In Situ Preparation of Lithographic Resists Containing Glutarimide Groups*

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Synopsis

Poly(acrylic acid) and poly(methacrylic acid) homopolymers, copolymers, and 1-μ-thick films have been converted in high yield to their corresponding cyclic imide derivatives by an *in situ* gas–solid phase reaction at 200°C with ammonia, methylamine, and ethylamine, respectively. Under similar reaction conditions with H_2S or CH_3SH as the reactive gas, sulfur was incorporated into the polymers in low yield. Under UV and electron beam irradiation, these cyclic derivatives degraded with main chain scission to eliminate isocyanic acid or alkyl isocyanate and to form olefins and ketenes. Poly(diacrylimide) was the exception and crosslinked. The poor solubility in organic solvents and the very high solubility in aqueous solutions of base limited the use of these films as positive resists. However, poly(methyl methacrylate) copolymers, containing 20%–25% cyclic groups, exhibited adequate solubility and sensitivity to be utilized as lithographic resists.

INTRODUCTION

Polymers are used in lithographic processes; the substrate to be patterned is coated with a polymer film which is selectively irradiated.[1] Depending on the chemical structure of the polymer, the irradiated regions of the resist film will either degrade with increased solubility in organic solvents (positive resist) or will crosslink to become insoluble (negative resist).[2]

For electron beam or x-ray lithography, the G value (number of scission or crosslinking events occurring per 100 eV of absorbed energy) and polymer properties such as film quality, adhesion, solubility, chemical resistance to acid and alkaline etchants, and thermal stability determine to a large extent whether a polymer can be utilized as a resist. In general, most polymeric materials, as resists, have been deficient in one or more of these essential properties. Thus, efforts have been directed toward the design of resist polymers with improved physical and chemical properties.

Relatively minor but specific chemical modification of the polymer structure has been shown to improve certain properties of the polymer. The adhesion and etch resistance of poly(methyl methacrylate), a material that has been extensively studied as a positive electron beam resist, is improved by incorporating acid groups into the polymer structure.[3] The acid side groups are thermally unstable and condense with the loss of water molecules to cyclic anhydride structures.[4,5] The cyclic anhydrides have higher thermal stabilities and interact more efficiently with electrons than the original polymers.[5,6]

Anhydrides are readily converted to cyclic imides.[7–9] In this study the *in situ* conversion of poly(methacrylic and acrylic anhydrides) to poly(dimethacrylimide), poly(diacrylimide), and the respective N-methyl and N-ethyl derivatives

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was carried out. These polymers were found to be sensitive to UV, electron beam, and x-ray radiation[8] and to be thermally stable above 200°C.[10,11] In addition, the reaction of the above anhydrides with H_2S was investigated in an attempt to synthesize poly(diacryloyl and polydimethacryloyl sulfides) by a similar *in situ* technique. The preparation, characterization, and radiation properties of these polymers are reported in this paper.

EXPERIMENTAL

IR spectra were obtained with a Perkin-Elmer 257 grating infrared spectrometer. Proton NMR spectra were obtained on a Varian HA-100 NMR spectrometer. The chemical shifts were measured in dimethyl sulfoxide-d_6 using hexamethyldisiloxane as an internal reference. Carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer using approximately 5% polymer solutions in pyridine-d_5.

Elemental analyses were performed by Childers Laboratories, Milford, New Jersey. Glass transition temperatures were measured with a du Pont 990 differential thermomechanical analyzer equipped with a quantitative DTA cell. Thermogravimetric analyses were carried out under helium at 5°C/min heating rate with a du Pont 951 thermal analyzer.

Poly(acrylic acid), molecular weight 1,000,000 and poly(methacrylic acid), molecular weight 250,000, were obtained from Polysciences Inc. Polymer solutions, 5%–7% (w/v), were prepared in 2-methoxyethanol. These solutions were filtered through 1.2-μ Millipore filters under nitrogen pressure prior to spin coating.

Poly(methyl methacrylate-*co*-methacrylic acid) copolymers were prepared in dry tetrahydrofuran solvent using freshly distilled methyl methacrylate and methacrylic acid monomers. Polymerizations were carried out for 48 hr at 70°C with *t*-butyl hydroperoxide as initiator. Polymers were recovered from hexane, a nonsolvent, and the product was dried in a vacuum oven at 60°C for 24 hr. Molecular weights ranged from 200,000 to 400,000 and were determined by low-angle laser light-scattering photometry, gel permeation chromatography, and viscometry.[12] The acid content of the copolymers was determined quantitatively by carbon-13 NMR analysis.[13]

Synthesis of Cyclic Polyimides

Poly(acrylic and methacrylic acid) polymers were spin coated on SiO_2 and potassium chloride windows, then converted to cyclic derivatives by a gas–solid phase reaction with ammonia, methylamine, and ethylamine, respectively. These reactions were carried out in a 150-ml Parr pressure reactor assembled to permit manipulation under vacuum and pressure. The polymers and films were first baked in air or vacuum at 200°C to yield almost exclusively glutaric anhydride-type structures, confirmed by infrared and NMR spectroscopy. The reaction vessel was evacuated to 10^{-3} mm Hg pressure, pressurized with the appropriate gaseous amine to 150–300 mm Hg, and then heated in an oil bath at 200°C/1 hr. After cooling to ambient temperature, the modified polymers and films were characterized by elemental analysis and by infrared[10,11,14] and NMR spectroscopy.[15,16]

Electron beam irradiation of the modified polymers was carried out at 20–25

keV at a dose of 1×10^{-5} C/cm^2 with a scanning raster-type electron beam. Films were developed in appropriate solvents. Thickness measurements were carried out on a Rank Talystep instrument.

Photochemical irradiation of the cyclic polymers was carried out with two medium-pressure mercury lamps for several hours at −100°C under continuous vacuum at 10^{-3} mm Hg.[8] The degradation products were analyzed by infrared analysis and mass spectroscopy.

RESULTS AND DISCUSSION

The aminolysis of poly(acrylic acid) and poly(methacrylic acid) at 200°C is a convenient and relatively simple in situ method for preparing polycyclic imides.[9,17,18] Synthetic routes, such as the free radical-initiated cyclopolymerization of dimethacrylimide monomers, yield low molecular weight polymers with mixed structures, mostly glutarimide units with a small proportion of succinimide units.[10,11,14,15,19] The film properties of these cyclo polymers are poor because of the low molecular weight and the limited solubility in organic solvents.

Heating a polyacid with an amine involves intermediate anhydride, amine salt, or monoamide formation before condensation to the imide.[8] These intermediate products predominate at temperatures below 200°C. During the thermal treatment at 200°C, the major reaction is anhydride formation, which occurs by elimination of water between pairs of carboxyl groups.[20] For condensation reactions involving neighboring groups, the maximum extent of reaction had been calculated as 86.5%.[21] Nitrogen analysis and NMR analysis, Figures 1(a) and 1(b), have shown that the maximum conversion to cyclic imides by the *in situ* synthesis is between 80% and 85%.

ANAL. Calcd for poly(dimethacrylimide), $(C_8H_{11}NO_2)_n$: %N, 9.14. Found: %N, 7.50; conversion, 82.1%.

ANAL. Calcd for poly(diacrylimide), $(C_6H_7NO_2)_n$: %N, 11.19. Found: %N, 9.56; conversion, 85.4%.

Apparently, all COOH groups cannot dehydrate by an intramolecular mechanism, but some must do so by intermolecular anhydride formation. A few such intermolecular linkages will convert the linear macromolecules into a network, insoluble polymer, unless chemical degradation predominates to yield soluble, branched molecules.[22]

The proton NMR spectrum of poly(dimethacrylimide) in DMSO-d_6 at 25°C, Figure 1(a), shows a large peak at 1.29δ, assigned to the methyl protons of the six-membered rings; a broad band at 1.90δ, assigned to the methylene protons, a peak at 2.48δ, atributed to the deuterated DMSO solvent, and a broad N—H band at 6.46δ. The carbon-13 NMR spectrum of poly(dimethacrylimide) in pyridine-d_5, Figure 1(b), shows the methyl groups in the region of 25 ppm from TMS. The quaternary backbone carbons are at 40 ppm, the CH_2 ring methylenes are at 43 ppm, the nonring CH_2's are at 49 ppm, and the carbonyl groups are at 176 ppm. Free acid groups are indicated at 25 and 50 ppm.

The glass transition temperature of poly(methacrylic acid) is of the order of 130°C[23] and increases with increasing glutarimide content. Consequently, the glass transition temperatures of poly(dimethacrylimide) and poly(N-methyldimethacrylimide) were found to be 237° and 212°C, respectively. Poly(dimethacrylimide) was thermally more stable losing 11% of its original weight at 300°C.

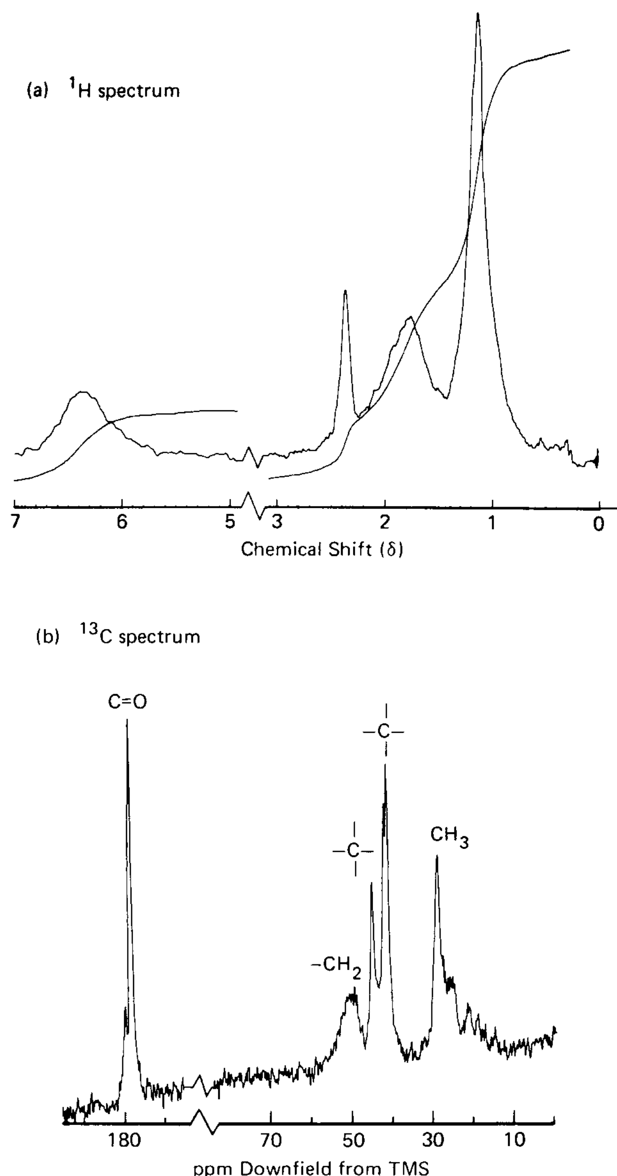
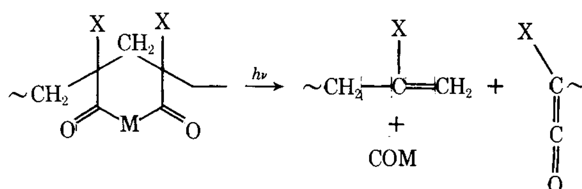


Fig. 1. NMR Spectra of Poly(Dimethacrylimide) in (a) DMSO-d_6 and (b) Pyridine-d_5 at 25°C.

The gas–solid phase reaction of poly(acrylic and methacrylic acids) with sulfur- and phosphorous-containing gases was also explored to determine whether this reaction would provide a general synthetic route for the preparation of cyclic sulfur- and phosphorous-containing polymers. Reactions with hydrogen sulfide or methyl mercaptan were sluggish and yielded cyclic polymers containing a small amount of sulfur. Elemental analysis indicated that 3%–5% of the cyclic rings contained sulfur. The reaction with phosphine did not produce a cyclic phosphorous derivative. Higher gas pressures and longer reaction times did not increase the conversion. Although carbonyl sulfide was positively identified by infrared and mass spectrometry during the UV photolysis of these polymers,

carbon-13 NMR and ESCA studies were unable to confirm a thioanhydride structure. These studies are continuing.

Hiraoka has demonstrated that glutaric anhydride-type polymers undergo photochemical degradation by decarboxylation which results in main chain scission with the formation of olefins and ketenes.[24] Poly(dimethacrylimides) exhibit the same photodegradation behavior,[25] i.e.,



where X = H or CH_3 and M = NH, N—CH_3, or N—C_2H_5.

The infrared absorption bands at 2270 and 2280 cm^{-1} are attributed to HN=C=O and RN=C=O (R = CH_3 and C_2H_5), respectively. Absorption bands at 2125 and 2145 cm^{-1} are assigned to the ketene endgroups. These volatile photoproducts were also identified by mass spectrometer measurements. The volatile photoproducts of poly(dimethacrylimide) are carbon monoxide, carbon dioxide, ammonia, and trace amounts of isocyanic acid. Isocyanic acid in the presence of water decomposed into carbon dioxide and ammonia. Poly(diacrylimide), when photolyzed, did not produce isocyanic acid but became insoluble, indicative of crosslinking reactions.

Under electron beam irradiation, all the polymer films, except poly(diacrylimide), which crosslinked, behaved as positive resists; they degraded to lower molecular units in the exposed regions. The crosslinking behavior of poly(diacrylimide) is attributed to the elimination of hydrogen from the nitrogen atom to produce a free radical. The free radical attacks the main polymer chain to form crosslinked structures. The products produced during electron beam irradiation were the same as those identified during photochemical irradiation. The positive resist behavior of poly(N-alkyldiacrylimides) was unexpected and appears to be a very specific and unusual example of the violation of the Miller Rule.[2] This rule states that when each carbon arom of the polymer main chain is substituted by at least one hydrogen atom, the polymer crosslinks. Even poly(acrylic acid), which has a negative resist structure, becomes a positive resist upon heating because of the formation of six-membered anhydride structures.[24,26]

The electron beam irradiation of cyclic imides and sulfides gives rise to a sig-

TABLE I
Evaluation of Amine- and Sulfur-Modified 75/25 P (MMA/MAA) Copolymers as Electron Beam Resists[a]

Modified polymer	Developer solvent	S/S_0
NH_3	ethylcellosolve acetate/ethanol	3.5
CH_3NH_2	ethylcellosolve acetate/ethanol	3.5
H_2S	cyclopentanone/isopropanol	3.0
P(MMA/MAA) (standard)	methylcellosolve/isopropanol	3.0

[a] Exposure at 20 keV at 1×10^{-5} C/cm^2; MAA is methacrylic acid.

nificantly low concentration of free radicals, in spite of an efficient main chain cleavage. This is attributed to the very high electron affinity of the free radicals to capture secondary electrons.[27] Also, instability of the intermediates in the presence of electrons renders degradation studies difficult and requires the combination of many methods before a reaction mechanism can be determined unequivocally.

After exposure, the resist films could not be adequately developed in organic solvents, or even stripped, unless hot alkaline solutions were used. The films were partially soluble in dimethylformamide and dimethyl sulfoxide, but they were not soluble in other solvents. Clear images could be developed in alkaline buffer solutions (pH 9.5–10), but the solubility rate ratios were low. In pH 12 solutions the films pitted and cracked. Aqueous solutions of sodium silicate have been used as developer solutions for a poly(methacrylamide) polymer containing some dimethacrylimide units.[28] However, these solutions were not suitable developers for polymers having a high methacrylimide content.

To improve the solubility, 75/25 methyl methacrylate-*co*-methacrylic acid copolymers were converted to ester–imide copolymers. The high ester content permitted the copolymers to be developed satisfactorily in organic solvent mixtures (cf. Table I) and to be utilized as sensitive electron beam resists.

CONCLUSIONS

This study has demonstrated a unique technique for modifying chemically preformed polymer films to alter their physical and chemical properties to optimize them for a particular end use. Modification of poly(acrylic and methacrylic acid) films has been found to provide unique pathways to cyclic polymer films which display high radiation sensitivity and good thermal properties. The limited solubility of these films in organic solvents has restricted their use as lithographic resists. However, when 20%–25% cyclic imide or cyclic groups containing sulfur are incorporated in copolymer structures, such as poly(methyl methacrylate-*co*-methacrylic acid), the solubility is improved. These polymer films have been found to be more sensitive and thermally stable resists than the original copolymers.

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