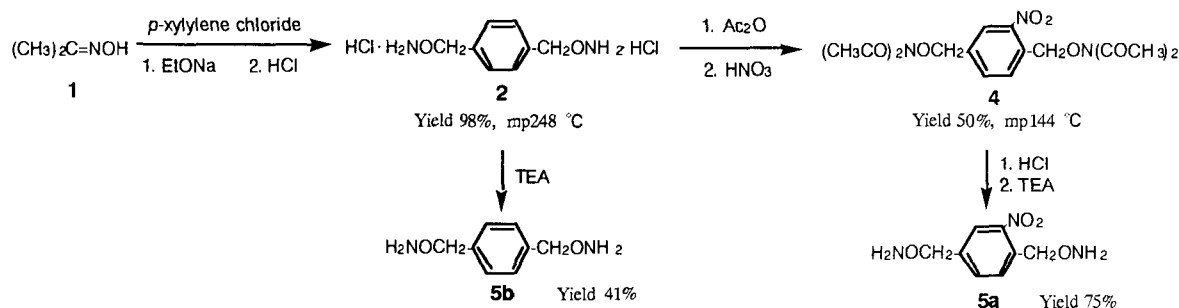
Measurements. Infrared spectra were obtained using a JASCO VALOR-III Fourier transform infrared spectrometer. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX 400WB spectrometer operating at 400 and 100 MHz, respectively. Elemental analysis was carried out by Shonan Analysis Center (Yokohama). Inherent viscosity was measured with an Ostwald viscometer in DMAc solution at concentration of 0.5 g/dL at 30 °C. The film thickness was determined with a Dektak ³ST Surface Profiler (Veeco Sloan Technology Co.).

Synthesis of Diamine 5a and 5b. The diamines **5a** and **5b** were prepared according to the route illustrated in Scheme 1. The diamine **5a** is a yellow liquid: IR (neat) 3317, 3245, 1589, 1529, 1346 cm⁻¹; ¹H NMR (CDCl₃) δ 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, bs, NH₂), 5.06(2H, s, CH₂ (attached to C-4)), 4.74(2H, s, CH₂ (attached to C-1)); ¹³C NMR (CDCl₃) δ 148.1(C-2),

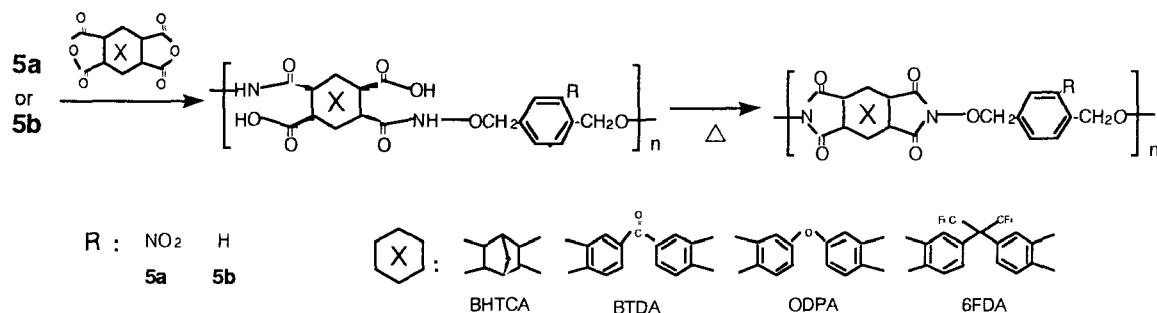
138.9(C-4), 133.6(C-1), 132.9(C-5), 129.4(C-6), 124.3(C-3), 76.2(CH₂, C-1 side), 74.2(CH₂, C-4 side). Anal. Calcd for C₈H₁₁O₄N₃: C, 45.06; H, 5.21; N, 19.71. Found: C, 45.20; H, 5.17; N, 19.50. The diamine **5b** is a white solid: mp 52-53 °C; IR (KBr) 3310, 3248, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 7.36(4H, s, Ph), 5.40(4H, bs, NH₂), 4.69(4H, s, CH₂); ¹³C NMR (CDCl₃) δ 137.42(C-1), 128.69(C-2), 77.84(CH₂).

Polymerization. In a three-necked flask were placed a dianhydride (2 mmol), DMAc (6 mL) and diamine (2 mmol). The mixture was stirred for 2 days at ambient temperature under nitrogen. The resulting viscous solution was poured into H₂O and the precipitate formed was dried in vacuum for 12 h at 30 °C and 6 h at 80 °C. A yield of 70-85% was achieved. The polyimide film was prepared from the poly(amic acid) solution by cast on a cover glass followed by heating *in vacuo* at 50 °C for 1 h, then at 80 °C and 170 °C for 2 h, respectively.

Film Photolysis. The polyimide film spin-cast on a cover glass or a silicon wafer was irradiated with a 500 watt Xenon lamp. Intensity on the exposed surface was 1.5 mW/cm² in the range of 240-270 nm. The exposed film was developed for 4 minutes in the 2:3 mixed solvent of 2-butanone and isopropanol, or was directly observed with IR spectroscopy.



Scheme 1



Scheme 2

Results and Discussion

The polymerizations of **5a** and **5b** with four kinds of dianhydrides were carried out as described in Scheme 2, and IR spectra of the resulting polyimides confirmed the complete imidization. All the polyimides were soluble in polar aprotic solvents such as DMAc, and especially BHTCA-**5a** and 6FDA-**5a** showed higher solubility than others.² Properties of the polymers prepared here are partially listed in Table 1.

The photochemical degradation of poly(amic acid)s from BHTCA-**5a** and BHTCA-**5b** was investigated in DMAc solution. The polymer solution was placed in a quartz cell, then exposed with a Xe lamp at specified time intervals and transferred into a viscometer for determination. The viscosity decrease with irradiation time for both polymers was readily apparent, but the decrease slope of the former was greater than that of the latter. This result suggests that the nitro group substituted at benzene ring enhanced the decomposability of the poly(amic acid).

In Figure 1 are shown the characteristic curves of polyimides from **5a** and **5b**, which present positive working photoresists. Their photosensitivity values are also summarized in Table 1. It is noted that the polyimides from **5a** were at least 1-2 order of magnitude more sensitive than those from **5b** for utilization of the same dianhydride.

Furthermore, there was a much larger difference in sensitivities even though the polyimides were composed of the same diamine. Much higher sensitivity compared to other polyimides was observed in polyimides such as 6FDA-**5a** and BHTCA-**5a**, which contained either a bulky trifluoromethyl (-CF₃) substituent or a polycyclic structure along the polymer backbone. It has been known that the introduction of a bulky substituent or a polycyclic structure into the

Table 1. Properties of Polymers

diamine	dianhydride	η_{inh}^a , dL/g	T_d^b , °C	Sensitivity, mJ/cm ²
5a	BHTCA	0.39	283	85
5a	BTDA	0.67	279	1.0×10^3
5a	ODPA	0.47	273	1.9×10^3
5a	6FDA	0.37	270	95
5b	BHTCA	0.34	288	1.7×10^3
5b	BTDA	0.89	289	$> 1.0 \times 10^4$
5b	ODPA	0.80	278	$> 1.0 \times 10^4$

^a Poly(amic acid)s; ^b Decomposition temperature measured by TGA at a heating rate of 10 °C/min in N₂

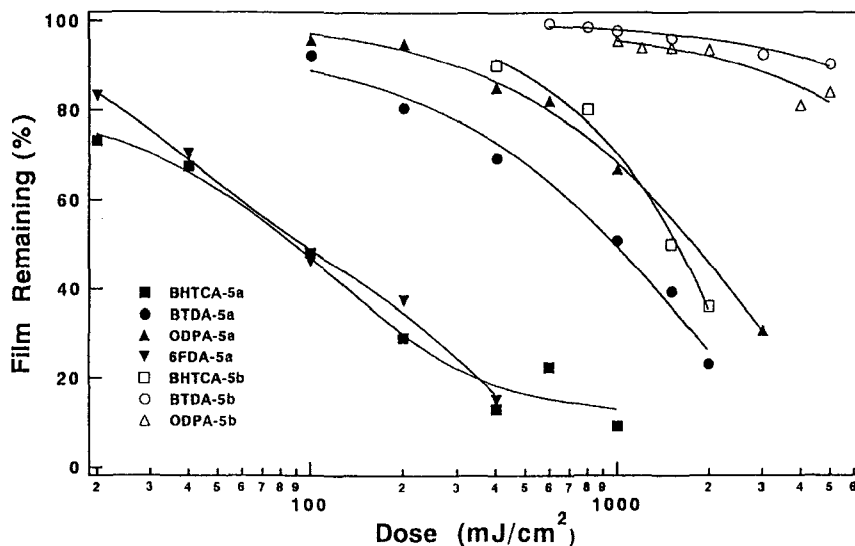
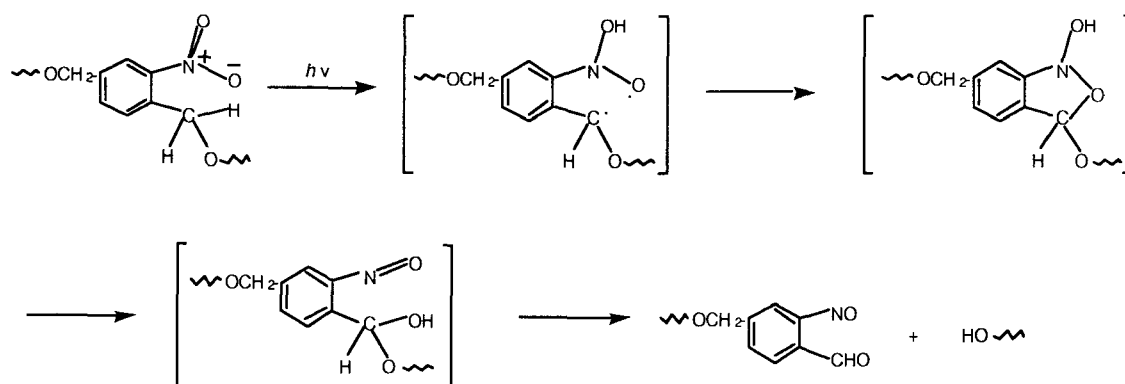


Figure 1. Characteristic curves for polyimides exposed to the light from Xe lamp

polyimides may inhibit polymer-polymer interaction by enlarging the distances between polymer chains and lead to an increase in solubility.³⁻⁴ Because the sensitivity obtained from the characteristic curve is expressed by the solubility of the segments which results from the photodecomposition of the polymer chains, the difference in photosensitivity of the polyimides comes from the different solubility of their segments. The segments containing a bulky substituent or a polyalicyclic structure moiety have greater solubility in development solvent, so that their polyimides exhibit higher sensitivities.

The area decrease of NO₂ group peaks at 1533 and 1350 cm⁻¹ in FTIR was observed in all of the studied polyimides from **5a** during irradiation. At the same time, new vibrational absorptions such as a hydroxy stretching band at 3240 cm⁻¹ and an aldehyde carbonyl stretching band at 1732 cm⁻¹ appeared in the spectra. The evidence for the formation of aldehyde and alcohol was also obtained from the ¹H NMR spectrum of a model compound **4** (shown in Scheme 1) after irradiation.

Thus, a primary mechanism for the decomposition 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 with *o*-nitrosobenzaldehyde and alcohol as terminal group, which might be soluble in the developer if their molecular weight were low enough.



In addition to the mechanism shown in Scheme 3, it is believed that one of other processes leading to the main chain scission included the cleavage of N-O bond on the backbone, though its decomposition rate was relatively low.

Reference

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