Synthesis and Chemically Amplified Photo-Cross-Linking Reaction of a Polyimide Containing an Epoxy Group

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ABSTRACT: A new polyimide, PI(6FDA/ep-AHHFP), containing an epoxy group was synthesized by the reaction of epichlorohydrin with PI(6FDA/AHHFP), which was prepared from 4,4′-(1,1,1,3,3,3-hexafluoro-2-propylidene)diphthalic anhydride (6FDA) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (AHHFP) in the presence of benzyl(trimethyl)ammonium chloride at 110−120 °C. This polyimide having an epoxy group is highly soluble in most common solvents. Photochemical reactivity of PI(6FDA/ep-AHHFP) was examined in the presence of diphenyliodonium hexafluoroarsenate as an acid generator. The conversion and the curing rate were determined by the absorbance change in the IR band at 905 cm^{-1} for the epoxy group. The activation energy for cross-linking reaction of PI(6FDA/ep-AHHFP) was found to be ∼6 kJ/mol. The reaction radius of an acid in PI(6FDA/ep-AHHFP) containing diphenyliodonium hexafluoroarsenate as a photoacid generator was determined to be about 19−30 Å in the chemical amplification process when heated for 5−40 min at 50−195 °C. The quantum yield for cross-linking of PI(6FDA/ep-AHHFP), Φ_{gel}, obtained from the characteristic curve was 3.0. The sensitivity, D_{gel}, and contrast, γ, after postcure at 100 °C for 30 min were 4.8×10^{-10} einstein cm^{-2} and 5.7, respectively. The quantum yield for cross-linking, Φ_{GPC}, was determined to be 2.6 from gel permeation chromatography measurements.

Introduction

The use of polyimides as high-temperature insulators and dielectrics, coatings, adhesives, and matrices for high-performance composites is well-known. The studies of photosensitive polyimides have become important in recent years. Being insoluble in most common solvents, polyimides are usually processed in the form of their precursors, poly(amic acids), which are then thermally converted to the imide structure. Since polyimide precursors suffer from high shrinkage (∼50%) during curing, there is great interest in fully imidized photosensitive polyimides which offer lower shrinkage (<20%). Thus, soluble polyimides are of advantage to their precursors because they require no thermal curing for imidization and because they are capable of being applied to the manufacture of devices sensitive to heat. Therefore, photosensitive polyimides that are soluble in organic solvents are desirable.[1]

Photosensitive polyimides are very attractive since they can reduce the number of processing steps by eliminating several steps involving photoresists.[2−5] However, their sensitivities are still low.[6,7] One strategy for the improvement of the photoreactivity of photosensitive polyimides is utilization of long-lived active intermediates,[8] and the other strategy is elimination of a charge transfer. The polyimides prepared from aliphatic diamines are examples of the latter.[9] The chemical amplification concept is another useful technique for the design of highly sensitive resist systems with high resolution, which is based on the acid-catalyzed cross-linking, deprotection, and depolymerization reactions.[10,11] Incorporation of an epoxy group into a polyimide is expected to increase its photoreactivity by the chemical amplification mechanism.

In this article, preparation of a novel photosensitive polyimide system from PI(6FDA/AHHFP) and epichlorohydrin is reported and the mechanism of the photopolymerization of the epoxy group is discussed.

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Experimental Section

Materials. 4,4′-(1,1,1,3,3,3-Hexafluoro-2-propylidene)diphthalic anhydride (6FDA) was purified by recrystallization from distilled acetic anhydride and dried overnight at 150 °C under reduced pressure. 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (AHHFP) was purified by recrystallization from diethylene glycol dimethyl ether (diglyme) and dried at 50 °C under reduced pressure overnight before use. *N*-Methyl-2-pyrrolidone (NMP) and epichlorohydrin were distilled before use and stored over molecular sieves. Diphenyliodonium hexafluoroarsenate (DPI-AsF_6), benzyl(trimethyl)ammonium chloride (BTMA), and other materials were obtained from commercial sources and used without further purification.

Instrumentation. IR spectra were measured with a Jasco IR-700 spectrometer. NMR spectra were recorded with a JEOL GX-400 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. UV absorption spectra were measured on a Uvidec-660 spectrophotometer. Molecular weights were measured on a Jasco BIP-IV gel permeation chromatography (GPC) with a Shodex K-80M column in dichloromethane as an eluent.

Synthesis of Polyimide. PI(6FDA/AHHFP) was prepared as follows: 6FDA (4.4424 g, 0.01 mol) and AHHFP (3.6626 g, 0.01 mol) were mixed in 32 g of NMP at room temperature for 12 h to give a poly(amic acid), PAA(6FDA/AHHFP).[12] *m*-Xylene (10 g) was added to the poly(amic acid) solution, which was then thermally imidized at 160 °C for 2 h. During this step, the water released by the ring-closure reaction was separated as a *m*-xylene azeotrope. After the reaction was completed, the PI(6FDA/AHHFP) was precipitated from the NMP solution into water and dried at 60 °C in vacuo overnight. IR (film): 3400, 1780, 725 cm^{-1}.

Preparation of Polyimide Containing An Epoxy Group. PI(6FDA/AHHFP) (7.75 g, 0.01 mol) was dissolved in epichlorohydrin (139 g, 1.50 mol) and heated at 110−120 °C in a three-necked round-bottomed flask equipped with a stirring bar and a thermometer. Solid BTMA (0.37 g, 0.002 mol) was added in a batch, and the mixture was heated at reflux. The reaction was completed in about ∼1 h. Unreacted epichlorohydrin was removed by distillation at reduced pressure; the crude product was dissolved in tetrahydrofuran (THF) and reprecipitated into cold water. The synthetic route to PI(6FDA/ep-AHHFP) is shown in Scheme 1. The structure of PI(6FDA/ep-AHHFP) was identified by IR and NMR spectroscopies. IR (film): 1780, 725, 905 cm^{-1}. NMR ($CDCl_3$): δ

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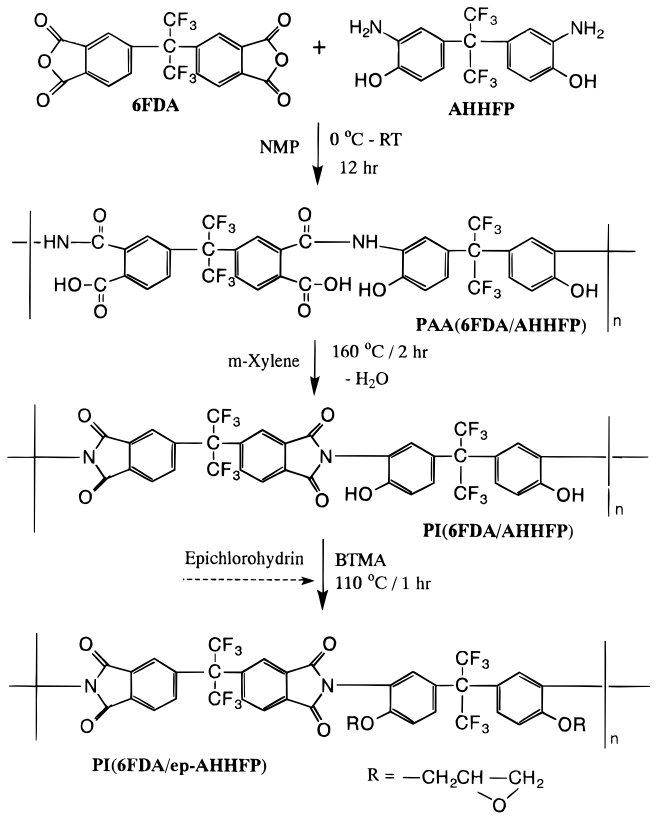
Scheme 1. Synthetic Route of PI(6FDA/ep-AHHFP)



7.0−8.0 (12H, Ar), 4.0−4.5 (4H, OCH_2), 3.2−3.3 (2H, CH_2CH), 2.5−3.0 (4H, CH_2 in epoxy ring) ppm.

Photoirradiation. Photoreaction was performed using a 450-W high-pressure Hg lamp and glass filters (Toshiba, UVD36A and UV-33). Actinometry was carried out with a photometer (Advantest, TQ8210). The incident light intensity was 2.02×10^{-9} einstein cm^{-2} s^{-1} for GPC experiments and 9.15×10^{-9} einstein cm^{-2} s^{-1} for film thickness and IR measurements.

Measurements of Photoreaction. A sample solution was prepared by dissolving PI(6FDA/ep-AHHFP) (1.0 g) and DPI-AsF_6 (0.05 g) in dichloroethane (10 mL), and the resultant mixture was filtered through 0.2 μm Teflon filter (Millipore Inc.). The films (~5 μm thick) were postbaked after exposure through filters at various temperatures. The reaction was monitored by the change in the absorption of epoxy group at 905 cm^{-1} in the IR spectra.

The films (~1 μm thick) for measurements of changes in film thickness were exposed through filters and postbaked for 30 min in an oven at 100 °C. The films were developed with cyclohexanone for 5 min and rinsed with isopropyl alcohol for 3 min. Film thickness was measured using a Talistep film thickness gauge (Rank Taylor Hobson, Inc.).

Films with an average coating weight of about ~1.2 mg were used for measurements of changes in molecular weight. The films were exposed through filters for given times and post-baked for 5 min at 100 °C. Changes in the molecular weight of PI(6FDA/ep-AHHFP) during the photoirradiation were measured with a GPC using dichloromethane as an eluent. Calibration for the molecular weights was carried out by using monodisperse polystyrene standards.

Results and Discussion

Synthesis of PI(6FDA/ep-AHHFP). Although there is extensive literature about glycidyl ether compounds, their reactions involving imide rings have been rarely reported. The reason is that the imide groups are susceptible to hydrolysis when sodium hydroxide is used as the base. It has been reported that glycidyl ether can be obtained directly if a quaternary ammonium halide is used as a phase transfer catalyst in a large excess of epichlorohydrin.[13−15] Therefore, we chose the synthetic route shown in Scheme 1. The obtained polymer can be dissolved in common solvents such as NMP, dimethylformamide, THF, and dichloromethane. In its IR spectrum, the absorption at 905 cm^{-1} can be assigned to the absorption of an epoxy ring and those at 1780 cm^{-1} 725 cm^{-1} to the imide moieties. Figure 1 shows the ^{1}H-NMR spectrum of the polyimide. The signals at 7.0−8.0 ppm are assigned to 12 aromatic protons, the signals at 4.0−4.5 ppm to four methylene protons attached to the oxygen of the ether linkage (H_a), the signals at 3.2−3.3 ppm to two protons attached to the asymmetric carbons of the epoxy rings (H_b), and the signals at 2.5−3.0 ppm to four protons attached to the epoxy ring (H_c). This spectrum shows good consistency with that of other epoxy compounds,[14,16] confirming the formation of PI(6FDA/ep-AHHFP). The integration shows that the content of the epoxy group is almost quantitative.

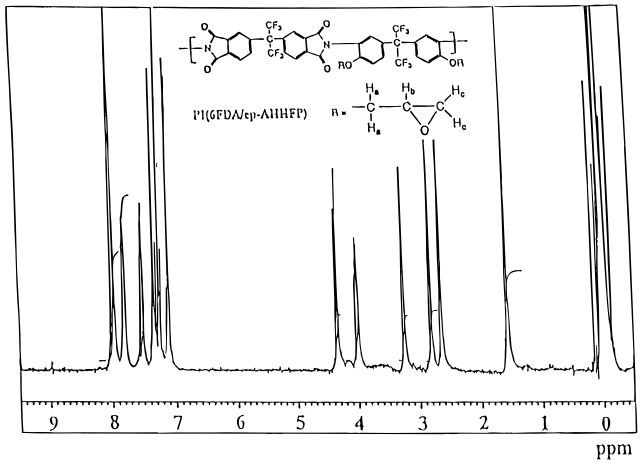


Figure 1. ^{1}H-NMR spectrum of PI(6FDA/ep-AHHFP).

Photoreaction. In order to determine the kinetics of the reaction during the postcure process, the rate of disappearance of the epoxide group during postcure was measured by IR.

Crivello and Lam[17] reported that diaryliodonium salts are one of the photoacid generators to polymerize epoxy groups. Although their absorption spectra show major bands at 200 and 240−250 nm, these compounds also possess some photosensitivity even at wavelengths as high as 365 nm. The quantum yield of acid generation from DPI-AsF_6 in a PI(6FDA/ep-AHHFP) matrix was determined by the use of the sodium salt of resorufin as an acid indicator. The absorbance at 590 nm (ϵ = 82 700 in dimethyl sulfoxide) was decreased by photoirradiation, indicating that the acid generated from DPI-AsF_6 reacted with the sodium salt of resorufin. The methodology developed is based on the observation by Mckean et al.[18] and Naitoh et al.[19] The quantum yield of acid generation from DPI-AsF_6 was determined to be ~0.10, which is about half of the value in solution reported by Crivello and Lam.[17,20,21] Figure 2 shows the UV absorption spectrum of a film composed of PI(6FDA/ep-AHHFP) and DPI-AsF_6. Optical density of the film is less than 0.3 above 330 nm, and the light below 330 nm was cut off by glass filters (UVD36A and UV-33) during photoirradiation in order that the film absorbed the light homogeneously. In this condition, the photoacid generator absorbs light independently from the matrix. The mechanism of the reaction of the epoxy groups catalyzed by the photochemically generated acid

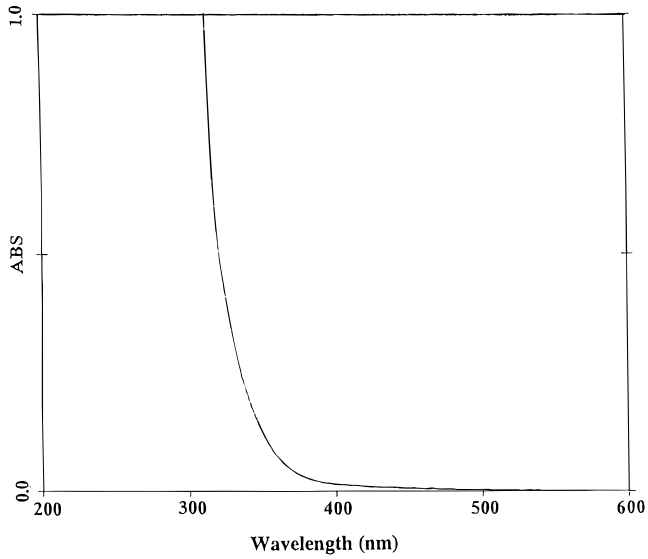
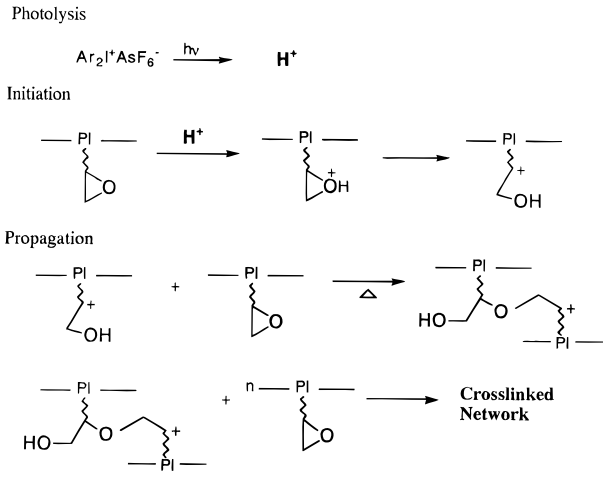


Figure 2. UV spectrum of a film composed of PI(6FDA/ep-AHHFP) and 5 wt % DPI-AsF_6.

Scheme 2. Mechanism of Photoreaction of PI(6FDA/ep-AHHFP)



is suggested in Scheme 2. Acids (H^+) liberated by photoirradiation carry out ring-opening polymerization during postcure.

Change in IR Absorption of the Epoxy Group. We studied the influence of concentration of the photoinitiator and the curing temperature on photochemical cross-linking by IR spectroscopy. Figure 3 shows the changes in the IR spectra of PI(6FDA/ep-AHHFP) before (a) and after (b) photoirradiation (1 h) followed by postcure (195 °C, 40 min). During the photoirradiation and the subsequent postcure, the absorbance at 905 cm^{-1} characteristic to the cyclic ether structure decreased, indicating acid-catalyzed ring opening.[22−25] An absorption band at 1510 cm^{-1} of the aromatic ring was chosen as an internal standard since its intensity is regarded as almost constant during the cross-linking reactions.

Figure 4 shows a decrease in the epoxy group concentration versus time during postcure at 100 °C for samples with various irradiation times (0−60 min). The films were irradiated with the incident light intensity of 9.15×10^{-9} einstein cm^{-2} s^{-1} and postbaked at 100 °C for given times. On postcure, the epoxy group reacted quickly in the first stage followed by a slower rate. Figure 4 shows that conversion reaches some saturation point at ~40 min of postcure. A considerable

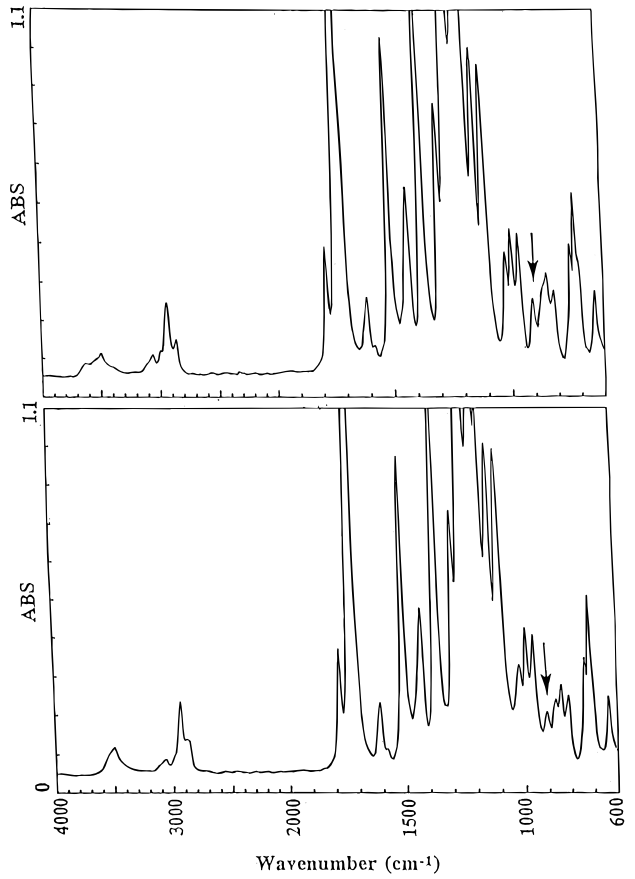


Figure 3. IR spectra of PI(6FDA/ep-AHHFP) (a, top) before and (b, bottom) after 1-h irradiation with postcure at 195 °C for 40 min. The of epoxy group absorptions at 905 cm^{-1}, shown by the arrows, are used to trace the reaction using the absorption at 1510 cm^{-1} as an internal standard.

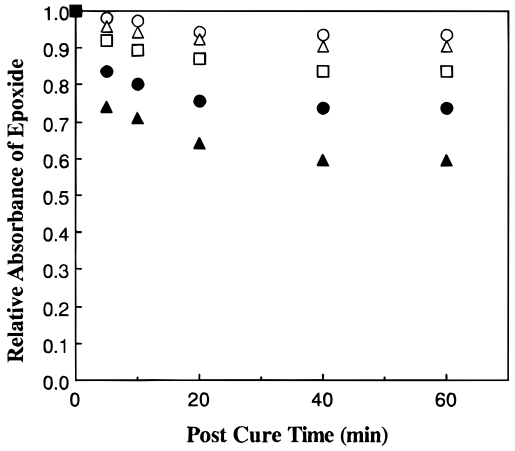


Figure 4. Changes in residual fractional concentration of epoxy groups by photoirradiation and postcure at 100 °C in the presence of 5 wt % DPI-AsF_6. Photoirradiation time: 5 (○), 10 (△), 20 (□), 40 (●), and 60 min (▲).

number of epoxy groups remain in the polymer film due to immobility of these groups in the cross-linked matrix.

The epoxy polymerization leading to cross-linking occurs as a result of the photogeneration of protons within the exposed area of the polymer film. The protons catalyze the cross-linking reaction that occurs only when thermal activation is provided by heating in the postexposure bake step. This is confirmed by a control experiment, in which no change is observed upon heating a film to 200 °C in the absence of acid. The pure thermal reaction occurs only at a temperature

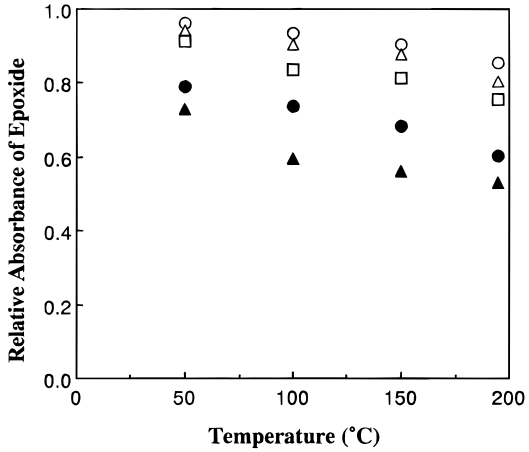


Figure 5. Effects of the postcure temperature on the conversion at which reaction saturated. Photoirradiation time: 5 (○), 10 (△), 20 (□), 40 (●), and 60 min (▲).

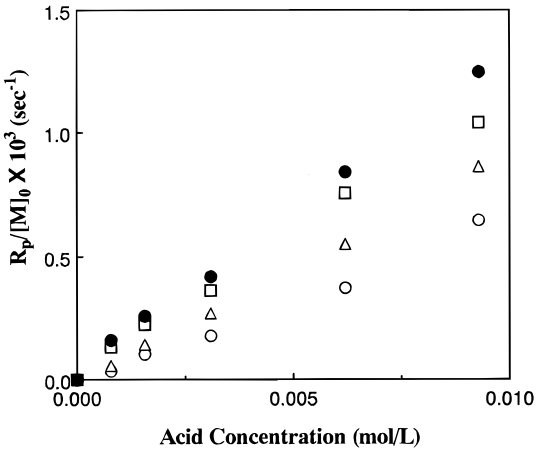


Figure 6. Relationship between $R_p/[M]_0$ and acid concentration, $[H^+]$, for the postcure reaction. Postcuring temperature: 50 (○), 100 (△), 150 (□), and 195 °C (●).

exceeding 200 °C. On the basis of these plots, we can obtain Figure 5, which shows the saturation points of the reaction for various postcure temperatures. As the temperature rises, a shorter irradiation time is sufficient to reach the same conversion. Consequently, higher postcure temperatures resulted in higher conversions.

The rate of polymerization, R_p, at a given time of the reaction, was calculated from the slope of the absorbance change in IR spectra

$$R_p = [M]_0 \frac{\Delta_{conversion}}{t_2 - t_1} \quad (1)$$

where $[M]_0$ is the initial concentration of the epoxy groups and $\Delta_{conversion}/(t_2 - t_1)$ is the slope of the conversion versus time curves. The R_p value depends, among other parameters, on the reactivity, the concentration of photoinitiator, the condition of postcure, and the light intensity. We calculated the rates, $R_p/[M]_0$, at the point of the maximum change of slopes (at 5-min postcure) of the absorbance decrease versus time curves. It should be pointed out, however, that these values are generally representative for only the initial stages of the polymerization prior to the gel point. The initial rate of the epoxy polymerization, R_p, during the postcure is directly related to the concentration of acid, $[H^+]$, present in the irradiated system. The reaction is described by a simple kinetic expression,[26] $R_p = k_p[M]_0[H^+]$, where $[M]_0$ (=3.23 mol/L) is the initial concentration of the epoxy group and k_p is the initial rate constant.

In Figure 6, a series plots of $R_p/[M]_0$ versus acid concentration are shown for various postcure temperatures. The acid concentration, $[H^+]$, was calculated from the initial DPI-AsF_6 concentration ($[DPI\text{-}AsF_6]_0$ = 0.152 mol/L), based on a film density of 1.43, the number of absorbed photons, and the quantum yield for proton formation of DPI-AsF_6 (Φ_d = 0.10). The rate of epoxy polymerization is shown to be linear with respect to acid concentration, i.e., to the irradiation time. The slope corresponds to the initial rate constants, k_p. The Arrhenius plot of ln k_p against the inverse postcure temperature, $1/T$, is shown in Figure 7. From this plot, the activation energy for epoxy polymerization of PI-(6FDA/ep-AHHFP) in the initial stages of postcure is calculated to be ~6 kJ/mol. Activation energy for a photoinitiated cationic polymerization of epoxides has been reported as 8.9−15.2 kJ/mol.[25] This small value for activation energy is thought to be due to the

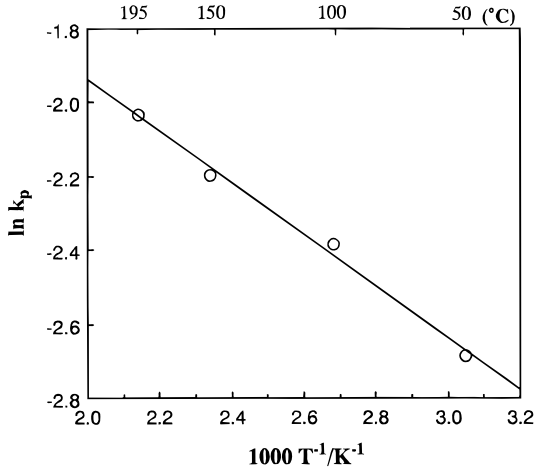


Figure 7. Arrhenius plots of initial rate constants, k_p, for epoxy polymerization vs postcuring temperature.

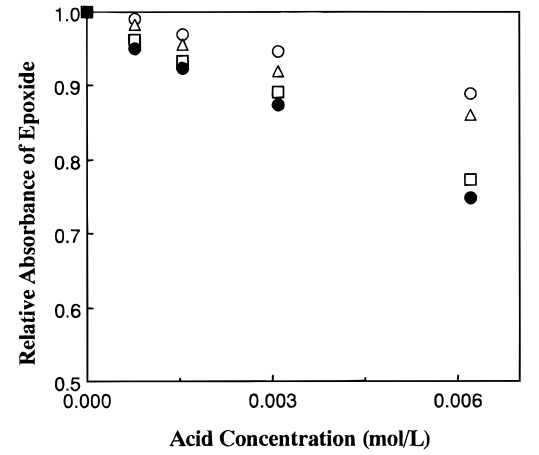


Figure 8. Effect of acid concentration on epoxy polymerization at initial postcure stage (5 min). Postcuring temperature: 50 (○), 100 (△), 150 (□), and 195 °C (●).

difference in the matrix, because the existence of polyimide chain makes the matrix rigid.

The effect of the acid concentration, $[H^+]$, (which is proportional to the photoirradiation time) on the epoxy polymerization is directly compared now by plotting epoxy conversion against acid concentration for various postcure temperatures. Figures 8 and 9 show the influence of the photogenerated acid concentration on the conversion of epoxy polymerization at the initial

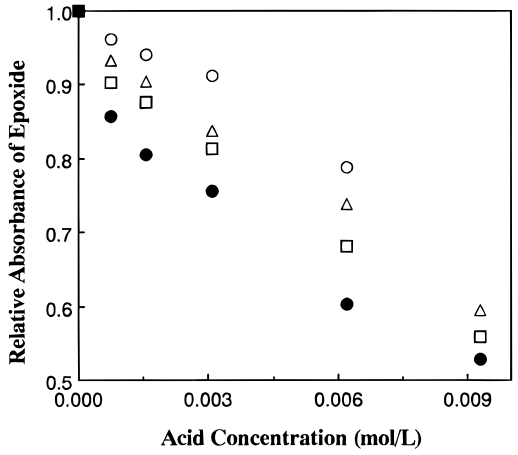


Figure 9. Effect of acid concentration on epoxy polymerization at final postcure stage (40 min). Postcuring temperature: 50 (○), 100 (△), 150 (□), and 195 °C (●).

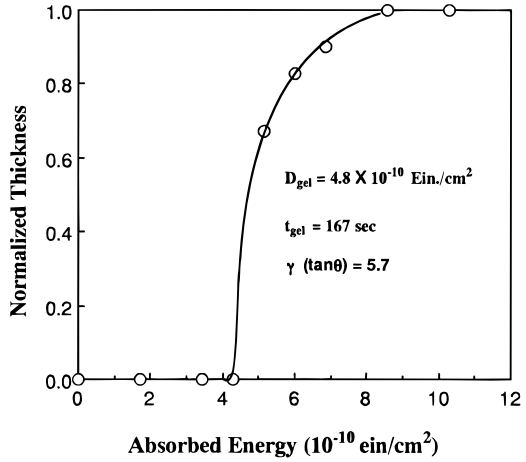


Figure 10. Characteristic curve for PI(6FDA/ep-AHHFP) in the presence of 5 wt % DPI-AsF$_6$ with postcure at 100 °C for 30 min.

stage (postcure of 5 min) and final stage (postcure of 40 min), respectively, for various postcure temperatures. These plots give straight lines, especially for the initial stage of postcure. Thus, the extent of postcuring reaction of the epoxy groups in film is proportional to the photogenerated acid concentration and to the photoirradiation time. This relationship means that the photogenerated acids reacted on some range in each temperature, but the range is limited. One of the reason for the limit of the reaction range is thought to be the change in the T_g of the matrix polymer during progress in the cross-linking reaction. However, we can estimate the acid concentration necessary for full conversion as the stage where each reaction range of an acid overlaps another. From Figure 9, we can calculate the condition for full conversion. For example, we obtain for a postcure temperature of 100 °C the acid concentration, $[H^+]$, necessary for full conversion of 0.024 mol/L, which gives the kinetic chain length, ν, of epoxy polymerization of 3.23/0.024 = 135.6. It corresponds to the photoirradiation time of ~155 min followed by the postcure of 40 min.

It is interesting to know the reaction radius per proton in the solid matrix, which cross-links during the postcure process. It should be noted here that epoxy polymerization in the present system induces cross-linking, as will be experimentally ascertained later. We calculated the reaction range by the following methods.[27] The concentrations of the epoxy group and the acid in the film were calculated by estimating that the density of film is 1.43. Before postcure of the epoxy group, 1.94×10^{24} molecules of the epoxy group exist in 1 L of the homogeneous film, based on the initial epoxy concentration ($[M]_0 = 3.23$ mol/L). From Figures 8 and 9, we can calculate the number of epoxy groups opened per one acid at initial and final stages of the reaction. It corresponds to the kinetic chain length, ν. The calculated ν, reaction volume, V_R, and reaction radius, r_R, per one photogenerated acid are listed in Table 1. The data of ν in Table 1 give a clear indication of chain reaction since approximately 58−214 of epoxy groups are reacted per one acid. The reaction radius, r_R, per one acid in PI(6FDA/ep-AHHFP) with DPI-AsF$_6$ therefore is determined to be about 19−30 Å through the chemical amplification process when heated for 5−40 min at 50−195 °C. The cross-linking reaction through diffusion of an acid is thought to be controlled by the molecular motion of the matrix, which becomes restricted as the progress in the cross-linking reactions. The matrix reaches the state where molecular motion for the cross-linking reaction is restricted sooner if a larger amount of acid is present. So, the kinetic chain length, reaction volume, and reaction radius are saturated for the more cross-linked matrix. These results provide interesting observations about the fundamental behavior of an acid in the solid state as well as the patterning characteristics of resist materials incorporating a chemical amplification process including cross-linking reactions.

Table 1. Calculated Kinetic Chain Length, ν, Reaction Volume, V_R, and Reaction Radius, r_R, per One Photogenerated Acid for Postcure of PI(6FDA/ep-AHHFP)

postcuring temp (°C)		postcuring time (min) 5	40
50	ν	58.2	103.4
	V_R (Å^3)	3.00×10^4	5.32×10^4
	r_R (Å)	19.3	23.3
100	ν	77.6	135.6
	V_R (Å^3)	4.00×10^4	7.00×10^4
	r_R (Å)	21.2	25.6
150	ν	116.2	168.0
	V_R (Å^3)	6.00×10^4	8.66×10^4
	r_R (Å)	24.3	27.4
195	ν	135.6	213.2
	V_R (Å^3)	7.00×10^4	10.98×10^4
	r_R (Å)	25.6	29.7

Characteristic Properties of Photosensitive Polyimide. Figure 10 shows a typical sensitivity curve of the PI(6FDA/ep-AHHFP) containing 5 wt % DPI-AsF$_6$. The exposed area of the film became insoluble in the developer (cyclohexanone) after photoirradiation followed by postcure (100 °C, 30 min). The normalized film thickness is plotted versus absorbed dose. Sensitivity, which is defined as the dose to give 50% of the initial thickness in the exposed regions, D_{gel}, is measured as shown in Figure 9. We use this value (D_{gel}) as the gel dose. The slope, tan θ, gives the contrast, γ, a relative measure of the difference in solubility between the exposed and unexposed regions. The quantum yield for cross-linking, Φ_{gel}, can be determined from the gel dose, $D_{gel} = I_{abs} t_{gel}$, by using eq 2,[28] where M_{w0} is the weight-

$$\Phi_{gel} = ld/(M_{w0} D_{gel}) = ld/(M_{w0} I_{abs} t_{gel}) \qquad (2)$$

average molecular weight before photoirradiation, I_{abs} is the rate of radiation absorption, t_{gel} is the gel time calculated from the characteristic curve, l is the film

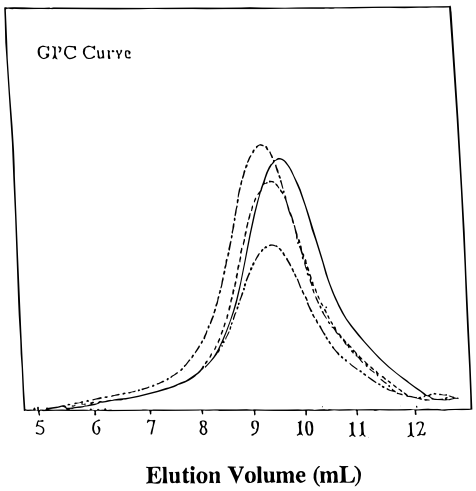


Figure 11. Change in GPC curves for PI(6FDA/ep-AHHFP) with 5 wt % DPI-AsF_6 with postcure of 5 min at 100 °C. Photoirradiation time: 0 (—), 1 (– – –), 2 (– · –), and 5 min (– ·· –).

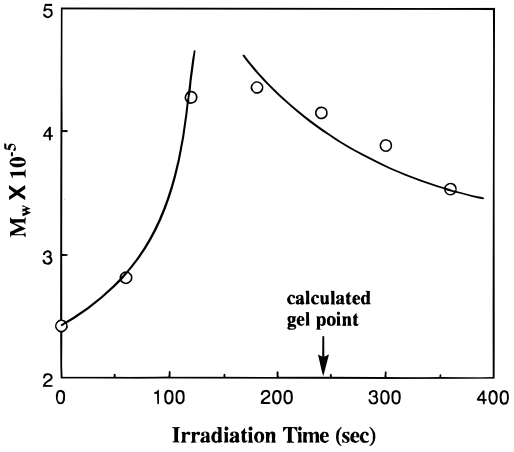


Figure 12. Change in M_w of PI(6FDA/ep-AHHFP) with 5 wt % DPI-AsF_6 during photoirradiation with postcure of 5 min at 100 °C.

thickness, and d is the density. We calculated the gelation time, t_{gel}, to be 167 s and the rate of radiation absorption, I_{abs}, to be 2.86×10^{-12} einstein cm^{-2} s^{-1}. By use of these values together with $M_{w0} = 99\,300$, $l = 1.0$ μm, and $d = 1.43$, the quantum yield for the cross-linking of PI(6FDA/ep-AHHFP), Φ_{gel}, was calculated to be ~3.0.

Change in Molecular Weight Measured by GPC. In order to detect the change in molecular weights of PI(6FDA/ep-AHHFP) during postcure after photoirradiation, the molecular weights of PI(6FDA/ep-AHHFP) were measured by GPC for various photoirradiation times (Figure 11). When the films of PI(6FDA/ep-AHHFP) with 5 wt % DPI-AsF_6 were irradiated and postcured for 5 min at 100 °C, the cross-linking reaction proceeded, increasing its weight average molecular weight, M_w. In Figure 12 is shown the change in M_w of PI(6FDA/ep-AHHFP) with on the photoirradiation time. According to the David theory on photo-cross-linking reaction,[29] the change in M_w of a cross-linked polymer before the gel point satisfies the following equation,

$$M_w = M_{w0}/(1 - 2u_{w0}x) \qquad (3)$$

where M_{w0} and u_{w0} are the weight-average molecular weight and weight-average degree of polymerization

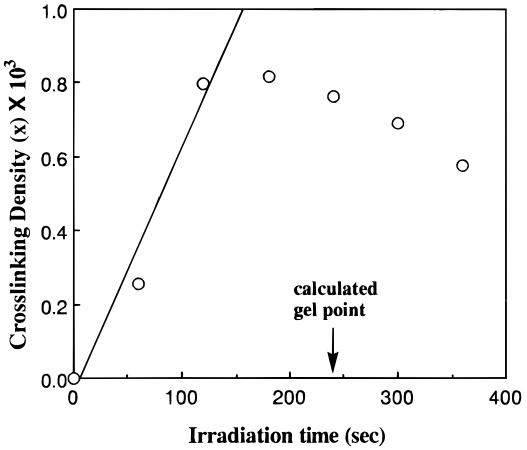


Figure 13. Cross-linking density (x) vs photoirradiation time with postcure of 5 min at 100 °C for photo-cross-linking of PI(6FDA/ep-AHHFP) with 5 wt % DPI-AsF_6.

before irradiation, respectively, and x is the cross-linking density, i.e., the number of cross-links per epoxy unit. The M_w should increase to infinity before gelation. Therefore, the decrease in the apparent molecular weights observed by GPC for irradiation times longer than ~180 s is due to precipitation of the higher molecular weight portion, which was observed for those samples even before the gelation point calculated from $x = 1/2u_{w0}$. Figure 13 shows the change in the cross-linking densities of PI(6FDA/ep-AHHFP) during photoirradiation calculated from eq 3. From the slope of the straight line in Figure 13, the quantum yield for cross-linking, Φ_{GPC}, was determined to be ~2.6. This value is in good agreement with $\Phi_{gel} = 3.0$ obtained from gel dose measurements. The very high sensitivity of this polymer is attributed to the fact that the cross-linking reaction is a chain reaction. Thus, the effective quantum yield for chemical amplification systems is usually much larger than unity. By using the initiation quantum yield of 0.1 for acid generation, the number of cross-links per one photogenerated acid would become to be 26.0 for the present system. This value is approximately one-third of the number of epoxy groups reacted per one acid ($\nu = 77.6$) determined from IR experiments at the same condition (postcure, 5 min at 100 °C). The kinetic chain length from IR measurements is much larger than the number of cross-links obtained from GPC measurements, because IR spectra survey the absorbance change of epoxy groups but the change of epoxy groups is not always related to the increase in molecular weight, probably due to the occurrence of intramolecular cyclization.

Conclusions

A novel photosensitive polyimide PI(6FDA/ep-AHHFP) was synthesized by the reaction of PI(6FDA/AHHFP) with epichlorohydrin using BTMA as a phase transfer catalyst. This polyimide having epoxy groups is highly soluble in most common solvents. The photochemical reactivity of PI(6FDA/ep-AHHFP) was examined in the presence of DPI-AsF_6. PI(6FDA/ep-AHHFP) containing DPI-AsF_6 was found to work as a negative-tone photosensitive polyimide with high sensitivity and contrast. IR spectroscopy was used to study postcure reactions. The activation energy for epoxy polymerization of PI(6FDA/ep-AHHFP) was 6 kJ/mol. The reaction radius induced by one photogenerated acid in PI(6FDA/ep-AHHFP) with DPI-AsF_6 was estimated

to be about 19−30 Å through the chemical amplification process when heated for 5−40 min at 50−195 °C. The quantum yield for cross-linking of PI(6FDA/ep-AHHFP), Φ_{gel}, was calculated to be ∼3.0 from the characteristic curve. The sensitivity, D_{gel}, and contrast, γ, after postcure at 100 °C for 30 min are 4.8×10^{-10} einstein cm^{-2} and 5.7, respectively. The quantum yield for cross-linking, Φ_{GPC}, was determined to be ∼2.6 from GPC measurements. The very high sensitivity of this polymer is attributed to the fact that the cross-linking reaction is a chain reaction using the chemical amplification technique.

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