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# A New Photoresist Based on Calix[4]resorcinarene Dendrimer

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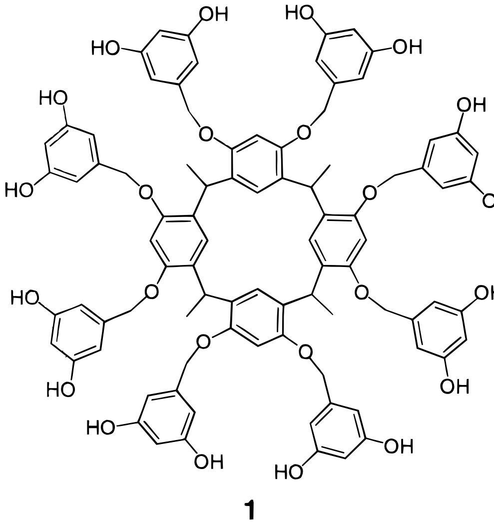
A new dendrimer (**1**), which contains phenol groups in the exterior for solubilization in aqueous alkaline solution and calix[4]resorcinarene in the interior to increase the molecular weight and number of the phenol group even in the lower generation, was designed as new negative-working, alkaline-developable photoresist material. A negative-working photoresist based on **1**, 2,6-bis(hydroxymethyl)phenol as cross-linker, and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate as a photoacid generator has been developed. This resist gave a clear negative pattern through postbaking at 110 °C after exposure to UV light, followed by developing with a 0.3% aqueous tetramethylammonium hydroxide solution at room temperature.

## Introduction

Resists consisting of a cresol-formaldehyde novolac resin and diazonaphthoquinone have been the workhorses of microelectronics for their high resolution, high thermal stability, and resistance to dry-etching conditions.[1] Novolac resins have *ortho*- and *para*-backbone linkages and broad molecular distribution that influence the lithographic performance of the resist, such as the dissolution kinetics and the thermal flow resistance. Therefore, the optimum resist performance is obtained with a complex mixture of novolac fractions with different molecular weights.[2]

To remedy these problems, we proposed the use of cyclic oligomers of phenols, calixarenes as the matrix materials, which have definite structure and molecular weights. In the preceding papers,[3,4] we reported successful preparation of a negative-working photoresist based on calix[4]resorcinarene (**2**), 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) as a cross-linker, and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator. Although **2** gave a fine negative pattern after development by aqueous tetramethylammonium hydroxide (TMAH) solution, the film was not stable because of its crystallinity.

Dendrimers are polymers with a new molecular architecture, which is characterized by a central polyfunctional core, from which arise successive layers of monomer units with a branch occurring at each monomer unit. They are monodisperse materials such as the calixarene, and their molecular weights reache several thousand such as the novolac resin. Thus, the dendrimer possessing a phenolic shell and calixarene core is another analogue of the novolac resin. In addition, some dendrimers are known as amorphous materials which is advantageous to improve the film stability of **2**. We designed a dendrimer (**1**) which contains phenol groups in the exterior for solubility in aqueous alkaline solution and tetramethyl calix[4]resorcinarene in the interior to increase the number of the phenol group even in the lower generation.



**1**

In this article, we report the development of a new negative-working, alkaline-developable photoresist con-

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sisting of a calix[4]resorcinarene dendrimer (**1**), a photoacid generator and a cross-linker.

## Experimental Section

**Measurements.** Melting points were measured on a Laboratory Devices Mel-Temp II melting apparatus and were uncorrected. Infrared spectra were recorded on a Horiba FT-210 spectrophotometer. $^1$H NMR spectra were obtained with use of a JEOL EX270 or JEOL JNM-GX270 spectrometer. Tetramethylsilane was used as the internal standard, except for high-temperature measurements in which dimethyl sulfoxide-$d_6$ (DMSO-$d_6$) was used as the internal standard. Fast atom bombardment (FAB) mass spectra were recorded by using xenon ionization techniques with a 3-nitrobenzyl alcohol as the matrix on a JEOL AX-505 spectrometer. UV matrix-assisted laser disorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained by means of a Kratos Kompact MALDI III mass spectrometer (Shimadzu Co.) operated in the linear-positive mode. The samples were dissolved in tetrahydrofuran (THF) and mixed with 2,5-dihydroxybenzoic acid as the matrix. The UV spectra were obtained on a Shimadzu UV-2200 spectrophotometer. Thermogravimetric (TG) analyses were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyzer at a heating rate of 10 °C·min$^{-1}$. The differential scanning calorimetry (DSC) were performed on a Seiko SSC/5200 (DSC 220) instrument at a heating rate of 20 °C·min$^{-1}$ under nitrogen atmosphere. The film thickness was measured by a Dektak 3030 system (Veeco Instruments Inc.). The scanning electron micrographs were obtained with a JEOL 5300 scanning electron microscope.

**Materials**. A cross-linker, BHMP,[5] was prepared by the reaction of phenol with formaldehyde in water. The photoacid generator, DIAS,[6] was prepared by the reaction of diphenyliodonium chloride with sodium 9,10-dimethoxyanthracene-2-sulfonate, which was obtained by the reduction of sodium anthraquinone-2-sulfonate with zinc and aqueous sodium hydroxide solution, followed by the methylation with dimethyl sulfate.[7] $C_{4v}$ *C*-tetramethyl calix[4]resorcinarene (**2**) was prepared according to the reported procedure.[8] 3,5-Dihydroxybenzoic acid (Merck) and 18-crown-6 (Tokyo Kasei Co.) were commercially available and used as received. THF and 1,4-dioxane were refluxed over sodium-benzophenone ketyl and distilled just before use. The other chemicals were commercially available and used without further purification.

**Methyl 3,5-Diallyloxybenzoate (4).** A mixture of methyl 3,5-dihydroxybenzoate (7.0 g, 41.7 mmol), 3-bromopropene (10.8 mL, 125 mmol), $K_2CO_3$ (17.3 g, 125 mmol), and KI (0.21 g, 1.25 mmol) in 150 mL of acetone was stirred at 60 °C for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure. The residue was dissolved in diethyl ether and washed with saturated aqueous $Na_2CO_3$ solution. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Yellow oil was obtained. Yield 9.31 g (37.5 mmol, 90%). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.70; H, 6.50. Found: C, 67.73; H, 6.64. IR (KBr): $\nu$ (cm$^{-1}$) 1720 (C═O). $^1$H NMR (270 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.08 (d, 2H, ArH, $J = 2.3$ Hz), 6.89 (t, 1H, ArH, $J = 2.3$ Hz), 5.97−6.11 (m, 2H, −CH═C), 5.42 (dd, 2H, ═CH$_2$, $^3J_{\mathrm{trans}} = 17.2$ Hz, $^2J = 1.3$ Hz), 5.31 (dd, 2H, ═CH$_2$, $^3J_{\mathrm{cis}} = 10.6$ Hz, $^2J = 1.3$ Hz), 4.54 (d, 4H, −OCH$_2$−, $J = 5.0$ Hz), 3.84 (s, 3H, −CH$_3$).

**3,5-Diallyloxybenzyl Alcohol (5).** A solution of **4** (5.0 g, 20 mmol) in THF (20 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (1.5 g, 40 mmol) in 100 mL of THF. The mixture was refluxed for 5 h under a nitrogen atmosphere and then left overnight at room temperature. Water (9 mL) was added dropwise, then the mixture was filtered and evaporated under reduced pressure. The residue was dissolved in diethyl ether and washed with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Colorless oil was obtained. Yield 3.25 g (14.8 mmol, 73%). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.82; H, 7.62. $^1$H NMR (270 MHz, DMSO-$d_6$): $\delta$ (ppm) 6.51 (d, 2H, ArH, $J = 2.3$ Hz), 6.39 (t, 1H, ArH, $J = 2.3$ Hz), 5.96−6.10 (m, 2H, −CH═C), 5.39 (dd, 2H, ═CH$_2$, $^3J_{\mathrm{trans}} = 17.5$ Hz, $^2J = 1.3$ Hz), 5.25 (dd, 2H, ═CH$_2$, $^3J_{\mathrm{cis}} = 10.6$, $^2J = 1.3$ Hz), 5.18 (t, 1H, −OH, $J = 5.9$ Hz), 4.52 (d, 4H, −OCH$_2$−, $J = 5.0$ Hz), 4.43 (d, 2H, −C*H*$_2$OH, $J = 5.9$ Hz).

**3,5-Diallyloxybenzyl Chloride (6).** A solution of **5** (0.85 g, 3.9 mmol), pyridine (0.31 mL, 3.9 mmol), and thionyl chloride (0.58 mL, 8.0 mmol) in $CHCl_3$ (50 mL) was stirred at room temperature for 2 h. The reaction mixture was washed with water and concentrated under reduced pressure; then the residue was dried under a vacuum for 1 h to give a colorless oil. Yield 0.89 g (3.7 mmol, 94%). $^1$H NMR (270 MHz, $CDCl_3$, 30 °C) $\delta$ (ppm) 6.55 (d, 2H, ArH, $J = 2.3$ Hz), 6.45 (t, 1H, ArH, $J = 2.3$ Hz), 5.97−6.11 (m, 2H, internal CH), 5.41 (ddt, 2H, terminal CH, $^3J_{\mathrm{trans}} = 17.1$ Hz, $^2J = 1.5$ Hz, $^4J = 1.5$ Hz), 5.28 (ddt, 2H, terminal CH, $^3J_{\mathrm{cis}} = 10.2$ Hz, $^2J = 1.5$ Hz, $^4J = 1.5$ Hz), 4.50−4.53 (m, 6H, O−CH$_2$ and CH$_2$Cl).

**Protected Dendrimer (7).** Calix[4]resorcinarene (**2**) was dried at 120 °C for 4 h just before use. A mixture of **2** (0.449 g, 0.82 mmol), **6** (1.947 g, 8.2 mmol), $K_2CO_3$ (1.155 g, 8.4 mmol), and 18-crown-6 (0.245 g, 0.93 mmol) in 2-butanone (50 mL) was refluxed for 70 h under an argon atmosphere. After removal of the solvent, the residue was extracted with dichloromethane. The organic layer was washed with water and dried over $Na_2SO_4$ and evaporated to dryness. The crude product was purified by dry column chromatography (hexane/ethyl acetate, 2:1, v/v) to give a yellow oil which solidified on standing after a few weeks. Yield 1.67 g (0.77 mmol, 94%). mp 85−86 °C. $^1$H NMR (270 MHz, DMSO-$d_6$, 100 °C) $\delta$ (ppm) 6.69 (s, 8H, ArH), 6.38−6.41 (m, 24H, ArH), 5.32 (dd, 16H, terminal CH, $^3J_{\mathrm{trans}} = 17.1$ Hz, $^2J = 1.5$ Hz), 5.90−6.04 (m, 16H, internal CH), 5.19 (dd, 16H, terminal CH, $^3J_{\mathrm{cis}} = 11.4$ Hz, $^2J = 1.5$ Hz), 4.71−4.87 (m, 20H, O−CH$_2$ and Ar−CH), 4.41−4.43 (m, 32H, O−CH$_2$), 1.44 (d, 12H, CH$_3$, $J = 7.3$ Hz). $^{13}$C{$^1$H} NMR (67.8 MHz, DMSO-$d_6$, 100 °C) $\delta$ (ppm) 158.8, 153.9, 139.3, 133.0, 127.1, 124.3, 116.3, 105.9, 100.6, 100.0, 69.9, 68.0 30.3 (bridge CH), 19.3 (bridge CH$_3$). Anal. Calcd for $C_{136}H_{144}O_{24}$: C, 75.53; H, 6.71. Found: C, 75.58; H, 6.74. FAB-MS (*m*/*z*) 2162 (M + H)$^+$.

**Deprotected Dendrimer (1).** A mixture of **7** (2.23 g, 1.03 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.23 g, 0.33 mmol), and ammonium formate (4.15 g, 66 mmol) in 1,4-dioxane (50 mL) was refluxed for 20 h under an argon atmosphere. After cooling, the reaction mixture was diluted with diethyl ether and extracted with 10% NaOH solution. The aquaous layer was acidified with concentrated hydrochloric acid to pH 3 and then extracted with ethyl acetate. The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was dissolved in methanol and purified by reprecipitation with hexane. The precipitate was collected by filtration and dried under a vacuum to give a tan solid. Yield 1.16 g (0.76 mmol, 74%). mp 248 °C (dec). $^1$H NMR (270 MHz, DMSO-$d_6$, 100 °C) $\delta$ (ppm) 8.71 (s, 16H, OH), 6.66 (s, 4H, ArH), 6.57 (s, 4H, ArH), 6.15−6.20 (m, 32H, ArH), 4.63−4.71 (m, 20H, CH$_2$ and Ar−CH), 1.42 (d, 12H, CH$_3$, $^3J = 7.2$ Hz). $^{13}$C{$^1$H} NMR (67.8 MHz, DMSO-$d_6$, 50 °C) $\delta$ (ppm) 158.1, 154.3, 139.9, 124.5, 107.1, 105.2, 101.7, 99.8, 70.1, 30.4 (bridge CH), 20.1 (bridge CH$_3$). Anal. Calcd for $C_{88}H_{80}O_{24}\cdot 4H_2O$: C, 66.32; H, 5.57. Found: C, 66.44; H, 5.30. FAB-MS (*m*/*z*) 1521 (M$^+$).

**Dissolution Rate Measurements.** Dendrimer **1** was dissolved at 20 wt % in cyclohexanone, to which were added BHMP and DIAS (20 wt % and 10 wt % of the total solid, respectively). Films spin-cast on Si wafer were prebaked at 80 °C for 10 min and exposed through a filtered super-high-pressure mercury lamp SH-200 (Toshiba Lighting and Tech-

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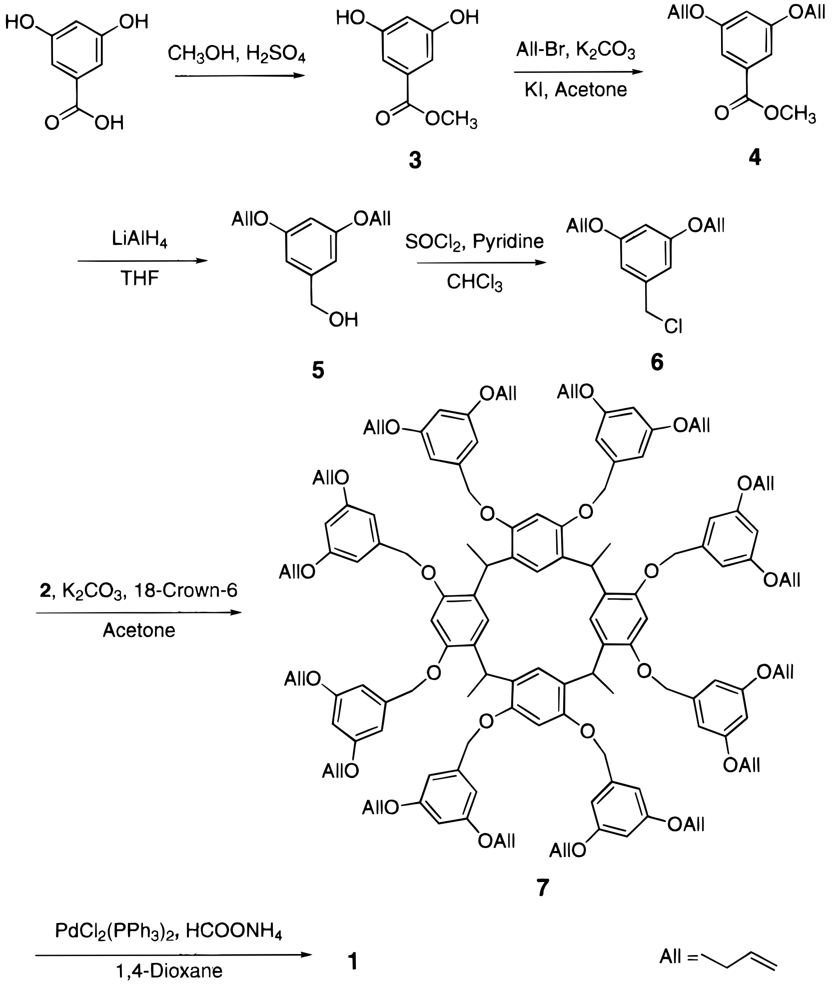
**Scheme 1**



nology Corporation). Imagewise exposure was carried out in a contact mode. Exposed films were subjected to development with 0.3% aqueous TMAH solution at room temperature. The dissolution rate was determined by measuring the change of film thickness per unit development time.

**Photosensitivity.** Three-micrometer films on silicon wafers were exposed at 365-nm wavelength to the filtered super-high mercury lamp, postexposure baked at 110 °C for 3 min, developed in a 0.3% aqueous TMAH solution at room temperature, and rinsed with water. The characteristic curve was obtained by plotting normalized thickness against exposed energy.

## Results and Discussion

**Synthesis of Dendrimer 1.** Dendrimer **1** was prepared according to Scheme 1 starting from 3,5-dihydroxybenzoic acid by modifying the Fréchet's convergent growth method.[9] The starting material was converted to methyl ester, the hydroxyl groups were protected with allyl ethers (**4**), and then the reduction of the ester group gave 3,5-diallyloxybenzyl alcohol (**5**). The alcohol **5** was treated with thionyl chloride to give chloride (**6**). The reaction of **6** and $C_{4v}$ *C*-tetramethyl calix[4]resorcinarene (**2**) was carried out with potassium carbonate and 18-crown-6 in 2-butanone to give the allyl-protected dendrimer (**7**). The cleavage of the allyl ether of **7** was accomplished with bis(triphenylphosphine)palladium(II) dichloride and ammonium formate in 1,4-dioxane to give the dendrimer with exterior hydroxyl groups (**1**).[10] All these steps had excellent yields (73−94%).

Figure 1 shows $^1$H NMR spectra of **1**, **7**, and **2** measured in DMSO-$d_6$. At ambient temperature, the spectrum of **2** displayed a doublet at 1.35 ppm for methyl protons, a quartet at 4.46 ppm for bridging methine protons, two singlets at 6.15 and 6.86 ppm for aromatic protons, and a singlet at 8.47 ppm for OH protons. On the other hand, the $^1$H NMR spectra of dendrimers **7** and **1** showed very broad peaks, indicating that the mutual interconvertion between two equivalent boat conformers occurs slowly on the NMR time scale. Thus the time-averaged simple spectra were observed at higher temperatures. The dendrimer **7** possesses a high symmetrical structure, as shown by the spectrum determined at 100 °C (Figure 1b). A well-defined vinylic multiplet for the allylic groups in the olefinic region, a doublet at 1.42 ppm for methyl protons, and an AB quartet at 4.7−4.9 ppm for benzyl methylene protons are compatible with a conformation with overall $C_{4v}$ symmetry. The disappearance of the allylic signals in the spectrum of **1** (Figure 1c) indicated that the deprotection could be achieved completely. A doublet at 1.42 ppm for methyl protons, an AB quartet at 4.6−4.7 ppm

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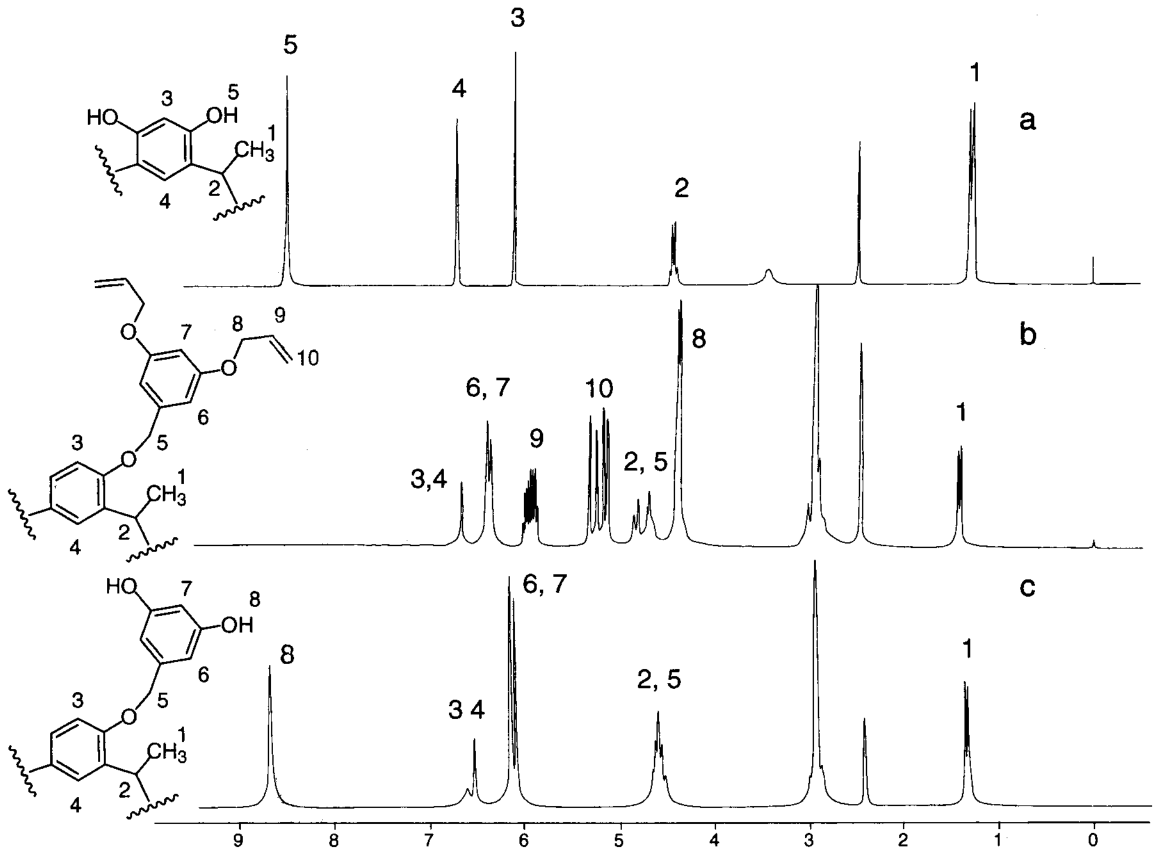

**Figure 1.** $^{1}$H NMR spectra of (a) **2** at room temperatureand (b) **7** and (c) **1** at 100 °C, measured in DMSO-$d_6$.

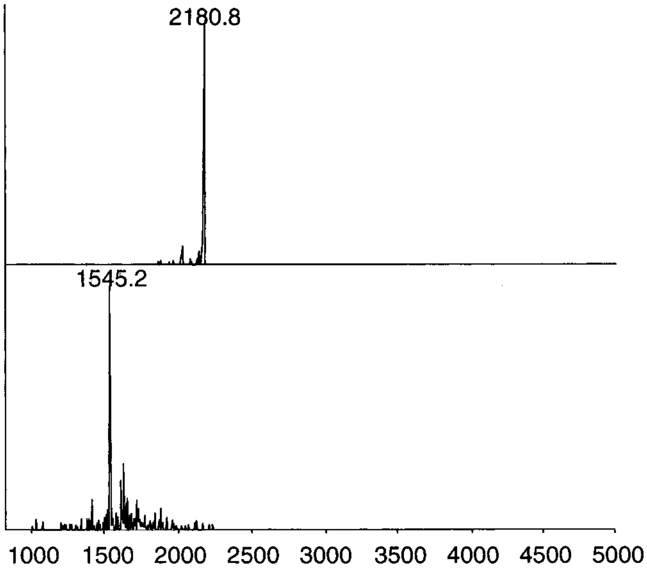

**Figure 2.** MALDI-TOF mass spectra of **7** (top) and **1** (bottom).

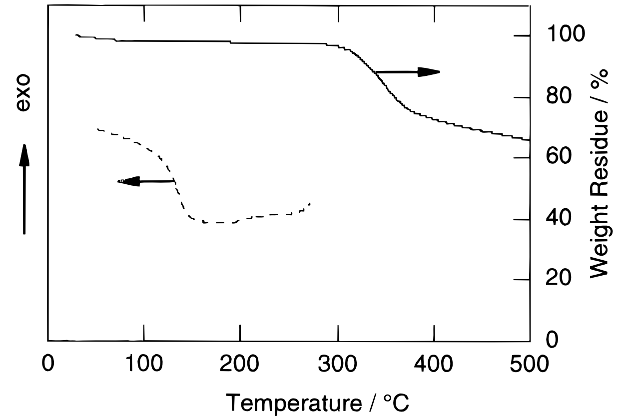

**Figure 3.** TG (solid line) and DSC (broken line) curves of dendrimer **1**.

for benzyl methylene protons, and a singlet at 8.71 ppm for OH protons were found. Two singlets at 6.57 and 6.66 ppm were assigned to the extraannular and intra-annular aromatic protons of calix[4]resorcinarene core unit, respectively. Furthermore, the structure of **1** was confirmed by its $^{13}$C NMR spectrum consisting of 11 carbon signals.

The formation and purity of dendrimers **7** and **1** was also confirmed by MALDI-TOF mass spectra (Figure 2). In the spectrum of **7**, only one peak was found at 2180.8, which is consistent with the theoretical molecular weight of **7** ([M + Na$^+$] = 2183.99). Thus the purity of **7** was confirmed. Although the spectrum of **1** shows some noises, the main peak at 1545.2 agrees with the calculated molecular weight of **1** ([M + Na$^+$] = 1543.49). No peaks indicating incomplete deprotection were observed.

Figure 3 shows TG and DSC curves of **1**. The 10% weight-loss temperature was 335 °C under a nitrogen atmosphere. Thus dendrimer **1** has high thermal resistance. The DSC curve shows the glass transition temperature ($T_g$) at 133 °C. In addition, no melting point was observed up to 300 °C in the DSC curve. This indicates **1** is amorphous, which is preferable for the film formation.

To study the formation of film and the dissolution behavior of a film of **1** in an alkaline solution, **1** was dissolved at 30 wt % in diglyme at room temperature,

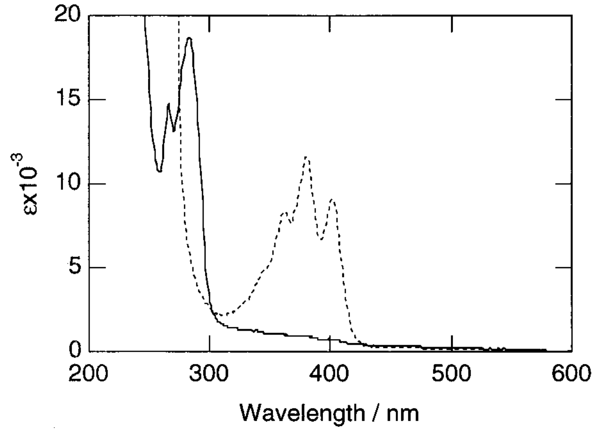

**Figure 4.** UV spectra of **1** (solid line) and DIAS (broken line) in acetonitrile solution. Each sample concentration was 1.0 × $10^{-5}$ mol $L^{-1}$. Path length was 1.0 cm.

and spin-coated on a Si wafer. The wafer was prebaked (80 °C for 10 min) to remove the residual solvent. A clear, tough transparent film was obtained, which was stable for an one month, whereas the film of **2** became opaque within 1 h. The film of **1** dissolved completely in a 0.1% aqueous TMAH solution at room temperature within 5 s. Such a high solubility in the alkaline solution should promise that **1** could act well as a negative-working photoresist if combined with a suitable cross-linking reaction. Thus we decided to formulate a negative-type photoresist consisting of **1**, a cross-linker, and a photoacid generator.

**Lithographic Evaluation.** We have shown[3] that DIAS worked well as a photoacid generator for **2**, which is transparent in the range of the absorption of DIAS. We measured a UV spectrum of **1** in acetonitrile (Figure 4) to find out whether DIAS could be used for **1**. The spectrum indicates that **1** has a strong absorption around 280 nm because of $\pi$-$\pi^*$ transitions and is almost transparent above 300 nm. Thus DIAS, which has a strong absorption in the range of 300−420 nm, can be used as the photoacid generator.

Some polyfunctional benzyl alcohols such as BHMP could be used as a cross-linker for matrixes having phenolic functional groups such as poly(4-hydroxystyrene),[7] hydroxypolyimide,[11] and **2**.[3] This acid-catalyzed cross-linking reaction was studied in detail, and the reaction was proposed to proceed via a direct C-alkylation as well as an initial *O*-alkylation, followed by a subsequent acid-catalyzed rearrangement to the final *C*-alkylated product. Furthermore, both thermal cross-linking and acid-catalyzed cross-linking processes were proposed for this alkylation.[12] Thus we decided to use BHMP for **1** on the basis of its availability and high reactivity.

Figure 5 shows the change of the UV spectrum corresponding to the film of **1** containing DIAS (10 wt %) and BHMP (20 wt %) upon UV (365 nm) irradiation. The absorption band around 390 nm decreased rapidly upon irradiation and became very similar to the spectrum of 9,10-dimethoxyanthracene-2-sulfonic acid over 200 mJ·cm$^{-2}$. Thus the resist consisting of **1** as a matrix and DIAS and BHMP, a photoacid generator and cross-linker, respectively, would be expected to show high sensitivity toward 365-nm UV light.

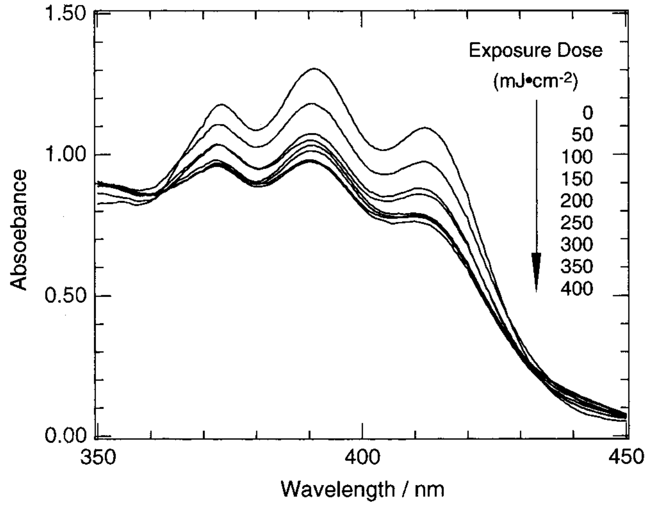

**Figure 5.** UV spectra of a film of **1** containing DIAS and BHMP.

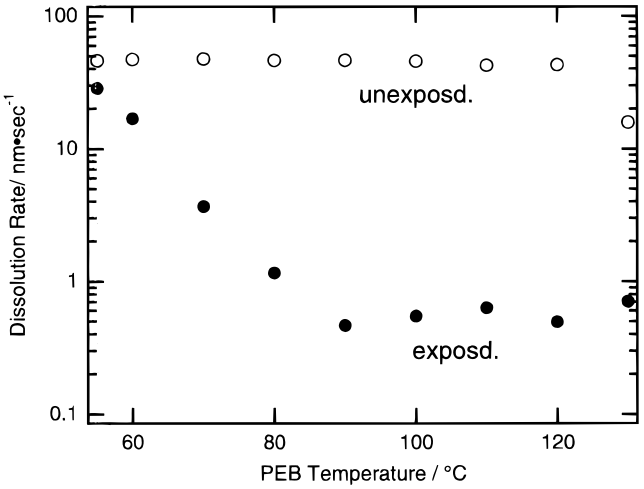

**Figure 6.** Effect of PEB temperature on the dissolution rate of dendrimer **1** film containing BHMP and DIAS. Exposure, 10 mJ·cm$^{-2}$ (365 nm); PEB time, 3 min; developer, 0.3% aqueous TMAH (20 s).

To optimize postexposure bake (PEB) conditions, we measured dissolution rates of both the exposed and the unexposed areas at various PEB temperatures. The dissolution rate was estimated by measuring the film thickness after development. The resist, which consists of **1** (70 wt %), BHMP (20 wt %), and DIAS (10 wt %) in cyclohexanone, was spin-cast on silicon wafers, exposed to 365-nm UV light (10 mJ·cm$^{-1}$), postexposure baked for 3 min, and developed with a 0.3 wt % aqueous TMAH solution for 20 s. The results were shown in Figure 6. The dissolution rate of the exposed area was reduced with the increase of the PEB temperature and became almost constant above 90 °C. At 100−120 °C, the exposed area was dissolved 100 times slower than the unexposed area. On the other hand, the rate of the unexposed area was constant below 120 °C of the PEB temperature, but decreased at 130 °C. This temperature is higher than the melting point of BHMP and the cross-linking took place thermally by the melt BHMP. Thus the suitable PEB temperature were 100−120 °C.

We also examined the effect of the PEB time on the dissolution rates with the constant PEB temperature

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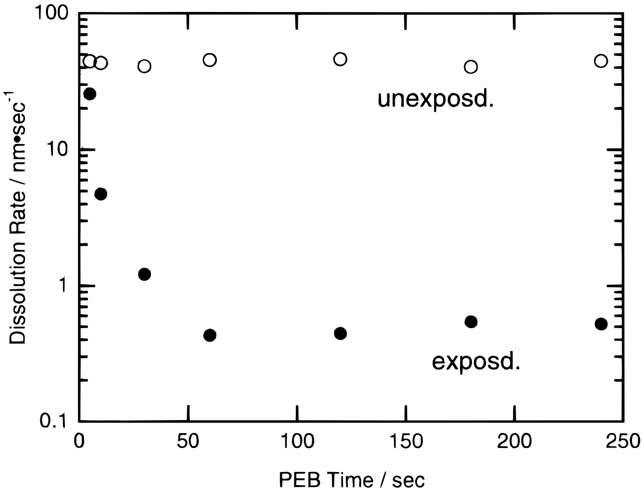

**Figure 7.** Effect of PEB time on the dissolution rate of dendrimer **1** film containing BHMP and DIAS. Exposure, 10 mJ·cm$^{-2}$ (365 nm); PEB temperature, 110 °C; developer, 0.3% aqueous TMAH (20 s).

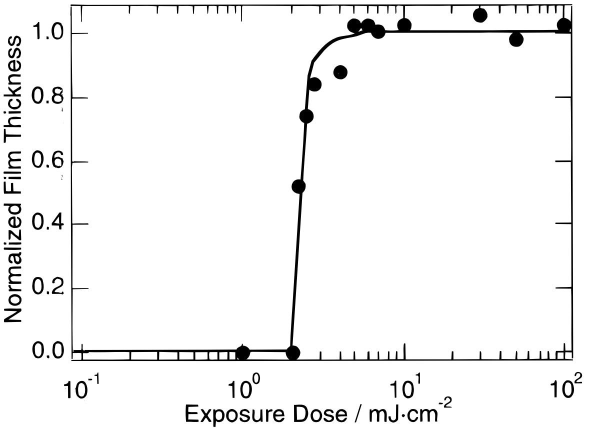

**Figure 8.** Exposure characteristic curves for the systems of **1** containing BHMP and DIAS.

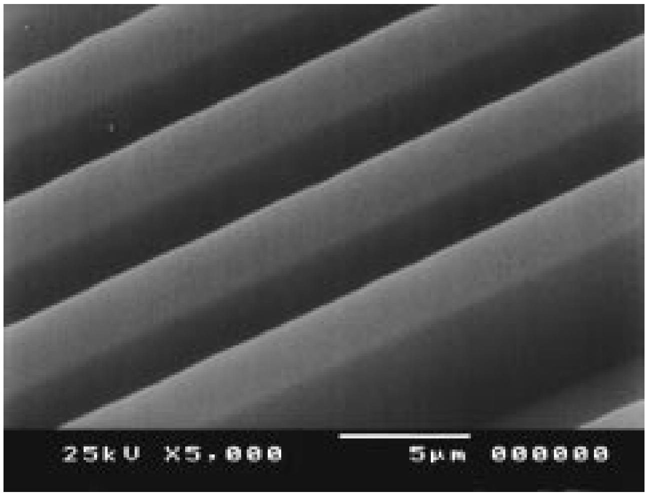

**Figure 9.** Scanning electron micrograph of the contact-printed negative image obtained from the system consisting of **1**.

of 110 °C (Figure 7). Although the dissolution rate of the unexposed area was unchanged for the PEB time of up to 250 s, the dissolution rate of the exposed area was reduced with prolonged PEB. The difference reached 60 times at 60 s, but the longer PEB time did not give any improvements. Thus the PEB should be performed for more than 60 s at 110 °C for maximum dissolution rate differentiation.

After these preliminary studies, we formulated a resist consisting of **1** (70 wt %), BHMP (20 wt %), and DIAS (10 wt %) in cyclohexanone. The film spin-cast on silicon wafer, exposed to 365-nm UV light (10 mJ·cm$^{-1}$), postexposure baked at 110 °C for 3 min, and developed in a negative mode with the 0.3 wt % aqueous TMAH solution for 20 s. The sensitivity curve for a 1-$\mu$m-thick film (Figure 8) indicates that the sensitivity ($D^{0.5}$) and the contrast ($\gamma^{0.5}$) were 2.3 mJ·cm$^{-2}$ and 13, respectively.

Figure 9 shows a scanning electron micrograph of the contact-printed negative image that was obtained using the dendrimer resist, prebaked at 80 °C for 600 s (thickness, 5 $\mu$m), exposed to 10 mJ·cm$^{-2}$ of 365 nm UV radiation, postbaked at 110 °C for 180 s, and developed in a negative mode with the 0.3 wt % aqueous TMAH solution at room temperature. The resist is capable of resolving a 3-$\mu$m feature when a 5-$\mu$m-thick film is used. Thus, this resist gave a fine pattern even for such thick film.

## Conclusion

Calix[4]resorcinarene dendrimer (**1**) was prepared as a new photoresist material. This compound acted as an excellent photoresist matrix with the photoacid generator, DIAS, and the cross-linker, BHMP. The resist showed the high sensitivity and contrast as 2.3 mJ·cm$^{-2}$ and 17, respectively.

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