Synthesis and Characterization of Photosensitive Polyimides for Optical Applications

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ABSTRACT: The objective of this research was to prepare colorless photosensitive polyimides for optical applications. In the first approach to these materials two new photosensitive end-capping agents, i.e., 6-(4-aminophenoxy)hexyl methacrylate and di[2-(methacryloyloxyethyl)] 5-aminoisophthalate, for polyimides were prepared. These agents were used along with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl to prepare a series of methacrylate end-capped imide oligomers. However, the oligomers required long exposures to UV radiation to affect cure. To improve their photosensitivity, multifunctional additives and photoinitiators were used. A tetrafunctional end-capped oligomer that contained 10 wt % trimethylolpropane triacrylate and 5 wt % trimethylbenzoyldiphenyl phosphine oxide (TMDPO) was photosensitive and displayed good photopatterning properties. A second approach to the desired materials involved the synthesis of a diamine monomer, i.e., 2,2′-dimethacryloyloxy-4,4′-diaminobiphenyl, in which methacrylate moieties were attached to the 2- and 2′-positions of a biphenyl structure. The monomer was polymerized with commercially available dianhydrides such as 6FDA and 4,4′-oxydiphthalic anhydride. The polyimides obtained were soluble in common organic solvents such as THF, acetone, and chloroform and could be solution cast into thin, water-white films that were highly transparent in the visible light region. The polymers were photosensitive when combined with 5 wt % TMDPO and displayed good photopatterning properties. The polymers, which afforded line patterns 10−30 μm wide and 5−20 μm thick, did not develop color or shrink during UV exposure and subsequent thermal treatments.

Introduction

Polyimides are widely used in microelectronic devices due to their excellent thermomechanical and planarization properties, low dielectric constants, and high dissipation factors.[1] Although multilayer processing of polyimide films can be carried out by either dry or wet-etch, pattern-transfer techniques, these imaging schemes increase the number of process steps and decrease manufacturing throughput. To overcome these disadvantages, many types of photosensitive polyimides and their precursors have been developed where the polymer also functions as the photoresist.[2,3] However, photosensitive polyimides have not been specifically developed for optical applications, such as color filters and retardation layers for liquid crystal displays. Although a few colorless photoreactive polyimide precursors have been prepared from fluorine-containing monomers,[4,5] most polyimides cannot be used in these applications because they form yellow/orange films that darken upon exposure to radiation and high temperatures.

Two new series of polyimides that form water-white, transparent films have recently been prepared in this laboratory through the use of 2,2′-disubstituted-4,4′-diaminobiphenyls[6] and 2,2′-disubstituted-4,4′,5,5′-tetracarboxylicbiphenyl dianhydrides.[7−9] The properties of the soluble polyimides prepared from one of the diamines in these series, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB), have been extensively studied.[10,11] The steric hindrance between the pendent groups located at the 2- and 2′-positions of the biphenyl units in the monomers forces the rings out of plane. The resulting twist in the backbones of the polymers prepared from such monomers hinders chain packing and, thus, reduces crystallinity and intermolecular interactions and enhances solubility. The twist also breaks up the extended conjugation along the backbone.[12] Solution-cast films of the polyimides display negative birefringence due to the high degree of in-plane chain orientation.[13] Thus, the films have found use as retardation layers in liquid crystal displays (LCDs).[14−16] The objective of this research was to modify these novel polyimides so as to make them photosensitive. It was postulated that such modification would greatly facilitate their use in retardation layers. For example, this would allow them to be photopatterned above or below individual pixels in an LCD.

In the first approach to the desired materials an attempt was to be made to prepare two new photosensitive end-capping agents, i.e., 6-(4-aminophenoxy)hexyl methacrylate and di[2-(methacryloyloxyethyl)] 5-aminoisophthalate, for polyimides. These agents were to be used in the preparation of end-capped imide oligomers. In the second part of this research, an attempt was to be made to prepare a new diamine monomer, i.e., 2,2′-dimethacryloyloxy-4,4′-diaminobiphenyl (DMDB), in which methacrylate moieties were attached to the 2- and 2′-positions of a biphenyl structure. The monomer was then to be polymerized with commercially available dianhydrides such as 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) and 4,4′-oxydiphthalic anhydride (ODPA). It was postulated that polyimides obtained from this diamine would be soluble in common organic solvents and would form clear films that would be highly transparent in the visible light

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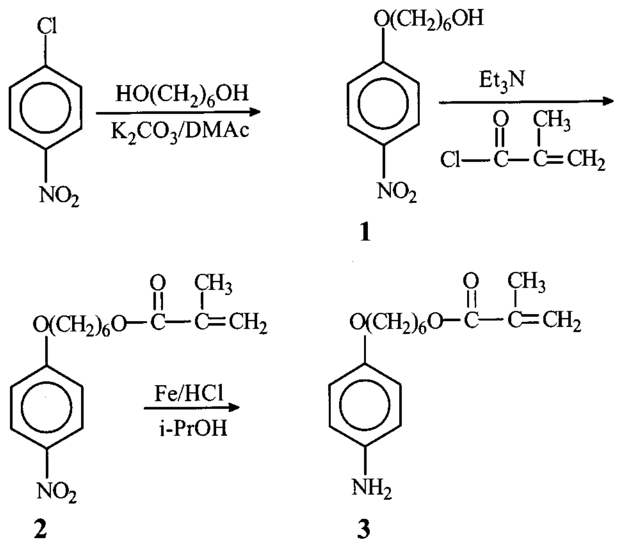
Scheme 1



region. The polyimides obtained in both approaches were to be thoroughly characterized. In particular, the photosensitivities of the polymers and their optical properties were to be carefully examined.

Results and Discussion

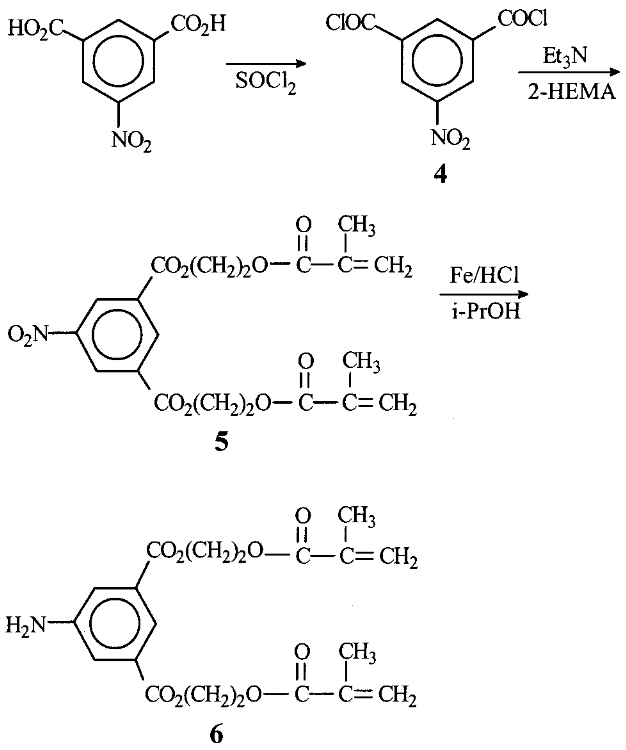
Synthesis of Methacrylate End-Capped, Photosensitive Imide Oligomers. The first approach to photosensitive polyimides involved the preparation of photosensitive end-capped imide oligomers. The use of reactive end-capped imide oligomers as precursors to cross-linked polyimides has been extensively studied.[17] An advantage to this approach is that the oligomers are preimidized so that no further intramolecular cyclizations, which can cause shrinkage in thin films, are required. The solubility of oligomers is also higher than that of the corresponding polymers.

An end-capping agent containing methacrylate moieties, i.e., 6-(4-aminophenoxy)hexyl methacrylate (**3**), was prepared via the route shown in Scheme 1. This synthesis began with the reaction of 4-nitrochlorobenzene with an excess of 1,6-hexanediol to yield the monosubstituted nitrobenzene **1**. The intermediate was treated with methacryloyl chloride in methylene chloride at 0 °C in the presence of triethylamine to yield 6-(4-nitrophenoxy)hexyl methacrylate (**2**). In the last step, the nitro groups in compound **2** were reduced. Because of the presence of the methacrylate groups, specific reduction conditions had to be used. Reduction with iron in acidic 2-propanol gave a 70% yield of 6-(4-aminophenoxy)hexyl methacrylate (**3**). Iron is suitable for the reduction of complex nitro derivatives since it does not reduce many other functional groups.[18−20]

An end-capping agent containing two dimethacrylate moieties, i.e., di[2-(methacryloyloxy)ethyl] 5-aminoisophthalate (**6**), was prepared via the route shown in Scheme 2. Thus, 5-nitroisophthalic acid was treated with excess thionyl chloride to form the acid chloride **4**. Treatment with 2-hydroxyethyl methacrylate in methylene chloride at 0 °C afforded the nitro compound **5**, which was reduced to **6** with iron in acidic 2-propanol.

Methacrylate end-capped imide oligomers were prepared by a two-step method (Scheme 3). In the first step, the diamine PFMB (**7**) was treated with an excess amount of 6FDA (**8**) at ambient temperature in NMP, producing an anhydride-terminated amic acid oligomer (**9**). The molecular weight of the oligomer was controlled by varing the molar ratio of the diamine to the dianhydride. Oligomers were prepared with calculated number-average molecular weights ($\bar{M}_n$) of 4000, 6000, 8000, and 10 000 (Table 1). The end-capping agent, i.e., **3** or **6**, was then allowed to react with the anhydride chain ends to form methacrylate end-capped amic acid oligomers. The amic acid oligomers were converted to the methacrylate-terminated imide oligomers by chemical imidization with pyridine and acetic anhydride. The oligomers were isolated by precipitation in ethanol. The ^{1}H NMR and FTIR spectra of the monofunctional and difunctional end-capped imide oligomers were consistent with the proposed structures.

Scheme 2



All the imide oligomers were soluble in common organic solvents such as acetone and THF and could be solution cast into water-white films. The minimum calculated oligomer $\bar{M}_n$ that afforded flexible thin films was 6000 amu (Table 1). Samples with this $\bar{M}_n$ (**10c** and **11a**) were used in the photoresist studies in order to obtain the highest photosensitivities.

Synthesis of Photosensitive Polyimides Containing Pendent Methacrylate Moieties. The monomer DMDB (**17**) was prepared according to Scheme 4. Thus, 2-methoxy-4-nitroaniline (**12**) was converted to the diazonium salt with sodium nitrite and sulfuric acid at 0 °C. The diazonium salt was treated with potassium iodide to afford the iodo compound **13**, which was then dimerized using Ullmann conditions to give compound **14**. Intermediate **14** was converted to the diphenol **15** with molten pyridine hydrochloride at 200 °C. The diphenol was treated with methacryloyl chloride in THF in the presence of triethylamine at 0 °C to afford the dinitro compound **16**, which was reduced with iron in acidic 2-propanol.

To determine the preferred conformation of DMDB, an energy minimization of the molecular structure of the monomer was carried out using Polygraf 3.1. The

Scheme 3

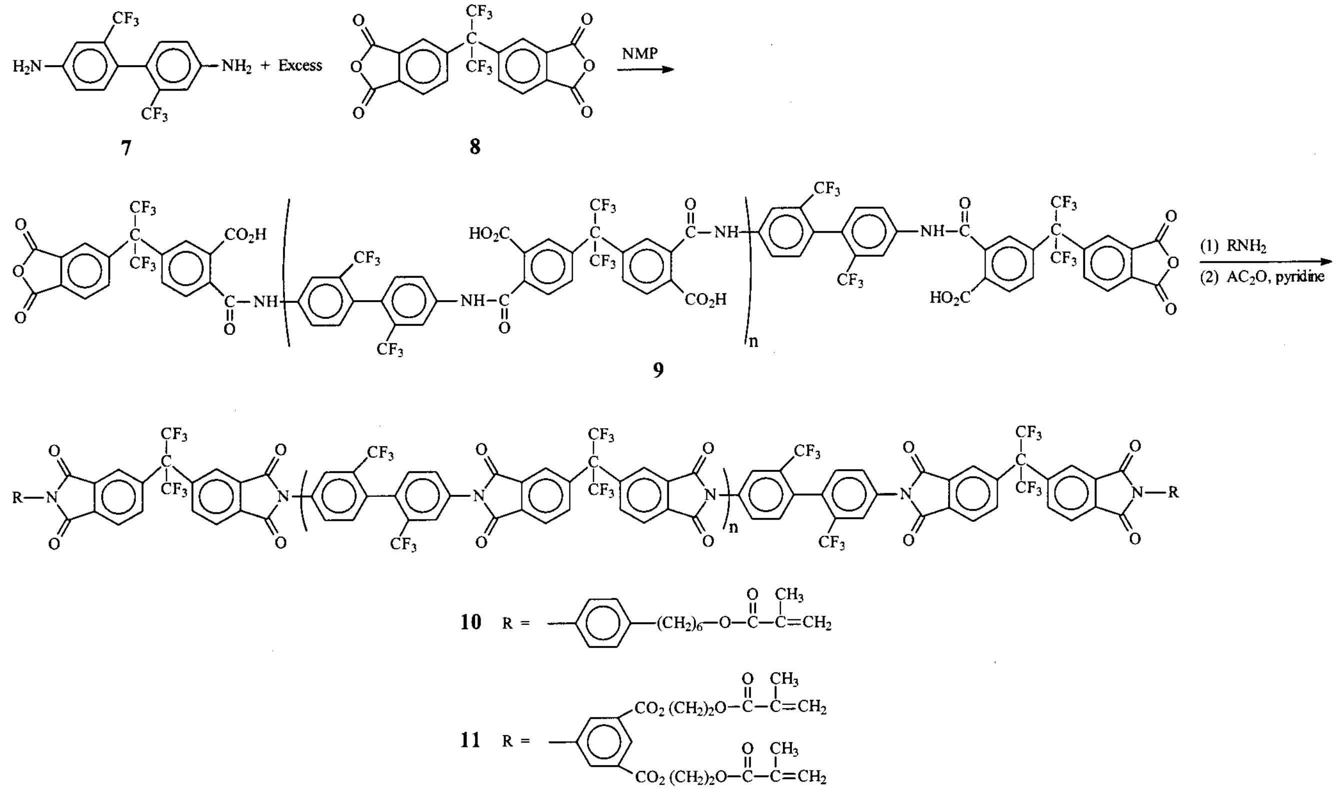


Table 1. Methacrylate End-Capped Imide Oligomers

oligomer	end-capping agent	target M_n[a]	$[\eta]$[b] (dL/g)	film quality[c]
10a	3	10000	0.74	e
10b	3	8000	0.63	e
10c	3	6000	0.48	g
10d	3	4000	0.22	p
11a	6	6000	0.43	g
11b	6	4000		p

[a] Calculated $M_n = M_0(1 + r)/(1 - r)$, where r = mole (amine)/mol (anh). [b] Intrinsic viscosity measured in NMP at 30 ± 0.1 °C. [c] e = excellent, fingernail creasable; g = good, flexible; p = poor, brittle.

dihedral angle between the two phenyl rings was found to be 30°.

Diamine **17** was polymerized with pyromellitic dianhydride (PMDA), 3,3′,4,4′-tetracarboxylicdiphenyl sulfone dianhydride (DSDA), 6FDA, and 3,3′,4,4′-tetracarboxylicbiphenyl dianhydride (BPDA) (Scheme 5). The polymerizations were carried out in NMP with a solids concentration of 15 wt % at ambient temperature. The poly(amic acids) (PAAs) obtained were then chemically imidized with an equimolar mixture of pyridine and acetic anhydride. The polymers (**20**), which were soluble in the polymerization mixtures, were isolated by precipitation in ethanol. The ^1H NMR and FTIR spectra of the polyimides were consistent with the proposed structures. The intrinsic viscosities of the DMDB-based polyimides ranged from 1.17 to 1.93 dL/g in NMP at 30 °C (Table 2).

The thermogravimetric analysis (TGA) thermograms of the polymers in nitrogen showed that they decomposed in two steps (Figure 1). The initial weight loss was attributed to the decomposition of the methacrylate ester moieties. The thermal degradation of the polyimide backbone chain took place above 500 °C.

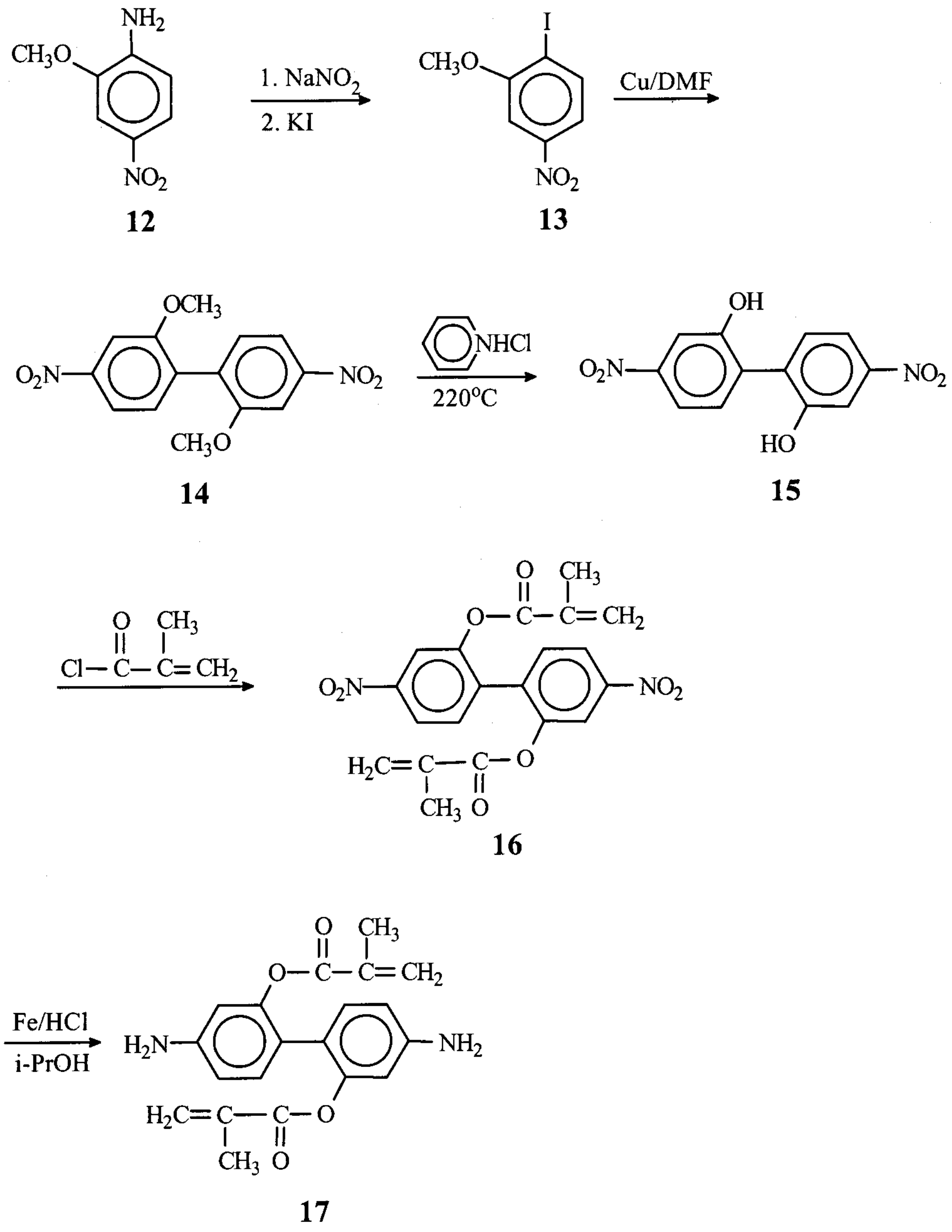
All of the polymers were soluble in DMF, DMAc, and DMSO (Table 3). Except for **20a**, which was only partially soluble, the polymers were also soluble in NMP. Polymers **20b**−**e** were soluble in THF. The polymer prepared from 6FDA (**20e**) was even soluble in acetone. The excellent solubility can be attributed to the twisted biphenyl units containing the polar methacrylate substituents.

The polymers could be cast into flexible, tough, transparent, colorless films from THF solutions at atmospheric pressure or from NMP solutions under reduced pressure at ambient temperature. Thin films (5 μm thick) of the polyimides began to transmit light in the range 338−350 nm. The films transmitted 80% of light above 392−415 nm (Table 4).

Since polymer **20e** was the most soluble, it was selected for further evaluation. To determine the feasibility of photopolymerizing the pendent methacrylate groups, a 5 μm film was irradiated with 2000 mJ/cm^2 of 365 nm UV light. The changes in the film were monitored with FTIR. The absorption bands at 1635 and 1318 cm^{-1} due to carbon−carbon double bonds decreased significantly during the irradiation. This is consistent with the polymerization of the carbon−carbon double bonds.

Photosensitivities of the End-Capped Imide Oligomers and Substituted Polyimides. The photosensitivities of the monofunctional end-capped imide oligomer **10c**, the difunctional end-capped imide oligomer **11a**, and the DMDB-based polyimide **20e** were determined. This was accomplished by irradiating a thin film (5 μm) of each material with 365 nm light and then determining the insoluble residue produced. (Films 5 μm thick were used throughout this study because this is the thickness of commercial retardation layers.[16]) The monofunctional end-capped imide oligomer was not very photosensitive. Even at high UV doses, only small gel

Scheme 4



fractions (<10%), which indicate low photosensitivity, were obtained. It is speculated that the concentration of cross-linkable groups was too low. Although the photosensitivity of the difunctional end-capped imide oligomer was higher, it was still not high enough to give a well-defined pattern (Figure 2).

Additives have been incorporated in photosensitive polymers to enhance their photospeed and resolution capability. These include photoinitiators, sensitizers, and mono- or polyfunctional methacrylate or acrylate monomers. For example, trimethylolpropane triacrylate (TMPTA) has been used to enhance the photosensitivity of photoresists.[21] 2,4,6-Trimethylbenzoyldiphenyl phosphine oxide (TMDPO) is a highly efficient photoinitiator suitable for thick films and white pigmented acrylate formulations. It is known to undergo very little yellowing. It also does not induce premature thermal polymerization, since it is thermally stable up to 180 °C.[22] In an attempt to increase the photosensitivity of the oligomers, 5 wt % of TMDPO was added to a solution of **11a**, while 5 wt % of TMDPO and 10 wt % of TMPTA were added to another. The solutions were poured on a glass plate, which was coated with the coupling agent, γ-aminopropyltrimethoxysilane.[4] The photosensitivities of the films that formed on drying were increased dramatically with these additives (Figure 2). In the second case, the contrast at 0.5 gel fraction ($\gamma^{0.5}$) was 1.5, and the exposure energy needed to attain a 0.5 gel fraction ($D_g^{0.5}$) was ca. 950−1000 mJ/cm^2.

The photosensitivity of a thin film of polyimide **20e** was also low, indicating that the cross-linking reaction was inefficient. The contrast at 0.5 gel fraction ($\gamma^{0.5}$) was 0.9, and the exposure energy needed to attain a 0.5 gel fraction ($D_g^{0.5}$) was ca. 4500−5000 mJ/cm^2 (Figure 3). On the other hand, a film that contained 5 wt % of TMDPO showed higher contrast and sensitivity, i.e., the contrast at 0.5 gel fraction ($\gamma^{0.5}$) was 2.7, and the exposure energy needed to attain 0.5 gel fraction ($D_g^{0.5}$) was ca. 800−850 mJ/cm^2. Although this value is higher than that of commercial poly(amic ester) photoresists (650−700 mJ/cm^2),[23] it is low enough for most applications. This low photosensitivity of the pure polymer was

Scheme 5

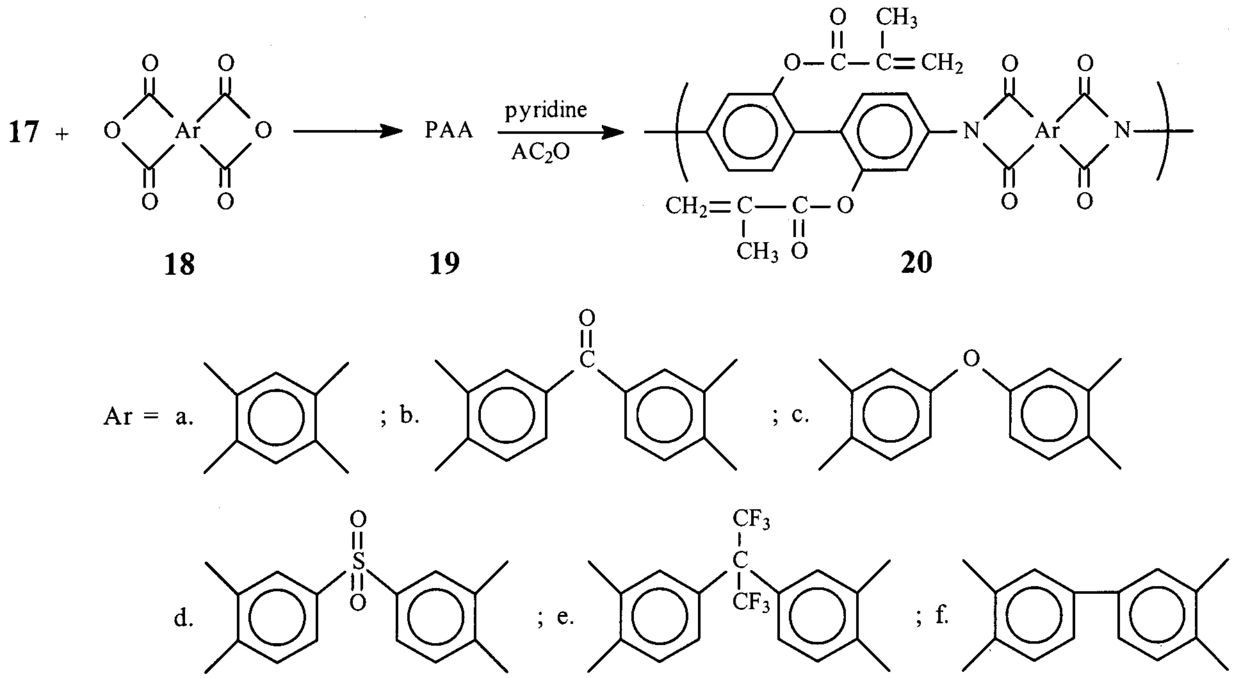


Table 2. Viscosity and Thermal Stability of Polyimides Based on DMDB

polymer	dianhydride monomer	$[\eta]^a$ (dL/g)	TGA[b] (°C)
20a	PMDA	1.93[c]	428
20b	BTDA	1.47	413
20c	ODPA	1.25	404
20d	DSDA	1.17	396
20e	6FDA	1.38	398
20f	BPDA	1.72	420

[a] Determined in NMP at 30.0 ± 0.1 °C. [b] Temperature at which samples lost 5% of their weight when subjected to TGA in nitrogen with a heating rate of 10 °C/min. [c] Intrinsic viscosity of NMP soluble portion.

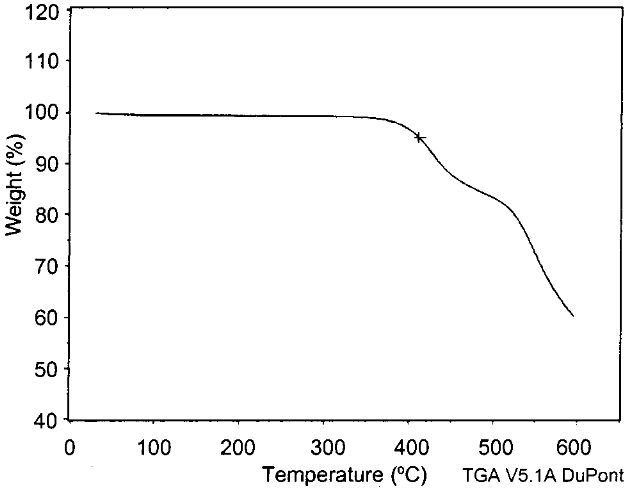


Figure 1. TGA thermogram of **20e** obtained in nitrogen with a heating rate of 10 °C/min.

Table 3. Solubility of Polyimides Based on DMDB

polymer	dianhydride monomer	acetone	NMP	DMF	$CHCl_3$	THF	DMSO
20a	PMDA	−[a]	+[b]	+	−	−	+
20b	BTDA	−	+	+	−	+	+
20c	ODPA	−	+	+	+	+	+
20d	DSDA	−	+	+	+	+	+
20e	6FDA	+	+	+	+	+	+
20f	BPDA	−	+	+	−	−	+

[a] − = solubility less than 2−3 g/L at room temperature. [b] + = solubility greater than 2−3 g/L at room temperature.

Table 4. UV Transmittance of 5 μm Films of Polyimides Based on DMDB

polymer	dianhydride monomer	transparency onset (nm)[a]	80%[b] transmission (nm)
20a	PMDA	350	415
20b	BTDA	347	410
20c	ODPA	340	395
20d	DSDA	348	493
20e	6FDA	338	392
20f	BPDA	345	413

[a] Wavelength at which the film began to transmit UV light. [b] Wavelength at which the film transmitted 80% of UV light.

speculated to arise from the direct attachment of the methacrylate groups to the rigid backbone, which hindered the cross-linking reaction.

Effect of Thermal Treatments on the UV Transmittance of Photolytically Cured Imide Films. The effects of exposure to elevated temperatures on the UV transmittances of a cross-linked film of the end-capped imide oligomer **11a** containing TMDPO (5 wt %) and TMPTA (10 wt %) (Figure 4) and a film of polyimide **20e** containing TMDPO (5 wt %) (Figure 5) were determined with a Perkin-Elmer Lambda 4B spectrometer. The films were exposed to 2000 and 1500 mJ/cm^2 of UV irradiation, respectively, and heated at various temperatures for 2 h. Both samples, which were 5 μm thick, did not develop color when heated at 300 °C.

Patterning Properties of the Photosensitive Imide Systems. To determine the photoimageability of the photosensitive imide systems, thin films were covered with a mask and exposed to UV radiation. After irradiation, the 5 μm films were heated at 90 °C for 1 h and then immersed in a mixture of NMP and water (80:20) to dissolve the unexposed material. After rinsing with water and drying, the films were analyzed with scanning electron microscopy (SEM). The SEM micro-

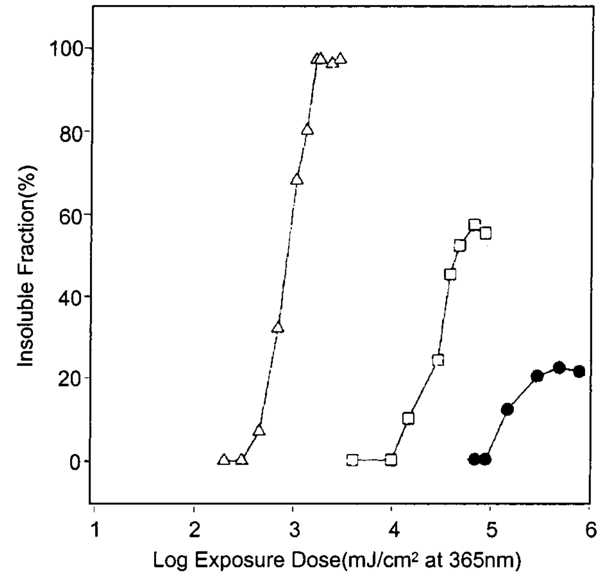


Figure 2. Plots of the insoluble fractions of thin films of oligomer **11a** vs UV exposure dose: ●, no additives; △, 5% TMDPO; □, 10% TMPTA and 5% TMDPO.

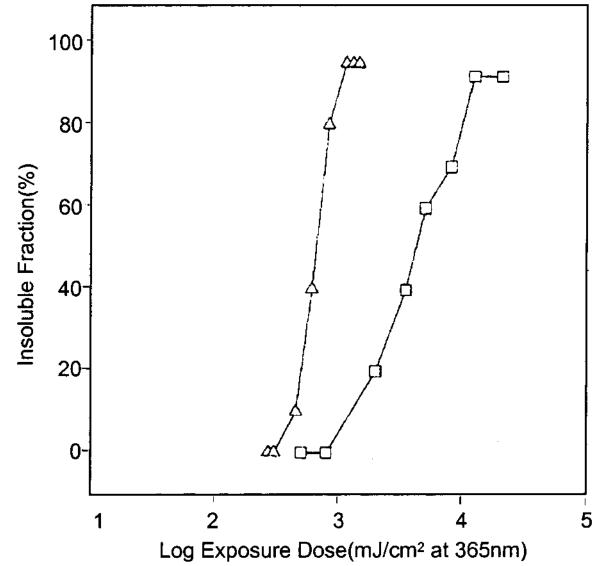


Figure 3. Plots of the insoluble fractions of thin films of polyimide **20e** vs UV exposure dose: □, no additives; △, 5% TMDPO.

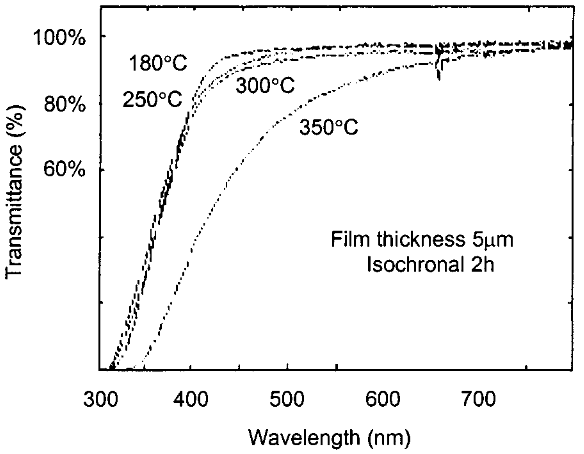


Figure 4. UV transmittance spectra of a 5 μm thick film of **11a** containing TMPTA (10 wt %) and TMDPO (5 wt %) after heating at elevated temperatures.

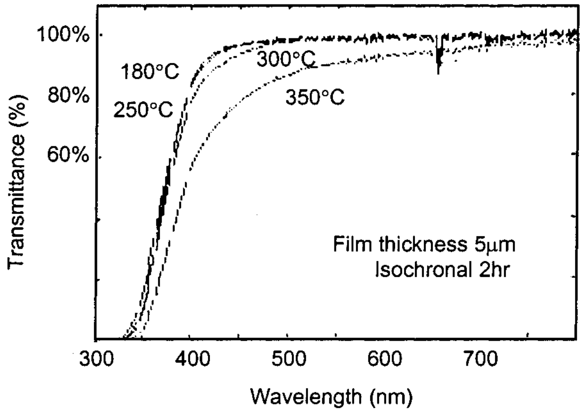


Figure 5. UV transmittance spectra of a 5 μm thick film of **20e** containing TMDPO (5 wt %) after heating at elevated temperatures.

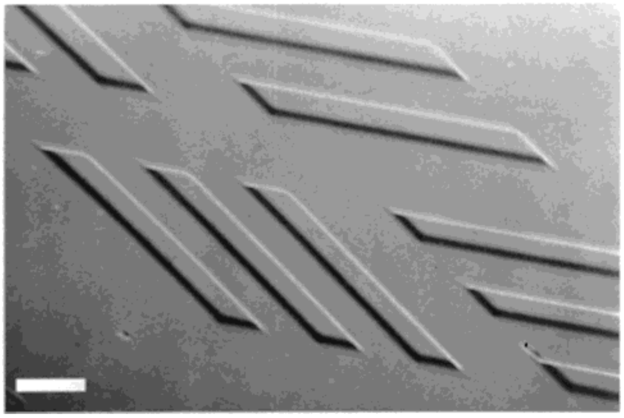


Figure 6. SEM micrograph of patterned **11a** containing TMPTA (10 wt %) and TMDPO (5 wt %); film thickness, 5 μm; exposure dose, 2000 mJ/cm^2; developer, NMP:water (80:20); developing time, 5 min; rinse, water. (Scale: the length of the white bar in the photo is equivalent to 33 μm.)

graph of the pattern obtained from a 5 μm thick film of the difunctional end-capped imide oligomer **11a** containing TMDPO (5 wt %) and TMPTA (10 wt %) after UV exposure and development with an NMP/water (80:20) mixture is shown in Figure 6. In this case, highly resolved line patterns less than 30 μm in width were obtained. (The micrograph of the pattern obtained with a film of **11a** that did not contain any additives showed very poor resolution.) Comparison of the SEM micrographs of patterns obtained from films of pure **20e** and films of **20e** containing 5 wt % TMDPO showed that a photoinitiator is required to obtain highly resolved patterns. In the latter case, resolved line patterns as thin as 10 μm could be obtained (Figure 7). Although the line edges were rounded, we speculate that this level of resolution is quite sufficient for patterning films above or below individual pixels (100 × 300 μm) in an LCD.

The SEM micrograph of a pattern developed from a 20 μm thick film of **21e** containing TMDPO (5 wt %) showed that even thick, well-defined patterns could be generated with this material. This is because the light absorption of DMB-6FDA is very low at 365 nm. The resolution was greatly improved by using an ultrasonic development process with the film. However, with ultrasonic development the development temperature was difficult to control, and there was a lack of uniformity in resolution over a wide area. A striking feature

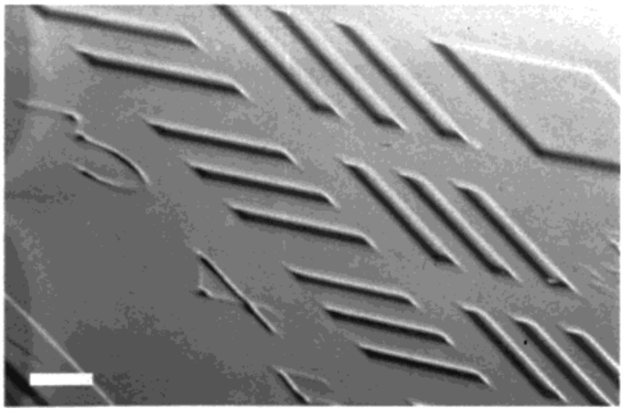


Figure 7. SEM micrograph of patterned **20e** containing TMDPO (5 wt %); film thickness, 5 μm; exposure dose, 1000 mJ/cm^2; developer, NMP:water (80:20); developing time, 5 min; rinse, water. (Scale: the length of the white bar in the photo is equivalent to 33 μm.)

of the DMB-based polyimide system was the retention of the film thickness after development and thermal curing. In fact, no reduction in film thickness was observed.

Experimental Section

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 200 MHz on a Varian Gemini-200 spectrometer. Infrared (IR) spectra were obtained with a Mattson Galaxy series FTIR 5000 spectrophotometer. Solid samples were imbedded in KBr disks. The IR spectra of the polymers were obtained directly from their films. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Intrinsic viscosities were determined on *N*-methyl-2-pyrrolidinone solutions using a Cannon-Ubbelohde no. 100 viscometer at 30.0 ± 0.1 °C. Thermogravimetric analyses (TGA) were obtained in nitrogen and air with a TA Hi-Res TGA 2950 thermogravimetric analyzer using a heating rate of 10 °C/min. High-pressure liquid chromatography (HPLC) analyses (Waters component system) were performed using a MicroPak CH-18 column (30 mm × 4 mm) in 70/30 (vol/vol) acetonitrile/H_2O at 100 psi with a diode array detector (UV detector). Transmission UV−vis spectra were obtained with a Perkin-Elmer Lambda 4B spectrometer in the reflectance mode. The scanning electron micrographs of patterning profiles were obtained with a JEOL JSM-U3 scanning electron microscope. The sample was homogeneously coated with a very thin layer of gold using a SEM coating unit prior to use. Ultraviolet exposure was carried out using UVP high-intensity long-wavelength UV lamp (100 W).

6-(4-Nitrophenoxy)hexanol (1). 4-Nitrochlorobenzene (47.1 g, 0.300 mol) and an excess amount of 1,6-hexanediol (213 g, 1.80 mol) were added to a 3 L, round-bottom flask equipped with a reflux condenser, nitrogen inlet, and overhead stirrer. DMAc (250 mL) was added, and the mixture was heated to 155 °C. Potassium carbonate (247 g, 1.80 mol) was poured into the solution in a slow stream. The reaction mixture was heated at reflux for 24 h. The homogeneous mixture was poured hot into ice and carefully neutralized to pH 7 with hydrochloric acid. After the product was collected by filtration and washed with warm water, it was dried at 50 °C under reduced pressure to give 55.0 g (77%) of white crystals; mp 55−57 °C. ^{1}H NMR ($CDCl_3$): δ 1.42−1.89 (m, 8H, aliphatic), 3.62 (t, 2H, aliphatic), 4.05 (t, 2H, aliphatic), 6.91 (d, 2H, aromatic), 8.15 (d, 2H, aromatic). IR (KBr): 3200−3500 (OH), 2345, 1650, 1360 (NO_2) cm^{-1}. Elem. Anal. Calcd for $C_{12}H_{17}N_1O_4$: C, 60.24; H, 7.16. Found: C, 60.17; H, 7.22.

6-(4-Nitrophenoxy)hexyl methacrylate (2). Methacryloyl chloride (3.66 g, 0.0350 mol) in methylene chloride (30 mL) was added dropwise to 6-(4-nitrophenoxy)hexanol (8.37 g, 0.0350 mol) and triethylamine (4.50 mL, 0.0350 mol) in methylene chloride (200 mL) over 1 h at 0 °C. After stirring for another 1 h, the mixture was warmed to room temperature and stirred for 2 h. Triethylammonium chloride was removed by filtration. The methylene chloride layer was washed three times with a 0.1 N NaOH aqueous solution and once with brine. The solution was dried over Na_2SO_4 overnight and filtered. Methylene chloride was removed from the filtrate under reduced pressure to yield 8.63 g (80%) of a yellow oily liquid. ^{1}H NMR ($CDCl_3$): δ 1.42−1.82 (m, 8H, aliphatic), 1.87 (s, 3H, CH_3), 3.99 (t, 2H, aliphatic), 4.09 (t, 2H, aliphatic), 5.49−6.02 (m, 2H, vinyl), 6.87 (d, 2H, aromatic), 8.11 (d, 2H, aromatic). IR (KBr): 3350, 1730 (C═O), 1610, 1360 (NO_2) cm^{-1}. Elem. Anal. Calcd for $C_{16}H_{21}N_1O_5$: C, 62.53; H, 6.89. Found: C, 62.61; H, 6.97.

6-(4-Aminophenoxy)hexyl Methacrylate (3). To a warm stirred solution of 6-(4-aminophenoxy)hexyl methacrylate (3.07 g, 0.0100 mol) in a mixture of 40 mL of 2-propanol and 10 mL of water was added 0.3 mL of hydrochloric acid and iron powder (325 mesh) (5.59 g, 0.100 mol) in one portion with mechanical stirring. The reaction mixture self-heated to reflux after the addition. After 30 min, an additional mixture of 0.3 mL of hydrochloric acid and iron powder (5.59 g, 0.100 mol) was added in one portion. After the mixture was stirred and heated at 70 °C for 3 h, it was filtered hot. The filtrate was concentrated on a rotary evaporator. The residue was extracted with methylene chloride. The extract was washed with a 0.1 N NaOH solution and once with brine. After drying over anhydrous magnesium sulfate, the methylene chloride was removed under reduced pressure to give 2.1 g (72%) of a yellow oily liquid. ^{1}H NMR ($CDCl_3$): δ 1.42−1.82 (m, 8H, aliphatic), 1.89 (s, 3H, CH_3), 3.42 (s, 2H, NH_2), 3.82 (t, 2H, aliphatic), 4.11 (t, 2H, aliphatic), 5.50−6.04 (m, 2H, vinyl), 6.60 (d, 2H, aromatic), 6.69 (d, 2H, aromatic). IR (KBr): 3250−3400 (NH_2), 2950, 1730 (C═O), 1635 (C═C) cm^{-1}. Elem. Anal. Calcd for $C_{16}H_{23}N_1O_3$: C, 69.29; H, 8.36. Found: C, 69.34; H, 8.22.

5-Nitroisophthaloyl Chloride (4). 5-Nitroisophthalic acid (10.0 g, 0.0474 mol) was added to thionyl chloride (100 mL) in a 300 mL, round-bottom flask equipped with a reflux condenser, a nitrogen inlet, and an overhead stirrer. The mixture was heated at reflux for 5 h. The excess thionyl chloride was removed under reduced pressure to give a white product, which was recrystallized from hexane to yield 9.9 g (85%) of white crystals; mp 82−84 °C (lit.[24] mp 80−83 °C). ^{1}H NMR (acetone-d_6): δ 8.53 (s, 2H, aromatic), 8.02 (s, 1H, aromatic).

Di[2-(methacryloyloxy)ethyl] 5-Nitroisophthalate (5). 5-Nitroisophthaloyl chloride (8.37 g, 0.0240 mol) in methylene chloride (40 mL) was added dropwise to a solution of 2-hydroxyethyl methacrylate (6.24 g, 0.0480 mol) and triethylamine (5.2 mL, 0.048 mol) in methylene chloride (200 mL) over 1 h at 0 °C. After stirring for another 1 h at 0 °C, the mixture was warmed to room temperature and stirred for 2 h. The triethylammonium chloride was removed by filtration. The methylene chloride layer was washed three times with a 0.1 N NaOH aqueous solution and once with brine. The solution was dried over Na_2SO_4 overnight and filtered. The methylene chloride was removed under reduced pressure to yield a white solid, which was crystallized from 2-propanol to give 9.7 g (80%) of white crystals; mp 57−59 °C. ^{1}H NMR (acetone-d_6): δ 1.89 (s, 6H, aliphatic), 4.49−4.57 (m, 8H, aliphatic), 5.50−6.10 (m, 4H, vinyl), 8.42 (s, 2H, aromatic), 8.15 (s, 1H, aromatic). IR (KBr): 3350, 1725 (C═O), 1610, 1380 (NO_2) cm^{-1}. Elem. Anal. Calcd for $C_{20}H_{21}N_1O_{10}$: C, 55.17; H, 4.86. Found: C, 55.29; H, 4.84.

Di[2-(methacryloyloxy)ethyl] 5-Aminoisophthalate (6). To a warm stirred solution of di[2-(methacryloyloxy)ethyl] 5-nitroisophthalate (4.12 g, 0.0100 mol) in a mixture of 60 mL of 2-propanol and 15 mL of water was added 0.5 mL of hydrochloric acid and iron powder (325 mesh) (5.59 g, 0.100 mol) in one portion. The mixture self-heated to reflux after the addition. After 30 min, an additional mixture of 0.5 mL of hydrochloric acid and iron powder (5.59 g, 0.100 mol) was added in one portion. After the mixture was stirred and heated at 70 °C for 3 h, it was filtered hot. The filtrate was concentrated on a rotary evaporator. The residue was extracted with methylene chloride. The extract was washed with a 0.1 N NaOH solution and once with brine. After drying over anhydrous magnesium sulfate, methylene chloride was removed under reduced pressure to give a white product, which was recrystallized from 2-propanol to yield 3.4 g (63%) of white crystals; mp 64−65 °C. ^{1}H NMR (acetone-d_6): δ 1.89 (s, 6H, aliphatic), 4.49−4.57 (m, 8H, aliphatic), 5.52−6.11 (d, 4H, vinyl), 7.52 (s, 2H, aromatic), 8.03 (s, 1H, aromatic). IR (KBr): 3350−3500 (NH_2), 2950, 1730 (C=O), 1635 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{20}H_{23}N_1O_8$: C, 59.25; H, 5.72. Found: C, 59.32; H, 5.83.

3-Methoxy-4-iodonitrobenzene (7). To a mixture of 3-methoxy-4-aminonitrobenzene (25 g, 0.15 mol) and water (100 mL) was added dropwise concentrated sulfuric acid (60 mL). The solution was heated to 200 °C and then cooled to 0 °C using ice and salt. Sodium nitrite (13.0 g, 0.18 mol) dissolved in water (50 mL) was added dropwise while the solution was cooled below 0 °C. After the addition, the solution was stirred at 0 °C for 30 min and then filtered. The filtrate was added slowly to a solution of potassium iodide (KI) (50 g, 0.30 mol) in water (700 mL) with vigorous stirring. The solid was collected by filtration and washed with a dilute aqueous sodium bisulfite solution and then with water. The solid was recrystallized from methanol to give 30 g (72%); mp 133−135 °C (lit.[25] mp 127−128 °C). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H, CH_3), 7.50−7.59 (m, 2H, aromatic), 7.90 (d, 1H, aromatic).

2,2′-Dimethoxy-4,4′-dinitrobiphenyl (8). After a mixture of 3-methoxy-4-iodonitrobenzene (30.0 g, 0.11 mol), activated copper (36.0 g, 0.60 mol), and DMF (80 mL) was stirred and heated at reflux for 15 h, additional DMF (100 mL) was added. The solution was heated to reflux and then filtered while hot. After the filtrate was allowed to cool to ambient temperature, the solid that formed was collected by filtration and sublimed at 180 °C under reduced pressure to give 11.8 g (69%) of yellow crystals; mp 258−260 °C (lit.[26] mp 256−258 °C). ^{1}H NMR (DMSO): δ 3.82 (s, 6H, CH_3), 7.30 (d, 2H, aromatic), 7.79 (d, 2H, Ar−H), 7.87 (d, 2H, aromatic).

2,2′-Dihydroxy-4,4′-dinitrobiphenyl (9). A mixture of 2,2′-dimethoxy-4,4′-dinitrobiphenyl (30.4 g, 0.100 mol) and pyridine hydrochloride (300 g) was stirred at 220 °C until totally homogeneous and then poured into water (500 mL). The precipitate that formed was collected by filtration and recrystallized from methanol to yield 22.9 g (83%) of yellow crystals; mp 259−261 °C (lit.[26] mp 253−254 °C). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H, CH_3), 7.50−7.59 (m, 2H, aromatic), 7.90 (d, 1H, aromatic).

2,2′-Dimethacryloyloxy-4,4′-dinitrobiphenyl (10). Methacryloyl chloride (3.66 g, 0.0350 mol) in THF (30 mL) was added dropwise to a solution of 2,2′-dihydroxy-4,4′-dinitrobiphenyl (4.83 g, 0.0175 mol) and triethylamine (3.54 g, 0.0350 mol) in THF (150 mL) over 1 h at 0 °C. After stirring for another 1 h, the mixture was allowed to warm to room temperature and stirred for 2 h. After the THF was removed under reduced pressure, the residue was dissolved in methylene chloride (100 mL), which was washed three times with a 0.1 N NaOH aqueous solution and once with brine. The solution was dried over anhydrous sodium sulfate overnight and filtered. The methylene chloride was removed under reduced pressure to give a yellow solid, which was recrystallized from methanol to yield 5.8 g (80%) of yellow crystals; mp 153−155 °C. ^{1}H NMR (acetone-d_6): δ 1.95 (m, 6H, $-CH_3$), 5.61−6.09 (m, 4H, vinyl), 6.55 (m, 4H, aromatic), 6.91 (d, 2H aromatic). IR (KBr): 1730 (C=O), 2950, 1635 (C=C), 1360 (NO_2) cm^{-1}. Elem. Anal. Calcd for $C_{20}H_{16}N_2O_8$: C, 58.26; H, 3.91. Found: C, 58.17; H, 3.84.

2,2′-Dimethacryloyloxy-4,4′-diaminobiphenyl (DMDB) (11). To a warm stirred solution of 2,2′-dimethacryloyloxy-4,4′-dinitrobiphenyl (4.1 g, 0.010 mol) in a mixture of 40 mL of 2-propanol and 10 mL of water was added 0.3 mL of hydrochloric acid and iron powder (325 mesh) (5.59 g, 0.100 mol) in one portion. The mixture self-heated to reflux after the addition. After 30 min, an additional mixture of 0.5 mL of hydrochloric acid and iron powder (5.59 g, 0.100 mol) was added in one portion. After the mixture was stirred and heated at 70 °C for 3 h, it was filtered hot. The filtrate was concentrated on a rotary evaporator. The residue was extracted with methylene chloride. The extract was washed with a 0.1 N NaOH solution and once with brine. After drying over anhydrous magnesium sulfate, methylene chloride was removed under reduced pressure to give a yellow product, which was recrystallized from 2-propanol to yield 2.4 g (68%) of yellow crystals; mp 153−155 °C. ^{1}H NMR (acetone-d_6): δ 1.95 (m, 6H, $-CH_3$), 5.61−6.09 (m, 4H, vinyl), 6.55 (m, 4H, aromatic), 6.91 (d, 2H aromatic). IR (KBr): 3350−3450 (NH_2), 1730 (C=O), 2950, 1635 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72. Found: C, 68.25; H, 5.83.

2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) (12). The compound was prepared from 2-bromo-5-nitrobenzotrifluoride by the described procedure;[12] mp 180−181 °C (lit.[12] mp 181−182 °C).

General Procedure for the Preparation of Methacrylate End-Capped Imide Oligomers. To a solution of PFMB in NMP, excess 6FDA solid (according to the target molecular weight) was added. The mixture (solids content 15% w/w) was stirred at room temperature under nitrogen for 24 h. The end-capping agent 6-(4-aminophenoxy)hexyl methacrylate or di-[2-(methacryloyloxy)ethyl] 5-aminoisophthalate was then added. After the reaction was allowed to continue for 24 h, a mixture of pyridine and acetic anhydride was added. After the reaction was allowed to proceed for another 24 h at room temperature, the solution was poured into methanol with stirring. The precipitate that formed was collected by filtration, washed with methanol, and agitated in methanol in a blender. The polyimide was collected by filtration and dried under reduced pressure at 90 °C for 24 h.

Polymerization of 2,2′-Dimethacryloyloxy-4,4′-diaminobiphenyl (DMB) with Dianhydrides. 6FDA (0.6882 g, 1.549 mmol) was added to a stirred solution of DMB (0.5459 g, 1.549 mmol) in NMP (solids content 15% w/w) under nitrogen at room temperature. After the solution was stirred for 24 h, pyridine (0.183 g, 2.32 mmol) and acetic anhydride (0.237 g, 2.32 mmol) were added. The resulting solution was stirred for an additional 24 h at room temperature. The polymer was isolated by precipitation in methanol with stirring. The precipitate was collected by filtration, washed with methanol, and agitated in methanol in a blender. The polyimide was collected by filtration and dried under reduced pressure at 90 °C for 24 h. The intrinsic viscosities of the polymers were measured at 30 °C in NMP with an Ubbelohde viscometer.

Determination of Photosensitivity and Contrast. After each of the photoreactive polyimides was dissolved in NMP or THF (solids content 2−4% w/w), 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) and trimethylolpropane triacrylate (TMPTA) were added in appropriate amounts, if required. The solution was then poured on a glass plate, which had been treated with a γ-aminopropyltrimethoxysilane solution in 2-propanol (0.5%) to increase the adhesion force. The coated glass was then heated for 1 h at 90 °C under reduced pressure. The film was exposed to a 365 nm wavelength light emitting from a high-pressure mercury lamp (100 W). The film was placed 10 cm from the lamp, which delivered a UV dose of 10 600 μJ/s at this distance. After being heated for another 1 h at 90 °C under reduced pressure, the film was immersed in a THF/water or NMP/water mixture for 3−5 min and rinsed with water. After development, the weight of the remaining film was plotted against the log of the exposure dose. The sensitivity (D_g^p) and contrast (Y_n) of the resist were determined from the curve.

Preparation of the Polyimide Patterns. The polymer solution was coated and prebaked using the procedure described for the photosensitivity study. The films were exposed to 365 nm wavelength light emitting from a high-pressure mercury lamp (100 W) through a chromium-negative mask on a quartz substrate. The films were postbaked and developed. After the film patterns were heated at 250 °C for 2 h, they were evaluated with scanning electron microscopy (SEM).

Summary and Conclusions

In the first part of this work, two photosensitive end-capping agents, i.e., 6-(4-aminophenoxy)hexyl methacrylate and di[2-(methacryloyloxy)ethyl] 5-aminoisophthalate, were prepared. The hydrogenation of the nitro-substituted precursors to these amines was the key step in their synthesis. The end-capping agents were treated with oligomers prepared from PFMB and 6FDA to afford methacrylate end-capped imide oligomers. The oligomers formed films that displayed high optical transparency but required long exposures to UV radiation to affect cure. To improve their photosensitivity, a photoinitiator (TMDPO) and a multifunctional additive (TMPTA) were added. The difunctional end-capped imide oligomers containing 10 wt % TMPTA and 5 wt % TMDPO showed high photosensitivity and contrast. The material could also be photoimaged to give well-defined patterns.

In the second part of this work, a new diamine monomer (DMB) that contained methacrylate moieties was synthesized. Novel polyimides containing pendent methacrylate moieties were prepared by the two-step condensation polymerization of the functionalized diamine and commercially available dianhydrides such as 6FDA and ODPA. The polymer intrinsic viscosities ranged from 1.17 to 1.93 dL/g in NMP. The polymers were soluble in commom organic solvents such as acetone and THF and could be cast into flexible, tough, and optically clear films from THF or chloroform solutions. Similar to the oligomers, 5 wt % of TMDPO had to be added to obtain photosensitive films that could be photoimaged into 10 μm thick patterns. However, the use of multifunctional additives was not required. The films did not develop color or shrink during UV exposure and thermal curing.

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