

The Synthesis and Photo-Induced Deprotection Reaction of Calix[4]resorcinarene Derivatives Containing *t*-Butyl Ester Moieties

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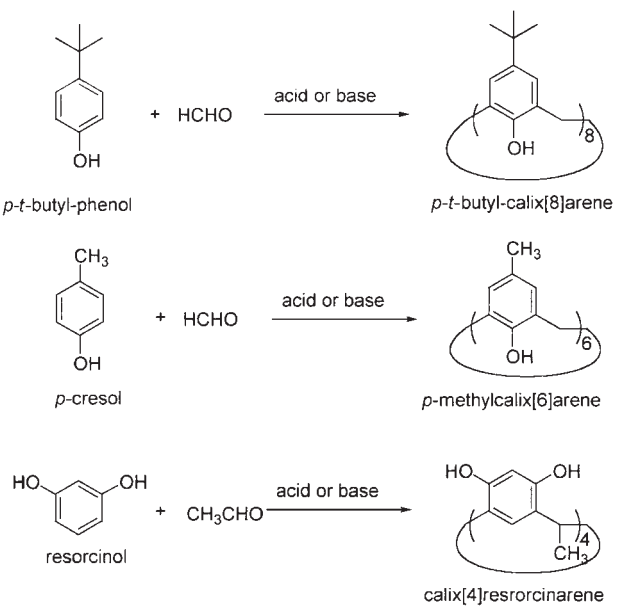
The syntheses and photoinduced deprotection reactions of calix[4]resorcinarene derivatives with pendant *t*-butyl ester moieties were examined. Calix[4]resorcinarenes, **1a**–**1h**, were prepared by the condensation reaction of resorcinol with certain aldehydes in the presence of hydrochloric acid as a catalyst in ethanol at 80 °C for 30 min in good yields. The substitution reaction of **1a**–**1h** with *t*-butyl bromoacetate using cesium carbonate as a base and tetrabutylammmonium bromide (TBAB) as a phase transfer catalyst was performed to afford the corresponding calix[4]resorcinarene derivatives, **2a**–**2h** with pendant *t*-butyl ester groups. It was found that **2a**, **2e**, **2f**, **2g**, and **2h** had film forming properties. The photoinduced deprotection reaction of calixarene derivatives **2a**, **2e**, **2f**, **2g**, and **2h** was examined in the presence of bis-[4-(diphenylsulfonio)phenyl] sulfide (DPSP) as a photoacid generator in the film state upon UV irradiation for 5 min followed by heating at 170 °C. It was found that the deprotection reaction of the *t*-butyl ester groups of **2a**, **2e**, **2f**, **2g**, and **2h** proceeded smoothly to produce the corresponding calixarene derivatives, **3a**, **3e**, **3f**, **3g**, and **3h** with carboxylic acid groups, quantitatively.

It is well known that calixarenes are attractive compounds as host molecules in the field of the host–guest chemistry.[1] The synthesis and chemical modification of the various calixarenes have been reported. Calixarenes are cyclic oligomers containing hydroxy groups and are easily prepared by the reaction of phenols with aldehydes.[2] For example, the reaction of formaldehyde with *p*-*t*-butylphenol, *p*-cresol, and resorcinol in the presence of either acid or base gives the corresponding calix[*n*]arenes, *p*-*t*-butyl-calix[8]arene (BCA), *p*-methylcalix[6]arene (MCA), and calixresorcin[4]arene (CRA), as shown in Scheme 1.



Scheme 1.

Furthermore, calixarenes have many potential applications because they have many hydroxy groups in small size molecules and have some unique properties, such as high thermal stability, high glass transition temperature (T_g),[3] and high melting temperature (T_m).[4] Certain calixarenes and their derivatives are amorphous in the solid state and have good film-forming properties.[5,6]

Ueda et al. and Fujita et al. have reported applications of calixarenes as negative- and positive-type photoresists, respectively.[7–10] We have also reported the synthesis and photochemical reactions of calix[*n*]arene derivatives containing certain polymerizable groups, such as (meth)acrylates,[3] viny ether,[4] propargyl ether,[4] oxetane,[11] oxirane,[11] and spiro ortho ester groups.[12] It was found that these calixarene derivatives had excellent thermal stability and high photochemical reactivity. Furthremore, we have investigated the synthesis and photoinduced deprotection of calix[*n*]arene derivatives containing suitable protective groups for hydroxy groups, such as *t*-butoxycarbonyl, trimethylsilyl ether, and cyclohexenyl ether groups prepared from calixarenes, CRA, MCA, and BCA[13] using photoacid generator. These synthesized calixarene derivatives also had high photochemical reactivity in the film state. In particular, *t*-butoxycarbonyl groups showed the highest deprotection rate, and CRA derivatives were found to be a better matrix than any other calixarene derivatives. These results indicated that calix[*n*]arene derivatives would be applicable to useful EB-

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and photo-resist materials. However, the film-forming properties of CRA derivatives were not good enough due to their poor solubility.

Therefore, we designed new CRA derivatives with pendant *t*-butyl ester groups. Our approach as the applications of the CRA derivatives is to obtain the CRA derivatives containing carboxylic acids groups by the photoinduced deprotection reaction that will function as a positive alkaline developable resist. In this article, we examined the syntheses and properties of the new CRA pendant *t*-butyl ester group derivatives. The photoinduced deprotection reaction of the synthesized CRA derivatives was also investigated in the film state.

Experimental

Materials. The solvent, *N*-methylpyrroridone (NMP) was dried with CaH_2 and was purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Cesium carbonate (Cs_2CO_3), pentadecanol, heptadecanol, resorcinol, undecanal, tridecanal, paraldehyde, *p*-hydroxybenzaldehyde, *o*-hydroxybenzaldehyde, 3-ethoxy-4-hydroxybenzaldehyde, pyridinium chlorochromate (PCC), and *t*-butylbromoacetate (BBAc) were used without further purification. Pentadecanal ($C_{14}H_{29}CHO$) and heptadacanal ($C_{16}H_{33}CHO$) were synthesized according to the reported method.[14,15]

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The ^{1}H NMR spectra were recorded on JNM FX-270 (270 MHz for ^{1}H NMR and 68 MHz for ^{13}C NMR) and JEOL Model JNM α-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) instruments in $CDCl_3$ and DMSO-d_6 using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. The T_gs of the calixarene derivatives were measured on a Seiko Instruments differential scanning calorimeter (DSC) Model EXSTAR6000/DSC6200 at a heating rate of 10 °C/min under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) Model EXSTAR6000/TG/DTA6200 at a heating rate of 10 °C/min under nitrogen. Matrix-assisted laser desorption ionization time-of flight mass (MALDI-TOF-MS) experiments were performed on a SHIMAZU/KRATOS MALDI-TOF-MS spectrometer using dihydroxy benzoic acid as a matrix and chloroform as a solvent.

Synthesis of Calixarenes, *C*-Methyl-calix[4]resorcinarene (1a), *C*-Decyl-calix[4]resorcinarene (1b), *C*-Dodecyl-calix[4]resorcinarene (1c), *C*-Tetradecyl-calix[4]resorcinarene (1d), and *C*-Hexadecyl-calix[4]resorcinarene (1e). A typical procedure for the reaction of resorcinol with aldehyde was as follows:[16,17] Resorcinol (33.0 g, 300 mmol) and conc. HCl (40 mL) were added to ethanol (120 mL), and the mixture was stirred at 5 °C for 30 min. Paraldehyde (12.1 g, 100 mmol) was added dropwise to the mixture, followed by refluxing for 30 min. After that, the resulting mixture was cooled to room temperature, and the solid was collected by filtration. The crude product was washed with water and methanol three times, followed by recrystallization from methanol twice and dried at 60 °C for 24 h in vacuo to obtain a colorless solid, *C*-methyl-calix[4]resorcinarene (**1a**). Yield = 49% (20. 8 g). IR (film, cm^{-1}): 3411 (ν OH), 2928, 2870 (ν CH), 1619, 1517, 1424 (ν C=C aromatic). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.32 (d, J = 6.60 Hz, 12H, CH_3), 4.44 (q, J = 6.60 Hz, 4H, CH), 6.11 (s, 4H, aromatic H), 6.77 (s, 4H, aromatic H), 8.54 (s, 8H, –OH). MALDI TOF-MS m/z 567.32 (M + Na)$^+$.

***C*-Decyl-calix[4]resorcinarene (1b):** Yield = 86% (recrystallization from methanol/water = 5/1 (v/v)). IR (film, cm^{-1}): 3237 (ν OH), 2925, 2854 (ν CH), 1619, 1500, 1460 (ν C=C aromatic). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.50 Hz, 12H, –CH_3), 1.27 (s, 56H, –C_7H_{14}–), 1.38 (s, 8H, –CH_2–CH_3), 2.21–2.28 (m, 8H, >CH–CH_2–), 3.60–4.12 (m, 4H, >CH–), 6.12 (s, 4H, aromatic H), 7.10–7.26 (m, 4H, aromatic H), 9.31–9.62 (m, 8H, –OH). MALDI TOF-MS m/z 1070.99 (M + Na)$^+$.

***C*-Dodecyl-calix[4]resorcinarene (1c):** Yield = 89% (recrystallization from methanol). IR (film, cm^{-1}): 3223 (ν OH), 2925, 2853 (ν CH), 1619, 1501, 1462 (ν C=C aromatic). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.50 Hz, 12H, CH_3), 1.27 (broad s, 64H, –C_8H_{16}–), 1.38 (broad s, 8H, –CH_2–CH_3), 2.28 (broad s, 8H, >CH–CH_2–CH_2–), 2.89 (broad s, 8H, >CH–CH_2–), 4.30 (broad s, 4H, >CH–), 6.11 (s, 4H, aromatic H), 7.10–7.26 (m, 4H, aromatic H), 9.32–9.65 (m, 8H, –OH). MALDI TOF-MS m/z 1199.71 (M + K)$^+$.

***C*-Tetradecyl-calix[4]resorcinarene (1d):** Yield = 20% (recrystallization from ethanol). IR (film, cm^{-1}): 3226 (ν OH), 2923, 2853 (ν CH), 1619, 1502, 1456 (ν C=C aromatic). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.50 Hz, 12H, CH_3), 1.26 (broad s, 80H, –$C_{10}H_{20}$–), 1.38 (broad s, 8H, –CH_2–CH_3), 2.19 (broad s, 8H, >CH–CH_2–CH_2–), 2.83 (broad s, 8H, >CH–CH_2–), 4.30 (broad s, 4H, >CH–), 6.11 (s, 4H, aromatic H), 7.10–7.26 (m, 4H, aromatic H), 9.32–9.65 (m, 8H, –OH). MALDI TOF-MS m/z 1295.96 (M + Na)$^+$.

***C*-Hexadecyl-calix[4]resorcinarene (1e):** Yield = 49% (recrystallization from ethyl acetate). IR (film, cm^{-1}): 3249 (ν OH), 2923, 2853 (ν CH), 1619, 1499, 1455 (ν C=C aromatic). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.50 Hz, 12H, CH_3), 1.26 (broad s, 96H, –$C_{12}H_{24}$–), 1.38 (broad s, 8H, –CH_2–CH_3), 2.16 (broad s, 8H, >CH–CH_2–CH_2–), 3.15 (broad s, 8H, >CH–CH_2–), 4.28 (broad s, 4H, >CH–), 6.11 (s, 4H, aromatic H), 7.10–7.26 (m, 4H, aromatic H), 9.30–9.56 (m, 8H, –OH). MALDI TOF-MS m/z 1408.19 (M + Na)$^+$.

Synthesis of Calixarenes, *C*-4-Hydroxyphenyl-calix[4]resorcinarene (1f), *C*-3-Ethoxy-4-hydroxyphenyl-calix[4]resorcinarene (1g), and *C*-2-Hydroxyphenyl-calix[4]resorcinarene (1h). The calixarene derivative **1f** was synthesized by the reaction of resorcinol (5.50 g, 50 mmol) and *p*-hydroxybenzaldehyde (6.11 g, 50 mmol) in a similar way as **1a** as mentioned above. The resulting product was washed with acetone (100 mL) three times, and dried at 60 °C for 24 h in vacuo to obtain *C*-4-hydroxyphenyl-calix[4]-resorcinarene (**1f**) (solid). Yield = 61%. IR (film, cm^{-1}): 3407 (ν OH), 3020 (ν CH), 1675, 1610, 1510 (ν C=C aromatic). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 5.41–5.56 (m, 4H, CH), 6.09–6.45 (m, 24H, aromatic H), 7.80–8.41 (m, 12H, –OH). MALDI TOF-MS m/z 876.77 (M + Na)$^+$.

***C*-3-Ethoxy-4-hydroxyphenyl-calix[4]resorcinarene (1g) (Solid):** Yield = 87% (recrystallization from ethanol). IR (film, cm^{-1}): 3407 (ν OH), 2979, 2930 (ν CH), 1614, 1519 (ν C=C aromatic). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 1.25 (t, J = 7.20 Hz, 12H, CH_3), 3.58 (s, 8H, O–CH_2–), 5.41–5.56 (m, 1H, >CH–), 6.09–6.45 (m, 20H, aromatic H), 7.80–8.41 (m, 12H, –OH). MALDI TOF-MS m/z 1057.01 (M + Na)$^+$.

***C*-2-Hydroxyphenyl-calix[4]resorcinarene (1h) (Solid):** Yield = 70%. IR (film, cm^{-1}): 3407 (ν OH), 3020 (ν CH), 1675, 1610, 1510 (ν C=C aromatic). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 5.42–5.52 (m, 4H, >CH–), 5.91–6.62 (m, 24H, aromatic H), 8.35–8.72 (m, 12H, –OH). MALDI TOF-MS m/z 876.87 (M + Na)$^+$.

Synthesis of Calixarene Derivative *O*-[(*t*-Butoxycarbonyl)-methyl]-*C*-methyl-calix[4]resorcinarene (2a). *A typical procedure*: The mixture of **1a** (0.65 g, 1.2 mmol), BBAc (2.93 g, 15

mmol), TBAB (0.16 g, 0.05 mmol) as a phase transfer catalyst, and Cs_2CO_3 (2.45 g, 7.5 mmol) as a base in NMP (10 mL) was stirred at 80 °C for 48 h. After that, hexane (30 mL) was added to the reaction mixture. The resulting mixture was washed with water (40 mL) six times. The organic phase was dried over $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by silica-gel column chromatography eluted with ethyl acetate/hexane (volume ratio 1/1) to obtain solid *O*-[(*t*-butoxycarbonyl)methyl]-*C*-methyl-calix[4]resorcinarene (**2a**). Yield = 25% (0.72 g). IR (film, cm^{-1}): 2978, 2925, 2853 (ν CH), 1758, 1731 (ν C=O), 1611, 1586, 1499, 1457 (ν C=C aromatic), 1157 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.46 (s, 84H, $–CH_3$), 3.75–4.64 (m, 20H, >CH–, $–O–CH_2–$), (m, 1H, >CH), 6.10–7.19 (m, 8H, aromatic H). MALDI TOF-MS *m*/*z* 1032.45 $(M + Na)^+$.

Synthesis of Calixarene Derivatives *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-decyl-calix[4]resorcinarene (2b), *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-dodecyl-calix[4]resorcinarene (2c), *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-tetradecyl-calix[4]resorcinarene (2d), and *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-hexadecyl-calix[4]resorcinarene (2e). The reaction of a mixture of **1b** (1.31 g, 1.4 mmol), BBAc (2.93 g, 15 mmol), TBAB (0.16 g, 0.05 mmol), and Cs_2CO_3 (2.45 g, 7.5 mmol) in NMP (10 mL) was carried out in a similar way as the synthesis of **2a**, mentioned above. The obtained residue was purified by silica-gel column chromatography eluted with ethyl acetate/hexane (volume ratio 2/1) to obtain the oily product *O*-[(*t*-butoxycarbonyl)methyl]-*C*-decyl-calix[4]resorcinarene (**2b**). Yield = 64% (1.56 g). IR (film, cm^{-1}): 2978, 2925, 2853 (ν CH), 1757, 1731 (ν C=O), 1611, 1586, 1499, 1456 (ν C=C aromatic), 1157 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.90 (t, $J = 7.0$ Hz, 3H, $–CH_2–CH_3$), 1.22 (broad s, 72H, $–C_9H_{18}–$), 1.45 (s, 36H, $–C(CH_3)_3$), 1.84 (broad s, 8H, >CH–$CH_2–$), 4.15–4.58 (m, 20H, >CH–, $–O–CH_2–$), 6.26–6.56 (m, 8.0H, aromatic H). MALDI TOF-MS *m*/*z* 1537.46 $(M + K)^+$.

***O*-[(*t*-Butoxycarbonyl)methyl]-*C*-dodecyl-calix[4]resorcinarene (2c) (Oily Product):** Yield = 51%. IR (film, cm^{-1}): 2978, 2925, 2854 (ν CH), 1757, 1730 (ν C=O), 1611, 1580, 1499, 1457 (ν C=C aromatic), 1157 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.87 (t, $J = 7.0$ Hz, 12H, CH_3), 1.24 (broad s, 88H, $–C_{10}H_{22}–$), 1.45 (s, 72H, $–C(CH_3)_3$), 1.84 (broad s, 8H, >CH–$CH_2–$), 4.15–4.59 (m, 20H, >CH–, $–OCH_2–$), 6.19–6.59 (m, 8H, aromatic H). MALDI TOF-MS *m*/*z* 1648.01 $(M + K)^+$.

***O*-[(*t*-Butoxycarbonyl)methyl]-*C*-tetradecyl-calix[4]resorcinarene (2d) (Oily Product):** Yield = 41%. IR (film, cm^{-1}): 2978, 2925, 2853 (ν CH), 1757, 1731 (ν C=O), 1611, 1586, 1499, 1457 (ν C=C aromatic), 1157 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.87 (t, $J = 7.0$ Hz, 12H, CH_3), 1.23 (broad s, 96H, $–C_{12}H_{24}–$), 1.46 (s, 72H, $–C(CH_3)_3$), 1.81 (broad s, 8H, >CH–$CH_2–$), 4.15–4.54 (m, 20H, >CH–, $–OCH_2–$), 6.19–6.58 (m, 8H, aromatic H). MALDI TOF-MS *m*/*z* 1743.02 $(M + Na)^+$.

***O*-[(*t*-Butoxycarbonyl)methyl]-*C*-hexadecyl-calix[4]resorcinarene (2e) (Solid):** Yield = 64%. IR (film, cm^{-1}): 2978, 2925, 2853 (ν CH), 1757, 1758, 1731 (ν C=O), 1611, 1586, 1499, 1457 (ν C=C aromatic), 1157 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.87 (t, $J = 7.0$ Hz, 12H, CH_3), 1.24 (broad s, 112H, $–C_{14}H_{28}–$), 1.46 (s, 72H, $–C(CH_3)_3$), 1.81 (broad s, 8H, >CH–$CH_2–$), 4.10–4.54 (m, 20H, >CH–, $–OCH_2–$), 6.19–6.58 (m, 8H, aromatic H). MALDI TOF-MS *m*/*z* 1857.06 $(M + Na)^+$.

Synthesis of Calixarene Derivatives *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-4-hydroxyphenyl-calix[4]resorcinarene (2f), *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-3-ethoxy-4-hydroxyphenyl-calix[4]resorcinarene (2g), and *O*-[(*t*-Butoxycarbonyl)methyl]-*C*-2-hydroxyphenyl-calix[4]resorcinarene (2h). The reaction of a mixture of **1f** (1.31 g, 1.4 mmol), BBAc (4.40 g, 22.5 mmol), TBAB (0.24 g, 0.075 mmol), and Cs_2CO_3 (2.45 g, 7.5 mmol) in NMP (10 mL) was carried out in a similar way as the synthesis of **2a** mentioned above. The obtained residue was purified by silica-gel column chromatography eluted with ethyl acetate/hexane (volume ratio 1/1) to obtain solid *O*-[(*t*-butoxycarbonyl)methyl]-*C*-4-hydroxyphenyl-calix[4]resorcinarene (**2f**). Yield = 35% (1.00 g). IR (film, cm^{-1}): 2978, 2933 (ν CH), 1752, 1730 (ν C=O), 1608, 1587, 1508 (ν C=C aromatic), 1156 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.47 (t, $J = 7.0$ Hz, 3H, $–C(CH_3)_3$), 4.01–4.55 (m, 20H, >CH–, $–OCH_2–$), 5.65–6.67 (m, 24H, aromatic H). MALDI TOF-MS *m*/*z* 1576.27 $(M + K)^+$.

***O*-[(*t*-Butoxycarbonyl)methyl]-*C*-3-ethoxy-4-hydroxyphenyl-calix[4]resorcinarene (2g) (Solid):** Yield = 41%. IR (film, cm^{-1}): 2978, 2933 (ν CH), 1752, 1730 (ν C=O), 1608, 1587, 1508 (ν C=C aromatic), 1156 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.42–1.49 (m, 30H, $–CH_2CH_3$, $–C(CH_3)_3$), 3.73 (broad s, 8H, $–OCH_2CH_3$), 4.10–4.61 (m, 20H, >CH–, $–OCH_2–$), 5.77–6.46 (m, 20H, aromatic H). MALDI TOF-MS *m*/*z* 1763.48 $(M + K)^+$.

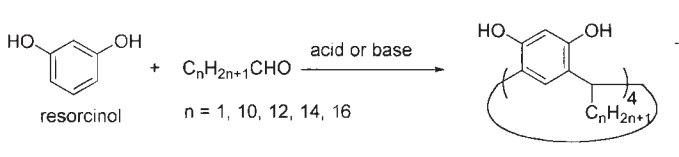
***O*-[(*t*-Butoxycarbonyl)methyl]-*C*-2-hydroxyphenyl-calix[4]-resorcinarene (2h) (Solid):** Yield = 39%. IR (film, cm^{-1}): 2978, 2933 (ν CH), 1752, 1730 (ν C=O), 1608, 1587, 1508 (ν C=C aromatic), 1156 (ν C–O–C). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.45 (s, 108H, $–CH_3$), 4.04–4.19 (m, 28H, >CH–, $–OCH_2–$), 6.20–6.90 (m, 24H, aromatic H). MALDI TOF-MS *m*/*z* 1576.09 $(M + K)^+$.

Photoinduced Deprotection of the Calixarene Derivatives 2a, 2b, 2c, 2d, 2f, and 2g. *Typical procedure*: **2a** (175 mg, 0.12 mmol) and DPSP (5 mg, 5 mol% to the *t*-butyl ester unit) were dissolved in $CHCl_3$ (1.0 mL). The solution was cast on a KBr plate and dried to a film state on the plate in vacuo. The film containing the photoacid generator was irradiated wiht a 250-W high-pressure mercury lamp (Ushio Electric Co.) without a filter under nitrogen and followed by heating at 170 °C for 1 h. The rate of decrease of the *t*-butyl ester group was measured by FT-IR spectroscopy at 1370 cm^{-1}.

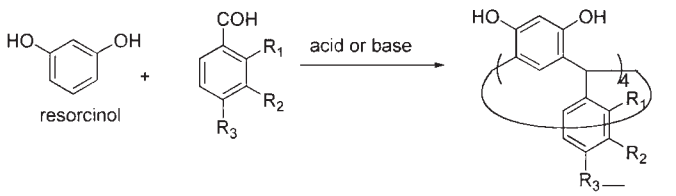
Result and Discussion

Synthesis of *C*-Alkyl-calix[4]resorcinarenes (1a–1e) and *C*-Hydroxyphenyl-calix[4]resorcinrarenes (1f–1h). Several *C*-alkyl-calix[4]resorcinarenes, **1a**–**1e**, and *C*-hydroxyphenyl-calix[4]resorcinarenes, **1f**–**1h**, were prepared by the condensation of resorcinol with acetaldehyde, decanal, dodecynal, tetradecynal, hexadecynal, 4-hydroxybenzaldehyde, 3-ethyl-4-hydroxybenzaldehyde, and 2-hydroxybenzaldehyde in the presence of hydrochloric acid as a catalyst in ethanol at 80 °C for 30 min, respectively (Scheme 2). The structures of the obtained calix[4]resorcinarenes **1a**–**1h** were confirmed by ^{1}H NMR, IR, and TOF-MS spectroscopy. These results are summarized in Table 1.

Synthesis of the Calixarene Derivatives Containing a *t*-Butyl Ester Moiety 2a–2h. The substitution reaction of **1a**–**1h** with BBAc was examined using Cs_2CO_3 as a base in the presence of tetrabutylammonium bromide as a phase transfer catalyst in NMP at room temperature for 5 h, affording the corresponding calixarene derivatives **2a**–**2h** containing *t*-butyl ester moieties in 25–64% yields (Scheme 3). The structures of the obtained **2a**–**2h** were confirmed by ^{1}H NMR, IR, and TOF-MS spectroscopy. Furthermore, the T_gs of the **2a**–**2h** were observed



C_nH_{2n+1}	calix[4]resorcinarene
n = 1	**1a**
n = 10	**1b**
n = 12	**1c**
n = 14	**1d**
n = 16	**1e**



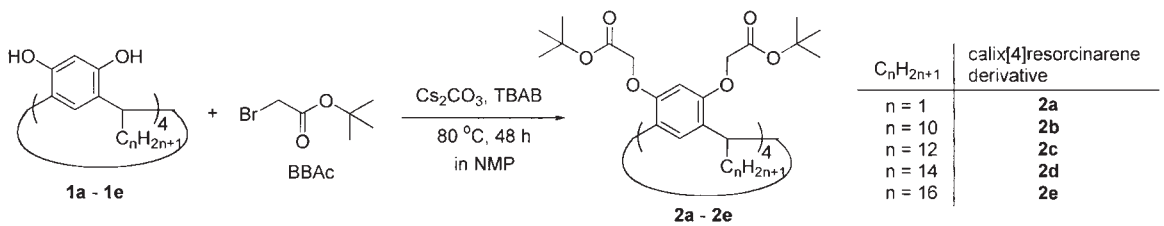
R_1	R_2	R_3	calix[4]resorcinarene
H	H	OH	**1f**
H	OCH_2CH_3	OH	**1g**
OH	H	H	**1h**

Scheme 2.

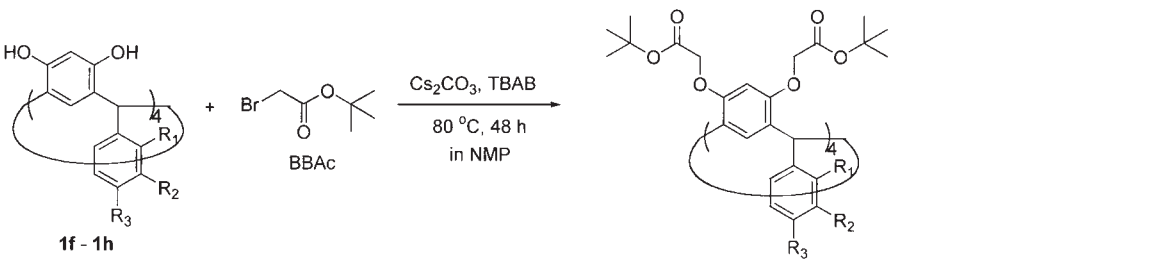
Table 1. Synthesis of Calix[4]resorcinarenes[a)]

Run	Calix[4]resorcinarene	Yield /%	T_d^{10} [b)] /°C
1	*C*-methyl-calix[4]resorcinarene (**1a**)	49[c)]	295
2	*C*-decyl-calix[4]resorcinarene (**1b**)	86[d)]	295
3	*C*-dodecyl-calix[4]resorcinarene (**1c**)	89[c)]	295
4	*C*-tetradecyl-calix[4]resorcinarene (**1d**)	20[e)]	295
5	*C*-hexadecyl-calix[4]resorcinarene (**1e**)	49[f)]	295
6	*C*-4-hydroxyphenyl-calix[4]resorcinarene (**1f**)	61[g)]	295
7	*C*-3-ethoxy-4-hydroxyphenyl-calix[4]resorcinarene (**1g**)	87[g)]	297
8	*C*-2-hydroxyphenyl-calix[4]resorcinarene (**1h**)	70[g)]	303

a) Reaction condition: resorcinol; 50 mmol, aldehydes; 50 mmol, HCl (conc. 7.0 mL) in ethanol (20 mL), reaction temperature at 80 °C for 30 min. b) Temperatures with 10% weight loss (T_d^{10}) was determined by TGA. c) Recrystallization from methanol. d) Recrystallization from methanol/$H_2O = 5/1$. e) Recrystallization from ethanol. f) Recrystallization from ethyl acetate. g) Acetnoe-insoluble part.



C_nH_{2n+1}	calix[4]resorcinarene derivative
n = 1	**2a**
n = 10	**2b**
n = 12	**2c**
n = 14	**2d**
n = 16	**2e**



R_1	R_2	R_3	calix[4]resorcinarene derivative
H	H	OCH_2COO-*t*-Bu	**2f**
H	OCH_2CH_3	OCH_2COO-*t*-Bu	**2g**
OCH_2COO-*t*-Bu	H	H	**2h**

Scheme 3.

Table 2. Synthesis of Calix[4]resorcinarene Derivatives[a)]

Run	Calix[4]resorcinarene derivatives	Yield /%	T_g[b)] /°C	T_d^{10}[c)] /°C
1	*C*-methyl-calix[4]resorcinarene derivative (**2a**)	64[d)]	130	212
2	*C*-decyl-calix[4]resorcinarene derivative (**2b**)	51[e)]	—[i)]	214
3	*C*-dodecyl-calix[4]resorcinarene derivative (**2c**)	41[e)]	—[i)]	213
4	*C*-tetradecyl-calix[4]resorcinarene derivative (**2d**)	64[f)]	—[i)]	213
5	*C*-hexadecyl-calix[4]resorcinarene derivative (**2e**)	25[g)]	50	214
6	*C*-4-hydroxyphenyl-calix[4]resorcinarene derivative (**2f**)	41[h)]	139	198
7	*C*-3-ethoxy-4-hydroxyphenyl-calix[4]resorcinarene derivative (**2g**)	27[h)]	49	199
8	*C*-2-hydroxyphenyl-calix[4]resorcinarene derivative (**2h**)	39	41	197

a) The reaction of calix[4]resorcinarenes was prepared by the substitution reaction of **1a**–**1h** with *t*-bromoacetate (BBAc) using Cs_2CO_3 as a base in the presence of TBAB as a phase transfer catalyst in NMP at room temperature for 5 h. b) Glass transition temperature (T_g) was determined by DSC. c) Temperatures with 10% weight loss (T_d^{10}) was determined by TGA. d) Recrystallization from methanol. e) Recrystallization from methanol/H_2O = 5/1. f) Recrystallization from ethanol. g) Recrystallization from ethyl acetate. h) Acetnoe-insoluble part. i) Not observed.

Table 3. Solubility of Various Calix[4]resorcinarene Derivatives[a)]

	Calix[4]resorcinearenes and calix[4]resorcinearene derivatives															
Solvent	**1a**	**2a**	**1b**	**2b**	**1c**	**2c**	**1d**	**2d**	**1e**	**2e**	**1f**	**2f**	**1g**	**2g**	**1h**	**2h**
Water	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Methanol	+	++	++	++	+	++	+	++	+−	++	−	+	−	+	−	+
2-Propanol	++	++	++	++	++	++	+	++	−	++	−	−	−	−	−	−
DMSO	+	++	+	++	+	+	+−	+	++	+	+	++	+	++	+	++
DMAc	++	++	++	++	++	++	++	++	++	++	++	++	−	++	++	++
NMP	++	++	++	++	++	++	++	++	++	++	++	++	−	++	++	++
DMF	+	++	++	++	++	++	++	++	++	++	++	++	−	++	++	++
Acetone	++	++	++	++	++	++	++	++	++	++	+−	++	+−	++	+−	++
1,4-Dioxane	−	++	++	++	++	++	++	++	++	++	−	+	−	+	−	+
Teterahydrofuran	+	++	++	++	++	++	++	++	++	++	+−	++	+−	++	+−	++
Ethyl acetate	++	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Acetonitrile	+	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
2-Heptanone	−	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Ethyl lactate	−	+	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Anisole	−	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Chloroform	−	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
PGMEA	−	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Cyclohexanone	−	++	++	++	++	++	++	++	++	++	−	++	−	++	−	++
Hexane	−	++	−	++	−	++	−	−	++	++	−	−	−	−	−	−
2.5 wt % TMAH[b)]	++	−	+−	−	+−	−	+−	−	+−	−	++	−	++	++	++	−
5.0 wt %TMAH	++	−	+−	−	+−	−	+−	−	+−	−	++	−	++	++	++	−
Film-forming property[c)]	N	G	G	N	G	N	G	N	N	G	N	G	N	G	N	G

a) ++: soluble at room temperature, +−: soluble by heating, +: partially soluble or swelling, −: insoluble. b) TMAH: teteramethylammonium hydroxide. c) G: good film forming property, N: not good film forming property.

in the range between 41–139 °C. These results are summarized in Table 2.

The Solubility and Film Forming Properties of the Calix[4]resorcinarenes 1a–1h and Calix[4]resorcinarene Derivatieves 2a–2h. The solubilities of the resulting calixarenes and calixarene derivatives were examined (Table 3). All of the calix[4]resorcinarenes and their derivatives were soluble in DMSO, but insoluble in water. Although all calix[4]resorcinarenes were soluble in an aqueous solution of 2.5 wt % TMAH and 5.0 wt % TMAH, all of their derivatives were insoluble in these solutions. It was observed that **1b**–**1e** and **2b**–**2e** had good solubility due to the pendant long chain alkyl groups. On the other hand, calix[4]resorcinarenes **1f**–**1h** had poor solubilities, although their derivatives **2f**–**2h** had good solubilities in common organic solvents. These results show that the calix[4]resorcinarene derivatives with *t*-butyl ester groups had better solubilities than those of calix[4]resorcinarenes.

Furthermore, the film forming properties were examined by the preparation as follows: **1a**–**2h** (50 mg) were dissolved in chloroform (1.0 mL), and then cast on a glass plate and dried in vacuo at room temperature. It was observed that the film forming properties were different between calix[4]resorcinarens and their derivtatives, respectively. **2a**, **2e**, **2f**, **2g**, and **2h** containing *t*-butyl ester groups had good film forming prop-

erties.

2a, **2e**, **2f**, **2g**, and **2h** had both good solubilities as well as good film forming properties. These calix[4]resorcinarene derivatives are therefore expected to be useful as positive photoresists.

The Thermal Properties of Calixarene Derivatives 2a, 2e, 2f, 2g, and 2h. The thermal decomposition of **2a**, **2e**, **2f**, **2g**, and **2h** was measured by TGA. As shown in Fig. 1, similar TGA profiles of these compounds were obtained. It was observed that the decomposition started around 200 °C due to the pendant *t*-butyl ester groups. These results showed that the thermal stability is in the following order: **2e** > **2a** > **2g** > **2f** = **2h**.

The Photoinduced Deprotection of 2a, 2f, 2e, 2g, and 2h. Wilson et al. have reported the photoinduced deprotection reaction of the polymers bearing *t*-butoxycarbonyl groups using a photoacid generator (PAG) as a chemically amplified photoresist system.[18] Based on the above, we previously examined the photoinduced deprotection of the calix[*n*]arene derivatives with *t*-butoxycarbonyl groups affording the calix[*n*]arenes, carbon dioxide, and isobutene.[13] However, the solubility change of these calixarene derivatives was not good enough due to their structures. In this article, the photoinduced deprotection of **2a**, **2e**, **2f**, **2g**, and **2h** containing *t*-butyl ester groups with a positive solubility change was examined (Scheme 4).

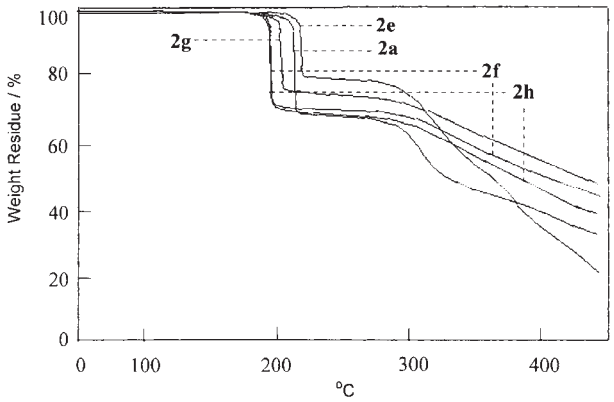
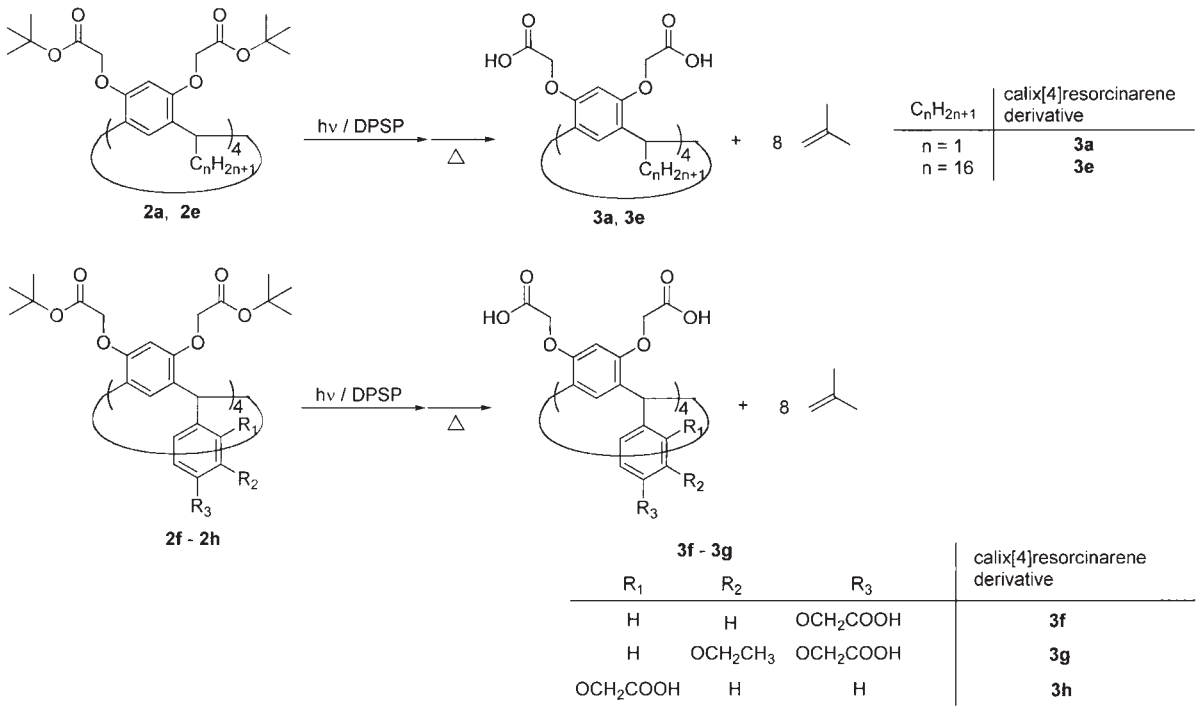


Fig. 1. TGA profiles of calix[4]resorcinarene derivatives, **2a**, **2e**, **2f**, **2g**, and **2h**.

In this reaction system, it is expected that novel alkaline-developable carboxylic acid groups containing calix[4]arene derivatives will be produced to release isobutene by the deprotection reaction. The photoinduced deprotection of **2f** was carried out under UV irradiation with a 250-W high-pressure mercury lamp in the film state prepared with 5 mol% of DPSP as a photoacid generator for 5 min, followed by heating at 170 °C. Figure 2 depicts the IR spectra before and after the photoinduced deprotection reactrion of **2f**. Before the deprotection reaction, a peak around 1700 cm^{-1} was assigned to the stretching vibration of *t*-butyl ester carbonyl groups (Fig. 2[A]). After 5 minutes of heating, the new broad peak appeared around 3000 cm^{-1}, which was assignable to the stretching vibration of carboxylic acid groups (Fig. 2[B]). This result shows that the deprotection reaction of *t*-butyl ester groups proceeded to produce the carboxylic acid groups while releasing isobutene. Further, the after 30 minutes of heating, a peak around 1680 cm^{-1} was observed, which was assigned to the stretching vibration of carboxylic acid groups (Fig. 2[C]). However, it is impossible to calculate the rate of conversion in the photoinduced deprotection reaction of **2f** from these peaks. The peak at 1370 cm^{-1} was assigned to the deformation vibration of *t*-butyl groups, and its decrease was observed with increasing heating time. From this peak, it is possible to calculate the conversion of the photoinduced deprotection reaction of **2f** measured by IR



C_nH_{2n+1}	calix[4]resorcinarene derivative
n = 1	**3a**
n = 16	**3e**

R_1	R_2	R_3	calix[4]resorcinarene derivative
H	H	OCH_2COOH	**3f**
H	OCH_2CH_3	OCH_2COOH	**3g**
OCH_2COOH	H	H	**3h**

Scheme 4.

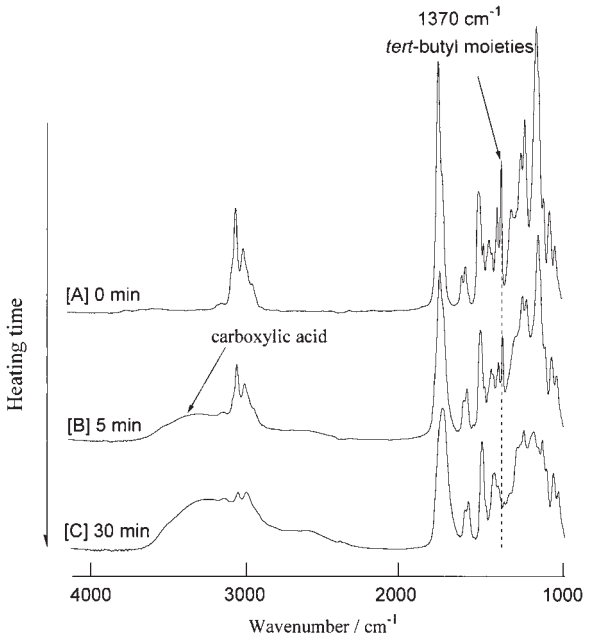


Fig. 2. IR spectra of photo-induced deprotection reaction of calix[4]resorcinarene derivative, **2f**. [A]: Before photoinduced deprotection. [B]: After 5 minutes heated at 170 °C. [C]: After 30 minutes heated at 170 °C.

spectroscopy. After 30 minutes of heating, the photoinduced deprotection reaction was completed (Fig. 2[C]).

As described above, when we determined the thermal decomposition of *t*-butyl ester groups of calix[4]arene derivatives by TGA, it was observed that the decomposition of the *t*-butyl ester moieties occurred around 200 °C. Therefore, we examined the heating temperature effect on the photo-induced deprotection reaction of **2f** with DPSP in the film state at 130, 150, and 170 °C. It was observed that the photo-induced deprotection reaction increased with the temperature. In the case of no heating, this reaction did not occur. These results are illustrated in the Fig. 3.

Furthermore, we examined the effect of the UV irradiation time on this photo-induced deprotection reaction. The film of **2f** in the presence of DPSP (5 mol%) was irradiated with a 250-W high-pressure mercury lamp in the range between 0–120 s, and then heated at 170 °C for 5 min. These results are illustrated in Fig. 4. This result shows that the conversion of the deprotection reaction increased up to 80 s of UV irradiation. However, after that, a constant conversion was obtained independent of the reaction time. In the absence of UV irradiation, this reaction did not occur. Accordingly, it seems that UV irradiation for more than 120 s is enough time, because DPSP can decompose completely in this reaction system.

Next, we examined the effect of the photoacid generator concentration in the range between 0.2–5.0 mol% in the photo-induced deprotection reaction under the same conditions. These results are illustrated in Fig. 5.

In all cases, the deprotection reaction proceeded completely in 60 min, although there was an induction period for 0.2, 1.0, and 5.0 mol%. This shows that the deprotection reaction rate increased with increasing the photoacid generator concentration.

Consequently, the photoinduced deprotection reaction proceeded smoothly using 5 mol% of DPSP upon UV irradiation for 5 min in the film state, followed by heating at 170 °C for 60 min.

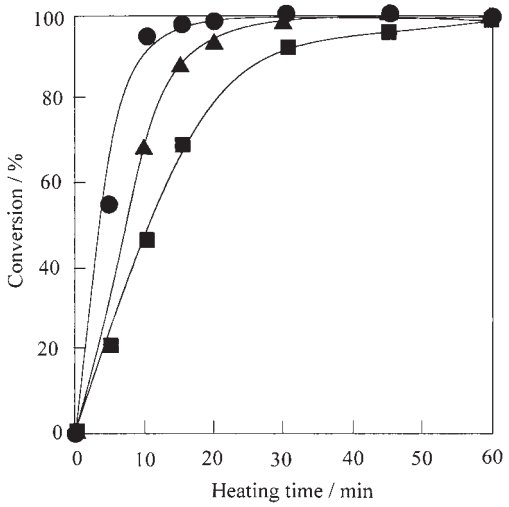


Fig. 3. Photo-induced deprotection reaction of **2f** in the presence of DPSP (5 mol%) under UV irradiation (15 mW/cm^2 at 365 nm) for 5 min, and then heated at various temperatures. [●]: 170 °C. [▲]: 150 °C. [■]: 130 °C.

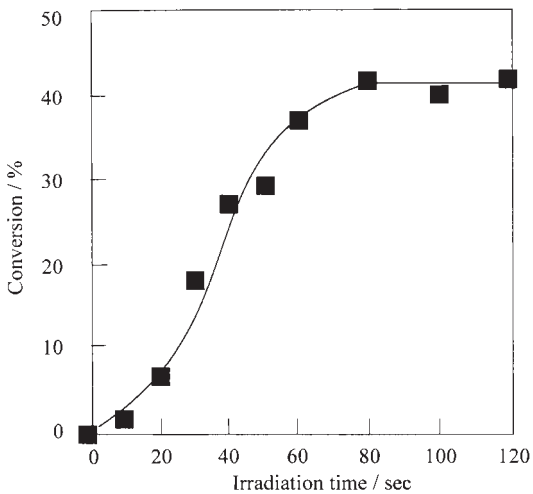


Fig. 4. The effect of the UV irradiation time in the photo-induced deprotection reaction of **2f** under UV irradiation (15 mW/cm^2 at 365 nm) for various seconds, and then heated at 170 °C for 30 min.

Furthermore, the photo-induced deprotection reaction of other calix[4]arene derivatives **2a**, **2e**, **2g**, and **2h** was performed with the same method as mentioned above, affording the corresponding calix[4]arene derivatives **3a**, **3e**, **3g**, and **3h**, respectively. As shown in Fig. 6, the rates of these deprotection reactions were as follows: **2f** = **2h** > **2a** > **2g** > **2e**. The conversion of **2a**, **2g**, **2f**, and **2h** reached over 90% within 10 minutes and that of **2e** 92% in 60 minutes. This result indicates that the rate of the photoinduced deprotection reaction of calix[4]arene derivatives can be assumed from their structure. That is, the photo-induced deprotection reaction can proceed more rapidly with an increase in the number of the deprotected groups in a calixarene derivative.

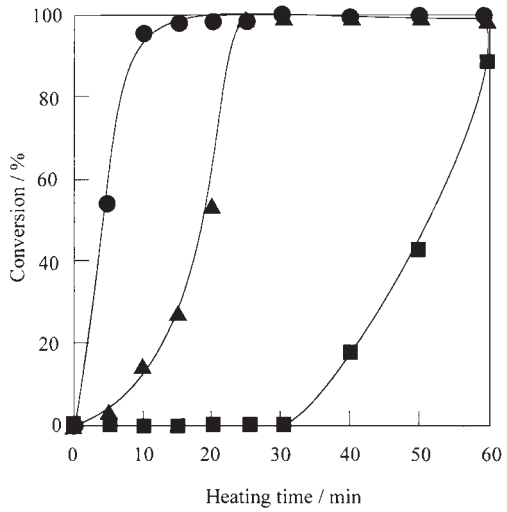


Fig. 5. The effect of the photoacid generator concentration in the photoinduced deprotection reaction of **2f** under UV irradiation (15 mW/cm^2 at 365 nm) for 5 min, and then heated at 170 °C. [●]: 5.0 mol%. [▲]: 1.0 mol%. [■]: 0.2 mol%.

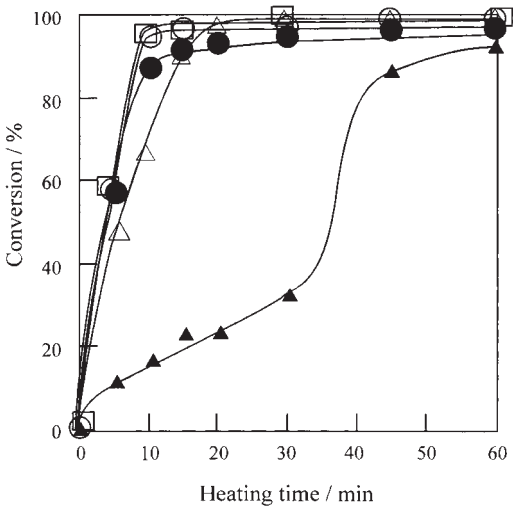


Fig. 6. The photo-induced deprotection reaction of calix[4]-resorcinarene derivatives under UV irradiation (15 mW/cm^2 at 365 nm) for 5 min, and then heated at 170 °C. [●]: **2a**. [▲]: **2e**. [○]: **2f**. [△]: **2g**. [□]: **2h**.

In summary, this article deals with the synthesis and photo-induced deprotection reaction of calix[4]resorcinarene derivatives with pendant *t*-butyl ester moieties. Certain calix[4]resorcinarenes were synthesized by the reaction of resorcinol with certain aldehydes in the presence of hydrochloric acid as a catalyst in ethanol at 80 °C for 30 min in good yields. From the reaction of these synthesized calix[4]arenes with *t*-bromoacetate, we obtained the corresponding calixarene derivatives **2a**–**2e** in 25–64% yields. **2a**, **2f**, **2g**, and **2e** showed the good solubility in the common organic solvents and good film forming properties. The photoinduced deprotection reaction of **2a**, **2f**, **2g**, and **2e** was performed in the presence of photoacid generator upon UV irradiation in the film state to afford **3a**, **3f**, **3g**, and **3e**. It is expected that **2a**, **2f**, **2g**, and **2e** might be applicable to novel positive alkaline developable resist materials with high resolution.

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