

Sulfur-Containing Poly(meth)acrylates with High Refractive Indices and High Abbe's Numbers

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Four new sulfur-containing monomers consisting of cyclic dithiocarbonate, norbornene, and (meth)acrylate units were synthesized to develop high refractive index polymers with high Abbe's numbers for optical lenses. A series of poly(meth)acrylates were successfully prepared by the radical polymerization of these monomers. The obtained polymers exhibited a relatively high degradation temperature (5% weight loss) at around 290 °C in both air and nitrogen, while their glass transition temperatures were in the range of 44–109 °C. All the polymer films prepared by spin cast from the polymer solutions exhibited a good transparency in the visible region (wavelengths: 400–800 nm) and high refractive indices in the range of 1.592–1.640 (at 589 nm) with large Abbe's numbers in the range of 40.5–44.5.

Introduction

Polymeric materials for optical applications such as lenses, prisms, and waveguides have been rapidly developed in recent years because of their lightweight, impact resistance, processability, and dying ability.^{1,2} Polymeric optical lenses are divided into two types of polymers: (1) thermoplastics such as poly(methyl methacrylate), polycarbonate, and cycloolefin polymers for industrial uses³ and (2) thermosets such as poly[ethylene glycol bis(allylcarbonate)] (CR-39)⁴ and resins from epysulfides, polythiols, and polyisocyanates⁵ for consumer use. The former is used in camera, pickup, and projector lenses where injection molding is applied. On the other hand, eyeglasses are manufactured by cast molding the latter.

Although various physical properties are required for such applications, the refractive index (n) is essentially important. High refractive synthetic resins can yield thinner lenses with the same focal distance as that of low refractive materials. Abbe's number (ν_D), which is a key measure for refractive index dispersion, is also an important parameter for optical materials used in the visible region. Abbe's number is given by

$$\nu_D = (n_D - 1)/(n_F - n_C) \quad (1)$$

where n_D , n_F , and n_C are the refractive indices of the material at the wavelength of the sodium *D* (589.3 nm), hydrogen *F* (486.1 nm), and hydrogen *C* (656.3 nm) lines, respectively.⁶

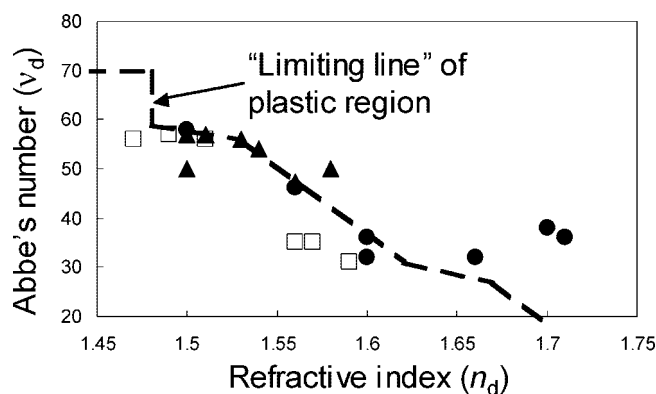


Figure 1. Plastic region in the n_d – ν_d diagram. (---) Present limit of the region of transparent plastic. (□) General-purpose resin for optical materials. (▲) Reported thermoplastic with high refractive indices and high Abbe's number. (●) Reported thermosets with high refractive indices and high Abbe's numbers.

The larger Abbe's number corresponds to a lower dispersion in the refractive index.⁷ Highly refractive materials generally exhibit a small Abbe's number.⁸ The dotted line in Figure 1 displays the relationship between the refractive indices (n_D) and Abbe's numbers for conventional optical polymers;⁹ this line is called "the limiting line". Although no theoretical reason was reported for the limiting line, only few synthetic resins were reported to go beyond the line.

Several reports are available on sulfur-containing thermosets exhibiting both high n_D and high ν_D values because a sulfur atom possesses a large atomic refraction. Okubo et al. reported such optical polymers synthesized by the radical polymerization of 2,5-bis(2-thia-3-butenyl)-1,4-dithiane and the polyaddition of oligo[2,5-bis(thiomethyl)-1,4-dithiane] and di- or triisocyanates.¹⁰ Shen et al. also reported episul-

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fide-type copolymers exhibiting high n_D and high v_D values.¹¹ On the other hand, poly(meth)acrylates, which are typical thermoplastics, are easy to polymerize and yield transparent films suitable for optical materials. However, (meth)acrylate-type optical polymers with high refractive indices have thus far not been the subject of detailed investigation. Thus, the development of high refractive index thermoplastics with high Abbe's numbers and based on poly(meth)acrylates is a challenging project.

To reduce the refractive index dispersion, we focused on an alicyclic group, which is also known to show a refractive index higher than that of an aliphatic moiety.^{12,13} Therefore, we designed a novel sulfur-containing alicyclic compound having a (meth)acrylate unit. This article reports the syntheses and polymerization of (meth)acrylates having sulfur-containing alicyclic structures such as 2-{exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl acrylate (**4**), 2-{exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl methacrylate (**5**), 2-[2-{exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyloxycabamoyl]ethyl methacrylate (**6**), and 2-{exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl thiomethacrylate (**7**). These polymers exhibited high transparency (<400 nm), high refractive indices in the range of 1.592–1.640 (at 589 nm), and large Abbe's numbers in the range of 40.5–44.5.

Experimental Section

Materials. Tetrahydrofuran (THF) and toluene were dried over sodium and distilled before use under nitrogen. α,α' -Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol at 60 °C. All the other reagents and solvents were used without further purification.

Measurements. The FT-IR spectra were obtained on a Horiba FT-720 spectrometer. The ¹H and ¹³C NMR spectra were recorded with a Bruker DPX300S spectrometer using CDCl₃ or DMSO-*d*₆ as a solvent and tetramethylsilane as a reference. Number- and weight-average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) on a Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Plgel 5 μ m MIXED-C) eluted with CHCl₃ at a flow rate of 1.0 mL/min calibrated by standard polystyrene samples and on a JASCO PU-2080 Plus system equipped with two polystyrene gel columns (TSK GELS GMH_{HR}-M) eluted with *N,N*-dimethylformamide (DMF) at a flow rate of 1.0 mL/min calibrated by standard polystyrene samples. Preparative high-pressure liquid chromatography was performed with a Japan Analytical Industry LC-908 equipped with two consecutive gel columns, JAIGELS 1H and 2H, detected with refractive index and ultraviolet at 254 nm using CHCl₃ as an eluent with a flow rate of 3.8 mL/min. The UV-vis transmittance spectra were recorded on a JASCO V-560 UV-vis spectrometer in the range 250–800 nm. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. The refractive indices of polymer films were measured at the wavelengths of 486, 589,

and 656 nm by changing monochromatic filters with an Abbe refractometer (Atago, DR-M4). A halogen lamp with high brightness was used as a white light source.

Synthesis of Exo-3,5-dithiatriacyclo[5.2.1.0]dec-8-ene-4-one (**1**).

A solution of norbornadiene (3.66 g, 19.9 mmol), diisopropyl xanthogen disulfide (13.5 g, 25 mmol), and AIBN (2 g, 25 mmol) was refluxed in toluene (500 mg) for 24 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Recrystallization from hexane gave a colorless crystal (3.78 g, 41% yield). Mp 105–107 °C. IR (KBr, ν cm⁻¹): 3066 (alkene C–H), 2942–2996 (alkyl C–H), 1639 (C=O); ¹H NMR (CDCl₃, δ , ppm): 2.13 (dt, 1H, CH–CH₂–CH), 2.16 (dt, 1H, CH–CH₂–CH), 3.04 (m, 2H, CH–CHCH₂–CS), 3.86 (dd, 2H, CH₂–S), 6.17 (t, 2H, CH=CH). ¹³C NMR (CDCl₃, δ , ppm): 199.6 (C=O), 136.7 (C=C), 52.0 (C–S), 50.1 (CH–CCH₂–CH), 42.6 (CH₂). Elem. Anal. Calcd for C₈H₈OS₂: C, 52.14; H, 4.38. Found: C, 52.15; H, 0.15.

Synthesis of 2-{Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethanol (**2**).

A solution of **1** (2.07 g, 11.2 mmol), 2-mercaptoethanol (0.962, 12.3 mmol), and AIBN (36.8 mg, 0.224 mmol) in THF (2.7 mL) was heated at 60 °C for 1 h. Then, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was diluted with distilled water and extracted with ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (an eluent, ether) and isolated. Colorless oil was obtained (2.83 g, 96% yield). IR (KBr, ν cm⁻¹): 3700–3200 (br, O–H), 2958–2873 (alkyl C–H), 1651 (C=O), 1045 (C–O). ¹H NMR (CDCl₃, δ , ppm): 1.52 (dt, 1H, CH–CH₂–CH), 1.92 (m, 2H, CHS–CH₂–CH), 2.20 (m, 1H, CH–CH₂–CH), 2.24 (t, 1H, OH), 2.40 (m, 1H, CH₂–CHCH₂–CH), 2.45 (dd, 1H, CHS–CHCH₂–CH), 2.75 (q, 2H, CH₂–CH₂–S), 2.87 (ddd, 1H, S–CHCH–CH₂), 3.76 (t, 2H, CH₂–OH), 4.05 (d, 2H, COS–CH). ¹³C NMR (CDCl₃, δ , ppm): 199.2 (C=O), 61.5 (CH₂–OH), 56.7 (CH–SCO), 56.0 (CH–SCO), 51.0 (CH₂OH–CH₂), 45.0 (CH₂S–CHCH₂–CH), 44.9 (CHS–CHCH₂–CH), 37.9 (CHS–CH₂–CH), 35.6 (CH₂–CHCH₂–CH), 30.2 (CH–CH₂–CH). Elem. Anal. Calcd for C₁₀H₁₄O₂S₃: C, 45.77; H, 5.38. Found: C, 45.79; H, 5.38.

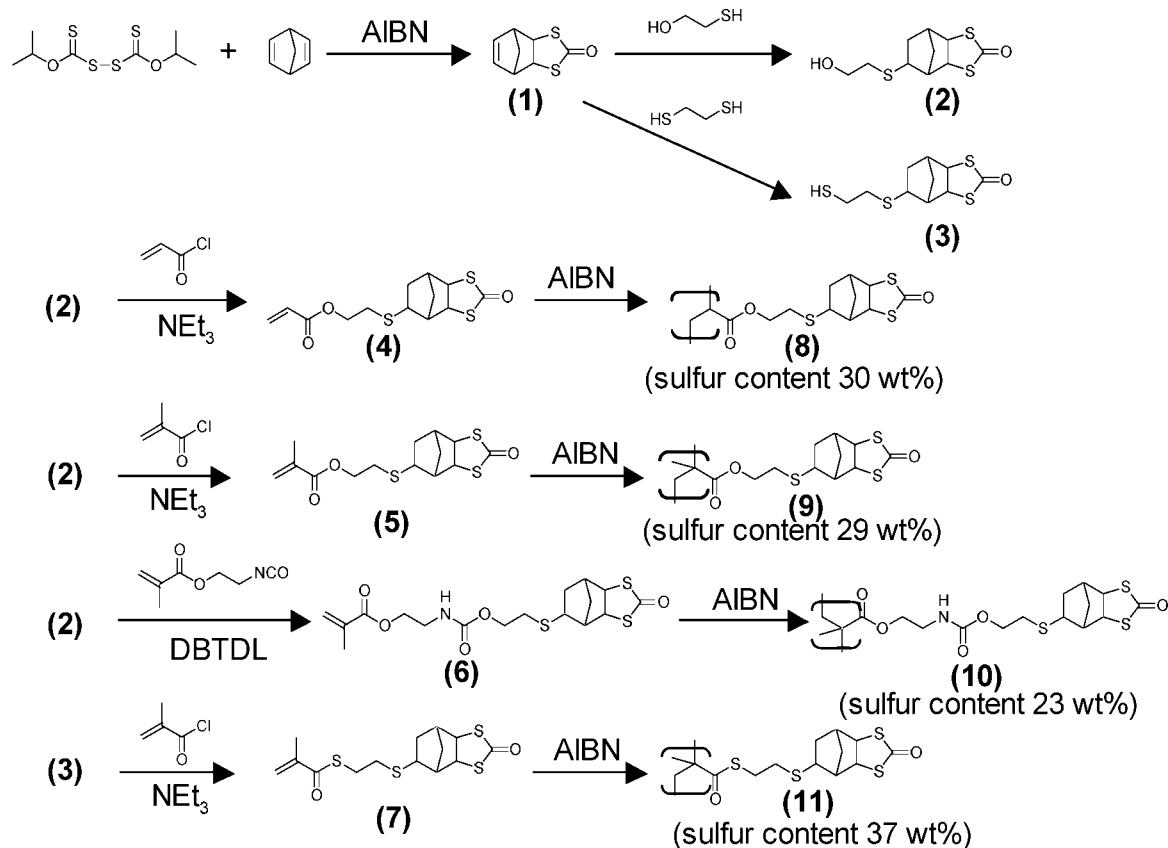
Synthesis of 2-{Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethanethiol (**3**).

To a solution of AIBN (67 mg, 0.41 mmol) in dry THF (8 mL), 1,2-ethanedithiol (2.90 g, 30.8 mmol) was added under a N₂ atmosphere. Then, the solution was heated at 65 °C, and the solution of **1** (3.78 g, 20.5 mmol) in dry THF (41 mL) was added dropwise. After the solution was stirred for 1 h at 65 °C, the mixture was concentrated. The crude product was purified by column chromatography on silica gel (eluent, ether/hexane = 1/1). White powder was obtained (2.56 g, 45% yield). Mp 87 °C. IR (KBr, ν cm⁻¹): 2954, 2866 (alkyl C–H), 2561 (thiol S–H), 1643 (alicyclic ketone C=O), 1461, 1442, 1427 (alkyl C–H) cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 1.52 (m, 1H, CH–CH₂–CH), 1.73 (m, 1H, SH), 1.91 (m, 2H, CHS–CH₂–CH), 2.23 (m, 1H, CH–CH₂–CH), 2.38 (m, 1H, CH₂–CHCH₂–CH), 2.45 (m, 1H, CHS–CHCH₂–CH), 2.75 (m, 4H, CH₂–CH₂–SH), 2.84 (m, 1H, S–CHCH₂–CH₂), 4.04 (d, 2H, CH–SCO–S–CH). ¹³C NMR (CDCl₃, δ , ppm): 198.5 (C=O), 56.6 (CH–SCO), 55.9 (CH–SCO), 51.0 (CHS–CHCH₂–CHS), 45.2 (S–CHCH₂–CH), 44.9 (S–CH₂–CH₂SH), 38.0 (CHS–CH₂–CH), 36.9 (CH₂–CHCH₂–CH), 30.2 (CH–CH₂–CH), 25.2 (CH₂–SH). Elem. Anal. Calcd for C₁₀H₁₄OS₄: C, 43.13; H, 5.07. Found: C, 43.10; H, 5.00.

Synthesis of 2-{Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl Acrylate (4**).** To a solution of **2** (4.5 g, 17.2 mmol) and phenothiazine as the polymerization inhibitor in dry THF (170 mL) was added triethylamine (10.6 mL, 76.5 mmol) under a N₂

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Scheme 1. Synthesis of Polyacrylates



atmosphere. Then, the solution was cooled at 0 °C, and the solution of acryloyl chloride (9.34 g, 103.2 mmol) in dry THF (60 mL) was added dropwise. After the solution was stirred for 24 h at room temperature, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was diluted with distilled water and extracted with ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated. The crude product was recrystallized by ethyl acetate/hexane to give a white crystalline (3.43 g, 63% yield). Mp 79 °C. IR (KBr, ν cm⁻¹): 2966 (alkyl C-H), 1720 (vinyl ester C=O), 1651 (alicyclic ketone C=O), 1465 (alkyl C-H), 1300, 1200 (ester C-O), 983, 903 (vinyl C=C). ¹H NMR (CDCl₃, δ , ppm): 1.50 (m, 1H, CH-CH₂-CH), 1.92 (m, 2H, CHS-CH₂-CH), 2.22 (dd, 1H, CH-CH₂-CH), 2.40 (m, 1H, CH-CHCH₂-CHS), 2.44 (m, 1H, CHS-CHCH₂-CHS), 2.82 (m, 2H, S-CH₂-CH₂), 2.88 (m, 1H, S-CHCH-CH₂), 4.04 (d, 2H, COS-CH-CH), 4.32 (td, 2H, COO-CH₂-CH₂), 5.88 (dt, 1H, CH₂=CH), 6.12 (ddd, 1H, CH₂=CH), 6.44 (dt, 1H, CH₂=CH). ¹³C NMR (CDCl₃, δ , ppm): 198.3 (C=O), 166.3 (COO), 132.2 (CH₂=CH), 128.4 (CH₂=CH), 63.7 (O-CH₂), 56.6 (CH-SCO), 55.9 (CH-SCO), 51.0 (CH-S-CH₂), 45.5 (CHS-CCH₂-CH), 45.0 (CHS-CH₂-CH), 38.1 (CH₂-CHCH₂-CH), 31.3 (S-CH₂-CHO), 30.1 (CH-CH₂-CH). Elem. Anal. Calcd for C₁₃H₁₆O₃S₃: C, 49.34; H, 5.10. Found: C, 49.35; H, 4.94.

Synthesis of 2-[2-(Exo-3,5-dithiatriicyclo[5.5.1.0^{2,6}])dectyl-4-one-8-sulfanyl]ethyl Methacrylate (5). To a solution of **2** (1.64 g, 6.25 mmol) and phenothiazine as the polymerization inhibitor in dry THF (60 mL), triethylamine (2.85 g, 28.1 mmol) was added under N₂ atmosphere. Then, the solution was cooled at 0 °C, and the solution of methacryloyl chloride (3.92 g, 37.5 mmol) in dry THF (25 mL) was added dropwise. After the solution was stirred for 24 h at room temperature, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was diluted with distilled water and extracted with chloroform. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated. The crude product

was recrystallized to give a white crystalline (79.3 mg, 4%). Mp 70 °C. IR (KBr, ν cm⁻¹): 2970, 2862 (alkyl C-H), 1712 (vinyl ester C=O), 1643 (alicyclic ketone C=O), 1373 (methyl C-H), 1296, 1184 (ester C-O), 941, 903 (vinyl C-H) cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 1.51 (m, 1H, CH-CH₂-CH), 1.90 (m, 2H, CHS-CH₂-CH), 1.96 (m, 3H, CH₃), 2.22 (m, 1H, CH-CH₂-CH), 2.40 (m, 1H, CH₂-CHCH₂-CHS), 2.45 (m, 1H, CH-CHCH₂-CHS), 2.82 (m, 2H, COO-CH₂-CH₂), 2.89 (m, 1H, S-CHCH₂-CH), 4.04 (d, 2H, CH-SCO-S-CH), 4.31 (t, 2H, COO-CH₂), 5.61 (t, 1H, CH₂=C), 6.12 (t, 1H, CH₂=C). ¹³C NMR (CDCl₃, δ , ppm): 198.0 (C=O), 167.3 (COO), 136.2 (CH₂=CH), 126.2 (CH₂=CH), 63.6 (O-CH₂), 56.2 (CH-SCO), 55.3 (CH-SCO), 51.0 (CHS-CH₂-CH), 45.4 (CH₂S-CH), 44.5 (CHS-CH₂CH-CH), 37.6 (CH₂-CHCH₂-CH), 31.1 (S-CH₂-CH₂O), 29.8 (CH-CH₂-CH), 18.0 (-CH₃). Elem. Anal. Calcd for C₁₄H₁₈O₃S₃: C, 50.88; H, 5.49. Found: C, 50.65; H, 5.33.

Synthesis of 2-[2-(Exo-3,5-dithiatriicyclo[5.5.1.0^{2,6}])dectyl-4-one-8-sulfanyl]ethyl methacrylate (6). To a solution of **2** (1.03 g, 3.90 mmol), di-*n*-butyltin dilaurate (0.37 g, 5.85 × 10⁻⁴ mmol), and phenothiazine as the polymerization inhibitor in dry THF (4 mL) was added 2-isocyanate ethyl methacrylate (605 mg, 3.90 mmol) dropwise and warmed at 65 °C for 1 h. Then, the mixture was concentrated. The crude product was recrystallized by methanol to give a white crystalline (0.85 g, 52%). Mp 115–116 °C. IR (KBr, ν cm⁻¹): 3379 (amide N-H), 2958 (alkyl C-H), 1716 (vinyl ester C=O), 1635 (alicyclic ketone C=O), 1527 (amide C=O), 1254, 1180 (ester C-O), 945, 906 (vinyl C-H). ¹H NMR (CDCl₃, δ , ppm): 1.50 (dt, 1H, CH-CH₂-CH), 1.90 (m, 1H, CHS-CH₂-CH), 1.96 (t, 3H, CH₃-C=CH₂), 2.22 (dt, 1H, CH-CH₂-CH), 2.39 (d, 1H, CHS-CHCH₂-CHS), 2.44 (dd, 1H, CH₂-CHCH₂-CHS), 2.77 (td, 2H, S-CHCH-CHCH-S), 2.87 (ddd, 1H, S-CHCH-CH₂), 3.51 (q, 2H, NH-CH₂), 4.05 (d, 2H, COO-CH₂-CH₂-S), 4.24 (q, 4H, COO-CH₂-CH₂-NHCO-CH₂-CH₂), 5.00 (br, 1H, NH),

5.61 (m, 1H, $CH_2=C$), 6.13 (s, 1H, $CH_2=C$). ^{13}C NMR ($CDCl_3$, δ , ppm): 198.3 (C=O), 167.7 (COO), 156.4 (NH-COO), 136.3 ($CH_2=CH$), 126.5 ($CH_2=CH$), 64.2 (COO- CH_2), 64.1 (NHCOO- CH_2), 56.5 (CH-SCO), 55.9 (CH-SCO), 51.0 (CH_2-NH), 45.4 (S- $CHCH_2-CH$), 45.0 (CHS- $CHCH_2-CHS$), 40.7 (CHS- CH_2-CH), 38.0 (CH_2-CHCH_2-CHS), 31.7 (COO- CH_2-CH_2), 30.1 (CH- CH_2-CH), 18.7 (CH_3). Elem. Anal. Calcd for $C_{17}H_{23}NO_5S_3$: C, 48.90; H, 5.55; N, 3.35. Found: C, 48.71; H, 5.39; N, 3.22.

Synthesis of 2-[Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl]ethyl Thiomethacrylate 7. To a solution of **3** (1.68 g, 6.03 mmol) and phenothiazine as the polymerization inhibitor in dry THF (65 mL), triethylamine (2.92 g, 28.9 mmol) was added under a N_2 atmosphere. Then, the solution was cooled at 0 °C, and the solution of methacryloyl chloride (2.7 g, 26.0 mmol) in dry THF (20 mL) was added dropwise. After the solution was stirred for 24 h at room temperature, the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with distilled water and extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (eluent, ether/hexane = 1/3) to give a colorless oil (1.49 g, 71%). IR (KBr, ν cm^{-1}): 3089 (vinyl C-H), 2965 (alkyl C-H), 2865 (methyl C-H), 1758, 1735 (thioester C=O), 1658 (alicyclic ketone C=O), 1373 (methyl C-H), 975, 891 (vinyl C-H). 1H NMR ($CDCl_3$, 25 °C): δ 1.51 (m, 1H, CH- CH_2-CH), 1.91 (m, 2H, CHS- CH_2-CH), 1.98 (m, 3H, $CH_2=CCH_3$), 2.22 (dd, 1H, CH- CH_2-CH), 2.44 (t, 2H, CH_2-CHCH_2-CHS , CHS- $CHCH_2-CHS$), 2.71 (m, 2H, CH_2S-CH_2-CHS), 2.99 (m, 1H, $CH_2S-CHCH_2-CH$), 3.12 (m, 2H, COS- CH_2-CH_2), 4.10 (m, 2H, S- $CHCH-CHCH-S$), 5.63 (m, 1H, $CH_2=CCH_3$), 6.08 (s, 1H, $CH_2=CCH_3$). ^{13}C NMR ($CDCl_3$, δ , ppm): 198.6 (C=O), 193.2 (COO), 143.8 ($CH_2=CCH_3$), 124.1 ($CH_2=CH$), 56.6 (CH-SCO), 56.1 (CH-SCO), 51.0 (CH_2-SCO), 45.0 (S- $CHCH_2-CH$), 45.0 (CHS- $CHCH_2-CHS$), 37.9 (CHS- CH_2-CH), 32.6 (CH_2-CHCH_2-CHS), 30.2 (S- CH_2-CH_2SCO), 29.2 (CH- CH_2-CH), 18.5 (CH_3). Elem. Anal. Calcd for $C_{14}H_{18}O_2S_4$: C, 48.52; H, 5.24. Found: C, 48.72; H, 5.18.

Polymerization. A typical polymerization procedure is as follows: a solution of monomer and AIBN in the ampule tube was deoxygenated by freeze-pump-thaw cycles, and the ampule tube was sealed. The mixture was then heated with stirring at 65 °C for 24 h. The resulting solution was cooled to room temperature and precipitated with methanol to isolate a solid polymer of white powder. The obtained polymer was dried at 60 °C in vacuo overnight.

Poly 2-[Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl]ethyl Acrylate (8). IR (KBr, ν cm^{-1}): 2954, 2866 (alkyl C-H), 1732 (vinyl ester C=O), 1651 (alicyclic ketone C=O), 1446 (alkyl C-H), 1250, 1157 (ester C-O) cm^{-1} . 1H NMR (DMSO, 100 °C, δ ppm): 1.16–1.98 (m, 2H, COCH- CH_2) 1.46 (m, 1H, CH- CH_2-CH), 1.82 (m, 1H, CH- CH_2-CH), 2.05 (m, 2H, CHS- CH_2-CH), 2.44 (m, 3H, CH- CH_2-CH , CO- CH), 2.84 (m, 2H, S- CH_2-CH_2), 3.00 (m, 1H, S- $CHCH-CH_2$), 4.20 (m, 2H, CHS-CO- CHS), 4.28 (m, 2H, COO- CH_2-CH_2). Elem. Anal. Calcd for $C_{13}H_{16}O_3S_3$: C, 49.34; H, 5.10. Found: C, 49.41; H, 5.08.

Poly 2-[Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl]ethyl Methacrylate (9). IR (KBr, ν cm^{-1}): 2958 (alkyl C-H), 1728 (vinyl ester C=O), 1655 (alicyclic ketone C=O), 1461 (alkyl C-H), 1389 (methyl C-H), 1257, 1145 (ester C-O) cm^{-1} . 1H NMR (DMSO, 100 °C, δ ppm): 1.20–1.39 (m, 2H, CCH₃- CH_2) 1.08 (br, 1H, CH- CH_2-CH), 1.47 (m, 1H, CH- CH_2-CH), 1.75–1.98 (m, 3H, - CH_3), 2.06 (m, 2H, CHS- CH_2-CH), 2.42 (s, 1H, CH_2-CHCH_2-CHS), 2.45 (m, 1H, CH- $CHCH_2-CHS$), 2.86 (m, 2H, COO- CH_2-CH_2), 3.00 (m, 1H, S- $CHCH_2-CH$),

4.13 (m, 2H, CH-SCO-S-CH), 4.29 (m, 2H, COO- CH_2). Elem. Anal. Calcd for $C_{14}H_{18}O_3S_3$: C, 50.88; H, 5.49. Found: C, 51.04; H, 5.39.

Poly 2-[2-[Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl]ethylmethacrylate (10). IR (KBr, ν cm^{-1}): 3363 (amide N-H), 2954 (alkyl C-H), 1720 (vinyl ester C=O), 1650 (alicyclic ketone C=O), 1527 (amide C=O), 1254, 1149 (ester C-O) cm^{-1} . 1H NMR (DMSO, 100 °C, δ ppm): 0.90–1.39 (m, 2H, CCH₃- CH_2), 1.03 (br, 1H, CH- CH_2-CH), 1.44 (m, 1H, CH- CH_2-CH), 1.73–2.14 (m, 5H, CHS- CH_2-CH , - CH_3), 2.40 (s, 1H, CH_2-CHCH_2-CH), 2.42 (d, 1H, CHS- $CHCH_2-CHS$), 2.79 (m, 2H, CHS-CO- CHS), 3.00 (m, 1H, CH_2O-CH_2-SCH), 3.32 (m, 2H, CH_2-NH), 4.01 (m, 2H, COO- CH_2), 4.17 (m, 2H, COO- CH_2), 4.29 (q, 2H, NHCOO- CH_2-CH_2), 6.58 (br, 1H, NH). Elem. Anal. Calcd for $C_{17}H_{23}NO_5S_3$: C, 48.90; H, 5.55; N, 3.35. Found: C, 48.67; H, 5.55; N, 3.35.

Poly 2-[Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl]ethyl Thiomethacrylate (11). IR (KBr, ν cm^{-1}): 2969 (alkyl C-H), 2866 (methyl C-H), 1762, 1735 (thioester C=O), 1651 (alicyclic ketone C=O), 1388 (methyl C-H). 1H NMR ($CDCl_3$, 25 °C): δ 1.00–2.15 (m, 5H, CO-CCH₃- CH_2) 1.65 (s, 1H, CH- CH_2-CH), 1.91 (m, 2H, CHS- CH_2-CH), 2.23 (d, 1H, CH- CH_2-CH), 2.47 (br, 2H, CH_2-CHCH_2-CHS , CHS- $CHCH_2-CHS$), 2.68 (br, 2H, CH_2S-CH_2-CHS), 2.92 (m, 1H, $CH_2S-CHCH_2-CH$), 3.02 (m, 2H, COS- CH_2-CH_2), 4.16 (m, 2H, S- $CHCH-CHCH-S$). Elem. Anal. Calcd for $C_{14}H_{18}O_2S_4$: C, 48.52; H, 5.24. Found: C, 48.33; H, 5.15.

Calculations. The refractive indices of the models for polymers were calculated on the basis of the Lorentz-Lorenz theory in the same way as in a previous report.¹⁴ To predict the optical absorption in the UV-visible region, one-electron transition energies and the corresponding oscillator strengths of the models were also calculated using the time-dependent DFT (TD-DFT).¹⁵ The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) was used for the calculations of frequency-dependent linear polarizabilities, transition energies, and corresponding oscillator strengths. The three-parameter Becke-style hybrid functional (B3LYP) was adopted as the functional, and all the calculations were performed using the software package Gaussian 03 (revisions C02 and D01).¹⁶ A typical packing coefficient (K_p) of 0.681¹⁷ was used for evaluating the intrinsic molecular volumes of models to predict the refractive indices.

Results and Discussion

Synthesis of Monomers. In this study, the new monomers, **4**, **5**, **6**, and **7**, having a cyclic dithiocarbonate, a norbornene,

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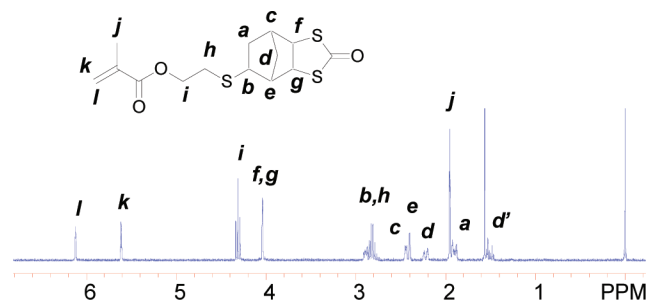


Figure 2. ^1H NMR spectrum of **5** (CDCl_3 , 25 $^\circ\text{C}$).

and a (meth)acrylate group were designed. Each monomer has a different sulfur content in the range of 23–37 wt %. All monomers were prepared using three steps, as shown in Scheme 1. 2-{Exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]deacyl-4-one-8-sulfanyl}ethanol **2** was prepared from norbornadiene and diisopropyl xanthogen disulfide in the presence of AIBN,¹⁸ followed by the ene-thiol reaction with 2-mercaptoethanol in the presence of AIBN. Monomer **6** was prepared from 2-methacryloylethylisocyanate and compound **2**. On the other hand, monomers **4** and **5** were prepared by the acylation reaction of **2** with acryloyl chloride and methacryloyl chloride, respectively. Furthermore, for obtaining a high sulfur content, monomer **7** was also prepared from methacryloyl chloride and 2-{exo-3,5-dithiatriacyclo[5.5.1.0^{2,6}]deacyl-4-one-8-sulfanyl}ethanethiol **3**, which was obtained by the ene-thiol reaction of **1** with 1,2-ethanedithiol in the presence of AIBN. This reaction produced byproducts such as the disubstitution product of ethanedithiol, which was insoluble in CHCl_3 . Thus, this byproduct was easily removed by filtration from CHCl_3 solution.

The structures of these monomers were determined on the basis of elemental analysis as well as IR and NMR spectroscopies. The IR spectra of monomers showed characteristic absorptions at 1712–1720 and 1635–1651 cm^{-1} due to the ester and acyclic ketone carbonyl groups, respectively.

Figure 2 shows the ^1H NMR spectrum of **5**, consisting of one triplet signal at 4.31 ppm and two triplet signals at 5.61 and 6.12 ppm that are attributed to the methylene next to the ester group and the vinyl protons, respectively. Assignments of other protons are summarized in Figure 2.

Preparation and Characterization of Polymers. Polymerization was carried out by free radical polymerization using AIBN as the radical initiator in DMF for monomers **4**, **5**, and **6** and in chloroform for monomer **7**. The results are summarized in Table 1. The polymerization proceeds smoothly and yields high molecular weights of the corresponding polymers. The higher the concentration of the polymerization solutions, the higher the molecular weight of the polymers. On the other hand, the polymerization of **4** forms a gel in a high concentration solution, probably because of α -hydrogen abstraction, while the low concentration solution provides a soluble polymer. Each polymerization produced a white powder; polymers **8**, **9**, and **10** were soluble in DMF, *N,N*-

Table 1. Radical Polymerization of **4**, **5**, **6**, and **7**

monomer	run no.	solvent	concn (mol/L)	M_n	PDI	yield (%)
4	1	DMF	1.0	gel		
	2	DMF	0.5	29 000 ^a	1.9 ^a	100
5	3	DMF	0.7	61 000 ^a	2.3 ^a	76
	4	DMF	0.5	27 000 ^a	1.6 ^a	59
6	5	DMF	0.7	65 000 ^a	3.2 ^a	83
	6	DMF	0.5	27 000 ^a	1.9 ^a	83
7	7	CHCl_3	0.5	20 000 ^b	2.3 ^b	100
	8	CHCl_3	1.0	76 000 ^b	3.8 ^b	82

^a Determined by GPC (DMF, PSt standard). ^b Determined by GPC (CHCl_3 , PSt standard).

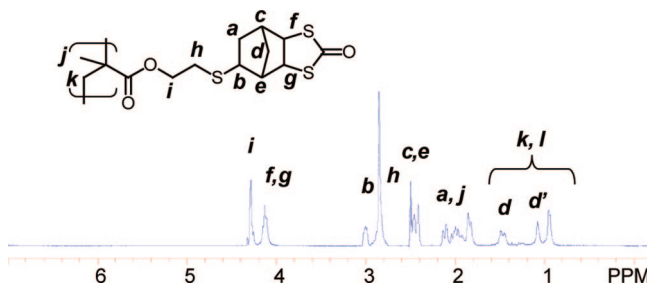
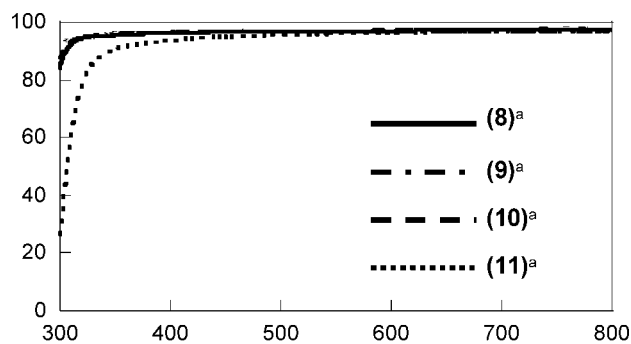


Figure 3. ^1H NMR spectrum of **9** ($\text{DMSO}-d_6$, 100 $^\circ\text{C}$).

Table 2. Thermal Properties of **8**, **9**, **10**, and **11**

polymer	5% weight loss temp ($^\circ\text{C}$) (under N_2 atm) ^a	5% weight loss temp ($^\circ\text{C}$) (under air atm) ^a	T_g ($^\circ\text{C}$) ^b
8	312	310	84.4
9	305	305	104.7
10	300	299	43.5
11	291	293	109.0

^a Determined by TGA. ^b Determined by DSC.



^aPolymer film on quartz substrate

Figure 4. UV-vis transmittance spectra of the polymer films.

dimethylsulfoxide, and *N,N*-dimethylacetamide, while polymer **11** was soluble in CHCl_3 , tetrachloromethane, and chlorobenzene.

The structures of the polymers obtained were characterized by ^1H NMR and FT-IR spectroscopies. The IR spectra of polymers exhibit the characteristic ester and acyclic ketone carbonyl stretching at 1712–1720 and 1635–1651 cm^{-1} , respectively. The IR absorption at around 990 cm^{-1} due to vinyl groups disappears. Figure 3 shows the ^1H NMR spectrum of polymer **9**. The signals except for those due to the acrylate group are slightly shifted as compared to those of the monomers and become broader. The signals of the methacrylate group ($\delta = 4.31\text{--}6.12$) disappear, and the signals of the main chain are spread at $\delta = 1.20\text{--}1.39$ because of the tacticity of the polymer. This spectrum

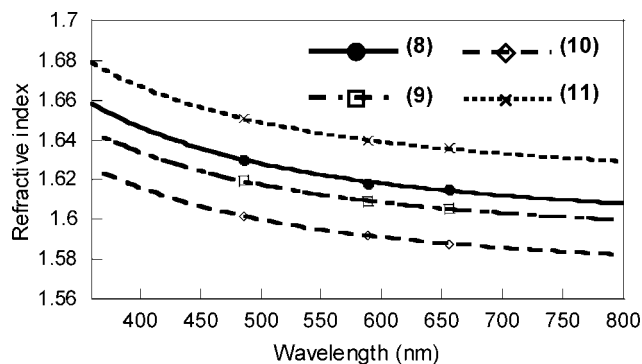
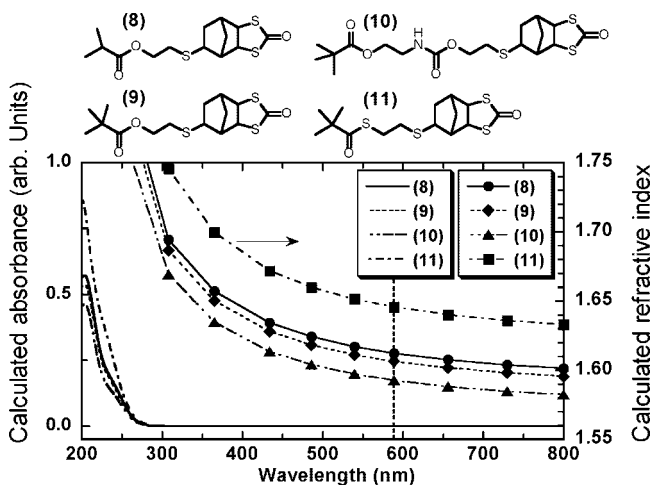
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Table 3. Refractive Indices (n) and Abbe's Numbers (ν) of Polymers

polymer	sulfur content (wt %)	$d^a(\mu\text{m})$	experimental						calculated ^f	
			n_F^b	n_D^c	n_C^d	ν_D^e	n_∞^f	D^f	n_D	ν_D
8	30.4	325	1.630	1.618	1.615	40.2	1.595	8201	1.612	36.6
9	29.1	300	1.619	1.609	1.606	44.5	1.589	7270	1.606	37.1
10	23.0	230	1.602	1.592	1.588	42.9	1.571	7203	1.593	37.7
11	37.0	500	1.651	1.640	1.636	42.1	1.617	8033	1.646	32.7

^a Film thickness. ^b Measured at 486 nm. ^c Measured at 589 nm. ^d Measured at 656 nm. ^e Estimated from curve fitting using the simplified Cauchy's formula. Calculated using eq 1. ^f Calculated from the wavelength-dependent molecular polarizabilities from DFT calculations with a constant packing coefficient ($K_p = 0.681$). The unit of D is nm^2 . The same model compounds were used for calculations in the polymers **8** and **9**.

Figure 5. Experimental refractive index dispersion of polymers **8**–**11**.Figure 6. Calculated absorption spectra and refractive index dispersion of model compounds for **8**–**11**. The model compounds used for the calculations are shown at the top.

suggests that the polymerization proceeds completely without the destruction of the monomers.

Properties of Polymers. The thermal properties of polymers were evaluated by TGA and DSC. As shown in Table 2, all the polymers exhibit a relatively high degradation temperature (5% weight loss) of around 290 °C in both air and nitrogen, while their glass transition temperatures (T_g) are in the range of 44–109 °C. From these results, the T_g would depend on the length of the alkyl spacers between the main chain and the norbornene moiety. Polymer **10** with a long spacer shows a low T_g , while polymers **8** and **9** with short spacers exhibit higher T_g values. These facts indicate that a long spacer with higher degrees of flexibility lowers the T_g . Moreover, polymer **9** shows a higher T_g as compared to that of polymer **8** because the methyl moiety in methacrylate reduces the mobility of polymer chains apart from increasing the chain rigidity.

Figure 4 shows the UV–vis optical transmission spectra of the polymer films formed on silica (amorphous SiO_2) substrates. The films of polymers **8**, **9**, and **10** were prepared by spin-casting from their *N,N*-dimethylacetamide solutions, and that of polymer **11** was obtained by spin-casting from its hot cyclohexanone solution. All films exhibit good transparency in the visible region (wavelengths: 400–800 nm). Although polymer **11** exhibits low transparency near 350 nm, it shows good transparency (>90%) over the entire visible region (>360 nm). One important reason for the high transparency is the absence of aromatic rings in the molecular structures.

The refractive indices of the polymer films determined at 486, 589, and 656 nm are listed in Table 3. The wavelength-dependent refractive indices (n_λ) thus obtained are plotted in Figure 5 with fitted curves that are obtained by using the simplified Cauchy's equation:¹⁹

$$n_\lambda = n_\infty + D/\lambda^2 \quad (2)$$

The coefficients of n_∞ and D and Abbe's numbers (ν_D) are also presented in Table 3. All the polymers show significantly higher values of n_D and ν_D as compared to those of conventional optical polymers. For instance, polymer **11** shows a high n_D and ν_D of 1.64 and 42.1, respectively, whereas the values of (n_D , ν_D) for PMMA, polystyrene, and polycarbonate are (1.491, 57), (1.590, 30), and (1.581, 29), respectively.

The n_D values of the synthesized polymers depend on the amount of sulfur atoms having a high atomic refraction. Moreover, the alicyclic and planar structures of the tricyclo moiety contribute to a reduction in the molecular volume and to an increase in the refractive indices without a decrease in Abbe's numbers. Among the three different polymerization groups, methacrylate and thiomethacrylate polymers display the most balanced values of n_D and ν_D as compared to that of the acrylate polymer.

Figure 6 shows the calculated absorption spectra and refractive index dispersions of models **8**–**11**. The calculated n_D and ν_D values are also incorporated in Table 3. The very short cutoff wavelengths (λ_{cutoff}) of around 310 nm for **8**, **9**, and **11** in Figure 3 are well reproduced in the calculated spectra, though λ_{cutoff} for **10** is slightly underestimated. The analysis of TD-DFT calculations indicates that the one-electron transitions appearing above $\lambda = 250$ nm are typical charge-transfer transitions with very small oscillation strengths (f), which is an essential cause of the high transparency. For instance, the f values of the transitions from the highest

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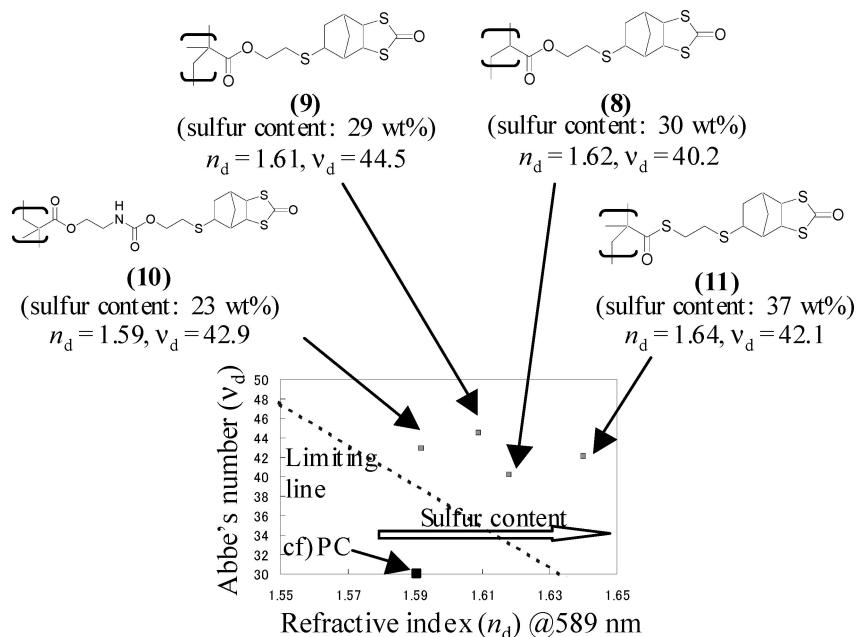


Figure 7. Plots of the refractive indices at 589 nm (n_D) against Abbe's numbers (v_D).

occupied molecular orbital located around the sulfur atom connecting the norbornane moiety and the $-\text{CH}_2-\text{CH}_2-$ chain to the lowest unoccupied molecular orbital around the carbonyl moiety are negligibly small. The relatively long λ_{cutoff} of **11** could be partly explained by the larger f values of the localized excitation around the carbonyl thioether ($-\text{CO}-\text{S}-$) moiety. This is reflected on the stronger absorption at 200–250 nm in the calculated spectrum (Figure 6).

As shown in Figure 5, the refractive indices and their dispersions for polymers **8–11** depicted in Table 3 are well reproduced in the calculations. Note that the prediction errors in the calculated n_D values are less than 0.4%, even though a constant K_p value (0.681) was used for the estimation of the molecular packing. The slightly lower n_D value of **9** as compared to that of **8** and the decrease in n_D in **10** due to the insertion of $-\text{COO}-\text{C}_2\text{H}_4-\text{NH}-$ in **9** are well reproduced by the calculations. In contrast, it should be noted that all experimental v_D values are significantly higher than the calculated ones by 11–29%. As we have reported, DFT calculations with a large basis set can quantitatively reproduce the experimental Abbe's numbers of organic compounds.²⁰ In addition, the basis for the limiting line (i.e., an empirical rule in which higher refractive compounds exhibit lower Abbe's numbers) was also confirmed by the calculations. One can find the same tendency in the calculated values: the higher the n_D , the smaller the v_D . However, polymers **8–11** exhibit similar v_D values regardless of the difference in n_D . The significantly higher v_D values as compared to those predicted by calculations apparently demonstrate that these polymers possess extraordinarily high

refractive index and low dispersion, although the essential reasons are still unclear. Since the wavelength dependence of the n_λ values is perfectly fitted by eq 2, as shown in Figure 5, the measurements should be sufficiently reliable.

Figure 7 shows the plots of v_D against n_D for the synthesized polymers. It should be noted that all the data points for **8–11** are clearly located in the region opposite that of the conventional optical polymers. In particular, polymer **11**, having the highest sulfur content (37.0 wt %) among the four polymers, is located at the most distant position from the line, which indicates that the substitution of sulfur for oxygen in the carbonyl ester moiety ($-\text{CO}-\text{O}- \rightarrow -\text{CO}-\text{S}-$) significantly increases the refractive index without deteriorating the dispersion. The side-chain structure of **11** could be the key to overcome and go beyond the limiting line in the judicious design of sulfur-containing polymers.

Conclusions

Sulfur-containing poly(meth)acrylates with good optical transparency in the visible region, high refractive indices (n_D), and high Abbe's numbers (v_D) were successfully prepared from four newly prepared monomers containing cyclic dithiocarbonate, norbornane, and (meth)acrylate units. The polymer films prepared on silica substrates demonstrated n_D and v_D values higher than 1.592 and 40.2, respectively, which indicates that the introduction of cyclic dithiocarbonate and thioether moieties is effective in increasing n_D without decreasing v_D . The well-balanced good properties of the polymer films make them good candidates for advanced optical applications.

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