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Synthesis and Photoimaging Study of a New Poly(methacrylate) with Tethered Silacyclobutane Moiety

Xiaosong Wu, Oleg Grinevich,† and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University,
Bowling Green, Ohio 43403, and Spectra Group Limited, Inc., 1722 Indian Wood Circle,
Suite H, Maumee, Ohio 43537

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A new methacrylate with a tethered silacyclobutane moiety, 6-(methylcyclotrimethylenesilyl)hexyl methacrylate, has been synthesized. Radical polymerization (thermal) yielded a linear poly(methacrylate) without affecting the silicon-containing four-membered ring. Photoactivated ring-opening polymerization of the silacyclobutane functionality was employed to cross-link the polymer thin film, yielding, after development, a negative photoimage. Evidence of solid-state ring-opening polymerization was provided by infrared spectroscopy. Postbaking was found to be important. With 0.1% molar $Pt(acac)_2$ with respect to monomer, the system exhibited D_c of 900 mJ/cm^2.

Introduction

Since the first synthetic polymeric photoresist, poly(vinyl cinnamate),[2] photoreactive polymers have been explored in printing and in the electronic circuit industry. They are classified as positive or negative working systems based on the opposite ways they replicate an original. Of the negative resists,[3] most are based on cross-link formation, brought about by, for example, [2 + 2] cycloaddition,[2] decomposition of organic azides to nitrenes[4] or radical coupling.[5] Processes involving incorporation of ionic and ionizable groups[6] and polarity changes[7] have also been applied to form negative images. One example, from our lab, was a study of a synthetic acrylic polymer with a pendant ethyl phenylglyoxylate chromophore.[8] Photoinduced hydrogen abstraction followed by radical coupling is responsible for the cross-link formation in this case.

Plasma etching has become the dominant pattern-transfer method in the semiconductor chip industry due to its unique anisotropic etching. Multilevel resist (MLR) systems have been developed to meet the needs for modern integrated circuit (IC) fabrication as the minimum feature size has been reduced to the submicrometer regime. In such multilevel processing, an etch-resistant layer serves as a mask during the dry transfer of the pattern into the planarizing layer. Since the incorporation of silicon into organic polymers increases resistance to erosion in an oxygen plasma,[9] silicon-containing polymers have found many applications in multilevel systems. Resistance in such cases results from formation of a protective layer of silicon dioxide on the polymer surface while the polymer is being treated with an oxygen discharge. In a so-called bilevel system,[10] polysilanes and polysiloxanes have been used to combine the function of the resist layer with the intermediate masking layer. A single layer resist process, in which selective silylation of the exposed area was carried out to protect this area in the following plasma etching step, has been developed.[11]

The platinum-catalyzed ring-opening polymerization of silacyclobutane and 1,3-disilacyclobutane[12−15] is well-known. This reaction has been utilized to synthesize poly(silylenemethylenes)[16] and to cross-link siloxanes,[17,18] silacyclobutasilazanes,[19,20] and polycarbosilanes.[21] All these reactions were carried out thermally.

We have recently reported that facile photoactivated ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) takes place upon near UV

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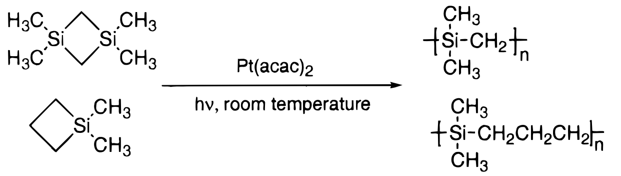
Scheme 1



irradiation in the presence of $Pt(acac)_2$.[22] This is also the case with 1,1-dimethyl-1-silacyclobutane (DMSCB, Scheme 1). Coordinative unsaturation created by sequential cleavage of the Pt−O bond provides for reaction with monomer to activate the Si−C bond, initiating and propagating the polymerization reaction. By the help of inhibition experiments and O_2 effects, both homogeneous and heterogeneous catalytic species have been identified in such processes. On the basis of this discovery, we now report a novel negative-tone photoimaging system based on a new poly(methacrylate) possessing a tethered silacyclobutane functionality. This provides a unique opportunity to utilize the chemistry in a photoimaging process, as well as the possibility of finding applications in multilevel systems.

Experimental Section

Materials. The following reagents and solvents were used as purchased: 3-chloropropylmethyldichlorosilane (Gelest), magnesium powder (Aldrich), DMF (anhydrous, Aldrich), *tert*-butyldimethylsilyl chloride (Aldrich), 6-chloro-1-hexanol (Aldrich), methanol (anhydrous, Aldrich), Dowex 50W-X8 resin (Baker), methacryloyl chloride (Aldrich), CH_2Cl_2 (anhydrous, Aldrich), triethylamine (Aldrich), AIBN (Alfa), and $Pt(acac)_2$ (Alfa). Silica gel (40 μm) used for flash chromatography was obtained from Scientific Adsorbents Inc. Diethyl ether and benzene were freshly distilled from the dark blue sodium benzophenone ketyl. 1-Chloro-1-methyl-1-silacyclobutane (**1**) was synthesized following a literature procedure.[23]

Instruments. NMR spectra were obtained with a Varian Gemini 200 NMR or a Unity Plus 400 NMR spectrometer and chemical shifts are in parts per million with the corresponding deuterated solvents as the internal standard. In the case of ^{29}Si spectra, TMS was used as an external standard. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. GC/MS measurements were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 ms column (J&B Scientific). GPC was performed with a HP 1050 series HPLC equipped with a HP 1047A refractive index detector and a PLgel 5 μm mixed-C 300 × 7.5 mm column with a 5 μm guard column. HPLC-grade THF was used as eluent. PMMA standard samples were obtained from Scientific Polymer Products, Inc. Original film thickness was measured on a Gaertner Model L116C ellipsometer. SEM micrographs were obtained on a Hitachi S-2700 scanning electron microscope. AFM micrographs were obtained using a Metris-2000 Atomic Force Microscope manufactured by Burleigh Instruments, Inc. Silicon tips with a spring constant of $k = 0.1$ N/m were used. A 30 × 30 μm scan module was used.

6-Chlorohexyl *tert*-Butyldimethylsilyl Ether (2). To a 100 mL flask were added DMF (20 mL), *tert*-butyldimethylsilyl chloride (3.3 g, 22 mmol), imidazole (3.1 g, 46 mmol), and finally, 6-chloro-1-hexanol (2.5 g, 18 mmol). After the mixture was stirred for 2 h at ambient temperature, 20 mL of hexane and 20 mL of H_2O were added, and the organic was layer separated. The aqueous layer was washed with another 20 mL of hexane, and the combined organic fractions were dried over anhydrous $MgSO_4$. Flash chromatography using hexane (hex)/ethyl acetate (EA) = 8/1 as eluent ($R_f = 0.70$) gave 4.0 g of **2**, yield 88%: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.019 (s, 6H), 0.866 (s, 9H), 1.24−1.57 (m, 6H), 1.68−1.82 (m, 2H), 3.50 (t, $J = 6.8$ Hz, 2H), 3.58 (t, $J = 6.2$ Hz, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ −5.31, 18.33, 25.12, 25.94, 26.67, 32.62, 45.03, 62.99; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 18.44; IR (neat, cm^{-1}) 2932, 2858, 1463, 1256, 1108, 836, 775; MS (EI, 70 eV) 55 (100), 73 (10), 75 (12), 83 (40), 93 (10), 95 (4), 123 (8.7), 125 (3.4), 193 (0.14, $M^+ - 57$ with ^{35}Cl).

6-(Methylcyclotrimethylenesilyl)hexyl *tert*-Butyldimethylsilyl Ether (3). To a 100 mL three-necked flask purged with N_2 and equipped with an addition funnel, a condenser, and a magnetic stirrer, were added magnesium (1.92 g, 80 mmol) and dry diethyl ether (40 mL). **2** (10.0 g, 40 mmol) was added dropwise to the mixture. 1,2-Dibromoethane was used to initiate the reaction after the addition of a small portion of **2**. The reaction mixture was refluxed for another 4 h, cooled, and filtered into another N_2 purged, two-necked 100 mL flask. **1** (4.2 g, 35 mmol) was added via a syringe to the above solution. After refluxing for 5 h, the reaction mixture was treated with aqueous ammonium chloride solution (20 mL, 10%). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in a vacuum. Flash chromatography on silica gel (6/1 Hex/EA) gave 8.9 g (85%) **3**: $R_f = 0.90$; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.027 (s, 6H), 0.217(s, 3H), 0.670−0.750 (m, 2H), 0.873 (s, 9H), 0.825−1.02 (m, 4H), 1.25−1.59 (m, 8H), 1.96−2.12 (m, 2H), 3.58 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ −5.27, −1.67, 13.53, 16.51, 18.19, 18.37, 23.61, 25.50, 25.98, 32.76, 33.02, 63.32; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 18.31, 20.47; IR (neat, cm^{-1}) 2929, 2857, 1472, 1256, 1102, 835, 774; MS (EI, 70 eV) 43 (12), 59 (9.0), 73 (21), 75 (16), 85 (8.5), 119 (9.4), 131 (22), 133 (19), 147 (6.1), 159 (100), 160 (17), 161 (14), 215 (0.17, $M^+ - 85$).

6-(Methylcyclotrimethylenesilyl)-1-hexanol (4). **3** (2.5 g, 8.3 mmol) was added to a mixture of methanol (30 mL) and Dowex 50W-X8 resin (1.7 g, 8.5 mequiv). The mixture was then stirred at ambient temperature for 6 h. After filtration, the solvent was removed at reduced pressure and the crude oil was subject to column chromatography on silica gel (4/1 Hex/EA) to give 1.0 g of **4** (68%): $R_f = 0.25$; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.212 (s, 3H), 0.662−0.737 (m, 2H), 0.830−1.04 (m, 4H), 1.28−1.45 (m, 6H), 1.47−1.60 (m, 2H), 1.55 (s, 1H), 1.94−2.11 (m, 2H), 3.61 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ −1.69, 13.49, 16.48, 18.19, 23.57, 25.43, 32.65, 32.95, 63.01; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 20.38; IR (neat, cm^{-1}) 3334, 2925, 2855, 1461, 1408, 1249, 1120, 1057, 876, 780, 720.

6-(Methylcyclotrimethylenesilyl)hexyl methacrylate (5). Methacryloyl chloride (0.59 mL, 6.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise via an addition funnel to a solution of **4** (1.0 g, 5.4 mmol) and triethylamine (0.83 mL, 6.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was then stirred overnight at ambient temperature, after which time 20 mL of H_2O was added. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and concentrated in a vacuum. Flash chromatography on silica gel (6/1 Hex/EA) afforded 0.85 g of **5**: $R_f = 0.75$; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.215 (s, 3H), 0.664−0.739 (m, 2H), 0.825−1.00 (m, 4H), 1.28−1.44 (m, 6H), 1.51−1.68 (m, 2H), 1.91−1.92 (m, 3H), 1.94−2.11 (m, 2H), 4.11 (t, $J = 6.6$ Hz, 2H), 5.50−5.54 (m, 1H), 6.07−6.08 (m, 1H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ −1.67, 13.51, 16.48, 18.19, 18.33, 23.52, 25.70, 28.52, 32.82, 64.81, 125.13, 136.50, 167.51; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 20.36; IR (neat, cm^{-1}) 2926, 2856, 1721, 1639, 1453, 1321, 1297, 1249, 1165, 1120, 938, 875, 814, 783; MS (EI, 70 eV) 41 (100), 43 (47), 45 (18), 55 (13), 58 (11), 59 (20), 61 (11), 69 (74), 75 (19), 77 (23), 83 (14), 84 (16), 85 (43), 86 (15), 87 (11), 96 (24), 98 (20), 99 (24), 101 (12), 111 (13), 114 (16), 115 (17), 125 (10), 129 (15), 142 (60), 143 (37), 171 (11), 253 (0.17, $M^+ - 1$).

Poly(6-(Methylcyclotrimethylenesilyl)hexyl methacrylate) (6). **5** (1.0 g, 3.9 mmol) and AIBN (20 mg, 0.12 mmol) were dissolved in dry benzene (10 mL). The solution was treated by three cycles of freeze−pump−thaw and then stirred at 60 °C for 48 h. The resulting solution was concentrated, precipitated into methanol and further purified by precipitat-

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ing from benzene solution with methanol two additional times. **6** (0.61 g, yield 61%) was obtained as a clear gum. $M_w = 5.9 \times 10^4$, $M_n = 1.7 \times 10^4$; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.234 (s, 3H), 0.670−0.750 (m, 2H), 0.855−0.992 (m, 7H), 1.36 (br, 8H), 1.59 (br, 2H), 1.96−2.12 (m, 2H), 3.90 (br, 2H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ −1.59, 13.57, 16.55, 18.24, 23.56, 25.79, 28.07, 32.89, 44.72, 45.12, 64.99, 177.41; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 20.49; IR (thin film on KBr plate, cm^{-1}) 2923, 2854, 1729, 1247, 1149, 1119, 874, 780.

Sample Preparation and Imaging Experiments. Polymer **6** and Pt(acac)$_2$ were dissolved in xylene to make a 10 wt % solution. This solution was then spin-coated onto 13 mm × 13 mm precut silicon wafers, n-type p-doped ⟨100⟩, with a Headway Research spinner at ambient conditions by spinning at 6500 rpm for 30 s. The same solution was also spin-coated for 30 s on a KBr plate at 3000 rpm for IR studies.

Irradiation of the films was carried out using a 200-W high-pressure mercury arc lamp as the irradiation source. Defocused UV irradiation was filtered through a water filter and a UV cutoff filter centered at 362 nm with 40 nm bandwidth. The distance from the film to the lamp remained fixed at 11 cm. Photon flux from the irradiation source was measured by a Scientech 365 Powermeter.

Imaging experiments for the sensitivity study were performed by exposing thin films on silicon wafers through a round opening having a diameter of 10 mm. Postbaking was done at 80 °C as indicated. Development was achieved by dipping the exposed wafers into benzene for 20 s. The IR spectra of the samples were recorded, and the areas under the bands resulting from the ester carbonyl stretching frequency integrated. The ratio of the integration to that of the original film was plotted against irradiation dosage to construct the sensitivity curve.

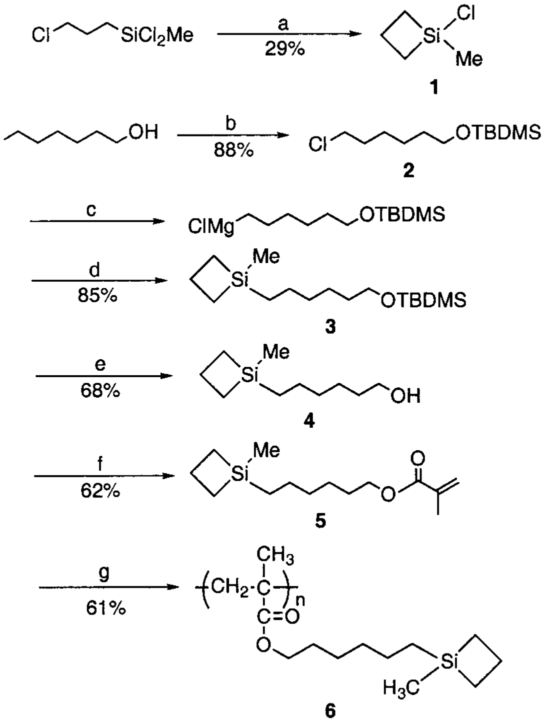
The 7.5 × 7.5 μm patterns were obtained through using T-2000 TEM grids purchased from Electron Microscopy Sciences as masks. The irradiation was carried out in the soft contact mode between the mask and the polymer film. Patterns were analyzed by AFM and SEM.

Results and Discussion

Monomer and Polymer Synthesis. 6-(Methylcyclotrimethylenesilyl)hexyl methacrylate, **5**, was synthesized according to Scheme 2. During our investigation of the photoactivated ring-opening polymerization of disilacyclobutane and silacyclobutane derivatives, we observed that replacement of the methyl group with more electronegative groups on silicon, such as phenyl, chlorine and alkoxyl groups, lowers the reactivity substantially. This is consistent with previous reports.[15,24,25] We designed monomer **5** in which alkyl groups are directly attached to silicon to ensure the activity of the silacyclobutane toward photoactivation. Silacyclobutane was chosen over 1,3-disilacyclobutane for two reasons. First, the compound **1** could be synthesized in a single step. Second, silacyclobutane is more reactive toward ring opening as a result of its greater ring strain.[26,27]

6-Chloro-1-hexanol was protected as the *tert*-butyldimethylsilyl (TBDMS) ether,[28] making the Grignard coupling reaction possible. Several methods were attempted to remove the protecting group. It turned out that using the strongly acidic cation-exchange resin, Dowex 50W-X8, worked well in our case.[29] Workup was made much easier because the resin could be removed by filtration. For unknown reasons, we were unable to obtain the GC/MS of this compound (**4**). The silacyclobutane moiety survived these synthetic steps.

Scheme 2



(a) Mg, Et$_2$O (b) *t*-butyldimethylsilyl chloride, imidazole, DMF, r.t. (c)Mg, Et$_2$O, refluxing (d) **1**, Et$_2$O, r.t. (e) Dowex 50W-X8, methanol, r.t. (f) methacryloyl chloride, CH$_2$Cl$_2$, r.t. (g) AIBN, benzene, 60°C

Polymer **6** was obtained thermally using 2,2′-azobis(isobutyronitrile) (AIBN) to initiate polymerization. The average degree of polymerization (DP) was 67. Figure 1 shows the ^{1}H NMR of both the monomer and polymer. The two olefinic protons completely disappear in the spectrum of the polymer, indicating complete consumption of the monomer. Accordingly, the peak of this methylene group and that of the methyl group attached to double bond in the monomer shift upfield and overlap with the resonances from the aliphatic part and silacyclobutane component of the molecule, respectively. More importantly, the singlet at about 0.22 ppm, along with the multiple peaks at 0.67−0.75 and 0.86−0.99 ppm, remain unchanged during the radical polymerization, clearly showing that the silacyclobutane functionality remains intact under these conditions. Kriner had previously proposed a zwitterionic mechanism for the thermal ring-opening polymerization of disilacyclobutanes based on such observation.[15] Our result is in agreement with Kriner's observations. In fact, this is a key point in our strategy to make a linear poly(methacrylate) while keeping the photoreactive silacyclobutane intact.

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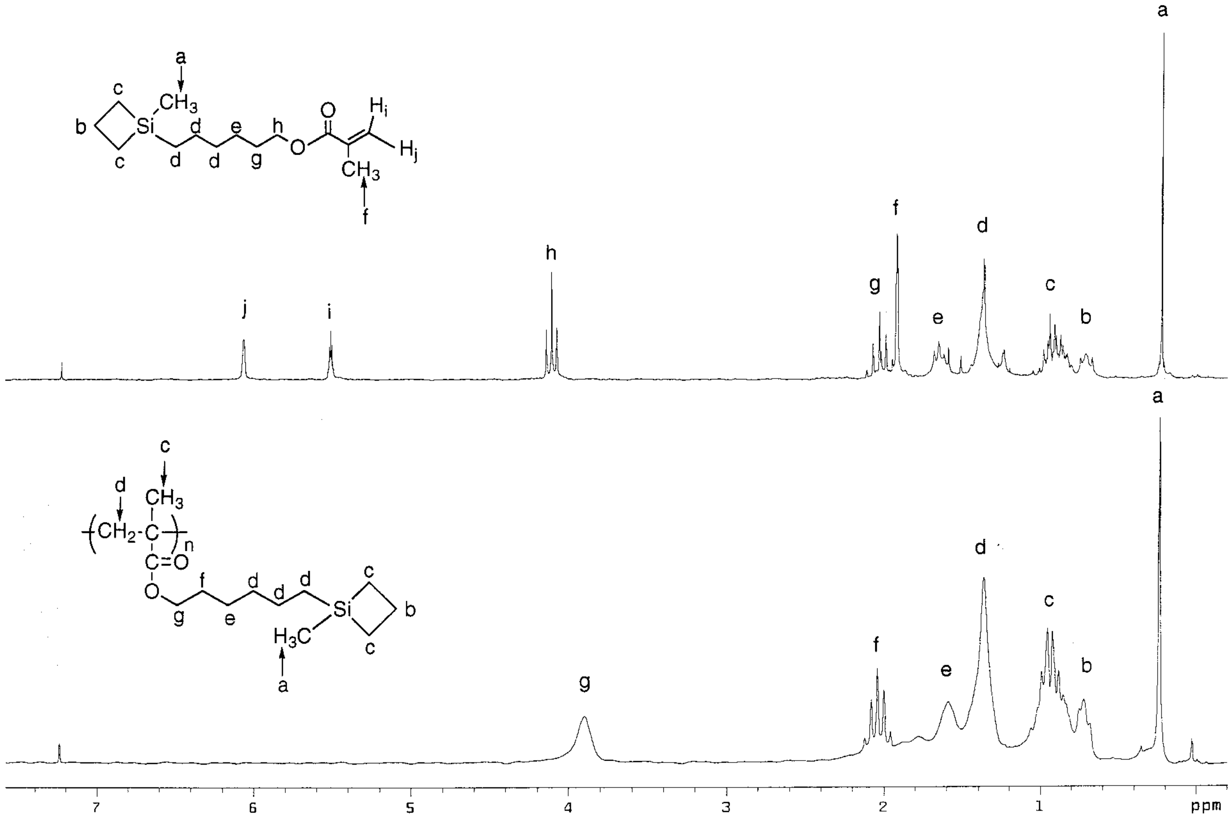


Figure 1. ^1H NMR spectra of monomer **5** and polymer **6** in $CDCl_3$.

Photoactivated Ring-Opening Polymerization in the Solid State. Thermal ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane results in distinct changes in the infrared spectrum.[13] The characteristic absorption of the monomer at 1119 cm^{-1} disappears after ring opening, and a new peak at 1140 cm^{-1} attributed to the open-chain structure of $SiCH_2CH_2CH_2$-Si emerges. This provides a useful tool for following the ring-opening process in the solid state when the poly(methacrylate) is subject to irradiation. Due to the opaqueness of the Si wafer in this region of the spectrum, this part of study was carried on a thin film on a KBr plate (see Experimental Section).

Figure 2 shows the IR spectra of the thin film after irradiation and following postbaking. Since the 1140 cm^{-1} absorption of the ring-opened structure overlaps with the C−O band, we are unable to detect it. The absorption at 1247 cm^{-1}, attributed to Si−CH_3 deformation, remains constant during the process and serves as an internal standard. Therefore, the ratio of the integration of the 1119 cm^{-1} peak to that of 1247 cm^{-1} peak is used to quantify the consumption of silacyclobutane functionality. Compared to the original film (A), 10 min of irradiation (not shown), and 20 min of irradiation (B) resulted in continuous disappearance of 1119 cm^{-1} peak. The Si-containing four-membered rings were opened 22% and 31%, respectively. Postbaking at 80 °C for 30 min (C) proved to be efficient in promoting the ring opening and 61% silacyclobutane was consumed. Prolonged thermal treatment resulted in complete disappearance of the 1119 cm^{-1} peak. Control experiments carried out by treating samples thermally for the same period of time but with no prior irradiation showed no change in the IR spectra. We conclude that direct thermal ring-opening polymerization does not occur under these conditions. Instead, the active species produced photochemically continues the reaction in the dark. When the temperature is elevated from ambient temperature to 80 °C, this reaction is accelerated. This is consistent with previous observations[22] that continuous irradiation is not necessary for the photoactivated ring-opening polymerization of TMDSCB. Once initiated, the reaction proceeds without photolysis, and chemical amplification thus becomes possible. The effect of postbaking will be further explored below.

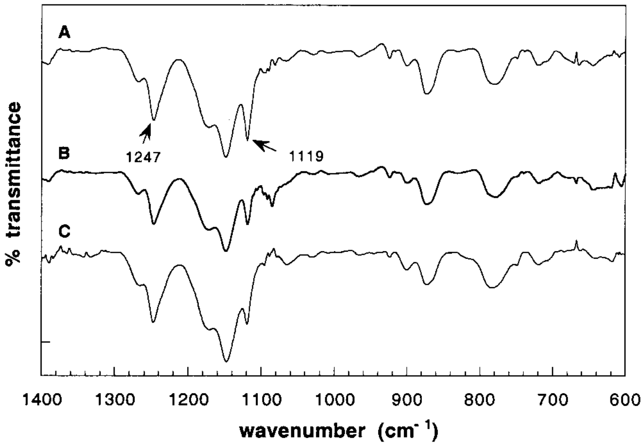
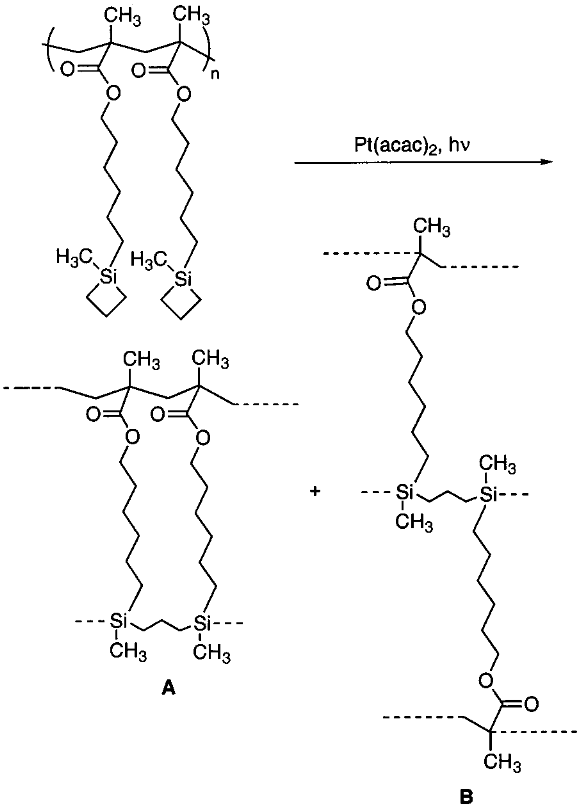


Figure 2. IR spectra of polymer thin film on KBr plate: (A) before irradication; (B) after irradiation for 20 min, an accumulated dose of 3060 mJ/cm^2; and (C) after irradiation as in B and postbaking at 80 °C for 30 min.

From the IR study above, we now propose solid-state ring-opening polymerization (Scheme 3). The resulting cross-linking can occur between any two silacyclobutane

Scheme 3



moieties, belonging either to the same polymer chain (type **A**) or to different chains (type **B**), provided that they are in spatial proximity.

Photoimaging Study. The IR study above indicates that photoactivated ring-opening polymerization occurs in the solid state. This results in at least partial cross-linking of the thin film and presents an opportunity to utilize the polymer as a negative photoresist. If the difference in solubility between the exposed and unexposed area is sufficiently large, only the exposed area will remain after the development step, and this will form a negative photoimage. In our case, benzene turned out to be a good developing solvent.

For the sensitivity study, a thin film spin-coated on Si wafer was irradiated through a round opening having a diameter of 10 mm. After different periods of exposure, the soluble part of polymer was washed away during subsequent development and round areas of differing colors were left, indicating that the areas formed were of differing film thickness. Because the polymer has a distinct carbonyl stretching frequency at 1729 cm^{-1}, it is convenient to measure the area of this carbonyl group stretching frequency before irradiation (A_0) and after irradiation and development (A). The ratio of these two values, A/A_0, allows one to compare the relative thickness of polymer films remaining. The sensitivity curve, Figure 3, was constructed from a plot of A/A_0 against irradiation dose. D_c is the minimum exposure dose after which the sensitivity curve levels off.

It is evident from Figure 3 that postbaking is critical to the use of the material for photoimaging. While maintaining a constant catalyst concentration (0.1% mol wt silacyclobutane functionality), 30 min of postbaking at 80 °C not only cut the D_c from 3800 to 900 mJ/cm^2, but also increased the maximum A/A_0 value from 0.49 to 0.95. The latter value is significant in that it means one has essentially built a cross-linked thin film as thick as the original film. This was evidenced concurrently in that the image was similar in color to the original film. It is well-accepted that solid-state reactions are slow,[30] and it takes a longer time for active species to diffuse through a polymer matrix. In our case, cross-linking is caused by a chain reaction in which this effect is even more pronounced. Therefore, postbaking is necessary to complete the reaction in such a system. We have seen that the IR spectrum changes after postbaking. We have now shown that postbaking also plays an important role in photoimaging.

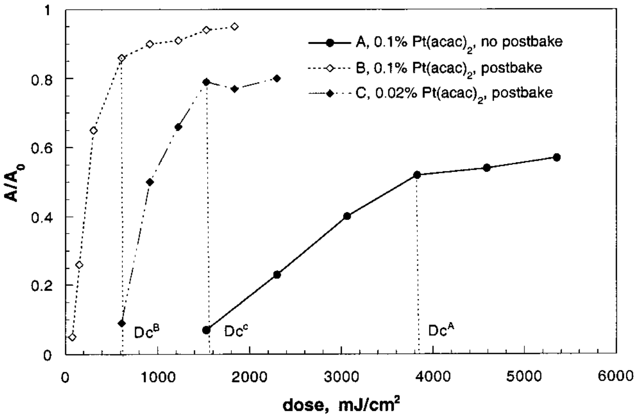


Figure 3. Sensitivity graphs for negative-tone image formation. A/A_0 is the normalized integration of the ester carbonyl stretch at 1729 cm^{-1} in IR.

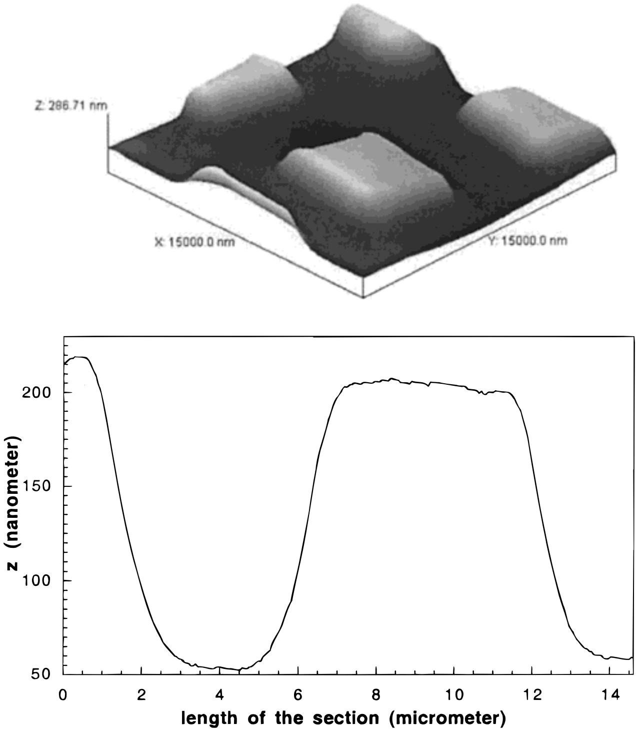


Figure 4. AFM three-dimensional and cross-section view of negative-tone pattern: 0.1% mol Pt(acac)$_2$, irradiated for 10 min, postbaking for 30 min, and developing in benzene for 20 s.

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[30] Thompson, L. F. In *Introduction to Microlithography*, 2nd ed.; Thompson, L. F., Willson, C. G., Bowden, M. J., Ed.; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1994; pp 326−327.

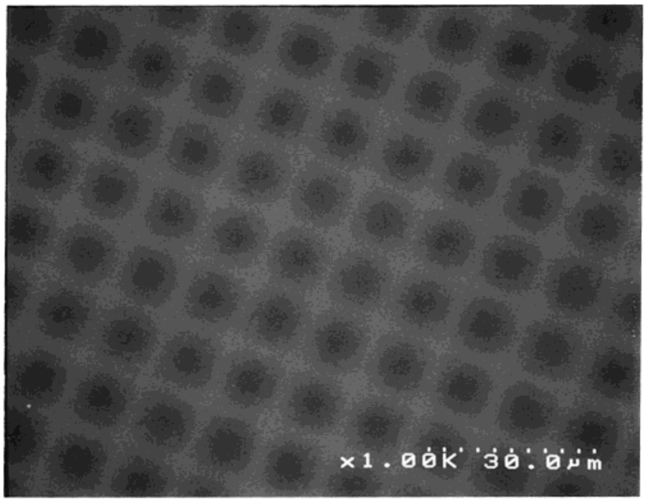

Figure 5. SEM backscattered image of the same sample as used in Figure 4.

Catalyst concentration is not as crucial as the postbaking step, although a decrease in the amount of catalyst lowers the reaction efficiency under the current conditions. With 0.02% mol wt silacyclobutane (Figure 3), D_c is about 1500 mJ/cm^2 and about 79% of the original film can be formed.

Negative-tone patterns were prepared by exposing the sample for a dose exceeding D_c and AFM and SEM results are shown in Figures 4 and 5. On the basis of the average of four measurements, the original film thickness is 174 nm. AFM showed that films as thick as 152 nm remained, and this accounted for about 87% of the original thickness. An SEM backscattered image is useful to differentiate the atomic number difference of specific sections of the image. After development, the unexposed areas are washed away, leaving only a bare silicon surface. These areas display a brighter color since silicon has a larger atomic number than H, C, and O, the elements that account for most of the cross-linked polymer. The backscattered SEM (Figure 5) replicates the masking grid very well. This provides us complementary composite information on the pattern.

Conclusion

We have designed a synthetic route leading to a silacyclobutane-containing methacrylate. The silacyclobutane ring remains intact during radical polymerization. A recently discovered photochemical process, photoactivated ring-opening polymerization, proves to be efficient in cross-linking exposed areas of a film upon imagewise irradiation. Postbaking before development results in more than 4-fold improvement in sensitivity.

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