Fluorine-Containing Photoreactive Polyimides. 7. Photochemical Reaction of Pendant 1,2-Naphthoquinone Diazide Moieties in Novel Photoreactive Polyimides[1]

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ABSTRACT: Novel photoreactive polyimides with 1,2-naphthoquinone diazide (NQD) groups in the side chain were synthesized by esterification of the hydrophilic polyimide, which had been prepared by the polycondensation of a fluorinated acid dianhydride and diamine with various amounts of NQD. These polyimides showed unique lithographic behavior. Either positive behavior was observed with an aqueous base developer or negative behavior could be achieved with an organic solvent developer, depending on the content of NQD. The reaction leading to the negative-working mode resulted from the low content of absorbed water in the hydrophobic fluorinated polyimide film. The cross-linking reactions leading to insolubility were a coupling reaction of the ketene and the reaction of a ketocarbene and a ketene, which are unstable intermediates in the photochemical reaction of NQD. It was further found by the study of water diffusion in the fluorinated polyimide film that the time needed to reach equilibrium with the surrounding atmosphere is shorter than 1.3 s for a dry 5-μm-thick film of the fluorinated polyimides.

Introduction

1,2-Naphthoquinone diazide (NQD) derivatives are familiar and important compounds in the field of photolithography for the formation of positive images[2] in combination with novolac resins. The mechanism providing positive images is based on the photochemical conversion of hydrophobic NQD to hydrophilic indenecarboxylic acid via ketocarbene and ketene intermediates.[3-5] On the other hand, several process variations enable us to reverse the tone of the image to create negative images.[6] The complexity of NQD's photochemical reaction offers a variety of applications.

Polyimides are an important class of high-performance polymers. The qualities of a high thermal stability and a low dielectric constant are especially desirable in the manufacturing of semiconductors. However, the process for multilayer fabrication using conventional polyimides is complicated. Recently, photoreactive polyimides have been attracting considerable technical interest, particularly in simplifying semiconductor fabrication. In previous research we have reported fluorine-containing polyimide precursors that are more easily processed because of their optical transparency and solubility in common organic solvents.[7,8] However, most photoreactive polyimides and their precursors reported so far are negative-working, and the number of reports on positive-working polyimides and their precursors, which become soluble on exposure to light, is very limited.

This article describes the preparation of novel photoreactive polyimides carrying the hydrophobic fluorinated group and NQD in their structures. The photochemical reactions and the mechanisms leading to the negative or positive-working mode, depending on the content of NQD, are also investigated and discussed. Finally, diffusion of water molecules in the fluorinated polyimides is studied.

Experimental Section

Materials. Organic solvents used in this study were obtained from Wako Pure Chemical Industries, Ltd., and dried with molecular sieves prior to use. 5,5′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzofurandione (6FDA) was obtained from American Hoechst Co., while 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (AHHFP) and 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane (AMHFP) were obtained from Central Glass Co., Ltd. These materials were dried overnight at 40 °C under reduced pressure prior to polymerization. 5-(Chlorosulfonyl)-1,2-naphthoquinone diazide was supplied by Toyo Gosei Kogyo Co., Ltd. Poly(*p*-hydroxystyrene) ($\bar{M}_n = 4000$, $\bar{M}_w = 7500$) was obtained from Maruzen Petrochemical Co., Ltd., and esterified by NQD without purification.

Measurement. IR spectra were measured on a Hitachi infrared spectrometer (Model 260-10). UV spectra of the films were recorded on a Hitachi spectrometer (Model 200-20). NMR spectra were recorded in deuteriochloroform on a JEOL GSX-400 spectrometer. Molecular weights of the polymers were determined on a TOSO HLC-802UR gel permeation chromatograph (GPC) with a TSK-GEL H-type column (styrene gel column) at 40 °C in tetrahydrofuran using styrene as a standard. Peak intensity was measured by a refractometer. Field desorption mass spectra (FDMS) were measured by a double-focus Hitachi M-80A mass spectrometer. A Nikon surface finish microscope was used to measure film thickness. The water content of the film was measured by an AQ-5 Hiranuma Aquacounter using the Karl Fischer reagent. Thermogravimetry (Du Pont 951) was used to measure the diffusion constants of water molecules in the film.

Exposure Apparatus. Polyimide films were exposed to 365-nm light with a filtered superhigh-pressure mercury lamp (250 W) in an exposure apparatus with a quartz window and an exhaust pipe (Figure 1).

Synthesis of the Polyimide with NQD. The polyimide (6FDA-AHHFP), which was soluble not only in alcohol but also in an alkaline aqueous solution, was prepared by polycondensation of 10 g of 6FDA and 8.24 g of AHHFP in 73 g of *N*-methyl-2-pyrrolidone (NMP) at room temperature for 12 h to prepare the poly(amic acid). *m*-Xylene (24 g) was added to the poly(amic acid) solution, which was then thermally cyclized at 150 °C for 1.5 h. During this step, the water released by the ring-closure reaction was separated as a *m*-xylene azeotrope. After the reaction was complete, 6FDA-AHHFP was precipitated from the NMP solution with water and dried at 40 °C in vacuo overnight. The weight-average and number-average molecular weights of synthesized 6FDA-AHHFP were determined as 34 000 and 17 600 from GPC, respectively.

6FDA-AHHFP (3 g) was dissolved in 27 g of diethylene glycol dimethyl ether (diglyme) and reacted with various concentrations of 5-(chlorosulfonyl)-1,2-naphthoquinone diazide (NQDC) in the presence of equimolar triethylamine at room temperature for 24

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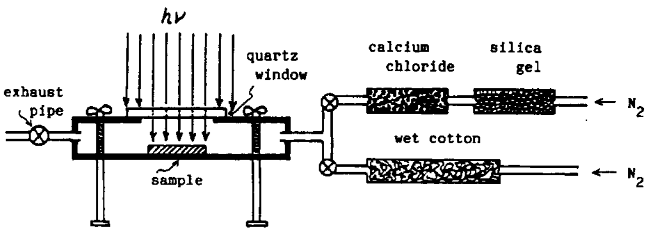
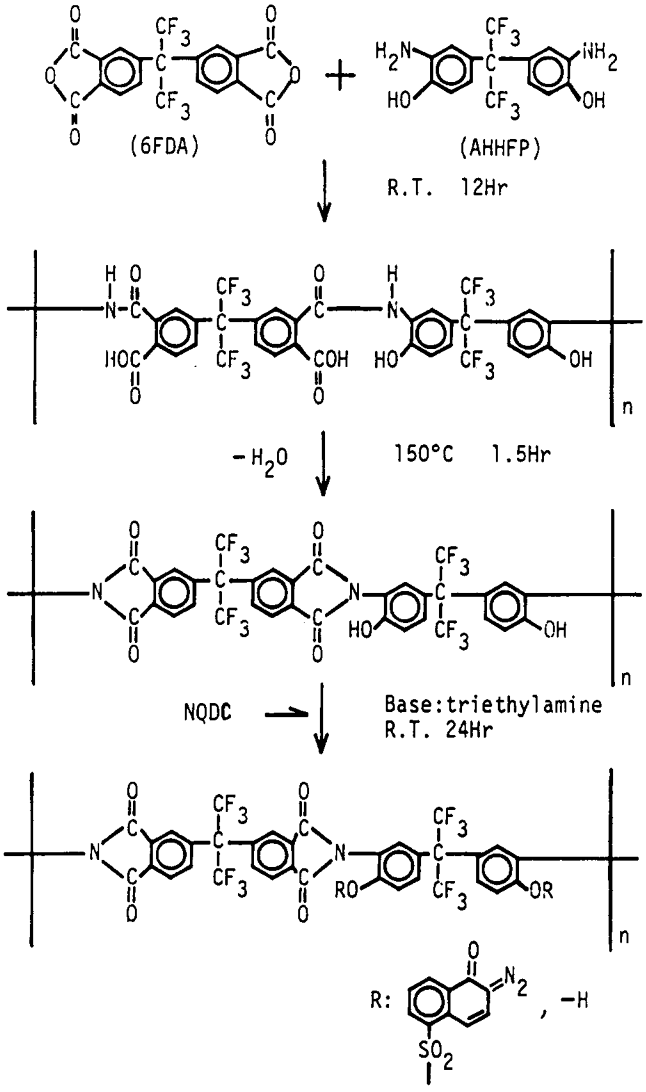


Figure 1. Exposure apparatus with a quartz window and an exhaust pipe.

Scheme I
Synthesis Scheme of the Fluorinated Polyimides with Various Amounts of NQD



h. After filtration to remove the triethylamine salt, polyimides with varying amounts of NQD in the side chain were precipitated from the solution with water, methyl alcohol, or mixed methyl alcohol/water solution (1:1 volume ratio). IR ν(OH) at 3700–2500 cm^{-1}, ν(N═N) at 2115 cm^{-1}, imide ν(C═O) at 1790 and 1740 cm^{-1}, imide ν(C–N) at 1370 cm^{-1}. Anal. Calcd for $C_{54}H_{22}N_6O_{12}S_2F_{12}$: C, 52.34; H, 1.79; N, 6.79. Found: C, 52.12; H, 1.76; N, 6.83.

Table I
Dissolution Rates and Concentrations of H_2O of the Fluorinated Polyimides with Various Amounts of NQD

concn of NQD, %	dissoln rate, μm/s × 10^3 exp	dissoln rate, μm/s × 10^3 unexp	conc of H_2O, g/mL × 10^2
0			2.90
3	2.80	1.60	2.38
4	2.30	0.84	
7	2.00	0.46	
9	1.30	0.24	
15	0.56	0.11	
32	0	0	1.50
73	0	0	1.17
100	0	0	0.70

Synthesis of Poly[5-((*p*-vinylphenoxy)sulfonyl)-1,2-naphthoquinone diazide]. Esterification of poly(*p*-hydroxystyrene) by NQD was carried out in diglyme at room temperature with triethylamine as the catalyst. A solution of 5 g of poly(*p*-hydroxystyrene) and 16.76 g of NQDC in 195.77 g of diglyme was mechanically stirred for 30 min. Triethylamine (6.31 g) was added to this solution dropwise, and the reaction mixture was further stirred overnight at room temperature. After filtration to separate the triethylamine ((*p*-vinylphenoxy)sulfonyl)-1,2-naphthoquinone diazide] was precipitated from the solution with methyl alcohol. IR: ν(C–H) at 2950 cm^{-1}, ν(N═N) at 2115 cm^{-1}, ν(S═O) at 1375 cm^{-1}. Anal. Calcd for $C_{18}H_{13}N_2O_4S$: C, 61.18; H, 3.71; N, 7.93. Found: C, 61.28; H, 3.61; N, 7.78.

Synthesis of 2-Diazo-5-(phenoxysulfonyl)-1-oxo-1,2-dihydronaphthalene (DPOD). Triethylamine (1.62 g) was slowly added to a solution of 4.26 g of NQDC and 1.08 g of phenol in 47.42 g of tetrahydrofuran. After 12 h of stirring at room temperature followed by filtration to remove the triethylamine salt, the reaction mixture was poured into water. Finally, DPOD was concentrated by purification using a silica gel column (Wako Pure Chemical Industries, Ltd., C-300) with methylene chloride. IR ν(N═N) at 2125 cm^{-1}, ν(S═O) at 1376 cm^{-1}; ^{1}H NMR δ 6.93 (m, 2 H, 2,6-H of phenol), 7.46 (t, 1 H, 7-H of naphthoquinone diazide), 7.56 (q, 1 H, 4-H of naphthoquinone diazide), 8.14 (q, 1 H, 8-H of naphthoquinone diazide), 8.65 (m, 1 H, 6-H of naphthoquinone diazide), FDMS m/z = 326.

Determination of NQD Concentration. The concentration of NQD in each polyimide was determined by the absorption ratio of 2115 cm^{-1} (ν(N═N)) versus 1790 cm^{-1} (imide ν(C═O) in the infrared spectrum.

Separation of Photoreaction Products. Equimolar quantities of 2-diazo-5-(phenoxysulfonyl)-1-oxo-1,2-dihydronaphthalene (DPOD) to the methyl and hydroxyl groups in the diamine segments of 6FDA-AMHFP and 6FDA-AHHFP were incorporated in the films. The 6FDA-AMHFP film with DPOD was dried at 45 °C for 1 h under reduced pressure in order to prepare an almost waterless reaction field and then exposed to light. At the same time, the 6FDA-AHHFP film with DPOD was held under wet nitrogen for 15 min to prepare an extremely wet reaction field and then exposed to light. These exposed films were dissolved in tetrahydrofuran, and then the solution was poured into methyl alcohol and chloroform for the 6FDA-AMHFP and 6FDA-AHHFP systems, respectively. Evaporation, followed by filtration to separate the unreacted polyimide reaction field, yielded the photoreaction products of DPOD. The photoreaction products were separated on silica gel thin-layer chromatography (TLC) plates (Art. 5554 DC-Alufoligen Kieselgel 60 F254, Merck) using chloroform–hexane (1:1 volume ratio).

Results and Discussion

Change of the Solubilities by Exposure to Light. Polyimides containing NQD moieties were prepared in three steps, starting with the condensation of the dianhydride (6FDA) and the diamine (AHHFP). The next step was the thermal cyclization of the poly(amic acid) according to the method described in the Experimental Section. In the last step, the polymer, 6FDA-AHHFP, was reacted with various amounts of 1,2-naphthoquinone diazide (NQD), resulting in polyimides with various amounts of 1,2-naphthoquinone diazide in the side chain.

Dissolution rates of the exposed and unexposed 1-μm films of each polyimide in a 0.5 wt % aqueous solution of tetramethylammonium hydroxide were then measured (Table I). The exposure energy required for the complete disappearance of the 2115-cm^{-1} (ν(N═N)) IR absorption peak for the polyimide with 100 mol % NQD (PI-100) was given to each polyimide film. The dissolution rates of the

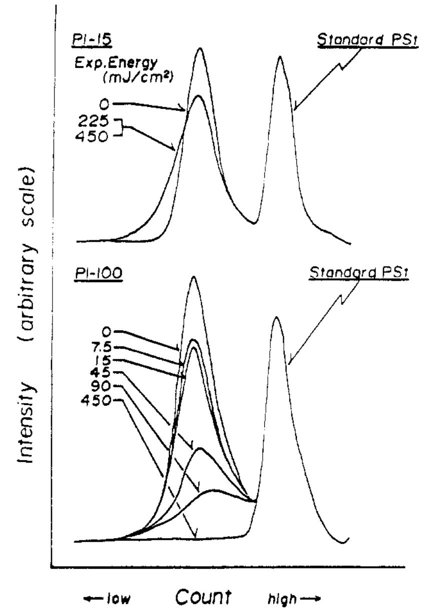


Figure 2. GPC spectra of PI-15 and PI-100 exposed under several energies at 365-nm wavelength.

exposed films were faster than those of the unexposed films in the case of 6FDA-AHHFP with <15 mol % NQD; i.e., in this range of NQD concentration, the polyimides behave as a positive type in an alkaline aqueous solution. On the other hand, 6FDA-AHHFPs with >32 mol % NQD show no enhanced solubility on exposure and behave as a negative type in organic solvents. This phenomenon is unique, and a similar one has not been reported so far. It is therefore interesting to investigate the reason for fluorinated polyimides showing dual-mode lithographic behavior that only depends on the concentration of the NQD.

Interpolymer cross-linking is a possible mechanism for this insolubility. The molecular weights and polydispersities of the polyimides with 15 mol % NQD (PI-15) and 100 mol % NQD (PI-100) before and after exposure were measured by GPC. The GPC spectra are shown in Figure 2. The shape of the PI-15 peak tended to broaden toward the lower count under increased exposure energy. However, the area percent for PI-15 versus internal standard polystyrene was entirely unchanged. This result shows that NQD in PI-15 photodecomposed to indenecarboxylic acid, and the broadening of the peak is attributed merely to changes in the interaction between the polyimide and polystyrene gel due to polarity changes. In the case of PI-100, the shape of the peak changed only slightly and the area percent of the peak decreased under increased exposure energy because of the removal of gel components by filtration before the GPC measurement. Moreover, the removed gel components were insoluble in any kind of organic solvent. From these results, it is suggested that the negative-working mode of PI-100 is due to an interpolymer cross-linking reaction by NQD.

Concentration Dependence of NQD Moieties on the Cross-Linking Reaction. To investigate the effect of the polymer's NQD concentration on the interpolymer cross-linking reaction, poly[5-((*p*-vinylphenoxy)sulfonyl)-1,2-naphthoquinone diazide], whose NQD moieties might be sufficiently close to interact with one another, was synthesized, and its film solubility was evaluated after exposure to light. The polymer solution in diglyme was spun onto a silicon wafer and then dried at 80 °C for 30 min to form a photosensitive 1-μm-thick layer. The film was soluble in the aqueous base and organic solvent developers even after 5-min exposure to light (this exposure energy was sufficient to decompose the NQD moieties completely), in contrast to the insoluble characteristic of the exposed PI-100 film. It was therefore confirmed that the concentration of NQD moieties in the film (as the distance between NQD moieties) was not directly related to the cross-linking reaction.

Influence of Moisture in the Film. Polyimide PI-20, having a 20 mol % NQD concentration falling between those of the positive-working PI-15 and the negative-working PI-32, was dissolved in diglyme previously dried with molecular sieves. The solution was spin-coated onto a silicon substrate and dried at 80 °C for 30 min. The films were set in an apparatus with a quartz window and an exhaust pipe (Figure 1) and then exposed to light under dry or wet nitrogen. The films exposed to light under dry nitrogen were insoluble in aqueous developers, while those exposed under wet nitrogen were soluble. From this result, it is recognized that the photochemical reaction of PI-20 clearly depends on atmospheric moisture content and that water plays an important role in the photochemical reaction of the NQD moieties.

The water contents of the fluorinated polyimide films, which had different concentrations of NQD moieties in their side chains, were quantitatively analyzed by an Aquacounter using the Karl Fischer reagent. The films were kept in a 25 °C atmosphere with 60% humidity for 12 h before measurement. Table I shows the relationship between the water and the NQD contents in the films. This result clearly indicates that the films containing less NQD (more hydroxyl groups) have higher concentrations of water.

Identification of Photo-Cross-Linking Structure. Several photoreaction mechanisms of NQD to achieve the negative-working mode have been reported.[6,9] In these mechanisms, unreacted NQD participates in the reaction with the products or the transient species formed by the photoconversion of NQD. Examples of such mechanisms are the formation of lactone rings[10] and azo compounds[6] (Scheme II). If NQD's photochemical reaction in PI-100 also undergoes the reaction mechanism the unreacted NQD is subjected to, the quantum yield of NQD photochemical conversion for PI-100 will become larger than that for PI-15.

The photochemical conversion of NQD is expressed by the kinetic scheme of eqs 1–3. According to this scheme, the rate of conversion of NQD should follow eq 4, and the plot of the term on the left-hand side against exposure time should follow a straight line. The slope of the straight line gives the quantum yield of NQD photochemical conversion after being calibrated with ϵ, l, I_0.

$$\mathrm{NQD} \xrightarrow{h\nu} \mathrm{NQD}^* \tag{1}$$

$$\mathrm{NQD}^* \xrightarrow{k_1} \text{ketocarbene} \tag{2}$$

$$\mathrm{NQD}^* \xrightarrow{k_2} \mathrm{NQD} \tag{3}$$

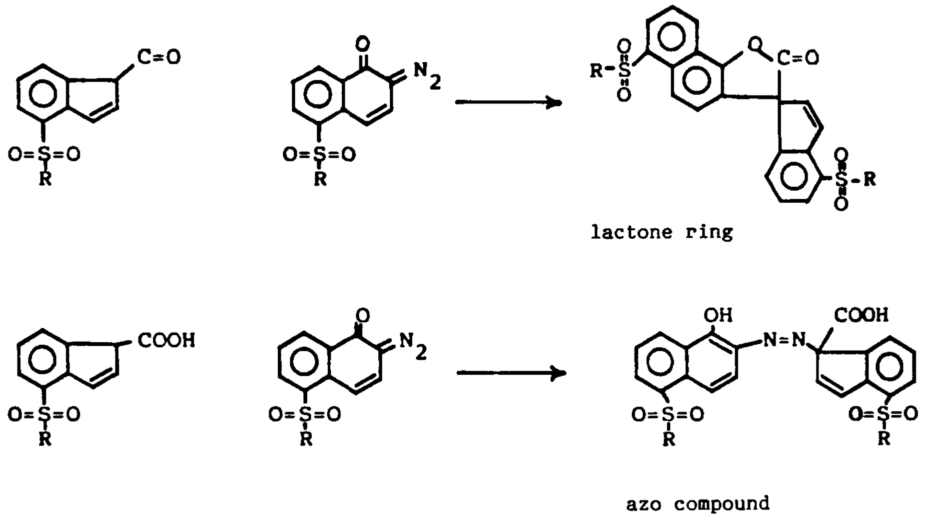
Under steady-state conditions

$$\mathrm{d}[\mathrm{NQD}^*]/\mathrm{d}t = I_0[1 - \exp(-2.303\epsilon[\mathrm{NQD}]l)] - k_1[\mathrm{NQD}^*] - k_2[\mathrm{NQD}^*] = 0$$

$$[\mathrm{NQD}^*] = I_0[1 - \exp(-2.303\epsilon[\mathrm{NQD}]l)]/k_1 + k_2$$

$$-\mathrm{d}[\mathrm{NQD}]/\mathrm{d}t = k_1[\mathrm{NQD}^*] = I_0[1 - \exp(-2.303\epsilon[\mathrm{NQD}]l)]k_1/k_1 + k_2$$

Scheme II
Example of the Photoreaction Mechanism That Unreacted NQD Is Subjected To



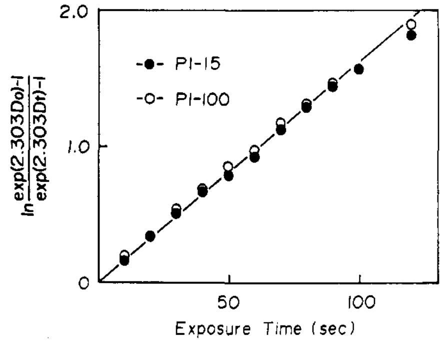


Figure 3. Plot of ln $[\exp(2.303D_0) - 1/\exp(2.303D_t) - 1]$ vs the exposure time at 365-nm wavelength for PI-15 and PI-100.

$$\int_{[NQD]_0}^{[NQD]_t} \{1/[1 - \exp(-2.303\epsilon[NQD]l)]\}\, d[NQD] = -\int_0^t (k_1 I_0/k_1 + k_2)\, dt$$

For the photodecomposition reaction

$$\ln [\exp(2.303\epsilon[NQD]_0 l - 1))/[\exp(2.303\epsilon[NQD]_t l - 1)] = (2.303\epsilon l k_1 I_0/k_1 + k_2)t \quad (4)$$

where $k_1/(k_1 + k_2)$ is the quantum yield for photodecomposition, k_1 and k_2 are the rate constants of decomposition and deactivation, ϵ is the molar extinction coefficient, [NQD] is the concentration of NQD, l is the path length of the film, and I_0 is the incident energy. NQD's photochemical conversion rates in PI-15 and PI-100 thin films (<1 μm) were measured by exposure to 365-nm monochromated light. As can be seen in Figure 3, these plots follow straight lines, indicating that these NQD photoconversions can be expressed by eq 4. Also, the two slopes were almost identical. Because ϵ, l, and I_0 are common to both polymers, the quantum yields for the photoconversion of NQD in the polymers were also identical. The unreacted NQD is not therefore involved in these cross-linking reactions. Moreover, the absorption band due to azo compounds was not observed for wavelengths longer than 500 nm in the PI-100 film's electronic spectrum, regardless of how the film was exposed to light. Consequently, the main reaction of PI-100 needed to form cross-linking is distinct from the cross-linking reactions shown above, where the unreacted NQD contributes to the cross-linking reaction.

To further study the photochemical reaction of NQD moieties in the fluorinated polyimides, thin-layer chromatography (TLC) and mass spectrometry were used to investigate the photoreaction products of DPOD in hydrophilic 6FDA-AHHFP films and hydrophobic 6FDA-AMHFP films that substituted methyl groups for 6FDA-AHHFP's hydroxyl groups. This is considered a model reaction for the fluorinated polyimide with NQD side-chain moieties. The photoreaction products of DPOD in the two kinds of reaction fields were located on silica gel TLC plates (Figure 4). The silica gel TLC of the products in the nearly dry reaction field indicates three pale yellow major products (components X_1, X_2, and X_3), which are not detected under wet conditions.

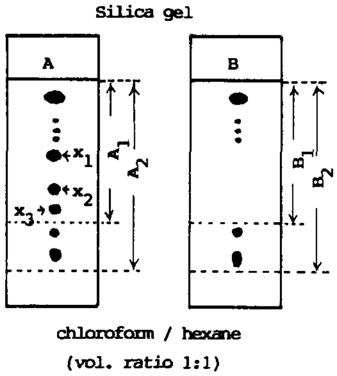


Figure 4. TLC of photoreaction products of DPOD: (A) in a nearly waterless reaction field; (B) in a wet reaction field.

The products were also characterized by field desorption mass spectroscopy (FDMS). Figure 5 shows the mass spectra of the reaction products indicated in areas A_1, A_2, B_1, and B_2 on the silica gel TLC (see Figure 4). A strong peak (mass $[m/z] = 596$) due to the reaction product was detected by FDMS of area A_1, while only insignificant peaks were detected in the large region beyond $m/z = 100$ in area B_1. On the other hand, the stronger peak at $m/z = 316$, assigned to 3-indenecarboxylic acid, was detected in the FDMS of area B_2, compared to the peaks at $m/z = 316$ and 596 in the FDMS of area A_2.

Despite confirmation of the three major products (X_1, X_2, and X_3) in area A_1 on TLC (Figure 4), only the major peak at $m/z = 596$ was detected in the mass spectrum of this area (Figure 5). The main photoreaction products of DPOD, formed in comparatively dry conditions, are therefore three kinds of isomers ($m/z = 596$) and 3-indenecarboxylic acid. Furthermore, the three isomers must participate in the cross-linking reaction.

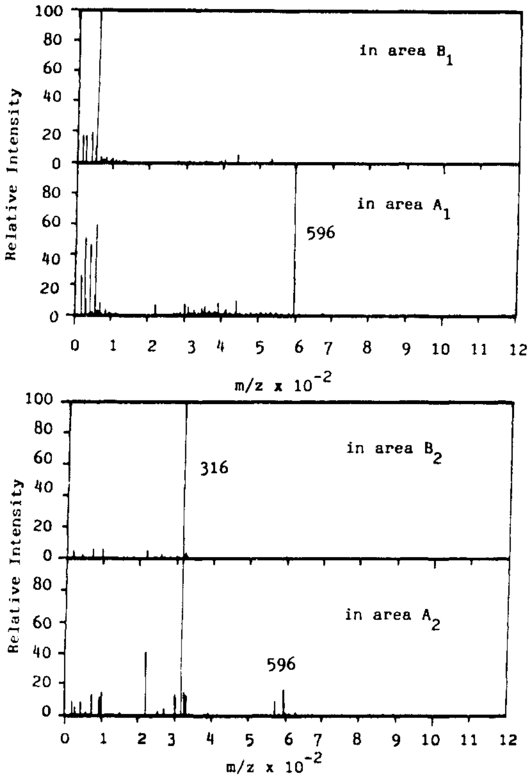


Figure 5. Field desorption mass spectra of the reaction products indicated in the areas A_1, A_2, B_1, and B_2 of the silica gel TLC in Figure 4.

Yates et al.[11] reported that 1,3-dioxole was obtained by the conversion of NQD in boiling xylene. Wiberg et al.[12] additionally reported the formation of butenolides during photolysis of NQD. Further, some ketenes are reported to undergo dimerization.[13] All of these reactions do not require the unreacted NQD. Furthermore, the peak at $m/z = 596$ from the mass spectra of the photoreaction products of DPOD agrees exactly with dioxole, butenolide, and ketene dimer. The reaction mechanisms of PI-15 and PI-100 can therefore be considered as those shown in Scheme III. In this reaction, the NQD in PI-15 that is exposed to light converts rapidly to a ketene intermediate via ketocarbene and then to 3-indenecarboxylic acid by reaction with a sufficient quantity of water that exists in the hydrophilic film having hydroxyl groups. PI-15 film becomes soluble in aqueous alkaline developer after exposure to light, due to its photoconversion to hydrophilic 3-indenecarboxylic acid from hydrophobic NQD. However, because little water is absorbed in the PI-100 film due to its hydrophobicity governed by the fluorine atoms, the ketene intermediate cannot convert to 3-indenecarboxylic acid, and cross-linking structures such as 1,3-dioxole, butenolide, and ketene dimer are formed in the film.

Water Diffusion in the Polyimide Films. The PI-15 film contains more water than the PI-100 film because it is more hydrophilic due to the presence of hydroxyl groups. Consequently, PI-15 converts smoothly to indenecarboxylic acid on exposure by having a sufficient amount of water. The conversion of NQD to indenecarboxylic acid allows PI-15 to be soluble in an aqueous alkaline solution. On the other hand, the hydrophobic propeity of the trifluoromethyl group in PI-100 is noteworthy because no hydroxyl group is present. Therefore, various ketenes in PI-100 transiently formed by exposure are not converted to indenecarboxylic acid by the lack of water but react through another mechanism to form a cross-linking such as those resulting from the reaction with ketocarbene and the coupling reaction.

It is important to investigate the diffusion of water, which plays a major role in determining the kind of NQD reaction on exposure in the polyimide film. This diffusion is interesting not only from the point of view of fundamentals but also from that of application.

Thermogravimetry (TGA) was used to measure the diffusion constants of water molecules at a temperature of 80 °C. Each 6FDA-AHHFP and PI-100 film was coated with the diglyme/polymer solution on a glass substrate and then dried in an oven at 80 °C for 30 min. The films were further dried at 40 °C in an oven under reduced pressure overnight and then exposed to a humid atmosphere (25 °C, humidity = 100%) for 24 h. The film thicknesses prepared for the measurement were 33 μm for 6FDA-AHHFP and 40 μm for PI-100.

If the step determining the rates of sorption and desorption of water vapor is the diffusion process in a polymer film, the Fick's diffusion law can be adapted to them. Fick's second law of diffusion (general diffusion equation) is expressed as

$$\mathrm{d}c/\mathrm{d}t = d/\mathrm{d}x(D\,\mathrm{d}c/\mathrm{d}x) \tag{5}$$

where c is the concentration of water in the film and D is the diffusion coefficient. When D is independent of concentration, this equation can be solved analytically to give an expression for the time dependence of the weight change during sorption and desorption. For the customary boundary conditions of instantaneous equilibration of a polymer surface with the surrounding vapor, the equation is

$$Q/Q_\mathrm{e} = 1 - 8/\pi^2\sum_{n=0}^{\infty}1/(2n+1)^2\exp\{-(2n+1)^2\pi^2Dt/l^2\} \tag{6}$$

where Q is the weight change at time t, Q_e is the equilibrium weight change, and l is the film thickness. Since the series involved in eq 6 converges rapidly, terms except $n = 0$ can be omitted. Consequently, eq 6 becomes

$$D\pi^2t/l^2 = \ln\,(Q_\mathrm{e}/Q_\mathrm{e} - Q) + \ln 8/\pi^2 \tag{7}$$

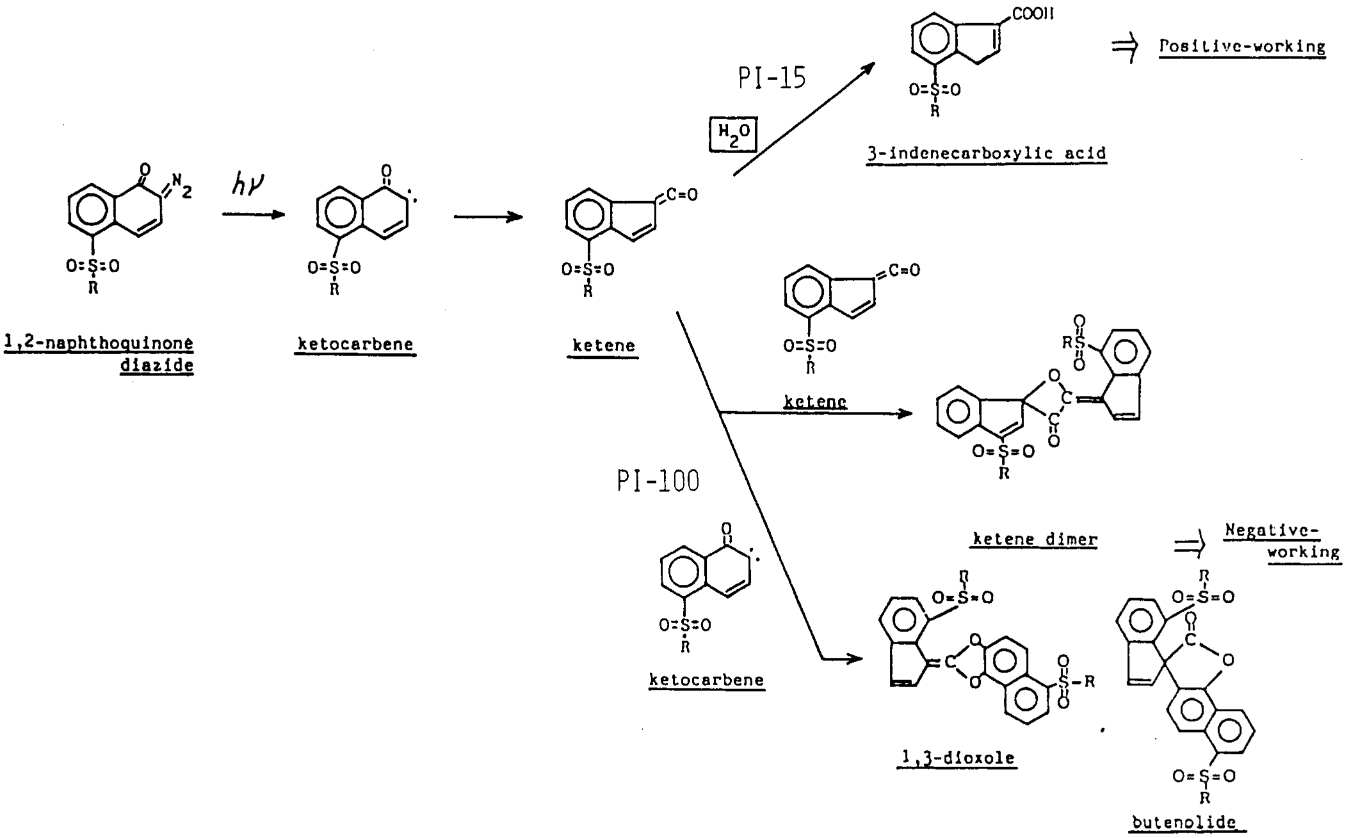
$$\mathrm{d}\log\,(Q_\mathrm{e} - Q)/\mathrm{d}t = (-\pi^2/2.3)D/l^2 \tag{8}$$

The D value can be determined by the slope of the plot between $\log\,(Q_\mathrm{e} - Q)$ and t when it is independent of concentration. Figure 6 shows the weight loss percent of 6FDA-AHHFP and PI-100 films, which were obtained from the TGA curves, due to desorption of water against time t. The curves indicate that the 6FDA-AHHFP film absorbs more water than the PI-100 film, a result similar to that obtained from the Aquacounter (Table I).

Figure 7 further shows plots of $\ln\,(Q_\mathrm{e} - Q)$ against time t. Since the plots are linear, the diffusion coefficient D of water vapor in the polyimide film is independent of concentration, and eq 8 accurately predicts this diffusion behavior. From the slope of the linear line, D values of 8.82×10^{-8} and 1.76×10^{-7} cm^2/s were determined for 6FDA-AHHFP and PI-100, respectively. These values are higher than that for novolac-based resin.[14] This result is assumed responsible for the increase in free volume due to the introduction of hexafluoropropyl groups and the nonsymmetrical m,m' linkage in the polymer backbone. This assumption adequately explains why these polyimides show high solubility and transparency.

Equation 5 and the D value obtained by the experimental result clearly explain the kinetics of drying of the thin polyimide films. The curves shown in Figure 8 represent the water desorption behavior in 6FDA-AHHFP and PI-100 films at 80 °C obtained by extra-

Scheme III
Photoreaction Scheme of PI-15 and PI-100 Films



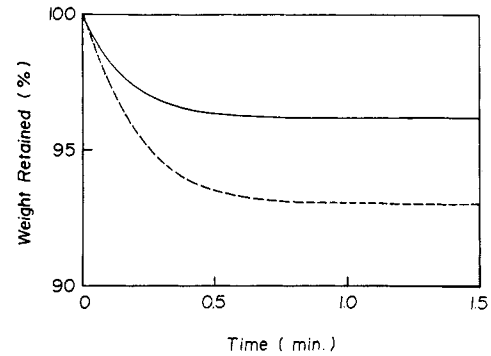


Figure 6. TGA curves of 6FDA-AHHFP and PI-100 films at 80 °C: (- - -) 6FDA-AHHFP; (—) PI-100.

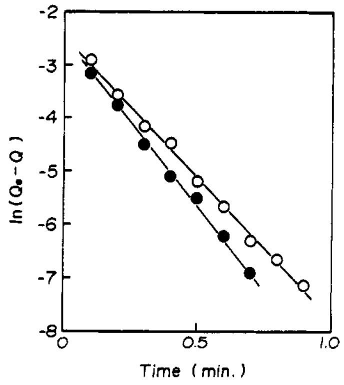


Figure 7. Plots of ln $(Q_e - Q)$ vs t for diffusion of water vapor in 6FDA-AHHFP and PI-100 films: (○) 6FDA-AHHFP; (●) PI-100.

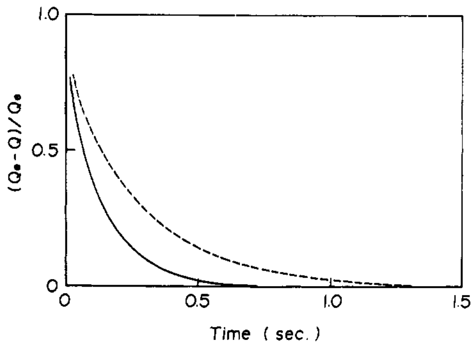


Figure 8. Water desorption behavior in 6FDA-AHHFP and PI-100 films at 80 °C by extrapolation to a 5-μm thickness: (- - -) 6FDA-AHHFP; (—) PI-100.

polating the 33- and 40-μm results to those for 5-μm thickness. From this result, the time required to dry the films at 80 °C was shorter than 1.3 s. The time required to recover humidity in the dry film is almost the same as that required to dry the wet film.[15]

To achieve a practical patterning process, the film dried by prebaking at 80 °C could absorb water as soon as it was taken out of the oven, and the water in it immediately reached equilibrium with the atmosphere. This fact is very helpful in understanding the photochemical reaction that always converts NQD to 3-indenecarboxylic acid in PI-15 film.

Summary

1. Novel soluble polyimides containing NQD in their side chains were synthesized.
2. These polyimides showed unique lithographic behavior: they were either positive-working with an aqueous base developer or negative-working with an organic solvent developer, depending on the content of NQD.
3. The films containing more NQD (fewer hydroxyl groups) show a lower content of water, and the hydrophobicity of these films may be due to their fluorinated structure.

4. The reaction leading to the negative-working mode must be due to the low content of absorbed water as well as the increased content of NQD in the fluorinated polyimide.

5. Compared with NQD's photochemical conversion in PI-15 to indenecarboxylic acid via ketocarbene and ketene intermediates, most ketenes in PI-100 transiently formed by exposure are not converted to indenecarboxylic acid through the absence of water but react with other ketenes or ketocarbene to form interpolymer cross-linking.

6. Diffusion behaviors of water molecules in the polyimide films for 80 °C. The films dried by prebaking could quickly reach equilibrium with the surrounding atmosphere.

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