A Structure Design of Novel Photobase Generator and Application of a Photobase Generator to Negative Photosensitive Polyimides

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1. Introduction

Polyimides (PIs) are used as engineering plastics because of their excellent mechanical properties. PIs are applied for photosensitive materials, *i.e.* photosensitive polyimides (PSPIs). Most of PSPIs are negative-type photosensitive materials with cross linked system which needs high temperature cure process to remove crosslink sites.

However those systems are difficult to apply for photosensitive cover lay in regards of flexible printed circuit (FPC) that is damaged against high temperature cure process.

PIs are synthesized from polyamic acids (PAAs) precursors under base catalyst condition. Therefore we have adopted photo base generators (PBGs) as a catalyst of PAA. We have developed the PBGs for alkaline developable negative-type PSPI (Scheme 1, Fig 1).

2. Experimental

2-1. Synthesis of Photo Base Generators

1Ph-BA was prepared as described in the literature.[1][2] C8 was prepared by the following patent.[3] C7M, C8M, C7MPh, C8MPh, TX-8 were prepared as described in Scheme 2~6. The abbreviations in Scheme 2~6 are as follows: MeMgI (Methyl magnesium iodide), PTSA (p- toluene sulfonic acid), NaIO₄ (Sodium periodate), RuCl₃ (Ruthenium(III) chloride), NH₂OH · HCl (Hydroxylamine hydrochloride), TCBC (Trichlorobenzoylchloride), DMAP (Dimethylaminopyrine), NEt₃ (Triethylamine),

POCl₃ (Phosphorus chloride oxide), PhMgBr (Phenylmagnesiumbromide), Pd₂(dba)₃ (Tris (dibenzylideneacetone)dipalladium(0)), P(tBu)₃ HBF₄ (Tri-t-butylphosphinetetrafluoroborate), Cy₂NM₂ (Dicyclohexylmethylamine).

Scheme 1 PBG as a catalyst of PAA and alkaline developable negative-type PSPI

Fig.1 PBG samples

2-2. Steady state spectroscopy

UV spectra of PBGs were measured as polymethacrylonitrile (PMAN) films prepared by the following procedure. PMAN films (4 μm thickness) were prepared by spin-casting of methylethylketone (MEK) (500mg) solution containing PMAN (100 mg), PBG (10 mg) and 2,4-Diethyl-9H-thioxanthen-9-one (DETX) (3 mg) on the CaF₂ plate followed by baking at 70°C for 5 min.

Scheme 2 Synthesis of PBG3:C7M

Scheme 3 Synthesis of PBG4:C8M

Scheme 4 Synthesis of PBG5:C7MPh

Scheme 5 Synthesis of PBG6:C8MPh

Scheme 6 Synthesis of PBG7:TX-8

2-3. Photolysis experiment

The photolysis of PBGs in PMAN films was conducted. High mercury lamp was used for the irradiation. The wave-length below 325 nm was cut by the filter. PMAN films (4 μm thickness) were prepared by spin-casting of MEK (500 mg) solution containing PMAN (100mg), PBG (10 mg) and DETX (3 mg) on the CaF_2 plate followed by baking at 70°C for 5 min. The absorption intensities were measured by FT-IR spectra at 1760 cm^{-1} (A_{1760}) correspond to oxime. The photolysis rate was determined by the following equation.

Photolysis Rate=

$$\frac{(A_{1760}(\text{samp}) - A_{1760}(\text{init}))}{(A_{1760}(\text{fin}) - A_{1760}(\text{init}))} \times 100$$

Subscripts between parentheses following A in the equation indicates the state of the polymer films; e.g. (samp) is the polymer sample at each exposure dose; (init) is unexposed film; (fin) is completely photolysis film.

2-4. Thermal stability experiment

The thermal stability experiment was carried out by TG/DTA under air condition.

2-5. Synthesis of poly(amic acid) PAA-1

Poly(amic acid)-1 (PAA-1) was synthesized as follows. 4,4'-Oxydiphthalic anhydride (ODPA) (10.3 g, 33.2 mmol) solution in γ -butyrolactone (γ BL) (60.0 ml) was added to 1,3-bis(4-aminophenoxy)benzene (TPE-R) (9.41 g, 9.41 mmol) with stirring. The mixture was stirred at room temperature for 12 hour to give a viscous solution. The yield was quantitative. Number-average molecular weights (M_n) and weight-average molecular weights (M_w) were 30,000 and 63,000, respectively, determined by gel permeation chromatography (GPC).

2-6. Synthesis of poly(amic acid) PAA-2

Poly(amic acid)-2 (PAA-2) was synthesized as follows. To a ODPA (6.2 g, 20.0 mmol) solution in N-methylpyrrolidone (NMP) (47.24 ml) was added 1,3-bis(3-aminophenoxy)benzene (APB) (5.61 g, 19.2 mmol) with stirring. The mixture was stirred at room temperature for 12 hour to give a viscous solution. The yield was quantitative. M_n and M_w were 20,000 and 70,000, respectively, determined by GPC.

2-7. Imidization degree

To a polymer solution of PAA-1 (2.5 g) were added PBG (50 mg), DETX (14 mg) and γ BL (0.5 g). These solutions were spin-casted on a silicon wafer, and baked at 95 °C for 15 min. The films were exposed at 2,000 mJ/cm^2 by using high pressure mercury lamp. We have achieved the post-exposure-baking at 140 °C for 30min

and at 330 °C for 30min sequentially. Absorption intensities of FT-IR spectrum at 1380 cm⁻¹ (A₁₃₈₀) assigned as imide were measured. The imidization degree was determined using the following equation.

$$\text{Imidization degree} = \frac{(A_{1380(\text{samp})} - A_{1380(\text{init})})}{(A_{1380(\text{fin})} - A_{1380(\text{init})})} \times 100$$

Subscripts between parentheses following A in the equation indicate the state of the polymer films; e.g. (samp) is the polymer sample at post-exposure-baking at 140°C for 30 min; (init) is non-baked film; (fin) is completely imidized film (Post-exposure-baked at 330°C for 30 min).

2-8. Photosensitivity

PAA-2 polymer films (17.0 μm) were prepared by PAA-2 (5.0 g), PBG (100 mg) and DETX (30 mg), followed by casting on copper films and then prebaked at 95 °C for 12 min. These films were exposed at 500mJ/cm², post-exposure-baked at 110 °C for 30 min. The development of the exposed films was performed with 1wt% Na₂CO₃ aq. at 30°C. The films were rinsed by distilled water. The normalized film thickness was calculated.

2-9. Film property experiment

PAA-2 polymer films (17.0 μm) were prepared with the same method of 2-7. The films were exposed at 500mJ/cm², post-exposure baked at 120°C for 60 min and at 180 °C for 60 min. Film property experiment was carried out by bending test.

2-10. Thermal stability of PBGs in the presense of carboxylic acid

To a PBG (0.025 mmol) solution in DMSO-d₆ (0.7 ml) was added terephthalic acid (TPA) (0.05 mmol). This solutions were set in a NMR tubes. The NMR tubes were heated between 60°C and 180°C for 20 min. The NMR spectra were measured at every 20°C.

3. Results

PBGs having acyloxyimino (AOI) group are transformed into imine or amine as shown Scheme 7. When **PBG1** (1PhBA) that generates benzylamine was applied for PSPI, the

resulting PI film became brittle. From GPC data, decrease of Mw was confirmed after curing at 180°C. Mw of PI film without/with 1PhBA was 71,000 and 21,000, respectively.

When various base species were added to PAA, PI films prepared with imidazole, amine, pyridine showed the same mechanical properties with the blank film. However the PI film prepared with piperidine became brittle.

It was assumed that the NH group influenced the negative effect on the mechanical properties of PI film. It was assumed that the imine group was generated from cyclic AOI group. Then some cyclic AOI groups (**PBG2~7**) were designed and applied as a catalyst of PSPI.

Table 1 shows evaluation of PBGs. UV-vis spectra of PBGs were measured. λ_{max} of TX-8 which has a thioxanthone group was 380nm, however the others showed below 300nm.

C8 showed efficient photolysis in PMAN film. However TX-8 showed slow photolysis, and C7M, C8M showed hardly photolysis. It is suggested that cyclic AOI compounds having a Ph group at E-position (the trans position against oxime N-O bond) of C=N are decomposed efficiently and group (e.g. thioxanthone group) at E-position are not decomposed efficiently. It is assumed that TX-8 is not transformed to a structure which is able to decompose at excited state because of fixed group.

The thermal stability of PBGs was evaluated by 5% weight loss temperature. 5% weight loss temperature of C8M and C7M were 184°C and 169°C, respectively. DTA analysis of C8M and C7M did not give the exothermic peak. So, it is assumed that C8M and C7M are volatilized without decomposition.

On the other hand, 5% weight loss temperatures of other samples were followed in the order of TX-8 > C8 > C7MPh > C8MPh. It was suggested that cyclic AOI compounds with small substituent or fixed group are more stable than those with steric hindrance substituents.

Catalytic ability of PBGs was evaluated by imidization of PAA-1 film. Diethythioxanthone

	UV spectra λ max (nm)	Photolysis (%)(a)	DTA analysis($^{\circ}$ C) (b)	5% weight loss Temp.($^{\circ}$ C)(c)	Degree of imidization (2000mJ/cm2) (%)(d)	Degree of imidization (0mJ/cm2) (%)(e)	Imidization difference(%) (f)	Normalized Film thickness (%)(g)	Film Property (i)
C8	246	89	215	212	63	42	21	93	x
C7M	235	11	No peak top	165	n.d.	n.d.	n.d.	n.d.	n.d.
C8M	234	7	No peak top	144	n.d.	n.d.	n.d.	n.d.	n.d.
C7MPh	250	83	189	181	38	32	4	78	O
C8MPh	256	85	220	210	48	35	13	93	Δ
TX-8	262,321,385	38	286	258	49	47	2	—(h)	O

- (a) Photolysis rate of PBGs exposed at 2000mJ/cm² in PMAN film.
 (b) Exothermic peak top of PBGs determined by TG analysis.
 (c) 5% weight loss temperature of PBSs determined by TG analysis.
 (d) Degree of imidization of PAA films exposed at 2000mJ/cm² and post-exposure-baked at 140 $^{\circ}$ C for 30 min. (Degree of imidization of PBG-free PAA was 28%)
 (e) Degree of imidization of PAA films exposed at 0 mJ/cm² and post-exposure-baked at 140 $^{\circ}$ C for 30min.
 (f) Imidization degree difference of PBGs between irradiated area and no-irradiated are.
 (g) No Patterning.
 (h) Film property experiment (x; self-support impossible, Δ ; folding back impossible at bending test,, O; folding back possible at bending test).
 (i) Not determined.

Table 1. Evaluation of PBG7:TX-8

Scheme 7 Photolysis of acyloxyimino group

(DETX) was adopted as a photo-sensitizer. The degree of imidization of photo irradiated area (2000mJ/cm², PEB;140 $^{\circ}$ C/30min) was compared with that of no-irradiated area (0mJ/cm², PEB;140 $^{\circ}$ C/30min). The degree of imidizations of photo irradiated area showed the following order, C8>TX-8>C8MPh>C7MPh. However, that of no-irradiated area showed the following order, TX-8>C8>C8MPh>C7MPh. Hence the differences of between irradiated area and no-irradiated area showed the following order, C8>C8MPh>C7MPh>TX-8. Although TX-8 showed the highest thermal stability in TG/DTA analysis, the dark-reaction proceeded in case of TX-8. It was assumed that TX-8 became unstable state by COOH of PAA side-chain, so the thermal decomposition occurred and caused

dark-reaction. In case of C8, the degree of imidization in irradiated area was high and that of no-irradiated area was also high. On the other hand, in case of C8M-Ph, the degree of imidization in irradiated area was smaller than in case of C8, however dark-reaction was also smaller. As a result, the difference between irradiated area and no-irradiated area was larger than any other samples. So it is suggested that C8M-Ph is suitable as the catalyst of PSPI.

The photosensitivity of PBGs was evaluated with the normalized film thickness. The normalized film thicknesses showed the following order, C8MPh>C8>C7MPh. The film residue of TX-8 was not observed after development.

The film property was evaluated by bending test. The film properties of PBG showed the following order, TX-8 $\doteq$ C7MPh>C8MPh>C8. It is supposed that the decrease of film property results from PAA degradation by the thermolysis product of PBGs. However, these results were not

associated with thermal stability results. Hence, we evaluated the thermal decomposition of PBGs in the presence of a carboxylic acid.

The thermal decomposition of PBGs was evaluated in the presence of TPA. Thermal stabilities of PBGs in the presence of TPA showed the following order, C8MPh>C7M>C8>C7MPh>C8M>TX-8. The thermal stability of TX-8 decreased especially in case of in the presence of TPA. However, these results were also not associated with the film property results obtained by bending test.

We suppose that the film properties are influenced by the molecular structures of PBG thermolysis products and/or PAA's degradability. Although TX-8 was not stable in the presence of a carboxyl acid, the film property of TX-8 was comparatively high. It is assumed that the thermolysis product of TX-8 is not induced the PAA's degradation.

We suppose that the thermal stability of PBGs in the presence of carboxyl acid is also important. We consider that these stabilities were associated with properties of substituents, *i.e.* electron-withdrawing and electron-donating group. For example, nitro group (electron withdrawing group) or methoxy group (electron-donating group) will be able to control the stability.

4. Conclusion

The large absorption of PBGs

corresponding i-line was accomplished by the introduction of a thioxanthone group. It is suggested that cyclic AOI compounds having a Ph group at E-position of C=N(the trans position against oxime N-O bond) decompose efficiently by irradiation. And cyclic AOI compounds having fixed group (e.g. thioxanthone group) at E-position do not decompose efficiently by irradiation. On the other hand, it is suggested that cyclic AOI compounds with small substituent or fixed group are more stable than those with bulky substituents. Hence, the molecular design for a balance between PBG's photolysis and PBG's thermal stability is important. Therefore we consider that thermal stability of PBGs in the presence of carboxyl acid is important for applying PSPIs.

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5. References

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