

Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperatures. III. Casting and Polymer Properties of Monomer Systems Including Inner-Plasticizing Comonomers

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Synopsis

Previously, it was found that organic glass material having no optical strain could be cast efficiently in a very short time by radiation-induced cast polymerization of glass-forming monomers. In this report, practical useful monomer systems having glass-forming property and good physical properties were investigated. Several inner plasticized comonomer systems of excellent impact resistance were found which could be glassified and applied to radiation casting. These systems included butyl acrylate or hexanediol monoacrylate as inner plasticized component. Physical properties other than impact resistance were tested. The casting polymerization was studied, and it was found that polymers without optical strain could be obtained in a remarkably short time.

INTRODUCTION

The authors have studied the radiation-induced polymerization of glass-forming monomers by radical mechanism and found various marked characteristics.^{1,2} In previous reports,^{3,4} application of glassy-state polymerization to casting of organic glass was investigated, and successful results were obtained in preparing polymer articles with no optical strain in a far shorter time than by the conventional catalytic method. This new casting technique could be generally applicable to all glass-forming monomer systems. It is important to find a practical useful system with good physical properties and applicable to radiation casting methods. One approach may be improving the physical properties of polymers obtained from glass-forming monomers such as hydroxyethyl methacrylate and glycidyl methacrylate, and another may be giving the glass-forming property to nonglass-forming monomer such as methyl methacrylate the polymer of which has good physical properties. The authors screened both ways and found that the results of the two approaches gave almost the same composition system having good glass-forming and good physical properties. This report concerns the search for a monomer system for organic glass material having glass-forming property as well as good impact resistance and heat resistance at least equal to or better than that of poly(methyl methacrylate).

EXPERIMENTAL

Commercially available vinyl monomers with low boiling point were purified by distillation and used for experiment. Other monomers having high boiling points were used after passing through columns filled with adsorption ion exchange resin to remove hydroquinone. Hexanediol monomethacrylate (HDMM) and hexanediol monoacrylate (HDMA) were synthesized by the reaction of hexanediol with methacrylic acid and acrylic acid. The synthesized HDMA and HDMM contained small quantities of hexanediol diacrylate (HDDA) or dimethacrylate (HDDM) and hexanediol (HD).

The glass-forming property of monomers was tested by observation of glassification in a test tube filled with sample in the cooling bath at a definite temperature. The glass transition temperature was determined by differential thermal analysis. The induction period of glassification was measured by observation of the time to the beginning of crystallization in the cooling bath at a definite temperature.

Polymerization was carried out by 100,000 Ci γ -ray irradiation from a ^{60}Co source in a reaction bath kept at a finite temperature using a casting frame constructed as described in previous reports.^{3,4} The optical strain formed in the polymer was checked by a photoelastic strain gauge with polarizing plates.

Impact resistance of polymer was estimated by three methods: Izod impact resistance test according to JIS-K6911; FDA drop-impact resistance test according to FDA standard for spectacle lenses; and JIS drop-impact resistance test according to JIS-K6718.

Heat durability was tested by a method similar to BS 1524-1955 in which a sample with a weight at one end was held horizontally at a definite temperature and the changes in the center angle of the sample by loading and heating were measured.

The weather resistance was estimated by measuring the changes in impact strength and appearance after sunshine exposure and in the xenon Weatherometer (Toyo-rika Co.) test according to ASTM E-239-70 for a definite time.

RESULTS AND DISCUSSION

Screening for Binary Monomer System

The screening was done by estimating impact resistance as the most important mechanical property for lenses and glazing material and also by estimating the glass-forming property for the applicability to radiation casting.

Hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) are typical glass-forming monomers and are effectively applicable to radiation casting techniques as studied in the previous reports. However, HEMA and GMA are very poor in mechanical strength, as shown in Table I, and not practically useful materials. So, impact resistance of HEMA and GMA polymer was improved by adding another comonomer. The results are shown in Table I. The standard screening conditions were: Izod impact resistance more than 15 kg-cm/cm², hard

TABLE I
Physical Properties of Binary Comonomer Systems Having Glass-Forming Property^a

Run no.	Monomer composition	Izod impact resistance, kg-cm/cm ²		
		Max. value	Min. value	Mean value
1	GMA85-MMA15	4.2	2.2	3.5
2	GMA75-MMA25	8.2	5.1	6.8
3	GMA65-MMA35	11.6	6.5	9.2
4	GMA95-EA5	2.6	1.0	2.0
5	GMA85-EA15	6.5	2.6	4.3
6	GMA75-EA25	19.7	9.3	14.6
7	GMA85-MA15	15.8	3.4	12.7
8	GMA75-MA25	18.6	5.3	15.2
9	GMA75-BMA25	4.6	2.2	3.5
10	GMA75-iso-BMA25	3.9	2.2	2.8
11	GMA75-EMA25	12.7	2.6	9.9
12	GMA75-CHMA25	1.5	0.8	1.1
13	GMA75-VAC25	15.4	4.5	6.6
14	GMA75-St25	9.2	4.2	7.1
15	GMA75-VT25	11.5	4.3	7.7
16	GMA95-AN5	3.6	1.5	2.5
17	GMA85-AN15	8.6	4.8	6.3
18	GMA75-AN25	25.4	13.3	20.4
19	GMA80-DAA20	2.3	0.9	1.8
20	GMA75-HDDA25	7.8	5.4	6.0
21	GMA75-HPMA25	2.4	1.0	1.7
22	GMA75-EDMA25	3.8	1.2	2.9
23	GMA88-DAP12	3.8	2.1	2.9
24	HEMA75-MMA25	3.4	1.4	2.6
25	HEMA95-EA5	3.7	0.9	1.5
26	HEMA85-EA15	6.6	0.9	3.5
27	HEMA75-EA25	18.2	1.7	7.8
28	HEMA75-BA25	9.0	2.5	3.9
29	HEMA75-BMA25	8.4	2.2	4.5
30	HEMA75-iso-BMA25	3.7	1.1	2.3
31	HEMA75-EMA25	3.3	1.1	2.2
32	HEMA75-CHMA25	2.7	0.9	1.2
33	HEMA75-VAC25	6.8	0.8	3.0
34	HEMA75-VT25	2.3	1.0	1.6
35	HEMA95-AN5	7.0	0.9	2.0
36	HEMA85-AN15	12.6	1.2	4.4
37	HEMA75-AN25	24.0	3.6	12.1
38	HEMA80-DAA20	2.2	0.6	1.2
39	HEMA75-HDDA25	7.4	3.7	5.6
40	HEMA75-HPMA25	2.7	0.9	1.2
41	HEMA75-EDMA25	3.4	1.4	2.6
42	HEMA90-DAP10	4.1	1.4	2.4
43	EMA75-BA25	19.4	3.6	12.1

^a GMA: glycidyl methacrylate; MMA: methyl methacrylate; EA: ethyl acrylate; MA: methyl acrylate; BMA: butyl methacrylate; iso-BMA: isobutyl methacrylate; EMA: ethyl methacrylate; CHMA: cyclohexyl methacrylate; VAc: vinyl acetate; St: styrene; VT: vinyl toluene; AN: acrylonitrile; DAA: diacetone acrylamide; HEMA: hydroxyethyl methacrylate; MPMA: hydroxypropyl methacrylate; HDDA: hexanediol diacrylate; EDMA: ethylene dimethacrylate; DAP: diallyl phthalate.

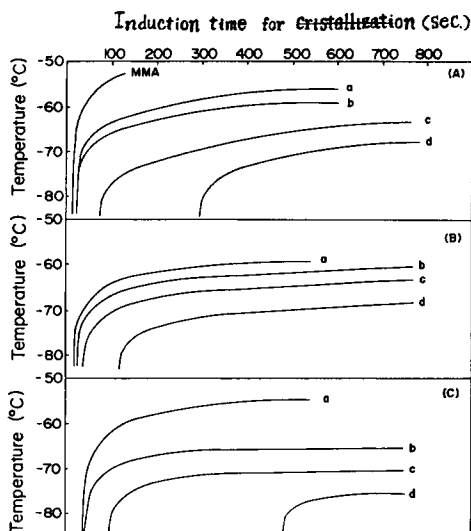


Fig. 1. Relation between induction time for glassification and temperature in methyl methacrylate in the presence of glass-forming monomers: (A) methyl methacrylate-tetraethylene glycol dimethacrylate system, tetraethylene glycol dimethacrylate concentration: (a) 9 vol-%, (b) 16 vol-%, (c) 28 vol-%, (d) 37 vol-%; (B) methyl methacrylate-diethylene glycol diacrylate system, diethylene glycol diacrylate concentration: (a) 9 vol-%, (b) 16 vol-%, (c) 28 vol-%, (d) 37 vol-%; (C) methyl methacrylate-hydroxyethyl methacrylate system, hydroxyethyl methacrylate concentration: (a) 9 vol-%, (b) 16 vol-%, (c) 28 vol-%, (d) 37 vol-%.

resin property, enough glass-forming property, and homogeneity of the polymerization phase (transparency of polymer). Although the glass-forming properties were relatively rich in HEMA or GMA, the Izod impact resistances of most systems were poor, as shown in Table I.

Adding other comonomers to methyl methacrylate (MMA) as the representative monomer for organic glass was also tried to produce glass formation. Figure 1 shows the induction period to glassification in these systems determined in the same manner as the previous works.⁵ The longer the induction time, the more stable the glass-forming property of the monomer system was. However, glass-forming properties in these systems were not sufficient in MMA-rich compositions at low temperature region such as -70° – -80° C, as seen in Figure 1 because induction time was not long enough in comparison with the required polymerization time.

It was concluded that suitable systems satisfying all standard conditions could hardly be found by means of binary combination of comonomers.

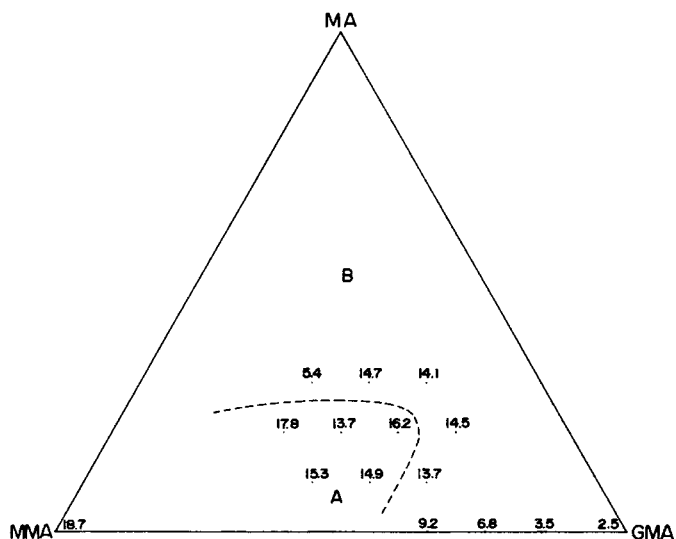
Screening for Three-Component System Including Lower Alkyl Methacrylate and Acrylate

Screening tests were made for three-component systems under the same screening standards, because, in general, glass-forming property increases and a balance of various physical properties is reached more easily with an increasing number of components. The results were shown in Table II. As seen in the

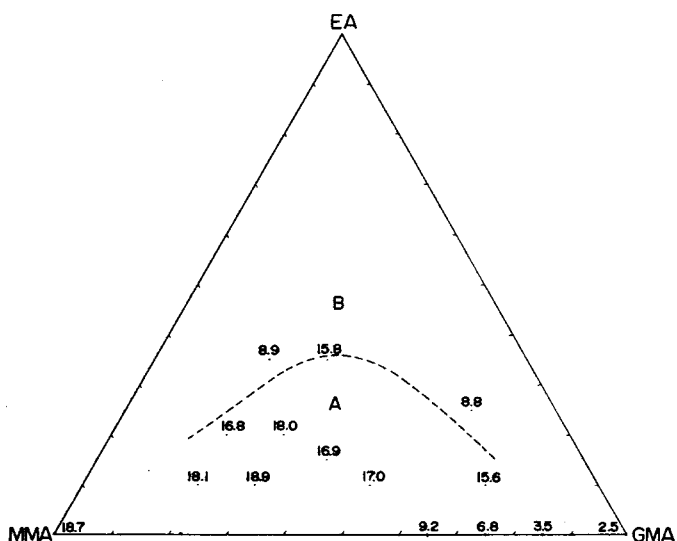
TABLE II
Physical Properties of Three-Component Comonomer Systems Having Glass-Forming Property^a

Run no.	Monomer composition, vol-%	Izod impact resistance, kg-cm/cm ²		
		Max. value	Min. value	Mean value
1	MMA30-VAC20-GMA50	12.3	2.8	14.0
2	MMA30-VAC10-GMA60	13.4	4.5	11.6
3	MMA40-VAC10-GMA50	13.5	6.5	12.8
4	MMA40-VAC20-GMA40	15.5	7.7	14.5
5	MMA50-VAC10-GMA40	16.5	12.3	14.4
6	MMA20-VAC20-GMA60	10.3	4.4	10.0
7	MMA50-St10-GMA40	15.5	9.6	14.9
8	MMA30-St10-GMA60	15.0	9.8	13.2
9	MMA40-St10-GMA50	15.7	3.7	14.7
10	MMA30-St20-GMA50	14.9	7.6	13.6
11	MMA20-St20-GMA60	13.7	10.2	12.2
12	MMA50-St20-GMA30	15.5	3.7	13.8
13	MMA40-St30-GMA30	13.9	8.8	9.6
14	MMA30-St30-GMA40	15.0	10.9	12.6
15	MMA30-VT10-GMA60	14.0	6.0	11.5
16	MMA50-VT10-GMA40	16.0	11.3	14.9
17	MMA20-VT20-GMA60	10.9	2.6	7.5
18	MMA40-VT10-GMA50	15.1	4.5	13.1
19	MMA30-VT20-GMA50	12.3	8.9	10.3
20	MMA40-VT20-GMA40	12.7	7.6	10.4
21	MMA30-EMA10-MA60	20.4	3.6	17.7
22	MMA30-EMA10-MA30	18.8	2.7	14.5
23	MMA40-EMA10-MA50	11.6	2.0	10.3
24	MMA50-EMA10-MA40	20.2	1.0	8.0
25	MMA30-EMA20-MA50	19.1	2.7	9.9
26	MMA10-EMA60-MA30	7.5	2.0	4.0
27	MMA30-EMA60-MA30	18.9	12.8	16.4
28	MMA30-EMA40-MA30	15.8	5.1	9.4
29	GMA40-EA20-EMA40	16.6	6.6	14.7
30	GMA30-EA20-EMA50	18.0	13.9	16.0
31	GMA50-EA20-EMA30	17.3	10.9	15.5
32	GMA50-EA30-EMA20	20.2	7.9	16.0
33	GMA30-EA30-EMA40	20.0	5.1	15.2
34	GMA40-EA30-EMA30	18.0	7.5	15.6
35	GMA60-EA10-EMA30	16.9	11.0	13.8
36	GMA40-EA10-EMA50	14.6	8.8	13.1
37	GMA50-EA10-EMA40	15.7	9.8	13.0
38	GMA60-EA20-EMA20	21.1	7.9	17.2
39	GMA70-AN15-St15	22.0	6.1	17.5
40	GMA70-AN15-EA15	20.8	14.1	17.0
41	GMA70-AN15-BA15	23.0	9.5	17.6
42	MMA40-AN20-GMA40	22.1	15.2	20.6
43	MMA40-AN10-GMA50	17.9	19.5	13.5
44	GMA70-St15-BA15	12.4	3.6	8.9
45	GMA70-St15-EA15	15.5	4.6	11.6
46	GMA70-EA15-BA15	21.6	7.8	15.1
47	GMA	3.6	1.4	2.5
48	HEMA	6.0	1.0	2.8

^a Symbols of monomers same as in Table I.



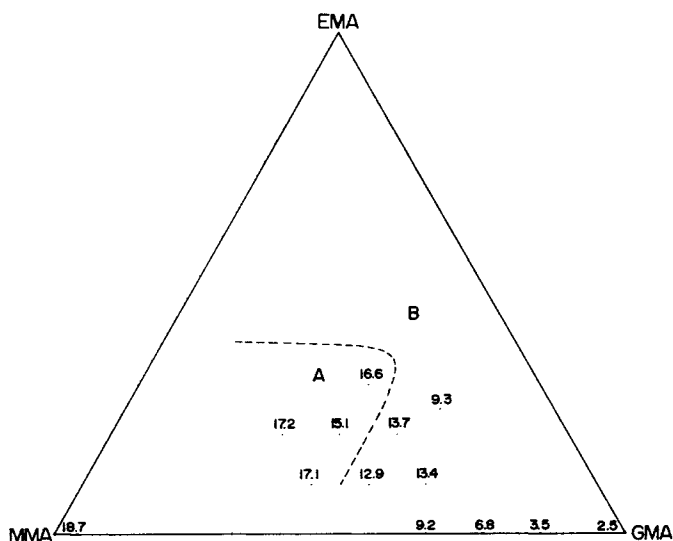
(a)



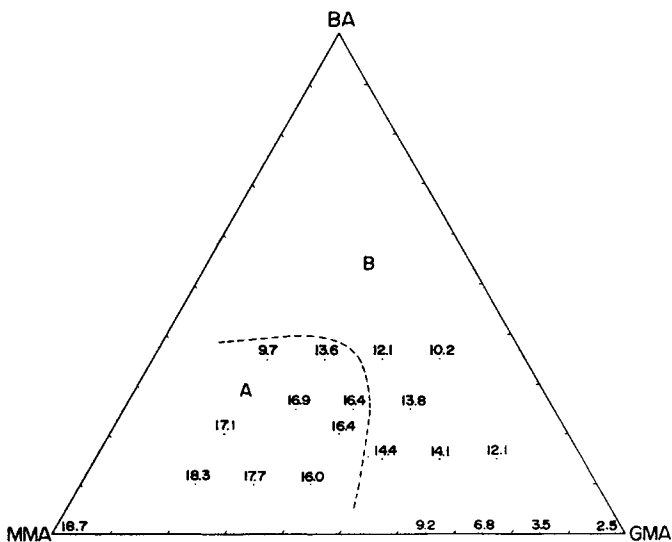
(b)

Fig. 2. Relation between impact resistance and composition of three-component systems consisting of glycidyl methacrylate-methyl methacrylate and lower alkyl acrylate and methacrylate: (a) glycidyl methacrylate-methyl methacrylate-methyl acrylate (MA) system; (b) glycidyl methacrylate-methyl methacrylate-ethyl acrylate (EA) system; (c) glycidyl methacrylate-methyl methacrylate-ethyl methacrylate (EMA) system; (d) glycidyl methacrylate-methyl methacrylate-butyl acrylate (BA) system; A: region of relatively good impact resistance to pass the screening test; B: region of relatively poor impact resistance. Figures in the four three-component system maps show Izod impact resistance in $\text{kg}\cdot\text{cm}/\text{cm}^2$.

table, several compositions having relatively good impact resistances could be obtained in three-component systems consisting of GMA and two combinations of monomers selected from the group of lower alkyl methacrylate and acrylate such as methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl acrylate



(c)



(d)

Fig. 2. (continued from previous page)

(BA), methyl acrylate (MA), and ethyl acrylate (EA). GMA was necessary to impart glass-forming property and resin hardness. MA was effective in imparting resin hardness keeping good impact resistance.

BA was most effective in producing excellent impact resistance, though it decreased resin hardness. Consequently, it was necessary to reach a balance of glass-forming property, impact resistance, and polymer hardness by suitable selection of comonomer composition. A map of impact resistance in three-component systems is shown in Figure 2. HEMA could be substituted for GMA to some degree. Acrylonitrile was found to give an impact resistance of more than 17 kg-cm/cm². However, as a brown coloration was often observed in acryloni-

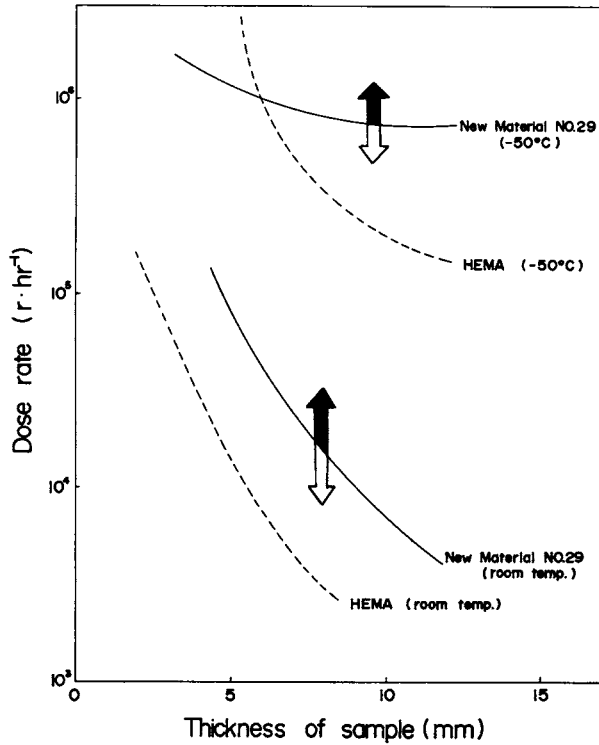


Fig. 3. Effect of dose rate and sample thickness on the optical strain formation in no. 29 multi-component system: \blacktriangle region in which optical strain formed; \triangleleft region in which no optical strain formed; (—) boundary curve of strain-forming condition in system no. 29; (- - -) boundary curve of strain-forming condition in hydroxyethyl methacrylate; total dose: 1×10^6 R; sample scale: 20 cm \times 10 cm.

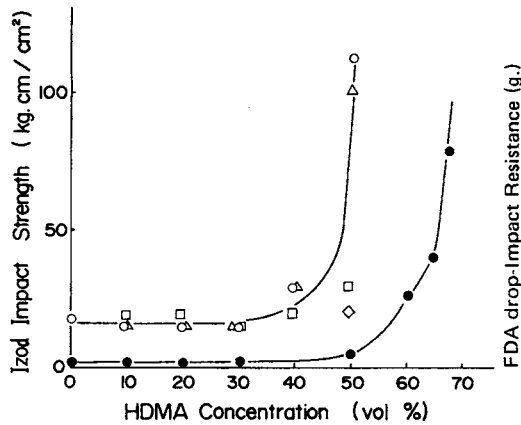


Fig. 4. Effect of hexanediol monoacrylate (HDMA) addition on Izod impact resistance: \square methyl methacrylate-hexanediol monoacrylate (ratio in side axis) and hexanediol diacrylate (30 vol-% to other monomers); Δ methyl methacrylate-hexanediol monoacrylate (ratio in side axis) and hexanediol diacrylate (15 vol-% other monomers); \circ methyl methacrylate-hexanediol monoacrylate (ratio in side axis) and hexanediol diacrylate (0 vol-% to other monomer); \bullet hydroxyethyl methacrylate-hexanediol monoacrylate; irradiation dose: 2.1×10^6 R.

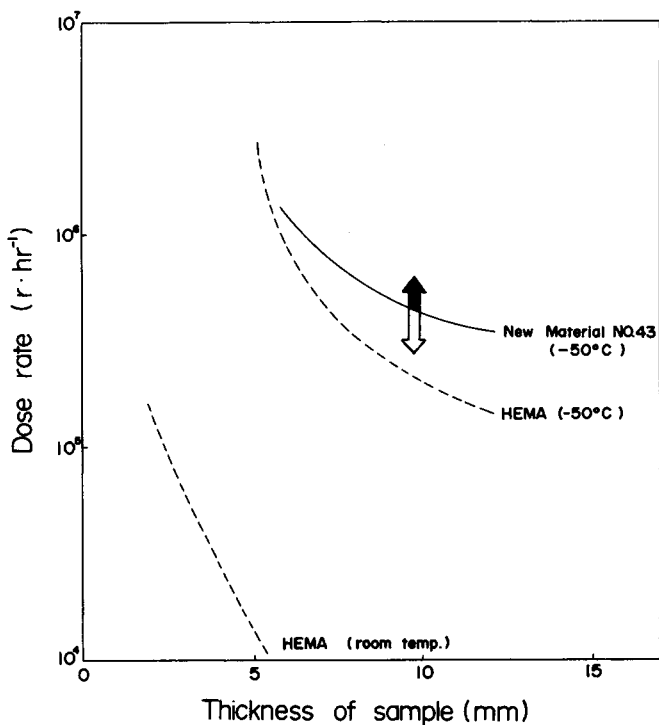


Fig. 5. Effect of dose rate and sample thickness on optical strain formation in multicomponent system no. 43: \leftarrow region in which optical strain formed; \rightleftharpoons region in which no optical strain formed; (—) boundary curves of strain forming-condition in system no. 43; (---) boundary curve of strain-forming condition in hydroxyethyl methacrylate; total dose: 1×10^6 R; sample scale: $20 \text{ cm} \times 10 \text{ cm}$.

trile-including systems, they were excluded. The lower alkyl methacrylate and acrylate groups mentioned above are characteristic in having relatively soft, flexible alkyl side chains, acting as an inner plasticizer, and also having supercooling tendency to some extent. Though these compositions all satisfied the screening standard conditions, the most excellent system and composition in this series, called system no. 29, was a three-component system consisting of 35 vol-% glycidyl methacrylate, 35 vol-% methyl methacrylate, and 30 vol-% butyl acrylate. It should be noted that suitable systems included both GMA and MMA. This means that GMA and MMA were necessary as the most suitable components. The fact suggests that two kinds of screening, one to improve the impact resistance of GMA and another to impart the glass-forming property to MMA, agreed in the same result. Butyl acrylate contributed mainly impact resistance, while MMA and GMA were necessary to keep the resin hard. Glass-forming property was produced mainly by GMA and also by an increase in the number of components.

Cast polymerization by radiation was applied to this system. The results are shown in Figure 3, in which the boundary condition curve of optical strain formation is shown in the same manner as in the previous reports.^{3,4} It is obvious that radiation casting is successfully applicable to system no. 29, in which a polymer article with no optical strain could be obtained very easily and in a very

TABLE III
Best Comonomer Compositions with the Most Suitable Physical Properties in Inner-Plasticized Systems^a

Components	Monomer	Composition range used, vol-%	Impact resistance		Heat durability (change in center angle)		
			Izod method, kg-cm/cm ²	FDA test, g	θ at 50°C, deg	θ at 100°C, deg	
GMA-MMA-EA		GMA: 30-70					
GMA-MMA-MA		MMA: 10-50	15-17	15.8 \geq			
GMA-MMA-EMA		others: 10-50					
		GMA: 20-50					
GMA-MMA-BA		MMA: 25-70	16-21	15.8 \geq			
		BA: 10-35					
GMA-MMA-BA		30-35-35 ^b	34.6	200<	55	65	
MMA-HDMA		MMA: 70-90	18-20	15.8 \geq			
		HDMA: 10-30					
MMA-HDMA-HDDA-HD		60-31-8.7-4.3 ^c	19.6	200<	25	22-26	
GMA-MMA-HDMA		30-35-35	10-27	15.8>			
HEMA-MMA-HDMA-HDDA-HD		30-35-26.6-17.9-4.7 ^d	51	200<	13	13	

^a Symbols of monomers same as in Table I. Under FDA test, g is the weight of the steel ball which destroyed a sample 5 cm X 5 cm X 2.1 mm thick when falling from a height of 127 cm. Balls of 10, 15.8, 20, 30, 40, 50, 100, and 200 g in weight were used, and the mean value of three tests was adopted.

^b System no. 29.

^c System no. 42.

^d System no. 43.

short time. It was noted especially that the boundary condition of strain formation in system no. 29 was not considerably lowered with increasing sample thickness, which is very beneficial in large-scale casting.

Screening for Monomer Systems Including Longer Hydroxy Alkyl Methacrylate (Acrylate)

It was also found that methacrylic and acrylic components with relatively long hydroxyalkyl chains were effective in increasing the impact resistance. That is, long hydroxyalkyl monomers such as hexanediol monomethacrylate (HDMM) and hexanediol monoacrylate (HDMA) increased impact resistance of HEMA markedly at higher concentrations, as shown in Figure 4. However, the copolymer hardness decreased and the polymer became soft with increasing long hydroxyalkyl component. The same tendency was observed in HDMA(HDMM)-MMA systems, as shown in Figure 4, and the copolymer became a soft resin at an HDMA concentration of more than 50%. It was necessary to reach a balance between impact resistance and polymer hardness for practical use. It was found that suitable quantities of HDDA and HD (hexanediol) were effective in reaching such a balance, and the most suitable composition in this series was found to be the system consisting of 60 vol-% MMA, 31 vol-% HDMA, 8.7 vol-% HDDA, and 4.3 vol-% HD; and the system consisting of 30 vol-% HEMA, 35 vol-% MMA, 26.6 vol-% HDMA, 17.9 vol-% HDDA, and 4.7 vol-% HD. The former system was designated no. 42, and the latter was designated no. 43. These systems also satisfied several standard conditions such as good impact resistance, polymer hardness, and glass-forming property.

Casting of system no. 43 was investigated, and the results are shown in Figure 5. It is clear that these systems are also efficiently applicable to radiation casting and show the merit of shortening the casting time cycle for preparing the article with no optical strain. These results support the possibility that a new casting process by radiation polymerization in the supercooled phase could be generally applicable to any kind of monomer system for organic glass, when glass-forming property or supercooled tendency is present. It is expected that the use of butanediol monoacrylate, pentanediol monoacrylate, and heptanediol monomethacrylate instead of HDMA will give similar results. A summary of most suitable systems in all inner-plasticized systems is given in Table III.

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