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Design and Synthesis of Photoactive Polymer Systems Based on Amine-Catalyzed Intramolecular Imidization of Polymer Side Chains

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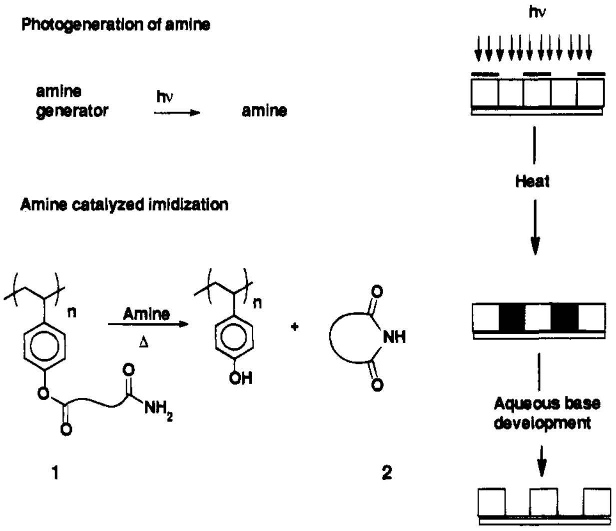
ABSTRACT: A novel family of functionalized polystyrenes that can undergo base-catalyzed intramolecular side-chain imidization is reported. The thermal behaviors of poly(4-vinylphenyl succinamate), poly(4-vinylphenyl glutaramate), poly(4-vinylphenyl 3,3-dimethylglutaramate), and poly(4-vinylphenyl phthalamate), as well as their optical properties and chemical reactivities in the presence of an added amine have been studied. With the exception of poly(4-vinylphenyl phthalamate), the polymers are thermally stable up to 200 °C and have a relatively low optical density below 300 nm. A general trend for the ease of imidization of the polymers is summarized as follows: poly(4-vinylphenyl phthalamate) > poly(4-vinylphenyl succinamate) > poly(4-vinylphenyl 3,3-dimethylglutaramate) > poly(4-vinylphenyl glutaramate). Photoactive polymer systems were obtained by mixing either poly(4-vinylphenyl succinamate) or poly(4-vinylphenyl 3,3-dimethylglutaramate) with some bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine used as an amine photogenerator. Imaging of films of the polymers, as well as the effect of structure on their reactivity is discussed.

Introduction

Since the concept of chemical amplification has been introduced to photolithography by Fréchet, Ito, and Willson[1] in 1982, the development of highly sensitive resist materials suitable for modern microlithography[2] has proceeded very rapidly. Among those successful imaging systems that have been commercialized,[3] the best known chemically amplified resists[2−6] are based on polymers containing [4-(*tert*-butyloxycarbonyl)oxy]styrene moieties.[1,7] This polymer is susceptible to acid catalyzed thermolysis of its side-chain *t*-BOC protecting group in a process that results in a significant change in polarity and solubility.

Although a large number of photopolymers known to date are highly sensitive to light-induced free radical[8] or cationic[9] modification processes, complementary examples for radiation-induced anionic or nucleophilic processes are rare. This is due to the lack of commercial sources of photogenerated base. Recently, our laboratory has developed several novel routes for the photogeneration of amines within a polymer matrix.[10] In addition, we have demonstrated that photogenerated amines may be of use in the design of chemically amplified resists based on amine-catalyzed decarboxylations[11] or in the preparation of photo-imidizable materials that may be used in electronics packaging.[12] Because of the importance of base-catalyzed reactions in polymer-modification and curing processes,[13] we also expected that amine photogeneration could be widely applied to many different areas of polymer science and technology. In particular our interest in the application of phototriggered catalytic chemistry[4] to imaging materials has led us to investigate the possibility of using amines as catalysts in the intramolecular imidization of amide−esters. In this paper, we report the design and the synthesis of a novel family of aqueous base developable imaging materials based on the intramolecular imidization of amide−esters.

Scheme 1



The thermal imidization of amide−esters usually occurs at relatively high temperatures. However, in the presence of bases such as hydroxide ions, imidization proceeds effectively at ambient or moderate temperatures.[14] The basis of our design for polymer **1** is that its intramolecular imidization would lead to splitting of the side chain of the functionalized polymers leading to two aqueous base soluble products, poly(4-hydroxystyrene) and the corresponding imide **2** (Scheme 1). This transformation is accompanied by a large change in polarity that allows image development in an aqueous base developer without swelling, as demonstrated by Iwayanagi on a different polymer system.[15] A schematic illustration of this approach is shown in Scheme 1. The resist material consists of polymer **1** containing a small amount of amine photogenerator. Since the polymer and the amine photogenerator are relatively hydrophobic, they have little affinity for aqueous base developers. Upon exposure to radiation, amines generated in the

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exposed areas will catalyze the imidization of **1** by liberating poly(4-hydroxystyrene) and a low molecular weight cyclic imide. Because both of the imidization products are aqueous base soluble, development in such a developer will lead to the fast removal of the exposed areas and therefore will afford a positive tone image. However, because the unexposed polymer itself is also relatively sensitive to base, its structure must be chosen to avoid extensive reaction with the aqueous base developer during the development process. Therefore polymer **1** should be stable in aqueous base developers at room temperature while showing good reactivity with the photogenerated amines at elevated temperatures.

In order to create an efficient photoimageable material based on the amine-catalyzed imidization, some additional factors must be considered for the structural design of the polymer:

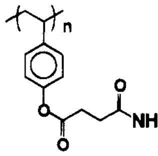
(i) The polymer should have a low absorption in the deep UV region, especially at the exposure wavelength near 250 nm. This factor is critical for the amine photogeneration process.

(ii) The polymer should be thermally stable, at least up to a suitable postbake temperature. However, it should be readily modified in the presence of amines.

(iii) The modification process should be amine-catalyzed; therefore, the photogenerated amine should not be consumed during the modification step.

(iv) The polymer should have a reasonably high T_g.

To demonstrate the feasibility of applying the base-catalyzed imidization to polymer imaging, four functionalized polystyrenes with amide–ester side chains **3–6** were synthesized and their properties were evaluated.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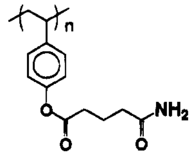
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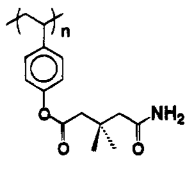
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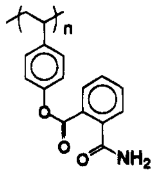
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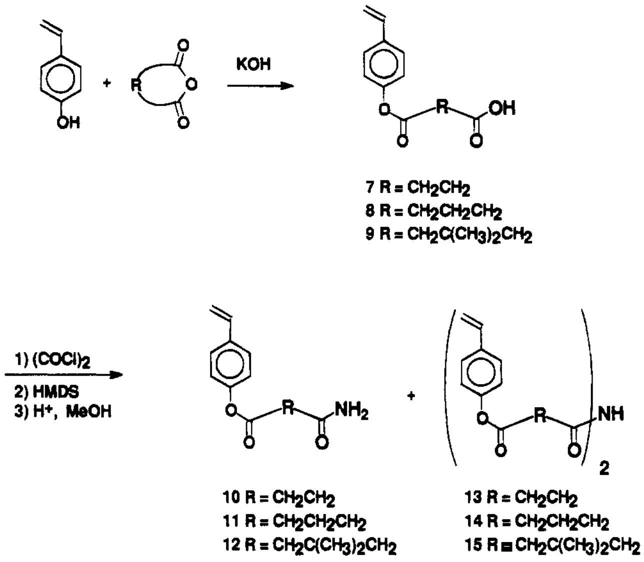
Results and Discussion

Preparation of the Functionalized Polystyrenes 3–6. Synthetic strategies to obtain monomeric precursors of the functionalized polystyrenes **3–6** are summarized in Schemes 2 and 3. Reaction of 4-hydroxystyrene with the corresponding acid anhydride in the presence of 1 equiv of potassium hydroxide led to the monoesters **7–9**. The stoichiometry of the reagents is crucial in this reaction because excess potassium hydroxide would hydrolyze the monoesters *in situ* to provide the corresponding diacids and 4-hydroxystyrene. Conversion^{16} of monoesters **7–9** to the corresponding acid chlorides by reaction with oxalyl chloride was followed by aminolysis with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and desilylation in methanol to afford the desired monomers **10–12** in moderate yields, along with very small amounts of divinyl imides **13–15**. Since the divinyl compounds would act as cross-linkers in the eventual radical polymerization of the monomers, they were removed either by flash chromatography on silica gel or by extraction with dilute (0.5%) aqueous NaOH solution. Because of the low conversion of phthalic anhydride and 4-hydroxystyrene into mono(4-vinylphenyl) phthalate, an alternative one-pot synthetic procedure shown in Scheme 3 was used to synthesize 4-vinylphenyl phthalamate (**16**). Treatment of phthaloyl dichloride with 1 equiv of 4-hydroxystyrene in the presence of 1 equiv of 4-(dimethylamino)pyridine (DMAP) and excess pyridine, followed by aminolysis with HMDS and desilylation in methanol provided the desired 4-vinylphenyl phthalamate (**16**) in moderate yield.

Scheme 2



Scheme 3

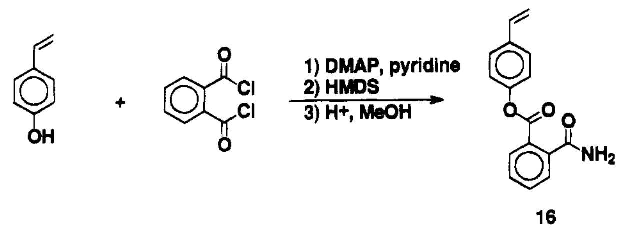


Table 1. Thermal Degradation Behavior of Polymers 3–6 Based on the Results of the DSC Analyses

	starting dec temp (peak) (°C)
polymer **3**	210 (250)
polymer **4**	210 (255)
polymer **5**	220 (260)
polymer **6**	160 (186)

Radical polymerization of the substituted styrene monomers under standard conditions with benzoyl peroxide as the initiator led to polymers **3–6**. The polymers are insoluble in nonpolar solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene but readily soluble in polar aprotic solvent such as DMSO, DMF, NMP, and *N,N*-dimethylacetamide.

Thermal Properties of the Functionalized Polystyrenes 3–6. The thermal behavior of the functional polymers was investigated under nitrogen by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC measurements were carried out from 50 to 350 °C at a heating rate of 10 °C/min, and the data are summarized in Table 1. The DSC curve for poly(4-vinylphenyl succinamate) (**3**) shows a broad exothermic peak starting at 210 °C and reaching a maximum near

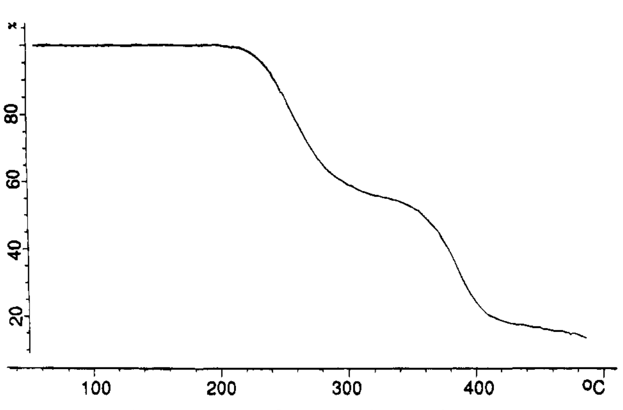


Figure 1. TGA curve of poly(4-vinylphenyl succinamate) (**3**).

Table 2. Thermal Degradation Behavior of Polymers 3–6 Based on the Results of the DSC Analyses

	% wt loss (temp, °C)	
	theory[a]	exptl result
polymer **3**	45	45 (220–320)
polymer **4**	48	44 (220–320)
polymer **5**	54	52 (260–350)
polymer **6**	55	52 (220–380)

[a] The theoretical amounts are calculated by assuming loss of the cyclic imides from the polymer side chains.

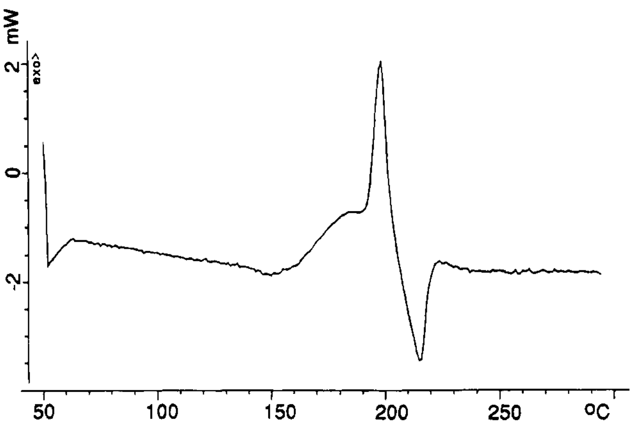


Figure 2. DSC trace of poly(4-vinylphenyl phthalamate) (**6**).

250 °C. This exotherm is attributed to the thermally induced intramolecular imidization of poly(4-vinylphenyl succinamate) (**3**). This assignment is supported by thermogravimetric analysis in which a 45% weight loss is observed between 220 and 320 °C (Figure 1). This weight loss corresponds to the evaporation of succinimide from the sample. Similar thermal decompositions were also observed for polymers **4** and **5** (Table 2). However, poly(4-vinylphenyl phthalamate) (**6**) is relatively unstable and imidizes at a significantly lower temperature. A DSC study of this process (Figure 2) shows a broad exothermic peak near 160 °C followed by a sharp exothermic transition at 200 °C and an endothermic transition at 230 °C. The broad exothermic peak is due to the intramolecular imidization of the phthalamate side chain while the sharp exothermic transition is attributed to the crystallization of phthalimide, which is the imidization product. Melting of the crystallized phthalimide is responsible for the endothermic transition near 230 °C. Because of the low volatility of phthalimide, no significant weight loss at the decomposition temperature of the polymer side chain is observed until the sample is heated above 220 °C in the TGA studies.

Scheme 4

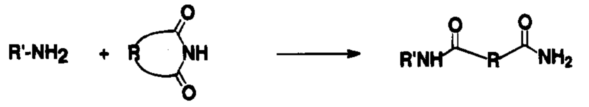


Table 3. Hexylamine-Catalyzed Imidization of Polymers 3 and 5 in DMSO-d_6 at 100 °C

	conversion (%)			
	10 min	20 min	70 min	130 min
polymer **3**[a]	68	89		
polymer **5**[b]	11		57	72

[a] The concentration of hexylamine was 0.04 M, and the concentration of poly(4-vinylphenyl succinamate) (**3**) was 0.40 M. [b] The concentration of hexylamine was 0.04 M, and the concentration of poly(4-vinylphenyl dimethylglutaramate (**5**) was 0.34 M.

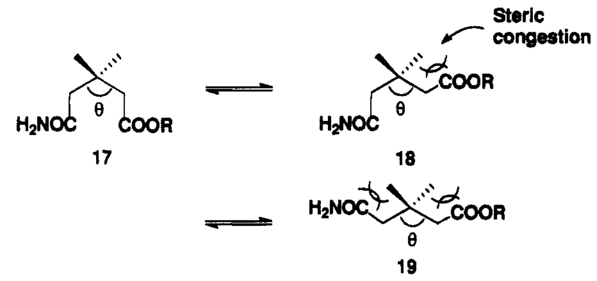
Chemical Reactivity of the Polymer Side Chains: Study of Imidization Reaction. The chemical reactivity of the side chains of polymers **3**–**6** toward amines and aqueous alkaline solutions is of particular importance for the design of our new imaging materials. Ideally, the side chains should imidize readily in the presence of amines at higher temperatures but be stable toward alkaline developers at room temperature. The balance between the propensity toward imidization of the polymer side chains and their stability in aqueous base developers is key to the success of this new design of radiation-sensitive materials. In order to provide sufficient sensitivity in imaging processes, the amine-promoted imidization should be catalytic. This point is important because only small amounts of amine will be generated within the polymer matrix during irradiation and their effect would be amplified in a catalytic process. However, it has been reported that amines may react with cyclic imides to give rise to aqueous base insoluble bis(amide)s (Scheme 4).[17] Since cyclic imides are the major products in the imidization reactions, these potential amine quenchers may consume the photogenerated amine and may therefore inhibit the catalytic process. In order to cope with this potential problem, a polymer system with amide–ester side chains that imidize at a rate that is faster than that of the competing quenching side reaction has to be used. It is known that the structure and conformation of the substrates greatly affect the rate and outcome of cyclization reactivity.[18] As will be described below, the design of the four functional polymers **3**–**6** we have selected allows the study of these effects and therefore provides for optimization of the basic design.

The study of the chemical reactivity of polymers **3**–**6** toward amines was carried out in DMSO-d_6 at 100 °C and monitored by ^{1}H NMR spectroscopy. Polymer **3** shows a fast decay (Table 3) in the presence of 10 mol % of hexylamine with a half-life of *ca.* 5 min. Along with the decay of the polymer, a new singlet signal for the ethano bridge protons of succinimide is observed at 2.55 ppm. No formation of bis(amide) is observed by NMR during the reaction period. Bis(amide) is only seen upon prolonged heating of the reaction mixture after the imidization has been completed.

Unlike poly(4-vinylphenyl succinamate) (**3**), poly(4-vinylphenyl glutaramate) (**4**) shows low reactivity toward amine-catalyzed intramolecular imidization. Heating of **4** at 100 °C for 70 min leads to no more than 10% of imidization. In addition, small amounts of unidentified products appear during this reaction.

Introduction of two methyl groups at the 3-position of the glutaramate increases the rate of imidization.

Scheme 5



Poly(vinylphenyl 3,3-dimethylglutaramate) (**5**) cyclizes at a moderate rate (Table 3) under similar conditions with a half-life of *ca.* 1 h. More importantly, no significant side product other than poly(4-hydroxystyrene) and 3,3-dimethylglutarimide can be observed when the reaction is monitored by ^{1}H NMR spectroscopy. We attribute this rate enhancement to the well-known *gem* dimethyl effect which has been explained by both Ingold[19] and Schleyer.[20] As shown in Scheme 5, methyl groups on the propano bridge compress the internal bond angle θ and increase the population of the reactive *syn*-rotamers **17** which favor the intramolecular cyclization in contrast to sterically congested rotamers **18** and **19** for which cyclization is disfavored.[21]

Poly(4-vinylphenyl phthalamate) (**6**) is relatively unstable thermally and cyclizes slowly in DMSO-d_6 at room temperature even in the absence of amines. This is likely the result of the *cis* configuration of the amido and ester groups, as well as the possibility of a favorable five-membered ring cyclization, two factors that facilitate the imidization.

Stability of the Polymers in Aqueous Base Developers. The dissolution behavior of functional polymers **3**, **5**, and **6** was studied on 1 μm films of each of the polymers containing some bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine,[10] an amine photogenerator. Dissolution of the polymer films in aqueous base developer led to a gradual thinning of the films. By monitoring the film thickness left on the surface of the substrate against the development time, a dissolution curve was constructed. As shown in Figure 3, poly(4-vinylphenyl phthalamate) (**6**) is particularly sensitive to aqueous developers and dissolves completely within 2 min. Poly(4-vinylphenyl succinamate) (**3**) shows a moderate reactivity and dissolves only after an induction period of 1 min. In contrast, poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**) is so stable in the developer that no significant thinning of the film was observed under the experimental conditions. We attribute the dissolution of the polymers to the hydroxide-catalyzed imidization which affords poly(4-hydroxystyrene) and the corresponding imides, both of which are soluble in aqueous bases.

According to these data it appears that intramolecular imidization of the amide−esters into five-membered cyclic imides proceeds faster than that into six-membered ones. However, substituents on the amide−esters can modify their reactivity so that a six-membered ring imidization can also become competitive, as reflected by the dissolution behavior in aqueous base developers.

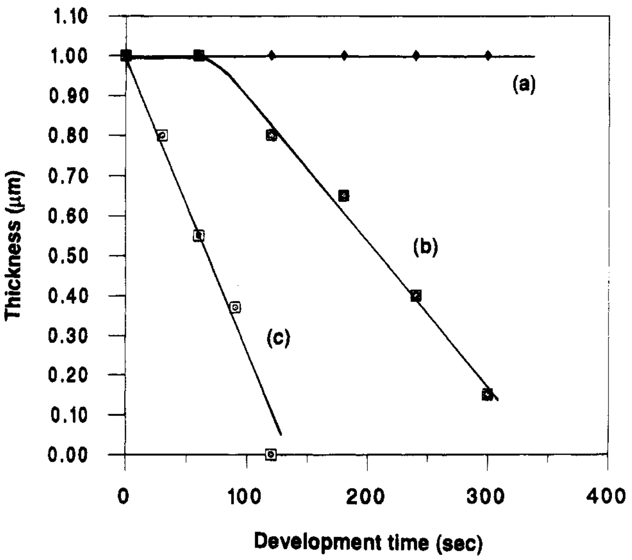


Figure 3. Dissolution curves of polymers **3**, **5**, and **6** in a dilute Shipley AZ312MIF (tetramethylammonium hydroxide) developer (25 v/v %): (a) poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**); (b) poly(4-vinylphenyl succinamate) (**3**); (c) poly(4-vinylphenyl phthalamate) (**6**).

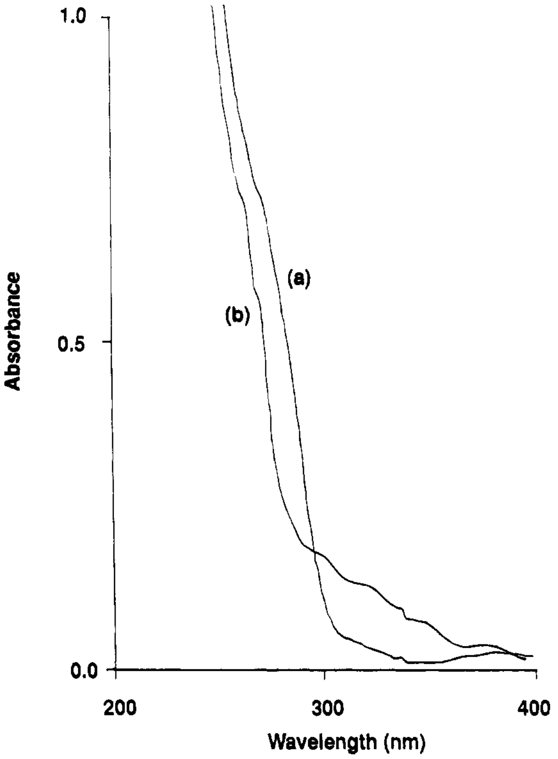


Figure 4. UV spectra obtained from (a) a 0.5 mm thick film of the resist derived from poly(4-vinylphenyl phthalamate) (**6**) and 5 mol % of bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine as a base generator and (b) a 1.0 mm thick film of the resist derived from poly(4-vinylphenyl succinamate) (**3**) and 8 mol % of the base generator.

Optical Properties of Films of 3 or 6 Containing an Amine Photoprecursor. The UV spectra of thin films of the imaging materials consisting of the polymers and bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine reveal significant UV absorption by **6** below 300 nm (Figure 4). For deep UV imaging near 250 nm, the high optical density of the film would prevent the UV light from penetrating through the full thickness of the polymer matrix. This disadvantage is particularly serious in the case of positive tone imaging because modification of the polymer down to the surface of the substrate is required to afford good images. Replacement of the conjugated spacer by a nonconjugated one reduces the UV absorption of the matrix. As shown in Figure 4, an imaging material based on polymer **3** has a much lower optical density below 300 nm than was the case for materials derived from **6**.

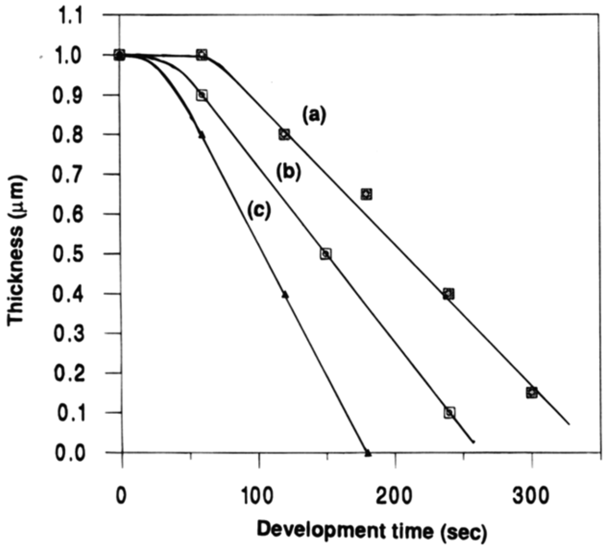


Figure 5. Photochemical and temperature effects on the dissolution behavior of the resist films containing poly(4-vinylphenyl succinamate) (**3**) and bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine) (8 mol %) in a dilute (25 v/v %) Shipley AZ312MIF (tetramethylammonium hydroxide) developer: (a) without irradiation; (b) irradiation at 254 nm (170 mJ/cm^2) and postbaking at 130 °C for 10 min; (c) irradiation at 254 nm (170 mJ/cm^2) and postbaking at 140 °C for 10 min.

Lithographic Evaluation. The lithographic behavior of the positive tone imaging materials based on poly(4-vinylphenyl succinamate) (**3**) and poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**) containing bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine (8 and 10 mol %, respectively) was evaluated using 1 μm thick films spin-coated onto silicon wafers. Because of the lack of stability of polymer **6** in aqueous base developers and the low reactivity of polymer **4** toward amines, these two polymers were not tested lithographically. In the absence of irradiation, the dissolution rates of the films in aqueous base developers are independent of the baking conditions. Upon irradiation at 254 nm, hexane-1,6-diamine is generated inside the polymer matrix and is therefore able to catalyze the imidization during the subsequent heating step (postbake). The extent of imidization reflects on the final dissolution rates of the resists in aqueous base developer. As seen in Figure 5, the dissolution rate of films based on polymer **3** increases after exposure. Moreover, the dissolution is affected by the postbake temperature: a higher postbake temperature will lead to a larger extent of imidization and therefore a higher dissolution rate. A similar dissolution behavior was also observed for films derived from polymer **5**.

The sensitivity curve shown in Figure 6 for polymer **3** (curve a) was obtained using an aqueous potassium borate developer (Shipley AZ400K). This figure is a plot of the normalized film thickness remaining on the substrate after development versus the exposure dose. As shown by this sensitivity curve, the lithographic process generates a positive tone image with a sensitivity of 350 mJ/cm^2 at 254 nm with a contrast of 1.5. The addition of electrolytes such as sodium chloride to the developer does not enhance the sensitivity. Figure 7 shows a relief image generated using a film of **3** spin-coated onto a silicon wafer. It must be emphasized here that it may be possible to further enhance the sensitivity of this type of imaging material through the use of different developers or process conditions.

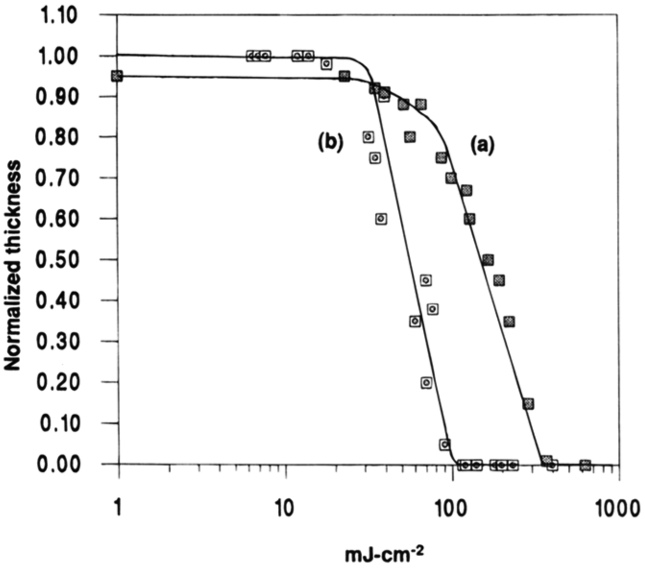


Figure 6. Sensitivity curves of the resists derived from polymers **3** and **5**. (a) The resist derived from poly(4-vinylphenyl succinamate) (**3**) was exposed to UV light at 254 nm, postbaked at 140 °C for 10 min, and developed in a dilute (40 v/v %) Shipley AZ400K developer for 80 s. (b) The resist derived from poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**) was exposed to UV light at 254 nm, postbaked at 120 °C for 12 min, and developed in a mixture of ethanol and Shipley AZ312MIF aqueous tetramethylammonium hydroxide developer for 70 s.

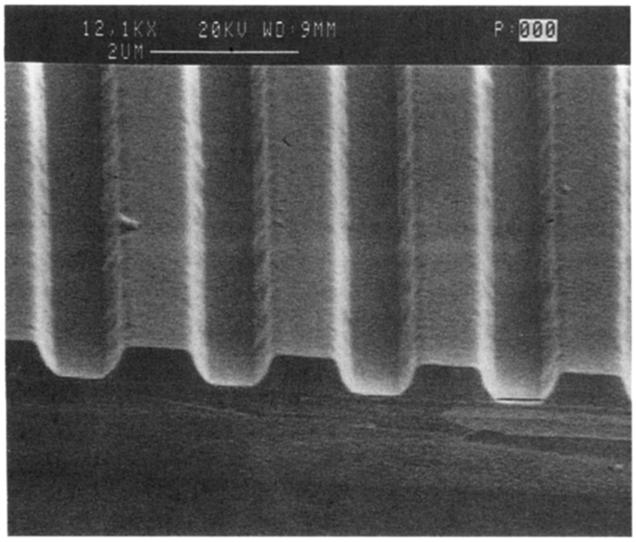


Figure 7. SEM image obtained with resist derived from poly(4-vinylphenyl succinamate) (**3**) using bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine as an amine photogenerator. After exposure to *ca.* 0.5 J/cm^2, the image was postbaked at 140 °C and developed in a dilute (40 v/v %) AZ400K aqueous potassium borate developer for 80 s.

The sensitivity curve for polymer **5** (curve b) is shown in Figure 6. Because of the higher stability of the background polymer matrix toward basic developers, stronger developer solutions may be used in the development process. Figure 6 shows a sensitivity curve for **5** that demonstrates a positive tone sensitivity of 100 mJ/cm^2 at 254 nm with a contrast of 1.9.

Conclusion

We have successfully designed a family of base-sensitive functionalized polystyrenes bearing amide−ester side chains that can be used as imaging materials in lithographic processes. Although poly(4-vinylphenyl succinamate) (**3**) is chemically more reactive and imidizes faster than poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**) in the presence of amines in DMSO solution, polymer **3** appears to be less sensitive than polymer **5** in the solid-state lithographic experiments. We ascribe these results to the intrinsic reactivity of polymer **3** with hydroxide ions in the aqueous base developers. Reaction of the polymer with hydroxide leads to poly(4-hydroxystyrene) and succinimide which enhance the dissolution rate of the polymer matrix into the basic developer. This background dissolution reduces the solubility difference between the exposed and unexposed areas that were created in the photolithographic process. In addition, we also observed the substituent effect (*gem* dimethyl effect) on the imidization of the glutaramate side chain. Introduction of methyl groups on the glutaramate unit enhances the rate of imidization and therefore increases the reactivity of the polymers. This type of rate enhancement may also depend on the size of the substituents. By changing the size of the substituents, the hydrophobicity that affects the stability of the polymers in an aqueous base developer and the imidization reactivity of the polymer might be modified further. It is clear that the systems reported in this work are not nearly as efficient in terms of chemical amplification as those that utilize the acid-catalyzed processes we pioneered more than 15 years ago.[1,2] However the use of photogenerated base[10,11] in imaging materials may obviate the deactivation of photogenerated catalysts that is reported to be caused by the airborne impurities commonly found in the clean room environment of semiconductor manufacturing facilities.[2,22]

Experimental Section

General Directions. Melting points were measured on a Gallenkamp melting point apparatus. IR spectra were recorded on a Nicolet IR/44 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on solutions in CDCl$_3$ or acetone-d_6 on an IBM-Bruker AF300 (300 MHz) spectrometer using the solvent proton signal or the solvent carbon signal as an internal standard. Size exclusion chromatography was performed on a liquid chromatograph consisting of a Waters 510 pump, a U6K injector (Waters), a Viscotek 110 differential viscometer and a differential refractometer-refractoMonitor (Milton Roy) with the detectors being connected in parallel. Four 5 μm PL gel columns connected in series in order of increasing pore size (100 Å, 500 Å, 1000 Å, and mixed bed C) were used with THF as the mobile phase at 40 °C. The molecular weight data are relative to polystyrene standards. In order to better compare the relative molecular weight of the various functionalized polystyrenes by GPC in THF, they were first transformed into the corresponding poly(4-hydroxystyrene) by mild heating in the presence of diisopropylethylamine or piperidine in DMF. The conversion is quantitative as monitored spectroscopically. Thermal behavior of the polymers was monitored by a Mettler DSC 30 thermal analysis unit and a Mettler TG 50 thermobalance. Microanalyses were performed by M. H. W. Laboratories, Phoenix, AZ. Lithographic experiments were performed on an Oriel illuminator equipped with a 254 nm band-pass filter. The amine photogenerator, bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine, was prepared according to the previously published procedure.[10] Highly pure poly(4-hydroxystyrene) was prepared by aminolysis of [(*tert*-butyloxycarbonyl)oxy]styrene[7] in the presence of hydrazine hydrate in ethanol.

Synthesis of 4-Vinylphenyl Phthalamate (16). To a solution of 4-hydroxystyrene (1 g, 8.3 mmol) and phthaloyl dichloride (2 g, 1.1 equiv) in CH$_2$Cl$_2$ (20 mL) was added a solution of 4-(dimethylamino)pyridine (DMAP) (1.1 g, 1.1 equiv) and pyridine (5 mL) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 3 h after which the mixture was chilled in an ice bath and subsequently added dropwise a solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (3 equiv) in CH$_2$Cl$_2$ (10 mL). The reaction mixture was stirred for an additional 6 h and quenched with ice-cold dilute H$_2$SO$_4$ (5%, 100 mL). The organic phase was taken up into CH$_2$Cl$_2$, washed with saturated aqueous NaCl solution, dried over anhydrous Na$_2$SO$_4$, and evaporated to dryness to give a crude silylated amide−ester obtained as an oil. This crude material was then dissolved in MeOH, and the solution was allowed to stand at room temperature for 2 h. Removal of the methanol under reduced pressure gave a slightly yellowish solid. Recrystallization of the solid from chloroform/hexanes provided **16** as colorless crystals in 76% yield: mp 126−127 °C; IR 3409, 3180 (NH$_2$, amide), 1741 (C=O, ester), 1653 cm^{-1} (C=O, amide); ^{1}H NMR δ (CDCl$_3$) 5.24 (d, J = 11.4 Hz, 1H), 5.70 (d, J = 17.7 Hz, 1H), 6.02 (bs, 1H), 6.14 (bs, 1H), 6.69 (dd, J_1 = 17.7 Hz, J_2 = 11.4 Hz, 1H), 7.17−7.21 and 7.39−7.43 (AA′BB′, 4H), 7.51−7.58 (m, 3H), 8.00−8.02 (m, 1H); ^{13}C NMR δ (CDCl$_3$) 114.30, 121.71, 127.39, 127.68, 129.36, 130.35, 130.58, 132.50, 135.75, 136.07, 137.59, 150.51, 165.71, 171.00. Anal. Calcd for C$_{16}$H$_{13}$NO$_3$: C, 71.9; H, 4.9; N, 5.2; O, 18.0. Found: C, 72.0; H, 5.0; N, 5.3.

Synthesis of 4-Vinylphenyl Succinamate (10). (a) Preparation of Mono(4-vinylphenyl)succinate (7). To a solution of 4-hydroxystyrene (5.1 g, 43 mmol) and KOH (86%, 3 g, 45 mmol) in dry THF (100 mL) was added succinic anhydride (4.5 g, 45 mmol) under nitrogen. The mixture was stirred for 15 min and quenched by an ice-cold dilute HCl solution. The product was extracted into ethyl acetate, dried over anhydrous Na$_2$SO$_4$, and rotary evaporated to dryness to give a white solid. Recrystallization of the white solid gave **7** as colorless crystals (7.7 g, 83%): mp 101−102 °C; IR 3230−3300 (COOH), 1758 (C=O), 1705 cm^{-1} (C=O); ^{1}H NMR δ (CDCl$_3$) 2.78−2.82 and 2.85−2.89 (AA′BB′, 4H), 5.23 (d, J = 11.6 Hz, 1H), 5.69 (d, J = 17.6 Hz, 1H), 6.68 (dd, J_1 = 17.6 Hz, J_2 =11.6 Hz, 1H), 7.03−7.05 and 7.38−7.41 (AA′BB′, 4H), 10.4−11.4 (bs, 1H); ^{13}C NMR δ (CDCl$_3$) 29.26, 29.43, 114.44, 121.85, 127.55, 135.88, 136.29, 150.50, 171.00, 178.25.

(b) Preparation of 4-Vinylphenyl Succinamate (10). To a solution of 4-vinylphenyl succinate (7 g, 32 mmol) in benzene (100 mL) was added a solution of oxalyl chloride (2 equiv) in benzene (20 mL). After addition, three drops of DMF was added to catalyze the reaction. Stirring was continued for 2 h after which the solvent and excess oxalyl chloride were removed under reduced pressure. The residue was taken up into benzene (30 mL), filtered, and concentrated to provide a crude acid chloride. The crude chloride was redissolved in CH$_2$Cl$_2$ (100 mL), and the solution was added dropwise a solution of HMDS (16.5 g, 3 equiv) in CH$_2$Cl$_2$ (30 mL) at 0 °C. The reaction mixture was stirred for another 8 h at room temperature and then quenched with ice-cold dilute H$_2$SO$_4$. The organic phase was extracted with CH$_2$Cl$_2$, dried over anhydrous Na$_2$SO$_4$, and evaporated to dryness to provide a crude silylated amide−ester as an oil. Desilylation of the crude intermediate in MeOH at room temperature for 2 h provided a white solid that was purified by flash chromatography on silica gel, eluting with hexanes/ethyl acetate (gradually from 1:1 to 1:2.5) to give compound **10** as colorless crystals (5.7 g, 82%): mp 125−126 °C; IR 3371, 3191 (NH$_2$, amide), 1758, 1658 cm^{-1} (C=O); ^{1}H NMR δ (CDCl$_3$) 2.62 (t, J = 6.7 Hz, 2H), 2.91 (t, J = 6.7 Hz, 2H), 5.23 (d, J = 10.8 Hz, 1H), 5.60 (bs, 2H), 5.69 (d, J = 17.6 Hz, 1H), 6.67 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 7.02−7.05 (d, J = 8.5 Hz, 2H), 7.31−7.41 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ (CDCl$_3$) 29.66, 30.31, 114.27, 121.74, 127.37, 135.69, 136.08, 150.37, 171.67, 173.76. Anal. Calcd for C$_{12}$H$_{13}$NO$_3$: C, 65.7; H, 6.0; N, 6.4; O, 21.9. Found: C, 65.6; H, 6.2; N, 6.4.

Synthesis of 4-Vinylphenyl Glutaramate (11). (a) Preparation of Mono(4-vinylphenyl) Glutarate (8). Following the procedure for mono(4-vinylphenyl) succinate above, 4-hydroxystyrene (5 g, 42 mol) and glutaric anhydride (4.8 g, 1 equiv) were reacted in the presence of KOH (86%, 2.7 g, 1.1 equiv) to provide mono(4-vinylphenyl) glutarate (7.3 g, 75%): mp 77−78 °C; IR 2300−3300 (COOH), 1755, 1705 cm^{-1} (C=O); ^{1}H NMR δ (CDCl$_3$) 2.03−2.12 (m, 2H), 2.52 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.3 Hz, 2H), 5.24 (d, J = 11.2 Hz, 1H), 5.70

(d, J = 17.6 Hz, 1H), 6.69 (dd, J_1 = 17.6 Hz, J_2 = 11.0 Hz, 1H), 7.02–7.06 and 7.38–7.43 (AA′BB′, 4H), 10.7–11.4 (bs, 1H); ^{13}C NMR δ (CDCl$_3$) 19.84, 33.04, 33.33, 114.24, 121.71, 127.34, 135.54, 136.00, 150.21, 171.53, 179.41. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.7; H, 6.0; O, 27.3. Found: C, 66.7; H, 6.1.

(b) Preparation of 4-Vinylphenyl Glutaramate (11). Following the procedure for **10** above, mono(4-vinylphenyl) glutarate (5 g, 21 mmol) was transformed to the acid chloride followed by aminolysis with HMDS and methanolysis to provide a crude solid. The crude solid was dissolved in CH_2Cl_2, washed with dilute KOH followed by a dilute HCl solution, dried over anhydrous Na_2SO_4, concentrated, and flash chromatographed on silica gel, eluting with hexanes/ethyl acetate (gradually changed from 1:1 to 1:2.5) to give **11** (3.7 g, 75%): mp 126–127 °C; IR 3368, 3188 (NH$_2$, amide), 1747 (C=O, ester), 1652 cm^{-1} (C=O, amide); ^{1}H NMR δ (CDCl$_3$) 1.99–2.09 (m, 2H), 2.33 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H), 5.22 (d, J = 10.8 Hz, 1H), 5.68 (d, J = 17.6 Hz, 1H), 5.72 (bs, 1H), 5.99 (bs, 1H), 6.70 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 6.99–7.03 and 7.37–7.41 (AA′BB′, 4H); ^{13}C NMR δ (CDCl$_3$) 20.57, 33.40, 34.51, 114.25, 121.71, 127.29, 135.53, 135.92, 150.18, 171.90, 174.84. Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.9; H, 6.5; N, 6.0; O, 20.6. Found: C, 67.1; H, 6.6; N, 6.0.

Synthesis of 4-Vinylphenyl 3,3-Dimethylglutaramate (12). (a) Preparation of Mono(4-vinylphenyl) 3,3-Dimethylglutarate (9). Following the procedure for mono(4-vinylphenyl) succinate above, 4-vinylphenol (5 g, 42 mmol) and 3,3-dimethylglutaric anhydride (5.9 g, 42 mmol) were reacted in the presence of KOH (86%, 2.75 g, 42 mol) to provide a colorless oil. The unreacted 4-hydroxystyrene was silylated by chlorotrimethylsilane in the presence of pyridine in benzene and removed by chromatography to provide mono(4-vinylphenyl) 3,3-dimethylglutarate (4.2 g, 55%) as a colorless oil (the product contained 10% 3,3-dimethylglutaric acid): ^{1}H NMR δ (CDCl$_3$) 1.11 (s, 6H), 2.52 (s, 2H), 2.67 (s, 2H), 5.20 (d, J = 10.8 Hz, 1H), 5.66 (d, J = 17.6 Hz, 1H), 6.62 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 6.09–7.10 and 7.35–7.38 (AA′BB′, 4H).

(b) Preparation of 4-Vinylphenyl 3,3-Dimethylglutaramate (12). Following the procedure for **11**, conversion of mono(4-vinylphenyl) 3,3-dimethylglutarate to the corresponding acid chloride followed by aminolysis with HMDS, desilylation in methanol, and purification through extraction and chromatography on silica gel provided 4-vinylphenyl 3,3-dimethylglutaramate **12** as colorless crystals in 61% yield: mp 56–58 °C; IR 3379, 3190 (NH$_2$, amide), 1747 (C=O, ester), 1659 cm^{-1} (C=O, amide); ^{1}H NMR δ (CDCl$_3$) 1.21 (s, 6H), 2.34 (s, 2H), 2.64 (s, 2H), 5.22 (d, J = 10.9 Hz, 1H), 5.69 (d, J = 17.6 Hz, 1H), 5.93 (bs, 1H), 6.30 (bs, 1H), 6.68 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 6.99–7.03 and 7.39–7.42 (AA′BB′, 4H); ^{13}C NMR δ (CDCl$_3$) 28.76, 33.75, 44.71, 46.56, 114.40, 121.75, 127.36, 135.75, 135.88, 149.97, 171.75, 173.82. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.9; H, 7.3; N, 5.4; O, 18.4. Found: C, 69.0; H, 7.1; N, 5.4.

Free Radical Polymerization of 4-Vinylphenyl Phthalamate. A solution of 4-vinylphenyl phthalamate (**16**) (1.5 g, 5.6 mmol) and benzoyl peroxide (28 mg, 2 mol %) in de-aerated THF (5 mL) was heated at 80–85 °C under nitrogen for 20 h during which the polymer product precipitated from the solution mixture. The solvent was decanted, and the residual polymer was rinsed with THF (5 mL), dissolved in a small volume of *N*,*N*-dimethylacetamide, and reprecipitated in CH_2Cl_2 to provide a viscous gel-like polymer. The polymer was stirred in pentane overnight to give **6** as a white powder in 70% yield: M_n = 15 000, M_w = 38 000, M_w/M_n = 2.5; IR 3409, 3180 (NH$_2$, amide), 1740 (C=O, ester), 1651 cm^{-1} (C=O, amide); ^{1}H NMR δ (DMF-d_6) 1.10–2.60 (3H, alkyl); 6.30–6.95 (2H, ArH), 6.95–7.30 (2H, ArH), 7.50–7.80 (4H, ArH), 7.82 (bs, 1H, NH), 8.17 (bs, 1H, NH); ^{13}C NMR δ (DMF-d_6) 40.85, 42–48 (b), 122.19, 128.35, 129.10, 130.00, 130.57, 131.49, 132.10, 138.45, 142–144 (b), 149.97, 167.18, 170.97. Anal. Calcd (based on the monomer formula) for $C_{16}H_{13}NO_3$: C, 71.9; H, 4.9; N, 5.2; O, 18.0. Found: C, 71.7; H, 5.1; N, 5.0.

Free Radical Polymerization of 4-Vinylphenyl Succinamate. A solution of 4-vinylphenyl succinamate (**10**) (1 g, 4.6 mmol) and benzoyl peroxide (80 mg, 7 mmol) in de-aerated toluene (5 mL) was heated under nitrogen at 80–85 °C for 20 h during which gel-like polymers precipitated from the reaction mixture. This viscous precipitate was rinsed with toluene, dissolved in *N*,*N*-dimethylacetamide, and reprecipitated in CH_2Cl_2 to give a viscous gel. The gel was stirred in pentane overnight to provide **3** as a white solid (0.8 g) in 80% yield: M_n = 17 000, M_w = 63 000, M_w/M_n = 3.6; IR 3440, 3346, 3199 (NH$_2$, amide), 1756 (C=O, ester), 1668 cm^{-1} (C=O, amide); ^{1}H NMR δ (DMSO-d_6) 0.9–2.1 (3H, alkyl), 2.48 (bs, 2H, –CH$_2$–), 2.70 (bs, 2H, –CH$_2$–), 6.20–6.80 (4H, ArH), 6.85 (bs, 1H, NH), 7.36 (bs, NH); ^{13}C NMR (DMSO-d_6) δ 29.02, 29.56, 38–43 (broad), 121.08, 127.94, 142.03 (b), 148.44, 171.15, 172.76. Anal. Calcd for $(C_{12}H_{13}NO_3)_n$: C, 65.7; H, 6.0; N, 6.4; O, 21.9. Found: C, 65.7; H, 5.9; N, 6.2.

Free Radical Polymerization of 4-Vinylphenyl Glutaramate. Following the procedure for poly(4-vinylphenyl succinamate) above, 4-vinylphenyl glutaramate (**11**) was polymerized in dioxane to provide **4** as a white solid in 70% yield: IR 3440, 3352, 3195 (NH$_2$, amide), 1753 (C=O, ester), 1665 cm^{-1} (C=O, amide); ^{1}H NMR δ (DMSO-d_6) 0.8–2.1 (5H, including a broad singlet at 1.8 ppm for 2H, –CH$_2$–), 2.20 (bs, 2H, –CH$_2$–), 2.55 (bs, 2H, –CH$_2$–), 6.20–7.20 (5H, including a broad singlet at 6.8 ppm for 1H, NH), 7.40 (bs, 1H, NH); ^{13}C NMR δ 20.42, 33.00, 33.93, 38–42 (broad), 121.34, 128.10, 141.85, 148.42, 171.44, 173.78. Anal. Calcd for $(C_{13}H_{15}NO_3)_n$: C, 66.9; H, 6.5; N, 6.0. Found: C, 66.7; H, 6.4; N, 5.8.

Free Radical Polymerization of 4-Vinylphenyl 3,3-Dimethylglutaramate. Following the procedure above 4-vinylphenyl 3,3-dimethylglutaramate (**12**) was polymerized in dioxane to provide a viscous gel. The gel was dissolved in *N*,*N*-dimethylacetamide, precipitated first in pentane, and then reprecipitated in water to provide **5** as a white powder in 85% yield: M_n = 4600, M_w = 5400, M_w/M_n = 1.2; higher molecular weight polymer could be obtained by modification of the polymerization conditions. IR 3440, 3353, 3195 (NH$_2$, amide), 1752 (C=O, ester), 1667 cm^{-1} (C=O, amide); ^{1}H NMR δ (DMSO-d_6) 0.7–2.2 (11H, including a broad singlet at 1.12 ppm for 6 H, *gem* methyl and a broad singlet at 2.14 ppm for 2H, –CH$_2$–), 2.62 (bs, 2H, –CH$_2$–), 6.02–7.15 (5H, including a broad singlet at 6.83 for 1H, NH), 7.30 (bs, 1H, NH); ^{13}C NMR δ 27.20, 32.55, 38–42 (b), 44.73, 46.36, 121.37, 128.11, 142.28 (b), 148.33, 170.12, 172.70. Anal. Calcd for $(C_{15}H_{19}NO_3)_n$: C, 68.9; H, 7.3; N, 5.4; O, 18.4. Found: C, 68.8; H, 7.2; N, 5.5.

Lithographic Experiments. Solutions of polymer **3** (18.6 wt %) and polymer **5** (24.6 wt %) containing bis((2,6-dinitrobenzyl)oxycarbonyl)hexane-1,6-diamine (8 and 10 mol %, respectively) in *N*,*N*-dimethylacetamide were spin-coated as ca. 1 μm thick films (3000 rpm, 1.5 min) onto two different substrates: (a) silicon wafers for lithography and (2) quartz disks for UV measurements. The resulting films were dried (prebake) at 90 °C for 3 min.

The sensitivity curve for polymer **3** (curve a) in Figure 6 was obtained by exposure of the resist films at 254 nm through a multitransmission mask (Ditric Optics Inc). After exposure, the films were postbaked at 140 °C for 10 min and developed in a dilute Shipley AZ400K (40 v/v %) developer for 80 s.

The sensitivity curve for polymer **5** (curve b) in Figure 6 was obtained by exposure at 254 nm through a multitransmission mask followed by postbaking at 120 °C for 12 min and development in a mixture of ethanol and Shipley AZ312MIF developer (3:80) for 70 s.

SEM images such as that shown for polymer **3** (Figure 7) were obtained by printing through an ordinary transmission mask with an exposure of *ca.* 0.5 J/cm^2 followed by postbaking at 140 °C (5–8 min) and development in a dilute Shipley AZ400K (40 v/v %) solution for 60–90 s.

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