

Synthesis of Novel Self-Developing Photosensitive Polyimide

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Abstract : Aromatic diamine monomers containing allylic ester linkage, 1,5-bis(4-aminobenzoate)-1,2,3,4-tetrahydronaphthalene (4-DABTN) and 1,5-bis(3-aminobenzoate)-1,2,3,4-tetrahydronaphthalene (3-DABTN) were synthesized through the reaction of 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene and 4- or 3-nitrobenzoyl chloride. By the reaction of these diamines with pyromellitic dianhydride (PMDA) or 4,4-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), poly(amic acid)s were obtained. The inherent viscosities of the poly(amic acid)s were between 0.55 and 1.31 dL/g. The poly(amic acid)s were converted to polyimides by chemical imidization. The thermogravimetric analysis (TGA) thermograms of these polyimides showed temperatures of 5% weight loss between 323 and 389°C in nitrogen atmosphere. The model compound, 1,5-bis(4-nitrobenzoate)-1,2,3,4-tetrahydronaphthalene (4-DNBTN), was decomposed to 4-nitrobenzoic acid and 5-(4-nitrobenzoate)-3,4-dihydronaphthalene upon addition of CF_3COOH .

Introduction

Polyimides have been employed in diverse areas of electronics and information technology because of high thermal stability and excellent physical properties.¹ Lithography of polyimides is an inevitable process in using polyimides for microelectronics. Photosensitive polyimides make it unnecessary to use photoresists for patterning polyimides and diminish the number of steps in fabrication of various electronics devices.² In addition, the development of technology of photosensitive polyimides is expected to play a great role in manufacturing photonics devices in near future.

Since the first photosensitive polyimide was reported by Kerwin and Goldrick in 1971,³ most of the negative type photosensitive polyimide are prepared from poly(amic acid)s, where cross-link-

ing sites are introduced to amic acids through ester or ammonium salt linkage. However, positive working photosensitive polyimides would be more desirable for higher resolution, use of alkaline aqueous developers, and high throughput patterning processes such as direct laser writing. It is also possible with positive resists to irradiate again after a first development step in order to correct or modify the imaged pattern. Kubota *et al.* reported the first positive imaging photosensitive poly(amic acid), in which an *o*-nitrobenzyl group was linked to the carboxylic acid by ester bond.⁴ Several attempts to synthesize positive working photosensitive polyimides which consist of poly(amic acid)s and *o*-diazonaphthoquinone (DNQ)⁵ or 1,4-dihydropyridine derivatives,⁶ polyimide containing hydroxy groups and DNQ,⁷ and polyimide based on polyisoimide precursor⁸ have been reported.

Significant advances are continually being made in microelectronic device fabrication, and espe-

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cially in lithography, the technique that is used to generate the high resolution circuit elements is characteristic of today's integrated circuits.⁹ These accomplishments have been achieved using conventional photolithography as the technology of choice. Incremental improvements in tool design and performance have allowed the continuous use of 350~450 μm light to produce ever smaller features.¹⁰ Unfortunately, conventional photore-sists are not appropriate for use with the new lithographic technologies that will be necessary for sub-0.5 μm lithography. The most notable deficiencies of the conventional novolac-quinone-diazide resists are the sensitivity and absorption properties of the materials. For most resists, the quantum yield is significantly less than 1.0, and since the new lithographic tools in general have low brightness sources, high sensitivity resists are required.

One approach to improve the sensitivity involves the concept of chemical amplification,¹¹ which employs the photogeneration of an acidic species that catalyze many subsequent chemical events such as deblocking of a protective group or depolymerization of the matrix polymer. The overall quantum efficiency of such reactions is thus effectively much higher than that for initial acid generation. The mechanism of chemically amplified depolymerization resist depends upon the incorporation of C-O bond into the polymer backbone which can be cleaved by either hydrolysis or acidolysis. Much of the work related to the design of chemically amplified resists that depolymerize upon catalytic cleavage of the polymer backbone has been done by Frechet *et al.*¹²⁻¹⁴ In these systems, the polymer film depolymerizes through thermally induced acid catalyzed cleavage of tertiary, secondary allylic, or secondary benzylic C-O bond, to form a stable carbocation with at least one alpha hydrogen. This carbocation can then eliminate to form an alkene with concomitant regeneration of the acid catalyst. Polycarbonates which incorporate tertiary carbonate units along the polymer backbone¹² have a thermal stability of 200 °C at which point they undergo decomposition to carbon dioxide and dienes.¹³ This decomposition may be accelerated by mild heating in the presence of photogenerated acid. Poly-

esters with tertiary, secondary allylic, and secondary benzylic units and polyethers containing the latter two groups were also prepared and evaluated as resist materials when used with onium salt photoacid generator materials.¹⁴ Resist systems formulated from these polymers and photoacid generator undergo acidolytic cleavage to afford a neutral olefin or aromatic compound plus a diacid or diol.

The primary aim of the work reported here was to synthesize new polyimides for positive working photosensitive polyimides based on chemically amplified thermolysis of backbone. Two diamines containing ester linkage and tetrahydronaphthalene moiety were synthesized to prepare photosensitive polyimides from pyromellitic dianhydride (PMDA) and 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA). Due to this allylic ester structure, these polyimides can undergo thermally activated multiple main chain cleavages catalyzed by photoacid generator.

Experimental

Materials. Pyromellitic dianhydride (PMDA) and 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (TCI Co.) were sublimed under reduced pressure before use. 1,5-Dihydroxy-1,2,3,4-tetrahydronaphthalene, 4-nitrobenzoyl chloride, 3-nitrobenzoyl chloride, and palladium on activated carbon (10%) (Aldrich Chem. Co.) were used without further purification. 1-Methyl-2-pyrrolidinone (NMP) (Aldrich Chem. Co.) was dried with calcium hydride and subsequently distilled under reduced pressure. All the chemicals used in this study were reagent grade and used without further purification.

Preparation of 1,5-bis(4-nitrobenzoate)-1,2,3,4-tetrahydronaphthalene (4-DNBTN). A solution of 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (5.00 g, 30.45 mmol) in tetrahydrofuran (THF) (350 mL) and triethyl amine (6.29 g, 62.12 mmol) was placed in a three necked round bottomed flask equipped with nitrogen inlet. Then 4-nitrobenzoyl chloride (11.52 g, 62.12 mmol) was added with stirring and the reaction mixture was refluxed for 3 h under nitrogen atmosphere. The reaction mixture was cooled down to room

temperature and the precipitated white salt was filtered off. After THF was removed by rotary evaporator, the residue was washed with 3% HCl aqueous solution, 3% NaHCO₃ aqueous solution, and water sequentially. The crude product obtained was recrystallized and dried under reduced pressure to afford 12.11 g (86%) of yellow powder: mp 176~178 °C IR (KBr) 3112 (CH aromatic stretching), 2930 (CH aliphatic stretching), 1744, 1719 (C=O), 1528, 1350 (N=O), and 1267 cm⁻¹(C-O); ¹H-NMR (CDCl₃) δ 8.1~8.5 (8H, aromatic), 7.3~7.5 (3H, aromatic), 6.3 (H, aliphatic), and 1.8~2.9 ppm (6H, aliphatic); Anal. Calcd for C₂₄H₁₈N₂O₈: C, 62.34%; H, 3.92%; N, 6.06%. Found: C, 62.07%; H, 3.86%; N, 5.99%.

Preparation of 1,5-bis(3-nitrobenzoate)-1,2,3,4-tetrahydronaphthalene (3-DNBTN). The dinitro intermediate, 1,5-bis(3-nitrobenzoate)-1,2,3,4-tetrahydronaphthalene (3-DNBTN) was prepared by the reaction of 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene and m-nitrobenzoyl chloride according to the method described above. The yield was 79%: mp 79~80 °C; IR (KBr) 3094 (CH aromatic stretching), 2945 (CH aliphatic stretching), 1748, 1719 (C=O), 1533, 1351 (N=O), and 1256 cm⁻¹(C-O); ¹H-NMR (CDCl₃) δ 7.1~9.2 (11H, aromatic), 6.4 (H, aliphatic), and 1.8~3.0 ppm (6H, aliphatic); Anal. Calcd for C₂₄H₁₈N₂O₈: C, 62.34%; H, 3.92%; N, 6.06%. Found: C, 62.09%; H, 3.88%; N, 6.00%.

Preparation of 1,5-bis(4-aminobenzoate)-1,2,3,4-tetrahydronaphthalene (4-DABTN). A solution of 4-DNBTN (3.0 g, 6.5 mmol) in ethyl acetate (150 mL) containing palladium on activated carbon (10%, 0.15 g) was placed in a hydrogenation apparatus. The mixture was agitated under hydrogen at room temperature for 3 h. The mixture was filtered and the solvent was removed on rotary evaporator. The residue was recrystallized in ethanol and dried under reduced pressure to afford 2.15 g (82%) of white crystal: mp 191~193 °C; IR (KBr) 3393, 3334, 3234 (NH stretching), 2945 (CH aliphatic stretching), 1701 (C=O), 1605 (NH bending), 1258 (C-O), and 1162 cm⁻¹(C-N); ¹H-NMR (CDCl₃) δ 6.5~7.9 (11H, aromatic), 5.9~6.3 (4H, NH₂), 6.1 (H, aliphatic), and 1.6~2.8 ppm (6H, aliphatic); Anal.

Calcd for C₂₄H₂₂N₂O₄: C, 71.63%; H, 5.51%; N, 6.96%. Found: C, 71.43%; H, 5.26%; N, 6.67%.

Preparation of 1,5-bis(3-aminobenzoate)-1,2,3,4-tetrahydronaphthalene (3-DABTN). 1,5-Bis(3-aminobenzoate)-1,2,3,4-tetrahydronaphthalene (3-DABTN) was prepared from the hydrogenation reaction of 3-DNBTN according to the method described above. The yield was 85%: mp 74~75 °C; IR (KBr) 3451, 3360, 3225 (NH stretching), 2934 (CH aliphatic stretching), 1733, 1696 (C=O), 1601 (NH bending), 1214 (C-O), and 1060 cm⁻¹(C-N); ¹H-NMR (CDCl₃) δ 6.8~7.6 (11H, aromatic), 6.2 (H, aliphatic), 5.3~5.7 (4H, NH₂), and 1.8~2.8 ppm (6H, aliphatic); Anal. Calcd for C₂₄H₂₂N₂O₄: C, 71.63%; H, 5.51%; N, 6.96%. Found: C, 70.37%; H, 5.19%; N, 6.54%.

Synthesis of Polyimides. A 50 mL round-bottom flask with a nitrogen inlet were charged with 4-DABTN (1.500 g, 3.727 mmol) and NMP (15 mL). After 4-DABTN was dissolved completely, PMDA (0.813 g, 3.727 mmol) was slowly added. The reaction mixture was stirred under nitrogen for additional 24 h at room temperature. Other poly(amic acid)s were also prepared from the reaction of 4-DABTN or 3-DABTN with PMDA or 6FDA.

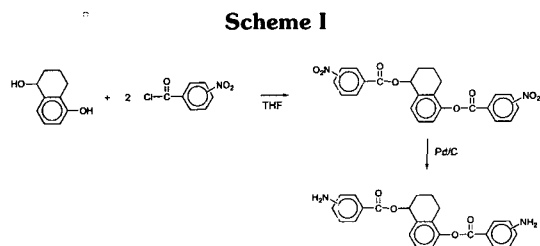
For thermal imidization, the poly(amic acid) was cast on a glass plate. The poly(amic acid) film was dried at 70 °C under reduced pressure and heated gradually to 250 °C. For chemical imidization, the poly(amic acid) was diluted with NMP. After acetic anhydride and triethyl amine were added, the reaction mixture was vigorously stirred at room temperature for 24 h under nitrogen. The polymer was isolated by precipitation in ethanol with stirring. The precipitate was collected by filtration, washed with ethanol and dried under reduced pressure. The polyimide was dissolved in NMP and the polyimide solution was coated on the glass substrate, and dried at 150 °C under vacuum. This film was taken off from the glass with aid of deionized water.

Measurements. ¹H-NMR spectra were measured using a Varian Unity Plus 300 NMR spectrometer in DMSO-d₆ and CDCl₃ solvents. Chemical shifts were calibrated with the chemical shift of the used solvent. FT-IR spectra were measured

using a Bruker IFS 66 FT-IR spectrometer with the KBr pallet disc. The inherent viscosity of poly-(amic acid)s was measured in NMP at 30°C using a Cannon-Fenske capillary viscometer. Thermogravimetric analysis (TGA) was carried out for the polyimide films using a Shimadzu TGA-50 thermogravimetric analyzer under a dry nitrogen flow. The sample was heated up to 800°C with a heating rate of 10°C/min.

Results and Discussion

Monomer Synthesis. The syntheses of diamines containing tetrahydronaphthalene ester moiety were carried out according to Scheme I. The dinitro intermediate, 4-DNBTN, was synthesized through the reaction of 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene and 4-nitrobenzoyl chloride. 3-DNBTN was also synthesized from 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene and 3-nitrobenzoyl chloride. The dinitro intermediate, 4-DNBTN, was converted to corresponding 4-DABTN through the hydrogenation reaction using palladium as a catalyst. FT-IR and $^1\text{H-NMR}$ of 4-DABTN were shown in Figure 1 and Figure 2. In Figure 1, prominent bands arising from NH_2 group show at 3393, 3334, and 3234 cm^{-1} . A sharp band at 1701 cm^{-1} assigned to $\text{C}=\text{O}$ group was observed. Figure 2 shows the aromatic proton peaks at 6.8~7.6 ppm and aliphatic proton peaks of tetrahydronaphthalene unit at 1.6~2.8 ppm. 3-DNBTN was converted to corresponding 3-DABTN in the same way as 4-DABTN. FT-IR and $^1\text{H-NMR}$ of 3-DABTN were shown in Figure 3 and Figure 4. The FT-IR spectrum shows absorption bands assigned to N-H bond at 3451, 3360, and 3225 cm^{-1} . The absorption band of $\text{C}=\text{O}$ group was observed at 1733 and 1696 cm^{-1} . Peaks in Figure 4 are assigned to the aromatic protons at



6.8~7.6 ppm and aliphatic proton peaks of tetrahydronaphthalene unit at 1.8~2.8 ppm.

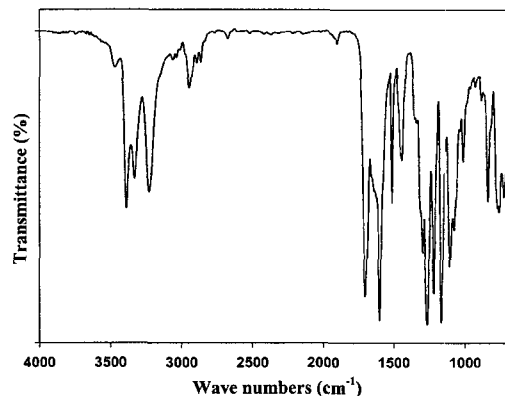


Figure 1. IR spectrum of 4-DABTN.

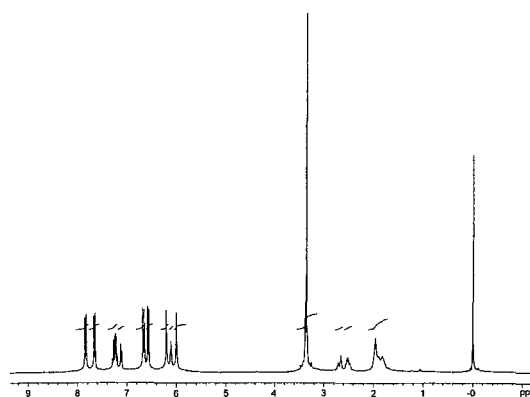


Figure 2. $^1\text{H-NMR}$ spectrum of 4-DABTN.

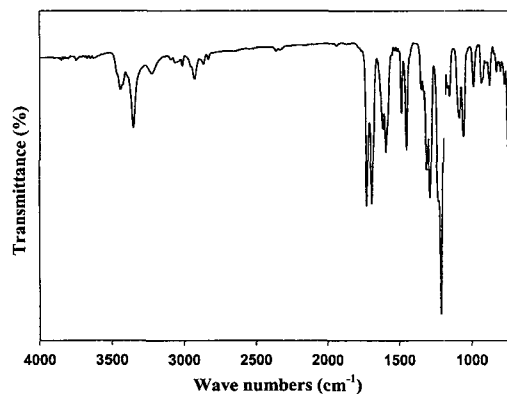
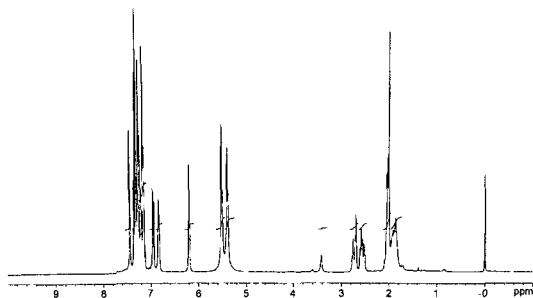


Figure 3. IR spectrum of 3-DABTN.


 Figure 4. $^1\text{H-NMR}$ spectrum of 3-DABTN.

Synthesis of Polyimides. The polymerization of 4-DABTN or 3-DABTN with PMDA or 6FDA through the standard poly(amic acid) synthetic route produced a highly viscous solution (Scheme II). The inherent viscosity of poly(amic acid)s is summarized in Table I.

For conversion of poly(amic acid)s to the corresponding polyimides, both thermal and chemical imidization were tried. But in case of thermal imidization, the resulting polyimide films were very brittle. We expect that acid groups of poly(amic acid) may catalyze main chain cleavage during the thermal imidization. However, tough polyimide films were obtained by the chemical imidization and solution film casting of resulting polyimides. FT-IR spectra of the polyimide films were shown in Figure 5. Several characteristic absorption bands of imide groups were observed at 1780 cm^{-1} (C=O asymmetrical stretching), 1380 cm^{-1} (C-N stretching), and 725 cm^{-1} (C=O bending).

In Figure 6, TGA thermograms showed 5% weight loss between $323\sim 389\text{ }^\circ\text{C}$ under nitrogen atmosphere. These results indicate that polyimides containing tetrahydronaphthalene ester moi-

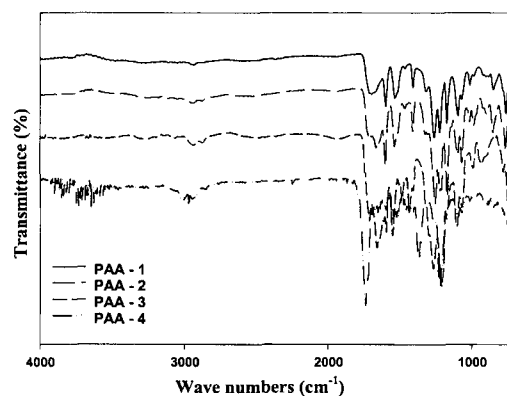
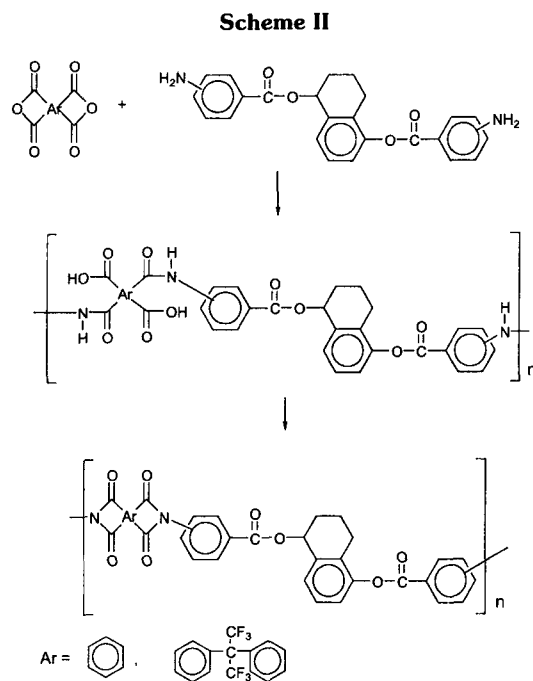


Figure 5. IR spectrum of poly(amic acid)s.

Table I. Properties of Poly(amic acid)s and Polyimides

Diamine	Dianhydride	Poly(amic acid)s		Polyimides	
		Poly(amic acid)s	Inherent Viscosity(dL/g)	Polyimides	TGA ^a
4-DABTN	PMDA	PAA-1	0.56	PI-1	389
4-DABTN	6FDA	PAA-2	0.55	PI-2	323
3-DABTN	PMDA	PAA-3	1.31	PI-3	382
3-DABTN	6FDA	PAA-4	0.86	PI-4	343

^a Temperature at which 5% weight loss occurred with a heating rate of $10\text{ }^\circ\text{C/min}$ in nitrogen.

Scheme III

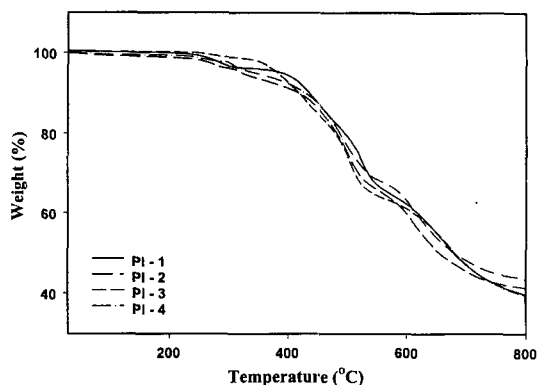
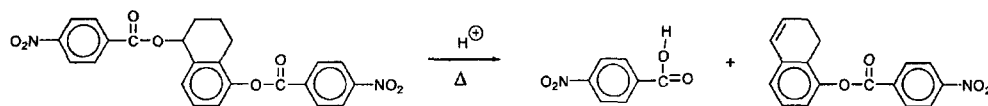


Figure 6. TGA thermogram of polyimides in nitrogen.

ety have relatively low thermal stability, compared to conventional polyimides.

Acid-Catalyzed Decomposition. Polyimides containing allylic ester structure may be patterned with a small amount of photoacid generator. In the exposed area, radiation of appropriate wavelength causes decomposition of the photoacid generator with the liberation of catalytic amounts of strong acid, then these strong acid decompose allylic ester structure. So, this leads to the positive imaging of the polyimide. In this study, acid-catalyzed decomposition of 4-DNBTN as a model compound was carried out. 4-DNBTN was dissolved in CDCl_3 and small amount of CF_3COOH as an acid catalyst was added. Figure 7 is the $^1\text{H-NMR}$ spectra before and after CF_3COOH treatment of 4-DNBTN. After CF_3COOH treatment, aliphatic proton peaks of tetrahydronaphthalene moiety at 2.0 and 6.4 ppm disappeared and new proton peaks of carbon-carbon double bond were observed at 6.1 and 6.5 ppm. From this result, we are confident that 4-DNBTN was decomposed to 4-nitrobenzoic acid and 5-(4-nitrobenzoate)-3,4-dihydronaphthalene with the assistance of the acid catalyst (Scheme III).

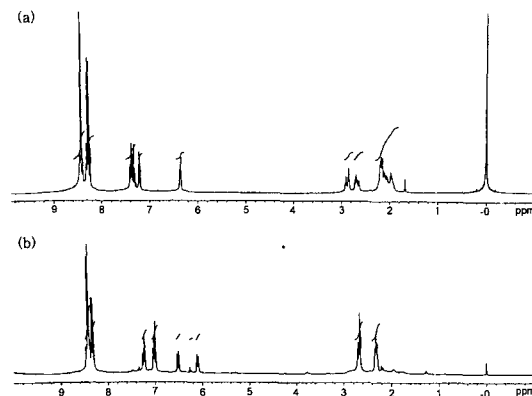


Figure 7. $^1\text{H-NMR}$ spectra of 4-DNBTN. (a) before CF_3COOH treatment and (b) after CF_3COOH treatment.

Conclusions

New diamine monomers containing allylic ester linkage were synthesized from 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene and 4- or 3-nitrobenzoyl chloride. Poly(amic acid)s were obtained by the reaction of these diamines with PMDA or 6FDA. Acid catalyzed thermolysis of the model compound demonstrated the feasibility of these polyimide as photosensitive polyimides.

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