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Synthesis of Novel Positive Type Photosensitive Polyimide

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Abstract : Tricyclic aliphatic dianhydride monomer, tricyclo[4.2.2.0]dec-9-ene-*exo,endo*-3,4:7,8-tetracarboxylic dianhydride (TCDDA), was synthesized by photochemical reaction and poly(amic acid)s from TCDDA and diamines such as 1,4-bis-(4-aminophenoxy)benzene (BAB), 2,2-bis(4-(4-aminophenoxy) phenyl) propane (BAPP), 2,2-bis(4-(4-aminophenoxy)phenyl)hexafluoropropane (BAPHF), bis(4-(4-aminophenoxy) phenyl)sulfone (BAPS), and 1,4-bis-(4-aminophenoxy)biphenyl (BABP) were prepared. The inherent viscosities of the poly(amic acid)s were between 0.39 and 0.50 dL/g. The poly(amic acid)s were converted to polyimide films by thermal imidization. The glass transition temperatures (T_g) of the polyimides were in the range of 201~263°C. The thermogravimetric analysis (TGA) thermogram of these polyimides showed the temperatures of 5% weight losses between 375 and 393°C in nitrogen atmosphere. To show their utility for image generation, degradations of these polyimides in UV exposure were investigated by UV spectroscopy.

Introduction

Polyimides have found usage as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance,

and dimensional stability.¹ Attempts are being made to use polyimides for different applications in variety of advanced technologies. Interest in these materials is particularly high in areas related to electronics, where miniaturization, large-scale integration, and high speed signal processing in semiconductor-based components are important technical issues. In order to satisfy these high ex-

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pectations, stringent and highly varied requirements have been placed on the properties of polyimide, including, high thermal resistance, high purity, high chemical resistance, high adhesion, high planarity, low dielectric constant, low thermal expansion, and, in some cases, high transparency and high refractivity. It is impossible for a single system to satisfy all of these requirements, so at present polyimides having different chain structures are used, according to the particular application.^{2,3}

In many applications, polyimide layers must be patterned to open connection or bonding windows, or to delineate dielectric or masking structures. Several options are available to pattern polyimides. These options include direct ultraviolet (UV) laser photoablation, reactive ion etching (RIE) or scanning laser ablation (SLA) through a soft or a hard mask, wet etching, and the use of a photosensitive polyimide. The choice of a patterning technology is a trade-off between the quality of the desired pattern (resolution, shape, sidewall slope, and roughness) and practicability in the industrial environment. Final property of the cured polymer is also an important parameter, since RIE and photoablation can be performed on any type of polyimide, but wet etching and direct photopatterning require specific formulations.^{4,7}

The use of photosensitive polyimide is a growing trend for some applications of polyimides, in which processing cost is an overriding factor and pattern geometries are compatible with their performances.⁸ This is especially the case for protection layers and high-density interconnects. It is evident that pattern definition is simpler with a photosensitive polyimide, since it only needs UV light exposure and development of the film before full cure. Photosensitive polyimide patterning can be performed on existing equipment used for usual photoresist patterning. By eliminating the use of a resist, the polyimide patterning process can be shortened by up to one-half. It is a simplified process and thus increases process stability and yield. Patterning photosensitive polyimide is inherently a clean process compared to particle-generating processes such as RIE or photoablation. Photosensitive polyimide process does not need toxic etchants compared to wet etching. Photosensitive polyimide patterning is an open-air process and,

unlike RIE, is compatible with large area processing.

The first photosensitive polyimide was a system obtained by adding bichromate to poly(amic acid) reported by Kerwin and Goldrick in 1971.⁹ However, since the shelf-life of the solution was extremely short and metallic residue was present in the polyimide film after curing, the bichromate type polyimide was not practical. Later, Rubner *et al.* reported a practical system: the poly(amic acid) was esterified by some acryloyl groups.¹⁰⁻¹² The system showed excellent storage stability. It was also possible to make a pattern from thick film.

However commercially available photosensitive polyimides are all of negative type. 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.¹³ Kubota *et al.* reported the first positive imaging photosensitive poly(amic acid), in which an ortho-nitrobenzyl group was linked to the carboxylic acid by ester bond. It is also possible with positive resists to irradiate again after a first development step in order to correct or modify the imaged pattern.¹⁴ Several attempts to synthesize positive working photosensitive polyimides¹⁵ or related polymers such as polybenzoxazoles have been reported.

The primary aim of the work reported here was to synthesize new polyimides for positive working photosensitive polyimide. Tricyclic aliphatic dianhydride monomer, tricyclo[4.2.2.0]dec-9-ene-*exo*, *endo*-3,4:7,8-tetracarboxylicdianhydride (TCDDA), was synthesized by photochemical reaction and soluble poly(amic acid)s from TCDDA and several diamines containing diphenyl ether group were prepared. Photoimaging can be accomplished, even after complete thermal curing to form the polyimide structure. To show their utility for image generation, degradations of these polyimides in UV exposure were investigated by UV spectroscopy.

Experimental

Materials. 2,2-Bis(4-(4-aminophenoxy)phenyl)propane (BAPP), 2,2-bis(4-(4-aminophenoxy)

phenyl)hexafluoropropane (BAPHF), bis(4-(4-aminophenoxy)phenyl)sulfone (BAPS), 1,4-bis(4-aminophenoxy)benzene (BAB), and 1,4-bis(4-aminophenoxy)biphenyl (BABP) were purchased from TCI Co., Ltd. and used without further purification after vacuum drying at 100°C for 1 day. Maleic anhydride and benzene (thiophene-free) were purchased from Aldrich Chem. Co., Ltd. 1-Methyl-2-pyrrolidinone (NMP) (Aldrich Chem. Co., Ltd.) was dried with calcium hydride (CaH₂) and subsequently distilled under reduced pressure. Other chemicals were reagent grade and used without further purification.

Synthesis of Tricyclo[4.2.2.0]dec-9-ene-*exo*,*endo*-3,4:7,8-tetracarboxylic dianhydride (TCDDA). TCDDA was prepared according to a method of Grovenstein, Jr. and co-workers.¹⁶ A solution of maleic anhydride (118 g, 1.20 mol) in acetone (100 mL) and benzene (125 mL, thiophene-free) was placed in a water-cooled quartz cell which encircles a medium-pressure Hanovia lamp. After 25 h of irradiation, white crystals deposited on the wall of the cell were collected and washed with acetone to give 10.5 g of product. Another 6.5 g of product was recovered by evaporation of the reaction solution, boiling the residue with 200 mL of acetone to dissolve unreacted maleic anhydride, and separation of the adduct by filtration. The total yield was about 17.0 g (10%): mp 355~357°C.

Synthesis of Poly(amic acid)s. To a 50 mL, 3 neck, round bottom flask equipped with an overhead stirrer and N₂ inlet, were added 1,4-bis(4-aminophenoxy)benzene (BAB) (1.066 g, 3.647 mmol) and NMP (13 mL). After BAB was dissolved completely, TCDDA (1.0 g, 3.647 mmol) was added slowly with stirring. The reaction mixture was stirred for 24 h at room temperature. The poly(amic acid) solution should be kept in a refrigerator in order to prevent its decomposition. Other poly(amic acid)s were prepared in the same manner.

Preparation of Polyimide Films. The poly(amic acid)s were coated on the glass substrate, followed by softbaking on a hot plate at 80°C for 1 h. The softbaked precursor films were thermally imidized in a drying oven under dried N₂ gas flow by a step imidization protocol; 100°C for 30 min,

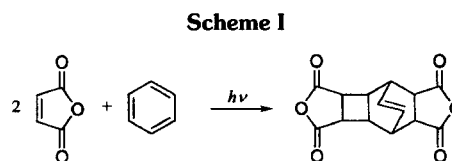
130°C for 30 min, and 250°C for 60 min. The heating rate was 2°C/min for all processes. After the thermal imidization, the samples were cooled to room temperature. The polyimide films were isolated with the aid of deionized water, followed by drying for 2 days at 50°C in a vacuum oven.

Measurements. ¹H-NMR and ¹³C-NMR spectra were measured using a Varian Unity Plus 300 NMR spectrometer in DMSO-d₆ and CDCl₃. 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 pellet disc. The inherent viscosity of poly(amic acid)s was measured in NMP at 30°C using a Cannon-Fenske capillary viscometer. DSC thermograms of polyimide films were measured using a TA Instruments 2100 differential scanning calorimeter. During the measurement, dried N₂ gas was purged with a constant flow rate. The 10°C/min of ramping rate was employed. Thermogravimetric analysis (TGA) was carried out for the polyimide films using a Shimadzu TGA-50 thermogravimeter under a dry nitrogen flow. The sample was heated up to 800°C with a heating rate of 10°C/min. UV spectra were obtained using a Perkin-Elmer Lambda-20 spectrometer.

Results and Discussion

Synthesis of TCDDA. TCDDA was synthesized through the photochemical reaction from maleic anhydride and benzene as shown in Scheme 1.¹⁶ ¹H-NMR and ¹³C-NMR spectra of TCDDA obtained were in agreement with the structure as shown in Figure 1. The UV spectrum of TCDDA is shown in Figure 2. TCDDA showed absorption maximum at 266 nm.

Synthesis of Poly(amic acid)s. The polymerization of the TCDDA monomer and several diamines containing diphenyl ether groups through the standard poly(amic acid) synthetic route typically proceeded well to give a highly viscous solu-



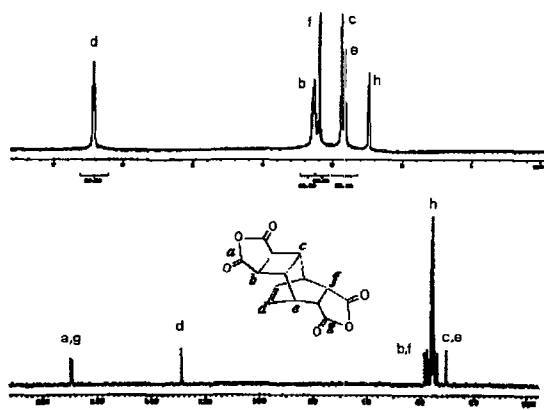


Figure 1. ¹H-NMR and ¹³C-NMR spectra of TCDDA.

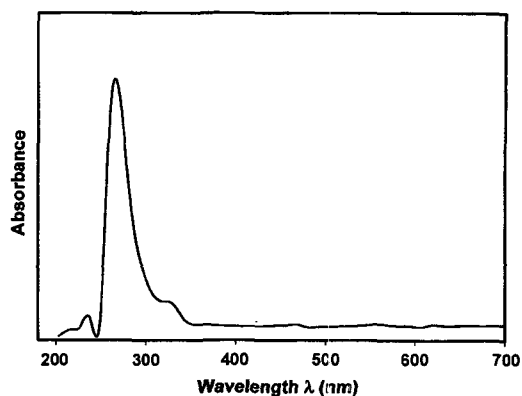
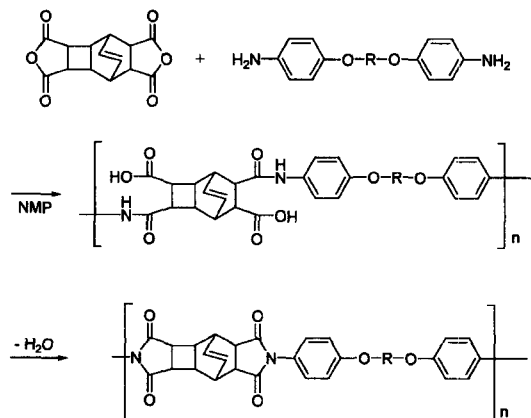


Figure 2. UV spectrum of TCDDA.

Scheme II



percent due to different chemical and structural nature of diamines, all poly(amic acid)s gave tough films when thermally imidized to corresponding polyimides. Table I shows the chemical structures of diamines and inherent viscosities of the poly(amic acid)s.

Preparation of Polyimide Films. All poly(amic acid)s thermally converted to polyimides by a step imidization process. FT-IR spectra of all polyimides are shown in Figure 3. Several characteristic absorption bands were used for the quantification of five-membered aromatic imides. The strongest absorption occurred at 1720 cm⁻¹ (C=O symmetrical stretching). 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).

tion (Scheme II). Although the viscosities of poly(amic acid)s were different at the same weight

Table I. Viscosities of Poly(amic acid)s

Dianhydride	Diamine		Inherent Viscosity (dL/g)
TCDDA		(BAB)	0.42
TCDDA		(BABP)	0.50
TCDDA		(BAPP)	0.36
TCDDA		(BAPS)	0.43
TCDDA		(BAPHF)	0.39

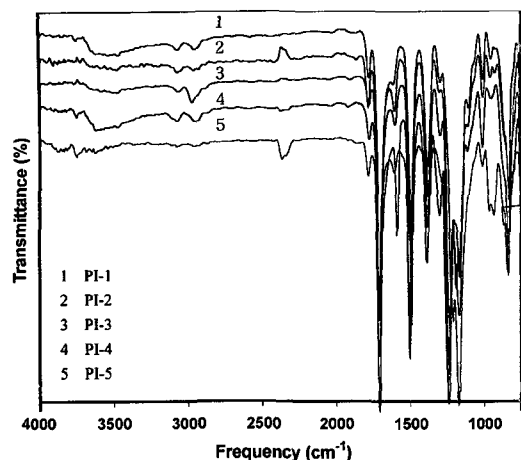


Figure 3. FT-IR spectra of polyimide films.

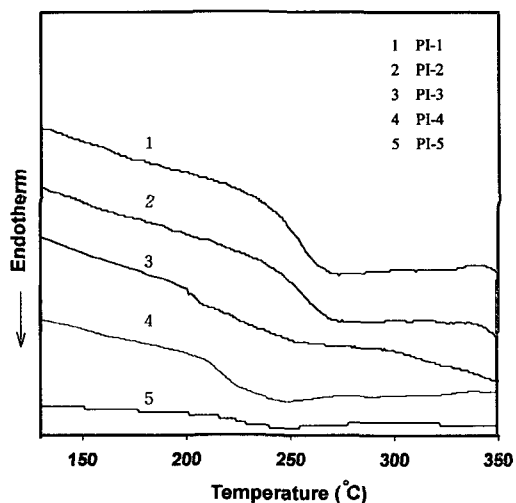


Figure 4. DSC thermograms of polyimides.

Thermal property was dependent upon the structure of the diamine moiety. Their thermal stabilities were not so good, because they had aliphatic structure and ether linkages in polymer chain.

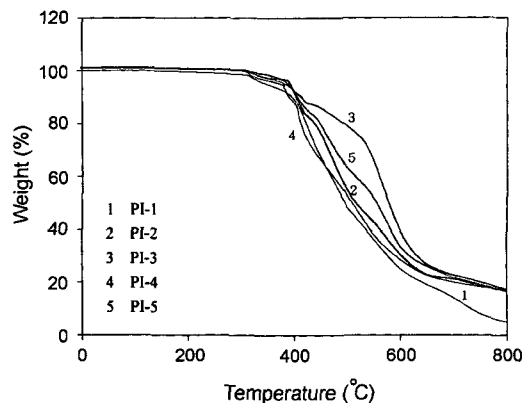


Figure 5. TGA thermograms of polyimides.

DSC thermograms of polyimide films are shown in Figure 4. The glass transition temperatures (T_g) were in the range of 201~264°C (Table II). Their glass transition behaviors depend on the diamine structures, and TCDDA-BABP polyimide had the highest T_g among them due to rigid main chain structure. Thermogravimetric curves of polyimides are shown in Figure 5. Decomposition occurred in the range of 375~393°C. These results indicate that polyimides containing TCDDA monomer have relatively low thermal stability compared with conventional aromatic polyimides (Table II).

Photodegradation of Polyimides. Polyimides containing TCDDA moiety may be patterned with UV irradiation. In the exposed area, irradiation of UV with an appropriate wavelength causes decomposition of the TCDDA moiety, and this leads to the positive imaging of the polyimide. To identify photosensitivity of the polyimides, poly(amic acid)s were coated on the glass substrate, followed by softbaking at 80°C for 1 h. The softbaked precursors were thermally imidized and irradiated at 254 nm of UV. Photodegradation of the polyimides containing TCDDA moiety is sup-

Table II. Thermal Properties of Polyimides

Polyimides	Dianhydride	Diamine	T_g (°C)	Temp. of 5% Weight Loss (°C)
PI-1	TCDDA	BAP	262	393
PI-2	TCDDA	BABP	264	388
PI-3	TCDDA	PAPP	201	390
PI-4	TCDDA	BAPS	223	375
PI-5	TCDDA	BAPHF	228	380

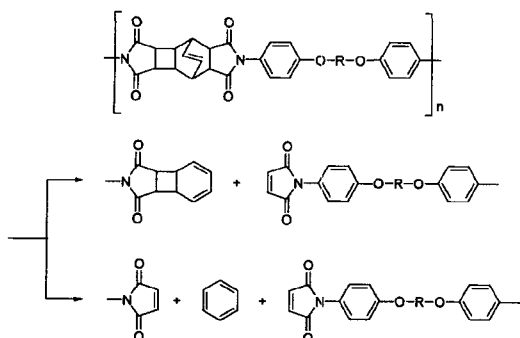


Figure 6. Photodegradation mechanism of polyimides containing TCDDA moiety.

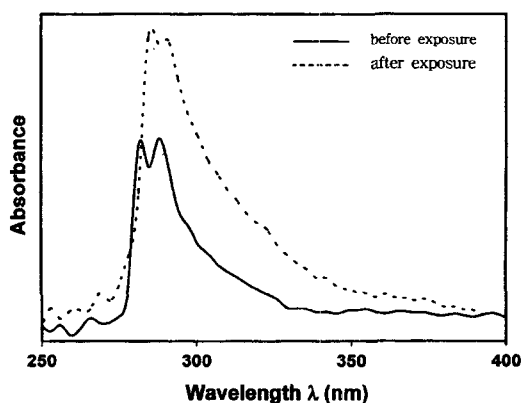


Figure 7. Change in UV absorption of the polyimides containing TCDDA moiety.

posed to occur in two ways as shown in Figure 6. As photodegradation occurs in the main chain of the polyimide, the maleimide moieties increase. After irradiation, UV absorption peak of the polyimides increased with time as the maleimide moieties were increased by cleavage of the TCDDA structure in the polyimide main chains (Figure 7). So, these polyimides are decomposed by irradiation at a wavelength that corresponds to energy absorption by the TCDDA, and can be used as positive-imaging materials.

Conclusions

A new dianhydride monomer, TCDDA, was synthesized from maleic acid and benzene. Polyimide films were obtained by the reaction of TCDDA with various aromatic diamines contain-

ing ether moiety. The change of UV absorption before and after the UV irradiation of the polyimide films demonstrated the feasibility of these polyimide as photosensitive materials.

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