

Ophthalmic Lens Material Prepared by Unsaturated Nitrile–Polyfunctional Methacrylate–Styrenic Monomer Copolymerization

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ABSTRACT: A resin having excellent ophthalmic lens performance was produced by radical polymerization of a mixture of bifunctional methacrylate, such as tetraethylene glycol dimethacrylate or triethylene glycol dimethacrylate, a styrenic monomer such as styrene or α -methylstyrene, and acrylonitrile. We provide a totally balanced resin composition suitable for an ophthalmic lens, having a high refractive index, large Abbe number, high impact strength, low specific gravity, heat resistance, cutting processability, tintability, and durability. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1227–1235, 1998

Key words: ophthalmic lens; impact resistance; heat resistance; methacrylate copolymer; cast polymerization

INTRODUCTION

Optical materials such as lenses for spectacles need to be colorless and transparent. Transparent synthetic resins are extending their range of application as materials for lenses 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 ophthalmic lenses. Of these, the refractive index is quite important. For example, transparent synthetic resins having a high refractive index can be rendered thinner than can materials having a low refractive index to give the same focal distance and can advantageously make lightweight lenses. Impact resistance is also important and advantageous for plastic lenses compared with brittle glass materials.

A diethylene glycol bis(allyl carbonate) resin, a poly(methyl methacrylate) resin, and a polycarbonate resin have been generally known, to date,

as resins used in plastic lenses. However, the diethylene glycol bis(allyl carbonate) and poly(methyl methacrylate) resins have low refractive indices of 1.49–1.50.^{1,2} When these resins are therefore shaped into plastic lenses, a center thickness, an edge thickness, and curvatures of the lenses become great compared with those of inorganic optical glass lenses. The polycarbonate resin has a high refractive index of 1.58–1.59,^{3,4} but is prone to birefringence in shaping and, thus, is defective in optical homogeneity.

Moreover, because the poly(methyl methacrylate) and polycarbonate resins are thermoplastic resins of noncrosslinked structures, they fuse in processing such as in cutting or grinding. They have not been satisfactory as materials in the field in which such processings are required, for example, as materials for lenses in precision optical machinery, optical elements, or ophthalmic lenses.

To remedy the above drawbacks of the thermoplastic resins, a method has been so far known which produces resins having a crosslinked structure using ethylene glycol dimethacrylate as a crosslinking agent.⁵ The resin obtained by using ethylene glycol dimethacrylate is, however, poor in impact resistance.

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Sakamoto et al. disclosed an example using halogenated styrene derivatives having a high refractive index.⁶ It has, nevertheless, drawbacks in that the specific gravity of the optical material is high and the light resistance is poor.

From the viewpoint of transparency, a wide variety of monomers, and economic availability, we focused on the (meth)acrylate–styrenic copolymer and made efforts to produce excellent optical materials. In our previous work, we found that acrylonitrile–styrene–polyfunctional methacrylate exhibits an excellent performance suitable for optical materials.⁷ We provide in this article an ophthalmic lens material having a high refractive index, excellent heat resistance, excellent impact strength, and low specific gravity.

EXPERIMENTAL

Materials

All monomers and initiators in this article were purchased from Tokyo Chemical Ind. Co., Ltd. (Tokyo, Japan) and Kyoisha Chemical Co. (Osaka, Japan) and used without further purification.

Copolymerization

A mixture of 50 g of tetraethylene glycol dimethacrylate, 40 g of styrene, 10 g of acrylonitrile, 0.1 g of 2,2'-azobis(2,4-dimethylvaleronitrile), and 0.1 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole was cast into a mold consisting of two glass plates and a silicone rubber gasket, maintained at 50°C for 6 h, and then heated to 110°C for 16 h to conduct polymerization. The substance was further maintained at 110°C for 2 h to conduct postpolymerization. The resulting resin was a colorless and transparent sheet, the thickness of which was 1.5 mm.

Typical Preparative Method of Lens

To a mixture of 36 g of tetraethylene glycol dimethacrylate, 9 g of 1,3-butanediol dimethacrylate, 46 g of styrene, 9 g of acrylonitrile, 0.1 g of 2-(2-hydroxy-5-methylphenyl)benzotriazole, and 0.1 g of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine were added 0.2 g of lauroyl peroxide and 0.3 g of *tert*-butyl peroxy-2-ethylhexanoate. The resulting mixture was cast into a space produced by a glass mold having an inner diameter of 78

mm and designed to give a lens having a diopter of -3.00 D and a silicone rubber gasket.

The content was maintained in a constant temperature vessel at 50°C for 4 h, then gradually heated to 120°C for 15 h, and further maintained at 120°C for 30 min to conduct cast polymerization. Subsequently, the glass mold and the gasket were removed from the polymerized product to afford a lens having a diameter of 75 mm and a diopter of -3.00 D. The optical surface condition of the lens was good.

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. The measurement was conducted at 25°C and 60% RH atmosphere.

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.

Cutting Processability

A 1.5-mm-thick sheetlike polymer obtained by cast polymerization was cut by a diamond cutter, and defects such as crack, fissure, and fusion of the cut surface that occurred at that time were observed. In Table I, circle (○) indicates that no defects were observed, a triangle (△), that small defects were observed; and a cross (×), that many or large defects were observed.

Heat Resistance

A 1.5-mm-thick sheetlike polymer obtained by cast polymerization was analyzed by a thermal mechanical analyzer (TMA) in accordance with JIS K7196. The softening temperature at which a needle began to penetrate 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, namely, a 1.5-mm-thick sheetlike polymer obtained by cast polymerization was scratched by a

Table I Properties of Homopolymer of Crosslinking Monomer

Crosslinking Monomer	Refractive Index	Impact Resistance (cm)			Heat Resistance (°C)	Cutting Processability
		127	100	80		
2EG	1.5077	×	—	×	244.2	× ~ △
3EG	1.5081	×	×	○	228.0	△
4EG	1.5063	○	—	—	223.2	△ ~ ○

Thickness of the sample sheets: 1.85 mm/2EG, 1.70 mm/3EG, 1.80 mm/4EG. Cutting processability: ×, bad, △, not so good; ○, good.

pencil with an angle of 45° to the sheet and 1 kg of weight kept. The hardness of the pencils used are designated by JIS S6006 and classified from 9H, hardest, to 8H, 7H, 6H, 5H, 4H, 3H, 2H, H, F, HB, B, 2B, 3B, 4B, 5B, and 6B, 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, namely, a steel ball having a weight of W (g) was dropped on a lens having a center thickness of T_c (mm) from a height of H (cm) and an unbroken lens was measured as W (g) $\times H$ (cm)/ T_c (mm), the results of which were transformed into the impact energy (J).

Tintability

A lens was dipped into hot water (above 85°C) containing a dispersed dye (for instance, dispersed brown) and a carrier for 10 min, and the features of the dyed lens were observed. A lens tinted homogeneously and densely was evaluated as excellent.

Durability

Durability was evaluated by a weathering test using a fade tester. After irradiation of a xenon arc for 250 h, the yellowness index was measured. A value below 2 was regarded as excellent durability.

RESULTS AND DISCUSSION

Effect of Crosslinker on Polymer Properties

Bifunctional methacrylate such as ethylene glycol dimethacrylate (1EG) was already examined as a crosslinker in our previous work.⁷ However, the resin using 1EG as a crosslinker showed poor impact resistance because of its too short crosslinking distance. Unlike 1EG, di(ethylene glycol)-dimethacrylate (2EG), tri(ethylene glycol)dimethacrylate (3EG), and tetra(ethylene glycol)dimethacrylate (4EG), which have a longer chain between two double bonds, are expected to have a higher impact resistance than has 1EG because of the increase of flexibility. The homopolymers of 2EG, 3EG, and 4EG were examined. The results are summarized in Table I.

Table II Totally Balanced Lens Materials by Use of 3EG and 4EG

Properties	Monomer Composition (wt %)		
	4EG/St/AN 40/50/10	3EG/St/AN 40/50/10	ADC 100
Refractive index	1.549	1.550	1.504
Abbe number	42.4	38.2	58.0
Light transmittance (%)	91.6	91.7	92.0
Yellow index	1.41	1.39	1.44
Specific gravity	1.13	1.14	1.32
Surface hardness	2H	3H	4H
Impact strength ^a	50 g \times 90 cm 0.44 J	16.2 g \times 110 cm 0.175 J	16.2 g \times 150 cm 0.24 J
Heat resistance (°C)	98	96	99

^a Center thickness of each lens tested was 1.5 mm.

Table III Detailed Investigation of Monomer Composition

Monomer Composition (wt %)	Refractive Index	Abbe Number	Specific Gravity	Surface Hardness	Heat Resistance (°C)	Impact Strength	
						g × cm	J
Basic composition							
4EG/St/AN = 40/50/10	1.549	42.4	1.13	4H	99	95 × 120	1.17
Reduction of AN							
4EG/St = 50/50	1.553	39.5	1.14	3H	95	50 × 100	0.49
4EG/St = 40/60	1.563	36.5	1.13	2H	95	50 × 110	0.54
4EG/St/AN = 40/55/5	1.555	37.8	1.13	2H	94	50 × 110	0.54
Substitution of AN							
4EG/St/9EG = 40/50/10	1.553	40.9	1.14	4H	98	95 × 100	0.93
4EG/St/14EG = 40/50/10	1.553	37.6	1.14	4H	93	95 × 127	1.18
Incorporation of HD							
HD/St/AN = 40/50/10	1.550	38.3	1.11	4H	115	16 × 127	0.20
4EG/St/HD = 40/50/10	1.552	40.8	1.14	4H	115	16 × 110	0.17
Incorporation of 9PG							
9PG/St/AN = 40/50/10	1.540	39.7	1.11	2H	57	225 × 120	2.65
4EG/St/9PG = 40/50/10	1.550	41.3	1.13	2H	64	50 × 120	0.59
Incorporation of allyl monomer							
4EG/St/AN/DAP = 40/50/5/5	1.555	36.4	1.13	2H	79	95 × 80	0.74
4EG/St/AN/DAP = 40/45/10/							
5	1.548	40.4	1.14	2H	70	95 × 80	0.74
4EG/St/DAP = 40/50/10	1.558	36.8	1.14	H	66	95 × 127	1.18
4EG/St/AN/ADC = 40/50/5/5	1.552	42.1	1.14	2H	69	50 × 120	0.59
4EG/St/AN/ADC = 40/45/10/							
5	1.547	41.9	1.14	2H	69	225 × 90	1.98
4EG/St/ADC = 40/50/10	1.551	40.6	1.14	H	59	50 × 90	0.44

9EG, nona(ethylene glycol) dimethacrylate; 14EG, tetradeca(ethylene glycol) dimethacrylate; HD, 1,6-hexanediol dimethacrylate; 9PG, nona(propylene glycol) dimethacrylate; ADC, di(ethylene glycol) dimethacrylate.

The refractive indices were not practically different. As the chain length between two double bonds became longer, the heat resistance became

lower. This result does not necessarily coincide with the glass transition temperature measured by Bowman et al.⁸ However, the longer the chain

Table IV Effect of Various Alkylene Glycol Dimethacrylate on Heat Resistance

Dimethacrylate	Content (wt %) ^a	Heat Resistance (°C)
1,6-Hexanediol dimethacrylate	10	101.7
Neopentylglycol dimethacrylate	10	103.9
Trimethylolpropane trimethacrylate	5	103.5
	10	119.0
	15	118.4
1,3-Butanediol dimethacrylate	5	114.0
	10	114.5
	15	113.6
Ethylene glycol dimethacrylate	5	118.5
	10	122.5

Base monomer composition; 4EG/St/AN = 40/50/10.

^a The content of dimethacrylate was designated by the ratio of addition amount to 100 parts by weight of base monomer composition.

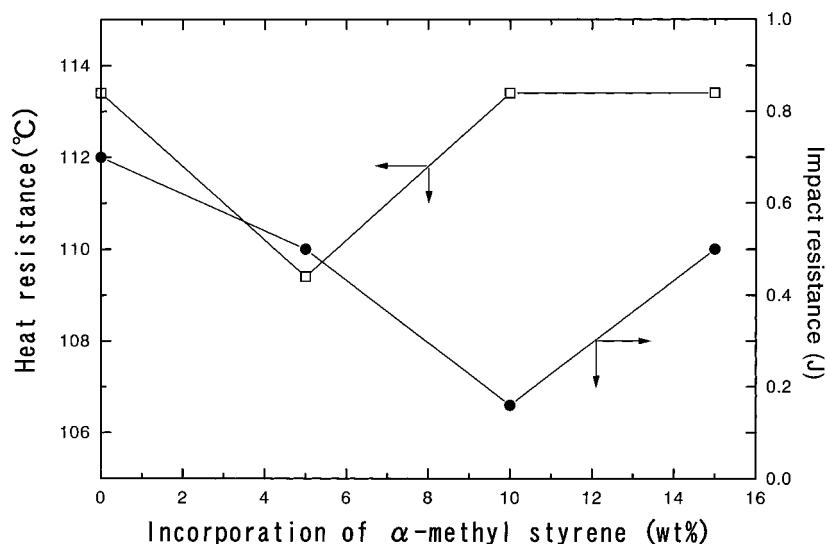


Figure 1 Heat resistance and impact resistance to α -St incorporation on the basis of 10 wt % of 1,3-BG.

length between the two double bonds, the better the impact resistance and cutting processability became. Moreover, the volume shrinkage during polymerization should be reduced by using longer-chain dimethacrylate.⁸ From this knowledge, we designed a totally balanced lens materials by using 3EG and 4EG as crosslinkers as shown in Table II. Kodama and Ide reported that the impact resistance was strongest at 10 mol % of 4EG in the 4EG and MMA copolymer.⁹ We found that a new composition in a higher content of longer-chain dimethacrylate could give a quite large impact resistance. In a bulk polymerization of the

dimethacrylates, unpolymerized vinyl groups were left as pendant double bonds.¹⁰ The residual pendant double bonds may play a role in exhibiting high impact resistance when a large amount of 3EG or 4EG was copolymerized. Residual pendant double bonds act as a plasticizer like a long aliphatic alkyl pendant to soften the polymer.

Optimization for Ophthalmic Lenses

Based on a tetra(ethylene glycol)dimethacrylate-styrene-acrylonitrile copolymer which is

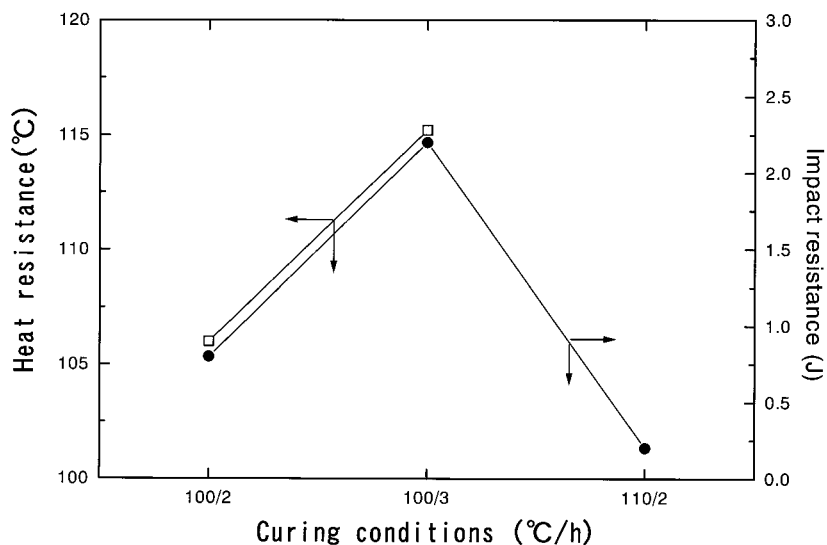


Figure 2 Heat resistance and impact resistance in some curing conditions on the basis of 10 wt % of 1,3-BG and 10 wt % of α -St.

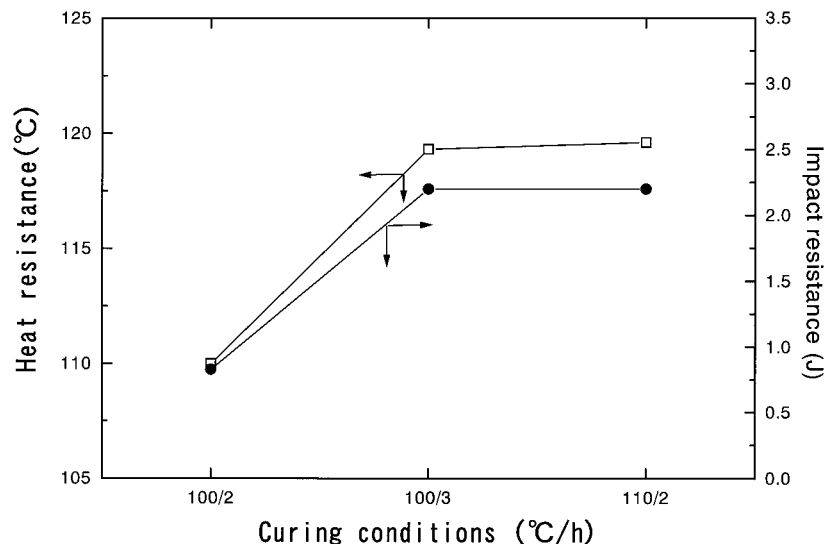


Figure 3 Heat resistance and impact resistance in some curing conditions on the basis of 10 wt % of 1,3-BG and 15 wt % of α -St.

believed to be a totally balanced lens material as described above, we optimized the monomer composition in detail for an ophthalmic lens. Although acrylonitrile (AN) is a good monomer to give the polymer excellent impact strength, it has a relatively low boiling point and is toxic. Therefore, it is preferable to reduce the amount of AN or substituted AN with another monomer. From this point of view, some attempts were made as summarized in Table III. When AN was reduced by half or was not used and styrene was increased, the refractive index slightly increased but impact

strength, surface hardness, and heat resistance slightly decreased. When 1,6-hexanediol dimethacrylate (HD) was used for the substitution of AN or 4EG, the heat resistance was greatly improved but impact strength was largely weakened. When AN was substituted by nona(ethylene glycol)dimethacrylate (9EG) or tetradeca(ethylene glycol)-dimethacrylate (14EG), the total balance of the polymer obtained was similar to that of the basic composition.

When 4EG was substituted by nona(propylene glycol)dimethacrylate (9PG), the impact strength

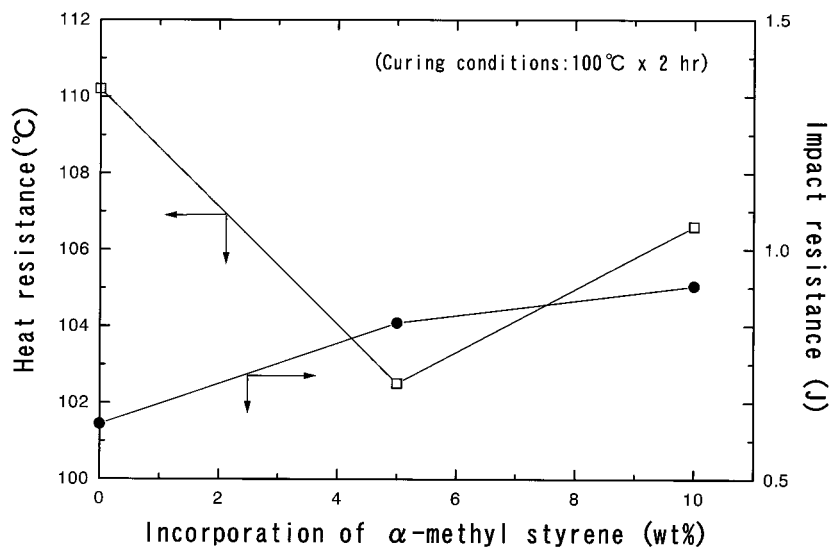


Figure 4 Heat resistance and impact resistance to α -St incorporation on the basis of 10 wt % of 1EG.

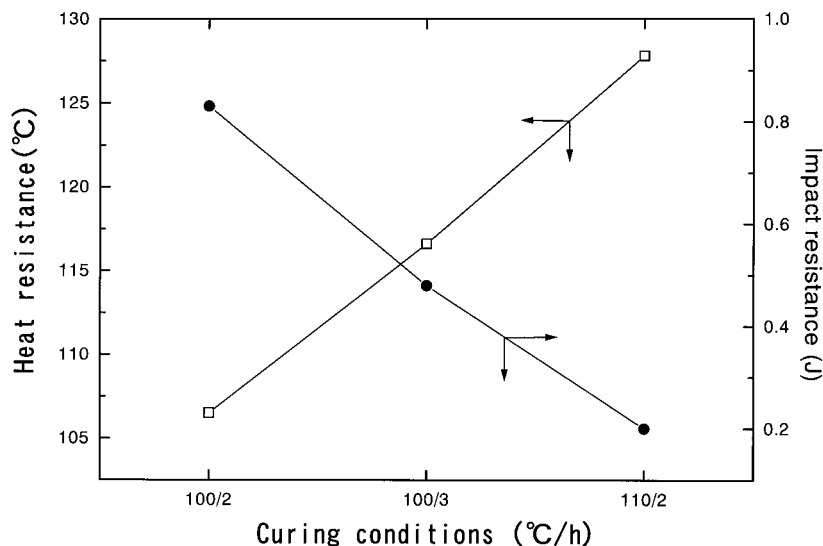


Figure 5 Heat resistance and impact resistance in some curing conditions on the basis of 10 wt % of 1EG and 10 wt % of α -St.

was greatly improved but heat resistance was badly decreased. When AN was substituted by 9PG, both impact strength and heat resistance were badly decreased.

When an allyl monomer such as diallyl phthalate (DAP) or di(ethylene glycol) bis(allylcarbonate) (ADC) was used together with or substituted by AN, heat resistance and surface hardness badly decreased. In the case of DAP, haze was also observed.

We confirmed that the basic composition was totally balanced except for heat resistance compared to ADC, which is now widely used for ophthalmic lens material. Heat resistance and impact

resistance are, in general, incompatible with each other. We have to search for a monomer which improves the heat resistance so as not to decrease the impact strength by any means. We have seen that HD increases the heat resistance as shown in Table III. We added some analogies to the basic composition and examined the effect on heat resistance (Table IV). From Table IV, trimethylolpropane trimethacrylate (TMPTM), 1,3-butanediol dimethacrylate (1,3-BG), and 1EG were found to be more effective than was HD. Besides the additional crosslinking monomer, we used α -methylstyrene (α -St), because incorporation of α -St makes the polymerization reaction easy to be con-

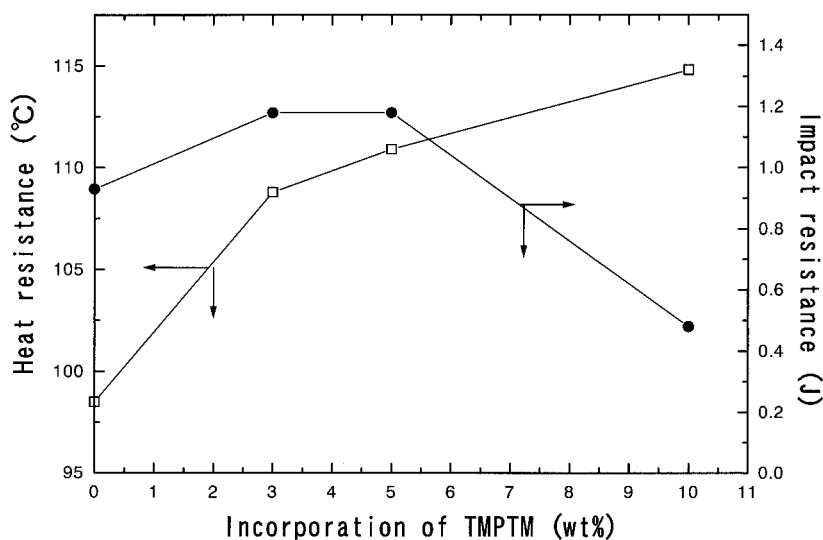


Figure 6 Heat resistance and impact resistance to the incorporation of TMPTM.

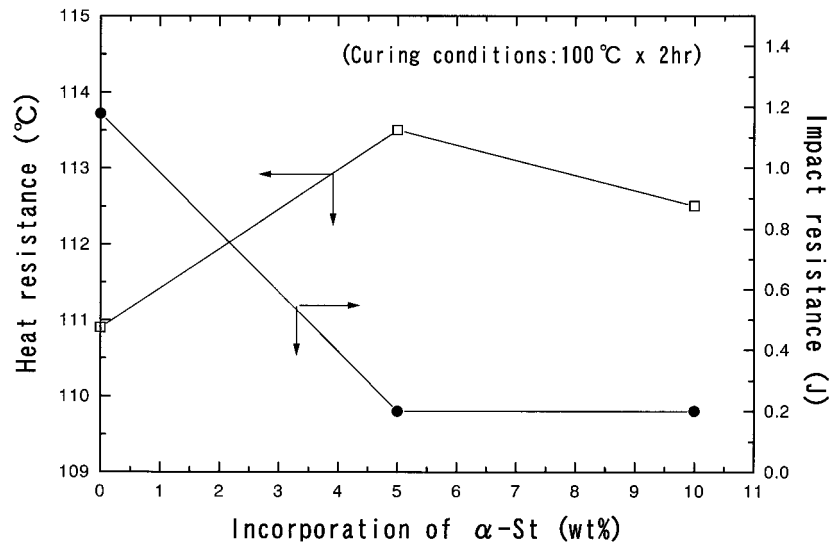


Figure 7 Heat resistance and impact resistance to α -St incorporation on the basis of 5 wt % of TMPTM.

trolled and increases the casting yield without decreasing heat resistance. Lenses must be durable during the hard-coating process which is mostly conducted at 100–120°C. Investigation was carried out in some combinations with the amount of crosslinker, α -St, and heat resistance and impact resistance. The results are summarized in Figures 1–7. In the case of 10 wt % incorporation of 1,3-BG, 10–15 wt % incorporation of α -St gave good impact resistance. (Fig. 1) From the viewpoint of the curing conditions, a longer period and

higher temperature is good for both heat resistance and impact resistance in the case of 10 wt % of 1,3-BG and 15 wt % of α -St. (Figs. 2 and 3). In the case of 10 wt % incorporation of 1EG, the impact resistance was not so different from the incorporation of α -St (Fig. 4). Both heat resistance and impact resistance depended on the curing conditions (Fig. 5) Five weight percent of TMPTM seemed to be the best balanced from the results of heat resistance and impact resistance (Fig. 6). Incorporation of α -St together with 5 wt

Table V Final Composition and Properties of Most Preferable Material for Lens

Monomer Composition	4EG/AN/St/ α – St/1,3-BG 40/10/35/15/10
Optical properties	
Refractive index	1.547
Abbe number	40
Light transmission (%)	91
Yellow index	Below 2.0
Physical properties	
Specific gravity	1.13
Impact strength (g \times cm/mm thick)	225 \times 100/1.3
(J)	2.21
Surface hardness	3H
Heat resistance (°C)	117
Processability	
Cutting & grinding	Excellent
Tintability	Excellent
Durability	
Weathering test	Excellent

% incorporation of TMPTM remarkably worsened the impact resistance (Fig. 7).

CONCLUSIONS

After consideration of the above discussion, we finally provide the best composition for ophthalmic lenses. We chose 4-EG and 1,3-BG as the crosslinking monomers, styrene and α -St as high index monomers, and AN as a soft monomer. The resulting polymer had excellent impact resistance (2.21 J/1.3 mm) and good heat resistance (117°C), a high refractive index (1.547), high Abbe number (40), very low specific gravity (1.13), excellent processability, tintability, and durability as shown in Table V. In addition, this material is believed to be economical and practical for ophthalmic lenses.

REFERENCES

1. J. Brandrup and E. H. Immergut, Ed., *Polymer Handbook*, 3rd ed., Vol. 6, Wiley, New York, 1989, p. 451.
2. Y. Otsuka, *Kobunshi*, **27**(2), 90 (1978).
3. F. Ide, *Plastics Age*, **33**(10), 115 (1987).
4. F. Ide, *Plastics Age*, **35**(4), 152 (1989).
5. K. Araki, *Jpn. Tokkyo Koho* 49-64691.
6. S. Sakamoto, T. Fukuda, and M. Saito, *Jpn. Tokkyo Koho* 62-34102.
7. T. Matsuda, Y. Funae, M. Yoshida, T. Yamamoto, and T. Takaya, *J. Appl. Polym. Sci.*, **65**, 2247 (1997).
8. C. N. Bowman, A. L. Carver, S. N. Kennet, M. M. Williams, and N. A. Peppas, *Polymer*, **31**, 35 (1990).
9. T. Kodama and F. Ide, *Kobunshi Kagaku*, **27**, 65 (1970).
10. Y. Mizukami, *Kyushu Shikaishi*, **40**, 807 (1986).