Bull. Chem. Soc. Jpn., ***78***, *731–737 (2005)*

Novel Molecular Photo-resists Based on the Cyclodextrin Derivatives Containing Fluorine Atoms and *t*-Butyl Ester Groups

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In this paper, we describe the syntheses, properties, and photo-induced deprotection of β-CD derivatives containing *t*-butyl ester groups and fluorine atoms. The β-CD derivative was obtained from the reaction of β-CD and *t*-butyl-α-(trifluoromethyl)acrylate. The obtained β-CD derivative had excellent solubility, good film-forming property, high thermal stability, and good transmittance with the VUV spectra. When the photo-chemical reaction of the β-CD derivative was performed with a photo acid generator in the film state upon UV irradiation, it was found that the photoinduced deprotection of *t*-butyl ester groups and decomposition of acetal moieties of gluconopyranose unit proceeded smoothly. Furthermore, we examined the patterning property of the β-CD derivative as the photo resist using triphenylsulfonium fluorosulfonate as a photo acid generator, and 2-heptanone as the solvent. From this result, it was observed that the resolution of a 100 nm line and space pattern could be obtained.

The development of new photolithography systems is strongly required for reducing the size on computer chips. It is well known that Moore's Law expresses advanced lithographic images with new shorter wavelength lasers, such as 193 nm and 157 nm and electron beams (EB).[1,2] In these technologies, the new resist materials for photolithography are required to have high transparency at the exposure wavelength and high stability under dry etching condition. Therefore, the chemical amplification resist system can be expected to be future photolithographic technology using a new irradiation method.[3–7] In this system, the generating acid was employed from a photo-acid generator when the light was irradiated, which promoted deprotection of the protecting groups, such as *t*-butyl ester, acetal, trimethylsilyl, and tetrahydropyranyl groups to achieve higher resolutions of the resist materials.[3,8–10] Recently, many new chemical amplification photoresist materials have been reported using various polymers containing fluorine atoms and alicyclic groups, such as adamantane and norbornane.[11,12] However, it seems that the molecular size is one of the important factors to achieve ultra-high resolution. Fujita et al. reported on a new type of EB-resist composed from calixarene derivatives; they achieved 50 nm-resolution as an EB-resist.[13,14]

Furthermore, we reported on the synthesis and photochemical reaction of negative-type photoresist calix[*n*]arene derivatives containing photo-polymerization groups, such as vinyl ether,[15] 2-propynyl ether,[15] (meth)acrylate,[15] oxetane,[16] oxirane,[16] and spiro orthoester groups,[17] and positive-type ones containing protective groups, such as trimethylsilyl ether,[18] cyclohexenyl ether,[18] *t*-butyl,[18,19] and acetal[20] as new useful chemical amplification materials. These results indicated that calix[*n*]arene derivatives would be applicable as useful EB- and photo-resist materials due to the small-size molecules with many photoreactive groups.

Meanwhile, cyclodextrins (CDs) are cyclic oligosaccharides containing α-1,4-linked six (α-), seven (β-), and eight (γ-) glucose units. CDs have many primary and secondary hydroxy groups in small-size molecules, as well as calixarenes. Therefore, we can consider to introduce photo-reactive groups into the CDs by chemical reactions of the hydroxy groups. Furthermore, it is expected that CDs have good thermal stability, film-forming property, and high transparency in the visible region due to their structures.

From these backgrounds, we designed new CD derivatives containing fluorine atoms and *t*-butyl ester moieties as novel high-performance photoresist materials. We examined the Michael addition reaction of β-cyclodextrin (β-CD) and *t*-butyl-α-(trifluoromethyl)acrylate (BTMA). Furthermore, the photochemical reaction and patterning property of the synthesized CD derivatives were investigated.

Experimental

Materials. 1-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethylformamide (DMSO), and dimethylformamide (DMF) were purchased from Tokyo Kasei Kogyo Co. They were dried with CaH_2 and purified by distillation before use. Chloroform ($CHCl_3$) was purchased from Wako Chemical Co. It was dried with P_2O_5, followed by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Cesium carbonate (Cs_2CO_3), tetrahydrofuran (THF), ethyl acetate, 2-heptanone, and hexane were purchased from Tokyo Kasei Kogyo Co., and used without further purification. β-cyclodextrin was purchased from Wako Chemical Co., and recrystallized from H_2O. The photo-acid generator norbor-

Published on the web April 8, 2005; DOI 10.1246/bcsj.78.731

naoicimidyl trifluorosulfonicacid (NDI-105) was obtained from Midori Kagaku Co., Ltd., and was used without further purification. *t*-butyl-α-trifluromethylacrylate (TBFA) was donated from JSR Co. It was dried with CaH_2, followed by distillation before use.

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The NMR spectra were recorded on JEOL Model JNM α-500 (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, and 475 MHz for ^{19}F NMR) instruments in DMSO-d_6 and $CDCl_3$. The T_gs 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 using dihydroxybenzoic acid as a matrix and chloroform as the solvent. The vacuum ultraviolet (VUV) was measured on a Jasco model VU-21.

Reaction of β-Cyclodextrin (β-CD) and *t*-Butyl-α-(trifluoromethyl)acrylate (BTMA). A Typical Procedure: A mixture of β-CD (0.11 g, 0.1 mmol), Cs_2CO_3 (0.0011 g, 0.005 mmol), and TBAB (0.023 g, 0.01 mmol) in DMSO (4 mL) was stirred at 25 °C for 6 h. BTMA (0.14 g, 0.70 mmol) was added slowly to the reaction mixture, and it was stirred at 25 °C for 12 h. The resulting solution was diluted with THF (2.0 mL) and poured into an aqueous solution of 2.5 wt % citric acid (80 mL) to precipitate a powdery compound. The obtained product was reprecipitated twice from THF (2 mL) into excess hexane, and dried in vacuo at 60 °C for 24 h to obtain a colorless solid β-CD derivative. The degree of the reaction of hydroxy groups of β-CD was calculated to be 38% by ^{1}H NMR integration of the signal for the methine protons of acetal moieties in the resulting CD-derivative at 4.78–4.90 ppm and methyl protons of the *t*-butyl moieties at 1.43 ppm. Yield = 0.22 g (88%). IR (film, cm^{-1}): 3435 (ν OH of CD), 1742 (ν C=O of ester), 1371 (ν C–H of *t*-butyl group), 1254 and 1114 (ν C–O–C of ester), 909 (ν cyclic ether), 842 (ν C–H of glucopyranose), and 747 (ring-breathing vibration of glucopyranose). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 1.43 (s, 11.0H, $-C(CH_3)_3$), 3.29–3.60 (m, 13.0H, –CH< of cyclodextrin and $-CH_2-$ of BTMA), 4.40–4.55 (m, 1.4H, CF_3–CH< and –OH of primary hydroxy group), 4.78–4.90 (m, 1.0H, >CH– of acetal moieties in β-CD), 5.55–5.90 (m, 1.0H, –OH of secondary hydroxy group). ^{13}C NMR (125 MHz, DMSO-d_6, TMS) δ 27.32 ($-\underline{C}H_3$), 60.04 (>CH–$\underline{C}H_2$–O of cyclodextrin), 72.13–73.10 (broad >$\underline{C}$H– of cyclodextrin), 81.70 (broad >$\underline{C}$H– of cyclodextrin), 82.77 (broad quaternary carbon), 83.95 (broad $-\underline{C}H_2-CH(CF_3)-$), 123.89 (broad $-\underline{C}F_3$), 126.09 (broad, >$\underline{C}$H–CF_3), 165.05 (>C=O). ^{19}F NMR (470 MHz, $CDCl_3$–$CFCl_3$) δ 251.7 (s, CF_3).

The Transparency of β-CD Derivative. The β-CD derivative (50 mg) was dissolved in 2-heptanone (400 mL). The solution was coated on to a substrate (MgF_2) by a bar coater with a wet film thickness of 200 nm. The coated substrate was heated at 100 °C for 90 s to remove the solvent, and its transparency was measured by VUV spectra.

Photo-Induced Deprotection of the β-CD Derivatives. Typical Procedure: β-CD (50 mg, 0.12 mmol) and NDI-105 (5 mg, 10 wt %) were dissolved in THF (0.5 mL). The solution was cast on a KBr plate and dried into a film state on the plate in vacuo for 3 h. The film containing the photo-acid generator was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co.,) (15 mW/cm^2 at 365 nm) without a filter under nitrogen, followed by heating at 120 °C for 2 h. The rate of decrease of the *t*-butyl group at 1371 cm^{-1} was measured by FT-IR spectroscopy.

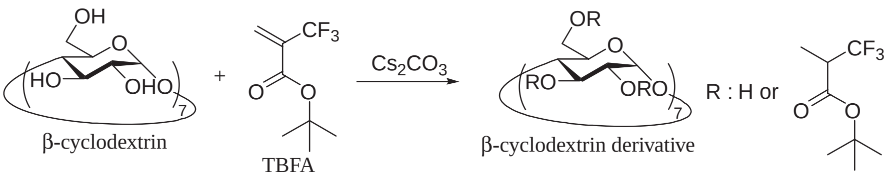
Patterning Property of β-CD Derivatives. A photo-resist was prepared from 10 wt % of β-CD derivative, 0.5 wt % of triphenylsulfonium fluorosulfonate as a photo acid generator, and 400 mL of 2-heptanone as the solvent, and it was coated on to a substrate by a bar coater with a wet film thickness of 150 nm. The coated substrate was heated at 130 °C for 90 s to remove the solvent, and exposed by a KrF laser with 72 mJ/cm^2, followed by at 100 °C for 90 s. After that, the exposed polymer film on the substrate was developed with 2.38 wt %-(tetramethylammonium hydroxide) (TMAH) for 20 s.

Results and Discussion

Synthesis of Cyclodextrin Derivatives Containing Fluorine Atoms and *t*-Butyl Ester Groups. We examined the reaction of β-cyclodextrin (β-CD) with *t*-butyl-α-(trifluoromethyl)acrylate (BTMA) to give the β-CD derivatives containing fluorine atoms, *t*-butyloxycarbonyl groups, and hydroxy groups. It is expected that the fluorine atoms induced high transparency at 150–200 nm region, *t*-butyloxycarbonyl groups induced a change of the solubility before and after photo-irradiation, and the hydroxy groups induced the hydrophilic nature of the corresponding materials backbone and provided good adhesion and substrate wettability. The reaction of β-CD and BTMA was carried out in the presence of TBAB as a phase-transfer catalyst using Cs_2CO_3 as a base for 12 h, as shown in Scheme 1. These condsitions and results are summarized in Table 1.

When the reaction was carried out in DMAC, DMF, NMP, and DMSO at 25 °C, the corresponding β-CD derivatives were obtained in 9–88% yields (runs 1–4 in Table 1), and it was observed that DMSO is the most suitable reaction solvent in this reaction system.

The structures of the reaction products were confirmed by IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and TOF-Mass spectroscopy. Figure 1 illustrates the ^{1}H NMR spectrum of the β-CD derivative obtained by this reaction in DMSO (run 4 in Table 1). This figure shows signals assignable to methyl protons of the *t*-butyl moieties at 1.43 ppm, methine and methylene protons of the β-CD and BTMA moieties at 3.29–3.60 ppm, the primary



Scheme 1.

hydroxy protons at 4.40–4.55 ppm, the methine protons of the acetal moieties of β-CD at 4.78–4.90 ppm, and the secondary hydroxy protons of β-CD at 5.55–5.90 ppm, respectively. Furthermore, in the IR spectrum, the β-CD derivative shows the characteristic peaks at 1742 and 1371 cm^{-1}, assignable to the C=O of carbonyl moieties and the C–H of *t*-butyl moieties, respectively. These results mean that the obtained β-CD derivative has trifluoromethyl groups and *t*-butyloxycarbonyl groups, as shown in Scheme 1. Figure 2 depicts the MALDI-TOF mass spectrum of the β-CD derivative (run 4 in Table 1); it was found that the mass differences in the peaks were exactly the molar mass of the *t*-butyl-α-(trifluoromethyl)acrylate repeating units (M = 196), and the degrees of introducing the BTMA moieties were in the range between 4 (β-CD(4)) and 10 (β-CD(10)). That is, the Michael addition reaction of BTMA to hydroxy groups of β-CD was performed.

Table 1. The Reaction of β-CD with BTMA[a)]

Run	Solvent	Reaction temperature	Yield[b)]	DR-1[c)]	DR-2[d)]
		°C	%	%	%
1	DMAc	25	21	31.3	28.0
2	DMF	25	9	23.4	25.5
3	NMP	25	32	41.4	24.0
4	DMSO	25	88	75.7	17.6
5	DMSO	40	57	54.0	18.0
6	DMSO	60	48	44.4	12.5
7	DMSO	80	39	40.4	13.5

a) The reaction was carried out in the presence of TBAB as a phase transfer catalyst for 24 h. b) Hexane-insoluble parts. c) DR-1: the degree of the reaction of primary hydroxy groups. d) DR-2: the degree of the reaction of secondary hydroxy groups.

Furthermore, the degrees of the reaction of primary hydroxy groups (DR-1) and secondary hydroxy groups (DR-2) of the β-CD derivative (run 4 in Table 1) were calculated to be 75.7 and 17.6% by ^{1}H NMR integration of the signal for the primary hydroxy protons, secondary hydroxy protons, and methyl protons of the *t*-butyl moieties, respectively. It was observed that the values of DR-1 and DR-2 increased along with the yields. Furthermore, we examined the effect of the reaction temperatures on this reaction, and it was found that the yields of the reaction products decreased with increasing reaction temperatures (runs 5–7 in Table 1). It might be indicated that the polymerization of TBFA proceeded at higher reaction temperature. Consequently, the appropriate temperature for this reaction of β-CD with BTMA was 25 °C under this reaction condition.

Thermal Property of the $\boldsymbol{\beta}$-CD Derivative. The thermal decomposition of the obtained β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) was measured by TGA, as shown in Fig. 3. It was observed that the decomposition started at around 165 °C due to the pendant *t*-butyl ester groups. These results showed that β-CD derivative had reasonable thermal stability. Furthermore, the glass transition temperature (T_g) of this derivative was determined by DSC. Generally, T_gs of the fluorine-containing polymers decreased with increasing the fluorine-contents. However, the high T_g of the β-CD derivative was observed to be 126.5 °C due to its cyclic structure. These results show that the obtained CD derivatives had suitable properties as photo-resist materials.

Solubility and Film-Forming Property of the $\boldsymbol{\beta}$-CD Derivative. The solubility of the resulting β-CD derivative was examined (Table 2). The β-CD derivative was insoluble

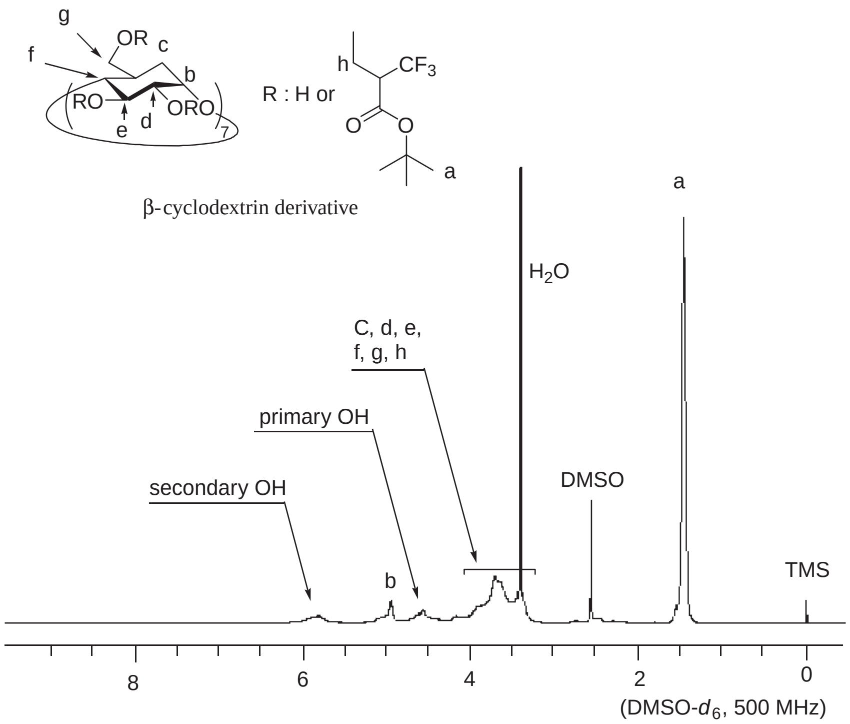


Fig. 1. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) obtained by the reaction of β-cyclodextrin (β-CD) and *t*-butyl α-(trifluoromethyl)acrylate (BTMA).

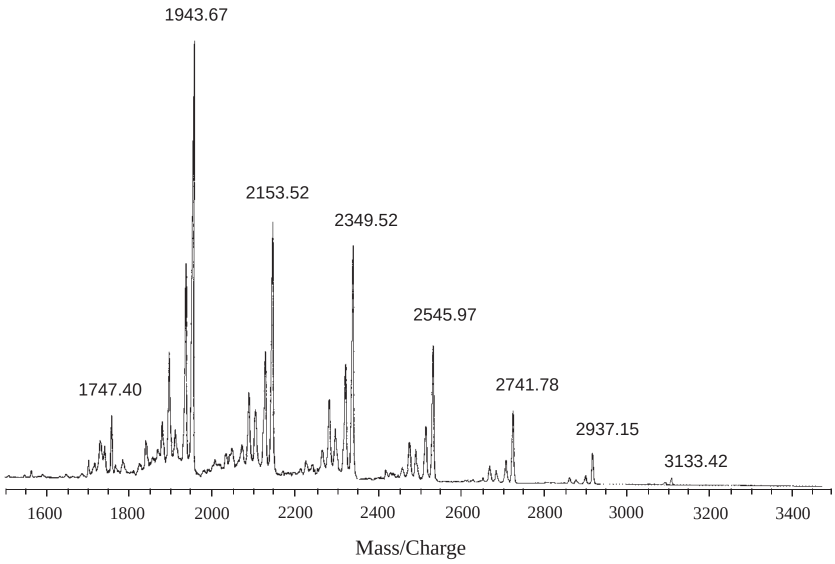


Fig. 2. MALDI-TOF mass spectrum of β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1).

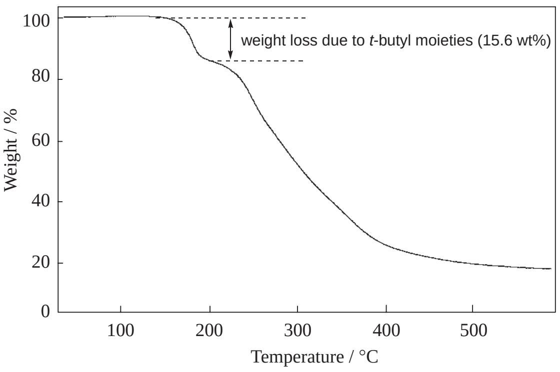


Fig. 3. TGA profiles of β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1).

Table 2. The Solubility of β-CD Derivative[a)]

Solvent	Solubility	Solvent	Solubility
Water	−	Ethyl acetate	++
Methanol	++	Acetonitrile	−
2-Propanol	+	2-Heptanone	+
DMSO	++	Anisole	+−
DMAc	++	Chloroform	++
NMP	++	PGMEA[b)]	+
DMF	++	Cyclohexane	++
Acetone	++	Hexane	−
1,4-Dioxane	++	2.5 wt % THAH[c)]	−
THF	++	5.0 wt % TMAH	−

a) ++: soluble at room temperature, +−: soluble by heating, +: partially soluble or swelling, −: insoluble. b) PGMEA: propylene glycol monomethyl ether acetate. c) TMAH: tetramethylammonium hydroxide.

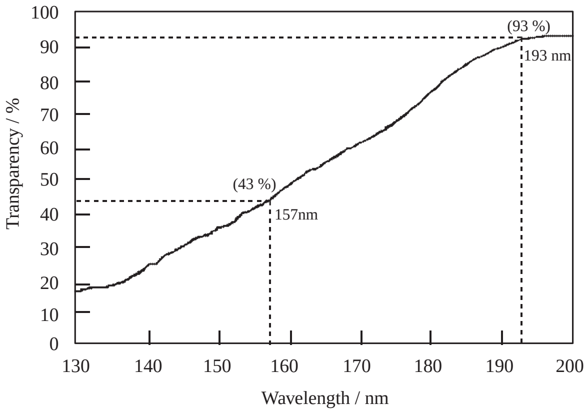


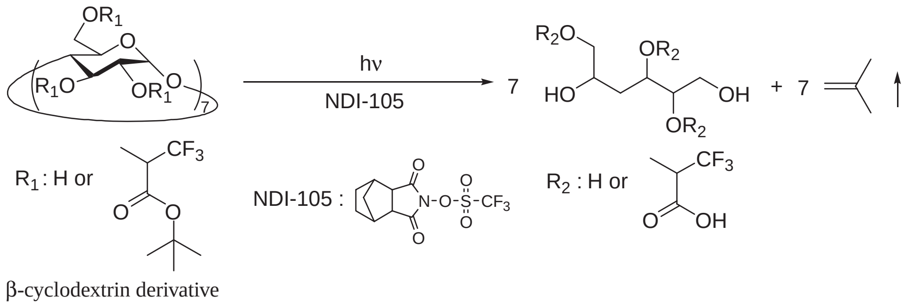
Fig. 4. VUV spectrum of β-CD derivative film (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) (film thickness: 150 nm).

in water and the aqueous solution (2.5 wt % TMAH and 5.0 wt % TMAH), but soluble in common organic solvents, except for acetonitrile and hexane.

Furthermore, the film-forming property was examined by the following preparation: the β-CD derivative (50 mg) was dissolved in chloroform (1.0 mL), and then the resulting solutions were cast on a glass plate and dried in vacuo at room temperature. It was observed that the β-CD derivative had good film-forming property and good transparency in the visible region. Consequently, the synthesized β-CD derivative basically has excellent properties for applications as a useful positive working photoresist.

The Transparency of the β-CD Derivative. The transmittance of the β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) was measured with a VUV spectrometer, and it was observed that the transmittance of the resulting β-CD derivative film was 43% at 157 nm and 93% at 193 nm, respectively, as shown in Fig. 4. This means that the β-CD derivative with pendant *t*-butyl ester groups can be used as single-layer photoresists for 193-nm lithography.

Photo-Induced Deprotection of the β-CD Derivative. The photo-induced deprotection of the β-CD derivative containing *t*-butyl ester groups (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) with a positive solubility change was exam-



Scheme 2.

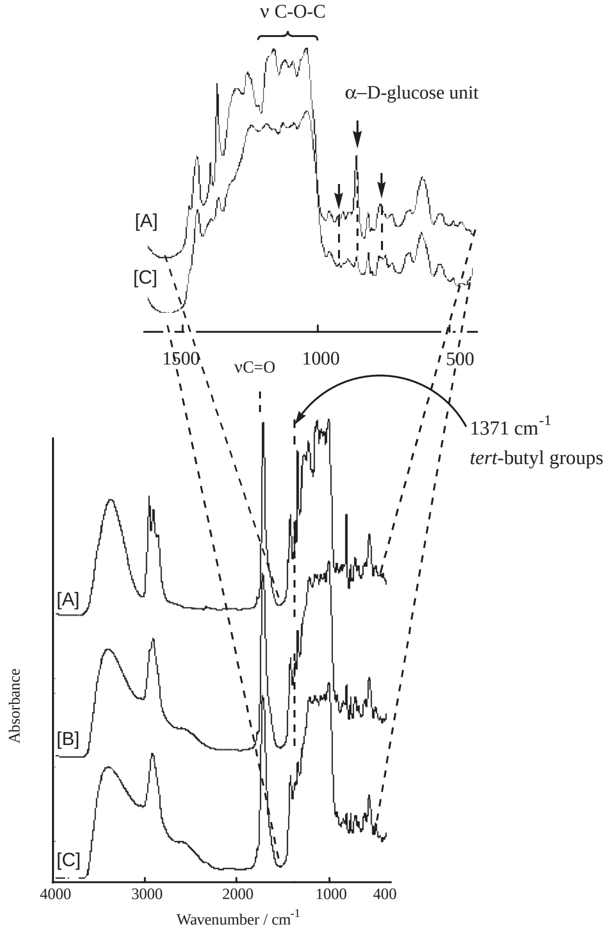


Fig. 5. Change of IR spectra before and after the photo-induced deprotection of β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1). [A]: Before the deprotection. [B]: After 15 min of heating. [C]: After 30 min of heating.

ined (Scheme 2). In this reaction system, it is expected that novel alkaline-developable carboxylic acid groups will be produced to release isobutene by deprotection. Photo-induced deprotection was carried out under UV irradiation with a 250-W high-pressure mercury lamp in a film state prepared with 5 mol % of NDI-105 as a photoacid generator for 5 min, followed by heating at 120 °C for 2 h. Figure 5 depicts the IR spectra before and after the photo-induced deprotection of the β-CD derivative. Before deprotection, a peak at around 1700 cm^{-1} was assigned to the stretching vibration of *t*-butyl ester carbonyl groups (Fig. 5[A]). After 15 min of heating, a new broad peak appeared around at 3000 cm^{-1}, which was assignable to the stretching vibration of carboxylic acid groups (Fig. 5[B]). This result shows that deprotection proceeded to produce the carboxylic acid groups while releasing isobutene. Furthermore, after 30 min of heating, a peak around at 1680 cm^{-1} was observed, which was assigned to the stretching vibration of carboxylic acid groups (Fig. 5[C]). However, it was impossible to calculate the rate of the conversion in the photo-induced deprotection from these peaks. The peak at 1370 cm^{-1} was a deformation vibration of *t*-butyl groups, and its decrease was observed with increasing the heating time. From this peak, it was possible to calculate the conversion of the photo-induced deprotection of the β-CD derivative by IR spectroscopy. After 120 min of heating, the photo-induced deprotection was completed (Fig. 5[C]). Furthermore, before irradiation, it was observed that the peaks at around 1100 cm^{-1} corresponded to the stretching vibration of the C–O–C groups, and the peaks at 909, 842, and 747 cm^{-1} were assignable to the stretching vibration of cyclic ether, the deformation vibration of C–H of the β-CD moieties, and the ring-breathing vibration of glucopyranose moieties, respectively.[21,22] These characteristic peaks of the β-CD derivative decreased after irradiation, as shown in this figure. This result shows that the decomposition reaction of the acetal moieties of glucopyranose proceeded to produce new hydroxy groups, as shown in Scheme 2. Furthermore, the characterstic signals assignable to methyl protons of the *t*-butyl moieties and methine protons of the acetal moieties of β-CD at 1.43 ppm and 4.78–4.90 ppm completely disappeared after photo-irradiation of the β-CD derivative, which were confirmed by ^{1}H NMR spectroscopy of the irradiated product. This irradiated product was treated with an aqueous solution of 2.5 wt % tetramethylammonium hydroxide, and its solubility was very good.

On the other hand, we observed that the decomposition of *t*-butyl ester groups of the obtained β-CD derivative occurred around at 160 °C by the TGA. Therefore, the heating-temperature effect on the photo-induced deprotection of the β-CD derivative was examined at 80, 120, and 160 °C in the film state. These results are illustrated in Fig. 6. It was observed that the rate of the photo-induced deprotection of β-CD increased with the heating temperature. However, in the absence of heating after photo-irradiation, this reaction did not occur.

Patterning Property of the β-CD Derivative. The patterning property of the β-CD derivative was measured by an SEM image obtained from a film prepared as follows. A pho-

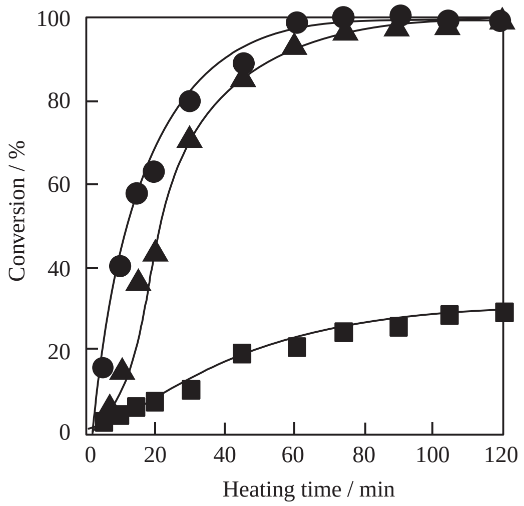


Fig. 6. Effect of heating time on the photo-induced deprotection of β-CD derivative film (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) under UV irradiation (15 mW/cm^2 at 365 nm) without a filter under nitrogen and followed by the heat at certain temperature for 2 h. [●]: 160 °C, [▲]: 140 °C, [■]: 80 °C.

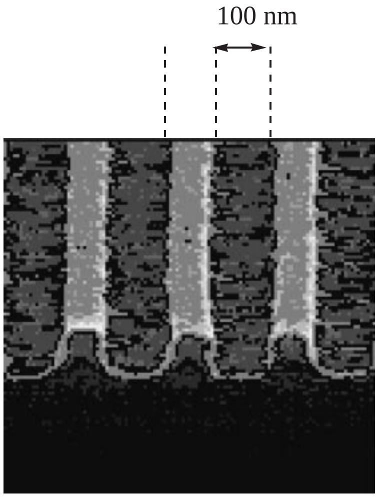


Fig. 7. SEM image obtained from the film prepared from β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1) and triphenylsulfonium fluorosulfonate as a photo acid generator.

to-resist was prepared from the β-CD derivative (DR-1 = 75.7%, DR-2 = 17.6%, run 4 in Table 1), triphenylsulfonium fluorosulfonate (TPSFS) as a photo acid generator, and 2-heptanone as the solvent, and it was coated on to a substrate by a bar coater with a wet film thickness of 150 nm. It is expected that TPSFS is a useful photo acid generator, just as the NDI-105. The coated substrate was exposed by KrF, followed by heating at 100 °C for 90 s. After that, the exposed polymer film on the substrate was developed with 2.38 wt %-TMAH for 20 s. As a result, a clear pattern with a 100 nm line width was obtained, as shown in Fig. 7.

Conclusion

This article deals with the synthesis and photo-induced deprotection of β-CD derivatives containing *t*-butyl ester groups and fluorine atoms. β-CD derivatives were synthesized by the reaction of β-CD with *t*-butyl-α-(trifluoromethyl)acrylate. The synthesized β-CD derivatives had good solubility, good film-forming properties, and good transmittance with VUV spectra. When the photo-irradiation reaction of β-CD dedrivatives was examined in the presence of a photo acid generator in the film state upon UV irradiation, the photo-induced deprotection of *t*-butyl ester and a decomposition reaction of the acetal moieties of gluconopyranose proceeded, and it was observed that the obtained product had good solubility in an alkali aqueous solution. Furthermore, the resolution of a 100 nm line and space pattern was obtained using the photo-resist prepared by the β-CD derivative and the photo acid generator. It was expected that the synthesized β-CD derivative would be applicable to applications of useful positive working photo-resist materials.

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