Chem. Mater. **1996,** *8,* 1029−1034

Novel Negative-Type Soluble Photosensitive Polyimides: Synthesis and Characterization

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Received July 11, 1995. Revised Manuscript Received February 22, 1996[⊗]

In the present paper, we describe the synthesis and characterization of a novel negative-type soluble photosensitive polyimide (PSPI). A group of new photosensitive polyimides has been prepared by condensation of dianhydrides bearing photoreactive ester groups and aromatic diamines in *N*-methylpyrrolidone (NMP), followed by chemical imidization using acetic anhydride without acid acceptors such as pyridine or triethylamine. Thus, the starting monomer used in the synthesis of a commercial aromatic polyimide has been chemically modified with four different photosensitive groups (chlorine-free synthesis). All the intermediates as well as the resulting polymers have been characterized. The PSPI esters were found to be soluble in *N*-alkyl-substituted amides. Their irradiation with UV light induces cross-linking of the photoreactive ester groups. These systems change from being weakly to being heavily cross-linked during irradiation and do not swell during development. The remaining PSPI esters do not require thermal imidization because they are already imidized, and shrinkage is about 20% due to volatilization of photoreactive groups.

Introduction

Photosensitive polyimide has recently attracted considerable attention in the microelectronics industry due to the simple fabrication process based on their direct patternability.[1−3] Since these reports, several types of photoreactive polyimides and their precursors have been studied. Being insoluble in most common solvents, polyimides are usually processed in the form of their precursor poly(amic acids),[4−6] which are then thermally converted to the imide structure. Kerwin and Goldrick first reported on this kind of photopolymers, which includes poly(amic acid) and sodium dichromate as a photoreactive additive.[7] The application of this material to electronic devices seems to be fruitless because of instability of the polymer solution and contamination by residual chromic ions. The first reports on a material applicable to microelectronics devices were by Rubner et al.[8,9] They described negative-type photosensitive polyimide precursors, in which a photoreactive methacryl group was introduced to the polymer side chain by esterification of carboxyl groups of a poly(amic acid). Alternatively, Yoda and Hiramoto demonstrated a different way of introducing the photoreactive groups.[10] In their material, an amino compound with a photoreactive methacryl group is added to a poly(amic acid) as a photoreactive additive, and the methacryl group is incorporated by a salt formation reaction between the amino group of the photosensitive additive with the carboxylic acid group of the poly(amic acid). Kataoka et al. described highly photosensitive materials containing aromatic azide compounds as a photosensitive additive.[11−12]

Low curing temperatures for PSPI are desired for applications in microelectronics because high temperatures may cause some problems, especially when the polyimide is used in manufacture of liquid-crystal image sensors and some hybrid integrated circuits which are sensitive to heat.[13] The lowest practical temperature that leads to complete curing is 350 °C for all types of PSPI (according to ref 13). During the curing of PSPI precursors at least three processes take place. Residual solvent evaporates, water or alcohols (depending on the type of precursor) are eliminated in the cyclization

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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S0897-4756(95)00318-8 CCC: $12.00

reaction to the polyimide, and photoreacted groups are depolymerized and released. The release of these components results in film thickness shrinking by about 50% during the curing of PSPI precursors of the ester-like type. This shrinkage is the reason for the "crowning" effect in holes or lines.[13]

Therefore, there is a great interest in fully imidized PSPIs which offer lower shrinkage (<20%) and should not need curing temperatures as high as those for precursors. However, few examples have been reported up to now.[14−18] A soluble, intrinsically photosensitive polyimides (negative working) based on benzophenone and thioxanthone chromophores were first reported by Pfeifer and Rhode at the 1985 Ellenville Polyimide Conference.[14] In this case, the cross-linked network is not volatized, as is the case with ester- or salt-like photo-cross-linkable precursors. Copolyimides which contain diaminobenzoic acid as comonomer are also soluble. They can be made photoreactive by esterification of the free carboxylic acid with methacrylic acid glycidyl ester, as reported by Lee and Lee.[18]

To date, the properties of the commercially available PSPI are not as good as desired for multilevel interconnect applications.[13] Most negative-acting PSPIs swell in the developing solution, resulting in poor resolution characteristics. Swelling, shrinkage, and storage stability are still of concern in some of the negative systems.

In this article, we report the preparation of a new, soluble photosensitive homopolyimides carrying photosensitive groups as a side chain of the fully imidized polyimide backbone. The photosensitive functional groups were incorporated in the dianhydride comonomer through the reaction between an alcohol group of benzhydrol tetracarboxylic dianhydride (BHTDA) and an acid group of four photosensitive groups, methacrylic, acrylic, furylacrylic, and cinnamic in solution in dichloromethane (DCM).

Experimental Section

Materials. BHTDA **1**, kindly provided by CEMOTA, was purified by Soxhlet extraction with diethyl ether[19] and dried in a vacuum oven to give the product, mp 183 °C, in 75% yield; ^{1}H NMR (dimethyl sulfoxide-d_6) δ 8.1−8.4 ppm (m, Ar H, 6H) 6.81 ppm (d, OH, 1H), 6.23 ppm (d, −CH−, 1H); ^{13}C NMR (DMSO-d_6) δ 163.17, 162.97, 153.21, 134.01, 131.93, 130.43, 125.79, 122.81, 72.66; IR (KBr) ν 3517(s, OH) cm^{-1}, 1858 and 1784 (s, C=O) cm^{-1}. Anal. Calcd for $C_{17}H_8O_7$: C, 62.96; H, 2.46. Found: C, 62.75; H, 2.68.

The aromatic diamines, oxydianiline (ODA) and methylene dianiline (MDA), were obtained from Merck and used without further purification. All of the other reagents and solvents are commercially available and were used after appropriate purification in the normal manner.

Analytical Equipment and Techniques. IR spectra were recorded on a Bruker IFS 45 infrared Fourier transform spectrometer. The FT-IR samples were prepared by casting films of the materials on KBr plates. UV spectra were taken on a Varian Cary 219 spectrophotometer. The spectra were recorded in quartz cells (10 mm path length). ^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were obtained with a Bruker ACE 200 spectrometer. Chemical shifts were given in parts per million from tetramethylsilane at 0 ppm. The structures of compounds were confirmed by elemental analysis (Analytical Department of the University of Pierre and Marie Curie, Paris, France). Viscosity was measured at 30 °C using a Canon Ubbelohde type viscometer. The film thickness was recorded with a Mettler TMA 40. Ultrasonic development was carried out by using a Bransonic ultrasonic cleaner model B2200 (47 kHz). Thermogravimetric analysis (TGA) was performed under N_2 atmosphere on a Mettler DSC 30 at a heating rate of 10 °C/min. Dielectrical measurements were carried out in the temperature range 30−350 °C and at 1−200 kHz frequencies with an Analyzer 2970 TA Instrument.

(A) Synthesis of BHTDA Derivatives (Scheme 1). *Synthesis of Cinnamoyloxymethylene Ester Dianhydride (2).* The synthesis of **2** is given as a typical synthetic example.[19] To a solution of cinnamic acid (2 g, 13 mmol) in 10 mL of DCM was added at 0 °C a solution of dicyclohexylcarbodiimide (DCCI, 3 g, 14 mmol) in 10 mL of DCM. The reaction mixture was stirred at this temperature for 30 min, then **1** (4.18 g, 14 mmol) and *N*,*N*-(dimethylamino)pyridine (DMAP, 1 g, 8 mmol as a catalyst were added. After complete addition, the solution was stirred for 1 h at 0 °C, and for several hours at room temperature. The dicyclohexylurea (DCU) does not dissolve in this solvent and was removed from the reaction mixture by filtration. The reaction mixture was extracted with HCl(aq) (0.5 M, 1 × 20 mL) and water (2 × 25 mL) and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation at room temperature, and the yellow solid was dissolved in acetic anhydride. After 24 h, acetic anhydride was removed by rotary evaporation and the product was purified by successive precipitation from DCM into petroleum ether and subsequently dried at 40 °C under vacuum to yield **2** as a white powder (yield 4.9 g, 80%).

For **2**: ^{1}H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.87 (d, 1H, vinyl), 7.8−7.4 (m, 5H, ArH), 7.35 (s, 1H, −CH−), 6.95 (d, 1H, vinyl); IR (KBr) ν 1853, 1781 (s, C=O anhydride), 1722 (s, C=O ester), 1637 (s, C=C) cm^{-1}.

Synthesis of Furylacryloyloxymethylene Ester Dianhydride (3). Compound **3** was prepared from furylacrylic acid by following the same procedure as described for **2**.

For **3**: ^{1}H NMR (DMSO-d$_6$) δ 8−8.5 (m, 6H, ArH), 7.9 (s, 1H, furan), 7.87 (d, 1H, vinyl), 7.41 (s, 1H, −CH−), 7 (d, 1H, furan), 6.62 (m, 1H, furan), 6.5 (d, 1H, vinyl); IR (KBr) ν 1853, 1781 (s, C=O anhydride), 1719 (s, C=O ester), 1636 (s, C=C) cm^{-1}.

Synthesis of Methacryloyloxymethylene Ester Dianhydride (4). Compound **4** was prepared from methacrylic acid by following the same procedure as described for **2**.

For **4**: ^{1}H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.35 (s, 1H, −CH−), 6.49 (d, 1H, vinyl), 5.9 (d, 1H, vinyl), 2.1 (s, 3H, CH_3); IR (KBr) ν 1853, 1781 (s, C=O anhydride), 1722 (s, C=O ester), 1638 (s, C=C) cm^{-1}.

Synthesis of Acryloyloxymethylene Ester Dianhydride (5). Compound **5** was prepared from acrylic acid by following the same procedure as described for **2**.

For **5**: ^{1}H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.35 (s, 1H, −CH−), 6.5 (m, 2H, vinyl), 6.11 (m, 1H, vinyl); IR (KBr) ν 1853, 1781 (s, C=O anhydride), 1722 (s, C=O ester), 1624 (s, C=C) cm^{-1}.

(A) Synthesis of Model Imide Compounds (Scheme 2). *Synthesis of Bis(N-phenylphthalimid-3-yl)methyl Cinnamate (6).* The synthesis of **6** is given as a typical synthetic example.[19] An amine solution was prepared by dissolving 0.41 g (4.4 mmol) of aniline in NMP. BHTDA cinnamate ester 1.0 g (2.2 mmol) was gradually added to the amine solution under a nitrogen atmosphere. The reaction mixture was stirred for 12 h at ambient temperature, to which was then added 2.0 mL of acetic anhydride as a dehydrating agent for chemical imidization. The solution was mechanically stirred for 24 h at room temperature. After the reaction was completed, the solution was poured into 50 mL of dry, ice-cold methanol. The precipitated product was washed with large amounts of distilled water to remove occluded acetic acid and purified by

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chromatography on a silica column ($CHCl_3$/hexane 1/1) followed by recrystallization from *n*-hexane/DCM. The product was dried under high vacuum for 16 h to yield **6** as a white powder (yield 0.89 g, 67%).

For **6**: ^1H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.87 (d, 1H, vinyl), 7.5 (m, 15H, ArH), 7.35 (s, 1H, −CH−), 6.95 (d, 1H, vinyl); IR (KBr) ν 1779, 1722 (s, C=O imide, ester), 1635 (s, C=C) cm^{-1}. Anal. Calcd for $C_{38}H_{24}N_2O_6$: C, 75.49; H, 3.90; N, 4.63. Found: C, 75.37; H, 3.95; N, 4.61.

Synthesis of Bis(N-phenylphthalimid-3-yl)methyl Furylacrylate (7). Compound **7** was prepared from **3** by following the same procedure as described for **6**.

For **7**: ^1H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.9 (s, 1H, furan), 7.87 (d, 1H, vinyl), 7.5 (m, 10H, ArH), 7.41 (s, 1H, −CH−), 7.1 (d, 1H, furan), 6.62 (m, 1H, furan), 6.5 (d, 1H, vinyl); IR (KBr) ν 1779, 1729 (s, C=O imide, ester), 1636 (s, C=C) cm^{-1}. λ_{max} (chloroform) 310 nm (ϵ 3.7 × 10^4). Anal. Calcd for $C_{36}H_{22}N_2O_7$: C, 72.72; H, 3.70; N, 4.04. Found: C, 72.18; H, 4.04; N, 5.45.

Synthesis of Bis(N-phenylphthalimid-3-yl)methyl Methacrylate (8). Compound **8** was prepared from **4** by following the same procedure as described for **6**.

For **8**: ^1H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.5 (m, 10H, ArH), 7.35 (s, 1H, −CH−), 6.49 (d, 1H, vinyl), 5.9 (d, 1H, vinyl), 2.1 (s, 3H, CH_3); IR (KBr) ν 1780, 1727 (s, C=O imide, ester), 1638 (s, C=C) cm^{-1}. Anal. Calcd for $C_{33}H_{22}N_2O_6$: C, 73.06; H, 4.05; N, 5.16. Found: C, 72.91; H, 4.32; N, 5.05.

Synthesis of Bis(N-phenylphthalimid-3-yl)methyl Acrylate (9). Compound **9** was prepared from **5** by following the same procedure as described for **6**.

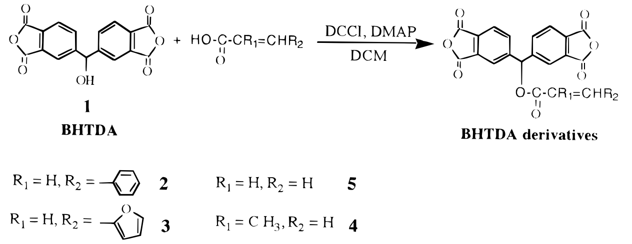
For **9**: ^1H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.5 (m, 10H, ArH), 7.35 (s, 1H, −CH−), 6.5 (m, 2H, vinyl), 6.11 (m, 1H, vinyl); IR (KBr) ν 1780, 1736 (s, C=O imide, ester), 1624 (s, C=C) cm^{-1}. Anal. Calcd for $C_{32}H_{20}N_2O_6$: C, 72.72; H, 3.78; N, 5.30. Found: C, 72.54; H, 3.89; N, 5.29.

(C) Synthesis of PSPI Esters (Scheme 3). *Synthesis of PSPI Cinnamate Ester (10).* The synthesis of PSPI cinnamate ester **10** is given as a typical example.[19] BHTDA cinnamate ester (2.0g, 4.4 mmol) was added to a solution of 0.87 g (4.4 mmol) MDA or 0.88 g of ODA in NMP (70 wt %). The reaction mixture was stirred mechanically for 24 h at ambient temperature. Acetic anhydride (5.0 mL) was added to the amic acid solution. The solution was stirred overnight. After the reaction was completed, the solution was added dropwise to 100 mL of methanol to precipitate the photosensitive polyimide (PSPI) ester. The product was washed with large amounts of distilled water to remove occluded acetic acid. The isolated PSPI ester was in the form of a beige powder and was dried under high vacuum for 16 h at 40 °C to yield **10**. IR (KBr) ν 1779, 1722 (s, C=O imide, ester), 1635 (s, C=C) cm^{-1}. The inherent viscosity of this polymer was 0.80 dL/g in NMP (C = 1 g/dL) at 30 °C.

All of the procedures were carried out under dry nitrogen gas or argon or in a vacuum to avoid ambient moisture because of the hydrolytic instability of the anhydride groups. The photosensitive products were shielded from direct sunlight during preparation and purification stages to minimize the photopolymerization process.

Film Formation and UV Exposure. The preparation of PSPI systems is carried out under nitrogen by dissolving the polyimide powder (25 wt %) in a mixture of solvents (NMP/γ-butyrolactone 1/1). Michler's ketone (4 wt %) and triethanolamine (4 wt %) were added as photosensitizers. The concentrated solutions were filtered through a 1.0 μm Teflon filter under pressure and cast on clean glass substrates using a 150 μm Filmograph. The films were dried under reduced pressure of 1−2 mmHg at 100 °C for 10 min. The thickness of the film was around 30 μm. The photoresists casted on the substrate were exposed to a 125 W mercury lamp, giving a strong emission at 365 nm. The distance from the lamp to the sample was 9 cm. After imagewise exposure in the contact mode with a quartz mask, the resists were developed in CEMSOLV8 (60% γ-butyrolactone, 37% xylene, 3% ethylbenzene) for 2 min at 30 °C by ultrasonic development and rinsed with water. To obtain characteristic curves, the resists were stepwise exposed to UV light and processed using a method similar to that mentioned above. After development the remaining film thickness was plotted against the exposure dose.

Scheme 1. Synthesis of BHTDA Derivatives



Results and Discussion

Monomer Synthesis. The starting monomer BHTDA (**1**) used in the synthesis of a commercial aromatic polyimide polybenzhydrolimide[20] has been chemically modified by esterification with four different photosensitive groups. The synthetic scheme is shown in Scheme 1.

BHTDA was chosen as a dianhydride for the preparation of new photosensitive monomers. It has a good solubility as a result of the chemical interaction between hydroxyl groups and solvent. The BHTDA derivatives were prepared by reaction of photoreactive acids such as cinnamic, furylacrylic, methacrylic, or acrylic acid with BHTDA and DCCI using DMAP as a catalyst in solution in DCM. This method is useful for large-scale synthesis. Although the BHTDA derivatives are free from contamination by ionic impurities such as chlorides, it is impossible to avoid the formation of DCU. The presence of DCU in photoreactive monomers was estimated to be less than 10% from the ^1H NMR spectrum by comparing the ratio of the cyclohexyl protons to the aromatic protons. The esterification reaction carried out using the acid chloride of the respective photoreactive groups in DCM with triethylamine as a catalyst does not produce the desired BHTDA derivatives, probably because the strongly electron-withdrawing anhydride groups in the BHTDA causes a reduction in the nucleophilicity of the hydroxyl group vis-a-vis the photoreactive acid chloride.[19] The hydrolysis of dianhydride and self-condensation of dianhydride alcohol were supposed not to occur simultaneously with esterification because of the low temperature, the absence of water, and the presence of an excess of the acetic anhydride as dehydrating agent.[21−23] Each of the IR spectra of the BHTDA derivatives was examined in the region 3200−3600 cm^{-1} for the presence of a broad intense peak assignable to the O−H stretching mode. The absence of this peak verified that the compounds were not substantially contaminated by water or unreacted alcohol **1** (see Figure 1). The four kinds of monomers synthesized were characterized by ^1H and ^{13}C

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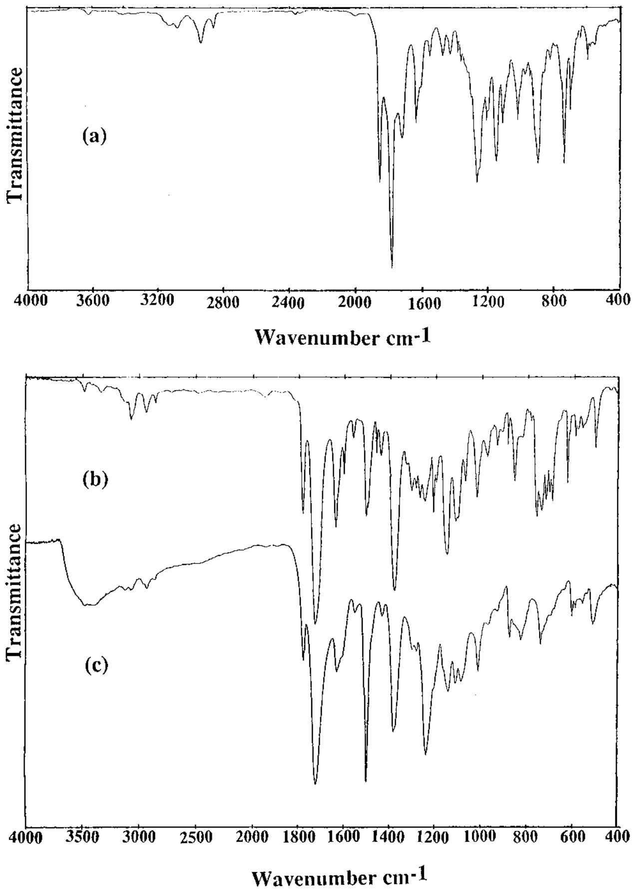
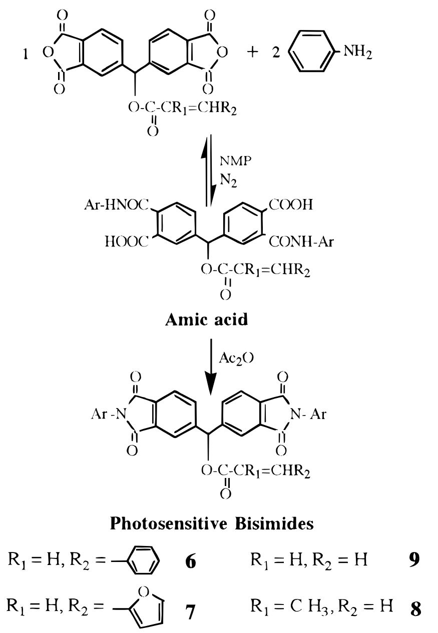
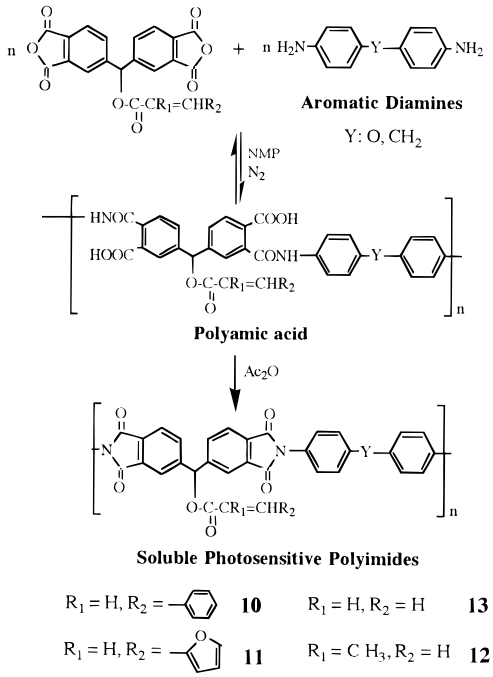


Figure 1. FT-IR spectra of (a) 3, (b) 7, and (c) PSPI 11.

Scheme 2. Synthesis of the Model Bisimide Compounds



Scheme 3. Synthesis of Soluble Photosensitive Polyimides



NMR, IR, and elemental analysis. All assignments of the signals are in agreement with the structures of **2**–**5**.

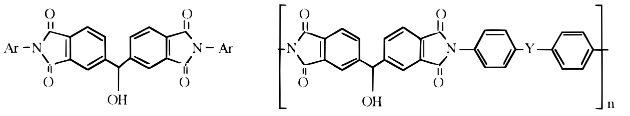
We now wish to report on new negative-type photosensitive polyimides, on the basis of soluble, fully imidized polyimide backbone with a photoreactive group attached to its side chain or on the basis of photosensitive compositions containing photoreactive bisimides and a commercially available polyimide: polybenzhydrolimide. The similarity of the structures led to interesting photosensitive compositions, which will be studied further in the future. The bisimides containing photosensitive groups are highlighted in Scheme 2.

Model Compound Synthesis. The two-step synthesis of bisimide esters is used as a reaction model for the preparation of PSPI esters. The bisimide is prepared by reacting BHTDA derivatives with aniline in NMP solution under a dry nitrogen atmosphere to avoid the hydrolysis of anhydride groups. After complete reaction, the amic acid is chemically imidized using acetic anhydride as the dehydrating agent. There are two methods for the imidization of amic acid; one is heat imidization with an azeotropic agent, and the other is catalytic chemical imidization with acetic anhydride as a dehydrating agent in the presence of a catalyst. In the case of the heat imidization, the absorption band at 1635 cm^{-1} due to the vinyl group decreased after heating. This change suggests that the cross-linking occurs by the reaction of the C=C moiety. On the other hand, the catalytic chemical imidization in the presence of triethylamine led to the formation of acetylated bisimide by trans-esterification reaction in the presence of acetic anhydride. Without catalyst this reaction does not occur at room temperature. Therefore, chemical imidization without catalyst is better than heat imidization. Esters are known to be attacked by amines, but in the case of BHTDA derivatives only aliphatic amines can react with activated esters simultaneously with imidization of dianhydrides to produce the bisimide alcohol, compound **14** (see Scheme 4).

The characterization of these bisimides was achieved by NMR and IR spectroscopy and elemental analysis (see Experimental Section). The IR spectra showed the presence of imide C=O at 1780 cm^{-1}, imide C–N at 1380 cm^{-1}, and vinyl C=C at 1635 cm^{-1} (see Figure 1).

Polymer Synthesis. There are two basic approaches in synthesizing the PSPI esters: first reacting BHTDA derivatives carrying photoreactive groups with diamines

Scheme 4. Stuctures of 14 and Poly(benzhydrolimide)



14 **Polybenzhydrolimides**

Table 1. Experimental Result of Photosensitive Polyimides

sample	dianhy	diamine	ratio (mol/mol)	yield (%)	$\eta_r{}^a$ (dL/g)
1	2	ODA	1/1	95	0, 8
2	2	MDA	1/1	93	0, 75
3	3	ODA	1/1	94	1
4	3	MDA	1/1	95	0, 8

[a] Inherent viscosity measured in NMP at 30 °C, $C = 1$ g/dL.

and, second, modifying a commercial soluble polyimide “polybenzhydrolimide” (see Scheme 4) with photosensitive compounds. Work on this is now in progress and will be discussed elsewhere. In this paper, we focus on the first approach.

New soluble polyimides were prepared by polycondensation of these BHTDA esters with aromatic diamines, MDA and ODA, in solution in NMP under dry conditions to avoid the hydrolysis of the dianhydride groups, which affects strongly the molecular weight, followed by a chemical imidization without a catalyst as shown in Scheme 3.

This technique eliminates a number of detrimental side reactions and has proved to be useful if a rigorous dianhydride:diamine stoichiometry was maintained (see Table 1). The viscosity increases gradually by the polycondensation reaction, and viscous solutions suitable for thick coatings were obtained. The characterization of the resulting polymers was realized with the help of bisimide models. The amide absorption peak at 1650 cm^{-1} served as a criterion for the degree of imidization, and complete cyclization to imide was achieved under the above-described chemical conditions (see Figure 1). The ^{1}H NMR spectrum for **10** shows signals for the cinnamoyloxy group at 6.95 (vinyl proton) and 7.87 (vinyl proton), and 7.40 (aromatic proton). Signals for the polymer backbone are at 7.7–8.5 (aromatic proton).

Attrib.	δ (ppm)	Attrib.	δ (ppm)	Attrib.	δ (ppm)
1 et 2	128,893	a	75,314	h	166,809
3	117,669	b	121,379	i	166,812
4	134,115	c	124,027	j	129,378
5	146,125	d	131,358	k	118,977
6	165,032	c	131,379	l	156,099
7	129,571	f	132,868	m	127,318
		g	147,029		

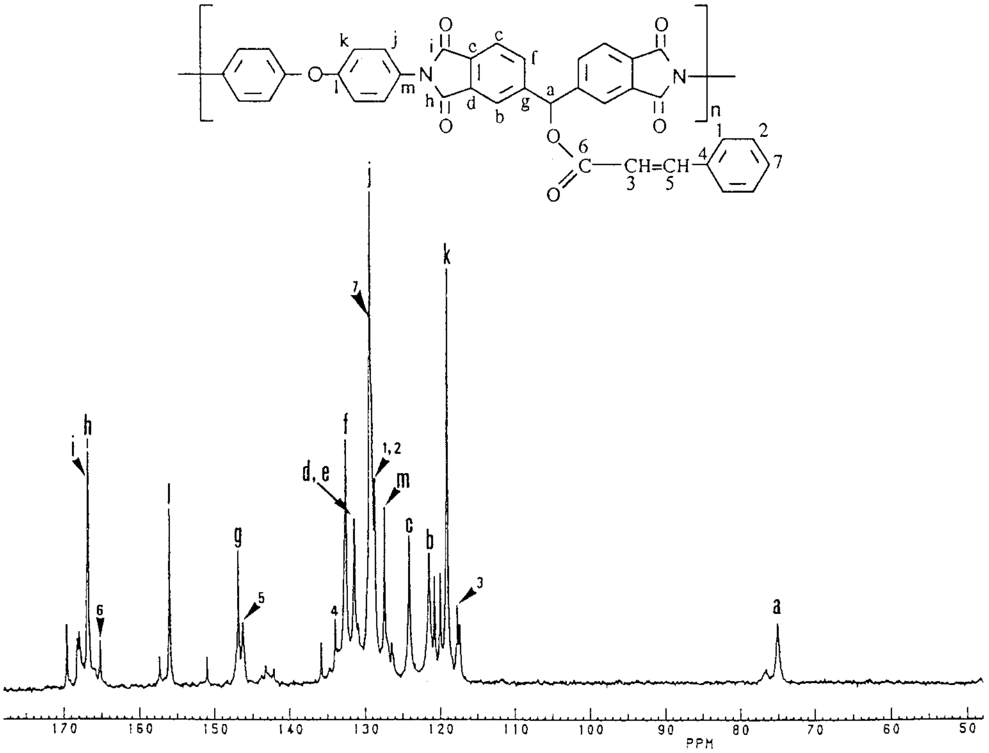


Figure 2. ^{13}C NMR spectrum of **10** in DMSO-d_6.

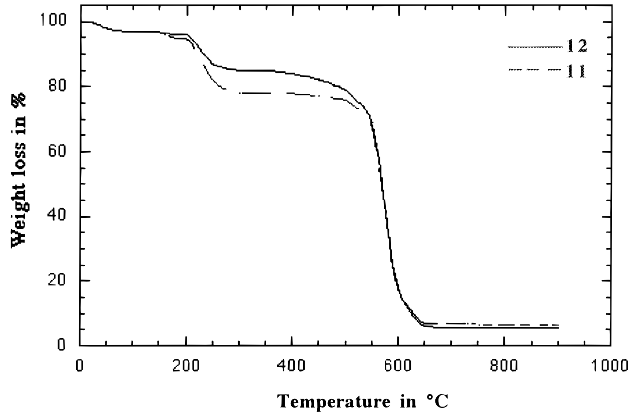


Figure 3. Thermogravimetric curves of photosensitive polyimides **11** and **12**. Heating rate = 10 °C/min in N_2.

The ^{13}C NMR spectra of polymer **10** is given as a typical characterization example in Figure 2.

Properties of Polyimides. The PSPI esters take up water from the air. Therefore, the photosensitive products were kept in dry boxes. Most of the water can be released again by means of an additional drying treatment under vacuum. However, for polyimides this process is not totally reversible. Some of the water can be consumed irreversibly by hydrolysis reactions of the polyimide. Water uptake has an effect on the mechanical properties and can cause stress relaxation.

Thermal Properties. Figure 3 shows the thermogravimetric behavior, under nitrogen, of the photosensitive polyimides **11** and **12**. A small weight loss in the temperature range 100−300 °C and a large weight loss at over 420 °C were observed. The former is due to heat decomposition of photoreactive group, and the latter is due to heat decomposition of the polyimide backbone. The weight loss in the region 100−300 °C is approximately 20% for **11** and 12% for **12** . The weight loss of **12** is lower than that of **11**. This is probably due to differences in the steric bulkiness between the methacryloyloxy group and the furylacryloyloxy group.

Electrical Properties. Dielectric measurements were carried out in the temperature range 30−350 °C and at frequencies of 1−200 kHz. The values of dielectric constants ϵ are particularly constant over the corresponding range of temperature. The dielectric constant ϵ of polymer **12** was evaluated as 4.2. This value is higher than those of commercially available negative photosensitive polyimides ($\epsilon < 3.5$), which is due to the lower rigidity of the chain and the greater polarity of photoreactive group.

Photosensitive Properties. The processing of photosensitive polyimide requires only three steps; soft cure, exposure, and development for patterning. The processing conditions, such as the exposure dose, the developing time and the solution temperature, are very critical in obtaining fine geometry. The developing solvent used was a CEMSOLV8, which gave the best results. During this step the unexposed polyimide is dissolved away without causing swelling in the exposed areas. Good resolution is obtained by simple dip development because of low image swelling. After patterning, the films were cured at 160 °C for 30 min to remove all of the volatiles, including the degradation products, from the photosensitive group. Therefore, during the cure process, the shrinkage of the film thickness is in the range of 20% depending only on the structure of the photoreactive group, because these PSPI ester systems consist of fully imidized polyimides.

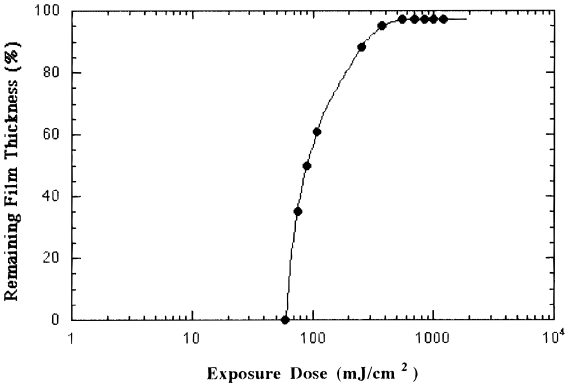


Figure 4. Exposure characteristic for **12** (initial film thickness 30 μm).

Figure 4 represents the sensitivity curve for the polyimide **12**. After each exposure the sample was developed, washed, and dried, and the remaining thickness was measured, and plotted versus the log dose. The sensitivity was determined as the minimum dose required for the exposed area of the film to become completely insoluble, and the contrast (γ value) was determined as the slope at that point. The residual film thickness for **12** after development is more than 95% at exposure doses in excess of 600 mJ/cm^2 at 365 nm, in the 30 μm prebaking film thickness. The sensitivities and the contrasts for PSPIs are in the ranges 0.6−1.4 J/cm^2 and 0.5−1.4, respectively.

Conclusions

We have successfully prepared a negative-type photosensitive polyimides. The PSPI esters were found to be soluble in *N*-alkyl-substituted amides, and after UV irradiation, the exposed area of the film became completely insoluble and no swelling effect was observed. Heat treatment temperature is much lower and heat treatment time is much shorter for these materials (fully imidized PSPIs) than those for conventional materials, resulting in a low shrinkage of the film thickness. Work is continuing to extend the limits of sensitivity, to optimize image dimensions, and to explore the structure−photosensitivity relationships of the class of copolyimides derived from BHTDA derivatives, 2,2-bis(3,4-dicarboxylphenyl)hexafluoroisopropane dianhydride (6FDA), and various aromatic diamines.

Acknowledgment. The authors would like to acknowledge the assistance of Dr. Joel Belleney and Mrs. Monique Contassot for their work related to spectroscopic characterization. They thank Professor Jean-Pierre Vairon and Dr. Bernard Sillion for helpful discussions. This research was supported by a grant from CEMOTA (Centre d'Etude des Matériaux Organiques pour les Technologies Avancées).

CM9503184