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Refractive index changes in polyacrylates bearing alkyl sulfur groups through the sulfur oxidation reaction

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ABSTRACT

Four polyacrylates with sulfur-containing side chains were prepared to examine the changes in refractive index (RI) induced by sulfur oxidation. Linear alkyl sulfides and alicyclic sulfides, such as 1,3-dithiolane and 1,4-dithiane, were introduced to impart large RIs to polyacrylates. Oxidation of the sulfur polymers by O_3 and *m*-chloroperoxybenzoic acid led to the formation of the corresponding sulfoxide and sulfone polymers, respectively. Sulfur oxidation occurred completely, which was highlighted by the oxidized polymer exhibiting a refractive index comparable to a polymer that was synthesized using a sulfone monomer. The RI of the linear sulfur polymer increased and decreased due to the formation of sulfoxide and sulfone polymers, respectively. The Abbe number of the polymer with a linear sulfide side chain was 33.4, which increased to 48.7 after oxidation.

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1. Introduction

The refractive index (RI) of materials is a significant optical parameter for photonic applications that can be precisely tuned to achieve clear images in ophthalmic lenses and for light confinement in an optical waveguide [1–3]. Organic polymer materials have attracted considerable attention because they provide flexible and thin films through a low temperature process [4]. The RI of polymer films can be adjusted with constituent atoms or by controlling the composition in composite polymers [5,6]. The introduction of fluorine and bromine atoms to hydrocarbons alters the RI in an opposite way. Many studies have introduced sulfur atoms to organic polymers to achieve high RIs, and several sulfur-containing resins (MR™ series, Mitsui) are in practical use [7–9]. The sulfur contribution can be explained by the large atomic refraction of sulfur (7.80), compared with carbon (2.13) or oxygen (1.64). High sulfur content for large RI often causes solubility and stability problems that limit polymer synthesis and film fabrication. High-RI materials have been developed considering the large molar refraction and small molar volume of the constituent group according to the Lorentz–Lorenz equation [10]. An alicyclic group is desirable for a small molar volume. Tetrahydrothiophene (THT) has a larger RI than diethyl sulfide (DES), despite its smaller molar refraction, which is attributed to its small molar volume, as shown in Table 1. A 1,3-dithiolane-attached polymer was reported to have higher sulfur content [11]. Okubo et al. introduced 1,4-dithiane to poly(*S*-alkylcarbamate) [12], and the Ueda group extensively studied poly(thioether sulfone)s [13]. Thiol addition polymerization to a vinyl sulfone group provided poly(thioether sulfone)s, yielding enhanced RI dispersion. The high atomic dispersion ($\Delta R = 0.22$) of a sulfide group was complemented by a sulfonyl group ($\Delta R = 0.07$). A sulfone group has an atomic refraction of 9.76, which is larger than a sulfide group; however, the former produces a lower RI due to its molar volume. Several sulfur and sulfur oxide molecules were compared, as listed in Table 1 [8,10]. The RIs of dimethylsulfone and THT were lower than dimethyl sulfide and sulfolane, respectively. The contribution of the molar volume to the RI represents an interesting result that a sulfoxide has a higher RI than a sulfide. From the data of small molecules, the change in RI relying on the oxidation state of sulfur prompted an oxidation study of sulfur-containing polymers. Although most efforts to date have focused on the high refractive index of sulfur-containing polymers, control of the RI based on the oxidation has not been reported. The further oxidation of a preformed sulfur polymer becomes a simple way to build a required RI. Various oxidation conditions were compared in this research for partial and complete oxidation of the sulfur polymers. The sulfur oxidation was monitored by infrared absorption spectroscopy and H-nuclear magnetic resonance spectroscopy.

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Table 1
The refractive indices of several sulfur, sulfoxide and sulfone molecules from a prediction and literature data.

Molecule	Mw (g/mol)	n_D[a]	Calculated[b]		
			n_D	Molar refractivity (cm^3)	Molar volume (cm^3)
Me_2S	62.1	1.435	1.425	19.3	75.5
Me_2SO	78.1	1.479	1.480	20.2	71.1
Me_2SO_2	94.1	1.423	1.402	20.1	82.6
Et_2S	90.2	1.442	1.440	28.6	108.5
THT[c]	88.2	1.503	1.515	26.6	88.2
THT-oxide[d]	104.2	1.520	1.549	27.4	86.2
Sulfolane	120.2	1.482	1.486	27.3	95.3

[a] Literature data from the Merk index.
[b] Industry standard physchem prediction models provided by ACD/Labs.
[c] Tetrahydrothiophene (THT).
[d] Tetrahydrothiophene 1-oxide (THT-oxide).

2. Experimental

2.1. Materials and characterization

All reagents were purchased from Sigma–Aldrich Chemical Co. (Yongin, Korea) and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. ^{1}H NMR and ^{13}C NMR spectroscopy experiments (Bruker AM-300 spectrometer) were used to characterize the molecular structures of the intermediate compounds and functional methacrylate monomers. The mass spectra were recorded on an Agilent 1200LC/1100 MSD SL mass spectrometer. A MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA) recorded the FTIR spectra. The refractive indices of the polymer films were measured by an Abbe Refractometer (DR-M4). TGA analysis was performed on a TAG/SDTA 851^e. The molecular weights of the polymers were determined by an Agilent PL-20 instrument using a polystyrene standard. Ozone was generated using a model PC57-10 laboratory ozonizer.

2.2. Synthesis of monomer methacrylates: *M-IV* (a general procedure)

To a stirred solution of intermediate alcohol, **Me** (1.50 g, 10 mmol) in dichloromethane (MC) (30 mL), methacrylic anhydride (94%, 1.66 mL, 10.5 mmol), triethylamine (1.53 mL, 11.0 mmol), and 4-dimethylaminopyridine (30 mg) were added in order. The mixture was stirred at room temperature for 12 h. The resulting mixture was diluted with MC, washed with water, and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The residue was subjected to column chromatography on silica gel to give an acrylate monomer, **M-IV** (1.94 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.92 (s, 3H), 2.82 (s, 4H), 2.98–3.08 (m, 1H), 3.15–3.25 (m, 2H), 4.32–4.42 (m, 2H), 5.58 (s, 1H), 6.14 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 27.5, 28.9, 31.1, 42.2, 64.1. LC-MS, m/z: 219.05 [M + 1].

M-I (89% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.92 (t, 3H), 1.38–1.48 (m, 2H), 1.51–1.60 (m, 2H), 1.95 (s, 3H), 2.58 (t, 2H), 2.79 (t, 2H), 4.30 (t, 2H), 5.59 (s, 1H), 6.13 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm) = 13.7, 18.4, 22.0, 30.3, 31.7, 32.1, 64.0, 125.9, 136.1, 167.2. LC-MS, m/z: 203.11 [M + 1].

M-II (90% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.84 (s, 3H), 2.03 (s, 3H), 2.58–2.82 (m, 6H), 4.19 (t, 2H), 5.49 (s, 1H), 6.01 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm) = 15.4, 18.3, 30.3, 31.7, 34.0, 63.8, 125.9, 135.9, 167.0. LC-MS, m/z: 221.07 [M + 1].

M-III (70% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.80 (s, 3H), 1.98 (s, 3H), 3.32–3.39 (m, 4H), 4.26 (s, 2H), 5.61 (s, 1H), 6.16 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm) = 18.3, 27.60, 39.6, 64.1, 71.8, 126.0, 136.0, 166.9. LC-MS, m/z: 219.05 [M + 1].

MO2-III (96% isolated yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.68 (s, 3H), 1.89 (s, 3H), 4.02–4.15 (m, 4H), 4.57 (s, 2H), 5.78 (s, 1H), 6.07 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm) = 14.5, 18.2, 49.3, 62.6, 71.9, 127.7, 135.436, 165.9. IR (KBr, cm^{-1}): ν_{max} 3383 (OH), 1326 (SO_2), 1126 (SO_2), 1073. LC-MS, m/z: 283.02 [M + 1].

2.3. Polymer synthesis: a general procedure

A flask was charged with a mixture of **M-III** (0.60 g), methyl methacrylate (MMA) (1.40 g), and a catalytic amount of AIBN (3.0 mol%), and the mixture was dissolved in tetrahydrofuran (THF) (9.0 mL) (20 wt.%). The reaction mixture was deoxygenated by N_2 flow for 10 min and then heated at 70 °C for 12 h under N_2 conditions. The resulting mixture was poured into methanol (40 mL) to precipitate a polymer product. The resulting solid was filtered, dissolved in THF (9 mL), and poured into methanol (40 mL). After standing overnight, the polymer was collected by filtration and dried in a vacuum oven (50 °C) to give an acrylate copolymer, **PM-III** (1.78 g, 89%).

2.4. Oxidation of a polymer: a general procedure

(i) O_3-oxidation: polymer **PM-III** (0.50 g) was dissolved in $CHCl_3$ (20 mL) and kept at −78 °C. The solution was treated with excess bubbling O_3 for 2 h and then with N_2 flow at room temperature to remove the dissolved O_3. The resulting mixture was concentrated to a volume of ca. 5 mL under reduced pressure and poured into methanol to precipitate a polymer. The polymer was collected by filtration and dried in a vacuum oven (50 °C) to give an oxidized polymer, **PM-III(O)** (0.49 g, 98%).

(ii) *m*-CPBA-oxidation: polymer **PM-III** (0.50 g) was dissolved in THF (20 mL), and *m*-CPBA (*m*-chloroperoxybenzoic acid, 78%) (0.91 g) was added at room temperature. The reaction mixture was heated at 70 °C for 9 h. The resulting mixture was poured into methanol to precipitate a polymer. The polymer was collected by filtration and dried in a vacuum oven (50 °C) to give an oxidized copolymer, **PM-III(O2)** (0.48 g, 96%).

PM-I: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.82 (br), 0.91 (t), 1.00 (br), 1.21 (br), 1.35–1.52 (m), 1.53–1.64 (m), 1.77–1.99 (m), 2.59 (m), 2.75 (m), 3.58 (s), 4.20 (br). IR (KBr, cm^{-1}): ν_{max} 1730 (C=O), 1270, 1240, 1192, 1149 (C—O), 1063. GPC (THF, polystyrene standard): Mn = 18.2 kDa, Mw = 40.4 kDa.

PM-I(O): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.75 (br), 0.95 (br), 1.47 (br), 1.60–2.05 (m), 2.65–3.05 (m), 3.54 (s), 4.24 (br). IR (KBr, cm^{-1}): ν_{max} 1727 (C=O), 1438, 1391, 1270, 1233, 1186, 1149 (C—O), 1035 (SO). GPC (THF, polystyrene standard): Mn = 20.1 kDa, Mw = 38.2 kDa.

PM-I(O2): ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 0.75 (br), 0.95 (br), 1.39–1.60 (br), 1.61–2.05 (m), 3.17 (br), 3.33 (br), 3.55 (s), 4.26 (br). IR (KBr, cm^{-1}): ν_{max} 1730 (C=O), 1323 (SO_2), 1270, 1240, 1192, 1149 (C—O), 1130 (SO_2), 1063. GPC (THF, polystyrene standard): Mn = 21.3 kDa, Mw = 41.5 kDa.

PM-II: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.83 (br), 1.00 (br), 1.20 (br), 1.42 (br), 1.75–2.05 (m), 2.68–2.83 (m), 3.58 (s), 4.10 (br). IR (KBr, cm^{-1}): ν_{max} 1729 (C=O), 1270, 1241, 1190, 1146 (C—O), 1063. GPC (THF, polystyrene standard): Mn = 16.5 kDa, Mw = 33.8 kDa.

PM-II(O): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.55–1.20 (br), 1.60–2.05 (m), 2.73 (s, CH_3—S), 3.61 (s, CH_3—O, CH_2—SO), 4.34 (br). IR (KBr, cm^{-1}): ν_{max} 1729 (C═O), 1434, 1391, 1268, 1240, 1186, 1144 (C—O), 1030 (SO). GPC (THF, polystyrene standard): Mn = 18.1 kDa, Mw = 34.0 kDa.

PM-II(O2): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.60–0.83 (br), 0.83–1.20 (br), 1.60–2.05 (m), 3.16 (br), 3.34 (br), 3.54 (s), 3.65 (br), 4.25 (br). IR (KBr, cm^{-1}): ν_{max} 1729 (C═O), 1318 (SO_2), 1268, 1241, 1190, 1146 (C—O), 1134 (SO_2), 1063. GPC (THF, polystyrene standard): Mn = 18.3 kDa, Mw = 34.8 kDa.

PM-III: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.89–0.95 (br), 0.96–1.08 (br), 1.30–1.52 (m), 1.60–2.05 (m), 3.55 (s), 3.72 (br), 4.36 (br). IR (KBr, cm^{-1}): ν_{max} 1730 (C═O), 1268, 1244, 1193, 1139 (C—O), 1064. GPC (THF, polystyrene standard): Mn = 24.2 kDa, Mw = 52.5 kDa.

PM-III(O): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.77 (br), 0.92 (br), 1.20–1.62 (br), 1.80–2.50 (m), 3.26–3.45 (m), 3.59 (s), 4.00 (br). IR (KBr, cm^{-1}): ν_{max} 1730 (C═O), 1268, 1245, 1192, 1140 (C—O), 1046 (SO). GPC (THF, polystyrene standard): Mn = 23.9 kDa, Mw = 49.0 kDa.

PM-III(O2): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.67–1.05 (m), 1.05–1.45 (m), 1.46–2.05 (m), 3.54 (br), 4.11 (br), 4.32 (br). IR (KBr, cm^{-1}): ν_{max} 1730 (C═O), 1137 (SO_2), 1268, 1244, 1193, 1139 (C—O, SO_2), 1064. GPC (THF, polystyrene standard): Mn = 27.5 kDa, Mw = 57.8 kDa.

PM-IV: ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.75 (br), 0.94 (br), 1.00–1.60 (m), 1.80–2.05 (m), 2.85 (br), 3.05 (br), 3.20 (br), 3.56 (s), 3.88–4.25 (m). IR (KBr, cm^{-1}): ν_{max} 1732 (C═O), 1271, 1242, 1193, 1152, 1064. GPC (THF, polystyrene standard): Mn = 29.3 kDa, Mw = 55.1 kDa.

PM-IV(O): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.53–0.92 (br), 1.00–1.50 (m), 1.65–2.10 (m), 3.54 (s), 3.80–4.30 (m). IR (KBr, cm^{-1}): ν_{max} 1690 (C═O), 1048, 1027, 1002. GPC (THF, polystyrene standard): Mn = 31.9 kDa, Mw = 58.1 kDa.

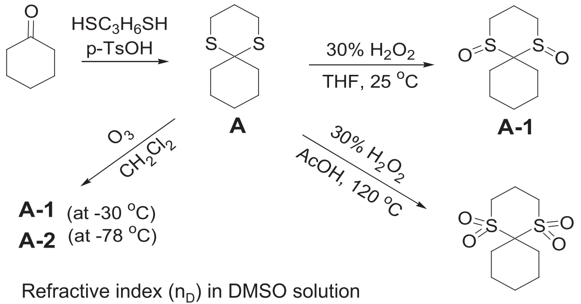
PM-IV(O2): ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 0.573 (br), 0.92 (br), 1.00–1.62 (m), 1.65–2.05 (m), 3.55 (br), 3.85 (br), 4.11–4.45 (m). IR (KBr, cm^{-1}): ν_{max} 1732 (C═O), 1331 (SO_2), 1271, 1241, 1193, 1150, 1130 (SO_2), 1064. GPC (THF, polystyrene standard): Mn = 33.1 kDa, Mw = 60.2 kDa.

3. Results and discussion

One efficient and simple method for the oxidation of sulfide groups is ozone (O_3) gas treatment because of the easy removal of excess O_3 and oxygen as a byproduct. Alkylated 1,3-dithiane (A) prepared from cyclohexanone was chosen. The oxidation of **A** resulted in the selective formation of a sulfoxide and a sulfone depending on the O_3 concentration at low temperatures, as shown in Fig. 1. A similar selective reaction was observed in the H_2O_2 oxidation of **A** [14]. Treatment of **A** with H_2O_2 at 25 °C and at 120 °C resulted in the selective formation of a sulfoxide, **A-1**, and a sulfone, **A-2**, respectively. The three solid molecules were dissolved separately in dimethyl sulfoxide (DMSO) with the same weight ratio for the RI measurement. As expected from Table 1, the refractive index (RI) of the sulfide group increased then decreased with the progress of oxidation. The RI of the DMSO solution increased with increasing sulfone **A** content, in which the effect was located between **A-1** and **A-2**, meaning that sulfide **A** had a lower RI than sulfoxide **A-1** and a higher RI than sulfone **A-2**.

3.1. The syntheses of acrylate monomers

From the preliminary oxidation result, this study focused on the alteration of the RI of polymer materials. A sulfur-containing polymer was previously developed with a high sulfur content for a large RI [11–15]. Fig. 2 shows the scheme for producing five different acrylate monomers. One and two sulfur atoms were introduced to an aliphatic linear and cyclic structure. The *S*-alkylation of 2-mercaptoethanol with 1-iodobutane gave an alcohol, **Ma**, and subsequent acrylation yielded a monomer acrylate, **M-I**. The selective *S*-alkylation of 2-mercaptoethanol occurred with 2-chloroethyl methyl sulfide, and acrylation with methacrylic anhydride provided **M-II**. Cyclic 1,3- and 1,4-sulfur substituted molecules such as 1,3-dithiolane and 1,4-dithiane derivatives were considered for high sulfur content. The acidic protection reaction of 2-hydroxyacetone with 1,2-ethanedithiol yielded a 1,3-ditholane derivative, **Mc**. A sulfone product, **Md**, was generated by heating **Mc** under reflux in acetic acid containing H_2O_2. The presence of SO_2 groups was confirmed by the two strong absorption bands at 1326 and 1126 cm^{-1} in the FTIR absorption spectrum. The corresponding sulfoxide from **Mc** was not isolated because it was unstable during isolation. Acrylation of the intermediate alcohols (**Mc** and **Md**) with methacrylic anhydride provided **M-III** and **MO2-III**, respectively. The 1,4-dithiane derivative **Me** was synthesized via the radical cyclization of propargyl alcohol and 1,2-ethanedithiol according to the method reported in the literature [16]. The alcohol



Refractive index (n_D) in DMSO solution

content	A	A-1	A-2
10 wt%	1.4843	1.4846	1.4806
30 wt%	1.5015	1.5035	1.4933

Fig. 1. The selective formation of a sulfoxide and a sulfone and their refractive indices in DMSO solutions.

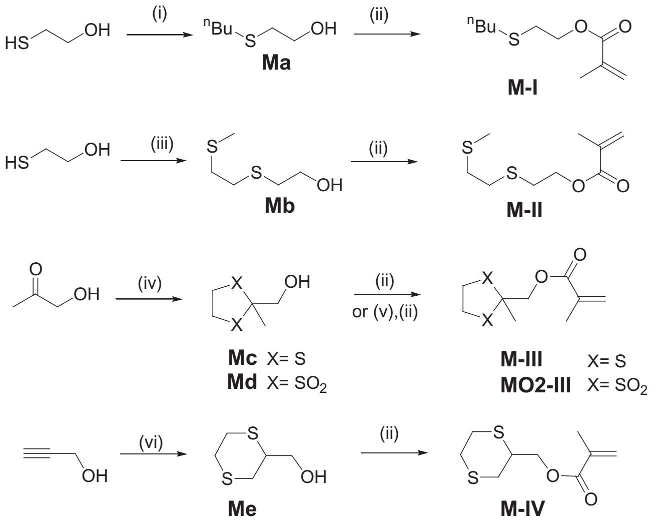


Fig. 2. The syntheses of sulfur acrylate monomers. Reaction conditions: (i) Bu-I, K_2CO_3, DMF, 25 °C; (ii) methacrylic anhydride, Et_3N, cat. DMAP; (iii) $CH_3SC_2H_4Cl$, K_2CO_3, DMF, 25 °C; (iv) cat. *p*-TsOH, 1,2-ethanedithiol, benzene reflux; (v) H_2O_2, AcOH, reflux, 20 h; (vi) HSC_2H_4SH, AIBN, benzene reflux, 8 h.

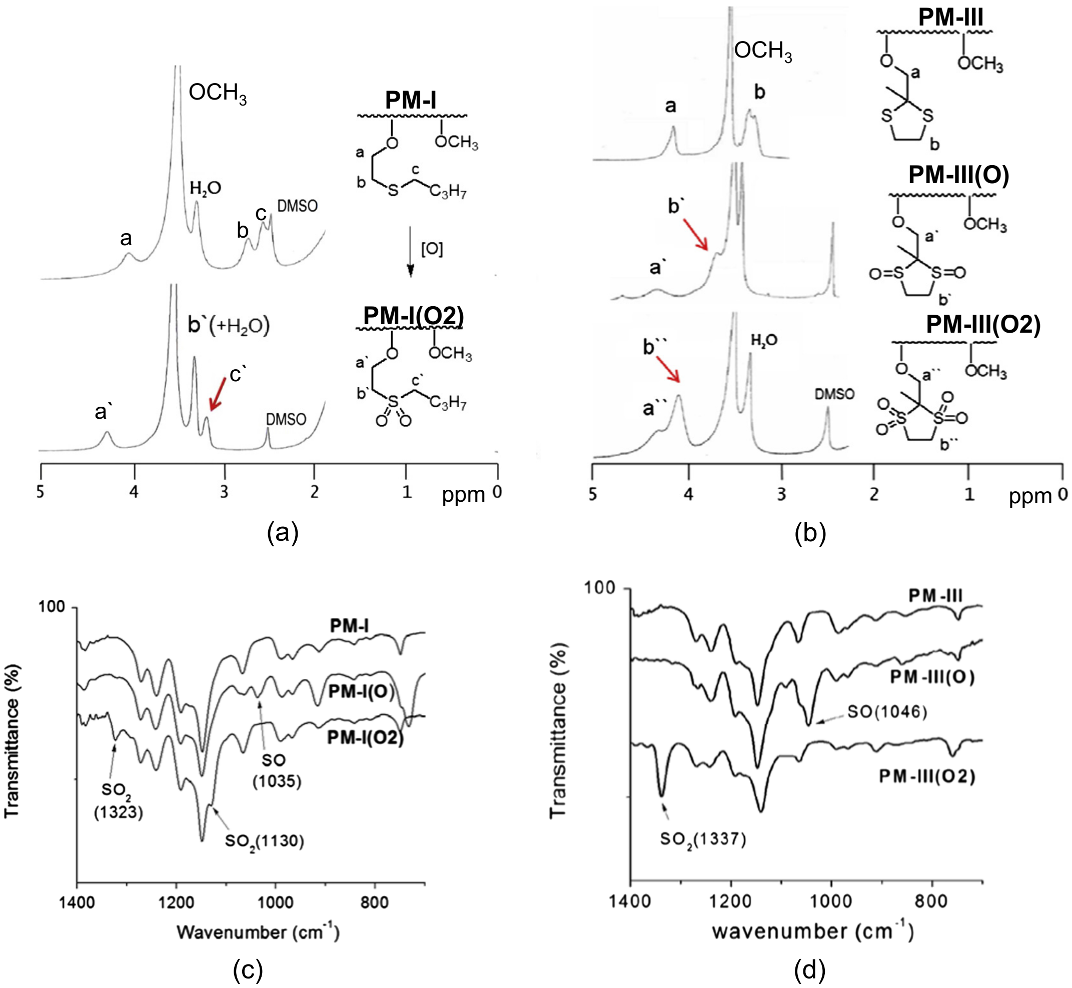


Fig. 3. The ^{1}H NMR and FTIR spectra of the sulfide, sulfoxide and sulfone polymers.

Table 2
GPC and TGA analyses of the sulfur, sulfoxide and sulfone polymer.

Polymer	Molecular weight (kDa)[a]			Degradation (°C)[e]	
	Mn[b]	Mw[c]	PDI[d]	5% loss	10% loss
PM-III	24.2	52.5	2.17	246	251
PM-III(O)	24.9	51.3	2.06	176	234
PM-III(O2)	27.5	57.8	2.10	248	282
PMO2-III	26.1	46.5	1.78	245	280

[a] Molecular weights through GPC analysis.
[b] Number average molecular weight.
[c] Weight average molecular weight.
[d] Polydispersity (Mw/Mn).
[e] Recorded by thermal gravimetric analysis.

Me was derived with an acrylate to produce the monomer **M-IV** in 89% yield.

3.2. The polymerization and oxidation of polyacrylates

Polymerization of the prepared acrylate monomer was conducted with methyl methacrylate (MMA) as the co-monomer under AIBN-mediated radical polymerization conditions. The formation of the copolymer excluded the solubility problem of a homopolymer caused by the high sulfur content, which may be worsened by sulfur oxidation. All of the polymers in this study were prepared from a monomer mixture with a MMA content of 70 wt.%. The copolymer **PM-I** was prepared from the monomer **M-I** at 30 wt.%. The copolymers **PM-II**, **PM-III** and **PM-IV** were produced from **M-II**, **M-III** and **M-IV**, respectively, at 30 wt.%. All of the prepared polymers were soluble in most polar aprotic solvents, such as chloroform, THF, DMF, and DMSO. Gel permeation chromatography (GPC) analysis of the polymers exhibited a number average molecular weight in the range of 20–30 kDa. The polymers were oxidized by the treatment of O_3 gas or by the use of peroxides, such as H_2O_2, Oxone® and *m*-CPBA [14,17]. When O_3 oxidation of the polymer **PM-III** was conducted in dichloromethane, a polymer, **PM-III**(**O**), was generated with sulfoxide functionality. The formation of sulfone groups was not observed, even under the reaction condition of high O_3 concentration at −78 °C. Similarly, the oxidation of **PM-III** occurred with H_2O_2 and Oxone®, yielding **PM-III**(**O**). The use of *m*-CPBA as an oxidizing agent exhibited an interesting result in that a sulfoxide or sulfone formed depending on the reaction temperature. The further oxidation of the sulfoxide groups in **PM-III**(**O**) occurred at a high temperature, yielding **PM-III**(**O2**). The selective oxidation of sulfur atoms was monitored by ^{1}H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, as shown in Fig. 3. All of the polymers were dissolved in DMSO-d6 for the NMR analysis because of the low solubility of the oxidized polymers. The chemical shifts of the methylene protons adjacent to S in **PM-I** were compared with those adjacent to SO_2 in **PM-I**(**O2**), as shown in Fig. 3(a). The complete disappearance of protons (b and c) at 2.6 and 2.8 ppm after the oxidation of **PM-I** indicated that

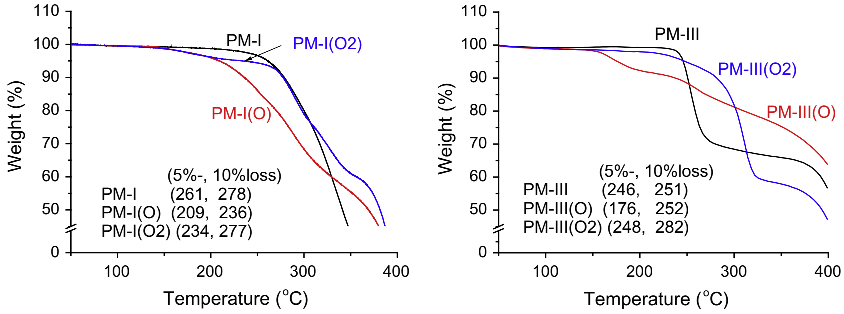


Fig. 4. Thermal stability of the sulfide, sulfoxide and sulfone polymers by thermogravimetric analysis.

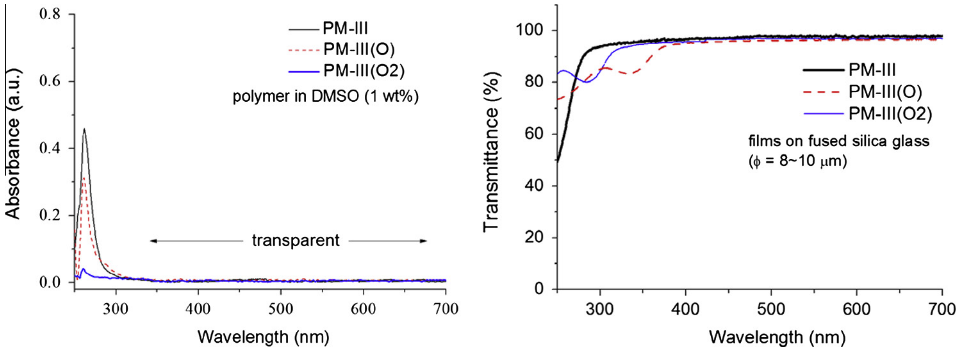


Fig. 5. UV–Vis absorption spectra of the polymers and optical transmittance of the polymer films.

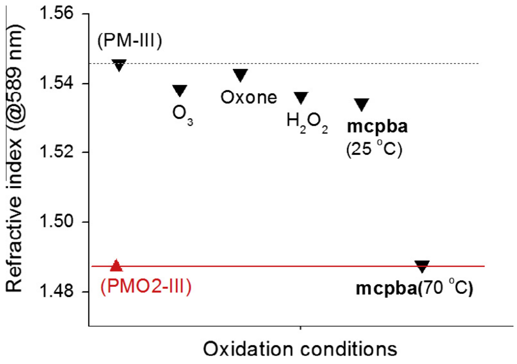


Fig. 6. The refractive index changes during oxidation of a sulfur polymer (PM-III).

all of the sulfur atoms in the polymer were oxidized. The two peaks at 3.2 and 3.4 ppm in the ^{1}H NMR spectrum of **PM-I(O2)** were assigned to the methylene protons (b′ and c′) adjacent to SO_2. The FTIR spectrum of **PM-I(O2)** was similar to **PM-I** except for two bands at 1323 and 1130 cm^{-1} (Fig. 3(c)). These two bands were attributed to the characteristic asymmetric and symmetric stretching vibrations of a sulfone group. Sulfoxide groups were produced by the oxidation of the polymer **PM-III**. The methylene protons (b) at 3.4 ppm in the **PM-III** spectrum, as shown in Fig. 3(b), moved to 3.8 ppm, which was assigned to the protons (b′) adjacent to the SO group in the **PM-III(O)** spectrum. The peak at 3.8 ppm in the **PM-III(O2)** spectrum for the protons (b″) adjacent to SO_2 group moved down field to 4.1 ppm. The presence of SO in the polymer **PM-III(O)** was confirmed by the characteristic absorption band (1046 cm^{-1}) of sulfoxide groups in the IR spectrum in Fig. 3(d). The IR spectrum of **PM-III(O)** exhibited pure sulfoxides without the formation of sulfone groups. The further oxidation of **PM-III(O)** resulted in the formation of **PM-III(O2)**, as illustrated by the strong absorption band at 1337 cm^{-1} for SO_2 groups. *m*-CPBA-oxidation oxidized the sulfur atoms of the sulfur-containing polyacrylates to sulfoxide and sulfone with high selectivity.

The molecular weights of the prepared polymers were measured by GPC and compared after oxidation, as listed in Table 2. The number average molecular weight of the polymer **PM-III** (24.2 kDa) increased to some degree due to oxygen coupling via the oxidation, giving 24.9 and 27.5 kDa for the sulfoxide and sulfone polymers, respectively. A polymer, **PMO2-III**, composed of a pure sulfone unit, was prepared from a sulfone monomer, **MO2-III**, for comparison with **PM-III(O2)**. The ^{1}H NMR and FTIR spectra of **PM-III(O2)** and **PMO2-III** were similar, as expected from the same structure and content of the sulfone units. The thermal decomposition temperature was recorded by thermogravimetric analysis by heating at a rate of 10 °C/min under a nitrogen atmosphere. The polymer **PM-I** exhibited a 5% weight loss at 261 °C, as shown in Fig. 4. The curves of the polymers **PM-I(O)** and **PM-I(O2)** declined at ca. 170 °C, indicating the decomposition of the sulfoxide and sulfone groups [18,19]. The cyclic sulfone polymer **PM-III(O2)** had a thermal stability comparable to **PM-III** with a 5% weight loss at 246 °C. **PM-III(O)** underwent appreciable degradation at temperatures higher than 150 °C to give a 5% loss at 176 °C. Similarly, the thermal behaviors of the sulfoxide polymers **PM-II(O)** and **PM-IV(O)** were observed with onset temperatures of degradation higher than 160 °C (supplementary data).

UV–Vis absorption spectrum of **PM-III** was examined during sulfur oxidation. All of the polymer solutions exhibited high transparency in the visible region, as shown in Fig. 5. The transmittance of the polymer films was measured with thin films (thicknesses of 8–10 μm). The transmittance of **PM-III**, **PM-III(O)**, and **PM-III(O2)** films was recorded as 97.0%, 95.2%, and 95.6%, respectively, at 400 nm. A small loss was observed below 400 nm, especially for **PM-III(O)**; however, all of the polymer films showed transmittance of more than 95% over 400 nm.

Table 3
The refractive indices and Abbe numbers of all of the prepared polymers.

Polymer	Acrylate monomer	S-content (%)	Refractive index (20 °C)				Abbe's number
			486 nm	589 nm	656 nm	n_∞	
PM-I	**M-I**	4.7	1.5197	1.5096	1.5036	1.4840	31.6
PM-I(O)			1.5240	1.5137	1.5086	1.4899	33.4
PM-I(O2)			1.5107	1.5019	1.4997	1.4863	45.6
PM-II	**M-II**	8.7	1.5349	1.5253	1.5192	1.5001	33.4
PM-II(O)			1.5422	1.5315	1.5271	1.5087	35.2
PM-II(O2)			1.5202	1.5120	1.5097	1.4969	48.7
PM-III	**M-III**	8.8	1.5598	1.5458	1.5401	1.5161	27.7
PM-III(O)			1.5478	1.5384	1.5345	1.5183	40.5
PM-III(O2)			1.4973	1.4877	1.4869	1.4742	46.9
PMO2-III	**MO2-III**		1.4971	1.4876	1.4868	1.4743	47.3
PM-IV	**M-IV**	8.8	1.5375	1.5317	1.5231	1.5056	36.9
PM-IV(O)			1.5358	1.5298	1.5204	1.5017	34.4
PM-IV(O2)			1.5011	1.4937	1.4892	1.4747	41.5

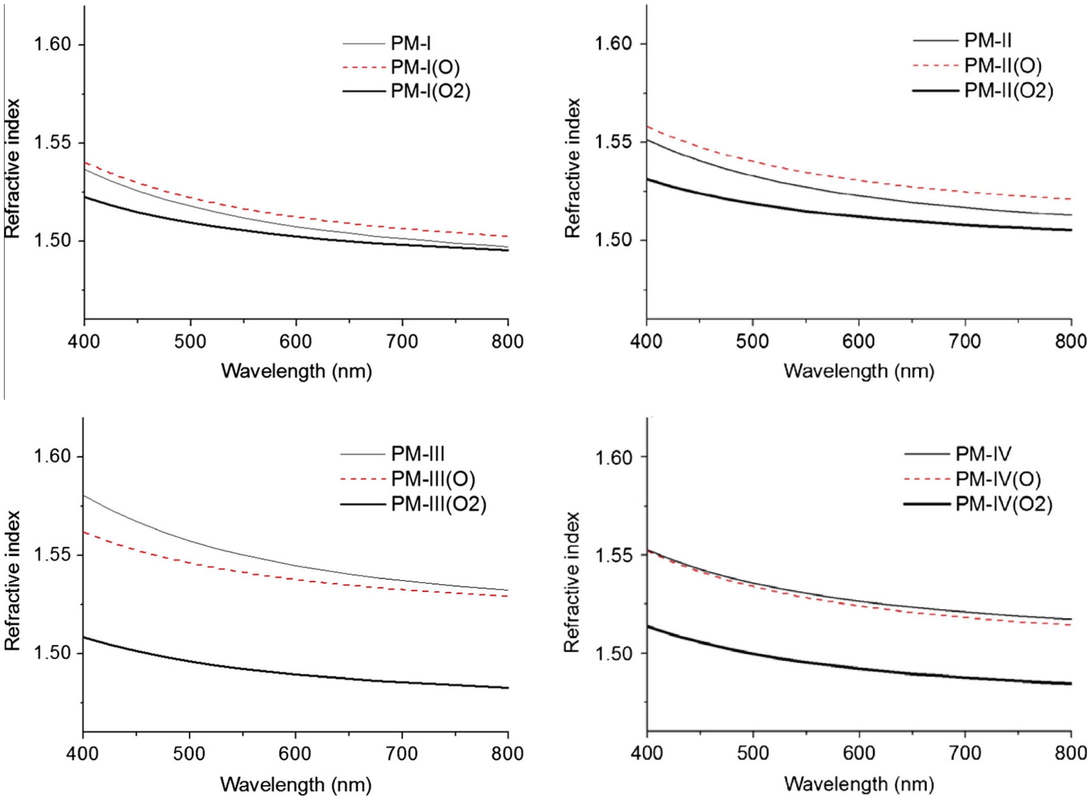


Fig. 7. The wavelength dispersion of sulfur polymers and oxidized sulfur polymers plotted by using a simplified Cauchy's formula.

3.3. The refractive index change in the polyacrylates by oxidation

A large molar volume of sulfone groups helps reduce the RI more than sulfide groups despite the larger molar refraction of the sulfone. The RI of a sulfoxide group is larger than a sulfide, which was stated through a preliminary study using the small molecule **A** or **THT**. The RI change in a sulfur-containing polyacrylate (PM-III) was examined through a range of sulfur oxidations. A polymer film was prepared using a DMSO solution (10 wt.%) to measure the RI using an Abbe refractometer. The RIs of the polymers **PM-III** and **PMO2-III** were 1.5458 and 1.4876, respectively, at 589 nm. The RI may change as the oxidation of **PM-III** proceeds and approach the RI of **PMO2-III**, composed of perfect sulfone groups. Fig. 6 shows that *m*-CPBA in hot THF completed the oxidation of **PM-III**, yielding **PM-III(O2)** with an RI of 1.4877. Therefore, the RI of **PM-III(O2)** became similar to **PMO2-III**. Oxidation by O_3 provided **PM-III(O)** through the formation of sulfoxide groups, as identified by the FTIR spectrum. The RI of **PM-III(O)** was 1.5384 and was lower than **PM-III**. Interestingly, the sulfoxide groups in the polymer **PM-III(O)** had an opposite RI effect compared with that in a small molecule. The similar RI effect of the sulfoxide group was observed in the cyclic sulfur polymer **PM-IV(O)**. The other oxidation conditions, including Oxone®, hot H_2O_2, and *m*-CPBA at 25 °C, exhibited RIs similar to **PM-III(O)**. Oxidation using hot *m*-CPBA was used to alter the RI of other sulfur-containing polymers. The RIs of the four polymers were measured at 486, 589 and 656 nm and are summarized in Table 3. The sulfur content was calculated from the copolymers. The same composition (30 wt.%) and molecular weight of monomers (M-II, M-III, and M-IV) afforded similar sulfur contents (8.7–8.8%). The polymer **PM-I** had a larger RI than **PM-II** due to its higher sulfur content. The cyclic sulfur polymers (PM-III and PM-IV) exhibited higher RIs than the acyclic polymer (PM-II) with similar sulfur content.

The effect of a decrease in RI was observed from the oxidation of all of the sulfone polymers with alicyclic and acyclic sulfide side chains. The RI of **PM-I** was increased due to O_3 oxidation and decreased due to *m*-CPBA-oxidation via the formation of **PM-I**(**O**) and **PM-I**(**O2**), respectively. A similar RI change was observed through the oxidation of **PM-II**. The change in the RI of acyclic sulfur polymers, such as **PM-I** and **PM-II**, agreed with the result from the oxidation of small molecules. However, the cyclic sulfoxide polymers (**PM-III**(**O**), **PM-IV**(**O**)) exhibited RIs lower than the corresponding sulfur polymers. The small volume of sulfoxide groups by inter-association was likely limited in the cyclic sulfur polymers, such as **PM-III**(**O**) and **PM-IV**(**O**), in which their volume effect was weaken [20], resulting in the reduction in the RI.

The refractive index dispersion of a polymer was evaluated using the Abbe number ($\nu_{\rm D}$) according to the equation [8]:

$$\nu_D = \frac{n_D}{n_F - n_C}$$

where $n_{\rm D}$, $n_{\rm F}$ and $n_{\rm C}$ are refractive indices at 589, 486 and 656 nm, respectively. The Abbe number of a sulfide polymer was smaller than the corresponding sulfone polymer, as listed in Table 3. A large Abbe number, meaning a small optical dispersion, was issued for high-RI materials [21–23]. The oxidation of a sulfide group improved the optical dispersion. An increment in $\upsilon_{\rm D}$ was observed through the oxidation of **PM-III** from 27.7 to 40.5 and 46.9 through the formation of sulfoxide and sulfone, respectively. The enhancement of $\upsilon_{\rm D}$ was similarly observed through the oxidation of the acyclic sulfur polymers **PM-I** and **PM-II**. The acyclic sulfone polymer **PM-II**(**O2**) exhibited a high $\upsilon_{\rm D}$ of 48.7. The optical dispersion was plotted from a fitted curve using the simplified Cauchy's formula [24]:

$$\nu_\lambda = n_\infty + D/\lambda^2$$

where n_∞ and D are the estimated RI at an infinite wavelength and the dispersion coefficient, respectively. A clear drift with a slope change in Fig. 7 reveals a reduced RI and improved optical dispersion through the formation of sulfone polymers from the corresponding sulfur polymers. The RI graphs indicated that the acyclic sulfone polymers **PM-I**(**O**) and **PM-II**(**O**) had larger RIs than the corresponding sulfur polymers, whereas the cyclic sulfone polymers **PM-III**(**O**) and **PM-IV**(**O**) had smaller RIs.

4. Conclusion

The change in RI of sulfur-containing polyacrylates during oxidation was investigated. A sulfide group of the polymer was transformed to a sulfoxide or sulfone by selective oxidation. The formation of a sulfoxide and a sulfone was dominant in the O_3 oxidation and *m*-CPBA oxidation, respectively. Oxidation occurred in all sulfide units, and the complete reaction was confirmed by ^{1}H NMR and FTIR spectroscopy. The RI of a sulfur polymer was changed depending on the level of oxidation, leading to the formation of the corresponding sulfoxide and sulfone polymers. The RI of acyclic sulfur polymers increased due to the formation of sulfoxide and decreased due to the formation of sulfone, whereas the cyclic sulfur polymers exhibited clear reductions in the RIs through the formation of both sulfoxide and sulfone. The optical dispersion measured by the Abbe number was improved due to oxidation for all of the sulfur polymers. The films of the prepared sulfur polymers showed high transmittance of more than 95% in the visible region over 400 nm. Thermal instability of the oxidized polymers was observed, which was due to the degradation of the sulfoxide groups. The 5% loss of **PM-I**, **PM-I**(**O**), and **PM-I**(**O2**) polymers was recorded at 261 °C, 209 °C, and 234 °C, respectively. The thermal degradation of the sulfoxide polymer **PM-III**(**O**) occurred with 5% loss at 176 °C. The sulfone polymer **PM-III**(**O2**) exhibited similar thermal stability to **PM-III**, affording 5% loss at 246 °C. The stable sulfone formation from sulfur polymers was shown to be a convenient synthetic approach to generate RIs appropriate for optical applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2015.04.005.

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