1304 *Macromolecules* **1997,** *30,* 1304−1310

Base-Sensitive Polymers as Imaging Materials: Radiation-Induced β-Elimination To Yield Poly(4-hydroxystyrene)

Edward J. Urankar,[†] **Isabella Brehm,**[†] **Q. Jason Niu,**[‡] **and Jean M. J. Fréchet***[,‡]

Baker Laboratory, Department of Chemistry, Cornell University,
Ithaca, New York 14850-1301, and Department of Chemistry,
University of California—Berkeley, Berkeley, California 94720-1460

Received September 30, 1996; Revised Manuscript Received December 13, 1996

ABSTRACT: A novel family of functionalized polystyrenes that are susceptible to base-catalyzed β-elimination is reported. A study of the thermal behaviors of poly[(((((2-cyano-1,1-dimethylethyl)oxy)-carbonyl)oxy)styrene], poly[(((2-cyanoethoxy)carbonyl)oxy)styrene], and poly[((((2-methylsulfonyl)ethoxy)-carbonyl)oxy)styrene] confirms that they undergo facile and quantitative elimination of their side chain groups in a process that is susceptible to base catalysis. Imaging of these polymer systems was accomplished using the novel ,4,4′-[bis[[(2-nitrobenzyl)oxy]carbonyl]trimethylene]dipiperidine as an amine photogenerator. Copolymerization of ((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene and ((*t*-butoxycarbonyl)oxy)styrene followed by selective deprotection of the *t*-BOC protecting groups with acid enabled the synthesis of a base-sensitive copolymer containing free phenol units with enhanced thin-film properties.

Introduction

The concept of chemical amplification in microlithography[1] has long been applied to the use of polymeric systems susceptible to cationic processes. This concept was first demonstrated with the development of the poly(*t*-BOC-styrene) resist[2] that operated on the basis of acid catalyzed thermolysis to poly(4-hydroxystyrene) with the evolution of carbon dioxide and isobutylene. Subsequently, many sources of photogenerated acid and numerous resist systems relying on acid-catalyzed processes[3,4] have been developed. Although chemically amplified resists have grown in importance because of their high-performance capabilities,[4] they have been found to be affected by the presence of airborne contaminants.[4,5] Since the resists operate on the basis of photogeneration of acid within the polymer film, airborne traces of *N*-methylpyrrolidinone may cause deactivation of the film surface via capture of the acid catalyst with concomitant degradation of imaging characteristics. Methods utilized to overcome this problem have included the removal of airborne contaminants using carbon filters,[6] the use of a protective overcoat,[7] the incorporation of additives[8] to the resist formulation, and the high-temperature annealing[9] of the resist film to decrease contaminant uptake. Because of the nature of common airborne contaminants, it was expected that a new family of resists designed to operate with photogenerated base, rather than acid, as the key catalyst might be less susceptible to this problem.

The development of a variety of photoprecursors to amines and other bases[10] has initiated interest in polymeric resist systems designed to operate with photogenerated base. These photoactive materials have been used successfully in resist systems that operate via an amine-catalyzed decarboxylation[11] reaction or intramolecular imidization of amide−ester polymer pendant groups.[12] Considerable interest and research has also focused on the utilization of photobase generators in the preparation of photosensitive polyimides from either poly(amic ester)[13] or polyisoimide[14] precursors. This report will focus on the design and synthesis of base sensitive polymers that are susceptible to β-elimination and the reactivity of these polymers toward photogenerated base will be evaluated.

The study of base labile protecting groups that may be removed by β-elimination has led to significant developments in peptide synthesis with the design of easily removed protecting groups for the amine terminus.[15] These designs made use of electron-withdrawing groups to increase the acidity of the β-hydrogens and promote cleavage in the presence of base. Because of their ease of preparation, high susceptibility toward base, and relative stability toward acid, these protecting groups are attractive alternatives to the well known and often used *t*-BOC protecting group, which is acid labile.[16] In designing our polymeric systems that would be susceptible to a base-catalyzed β-elimination, we chose to incorporate these protecting groups into a carbonate structure and block the phenolic groups of poly(4-hyroxystyrene) as shown in Scheme 1. In this manner, our reactive polymer **1**, in the presence of photogenerated base, can undergo the desired β-elimination upon heating to afford poly(4-hyroxystyrene), carbon dioxide, and an activated olefin. The choice of electron-withdrawing group used and the temperature needed to drive the elimination reaction should determine the volatility and the extent to which the olefin is removed from the polymer film. Although the active units and mode of deprotection are different, the basic design and thin-film properties of these materials is analogous to the family of *t*-BOC resists. Elimination of the volatile products and conversion to the phenolic polymer enable preferential dissolution of this material during aqueous base development to afford a positive tone image.

Results and Discussion

In order to demonstrate the ability of photogenerated amines to catalyze the β-elimination process, polymers

---

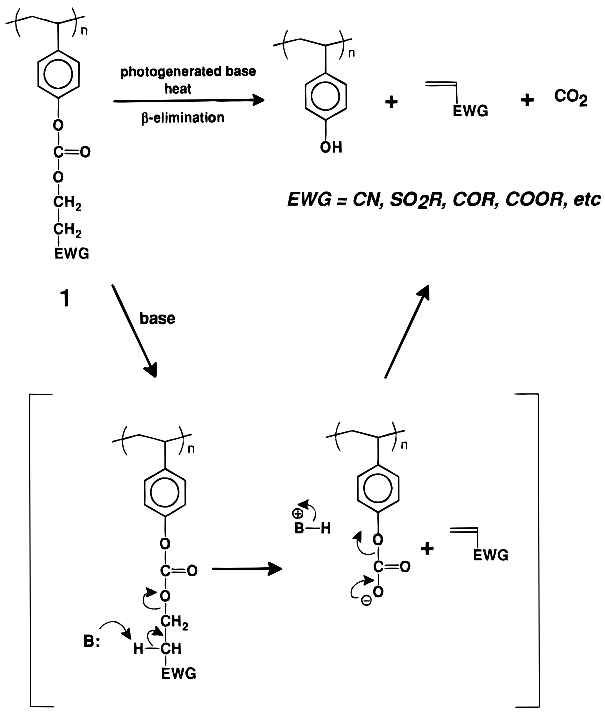
[†] Cornell University.

[‡] University of California—Berkeley.

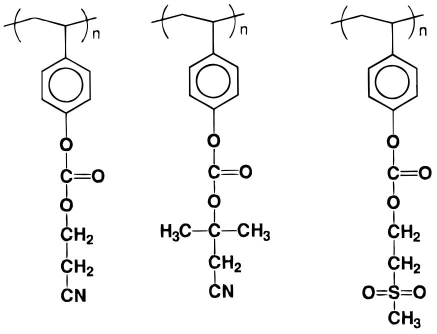
[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

S0024-9297(96)01446-5 CCC: $14.00

Scheme 1

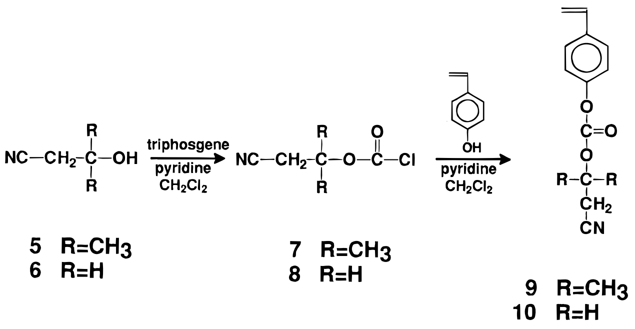


2−**4** were prepared and their thermal and lithographic properties evaluated. The nitrile functionality was chosen to activate polymers **2** and **3** due to its strong electron-withdrawing ability, small size, and favorable solubilizing properties. The use of the sulfone functionality in polymer **4**, is more problematic since the geometry and polar nature of the sulfone group affect the solubility of the resulting polymer in nonpolar solvents, a factor that may limit the use of **4** with the traditional solvents used in spin-coating. Earlier studies[17,18] have shown that the reactive matrix polymer need not carry an active protecting group on each repeat unit, which led us to investigate the use of a copolymer system (**15**) with free phenolic units as well as base labile protected pendant groups.

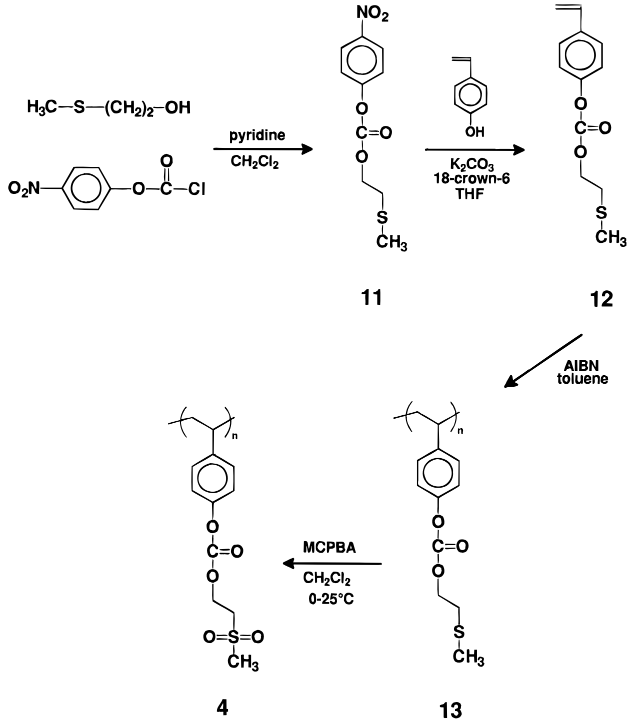


2 **3** **4**

Scheme 2



Scheme 3



Preparation of the Functionalized Polystyrenes. The synthetic strategy to obtain the desired nitrile-containing monomers for the synthesis of polymers **2** and **3** are shown in Scheme 2. Chloroformates **7** and **8** were obtained by reaction of the appropriately substituted alcohol and triphosgene. Isolation of the crude chloroformate was accomplished by washing with dilute acid followed by evaporation of the solvent. Characterization of the chloroformate by ^{13}C-NMR and FTIR spectroscopy suggested that the reactions with triphosgene proceeded in quantitative yield. Reaction of 4-hydroxystyrene with the corresponding chloroformate in the presence of an equivalent amount of pyridine led to the desired monomers **9** and **10**. Radical polymerization of the substituted styrene monomers in toluene using AIBN as a radical source afforded polymers **2** and **3**, which were highly soluble in common solvents such as THF, CHCl$_3$, and acetone.

Polymer **4** was prepared using a synthetic strategy in which the desired product is obtained by polymerization of the sulfide-containing monomer **12** (Scheme 3) followed by subsequent oxidation of the resulting polymer to the corresponding sulfone. This synthetic route is preferred over the alternative preparation of the sulfone functionalized styrene monomer because of easier isolation and purification steps for **12** and its precursors. 2-(Methylthio)ethanol was allowed to react with 4-nitrophenyl chloroformate to produce the desired activated carbonate **11** in quantitative yield. This activated carbonate was then treated with 4-hydroxystyrene in the presence of K$_2$CO$_3$ and 18-crown-6 to afford the desired sulfide-containing monomer **12**. Radical polymerization of **12** under standard conditions gave polymer **13**, which was easily dissolved in solvents such as chloroform and dichloromethane. Oxidation of the sulfide to sulfone was accomplished by treatment with *m*-chloroperbenzoic acid in dichloromethane. The sulfone polymer precipitates during this reaction and the *m*-chlorobenzoic acid byproduct may be removed from the precipitate of **4** by washing with methanol. The transformation of **13** into **4** is readily confirmed by observing the appropriate downfield shifts for the signals corresponding to the methylene group α to the sulfone in the ^{1}H and ^{13}C spectra. Polymer **4** is soluble in polar aprotic solvents such as DMSO, DMF, and *N*,*N*-dimethylacetamide but is insoluble in less polar solvents that readily dissolve polymers **2**, **3**, and **13**.

Preparation of the Partially Protected Copolymer. Upon reaction with base and subsequent heating, our polymer systems should undergo the desired β-elimination with evolution of carbon dioxide and activated olefin. Evolution of these volatile products from the resist will bring about a reduction of the film thickness in the exposed areas of the film. In the case of the *t*-BOC styrene resist system, which loses carbon dioxide and an isobutylene upon reaction with acid, a weight loss amounting to approximately 45% occurs in the polymer film.[19] This large weight loss undoubtedly causes some stress in the resist film, and some have suggested that it adversely affects adhesion as it produces film shrinkage.[17] A number of strategies[18] have been devised to reduce the amount of weight lost upon deprotection by reducing the number of active *t*-BOC groups through the use of copolymer structures. These efforts have led to the development of poly[((*t*-butoxycarbonyl)oxy)styrene-*co*-4-hydroxystyrene], which is now in commercial use.[4] The carbonate linkages partially block the pendant phenolic units and inhibit dissolution of the polymer in aqueous base developer. Photogeneration of the acid catalyst and deprotection of the blocked phenol groups restores the solubility of the polymer in the developer while minimizing the weight lost during deprotection. As an extension of this concept, we were interested in preparing a similar copolymer containing 4-hydroxystyrene units and our base-sensitive carbonate linkages. The synthetic strategy employed for obtaining this copolymer structure takes advantage of the acid stability demonstrated by the ((2-cyano-1,1-dimethylethyl)oxy)carbonyl protecting group previously described by Wünsch and Spangenberg[16] for use in peptide synthesis. Synthesis of a copolymer structure incorporating this group as a base-sensitive carbonate linkage would allow for the selective deprotection of a comonomer containing an acid labile protecting group. To demonstrate this concept, monomer **9** was copolymerized with *t*-BOC styrene as the acid-sensitive comonomer affording copolymer **14**. ^{1}H- and ^{13}C-NMR spectroscopy confirmed the incorporation of both monomers into the polymer structure. Deprotection of the acid-sensitive *t*-BOC linkages was accomplished by treatment with trifluoroacetic acid to yield copolymer **15** containing both free phenolic units and latent phenolic groups masked by the base-sensitive carbonate linkages (Scheme 4). Complete removal of the *t*-BOC groups was confirmed by the disappearance of the methyl and quaternary carbon signals of the *tert*-butyl groups at 28.1 and 83.5 ppm, respectively, in the ^{13}C-NMR spectrum of **15**. Selective deprotection of the *t*-BOC groups was demonstrated by comparison of the integrals in the ^{1}H-NMR spectrum for the aromatic protons and the protons of the methylene α to the nitrile. From the ratio of these integrals, the amount of monomer **9** incorporated into copolymers **14** and **15** was determined to be 43 mol %.

Scheme 4

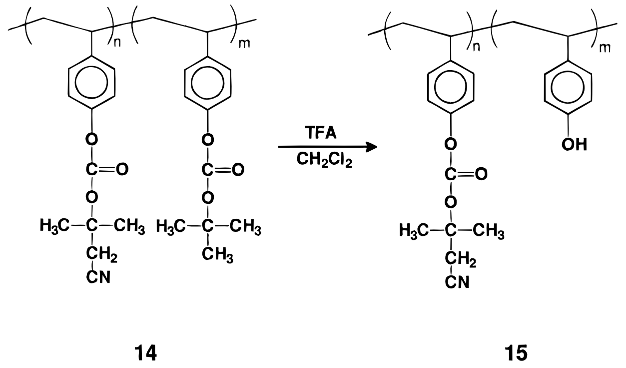


Table 1. Thermal Degradation Behavior of Polymers Based on the Initial Transition of the TGA

	% wt loss (dec temp onset)	
	theory[a]	exptl results
polymer **2**	44.7	44.4 (181 °C)
polymer **3**	51.0	51.7 (206 °C)
polymer **4**	55.5	55.0 (226 °C)
polymer **14**	47.6[b]	48.3 (191 °C)
polymer **15**	31.1[b]	31.2 (215 °C)

[a] The theoretical amounts are calculated assuming loss of eliminated olefins and carbon dioxide from polymer side chains. [b] Calculated from molar ratio of monomers determined from ^{1}H-NMR integrations.

Thermal Properties of the Functionalized Polystyrenes. The thermal behavior of the functionalized polystyrenes investigated by thermogravimetric analysis (TGA) is summarized in Table 1. All of the TGA measurements were conducted under nitrogen from 30 to 550 °C at a heating rate of 10 °C/min. Each of the polymers investigated exhibited a two-step decomposition curve that was reminiscent of that seen for poly(*t*-BOC-styrene)[19] due to the presence of labile β-hydrogens in the carbonate structure. The TGA curve for poly[(((2-cyanoethoxy)carbonyl)oxy)styrene] (**2**) shows an initial weight loss of 44.4% between 181 and 260 °C. This initial weight loss corresponds to the thermal elimination of the volatile acrylonitrile and carbon dioxide from the polymer structure and agrees well with the theoretical value calculated for this process. Similar decompositions seen for polymers **3** and **4** begin at slightly higher temperatures and are in good agreement with the theoretical weight loss values.

TGA of poly [((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene-*co*-((*tert*-butoxycarbonyl)oxy)styrene] (**14**) demonstrated two distinct transitions for the thermal removal of both heat labile carbonate linkages attached to its side chains (Figure 1).

The thermolysis of the *t*-BOC groups took place beginning at 191 °C, while the removal of the cyano-functionalized carbonate linkages took place at slightly higher temperature with a less sharp transition. The decomposition curve obtained for polymer **15**, in which the *t*-BOC groups were chemically removed, showed only the transition corresponding to thermolysis of the nitrile containing carbonate linkages starting at 215 °C, confirming the complete removal of the acid-sensitive *t*-BOC groups. The experimental weight loss values measured for **14** and **15** are in good agreement with the theoretical values calculated using the molar ratio of monomers determined from ^{1}H-NMR integrations.

To examine the effect of amines on the decomposition behavior of these types of polymers, the thermal behavior of polymer **2** containing a catalytic amount of an amine was studied. Figure 2 shows the TGA curve for polymer **2** under normal conditions (curve a) and

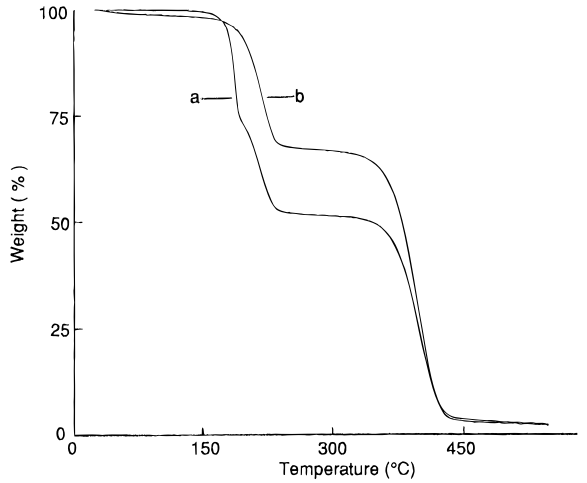


Figure 1. TGA curves for (a) poly[((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxystyrene-*co*-((*tert*-butoxycarbonyl)oxy)styrene] (**14**) and (b) poly[((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene-*co*-4-hydroxystyrene] (**15**).

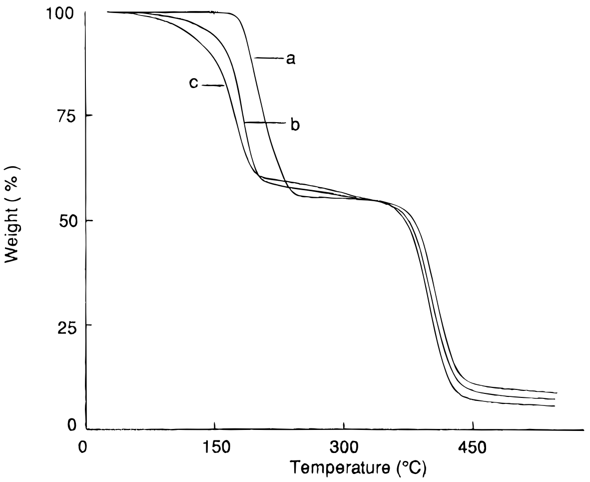


Figure 2. TGA curves for poly[((((2-cyanoethoxy)carbonyl)oxy)styrene] (**2**): (a) without added amine; (b) with 3.9 mol % 1,10-diaminodecane added; (c) with 3.9 mol % 4,4′-trimethylenedipiperidine added.

containing 3.9 mol % of two representative amine bases (curve b and c). The two amines 1,10-diaminodecane and 4,4′-trimethylenedipiperidine (curves b and c, respectively) were chosen because they represent examples of the types of amines that can be readily generated photochemically. Addition of these amines to polymer **2** caused a modest shift in the decomposition curve to lower temperatures. The largest change was seen for the addition of 4,4′-trimethylenedipiperidine, which decreased the decomposition temperature by approximately 35 °C to a value of 146 °C. Increasing the relative amounts of amine added to the polymer continued to shift this transition to lower temperatures.

Lithographic Evaluation. The ability of a photogenerated amine catalyst to effect the decomposition of the functionalized polystyrenes via a β-elimination was evaluated by spin-coating a 1 μm thick film of the polymer containing 11 wt % of 4,4′-[bis[[(2-nitrobenzyl)oxy]carbonyl]trimethylene]dipiperidine (**17**) onto silicon substrates. Photobase generator **17** was prepared using a procedure described by Mochizuki et al.[14] for a similar photoactive material. Exposure to 254 nm radiation liberates 4,4′-trimethylenedipiperidine within the polymer matrix and enables it to catalyze the elimination process in the subsequent baking step. By using double-sided polished silicon wafers, the elimination reaction could be monitored using FTIR spectroscopy. Figure 3 shows the results of monitoring the base-catalyzed decomposition of polymer **2** upon exposure to UV light and is representative of results seen for polymers **3**, **4**, and **15** under similar conditions. Prior to exposure, the strong carbonyl stretching absorption at 1760 cm^{-1}, characteristic of the carbonate structure of polymer **2**, and the nitrile absorption (2250 cm^{-1}) are apparent. Exposure to ca. 160 mJ/cm^2 of 254 nm irradiation followed by heating of the film at 160 °C for 10 min brought about the complete decomposition of the carbonate structure and elimination of the volatile products. This is confirmed by a FTIR spectrum of the film showing the disappearance of the carbonate bands (1760 and 1250 cm^{-1}) and appearance of a hydroxyl band (3400 cm^{-1}) from the resulting phenolic units. These results are also typical of the FTIR spectra obtained from experiments in which amines were added to solutions of the polymers which were then cast into films and subsequently baked to promote the elimination reaction. FTIR analysis of unexposed resist films that were heated at a similar temperature (160 °C) did not exhibit any signs of decomposition, as this is below the thermal elimination temperature for the polymer. Transformation of the matrix polymer to poly(4-hydroxystyrene) was also confirmed by ^{1}H-NMR analysis of the resist film after UV exposure and baking. Use of the photobase generator which produced 4,4′-trimethylenedipiperidine was critical to the elimination process as the performances of other photobase generators were less satisfactory. As an example, films of polymer **2** containing bis[[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine, which generates 1,6-hexanediamine upon exposure to UV light, did not show any appreciable decomposition upon irradiation and baking at temperatures of up to 170 °C. Other amine generators that liberate a secondary amine did demonstrate

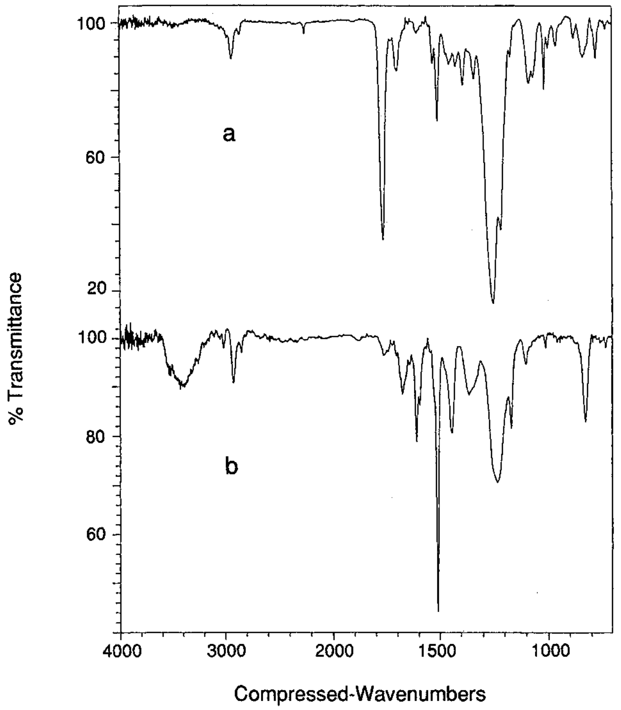


Figure 3. FTIR spectra for the resist containing 89 wt % polymer **2** and 11 wt % photoamine generator **17**: (a) baked at 160 °C for 10 min without exposure to UV irradiation; (b) after exposure to 168 mJ/cm^2 of 254 nm irradiation and baking at 160 °C for 10 min.

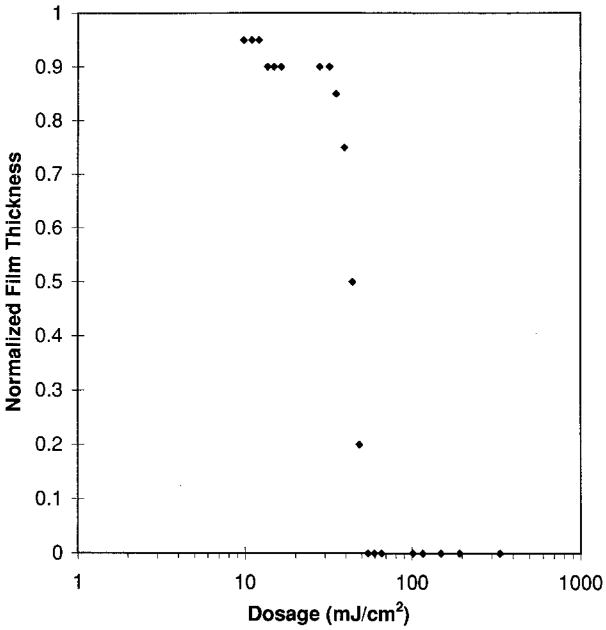


Figure 4. Sensitivity curve for resist containing 89 wt % polymer **2** and 11 wt % photoamine generator **17**. Exposure to 254 nm irradiation was followed by baking at 160 °C for 10 min and development in 0.54 N AZ312MIF developer for 15 s.

Table 2. Deep-UV Sensitivity Values of Resists[a] upon Aqueous Base Development

	sensitivity,[b] mJ/cm^2 (contrast)	postexposure bake conditions
polymer **2**	55 (3.7)	160 °C, 10 min
polymer **3**	50 (2.1)	170 °C, 10 min
polymer **4**	60 (3.3)	160 °C, 10 min
polymer **15**	100 (1.0)	170 °C, 10 min
polymer **15**	250 (1.4)	160 °C, 10 min

[a] Polymer films contain 11 wt % 4,4′-[bis[[(2-nitrobenzyl)oxy]carbonyl]trimethylene]dipiperidine (**17**). [b] Development of relief image by immersion into 0.54 N AZ312MIF developer for 15–30 s.

the ability to catalyze the elimination process, perhaps as a result of the increased basicity of the generated secondary amine. This trend is also seen in the TGA (Figure 2) as the decomposition temperature of a blend of **2** with the secondary amine is lowered by an additional 15 °C when compared to a blend of **2** with the primary amine. Volatility of the generated amines may also play a critical role in the lithographic process since 4,4′-trimethylenedipiperidine (bp 330 °C) has a significantly higher boiling point than 1,6-hexanediamine (bp 204 °C).

Formation of poly(4-hydroxystyrene) in the irradiated areas of the resist film leads to differential solubility as these exposed areas are highly soluble in isopropyl alcohol or commercial aqueous base developers. The sensitivity curve shown in Figure 4 for polymer **2** was obtained by development in aqueous tetramethylammonium hydroxide (AZ312MIF) to provide the positive tone relief image. The demonstrated sensitivities for polymers **2**–**4**, containing 11 wt % of 4,4′-[bis[[(2-nitrobenzyl)oyx]carbonyl]trimethylene]dipiperidine, were high, ranging from ca. 50 to 60 mJ/cm^2 (Table 2). Polymer **15**, which contained free phenol units, showed a lower sensitivity (100 mJ/cm^2) than homopolymer **3**. The incorporation of phenolic units within polymer **15** increases the optical density of the materials at 254 nm (0.202/μm) when compared to polymer **3** (0.149/μm). The higher optical density of polymer **15** allows less light to reach the photobase generator and may contribute to the lower sensitivity demonstrated by this material when compared to the homopolymer. However, decreasing the amount of base-sensitive carbonate linkages in the copolymer structure did result in the expected reduction in the percent of film thickness lost upon phototriggered deprotection. The fully protected polymer **3** lost 45% of its original film thickness while partial protection in **15** reduced this value to 29%. Unfortunately the use of high baking temperatures to facilitate the elimination process in these systems does not allow their use for the formation of very small size relief images. We are currently exploring ways to increase the sensitivity of the polymer films in order to lower the postexposure bake temperature required for the elimination process.

Experimental Section

Instrumentation. Instruments used included the following: Gallenkamp melting point apparatus; Nicolet IR/44 spectrophotometer; Hewlett-Packard 8452A diode array UV-visible spectrophotometer; IBM-Bruker AF300 spectrometer for both ^{1}H- and ^{13}C-NMR spectra recorded using the solvent signal as an internal standard; Mettler DSC 30 low-temperature differential scanning calorimeter (10 °C /min, T_g taken as the midpoint of the inflection tangent); Seiko Instruments SSC 5200 TGA thermal analysis system (10 °C/min under N_2); Waters size exclusion chromatograph (510 pump, U6K injector, Viscotek 110 differential viscometer, and a differential refractometer with the detectors connected in parallel with four 5 μm PL gel columns connected in series in order of increasing pore size 100, 500, 1000 A, and mixed bed C with THF as the mobile phase at 40 °C). The molecular weight data are relative to polystyrene standards. Microanalyses were performed by M. H. W. Laboratories, Phoenix, AZ.

Resist film thickness was measured with a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed by contact printing using an Oriel 87301 exposure system with a medium-pressure mercury lamp, a shutter system and an exposure timer. Photon flux was measured using an Optical Associates Inc. 354 exposure monitor. The output of the mercury lamp was filtered through a 254 nm narrow-bandwidth interference filter from Oriel Corp. Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 Multidensity resolution target, Ditric Optics Inc. The amine photogenerator, bis[[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine, was prepared according to the literature.[10]

Synthesis of 3-Hydroxy-3-methylbutyronitrile (5). This compound was prepared by the procedure of Jensen and Kjaer[20] with 1-chloro-2-methyl-2-propanol and excess sodium cyanide in ethanol. Distillation gave a clear liquid: bp 100 °C/12 mm; ^{1}H-NMR ($CDCl_3$) δ 1.31 (m, 6H), 2.46 (m, 2H), 3.25 (br, 1H); ^{13}C-NMR ($CDCl_3$) δ 28.6, 32.3, 68.8, 117.7.

Synthesis of 2-Cyano-1,1-dimethylethyl Chloroformate (7). To a solution of 3-hydroxy-3-methylbutyronitrile (**5**, 5.0 g, 50.5 mmol) and dry pyridine (4.35 g, 55 mmol) dissolved in CH_2Cl_2 (30 mL) under N_2 and cooled with a dry ice bath was added triphosgene (5.94 g, 20 mmol) dissolved in CH_2Cl_2 (30 mL). The triphosgene solution was added over a period of 20 min during which time the reaction mixture turns yellow and a precipitate eventually formed. The mixture was brought to room temperature (rt) , stirred for another 12 h, and finally washed with dilute HCl. The aqueous layer was extracted with additional CH_2Cl_2, and the organic layers were combined and dried over $MgSO_4$. Evaporation of the solvent at reduced presssure left 8.2 g of crude chloroformate, which was used without further purification. ^{1}H-NMR ($CDCl_3$) δ 1.62 (d, 6H), 2.87 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 25.0, 29.4, 85.8, 115.3, 148.1; IR (KBr) 2250 (CN), 1776 (C=O), 1169, 1111, 841 cm^{-1}.

Synthesis of ((((2-Cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene (9). To a solution of 4-hydroxystyrene (2.00 g, 16.7 mmol) and dry pyridine (1.40 g, 18 mmol) dissolved in CH_2Cl_2 (30 mL) under N_2 and cooled with an ice bath was added a solution of 2-cyano-1,1-dimethylethyl chloroformate (**7**, 2.95 g, 18 mmol) dissolved in CH_2Cl_2 (20 mL). The mixture was warmed to rt, stirred for an additional 12 h, and then washed with water. The aqueous layer was extracted with additional CH_2Cl_2, and the organic layers were combined and dried over $MgSO_4$. Concentration and purification of the crude product by flash chromatography on silica gel, eluting with CH_2Cl_2, provided ((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene (4.0 g, 98%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ 1.67 (s, 6H), 2.98 (s, 2H), 5.25 (dd, 1H), 5.70 (dd, 1H), 6.68 (dd, 1H), 7.12 and 7.40 (AA′BB′, 4H); ^{13}C-NMR ($CDCl_3$) δ 25.1, 80.3, 114.0, 116.0, 120.8, 126.9, 135.3, 149.9, 151.2; IR (neat) 2250 (CN), 1759 (C═O), 1508, 1257, 1210, 1127 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.68; H, 5.94; N, 5.68.

Synthesis of 2-Cyanoethyl Chloroformate (8). Following the procedure for 2-cyano-*tert*-butyl chloroformate above, 3-hydroxypropionitrile (**6**, 2.10 g, 30 mmol) and triphosgene (2.97 g, 10 mmol) were allowed to react in the presence of dry pyridine (2.40 g, 30 mmol) to provide 4.05 g of the crude chloroformate, which was used without further purification. ^{1}H-NMR ($CDCl_3$) δ 2.74 (t, 2H); 4.40 (t, 2H). ^{13}C-NMR ($CDCl_3$) δ 17.1, 65.2, 116.0, 149.8; IR (KBr) 2258 (CN), 1776 (C═O), 1148 cm^{-1}.

Synthesis of ((((2-Cyanoethoxy)carbonyl)oxy)styrene (10). Following the procedure for (((2-cyano-*tert*-butoxy)carbonyloxy)styrene above, 4-hydroxystyrene (3.05 g, 25 mmol) and 2-cyanoethyl chloroformate (4.05 g, 30 mmol) were allowed to react in the presence of dry pyridine (2.40 g, 30 mmol) to provide crude oil. Flash chromatography on silica gel using CH_2Cl_2 as eluent provided **10** as a colorless oil (3.7 g, 68%). Product could be crystallized from carbon tetrachloride/hexanes to yield a white solid: mp 49−51 °C; ^{1}H-NMR ($CDCl_3$) δ 2.80 (t, 2H), 4.42 (t, 2H), 5.27 (dd, 1H), 5.73 (dd, 1H), 6.70 (dd, 1H), 7.15 and 7.43 (AA′BB′, 4H); ^{13}C-NMR ($CDCl_3$) δ 17.7,62.3, 114.3, 116.3, 120.7, 127.0, 135.3, 135.6, 150.0, 152.7; IR (KBr) 2257 (CN), 1752 (C═O), 1274 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.12; H, 5.30; N, 6.19.

Synthesis of 2-(Methylthio)ethyl *p*-Nitrophenyl Carbonate (11). Following the procedure of Kunz,[16] 2-(methylthio)ethanol (7.30 g, 79 mmol) and 4-nitrophenyl chloroformate (14.50 g, 72 mmol) were allowed to react in the presence of dry pyridine (6.24 g, 79 mmol) in CH_2Cl_2, followed by two recrystallizations from ethanol to provide **11** as white needles (11.8 g, 64%): mp 56−57 °C; ^{1}H-NMR ($CDCl_3$) δ 2.19 (s, 3H), 2.84 (t, 2H), 4.44 (t, 2H), 7.38 and 8.28 (AA′BB′, 4H); ^{13}C-NMR ($CDCl_3$) δ 15.5, 32.1, 67.2, 121.5, 125.1, 145.2, 152.1, 155.2. Anal. Calcd for $C_{10}H_{11}NO_5S$: C, 46.69; H, 4.31; N, 5.44. Found: C, 46.78; H, 4.50; N, 5.48.

Synthesis of (((2-(Methylthio)ethoxy)carbonyl)oxy)styrene (12). A mixture of 4-hydroxystyrene (6.04 g, 50 mmol), 2-(methylthio)ethyl *p*-nitrophenyl carbonate (**11**, 12.85 g, 50 mmol), K_2CO_3 (7.60 g, 55 mmol), and 18-crown-6 (264 mg, 1 mmol) was stirred in refluxing THF for 14 h while under nitrogen. The mixture was poured onto water, and the product was extracted into ethyl ether which was washed with saturated sodium bicarbonate to remove the yellow 4-nitrophenol. The ether was washed with water, dried over $MgSO_4$ and concentrated to yield a crude oil which was purified by flash chromatography. Elution with CH_2Cl_2 provided **12** as a colorless oil (11.2 g, 94%). ^{1}H-NMR ($CDCl_3$) δ 2.18 (s, 3H), 2.83 (t, 2H), 4.40 (t, 2H), 5.27 (dd, 1H), 5.70 (dd, 1H), 6.69 (dd, 1H), 7.15 and 7.42 (AA′BB′, 4H); ^{13}C-NMR ($CDCl_3$) δ 15.1, 31.7, 66.5, 113.7, 120.5, 126.7, 135.0, 135.2, 150.1, 152.8; IR (neat) 1761 (C═O), 1508, 1255, 1218, 840 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.30; H, 5.83.

Free-Radical Polymerization of (((2-Cyanoethoxy)carbonyl)oxy)styrene. A solution of (((2-cyanoethoxy)carbonyl)oxy)styrene (**10**, 5.32 g, 24.5 mmol) and 2,2′-azobis(isobutyronitrile) (AIBN, 71.5 mg, 1.8 mol %) in dry toluene (10 mL) was heated under nitrogen at 65−70 °C for 20 h during which time the polymer precipitated out of solution. The solvent was decanted, and the precipitated polymer was reprecipitated from acetone into methanol to provide **2** as a white powder (3.65 g, 67%). $M_n = 18\,800$, $M_w = 99\,700$, $M_w/M_n = 5.3$. $T_g =$ 94.1 °C. ^{1}H-NMR (acetone-d_6) δ 1.2−2.2 (CH and CH_2), 3.0 (CH_2CN), 4.5 (CH_2O), 6.4−7.2 (ArH); ^{13}C-NMR (d_6-acetone) δ 18.1, 40.5−48.0 (br), 63.7, 118.0, 121.3, 129.1, 143−145 (br), 149.8, 153.7; IR (KBr) 2255 (CN), 1760 (C═O), 1255 cm^{-1}. Anal. Calcd (based on monomer formula) for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.51; H, 5.22; N, 6.40.

Free-Radical Polymerization of ((((2-Cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene. A solution of 2-((((cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene (**9**, 3.07 g, 12.5 mmol) and AIBN (44.8 mg, 2.2 mol %) in dry toluene (5 mL) was heated under nitrogen at 65−70 °C for 20 h to provide a viscous solution. The solution was diluted with CH_2Cl_2 and precipitated into methanol to provide **3** as a white powder (2.40 g, 78%). $M_n = 30\,600$, $M_w = 64\,700$, $M_w/M_n = 2.1$. $T_g = 117.5$ °C. ^{1}H-NMR ($CDCl_3$) δ 1.1−1.8 (CH, CH_2, and CH_3), 3.0 (CH_2CN), 6.2−7.0 (ArH); ^{13}C-NMR (acetone-d_6) δ 25.6, 41−48.0 (br), 81.3, 117.5, 121.8, 129.4, 143−145 (br), 149.9, 152.5; IR (KBr) 2250 (CN), 1758 (C═O), 1507, 1259, 1208, 1127 cm^{-1}. Anal. Calcd (based on monomer formula) for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.32; H, 6.02; N, 5.61.

Free-Radical Polymerization of (((2-(Methylthio)ethoxy)carbonyl)oxy)styrene. A solution of (((2-(methylthio)ethoxy)carbonyl)oxy)styrene (**12**, 7.85 g, 33 mmol) and AIBN (91.8 mg, 1.7 mol %) in dry toluene (10 mL) was heated under nitrogen at 65−70 °C for 20 h to provide a viscous solution. The solution was diluted with CH_2Cl_2 and precipitated into methanol to provide a viscous gel. Dissolution in CH_2Cl_2 and reprecipitation twice into ethyl ether followed by drying under vacuum provided **13** as a glassy solid (4.60 g, 58%). $M_n = 16\,100$, $M_w = 42\,600$, $M_w/M_n = 2.6$. ^{1}H-NMR ($CDCl_3$) δ 1.1−1.9 (CH and CH_2), 2.25 (CH_3S), 2.83 (CH_2S), 4.4 (CH_2O), 6.2−7.2 (ArH); ^{13}C-NMR (acetone-d_6) δ 11.0, 32.9, 40.5−46.0 (br), 67.7, 121.7, 129.4, 143−145 (br), 150.3, 154.3; IR (KBr) 2921, 1758 (C═O), 1509, 1256, 1215 cm^{-1}. Anal. Calcd (based on monomer formula) for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.69; H, 5.68.

Synthesis of Poly[(((2-(methylsulfonyl)ethoxy)carbonyl)oxy)styrene] (4). To a solution of poly[(((2-(methylthio-)ethoxy)carbonyl)oxy)styrene] (**13**, 600 mg, 2.5 mmol) in 30 mL of CH_2Cl_2 cooled with an ice bath was added excess solid *m*-chloroperbenzoic acid (MCPBA, 4.35 g, 5 equiv). After 15 min, the ice bath was removed and the reaction was stirred at rt for 12 h. The solvent was removed by evaporation and the residual white solid was washed with methanol to remove *m*-chlorobenzoic acid which was generated. The remaining solid was filtered, washed with methanol, and air-dried. Reprecipitation from DMSO into water produced **3** as a white powder (580 mg, 86%). $T_g = 84.1$ °C ^{1}H-NMR (DMSO-d_6) δ 1.0−2.0 (CH and CH_2), 3.10 (CH_3SO_2), 3.60 (CH_2SO_2), 4.60 (CH_2O), 6.2−7.2 (ArH); ^{13}C-NMR (DMSO-d_6) δ 41.6,52.5, 61.8, 120.6, 128.2, 142−144 (br), 148.5, 152.5; IR (KBr) 2933, 1764 (C═O), 1506, 1315 (SO_2), 1264, 1132 (SO_2) cm^{-1}. Anal. Calcd (based on monomer formula) for $C_{12}H_{14}O_5S$: C, 53.32; H, 5.22. Found: C, 53.15; H, 5.39.

Free-Radical Copolymerization of ((((2-Cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene and ((*tert*-Butoxycarbonyl)oxy)styrene. A solution of ((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene (**9**, 10.80 g, 44 mmol), ((*tert*-butoxycarbonyl)oxy)styrene (9.68 g, 44 mmol), and AIBN (204.3 mg, 1.4 mol %) in dry toluene (20 mL) was heated under nitrogen at 65−70 °C for 40 h to provide a viscous solution. After dilution in CH_2Cl_2 and two precipitations into methanol, **14** was obtained (white powder, 16.78 g, 82%). $M_n = 35\,900$, $M_w = 70\,200$, $M_w/M_n = 1.9$. $T_g = 121.9$ °C. ^{1}H-NMR (acetone-d_6) δ 1.4 −2.0 (CH, CH_2, and CH_3), 3.15 (CH_2CN), 6.2−7.0 (ArH); ^{13}C-NMR (acetone-d_6) δ 25.7, 28.1, 41−48.0 (br), 81.5, 83.5, 117.7, 122.1, 129.5, 143−145 (br), 150.3, 152.9; IR (KBr) 2985, 2933, 2260 (CN), 1758 (C═O), 1508, 1258, 1149 cm^{-1}. Anal. Calcd (based on monomer formula and molar ratio): C, 69.81; H, 6.80; N, 2.61. Found: C, 70.02; H, 6.76; N, 2.60.

Synthesis of Poly[((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene-*co*-4-hydroxystyrene] (15). To a solution of poly [((((2-cyano-1,1-dimethylethyl)oxy)carbonyl)oxy)styrene-*co*-((*tert*-butoxycarbonyl)oxy)styrene] (**14**, 6.03 g) dissolved in chloroform (80 mL) under nitrogen was added trifluoroacetic acid (4 mL). The reaction was stirred at reflux for 14 h. The solvent was removed by evaporation, and the resulting brown viscous oil was dissolved in acetone and precipitated three times into water to provide **15** as a white solid (3.74 g). $T_g = 141.5$ °C. ^{1}H-NMR (acetone-d_6) δ 1.2 −2.0 (CH, CH_2, and CH_3), 3.15 (CH_2CN), 6.2−7.1 (ArH), 8.0 (OH); ^{13}C-NMR (d_6-acetone) δ 25.5, 41−48.0 (br), 81.3, 115.6, 117.5, 121.4, 129.4, 137−139 (br), 143−145 (br), 150.3, 152.9, 155.9; IR (KBr) 3450 (OH), 2924, 2263 (CN), 1760 (C=O), 1514, 1260, 1208, 1126, 830 cm^{-1}. Anal. Calcd (based on monomer formula and molar ratio): C, 73.04; H, 6.39; N, 3.46. Found: C, 72.24; H, 6.49; N, 3.55.

Synthesis of 2-Nitrobenzyl *p*-Nitrophenyl Carbonate (16). To a solution of 2-nitrobenzyl alcohol (21.20 g, 138 mmol) and dry pyridine (11.06 g, 140 mmol) dissolved in dry THF (75 mL) under N_2 and cooled with an ice bath was added a solution of *p*-nitrophenyl chloroformate (28.14 g, 140 mmol) dissolved in dry THF (75 mL). A white precipitate formed immediately and the mixture was stirred under reflux for 24 h. The reaction was poured onto water and the product was extracted into CH_2Cl_2. The CH_2Cl_2 was washed twice with water, dried with $MgSO_4$, and evaporated to dryness to yield a white solid. Crystallization from a mixture of toluene and ethanol (1:1) provided **16** as a white powder (33.0 g, 75%): mp 131−133 °C; ^{1}H-NMR (acetone-d_6) δ 5.73 (s, 2H), 7.57 and 8.33 (AA′BB′, 4H), 7.69 (m, 1H), 7.84 (m, 2H), 8.17 (d, 1H); ^{13}C-NMR (d_6-acetone) δ 67.9, 123.1, 125.8, 126.1, 130.3, 130.4, 131.4, 134.9, 146.5, 152.9, 156.5. Anal. Calcd for $C_{14}H_{10}N_2O_7$: C, 52.84; H, 3.17; N, 8.80. Found: C, 53.00; H, 3.22; N, 8.80.

Synthesis of 4,4′-[Bis[[2-nitrobenzyl)oxy]carbonyl]trimethylene]dipiperidine (17). A mixture of 4,4′-trimethylenedipiperidine (3.20 g, 15 mmol), 2-nitrobenzyl *p*-nitrophenyl carbonate (**16**, 10.18 g, 32 mmol), and 1-hydroxybenzotriazole hydrate (1.35 g, 10 mmol) was stirred in refluxing THF for 14 h while under nitrogen. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and washed with 20% aqueous NaOH (500 mL). The CH_2Cl_2 was washed with water, dried over $MgSO_4$, and concentrated to a crude oil which was purified by flash chromatography. Elution with a mixture of acetone/CH_2Cl_2 (1:5) followed by precipitation of the resulting oil into hexane from CH_2Cl_2 provided **17** as a white solid (8.10 g, 95%): mp 87−89 °C; ^{1}H-NMR ($CDCl_3$) δ 1.1−1.6 (m, 12H), 1.68 (br, 4H), 2.79 (br, 4H), 4.13 (br, 4H), 5.51 (s, 4H), 7.46 (m, 2H), 7.54 (m, 2H), 7.63 (m, 2H), 8.05 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 23.5, 32.0, 35.7, 36.5, 44.3, 63.6, 124.8, 128.4, 128.8, 133.2, 133.5, 147.6, 154.5. Decomposition temperature 239 °C. Anal. Calcd for $C_{29}H_{36}N_4O_8$: C, 61.26; H, 6.38; N, 9.85. Found: C, 61.19; H, 6.15; N, 9.83.

Acknowledgment. Financial support for this research by the Office of Naval Research is acknowledged with thanks. Financial support for the undergraduate student exchange program between the University of Mainz and Cornell University from the D.A.A.D. and Hoechst Celanese Corp. is also acknowledged.

References and Notes

(1) Reichmanis, E.; Thompson, L. F., *Chem. Rev.* **1989**, *89*, 1273. Reichmanis, E.; Houlihan, F. M., Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394. Fréchet, J. M. J. *Pure Appl. Chem.* **1992**, *64*, 1239.

(2) Fréchet, J. M. J.; Ito, H.; Willson, C. G., *Proc. Microcircuit Eng.* **1982**, *260*. Willson, C. G.; Ito, H.; Fréchet, J. M. J.; Tessier, T. G.; Houlihan, F. M. *J. Electrochem. Soc.* **1986**, *133*, 181.

(3) Willson, C. G., *Introduction to Microlithography*, 2nd ed.; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Washington, DC, 1994; pp 139−268.

(4) MacDonald, S. A.; Willson, C. G.; Fréchet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.

(5) MacDonald, S. A.; Hinsberg, W. D.; Wendt, H. R.; Clecak, N. J.; Willson, C. G.; Snyder, C. D. *Chem. Mater.* **1993**, *5*, 348. Nalamasu, O.; Reichmanis, E.; Hanson, J. E.; Kanga, R. S.; Heimbrook, L. A.; Enerson, A. B.; Baiocchi, F. A.; Vaidya, S. *Polym. Eng. Sci.* **1992**, *32*, 1565. Kumada, T.; Kubota, S.; Koezuka, H.; Hanawa, T.; Morimoto, H. *J. Photopolym. Sci. Technol.* **1993**, *6*, 571.

(6) MacDonald, S. A.; Clecak, N. J.; Wendt, H. R.; Willson, C. G.; Snyder, C. D.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R.; McGuire, A. E.; Holmes, S.J., *Proc. SPIE*, **1991**, *1466*, 2.

(7) Nalamasu, O.; Cheng, M.; Timko, A. G.; Pol, V.; Reichmanis, E.; Thompson, L.F. *J. Photopolym. Sci. Technol.* **1991**, *4*, 299. Kumada, T.; Tanaka, Y.; Ueyama, A.; Kubota, S.; Koezuka, H.; Hanawa, T.; Morimoto, H. *Proc. SPIE* **1993**, *1925*, 31.

(8) Roschert, H.; Przybilla, K. J.; Spiess, W.; Wengenroth, H.; Pawlowski, G. *Proc. SPIE* **1992**, *1672*, 33. Funhoff, D. J. H.; Binder, H.; Schwalm, R. *Proc. SPIE* **1991**, *1672*, 46.

(9) Ito, H.; England, W. P.; Clecak, N. J.; Breyta, G.; Lee, H.; Yoon, D. Y.; Sooriyakumaran, R.; Hinsberg, W. D. *Proc. SPIE* **1993**, *1925*, 65. Ito, H.; England, W. P.; Sooriyakumaran, R; Clecak, N. J.; Breyta, G.; Hinsberg, W. D.; Lee, H.; Yoon, D. Y. *J. Photopolym. Sci. Technol.* **1993**, *6*, 547. Ito, H.; Breyta, G.; Hofer, D.; Pomerene, A.; Petrillo, K.; Seeger, D. *Polym. Prepr.*(*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35*, 935.

(10) Kutal, C.; Willson, C. G. *J. Electrochem. Soc.* **1987**, *134*, 2280. Song, K. H.; Urano, A.; Tsunooka, M.; Tanaka, M. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 417. Cameron, J. F.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919. Cameron, J. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4303. Ackmann, A.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1996**, 605. Ito, K.; Nishimura, M.; Sashio, M.; Tsunooka, M. *J. Polym. Sci., Part A.* **1994**, *32*, 2177. Cameron, J. F.; Willson, C. G.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.*, **1995**, 923. Hanson, J. E.; Jenson, K. H.; Gargiolo, N.; Motta, D.; Pingor, D. A.; Novembre, A. E.; Mixon, D. A.; Komentani, J. M.; Knurek, C. *Polym. Mater. Sci. Eng.* **1995**, *72*, 201. Cameron, J. F.; Willson, C. G.; Fréchet, J. M. J. *J. Am. Chem. Soc.*, in press.

(11) Leung, M.; Fréchet, J. M. J. *Polym. Mater. Sci. Eng.* **1993**, *68*, 30.

(12) Leung, M.; Fréchet, J. M. J.; Cameron, J. F.; Willson, C. G. *Macromolecules* **1995**, *28*, 4693.

(13) McKean, D. R.; Wallraff, G. M.; Volksen, W.; Hacker, N. P.; Sanchez, M. I.; Labadie, J. W. *Polym. Mater. Sci. Eng.* **1992**, *66*, 237. McKean, D. R.; Briffaud, T.; Volksen, W.; Hacker, N. P.; Labadie, J. W. *Polym. Prepr.*, (*Am. Chem. Soc., Soc., Div. Polym. Chem.*) **1994**, *35*, 387. Fréchet, J. M. J.; Cameron, J. F.; Chung, C. M.; Haque, S. A.; Willson, C. G. *Polym. Bull.*, **1993**, *30*, 369.

(14) Mochizuki, A.; Teranishi, T.; Ueda, M. *Macromolecules* **1995**, *28*, 365.

(15) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley-Interscience: New York, 1991, p 341.

(16) Tesser, G. I.; Balvert-Geers, I. C. *Int. J. Pep. Protein Res.* **1975**, *7*, 295. Kunz, H. *Chem. Ber.* **1976**, *109*, 3693. Wünsh, E.; Spangenberg, R. *Chem. Ber.* **1971**, *104*, 2427.

(17) Thackeray, J. W.; Canistro, D.; Denison, M.; Ferrari, J.; Hemond, R.; Medeiros, D.; Orsula, G. W.; Pavelchek, E. K.; Rajaratnam, M.; Sinta, R. *Proc. SPIE* **1992**, *1672*, 15. Mixon, D. A.; Bohrer, M. P.; Alonzo, J. C. *Proc. SPIE* **1994**, *2195*, 297.

(18) Kometani, J. M.; Galvin, M. E.; Heffner, S. A.; Houlihan, F. M.; Nalamasu, O.; Chin, E.; Reichmanis, E. *Macromolecules* **1993**, *26*, 2165. Ulrich, K. E.; Reichmanis, E.; Heffner, S. A.; Kometani, J. M.; Nalamasu, O. *Chem. Mater.* **1994**, *6*, 287.

(19) Ito, H.; Willson, C. G.; Fréchet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510. Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995.

(20) Kjaer, A.; Jensen, R. B. *Acta Chem. Scand.* **1958**, *12*, 1746.

MA961446W