

## Synthesis of Novel Polythiol for Plastic Optical Lens and its Ophthalmic Lens

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Novel polythiol materials of urethane lens series for plastic optical lens were synthesized from polyol materials via thioisouronium of thiourea with c-HCl in refluxing aqueous solution, in which polythiol material was carried out from hydrolysis of thioisouronium by ammonia water. Their structure properties were identified by EA, EI-MS, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and TGA. Their ophthalmic lenses as polythiourethane material were prepared by thermal curing to an injected glass mold using the evenly solutions of diisocyanates series (TDI, XDI, HDI or IPDI) with polythiols. Polythiourethane shows that the strong stretching mode for SH group of polythiol disappeared in FT-IR spectra after thermosetting polymerization. Thermal deformation starting temperature of ophthalmic lenses was determined by TMA. Ophthalmic lenses made from characteristic polythiol and diisocyanate series have transparency, colorless and good impact strength, in which thermal resistance and impact strength of ophthalmic lenses were influenced by diisocyanate series. Physical properties of ophthalmic lens have contrast thermal resistance with impact strength. The property of thermal resistance and impact strength for respective ophthalmic lenses was examined by TMA and drop ball test.

**Key Words:** Plastic optical lens, Polythiol, Polythiourethane, Refractive index, Abbe's number

### Introduction

Polythiourethane has been considerably interesting due to excellent physical and optical properties of plastic optical lenses since polythiol has been firstly used as materials of ophthalmic lenses,<sup>1</sup> in which polythiourethane optical lenses have good properties such as easy casting, high thermal resistance, good light resistance, good transmittance, good transparency, good weather resistance and good tintability. It has also easy etching and coating in the process of manufacturing lens. Polythiourthane lens is a hyperbranched thermosetting polymer obtained by polymerization of the evenly mixed polythiol with diisocyanate, it was prepared by thermal curing after casting into glass mold using clear solutions mixed from monomer resin and isocyanate series in the presence of catalyst. Refractive index of ophthalmic lenses was determined by sulfur contents including ophthalmic lens and also polythiol compounds can be more easily controlled a rate of polymerization in comparison with polyol compounds. Also, diisocyanates used in polythiourea material are known such as aryl, alkyl, cycloalkane and heterocycle diisocyanate series. In case of alkyl isocyanates, it decreases refractive index due to a low refractive index of itself, while in case of aryl diisocyanates, it isn't changed almost for refractive index of plastic optical lenses due to a high refractive index of aryl groups. Refractive indexes of plastic lens materials in plastic lens industry were divided into low refractive index (nd or nE, 1.50), middle refractive index (nd or nE, 1.56), high refractive index (nd or nE, 1.60), super high refractive index (nd or nE, 167 or more than 1.70) and functional materials (photochromic dyes and high impact strength materials). Plastic optical lens materials of middle refractive index are well-known as acryl and aryl series, while those of high refractive index are known as acryl

and urethane series. Plastic optical lens materials of super high refractive index are polythiourethane materials having refractive index of 1.67 formed from a mixed solution of urethane series with diisocyanate series<sup>2-5</sup> and also ophthalmic lens materials in the range of 1.70 - 1.76 as episulfide series bearing high sulfur content.<sup>6-7</sup> Super high refractive index of urethane series is not reached to more than 1.70 because of decrease for the refractive index of diisocyanates.

Even though polythiol has not been studied widely in optical lens industry, it is necessary to develop novel plastic materials in order to overcome a patent infringement of a well-known GST<sup>5</sup> (2,3-bis(2-mercaptoethylthio)-propane-1-thiol). Otherwise, GMT<sup>8</sup> (2-(2-mercaptoethylthio)-propane-1,3-dithiol) by comparison with GST was easily changed as a yellow color under heating condition at 70 °C and it has a smaller molecular weight. We have investigated in the mechanism of polythiols and synthesized new model compounds through the new synthetic route having larger molecular weight than GST.

Herein, we will report two novel polythiols, GMMT (2-{3-(2-mercaptoethylthio)-2-[2-(2-mercaptoethylthio)ethylthio]propylthio}ethanethiol) (**1**) and GSTT (2-{2,3-bis(2-mercaptoethylthio)ethylthio}propylthio}ethanethiol) (**2**) and its ophthalmic lenses, in which **1** and **2** are materials of urethane lens series having high refractive index and super high refractive index. **1** and **2** as optical lens materials of urethane lens series in ophthalmic lens were synthesized and identified their structures and properties by elemental analysis, EI-MS, TGA, FT-IR spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. Their plastic optical lenses were prepared and its properties were investigated by TMA and drop ball test. These studies are necessary in order to obtain excellent ophthalmic lenses and also the substitution effect for an import of the whole quantity

from advanced nations to domestic companies which are related to urethane optical lens materials for plastic optical lens.

## Experimental Section

**Materials.** DBTC (dibutyltin dichloride), epichlorohydrin, HDI (hexamethylene diisocyanate), HMPB (2-(2'-hydroxy-5-methylphenyl)-2H-benzotriazole), HTA (1-hydroxy-4-(*p*-toluidin)anthraquinone), IPDI (diisophorone diisocyanate), 2-mercaptoethanol, perinone dye, PNPP (polyoxy ethylene nonyl phenyl phosphate), TDI (tolylene-2,4-diisocyanate), thiourea and XDI (xylylene diisocyanate) are purchased as industrial reagents and used without purification. HCl, NaOH and TEA (triethylamine) were used as reagent grade and solvents used without purification. Distilled water passed through the ion exchange resin after the first distillation and it used after metal ion removed. GMT<sup>8</sup> and GST<sup>5</sup> were synthesized by a similar method as reported.

**General procedure.** Elemental analyses were carried out by EA1110 (CE Instrument, Italy), EI-MS data were obtained with JMS-AX505 WA (Jeol, Japan), FT-IR spectra were recorded on Perkin-Elmer Spectrum 1000 as KBr pellet. TGA (thermogravimetric analyzer) was recorded with thermal property with Du pont 990 Model 951 TGA as 10 °C/min under air condition. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Varian Oxford 300 MHz spectrometer and the chemical shifts were reported in ppm units with tetramethylsilane (TMS) as an internal standard. TMA (thermomechanical analysis) was performed with TMA Q400 (TA instruments, USA) as 5 °C/min under high pure nitrogen gas in order to obtain data of thermal expansion coefficient and thermal resistance. GC (Gas Chromatography) Analysis was performed on M660D (YoungLin, Korea) as column HP-1 (J & W Scientific) and heating condition of 20 °C/min in the range of 60 - 260 °C, HPLC analysis was measured on LC 20A (Shimazhu, Japan) as C18 reverse column (Ace 5, 250 × 4.6 mm, ACE-128-2548, particle size 5 mm), a mixed solvent (CH<sub>3</sub>CN : H<sub>2</sub>O = 7 : 3) and flow rate of 1 mL/min. Wavelength of UV detector was measured at 210 nm, oven temperature measured at 40 °C. Refractive index and Abbe' number data were performed with IT Abbe refractometer (ATAKO, Japan). Impact strength data were obtained by drop ball test of 95.1155 g (steel ball, diameter 30 mm) from a height of 170 cm with non-coated ophthalmic lenses having central lens thickness of 1.20, 1.27 and 2.34 mm (impact resistance of lenses in FDA should be passed 16 g drop ball (diameter 15.9 mm) test from a height of not less than 127 cm and it should be remained an intact without a crack and a damage).

**Synthesis of 2-[3-(2-mercapto-ethylthio)-2-[2-(2-mercapto-ethylthio)-ethylthio]propylthio}ethanethiol (GMTT) (1).** To GMT<sup>8</sup> (186.85 g, 0.932 mol) was added dropwise 25% aqueous NaOH solution (447.52 g, 2.797 mol) below 40 °C. Reaction temperature does not rise above 45 °C in the process of reaction during addition of 25% aqueous NaOH solution. After stirring a reaction solution for 1 hour at 45 °C, 2-chloroethanol (225.10 g, 2.797 mol) was added to a suspension solution at 45°C and it was cooled with an ice bath due to a temperature

raise during addition of 2-chloroethanol. After stirring for 2 hours at 45 °C, to this resulting polyol solution was added thiourea (255.49 g, 3.356 mol) and c-HCl (364.48 g, 4.196 mol) at about 30 °C. After refluxing at 110 °C for 3.5 hours, it was cooled to room temperature. To this resulting solution was added dropwise 25% ammonia water (370.87 g, 5.454 mol) below 30 °C and then toluene (400 mL). This suspension solution was hydrolyzed at 80 °C for 1.5 hours and cooled up to room temperature. The organic layer was separated, washed with c-HCl (100 mL) two times, and washed with H<sub>2</sub>O (100 mL) two times. The separated organic layer was evaporated under reduced pressure and completely removed solvent under vacuum to give a colorless liquid compound. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.87-2.90 (m, 7H, -CH-, -SCH<sub>2</sub>CH<sub>2</sub>SH), 2.68-2.82 (m, 14H, -CH-CH<sub>2</sub>-SCH<sub>2</sub>CH<sub>2</sub>H, -SCH<sub>2</sub>CH<sub>2</sub>SH, -SCH<sub>2</sub>CH<sub>2</sub>S-), 1.70-1.75 (m, 3H, -CH<sub>2</sub>CH<sub>2</sub>SH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz) δ 46.19 (-CH-), 36.88 (-CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH-), 36.38 (-CH-CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 36.03 (-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 31.97 (-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 31.52 (-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 24.71 (-SCH<sub>2</sub>CH<sub>2</sub>SH). FT-IR (KBr pellet, cm<sup>-1</sup>): 2539 (thiol, SH). EI-MS [M<sup>+</sup>]: Calcd. (380.76), Found (380). Elemental Analysis: C<sub>11</sub>H<sub>24</sub>S<sub>7</sub>, Calcd. (%): C, 34.70; H, 6.35; S, 58.95. Exp. (%): C, 34.55; H, 6.88; S, 58.58. Refractive index (nd at 20 °C): 1.6442.

**Synthesis of {2-[2,3-bis-(2-(2-mercapto-ethylthio)-ethylthio)-propylthio}ethanethiol (GSTT) (2).** GSTT was prepared by a similar synthetic procedure of GMTT. To GST<sup>5</sup> (172.67 g, 0.663 mol) was added dropwise 25% aqueous NaOH solution (318.13 g, 1.988 mol) below 40 °C. Reaction temperature does not rise above 45 °C when addition of 25% aqueous NaOH solution. After stirring a reaction solution for 2 hours at 45 °C, 2-chloroethanol (160.21 g, 1.990 mol) was added to a suspension solution at 45 °C and it was cooled with an ice bath due to a temperature raise during addition of 2-chloroethanol. To this polyol solution was added thiourea (181.61 g, 2.386 mol) and c-HCl (259.00 g, 2.982 mol) and refluxed at 110 °C for 3.5 hours. After this resulting solution was cooled to room temperature and then added dropwise ammonia water (267.00 g, 3.970 mol) below 30 °C and toluene (250 mL). This suspension solution was hydrolyzed at 80 °C for 1.5 hours and it was cooled up to room temperature. The organic layer was separated, washed with c-HCl (120 mL) two times, and washed with H<sub>2</sub>O (120 mL) two times. The separated organic layer was evaporated under reduced pressure and completely removed solvent under vacuum to give a colorless liquid compound. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.85-2.99 (m, 7H, -CH-, -SCH<sub>2</sub>CH<sub>2</sub>SH), 2.70-2.84 (m, 18H, -CH-CH<sub>2</sub>-SCH<sub>2</sub>CH<sub>2</sub>H, -SCH<sub>2</sub>CH<sub>2</sub>SH, -SCH<sub>2</sub>CH<sub>2</sub>S-), 1.74-1.79 (m, 3H, -CH<sub>2</sub>CH<sub>2</sub>SH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz) δ 46.11 (-CH-), 36.76 (-SCH<sub>2</sub>CHCH<sub>2</sub>S-), 36.42 (-SCH<sub>2</sub>CH-CH<sub>2</sub>S-), 36.26 (-CH-CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 35.91 (-CHCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 35.85 (-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 36.26 (-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH) 32.90 (-SCH<sub>2</sub>CH<sub>2</sub>S- CH<sub>2</sub>CH<sub>2</sub>SH), 31.87 (-SCH<sub>2</sub>CH<sub>2</sub>S CH<sub>2</sub>CH<sub>2</sub>SH), 31.77 (-CH- CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 31.42 (-CH-SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH), 24.71 (-SCH<sub>2</sub>CH<sub>2</sub>SH). FT-IR (KBr pellet, cm<sup>-1</sup>): 2540 (thiol, SH). EI-MS [M<sup>+</sup>]: Calcd. (440.89), Found (440). Elemental Analysis: C<sub>13</sub>H<sub>28</sub>S<sub>8</sub>, Calcd. (%): C, 35.41; H, 6.40; S, 58.18. Exp. (%): C, 35.23; H, 6.71; S, 58.33. Refractive index (nd at 20 °C): 1.6405.

**Ophthalmic lens of 1 with TDI (3).** To suction flask was added TDI (39.29 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **1** (60.71 g) was added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had colorless and strong impact strength. Refractive index (nd at 20 °C) was 1.6589, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 86.39 °C.

**Ophthalmic lens of 1 with XDI (4).** To suction flask was added XDI (41.15 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **1** (58.85 g) was added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and has a thermosetting polymerization. The resulting plastic lens had thin yellow color and strong impact strength. Refractive index (nd at 20 °C) was 1.6590, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 48.71 °C.

**Ophthalmic lens of 1 with TDI, HDI and IPDI (5).** To suction flask was added TDI (22.06 g), HDI (8.01 g), IPDI (8.01 g), HMPB (1.20 g), HTA (0.176 g), perinone dye (0.12 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **1** (61.92 g) were added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and cured. The resulting plastic lens had colorless and strong impact strength. Refractive index (nd at 20 °C) was 1.6585, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 83.32 °C.

**Ophthalmic lens of 1 with PETMP, HDI and IPDI (6).** To suction flask was added HDI (11.04 g), IPDI (34.03 g), HMPB (1.50 g), HTA (0.08 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **1** (40.24 g) and PETMP (14.69 g) were added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had colorless and strong impact strength. Refractive index (nd at 20 °C) was 1.6041, Abbe's number 40.32 and thermal deformation starting temperature (Ts) 52.47 °C.

The other ophthalmic lenses were prepared according to a similar procedure described above.

**Ophthalmic lens of 2 with TDI (7).** To suction flask was added TDI (35.86 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **2** (64.14 g) was added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had colorless and strong impact strength. Refractive index (nd at 20 °C) was 1.6586, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 69.92 °C.

**Ophthalmic lens of 2 with XDI (8).** To suction flask was added XDI (37.66 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **2** (62.34 g) was added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had thin yellow color and high impact strength. Refractive index (nd at 20 °C) was 1.6586, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 40.65 °C.

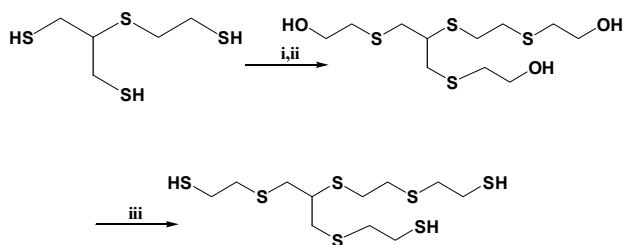
**Ophthalmic lens of 2 with TDI, HDI and IPDI (9).** To suction flask was added TDI (20.09 g), HDI (7.30 g), IPDI (7.30 g), HMPB (1.20 g), HTA (0.176 g), perinone dye (0.12 g), DBTC (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **2** (65.32 g) was added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had colorless and high impact strength. Refractive index (nd at 20 °C) was 1.6581, Abbe's number 27.9 and thermal deformation starting temperature (Ts) 67.67 °C.

**Ophthalmic lens of 2 with PETMP, HDI and IPDI (10).** To suction flask was added HDI (10.38 g), IPDI (31.99 g), HMPB (1.50 g), HTA (0.08 g), catalyst (0.08 g) and PNPP (0.10 g). After evenly mixing a mixture, **2** (43.82 g) and PETMP (13.81 g) were added to reaction vessel. After removing gas under vacuum for 30 minutes, it injected into a glass mold and had a thermosetting polymerization. The resulting plastic lens had colorless and high impact strength. Refractive index (nd at 20 °C) was 1.594, Abbe's number 40.55 and thermal deformation starting temperature (Ts) 50.66 °C.

## Results and discussion

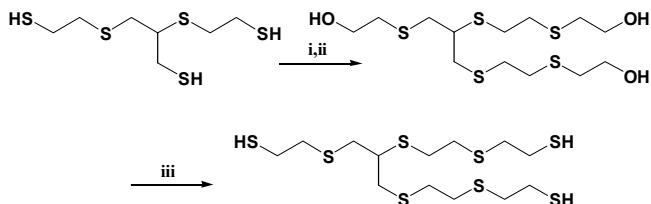
**Synthesis and analysis of thiol materials for plastic optical lens.** Plastic optical lens of urethane lens series made using polythiol was produced firstly at Mitsui Toatsu Chemicals, Inc.,<sup>1</sup> they are world-wide top class for the production of thiol materials for plastic urethane optical lens. In general, polythiol materials were synthesized by conversion of OH group into SH group. Compound including OH group can be converted into SH group via the reaction of SOCl<sub>2</sub> with thiourea<sup>9</sup> or HBr with thiourea.<sup>10-12</sup> In recent, it was synthesized by hydrolysis of KOH or ammonia water in refluxing base conditions via isothiouronium made using HCl and thiourea.<sup>13-14</sup> In this work, thiol materials were prepared by hydrolysis of ammonia via isothiouronium obtained using HCl and thiourea as shown in Scheme 1 and 2.<sup>15</sup> We have tried to obtain thiol compounds using terminal groups such as 3-mercaptopropanol, propanol, ethanol or glycol except the existence of terminal 2-mercaptopropanol units but thiol materials were not produced without terminal 2-mercaptopropanol group. Thiol materials were completed through an intermediate existence of three member ring bearing S atom and then formation and hydrolysis of isothiouronium chloride as shown in Scheme 3.

**1** and **2** were in accord with the estimated contents and molecular weight from elemental analysis and EI-MS, respec-



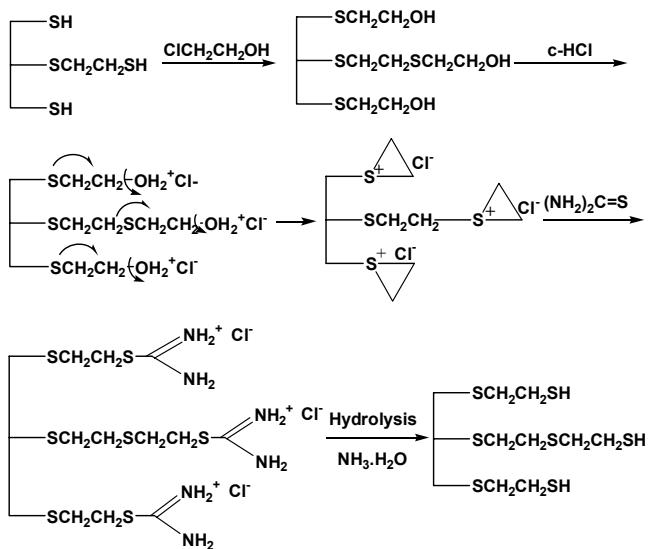
i:NaOH; ii: 2-Chloroethanol; iii: Thiourea/c-HCl at 110 °C and NH<sub>4</sub>OH at 80 °C

**Scheme 1.** Synthetic route of **1**.



i: NaOH; ii: 2-Chloroethanol; iii: Thiourea/c-HCl at 110 °C and NH<sub>4</sub>OH at 80 °C

**Scheme 2.** Synthetic route of **2**.

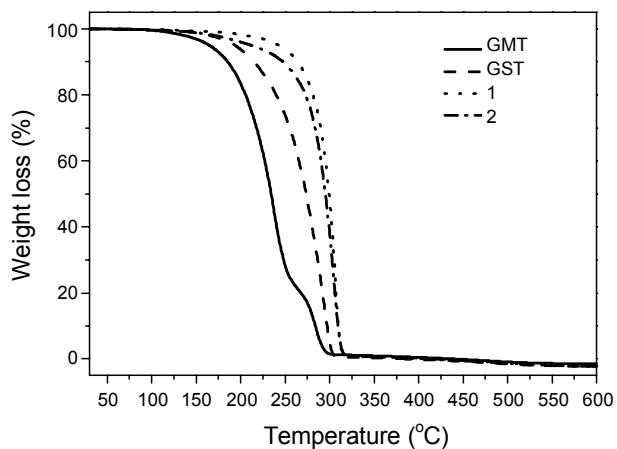


**Scheme 3.** Mechanism for synthetic route of **1**.

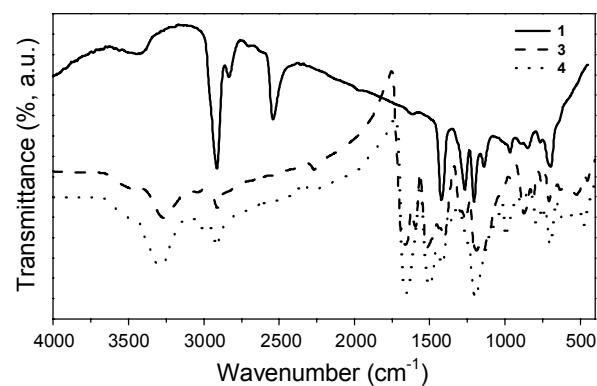
tively. The thermal stability of **1** and **2** were more stable than that of GMT and GST in TGA thermograms as shown in Figure 1. GMT was very unstable as thermal property and easily decomposed, while **1** is more stable in comparison with GST and **2**. All compounds are stable up to 150 °C except GMT, these results can be estimated for thermal property of thiol materials as the order of GMT < GST < **2** < **1**.

Analysis of <sup>1</sup>H NMR data for **1** and **2** indicated approximately three groups such as -CH- or -SCH<sub>2</sub>CH<sub>2</sub>SH at 2.85 - 3.00 ppm, -CHCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SH, -SCH<sub>2</sub>CH<sub>2</sub>SH, -SCH<sub>2</sub>CH<sub>2</sub>S- at 2.70 - 2.84 ppm and -CH<sub>2</sub>CH<sub>2</sub>SH at 1.78 ppm, even though their assignments were not exactly determined due to a complicated peaks for similar conditions of polythiols. Analysis of <sup>13</sup>C NMR data for **1** and **2** indicated that the characteristic peak of -CH- showed one peak at 46.19 ppm for **1** and 46.11 ppm for **2**, respectively, while that of terminal -SCH<sub>2</sub>CH<sub>2</sub>SH groups showed an equal peak at 24.71 ppm for **1** and **2**.

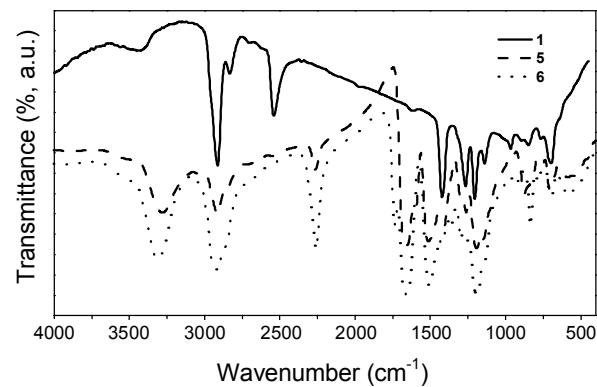
**Properties of ophthalmic lenses.** Ophthalmic lenses were prepared by thermal curing after casting into glass mold using well mixed solutions of thiol materials with diisocyanates in the presence of catalyst. **3** formed from the evenly mixed solutions of **1** with TDI shows that refractive index is 1.6591 and a Abbe's number 27.9, while **4** made from **1** with XDI has refractive index of 1.6590 and Abbe's number of 27.9. **7** prepared from **2** with TDI has refractive index of 1.6586 and Abbe's number of 27.9, while **8** made from **2** with XDI has refractive index of 1.6588 and Abbe's number of 27. However,



**Figure 1.** TGA thermograms of GMT, GST, **1** and **2**.



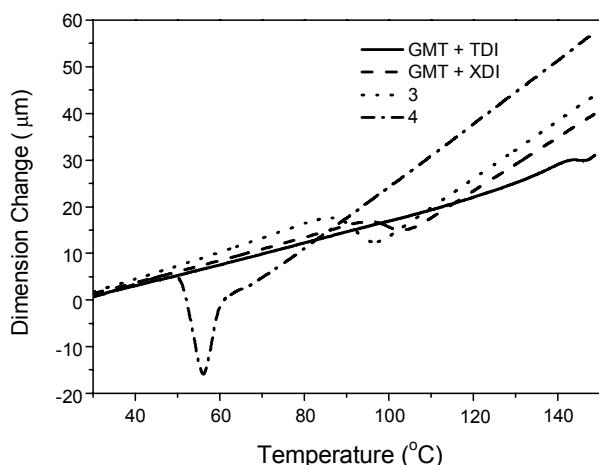
**Figure 2.** FT-IR spectra of **1**, **3** and **4**.



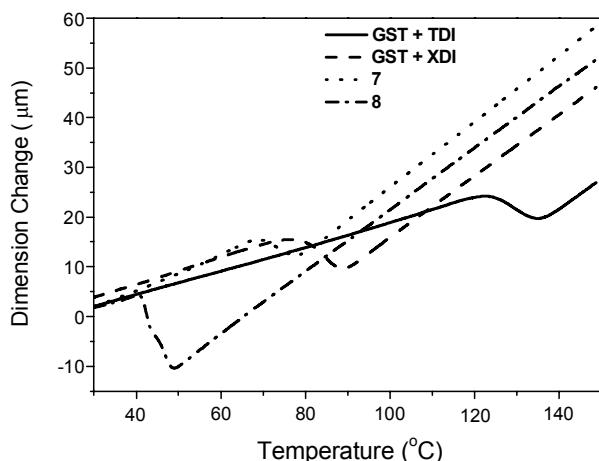
**Figure 3.** FT-IR spectra of **1**, **5** and **6**.

the preparation of optical lenses from the mixed solutions of **1** with IPDI and of **2** with IPDI, respectively, was not carried out successfully because they were mixed and polymerized each other. The preparation of ophthalmic lenses **5** and **6** by the improved methods of **1** with TDI, HDI and IPDI and **1** with PETMP, HDI and IPDI was carried out successfully, **5** made using the evenly mixed solutions of **1** with TDI, HDI and IPDI has super high refractive index of 1.6585 and Abbe's number of 27.9 and **6** made by **1** with PETMP, HDI and IPDI has high refractive index of 1.6041 and Abbe's number of 40.32. Data of ophthalmic lenses **9** and **10** made from **2** by the same procedure of **1** have listed in experimental section.

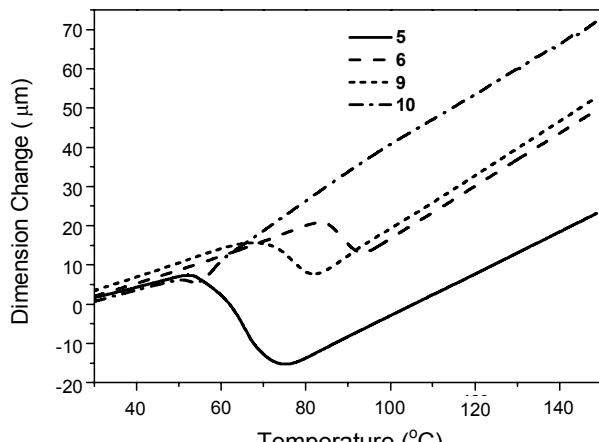
Figure 2 and 3 showed FT-IR spectra of ophthalmic lenses **3** and **4** carried out by **1** with diisocyanates. SH groups of polythiols in FT-IR spectra as shown in Fig. 2 and 3 are assigned to a strong stretching mode of SH in the region of  $2539\text{ cm}^{-1}$  for **1** and that of  $2545\text{ cm}^{-1}$  for **2**, respectively.<sup>15,16</sup>



**Figure 4.** TMA curves of GMT+TDI, GMT+XDI, **3** and **4**.



**Figure 5.** TMA curves of GST+TDI, GST+XDI, **7** and **8**.



**Figure 6.** TMA curves of **5**, **6**, **9** and **10**.

The strong stretching mode of SH groups for plastic optical lenses after polymerization of **1** with diisocyanates disappeared in FT-IR spectra, while stretching modes of NH and C=O bonds appeared newly in FT-IR spectra as shown in Figure 2 and 3. These results can confirm the existence of branch linked polythiourethane after forming bonds of SH with diisocyanate. The ester group for PETMP of ophthalmic lens **9** was assigned to the shoulder peak in the region of  $1739\text{ cm}^{-1}$  as shown in Figure 3.

Figure 4, 5 and 6 show thermograms of TMA for ophthalmic lenses of GMT + TDI, GMT + XDI, GST + TDI, GST + XDI, **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10**, respectively. Thermal distortion starting temperatures in TMA thermograms of GMT + TDI, GST + TDI, **3** and **7** are high considerably in comparison with GMT + XDI, GST + XDI, **4** and **8**. It can be estimated as the cross-linking difference by a steric effect between benzene group and benzyl group of polythiourethane made from polythiol with TDI and XDI.

Thermal resistance of ophthalmic lenses shows as order of  $\text{GMT} + \text{TDI} > \text{GST} + \text{TDI} > \text{GMT} + \text{XDI} > \text{GST} + \text{XDI} > \mathbf{3} > \mathbf{5} > \mathbf{7} > \mathbf{9} > \mathbf{6} > \mathbf{10} > \mathbf{4} > \mathbf{8}$  as shown in Figure 4, 5 and 6. They have a low thermal distortion temperature and thermal resistance of ophthalmic lens due to flexible long alkyl chains and low cross-linking density in comparison with GMT and GST as listed in Table 1. Thermal resistance and thermal distortion starting temperature of polythiol materials is in the order of  $\text{GMT} > \text{GST} > \text{GMST} > \text{GSTT}$ . Diisocyanates in ophthalmic lenses have an influence on thermal resistance as order of TDI > IPDI > XDI. The thermal properties of ophthalmic lenses were affected largely by not only thiol materials but also diisocyanate materials. In particular, ophthalmic lens made using TDI has the highest thermal resistance in comparison with XDI and IPDI as listed in Table 1. It may be affected by  $\pi$ - $\pi$  stacking for aromatic ring of TDI and its regular arrangements.

Impact strength of ophthalmic lenses made by thiol ma-

**Table 1.** Thermal distortion starting temperature of ophthalmic lenses prepared by thiol and diisocyanate materials as urethane materials.

Number	Thiol and diisocyanate materials	Refractive index (nd) at 20 °C	Thermal distortion starting temperature ( $T_s$ , °C)
No.1	GMT + TDI	1.6583	143.00
No.2	GMT + XDI	1.6582	95.86
No.3	GMT + IPDI	1.5838	116.10
No.4	GST + TDI	1.6589	122.65
No.5	GST + XDI	1.6589	76.19
No.6	GST + IPDI	1.5960	112.83
No.7	<b>3</b>	1.6591	86.39
No.8	<b>4</b>	1.6590	48.71
No.9	<b>5</b>	1.6585	83.32
No.10	<b>6</b>	1.6041	52.47
No.11	<b>7</b>	1.6586	68.92
No.12	<b>8</b>	1.6588	40.65
No.13	<b>9</b>	1.6581	67.67
No.14	<b>10</b>	1.5940	50.66

**Table 2.** Test of impact strength of ophthalmic lenses prepared by thiol and diisocyanate materials as urethane materials.

Number	Thiol and diisocyanate materials	Impact strength for optical lens thickness		
		1.20 mm	1.27 mm	2.34 mm
No.1	GMT + TDI	Fail	Fail	Fail
No.2	GMT + XDI	Fail	Fail	Fail
No.3	GMT + IPDI	Fail	Fail	Fail
No.4	GST + TDI	Fail	Fail	Fail
No.5	GST + XDI	Pass	Pass	Pass
No.6	GST + IPDI	Fail	Fail	Fail
No.7	<b>3</b>	Fail	Fail	Fail
No.8	<b>4</b>	Pass	Pass	Pass
No.9	<b>5</b>	Pass	Pass	Pass
No.10	<b>6</b>	Pass	Pass	Pass
No.11	<b>7</b>	Pass	Pass	Pass
No.12	<b>8</b>	Pass	Pass	Pass
No.13	<b>9</b>	Pass	Pass	Pass
No.14	<b>10</b>	Pass	Pass	Pass

terials showed as the order of **2 > 1 > GST > GMT** as listed in Table 2. Impact strength of non-coated ophthalmic lens made using thiol materials with XDI has passed the drop ball test of 95.1155 g from a height of 170 cm except GMT as shown in Table 2.

Impact strength of FDA for ophthalmic lens should be passed the drop ball test of 16 g from a height of 127 cm and it is to be remained an intact lens after drop ball test. Non-coated ophthalmic lenses made using GST, **1** and **2** have passed the drop ball test of 68 g from a height of 127 cm, but that made using GMT has not even passed the drop ball test of 32 g from a height of 127 cm. Even through ophthalmic lenses made using GMT and GST have a high thermal resistance, they have problems for impact strength. Here, if impact strength was increased, thermal resistance was decreased. It showed inversely between thermal resistance and impact strength each other.

Ophthalmic lenses of **5**, **6**, **9**, and **10** for improved methods using **1** and **2** as shown in Figure 6 have produced better ophthalmic lenses than those of **3**, **4**, **7** and **8**. In order to obtain excellent ophthalmic lenses via improved mixed ratios having excellent physical properties and optical properties, further studies for lens process test are being investigated.

In summary, novel thiol materials for plastic optical lens have been synthesized and their structures identified by EA, EI-MS, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. Their mechanisms have been studied via their synthetic route and polythiol materials in this work were only produced from polyalcohol compounds bearing 2-mercaptoethanol units. The thermal sta-

bility of thiol materials showed as the order of GMT < GST < **2 < 1** by TGA. Thermal resistance of ophthalmic lens showed as the order of GMT > GST > **1 > 2** by TMA data. Thermal resistance of ophthalmic lens was affected largely by not only thiol materials but also diisocyanates compounds. Diisocyanates have an influence on the thermal resistance as order of TDI > IPDI > XDI, while polythiol materials were shown as the order of GMT > GST > **1 > 2**. Impact strength of non-coated ophthalmic lenses made using thiol materials with XDI have passed the drop ball test of 95 g from the height of 170 cm except GMT. If the impact strength of lenses under the same conditions was increased, its thermal resistance was decreased. It contrasts thermal resistance with impact strength. Ophthalmic lenses **5** and **6** made by improved mixed ratios using **1** and **2** were prepared better ophthalmic lenses than **3** and **4**. In order to obtain excellent ophthalmic lenses, further studies for lens process are being investigated. It is possible of utility for the industrialization due to colorless, transparency and good physical and optical properties.

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