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Novel Materials for Large Change in Refractive Index: Synthesis and Photochemical Reaction of the Ladderlike Poly(silsesquioxane) Containing Norbornadiene, Azobenzene, and Anthracene Groups in the Side Chains

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ABSTRACT: We succeeded in the synthesis of certain poly(silsesquioxane)s (poly(SCC)) with excellent refractive indices properties, which have pendant norbornadiene (NBD), azobenzene (AZ), and anthracene (AT) moieties. The photochemical reactions of the obtained poly(SCC) derivatives were examined in the film state upon UV irradiation, and it was found that poly(SCC) derivatives with NBD groups, AZ groups, and AT groups had large change in values of the refractive index (Δn_D's) before and after photoirradiation which were in the range of 0.050−0.073, 0.007−0.009, and 0.094−0.116, respectively.

Introduction

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, azobenzenes[3−5] and spiropyrans[6−8] have been investigated as the refractive index change materials with photoreversibility. Furthermore, Horie and Nishikubo experimentally confirmed large refractive index change before and after photoirradiation of poly(methyl methacrylate) containing 2-phenyl-2,5-norbornadiene moieties.[9] Recently, Horie et al. reported on the large refractive index changes of poly(methyl methacrylate) films doped with norbornadiene (NBD) derivatives and the poly(vinyl ether)-bearing NBD moieties.[10] They also found that poly(vinyl cinnamate) showed a large refractive index change by photodimerization.[11] More recently, we reported on the large change in values of the refractive index (Δn_D's $= 0.028-0.061$) of calixarene derivatives containing NBD moieties before and after photoirradiation in the film state.[12] It might be indicated that the larger Δn_D was obtained due to the small size of the calixarene derivatives containing many photoisomerizable groups. That is, it is well-known that the relationship between the refractive index (n_D), density (ρ, g/cm^3), molecular weight (M, g), and molar refraction (R, cm^3/mol) is described by the Lorentz−Lorenz equation[13]

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

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 photoreactive groups show a high refractive index change before and after UV irradiation.

Meanwhile, poly(silsesquioxane)s are one of the ladderlike polymers, and their synthesis and properties have been reported by many researchers.[14] It is expected that poly(silsesquioxane)s are useful starting polymers for the synthesis of functional materials because they have excellent thermal stabilities, fire resistances, and good film-forming properties. Furthermore, poly(silsesquioxane)s with many pendant reactive groups are obtained easily by the polycondensation of trialkoxysilanes containing alkyl halide groups.[15]

Given these backgrounds, we examined the synthesis and photochemical reactions of poly(silsesquioxane) derivatives containing photoreactive groups in the side chains.

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP), triethylamine (NEt_3), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were dried with CaH_2 and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Potassium hydroxide (KOH) and toluene were used without further purification. (*p*-Chloromethyl)phenyltrimethoxysilane (CPTS) was dried with CaH_2 and purified by distillation before use. 3-Phenyl-2,5-norbornadiene-2-carboxylic acid (PNC) and 3-phenyl-2,5-norbornadiene-2-(4′-hydroxyphenyl) ketone (PNK) were obtained from Sanpo Kagaku Co., Ltd., and were recrystallized from hexane before use. 2-(Benzofuran-2-yl)-7,7-dimethyl-3-(5-carboxythiophene-2-yl)-5,6-bis(trifluoromethy)-2,5-norbornadiene (BTTN) and 2-(benzothiophene-2-yl)-7,7-dimethyl-3-(3,4-ethylenedioxyfuran-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (BETN) were donated from Daikin Environmental Lab., Ltd., and were used without further purification. 4-Phenylazophenol was used without further purification. 4-*tert*-Butylphenylazophenol was obtained by the previous reported.[16] 1-Carboxylanthracene, 2-carboxylanthracene, and 9-carboxylanthracene were used without further purification.

Measurements. Infrared (IR) spectra were measured on a Jasco model IR-420 spectrometer. The ^{1}H NMR spectra were recorded on JEOL model JNM α-600 (600 MHz for ^{1}H NMR and 150 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_g's) of the calixarene derivatives were

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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 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 Poly(silsesquioxane) (Poly(SCC)). A typical procedure: CPTS (2.46 g, 10.0 mmol) was added to the solution of NEt_3 (0.1 g, 1.0 mmol) in the mix solvent of water (20 mL) and toluene (40 mL). The reaction mixture was stirred at 60 °C for 12 h. After that, the resulting solution 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. Yield = 1.02 g (68%). $M_n = 10\,000$, $M_w/M_n = 2.89$. IR (film, cm^{-1}): 1606 and 1504 (ν C=C of aromatic), 1128 (ν Si−O−), 696 (ν C−Cl). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 3.34$ (br s, S−OCH_3), 4.45 (br s, −CH_2−Cl), 7.01 (br, aromatic H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 45.2$ (CH_2Cl), 127.8, 130.3, 134.1, and 139.6 (aromatic C). ^{29}Si NMR (119 MHz, $CDCl_3$, TMS): $\delta = -80.6$ ($SiO_{3/2}$).

Synthesis of Poly(silsesquioxane) Derivatives Containing NBD Groups (P−A−P−I). A typical procedure for the synthesis of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) derivatives containing NBD moieties (**P−A**) is as follows. The mixture of poly(SCC) (0.684 g), PNC (0.934 g, 4.4 mmol), and DBU (0.682 g, 4.4 mmol) in DMF (1.5 mL) was stirred at 70 °C for 6 h. Then, the resulting solution was poured into large amounts of 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, **P−A**. It was filtered with a membrane filter (0.45 μm) and then dried in vacuo at 60 °C for 24 h. The degree of introduction (DI) of the NBD moieties of **P−A** was calculated to be 100% by ^{1}H NMR integration of the signal for the aromatic protons at 6.30−7.81 ppm and methylene protons of the NBD at 1.40−2.30 ppm, and the yield was 70% (1.05 g). IR (film, cm^{-1}): 1698 (ν C=O of ester), 1608 (ν C=C of NBD), 1594 and 1490 (ν C=C of aromatic), 1218 (ν C−O−C), 1130 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 1.40-2.30$ (m, methylene protons of NBD), 3.50−4.10 (m, methine protons of NBD), 5.01 (br s, −CH_2−), 6.30−7.80 (m, aromatic H and −CH=CH− of NBD).

P−B was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and BTTN. Yield = 66%. DI = 100%. IR (film, cm^{-1}): 1710 (ν C=O of ester), 1608 (ν C=C of NBD), 1560 and 1509 (ν C=C of aromatic), 1324 (ν C−F), 1267 and 1213 (ν C−O−C of ester), 1133 (ν Si−O), 1022, 873, and 750 (ν benzofuran), 690 (thiofuran). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 1.21$ (s, methyl protons of NBD), 3.88 (s, methine protons of NBD), 5.23 (br, −CH_2−), 6.80−7.85 (m, aromatic H and benzofuran H).

P−C was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and BETN. Yield = 51%. DI = 100%. IR (film, cm^{-1}): 1710 (ν C=O of ester), 1608 (ν C=C of NBD), 1573 and 1482 (ν C=C of aromatic), 1363 (ν C−F), 1265 and 1245 (ν C−O−C of ester), 1214 (ν C−O−C of ether), 1132 (ν Si−O), 887 and 806 (furan), 755 (thiofuran). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 1.23$ (s, methyl protons of NBD), 3.78−4.40 (m, methine protons of NBD and −O−CH_2−CH_2−O−), 5.23 (br, −CH_2−COO−), 6.78−7.78 (m, aromatic H and thiofuran H).

P−D was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and PNK. Yield = 69%. DI = 100%. IR (film, cm^{-1}): 1625 (ν C=O of NBD), 1596 and 1506 (ν C=C of aromatic), 1249 (ν C=O of ester), 1133 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 2.00-2.50$ (m, methylene protons of NBD), 3.80−4.15 (m, methine protons of NBD), 4.94 (br s, −CH_2O−), 6.00−7.98 (m, aromatic H and −CH=CH of NBD).

P−E was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and 4-*tert*-butylphenylazophenol. Yield = 67%. DI = 100%. IR (film, cm^{-1}): 1600 and 1498 (ν C=C of aromatic), 1249 (ν C−O−C of ester), 1139 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 0.75-1.50$ (m, −CH_3), 4.84 (br, −CH_2O−), 4.94 (br s, −CH_2O−), 6.40−8.00 (m, aromatic H).

P−F was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and 4-phenylazophenol. Yield = 81%. DI = 100%. IR (film, cm^{-1}): 1600 and 1500 (ν C=C of aromatic), 1249 (ν C−O−C of ester), 1137 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 4.82$ (br, −CH_2O−), 4.84 (br, −CH_2O−), 6.30−8.19 (m, aromatic H).

P−G was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and 1-carboxylantharacene. Yield = 71%. DI = 100%. IR (film, cm^{-1}): 1714 (ν C=O of ester), 1614 and 1506 (ν C=C of aromatic), 1218 (ν C−O−C of ester), 1132 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 5.52$ (br, −CH_2O−), 7.50−9.49 (m, aromatic H).

P−H was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and 2-carboxylanthracene. Yield = 74%. DI = 100%. IR (film, cm^{-1}): 1714 (ν C=O of ester), 1608 and 1506 (ν C=C of aromatic), 1232 (ν C−O−C of ester), 1132 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 5.07$ (br, −CH_2OC(O)−), 6.00−8.80 (m, aromatic H).

P−I was obtained by the reaction of poly(SCC) ($M_n = 10\,000$, $M_w/M_n = 2.89$) and 9-carboxylanthracene. Yield = 88%. DI = 100%. IR (film, cm^{-1}): 1720 (ν C=O of ester), 1606 and 1523 (ν C=C of aromatic), 1195 (ν C−O−C of ester), 1128 (ν Si−O). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 5.30$ (br, −CH_2OC(O)−), 6.50−8.52 (m, aromatic H).

Photochemical Reactions of the Poly(SCC) Derivatives with Pendant NBD, AZ, and AT Moieties. A typical procedure for the photochemical reaction is as follows: A solution of poly(SCC) derivative in THF (1.0×10^{-4} mol/L) was cast on a quartz 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} were measured by a UV spectrophotometer.

Measurement of the Stored Thermal Energies in the Poly(SCC) Derivatives Containing NBD, AZ, and AT. Poly(SCC) derivative 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 Poly(SCC) Derivatives before and after Photoirradiation. 2-Methoxyethyl acetate solutions of the poly(SCC) derivatives were prepared, followed by being spin-coated on a silicon wafer and hard-baked at 170 °C for 30 min. The n_D's of the poly(SCC) derivative films with about 0.1 μm spin-coated on silicon wafer before and after photoirradiation were determined by ellipsometry.

Results and Discussion

Synthesis of Poly(silsesquioxane) with Pendant Chloromethyl Groups (Poly(SCC)). It was reported that ladderlike poly(silsesquioxane)s were obtained easily by the basic condensation of trimethoxysilanes. According to these previous reports,[15] the polycondensations of (*p*-chloromethyl)phenyltrimethoxysilane (CPTS) were synthesized (Scheme 1). These conditions and results are summarized in Table 1.

In all cases, the reaction mixtures were consistently homogeneous with products remaining in the solutions, and no gelation was observed. The SEC of the obtained polymers showed unimodal curves. It was observed that M_n's and yields of the polymers increased with until 12 h of reaction. At this point, the polymer with $M_n = 10\,000$ ($M_w/M_n = 2.89$) was obtained in a 68% yield. Accordingly, it seems that 12 h is an enough time to obtain the soluble polymer with a high M_n in

Scheme 1

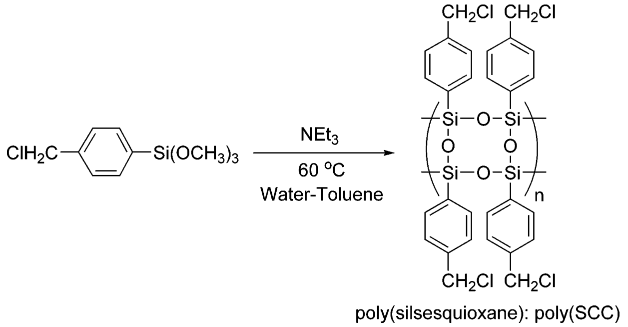


Table 1. Synthesis of Poly(silsesquioxane) with Pendant Chloromethyl Groups[a]

run	reaction time (h)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	6	68	7 800	2.25
2	12	68	10 000	2.89
3	24	60	10 300	2.49
4	48	65	10 400	2.29
5	72	57	10 000	2.44

[a] The reaction of (4-chloromethyl)phenyltrimethoxysilane (1.0 mmol) was carried out using NEt_3 (0.1 mmol) in the mix solvents of water (2 mL) and toluene (4 mL) at 60 °C. [b] Insoluble parts in methanol. [c] Estimated by SEC based on polystyrene standards in THF.

good yield. The obtained polymers were soluble in common organic solvents, such as DMSO, DMF, THF, and $CHCl_3$. The structures of the obtained polymers were confirmed by IR, ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy. In the IR spectra, the characteristic absorption peaks were observed at 1504 and 1604 cm^{-1} due to C=C stretching of the aromatic moieties, 1128 cm^{-1} due to the Si−O stretching of poly(SCC), and 696 cm^{-1} due to the C−Cl stretching of chloromethyl moieties. ^{13}C NMR spectra also showed the signals assignable to methylene carbons of the chloromethyl moieties at 45.2 ppm and aromatic carbons at 127.8−139.6 ppm. Furthermore, in the ^{29}Si NMR, only $SiO_{3/2}$ signal was observed at −80.6 ppm. These results show that the obtained products are ladderlike polymers. However, ^1H NMR spectra showed the signals assignable to methyl protons of methoxysilyl moieties at 3.34 ppm in addition to methylene protons of the chloromethyl moieties at 4.45 ppm and aromatic protons at 7.01 ppm (Figure 1A). This means that obtained ladderlike polymers had branched structures in part. From these spectroscopic data along with the solubility of the obtained polymers, the polycondensation of CPTS using NEt_3 proceeded to afford mainly ladderlike poly(silsesquioxane)s containing chloromethyl groups (poly(SCC)) in the side chains.

Synthesis of Poly(silsesquioxane) with Pendant Norbornadiene Moieties (P−A−P−D). The reactions of the resulting poly(SCC) (M_n = 10 000, M_w/M_n = 2.89) with PNC afforded the corresponding poly(SCC) derivative containing NBD moieties in the side chain (**P−A**) (Scheme 2). The structure of the obtained **P−A** was confirmed by IR and ^1H NMR spectroscopy. Figure 1 illustrated the ^1H NMR spectra of **P−A** along with the poly(SCC). The ^1H NMR spectrum of poly(SCC) showed the methylene protons of the chloromethyl moieties at 4.45 ppm (Figure 1A), while those of the poly(SCC) derivative did not (Figure 1B). This means that the reaction chloromethyl groups of poly(SCC) (M_n = 10 000, M_w/M_n = 2.89) and PNC proceeded quantitatively. Furthermore, the degree of the introduction (DI) of NBD moieties of **P−A** was calculated to be 100% by ^1H NMR integration of the signal for the aromatic protons at 6.30−7.81 ppm and methylene protons of the NBD at 1.40−2.30 ppm, and the yield was 70%.

In the same way, we examined the reaction of poly(SCC) with certain NBD derivatives, BTTN and BETN, affording the corresponding poly(SCC) derivatives **P−B** and **P−C** with DI = 100% in 66 and 51% yields, respectively, as shown in Scheme 2. Furthermore, in a similar manner as mentioned above, the reaction of poly(SCC) with PNK was performed to give the corresponding poly(SCC) derivative **P−D** with DI = 100% in a 69% yield.

Synthesis of Poly(silsesquioxane) with Pendant Azobenzene (AZ) Moieties (P−E and P−F). The reaction of the poly(SCC) (M_n = 10 000, M_w/M_n = 2.89) with 4-*tert*-butylazophenol afforded the corresponding poly(SCC) derivative containing azobenzene (AZ) moieties in the side chain (**P−E**) with DI = 100% in a 67% yield in a similar way as the synthesis for **P−A**

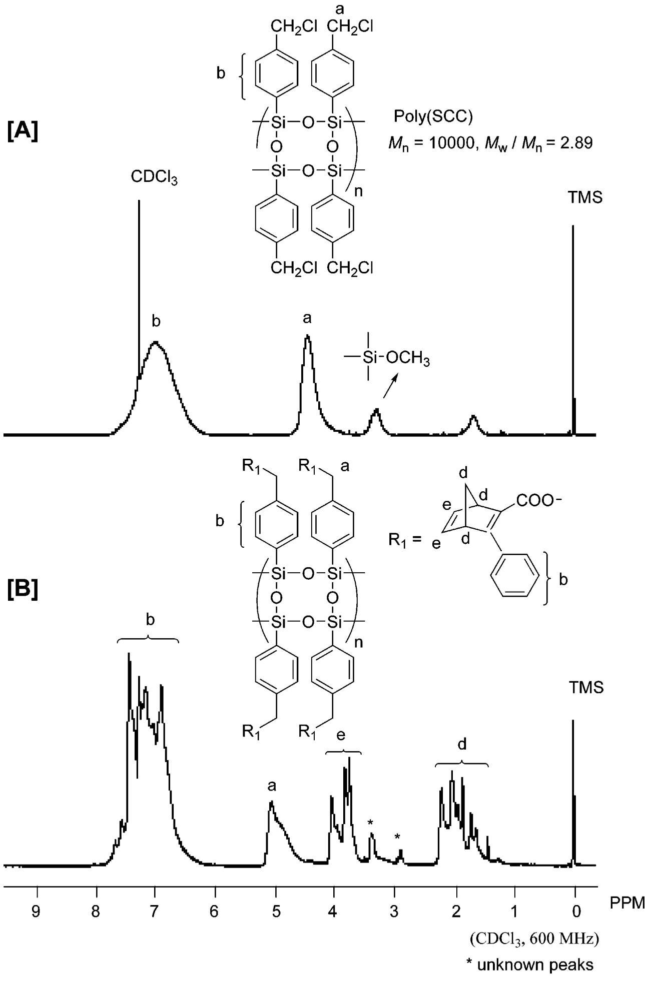
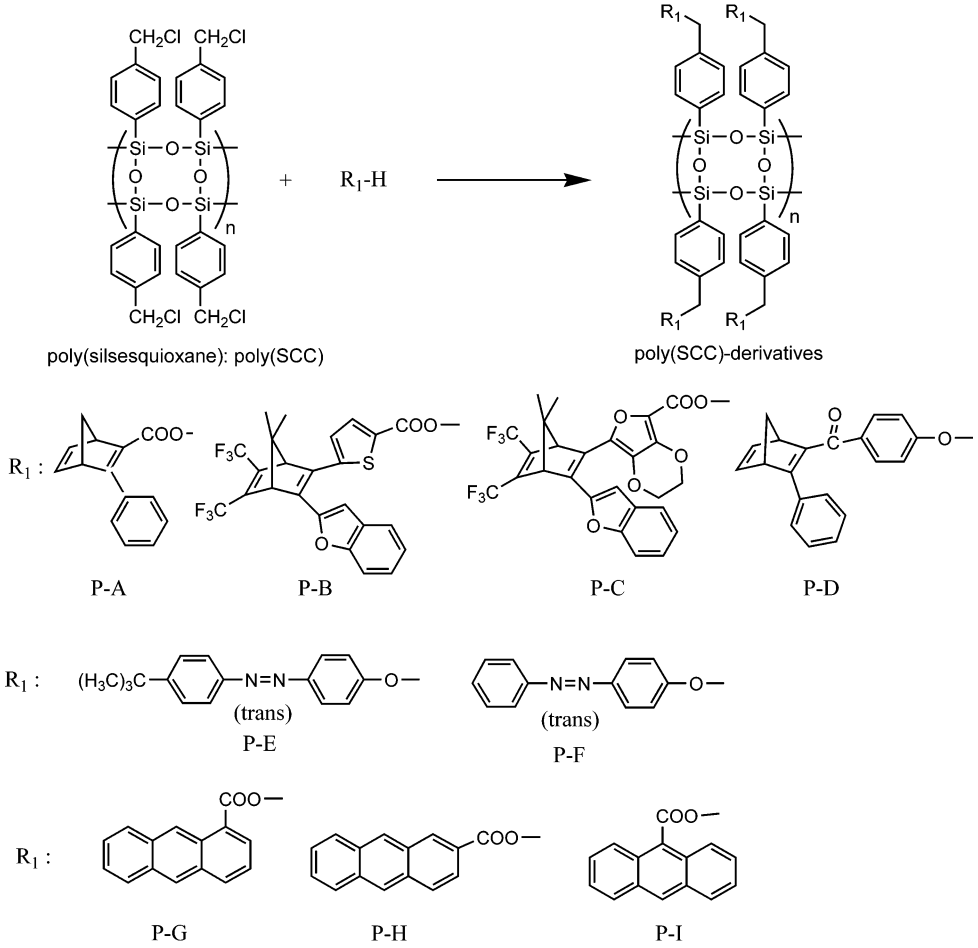


Figure 1. ^1H NMR spectra (600 MHz, $CDCl_3$) of poly(SCC) (M_n = 10 000, M_w/M_n = 2.89, run 2 in Table 1) and poly(SCC) derivative **P−A** obtained by the reaction of poly(SCC): (A) poly(SCC); (B) poly(SCC) derivative **P−A**.

Scheme 2



as mentioned above. The structure of the obtained **P−E** was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Furthermore, the poly(SCC) derivative **P−F** was obtained by the reaction of poly(SCC) with 4-phenylazophenol with DI = 100% in a 81% yield (Scheme 2).

Synthesis of Poly(silsesquioxane) with Pendant Anthracene (AT) Moieties (P−G−P−I). In a similar manner as described in the synthesis of **P−A**, the poly(SCC) derivative containing anthracene (AT) moieties in the side chain (**P−G**) with DI = 100% was obtained in a 70% yield by the reaction of poly(SCC) (M_n = 10 000, M_w/M_n = 2.89) with 1-carboxylanthracene. Furthermore, **P−H** and **P−I** were prepared by the reaction of 2-carboxylanthracene and 9-carboxylanthracene with DI = 100% in 74 and 88% yields, respectively (Scheme 2).

Furthermore, it was observed that all of the synthesized poly(SCC) derivatives were soluble in common organic solvents and had good film-forming properties.

Photochemical Valence Isomerization of Poly(SCC) Derivatives Containing NBD Moieties P−A−P−D. The photochemical valence isomerization of the poly(SCC) derivatives **P−A−P−D** with pendant NBD groups was examined in the film states. The resulting films were irradiated by a 500 W xenon lamp, and the decrease of λ_{max} of the NBD moiety was observed by a UV spectrometer. These results are illustrated in Figure 2. Figure 2A depicts the UV spectra changes of **P−A** when the resulting film was irradiated.

It was observed that an absorption maxima at 295 nm due to the NBD moiety decreased after only 5 min of photoirradiation. This result shows that the NBD groups isomerized quantitatively to the corresponding QC groups immediately (Scheme 3A). In this reaction, two isosbestic points at 239 and 249 nm were also observed. This shows that the photochemical valence isomerization of **P−A** occurred selectively without any side reaction under this irradiation condition. In a similar way as mentioned above, the photochemical valence isomerizations of other poly(SCC) derivatives **P−B**, **P−C**, and **P−D** were also examined. In the UV spectra, the λ_{max}s of these derivatives were different, but all of the NBD moieties isomerized quantitatively to the QCs within 5 min. Their UV spectra changes are illustrated in parts B, C, and D of Figure 2, respectively. Furthermore, a linear relationship was observed between the rates of the photochemical reaction ($\ln(a/a_0)$) and irradiation time, and the first-order rate constants in **P−A**, **P−B**, **P−C**, and **P−D** are summarized in Table 2. These results show that the rates in the photochemical valence isomerization is as follows: **P−B** ≥ **P−C** > **P−D** > **P−A**. This means that the rate of the photochemical isomerization of NBD moieties depends on their absorption maxima. That is, the λ_{max}s of **P−A**, **P−B**, **P−C**, and **P−D** were 295, 408, 408, and 335 nm, respectively.

Photochemical Isomerization of Poly(SCC) Derivatives Containing Azobenzene (AZ) Moieties P−E−P−F. In a similar way as mentioned above, the photochemical trans−cis isomerizations of poly(SCC) derivatives containing AZ moieties in the side chain **P−E** and **P−F** were also examined (Scheme 3B). Figure 3 depicts the UV spectra changes of **P−E** and **P−F** when the resulting films were irradiated.

It was observed that absorption peaks at 335 and 333.5 nm due to the *trans*-azobenzene moiety of P−E and P−F decreased

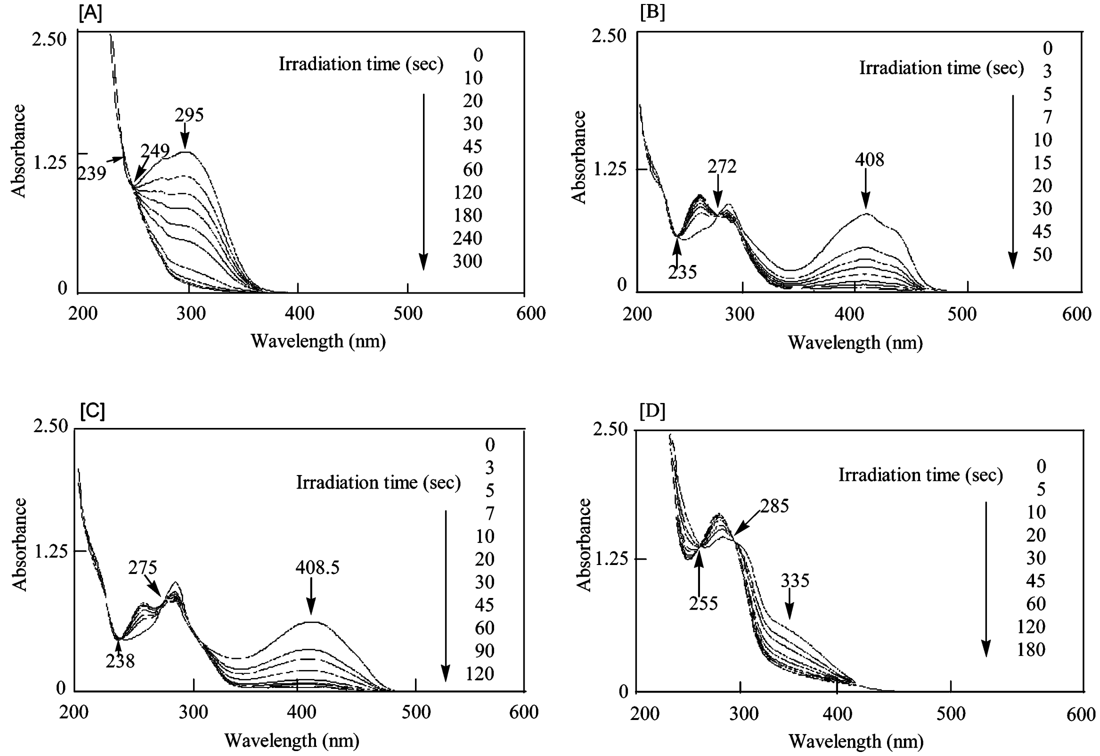


Figure 2. Change of UV spectra of poly(SCC) derivatives containing NBDs in the film state upon irradiation with a 500 W xenon lamp. Intensity: 1.20 mW/cm^2 at 310 nm. (A) **P−A**, (B) **P−B**, (C) **P−C**, and (D) **P−D**.

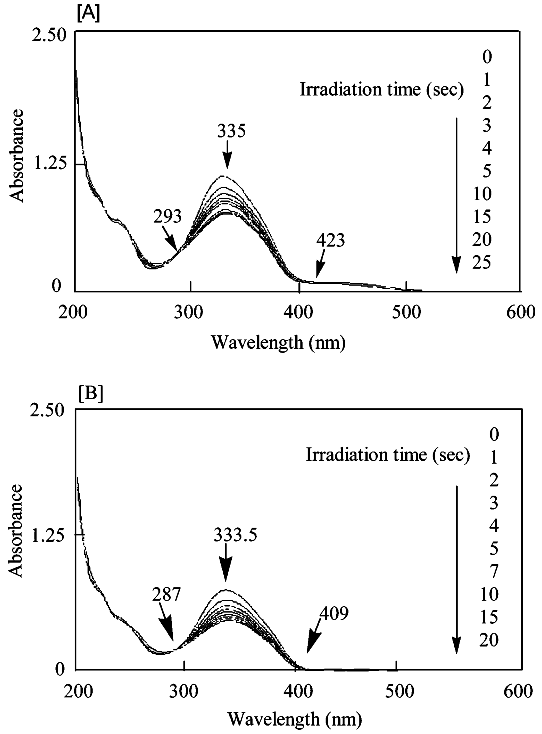


Figure 3. Change of UV spectra of poly(SCC) derivatives containing AZs in the film state upon irradiation with a 500 W xenon lamp. Intensity: 1.20 mW/cm^2 at 310 nm. (A) **P−E**; (B) **P−F**.

Table 2. First-Order Rate Constants of Polymers Containing NBD Moieties in the Film State

polymer	λ_{max} (nm)	isosbestic point (nm)	$k_{obd} \times 10^{-2}$ (s^{-1})
P−A	295.0	239.0, 249.0	0.97
P−B	408.0	235.0, 272.0	7.38
P−C	408.5	238.0, 275.0	7.19
P−D	335.0	255.0, 285.0	2.86
P−E	335.0	293.1, 423.3	10.9
P−F	333.5	287.3, 409.6	13.1
P−G	389.5	294.2, 453.1	1.08
P−H	385.5	446.4	1.46
P−I	369.0	446.5	1.45

after only 25 s of the photoirradiation. This result shows that the *trans*-azobenzene moieties isomerized quantitatively to the *cis*-azobenzene moieties immediately. Two isosbestic points approximately at 290 and 410 nm were also observed. This result showed that the photochemical isomerization of **P−E** and **P−F** occurred selectively without any side reaction under these irradiation conditions, and a linear relationship between the rates of the photochemical reaction (ln(a/a_0)) and irradiation time was observed. The first-order rate constants in **P−E** and **P−F** are summarized in Table 2. This means that photochemical reactivities of poly(SCC) derivatives with pendant AZ groups are relatively higher than those of poly(SCC) derivatives with pendant NBD.

Photochemical Dimerization of Poly(SCC) Derivatives Containing Anthracene (AT) Moieties P−G−P−I. Furthermore, the photochemical dimerization of poly(SCC) derivatives containing AT moieties in the side chain **P−G−P−I** were examined in the similar way with **P−A**. Figure 4 depicts the UV spectra changes of **P−G−P−I** by the irradiation in the film state.

It was observed that an absorption peak at approximately 390 nm due to the AT moieties decreased after 25 min of the photoirradiation. This result shows that the AT moieties converted quantitatively to the AT dimers (Scheme 3C). Each polymer also showed an isosbestic point at approximately 450 nm. This means that the photochemical reaction of **P−G−P−I** occurred smoothly without any side reaction upon photoirradiation, and a linear relationship between the rates of the photochemical reaction (ln(a/a_0)) and irradiation time was observed. The first-order rate constants in **P−G−P−I** are also summarized in Table 2. It seems that this photochemical reaction

Scheme 3

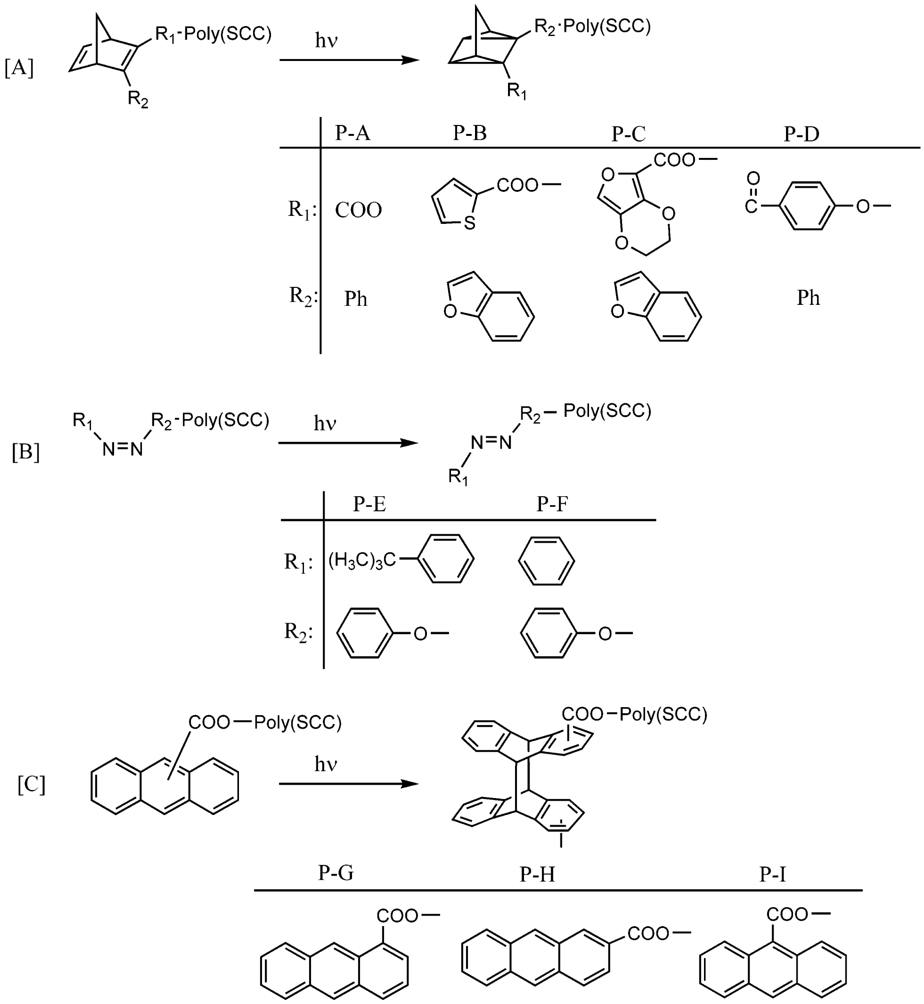


Table 3. Refractive Indices, Their Changes for Poly(SCC) Derivatives Films before and after Photoirradiation, Stored Thermal Energy, and Thermal Decomposition Temperatures[a]

poly(SCC) derivatives (photoisomerizable group)	n_b[b]	n_a[c]	Δn_D[d]	stored thermal energy[e]/kJ mol^{-1}	$T_d{}^5$[f]/°C
P−A (NBD)	1.602	1.552	0.050	50.6	329.2
P−B (NBD)	1.602	1.529	0.073	22.9	319.4
P−C (NBD)	1.596	1.523	0.073	11.5	325.0
P−D (NBD)	1.626	1.573	0.053	50.2	370.0
P−E (AZ)	1.630	1.623	0.007	1.5	323.0
P−F (AZ)	1.671	1.662	0.009	3.4	318.3
P−G (AT)	1.670	1.567	0.103	4.3	302.0
P−H (AT)	1.688	1.572	0.116	3.5	365.0
P−I (AT)	1.660	1.566	0.094	14.7	308.3

[a] The n_D's of the poly(SCC) 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 = refractive index value before irradiation. [c] n_a = refractive index value after irradiation. [d] $\Delta n_D = n_b - n_a$. [e] Calculated by DSC. [f] Measured by TGA.

proceeded between two AT groups, and it took a longer time for the complete dimerization.

Refractive Index Changes (Δn_D's) of the Poly(SCC) Derivatives before and after Photochemical Reactions. The n_D's of the poly(SCC) derivative films with about 0.1 μm spin-coated on a silicon wafer were measured by ellipsometry before and after photoirradiation. The comparisons of the refractive index changes (Δn_D's) of the poly(SCC) derivatives are summarized in Table 3.

It is well-known that the values of Δn_D's are dependent on the materials in which molar refraction and density change before and after photoirradiation.[13] That is, the changes of electronic distribution and molecular volume of poly(SCC) derivatives during the photoisomerization induced the refractive index changes. In our previous report as mentioned in the Introduction, calixarene derivatives containing NBD showed large refractive index changes (Δn_D's = 0.028−0.061) before and after photochemical valence isomerization.[12] In the case of poly(SCC) derivatives (**P−A−P−D**) containing NBD, Δn_D's were in the range between 0.050 and 0.073, which were larger than those of calixarene derivatives. This means that Δn_D's of NBDs might be supported by their structures. Furthermore, we examined the Δn_D before and after trans−cis photoisomerization of AZ based on poly(SCC) (**P−E** and **P−F**), and their Δn_D's were 0.007 and 0.009, respectively. It was also reported that Δn_D of poly(methyl methacrylate) with pendant NBD was about 0.01.[9] This means that Δn_D's of AZ are smaller than those of NBD.

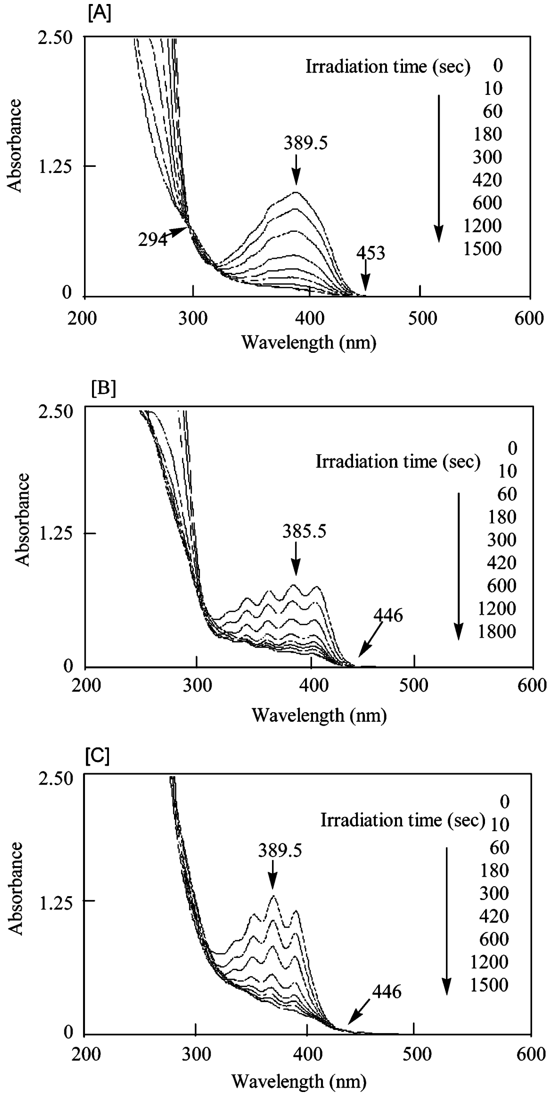


Figure 4. Change of UV spectra of poly(SCC) derivatives containing ATs in the film state upon irradiation with a 500 W xenon lamp. Intensity: 1.20 mW/cm^2 at 310 nm. (A) **P−G**; (B) **P−H**; (C) **P−I**.

Meanwhile, Knol and Müllen showed that the polymers with pendant 9-substituted AT had large Δn_D's before and after photodimerization of AT.[17] They also proposed that the synthesized polymers are applicable to the photolithography and channel waveguide; their Δn_D's were in the range between 0.013 and 0.076. In this time, we examined the Δn_D's of the poly(SCC) derivatives (**P−G−P−I**) with pendant 1-, 2-, and 9-substituted AT before and after photodimerization. It was found that their Δn_D's were in the range between 0.094 and 0.116, which were larger than those of NBD and AZ based on poly(SCC). This time, it was surprising that the value of Δn_D was 0.116 before and after irradiation of **P−H**, and it is largest as far as we know. It might be indicated that the large molecular volume change of ladderlike polymers with pendant photoisomerizable groups can occur during the photoirradiation. In addition, it was found that Δn_D of 1- and 2-substituted AT groups were higher than that of 9-substituted one.

Thermal Energy Storages and Thermal Properties of Poly(SCC) Derivatives. The values of the thermal energy storages for the QC, *cis*-azobenzene, and anthracene dimers in poly(SCC) derivatives were measured by DSC, and they were in the ranges 11.5−50.6, 1.5−3.4, and 3.5−14.7 kJ/mol. Furthermore, glass transition temperature (T_g) and 5 wt % loss of thermal decomposition temperature ($T_d{}^5$) of these poly(SCC) derivatives were determined by DSC and TGA, respectively. No apparent T_g was observed up to 250 °C in each polymer. $T_d{}^5$s were observed in the range 302.0−370.0 °C. All these results are summarized in Table 3. That is, the synthesized poly(SCC) derivatives had good thermal stability, which seem to be very useful new materials for the application of the optoelectronics fields.

Conclusion

We reported on the large change in values of the refractive index (Δn_D's) of synthesized poly(SCC) derivatives containing NBD, AZ, and AT moieties (**P−A−P−I**) before and after photoirradiation in the film state. It was observed that the values of Δn_D's of the poly(SCC) derivatives were very large. It was noteworthy that the largest value of Δn_D in the case of **P−H** was observed to be 0.116. It is expected that the obtained poly(SCC) derivatives are widely used for novel optoelectronics materials.

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