Imaging of Aliphatic Polycarbonates with Photogenerated Base

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A series of aliphatic polycarbonates based on the condensation copolymerization of the bischloroformate of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) with itself and the diols of 3-cyclohexene-1,1-dimethanol, 1,4-cyclohexanediol (CHD), in various molar ratios, *exo,exo*-tricyclo[2.2.1.0^{2,6}]heptane-3,5-diol, and 4,8-bis(hydroxymethyl)tricyclo[5.2.10^{2,6}]decane (BTD) were synthesized. Incorporation of cyclic and tricyclic repeat units produced polycarbonates with high glass transition temperatures (T_g's), high molecular weights, and low refractive indexes. The crystallinity of the TMCBD homopolymer was minimized in the CHD/TMCBD copolymers with little effect on T_g but with decreased thermal stability. Thermal analysis yields decomposition temperatures ranging from 354 °C for the TMCBD homopolymer to 292−298 °C for the CHD/TMCBD copolymers; all polymers undergo complete thermal degradation. Refractive indexes range from 1.493 for the 1:1 copolymer of BTD and TMCBD to 1.481 for the CHD/TMCBD copolymers. Thin films composed of an aliphatic polycarbonate and a base-releasing cobalt(III) photoinitiator can be imaged with deep-UV light. The polycarbonates selected for study were the 9:1 copolymer of CHD and TMCBD and the 1:1 copolymer of BTD and TMCBD. The first step of image formation is the efficient photoredox decomposition of the photoinitiator with the release of multiequivalents of Lewis base. In the case of $[Co(en)_3](BPh_4)_3$ (en is ethylenediamine, BPh_4^- is tetraphenylborate), photogenerated ethylenediamine cross-links the polymer chains via formation of bis(dicarbamate) linkages. Development with solvent dissolves the unirradiated areas to yield negative-tone images. For $[Co(NH_3)_6](BPh_4)_3$, photoreleased ammonia causes chain scission in the exposed regions of the film, and wet or dry development results in positive-tone images.

Introduction

Photosensitive films composed of a functionalized polymer and a photoinitiator play a central role in numerous commercial applications ranging from the ultraviolet curing of coatings to the microimaging of semiconductor chips.[1] Typically, the photoinitiator is an organic or organometallic compound that, upon exposure to radiation, generates one or more species which alter the chemical composition of the film. In essentially all systems reported to date, these photogenerated species are radicals and/or acids.[2]

During the past few years we have demonstrated that a promising alternative strategy for initiating useful chemistry involves the photochemical production of base.[3] Thus thin films of an epoxide-functionalized polymer containing a cobalt(III) am(m)ine complex such as $[Co(NH_3)_6](BPh_4)_3$ or $[Co(en)_3](BPh_4)_3$ (en is ethylenediamine, BPh_4^- is tetraphenylborate) undergo photoinitiated cross-linking upon deep-UV irradiation and subsequent heating.[4] Patternwise exposure and development in a solvent that dissolves the unirradiated areas results in negative-tone image formation with 1−2 μm resolution. The mechanism of this process involves the quantum efficient photoredox decomposition of the cobalt salt with the release of multiequivalents of Lewis base (eqs 1 and 2). In a thermally activated step, the base cross-links the polymer via nucleophilic attack on the epoxide rings of neighboring chains (eq 3). Other sources of photogenerated base, such as photosensitive carbamates, have been reported to yield analogous behavior.[5]

Our efforts to expand the scope of base-initiated chemistry in polymer films led us to investigate the photochemical properties of polycarbonate films containing cobalt(III) am(m)ine complexes. Polycarbonates are known to undergo nucleophilic attack at the carbo-

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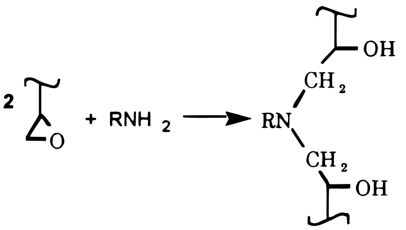
$$[Co(NH_3)_6](BPh_4)_3 \xrightarrow{h\nu} Co^{2+} + 6NH_3 + BPh_3 + Ph^{\bullet} + 2\,BPh_4^{-} \quad (1)$$

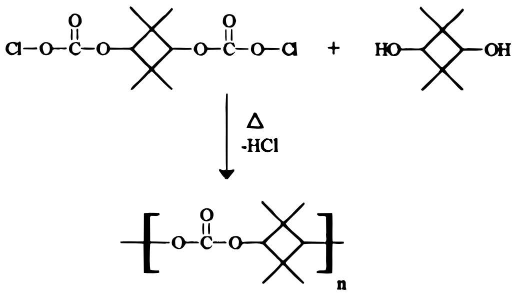
$$[Co(en)_3](BPh_4)_3 \xrightarrow{h\nu} Co^{2+} + 3en + BPh_3 + Ph^{\bullet} + 2\,BPh_4^{-} \quad (2)$$



(3)

nyl linkage,[6] and, therefore, we reasoned that they should be susceptible to reaction with photogenerated base. Aromatic polycarbonates, such as those derived from bisphenol A, possess desirable physical properties but absorb too strongly below 280 nm to be of practical interest for deep-UV applications. Accordingly, we have focused our attention upon aliphatic polycarbonates which are optically transparent down to 230 nm.

Aliphatic polycarbonates can be synthesized by transesterification,[7,8] by ring opening polymerization,[7,9] and by reaction of hydroxy compounds with bischloroformates (eq 4).[7,10] Practical applications of these polymers have been limited, however, because of low molecular weights and inferior thermal properties compared to their aromatic counterparts.[7] Recently, Kricheldorf and Weegen-Schultz reported that polymers with molecular weights exceeding 10^6 can be synthesized by ionic ring-opening polymerization of aliphatic cyclic polycarbonates with boron trihalide initiators.[11] Although these polymers are high molecular weight materials, their glass transition temperatures (T_g's) are low because the presence of methylene groups throughout the backbone yields flexible chains. Matzner et al. demonstrated that replacing the methylene units by a rigid cyclic group such as cyclobutane (e.g., eq 4) yields stiffer chains and correspondingly higher T_g values.[12]



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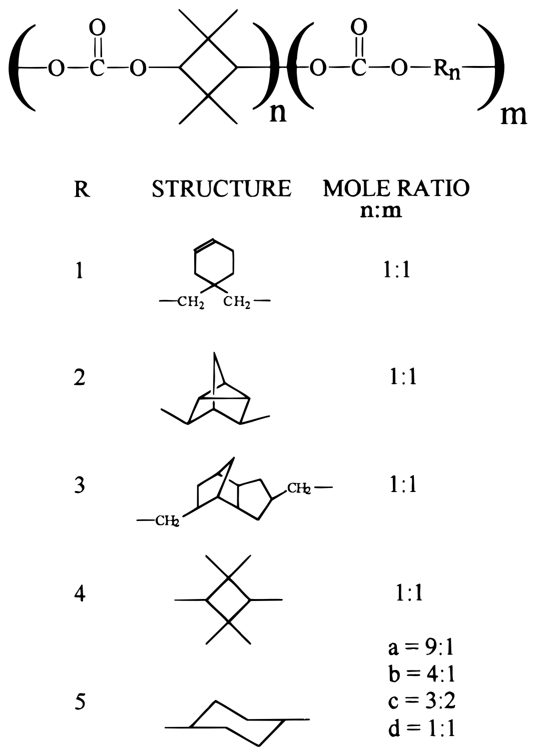
Scheme 1



Building upon these earlier studies, we have prepared and characterized a series of optically clear aliphatic polycarbonates with T_g's above 125 °C and molecular weights to 10^5 via condensation polymerization between the bis(chloroformate) of tetramethylcyclobutane and various aliphatic diols. The structures of the eight polymers reported here and their shorthand designations are listed in Scheme 1. We also have examined the photochemical responses of thin films of two aliphatic polycarbonates, R_3 and R_{5a}, containing a base-releasing photoinitiator. Both polymers can be imaged with deep-UV light in the presence of $[Co(NH_3)_6](BPh_4)_3$ or $[Co(en)_3](BPh_4)_3$. Quite interestingly, we find that either a positive tone or a negative tone response to light can be obtained depending upon the combination of polycarbonate and cobalt photoinitiator and the processing conditions employed.

Experimental Section

Reagents. Bisphenol A polycarbonate (Lexan), 3-cyclohexene-1,1-dimethanol, 4,8-bis(hydroxymethyl)tricyclo[5.2.10.^{2,6}]decane, 1,4-cyclohexanediol, anisole, *n*-butylamine, diphenyl carbonate, $[Co(NH_3)_6]Cl_3$, $[Co(en)_3]Cl_3 \cdot 3H_2O$, and sodium tetraphenylborate were purchased from Aldrich Chemical Co. Tetramethyl-1,3-cyclobutanediol was obtained from the Eastern Chemical Co. Pressurized liquid phosgene was purchased from Matheson Gas Products. *exo,exo*-Tricyclo[2.2.1.0^{2,6}]heptane-3,5-diol was prepared by a method previously described.[13]

Synthesis. *Cobalt Complexes.* The cobalt(III) am(m)ine complexes were converted to their tetraphenylborate salts by the following metathesis procedure: An aqueous solution of $NaBPh_4$ was added slowly with stirring to an aqueous solution of the cobalt complex; a slight stoichiometric excess (3.1:1) of BPh_4^- was used to ensure complete conversion. A yellow solid gradually precipitated, and the resulting mixture was stirred an additional 20 min. The solid was filtered, washed with

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(6) *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G.; Menges, G., Eds.; John Wiley: New York, 1988; Vol. 11, pp 648–718.

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dilute $NaBPh_4$ solution and distilled water, and then air dried in the dark. Analytical calculations for $[Co(NH_3)_6](BPh_4)_3 \cdot 5H_2O$: C, 71.57%; H, 7.28%; N, 6.96%. Found: C, 71.44%; H, 7.35%; N, 6.90%. Yield 65%. $[Co(en)_3](BPh_4)_3 \cdot 3H_2O$: C, 74.86%; H, 7.20%; N, 6.70%. Found: C, 74.43%; H, 7.29%; N, 6.66%. Yield 75%.

Polymers. The synthesis of 2,2,4,4-tetramethyl-1,3-cyclobutane bischloroformate was reported earlier.[14] Each of the commercially available diols was purified by sublimation. Glassware was dried for 24 h at 150 °C. The general polymerization procedure used to prepare the polycarbonates listed in Scheme 1 will be described in detail for R_{5a}. To a 100 mL three-neck flask containing a magnetic stir bar were added 1.05 g of 1,4-cyclohexanediol, 2.42 g of the bischloroformate, and 30 mL of reagent-grade chlorobenzene. The flask was fitted with a nitrogen feed, thermometer, and condenser, and the contents were heated with stirring to 130 °C for 5 min to remove water. The temperature was then lowered to 90 °C and 1.50 g of pyridine, dissolved in 10 mL of chlorobenzene, was added slowly by means of a dropping funnel. The reaction was run at 90 °C for 24 h, after which the polymer was precipitated by pouring the contents of the flask into 500 mL of methanol. The polymer was separated by filtration and dried under vacuum for 24 h.

Measurements. *Polymer Characterization.* Inherent viscosities were determined at 25 °C for solutions of the polymers (0.5 g/dL) in tetrahydrofuran (THF) using an Ubbelohde viscometer. Molecular weight determinations were performed with two Phenomix, 10 μm, 300 × 7.8 mm chromatography columns fitted in series with a Waters 590 HPLC pump and Waters 410 differential refractometer. A calibration curve based on polystyrene standards was used to estimate the molecular weight. Polymer concentrations were 1% by weight with THF as solvent and flow rates set at 1.0 mL/min.

Measurements of T_g and T_m, the melting temperature, of the polymers were made with a Seiko DSC 220C differential scanning calorimeter at a heating rate of 10 °C/min. T_g was taken as the midpoint of the change in slope of the baseline, while T_m was determined from the peak of the baseline change. The degradation temperature, T_d, taken as the midpoint of the change in slope of the baseline, was found by thermogravimetric analysis using a Seiko TG/DTA 220 thermobalance. The heating rate was 5 °C/min.

Proton NMR spectra were determined with a Bruker AC/WP200 FT spectrometer in 5-mm o.d. sample tubes. Deuterated chloroform, with 1% v/v tetramethylsilane as an internal standard, was used as solvent. For each polymer, the percentage of cyclobutane rings exhibiting the cis stereochemistry of the 1,3 substituents was determined from the areas of the resonances at 4.4 and 4.6 ppm.[14]

Thin Film and Model System Studies. Chloroform and THF proved to be suitable solvents for casting thin films of the polycarbonates polymers. Due to the limited solubility of $[Co(NH_3)_6](BPh_4)_3$ and $[Co(en)_3](BPh_4)_3$ in chloroform, only THF was used to cast polymer films containing these salts. Polymer solutions were mixed vigorously on a Fisher Vortex machine for 5–10 min and then filtered through a 0.2 μm disk filter. Films for UV–vis spectral studies were prepared by spin coating solutions of pure wt %, polycarbonate (5% by weight) or polycarbonate plus cobalt salt (5 and 1 wt %, respectively) onto 1-in. diameter quartz wafers at 1000 rpm for 30 s. The wafers were placed under a gentle stream of air for 5 min to remove solvent. A similar procedure was followed to deposit films onto sodium chloride plates for infrared spectral measurements. Photoimaging studies were performed on films that had been spin coated onto 1-in. diameter silicon or quartz wafers to 2000 rpm for 40 s and then baked at 50 °C for 3 min to remove solvent. Films for refractive index measurements were formed by coating the observation base of a Bausch and Lomb Abbé refractometer with a THF solution of the polymer (8 wt %) and then allowing the solvent to evaporate over 24 h.

Table 1. Diol Structure and Properties of Aliphatic Polycarbonates

polymer	$10^{-4}M_W$	yield (%)	n_{sp} (dL/g)	% cis	T_m (°C, mj/mg)	T_g (°C)	T_d (°C)	RI
R_1	3.30	24	0.14	48	N/A	28	334	1.484
R_2	1.64	80	0.21	54	150 4 mJ/mg	142	350	1.487
R_3	3.90	54	0.34	36	N/A	61	350	1.498
R_4	3.60	57	0.33	45	185 96 mJ/mg	147	354	N/A
R_{5a}	1.85	59	0.30	65	N/A	147	296	1.480
R_{5b}	1.91	40	0.38	66	N/A	141	294	1.483
R_{5c}	2.01	58	0.31	67	N/A	128	298	1.481
R_{5d}	11.5	98	N/A	43	N/A	139	292	1.481

Electronic absorption spectra were measured on a Varian DMS-300 spectrophotometer. Fourier transform infrared spectra were obtained on a Perkin-Elmer Series 1600 spectrometer. Film thickness measurements were taken with an Alpha Step 200 profilometer from Tencor Instruments. Deep-ultraviolet irradiations of films were conducted with an Optical Associates Model 150 illuminator containing a dichroic mirror system that optimized output in the 240–280 nm spectral region. The photon flux at 254 nm was measured with an Optical Associates calibrated power meter. Broad-band irradiation studies were performed using a 75 W Philips mercury vapor lamp with no filter. Gas chromatography/mass spectrometry (GC/MS) experiments were performed on a Hewlett-Packard Model 5971A mass spectrometer fitted with a DB5-ms column from J&W Scientific. Helium was the carrier gas, and the injection volume was 1 μL.

Results and Discussion

Physical Properties of Polycarbonates. Table 1 summarizes some important physical properties of the aliphatic polycarbonates examined in this study. One immediately obvious trend is the increase in T_g that results from the replacement of methylene units by rigid cyclic groups in the polymer backbone. Thus T_g rises from near room temperature for R_1 to 147 °C for R_4; the latter value is comparable to the T_g's of bisphenol A polycarbonates.[8] The regularity of the repeat unit in R_4 facilitates the crystallization of this homopolymer as evidenced by the large melt transition at 185 °C. Consequently, films of R_4 appear opaque when cast. To reduce crystallinity, we copolymerized tetramethyl-1,3-cyclobutanediol (TMCBD) with varying amounts of 1,4-cyclohexanediol (CHD). Members of the resulting R_{5a-d} series possess T_g's near that of the homopolymer but lack a detectable exotherm in differential calorimetry scans at the temperature corresponding to the melting of R_4. The fall in T_g as the TMCBD/CHD ratio decreases from 9:1 to 3:2 reflects the greater chain mobility that occurs upon replacing the cyclobutane ring by the more flexible cyclohexane ring. The anomalously high T_g for the 1:1 copolymer, R_{5d}, is caused by the large percentage of cyclobutane rings containing 1,3 substituents in the trans configuration.[13] All of the aliphatic polycarbonates undergo complete thermal degradation above their respective T_d values; Figure 1 illustrates the thermogravimetric trace for R_{5a}.

Optical Properties of Polycarbonates. The electronic absorption spectra of several aliphatic polycarbonates (R_1–R_4, R_{5a}, and R_{5b}) reveal that these materials possess excellent transparency in the deep-UV region. Films cast from 5% wt/wt solutions of polymer in chloroform exhibit negligible absorbance (<0.1) above 230 nm (Figure 2). In contrast, a comparably prepared film of bisphenol A polycarbonate shows significant absorbance (~0.3) out to 275 nm.

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(14) Geiger, C. C.; Davies, J. D.; Daly, W. H. *J. Polym. Sci., A: Chem.* **1995**, *33*, 2317.

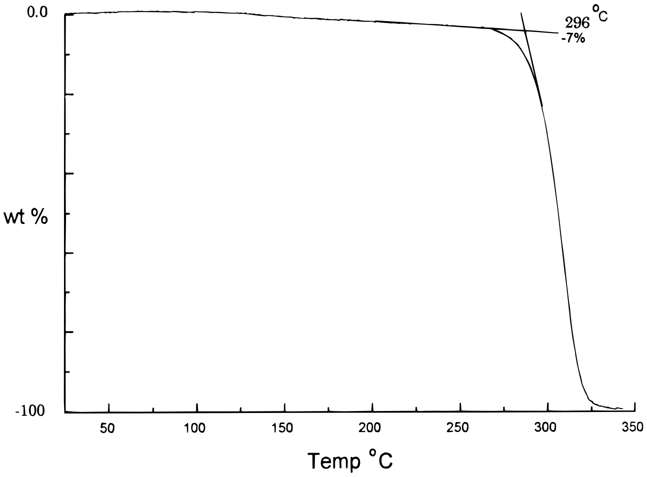


Figure 1. Thermogravimetric trace of R_{5a}.

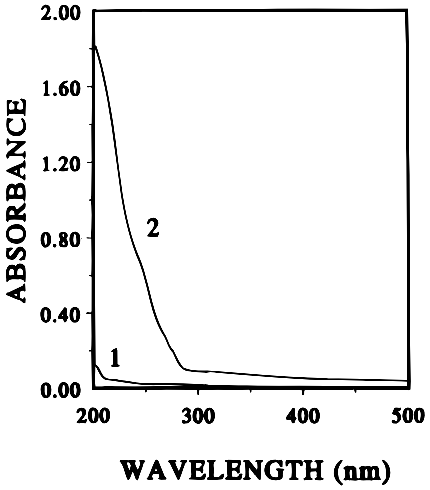


Figure 2. Electronic absorption spectra of thin films of (1) pure R_3 and (2) polycarbonate of bisphenol A, Lexan.

Refractive indexes for several aliphatic polycarbonates are listed in Table 1. The values fall within a relatively narrow range of 1.481−1.493. Notably, these values are considerably below the refractive index of 1.584 reported for bisphenol A polycarbonate.[6]

Photochemical Studies. Thin films of the aliphatic polycarbonates R_3 and R_{5a} absorb very weakly (absorbance <0.1 μm^{-1}) above 220 nm. In contrast, films of comparable thickness containing $[Co(NH_3)_6](BPh_4)_3$ or $[Co(en)_3](BPh_4)_3$ display strong absorption in the deep-UV region owing to the presence of ligand-to-metal charge-transfer and BPh_4^--localized $\pi-\pi^*$ transitions (Figure 2). Previous work has demonstrated that irradiation at 254 nm results in efficient photoredox decomposition of these cobalt complexes with release of the am(m)ine ligands (eqs 1 and 2).[4] We have exploited this photochemical generation of base to obtain both positive and negative tone images in polycarbonate films.

(i) Positive-Tone Image Formation. Silicon wafers coated with 0.5 μm films of R_3 containing $[Co(NH_3)_6](BPh_4)_3$ were frontside exposed to deep-UV light (516 mJ/cm^2 at 254 nm) through a mask at room temperature. Thereafter, the wafers were baked at 118 °C for 1 min and developed by spin rinsing with a stream of anisole for 40 s. The irradiated areas of the films dissolved completely in the developer, whereas the unirradiated regions retained 70−90% of their original thickness (Figure 3). Positive images also formed upon irradiation and development of R_3 films containing $[Co(en)_3](BPh_4)_3$, but image quality was very poor.

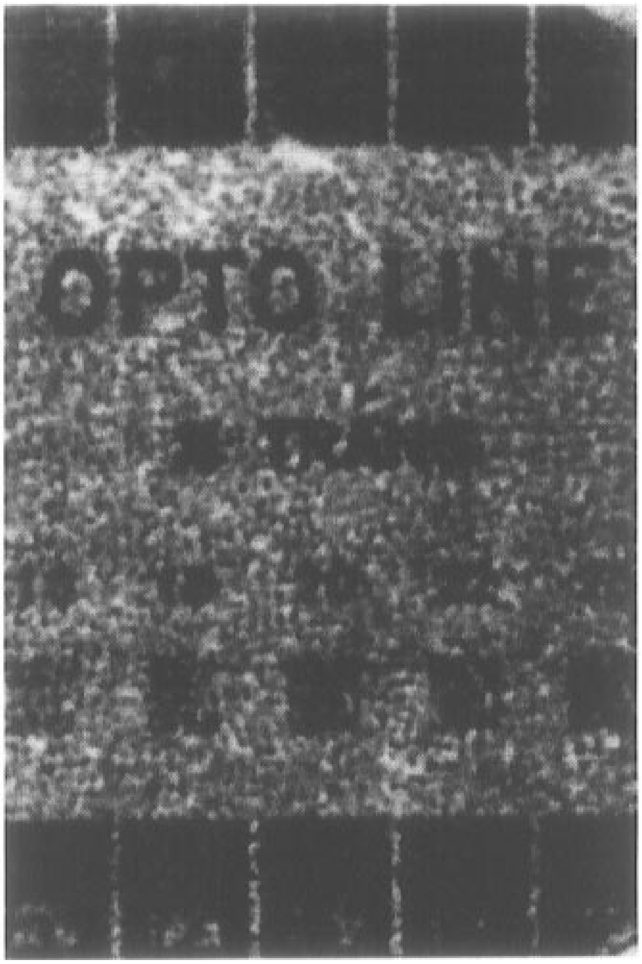
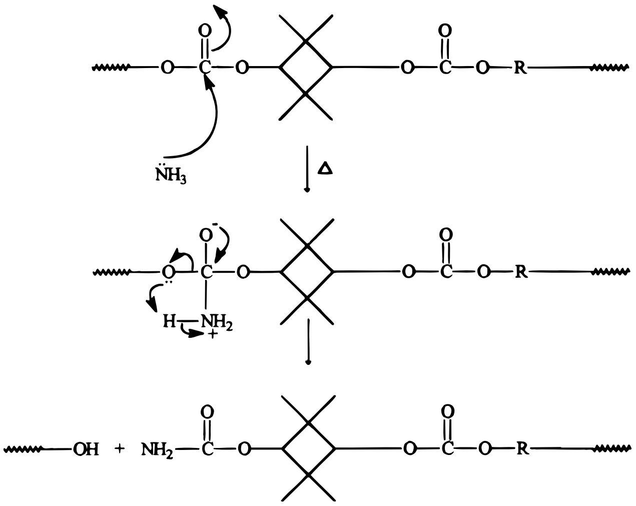


Figure 3. Positive-tone images formed upon deep-UV irradiation of a film of R_3 containing $[Co(NH_3)_6](BPh_4)_3$. The substrate (dark regions) is a 1-in. diameter silicon wafer.

Interestingly, under otherwise identical conditions, postirradiation baking of the $R_3-[Co(NH_3)_6](BPh_4)_3$ films at 150 °C for 3 min directly yielded positive-tone images without solvent development. Step heights up to 70% of the original film thickness were obtained, although some residual material remaining in the exposed areas was clearly visible under a microscope. Improved image quality in this “dry development” process was achieved by exposing films to 15 min of unfiltered radiation at 50−60 °C. These conditions resulted in complete removal of the irradiated areas of the film and yielded feature sizes to 20 μm, the resolution of our mask.

Positive-tone images result from the photoinitiated degradation of the polycarbonate. The proposed mechanism, shown in Scheme 2, involves the photochemical release of ammonia (eq 1) and subsequent thermally activated nucleophilic attack at the carbonyl linkage to produce carbamate and hydroxy endgroups. Further reactions yield low molecular weight components such as diols, bis(carbamates), or hydroxy carbamate difunctional moieties. Solventless development at elevated temperatures occurs via sublimation of these components. Attempts to collect and identify the gaseous products by GC-MS proved unfruitful. However, treat-

Scheme 2



ment of a THF solution of R_{5a} with excess ammonia at room temperature for 24 h led to a 50% reduction in solution viscosity. The latter result is fully consistent with the occurrence of main-chain scission.

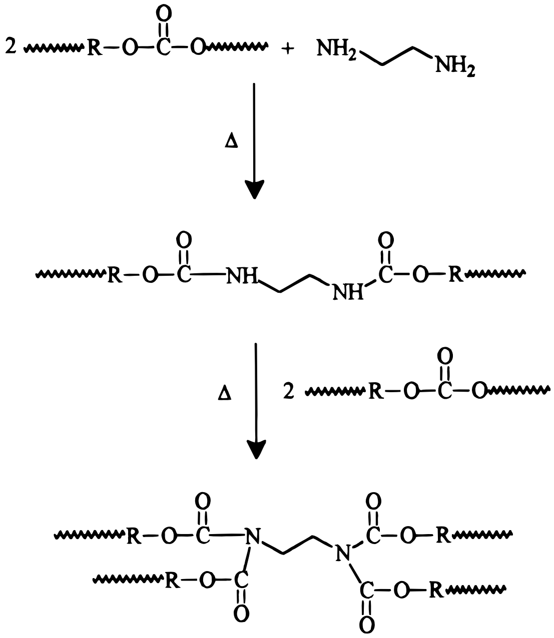
(ii) Negative-Tone Image Formation. Half-micron films of R_{5a} containing $[Co(en)_3](BPh_4)_3$ were coated onto quartz wafers and backside exposed to deep-UV radiation (516 mJ/cm^2 at 254 nm) through a mask at room temperature. Following postirradiation baking at 50 °C for 5 min, the films were developed by spin rinsing with a stream of 1:4 (v/v) 2-butanone/2-propanol solvent for 1 min. The unexposed regions dissolved to yield negative-tone images that retained 75−90% of the original film thickness. Under similar conditions, films of R_{5a} containing $[Co(NH_3)_6](BPh_4)_3$ produced negative-tone images of very poor quality.

We attribute the negative-tone response of films containing $[Co(en)_3](BPh_4)_3$ to the reactions of photogenerated ethylenediamine. As summarized in Scheme 3, this base can serve as a multifunctional cross-linking agent by forming dicarbamate linkages between adjacent polymer chains. Cross-linking increases the average molecular weight of the polymer and thereby decreases its solubility. Subsequent rinsing of the film with the developer solution preferentially dissolves the unexposed areas to yield negative-tone images. The negative-tone response of films containing $[Co(NH_3)_6](BPh_4)_3$ suggests that photogenerated ammonia also can form crosslinks between the polycarbonate chains. The very poor image quality, however, indicates that this process is considerably less favorable than in the case of the more basic ethylenediamine.

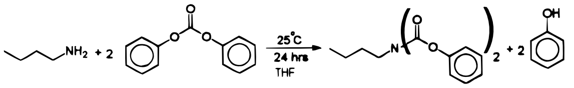
Infrared Spectral Studies. Films of pure R_3 were heated at 50 °C for 2 min, irradiated with deep-UV light for 2 min, and then heated at 150 °C for 5 min. Comparison of the infrared spectra of the film before and after this treatment revealed no significant differences. This finding indicates that the polycarbonates are thermally and photochemically stable under the conditions employed in the imaging studies.

In contrast, irradiating a R_{5a} film containing $[Co(en)_3](BPh_4)_3$ with deep-UV light for 2 min causes the intense carbonyl stretching band of the polycarbonate to shift from 1742 to 1737 cm^{-1}. Both the direction and magnitude of the shift are consistent with the formation of carbamates[15] via nucleophilic attack of photogenerated ethylenediamine on the carbonyl groups of the polymer (Scheme 3). Direct evidence for this reaction was obtained from studies of films spun from THF solutions of R_{5a} and ethylenediamine. Heating such a film of 50 °C for 5 min caused the carbonyl band to shift to 1737 cm^{-1}. Similar behavior occurred for a film spun from a solution that had stood for 24 h at room temperature; moreover, the solution thickened noticeably during this time period, as would be expected for cross-link formation.

Scheme 3



Mass Spectral Studies. According to Scheme 3, ethylenediamine behaves as a tetrafunctional cross-linking agent in its reactions with a polycarbonate. By analogy, a model system composed of *n*-butylamine and diphenyl carbonate should react according to eq 5. To



(5)

test this premise, we allowed the two compounds to react in THF at 25 °C for 24 h. Analysis of the products by GC/MS revealed two major peaks with retention times of 5.2 and 10.0 min. The first peak exhibited a mass spectral splitting pattern typical of a phenol with a parent ion at $m/z = 94$. The second peak yielded ions at $m/z = 313$ and 192, which can be assigned, respectively, as the dicarbamate and a fragmentation product resulting from the loss of a phenyl carbonate moiety. These results clearly support the mechanism of cross-link formation shown in Scheme 3.

Conclusions

Films of the aliphatic polycarbonates, R_3 and R_{5a}, can be imaged with deep-UV light in the presence of base-generating photoinitiators. Photoredox decomposition of $[Co(en)_3](BPh_4)_3$ in a film releases ethylenediamine (eq 2), which subsequently cross-links the polymer via formation of bis(dicarbamate) linkages (Scheme 3). This

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(15) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; p 196.

chemistry insolubilizes the film in the exposed areas to yield negative-tone images. Photochemical release of ammonia from $[Co(NH_3)_6](BPh_4)_3$ (eq 1), on the other hand, leads to positive-tone images. While ammonia can form a carbamate via attack on the polycarbonate (Scheme 2), its weaker basicity disfavors further reaction to form the dicarbamate. Consequently, the predominant reaction is chain scission and eventual production of low molecular weight fragments that volatilize away at elevated temperatures. To our knowledge, the present results constitute the first example in which photogenerated base initiates positive-tone image formation via main-chain scission.[16]

Aliphatic polycarbonates of the type investigated in this study possess a number of attractive properties including high molecular weight, low refractive index, high ultraviolet transparency, and good thermal behavior. Combining these polymers with base-generating photoinitiators has yielded an interesting new class of materials that deserves further study.

Acknowledgment. We thank the National Science Foundation (Grant DMR-9122653 to C.K.) for financial support.

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(16) Fréchet et al. reported a positive-tone image-reversal process in which photogenerated base neutralizes an acidic cross-linking agent: Matuszczak, S.; Cameron, J. F.; Fréchet, J. M. J.; Willson, C. G. *J. Mater. Chem.* **1991**, *1*, 1045.