

New Large Refractive-Index Change Materials: Synthesis and Photochemical Valence Isomerization of the Calixarene Derivatives Containing Norbornadiene Moieties

Hiroto Kudo, Wataru Ueda, Kiyomitsu Sejimo, Kouji Mitani, Tadatomi Nishikubo,* and Tetsuo Anada[1]

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686

[1]Department of Electrical, Electronics and Information Engineering, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686

Received January 22, 2004; E-mail: nishit02@kanagawa-u.ac.jp

We have examined the synthesis of cyclic oligomers with pendant norbornadiene (NBD) moieties based on the calixarenes [*p*-*tert*-butylcalix[8]arene (BCA), *p*-methylcalix[6]arene (MCA), calix[4]resorcinarene (CRA), 2,8,14,20-tetradecylcalix[4]resorcinarene (CRA_{10}), and 2,8,14,20-tetrakis(*p*-hydroxyphenyl)calix[4]resorcinarene (CRA_{ph})]. The photochemical valence isomerization of the obtained calixarene derivatives containing NBD moieties proceeded very smoothly to afford the corresponding quadricyclane (QC) moieties, and it was found that the large refractive-index changes (Δn's = 0.028–0.061) before and after photo-isomerization.

Refractive-index change materials have received great attention as important optoelectronic materials, such as write-read-erase recordings, switching devices, optical waveguides, memories, and holographic image records.[1,2] In these fields, photochromic materials containing photochemical reversible reaction moieties, such as azobenzenes[3–5] and spiropyrans,[6–8] have been investigated as the refractive-index change materials. However, these organic compounds were not suitable to applications as refractive-index change materials, because they had strong absorption band into visible region and did not have good durabilities in the reversible photochemical reaction. Large refractive-indices changes of the polymers containing nitrone moieties have been observed before and after UV irradiation.[9,10] However, the photochemical isomerization reaction of nitrone is irreversible.

On the other hand, Nishikubo et al.[11–14] 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 property. Furthermore, it was observed that the polymer containing quadricyclane (QC) moieties produced by the UV irradiation of NBD had good stability in the film state. Therefore, synthesized polymers are expected as a good photo-energy transformation system. As a start for these studies,[11] Nishikubo proposed that large refractive-indices changes of the polymers containing NBD would be induced by photo-isomerization reactions. In a series of the studies for the synthesis of the polymers containing the NBD, Horie and Nishikubo experimentally confirmed large refractive-index change before and after photo-irradiation of poly(methyl methacrylate) containing 2-phenyl-2,5-norbornadiene moieties.[15] More recently, Horie et al. reported on the large refractive-indices changes of poly(methyl methacrylate) films doped with NBD derivatives and the poly(vinyl ether)s-bearing NBD moieties.[16] They also found that poly(vinyl cinnamate) showed a large refractive-index change by photodimerization.[17] It is well known that the relationship between the refractive-index (n), density (ρ g/cm^3), molecular weight (M g), and molar refraction (R cm^3/mol) is described by the Lorentz–Lorentz Eq. 1.[18]

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}. \quad (1)$$

From this equation, we can consider that films with a large refractive-index change are prepared from materials in which R and ρ show large change values before and after photoirradiation. Therefore, it might be suggested that films prepared from materials containing the many photo-reaction groups show a high refractive-index change before and after UV irradiation.

Meanwhile, calixarenes are cyclic oligomers containing hydroxy groups, which are prepared easily by the reaction of phenols with aldehydes.[19] Calixarenes are great attractive materials as host molecules in the field of host–guest chemistry.[20] Recently, wide applications of calixarenes have been further expected, because they have many hydroxy groups in small-size molecules and some unique characteristic properties, such as high thermal stability, a high glass transition temperature (T_g),[21] a high melting temperature (T_m),[22] and good film-forming properties.[23,24] Applications as positive- and negative-type photoresist of the calixarene derivatives have been reported by Ueda[25,26] et al. and Fujita[23,24] et al., respectively. Furthermore, Nishikubo et al. have reported on the synthesis and photochemical reactions of new calix[n]arene derivatives[27,28] containing

Published on the web July 9, 2004; DOI 10.1246/bcsj.77.1415

photo-induced polymerizable groups, such as vinyl ether,[21] (meth)acrylate,[29] propargyl ether,[21] oxetane,[29] oxirane,[29] and spiro ortho ester groups,[30] and photo-induced deprotection groups, such as *tert*-butylcarbonate, trimethylsilyl ether,[31] cyclohexenyl ether groups,[31] and *tert*-buthyl ester groups.[32] It was also found that these obtained calixarene derivatives had excellent thermal stability and high photochemical reactivity in the film state due to the small size molecules. These results indicated that calixarene derivatives would be applicable to additional new photo-functional materials.

Given these backgrounds, we examined the refractive-index change of calixarene derivatives containing NBD before and after photoinduced isomerization. In this article, the largest value of refractive-index change in the field of organic materials or polymer films would be reported as far as we know.

Experimental

Materials. The reaction solvent, *N*-methyl-2-pyrroridone (NMP) was dried with CaH_2 and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Cesium carbonate (Cs_2CO_3), and 3-bromo-1,2-epoxypropane (Gly-Br) were used without further purification. 3-Phenyl-2,5-norbornadiene-2-carboxylic acid (PNC) was obtained from Sanpo Kagaku Co., Ltd., and was recrystallized from hexane before use. *p-tert*-Butylcalix[8]arene (BCA) and *p*-methylcalix[6]arene (MCA) were donated from Shin Nakamura Chemical Co., Ltd. BCA was purified by recrystallization from tetrahydrofuran (THF) and MCA was achieved by precipitation from THF into methanol. Calix[4]resorcinarene (CRA),[33] 2,8,14,20-tetradecylcalix[4]resorcinarene (CRA_{10}),[32] 2,8,14,20-tetra(4-hydroxyphenyl)-calix[4]resorcinarene (CRA_{ph})[32] were synthesized according to reported method.

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The ^{1}H NMR spectra were recorded on Varian Gemini-200 (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR) and JEOL Model JNM α-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) instruments in $CDCl_3$ and DMSO-d_6 using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. The glass transition temperatures (T_gs) of the calixarene derivatives were measured on a Seiko Instruments differential scanning calorimeter (DSC) Model EXSTAR6000/DSC6200 at a heating rate of 10 °C/min under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) Model EXSTAR6000/TG/DTA6200 at a heating rate of 10 °C/min under nitrogen. The refractive-index (NOS) of the calixarene derivatives with about 0.1 μm on spin coating on silicon-wafers was measured by Ellipsometry at 0.6328 μm with a Gaertener Scientific. Co. model L116C ellipsometer.

Synthesis of 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis(oxiranylmethoxy)calix[8]arene (BCA-Gly), 5,11,17,23,29,35-Hexamethyl-37,38,39,40,41,42-hexakis(oxiranylmethoxy)calix[6]arene (MCA-Gly), 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-octakis(oxiranylmethoxy)calix[4]resorcinarene (CRA_1-Gly), 2,8,14,20-Tetradecyl-4,6,10,12,16,18,22,24-octakis(oxiranylmethoxy)calix[4]resorcinarene (CRA_{10}-Gly), 2,8,14,20-Tetrakis(*p*-hydroxyphenyl)calix[4]resorcinarene (CRA_{ph}-Gly). A typical procedure for the synthesis of BCA-Gly is as follows: BCA (0.811 g, 0.625 mmol) was added to the solution of Cs_2CO_3 (2.281 g, 7.0 mmol) in NMP (5 mL). The reaction mixture was stirred at 50 °C for 3 h. Gly-Br (0.959 g, 7.0 mmol) was added dropwise to the resulting mixture, and it was stirred at 50 °C for 48 h. After that, $CHCl_3$ (20 mL) was added to the mixture, and the resulting suspension was washed with water 5 times. The organic phase was dried using $MgSO_4$ and concentrated by a rotary evaporator. The residue was poured into large amounts of methanol to precipitate a white powdery compound. It was filtered with a membrane filter (0.45 μm) and then dried in vacuo at 60 °C for 24 h, to obtain a colorless solid (**BCA-Gly**). Yield = 1.08 g (50%). IR (film, cm^{-1}): 1478 (ν C=C of aromatic), 1247 (ν Ph–O–C), 909 (ν C–O–C of cyclic ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.11 (s, 9H, $C(CH_3)_3$), 2.30–2.58 (m, 2H, $–CH_2–O–$ of oxirane moiety), 3.08–3.10 (m, 1H, >CH– of oxirane moiety), 3.40–4.15 (m, 4H, $–O–CH_2–$, $Ph–CH_2–$), 6.96 (s, 2H, aromatic H). MALDI TOF-MS m/z 1783.21 $(M + K)^+$.

MCA-Gly: Yield = 69%. IR (film, cm^{-1}): 1467 (ν C=C of aromatic), 1215 (ν Ph–O–C), 911 (ν C–O–C of cyclic ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 1.85–2.72 (m, 5H, CH_3, CH_2 of oxirane moiety), 2.90–3.05 (m, 1H, >CH– of oxirane moiety), 3.19–4.32 (m, 4H, $–O–CH_2–$, $Ph–CH_2–$), 6.67 (s, 2H, aromatic). MALDI TOF-MS m/z 1096.02 $(M + K)^+$.

CRA_1-Gly: Yield = 60%. IR (film, cm^{-1}): 1502 (ν C=C of aromatic), 1192 (ν Ph–O–C), 909 (ν C–O–C of cyclic ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.45 (s, 3H, $–CH_3$), 2.87–4.64 (m, 11H, $–O–CH_2–$, –CH< of oxirane moiety, $–CH_2–O–$ of oxirane moiety, Ph–CH<), 5.82–6.56 (m, 2H, aromatic H). MALDI TOF-MS m/z 993.16 $(M + H)^+$.

CRA_{10}-Gly: Yield = 80%. IR (film, cm^{-1}): 1501 (ν C=C of aromatic), 1192 (ν Ph–O–C), 912 (ν C–O–C of cyclic ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.85–1.57 (m, 21H, $–C_{10}H_{21}$), 2.76–4.40 (m, 11H, $–O–CH_2–$, –CH< of oxirane moiety, $–CH_2–O–$ of oxirane moiety, –CH<), 5.83–6.57 (m, 2H, aromatic H). MALDI TOF-MS m/z 1497.56 $(M + H)^+$.

CRA_{ph}-Gly: Yield = 75%. IR (film, cm^{-1}): 1508 (ν C=C of aromatic), 1179 (ν Ph–O–C), 913 (ν C–O–C of cyclic ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.51–3.34 (m, 6H, $–O–CH_2–$), 3.85–5.13 (m, 10H, –CH< of oxirane moiety, $–CH_2–O–$ of oxirane moiety, Ph–CH<), 6.17–7.27 (m, 6H, aromatic H). MALDI TOF-MS m/z 1304.38 $(M + H)^+$.

Synthesis of 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis{3-[(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy}calix[8]arene (BCA-NBD), 5,11,17,23,29,35-Hexamethyl-37,38,39,40,41,42-octakis{[3-(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy}calix[6]arene (MCA-NBD), 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-octakis{[3-(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy}calix[4]resorcinarene (CRA_1-NBD), 2,8,14,20-Tetradecyl-4,6,10,12,16,18,22,24-octakis{[3-(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy}calix[4]resorcinarene (CRA_{10}-NBD), and 2,8,14,20-Tetra[4-(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy]-4,6,10,12,16,18,22,24-octakis{[3-(3-phenyl-2,5-norbornadiene-2-carboxyl)-2-hydroxylbutan]-oxy}calix[4]resorcinarene (CRA_{ph}-NBD). A typical procedure for the synthesis of BCA-NBD is as follows. The mixture of BCA-Gly (0.87 g, 0.5 mmol), PNC (1.27 g, 6.0 mmol), and TBAB (0.097 g, 0.3 mmol) in NMP (6.0 mL) was stirred at 70 °C for 15 h. Then, AcOEt (30 mL) was added to the mixture, and the resulting solution was washed with water (20 mL) 5 times. The organic phase was dried over $MgSO_4$ and concentrated by a rotary evaporator. The residue was poured into large excess methanol to precipitate a white powdery compound. The obtained product was reprecipitated twice from $CHCl_3$ into excess methanol and dried in vacuo at 60 °C for 24 h to obtain a colorless solid, **BCA-NBD**. The degree of introduction (DI) of

the epoxide group of **BCA-NBD** was calculated to be 97% by ^{1}H NMR integration of the signal for the aromatic protons at 6.96 ppm and methylene protons of the NBD at 2.07 ppm. Yield = 0.426 g (26%). IR (film, cm^{-1}): 1086 (ν Ph–O–C of ether), 1236 (ν C–O–C of ester), 1481 (ν C=C of aromatic), 1594 (ν C=C in NBD), 1698 (ν C=O of ester), 3443 (ν OH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.04 (broad s, 9.0H, $C(CH_3)_3$), 2.07 (s, 1.9H, $-CH_2-$ in NBD), 3.56–4.02 (m, 8.5H, $-CH_2-CH-CH_2-O-$, Ph–CH_2-, >CH– of NBD), 6.82–7.43 (m, 8.5H, –CH=CH– of NBD, aromatic H).

MCA-NBD: DI (the degree of introduction of epoxide groups) = 97%. Yield = 70%. IR (film, cm^{-1}): 1235, 1217 (ν Ph–O–C of ether), 1455 (ν C=C of aromatic), 1593 (ν C=C of in NBD), 1696 (ν C=O of ester), 3478 (ν OH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.93–2.08 (m, 1.9H, CH_2 in NBD), 2.16 (s, 3.0H, $-CH_3$), 3.58–4.33 (m, 8.6H, $-CH_2-CH-CH_2-O-$, Ph–CH_2-, >CH– of NBD), 6.82–7.43 (m, 8.6H, –CH=CH– of NBD, aromatic H).

CRA-NBD: DI = 81%. Yield = 36%. IR (film, cm^{-1}): 1216 (ν Ph–O–C of ether), 1448 (ν C=C of aromatic), 1604 (ν C=C of in NBD), 1695 (ν C=O of ester), 3200–3600 (ν OH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.39 (s, 3.0H, CH_3), 2.03–2.28 (m, 3.3H, CH_2 in NBD), 6.27–7.48 (m, 13.6H, –CH=CH– of NBD, aromatic H).

CRA_{10}-NBD: DI = 80%. Yield = 38%. IR (film, cm^{-1}): 1100 (ν Ph–O–C of ether), 1236 (ν C–O–C of ester), 1455 (ν C=C of aromatic), 1604 (ν C=C in NBD), 1694 (ν C=O of ester), 3200–3600 (ν OH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.85–1.60 (m, 21.0H, $C_{10}H_{21}$), 1.90–2.26 (m, 3.2H, CH_2 in NBD), 3.38–4.43 (m, 14.2H, O–CH_2–CH–CH_2–O–, Ph–CH<, –CH< in NBD), 6.86–7.49 (m, 14.3H, CH=CH in NBD, aromatic H).

CRA_{ph}-NBD: DI = 86%. Yield = 42%. IR (film, cm^{-1}): 1219 (ν Ph–O–C of ether), 1455 (ν C=C of aromatic), 1609 (ν C=C in NBD), 1693 (ν C=O of ester), 3200–3600 (ν OH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.96–2.17 (m, 5.48H, CH_2 in NBD), 2.89–4.14 (m, 21.4H, O–CH_2–CH–CH_2–O–, Ph–CH<, –CH< in NBD), 6.86–7.36 (m, 19.1H, CH=CH in NBD, aromatic H).

The Photochemical Valence Isomerization of the Calixarene Derivatives with Pendant NBD Moieties, BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, and CRA_{ph}-NBD. A typical procedure for the photochemical valence isomerization is as follows: A solution of calixarene derivative with pendant NBD moieties in THF (1.0×10^{-4} mol/L) was cast on a quarts cell and dried in vacuo at room temperature to obtain a film. The resulting film was irradiated by a 500-W xenon lamp (Ushio Electric Co., UXL-500D-O) through a monochromator (Jasco Model CT-10). The rates of disappearance of λ_{max} at near 280 nm of the NBD moieties were measured by a UV spectrophotometer.

Measurement of the Stored Thermal Energy in the QC Groups in the Calixarene Derivatives. A calixarene derivatives solution in THF was cast on a poly(tetrafluoroethylene) plate and dried to form a film. The obtained film on the plate was irradiated for 30 min by a high-pressure mercury lamp without a filter at a distance of 30 cm. The irradiated film was packed in an aluminum sample tube for DSC analysis. The sample in the tube was heated at 3 °C/min.

Refractive-Index (n_D) Change of the Calixarene Derivatives before and after Photochemical Isomerization. First, 2-methoxyethylacetate solutions of the calixarene derivatives were prepared, followed by spin-coating on a silicon-wafer and hardbaked at 170 °C for 30 min. The n_D's of the calixarene derivative films with about 0.1 μm spin-coated on silicon-wafer before and after photoirradiation were determined by elipsometry.

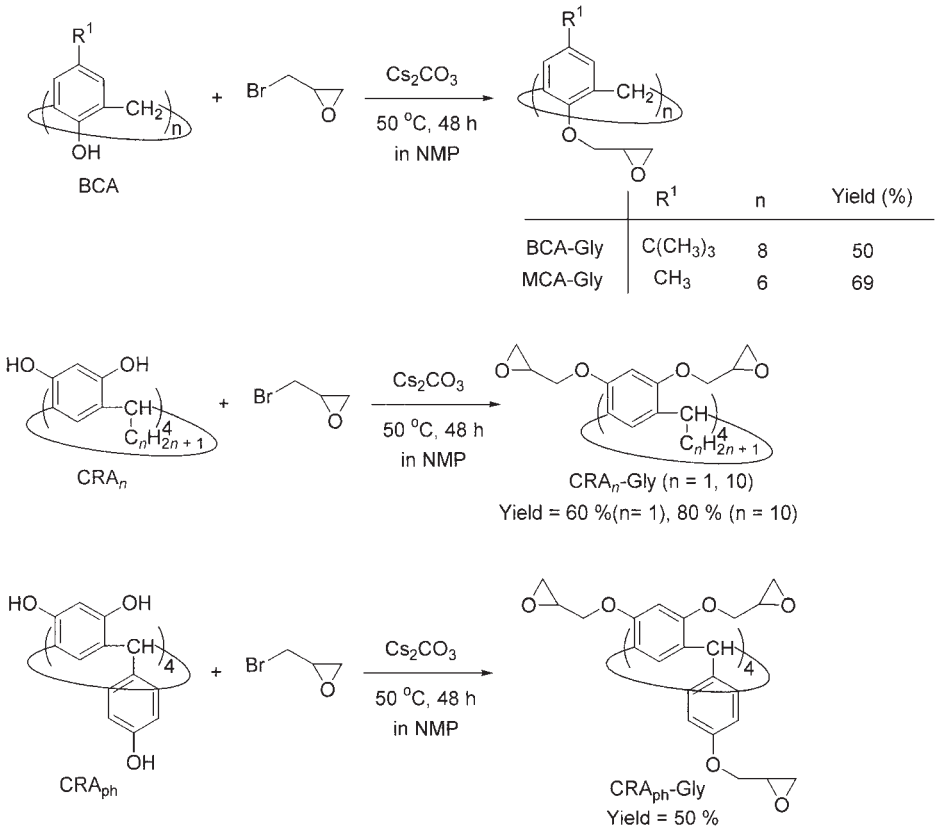
Results and Discussion

Synthesis of Calixarene Derivatives with Pendant Epoxide Groups, BCA-Gly, MCA-Gly, CRA_1-Gly, CRA_{10}-Gly, and CRA_{ph}-Gly. Calixarene derivatives (**BCA-Gly**, **MCA-Gly, CRA_1-Gly**, **CRA_{10}-Gly**, and **CRA_{ph}-Gly**) containing epoxide groups were synthesized by the reaction of calixarenes (BCA, MCA, CRA, CRA_{10}, CRA_{ph}) with Gly-Br using $CsCO_3$ in NMP at 50 °C for 48 h. The structures of the obtained products were confirmed by ^{1}H NMR, ^{13}C NMR, IR, and TOF-MS spectroscopy. These results showed that each reaction proceeded to give the corresponding calixarene derivatives containing epoxide groups, respectively, as shown in Scheme 1.

Synthesis of Calixarene Derivatives with Pendant Norbornadiene Moiety, BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, and CRA_{ph}-NBD. The reactions of the resulting **BCA-Gly**, **MCA-Gly**, **CRA_1-Gly**, **CRA_{10}-Gly**, and **CRA_{ph}-Gly** with 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNC) were carried out in the presence of TBAB as a catalyst in NMP at 70 °C for 15 h, to afford the corresponding calixarene derivatives containing the NBD moieties, (**BCA-NBD**, **MCA-NBD**, **CRA-NBD**, **CRA_{10}-NBD**, and **CRA_{ph}-NBD**) (Scheme 2). Their structures were confirmed by ^{1}H NMR spectroscopy. In the case of the **BCA-Gly**, the degree of the introduction (**DI**) of NBD moieties was calculated to be 97% by ^{1}H NMR integration of the signal for the aromatic protons at 6.96 ppm and methylene protons of the NBD at 2.07 ppm, and the yield was 26%. In the same way, we calculated the **DI**s of MCA-Gly, CRA_1-Gly, CRA_{10}-Gly, and CRA_{ph}-Gly, to be in the range of between 80 and 93%, and the yields were in the range between 30 and 70%. These results are summarized in Table 1. Furthermore, all of the synthesized calixarene derivatives were soluble in common organic solvents and had good film-forming properties.

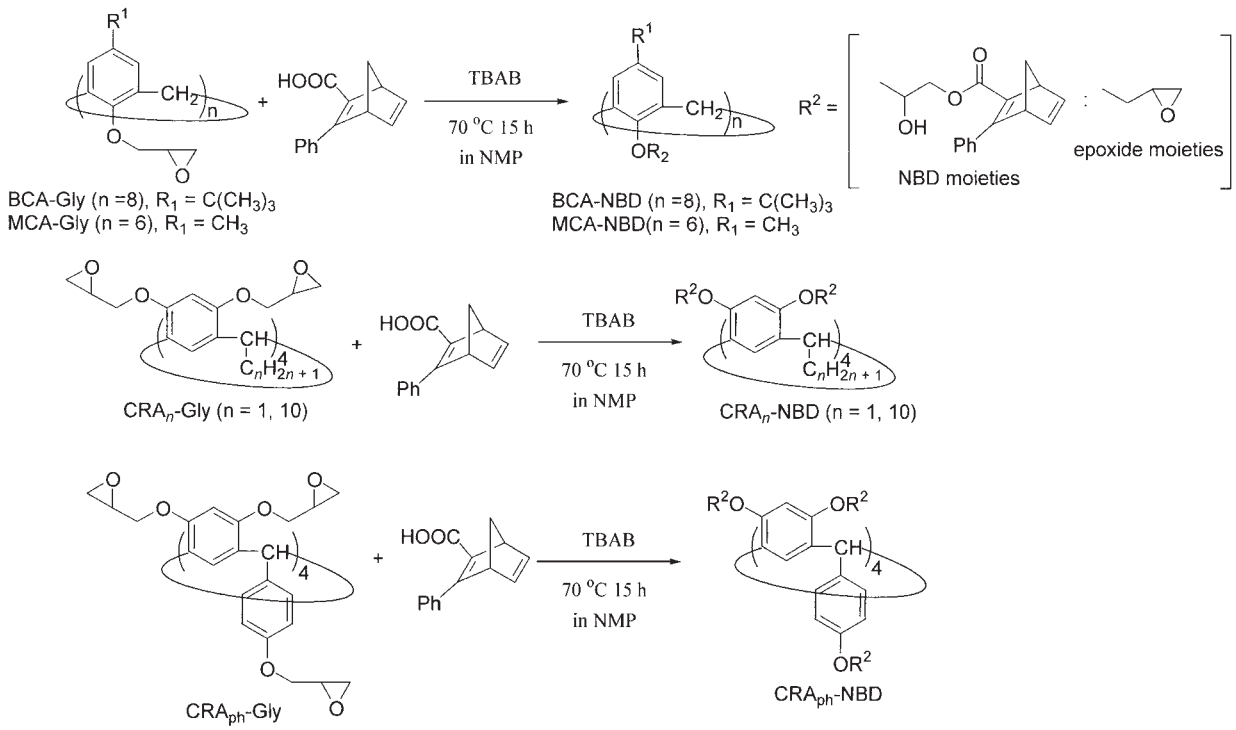
Photochemical Isomerization of BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, and CRA_{ph}-NBD. The photochemical valence isomerization of the calixarene derivatives with pendant NBD was examined as follows: after **BCA-NBD**, **MCA-NBD**, **CRA-NBD**, **CRA_{10}-NBD**, and **CRA_{ph}-NBD** were dissolved in THF (1.0×10^{-4} mol/L), the resulting solutions were cast on a quarts cell and dried in vacuo at room temperature to obtain films. When the resulting film was irradiated by a 500-W xenon lamp, λ_{max} of the NBD moiety was observed by a UV spectrometer (Scheme 3). These results are illustrated in Fig. 1. Figure 1(A) depicts the UV spectra change of **BCA-NBD** when irradiated in the film state.

It was observed that an absorption at 279 nm due to the NBD moiety decreased after only 5 min of photoirradiation. This result shows that the NBD groups isomerized quantitatively to the QC groups immediately. Isosbestic points at 249 nm were also observed. This shows that the photochemical isomerization of **BCA-NBD** occurred selectively without any side reaction upon photoirradiation. In a similar way as mentioned above, the photochemical valence isomerizations of other calixarene derivatives (**MCA-NBD**, **CRA-NBD**, **CRA_{10}-NBD**, and **CRA_{ph}-NBD**) were also examined. In the UV spectra, the λ_{max} values of these derivatives were different (Table 2), but all of the NBD moieties isomerized quantitatively to the QCs within 5 min. Their UV changes are illustrated in Fig. 1(B), (C), (D), and



	R^1	n	Yield (%)
BCA-Gly	$C(CH_3)_3$	8	50
MCA-Gly	CH_3	6	69

Scheme 1.



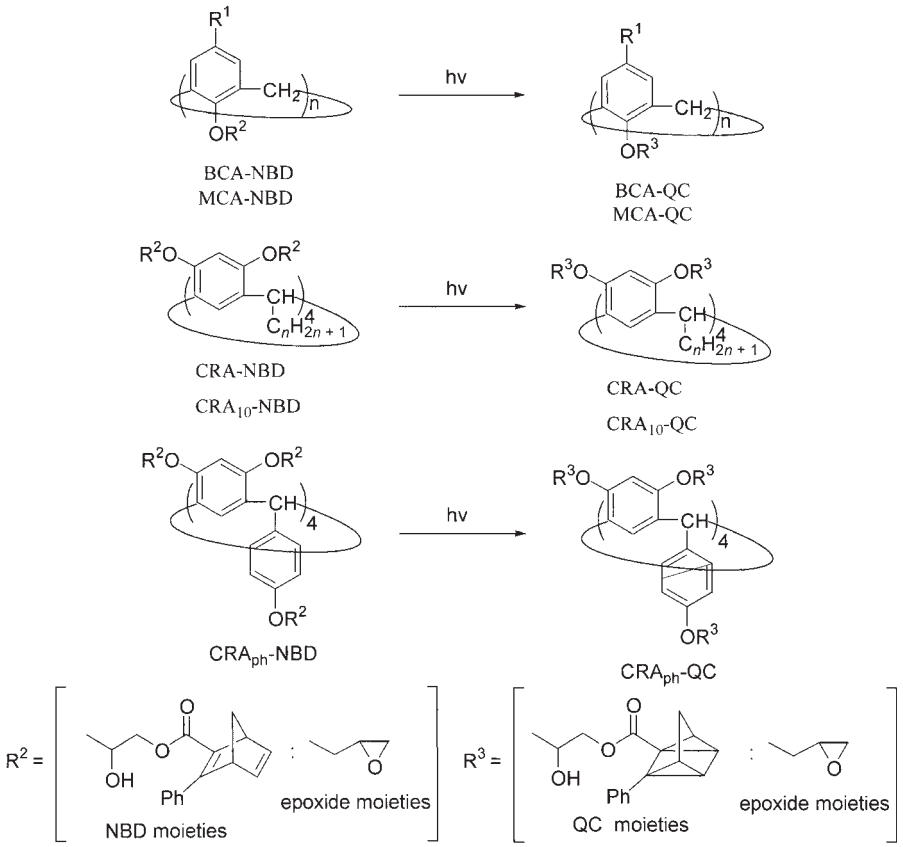
Scheme 2.

(E), respectively. Furthermore, a linear relationship was observed between the rates of the photochemical reaction ($\ln(a/a_0)$) and irradiation time, as shown in Fig. 2. The first-order rate constants in **BCA-NBD**, **MCA-NBD**, **CRA-NBD**, **CRA_{10}-NBD**, and **CRA_{ph}-NBD** are also summarized in Table 2.

Table 1. The Calixarene Derivatives Containinig NBD Moieties

Calixarene derivatives	NBD moieties/Epoxide moieties[a)]	Yield[b)]/%
BCA-NBD	93/7	26
MCA-NBD	97/3	70
CRA-NBD	81/19	36
CRA_{10}-NBD	80/20	38
CRA_{ph}-NBD	86/14	42

a) Calculated by ^{1}H NMR spectroscopy. b) Insoluble parts in methanol.



Scheme 3.

These results show that the order of the rates in the photochemical valence isomerization is as follows: **CRA_{ph}-NBD** > **CRA-NBD** > **CRA_{10}-NBD** > **BCA-NBD** > **MCA-NBD**. This means that the rate of the photochemical isomerization of the NBD moieties depends on the skeleton of the calixarenes.

Refractive-Index (n_D) Change of the Calixarene Derivatives before and after Photochemical Isomerization. The n_D's of the calixarene derivative films with about 0.1 μm spin-coated on silicon-wafer before and after photoirradiation were determined by elipsometry. A comparison of the refractive-index changes (Δn) of the calixarene derivatives is summarized in Table 3.

It was observed that the refractive-index changes are affected by the calixarene derivatives. As described in the introduction,[16,17] Horie et al. achieved a large refractive-index change of the polymer film with pendant NBD by photochemical isomerization. Furthermore, they achieved larger refractive-index change upon the photoisomerization of the polymer films with pendant cinnamoyl groups; its Δn was about 0.037.[17] This time, it was surprising that the value of Δn was 0.061 before and after irradiation of CRA_{ph}-NBD, and it is largest as far as we know. It might be indicated that the larger Δn was obtained due to the small size of the calixarene derivatives.

Furthermore, we examined the refractive-index value when the cycle photochemical valence isomerization of the CRA-NBD was repeated 10 times in the film state. Figure 3 depicts the relationship between the refractive indices values and cycle times of the photochemical valence isomerization. The value of Δn decreases slightly with the cycle times and remains at about 0.02 after 10 cycles. These results indicate that some side reactions occur in these repeat reactions.

Furthermore, the value of the thermal energy storages for the QC group in calixarene derivatives were about in the range between 33.8–89.3 kJ/mol. In addition, the glass transition temperature (T_g) and 5 wt % loss of thermal decomposition temperature (T_d^5) of these calixarene derivatives were determined by

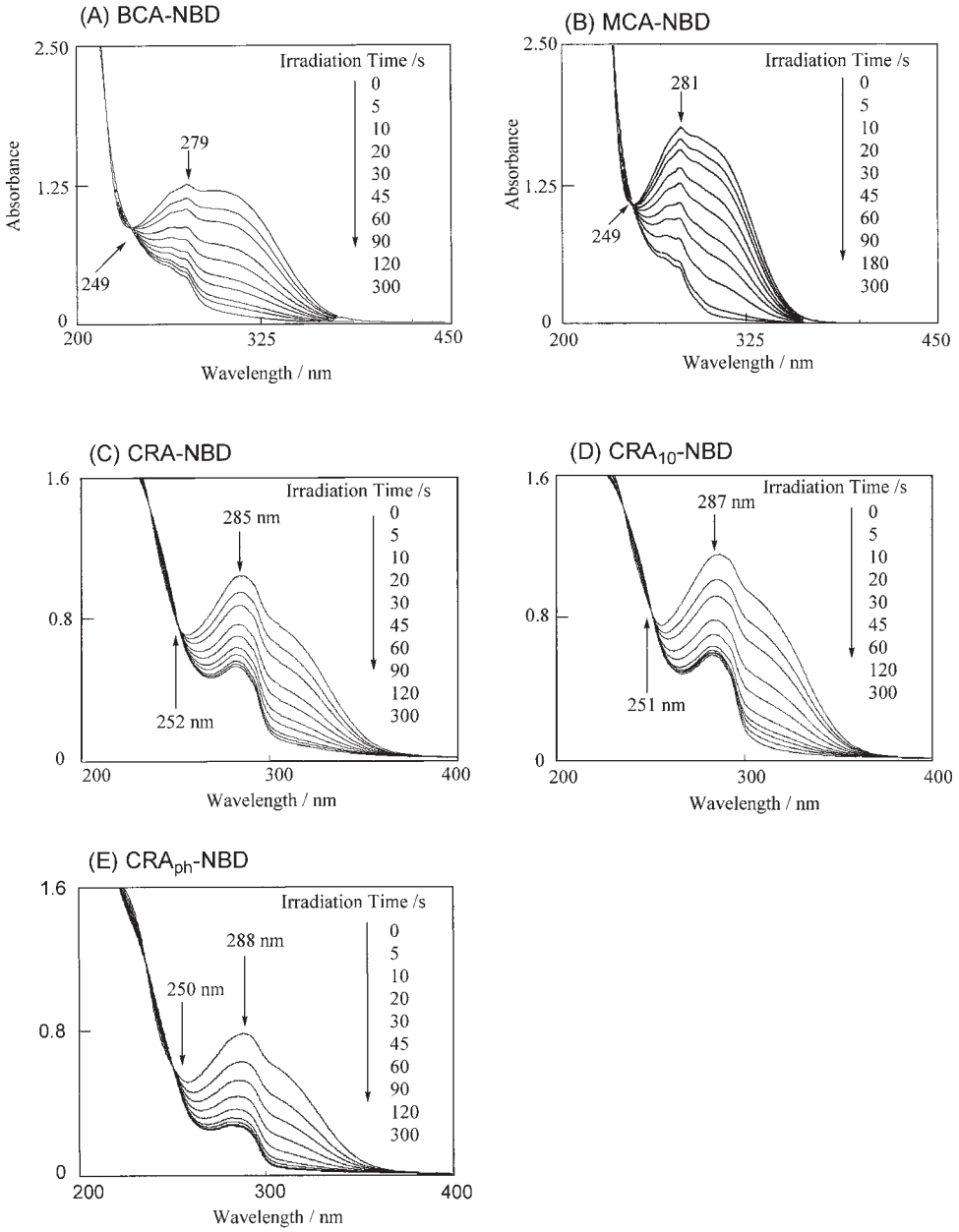


Fig. 1. Change of UV spectra of BCA-NBD in the film state upon irradiation with a 500-W xenon lamp. Intensity; 1.20 mW/cm^2 at 310 nm. (A): BCA-NBD, (B): MCA-NBD, (C): CRA-NBD, (D): CRA_{10}-NBD, (E): CRA_{ph}-NBD.

Table 2. The λ_{max} of the Calixarene Derivatives Containing NBD and First-Order Rate Constants of Photochemical Valence Isomerizations of the NBD Moieties

Calixarene derivatives	λ_{max}/nm	$k_{obd}/\times 10^3\ s^{-1}$
BCA-NBD	279	6.63
MCA-NBD	281	6.17
CRA-NBD	285	15.8
CRA_{10}-NBD	287	12.1
CRA_{ph}-NBD	288	34.0

DSC and TGA, respectively. No apparent T_g was observed up to 250 °C. T_d^5s were observed in the range of 311–369 °C. These results are also summarized in Table 3. This means that the synthesized calixarene derivatives with pendant NBD seems to be very useful new materials for the application of the optoelectronics fields.

Conclusion

We reported on the large values of the refractive-indices changes (Δn_Ds) of synthesized calixarene derivatives containing NBD moieties, (**BCA-NBD**, **MCA-NBD**, **CRA-NBD**, **CRA_{10}-NBD**, and **CRA_{ph}-NBD**) before and after photoirradiation in the film state. The values of Δn_Ds of the calixarene derivatives might be assumed from their structures. It was noteworthy that the largest value of Δn_D in the case of **CRA_{ph}-NBD** was observed to be 0.061. It is expected that the obtained calixarene derivatives are widely used for novel optoelectronics materials.

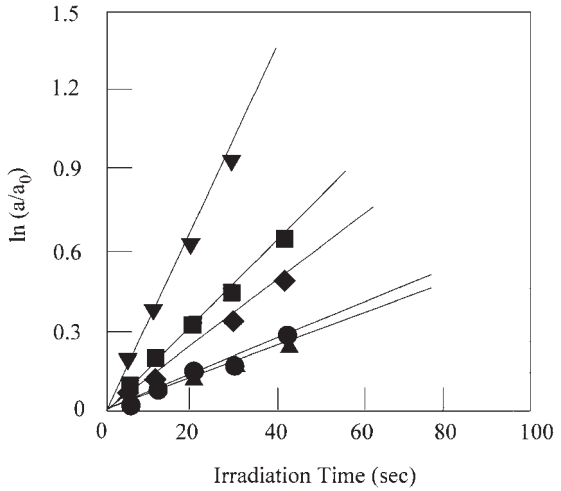


Fig. 2. First-order rates of photo-isomerization of calixarene derivatives BCA-NBD, MCA-NBD, CRA-NBD, CRA_{10}-NBD, and CRA_{ph}-NBD. (●): BCA-NBD, (▲): MCA-NBD, (■): CRA-NBD, (◆): CRA_{10}-NBD, (▼): CRA_{ph}-NBD.

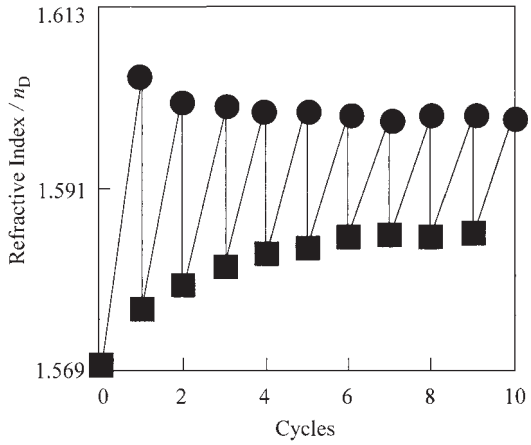


Fig. 3. Cycles of the photochemical valence isomerization and reversion between the pendant NBD moieties (CRA-NBD) and the produced QC moieties (CRA-QC) in the film state. The photochemical valence isomerization of CRA-NBD irradiation for 1 h and thermal reversion isomerization of CRA-QC at 140 °C for 30 min. (●): CRA-NBD, (■): CRA-QC.

Table 3. Refractive Indices and Their Changes for Calixarene Derivatives Films before and after Photo-Irradiation[a)]

Calixarene derivatives	n_b (NBD)[b)]	n_a (QC)[c)]	Δn[d)]	Stored thermal energy[e)] /kJ mol^{-1}	T_d[5 f)] /°C
BCA-NBD	1.592	1.564	0.028	33.8	311
MCA-NBD	1.626	1.597	0.029	46.9	332
CRA-NBD	1.682	1.633	0.049	85.5	367
CRA_{10}-NBD	1.614	1.569	0.045	89.3	368
CRA_{ph}-NBD	1.662	1.601	0.061	83.1	369

a) The n_D's of the calixarene derivative films with about 0.1 μm spin-coated on silicon-wafer before and after photoirradiation were determined by elipsometry at 632.8 nm. b) n_b (NBD) = refractive index value before irradiation. c) n_a (QC) = refractive index value after irradiation. d) $\Delta n = n_b$ (NBD) − n_a (QC). e) Calculated by DSC. f) Measured by TGA.

This work was supported by a Grant-in-Aid for Scientific Research, in Japan (No. 13450385) from the Ministry of Education, Culture, Sports, Science and Technology, which is gratefully acknowledgement.

References

1 S. Morino, S. Machida, T. Yamashita, and K. Horie, *J. Phys. Chem.*, **99**, 10280 (1995).

2 A. Toriumi, J. M. Herrmann, and S. Kawata, *Opt. Lett.*, **22**, 555 (1997).

3 L. Sharma, T. Matsuoka, T. Kimura, and H. Matsuda, *Polym. Adv. Technol.*, **13**, 481 (2002).

4 S. Yoneyama, T. Yamamoto, O. Tsutsumi, A. Kanazawa, T. Shiono, and T. Ikeda, *Macromolecules*, **35**, 8751 (2002).

5 V. Cimrova, D. Neher, R. Hildebrandt, M. Hegelich, A. Lieth, G. Marowsky, and R. Hagen, *Appl. Phys. Lett.*, **81**, 1228 (2002).

6 S. O. Konorov, A. B. Fedotov, and A. M. Zheltikov, *Appl. Phys. B: Laser and Optics*, **76**, 707 (2003).

7 K. Sasaki and T. Nagamura, *J. Appl. Phys.*, **83**, 2894 (1998).

8 K. Sasaki and T. Nagamura, *Appl. Phys. Lett.*, **71**, 434 (1997).

9 T. Kada, A. Obara, T. Tatanabe, S. Miyata, C. X. Liang, H. Machida, and K. Kiso, *J. Appl. Phys.*, **87**, 638 (2000).

10 K. W. Beeson, K. A. Horn, M. Mcfarland, and J. T. Yardley, *Appl. Phys. Lett.*, **58**, 1955 (1991).

11 T. Nishikubo, T. Shimokawa, and A. Sahara, *Macromolecules*, **22**, 8 (1989).

12 T. Nagai, M. Shimada, Y. Ono, and T. Nishikubo, *Macromolecules*, **36**, 1786 (2003).

13 N. Kawashima, A. Kameyama, T. Nishikubo, and T. Nagai, *React. Funct. Polym.*, **55**, 75 (2003).

14 A. Ikeda, A. Kameyama, T. Nishikubo, and T. Nagai, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 2778 (2001).

15 K. Kinoshita, K. Horie, S. Morino, and T. Nishikubo, *Appl. Phys. Lett.*, **70**, 2940 (1997).

16 Y. Kato, H. Muta, S. Takahashi, K. Horie, and T. Nagai, *Polym. J.*, **33**, 868 (2001).

17 S. Murase, K. Kinoshita, K. Horie, and S. Morino, *Macromolecules*, **30**, 8088 (1997).

18 G. H. Meeten, "Optical Properties of Polymers," Elsevier Applied Science, London (1989).

19 For example, Z. Asfari, V. Bohmer, and J. Harrowfield, "Calixarrewnes 2001," Kluwer Academic Publishers (2001).
20 For example, C. D. Guche, "Calixarenes," Royal Society of Chemistry, Cambridge (1989).
21 T. Nishikubo, A. Kameyama, K. Tsutsui, and M. Iyo, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 1805 (1999).
22 M. Iyo, K. Tsutsui, A. Kameyama, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 3071 (1999).
23 J. Fujita, Y. Onishi, Y. Ochiai, and S. Matsui, *Appl. Phys. Lett.*, **68**, 1297 (1996).
24 Y. Ochiai, S. Manako, H. Yamamoto, T. Teshima, J. Fujita, and E. J. Nomura, *Photopolym. Sci. Technol.*, **13**, 413 (2000).
25 T. Nakayama, K. Haga, O. Haba, and M. Ueda, *Chem. Lett.*, **1997**, 265.
26 M. Ueda, D. Takahashi, T. Nakamura, and O. Haba, *Chem. Mater.*, **10**, 2230 (1998).
27 T. Nishikubo, A. Kameyama, and H. Kudo, *Polym. J.*, **35**, 213 (2003).
28 H. Kudo, A. Kameyama, and T. Nishikubo, *Nippon Insatsu Gakkaishi*, **39**, 394 (2002).
29 T. Nishikubo, A. Kameyama, and K. Tsutsui, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1169 (2001).
30 T. Nishikubo, A. Kameyama, H. Kudo, and K. Tsutsui, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1293 (2002).
31 T. Nishikubo, A. Kameyama, K. Tsutsui, and S. Kishimoto, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1481 (2001).
32 H. Kudo, K. Mitani, T. Nishikubo, M. Mitsuishi, and T. Miyashita, *Bull. Chem. Soc. Jpn.*, **77**, 819 (2004).
33 A. G. S. Hogberg, *J. Org. Chem.*, **45**, 4498 (1980).