

A New Class of Inorganic Base-Generating Photoinitiators

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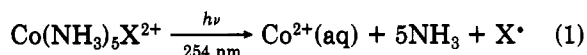
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Thin films composed of the copolymer of glycidyl methacrylate and ethyl acrylate and cobalt(III) ammine or alkylamine salts as photoinitiators undergo cross-linking upon deep-UV irradiation and subsequent heating. The mechanism of cross-linking involves nucleophilic attack by photoliberated am(m)ine base on the epoxide ring of the copolymer. The quantum efficiency for photodecomposition of the cobalt(III) salts is about 1% at 254 nm. Oxygen plasma etching studies suggest that the cobalt(III) salts are dispersed uniformly as submicron particles throughout the film.

Introduction

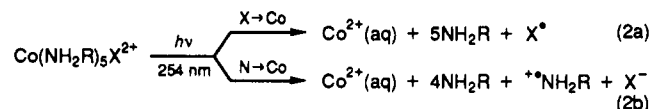
Recent efforts to develop new photoresists and photocurable coatings have resulted in the discovery of several interesting classes of inorganic photoinitiators. Examples include thermally stable fluorinated titanocene derivatives which undergo efficient radical production when irradiated at wavelengths of the argon ion laser,¹ a series of cationic iron sandwich complexes that photodecompose to a strong Lewis acid,² and cobalt(III) ammine complexes that photochemically liberate a Lewis base.³ Complexes belonging to the last category are especially intriguing since, as summarized in eq 1 (X is Cl⁻ or Br⁻) for photolysis in



aqueous solution, they yield a cationic Lewis acid, multiple equivalents of an uncharged Lewis base, and a radical.⁴ Any one or combination of these reactive species could initiate useful chemistry in a suitably designed system.

In 1987, we reported that incorporation of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ into a thin film of the copolymer of glycidyl methacrylate and ethyl acrylate (COP, Figure 1) affords a material that undergoes photoinitiated cross-linking upon deep-UV irradiation and subsequent heating.³ Patternwise exposure and development in a solvent that dissolves the unirradiated areas result in negative tone image formation with 1–2- μm resolution. Identifying the active cross-linking agent in this system poses an interesting mechanistic problem since, in principle, both the acidic Co^{2+} ion and the basic ammonia molecule can open the epoxide ring.⁵ In an effort to resolve this issue and also to expand the list of base-generating photoinitiators, we have examined the spectral and photochemical properties of complexes of general formula $\text{Co}(\text{NH}_2\text{R})_5\text{X}^{2+}$ (R is CH_3 or $n\text{-C}_3\text{H}_7$, X is Cl⁻ or Br⁻).⁶ While the ultraviolet photochemistry

of these complexes in aqueous solution (eq 2) mimics that



of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (eq 1), the liberated alkylamines are appreciably stronger bases than ammonia. Accordingly, we would expect members of the $\text{Co}(\text{NH}_2\text{R})_5\text{X}^{2+}$ family to be more effective than their ammine analogues in photoinitiating the cross-linking of COP via a base-mediated pathway, whereas roughly comparable photosensitivities should obtain if cross-linking involves attack by Co^{2+} .

In this article we report a detailed study of several cobalt(III) ammine and alkylamine photoinitiators dispersed in thin films of COP. The extent of photoinitiated cross-linking/insolubilization of the films has been determined as a function of 254-nm exposure dose. These dose-response data, in conjunction with the measured quantum efficiencies of photoinitiator decomposition, have been used to assign the mechanism of cross-linking. In addition, oxygen plasma etching of the films has yielded information about the size and distribution of photoinitiator clusters within the polymer matrix.

Experimental Section

Reagents and Equipment. Literature procedures were followed in the synthesis of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$,⁷ $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$,⁸ $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$,⁹ $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$,¹⁰ $[\text{Co}(\text{NH}_2\text{C}_3\text{H}_7)_5\text{Cl}]\text{Cl}_2$,¹¹ and *trans*- $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$,¹² complexes originally prepared with halide counterions were converted to perchlorate salts by two or three recrystallizations from aqueous solution containing $\text{NaClO}_4\text{-HClO}_4$. All complexes were characterized by elemental analysis. A solution of COP (12 wt %) in chlorobenzene was purchased from Mead Technologies, Inc., and high-purity *N*-methyl-2-pyrrolidinone (NMP) was obtained from Burdick and Jackson. All other chemicals were at least of reagent grade quality and used as received.

Electronic absorption spectra were recorded on a Varian DMS-300 spectrophotometer. Film thickness measurements were

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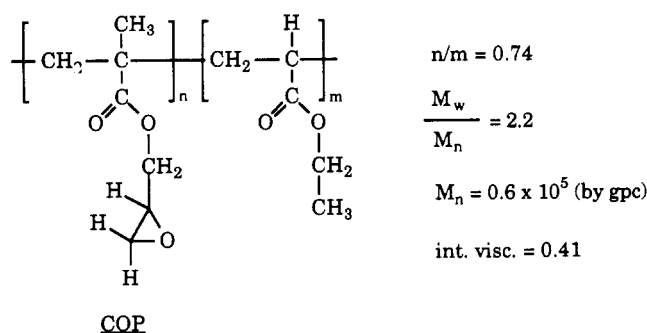


Figure 1. Structure of COP. Composition and physical properties were determined by the supplier.

taken with an Alpha-Step 200 profilometer from Tencor Instruments. Irradiations at 254 nm were performed with an Optical Associates, Inc. Model 150 illuminator in conjunction with a narrow-bandwidth interference filter. Photon flux was determined with an OAI calibrated power meter. Oxygen plasma etching experiments were conducted in a Plasmatherm reactor operating at a pressure of 0.2 Torr, a power to the bottom electrode of 150 W, a bias of -138 V, and an oxygen flow of 40 sccm. Films etched to various depths were viewed with an Amray field emission scanning electron microscope.

Quantum Yield Determinations. A weighed amount (typically 100 mg) of the cobalt(III) salt was dissolved with stirring in 1 mL of NMP. This solution was stirred for 5–10 min with 3 mL of the commercial COP material, and the resulting solution filtered through a 0.45- μm disk filter. Several 1-in.-diameter quartz wafers were spin-coated with the filtrate at either 600 or 2000 rpm for 30 s and then baked on a hotplate at 50 or 62 $^{\circ}\text{C}$ for 4 min to remove solvent. This procedure afforded thin films of COP containing the cobalt(III) photoinitiator. Following exposure to 254-nm radiation, each coated wafer was placed in a small vial containing 3 mL of acetone and a magnetic stir bar. The contents of the vial were stirred for 10 min to dissolve the film, and the resulting solution was analyzed for Co(II) by a modification of the procedure of Vydra and Pribil.¹³ In brief, 1.5 mL of acidified sodium acetate solution, 1 mL of acidified ferric chloride solution, and 1.5 mL of a 0.1% solution of 1,10-phenanthroline were added to the vial, and the entire contents stirred for 60 min in the dark. The liquid portion was then filtered through a 0.45- μm filter, and its absorbance measured at 510 nm. A similar procedure was performed on a nonirradiated wafer to provide a blank value. A previously constructed calibration plot was used to convert absorbance readings to Co(II) concentrations. The quantum yield of redox decomposition, $\varphi_{\text{Co}^{2+}}$, is calculated from the relation (mol of Co^{2+} generated)/(mol of light absorbed).

Lithographic Studies. Dose-response curves were determined for COP films containing each of the cobalt(III) complexes. Resist solutions (prepared as described in the preceding section, but at one-half the cobalt concentration) were spin-coated onto quartz wafers at 2000 rpm for 30 s and then baked at 62 $^{\circ}\text{C}$ for 4 min. Each wafer was backside exposed to 254-nm radiation through a step wedge, baked at 70 $^{\circ}\text{C}$ for 7 min, and then developed by spin-rinsing with a 5:3 (v/v) 2-butanone/ethanol solution for 10–15 s. The thickness profile of the undissolved film was measured with the profilometer, and the results were normalized to unity by dividing each value by the maximum film thickness obtained at high radiation doses.

Photoimaging studies were conducted on films spin-coated onto silicon wafers. The films were frontside exposed to 254-nm radiation through a chrome-on-quartz mask in contact with the film surface, baked at 62 $^{\circ}\text{C}$ for 10 min, and developed by spin-rinsing with a stream of 5:3 (v/v) 2-butanone/ethanol solution for 10–15 s followed by a similar rinse with 2-propanol. Images were observed and photographed under an optical microscope.

Plasma Etching Experiments. Silicon wafers coated with $\sim 0.6\text{-}\mu\text{m}$ films of COP-[Co(NH₂CH₂)₅Br](ClO₄)₂ or COP-[Co(NH₂CH₂)₅Cl](ClO₄)₂ were etched for various times in an oxygen plasma. This treatment resulted in film thickness losses of up

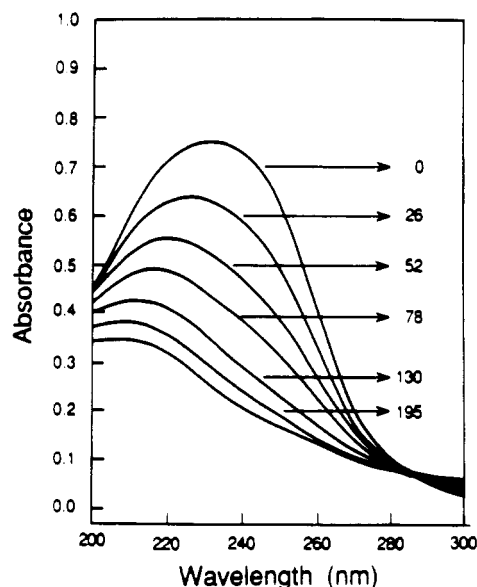


Figure 2. Ultraviolet spectral changes resulting from the 254-nm irradiation of a COP film containing [Co(NH₂CH₂)₅Cl](ClO₄)₂. Numbers correspond to exposure dose in mJ/cm².

to 33%. Following etching, the morphology of each film was examined with a scanning electron microscope.

Results and Discussion

Photochemical Studies. Complexes belonging to the Co(NH₃)₅X²⁺ and Co(NH₂R)₅X²⁺ families exhibit intense absorption bands in the ultraviolet region arising from ligand-to-metal charge-transfer transitions.⁴ These transitions, which formally involve the transfer of an electron from the acido group (X \rightarrow Co) or the am(m)ine nitrogen (N \rightarrow Co) to the metal, create a substitutionally labile Co(II) complex susceptible to ligand loss (e.g., eqs 1 and 2). Figure 2 depicts the spectral changes that accompany the deep-UV irradiation of [Co(NH₂CH₂)₅Cl](ClO₄)₂ dispersed in a thin film of COP. Excitation of the overlapping N \rightarrow Co and Cl \rightarrow Co charge-transfer transitions causes a steady bleaching of the broad, composite absorption band. Such behavior indicates the occurrence of photoredox chemistry which, by analogy to eq 2, generates one or more weakly absorbing Co(II) species. While our results provide no stoichiometric information about the Co-containing photoproduct(s) in the polymer matrix, we would expect the reduced metal to retain at least some coordinated methylamine ligands at room temperature.¹⁴ Dissociation of methylamine should occur, however, as the polymer film is heated. Both [Co(NH₃)₅Br](ClO₄)₂ and [Co(NH₂CH₂)₅Br](ClO₄)₂ also undergo photoredox decomposition in COP films upon 254-nm irradiation, although in these cases reaction arises mainly from Br \rightarrow Co charge transfer.^{4,6}

While exposing a COP film containing [Co(NH₂CH₂)₅Cl](ClO₄)₂ to 78 mJ/cm² of 254-nm radiation causes appreciable decomposition of the cobalt(III) salt (Figure 2), the film dissolves completely in a 2-butanone/ethanol developing solution. In contrast, heating a comparably irradiated film at 70 $^{\circ}\text{C}$ for 7 min renders it insoluble in the developer. Since heating alone does not insolubilize the film, it follows that some photoredox product of the cobalt(III) salt initiates cross-linking of the epoxy copolymer in a thermally activated step. Figure 3 depicts the dose-response curves for 0.6–0.7- μm COP films con-

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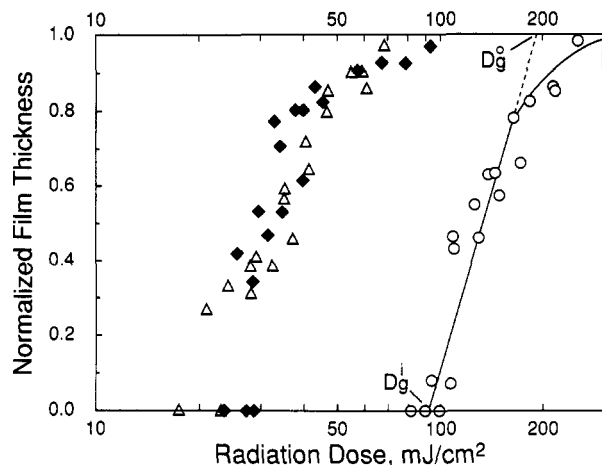


Figure 3. Dose-response curves for 0.6–0.7- μm films of COP containing $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ (\circ), $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$ (\blacklozenge), or $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ (Δ). Films were coated onto transparent quartz wafers, exposed from the back side to 254-nm radiation, baked at 70 °C, and developed by spin-rinsing with a 5:3 (v/v) 2-butanone/ethanol solution. The straight line drawn through the data points for $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ establishes the values of D_g^i and D_g^o (see Table I).

Table I. Lithographic Sensitivity Values for the Photoinitiated Cross-Linking of COP Films^a

photoinitiator	A_{254}^b	$D_g^{i,c}$ mJ/cm ²	$D_g^{o,d}$ mJ/cm ²
$[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$	0.33	26	46
$[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$	0.46	22	54
$[\text{Co}(\text{NH}_2\text{C}_3\text{H}_7)_5\text{Cl}]\text{Cl}_2$	0.48	14	80
$[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$	0.47	94	190
$[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$	0.19	130	208

^a See Experimental Section and caption to Figure 3 for experimental details. ^b Absorbance of film at 254 nm. ^c Minimum dose of 254-nm radiation required for detectable gel formation. ^d Projected dose of 254-nm radiation that causes 100% film thickness retention.

taining $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$, or $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$. The normalized film thickness remaining after exposure, baking, and development is plotted as a function of the logarithm of the radiation dose.¹⁵ Two important features of these curves should be noted. First, the lithographic sensitivities of films containing the methylamine complexes are very similar. Second, both of these films are considerably more sensitive than that containing $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$. For example, the interface gel dose, D_g^i , defined as the minimum dose required for detectable gel formation, is 26 mJ/cm² for $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$ and 94 mJ/cm² for the ammine complex. Likewise, the projected dose that causes 100% film thickness retention, D_g^o , is considerably smaller for the methylamine complex. Table I contains a summary of D_g^i and D_g^o values for several cobalt(III) photoinitiators investigated in this study. In general, those films containing alkylamine complexes exhibit the higher photosensitivity.¹⁶

(15) Measurements on three to five coated wafers were required to construct a complete dose-response curve for each complex. Although care was taken to maintain uniform coating, baking, irradiation, and development conditions, small variations in these processes from wafer to wafer are the likely source of the scatter in the data points.

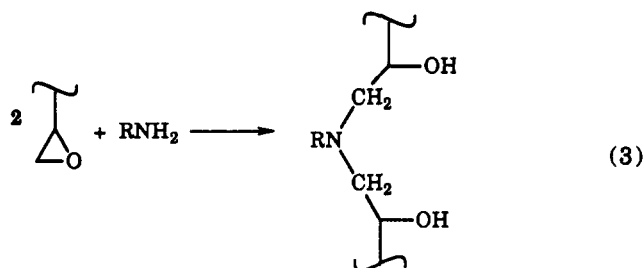
(16) Our comparisons of lithographic sensitivity do not take into account differences in film absorbance at the excitation wavelength (A_{254}). While normalization to equal absorbance would cause some changes in the D_g^i and D_g^o values listed in Table I, it would not affect the main conclusion that COP films containing the alkylamine complexes exhibit higher photosensitivity.

Table II. Quantum Yields for Photoredox Decomposition of Cobalt(III) Complexes in COP Films Exposed to 254-nm Radiation^a

complex	$\varphi_{\text{Co}^{2+}b}$
$[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$	0.008 \pm 0.001
$[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$	0.007 \pm 0.002
$[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$	0.012 \pm 0.004
	0.013 \pm 0.004 ^c

^a Unless noted otherwise, concentration of cobalt(III) complex in resist solution was $(5\text{--}6) \times 10^{-2}$ M; film was spin-coated at 600 rpm and baked at 50 °C. ^b Quantum yields were corrected for incomplete absorption of the exciting light. Average of three to six determinations. ^c Cobalt(III) complex concentration was 3×10^{-2} M; films were spin-coated at 2000 rpm and baked at 62 °C.

These dose-response data strongly suggest that photoliberated base plays a key role in the cross-linking/insolubilization of COP films. A plausible description of this process, involving nucleophilic attack of base on the pendant epoxide rings of neighboring polymer chains, is presented in eq 3. The higher lithographic sensitivity

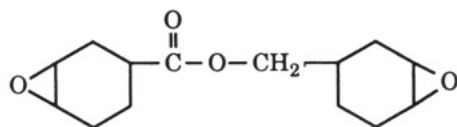


attained with complexes containing NH_2R relative to those containing NH_3 correlates with the greater base strength/nucleophilicity of alkylamines. Differences in the volatilities of the various bases also can influence dose-response behavior. Thus the low boiling point of NH_3 (-33.4 °C vs -6.3 °C for NH_2CH_3 and 47.8 °C for $\text{NH}_2(n\text{-C}_3\text{H}_7)$) facilitates its escape from the polymer film during postirradiation baking, thereby lessening the likelihood of reaction with epoxide groups.

Although eq 3 provides a ready explanation for the dose-response data in Figure 3 and Table I, the alternative view that a Co^{2+} species is the active cross-linking agent could be defended if the alkylamine complexes undergo photodecomposition in COP films more efficiently than their ammine counterparts. That is, the higher sensitivity of films containing $\text{Co}(\text{NH}_2\text{R})_5\text{X}^{2+}$ simply may reflect a larger concentration of photochemically generated Co^{2+} products. Quantum yield data summarized in Table II, however, clearly militate against this possibility. Thus $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$, and $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ decompose under 254-nm radiation with comparable $\varphi_{\text{Co}^{2+}}$ values of about 1%. It should be noted that these values are significantly below those for the photodecomposition of the complexes in aqueous solution. This disparity can be attributed to the much lower mobility of the primary radical-pair photoproducts in the viscous polymer matrix and the correspondingly greater probability of recombination with no net reaction.⁴

Two additional observations lend credence to the base-mediated cross-linking mechanism depicted in eq 3. First, the liberation of pyridine in a COP film by photoredox decomposition of *trans*- $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}\cdot 6\text{H}_2\text{O}$, followed by heating, causes no apparent cross-linking of the epoxide copolymer. Such behavior correlates nicely with the properties of pyridine in that low base strength and the absence of active hydrogens preclude this molecule from attacking the epoxide ring via the pathway followed by alkylamines and ammonia (eq 3). Second, photoin-

duced decomposition of $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ and $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$ in thin films of the low molecular weight epoxide, (3,4-epoxycyclohexyl)methyl-(3,4-epoxy)cyclohexane carboxylate (ECC), followed by heating,

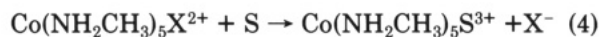


ECC

causes infrared spectral changes consistent with attack of photoliberated base on the epoxide ring. Specifically, the characteristic epoxide ring vibrations in the vicinity of 800 cm^{-1} decrease in intensity while an intense band, assignable to C-N and C-O stretching modes of the alcoholamine moiety, appears at about 1080 cm^{-1} .¹⁷

The photoinitiated chemistry described by eqs 1–3 can be utilized for micropattern delineation with deep-UV light. On a molecular level, the photoredox decomposition of a cobalt(III) am(m)ine photoinitiator in the irradiated areas of a COP film releases a Lewis base which, in a thermally activated step, causes cross-linking of the pendant epoxide groups of the copolymer. Rinsing the film with a developer solution dissolves the unexposed regions to afford a negative tone relief image. Figure 4 displays the line-space pattern that results from exposing a COP film containing $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ to 98 mJ/cm^2 of 254-nm radiation. Despite some swelling of the copolymer in the developer, the $2\text{-}\mu\text{m}$ features are clearly resolved.

Thermal Stability Studies. A few experiments were performed to assess the thermal stabilities of the cobalt(III) photoinitiators in solution and in COP films. No changes were evident in the electronic absorption spectrum of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ dissolved in NMP, acetone, or acetonitrile over several hours at room temperature. In contrast, solutions of $\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}^{2+}$ in these solvents changed color within a few hours. These color changes could arise from one or more of the following processes: (i) substitution of coordinated methylamine by solvent; (ii) substitution of coordinated halide ion by solvent (S in eq 4); (iii) redox decomposition of the com-



plex. Processes i and iii appear to be unimportant, at least initially, since only minor amounts of free NH_2CH_3 and Co^{2+} were detected in solutions that had undergone considerable change in color. The likely involvement of process ii is indicated by the steady rise in solution conductivity with time. Rapid, dissociative loss of halide ion from $\text{Co}(\text{NH}_2\text{CH}_3)_5\text{X}^{2+}$ complexes in coordinating solvents is facilitated by the steric crowding of the bulky (relative to H) alkyl groups.¹⁸

The relatively rapid substitutional chemistry of the $\text{Co}(\text{NH}_2\text{R})_5\text{X}^{2+}$ family in NMP necessitates that resist formulations containing these complexes and COP (see Experimental Section) be used immediately upon mixing. After the resist solution has been spin-coated onto a substrate and the solvent removed by baking, the resulting film possesses an effective shelf life of 12–24 h at room temperature. Storage for longer times results in thermal

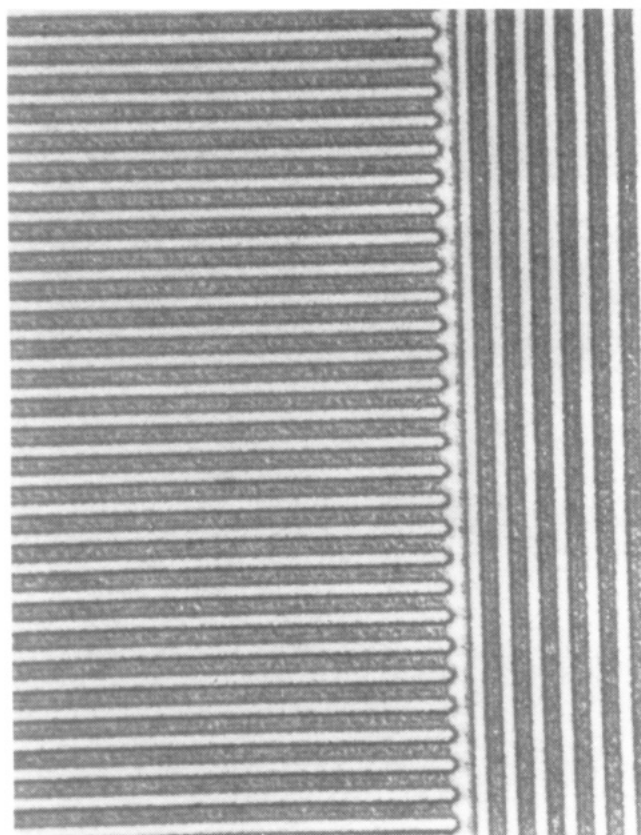


Figure 4. Optical photomicrograph (1000 times magnification) of the $2\text{-}\mu\text{m}$ line-space pattern obtained upon 254-nm irradiation of a COP film containing $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$.

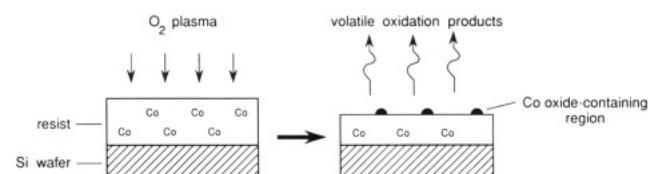


Figure 5. Schematic representation of the reactive-ion etching of a polymer film containing a cobalt(III) photoinitiator (here simply denoted as Co).

cross-linking that renders the film unsuitable for imaging applications.

Plasma Etching Studies. Resist solutions composed of COP, a cobalt(III) am(m)ine photoinitiator, and an NMP/chlorobenzene casting solvent afford good-quality films when spin-coated onto silicon or quartz substrates and baked to remove solvent. When viewed under an optical microscope at 1000–1500 times magnification, films containing $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ showed no evidence of photoinitiator aggregation. Similar inspection of COP- $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ films revealed some apparent crystallization of the cobalt salt, but the crystallites were widely separated ($>150\text{ }\mu\text{m}$) on an otherwise featureless surface. These visual observations and the ability to generate relief images with 1– $2\text{-}\mu\text{m}$ resolution (Figure 4) establish that the ionic cobalt(III) photoinitiators are dispersed in the polymer matrix with an average cluster size considerably below $1\text{ }\mu\text{m}$. Even at these dimensions, however, a cluster could contain tens to hundreds of individual cation/anion units. More importantly, the average size and thus the total number of clusters per unit volume of the film may vary with the identity of the cation. This would result in unequal distributions of effective photoactive sites (i.e., smaller clusters contain a greater fraction of their cations at the surface, where reaction of photoliberated base with epoxide is most probable) and

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thereby possibly contribute to the observed difference in lithographic sensitivities (Figure 3).

In an attempt to visualize individual photoinitiator clusters, we exposed 0.6- μm films of COP containing $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ or $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ to an oxygen plasma. As illustrated in Figure 5, this reactive-ion etching (RIE) technique converts nonmetallic elements to volatile oxides, which are removed under vacuum, while leaving behind nonvolatile cobalt oxide(s) as a "footprint" of the original cobalt(III) photoinitiator. Regions of the film rich in cobalt will therefore etch at a slower rate than regions containing little or no metal. If the cobalt(III) am(m)ine photoinitiator aggregates or phase separates to a significant extent in COP films, partial etching followed by examination under a scanning electron microscope will reveal the structure (size and spacing) of clusters with dimensions above about 0.1 μm . Information of this type recently was obtained for triarylsulfonium antimonate photoacid generators in polymer films¹⁹ and for polybutadiene particles in high-impact polystyrene.²⁰

Our RIE studies reveal no sign of macroscopic phase separation between COP and either $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ or $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$. Thus films etched to 15–33% of their original thickness exhibited a morphology (i.e., absence of features >0.1–0.2 μm in size) consistent with good solubility and uniform distribution of the ionic photoinitiators in the polymer matrix.²¹ This finding, in turn, reinforces our earlier conclusion that differences in lithographic sensitivity between ammine and alkylamine complexes (Figure 3) arise mainly from the different strengths and/or volatilities of the photoliberated Lewis bases.

(19) (a) Allen, R. D., manuscript in preparation. (b) For closely related work, see: Allen, R. D.; Schaedeli, U.; McKean, D. R.; MacDonald, S. A. *Proc. Polym. Mater. Sci. Eng.* **1989**, *61*, 185.

(20) Ramesh, N. S.; Padiyath, R.; Campbell, G. A.; Babu, S. V. *J. Polym. Sci. B: Polym. Phys.* **1991**, *29*, 1031.

(21) For comparison, the morphology of these etched films resembles that found for the most soluble triarylsulfonium antimonate/polymer combinations examined in another RIE study.^{19a}

Conclusions

Ultraviolet irradiation of thin films of COP containing $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Br}](\text{ClO}_4)_2$, or $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$ causes redox decomposition of the cobalt(III) complex with the liberation of several equivalents of Lewis base. The quantum efficiency of this process at 254 nm is about 1%. Subsequent heating of the irradiated film induces cross-linking and insolubilization via ring-opening attack of the base on the epoxide moiety (eq 3). The greater lithographic sensitivity of films containing the stronger base, methylamine, supports this mechanism. Oxygen plasma etching experiments indicate that the cobalt(III) salts are well dispersed as submicron particles in the polymer matrix.

Essentially all commercial photoinitiators currently in use liberate radicals and/or strong acids upon being irradiated. Our results with cobalt(III) am(m)ine complexes and the recent work of Cameron and Fréchet²² with photosensitive carbamates demonstrate the feasibility of photogenerating base to initiate useful chemistry.²³ Further studies are needed to delineate the scope and potential applications of this promising new photoinitiation strategy.

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Registry No. COP, 26591-04-8; O₂, 7782-44-7; $[\text{Co}(\text{NH}_2\text{C}_6\text{H}_5)_5\text{Br}](\text{ClO}_4)_2$, 61160-95-0; $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}](\text{ClO}_4)_2$, 15392-60-6; $[\text{Co}(\text{NH}_2\text{C}_3\text{H}_7)_5\text{Cl}]\text{Cl}_2$, 26764-69-2; $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, 14591-65-2; $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$, 15156-18-0.

(22) (a) Cameron, J. F.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919. (b) Cameron, J. F.; Fréchet, J. M. J. *J. Photochem. Photobiol., A (Chemistry)* **1991**, *59*, 105.

(23) For an interesting example of the use of photogenerated base in the imagewise formation of a dye, see: DoMinh, T. *Res. Chem. Intermed.* **1989**, *12*, 251.