Novel Imaging Materials: Synthesis and Characterization of Poly[*N*,*N*-dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium triphenylbutylborate] as a Single-Component Photoimaging System

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ABSTRACT: New polymeric materials based on *N*,*N*,*N*-trialkyl-*N*-(*p*-benzoylbenzyl)ammonium triphenylbutylborate have been synthesized and characterized. Model compounds provide spectroscopic evidence that these polymers are capable of forming free tertiary amines upon irradiation at 365 nm. Photochemical generation of base is much enhanced when triphenylbutylborate is used as the electron donor. Using this concept, the synthesized polymers have been utilized for imaging in a single-component system. Positive-tone images can be achieved by washing the polymeric film produced upon exposure to light with aqueous acidic solution and ethanol.

Introduction

Significant efforts have focused recently on the design and synthesis of new polymers to be used in photolithographic processes.[2,3] The main requirement for such photopolymers is that on exposure to light or radiation they undergo a chemical change that allows the nonirradiated portions of the photoresist to be distinguished from irradiated portions, usually on the basis of solubility. A decade ago, photoresist polymers were designed[4−6] based on an acid-catalyzed deprotection wherein acid was generated from iodonium or sulfonium salts upon irradiation[7] and the reaction amplified by a subsequent thermolysis reaction. The most widely used of these chemically amplified resists to date are based on poly(*p*-(*tert*-butoxycarbonyloxy)styrene)[4−6] or its analogs.[8−10] Upon irradiation of onium salts, acid is released, causing the loss of polymer side chains in a catalytic degradation process. A similar strategy has also been used to design resist materials based on the concept of electrophilic aromatic substitution.[11,12] In this approach, carbocationic species alkylate aromatic rings on a matrix polymer. This process results in cross-linking.

The use of photogenerated base in designing an imaging polymer has lagged behind those systems producing acids though there is no reason, a priori, for this to be the case. With the development of new base photogenerators,[13] a few examples of systems that generate primary and secondary polymeric amines have been reported.[14−16] Photochemical formation of tertiary amines, however, is less common.[17] Tertiary amines are, in some respects, better basic catalysts than primary and secondary amines, since the latter may be incompatible with certain resist chemistry.[18,19]

In recent studies, we found that *N*,*N*,*N*-trialkyl-*N*-(*p*-benzoylbenzyl)ammonium triphenylbutylborate produces free tertiary amine upon irradiation. The mechanism involved electron transfer from the borate to the benzophenone triplet state.[20,21] This result led us to conclude that this system may readily produce polymeric tertiary amine upon irradiation and eventually generate a new class of photoresist polymers. In this paper, we report the synthesis and characterization of poly(methyl methacrylate) with pendant benzophenone borate salts—a new class of photobase-generating polymers—and a preliminary evaluation of their capability to act as a single-component resist system.

Experimental Section

General Procedures. Melting point determinations were made using a Thomas Hoover capillary melting point apparatus; all temperatures are uncorrected. All new compounds were characterized by nuclear magnetic resonance (NMR), IR, and elemental analysis (Atlantic Microlab, Inc.). ^{1}H NMR spectra were taken on a Gemini GEM-200 (200 MHz). Chemical shifts are reported in parts per million (ppm) relative to TMS at 0.0 ppm on the δ scale. ^{13}C NMR spectra were recorded on a Gemini GEM-200 (50 MHz), and chemical shifts are reported in δ units, unless otherwise mentioned. ^{11}B NMR spectra were recorded on a Varian Unity+ 400 (128 MHz) with $B(OMe)_3$ as the external standard. IR spectra were obtained on a 6020 Galaxy FTIR spectrometer. Photolysis experiments were carried out in a Rayonet model photochemical reactor fitted with mercury lamps (300−400 nm). Unless otherwise mentioned, all reagents and solvents were obtained from Aldrich Chemical Co. and used as received.

Thermal analysis data were obtained using a Du Pont TGA-951 with a thermal analyzer 2100 system. TGA samples were heated at a rate of 20 °C/min with a purified N_2 gas flow of 20 cm^3/min. Phase transition temperatures were measured with a Perkin-Elmer DSC-2 instrument, calibrated with indium and tin, under a nitrogen flow with the heating and cooling rates of 20 °C/min. Polymer samples weighing 5−10 mg were used for this analysis. The glass transition (T_g) and melting (T_m) temperatures were taken as the onset of the transitions in either the first or second heating cycle, whichever was more prominent.

For imaging experiments, all films were spin-coated on 13 × 13 mm silicon wafers from 20 wt % polymer solution in *N*,*N*-dimethylformamide (DMF). The films were typically prebaked at ≈75 °C for 30 min. Films were exposed to UV irradiation from an encased 200 W high-pressure mercury arc lamp filtered through a 365 nm filter (bandwidth 40 nm). All exposures were performed in air at room temperature. All film-bearing silicon wafers were placed in a custom-made exposure setup capable of mask image projection onto the film surface in the soft contact mode. Transmission electron microscope (TEM) copper foil grids were used as masks. The

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smallest image feature size of the mask was 5 μm (mask T-2000 purchased from EMS). Development was achieved by selective removal of irradiated areas during sequential washing in 1.0 M aqueous hydrochloric acid, distilled water, and absolute ethanol. The resulting image quality was evaluated by atomic force microscopy (AFM; Digital Instruments Dimension 3000 scanning probe microscope). The AFM images were collected in Tapping Mode, using standard 125 μm etched silicon probes. Scans 50 × 50 μm were collected at a scan rate of 0.5 cycles/s.

Synthesis. *N,N*-Dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium Bromide (1). To a solution of 1.50 g (5.45 mmol) of 4-(bromomethyl)benzophenone[22] in 12 mL of a toluene−acetone mixture (5:1) was added 0.75 g (4.77 mmol) of 2-(dimethylamino)ethyl methacrylate dropwise with stirring at room temperature. A white precipitate formed almost immediately. The solution was stirred for another 30 min. The precipitate was separated by filtration and washed thoroughly with acetone. After drying under vacuum, **1** was obtained as white crystals in 72% yield (1.70 g), mp 155−156 °C. ^{1}H NMR (CD_3CN): δ 7.79 (m, 6H), 7.68 (m, 1H), 7.55 (m, 2H), 6.14 (s, 1H), 5.70 (s, 1H), 4.82 (s, 2H), 4.64 (m, 2H), 3.85 (t, J = 4.7 Hz, 2H), 3.15 (s, 6H), 1.93 (s, 3H). Anal. Calcd for $C_{22}H_{26}BrNO_3$: C, 61.14; H, 6.02; N, 3.24. Found: C, 60.90; H, 6.05; N, 3.23.

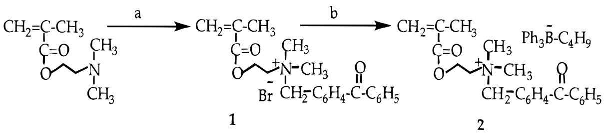
***N,N*-Dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium Triphenylbutylborate (2).** *N,N*-Dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium bromide (2.09 g (4.83 mmol)) was dissolved in 100 mL of a water−methanol mixture (4:1), and undissolved dust materials, if present, were filtered. The lithium salt of triphenylbutylborate (1.38 g (4.51 mmol)) in 10 mL of water was added dropwise into the mixture with stirring at room temperature. After 30 min, water (250 mL) was added, and the solution was stirred for 1 h and filtered.[23] After drying under vacuum, **2** was obtained as a white powder (2.65 g (85%)), mp 132−134 °C. ^{1}H NMR (CD_3CN): δ 7.83 (m, 4H), 7.59 (m, 5H), 7.26 (br s, 6H), 6.96 (m, 6H), 6.83 (m, 3H), 6.14 (s, 1H), 5.74 (s, 1H), 4.53 (br s, 2H, OCH_2), 4.46 (s, 2H, CH_2-Ph), 3.58 (m, 2H, NCH_2), 2.95 (s, 6H, NCH_3), 1.94 (s, 3H), 1.23 (m, 2H, BCH_2), 0.91 (m, 4H, $BCH_2C_2H_4$), 0.77 (t, J = 7.0 Hz, 3H, BCH_3). ^{11}B NMR (DMSO): δ −28.52. Anal. Calcd for $C_{44}H_{50}BNO_3$: C, 81.14; H, 7.68; N, 2.18. Found: C, 81.20; H, 7.63; N, 2.20.

Poly[*N,N*-dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium bromide] (3). A solution of 1.0 g (2.31 mmol) of **1** and 12 mg (0.068 mmol) of azobis(isobutyronitrile) (AIBN) in 10 mL of methanol was heated at 55 °C in a sealed tube for 72 h. The white precipitate was separated and washed thoroughly with methanol. After drying under vacuum, **3** was obtained as a white powder (0.65 g, 65% yield by weight). Anal. Calcd for $C_{22}H_{26}BrNO_3$: C, 61.14; H, 6.02; N, 3.24; Br, 18.49. Found: C, 60.46; H, 6.34; N, 2.98; Br, 16.64.

Poly[*N,N*-dimethyl-*N*-(*p*-benzoylbenzyl)-*N*-(2-methacryloylethyl)ammonium triphenylbutylborate] (4). A solution of 1.0 g (1.54 mmol) of **2** and 14 mg (0.08 mmol) of AIBN in 12 mL of dry acetonitrile was heated at 65 °C in a sealed tube for 120 h. Insoluble materials were filtered and the filtrate was poured into 150 mL of ether. The precipitate was separated by filtration. The resulting polymer was purified by redissolving in acetonitrile and precipitated into ether. After drying in vacuo overnight, **4** was obtained as a white powder (0.70 g (70% by weight)). ^{1}H NMR (CD_3CN): δ 7.38−7.80 (br m, 9H, benzophenone), 7.28 (m, 6H, aromatic), 6.95 (m, 6H, aromatic), 6.78 (m, 3H, aromatic), 4.39 (br, 2H, PhCH_2), 3.39 (m, 2H, OCH_2), 2.88 (br, 2H, CH_2N), 2.16 (s, 6H), 1.93 (m, 3H, α-methyl), 1.23 (m, 2H, polym chain), 1.16 (m, 2H, BCH_2), 0.90 (m, 4H), 0.73 (t, J = 7.0 Hz, 3H). Anal. Calcd for $C_{44}H_{50}BNO_3$: C, 81.14; H, 7.68; N, 2.15. Found: C, 80.35; H, 7.60; N, 2.51.

Copolymer 5. 2 (1.0 g (1.53 mmol)) and 4-methoxystyrene (0.20 g (1.53 mmol)) were dissolved in 10 mL of dry acetonitrile with 15 mg of AIBN (3 mol % to total monomer) in a polymerization tube and subjected to freeze−pump−thaw cycles. The tube was sealed and heated at 60 °C for 120 h. The clear reaction mixture was poured into 150 mL of ether with stirring to precipitate the polymer. The white precipitate was filtered, washed with ether, and dried under vacuum. ^{1}H NMR (CD_3CN): δ 7.42−7.92 (m, 9H, benzophenone), 7.28 (m, 6H, triphenylborate), 7.20 (m, 2H, styrene aromatics), 6.95 (m, 6H, triphenylborate), 6.83 (m, 5H, styrene aromatics and triphenylborate), 4.39 (br, 2H, PhCH_2), 3.62 (br, 5H, OCH_2 and OCH_3), 2.90 (br s, NCH_2), 2.22 (s, 6H), 1.98 (m, 3H), 1.42 (m, 1H, polym chain), 1.26 (m, 2H, BCH_2), 1.21 (m, 2H, polym chain), 0.96 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). Anal. Calcd for $(C_{44}H_{50}BNO_3)_{0.51}(C_9H_{10}O)_{0.49}$: C, 81.06; H, 7.64; N, 1.79. Found: C, 81.32; H, 7.72; N, 1.94.

Scheme 1[a]



[a] (a) 4-(Bromomethyl)benzophenone, toluene−acetone (5:1), room temperature; (b) lithium salt of triphenylbutylborate, water, room temperature.

Photolysis of Model Compound 6. 6 (0.75 g) was dissolved in 5 mL of dry acetonitrile and placed in a Pyrex glass tube containing a magnetic stir bar. The sample was placed in a Rayonet reactor and irradiated at 300−400 nm for 1 h with stirring. The irradiation time was held at 1 h in order to avoid secondary photochemistry. The mixture of photoproducts was subjected to careful silica gel chromatography with hexane−ethyl acetate (9:1) as eluent, and the products were characterized by a combination of ^{1}H NMR, mass spectrometry, elemental analysis, and comparison to authentic samples that were synthesized independently.

2-(Dimethylamino)ethyl Butyrate (8). ^{1}H NMR ($CDCl_3$): δ 4.10 (t, J = 5.82 Hz, 2H), 2.50 (m, 3H), 2.21 (s, 6H), 1.11 (s, 3H), 1.08 (s, 3H). MS m/z 159 (M^+), 115, 71, 58 (100%), 42.

4-Pentylbenzophenone (11). ^{1}H NMR ($CDCl_3$): δ 7.76 (m, 4H), 7.50 (m, 4H), 7.28 (d, J = 8.3 Hz, 1 H), 2.68 (t, J = 7.0 Hz, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). MS m/z 252 (M^+), 195, 181, 175, 105, 91, 77, 55, 41.

***p*-Dibenzoyldiphenylethane (12).** Yellowish crystals, mp 175−176 °C (lit.[24] mp 175−176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (q, J = 8.0 Hz, 8H), 7.57 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 4H), 7.29 (t, J = 8.0 Hz, 4H), 3.04 (s, 4H). MS m/z 390 (M^+), 195, 167, 105, 77, 51. Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.16; H, 5.64. Found: C, 85.97; H, 5.76.

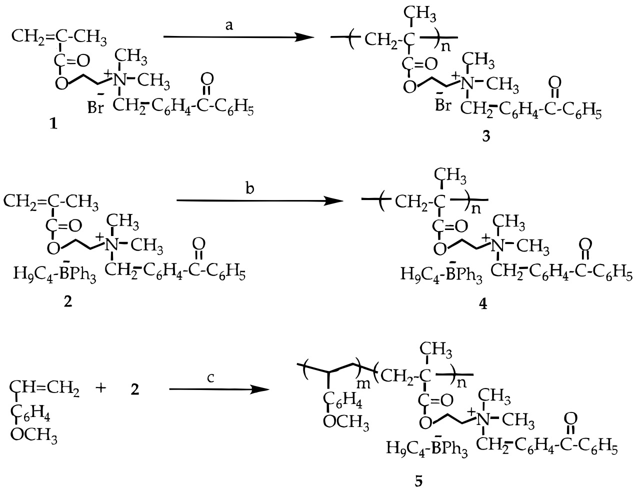
Results and Discussion

Synthesis of Monomers and Polymers. Compound **1** was synthesized in excellent yield by dropwise addition of (dimethylamino)ethyl methacrylate at room temperature to 4-(bromomethyl)benzophenone[22] in a toluene−acetone mixture at room temperature (Scheme 1). Acetone served as the solvent for 4-(bromomethyl)benzophenone. Compound **1** was obtained analytically pure and used in the next step without further purification. The reaction of **1** with the lithium salt of triphenylbutylborate[23] in water at room temperature gave **2** as an analytically pure compound in 85% yield. It was further recrystallized from ethanol before use in radical polymerization.

All polymerization reactions were carried out in sealed tubes using 3 mol % of AIBN with respect to monomers in dry solvents (methanol or acetonitrile) as shown in Scheme 2. Polymer **5** was prepared by copolymerization of 4-methoxystyrene and monomer **2** in a 1:1 molar feed ratio at 60 °C in dry acetonitrile. Incorporation of 50% 4-methoxystyrene into copolymer **5** was confirmed by ^{1}H NMR and elemental analysis.

Model compounds **6** and **7** were synthesized independently to study photochemical formation of free amine. The structure of compounds **6** and **7** was confirmed by

Scheme 2[a]



[a] (a) AIBN, methanol, 55 °C, 72 h; (b) AIBN, acetonitrile, 65 °C, 120 h; (c) AIBN, acetonitrile, 60 °C, 120 h.

^{1}H NMR. Additional structural confirmation was provided by FTIR spectroscopy by the appearance of carbonyl bands at 1656 cm^{-1}, elemental analysis, and GC–MS. The detailed synthetic procedure was published elsewhere.[25]

Characterization. The expected structures of all the polymers were confirmed by ^{1}H NMR spectra, which showed no signal in the 6.8–5.5 ppm region where the resonances of the vinylic protons belonging to acrylic monomers are expected. This result suggested that both homo- and copolymerizations occurred by a free-radical chain mechanism involving the acrylic double bond. It also indicated that no residual monomer is present in the final polymers (detailed assignments can be found in the Experimental Section). FTIR of all the polymers showed no bands in the region of 1417–1408 cm^{-1} due to CH_2 scissoring vibrations of the vinyl group of the acrylic functionalities in the monomers. On the other hand, the IR spectra exhibit no absorptions due to the trans C═C bond of the monomer in the 1000–900 cm^{-1} region.

Copolymer composition was determined by ^{1}H NMR and elemental analysis.[25] The relative content of the co-unit in the polymer was evaluated by comparing the integrated signal located in the 3.62 ppm region due to the methoxy group attached to the aromatic ring in the styrene unit with resonances at 1.98 ppm of the α-methyl groups in the methacrylate unit. The multiplicity of the α-CH_3 peaks around 1.94 ppm represented the different tacticities of all polymer backbones. The FTIR spectra of the copolymer exhibits bands at 1650 cm^{-1} representative of the typical ketone functionalities present in methyl methacrylate and 1250 cm^{-1} for the ether group in the styrene unit.

Due to the highly ionic nature of all the polymers, gel permeation chromatography (GPC) measurements could not be accomplished using our existing system with THF eluent. However, the dissolution behavior in THF and DMF revealed that all polymers have reasonably high molecular weights. Moreover, flexible films can easily be prepared from the polymer solutions in DMF, which again indicates the compounds have high molecular weights with considerable polydispersity.

Thermal Behavior. The DSC thermogram of homopolymers **3** and **4** showed T_m but no T_g. The absence of T_g and the presence of T_m in the DSC thermogram clearly demonstrated that these polymers were crystalline. This crystallinity resulted from the obvious ionic nature of the polymers. In contrast, the copolymer had a T_g of 80 °C as well as a melting transition, T_m. This implies that the copolymer has a semicrystalline nature arising due to incorporation of the methoxystyrene (MS) unit in the methyl methacrylate main chain. Therefore, it is clear that the crystallinity of the homopolymers is reduced by copolymerization with MS. This effect was also observed when the comonomer unit was methyl methacrylate.[25] Moreover, the methoxystyrene unit caused a significant increase in the chain rigidity of the methyl methacrylate backbone, resulting in a decrease in free volume and an increase in the cohesive energy density. Both effects contributed to an observable T_g in copolymer **5**.

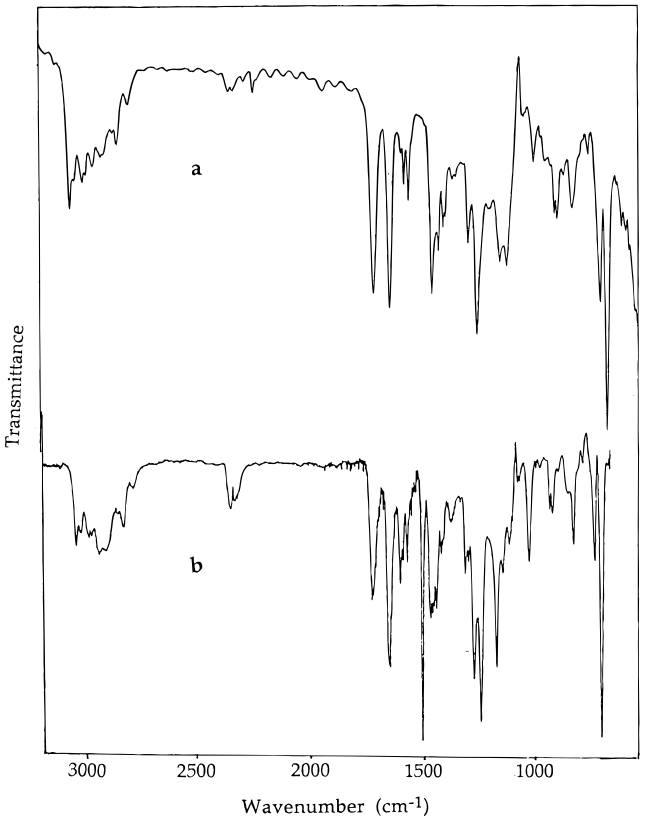


Figure 1. FTIR spectra of polymer **4** (a) and **5** (b) taken from thin film cast on NaCl plates.

Table 1. Physical Properties of Synthesized Polymers

sample	yield (%)	T_g (°C)	T_m (°C)	T_d (°C)
3	65		155	235
4	70		115	229
5	73	80	119	272

For device applications, a relatively low T_m and a low level of crystallinity are highly desirable since the polymers can then be processed at convenient temperatures without thermal degradation. On the other hand, the absence of a significant amount of crystallinity can result in poor mechanical properties above T_g. In this regard, the copolymer with MS units is of considerable practical interest.

The thermal stabilities of all the polymers were determined in nitrogen by thermal gravimetric analysis (TGA), and the results are collected in Table 1. The thermal stability limit, T_d, which was taken as the temperature at which 5% weight loss of a sample occurred, varied from 230 to 272 °C, indicating that each of them had an excellent thermal stability (Figure 2).

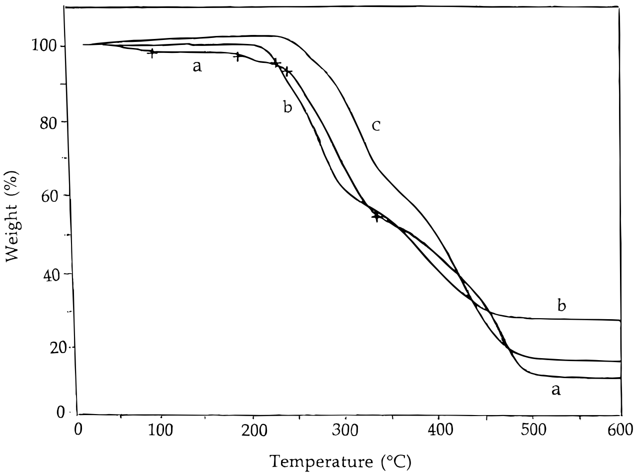
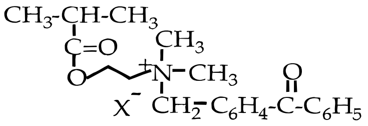


Figure 2. TGA diagram of polymer **3** (a), **4** (b) and **5** (c).

However, many industrial applications require materials that tolerate prolonged exposure at elevated curing temperature, i.e., 100 °C. Therefore, an isothermal study was done at 100 °C for all three materials. This study demonstrated that all polymers undergo no observable weight loss after 0.5 h of heating.

Photochemistry. As previously described,[20] benzophenone borate salts undergo intra- or intermolecular electron transfer to the benzophenone excited state subsequent to which C−N bond cleavage takes place with concomitant liberation of a free amine. A similar photochemistry for the newly synthesized polymers can be expected. Indeed, formation of free amine from polymer in acetonitrile upon irradiation was visually anticipated since we observed a color change from white to yellow. However, identification of amine by NMR was complicated due to the formation of broadened as well as overlapping peaks. On the other hand, FTIR cannot be used for detection of tertiary amine. Thus, for simplicity, the photochemistry of small model compounds **6** and **7** was explored in solution.



6. X=Ph3B-C4H9

7. X= Br

Photochemistry in solution was monitored by ^{1}H NMR spectroscopy. Model compound **6** was photolyzed in deuterated acetonitrile at 350 nm over the course of 1 h in the presence of oxygen. The extent of conversion to free tertiary amine was determined from ^{1}H NMR by observing the disappearance of the benzophenone methylene resonances at 4.45 ppm and the appearance of a new peak at 2.43 ppm due to the formation of the dimethylamino functionality (Figure 3). Similar photochemical behavior was observed for **7** when triphenylbutylborate was replaced by the bromide counteranion. However, the time course of the decomposition or conversion to free tertiary amine from **7** was rather slow, indicating that electron transfer from bromide to the benzophenone excited state was not as efficient as electron transfer from triphenylbutylborate. The photodecomposition of both model compounds in deuterated methanol was similar to that in acetonitrile under the same conditions.

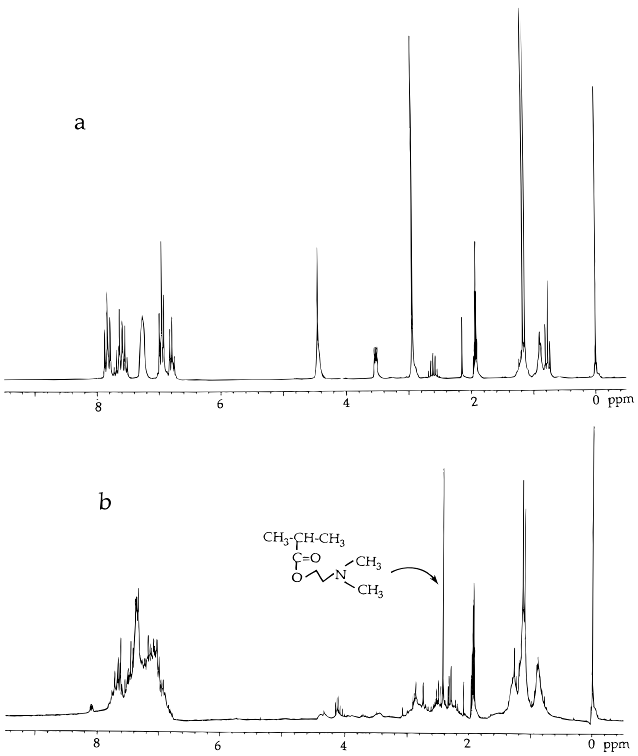


Figure 3. ^{1}H NMR of model compound **6** in deutrated acetonitrile (a) before photolysis and (b) after 60 min photolysis.

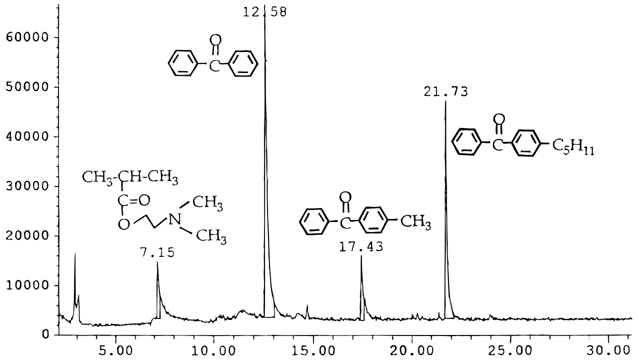
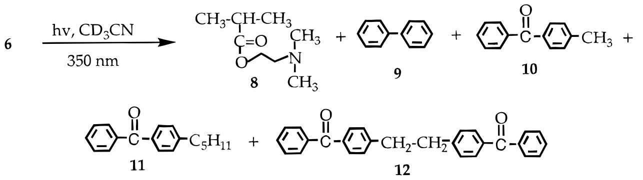
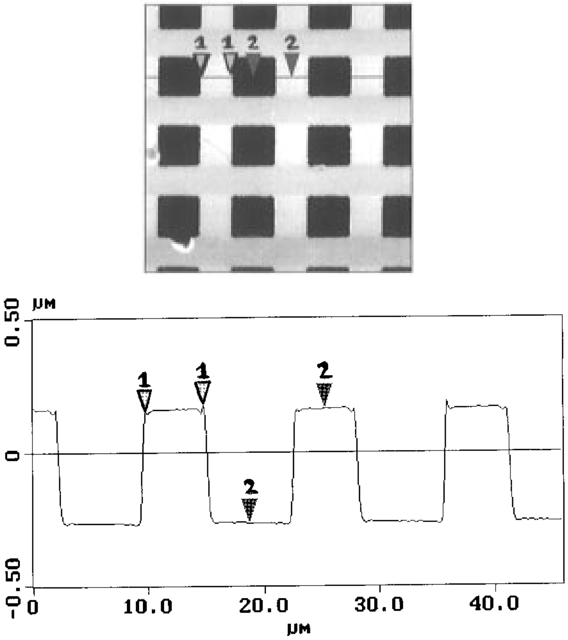


Figure 4. GC-MS chromatogram of photolysis products of **6**.

Scheme 3



The photolysis products were identified by thin-layer chromatography (silica gel, hexane−ethyl acetate) and HPLC comparison with authentic samples as well as by their GC−MS fragmentation patterns. The GC−MS chromatogram of photolysis products from **6** is shown in Figure 4. The photoproducts were subsequently separated by column chromatography and characterized by melting points, NMR, and GC−MS. The products formed from photolysis, including free tertiary amine **8**, are shown in Scheme 3. Products **10**, **11**, and **12** clearly indicate that the benzophenone methylene radical was the common intermediate formed, along with tertiary amine, during photolysis at 350 nm. The benzophenone methylene radical gave **10** by abstraction of a hydrogen atom from the solvent or tertiary amine.



1 - 1	Horiz distance (L)	5.031 µm
	Vert distance	21.623 nm
	Angle	0.246 deg
	Horiz distance	6.648 µm
2 - 2	Vertic distance	427.54 nm
	Angle	3.680 deg

Figure 5. Positive-tone images obtained upon irradiation of copolymer **5** (x-sectional view).

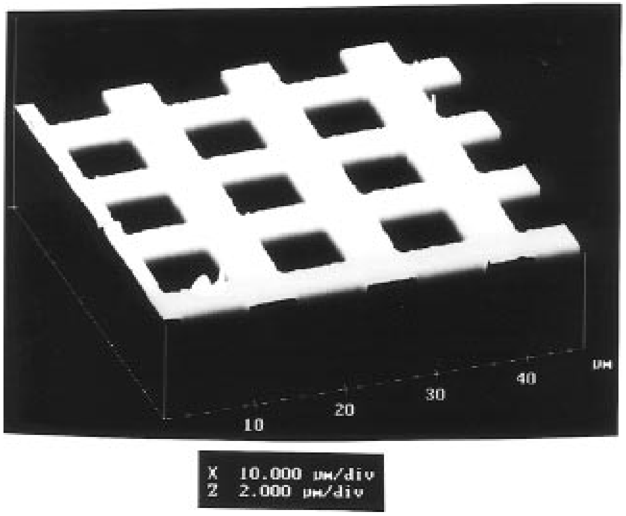


Figure 6. Positive-tone images obtained upon irradiation of copolymer **5** (3 D view).

Compound **11** is the result of cross coupling of the benzophenone methylene radical with a butyl radical formed by cleavage of the B−C bond from the triphenylbutylborane anion radical. Compound **12** is the dimerization product, which could not be identified by GC−MS; however, it could be separated by column chromatography and characterized by NMR and elemental analysis. We are presently investigating the quantum yield of amine formation from polymers as well as model compounds photochemically in both the solid and solution states. Detailed results will be reported in our upcoming paper.

Imaging. The preliminary evaluation of polymer **4** acting as single-component positive-tone photoimaging system has been previously performed by us.[26] The system showed promising results as a good-quality image with slight "footing" was formed. However, the low sensitivity of polymer **4** to the incident irradiation was considered as a drawback. In order to improve sensitivity and resolution, we synthesized copolymer **5**. Dosages of 3.0 J/cm^2 were required for **5** (original thickness after prebake was 0.5 μm). This represents an improvement from 4.5 J/cm^2 required for polymer **4** under the same conditions. It is worth noting that no lithography was possible in the case of polymer **3** due to the inefficient electron transfer from the bromide anion to the benzophenone moiety which was found in model compound studies.

An image of excellent quality has been produced utilizing polymer **5** as a single-component photoimaging system. The TEM grid image was faithfully reproduced with the dimensions of features shown in Figures 5 and 6. No "footing" or undercutting was observed.

Conclusions

We described the synthesis of novel polymers which have lithographic imaging capabilities. These polymers are readily prepared by straightforward synthetic techniques and all have high thermal stabilities. Polymeric base formation was proposed to occur by an intra- or intermolecular electron transfer mechanism. In the excited state, electron transfer takes place from triphenylbutylborate to benzophenone acceptor followed by C−N bond cleavage. Thus, homo- and copolymers bearing benzophenone borate moieties have the capability of producing a single-component resist system without addition of any photobase generator. A positive-tone image can be achieved easily by exposure of the polymer films in the UV region followed by development with aqueous acidic solution and ethanol.

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References and Notes

(1) Contribution No. 307 from the Center for Photochemical Sciences.
(2) Willson, C. G. *Introduction to Microlithography*, 2nd ed.; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Washington, DC, 1994; pp 139−268.
(3) Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; John Wiley & Sons: New York, 1989.
(4) Frechet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Eng.* **1982**, *82*, 260.
(5) Frechet, J. M. J.; Eichler, E.; Willson, C. G.; Ito, H. *Polymer* **1983**, *24*, 995.
(6) Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, M.; Eichler, E. *Macromolecules* **1983**, *16*, 510.
(7) Crivello, J. V.; Lam, J. H. *Macromolecules* **1977**, *10*, 1307.
(8) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394.
(9) Schwalm, R. *J. Electrochem. Soc.* **1989**, *136*, 3471.
(10) Pryzbilla, K. J.; Dammel, R.; Pawlowski, J. *Proceedings of the SPE Regional Technical Conference*; Society of Plastics Engineers, Inc.: New York, 1991, p 131.
(11) Stover, H. D. H.; Matuszczak, S.; Willson, C. G.; Frechet, J. M. J. *Macromolecules* **1991**, *24*, 1741.
(12) Frechet, J. M. J.; Matuszczak, S.; Reck, B.; Stover, H. D. H.; Willson, C. G. *Macromolecules* **1991**, *24*, 1746.
(13) Cameron, J. E.; Frechet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919; *J. Am. Chem. Soc.* **1991**, *113*, 4303.
(14) Frechet, J. M. J. *Pure Appl. Chem.* **1992**, *64*, 1239.

(15) Graziano, K. A.; Thompson, S. D.; Winkle, M. R. *SPIE Adv. Resist Tech. Process.* **1991**, *1466*, 75.
(16) Urankar, E. J.; Frechet, J. M. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 933.
(17) Hanson, J. E.; Jensen, K. H.; Gargiulo, N.; Motta, D.; Pingor, D. A.; Novembre, A. E.; Mixon, D. A.; Kometani, J. M.; Knurek, C. *ACS Symp. Ser.* **1995**, *614*, 137.
(18) Sakurai, T.; Kojima, S.; Inone, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3141.
(19) Drewes, S. E.; Ross, G. H. P. *Tetrahedron* **1988**, *44*, 4653.
(20) Hassoon, S.; Sarker, A.; Rodgers, M. A. J.; Neckers D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11369.
(21) Hassoon, S.; Sarker, A.; Polykarpov, A. Y.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem.* **1996**, *100*, 12386.
(22) Itoh, T.; Hall, H. K. *Macromolecules* **1990**, *23*, 4879.
(23) Adair, P. C.; Moore, M. J. U.S. Patent 4,751,102, 1988.
(24) McCombs, D. A.; Menon, C. S.; Higgins, J. *J. Polym. Sci., Part A-1* **1971**, *9*, 1261.
(25) Sarker, A. M.; Lungu, A.; Neckers, D. C. *Macromolecules* **1996**, *29*, 8047.
(26) Mejiritski, A.; Polykarpov, A. Y.; Sarker, A. M.; Neckers, D. C. *Chem. Mater.* **1996**, *8*(7), 1360.

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