

Synthesis of Novel Chemically Amplified Materials Based on Calix[4]arene Derivatives with Acetal Moieties

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The synthesis and photoinduced deprotection reaction of calix[4]resorcinarene derivatives with pendant acetal moieties were examined. *C*-methyl[(methoxymethylcarbonyl)oxy]calix[4]resorcinarene (CRA-Acetal) and *C*-4-hydroxyphenyl[(methoxymethylcarbonyl)oxy]calix[4]resorcinarene (CRA_{ph}-Acetal) were prepared from *C*-methylcalix[4]resorcinarene (CRA) and *C*-4-hydroxyphenylcalix[4]resorcinarene (CRA_{ph}). The synthesized CRA-Acetal and CRA_{ph}-Acetal had good solubilities, good film-forming properties, and high thermal stabilities. The photoinduced deprotection reaction of CRA-Acetal and CRA_{ph}-Acetal was examined in the presence of bis[4-(diphenylsulfonio)phenyl]sulfide (DPSP) as a photo-acid generator in the film state upon UV irradiation. It was found that the deprotection reaction of acetal groups of CRA-Acetal and CRA_{ph}-Acetal proceeded smoothly without further heating to produce the corresponding calixarene derivatives, CRA-COOH and CRA_{ph}-COOH with carboxylic acid groups.

New microelectronic devices have been developed for reducing the size on computer chips. The advanced process of lithographic imaging is expressed by Moore's law.¹ In these technologies, the development of new resist materials is strongly required for the advancement of the electron beam and new lasers with shorter wavelengths, such as 193 nm and 157 nm. Furthermore, chemical amplification resist systems are among the most important photolithographic technologies for the advancement of microelectronic devices.² In this system, the generating acid from a photo-acid generator is employed by photo-irradiation, and promotes deprotection reactions of the protecting groups, such as *t*-butyl ester and acetal groups, to achieve higher resolution of the resist materials.³ It is expected that future photolithographic technologies using new irradiation method will depend on this chemical amplification system. Recently, many new chemical amplification photo-resist materials have been reported that use various polymers containing alicyclic groups, such as adamantane and norbornene, fluorine atoms, and certain protecting groups, such as trimethylsilyl and tetrahydropyranyl groups.^{4–6}

Meanwhile, applications as positive- and negative-type photoresist materials of calixarene derivatives have been reported by Ueda^{7,8} et al. and Fujita^{9,10} et al., respectively. Because, calix[*n*]arenes, such as *p*-*t*-butylcalix[8]arene (BCA), *p*-methylcalix[6]arene (MCA), and calixresorcin[4]arene (CRA), have many hydroxy groups in small-size molecules and some unique characteristic properties, such as high thermal stability, high glass transition temperature (T_g), high melting temperature (T_m), and good film-forming properties. Nishikubo et al. have reported on the synthesis and photochemical reaction of calix[*n*]arene derivatives containing photo-reactive groups, such as viny ether,¹¹ propargyl ether,¹¹ (meth)acrylate,¹² oxetane,¹² oxirane,¹² and spiro ortho ester groups,¹³ as new useful negative-type photoresist materials. We have also investigated the synthesis and photoinduced deprotection of calix[*n*]arene

derivatives containing suitable protective groups, such as *t*-butoxycarbonyl, trimethylsilyl ether, and cyclohexenyl ether as new useful chemical amplification materials.¹⁴ These results indicated that calix[*n*]arene derivatives would be applicable for useful EB- and photo-resist materials due to the small-size molecules with many photoreactive groups. Furthermore, it was found that these CRA derivatives have good matrices for resist materials, because they had good film-forming properties, excellent thermal stabilities, and higher photochemical reactivities.

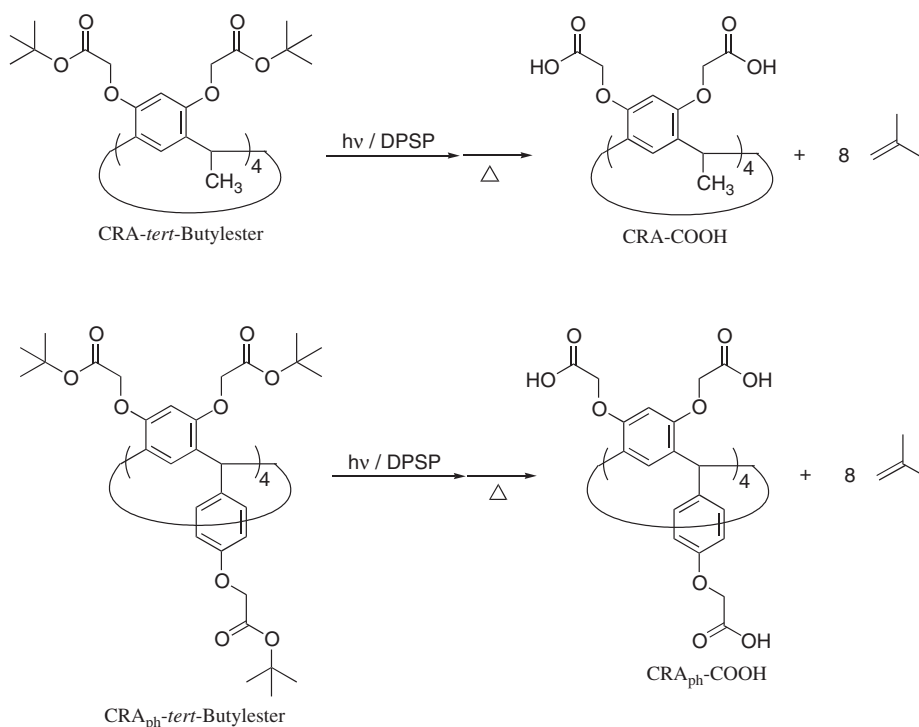
Recently, we also reported on the synthesis and photoinduced deprotection of *C*-methyl[(*t*-butylacetate)oxy]calix[4]-resorcinarene (CRA-*t*-Butylester) and *C*-4-hydroxyphenyl[(*t*-butylacetate)oxy]calix[4]resorcinarene (CRA_{ph}-*t*-butylester), as shown in Scheme 1.¹⁵ It was found that these derivatives based on CRA and CRA_{ph} showed good photochemical reactivity and good film-forming properties.

On the other hand, acetal groups are among the useful protecting groups for chemical amplification systems, because they are stable in basic aqueous solution, and would be easily decomposed by the acid in the mild conditions.

Given these backgrounds, in this article we examined the synthesis and photoinduced deprotection of CRA derivatives containing acetal moieties in a series of studies for developing chemical amplification materials based on calix[*n*]arenes.

Experimental

Materials. *N*-Methyl-2-pyrrolidone (NMP) was dried with CaH₂ and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Cesium carbonate (Cs₂CO₃), ethyl bromoacetate (EBAc), tetrahydrofuran (THF), ethyl acetate, and hexane were used without further purification. *C*-Methylcalix[4]resorcinarene (CRA) and *C*-4-hydroxyphenylcalix[4]resorcinarene (CRA_{ph}) were obtained from a reported method.¹⁵



Scheme 1.

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The ^1H NMR spectra were recorded on JEOL Model JNM α -500 (500 MHz for ^1H NMR) instruments in CDCl_3 and $\text{DMSO}-d_6$ using Me_4Si (TMS) as an internal standard reagent for ^1H NMR. The rate of the photoinduced deprotection reaction of the acetal group was measured by Real-Time-IR (RT-IR) spectroscopy (BIO RAD model Excalibur FTS3000MX spectrometers). The T_g s values of the calixarene derivatives were measured on a Seiko Instruments differential scanning calorimeter (DSC) (Model EXSTAR6000/DSC6200) at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) (Model EXSTAR6000/TG/DTA6200) at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) experiments were performed on a SHIMADZU/KRATOS MALDI-TOF-MS using dihydroxybenzoic acid as a matrix and chloroform as a solvent.

Synthesis of Calixarene Derivatives, C-Methyl(ethylcarbonyl)calix[4]resorcinarene (CRA-COOEt) and C-4-Hydroxyphenyl(ethylcarbonyl)calix[4]resorcinarene (CRA_{ph}-COOEt). A typical procedure: A mixture of CRA (5.50 g, 10 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 (25 mL) was stirred at room temperature for 12 h. EBAc (20.02 g, 120 mmol) was added slowly to the reaction mixture, and stirred at 75°C for 48 h under nitrogen. After that, ethyl acetate (100 mL) was added to the mixture, and the resulting suspension was washed five times with water (50 mL). The organic phase was dried over MgSO_4 and concentrated by a rotary evaporator. The solution was diluted with a few amounts of ethyl acetate and poured into hexane (100 mL) to precipitate a powdery compound. The obtained product was reprecipitated twice from THF into excess hexane, and dried in vacuo at 60°C for 24 h to obtain the calixarene derivative CRA-COOEt. The degree of introduction (DI) of the ethyl ester group of CRA was calculated to be 100% by ^1H NMR integration of the signal

for the aromatic protons at 6.25 ppm and methyl protons of the ethyl ester at 1.27 ppm. Yield = 11.14 g (91%). IR (film, cm^{-1}): 2978, 2972, 2874 (ν C-H), 1750 (ν C=O of ester), 1613, 1587, 1499 (ν C=C of aromatic), 1157 (ν C-O-C of ethyl ester). ^1H NMR (500 MHz, CDCl_3 , TMS) δ 1.27 (t, $J = 6.8$ Hz, 24H, $-\text{CH}_2\text{CH}_3$), 1.48 (d, $J = 5.7$ Hz, 12H, >CH-CH_3), 4.18–4.27 (m, 32H, $-\text{O-CH}_2-$, $-\text{O-CH}_2\text{CH}_3$), 4.71 (q, $J = 9.1$ Hz, 4H, >CH-CH_3), 6.25 (s, 8H, aromatic H). MALDI TOF-MS m/z ($\text{M} + \text{Na}$)⁺ Calcd for ($\text{C}_{64}\text{H}_{80}\text{O}_{24} + \text{Na}$): 1255.50. Found: 1257.41.

CRA_{ph}-COOEt (solid): The calixarene derivative CRA_{ph}-COOEt was synthesized by the reaction of CRA_{ph} (8.82 g, 10 mmol) and EBAc (30.12 g, 180 mmol) in a similar way as CRA-COOEt, as mentioned above. The DI of the resulting product CRA_{ph}-COOEt was calculated to be 100% by ^1H NMR integration of the signal for the methine and aromatic protons at 5.71–6.68 ppm, and methyl protons of the ethyl ester at 1.18–1.36 ppm. Yield = 16.82 g (89%). IR (film, cm^{-1}): 2983, 2935 (ν C-H), 1759, 1733 (ν C=O of ester), 1609, 1586, 1508 (ν C=C of aromatic), 1110 and 1080 (ν C-O-C of ethyl ester). ^1H NMR (500 MHz, CDCl_3 , TMS) δ 1.18–1.36 (m, 36H, $-\text{CH}_2\text{CH}_3$), 4.08–4.64 (m, 48H, $-\text{CH}_2\text{CH}_3$, $-\text{OCH}_2-$), 5.71–6.68 (m, 28H, >CH- and aromatic H). MALDI TOF-MS m/z ($\text{M} + \text{Na}$)⁺ Calcd for ($\text{C}_{100}\text{H}_{112}\text{O}_{36} + \text{Na}$): 1911.69. Found: 1914.62.

Synthesis of Calixarene Derivatives, C-Methyl(carboxymethoxy)calix[4]resorcinarene (CRA-COOH) and C-4-Hydroxyphenyl(carboxymethoxy)calix[4]resorcinarene (CRA_{ph}-COOH). Typical procedure: A solution of CRA-COOEt (1.23 g, 1.0 mmol), TBAB (0.32 g, 0.32 mmol), and KOH (0.73 g, 12.0 mmol) aqueous solution (10 mL) was stirred at 70°C for 6 h. After that, conc. HCl was added to the solution until pH became 2.0, and then water (50 mL) was added to the resulting mixture. The water-insoluble product was centrifuged to remove the supernatant. The obtained product was washed thrice with THF (50 mL), and dried in vacuo at 60°C for 24 h to obtain a colorless solid, CRA-COOH. Yield = 9.93 g (97%). IR (film,

cm^{-1}): 3435 (ν O–H, carbonyl), 2962, 2930 (ν C–H), 1690 (ν C=O of carboxyl), 1500 (ν C=C of aromatic). MALDI TOF-MS m/z ($M + \text{Na}$)⁺ Calcd for ($\text{C}_{48}\text{H}_{48}\text{O}_{24} + \text{Na}$): 1031.24. Found: 1035.34.

CRA_{ph}-COOH (solid): The calixarene derivative CRA_{ph}-COOH was prepared by the reaction of CRA_{ph}-COOEt (1.92 g, 1.0 mmol) in the presence of TBAB (0.54 g, 0.48 mol) in KOH (1.11 g, 18 mmol) aqueous solution (10 mL) in the similar way as **CRA-COOH**, as mentioned above. Yield = 1.50 g (96%). IR (film, cm^{-1}): 3442 (ν O–H, carbonyl), 2918 (ν C–H), 1730 (ν C=O of carboxyl), 1584, 1505 (ν C=C of aromatic). MALDI TOF-MS m/z ($M + \text{K}$)⁺ Calcd for ($\text{C}_{76}\text{H}_{64}\text{O}_{36} + \text{K}$): 1591.42. Found: 1595.46 ($M + \text{K}$)⁺.

Synthesis of Calixarene Derivatives, C-Methyl[(methoxymethylcarbonyl)calix[4]resorcinarene (CRA-Acetal) and C-4-Hydroxyphenyl[(methoxyethyl acetate)oxy]calix[4]resorcinarene (CRA_{ph}-Acetal). *Typical procedure:* A solution of CRA-COOH (2.52 g, 25 mmol), NEt₃ (4.01 g, 400 mmol), and DMF (20 mL) was stirred at room temperature for 1 h. Chloromethyl methyl ether (2.39 g, 300 mmol) was added to the solution and it was stirred under nitrogen at room temperature for 2 h. Then, ethyl acetate (100 mL) was added to the mixture, and the resulting suspension was washed five times with water (50 mL). The organic phase was dried over MgSO₄ and concentrated by a rotary evaporator to obtain a solid compound. The obtained product was washed twice with hexane, and dried in vacuo at 60 °C for 24 h to obtain the calixarene derivative **CRA-Acetal**. The degree of introduction (DI_a) of the acetal group of CRA was calculated to be 100% by ¹H NMR integration of the signal for the aromatic protons at 6.20–6.30 ppm and methyl protons of acetal at 3.30–3.50 ppm. Yield = 0.72 g (21%). IR (film, cm^{-1}): 2963, 2875, 2833 (ν C–H), 1763 (ν C=O of ester), 1613, 1587, 1501 (ν C=C of aromatic), 1153, 1078 (ν C–O–C of ester), 929 (ν O–C–O of acetal). ¹H NMR (500 MHz, CDCl₃, TMS) δ 1.51 (d, J = 11.3 Hz, 12H, >CHCH_3), 3.41 (s, 36H, –O–CH_3), 4.41 (broad s, 16H, $\text{–O–CH}_2\text{–C(O)–}$), 4.73 (d, J = 4.5 Hz, 4H, >CHCH_3), 5.28 (d, J = 20.0 Hz, 16H, $\text{O–CH}_2\text{–O}$), 6.27 (s, 8H, aromatic H). MALDI TOF-MS m/z ($M + \text{K}$)⁺ Calcd for ($\text{C}_{64}\text{H}_{80}\text{O}_{32} + \text{Na}$): 1383.46. Found: 1385.24 ($M + \text{Na}$)⁺.

CRA_{ph}-Acetal (solid): The calixarene derivative CRA_{ph}-Acetal was prepared by the reaction of CRA_{ph}-COOH (1.60 g, 10 mmol) and chloromethyl methyl ether (1.41 g, 180 mmol) in the presence of NEt₃ (2.42 g, 240 mmol) in DMF (20 mL) in a similar way as **CRA-Acetal**, as mentioned above. The DI_a was calculated to be 100% by ¹H NMR integration of the signal for the aromatic protons at 6.00–6.65 ppm and methyl protons of acetal at 3.20–3.50 ppm. Yield = 0.89 g (45%). IR (film, cm^{-1}): 2913, 2832 (ν C–H, carbonyl), 1769 (ν C=O of ester), 1608, 1584, 1507 (ν C=C of aromatic), 1153, 1074 (ν C–O–C of ester), 928 (ν O–C–O of acetal). ¹H NMR (500 MHz, CDCl₃, TMS) δ 3.32 (t, J = 25.0 Hz, 36H, –O–CH_3), 4.27–4.42 (m, 24H, $\text{Ph–O–CH}_2\text{–C(O)–}$), 4.55–4.59 (m, 4H, >CH–), 5.19–5.27 (m, 24H, $\text{O–CH}_2\text{–O–CH}_3$), 5.68–6.53 (m, 24H, aromatic H). MALDI TOF-MS m/z ($M + \text{K}$)⁺ Calcd for ($\text{C}_{100}\text{H}_{112}\text{O}_{48} + \text{K}$): 2119.73. Found: 2121.53 ($M + \text{K}$)⁺.

Photoinduced Deprotection of the Calixarene Derivatives, CRA-Acetal and CRA_{ph}-Acetal. *Typical procedure:* CRA-Acetal (145 mg, 0.12 mmol) and DPSP (5 mg, 5 mol% to acetal unit) were dissolved in CHCl₃ (1.0 mL). The solution was cast on a KBr plate and dried into a film state on the plate in vacuo for 3 h. A film containing the photo-acid generator was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co.) (15

mW/cm² at 365 nm) without a filter under nitrogen, followed by heating at 170 °C for 1 h. The rate of decrease of the acetal group at 929 cm^{-1} was measured by in situ RT-IR spectroscopy.

Results and Discussion

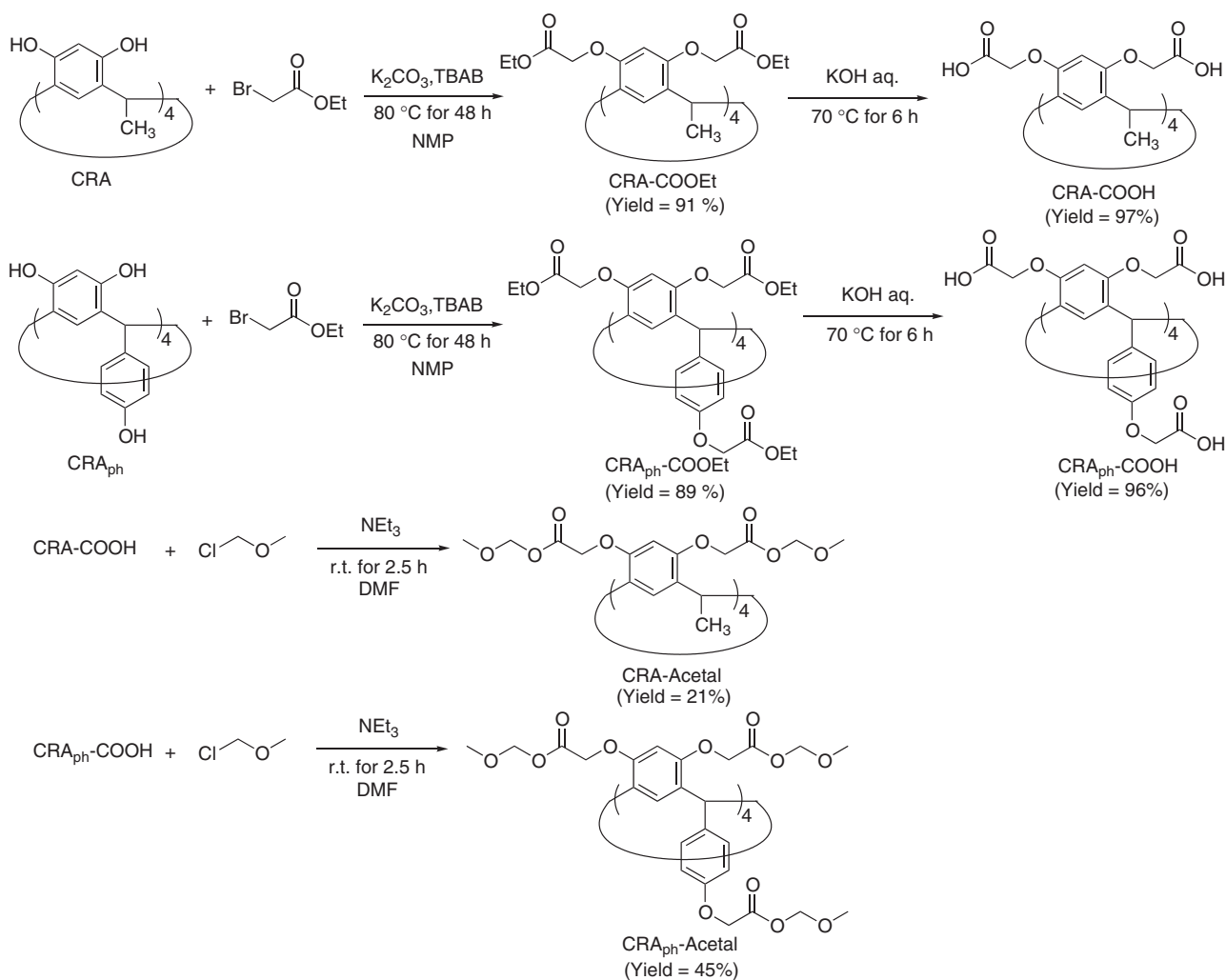
Synthesis of Calixarene Derivatives, C-Methyl[(methoxymethylcarbonyl)calix[4]resorcinarene (CRA-Acetal) and C-4-Hydroxyphenyl[(methoxyethyl acetate)oxy]calix[4]resorcinarene (CRA_{ph}-Acetal). The synthesis and properties of CRA and CRA_{ph} derivatives containing acetal groups as photoinduced deprotection groups were examined. Scheme 2 gives an outline of synthesis of the C-methyl[(methoxyethyl acetate)oxy]calix[4]resorcinarene (CRA-Acetal) and C-4-hydroxyphenyl[(methoxyethyl acetate)oxy]calix[4]resorcinarene (CRA_{ph}-Acetal). The reaction of CRA and ethyl bromoacetate was carried out using K₂CO₃ in the presence of TBAB as a phase-transfer catalyst in NMP for 48 h, affording the corresponding C-methyl[(ethyl acetate)oxy]calix[4]resorcinarene (CRA-COOEt) in 91% yield. In the same way, C-4-hydroxyphenyl[(ethyl acetate)oxy]calix[4]resorcinarene (CRA_{ph}-COOEt) was obtained from CRA_{ph} in 89% yield.

C-Methyl[(acetic acid)oxy]calix[4]resorcinarene (CRA-COOH) and C-4-hydroxyphenyl[(acetic acid)oxy]calix[4]resorcinarene (CRA_{ph}-COOH) were synthesized by hydrolyzation from CRA-COOEt and CRA_{ph}-COOEt in 97 and 96% yields, respectively.

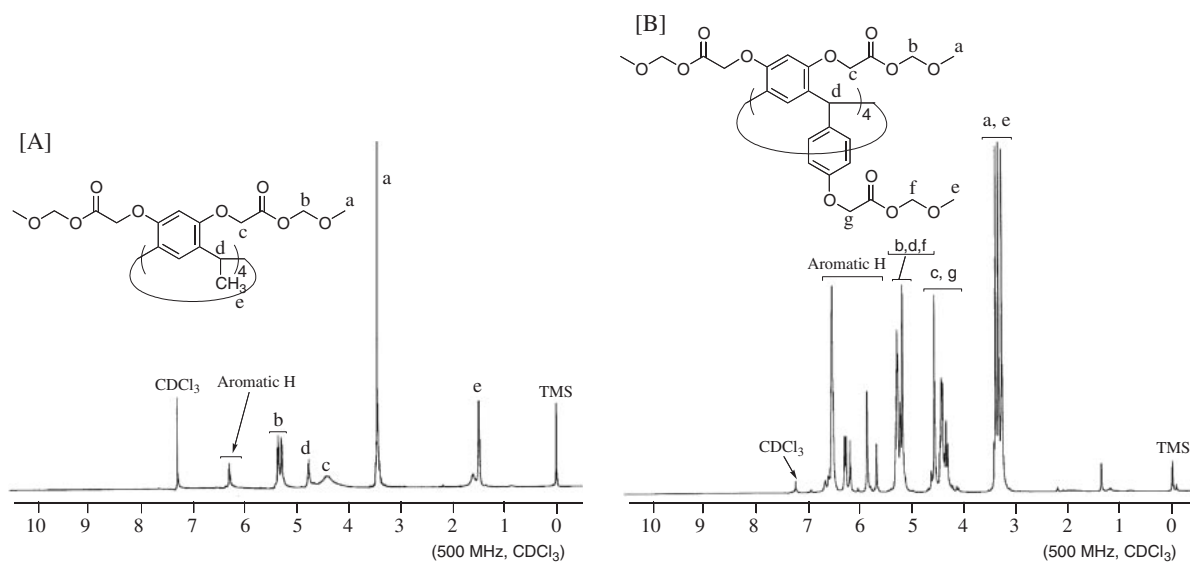
Reactions of CRA-COOH and CRA_{ph}-COOH with chloromethyl methyl ether were carried out using NEt₃ in DMF at room temperature for 2.5 h to obtain the corresponding products calixarene derivatives containing the acetal groups CRA-Acetal and CRA_{ph}-Acetal in 21 and 45% yields, respectively. The structures of all the obtained products were confirmed by the ¹H NMR, and IR spectroscopy. Figure 1 illustrates the ¹H NMR spectra of the CRA-Acetal and CRA_{ph}-Acetal. These results show the signals of CRA-Acetal and CRA_{ph}-Acetal corresponding with the structures as shown in Scheme 2.

The Solubility and Film-Forming Property of the Calix[4]resorcinarene Derivatives CRA-Acetal and CRA_{ph}-Acetal. The solubility of the resulting calixarenes and calixarene derivatives was examined (Table 1). All of the calix[4]resorcinarenes and their derivatives were insoluble in 1,4-dioxane, cyclohexane, and hexane. Although CRA-Acetal and CRA_{ph}-Acetal were insoluble in aqueous solution (2.5 wt % TMAH, 5.0 wt % TMAH, and 1.0 wt % Na₂CO₃), CRA-COOH and CRA_{ph}-COOH were soluble in these solvents. It was observed that CRA had good solubility in the common organic solvents. On the other hand, CRA_{ph} had poor solubility. However, both derivatives containing acetal moieties based on CRA and CRA_{ph} showed good solubilities in common organic solvents.

Furthermore, the film-forming property was examined by the preparation as follows: calixarenes and their derivatives (50 mg) were dissolved in chloroform (1.0 mL), after the resulting solutions were 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]resorcinarenes and their derivatives. CRA-Acetal and CRA_{ph}-Acetal had good film-forming properties. Consequently, the solubility and



Scheme 2.

Fig. 1. ¹H NMR spectra (500 MHz, CDCl₃) of the calixarene derivatives with pendant acetals. [A] CRA-Acetal. [B] CRA_{ph}-Acetal.

film-forming property of the synthesized calix[4]resorcinarene derivatives were proposed based on their structures. CRA-Ace-

tal and CRA_{ph}-Acetal had good properties for applications as useful positive working photoresist.

Table 1. The Solubility and Film-Forming Property of Calix[4]resorcinarene and Calix[4]resorcinarene Derivatives^{a)}

Solvent	Calix[4]resorcinarene and calix[4]resorcinarene derivatives							
	CRA	CRA-COOEt	CRA-Acetal	CRA-COOH	CRA _{ph}	CRA _{ph} -COOEt	CRA _{ph} -Acetal	CRA _{ph} -COOH
Water	—	—	—	+	—	—	—	+
Methanol	++	++	++	—	—	++	++	—
2-Propanol	++	++	++	—	—	++	++	—
DMSO	++	++	++	—	++	++	++	—
DMAc	++	++	++	—	+-	++	++	—
NMP	++	++	++	—	+-	++	++	—
DMF	++	++	++	—	+-	++	++	—
Acetone	++	++	++	—	—	++	++	—
1,4-Dioxane	—	—	—	—	—	—	—	—
Tetrahydrofuran	++	++	++	—	—	++	++	—
Ethyl acetate	++	++	++	—	—	++	++	—
2-Heptanone	++	++	++	—	—	++	++	—
Ethyl lactate	++	++	++	—	—	++	++	—
Chloroform	++	++	++	—	—	++	++	—
PGMEA	++	++	++	—	—	++	++	—
Cyclohexane	—	—	—	—	—	—	—	—
Hexane	—	—	—	—	—	—	—	—
2.5 wt % TMAH ^{b)}	++	—	—	++	—	—	—	++
5.0 wt % TMAH	++	—	—	++	—	—	—	++
1.0 wt % Na ₂ CO ₃	+	—	—	++	—	—	—	++
Film-forming property ^{c)}	No	Yes	Yes	No	No	Yes	Yes	No

a) ++: soluble at room temperature, +-: soluble by heating, +: partially soluble or swelling, -: insoluble. b) TMAH: tetramethylammonium hydroxide. c) Yes: good film-forming property, No: not good film-forming property.

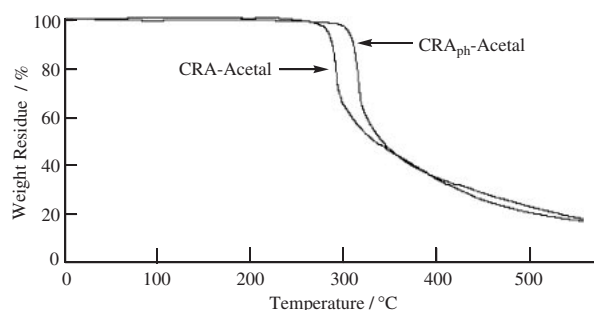


Fig. 2. TGA profiles of calixarene derivatives CRA-Acetal and CRA_{ph}-Acetal with pendant acetals.

The Thermal Property of Calixarene Derivatives CRA-Acetal and CRA_{ph}-Acetal. The thermal decomposition of CRA-Acetal and CRA_{ph}-Acetal was measured by TGA. As shown in Fig. 2, similar TGA profiles of these compounds were obtained. It was observed that the decomposition started at around 300 °C. These results showed that CRA-Acetal and CRA_{ph}-Acetal had high thermal stability. Furthermore, no apparent glass transition temperature (T_g) was observed up to 250 °C in these derivatives.

The Photoinduced Deprotection of CRA-Acetal and CRA_{ph}-Acetal. As described in the introduction, chemical amplification systems are expected as future photolithographic technologies using 193 nm ArF excimer laser, 157 nm F₂ excimer laser, and electron beam. In our previous report,¹² we examined the photoinduced deprotection of calix[*n*]arene derivatives containing *t*-butyl ester groups. It was found that the deprotection reaction of *t*-butyl ester groups proceeded to pro-

duce carboxylic acid groups while releasing isobutene by irradiation with a 250-W high-pressure mercury lamp, followed by heating at 170 °C for about 1 h. In the present work, the photoinduced deprotection of CRA-Acetal and CRA_{ph}-Acetal was examined by photo-irradiation at room temperature. In this reaction system, it is expected that novel alkaline-developable carboxylic acid groups in calix[4]arene derivatives are produced by a deprotection reaction while releasing dimethyl ethers.

The photoinduced deprotection of CRA-Acetal 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 photo-acid generator. The rate of decrease of the C–O–C groups of the acetal groups at 929 cm⁻¹ was measured using in situ by RT-IR spectroscopy. Figure 3 depicts the IR spectra before and after the photoinduced deprotection reaction of CRA. Before the deprotection reaction, some peaks at around 1700 cm⁻¹ were assignable to the stretching vibration of carbonyl groups (Fig. 3-A [a]). After 30-s irradiation, a new broad peak appeared at around 3000 cm⁻¹, which was assignable to the stretching vibration of carboxylic acid groups (Fig. 3-A [b]). This result shows that the deprotection reaction of the acetal groups proceeded to produce carboxylic acid groups while releasing dimethyl ether. Furthermore, after 90-s irradiation, a peak at around 1680 cm⁻¹ was observed, which was assignable to the stretching vibration of the carboxylic acid groups (Fig. 3-A [c]). However, it is impossible to calculate the rate of conversion in the photoinduced deprotection reaction from these peaks. The peak at 928 cm⁻¹ was assignable to the deformation vibration of *t*-butyl groups, and its decrease was observed with increasing the irradiation time. From this peak,

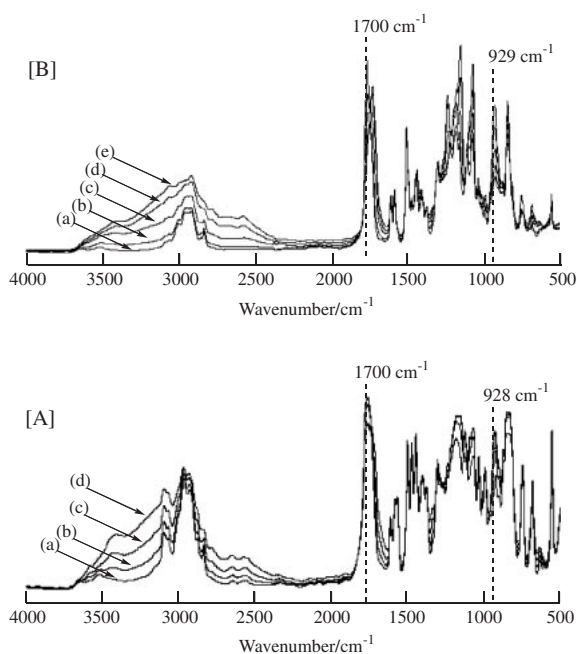


Fig. 3. IR spectra (KBr) of before and after photo-irradiation of the calixarene derivatives CRA-Acetal and CRA_{ph}-Acetal in the film state. [A] (a) CRA-Acetal, (b) after 30 s, (c) after 60 s, (d) after 90 s. [B] (a) CRA_{ph}-Acetal, (b) after 30 s, (c) after 60 s, (d) after 90 s, (e) after 120 s.

it is possible to calculate the conversion of the photoinduced deprotection reaction of CRA-Acetal measured by RT-IR spectroscopy. After 120-s of irradiation, the conversion of the photoinduced deprotection reaction reached 84% (Fig. 3-A [d]). In the same way as mentioned above, it was observed that the deprotection reaction of acetal of CRA_{ph}-Acetal proceeded to afford the corresponding product CRA_{ph}-COOH and its conversion reached 77% in 120-s (Fig. 3-B). In our previous article,¹⁵ we reported on the photoinduced deprotection reaction of CRA derivatives containing *t*-butyl ester groups; it was found that the deprotection proceeded upon UV irradiation in 5 min, followed by heating at 170 °C, but did not proceed at room temperature. In this time, the deprotection reaction of the acetal groups proceeded smoothly without heating. These results indicate that the synthesized CRA-Acetal and CRA_{ph}-Acetal have high photochemical reactivities, and are expected to be new positive working photoresist materials with higher resolutions.

Conclusion

This article deals with the synthesis and photoinduced deprotection reaction of calix[4]resorcinarene derivatives with pendant acetal groups. CRA-Acetal and CRA_{ph}-Acetal were synthesized from the *C*-methylcalix[4]resorcinarene (CRA) and *C*-4-hydroxyphenylcalix[4]resorcinarene (CRA_{ph}) in 21 and 45% yields, respectively. The synthesized CRA-Acetal and CRA_{ph}-Acetal had good solubilities, good film-forming properties, and high thermal stabilities. Furthermore, a photoinduced deprotection reaction of CRA-Acetal and CRA_{ph}-Acetal was performed in the presence of DPSP in the film state

upon UV irradiation, affording the corresponding products, CRA-COOH and CRA_{ph}-COOH, containing pendant carboxyl groups, respectively. It was expected that CRA-Acetal and CRA_{ph}-Acetal would be applicable to the applications of useful positive working photoresist materials with high resolution.

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