PHOTOSENSITIVE POLYIMIDES AND FUNCTIONAL POLYIMIDES INCLUDING A PHOTO-ACID GENERATOR

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ABSTRACT

A new photosensitive polyimide system composed of solvent-soluble polyimides bearing epoxy groups and photo-acid generators was prepared, and its mechanism and kinetics of photocrosslinking reactions are elucidated.

INTRODUCTION

Polyimides (PI) are well known because of the excellent thermal stability and have become indispensable materials for microelectronic applications such as passivation coatings, α-particle barriers, and interlayer dielectrics in the manufacture of integrated circuits. Their ability to planarize when used as an insulator is also important compared to inorganic materials. Recently, increasing research has been devoted to developing photosensitive polyimides because they can eliminate a number of processing steps required for patterning the usual polyimide films by using the usual photoresist materials [1]. Photosensitive polyimides are divided into four types according to the combination of whether they become insoluble or soluble after exposure to light (negative-tone type or positive-tone type, respectively) and whether the exposure to light and development are carried out on polyimide precursors or on solvent-soluble polyimides. Typical examples of these combinations are shown in Table 1.

Since photosensitive polyimide precursors suffer from high shrinkage during curing, there is great interest in fully imidized photosensitive polyimides which offer lower shrinkage. 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. However, sensitivities of photosensitive polyimides are still low [2,3]. One strategy for the improvement of the photoreactivity of photosensitive polyimides is utilization of long-lived active intermediates [4], and the other strategy is elimination of a charge transfer. The polyimides prepared from aliphatic diamines are examples of the latter [5]. 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 [1]. Incorporation of an epoxy group into a polyimide is expected to increase its photoreactivity by the chemical amplification mechanism.

In the present talk, the preparation of novel photosensitive polyimides containing a epoxy group and their mechanism of photopolymerization with photo-acid generators are discussed.

PHOTOCROSSLINKING OF PI(6FDA/ep-AHHFA) WITH DPI-AsF_6

A new polyimide, PI(6FDA/cp-AHHFA), containing an epoxy group (Fig. 1) 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)haxafluoropropane (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 by irradiating it in the presence of diphenyliodonium hexafluoroarsenate (DPI-AsF_6) and by successive post curing [6]. The conversion and curing rate were determined by the absorbance change in the IR band at 905 cm^{-1} for the epoxy group. Figure 2 shows typical results. On postcure at 100 °C after room-temperature photoirradiation, the epoxy group reacts quickly in the first stage followed by a slower rate. No epoxy group reacted even upon heating a film to 200 °C without irradiation to DPI-AsF_6. The occurrence of crosslinking during postcure was ascertained by the increase in molecular weight of PI(6FDA/cp-AHHFP) and the gelation. The epoxy polymerization occurs as a result of thermal activation of the photo-generated protons within the exposure area of the polymer film. The activation energy for crosslinking reaction of PI(6FDA/cp-AHHFP) was found to be about 6 kJ/mol.

The linear dependence of epoxide conversion on photogenerated acid concentration is shown in Fig. 3. The slopes in Fig. 3 give the number of epoxy groups opened per one acid, i.e., kinetic chain length, ν. The calculated ν, reaction volume, V_R, and reaction radius, r_R, per one photogenerated acid are listed in Table 2. They give a clear indication of chain reaction since approximately 58 - 214 of epoxy group are reacted per one acid. The reaction radius, r_R, per one acid is about 19 - 30 Å for this system through the chemical amplification process when heated for 4 - 40 min at 50 - 195 °C. The crosslinking 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 reaction. A typical sensitivity curve is shown in Fig. 4 for PI(6FDA/cp-AHHFP) with 5 wt% DPI-AsF_6. The quantum yield for crosslinking, ϕ_{gel}, was determined to be about 3.0 from the gel dose, $D_{gel} = I_{abs} t_{gel}$. This value is in good accord with the quantum yield for crosslinking measured with GPC, $\Phi_{GPC} \simeq 2.6$. When we consider that the quantum yield of acid generation is 0.1, the number of crosslinks per one photogenerated acid would become to be 26. This value is large enough, but is about one-third of the number of epoxy groups reacted per one acid ($\nu = 77.6$) at the same condition. The difference is probably due to the occurrence of intramolecular cyclization.

PHOTOCROSSLINKING OF PI(BTDA/ep-AHHFP) WITH DPI-AsF_6

In order to improve the low absorptivity of DPI-AsF_6 at 300 - 400 nm, a benzophenone group was introduced into the main chain of the polyimide to give the photosensitivity itself and also to give the possibility of sensitizing the reaction of photo-acid generators.

A benzophenone-containing polyimide with epoxy groups, PI(BTDA/cp-AHHFP), (Fig. 1) was prepared in a similar method as for PI(6FDA/cp-AHHFP) but by using BTDA instead of 6FDA. Photochemical reactivity of epoxy groups was examined by IR spectra in the presence of DPI-AsF_6 [7]. The PI(BTDA/ep-AHHFP) containing benzophenone groups with DPI-AsF_6 reacts to much higher extent than PI(6FDA/ep-AHHFP) with DPI-AsF_6 for the same conditions of photoirradiation and postcure. Polyimides with BTDA are known to abstract aliphatic hydrogen atoms in the polymer chains by photoirradiation [1]. PI(BTDA/cp-AHHFP) in the present case also showed to react considerably during photoirradiation at room temperature but before the postcure. However, interesting to say, the extent of epoxy reaction both at room temperature and at the postcure increased markedly with the increase in concentration of DPI-AsF_6. The increase in epoxy reaction at the postcure supports the presence of photosensitizing effect of benzophenone groups on the acid generation of DPI-AsF_6. The increase in epoxy reaction at room temperature would be due to some complex photochemical processes including benzophenone, DPI-AsF_6, and epoxy groups. The supposed reaction scheme is summarized in Fig. 5.

INFLUENCE OF PHOTO-ACID GENERATOR ON PHOTOREACTIVITY

An alternative method of improving the photosensitivity is to use a photo-acid generator having higher absorptivity for above 300 nm. Diphenyliodonium 9,10-dimethylanthracene-2-sulfonate (DIAS) was used for this purpose [8]. By using DIAS having absorption band in 350 - 410 nm for the photocrosslinking of PI(6FDA/cp-AHHFP) the irradiation time was shortened by twenty times as in shown in Fig. 6 for getting same conversion compared to the previous case with DPI-AsF_6. The kinetic chain length, ν, per one acid in PI(6FDA/cp-AHHFP) with DIAS was calculated about 4 - 31. The reaction radius, r_R, of an acid is about 8 - 16 Å when heated for 5 - 40 min at 50 - 195 °C, which is about a half for DPI-AsF_6.

A typical sensitivity curve for PI(6FDA/cp-AHHFP) with 5.0 wt% DIAS is shown in Fig. 7, where the abscissa is given based on incident energy. The incident gel dose, Do_{gel}, is about 117 mJ/cm^2 or 8.5×10^{-8} einstein/cm^2, which is 18 times smaller than that ($Do_{gel} = 1.5 \times 10^{-6}$ einstein/cm^2) for DPI-AsF_6.

The quantum yield for crosslinking, Φgel, was determined to be 0.084 for PI(6FDA/cp-AHHFP) with DIAS. By using the initiation quantum yield of 0.1 for acid generation, the number of crosslinks per one photo-generated acid would become to be about 0.84. When compared to the results with DPI-AsF_6 ($\Phi_{gel} \sim 3.0$), the value with DIAS is very small probably due to the difference in mobility of the acids in the solid film. In conclusion, PI(6FDA/ep-AHHFP) containing DIAS has been proved to work as a new negative-tone photosensitive polyimide.

ACKNOWLEDGMENT

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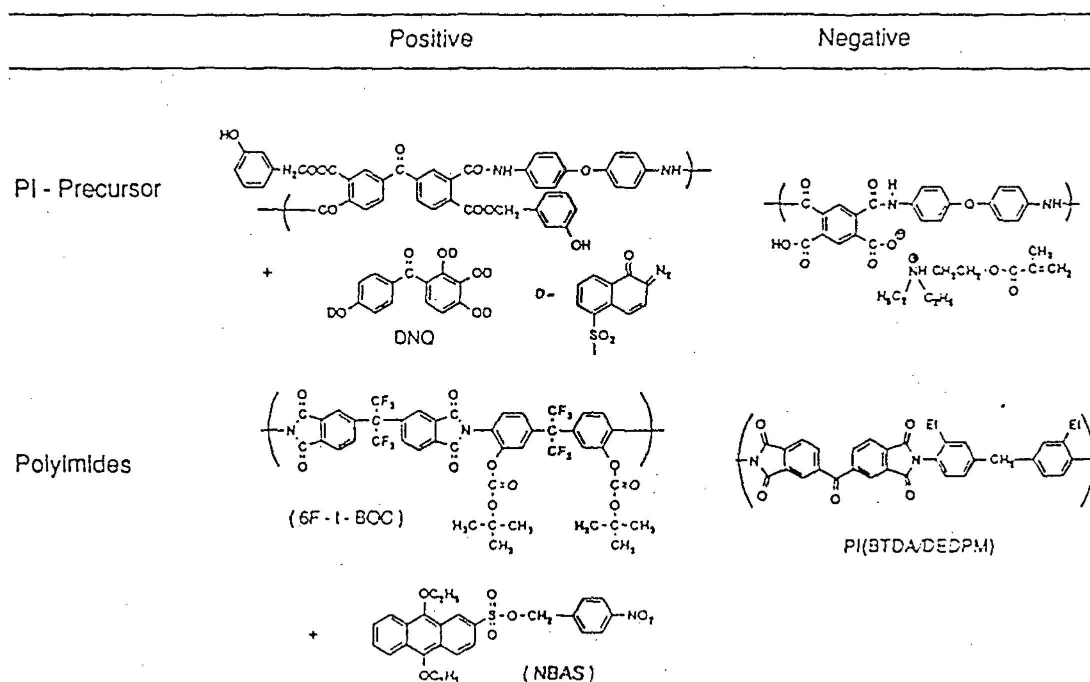
experimental part of the present work and for the discussion.

Table 1. Typical Photosensitive Polyimides (PI)



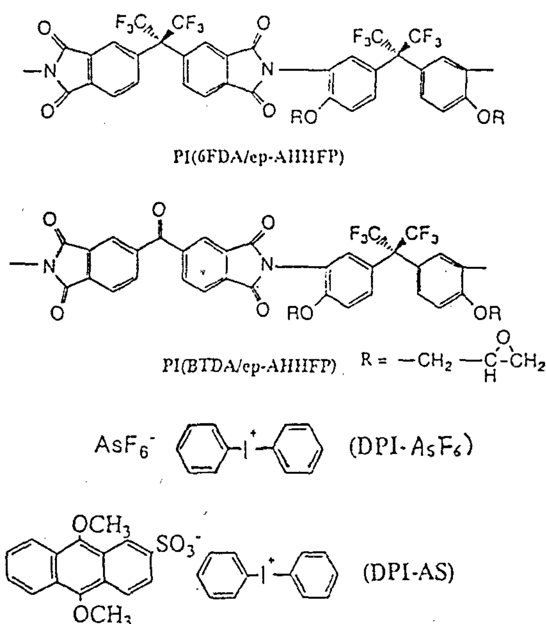


Figure 1. The structure of PI(6FDA/ep-AHHFP), PI(BTDA/ep-AHHFP), DPI-AsF_6 and DPI-As.

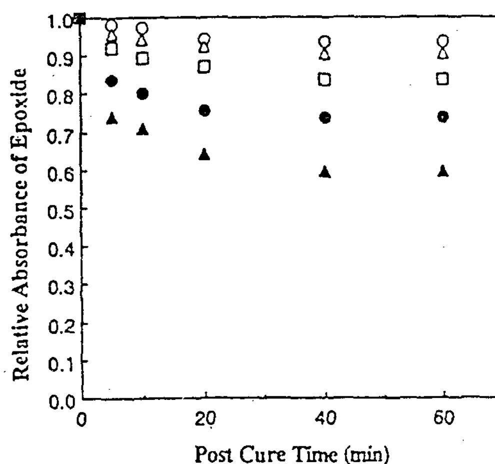


Figure 2. Changes in residual fractional concentration of epoxy groups by photoirradiation and postcure at 100 °C in the presence of 5 wt% DPI-AsF_6. Photoirradiation time: 5(○), 10(△), 20(□), 40(●), and 60 min (▲).

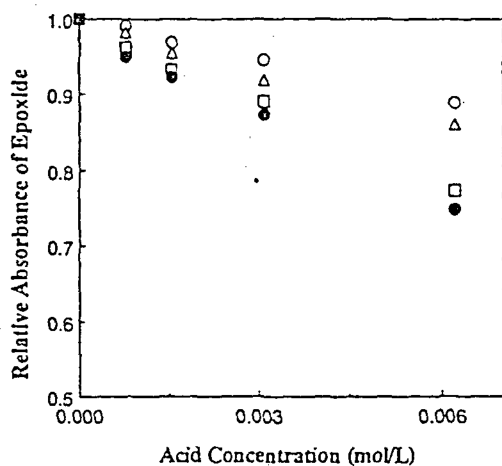


Figure 3. Effect of acid concentration on epoxy polymerization at initial postcure stage (5 min). Postcuring temperature: 50(○), 100(△), 150(□), and 195 °C (●).

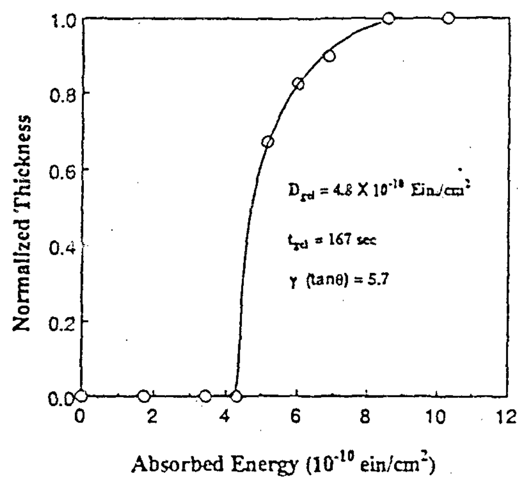


Figure 4. Characteristic curve for PI(6FDA/cp-AHHFP) in the presence of 5 wt% DPI-AsF_6 with postcure at 100 °C for 30 min.

Table 2 Calculated Kinetic Chain Length, ν, Reaction Volume, V_R, and Reaction Radius, r_R, per One Photogenerated Acid for Postcure of PI(6FDA/cp-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

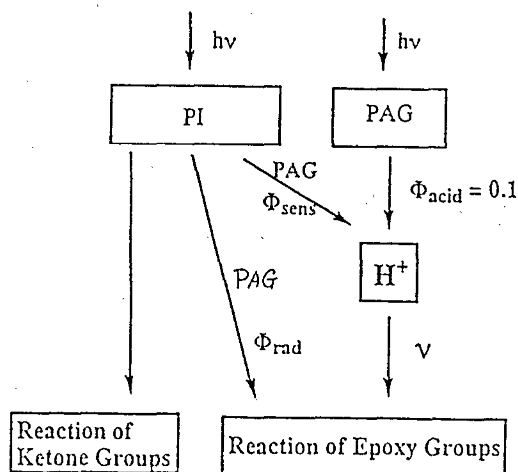


Figure 5. The reaction scheme of PI(BTDA/ep-AHHFP) with photo-acid generator (PAG), DPI-AsF_6.

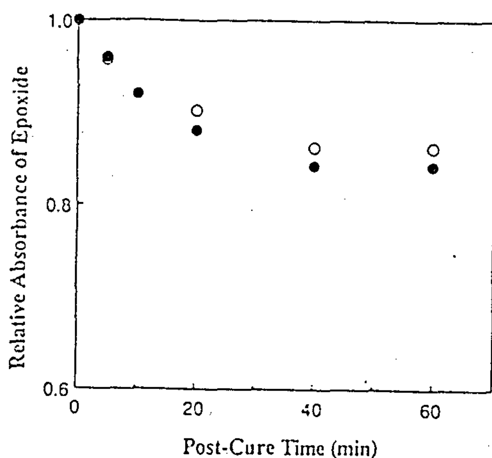


Figure 6. The comparison of the conversion using DIAS (O, 5 min of irradiation time) and DPI-AsF_6 (●, 100 min of irradiation time) as photo-acid generator at same incident energy (2.72×10^{-9} einstein cm^{-2} sec^{-1}) and same post-cure temperature (100 °C).

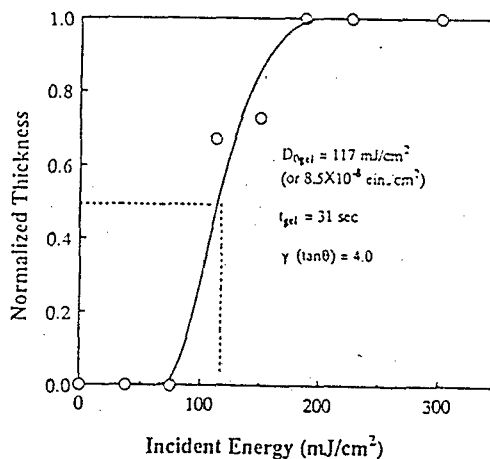


Figure 7. Characteristic curve for PI(6FDA/ep-AHHFP) in the presence of 5 wt% DIAS with post-cure at 100 °C for 30 min.

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