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Synthesis and Refractive-Index Properties of Star-Shaped Polysulfides Radiating from Calixarenes

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ABSTRACT: The continuous insertion reaction of phenoxypropylenesulfide (PPS) into the thioester moieties of calixarene derivatives (cores) generated from *p-tert*-butylthiacalix[4]arene (BTC[4]), 2,8,14,20-tetramethylcalix[4]resorcinarene (CRA[4]), and 2,8,14,20-tetra(4-hydroxybenzen-1-yl)calix[4]resorcinarene {CRA(Ar-OH)[4]} proceeded smoothly with tetrabutylammonium chloride (TBAC) as a catalyst to give well-defined star-shaped polysulfides with 4, 8 and 12 arms. The arm length and sulfur content of the star-shaped polysulfides were controlled by the feed ratio of PPS and core. The refractive-index values (n_D's) of the synthesized star-shaped polysulfides were determined in the film state by means of ellipsometry; the n_D's increased with increasing numbers of arms, length of arms, and sulfur content and with decreasing size of the core structure.

Introduction

The unique structures of nonlinear polymers,[1] such as star-shaped polymers, hyperbranched polymers, graft polymers, polyrotaxanes, and cyclic polymers, often result in unusual physical properties, such as high thermal stability, solubility, and density, which may lead to novel applications. Star-shaped polymers have particularly compact structures and high segment densities.[2] Various well-defined star-shaped polymers have been synthesized by living anionic polymerization,[3−5] living cationic polymerization,[6−9] and living radical polymerization.[10−16] Kennedy[17−20] et al. reported the first synthesis of a star-shaped polymer using a calixarene derivative as the core. Sawamoto et al.[21] and Taton et al.[22] also reported the synthesis of well-defined star-shaped polymers with 4, 6, and 8 arms, using calixarene derivatives as multifunctional initiators. Star-shaped polymers show higher viscosity, solubility, and thermal stability than linear polymers.[19,23−27]

Various high- and low-refractive-index polymers have been developed by many researchers, and are important materials in the field of optoelectronics such as optical lens, optical fibers, and optical waveguide. Polymers containing aromatic rings, heavy metals, halogens (Cl, Br, and I), and sulfur atoms have a high refractive index, while fluorine-containing polymers have a low refractive index.[28] That is, the value of the refractive index is determined by the constituents of the polymers. It is well-known that the relationship between refractive index (n_D), density (ρ g/cm^3), molecular weight (M g), and molar refraction (R cm^3/mol) of a polymer is described by the Lorentz−Lorenz equation[29] (1).

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

However, there has been little systematic study of the relationship between the value of n_D and polymer structure. We recently reported that star-shaped polysulfides have higher refractive index values than linear polysulfides at temperatures above the glass transition temperature (T_g) (Scheme 1).[30,31] This is because the segment motion of linear polymers is greater than that of star-shaped polymers at temperatures above the T_g.

In this paper, we designed and synthesized a series of high-refractive-index star-shaped polysulfides with different numbers of arms radiating from certain calixarene derivatives. Furthermore, we clarified the relationship between the refractive index and the structure of these polymers.

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP) and pyridine were dried with CaH_2 and purified by distillation before use. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate. Tetrabutylammonium chloride (TBAC) was used without further purification. Potassium thioacetate, tetrahydrofuran (THF), chloroacetyl chloride, ethyl acetate, and *n*-hexane were used without further purification. Phenoxypropylenesulfide (PPS), 2,8,14,20-tetramethylcalix[4]resorcinarene (CRA[4]) and 2,8,14,20-tetra(4-hydroxybenzen-1-yl)calix[4]resorcinarene {CRA(Ar-OH)[4]} were synthesized by reported methods.[30,31] *p-tert*-Butylthiacalix[4]arene (BTC[4]) was purchased from Tokyo Kasei Co. and was used without further purification.

Measurements. Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. NMR spectra were recorded on 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. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI−TOF−MS) experiments were performed on a Shimadzu/Kratos MALDI−TOF−MS using dihydroxybenzoic acid as the matrix and chloroform as the solvent. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC; Tosoh model HLC-8020) on TSK gel Multipore Hxl-M columns calibrated by means of narrow-molecular-weight polystyrene standards, using a refractive index detector without correction, with tetrahydrofuran (THF) as an eluent. The refractive index (NOS) of polymer films spun-coated to a thickness of about 0.1 μm on silicon wafers was measured by ellipsometry at 0.6328 μm with a Gaertner Scientific Co. model L116C ellipsometer.

Synthesis of Calixarene Derivatives Containing Chloromethyl Moieties. *Synthesis of 2,8,14,20,-Tetramethyl-4,6,10,12,16,18,22,24-octakis(chloroacetyloxy)calix[4]resorcinarene (CRA[4]-Cl).* To a solution of CRA[4] (2.14 g, 32 mmol as hydroxyl groups) in THF (100 mL) were added pyridine (7. 59 mL, 96 mmol), and then a solution of chloroacetyl chloride (23.65 g, 96 mmol) slowly at 0 °C under nitrogen. The mixture was stirred at room temperature for 24 h. The resulting mixture was concentrated in a rotary evaporator. Ethyl acetate (200 mL) was added to the residue, and the resulting suspension was washed with water, an aqueous solution of sodium hydrogen carbonate (5%), and water. The organic phase was dried

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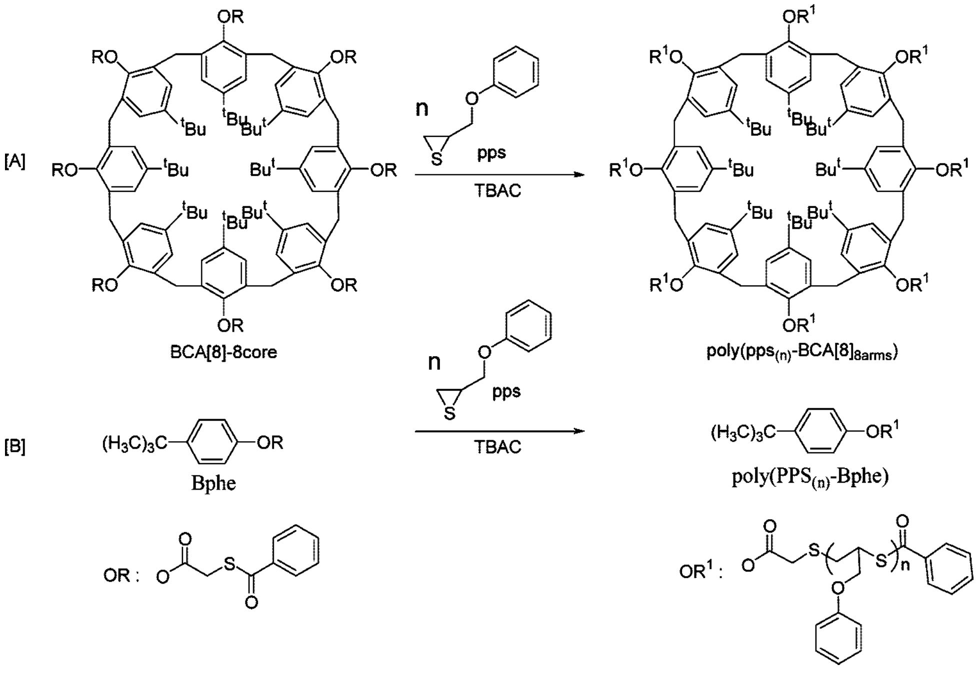
Scheme 1



over $MgSO_4$ and concentrated in a rotary evaporator. The residue was washed with hexane several times, followed by recrystallization from a mixture of $CHCl_3$ and *n*-hexane to obtain a colorless solid (CRA-Cl). Yield = 0.64 g (13%). IR (neat): v = 2968 (ν_{C-H} aliphatic), 1769 ($\nu_{C=O}$ ester), 1491 ($\nu_{C=C}$ aromatic), and 1234 (ν_{C-O-C} ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 1.51 (d, J = 7.5 Hz, 12.0 H, $-CH_3$), 4.09−4.36 (m, 20.0 H, >CH− and $-CH_2-Cl$), 6.32 (s, 4.0 H, aromatic H), 6.76 (s, 4.0 H, aromatic H). MALDI−TOF−MS: m/z (M + Na)$^+$ calcd for ($C_{48}H_{40}C_{18}O_{16}$+ Na), 1179.42; found, 1177.30.

Synthesis of 2,8,14,20-Tetra(4-chloroacetyloxybenzen-1-yl)-4,6,10,12,16,18,22,24-octakis(chloroacetyloxy)calix[4]resorcinarene{CRA[4]-(Ar-OH)-Cl}. CRA[4](Ar-OH)-Cl was synthesized by the reaction of CRA[4](Ar-OH) and chloroacetyl chloride in the same manner as described for the synthesis of CRA[4]-Cl. The product was washed with water, an aqueous solution of sodium hydrogen carbonate (5%), and water. The organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The residue was poured into a large amount of methanol to precipitate a white solid (CRA[4]-Cl). Yield = 21%. IR (neat): v = 2951 (ν_{C-H} aliphatic), 1773 ($\nu_{C=O}$ ester), 1490 ($\nu_{C=C}$ aromatic), and 1210 (ν_{C-O-C} ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 4.09−4.58 (m, 24.0 H, $-CH_2-Cl$), 4.72 (s, 4.0 H, >CH−), 6.08−7.26 (m, 24.0 H, aromatic H). MALDI−TOF−MS: m/z (M + Na)$^+$ calcd for ($C_{72}H_{56}C_{12}O_{24}$ + K), 1813.74; found, 1811.74.

Synthesis of 4,8,12,16-Tetra(chloroacetyloxy)-p-tert-butylthiacalix[4]arene (BTC[4]-Cl). BTC[4]-Cl was synthesized by the reaction of BTC[4] and chloroacetyl chloride in the same manner as described for the synthesis of CRA[4]-Cl. The obtained residue was recrystallized from $CHCl_3$ to obtain a yellow solid (BTC[4]-Cl). Yield = 14%. IR (KBr disk, cm^{-1}): 2965 (ν_{C-H} aromatic), 2868 (ν_{C-H} aliphatic), 1791 ($\nu_{C=O}$ ester), 1571,1437 ($\nu_{C=C}$ aromatic), 1114 (ν_{C-O-C} ether), 742 (ν_{C-S-C} sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) 1.31 (s, 36.0 H, $-C(CH_3)_3$), 3.40 (s, 8.0 H, $-CH_2-Cl$), 7.01 (s, 8.0 H, aromatic H).

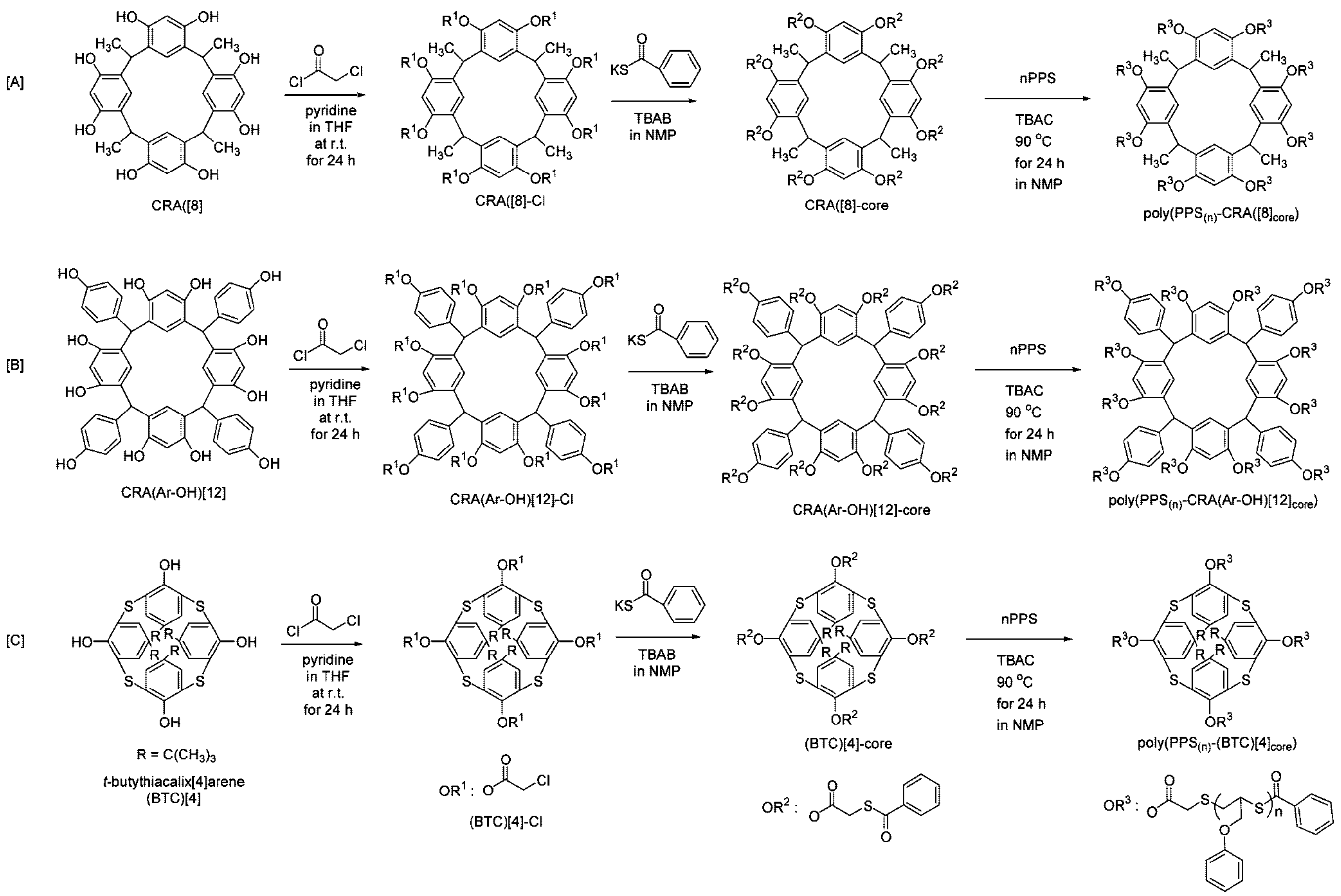
Synthesis of Calixarene Derivatives Containing Thioesters. *Synthesis of 2,8,14,20,-Tetramethyl-4,6,10,12,16,18,22,24-octakis-(benzoylthioacetyloxy)calix[4]resorcinarene (CRA[4]-8arms).* A mixture of potassium thioacetate (0.99 g, 6.0 mmol) and CRA[4]-Cl (0.3 g, 0.25 mmol) was stirred in the presence of tetrabutylammonium bromide (TBAB) (0.035 g, 0.1 mmol) in NMP (5 mL) at room temperature for 5 h. Ethyl acetate (100 mL) was added, and the resulting solution was washed with water. The organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The residue was purified by silica gel column chromatography eluted with chloroform to obtain a yellow solid (CRA[4]-8arms). Yield = 0.35 g (76%). Mp = 80.5−81.5 °C. IR (neat): v = 2972 (C−H aliphatic), 1763 (*C*═O ester), 1667 (C═O, thioester), 1595 and 1492 (C═C aromatic), 1123 (C−O−C, ether), 756 (C−S−C, sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 1.43 (d, J = 5.5 Hz, 12H, $-CH_3$), 3.35 − 3.97 (m, 16 H, $-CH_2-S-$), 4.43 (s, 4 H, >CH−), 6.32−7.94 (m, 40 H, aromatic H). MALDI−TOF−MS: m/z (M + Na)$^+$ calcd for ($C_{104}H_{80}O_{24}S_8$ + Na), 1993.26; found, 1994.43.

Synthesis of 2,8,14,20-Tetrakis(4-benzoylthioacetyloxybenzen-1-yl)-4,6,10,12,16,18,22,24-octakis(benzoylthioacetyloxy)calix[4]resorcinarene {CRA[4](Ar-OH)-12arms}. CRA[4](Ar-OH)-12arms was synthesized by the same method as described for the synthesis of CRA[4]-8arms. Yield = 56%. Mp = 86.5 − 88.0 °C. IR (neat): v = 3026 (C−H aliphatic), 1764 (*C*═O ester), 1667 (C═O, thioester), 1595 and 1504 (C═C aromatic), 1123 (C−O−C, ether), 772 (C−S−C, sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) = 3.67−4.19 (m, 24.0 H, $-CH_2-S-$), 5.71 (s, 4.0 H, >CH−), 6.20 − 8.00 (m, 64.0 H, aromatic H). MALDI−TOF−MS: m/z (M + Na)$^+$ calcd for ($C_{160}H_{112}O_{36}S_{12}$ + Na), 3018.37; found, 3016.89.

Synthesis of 4,8,12,16-Tetra(benzoylthioacetyloxy)-p-tert-butylthiacalix[4]arene (BTC[4]-4arms). BTC[4]-4arms was synthesized by the same method as described for the synthesis of CRA-[4]-8arms. Yield = 35%. Mp = 320.1 (degradation) °C. IR (neat); v = 3062 (C−H aromatic), 2964 (C−H aliphatic),1779 (*C* = O ester), 1671 (C═O, thioester), 1571 and 1475 (C═C aromatic), 1103 (C−O−C, ether), 688 (C−S−C, sulfide). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm) = 1.27 (s, 36 H, $-C(CH_3)_3$), 3.37 (s, 8 H, $-CH_2-S-$), 7.48–7.97 (m, 28H, aromatic H). MALDI−TOF−MS m/z (M + Na)$^+$ Calcd. for ($C_{160}H_{112}O_{36}S_{12}$ + Na): 3018.37. Found: 3016.89. Anal. Calcd. for $C_{76}H_{72}O_{12}S_8$ Calcd. C 63.66 H 5.06 Found C 63.57 H 5.10.

Synthesis of Star-Shaped Polysulfides. *Synthesis of Poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) Radiating from CRA[4]-8arms.* A typical procedure for the insertion reaction of excess PPS into CRA[4]-8arms was as follows: CRA[4]-8arms (0.019 g, 0.08 mmol as thioester groups), PPS (0.531 g, 3.2 mmol), and TBAC (0.033 g, 0.12 mmol) were dissolved in NMP (0.25 mL) in a polymerization tube. The tube was cooled, degassed, and sealed, and the mixture was allowed to react at 90 °C for 24 h. The reaction mixture was diluted by the addition of tetrahydrofuran (THF) and poured into methanol to

Scheme 2. Synthesis of Octa-, Dodeca-, and Tetrathioesters as Initiators for the Synthesis of Star-Shaped Polysulfides



precipitate a polymer; this was reprecipitated twice from THF into methanol and dried *in vacuo* at 60 °C for 24 h. The yield of poly{PPS$_{(40)}$-CRA[4]$_{8arms}$}(n = 40) was 94% (0.52 g). M_n = 23700 and M_w/M_n = 3.93. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ (ppm) = 2.70−2.99 (m, 960H, >CH− + −CH$_2$−S−), 4.05−4.41 (m, 640H, −CH$_2$−O−), 6.69−7.17 (m, 1600H, aromatic H of PPS), 7.49−7.89 (m, 40H, aromatic H of CRA[4]-8arms).

Synthesis of Poly(PPS$_{(n)}$-CRA(Ar-OH)[4]$_{12arms}$) Radiating from CRA[4]-12arms. A typical procedure for the insertion reaction of PPS (0.80 g, 4.8 mmol) into CRA(Ar-OH)[4]-12arms (0.0299 g, 0.12 mmol as thioester moieties) was similar to that described in the case of poly(PPS$_{(n)}$-CRA[4]$_{8arms}$). Yield = 0.94 g (94%). $M_{n(SEC)}$ = 23700, M_w/M_n $_{(SEC)}$ = 3.93, $M_{n(NMR)}$ = 82700. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ (ppm) = 3.00−3.15 (m, 1440H, >CH− + −CH$_2$−S−), 4.05 − 4.41 (m, 960H, −CH$_2$−O−), 6.82−7.00 (m, 2400 H, aromatic H of PPS), 7.29−7.89 (m, 60H, aromatic H of CRA[4]-8arms).

Synthesis of Poly(PPS$_{(n)}$-BTC[4]$_{4arms}$) Radiating from BTC[4]-4arms. A typical procedure for the insertion reaction of PPS (1.662 g, 5.0 mmol) into BTC[4]-4arms (0.072 g, 0.2 mmol as thioester moieties) was similar to that described in the case of poly(PPS$_{(n)}$-CRA[4]$_{8arms}$). Yield = 1.53 g (88%). $M_{n(SEC)}$ = 7800, M_w/M_n $_{(SEC)}$ = 1.83, $M_{n(NMR)}$ =34500. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ (ppm) = 1.34 (s, 36H, C(CH$_3$)$_3$), 2.89−3.18 (m, 600H, >CH− + −CH$_2$−S−), 4.04−4.42 (m, 400H, −CH$_2$−O−), 6.79−7.21 (m, 1000H, aromatic H of PPS), 7.35−7.98 (m, 20H, aromatic H of BTC[4]-4arms).

Measurement of Refractive Index (n_D) of Star-Shaped Polysulfides. THF solutions of the star-shaped polysulfides were prepared, and spin-coated onto silicon wafers. The films were dried *in vacuo* at 25 °C for 24 h. The n_D's of the spin-coated films (about 0.1 μm thick) were determined by ellipsometry at 632.8 nm.

Results and Discussion

Synthesis of Calixarene Core with Octa(thioester)s (CRA[4]-8arms), Dodeca(thioester)s (CRA(Ar-OH)[4]-12arms), and Tetra(thioester)s (BTC[4]-4arms). All the hydroxyl groups of CRA[4], CRA(Ar-OH)[4], and BTC[4] were converted to thioester groups as shown in Scheme 2. Calixarenes have certain conformations such as boat-type, crown-type, and chair-type. The conformation of CRA[4](Ar-OH) and BCA[8] are only crown-type, and those of CRA[4] and BTC[4] are mixture of three types.[32,33] First, the reaction of CRA[4] and chloroacetyl chloride was carried out in the presence of pyridine in THF at room temperature for 24 h, to give the corresponding CRA derivative, CRA[4]-Cl, in 13% yield. Next, the reaction of CRA[4]-Cl and potassium thioacetate was performed using TBAB as a catalyst in NMP, to give the CRA derivative containing octathioesters moieties (CRA[4]-8arms) in 76% yield (Scheme 2A). The structures of these compounds were confirmed by IR, and ^{1}H NMR spectroscopy, as well as MALDI−TOF mass spectroscopy and elemental analysis. Dodecathioesters CRA[4](Ar-OH)-12arms and tetrathioesters BTC[4]-4arms were similarly synthesized from CRA[4](Ar-OH) and BTC[4], respectively (Scheme 2, parts B and C).

Synthesis of Star-Shaped Polysulfides. Our research group[34−36] has developed living-like acyl transfer polymerization of thiiranes with thioesters. This reaction system was employed to synthesize well-defined polysulfides by control of the feed ratio of thiiranes. Using a similar method, the insertion reaction of excess PPS into CRA[4]-8arms was examined in the presence of TBAC as a catalyst at 90 °C for 24 h in NMP with various feed monomer molar ratios (Scheme 2A). In all cases, the reaction mixtures were homogeneous, with the

Table 1. Continuous Insertion Reaction of PPS with CRA[4]-8arms[a]

run	feed molar ratio/{PPS/ (CRA[4]-8arms X 8)}	yield[b] (%)	polymer composition[c]/ {PPS/(CRA[4]-8arms X 8)}	$M_{n(SEC)}$ (M_w/M_n)[d]	$M_{n\ (NMR)}$[e]	sulfur content (%)	nD[f]
1	5/1	89	5/1	2900 (1.53)	8700	17.9	1.636
2	10/1	81	10/1	4300 (1.56)	15300	18.5	1.629
3	15/1	89	15/1	7200 (1.64)	22000	18.7	1.624
4	20/1	85	20/1	10600 (1.64)	28600	18.8	1.631
5	30/1	80	30/1	11700 (1.64)	41900	19.0	1.637
6	40/1	94	40/1	27700 (1.81)	55200	19.0	1.640
7	50/1	96	50/1	36800 (2.10)	68500	19.0	1.653
8	60/1	92	60/1	57800 (4.26)	81800	19.0	1.661

[a] The reaction of PPS and CRA[4]-8arms was carried out in the presence of TBAC as a catalyst in NMP at 90 °C for 24 h. [b] Methanol-insoluble part. [c] Determined by ^{1}H NMR. [d] Estimated by SEC based on polystyrene standards; eluent: THF. [e] Calculated from ^{1}H NMR data. [f] Average values of refractive-index determined by ellipsometry at 0.6328 μm.

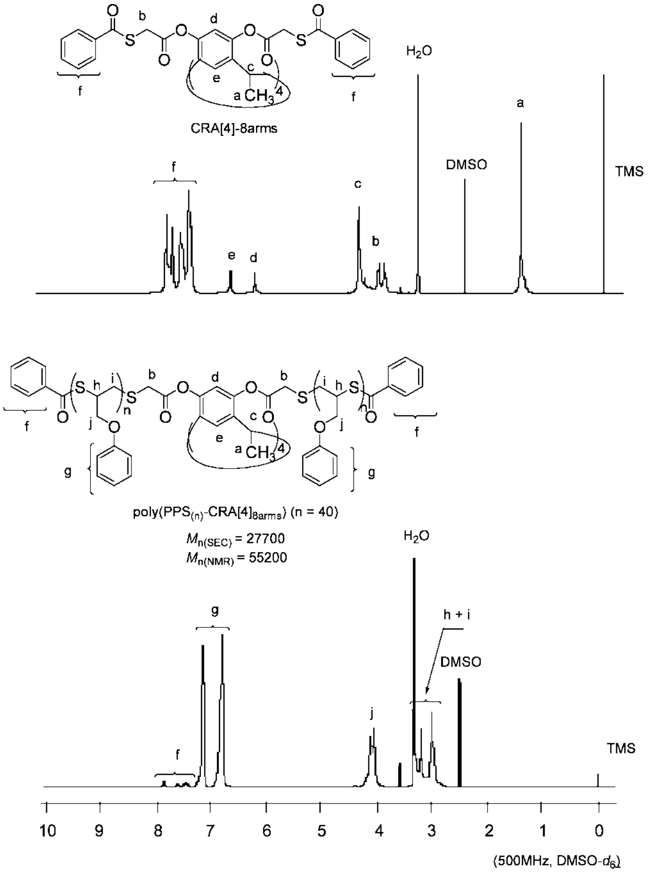


Figure 1. ^{1}H NMR spectra of calixarene-core initiator with octa(thioester)s CRA[4]-8arms and poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) (n = 40, $M_{n(SEC)}$ = 27700, M_w /$M_{n(SEC)}$ = 1.81, $M_{n(NMR)}$ = 55200, run 6 in Table 1).

products remaining in solution. The resulting polymers poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) (n = 5, 10, 15, 20, 30, 40, 50, 60) were isolated by precipitation with methanol in yields of 81−96%, as summarized in Table 1.

The structures of poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) were confirmed by IR and ^{1}H NMR spectroscopy. Figure 1 illustrates the ^{1}H NMR spectrum of poly(PPS$_{(40)}$-CRA[4]$_{8arms}$) ($M_{n(SEC)}$ = 27700, M_w /$M_{n(SEC)}$ = 1.81, $M_{n(NMR)}$ = 55200, run 6 in Table 1) obtained by using the feed ratio of PPS/CRA[4]-8arms = 40/1, along with that of CRA[4]-8arms. The signals assignable to aromatic groups of PPS and CRA[4]-8arms can be seen at 6.69−7.17 and 7.49−7.89 ppm, respectively, together with the signals of >CH− and −CH$_2$−S− at 2.99 − 3.21 ppm, and −CH$_2$O− at 4.12 − 4.41 ppm of the polymers obtained by the continuous insertion reaction of PPS. However, signals assignable to the core-structure (CRA[4]-8arms moiety) of poly(PPS$_{(40)}$-CRA[4]$_{8arms}$) are not apparent in this figure. This might be because the core part of the star-shaped polysulfide is insoluble in the organic solvent owing to the excluded volume arising from the long arms. These results show that poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) has the structure shown in Scheme 2[A].

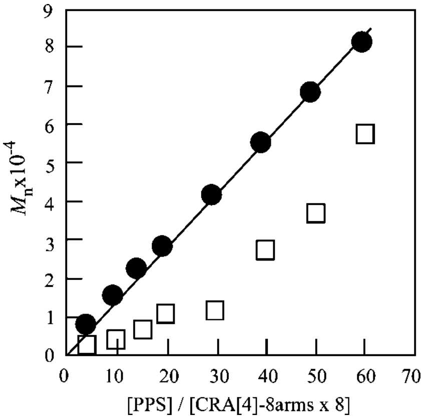


Figure 2. Relationships between $M_{n(SEC)}$ estimated by SEC, $M_{n(NMR)}$ calculated from ^{1}H NMR data and feed ratios of [PPS]/ [(CRA[4]-8arms) × 8] in the continuous insertion reaction of PPS into CRA[4]-8arms. Open squares: $M_{n(SEC)}$, filled circles: $M_{n(NMR)}$.

We could calculate the degree of polymerization of PPS (DE) by integration of the ^{1}H NMR signals of the aromatic protons at 6.69–7.17 ppm (the end of CRA[4]-8arms) and at 7.49–7.89 ppm (PPS). In all cases, the DE values were the same as the feed molar ratios of PPS; that is the length of the arms of poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) could be controlled by setting the feed ratio.

Furthermore, Figure 2 shows the relationship between M_n and feed molar ratio of PPS. We obtained linear relationships between feed molar ratio of PPS and the $M_{n(SEC)}$'s estimated by SEC, and $M_{n(NMR)}$'s calculated from the ^{1}H NMR signals. Furthermore, the slope of the relationship was larger for ^{1}H NMR than for SEC; that is, the values estimated from SEC for star-shaped polymers are lower than those estimated from ^{1}H NMR. This indicates that the hydrodynamic volumes of the star-shaped polymers are smaller than those of the polystyrene standards used for calibration. Thus, well-defined eight-armed, star-shaped polysulfides with desired lengths of the arms could be obtained by the continuous insertion reaction of PPS into CRA[4]-8arms in high yields.

Star-shaped polysulfides poly{PPS$_{(n)}$-CRA[4](Ar-OH)$_{12arms}$} (Scheme 2B) with twelve arms and poly(PPS$_{(n)}$-BTC[4]$_{4arms}$) (Scheme 2 C) with four arms were similarly synthesized. Their yields and M_n's are summarized in Table 2 and Table 3.

Refractive Indices (n_Ds) of the Eight-Armed Star-Shaped Polysulfides. A THF solution of polymer was spin-coated onto a silicon wafer and dried *in vacuo* at room temperature for 3 h to prepare a thin film with a thickness of about 0.1 μm. The refractive indices of the polymer films were determined by ellipsometry. These results are summarized in Tables 1, 2, and

Table 2. Continuous Insertion Reaction of PPS with CRA[4]-12arms[a]

run	feed molar ratio/ {PPS/(CRA[4]-12arms X 12)}	yield[b] (%)	polymer composition[c]/ {PPS/(CRA[4]-12arms X 12)}	$M_{n(SEC)}$ (M_w/M_n)[d]	$M_{n\,(NMR)}$[e]	sulfur content (%)	nD[f]
1	5/1	90	5/1	2400 (1.51)	13000	17.8	1.647
2	10/1	87	10/1	4900 (1.70)	23000	18.5	1.638
3	15/1	89	15/1	7600 (2.14)	32700	18.7	1.642
4	20/1	88	20/1	13200 (2.34)	42900	18.8	1.645
5	30/1	90	30/1	18300 (2.15)	62800	19.0	1.678
6	40/1	94	40/1	23700 (3.92)	82700	19.0	1.685
7	50/1	97	50/1	36200 (5.94)	102400	19.1	1.700
8	60/1	95	60/1	32100 (12.71)	122900	19.1	1.700

[a] The reaction of PPS and CRA[4]-12arms was carried out in the presence of TBAC as a catalyst in NMP at 90 °C for 24 h. [b] Methanol-insoluble part. [c] Determined from ^{1}H NMR. [d] Estimated by SEC based on polystyrene standards; eluent: THF. [e] Calculated by ^{1}H NMR data. [f] Average values of refractive index determined by ellipsometry at 0.6328 μm.

Table 3. Continuous insertion reaction of PPS with BTC[4]-4arms[a]

run	feed molar ratio/ {PPS/(BTC[4]-4arms X 4)}	yield[b] (%)	polymer composition[c]/ {PPS/(BTC[4]-4arms X 4)}	$M_{n(SEC)}$ (M_w/M_n)[d]	$M_{n\,(NMR)}$[e]	sulfur content (%)	nD[f]
1	10/1	50	5/1	1400 (1.20)	8000	19.0	1.618
2	20/1	72	20/1	3500 (1.61)	14700	19.1	1.620
3	30/1	86	30/1	5100 (1.72)	21200	19.2	1.621
4	40/1	89	40/1	6200 (1.81)	27600	19.2	1.621
5	50/1	88	50/1	7800 (1.83)	34500	19.2	1.623

[a] The reaction of PPS and BTC[4]-4arms was carried out in the presence of TBAC as a catalyst in NMP at 90 °C for 24 h. [b] Methanol-insoluble part. [c] Determined from ^{1}H NMR data. [d] Estimated by SEC based on polystyrene standards; eluent: THF. [e] Calculated from ^{1}H NMR data. [f] Average values of refractive index determined by ellipsometry at 0.6328 μm.

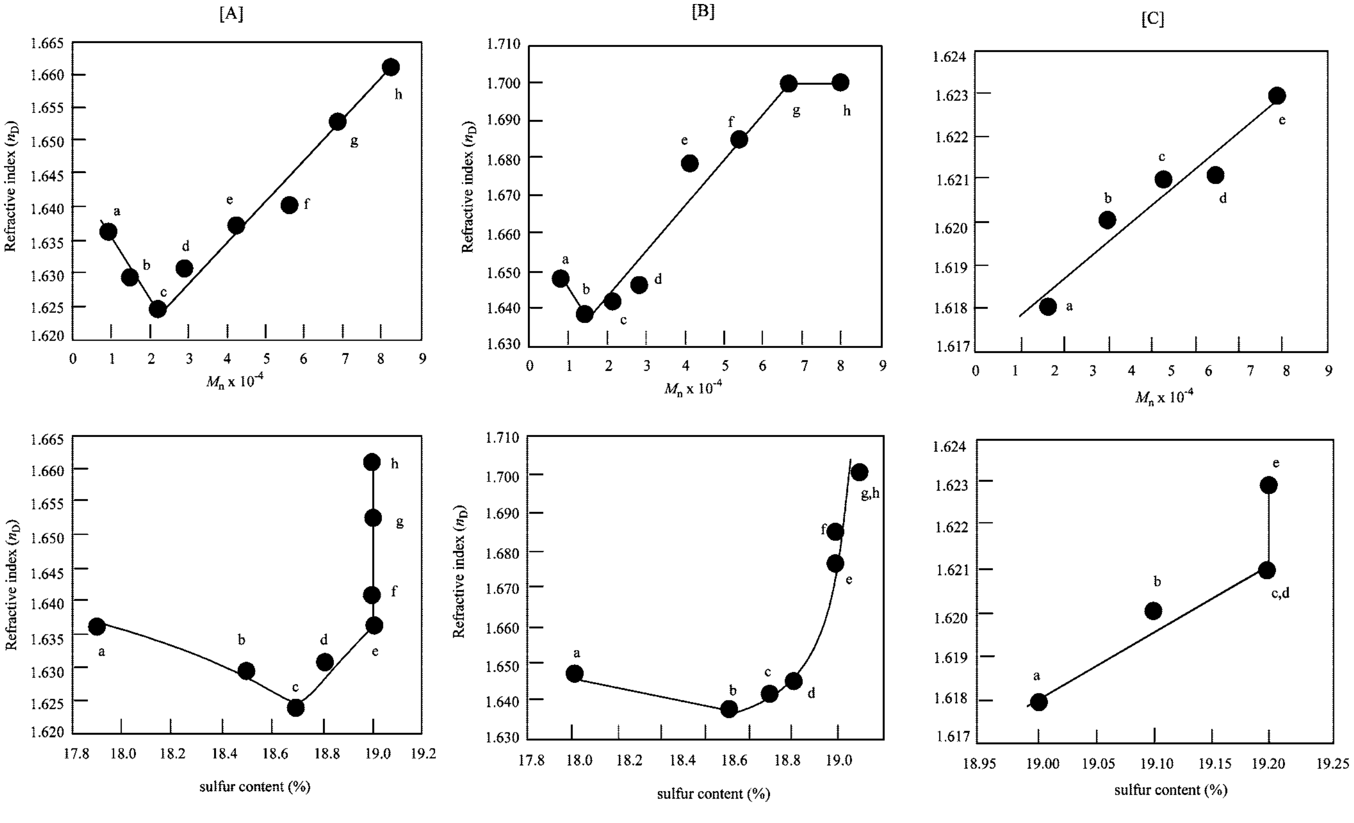


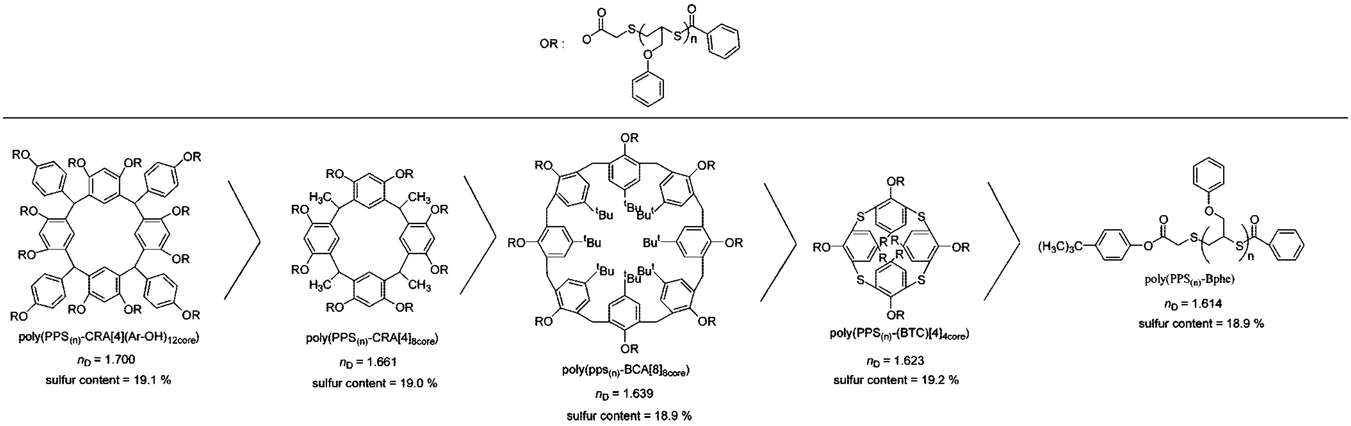
Figure 3. The relationships between the refractive-index values, $M_{n(NMR)}$, and sulfur contents of star-shaped polysulfides. [A]: poly(PPS$_{(n)}$-CRA[4]$_{8arms}$), [B]: poly(PPS$_{(n)}$-CRA[4](Ar-OH)$_{12arms}$), [C] poly(PPS$_{(n)}$-TCA[4]$_{4arms}$).

3. The relationship between n_D and $M_{n(NMR)}$ is illustrated in Figure 3.

In the case of poly(PPS$_{(n)}$-CRA[4]$_{8arms}$) (Figure 3A), a decrease of n_D was observed until $M_{n(NMR)} = 22000$ (a−c), then n_D increased with increasing M_n (c−h). This tendency is reasonably consistent with that of the relationship between the n_D and the sulfur content ratios. The sulfur content ratios increased up to $M_{n(NMR)} = 41900$ (c−e). In the range between a and c in Figure 3A, the decrease of the density might be caused with increasing the molecular weights. At constant sulfur content ratio, the n_D increased linearly (e−h) with increasing $M_{n(NMR)}$. The maximum value of n_D was 1.661 with sulfur content = 19.0%.

In the case of poly{PPS$_{(n)}$-CRA(Ar-OH)[4]$_{12arms}$} (Figure 3B), the n_D decreased from 1.647 to 1.638 (a, b) and then increased up to 1.700 with increasing M_n and sulfur content (b–g). Thereafter, n_D remained constant, independent of increase of M_n and sulfur content (g–h). Consequently, the maximum value of n_D is 1.700 with the sulfur content = 19.1%.

Scheme 3. Refractive Index Values and Sulfur Contents of Star-Shaped Polysulfides



In the case of poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) (Figure 3C), the n_D increased slightly with increasing M_n (a−e), and the maximum was seen with the sulfur content of 19.2%. These results show that the refractive-index values of star-shaped polysulfides are determined by the length of the arms, the number of arms, and the nature of the calixarene core structure.

The n_D's of poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$) and poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) increased with increase of their molecular weights. However, a similar relationship was not observed in the case of poly{PPS$_{(n)}$-CRA(Ar-OH)[4]$_{12\text{arms}}$}. Furthermore, it was observed that their n_D's increase even if the sulfur content ratios were same as shown in e−h in Figure 3A and c−h in Figure 3C. These results might be caused by their skeletons of calixarenes. That is, the densities of poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$) and poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) might increase with increase of their molecular weights.

In our previous study, we synthesized eight-armed star-shaped polysulfides poly(PPS$_{(n)}$-BCA$^{[8]}{}_{8\text{arms}}$) and linear polysulfides poly(PPS$_{(n)}$-Bphe), which have almost the same skeleton as poly(PPS$_{(n)}$-BCA$^{8}{}_{8\text{arms}}$), and their refractive index properties were examined (Scheme 1). The maximum sulfur contents of these star-shaped and linear polysulfides were almost the same, at 18.9%. However, poly(PPS$_{(n)}$-BCA$^{[8]}{}_{8\text{arms}}$) has a larger refractive index ($n_D = 1.639$) than poly(PPS$_{(n)}$-Bphe) ($n_D = 1.614$), because the star-shaped polymer has a more compact structure and higher segment density than the linear polymer. In contrast, the eight-armed star-shaped polysulfide poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$) has a larger refractive index of 1.661, while its sulfur content is almost the same at 19.0%. This means that poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$) has a larger density than poly(PPS$_{(n)}$-BCA$^{[8]}{}_{8\text{arms}}$), presumably because of its more compact core structure derived from CRA[4], as shown in Scheme 2A. Furthermore, the 12-armed star-shaped polysulfide poly{PPS$_{(n)}$-CRA[4](Ar-OH)$_{12\text{arms}}$} has an even larger refractive index ($n_D = 1.700$), although its sulfur content is similar, at 19.1%. This indicates that poly{PPS$_{(n)}$-CRA[4][4](Ar-OH)$_{12\text{arms}}$} has a higher density due to its many arms and compact core structure. In order to increase further the sulfur contents of the star-shaped polysulfides, we designed and synthesized poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) derived from BTC[4]. Though the sulfur content of poly(PPS$_{(n)}$-BTC[4]$_{4\text{core}}$) is highest (19.2%) among the present star-shaped polysuldides, its n_D is lower than than that of any other star-shaped polysulfide ($n_D = 1.623$). This indicates that poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) has a lower density because it has only four arms.

Consequently, the order of refractive index of the synthesized star-shaped and linear polysulfides is as follows: poly{PPS$_{(n)}$-CRA[4](Ar-OH)$_{12\text{arms}}$} > poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$) > poly(PPS$_{(n)}$-BCA$^{[8]}{}_{8\text{arms}}$) > poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$) > poly(PPS$_{(n)}$-Bphe) (Scheme 3). That is, the refractive index of star-shaped polysulfides increases with increasing number of arms, with increasing sulfur content, and with decreasing size of the core structure.

In summary, the continuous insertion reaction of phenoxypropylenesulfide (PPS) into the thioester moieties of calixarene derivatives (cores) generated from *p*-*t*-butylthiacalix[4]arene (BTC[4]), 2,8,14,20-tetramethylcalix[4]resorcinarene (CRA[4]), and 2,8,14,20-tetra(4-hydroxybenzen-1-yl)calix[4]resorcinarene {CRA(Ar-OH)[4])} derivatives proceeded smoothly in the presence of TBAC as a catalyst, affording the corresponding star-shaped polysulfides, poly(PPS$_{(n)}$-BTC[4]$_{4\text{arms}}$), poly(PPS$_{(n)}$-CRA[4]$_{8\text{arms}}$), and poly{PPS$_{(n)}$-CRA(Ar-OH)[4]$_{12\text{arms}}$}. It was found that the arm lengths of star-shaped polysulfides could be controlled easily by varying the feed ratio of PPS and core. The values of refractive index (n_D) of these star-shaped polysulfides increased with increasing numbers of arms, length of arms, and sulfur content and with decreasing size of the core structure.

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