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Development of Novel Photo-Functional Materials Based on Cyclic Oligomers

By Hiroto KUDO and Tadatomi NISHIKUBO*

Novel photo-functional materials, such as refractive-index-changing materials, argon fluoride (ArF) resist materials, and electron beam (EB) resist materials, were designed based on the structures of calixarenes, cyclodextrin, and noria. The synthesis and refractive-index properties of calixarene derivatives containing photo-reactive groups, including azobenzene, norbornadiene, anthracene, cinnamate, and chalcone, were examined, and refractive-index changes (Δn_D's) of between 0.007 and 0.061 were observed. The synthesis and patterning properties of a single-layer ArF photoresist system of β-CD derivative containing *t*-butyl ester and fluorine were examined, and a well-resolved 100 nm line and space pattern was obtained on a silicon wafer. A new ladder-like macrocycle, noria (water wheel in Latin), was also synthesized and its application as an EB resist material was examined. The noria derivatives noria-COO^{t}Bu containing *t*-butyl ester groups, noria-BOC containing *t*-butyloxycarbonyl group, and noria-acetal containing acetal groups had good physical properties and photo-reactivity. EB-resist based on noria-COO^{t}Bu and noria-BOC provided clear line and space patterns at a resolution of 70 and 50 nm, respectively.

KEY WORDS: Refractive Index / Calixarene / Cyclodextrin / ArF Resist / Noria / EB Resist /

The development of novel photo-functional materials has contributed substantially to progress in the electronic and optoelectronic industries. Photo-reactive groups, such as radical- or cation-polymerizable groups, photo-isomerizable groups, and photo-removable groups, are useful for obtaining ultraviolet (UV)-cured resins, refractive-index-changing materials, and photo-resist materials, respectively. The physical properties of photo-functional materials, such as film-forming characteristics, thermal stability, mechanical properties, and photo-reactivity, depend primarily on the polymer or oligomer structure. Generally, the photochemical reactivity increases with decreasing glass transition temperature (T_g), due to increase of the molecular motion of polymer chains and functional groups.

The photo-chemical reactivity of oligomers is usually greater than that of polymers, due to the lower T_g of oligomers compared with polymers. However, the mechanical properties, thermal stability and film-forming properties of oligomer derivatives are inferior to those of polymer derivatives. However, if a linear oligomer is changed to a cyclic oligomer by coupling reaction of the two ends, the physical properties of the resulting cyclic oligomer are expected to be superior to those of the linear oligomer. Therefore, we considered that photo-functional cyclic oligomers might combine the advantages of photo-functional polymers and photo-functional oligomers. That is, photo-functional cyclic oligomers might have both high photo-chemical reactivity and good physical properties.

Calixarenes are typical cyclic oligomers containing many hydroxyl groups, and are prepared easily by the reaction of phenols with aldehydes (Scheme 1).[1]

Although it is well known that calixarenes are attractive materials for use as host molecules in the field of host-guest chemistry,[2] they also seem to be applicable as photo-functional materials, because they are small molecules containing many reactive hydroxyl groups, and have intriguing combinations of properties, including high thermal stability, high T_g, and high melting temperature (T_m).[3] Certain calixarenes and their derivatives are amorphous in the solid state and have good film-forming properties.[4,5] Nishikubo *et al.* reported the synthesis, properties, and photo-reactivity of photo-functional materials based on calixarenes containing polymerizable groups, such as vinyl ether,[3] methacrylate,[6] propargyl ether,[3] oxetane,[7] oxirane,[7] and spiro ortho-ester groups.[8] It was shown that these calixarene derivatives have excellent thermal stability and high photo-chemical reactivity. Figure 1 illustrates the results of photo-cationic polymerization of calixarene derivatives containing oxirane groups derived from *t*-butylcalix[8]arene (BCA), *p*-methylcalix[6]arene (MCA), and calixresorcin[4]arene (CRA).[7]

It was observed that the order of photochemical reactivity is as follows: CRA derivative > BCA derivative > MCA derivative. This indicates that the photochemical reactivity increased with increasing numbers of photo-reactive groups and decreasing size of the calixarene structure, *i.e.*, with increasing density of the photo-chemical groups.

Furthermore, cyclodextrins (CDs)[9] are well-known cyclic oligosaccharides containing six (α-), seven (β-), or eight (γ-) α-1,4-linked glucose units (Scheme 2).

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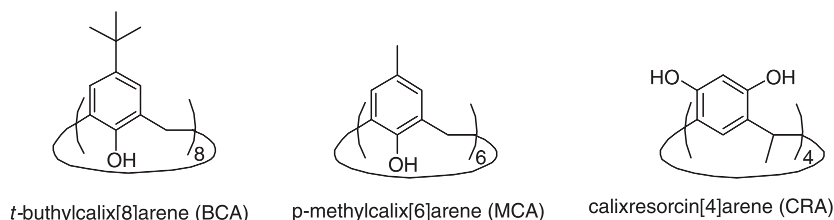


Scheme 1. Calixarenes.

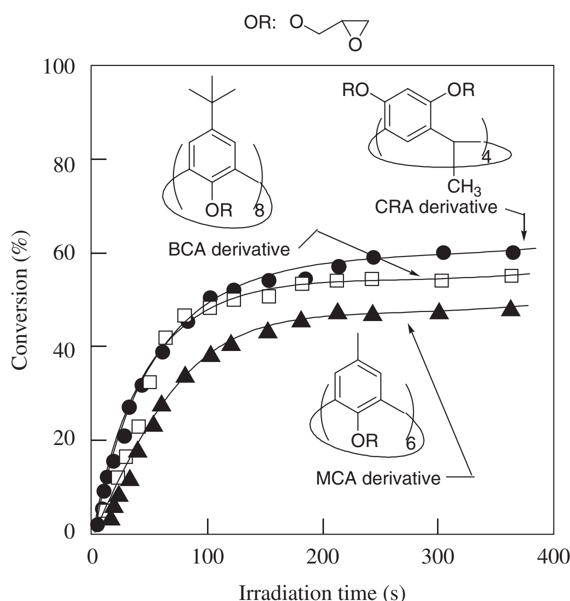
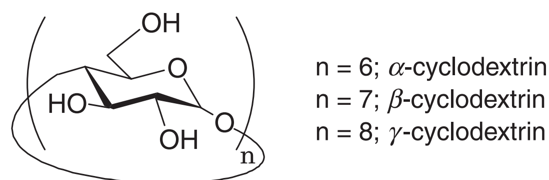


Figure 1. Rates of photochemical reaction of calixarenes containing pendant oxirane groups with DPSP (5 mol %): (●) BCA derivative, (□) MCA derivative, and (▲) CRA derivative.



Scheme 2. Cyclodextrin.

CDs contain many reactive primary and secondary hydroxyl groups, like calixarenes. Therefore, we also considered the introduction of photo-reactive groups on the hydroxyl groups of CDs to obtain candidate photo-functional materials.

Very recently, we also synthesized a new ladder cyclic oligomer, which we named noria (water wheel in Latin), by the condensation reaction of resorcinol and 1,5-pentanedial and investigated its application as a novel electron beam (EB) and extreme ultraviolet (EUV) resist material.

In this review article, we describe the synthesis, physical properties, and photo-chemical reactivity of photo-functional cyclic oligomers derived from calixarene, CD, and noria. Their applications to refractive-index-changing materials, ArF resist materials, and EB resist materials are also described.

CALIXARENE DERIVATIVES AS REFRACTIVE-INDEX-CHANGING MATERIALS

Synthesis, Physical Properties, and Refractive-Index-Changing Properties of Calixarene Derivatives

Refractive-index-changing materials are required for write-read-erase recording, switching devices, optical waveguides, memories, and holographic image recording.[10–13]

Nishikubo *et al.*[14–17] reported that polymers containing certain norbornadiene (NBD) moieties in the main and side chains showed high photochemical reactivity, and had a high photo-energy storage capability. NBD is converted to quadricyclane (QC) under UV irradiation, and the resulting polymers are expected to be good photo-energy transformation systems. Furthermore, Nishikubo[14] also proposed that polymers containing NBD would be useful as novel refractive-index-changing materials. Scheme 3 summarizes reported studies on refractive-index-changing materials. Horie and Nishikubo[18] experimentally confirmed a marked refractive-index change upon photo-irradiation of poly(methyl methacrylate) containing 2-phenyl-2,5-norbornadiene moieties; the value of the refractive index change (Δn_D) was about 0.01. Furthermore, Horie *et al.*[19] reported large Δn_D's (0.05–0.06) of films of poly(methyl methacrylate) doped with NBD derivatives and poly(vinyl ether)s bearing NBD moieties. They also found that poly(vinyl cinnamate) showed a large Δn_D (0.037) upon photodimerization.[20] Natansohn *et al.*[21,22] reported that the Δn_D upon photo-isomerization of polymer films containing azobenzene was about 0.01. Miyata *et al.*[23] reported that 4-*N*,*N*-dimethylaminophenyl-*N*-phenyl nitrone doped in poly(methyl methacrylate) films showed Δn_D's of 0.026–0.028. Sakurai *et al.*[24–28] found that films containing certain nitrone derivatives showed Δn_D's of 0.014–0.023 upon photo-isomerization. Knol and Müllen[29,30] showed that polymers with pendant 9-substituted anthracene (AT) had large Δn_D's in the range of 0.013 to 0.076 upon photo-dimerization of AT. Furthermore, materials which show a refractive index increase after photo-irradiation have been reported by several researchers. Toussaere *et al.*[31] reported that the photo-chemical isomerization of thiocyanate moieties under photo-irradiation; the Δn_D reached about 0.03. Horie *et al.*[32] examined films doped with phenylazide and found an Δn_D after photo-irradiation of 0.0161. Kern *et al.*[33,34] examined the photo-Fries rearrangement based on the polymer, and observed Δn_D's in the range from 0.042 to 0.070. Sakurai *et al.*[35] reported that

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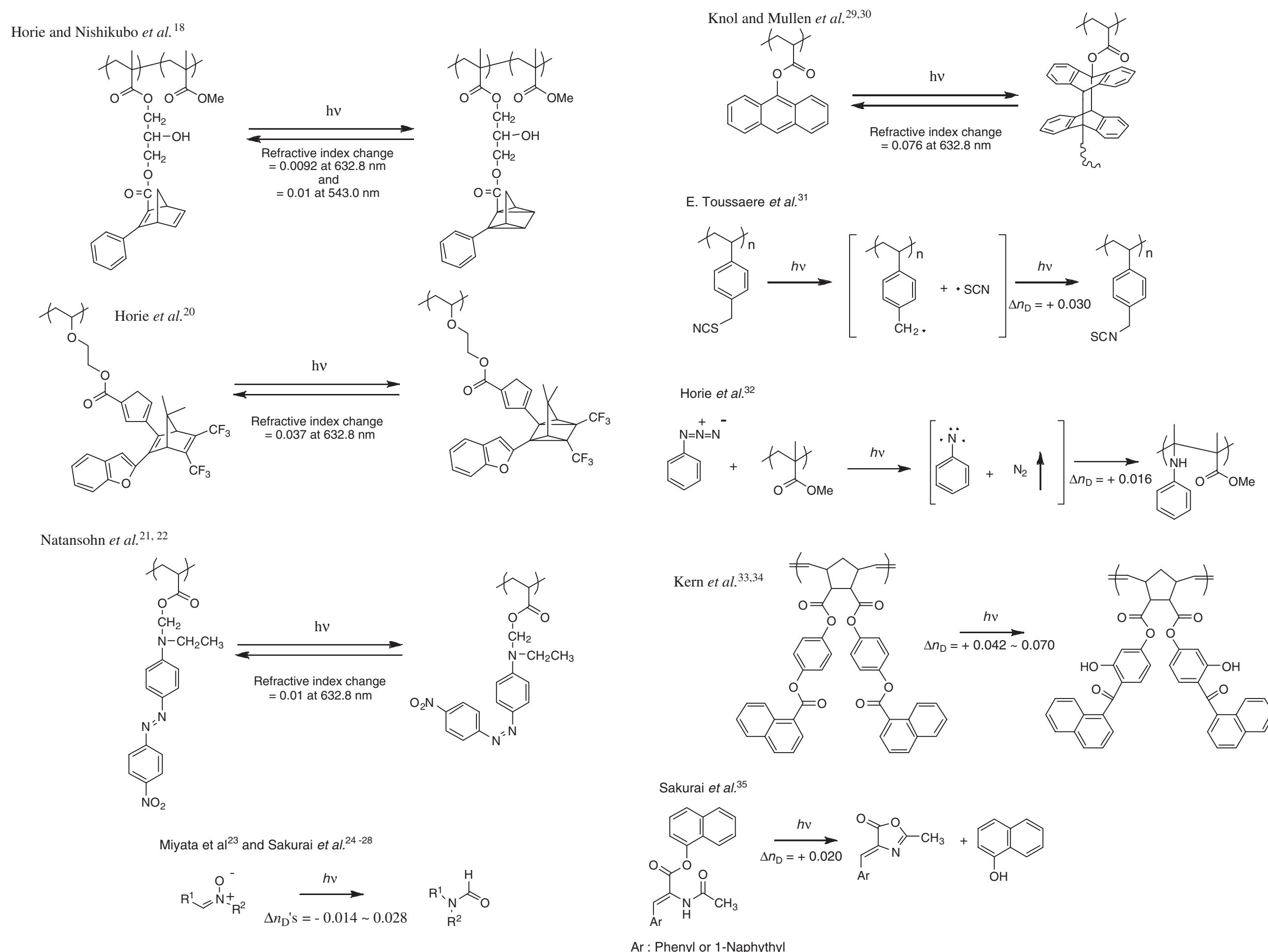

Scheme 3. Refractive-index-changing materials.

Δn_D of poly(methyl methacrylate) film doped with *N*-acetyl-α-dehydroarylalanine naphthyl ester reached about 0.02. However, it is difficult to apply these materials in the optoelectronics industry, because the photo-chemical reaction is accompanied with release of low-molecular compounds or gases.

It appears that the change of n_D was due to a molar refraction change upon photo-chemical reaction. As shown in eq. 1, refractive index (n_D) is dependent upon density (ρ g/cm^3), molecular weight (M), and molar refraction (R cm^3/mol), in accordance with the Lorentz-Lorenz equation.[36]

$$n_D = \sqrt{(M + 2\rho R)/(M - \rho R)} \qquad (1)$$

From this equation, we can consider that films showing larger Δn_D might be obtained from materials in which the values of R and ρ show large changes following photo-irradiation. If a material contains many photo-reactive groups, the resulting film might show a large Δn_D upon photo-irradiation.

We examined the synthesis of candidate refractive-index-changing calixarene derivatives containing NBD. A key feature in the design of oligomer-based photo-functional materials is hydroxyl groups. It can be speculated that the pendant hydroxyl groups of materials result in higher hydrophilicity and provide better adhesion to the substrate. From this viewpoint, we designed calixarene derivatives with pendant epoxy groups, and examined the reaction of the resulting calixarene derivatives and 3-phenyl-2,5-norbornadiene-2-carboxylic acid to obtain the corresponding calixarene derivatives with NBD moieties containing pendant hydroxyl groups (Scheme 4).[37] The synthesized calixarene derivatives BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, CRA(OH)-NBD were soluble in common organic solvents and had good film-forming properties. The photochemical valence isomerization of these calixarene derivatives with pendant NBD was examined in thin films. When the films were irradiated with a 500-W xenon lamp, a decrease of λ_{max} of the NBD moiety was observed by UV spectroscopy. It was observed that the absorption maximum at 279 nm due to the NBD moiety disappeared after only 5 min of photo-irradiation. This result indicates that the NBD groups rapidly isomerized quantitatively to QC groups, as shown in Scheme 5. Two isosbestic points at 235 and 249 nm were observed; this suggests that the photochemical isomerization of calixarene derivatives occurred selectively without any side reaction upon photo-irradiation. A linear relationship

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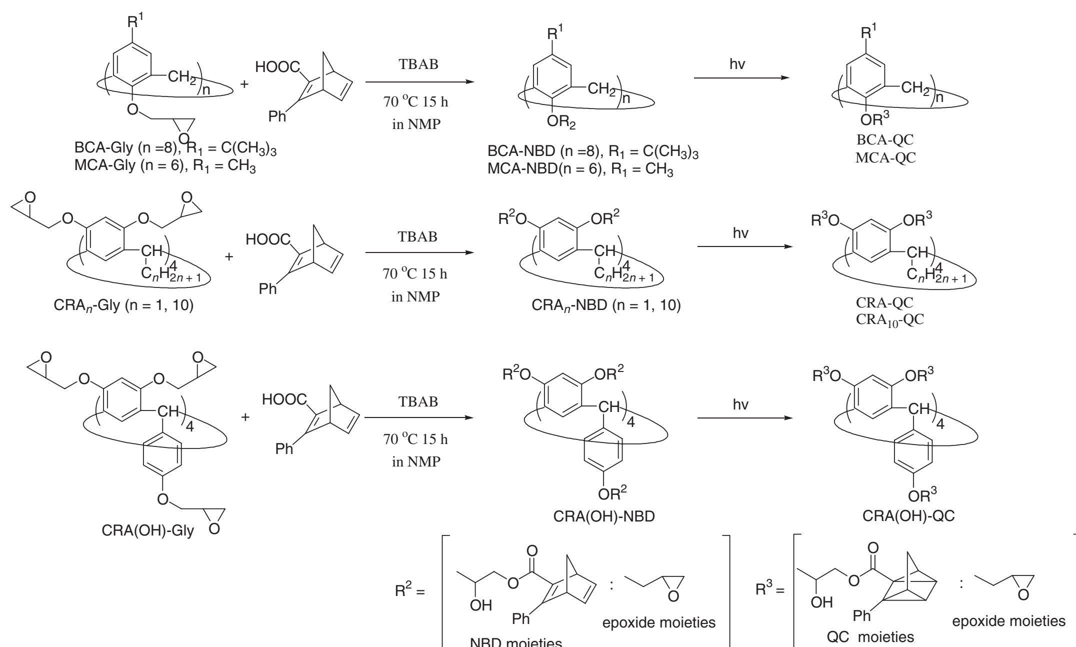
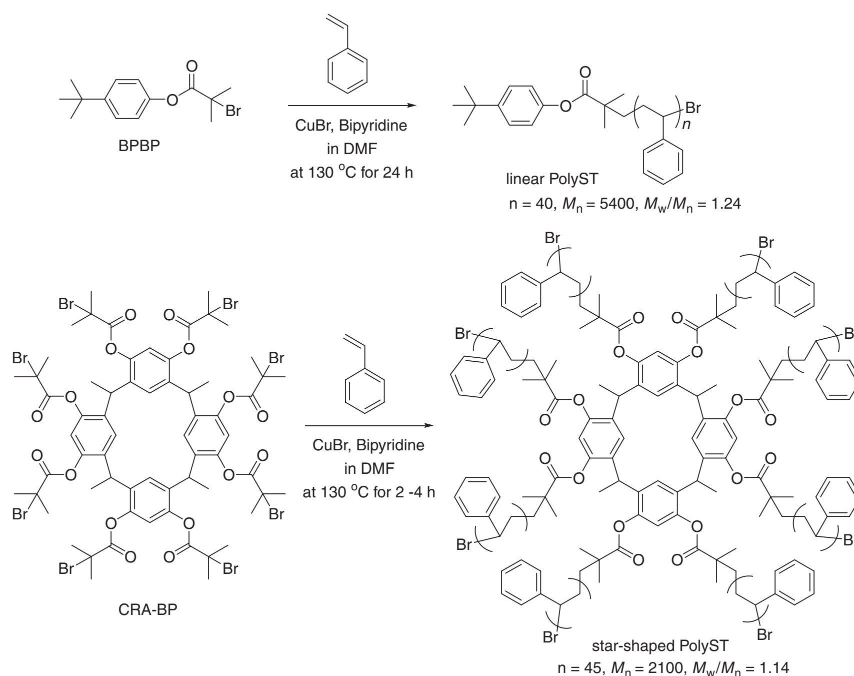


Scheme 4.



Scheme 5. Synthesis of linear polystyrene and star-shaped polystyrene.

was observed between the rate of the photochemical reaction [ln(a/a$_0$)] and irradiation time, as illustrated in Figure 2. The first-order rate constants for BCA-NBD, MCA-NBD, CRA-NBD, CRA$_{10}$-NBD, and CRA(OH)-NBD are summarized in Table I, which shows that the order of the rates of photo-chemical valence isomerization is as follows: CRA(OH)-NBD > CRA-NBD > CRA$_{10}$-NBD > BCA-NBD > MCA-NBD. Thus, the photo-chemical reactivity of the NBD moieties is consistent with the character of the calixarene skeleton. That is, the photo-chemical reactivity of calixarene derivatives increased with increasing number of NBD moieties and decreasing size of the calixarene structure.

The refractive index of the calixarene derivatives was measured by ellipsometry. 2-Methoxyethylacetate solutions of the prepared calixarene derivatives were spin-coated on a silicon-wafer, and hard-baked at 170 °C for 30 min to obtain films with about 0.1 μm thickness. The values of the refractive-index changes (Δn_D) are summarized in Table II.

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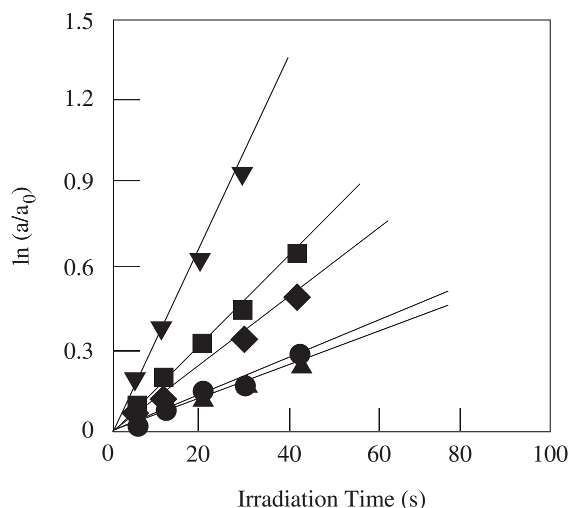

Figure 2. First-order rates of photo-isomerization of calixarene derivatives BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, and CRA(OH)-NBD. (●): BCA-NBD, (▲): MCA-NBD, (■): CRA-NBD, (□): CRA_{10}-NBD, (▼): CRA(OH)-NBD.

Table I. First-Order Rate Constants of Photochemical Valence Isomerization of Calixarene Derivatives

Calixarene derivative	$K_{obd} \times 10^3\ s^{-1}$
BCA-NBD	6.63
MCA-NBD	6.17
CRA-NBD	15.8
CRA10-NBD	12.1
CRA(OH)-NBD	34.0

Table II. Refractive Index Values and Their Change for Films of Calixarene Derivatives Before and After Photo-irradiation[a)]

Calixarene derivative	n_b[b)]	n_a[c)]	Δn_D[d)]
BCA-NBD	1.592	1.564	0.028
MCA-NBD	1.626	1.597	0.029
CRA-NBD	1.682	1.633	0.049
CRA_{10}-NBD	1.614	1.569	0.045
CRA(OH)-NBD	1.662	1.601	0.061

[a)] The n_D's of the calixarene derivative films about 0.1 µm thick, spin-coated on a silicon wafer, before and after photo-irradiation were determined by ellipsometry at 632.8 nm. [b)] n_b = refractive index value before irradiation. [c)] n_a = refractive index value after irradiation. [d)] $\Delta n_D = n_b - n_a$.

Large Δn_D's in the range from 0.028 to 0.061 were obtained. The order of Δn_D's was as follows: CRA(OH)-NBD > CRA-NBD > CRA_{10}-NBD > BCA-NBD > MCA-NBD, which agreed with the order of the photo-chemical reactivity. That is, the values of Δn_D and the photo-chemical reactivity of calixarene derivatives are consistent with those expected based on the structures.

Temperature Effect on the Refractive Index

It is well known that the value of n_D of a thin film is decreased by heating, because the density (ρ) of the films is dependent on the temperature. We further examined the effect of temperature on the refractive index of well-defined linear polystyrene ($M_n = 5400$, $M_w/M_n = 1.24$, $T_g = 92\,°C$) and star-shaped polystyrene ($M_n = 2100$, $M_w/M_n = 1.14$, $T_g = 102\,°C$) in the film state (Scheme 5).[38] Well-defined linear polymers and star-shaped polymers were synthesized using the atom transfer radical polymerization (ATRP) system.[39] Polymer films prepared by spin-coating on silicon wafers were placed on the heating plate of an ellipsometer, and changes in their refractive index were followed during heating.

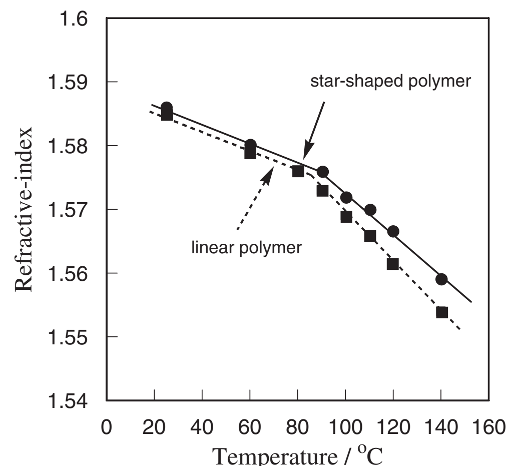

Figure 3. Relationship between refractive index (n_D) and temperature for linear and star-shaped poly-STs.

Figure 3 depicts the relationship between refractive index (n_D) and temperature for linear and star-shaped polySTs. The linear and star-shaped polySTs both showed a linear decrease of n_D as the temperature was increased, with an inflection point at 90–100 °C. The inflection point appeared to coincide with the glass transition temperature (T_g), which is 92 °C for the linear polyST and 102 °C for the star-shaped polyST. Thus, the values of n_D decreased as a result of the decrease of ρ during heating in the film state. At T_g, the slopes of the straight lines changed due to the effect of micro-Brownian motion. The slope of the relationship was larger for linear polyST than for star-shaped polyST. This is because the segment motion of linear polyST is more active than that of star-shaped polyST, and the decrease of ρ of linear polyST is larger than that of star-shaped polyST.

ARF RESIST MATERIALS BASED ON CYCLODEXTRIN

The development of new photolithography systems is important for reducing the size of computer chips. It is well known that advanced systems require new shorter wavelength lasers, such as 193 nm (ArF) and 13.5 nm (EUV).[40,41] In the ArF resist systems, the new resist materials for photolithography are required to have high transparency at the exposure wavelength and high stability under conditions of dry etching. The chemical amplification resist system is one new approach.[42–46] In this system, acid derived from a photo-acid generator promotes removal of the protecting groups, such as t-butyl ester, acetal, trimethylsilyl, and tetrahydropyranyl groups to achieve higher resolution.[47–50] Recently, many new chemical

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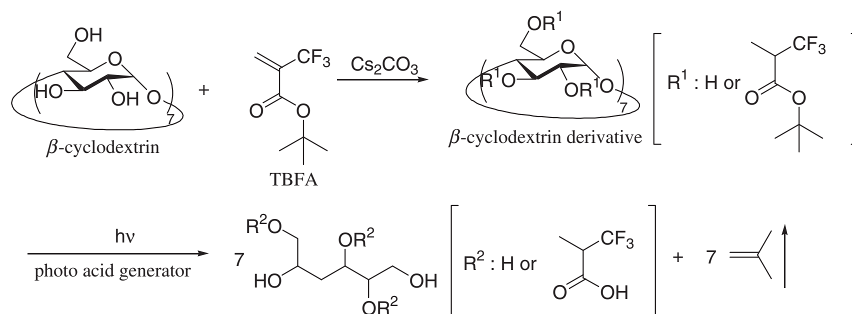


Scheme 6. Synthesis and photo-induced deprotection reaction of CD derivatives containing *t*-butyl ester groups.

amplification ArF photo-resist materials have been reported using various polymers containing fluorine and alicyclic groups, such as adamantane and norbornane.[51,52] It was suggested that molecular size is an important consideration to achieve higher resolution, from the viewpoints of both photo-reactivity and low line-edge roughness.[43]

We designed new CD derivatives containing fluorine and *t*-butyl ester moieties as candidate high-performance ArF photo-resist materials,[53] because we expected that CD derivatives would show good transmittance of vacuum ultraviolet (VUV) laser light. The Michael addition reaction of β-cyclodextrin (β-CD) and *t*-butyl-α-(trifluoromethyl)acrylate (BTMA) was examined using Cs_2CO_3 as a base and tetrabutylammonium bromide (TBAB) as a phase transfer catalyst in DMSO at 25 °C for 6 h, to give β-CD derivatives containing fluorine atoms, *t*-butyloxycarbonyl groups, and hydroxyl groups (Scheme 6).

The obtained β-CD derivative has trifluoromethyl groups and *t*-butyloxycarbonyl groups, with the degree of introduction onto primary hydroxyl groups and secondary hydroxyl groups of 76 and 18%, respectively. This β-CD derivative had good thermal stability (the decomposition of *t*-butyl ester groups started at around 160 °C as determined by thermogravimetric analysis) and good film-forming properties. The transmittance of the synthesized β-CD derivative was measured with a VUV spectrometer, and was 43% at 157 nm and 93% at 193 nm (Figure 4).

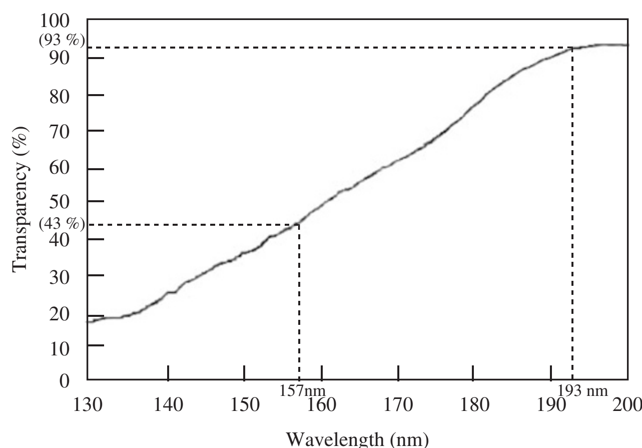


Figure 4. VUV spectrum of β-CD derivative film (film thickness: 150 nm).

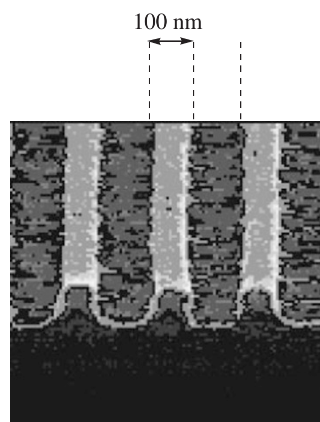
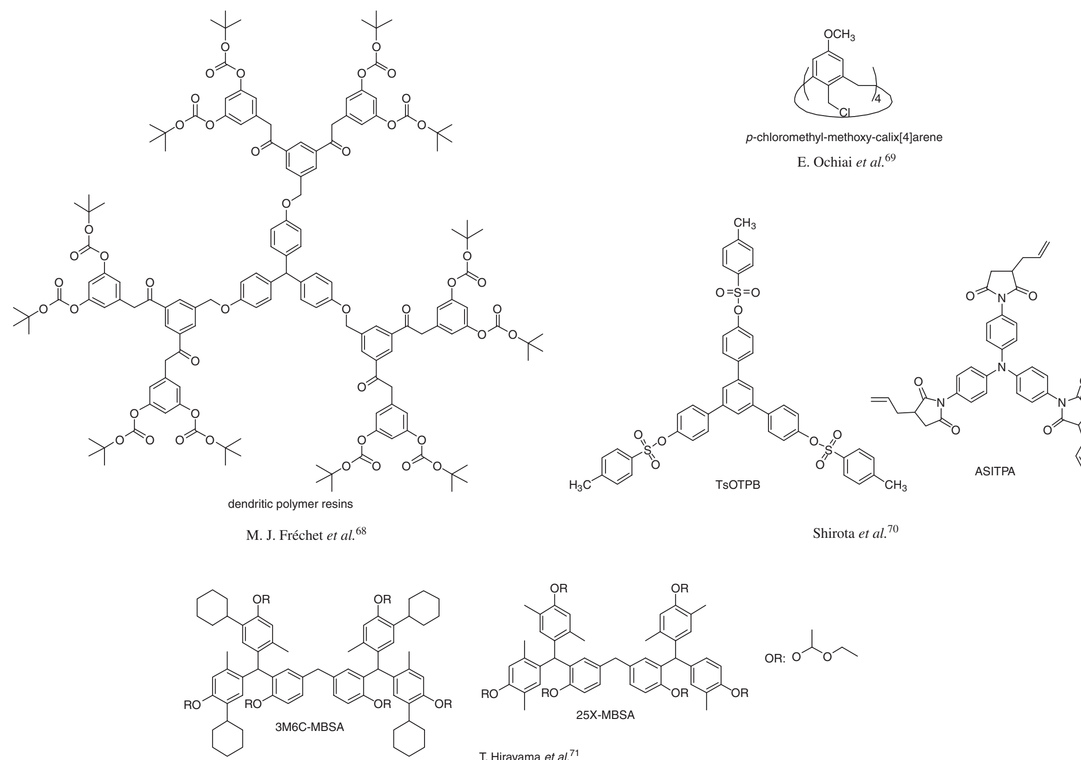


Figure 5. SEM image of film prepared from β-CD derivative.

This means that the β-CD derivative with pendant trifluoromethyl groups and *t*-butyl ester groups can be used as single-layer ArF photoresist system for a 193-nm laser. Wilson *et al.*[54] reported the photo-induced deprotection reaction of polymers bearing *t*-butyloxycarbonyl groups using photo-acid generator (PAG) as a chemically amplified photoresist. The patterning properties of the β-CD derivative were examined by means of SEM imaging as follows. A photo-resist was prepared using the β-CD derivative, with triphenylsulfoniumfluorosulfonate (TPSFS) as a photo acid generator, and was exposed to ArF, followed by heating at 100 °C for 90 s. The exposed film on the substrate was developed with 2.38 wt % tetramethylammonium hydride (TMAH) aqueous solution for 20 s. A clear line and space pattern with 100 nm width was obtained, as shown in Figure 5. In this ArF resist system, photo-induced deprotection reaction of *t*-butyl ester groups afforded the carboxylic acid groups and decomposition reaction of acetal moieties of glucopyranose produced new hydroxyl groups as shown in Scheme 6. Thus, the β-CD derivative showed excellent photo-sensitivity and good alkali-aqueous solubility after photo-irradiation.

SYNTHESIS OF NORIA AND ITS APPLICATIONS TO EB AND EUV RESIST MATERIALS

To achieve greater component densities, next-generation lithography systems will employ an electron beam (EB) or an



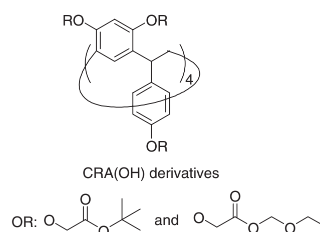
Scheme 7. EB molecular glass resist materials.

extreme ultraviolet (EUV) laser.[41,55] Resists for these systems will likely require new chemical amplification photo-resist materials containing alicyclic groups (adamantane and norbornene), fluorine atoms, and certain protecting groups (trimethylsilyl and tetrahydropyranyl groups).[48,56,57] Recently, molecular glass resists have attracted attention as candidates for high-resolution patterning.[58–67]

Fréchet *et al.*[68] reported EB resist materials based on dendritic polymer resins, resulting in 50–100 nm line and space patterns. Ochiai *et al.*[69] reported negative-type high-resolution resists based on *p*-chloromethylmethoxycalix[4]arene. Shirota *et al.*[70] examined the EB resist properties of 1,2,5-tris[4-(4-toluenesulfonyloxy)phenyl]benzene (TsOTPB) and 4,4′-tris(allylsuccinimido)triphenylamine (ASITPA), and obtained 70–150 nm line patterns. Hirayama *et al.*[71] developed amorphous low-molecular-weight polyphenols, such as 4,4′-methylenebis[2-[di(2-methyl-4-hydroxy-2,5-dimethylphenyl)methyl]phenol (3M6C-MBSA) and 4,4′-methylenebis[2-[di(4-hydroxy-2,5-dimethylphenyl)methyl]phenol(25X-MBSA) as EB resist materials, obtaining 50–70 nm line and space patterns (Scheme 7).

We anticipated that calixarene derivatives containing photo-degradable groups would be applicable as novel EB-resist materials, and examined the photo-induced deprotection and patterning properties of calixarene derivatives with *tert*-butyl groups[72] and acetal groups (Scheme 8).[73]

Indeed, these derivatives showed excellent reactivity in the photo-induced deprotection reaction. However, a clearly resolved line and space pattern could not be obtained,[74]



Scheme 8. CRA(OH) derivatives containing chemical amplification reactive groups.

because the line pattern was broken down during the etching process. This may reflect insufficient structural stability of calixarenes. We therefore considered the use of more rigid cyclic molecules, such as cavitands, carcerands, and other cyclic oligomers. Then, we succeeded in synthesizing a new ladder-type cyclic molecule, noria, by the reaction of resorcinol and 1,5-pentanedial in a one-pot procedure (Scheme 9).[75] The reaction of resorcinol and 1,5-pentanedial was performed in the presence of conc. HCl in ethanol at 80 °C for 48 h. The reaction mixture was poured into methanol, and the precipitated product was washed with ethyl ether several times, then dried *in vacuo* at 60 °C for 12 h to give noria as the sole product in 83% yield. Its structure was confirmed by IR, ^{1}H NMR, and MALDI TOF mass spectroscopy, as well as single X-ray crystal analysis of a noria derivative. It was found that noria has 24 hydroxyl groups, 6 cavities in the side, and a large hydrophobic hole through the center of the molecule, as shown in Scheme 9.

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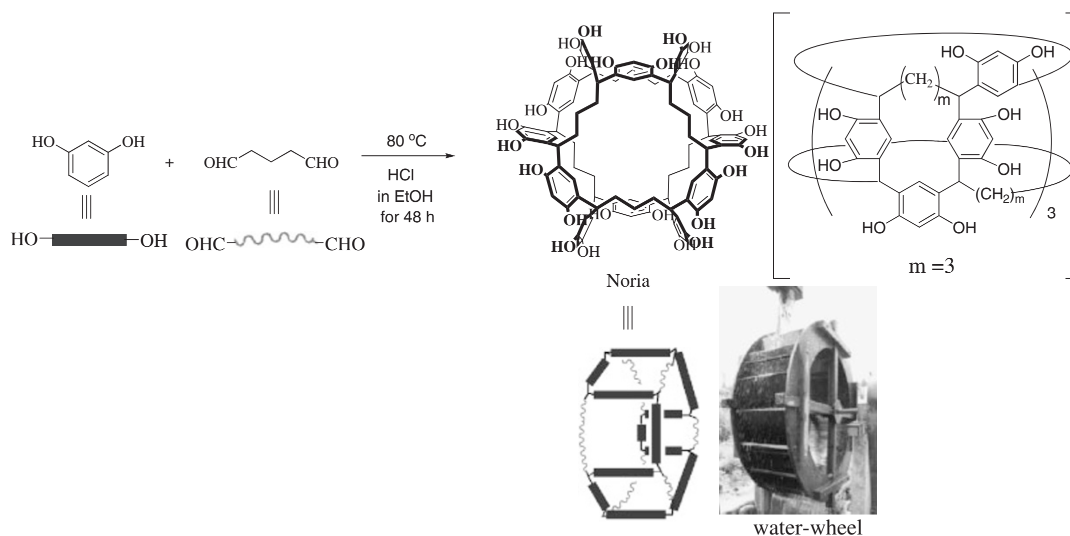
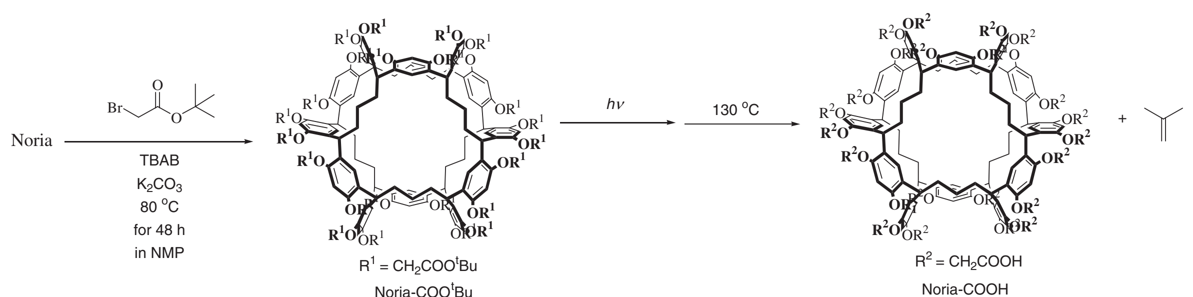


Scheme 9. Synthesis of noria.



Scheme 10. Synthesis of noria derivative (noria-COO^{t}Bu).

We synthesized the noria derivative containing *t*-butyl ester groups by reaction with *t*-butyl bromoacetate (BBA) in the presence of TBAB as a catalyst and K_2CO_3 as a base in NMP at 80 °C for 48 h, obtaining noria-COO^{t}Bu in 58% yield (Scheme 10).

Noria-COO^{t}Bu must have good solubility, good film-forming ability, and excellent thermal stability for application as a resist material. Table III summarizes the solubility characteristics of noria-COO^{t}Bu and noria. Noria was soluble in DMSO, DMAc, DMF, toluene, and cyclohexane, but insoluble in other organic solvents. On the other hand, noria-COO^{t}Bu was soluble in all common organic solvents, though not in water. Noria-COO^{t}Bu was insoluble in alkaline aqueous solution, whereas noria was soluble. Film-forming ability was examined using films cast on a glass plate (with noria or noria-COO^{t}Bu 50 mg in $CHCl_3$ 1.0 mL), and dried *in vacuo* at room temperature on a silicon wafer. It was found that noria-COO^{t}Bu had good film-forming ability, whereas noria did not. Thermogravimetric analysis (TGA) of noria-COO^{t}Bu showed that decomposition started at above 150 °C (Figure 9). The photoinduced deprotection of synthesized noria-COO^{t}Bu was examined in the film state. As shown in Scheme 10, alkali-developable carboxylic acid groups would be produced with release of isobutylene in the deprotection reaction of noria-COO^{t}Bu, affording the corresponding noria derivative noria-COOH.

The photo-induced deprotection of noria-COO^{t}Bu was carried out under UV irradiation with a 250-W high-pressure mercury lamp, using films prepared with 5 mol % photoacid generator for 30 min, followed by heating at 130 °C. Figure 6 depicts the IR spectra before and after the photoinduced deprotection reaction.

This result shows that the deprotection reaction of *t*-butyl ester groups proceeded, generating carboxylic acid groups with release of isobutylene, as shown in Scheme 10. From the peak at 1370 cm^{-1}, assignable to deformation vibration of *t*-butyl groups, it is possible to calculate the conversion rate of the photoinduced deprotection reaction, and the reaction was complete within 30 min. The resulting noria-COOH became soluble in alkaline aqueous solutions, such as 2.38 wt % Na_2CO_3 and tetramethylammonium hydride (TMAH), as summarized in Table III.

Patterning Properties of Noria-COO^{t}Bu and Noria-BOC

The patterning properties were examined using film prepared from noria-COO^{t}Bu (all hydroxyl groups were converted to *t*-butyl groups) and noria-COO^{t}Bu(71) (71% of hydroxyl groups were converted to *t*-butyl groups). A clear pattern with a

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Table III. Solubility and Film-forming Properties of Noria and Noria-COO^{t}Bu

Solvent	noria	noria-COO^{t}Bu	noria-BOC	noria-COOH	noria-Acetal
Water	−	−	−	++	−
DMSO	++	+−	+−	+	++
DMAc	++	++	++	+	++
DMF	+−	++	++	+	++
Methanol	−	++	++	−	+
2-Propanol	−	++	++	−	++
THF	−	++	++	−	++
1,4-Dioxane	−	++	++	−	++
Acetonitrile	−	++	++	−	++
Acetone	−	++	++	−	++
Ethyl acetate	−	++	++	−	++
Methyl ether ketone	−	++	++	−	++
o-Dichlorobenzene	−	++	++	−	++
Chloroform	−	++	++	−	++
Toluene	+−	++	++	−	++
2-Heptanone	−	++	++	−	−
Ethyl lactone	−	++	++	−	+−
γ-Butyrolactone	−	++	++	−	++
n-Hexane	−	++	++	−	−
Film-forming ability	No	Yes	Yes	No	Yes

++: soluble at room temperature. +: soluble on heating. +−: partially soluble.

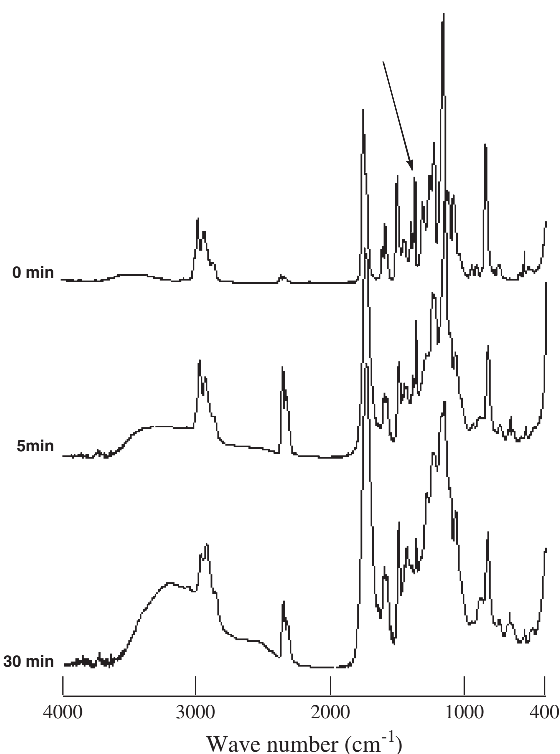

Figure 6. IR spectra showing the course of the photo-induced deprotection reaction of noria-COO^{t}Bu under UV irradiation (8 mW/cm^2 at 254 nm for 30 min), followed by heating at 130 °C for 30 min.

resolution higher than 100 nm could not be obtained with a conventional poly(hydroxyl styrene)-type polymer or with cyclic oligomer calixarene derivatives[72–74] under similar conditions. However, a clear pattern was obtained with noria-COO^{t}Bu(71) at 70 nm resolution.[76] These results are depicted in Figure 7.

This indicates that noria-COO^{t}Bu(71) shows higher hydrophilicity due to the remaining hydroxyl groups, resulting in better adhesion to the silicon wafer. That is, a high-resolution pattern could be obtained owing to the appropriate balance between *t*-butyl groups and hydroxyl groups in noria-COO^{t}Bu(71).

Furthermore, the synthesis and EB resist properties of a noria derivative (noria-BOC) containing *t*-butyloxycarbonyl (BOC) groups were examined. Noria-BOC was synthesized by the reaction of noria and di-*t*-butyloxydicarbonate, and its photo-induced deprotection reaction was examined by exposure to UV irradiation for 45 min with a 250-W high-pressure mercury lamp using a film prepared with 5 mol % of bis({[4-(2-hydroxy)ethoxy]diphenylsulfonoiophenyl}hexafluorophosphate)-sulfide (sp-150) as a photo-acid generator, followed by heating at 130 °C. The deprotection reaction of BOC groups proceeded smoothly to produce hydroxyl groups with release of CO_2 and isobutylene, as shown in Scheme 11.

Thermal decomposition of noria-BOC started at around 150 °C, presumably due to the pendant BOC groups (Figure 9). The solubility and film-forming properties of noria-BOC appear to be suitable for application of this compound as an EB resist material. These results are also summarized in Table III.

The patterning property of noria-BOC was measured by SEM imaging (Figure 8). A photo-resist was prepared from noria-BOC, with triphenylsulfonium perfluoro-1-butanesufonate (TPS nonaflate, 99+% electronic grade) as a photoacid generator (PAG, 5% over resist), and baked at 115 °C for 30 s (post application bake, PAB). These conditions yielded films approximately 100 nm thick. The coated substrate was exposed to an electron beam, then the wafers were baked at 140 °C for 150 s, developed in TMAH aqueous solution (0.26 N), rinsed with water and dried in a stream of N_2. A clear pattern with a

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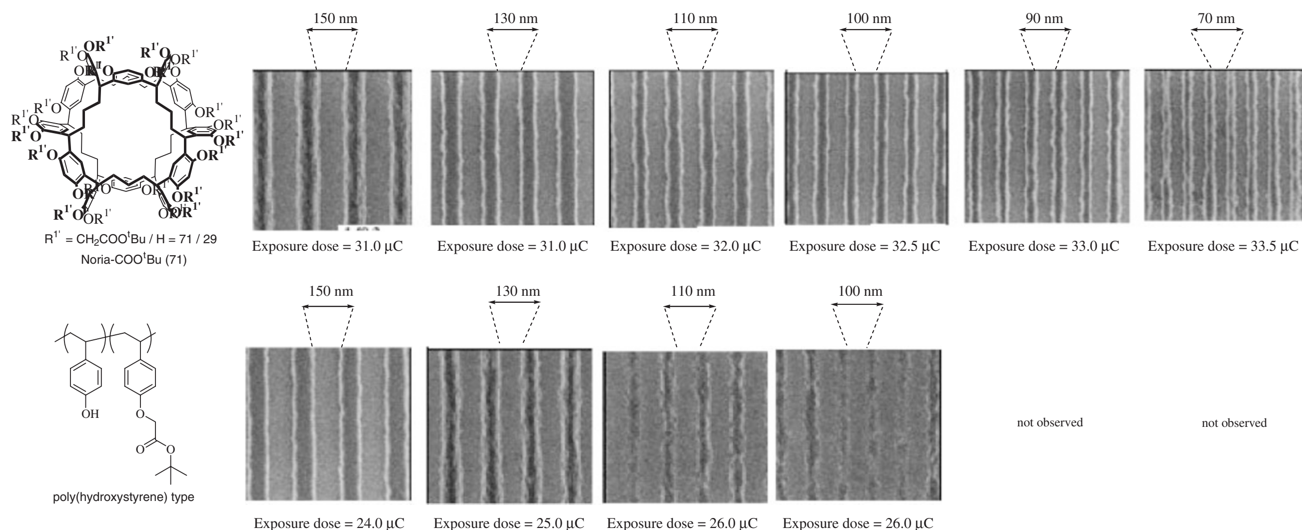
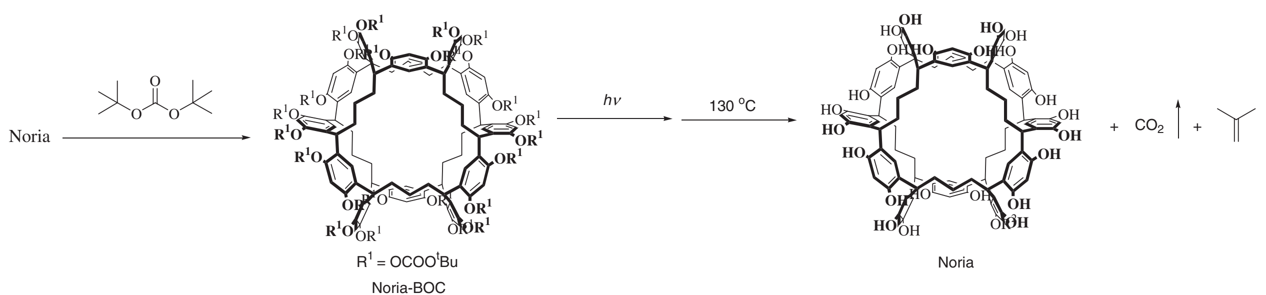


Figure 7. SEM images of patterning obtained with films prepared from noria-COO^{t}Bu(71) and a conventional poly(hydroxyphenyl)-type polymer. Exposure dose = 24.0 μC–33.5 μC, PAB: 130 °C for 90 s. PEB: 130 °C for 90 s.



Scheme 11. Synthesis of noria derivative (noria-BOC).

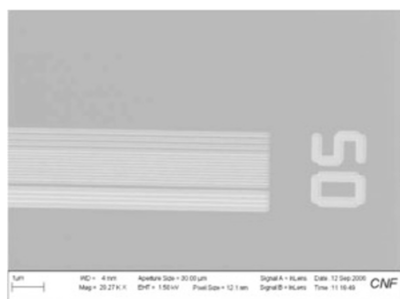


Figure 8. 50 nm line/space pattern obtained using 'Noria-Boc' resist after electron beam exposure.

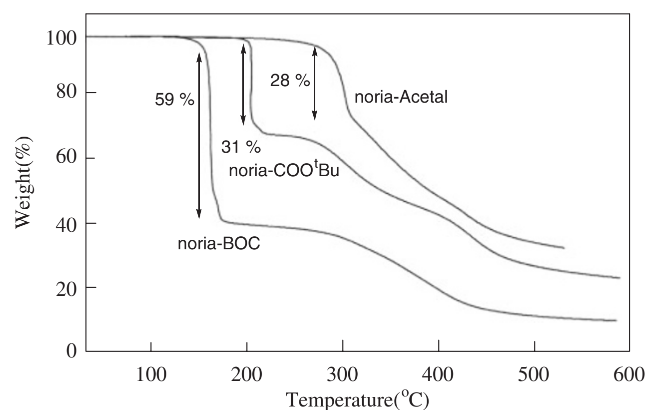
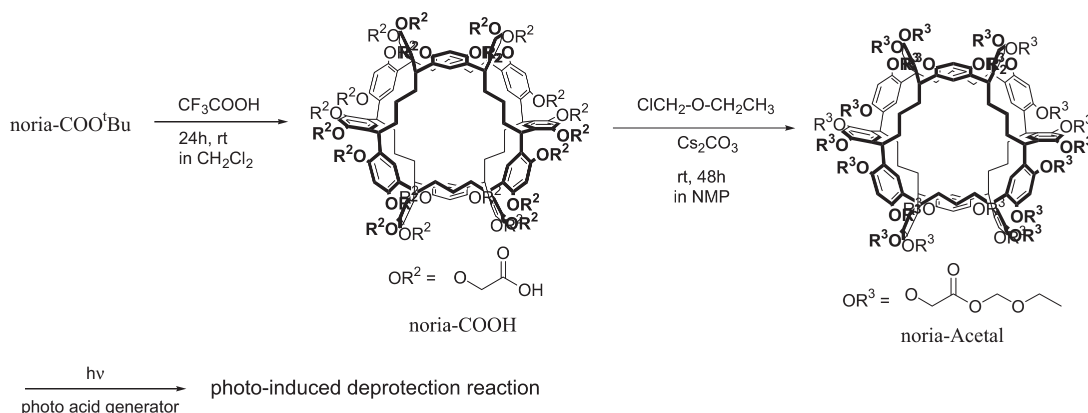


Figure 9. Thermal gravimetric analysis of noria-BOC, noria-COO^{t}Bu, and noria-Acetal.

50 nm line width was obtained.[77] Furthermore, the synthesis, physical properties, and photo-induced deprotection reaction of a noria derivative containing acetal moieties were examined.[78] The deprotection reaction of noria-COOtBu was carried out using trifluoroacetic acid to give the corresponding noria derivative (noria-COOH) with pendant carboxyl groups. The reaction of noria-COOH with chloromethyl ethyl ether using cesium carbonate as a base gave the corresponding noria derivative (noria-Acetal) with pendant acetal groups (Scheme 12). Noria-Acetal showed higher solubility than other noria derivatives, such as noria-COO^{t}Bu, noria-BOC, and noria-COOH. These results are also summarized in Table III. Figure 9 showed that the thermal stability was excellent; decomposition started at around 270 °C. Furthermore, the photo-induced deprotection reaction of noria-Acetal in thin films was examined in the presence of a photo-acid generator upon UV irradiation, and it was found that acetal groups were changed to carboxyl acid groups smoothly without external



Scheme 12. Synthesis of noria derivative (noria-acetal).

heating; the conversion reached 26% in 40 min. This means that noria-Acetal is a good candidate for a next-generation positive photo-resist with high resolution for EB or EUV resist systems. The outstanding mechanical properties of noria, noria-BOC, and noria-BAc as low-molecular compounds appear to be due to their ladder cyclic structure.

SUMMARY

Refractive-index-changing materials, ArF resist materials, and EB resist materials were developed based on calixarene, cyclodextrin, and noria.

In calixarene derivatives containing photo-reactive groups, such as azobenzene, norbornadiene, cinnamate, anthracene, and chalcone, the photo-chemical reactivity increased with increasing numbers of photo-chemical groups and decreasing size of the calixarene core. The refractive index of these films changed after photo-irradiation and their values (Δn_D's) were in the range from 0.028 to 0.061.

A β-CD derivative, synthesized by the reaction of β-CD with *t*-butyl α-(trifluoromethyl)acrylate, showed good solubility, good film-forming properties, and good VUV transmittance. Its photo-induced deprotection in the presence of a photo-acid generator resulted in decomposition reaction of the acetal moieties of gluconopyranose. A 100 nm line and space pattern was achieved using the β-CD derivative in a single-layer ArF photoresist system with a 193-nm laser.

We also synthesized a unique macrocycle, noria, by condensation reaction of resorcinol and 1,5-pentanedial. Noria is ladder cyclic oligomer with a large hole in the center, 6 cavities in the side, and 24 hydroxyl groups. The synthesis, properties, and photo-induced deprotection of noria derivatives, noria-COO^{t}Bu containing *t*-butyl ester groups, noria-BOC containing *t*-butyloxycarbonyl groups, and noria-acetal containing acetal groups, were examined. These noria derivatives had good solubility, good film-forming ability, good thermal stability, and good photo-reactivity. Photoresists prepared with noria-COO^{t}Bu(71) (ratio of *t*-butyl groups: 71%) and noria-BOC provided a clear line and space patterns at a resolution of 70 and 50 nm, respectively. These noria derivatives containing acid-labile groups are good candidates for next-generation EB resist materials, and should also be available as EUV resist materials. We believe our results provide a new direction for the development of photo-functional materials.

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REFERENCES

1. "Calixarenes 2001," Z. Asfari, V. Bohmer, J. Harrowfield, and J. Vicens, Ed., Kluwer Academic Publishers, 2001.
2. D. C. Gutsche, "Calixarens", Royal Society of Chemistry, Cambridge, 1989.
3. T. Nishikubo, A. Kameyama, K. Tsutsui, and M. Iyo, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 1805 (1999).
4. J. Fujita, Y. Onishi, Y. Ochiai, and S. Matsui, *Appl. Phys. Lett.*, **68**, 1297 (1996).
5. Y. Ochiai, S. Manako, H. Yamamoto, T. Teshima, J. Fujita, and E. Nomura, *J. Photopolym. Sci. Technol.*, **13**, 413 (2000).
6. M. Iyo, K. Tsutsui, A. Kameyama, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 3071 (1999).
7. T. Nishikubo, A. Kameyama, and K. Tsutsui, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1169 (2001).
8. T. Nishikubo, A. Kameyama, H. Kudo, and K. Tsutsui, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1293 (2002).
9. N. Szerman, I. Schroh, A. L. Ross, A. M. Rosso, N. Krymkiewicz, and S. A. Ferrarotti, *Bioresour. Technol.*, **98**, 2886 (2007).
10. S. Morino, S. Machida, T. Yamashita, and K. Horie, *J. Phys. Chem.*, **99**, 10280 (1995).
11. A. Toriumi, J. M. Herrmann, and S. Kawata, *Opt. Lett.*, **22**, 555 (1997).
12. T. Kada, A. Obara, T. Tanabe, S. Miyata, C. X. Liang, H. Machida, and K. Kiso, *J. Appl. Phys.*, **87**, 638 (2000).
13. K. W. Beeson, K. A. Horn, M. Mcfarland, and S. T. Yardley, *Appl. Phys. Lett.*, **58**, 1955 (1991).
14. T. Nishikubo, T. Shimokawa, and A. Sahara, *Macromolecules*, **22**, 8 (1989).
15. T. Nagai, M. Shimada, Y. Ono, and T. Nishikubo, *Macromolecules*, **36**, 1786 (2003).
16. N. Kawashima, A. Kameyama, T. Nishikubo, and T. Nagai, *React. Funct. Polym.*, **55**, 75 (2003).
17. N. Kawashima, A. Kameyama, T. Nishikubo, and T. Nagai, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1764 (2001).

©2009 The Society of Polymer Science, Japan

18. K. Kinoshita, K. Horie, S. Morino, and T. Nishikubo, *Appl. Phys. Lett.*, **70**, 2940 (1997).
19. Y. Kato, H. Muta, S. Takahashi, K. Horie, and T. Nagai, *Polym. J.*, **33**, 868 (2001).
20. S. Murase, K. Kinoshita, K. Horie, and S. Morino, *Macromolecules*, **30**, 8088 (1997).
21. A. Natansohn, P. Rochon, T. Gosselin, and S. Xie, *Macromolecules*, **25**, 2268 (1992).
22. A. Natansohn, S. Xie, and P. Rochon, *Macromolecules*, **25**, 5531 (1992).
23. T. Kada, A. Obara, T. Tatanabe, S. Miyata, C. X. Liang, H. Machida, and K. Kiso, *J. Appl. Phys.*, **87**, 638 (2000).
24. K. Tanaka, T. Igarashi, and T. Sakurai, *Macromolecules*, **37**, 5482 (2004).
25. K. Tanaka, K. Shima, H. Kondoh, T. Igarashi, and T. Sakurai, *J. Appl. Polym. Sci.*, **93**, 2517 (2004).
26. K. Tanaka, H. Shiraishi, E. Takayanagi, A. Korechika, T. Igarashi, and T. Sakurai, *J. Photochem. Photobiol., A*, **174**, 199 (2005).
27. K. Tanaka, M. Fukuda, T. Igarashi, and T. Sakurai, *Polym. J.*, **37**, 776 (2005).
28. K. Tanaka, E. Takayanagi, T. Igarashi, and T. Sakurai, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 88 (2006).
29. S. Paul, O. Halle, H. Einsieldel, B. Menges, K. Müllen, S. Knoll, and S. M. Neher, *Thin Solid Films*, **288**, 150 (1996).
30. S. Paul, S. Stein, S. Knol, and K. Müllen, *Acta Polym.*, **45**, 235 (1994).
31. G. Langer, T. Kavac, W. Kern, G. Kranzelbinder, and E. Toussaere, *Macromol. Chem. Phys.*, **202**, 3459 (2001).
32. S. Murase, K. Shibata, H. Furukawa, Y. Miyashita, and K. Horie, *Polym. J.*, **35**, 203 (2003).
33. U. Daschiel, T. Höfler, G. Jakopic, V. Schmidt, and W. Kern, *Macromol. Chem. Phys.*, **209**, 1190 (2007).
34. T. Höfler, T. Grießer, M. Gruber, G. Jakopic, G. Trimmel, and W. Kern, *Macromol. Chem. Phys.*, **209**, 488 (2008).
35. K. Tanaka, H. Nakajima, T. Igarashi, and T. Sakurai, *Macromolecules*, **38**, 7207 (2005).
36. "Optical Properties of Polymers," G. H. Meeten, Ed., Elsevier Applied Science, London, 1989.
37. H. Kudo, W. Ueda, K. Sejimo, K. Mitani, and T. Nishikubo, *Bull. Chem. Soc. Jpn.*, **77**, 1415 (2004).
38. H. Kudo, H. Aoki, and T. Nishikubo, *Chem. Lett.*, **37**, 282 (2008).
39. T. E. Patten, J. Xia, T. Abernathy, and K. Matyjaszewski, *Science*, **272**, 866 (1996).
40. A. M. Goethals, G. Vandenberghe, I. Pollentier, M. Ercken, P. De. Bisschop, M. Maenhoudt, and K. Ronse, *J. Photopolym. Sci. Technol.*, **14**, 333 (2001).
41. H. Ito, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 3863 (2003).
42. S. A. MacDonald, C. G. Willson, and J. M. J. Frechet, *Acc. Chem. Res.*, **27**, 151 (1994).
43. C. G. Willson, B. C. Trinque, B. P. Osborn, C. R. Chambers, Y. Hedieh, T. Chiba, P. Zimmerma, D. Miller, and W. Conley, *J. Photopolym. Sci. Technol.*, **15**, 583 (2002).
44. C. K. Ober, K. Douki, V. R. Vohra, Y. Kwark, X. Liu, W. Conley, D. Miller, and P. Zimmerman, *J. Photopolym. Sci. Technol.*, **15**, 603 (2002).
45. R. J. Hung, M. Yamachika, T. Chiba, H. Iwasawa, A. Hayashi, N. Yamahara, and T. Shimokawa, *J. Photopolym. Sci. Technol.*, **15**, 693 (2002).
46. Z. M. Fresco, N. Bensel, I. Suez, S. A. Backer, and J. M. J. Frechet, *J. Photopolym. Sci. Technol.*, **16**, 27 (2003).
47. For example, C. G. Willson, H. Ito, J. M. J. Frechet, T. G. Tessier, and F. M. Houlihan, *J. Electrochem. Soc.*, **133**, 181 (1986).
48. H. Ito, in "Radiation Curing in Polymer Science and Technology," J. P. Fouassie and J. F. Rabek, Ed., Elsevier, London, 1993, Vol 4, p 237.
49. S. A. MacDonard, C. G. Willson, and J. M. J. Frechet, *Acc. Chem. Res.*, **27**, 151 (1994).
50. H. Ito, N. Seehof, R. Sato, T. Nakayama, and M. Ueda, in "Micro- and Nano-Patterning Polymers," H. Ito, E. Reichmanis, O. Naramasu, and T. Ueno, Ed., American Chemical Society, Washington, DC, 1998, p 208.
51. T. Nakayama, K. Haga, O. Haba, and M. Ueda, *Chem. Lett.*, 265 (1997).
52. M. Ueda, D. Takahashi, T. Nakamura, and O. Haba, *Chem. Mater.*, **10**, 2230 (1998).
53. H. Kudo, N. Inoue, I. Nishimura, and T. Nishikubo, *Bull. Chem. Soc. Jpn.*, **78**, 731 (2005).
54. C. G. Willson, H. Ito, J. M. J. Frechet, T. G. Tessier, and F. M. J. Houlihan, *J. Electrochem. Soc.*, **133**, 181 (1986).
55. A. M. Goethals, G. Vandenberghe, I. Pollentier, M. Ercken, P. De. Bisschop, M. Maenhoudt, and K. Ronse, *J. Photopolym. Sci. Technol.*, **14**, 333 (2001).
56. S. A. MacDonard, C. G. Willson, and J. M. J. Frechet, *Acc. Chem. Res.*, **27**, 151 (1994).
57. H. Ito, N. Seehof, R. Sato, T. Nakayama, and M. Ueda, in "Micro- and Nano-Patterning Polymers," H. Ito, E. Reichmanis, O. Naramasu, and T. Ueno, Ed., American Chemical Society, Washington, DC, 1998, p 208.
58. J. Dai, S. W. Chang, A. Hamad, D. Yang, N. Felix, and C. K. Ober, *Chem. Mater.*, **18**, 3404 (2006).
59. T. Hirayama, D. Shiono, S. Matsumaru, T. Ogata, H. Hada, J. Onodera, T. Arai, T. Sakamizu, A. Yamaguchi, H. Shiraishi, H. Fukuda, and M. Ueda, *Jpn. J. Appl. Phys.*, **44**, 5484 (2005).
60. T. Kadota, H. Kageyama, F. Wakaya, K. Gamo, and Y. Shirota, *Chem. Lett.*, **33**, 706 (2004).
61. J. Fujita, Y. Onishi, Y. Ochiai, and S. Matsui, *Appl. Phys. Lett.*, **68**, 1297 (1996).
62. Y. Ochiai, S. Manako, H. Yamamoto, T. Teshima, J. Fujita, and E. Nomura, *J. Photopolym. Sci. Technol.*, **13**, 413 (2000).
63. T. Nakayama, K. Haga, O. Haba, and M. Ueda, *Chem. Lett.*, **26**, 265 (1997).
64. M. Ueda, D. Takahashi, T. Nakamura, and O. Haba, *Chem. Mater.*, **10**, 2230 (1998).
65. K. Takeshi, R. Nakayama, and M. Ueda, *Chem. Lett.*, **27**, 865 (1998).
66. T. Nakayama, M. Nomura, K. Haga, and M. Ueda, *Bull. Chem. Soc. Jpn.*, **71**, 2979 (1998).
67. J. B. Kim, H. J. Jun, and Y. G. Kwon, *Chem. Lett.*, **31**, 1064 (2002).
68. Tully, A. R. Trimble, and J. M. J. Frechet, *Adv. Mater.*, **12**, 1118 (2000).
69. M. Ishida, J. Fujita, T. Ogura, Y. Ochiai, E. Ohishima, and J. Momoda, *Jpn. J. Appl. Phys.*, **42**, 3913 (2003).
70. M. Yoshiiwa, H. Kageyama, Y. Shirota, F. Wakaya, K. Gamo, and M. Takai, *Appl. Phys. Lett.*, **69**, 2605 (1996).
71. T. Hirayama, D. Shiono, H. Hada, J. Onodera, and M. Ueda, *J. Photopolym. Sci. Technol.*, **17**, 435 (2004).
72. H. Kudo, K. Mitani, T. Nishikubo, M. Masaya, and T. Miyashita, *Bull. Chem. Soc. Jpn.*, **77**, 819 (2004).
73. H. Kudo, K. Mitani, S. Koyama, and T. Nishikubo, *Bull. Chem. Soc. Jpn.*, **77**, 2109 (2004).
74. T. Nishikubo, presented at the 88th Annual Meeting of the Chemical Society of Japan, Ikebukuro, Japan, March 26–30, 2008, 1C2-20 (2008).
75. H. Kudo, R. Hayashi, K. Mitani, N. C. Kasuga, and T. Nishikubo, *Angew. Chem., Int. Ed.*, **45**, 7948 (2006).
76. H. Kudo, D. Watanabe, T. Nishikubo, K. Maruyama, D. Shimizu, T. Kai, T. Shimokawa, and C. K. Ober, *J. Mater. Chem.*, **18**, 3588 (2008).
77. X. André, J. K. Lee, A. DeSilva, C. K. Ober, H. B. Cao, H. Deng, H. Kudo, D. Watanabe, and T. Nishikubo, *SPIE*, **6519**, 65194B (2007).
78. H. Kudo, D. Watanabe, and T. Nishikubo, *Kobunshi Ronbunshu*, **66**, 10 (2009).

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