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**Photogenerated base in polymer imaging. Synthesis and
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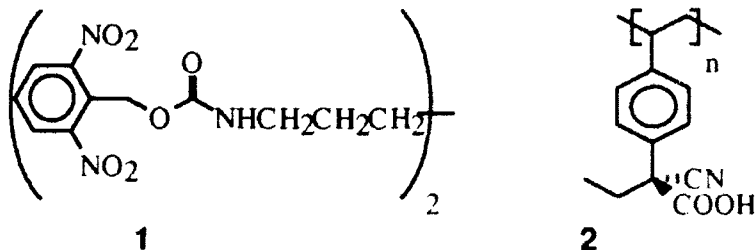
Abstract

Since the concept of chemical amplification was first introduced by us more than twelve years ago, a number of new resists based on acid-catalyzed thermolysis have been developed and commercialized. This report describes the first chemically amplified resist operating through photogenerated base. The concept is demonstrated with poly(2-cyano-2-(p-vinylphenyl)butanoic acid) which decarboxylates readily under basic conditions. A resist system consisting of this polymer and an amine photogenerator bis[(2,6-dinitrobenzyloxy)carbonyl]hexan-1,6-diamine has been formulated and tested in microlithography. The sensitivity of this resist is extremely high (1.4 mJ/cm^2) with a very high contrast of 13.7. This very high sensitivity confirms that chemical amplification is achieved as the photogenerated base is not consumed in the overall decarboxylation process. The mechanistic insights gained from the study of the decarboxylation process may be used in the design of other resists involving more readily accessible polymers.

Introduction

The concept of chemical amplification in microlithography was developed in the early 1980s by Fréchet, Willson and Ito [1] with the development of the poly(t-BOC-styrene) resist that operated on the basis of acid catalyzed thermolysis. This concept has been extended to numerous

functional polymers that are susceptible to acid-catalyzed processes [2]. Recently, our research group has successfully developed a series of effective amine-photogenerators [3,4] such as carbamate **1**. The quantum efficiency of these photoprecursors of amines ranges from 0.1 to 0.6. These results have encouraged us to design some novel polymers that are appropriate for lithographic processes under a novel base-catalyzed approach. This paper reports the design and the synthesis of a novel polymer, poly(2-cyano-2-(*p*-vinylphenyl)-butanoic acid) (**2**), and demonstrates for the first time the concept of chemical amplification using photogenerated base.



Design and Synthesis

The design of an effective polymer for chemically amplified photolithography through base catalysis requires that several important factors be considered: (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 base photogeneration process. (ii) The polymer should be thermally stable, at least up to a suitable postbake temperature. However, it should also be modified readily in the presence of base. The modification process has to be base-catalysed, therefore the photogenerated base should not be consumed during the modification step. (iii) The polymer should have a reasonably high *T_g*. (iv) The polarity of the polymer should be changed significantly after the modification has taken place. In an ideal situation, the

latent image should be developable with an aqueous developer. (v) Since the base-catalysed reaction is carried out in a solid polymer matrix, the mobility of the photogenerated base will be retarded. Therefore, in order to maintain the efficiency of the base-catalysed process, there should be a particular mechanism that can help the reaction to propagate in the polymer matrix.

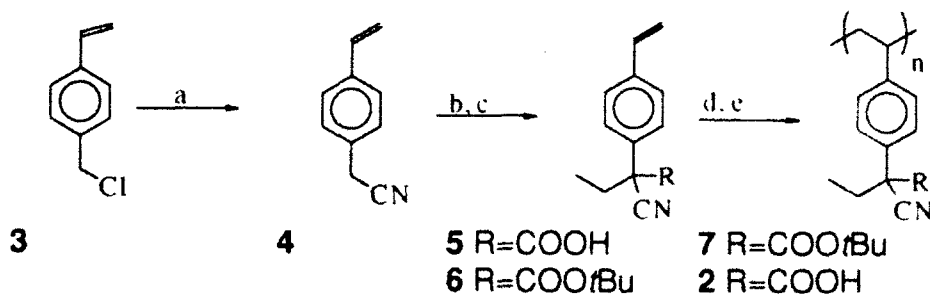
After considering all of these factors, the base-catalyzed decarboxylation of carboxylic acids was selected for investigation. The decarboxylation of carboxylic acids and their derivatives has long been known both in synthetic organic chemistry and in biochemistry [5]. Since the decarboxylation reaction is usually accelerated in the presence of bases, it was expected that *in situ* amine photogeneration could be employed to create a latent image in a polymer matrix containing pendant carboxylic acid groups. After base-induced decarboxylation, the product would be far less polar than the original carboxylic acid and would lose its solubility in aqueous base. Overall, this would provide for the differential dissolution of exposed and unexposed areas of the polymer film with relief image formation.

Synthesis of Poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (2)

The synthesis of poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (2) is shown in Scheme 1. Nucleophilic substitution of chloride 3 with cyanide in ethanol led to *p*-vinylbenzyl cyanide (4) [6]. Alkylation of 4 with ethylbromide under basic conditions [7], followed by reaction with dry-ice [8] afforded carboxylic acid 5. Radical polymerization of 5 in toluene with AIBN as an initiator led to a decarboxylated polymer. Examination of the thermal stability of 5 in the absence of AIBN revealed that carboxylic acid 5 decarboxylates slowly at 70 °C in toluene. To avoid this problem, 5 was transformed [9] into

the corresponding *tert*-butyl ester **6** which was subsequently polymerized in toluene with AIBN as an initiator to provide **7**. Deprotection of **7** in a solution of trifluoroacetic acid and dichloromethane [10] at room temperature gave the desired polymer **2**.

Scheme 1



(a) NaCN, (b) 1. NaOH, EtBr; 2. LDA, CO₂, (c) (COCl)₂, *t*-BuOH, (d) AIBN, (e) TFA

Properties and Thermal Stability of Poly(2-cyano-2-(*p*-vinylphenyl)-butanoic acid) (2)

In order to be potentially useful in the formulation of resist materials or imaging systems, the polymer must be thermally stable under the standard processing conditions that may include heating to temperatures over 100 °C. TGA studies confirm that polyacid **2** meets these requirements as it does not lose carbon dioxide at temperatures below 135°C. This is further confirmed by differential scanning calorimetry (DSC).

In the presence of 1.5 mol% of 1,10-diaminodecane, decarboxylation occurs at a lower temperature. In order to obtain more information about the decarboxylation reaction in imaging experiments, the reaction was also monitored by FTIR spectroscopy. Figure 1 shows the IR spectrum of a thin film of the resist containing 90 % of polyacid **2** and 10 % of bis[(2,6-dinitrobenzyl)oxy]carbonyl]hexan-1,6-diamine **1**. The sample was heated to 135 °C

for 10 min without exposure to UV light (Spectrum a). The characteristic absorptions between 3500 cm^{-1} to 2500 cm^{-1} and 1750 cm^{-1} to 1700 cm^{-1} indicate that the carboxylic acid functional group in the polymer matrix can survive under these purely thermal conditions. Spectrum b in Figure 1 shows the IR spectrum of a thin film of the resist after exposure to UV light (44 mJ/cm^2 at 254 nm) followed by postbaking at $135\text{ }^{\circ}\text{C}$ for 10 min. The disappearance of the characteristic absorptions of the carboxylic acid group strongly indicates that the photogenerated amine is capable of accelerating the decarboxylation process effectively in the polymer matrix.

In order to evaluate the sensitivity for the resist, contrasts curves for the resist were obtained under various processing conditions (Tables 1 and 2). Two typical contrast curves for the resist are shown in Figure 2. The best conditions found to date lead to a sensitivity of 1.4 mJ/cm^2 using a 0.25% v/v solution of AZ312MIF in water as the developer. Under these conditions the resist contrast is very high: 13.7. By using an aqueous solution of triethanolamine as a developer, the sensitivity of the resist is somewhat less at 6.4 mJ/cm^2 , but the contrast remains high at 8.7 and swelling is avoided.

Figure 3 shows a negative-tone image obtained from the resist containing 90 wt% of polyacid 2 and 10 wt% of PBG 1. This image was obtained by contact printing with an ordinary transmission mask, followed by postbaking at $125\text{ }^{\circ}\text{C}$ for 14 min, and development using aqueous triethanolamine.

Conclusion

This study clearly demonstrates the feasibility of achieving chemical amplification in resists that operate with photogenerated base [11]. The first material we have designed and tested shows extremely high sensitivity and

the large change in polarity that occurs as a result of the base-catalyzed decarboxylation process affords high resolution. Further studies will focus on image reversal as well as three-component systems compatible with current novolak based processes. In addition, experiments will be carried out to demonstrate the resistance of this new type of resist to the type of airborne contamination [12] that adversely affects chemically amplified systems involving photogenerated acid.

Acknowledgment

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Table 1. The imaging sensitivity of poly(2-cyano-2-(*p*-vinylphenyl)-butanoic acid) (2) with diluted AZ312MIF (0.25 %V/V) as a developer.^a

Postbaking temperature	Sensitivity, mJ/cm ² (contrast g) of polymer 2 for different postbaking time	
	5 min	10 min
135 °C	1.4 (13.7)	-
130 °C	5.2 (5.2)	1.3 (4.2)
125 °C	8.8 (11.8)	5.0 (11.8)
120 °C	13.6 (12.6)	

- a) The experimental conditions are summarized as the following: A resist containing poly(2-cyano-2-(*p*-vinylphenyl) butanoic acid) (238.4 mg) and bis[[2,6-dinitro-benzyl)oxy]-carbonyl]hexane-1,6-diamine (24 mg) in diglyme (950 mg) was spun and prebaked at 110 °C for 2 min to give a film with 1.0 micron thickness. After exposure to DUV light at 254 nm with a gradient mask and postbaked on a hot plate equipped with a Omega temperature controller, the latent images formed were developed by immersion of the film in a diluted AZ312MIF developer (0.25 %V/V).

Table 2. The imaging sensitivity of poly 2-cyano-2-(*p*-vinylphenyl)-butanoic acid (2) with a solution of triethanolamine as a developer.^a

Postbaking temperature	Sensitivity, mJ/cm ² (contrast g) of polymer 2 for different postbaking time	
	8 min	14 min
130 °C	11.0 (16.4) ^b	
125 °C	11.2 (7.5) ^b	6.4 (8.7) ^c
125 °C ^d	16.9 (6.1) ^b	

- a) The experimental conditions are summarized as the following: A resist solution with a formulation consisting of poly(2-cyano-2-(*p*-vinylphenyl) butanoic acid) (109.8 mg) and bis[[2,6-dinitrobenzyl)oxy]-carbonyl]hexane-1,6-diamine (10.8 mg) in diglyme (458.3 mg) was spun and prebaked at 110 °C for 2 min to give films with 1.0 micron thickness. After exposure to DUV light at 254 nm, postbaked at 125 °C for 14 min, dipped into water for 30 sec, developed by immersion of the films in a solution of triethanolamine (1.04 g/L) and rinsed with water, the sensitivity of the resist was determined.
- b) The concentration of the developer (triethanolamine) is 1.04 g/L.
- c) The concentration of the developer (triethanolamine) is 2.53 g/L.
- d) The image was developed directly in the developer without presoaked in water.

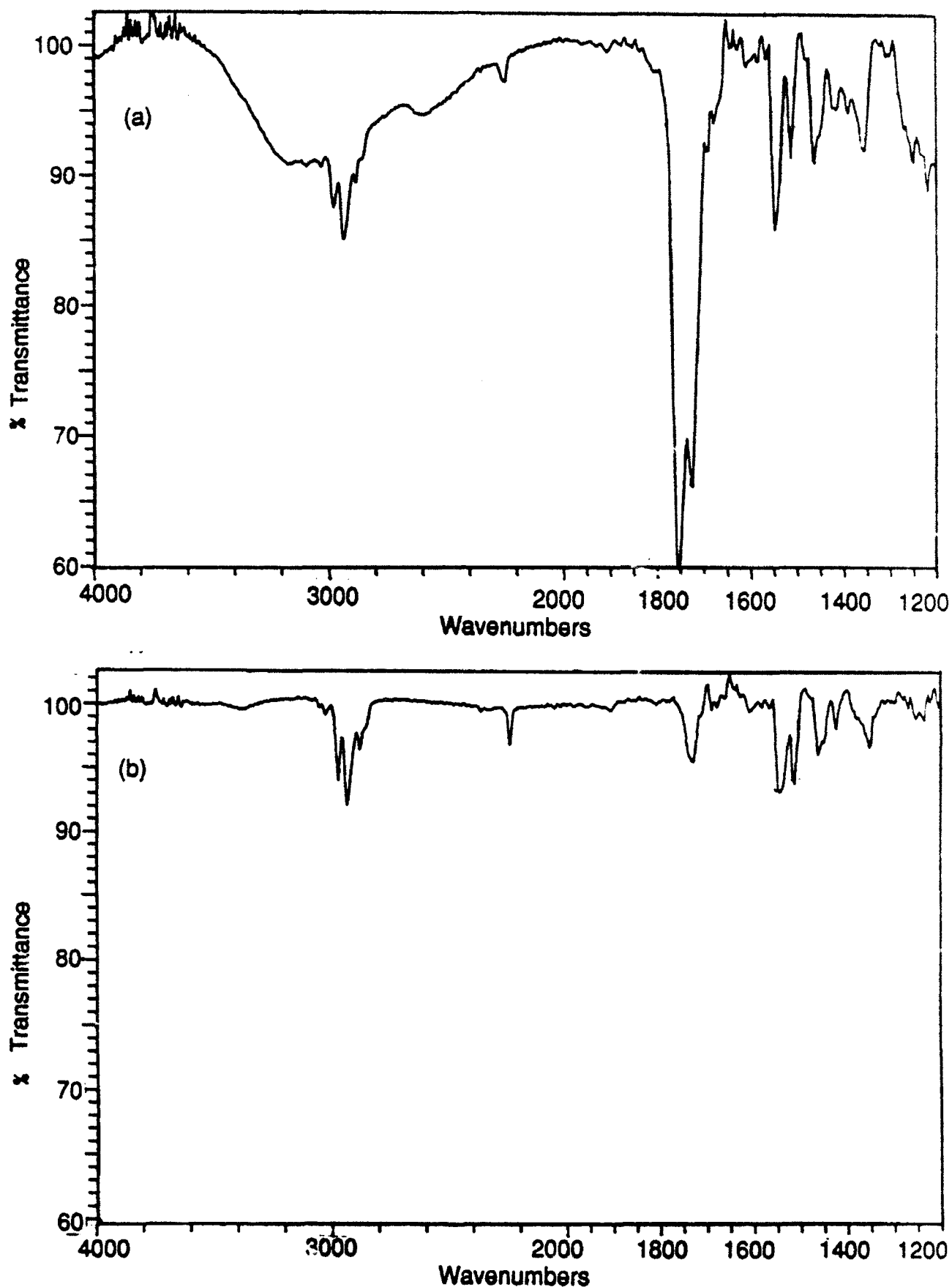


Figure 1. FTIR spectra for a resist containing 90% polymer 2 and 10% (by weight) of photobase generator 1. (a) Film heated at 135°C without irradiation. (b) Film irradiated with DUV light then heated at 135°C for 10 min.

Normalized
thickness

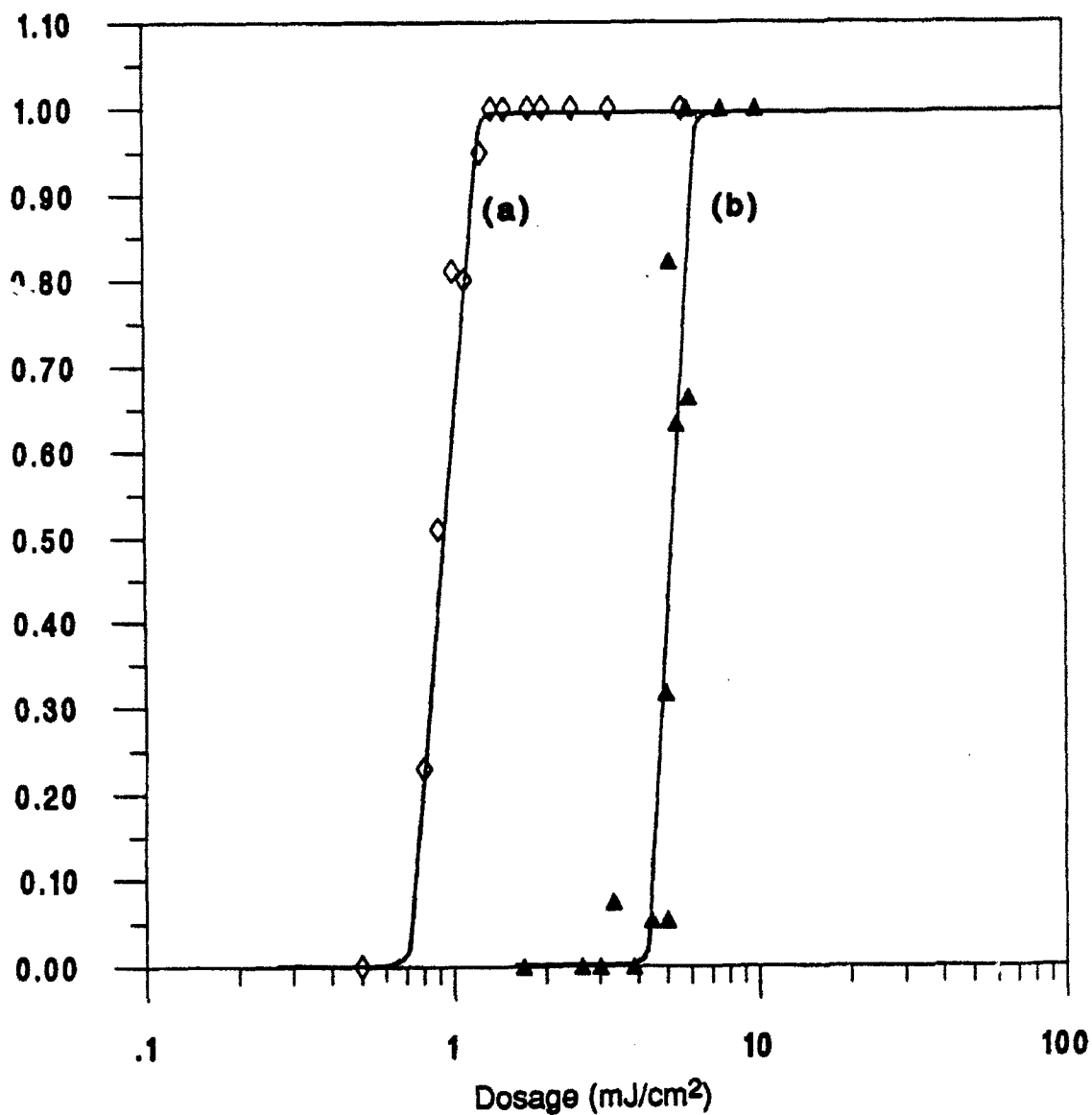


Figure 2. Contrast curves for the resist containing 90 wt% of polyacid 2 and 10 wt% of amine photogenerator 1: (a) The images were postbaked at 130 °C for 10 minutes and developed in a 0.25 v/v% solution of AZ312MIF developer (active ingredient is tetramethylammonium hydroxide). (b) The images were postbaked at 125 °C for 14 minutes, presoaked in water for 30 seconds and developed in a solution of triethanolamine (2.53g/L).



Figure 3. Scanning Electron Micrograph of an image obtained with a resist based on polymer **2** and photobase generator **1**. The resist was irradiated at 254nm using a contact printing exposure tool, postbaked at 125°C for 14 min., then developed in aqueous triethanolamine (2.53 g/L). Image resolution is only limited by the contact printing technique used.