# Optical Material of High Refractive Index Resin Composed of Sulfur-Containing Aromatic Methacrylates

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**ABSTRACT:** A resin with a high refractive index and a high Abbe number can be produced by radical polymerization of a polymerizable monomer mixture composed of essentially sulfur-containing aromatic methacrylates. An optical material composed of said resin is provided especially for lenses. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 50–54, 2000

**Key words:** optical material; ophthalmic lens; aromatic thiomethacrylate; high refractive index

## INTRODUCTION

Materials used to produce optical materials such as lenses, prisms, optical waveguides, and disk substrates need to be colorless and transparent. Especially in the case of lenses for spectacles, transparent synthetic resins are extending their range of application as materials that replace inorganic optical materials because they are lightweight and excellent in impact resistance, processability, and dyeability. Various characteristics are required of transparent synthetic resins as optical materials. Of these the refractive index is quite important.[1–3] For example, transparent synthetic resins having a high refractive index when used as lenses can be rendered thinner than materials having a low refractive index to give the same focal distance. The use of thin lenses contributes to reducing the volume of space occupied by lenses in optical assemblies, which can advantageously make a small, lightweight optical apparatus. The Abbe number is also important for plastic lenses[1–3] and is described in the equation below:

$$\nu = \frac{n_D - 1}{n_F - n_C}$$

A larger Abbe number means lower dispersion (i.e., a smaller chromatic aberration). Generally speaking, however, a material having a high refractive index usually has a small Abbe number whereas sulfur-containing aromatic methacrylates (MAs) have high refractive indices and a large Abbe number.[4] We provide an optical material suitable for ophthalmic lenses by optimizing the monomer composition.

## EXPERIMENTAL

### Materials

#### *Preparation of Aromatic Thiomethacrylate*

S-*Benzyl Thiomethacrylate (SBzMA).* Dichloromethane (897 mL) 7.6 wt % aqueous sodium hydroxide (1799 g), and benzyl mercaptane (250 g) were put in a 5-L flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. Keeping the temperature below 10°C with an ice bath under stirring, 273.6 g of methacryloyl chloride was added dropwise for 40 min. Then the

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reaction mixture was stirred below 10°C for 75 min. The organic layer was separated from the water layer, washed with water, and dried with anhydrous sodium sulfate. The resulting organic layer was condensed by a rotary evaporator.

This reaction mixture was distilled *in vacuo* to obtain 344.6 g of SBzMA. Yield: 89.2%; 102°C/0.5 Torr; homopolymer: $n_D$, 1.625; $\nu$, 31.6.

S-*[2-(Phenylthio)ethyl]Thiomethacrylate.* Phenylthioethanethiol (68.1 g) 13 wt % aqueous sodium hydroxide (209 g), *p*-methoxyphenol (23.8 mg), and dichloromethane (90 mL) were put in a 500-mL flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. Keeping the temperature below 10°C with an ice bath under stirring, 54.4 g of methacryloyl chloride was added dropwise for 50 min. Then the reaction mixture was stirred below 10°C for 1 h. The organic layer was separated from the water, washed with 5 wt % of aqueous sodium hydroxide, then washed with water and dried with anhydrous sodium sulfate. The resulting organic layer was condensed by a rotary evaporator. This reaction mixture was distilled *in vacuo* to obtain 21.3 g of *S*-[2-(phenylthio)ethyl]thiomethacrylate. Yield: 44.7%, 123–126°C/0.06 Torr; $n_D$,[19] 1.5970; elemental analysis: obsd. for C, 60.39%; H, 5.90%; S, 27.04%; calcd. for C, 60.47%; H, 5.92%; S, 26.90%. NMR: $\delta$ (ppm) 1.94 s 3H, 3.10 m 4H, 5.57 s 1H, 6.07 s 1H, 7.14–7.41 m 5H. MS (*m/e*): 239 (M + 1). IR: 1660 cm$^{-1}$ ($\nu$, C═O). Homopolymer: $n_D$, 1.649; $\nu$, 27.8.

### Typical Preparation Method of Copolymerization

A mixture of 35 g of SBzMA, 15 g of ethylene glycol dimethacrylate (EGDMA), and 0.25 g of 2,2′-azobis(2,4-dimethylvaleronitrile) was cast into a mold consisting of two glass plates and a silicone rubber gasket maintained at 50°C for 6 h, 60°C for 16 h, and 90°C for 1 h. The resulting resin was colorless and transparent. The refractive index was 1.589 and the Abbe number was 38.

### Measurement

#### *Refractive Index and Abbe Number*

A small piece of a 1.5 mm thick sheetlike polymer obtained by cast polymerization was measured for a refractive index using an Abbe's refractometer, and an Abbe number was found from a dispersion table.

#### *Entire Light Transmittance*

A 1.5 mm thick sheetlike polymer obtained by cast polymerization was measured for an entire light transmittance by using a hazemeter in accordance with ASTM D1003-59.

#### *Heat Resistance*

A 1.5 mm thick sheetlike polymer obtained by cast polymerization was analyzed by a thermal mechanical analyzer in accordance with JIS K7196. The softening temperature at which a needle penetrates into the sheet was regarded as the heat resistance temperature of the sample polymer.

#### *Surface Hardness*

Surface hardness was evaluated by pencil hardness measured in accordance with JIS K5400: a 1.5 mm thick sheetlike polymer obtained by cast polymerization was scratched by a pencil at an angle of 45° to the sheet and 1 kg of weight was kept. The hardness of the pencil used was designated by JIS S6006 and classified from 9H, the hardest, to 8H, 7H, 6H, 5H, 4H, 3H, 2H, H, F, HB, B, 2B, 3B, 4B, 5B, and 6B, the softest. The hardest pencil that did not scratch the test piece was assigned as its hardness.

#### *Impact Resistance*

Impact resistance was evaluated in accordance with ASTM F659: a steel ball having a weight $W$ (g) was dropped on a lens having a center thickness $T_c$ (mm) from a height $H$ (cm), and an unbroken lens was measured as $W \times H/T_c$, the results of which was transformed into the impact energy (J).

## RESULTS AND DISCUSSION

The Lorenz–Lorentz equation is used for designing high refractive index plastic lenses. It shows the relationship between the refractive index and molecular structure.

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{[R_D]}{M} \cdot \rho = \frac{[R_D]}{V} \quad (1)$$

**Table I High Index Optical Material Composed of *S*-Benzyl Thiomethacrylate Copolymer**

| Monomer Composition (wt %) | Refractive Index | Abbe Number | Pencil Hardness | Heat Resistance (°C) | Impact Resistance (100 cm) |
|---|---|---|---|---|---|
| SBzMA/EGDMA/MAN/St | | | | | |
| 50/30/10/10 | 1.577 | 38.9 | 4H | 80.2 | Broken |
| SBzMA/EGDMA/AN/St | | | | | |
| 50/30/10/10 | 1.575 | 39.3 | 4H | 81.7 | Broken |
| BzMA/EGDMA/MAN/St | | | | | |
| 50/30/10/10 | 1.547 | 41.4 | 5H | 84.5 | Unbroken |

SBzMA, *S*-benzyl thiomethacrylate; EGDMA, ethylene glycol dimethacrylate; MAN, methacrylonitrile; AN, acrylonitrile; St, styrene; BzMA, benzyl methacrylate. The impact resistance was evaluated by the drop-ball test in accordance with ASTM F659: a 16.2-g steel ball was dropped from the height of 100 cm onto the polymer sheet sample, the thickness of which was 1.5 mm.

where $n_D$ is the refractive index, $M$ is the molecular weight, $\rho$ is the density, $V$ is the molecular volume, and $R_D$ is the molecular refraction.

Equation (1) is solved for $n_D$:

$$n_D = \sqrt{\frac{1 + 2[R_D]/V}{1 - [R_D]/V}} \tag{2}$$

Dispersion, which is also a significant optical property, is usually expressed by the Abbe number described as the following equation:

$$\nu_D = \frac{6n_D}{(n_D^2 + 2)(n_D + 1)} \cdot \frac{[R_D]}{\Delta R} \tag{3}$$

Although detailed discussions are given in the literature,[5–8] larger density, a larger molecular refraction, and a smaller molecular volume lead to a larger refractive index as seen from eqs. (1) and (2). For example, the aromatic ring, halogen atoms except fluorine, the sulfur atom, and heavy metal atoms are effective in increasing refractive indices. However, heavy metal atoms have the defects of large specific gravity, low solubility toward organic compounds, and coloring. Equation (3) shows that a larger refractive index makes the refractive index and Abbe number smaller. Therefore, there is an optimum point between Abbe number.

We looked into the sulfur atom and aromatic ring. We described the optical material using a sulfur-containing aromatic MA. The sulfur atom and aromatic ring can both contribute to the increase of the refractive index. From the viewpoint of thermosetting resins for an ophthalmic lens of high refractive index, we further investigated the sulfur-containing aromatic MA copolymer. In addition to the increase of the refractive index, the sulfur-containing aromatic MA can be a liquid monomer. Therefore, it can be purified by distillation and have a facile property of mixing or solving with other monomers. Among the aromatic thiomethacrylates, we chose SBzMA and examined its features in detail in the copolymerization for optical materials.

In order to make the optical material a thermosetting resin, we used a crosslinker like EGDMA. In addition, we used methacrylonitrile (MAN) or acrylonitrile (AN) as a soft monomer to make the optical material have a high impact resistance. The $e$ value of copolymerization is 0.36 for benzyl methacrylate (BzMA), 0.24 for EGDMA, and 0.81 for MAN. All of these values are positive and not so different. Therefore, these monomers are not good for copolymerization, resulting in incomplete or inhomogeneous polymerization. To avoid this, we used styrene that had an $e$ value of $-0.81$ to proceed with the copolymerization completely and homogeneously. This was also the case of SBzMA speculating from the $e$ and $Q$ values of *S*-methyl thiomethacrylate of 0.60 and 0.42, respectively, in comparison with those of methyl MA of 0.58 and 1.23, respectively. It seems to be better if styrene is put in the copolymerization components. The results are summarized in Table I.

When SBzMA was substituted for BzMA, the refractive index increased and the Abbe number decreased as we expected. However, the impact strength and the heat resistance worsened. We reported in a previous article[9] that the use of EGDMA made the polymer impact resistance de-

**Table II Effect of *S*-Benzyl Thiomethacrylate Compared with Benzyl Methacrylate in Optical Polymer Material**

| Monomer Composition (wt %) | Refractive Index | Abbe Number | Pencil Hardness | Heat Resistance (°C) | Impact Resistance | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 127 | 100 | 80 | *T* (mm) |
| SBzMA/4EG/MAN/St | | | | | | | | |
| 50/30/10/10 | 1.577 | 39.0 | 4H | 59.4 | × | × | ○ | 1.55 |
| 50/40/5/5 | 1.571 | 40.8 | 4H | 70.0 | ○ | — | — | 1.50 |
| BzMA/3EG/MAN/St | | | | | | | | |
| 50/30/10/10 | 1.549 | 40.6 | 4H | 63.7 | × | × | ○ | 1.65 |
| 50/40/5/5 | 1.544 | 42.2 | 4H | 77.2 | × | — | — | 1.40 |

SBzMA, *S*-benzyl thiomethacrylate; 4EG, tetraethylene glycol dimethacrylate; MAN, methacrylonitrile; AN, acrylonitrile; St, styrene; BzMA, benzyl methacrylate; 3EG, triethylene glycol dimethacrylate. The impact resistance was evaluated by the drop-ball test in accordance with ASTM F659: a 16.2-g steel ball was dropped from the height of 127, 100, and 80 cm onto the polymer sheet sample with thickness *T*. The test piece was (○) not broken or (×) broken.

crease because the carbon chain between its two double bonds was too short. Monomers such as tri- or tetraethylene GDMA (3EG or 4EG), which have a longer carbon chain between their two double bonds, exhibit good impact resistance. Therefore, we examined the copolymerization of SBzMA with 3EG or 4EG in comparison with BzMA. The results are summarized in Table II.

Although there was a little difference between 3EG and 4EG, the sulfur atom increased the refractive index, decreased the Abbe number a little, and worsened the heat resistance. The impact resistance might have been improved, but it is not clear from Table II. So we examined the impact resistance further by substituting MAN with AN in Table III.

As a result, the impact resistance was apparently improved. We found that some optical polymer materials cleared the FDA criteria of 127 cm, but the heat resistance and the surface hardness were deteriorated.

In order to increase the refractive index of the optical polymer further, more sulfur atoms should be introduced in the monomer molecule. The one example of such a monomer is *S*-[2-(phenylthio)ethyl]thiomethacrylate, the homopolymer of which has a refractive index of 1.649 and an Abbe number of 27.9. When using

**Table III Copolymerization of *S*-Benzyl Thiomethacrylate with Tri- or Tetraethylene Glycol Dimethacrylate in Optical Polymer Material**

| Monomer Composition (wt %) | Refractive Index | Abbe Number | Pencil Hardness | Heat Resistance (°C) | Impact Resistance | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 127 | 100 | 80 | *T* (mm) |
| SBzMA/4EG/AN/St | | | | | | | | |
| 65/25/5/5 | 1.588 | 37.7 | 2H | 48.3 | × | × | ○ | 1.65 |
| 55/25/10/10 | 1.581 | 38.3 | 4H | 54.0 | ○ | — | — | 1.50 |
| 50/30/10/10 | 1.575 | 39.4 | 2H | 59.0 | ○ | — | — | 1.65 |
| 50/40/5/5 | 1.570 | 41.0 | 4H | 54.0 | ○ | — | — | 1.50 |
| SBzMA/3EG/AN/St | | | | | | | | |
| 55/25/10/10 | 1.582 | 37.6 | 4H | 61.9 | × | × | ○ | 1.55 |
| 50/30/10/10 | 1.576 | 38.6 | 4H | 52.7 | × | × | ○ | 1.45 |
| 50/40/5/5 | 1.571 | 39.9 | 3H | 59.0 | ○ | ○ | × | 1.45 |

SBzMA, *S*-benzyl thiomethacrylate; 4EG, tetraethylene glycol dimethacrylate; AN, acrylonitrile; St, styrene; BzMA, benzyl methacrylate; 3EG, triethylene glycol dimethacrylate. The impact resistance was evaluated by the drop-ball test in accordance with ASTM F659: a 16.2-g steel ball was dropped from the height of 127, 100, and 80 cm onto the polymer sheet sample with thickness *T*. The test piece was (○) not broken or (×) broken.

**Table IV High Index Optical Material Composed of Copolymer**

| Monomer Composition (wt %) | Refractive Index | Abbe Number | Entire Light Transmittance (%) |
|---|---|---|---|
| SPTEMA/EGDMA | | | |
| 70/30 | 1.600 | 38.0 | 91 |

SPTEMA, *S*-[2-(phenylthio)ethyl]thiomethacrylate; EGDMA, ethylene glycol dimethacrylate.

EGDMA as a crosslinker, we obtained an optical polymer having a high refractive index as shown in Table IV.

## CONCLUSION

In order to enhance the high refractive index, we synthesized the MAs that have a molecular structure introduced at the same time with a sulfur atom having a high atomic refraction and an aromatic ring with a high molecular refraction. We showed as expected that the copolymers of those MAs can be promising candidates for high index optical materials. Above all, *S*-[2-(phenylthio)ethyl]thiomethacrylate showed the highest refractive index (1.649) of its homopolymer.

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