Optical Material of High Refractive Index Resin Composed of Sulfur-Containing Aliphatic and Alicyclic Methacrylates

TATSUHITO MATSUDA, YASUAKI FUNAE, MASAHIRO YOSHIDA, TETSUYA YAMAMOTO, TSUGUO TAKAYA

Materials and Functions Research Laboratory, Nippon Shokubai Co. Ltd., Suita, Osaka 564, Japan

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ABSTRACT: A resin having a high refractive index and a high Abbe number was produced by radical polymerization of a polymerizable monomer mixture composed of essentially sulfur-containing aliphatic methacrylates or alicyclic methacrylates. We provide an optical material composed of said resin, specifically, a lens. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 45–49, 2000

Key words: optical material; ophthalmic lens; aliphatic thiomethacrylate; sulfur-containing alicyclic methacrylate; high refractive index

INTRODUCTION

Materials used to produce optical members such as lenses, prisms, optical waveguides, and disc substrates, need to be colorless and transparent. Especially, in case of lenses for spectacles, transparent synthetic resins are extending the range of their application as materials that replace inorganic optical materials because they are lightweight and have excellent 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 an optical apparatus lightweight and small-sized. The Abbe number is also important for plastic lenses.[1–3] The Abbe number is described as an equation below:

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

A larger Abbe number means lower dispersion, that is, smaller chromatic aberation. Generally speaking, however, a material having a high refractive index usually has a small Abbe number. However, sulfur-containing alicyclic methacrylates are known to have high refractive indices and large Abbe numbers.[4] We found that aliphatic methacrylates also have high refractive indices and large Abbe numbers. We provide an optical material suitable for ophthalmic lenses by optimizing the monomer composition.

MATERIALS AND METHODS

Preparation of Aliphatic Thiomethacrylate

S-*Methyl Thiomethacrylate*

Five hundred milliliters of dichloromethane was put in a 2-L flask equipped with a stirrer, a thermometer, a cooler, and two dropping funnels. While the temperature was kept at 0°C with an ice bath under stirring, 111.8 g of methacryloyl chloride and 75 g of 15% sodium methylthiolate with 500 mL of water were simultaneously added

Correspondence to: T. Matsuda.

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dropwise for 90 min. Then the reaction mixture was stirred for 1 h at temperature below 10°C. The organic layer was separated from water and condensed by an evaporator. This reaction mixture was distilled *in vacuo* to obtain 106.2 g of *S*-methyl thiomethacrylate (yield 85.6%, 68–70°C/60 Torr).

Preparation of Alicyclic Methacrylates

2-(Tricyclo[5,2,1,$0^{2.6}$]-3-decenylthio)ethyl Methacrylate

One hundred grams of dicyclopentadiene was put in a 500-mL flask, equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. While the temperature was kept below 10°C under stirring, 59.1 g of 2-mercaptoethanol was added dropwise for 30 min; then the temperature was raised to 25°C, and the mixture was stirred for 2 h. Forty-five grams of this reaction product was transferred into a 500-mL flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. To this was added 200 mL of chloroform and 43.3 g of triethylamine. Keeping the temperature at 10 to 15°C under stirring, 38.0 g of methacryloyl chloride was dropped for 110 min, and then the mixture was stirred for 30 min. This reaction mixture was washed with water and diluted with aqueous hydrogen chloride, water, aqueous sodium carbonate, and water. After drying with anhydrous sodium sulfate, the organic layer was distilled to obtain 38.1 g of 2-(tricyclo[5,2,1,$0^{2.6}$]-3-decenylthio)ethyl methacrylate (DTEMA) (64.0% yield, 163–165°C/3 Torr). Elemental analysis: obsd. C 69.21%, H 7.94%, S 11.40%; calcd. C 69.03%, H 7.97%, S 11.52%. nmr: δ (ppm) 6.12 s, 5.67 m, 5.58 s, 5.52 m, 4.27 m, 2.8–3.1 br.m, 2.74 m, 2.1–2.7 br.m, 1.94 s, 1.7–1.9 br.m, 1.6 br.d, 1.0–1.2 br.q. MS m/e 278M^+. IR: 2850–3050 cm^{-1}, 1720 cm^{-1}.

2-(Tricyclo[5,2,1,$0^{2.6}$]-3,4-dibromodecylthio)ethyl Methacrylate

One hundred grams of dicyclopentadiene was put into a 500-mL flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. While the temperature was kept below 10°C under stirring, 59.1 g of 2-mercaptoethanol was added dropwise for 30 min, and then the temperature was raised to 25°C, and the mixture was stirred for 2 h. Forty-five grams of this reaction product and 350 mL of chloroform were transferred into a 500-mL flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. To this was added 68.4 g of bromine for 2 h at room temperature, and then the mixture was stirred for 1 h. The reaction mixture was poured into aqueous sodium sulfite. The chloroform layer was washed with aqueous sodium hydroxide and water and then dried with anhydrous magnesium sulfate. Then, the chloroform was removed. The residual reaction product was purified by silica gel column chromatography to obtain 65.0 g of 2-(tricyclo[5,2,1,$0^{2.6}$]-3,4-dibromodecylthio)ethyl bromide (yield 70.2%). Sixty-five grams of this reaction mixture, 18.6 g of potassium methacrylate, 400 mL of dimethylformamide, and 0.05 g of phenothiazine were put into a 500-mL flask equipped with a stirrer, a thermometer, a cooler, and a dropping funnel. The reaction proceeded at 10–15°C for 5 h, and then the reaction mixture was poured into water, extracted by 300 mL of ether three times. The ether layer was washed by water and then dried by anhydrous sodium sulfate. After ether was removed, residual reaction product was purified by silica gel chromatography to obtain 43.9 g of 2-(tricyclo[5,2,1,$0^{2.6}$]-3,4-dibromodecylthio)ethyl methacrylate (Br_2DTEMA) (yield 66.7%). B.P. 195–196°C/1.5–2.0 Torr. Elemental analysis: obsd. C 43.61%, H 5.20%, S 7.44%, Br 36.28%; calcd. C 43.86%, H 5.06%, S 7.31%, Br 36.47%.

A Typical Copolymerization

A mixture of 35 g of Br_2DTEMA, 15 g of ethylene glycol dimethacrylate, 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; the mixture was maintained at 50°C for 6 h at 60°C for 16 h and at 90°C for 1 h. The resulting resin was colorless and transparent. The properties are summarized in Table I.

Measurement

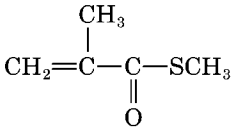
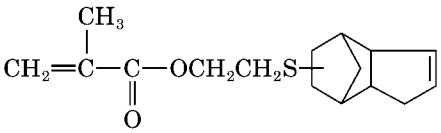
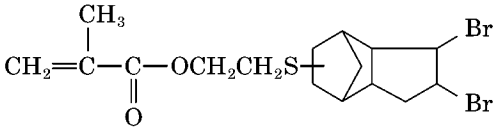
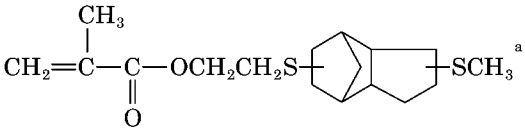
Refractive Index and Abbe Number

A small piece of a 1.5-mm-thick sheet-like 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 sheet-like polymer obtained by cast polymerization was measured for an entire

Table I Refractive Indices of Homopolymers of Sulfur-Containing Aliphatic and Alicyclic Methacrylate

Monomer	Refractive Index	Abbe Number	Entire Light Transmittance (%)
 (MTMA)	1.582	38.6	91
 (DTEMA)	1.557	47.4	91
 (Br_2DTEMA)	1.612	31.0	90
 [a]	1.580	50.0	90

[a] From ref. 4.

light transmittance by using a hazemeter in accordance with ASTM D1003-59.

RESULTS AND DISCUSSION

The Lorenz-Lorentz eq. (1), which shows the relationship between refractive index and molecular structure, is used to design high refractive index plastic lenses:

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{[R_D]}{M} \times \rho = \frac{[R_D]}{V} \tag{1}$$

where n_D is refractive index, M is molecular weight, ρ is density, V is molecular volume, and R_D is molecular refraction.

Equation (1) is solved on n_D:

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

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

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

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

We also looked into the sulfur atom. In this paper, we describe the optical material, using al-

Table II High Index Optical Material Composed of Aliphatic Sulfur-Containing Methacrylate Copolymer

Monomer Composition (wt %)	Refractive Index	Abbe Number	Entire Light Transmittance (%)
MTMA/EGDMA (70/30)	1.560	41.6	91
MTMA/Br_4BMEPP (70/30)	1.586	36.6	90
MTMA/St/EGDMA (60/20/20)	1.569	40.0	90
MTMA/BMTE (70/30)	1.590	36.0	91

MTMA, *S*-methylthio methacrylate; EGDMA, ethylene glycol dimethacrylate; Br_4BMEPP, 2,2-bis(3,5-dibromo-4-methacryloyloxyethoxyphenyl)propane; St, styrene; BMTE, 1,2-bis(methacryloylthio)ethane.

iphatic and alicyclic sulfur containing methacrylate. These compounds have the merit to take a wide variety in synthesis. Cawley et al.[4] reported that thermoplastic resins of alicyclic sulfur containing methtacrylate can be used for lens by injection-molding process. From the view point of thermosetting resins for ophthalmic lens of high refractive index, we investigated further the sulfur containing aliphatic and alicyclic methacrylate copolymers.

Poly(methylmethacrylate) (PMMA) is a thermoplastic suitable for plastic lens by injection molding because of its transparency and weatherability. However, the refractive index of PMMA is 1.49, which is low for ophthalmic lens, whereas, poly-*S*-methyl thiomethacrylate (MTMA), which has an analogous structure of PMMA has a high refractive index of 1.582 by the effect of sulfur atom and also has a high Abbe number of 38.6. Ophthalmic lenses, in general, require a high Abbe number of more than 30. The polymer of DTEMA, which has both an alicyclic condensed ring and a sulfur atom, has the refractive index of 1.557 and the Abbe number of 47.4. The refractive index is lower than MTMA, but the Abbe number is much higher. The polymer of bromine adduct of DTEMA has very high refractive index of 1.612 but has a low Abbe number of 31.0, whereas the polymer of methyl mercaptane adduct of DTEMA has a high refractive index and a high Abbe number of 1.580 and 58.0, respectively.[4] These data are summarized in Table I.

Referring to Table I, we designed thermosetting resins for ophthalmic lenses. First, we used *S*-methyl thiomethacrylate as a main monomer and some dimethacrylates as a crosslinker. In the case of ethylene glycol dimethacrylate with or without styrene, we obtained lens material, the refractive index of which is 1.560–1.569 and the Abbe number of which is 41.6 to 41.0. By using bromine containing dimethacrylate or sulfur containing bifunctional thiomethacrylate instead of ethylene glycol dimethacrylate, the refractive index of the polymer increased to 1.586–1.590, but the Abbe number decreased to 36.6–36.0 (Table II). Second, we used condensed alicyclic sulfur containing methacrylate as a main monomer instead of *S*-methyl thiomethacrylate. When DTEMA and Br_2DTEMA were used in combination with ethylene glycol dimethacrylate or 1,2-bis(methacrylyol-

Table III High Index Optical Material Composed of Alicyclic Sulfur-Containing Methacrylate Copolymer

Monomer Composition (wt %)	Refractive Index	Abbe Number	Entire Light Transmittance (%)
DTEMA/BMTE (70/30)	1.573	43.4	91
Br_2DTEMA/EGDMA (70/30)	1.580	37.7	91
Br_2DTEMA/St/EGDMA (60/20/20)	1.587	35.4	90
Br_2DTEMA/BzMA/EGDMA (60/20/20)	1.582	36.6	91
Br_2DTEMA/Br_4BMEPP (80/20)	1.608	30.4	90

DTEMA, 2-(tricyclo[5,2,1,$0^{2.6}$]-3-decenylthio)ethyl methacrylate; Br_2DTEMA, 2-(tricyclo[5,2,1,$0^{2.6}$]-3,4-dibromodecylthio)ethyl methacrylate; EGDMA, ethylene glycol dimethacrylate; Br_4BMEPP, 2,2-bis(3,5-dibromo-4-methacryloyloxyethoxyphenyl)propane; St, styrene; BMTE, 1,2-bis(methacryloylthio)ethane; BzMA, benzyl methacrylate.

thio)ethane, we obtained lens material the refractive index of which is 1.573–1.587 and the Abbe number of which is 35.4–43.4. Condensed alicyclic sulfur-containing methacrylates are superior to *S*-methyl thiomethacrylate as a main monomer for an optical material. They have a good balance between the refractive index and the Abbe number. When Br_2DTEMA was used in combination with the dimethacrylate, which contains tetrabromo bisphenol A, we did obtain the resin having very high refractive index, 1.608, although the Abbe number was greatly decreased to 30.4 (Table III). Too many bromine atoms may make the material heavy and might lead to a bad weatherability.

For practical lens material, other performances are required such as impact resistance, heat resistance, durability, and so on as well as refractive index, Abbe number, and entire light transmittance. We think, however, that the condensed alicyclic sulfur-containing methacrylate is able to be a promising main monomer for a high refractive index lens material.

REFERENCES

1. Otsuka, Y. Polymer Digest 1986, 1986(3), 2.
2. Otsuka, Y. Kobunshi 1984, 33(3), 266.
3. Ide, F. Plastic Age 1989, 35(4), 152.
4. Cawley, J. D.; Faber, J. W. H. U.S. Pat. 3,799,972, 1974.
5. Otsuka, Y. Kobunshi 1978, 27(2), 90.
6. Brandrup, J.; Immergut, E. H., Eds. Polymer Handbook, 2nd ed.; Wiley: New York, 1979; Vol. 3, p 241.
7. Miwa, S. Polymer Digest 1984, 1984(3), 31.
8. Endo, T.; Yoshida, H., Ed. Manufacture and Application of Plastic Lens; CMC: 1989; p 3.