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Design of Photosensitive Polyimides

by

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PHOTOGENERATED BASE AS CATALYST FOR IMIDIZATION REACTIONS: DESIGN OF PHOTOSENSITIVE POLYIMIDES.

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Abstract

The photogeneration of free amines or diamines from soluble organic precursors such as photoactive 2-nitrobenzyl carbamates is useful for the imidization of polymers containing amic acid or amic ester groups as part of their main-chain or their side-chain. The base-catalyzed reaction occurs at lower temperatures than the non-catalyzed thermal process and is applicable to the patterning of thin film coatings.

Introduction

The use of acid catalysis in the design of chemically amplified resist materials has led to numerous advances in the field of microlithography (1, 2). A variety of sources of photogenerated acid have been explored including the triarylsulfonium salts of Crivello et al. (3) and a large number of other organic compounds (4). We have recently described (5-8) a number of photoactive carbamates that may be used as efficient photoprecursors of amines (e.g. compounds **1** and **2**), diamines, or polymers containing numerous amino pendant groups (e.g. structure **3**). The first family (5, 6) of carbamates is based on the photoactive Ddz (α,α-dimethyl-3,5-dimethoxybenzyl carbamoyl group) (9) and the second (7, 8) is based on carbamates incorporating the well-known 2-nitrobenzyl or related chromophores (10). For both of these families, removal of the photolabile protecting groups from their carbamate precursors has been demonstrated in the solid state through experiments in which polymer films containing small amounts of the carbamates were exposed to UV light (5-8). The quantum yields measured for carbamates based on the Ddz chemistry are near 0.10, while higher quantum yields varying from 0.11 to 0.62 are obtained with the 2-nitrobenzyl carbamates depending on the structure of the basic 2-nitrobenzyl chromophore. For example, substitution of the 2,6-dinitrobenzyl for the 2-nitrobenzyl chromophore affords a five-fold increase in quantum yield, while the introduction of an α-methyl-benzyl group results in both increased quantum yield and reactivity enhancements in some applications (11). Other useful photoprecursors of amines have been described by Kutal and Willson (12).
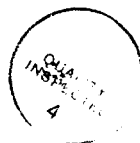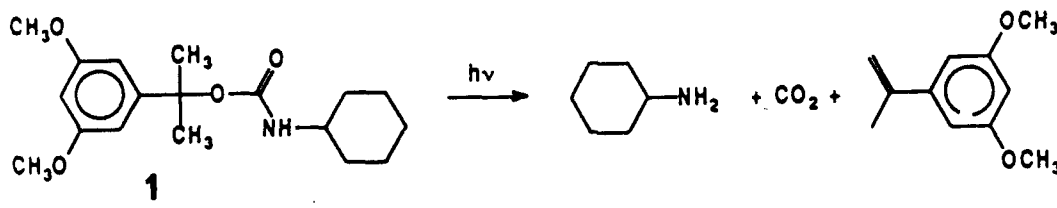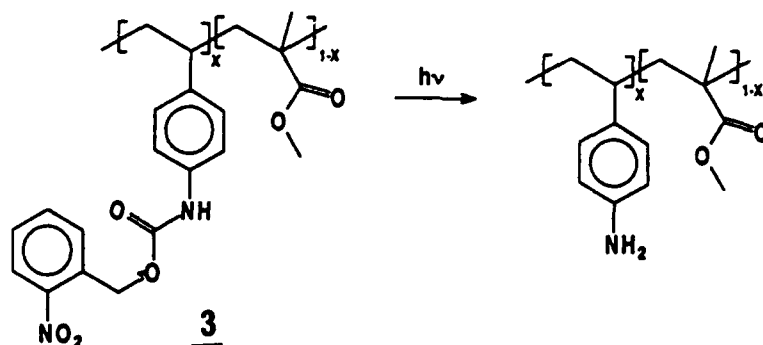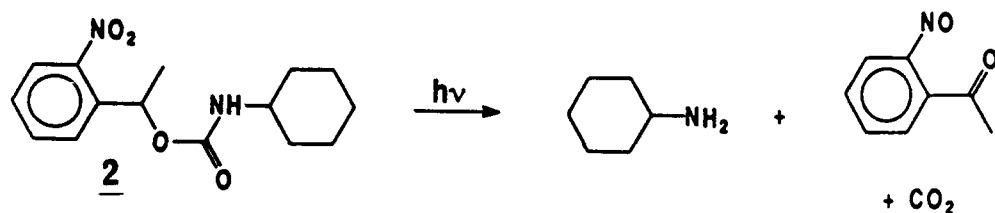
While the photogeneration of amines has found applications in image reversal processes (11) or in the patterning or photocuring of polymers formulations containing multifunctional e˙ ˈxides (13), numerous other applications are possible.

For example, a survey of the literature reveals that the process of imidization of a variety of polyamic acids and derivatives may be base-catalyzed. Early work at Cornell University by Sondheimer and Holley (14) has shown the effectiveness of base-catalysis in the imidization of monoamide-monoester derivatives of asparagine and glutamine. Similarly, the influence of dimethylformamide in the imidization of the diester derivatives of several polyamic acids was suggested by Nishizaki and co-workers (15), while the kinetics and mechanism of cyclization of polyamido esters to polyimides under catalysis by tertiary amines were reported (16) in 1978.

The first photosensitive polyimide was developed by Rubner (17) more than fifteen year ago using a design that involved the photocrosslinking of polyamic esters with acrylate pendant groups. Numerous other designs based on similar concepts have been reported since (18).

Results and Discussion

We have selected two different systems to demonstrate the concept of using photogenerated base to pattern polyimides. In this design, a radiation-sensitive coating is prepared using a soluble polyamic acid, or an ester derivative thereof, in combination with a base photogenerator such as **1**, **2**, **4**, or **5**. Exposure of the coating to light of the appropriate wavelength cause liberation of the base within the polymer and initiates the imidization reaction. As this reaction is very slow at room temperature, the exposed film is heated to a temperature which is sufficient to allow the base-catalyzed imidization process to take place, but is too low for appreciable imidization to occur in the absence of base. Therefore, a gradient of solubility is created as the exposed and unexposed areas of the film have different solubilities. Imaging is carried out by differential dissolution, and complete imidization can then be achieved thermally after image development.

Copolymer **7** containing carboxylic acid and amide functionalities on adjacent carbons is easily prepared by reaction of benzylamine with the regularly alternating

copolymer of maleic anhydride and styrene **6**. This reaction can be carried out at room temperature using a modification of an earlier procedure (19).

6 → (PhCH₂NH₂) → **7**
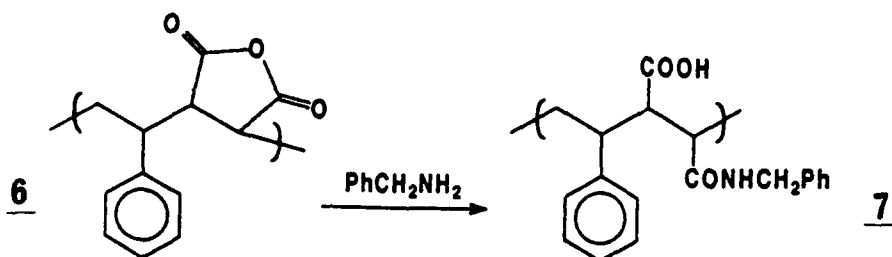
In order to facilitate its characterization, polymer **7** can be converted to an ester derivative such as **8** or **9**. Characterization of **8** and **9** is easily done using spectroscopic techniques as well as gel permeation chromatography (GPC). For example a styrene-maleic anhydride copolymer **6** with M_n = 18,300 and M_w/M_n = 1.9 (GPC data) afforded **8** with M_n = 25,800 and M_w/M_n = 1.6 (GPC data) after reaction with benzylamine followed by esterification using diazomethane. The structures proposed for the various polymers **6-9** are confirmed by NMR as well as IR spectrometry.


8 R = CH₃

9 R = Ph
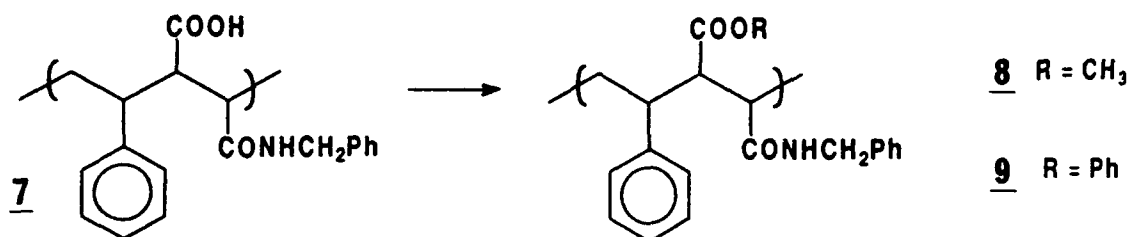
The imidization of copolymer **7** was first tested under purely thermal conditions by heating above 200°C. The reaction is readily monitored by infrared spectrometry. The broad bands corresponding to the COOH group of **7** disappear upon heating while the amide band near 1735 cm⁻¹ is replaced by an imide band near 1705cm⁻¹. However, in addition to the imide band, two other bands also appear in the carbonyl region of the spectrum: a small band at 1857 cm⁻¹ and a larger one at 1780 cm⁻¹. These absorptions are similar to those found in **6** and suggest the formation of a significant amount of anhydride units in the product. Therefore the product of thermolysis of **7** would have structure **10** with both imide and anhydride groups. A similar observation of partial imidization accompanied by partial anhydride formation was made when **7** was heated to 180°C in the presence of 1,6-diaminohexane.


7 → (Δ) → **10**
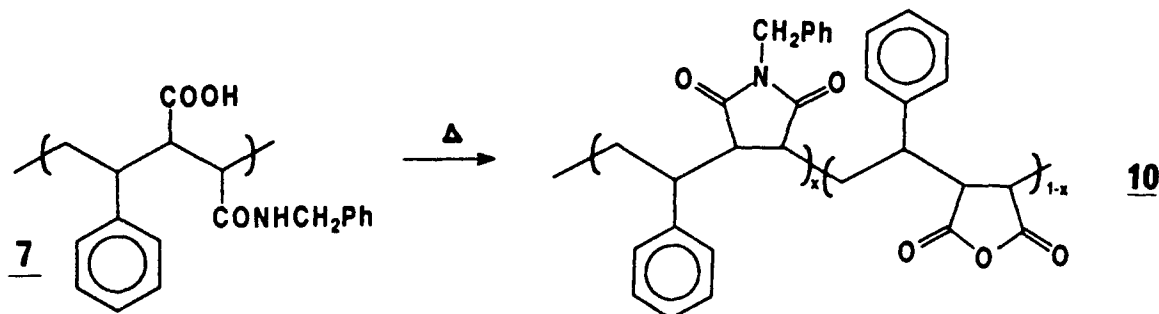
Since both the imidization reaction and the side reaction (anhydride formation) result in a significant change in the solubility properties of the polymer, the

process can be used to image polymers 7-9. In particular the change in solubility as 7 is transformed into 10 is interesting for imaging or resist chemistry as the starting polymer 7 is readily dissolved in very dilute aqueous base while the product is not.
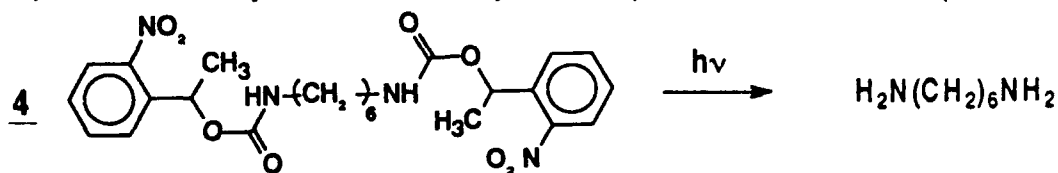
Therefore, photobase generator 4 which affords a diamine upon exposure to UV light was tested in the photoinitiated thermal transformation of 7 into 10. Thin films of copolymer 7 containing 10 mole % of photobase generator 4 were exposed through a mask to varying doses of 254 nm UV light. Despite the high quantum efficiency of the photobase generator itself (7), relatively high exposure doses were required due to the high absorbency of the medium. After exposure, the exposed films were heated at temperatures varying from 140 to 180°C to effect the base catalyzed thermal reaction. The use of silicon wafers polished on both sides allowed monitoring of the reaction by FT-IR. It was observed that the two reactions responsible for the formation of a product with structure 10 occurred to varying degrees depending on reaction conditions. Under some of the conditions that were tested, the amount of anhydride formation that was observed was estimated to exceed 50%. Attempts at accurate quantifying of the process were made difficult by the presence of some water in the starting polymer. Image development for the partly imidized films was made possible by the great solubility difference that exists between polymer 10 and its precursor 7. While the latter, with its free carboxylic acid group, is soluble in very dilute aqueous tetramethylammonium hydroxide (ca. 0.005 M), the partly imidized structure 10 is not. Therefore a negative-tone image of the mask is obtained. Typical sensitivities for this system are not high, with doses of ca. 700 mJ/cm^2 required for complete insolubilization to be observed. However, since the exact structure of 10 varies with imaging and thermolysis conditions, it is difficult to measure accurately the ultimate lithographic sensitivity of the system.

This chemistry is directly applicable to the preparation of polyimides from polyamic acids or derivatives. For example, in preliminary work for a collaborative project (20), we have demonstrated the use of photogenerated base in the design of a photosensitive polyimide.

R' = CH$_2$CH$_3$ or CH$_2$CO$_2$Et

11   12
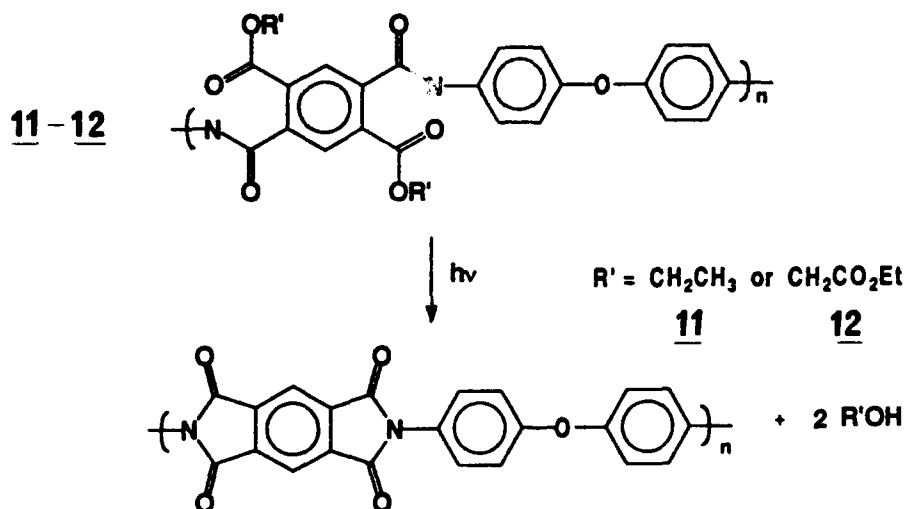
Therefore, polyamic esters such as **11** and **12** can be used in combination with a photobase generator such as **2** or **4** to prepare radiation-sensitive films. Irradiation through a mask liberates the amine in those areas of the film that have been irradiated and affords a latent image. Subsequent heating of this image effects the partial imidization of the polymer to give products containing the repeating units shown below as structure **13**.

Image development can then be achieved using solvent mixtures containing N-methyl-pyrrolidone. The partly imidized areas of the film are less soluble in the developer than the unexposed areas containing the starting amic ester moieties, as a result a negative-tone image is obtained. Since only some of the repeating units of polymers **11** and **12** are imidized, insolubilization of the exposed areas of the film is not complete and significant thinning of the film occurs during development. Due to the high absorbency of the starting polymers, the photochemical step is inefficient and very high doses near or in excess of $1 J/cm^2$ are required to obtain images such as that shown in Figure 1. Other base photogenerators such as **1** are not suitable for this application since they operate exclusively below 300 nm where the absorbency of polymers such as **11** and **12** is too high to allow penetration of the film. This is not a problem in solution as demonstrated by the rapid gelation of solutions containing **12** and **1** upon exposure to deep UV light.

Figure 1. Image obtained with a photosensitive polyimide using 4

Experimental Procedure.

<u>Preparation of polymer **7**</u>.

A mixture of styrene-maleic anhydride copolymer (10 mmoles, M_n = 18,300 and M_w/M_n = 1.9 by GPC with polystyrene calibration) and 50 mL methanol was treated with 40 mmoles of benzylamine while stirring vigorously at room tempera-

ture. All of the copolymer was dissolved within 20 minutes and stirring was continued for another 20 min. The solution was then concentrated and the polymer was precipitated in 1% aqueous acetic acid. After filtration and washing, the polymer was redissolved in methanol and precipitated again to afford the desired polymer 7 (71%). GPC (polystyrene standards M_n = 25,800 and M_w/M_n = 1.5). [1]NMR analysis as well as FT-IR spectrometry are in agreement with the proposed structure; some water of hydration is tenaciously retained by the polymer.

Preparation of base photogenerator 4.

This compound was prepared from 1,6-diisocyanatohexane and (2-nitrophenyl)-ethanol as described previously (7).

Imaging of a resist based on polymer 7 and base photogenerator 4.

A 14 wt% solution of polymer 7 in ethylene glycol monomethyl ether was prepared. Compound 4 (10 wt% with respect to polymer 7) was dissolved and the solution was filtered then used to spin coat silicon wafers as well as KBr discs. The coated wafers were then pre-baked at 80°C for 10 min and the film thickness of the polymer coating was measured (0.95μm). The wafers were then exposed to various doses of 254nm UV light to photogenerate amine, and postbaked at temperatures varying from 140 to 180°C to effect the thermal imidization reaction. Development of the exposed images was accomplished using dilute aqueous base to remove the unexposed (unreacted) areas of the film. A typical developer was 1% aqueous AZ 312 MIF (AZ 312 is a commercial developer from Hoechst-Celanese consisting of 0.54 M aqueous tetramethylammonium hydroxide).

Imaging of polyamic ester 12

This was done as described above using a more dilute solution (ca. 10 wt%) of the polyamic ester 12 (15) in N-methyl-pyrrolidone. The photobase generator 2, prepared as described previously (7), was added to the solution in concentrations from 5 to 20% (with respect to polymer). After pre-baking for 5 min at 80°C, the films were exposed to varying doses of unfiltered UV light. A weak image observed after the exposure step intensified during post-bake at 150°C for 10 min. The exposed areas of the film became almost insoluble during the post-bake while the exposed areas remained soluble in solvents containing N-methyl-pyrrolidone. Therefore a negative image of the mask was obtained, though considerable film thinning was also observed during the development step.

Conclusion

The use of photobase generators such as 2-nitrobenzyl carbamates in the design of photosensitive polyimides has been demonstrated. The photogenerated amine acts as a catalyst in the imidization of precursor polymers containing active functionalities such as amic acid or amic ester groups. Though the reaction can be carried out in the solid state, sensitivity is low due to the high absorbency of the starting polymers at the wavelengths that are most effective for photogeneration of base. We are investigating several new promising photobase generators as well as the sensitization of existing compounds (5-8).

Acknowledgements.

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