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ABSTRACT

The use of photogenerated base in polymer modification processes has been investigated with the study of the amine catalyzed intramolecular imidization of reactive functional groups attached to a polystyrene matrix. The monomers are prepared by reaction of 4-hydroxystyrene with suitable anhydrides such as phthalic anhydride or the corresponding diacid chlorides, followed by amidation with hexamethyldisilazane. Following their free-radical polymerization, the functionalized polystyrenes have been tested in imaging experiments involving in situ photogeneration of amine from a photoactive carbamate precursor followed by low temperature imidization. The amine catalyzed imidization occurs as a much lower temperature than the uncatalyzed process thereby allowing photopatterning. Because the imidization process results in the formation of aqueous base soluble by-products, image development may be accomplished used standard water-based developers. While the new materials themselves can be used as resists, the concepts demonstrated in this study can be used to design novel photopatternable imaging and packaging materials for microelectronics.

INTRODUCTION

Since the concept of chemical amplification has been introduced to photolithography, the development of highly sensitive resist materials suitable for modern microlithography has proceeded rapidly during the last decade.[1] Among those successful imaging systems that have been commercialized[2], the best known chemically amplified resists are based on polymers containing 4-*t*-butyloxycarbonyloxystyrene moieties.[3] 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 or cationic[4] 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.[5] In addition, we have demonstrated that photogenerated amines may be of use in the design of chemically amplified resists based on amine-catalyzed decarboxylations and imidizations.[6] Because of the importance of base-catalyzed reactions in polymer-modification and curing processes,[7] 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 photo-triggered catalytic chemistry to imaging materials has led us to investigate the possibility of using amines as catalysts in the intramolecular imidization of amide-esters.[6b] 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.

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.[8] The basis of our design for polymer **1** is that its imidization would lead 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. 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 exposed areas will catalyze the imidization of **1** to provide poly(4-hydroxystyrene) and the corresponding 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 photoimagable 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 polymers with amide-ester side chains **3-6** were synthesized and their properties were evaluated.

RESULTS AND DISCUSSION

Preparation of Polymers 3-6. Synthetic strategies to obtained 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 one equivalent of potassium hydroxide led to the *mono*-esters **7-9**. The stoichiometry of the reagents is crucial in this reaction because excess potassium hydroxide would hydrolyze the *mono*-esters *in situ* to provide the corresponding diacids and 4-hydroxystyrene. Conversion[9] of *mono*-esters **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 crosslinkers 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 one equivalent of 4-hydroxystyrene in the presence of an equivalent of 4-dimethylaminopyridine (DMAP) and excess pyridine, followed by aminolysis with HMDS and desilylation in methanol provided the desired 4-vinylphenyl phthalamate (**16**) in moderate yield.

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 Polymers 3-6. The thermal behavior of the polymers was investigated under nitrogen by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC measurements were carried out from 50°C 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-vinylphenylsuccinamate) (**3**) shows a broad exothermic peak starting at 210°C reaching a maximum near 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 is observed until the sample is heated above 220°C in the TGA studies.

Chemical Reactivity. The chemical reactivity of polymers **3-6** towards amines and aqueous alkaline solutions is of particular importance for the design of our new imaging materials. Ideally, the polymers should imidize readily in the presence of amines at higher temperatures but be stable towards alkaline developers at room temperature. The balance between the sensitivity of the polymers and their stability in aqueous base developers is key to the success of this new design of radiation-senstive materials. In order to provide sufficient sensitivity in imaging processes, the amine promoted imidization should be catalytic. This point is important because most photochemical reactions are relatively inefficient and only small amounts of amine will be generated inside the polymer matrix during irradiation. However, it has been reported that amines may react with cyclic imides to give rise to aqueous-base insoluble bisamides (Scheme 4).[10] 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 faster than the quenching 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.[11] As will be described below, the design of the four 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** towards amines was carried out in DMSO-d_6 at 100°C and monitored by ^1H 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 2.55ppm. No formation of bisamide is observed by NMR during the reaction period. Bisamide 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 towards amine-catalyzed intramolecular imidization. Heating of **4** at 100°C for 70 min lead to no more than 10 % of imidization. In addition, small amounts of unidentified products appear during in this reaction.

Introduction of two methyl groups at the 3-position of the glutaramate increases the rate of imidization. Poly(vinylphenyl 3,3-dimethylglutaramate) (**5**) cyclizes at a moderate rate (Table 3) under similar conditions with a half-life of *ca.* 1h. More importantly, no significant side product other than poly(4-hydroxystyrene) and 3,3-dimethylglutarimide can be observed when the reaction is monitored by ^1H NMR spectroscopy. We attribute this rate enhancement to the well known *gem* dimethyl effect which has been explained by both Ingold[12] and Schleyer[13]. 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.[13]

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 group, 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 polymers **3**, **5**, and **6** was studied on 1 μm films of each of the polymers containing some bis((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine, 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 minute. In contrast, poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**) is so stable in the devoloper 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.

Optical Properties. The UV spectra of thin films of the imaging materials consistting of the polymers and bis(2,6-dinitrobenzyloxycarbonyl)hexan-1,6-diamine reveal significant UV absorbtion 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 particular 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 reduce 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**.

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)hexan-1,6-diamine (8 mol% 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** towards 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, hexan-1,6-diamine is generated inside the polymer matrix and is therefore is able 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.

The sensitivity curve for polymer **5** (curve b) is shown in Figure 6. Because of the higher stability of the background polymer matrix towards 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 100mJ/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 used as imaging materials in lithographic processes. Although poly(4-vinylphenyl succinamate) (**3**) is chemically more reactive and imidizes faster than poly(4-vinylphenyl3,3-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.

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 is 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 254nm bandpass filter. The amine photogenerator, bis((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine, was prepared according to the previously published procedure.[5a] Highly pure poly(4-hydroxystyrene) was prepared by aminolysis of *tert*-butyloxycarbonyloxystyrene[2] 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_2Cl_2 (20 mL) was added a solution of 4-dimethylaminopyridine (DMAP) (1.1 g, 1.1 equiv.) and pyridine (5 mL) in CH_2Cl_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_2Cl_2 (10 mL). The reaction mixture was stirred for an additional 6 h and quenched with ice-cold dilute H_2SO_4 (5%, 100 mL). The organic phase was taken up into CH_2Cl_2, washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_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 allowed to stand at room temperature for 2h. 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: m.p. 126-127°C; IR cm^{-1} 3409, 3180 (NH_2, amide), 1741 (C=O, ester), 1653 (C=O, amide); ^1H 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 anhydrous (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_2SO_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 %): m.p. 101-102°C; IR cm^{-1} 3230-3300 (COOH), 1758 (C=O), 1705 (C=O); ^1H 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 were added to catalyze the reaction. Stirring was continued for 2 h after which the solvent and excess oxalyl chloride was 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_2Cl_2 (100 mL) and was added dropwise a solution of HMDS (16.5 g, 3 equiv) in CH_2Cl_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_2SO_4. The organic phase was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated to dryness to provide a crude silylated amide-ester as an oil. De-silylation 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/ethylacetate (gradually from 1:1 to 1:2.5) to give compound **10** as colorless crystals (5.7 g, 82 %): m.p. 125-126°C; IR cm^{-1} 3371, 3191 (NH_2, amide), 1758, 1658 (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 anhydrous (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 %): m.p. 77-78°C; IR cm^{-1} 2300-3300 (COOH), 1755, 1705 (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/ethylacetate (gradually changed from 1:1 to 1:2.5) to give **11** (3.7 g, 75 %): m.p. 126-127°C; IR cm^{-1}

3368, 3188 (NH_2, amide), 1747 (C=O, ester), 1652 (C=O, amide); ^1H 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 % of 3,3-dimethylglutaric acid): ^1H 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 to provide 4-vinylphenyl 3,3-dimethylglutaramate **12** as colorless crystals in 61 % yield: m.p. 56-58°C; IR cm^{-1} 3379, 3190 (NH_2, amide), 1747 (C=O, ester), 1659 (C=O, amide); ^1H 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 deaerated 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 white powder in 70 % yield: Mn=15000, Mw=38000, Mw/Mn=2.5; IR 3409, 3180 (NH_2, amide), 1740 (C=O, ester), 1651 (C=O, amide); ^1H 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 deaerated 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 over night to provide **3** as a white solid (0.8 g) in 80 % yield: Mn=17000, Mw=63000, Mw/Mn=3.6; IR cm^{-1} 3440, 3346, 3199 (NH_2, amide), 1756 (C=O, ester), 1668 (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 cm^{-1} 3440, 3352, 3195 (NH_2, amide), 1753 (C=O, ester), 1665 (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 and precipitated first in pentane, and then reprecipitated in water to provide **5** as white powder in 85% yield: Mn=4600, Mw=5400, Mw/Mn=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 (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)hexan-1,6-diamine (8 mol% and 10 mol% respectively) in N,N-dimethylacetamide were spin-coated as ca. 1μm 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 (pre-bake) 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 multi-transmission mask (Ditric Optics Inc). After exposure, the films were poskbaked at 140°C for 10 min and developed in a dilute Shipley AZ400K (40% v/v) developer for 80 sec.

The sensitivity curve for polymer **5** (curve b) in Figure 6 was obtained by exposure at 254 nm through a multi-transmission 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 sec.

The SEM image of polymer **3** in Figure 7 was obtained by contact printing through an ordinary transmission mask with an exposure of 690 mJ/cm^2 followed by postbaking at 140°C for 7.5 min, and development in a dilute Shipley AZ400K (40 v/v%) solution for 80 sec.

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FIGURE CAPTIONS

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

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

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

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)hexan-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.

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 seconds. (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 seconds.

Figure 7. SEM image obtained with resist derived from poly(4-vinylphenyl succinamate) (**3**) using bis((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine as an amine photogenerator.

Table I. Thermal Degradation Behavior of Polymers 3-6 based on the Results of the DSC Analyses

	starting decomposition temperature (peak) (°C)
polymer **3**	210 (250)
polymer **4**	210 (255)
polymer **5**	220 (260)
polymer **6**	160 (185)

Table II. Thermal Degradation Behavior of Polymers 3-6 based on the Results of the TGA Analyses

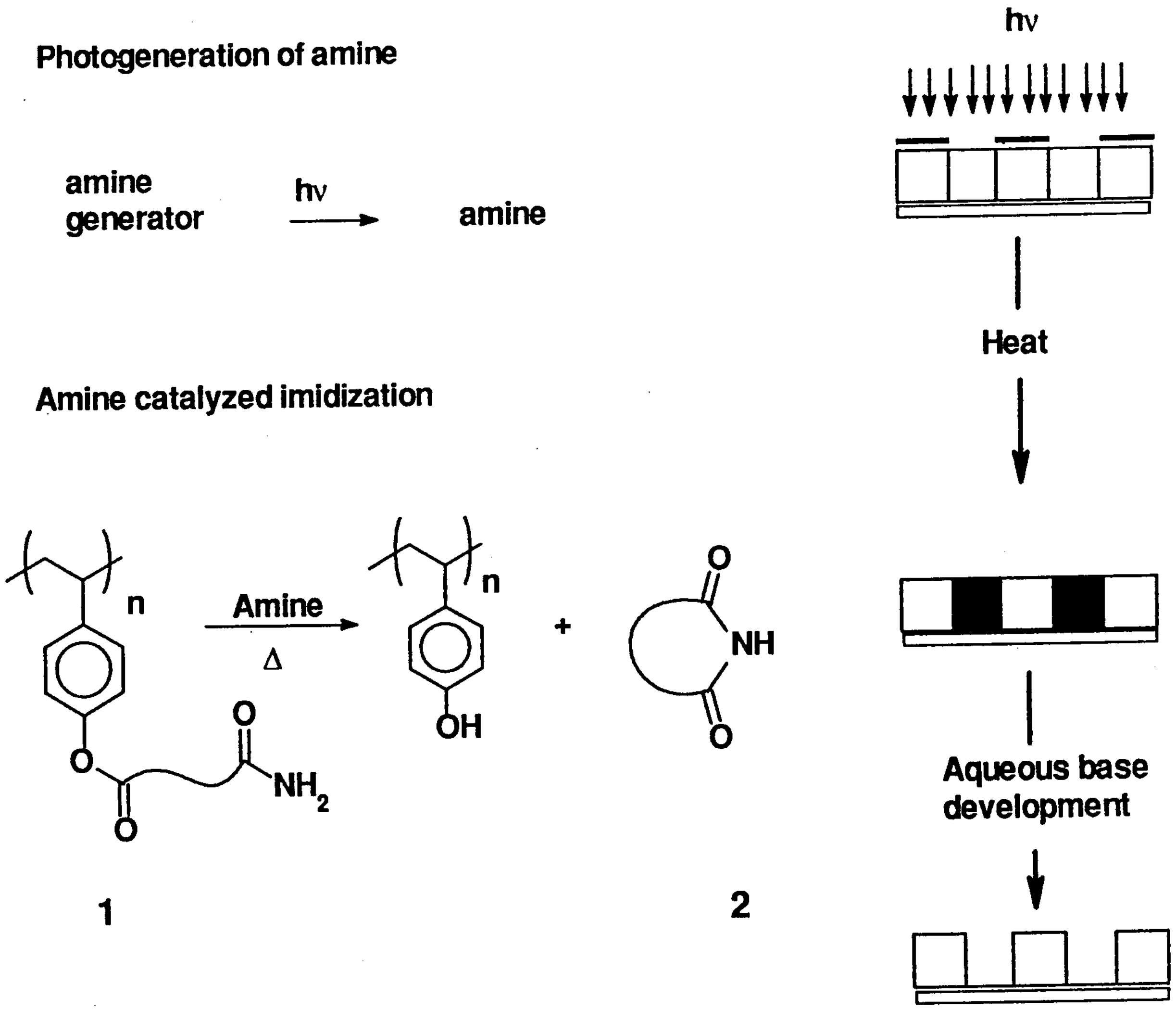
	% wt. loss (temp, °C)	
	theory [a]	experimental result
polymer **3**	45	45 (220-320)
polymer **4**	48	44 (220-320)
polymer **5**	54	52 (260-350)
polymer **6**	55	52 (220-380)

(a) The theoretical amounts are calculated by assuming loss of the cyclic imides from the polymer side-chains.

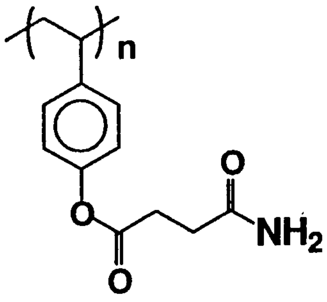
Table III. **Hexylamine Catalyzed Imidization of Polymers 3 and 5 in DMSO-d_6 at 100 °C**

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


Photogeneration of amine
amine generator
hν
amine
Amine catalyzed imidization
n
Amine
Δ
n
+
O
NH
O
O
NH2
O
O
OH
1
2
hν
Heat
Aqueous base development

Scheme 1



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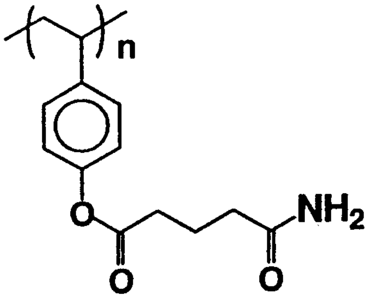

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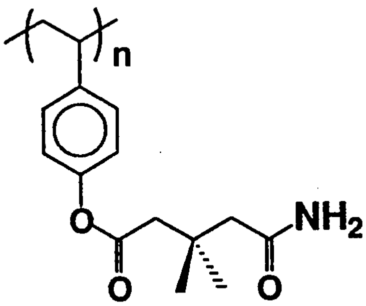

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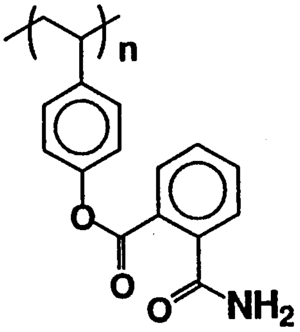

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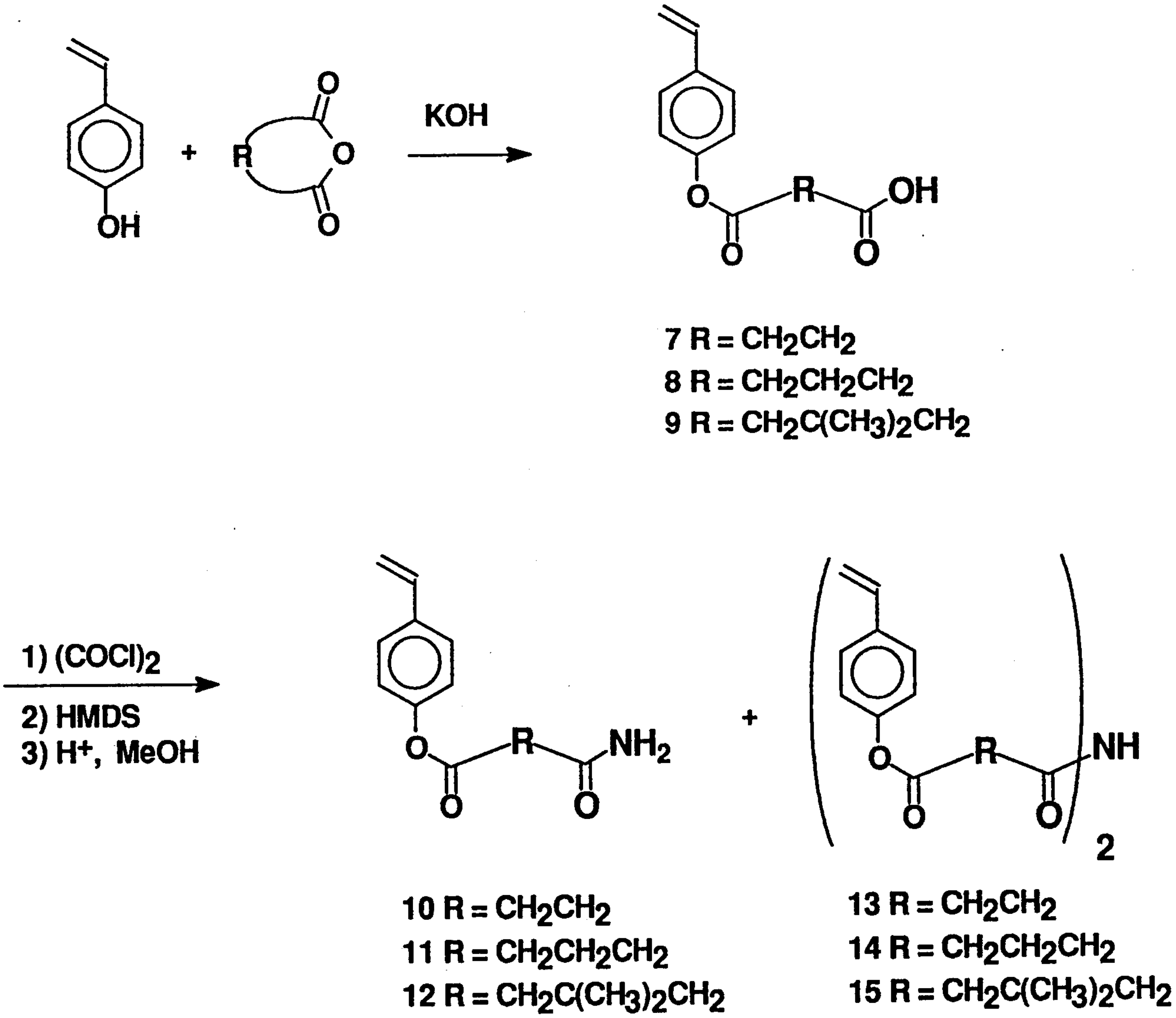
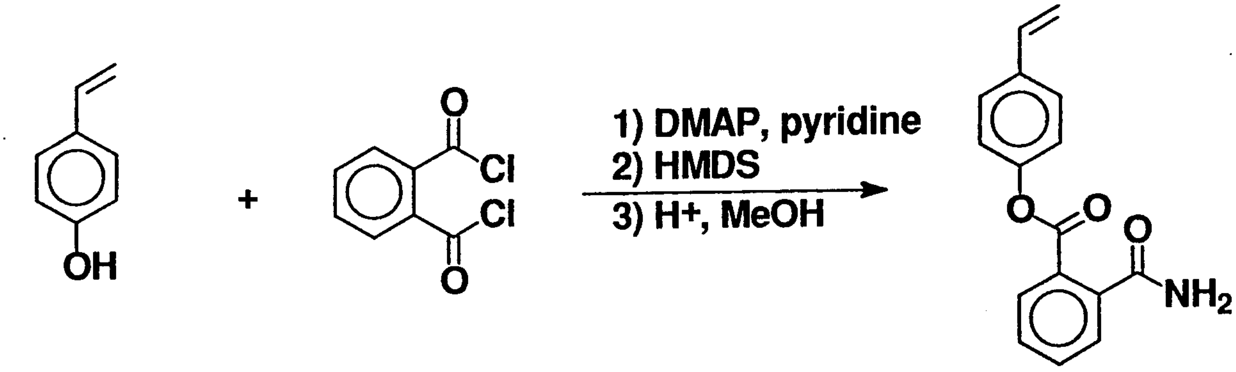


7 R = CH_2CH_2
8 R = $CH_2CH_2CH_2$
9 R = $CH_2C(CH_3)_2CH_2$

10 R = CH_2CH_2
11 R = $CH_2CH_2CH_2$
12 R = $CH_2C(CH_3)_2CH_2$

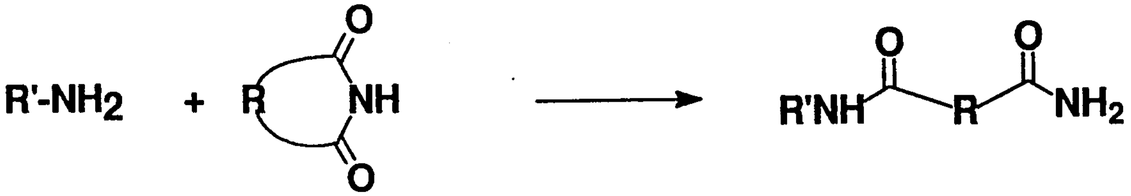
13 R = CH_2CH_2
14 R = $CH_2CH_2CH_2$
15 R = $CH_2C(CH_3)_2CH_2$

Scheme 2

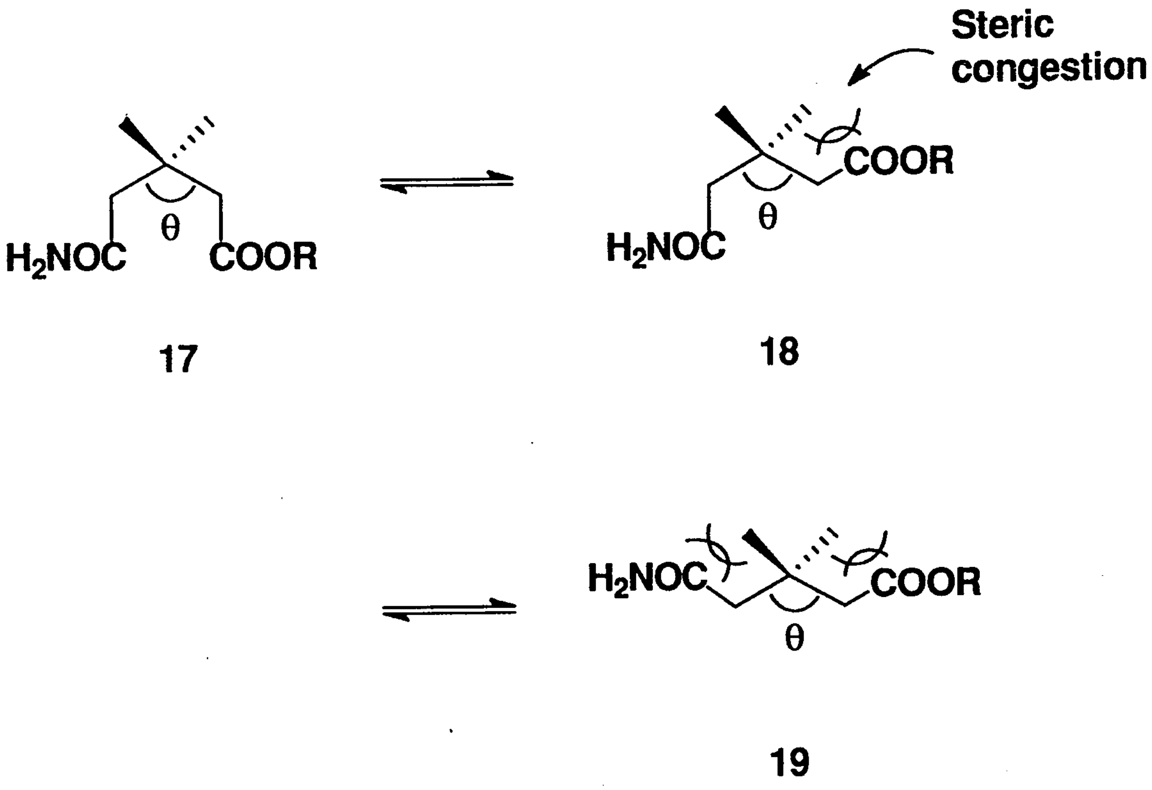


16

Scheme 3



Scheme 4



Scheme 5

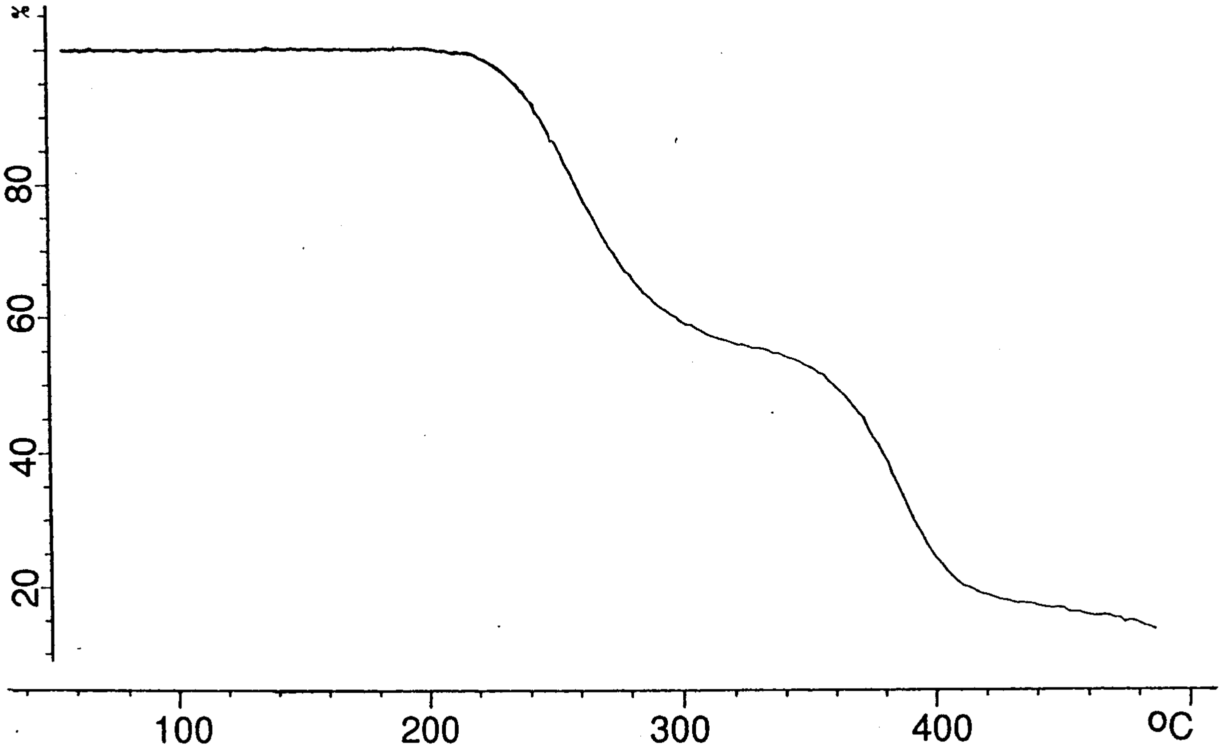


Figure 1. TGA curve of poly(4-vinylphenyl succinamate) (**3**).

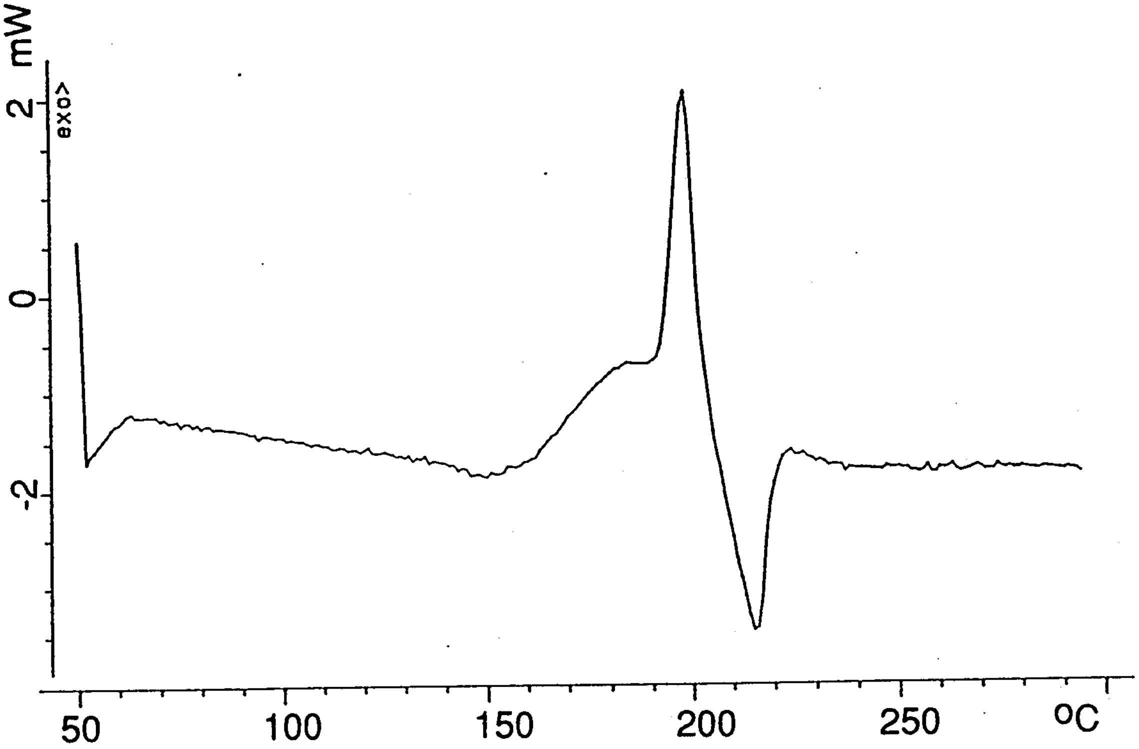


Figure 2. DSC trace of poly(4-vinylphenyl phthalamate) (**6**).

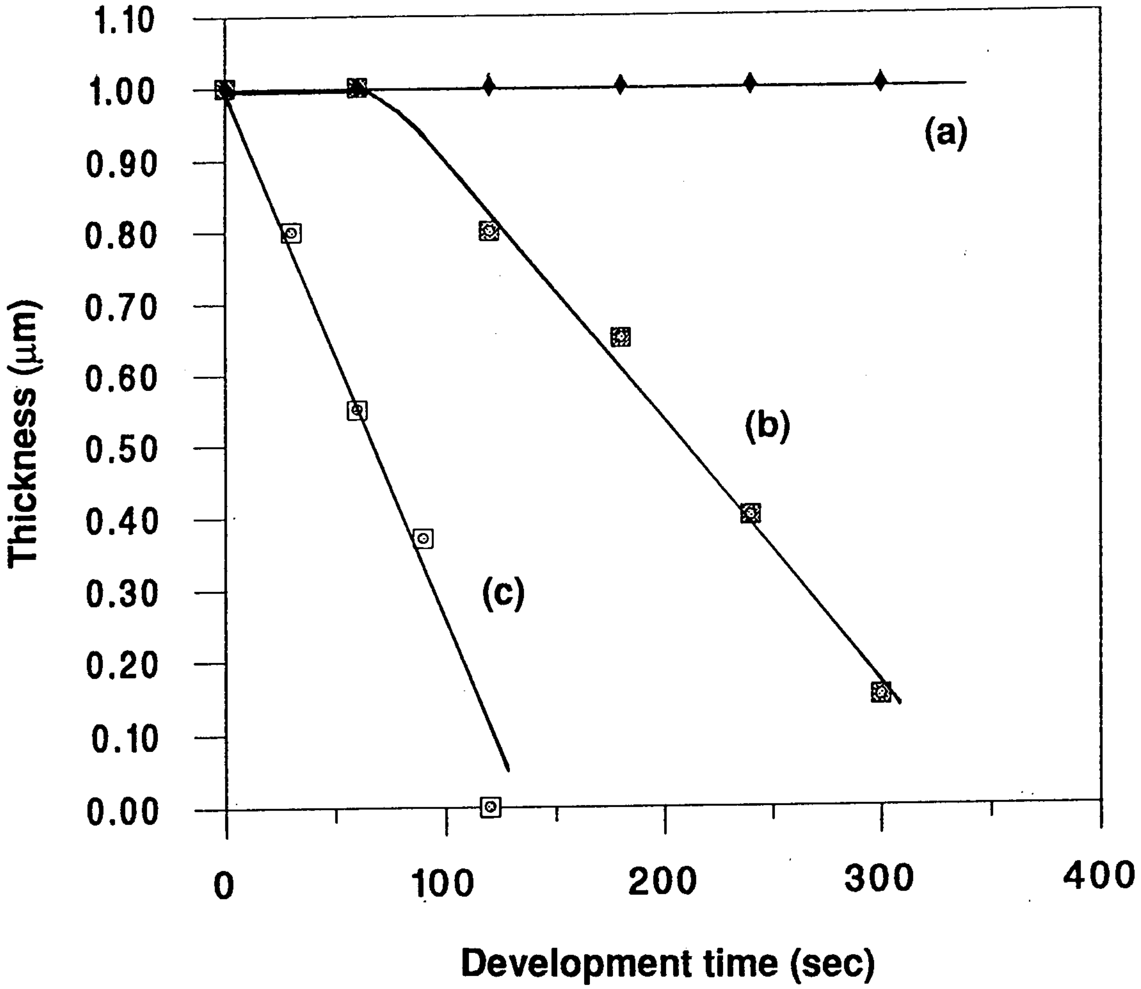


Figure 3. Dissolution curves of polymers **3**, **5**, and **6** in a dilute Shipley AZ312MIF (tetramethylammonium hydroxide) developer (25 v/v%): (a) poly(4-vinylphenyl 3,3-dimethylglutaramate) (**5**); (b) poly(4-vinylphenyl succinamate) (**3**); (c) poly(4-vinylphenyl phthalamate) (**6**).

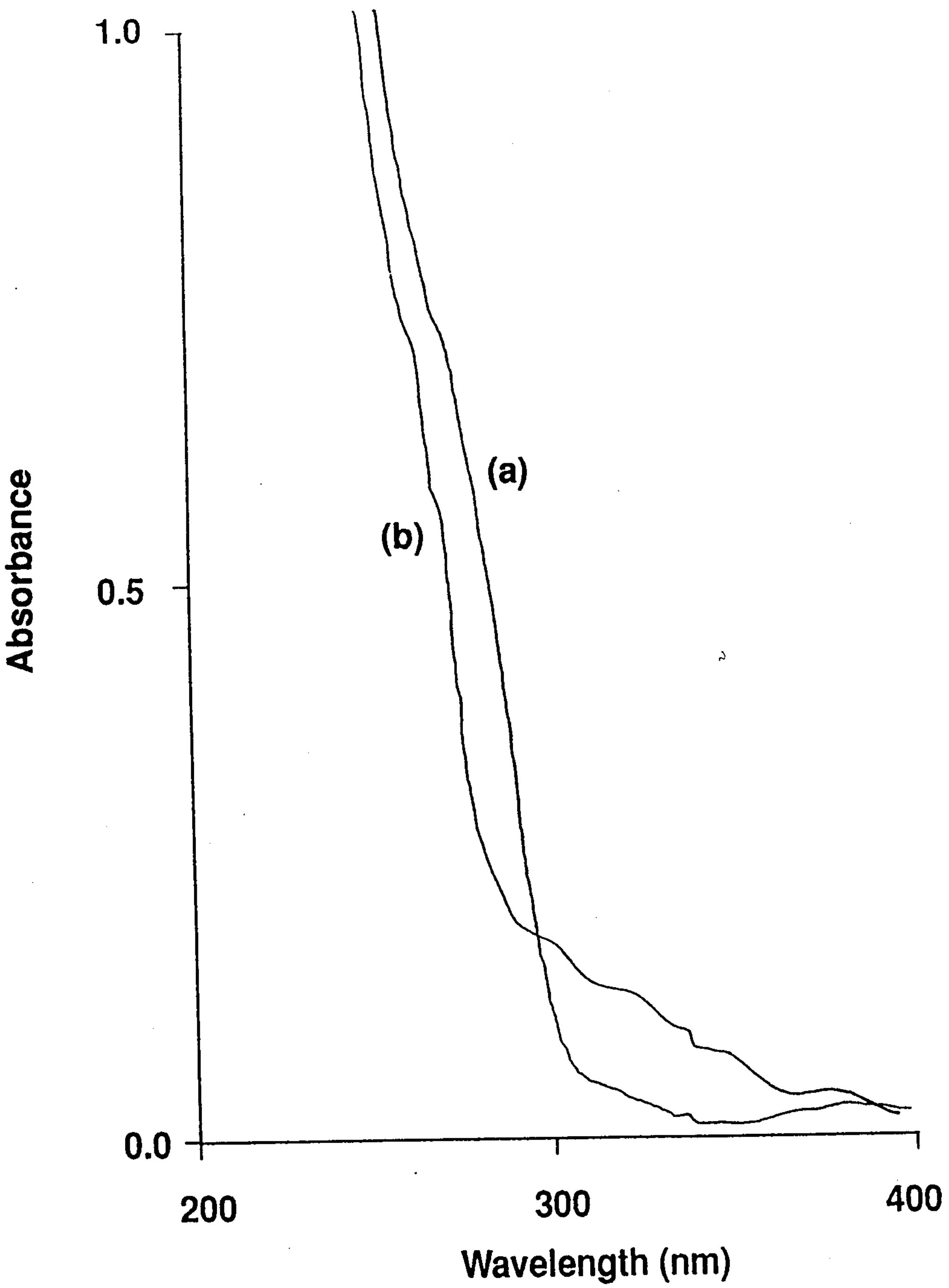


Figure 4. UV spectra obtained from: (a) a 0.5 μm thick film of the resist derived from poly(4-vinylphenyl phthalamate) (**6**) and 5 mol% of bis((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine as a base photogenerator and (b) a 1.0 μm thick film of the resist derived from poly(4-vinylphenyl succinamate)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

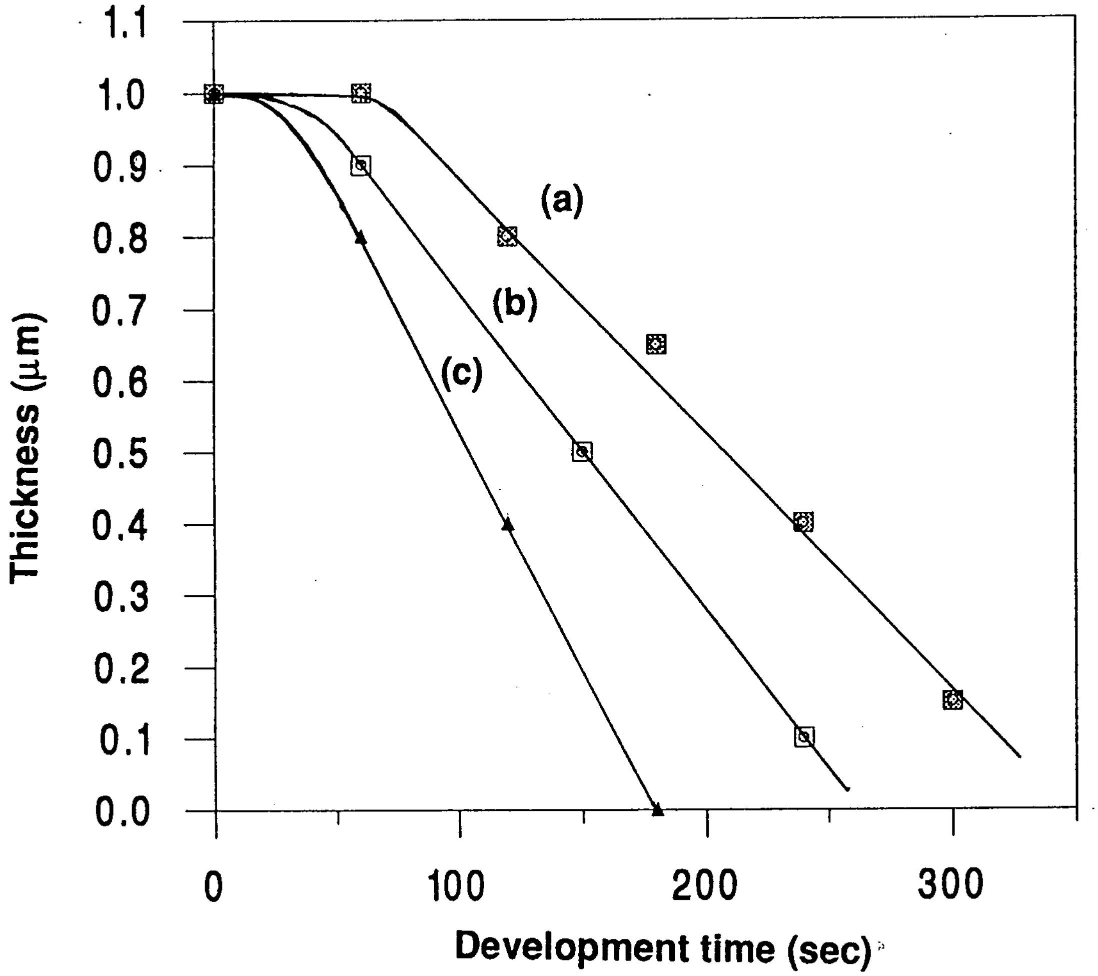


Figure 5. Photochemical and temperature effects on the dissolution behavior of the resist films containing poly(4-vinylphenyl succinamate) (**3**) and bis ((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine) (8 mol%) in a dilute (25 v/v%) Shipley AZ312MIF (tetramethylammonium hydroxide) developer: (a) 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.

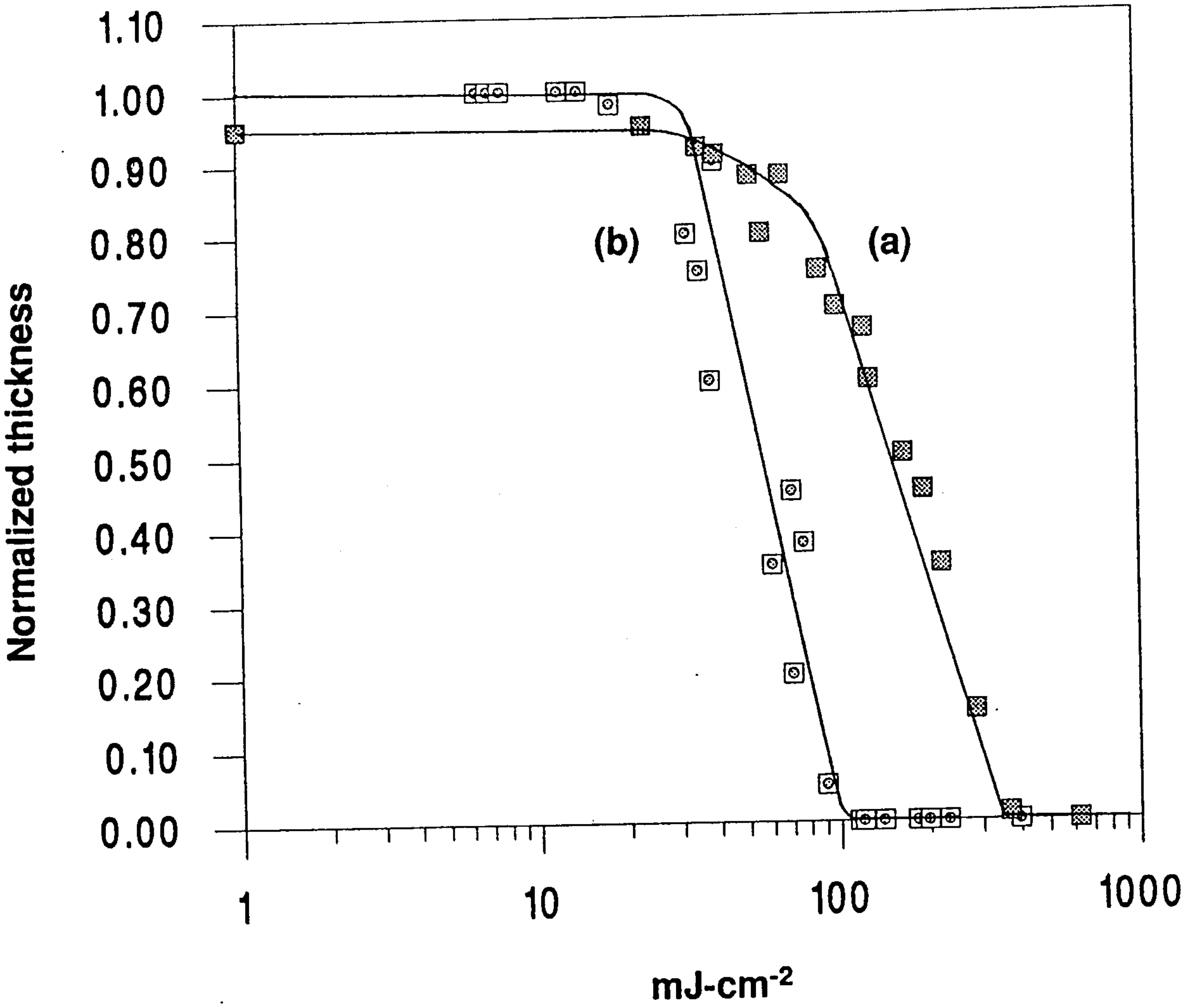


Figure 6. Sensitivity curves of the resists derived from polymers **3** and **5**: (a) The resist derived from poly(4-vinylphenyl succinamate) (**3**) was exposed to UV light at 254 nm, postbaked at 140 °C for 10 min and developed in a dilute (40 v/v%) Shipley AZ400K developer for 80 seconds. (b) The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

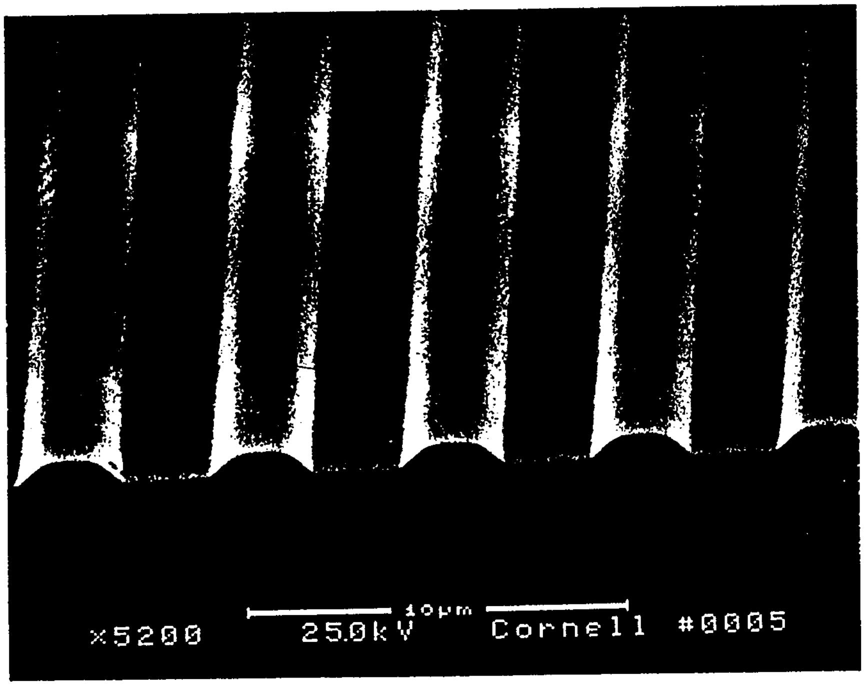


Figure 7. SEM image obtained with resist derived from poly(4-vinylphenyl succinamate) (**3**) using bis((2,6-dinitrobenzyl)oxycarbonyl)hexan-1,6-diamine as an amine photogenerator. After exposure of 690 mJ/cm^2, the image was post-baked at 140 °C for 7.5 min and developed in a dilute (40 v/v%) AZ400K aqueous potassium borate developer for 80 seconds.