

Optical Material Having High Refractive Index, Low Specific Gravity, and Excellent Impact Resistance Prepared by Unsaturated Nitrile–Polyfunctional Methacrylate–Styrenic Monomer Copolymerization

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Received 18 November 1996; accepted 16 February 1997

ABSTRACT: A resin having a low specific gravity, an excellent impact resistance, and a high refractive index was produced by radical polymerization of a mixture of difunctional methacrylate, such as tetraethylene glycol dimethacrylate or triethylene glycol dimethacrylate, styrenic monomer such as styrene or α -methyl styrene, and acrylonitrile. We provide a totally balanced optical material composed of the said resin, especially a lens. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2247–2255, 1997

Key words: optical material; lens; methacrylate copolymer; high refractive index; impact resistance

INTRODUCTION

Materials used in 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 a range of their 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. For example, transparent synthetic resins having a high refractive index, when used as lenses, can be rendered thinner than can materials having a low refractive index to give the same focal distance. The use of thin lenses contributes to reducing the volume of the space occupied by lenses in optical assemblies, which can advantageously

make an optical apparatus lightweight and small-sized. Impact resistance is also important and advantageous for plastic lenses compared with brittle glass materials. It is, moreover, advisable that an impact resistance is higher to obtain more durable optical 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, defective in optical homogeneity. Moreover, because the poly(methyl methacrylate) and polycarbonate resins are thermoplastic resins of non-crosslinked structures, they fuse in processing such as in cutting or grinding. They have not been satisfactory as materials in the field in which such

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processings are required, e.g., 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.

Sakamoto et al. disclosed an example using 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)acryl-styrenic copolymer and made efforts to produce excellent optical materials. As a result, we provide in this article an optical material having a high refractive index, excellent heat resistance, excellent impact strength, and low specific gravity.

EXPERIMENTAL

Materials

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.

Polymerization of Diethylene Glycol Bis(allylcarbonate)

A mixture of 100 g of diethylene glycol bis(allylcarbonate) and 2.5 g of diisopropyl peroxydicarbonate was cast into a mold consisting of two glass plates and a silicone rubber gasket and was polymerized at 40°C for 1 h, at 45°C for 1 h, at 50°C for 1 h, at 60°C for 16 h, at 90°C for 2 h, and then at 110°C for 2 h. The resulting resin was a colorless and transparent sheet.

Polymerization of Methyl Methacrylate

A mixture of 100 g of methyl methacrylate and 0.5 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was cast into a mold consisting of two glass plates and a silicone rubber gasket and was polymerized at 50°C for 6 h, at 60°C for 16 h, and then at 90°C for 2 h. The resulting resin was a colorless and transparent sheet.

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 75 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.

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

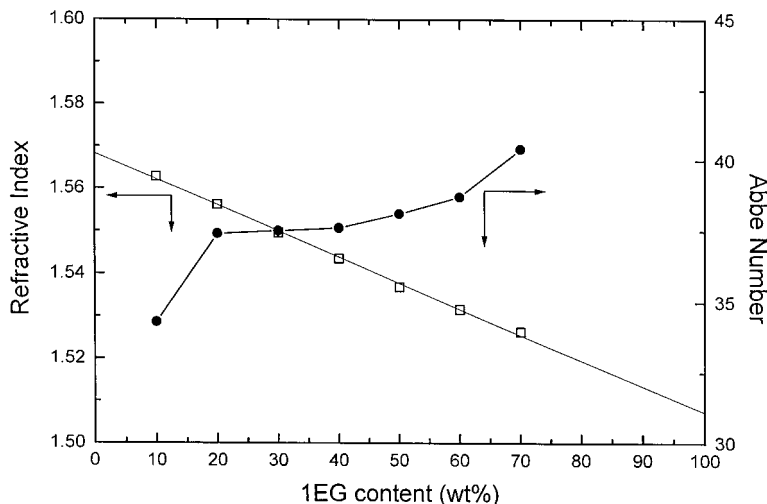


Figure 1 Optical properties as a function of crosslinking monomer wt %.

the cut surface that occurred at that time 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 penetrated 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 pencil with an angle of 45° to the sheet and 1 kg of weight kept. The hardness of the pencil used is 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,

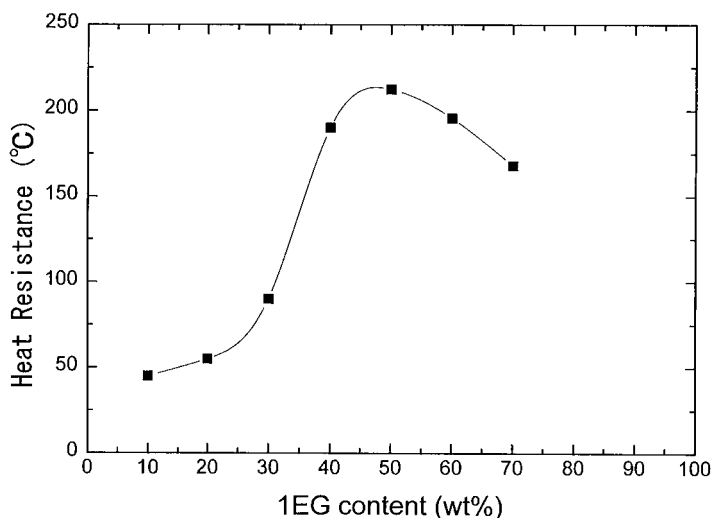


Figure 2 Heat resistance as a function of crosslinking monomer wt %.

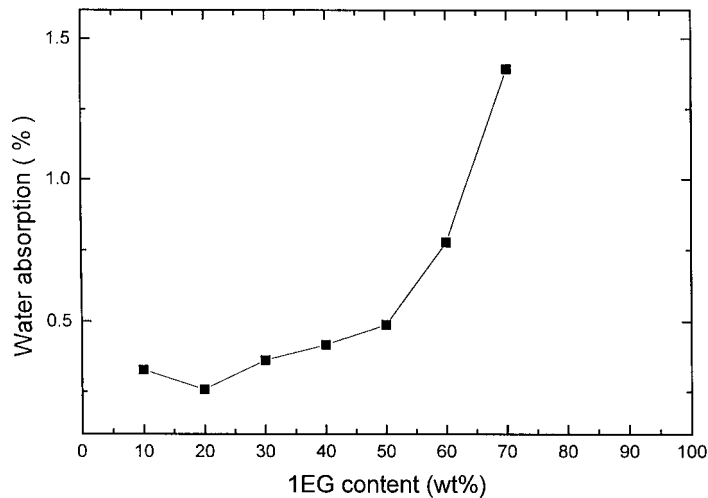


Figure 3 Water absorption as a function of crosslinking monomer wt %.

and an unbroken lens was measured as $W(g) \times H(cm)/Tc(mm)$, the results of which were transformed into the impact energy (J).

Tintability

A lens was dipped in hot water (higher than 85°C) containing a dispersed dye (for instance, dispersed brown) and a carrier for 10 min, and the dyed condition of the lens was observed.

Durability

Durability was evaluated by a weathering test using a fade tester. After irradiation of the xenon arc for 250 h, the yellowness index was measured.

A value below 2 was regarded as excellent durability.

RESULTS AND DISCUSSION

Monomeric Methacrylate and Bifunctional Methacrylate System

For optical materials such as the prism and lens, particularly ophthalmic lens, cutting processability, grinding processability, and heat resistance are essential. Therefore, a crosslinking monomer is required. Considering impact resistance, aliphatic multifunctional (meth)acrylate is better than is divinylbenzene which is hard but brittle.

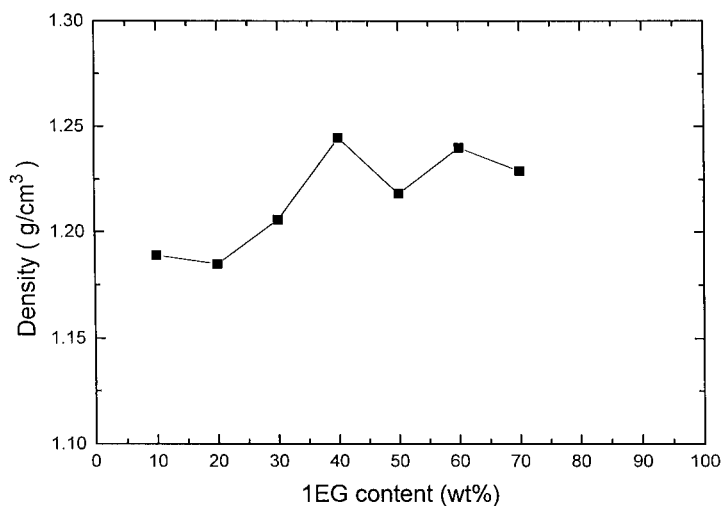


Figure 4 Density as a function of crosslinking monomer wt %.

Table I Surface Hardness, Processability, and Impact Resistance vs. Crosslinking Monomer Content Wt % in Benzyl Methacrylate and Ethylene Glycol Dimethacrylate Copolymer

	1EG Content (Wt %)						
	10	20	30	40	50	60	70
Surface hardness ^a	4H	4H	5H	5H	4H	4H	5H
Cutting processability ^b	△	△	△	×	×	×	×
Impact resistance ^c	×	×	×	×	×	×	×

^a Surface hardness was designated by pencil hardness. 5H is harder than is 4H.

^b Cutting processability was evaluated by observation of cutting surface and edge with a diamond cutter. ×: bad, △: not so good.

^c Impact resistance was evaluated by a drop ball test (16.2 g × 127 cm). The mark × means that the test piece was broken.

We examined the relationship between physical properties and crosslinking density by using a benzyl methacrylate (BzMA) and ethylene glycol dimethacrylate (1EG) copolymer as a model polymer.

Relationship Between Optical Property and the Content of Crosslinking Component

The refractive index and Abbe number were measured and plotted as 1EG content (wt %/

total monomer) was varied. The results are shown in Figure 1. As for the refractive index, all measured values were plotted on the line starting from the refractive index of the homopolymer of BzMA to that of 1EG, i.e., the refractive index of the copolymer is the sum of each contribution of the refractive index of each monomer component proportionally to its content. However, no linearity was observed between the Abbe number and the content of the crosslinking monomer.

Table II Effect of Soft Monomers on Impact Strength

Monomer Composition (Wt %)			Impact Strength (cm) ^a			Heat Resistance (°C)	Surface Hardness ^b	Cutting Processability ^c
			127	100	80			
BzMA	1EG	BMA						
60	30	10	×	—	×	90.2	2H	△
50	30	20	×	○	○	104.0	4H	△
70	20	10	×	—	×	54.5	4H	△
60	20	20	×	×	○	73.3	4H	△
BzMA	1EG	MAN						
60	30	10	×	×	○	92.7	3H	△
50	30	20	×	○	—	93.6	4H	△
70	20	10	×	—	×	70.2	4H	△
60	20	20	×	×	○	71.2	4H	△
BzMA	1EG	DAP						
60	30	10	×	—	×	91.2	4H	△
70	20	10	×	×	○	60.0	4H	△

BzMA: benzyl methacrylate; 1EG: ethylenglycol dimethacrylate; BMA: butyl methacrylate; MAN: methacrylo-nitrile; DAO: diallyl phthalate.

^a Cross means that the test piece was broken. Circle means that the test piece was not broken. Dash means that no test was conducted.

^b Surface hardness was evaluated by pencil hardness in accordance with JIS K5400. Larger numeral means harder surface.

^c Triangle means not so good processability. Small crack and fissure were observed on the cut surface or edge. Polymerization conditions: initiator: 2,2'-azobis(2,4-dimethylvaleronitrile), 0.5%; time: 50°C (6 h), 60°C (16 h), then 90°C (2 h).

Table III Styrene-containing Polymer for Optical Materials

Monomer Composition (Wt %)				Impact Strength (cm) ^a			Heat Resistance (°C)	Surface Hardness ^b	Cutting Processability ^c	Refractive Index	Abbe No.
				127	100	80					
St	BzMA	1EG	MAN								
10	50	30	10	×	○	○	84.5	5H	△-○	1.5465	40.2
10	60	20	10	×	○	○	80.2	4H	△-○	1.5512	39.0

St: styrene; BzMA: benzyl methacrylate; MAN: methacrylonitrile; 1EG: ethylene glycol dimethacrylate.

^a Impact strength was evaluated by the dropball test in which 16.2 g of a steel ball was dropped from 80, 100, and 127 cm high above 1.5 mm-thick test piece. Cross means that the test piece was broken. Circle means that the test piece was not broken. Dash means that no test was conducted.

^b Surface hardness was evaluated by pencil hardness in accordance with JIS K5400. Larger numeral means harder surface.

^c Circle means good processability. No crack and no fissure were observed by use of a diamond cutter. Triangle means not so good processability. Small crack and fissure were observed on the cutting surface or edge. Polymerization conditions: initiator: 2,2'-azobis(2,4-dimethylvaleronitrile), 0.5%; time: 50°C (6 h), 60°C (16 h), then 90°C (2 h).

Relationship Between Heat Resistance and the Content of Crosslinking Component

Heat resistance caused by forming a crosslinkage was improved drastically over 20 wt % of 1EG content but decreased after more than 50 wt % content as shown in Figure 2. Crosslinkage increases as 1EG content increases, resulting in improvement of the heat resistance. In the case of too much crosslinker, however, excess crosslinker may remain unpolymerized after gelation proceeds.⁷ Thus, crosslinkage density decreased, resulting in decrease of the heat resistance with more than 50 wt % of 1EG content.

Relationship Between Water Absorption and the Content of Crosslinking Component

Generally, methacrylate polymers are not good in water absorption compared with polystyrene.^{3,4}

Even when the crosslinking monomer component increased, the water absorption property itself was not improved as shown in Figure 3. On the contrary, a large amount of 1EG made the polymer more hydrophilic.

Relationship Between the Density of the Polymer and the Content of Crosslinking Component

The relationship between the density of the polymer and the content of the crosslinking component was examined. The density of the polymer was not affected much by the content of 1EG and the density was rather small throughout a wide range of 1EG content as shown in Figure 4. It is very advantageous for lightweight lens.

Surface Hardness

Surface hardness was evaluated by the pencil hardness method designated by JIS K5400. The

Table IV Effect of Styrenic Monomers

Monomer Composition (Wt %)			Impact Strength (cm) ^a			Heat Resistance (°C)	Specific Gravity	Cutting Processability ^b
			127	100	80			
2EG	AN	St						
50	10	40	○	○	○	118.4	1.14	○
2EG	AN	α -St						
50	10	40	×	○	○	115.2	1.14	○
2EG	AN	<i>p</i> -St						
50	10	40	—	—	×	121.2	1.12	○

St: styrene; α -St: α -methylstyrene, *p*-St: *p*-methylstyrene; AN: acrylonitrile; 2EG: di(ethylene glycol dimethacrylate).

^a Impact strength was evaluated by the dropball test in which 16.2 g of a steel ball was dropped from 80, 100, and 127 cm high above 1.5 mm-thick test piece. Cross means that the test piece was broken. Circle means that the test piece was not broken. Dash means that no test was conducted.

^b Circle means good processability. No crack and no fissure were observed by use of a diamond cutter. Polymerization conditions: initiator: 2,2'-azobis(2,4-dimethylvaleronitrile), 0.5%; time: 50°C (6 h), 60°C (16 h), then 90°C (2 h).

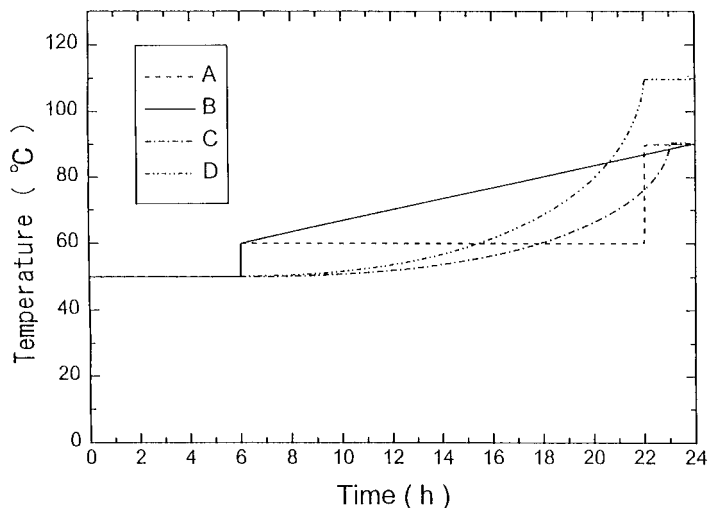


Figure 5 Polymerization pattern. Polymerization temperature was raised with (A) steps, (B) constant rate, (C) parabola curve-1 and (D) parabola curve-2.

results are summarized in Table I. Surface hardness was as good as 4H to 5H throughout a wide range of 1EG content and was not affected by the crosslinking density.

Processability

Processability was evaluated by a cutting trial with a diamond-cutting machine. The results are shown in Table I. A polymer sheet sample was cut rather fairly up to 30 wt % of 1EG content, but at 40 wt % and more of 1EG content, the polymer sheet sample was not cut fairly because of cracks or cleavage.

Impact Resistance

Impact resistance was evaluated by the drop ball test designated by FDA in which 16.2 g of a steel

ball was dropped from 127 cm high above the polymer sheet tested. Regardless of the content of crosslinking monomer, all the copolymers were broken as shown in Table I. Thus, more toughness should be required for the copolymer consisting of BzMA and 1EG.

Improvement of Impact Strength by Adding a Soft Monomer

As described above in the case of the monomeric methacrylate and bifunctional methacrylate system, toughness must be improved. To improve toughness, we may add the third monomer. A preferable third monomer increases the impact strength of the polymer without decreasing the refractive index. However, the monomers of high refractive index do not generally give polymers

Table V Effect of Polymerization Pattern on Impact Strength and Heat Resistance with BzMA/1EG/MAN(50/30/20) Copolymer

Pattern	Initiators V-65/V-40	Impact Strength (cm)				Heat Resistance (°C)	Surface Hardness
		127	100	80	60		
A	0.5/—	○	—	—	—	93.6	4H
B	0.2/0.1	×	×	○	○	72.6	5H
C	0.2/0.1	×	×	○	—	65.7	3H
D	0.2/0.1	×	×	○	—	85.6	4H
B	0.1/0.1	×	—	×	○	67.3	5H
C	0.1/0.1	×	×	○	—	66.7	4H
D	0.1/0.1	×	×	○	—	82.3	5H

V-65: 2,2'-azobis(2,4-dimethylvaleronitrile); V-40: 1,1'-azobis(cyclohexane-1-carbonitrile).

Table VI Effect of Polymerization Pattern on Impact Strength and Heat Resistance with BzMA/1EG/BMA(50/30/20) Copolymer

Pattern	Initiators V-65/V-40	Impact Strength (cm)				Heat Resistance (°C)	Surface Hardness
		127	100	80	60		
A	0.5/—	×	○	○	—	104.0	4H
B	0.2/0.1	×	—	—	×	73.0	4H
C	0.2/0.1	×	×	○	—	60.3	4H
D	0.2/0.1	×	—	×	—	90.6	4H
B	0.1/0.1	×	—	—	×	74.0	4H
D	0.1/0.1	×	—	×	—	71.0	5H

which are elastic and soft but weak or brittle against impact. Among them, butyl methacrylate (BMA) and methacrylonitrile (MAN) were selected as the third monomer, which do not reduce the refractive index much as long as the amount of the addition monomer is small. Diallyl phthalate was also added as a plasticizer. Results are summarized in Table II.

The plasticizer improved the impact resistance to some extent but reduced the heat-resistance temperature of the polymer very badly. To the contrary, soft monomers like BMA and MAN largely improved impact resistance by 20 wt % addition without reducing the heat-resistance temperature. Other properties such as surface hardness and cutting processability were not affected. In the case of MAN, the homogeneity of the polymer was found to be unsatisfactory for optical materials. This is due to the difference of the e value: BzMA 0.36, 1EG 0.24, and MAN 0.81.⁸ Random copolymerization may occur more easily between two methacrylates than between methacrylate and methacrylonitrile. Particularly at the latter period of polymerization, it may be difficult for methacrylonitrile to enter the microgel formed, resulting in increasing homopolymerization of the methacrylonitrile. That causes a microphase separation in the polymer. To avoid this phenomenon, we introduced styrene which has a $-0.8 e$ value.⁸ Styrene was expected to promote alternating copolymerization with both methacrylates and methacrylonitrile to make the homogeneity of the polymer better. Besides, styrene itself has a high refractive index and is economically inexpensive. The polymer obtained by adding styrene in the monomer composition was, in fact, transparent and homogeneous by examining it through a xenon lamp projection. Incorporation of styrene provided polymers which were totally balanced for ophthalmic lens as summarized in

Table III. Other styrenic monomers such as α -methylstyrene (α -St) and p -methylstyrene (p -St) were also examined as a comonomer (Table IV). Heat resistance decreased in the order of p -St, St, and α -St, while impact strength was decreased in the order of St, α -St, and p -St.

Effect of Polymerization Pattern and Temperature

As well as monomer composition and polymerization initiators, polymerization conditions often affect the properties of the polymer obtained. Above all, the polymerization pattern and temperature are quite important in cast polymerization. Rapid gel formation causes microgelation, resulting in making the crosslinking polymer inhomogeneous.⁹ Therefore, to make a crosslinking polymer homogeneous by cast polymerization, it is preferable that polymerization is conducted at a lower temperature at the beginning and then the temperature is increased gradually up to a higher temperature for curing. We conducted cast polymerization with the four different patterns shown in Figure 5. The initial 6 h were kept at 50°C with all polymerization patterns. After 6 h, the polymerization temperature was increased stepwise with pattern A, by a constant rate with pattern B, along with a parabola curve up to 90°C with pattern C, and by a parabola curve up to 110°C with pattern D (Fig. 5).

The results are summarized in Tables V and VI. Polymer sheets obtained by pattern A afforded the highest impact and heat resistance. It is thought that a long period at low temperature helps reduce strain and conducts homogeneous polymerization. There were no significant differences among other polymerization patterns. With the parabola curve patterns C and D, heat resistance was better in the case of higher final temperature, pattern D.

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