

# Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperatures. V. Casting and Polymer Properties of CR-39 Modified Monomer Systems

H. OKUBO, M. KATO, and I. KAETSU, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki-shi, Gunma-ken, Japan, and Tokyo Optical Company, Setagayaku, Tokyo, Japan*

## Synopsis

Classification, cast polymerization, and physical properties of monomeric system including diethylene-glycolbisallyl carbonate (CR-39) was investigated. Addition of other monomers to CR-39 was investigated CR39- polyfunctional monomer and CR-39-methyl methacrylate-polyfunctional monomer systems were found to form stable glassy state applicable to radiation-induced casting and good in physical property. Two-step polymerization method consisting of pre-irradiation and post-catalytic polymerization necessary to complete casting. It was found that these newly found CR-39 modified systems could be casted efficiently in much shorter time cycle than catalytic process without forming optical strain. Physical properties of casted polymer such as impact resistance and heat durability were sufficient for practical use.

## INTRODUCTION

In previous papers,<sup>1,2,3</sup> cast polymerization of glass-forming model monomers such as hydroxyethyl methacrylate and glycidyl methacrylate was investigated by radiation-induced polymerization in supercooled phase at low temperatures. It was found that cast polymer articles with no optical strain could be obtained in much shorter times than in the conventional catalytic method. The mechanism of optical strain formation and the reasons for the beneficial characteristics of radiation casting were discussed in the previous reports.<sup>2,3</sup> It is also important to find a practically useful organic glass system with excellent physical properties applicable to radiation casting because of glass-forming property. In the previous reports,<sup>4,5</sup> some methacrylate and acrylate modified systems including inner-plasticizing comonomer were found which satisfied the above properties. However, CR-39 polymer is also well known as representative organic glass material having good surface hardness and heat durability,<sup>6</sup> but it is not universally utilized because of the poor casting suitability by catalysts. To test the general availability of radiation casting methods, the authors tried in this report the composition screening of modified CR-39 resin system and its casting by

radiation resulting in glass-forming property and at least equal or better physical properties than CR-39 polymer.

## EXPERIMENTAL

All monomers used were purified by distillation or passing through adsorption ion exchange resin to remove inhibitors. Glass-forming property was judged from appearance using a cooling bath controlled at a definite temperature. Polymerization was carried out in a test tube or in a casting frame by irradiation from a  $^{60}\text{Co}$   $\gamma$ -ray source (100,000 Ci) or by catalyst at definite temperatures. The polymerization rate was determined by weighing. Optical strain of polymer was checked by a photoelastic strain gauge. The impact resistance was estimated by FDA test and by JIS impact strength method.<sup>4</sup> The heat durability was estimated<sup>4</sup> by measuring the change in the center angle in the equipment in which the sample was gripped at one end and loaded in the other end by a steel weight at elevated temperatures. The weather durability was estimated<sup>4</sup> by the change of impact resistance and appearance such as coloring and crack formation after exposure to sunshine and ultraviolet irradiation from a xenon Weatherometer.

## RESULTS AND DISCUSSION

### Polymerization and Physical Properties of CR-39-MMA and CR-39-MMA-GMA Systems

Screening was done to find the monomer system satisfying standard properties such as glass-forming property of monomer, homogeneity of polymerization phase, hardness of polymer, sufficient impact resistance, and heat resistance. The results are shown in Table I and Figure 1. It was found that the CR-39-MMA system formed unstable glassy state in all composition ranges, which began to crystallize in rising temperature steps after supercooling, while the CR-39-MMA-GMA (glycidyl methacrylate) system formed stable glassy state in GMA-rich compositions. The polymerization phase was often heterogeneous in binary systems consisting of CR-39 and vinyl monomer, but those in CR-39-MMA and CR-39-MMA-GMA systems were completely homogeneous.

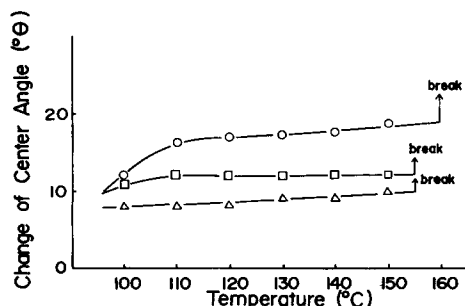


Fig. 1. Heat durability of CR-39-MMA and CR-39-MMA-GMA systems. Change in center angle by heating at various temperatures for 30 min: (O) CR-39 40 vol-%-MMA 50 vol-% copolymer; (□) CR-39 50 vol-%-MMA 50 vol-% copolymer; (Δ) CR-39 60 vol-%-MMA 40 vol-% copolymer.

Impact resistance of both systems was good in comparison with poly(methyl methacrylate), but heat resistance  $\alpha$  was inferior to that of CR-39 resin.

The polymerization of the CR-39-MMA system was studied in detail as shown in Figures 2-5. The polymerization of the CR-39 monomer itself hardly occurred

TABLE I  
Physical Properties of CR-39-Vinyl Monomer Systems<sup>a</sup>

Run no.	System	Homogeneity of polymerization phase	Glass-forming property	Izod impact strength, kg-cm/cm <sup>2</sup>	Hardness of polymer
1	CR-39-Styrene (50-50)	no	no		
2	CR-39-Hydroxyethyl methacrylate (50-50)	no	unstable	brittle	
3	CR-39-Hexanediol monoacrylate (50-50)	no	stable		soft
4	CR-39-Hexanediol diacrylate (50-50)	no	stable		soft
5	CR-39-Ethylene dimethacrylate (50-50)	no	no		
6	CR-39-Tetraethylene glycol dimethacrylate (50-50)	no	stable		soft
7	CR-39-Acrylic acid (50-50)	no	no		
8	CR-39-Methacrylic acid (50-50)	no	no		
9	CR-39-Butyl acrylate (50-50)	yes	unstable		soft
10	CR-39-Ethyl acrylate (50-50)	yes	unstable		soft
11	CR-39-Glycidyl methacrylate (25-75)	yes	stable	12.4	2B
12	CR-39-Glycidyl methacrylate (20-80)	yes	stable	brittle	3B
13	CR-39-Methyl methacrylate (67-33)	yes	unstable		
14	CR-39-Methyl methacrylate (50-50)	yes	unstable		
15	CR-39-Methyl methacrylate (33-67)	yes	unstable	13.2	F
16	CR-39-Methyl methacrylate (25-75)	yes	no	19.4	4H
17	CR-39-Methyl methacrylate (20-80)	yes	no	18.6	4H
18	CR-39-Glycidyl methacrylate-methyl methacrylate (50-50-50)	yes	stable		
19	CR-39-Glycidyl methacrylate-methyl methacrylate (25-25-50)	yes	stable	19.9	F
20	CR-39-Glycidyl methacrylate-methyl methacrylate (20-20-60)	yes	stable	19.3	2H
21	CR-39-Glycidyl methacrylate-methyl methacrylate (16-16-68)	yes	unstable		

<sup>a</sup> Hardness of polymer is expressed by the pencil hardness.

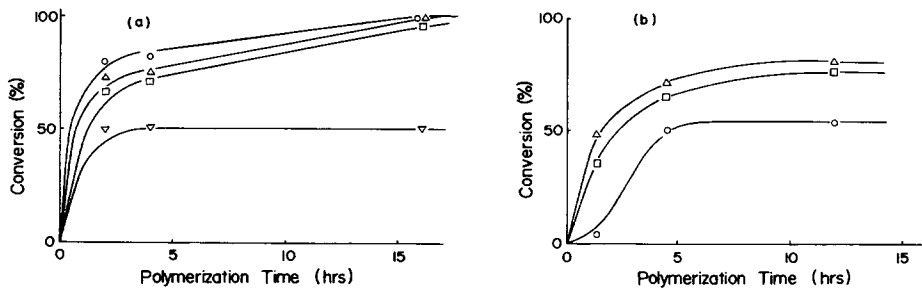


Fig. 2. Catalytic polymerization of CR-39-MMA system. (a) Catalytic polymerization by isopropylperoxy carbonate (IPP) at 60°C: ( $\Delta$ ) CR-39 40 vol-%-MMA 60 vol-%; ( $\square$ ) CR-39 50 vol-%-MMA 50 vol-%; ( $\Delta$ ) CR-39 60 vol-%-MMA 40 vol-%; ( $\circ$ ) CR-39 80 vol-%-MMA 20 vol-%. (b) Catalytic polymerization by benzoyl peroxide (BPO) at 60°C: ( $\Delta$ ) CR-39 40 vol-%-MMA 60 vol-%; ( $\square$ ) CR-39 50 vol-%-MMA 50 vol-%; ( $\circ$ ) CR-39 80 vol-%-MMA 20 vol-%.

TABLE II  
Homogeneity of Polymerization Phase in CR-39-Polyfunctional Monomer Systems<sup>a</sup>

Poly-functional monomer	60% <sup>b</sup>	50%	40%	20%
TMET	Heterog.	Heterog.	Slightly heterog.	Homog.
TMPT	Heterog.	Heterog.	Slightly heterog.	Homog.
A-TMMT	Heterog.	Slightly heterog.	Slightly heterog.	Homog.
A-TMPT	Heterog.	Heterog.	Heterog.	Heterog.
A-TMM-3	Heterog.	Heterog.	Slightly heterog.	Homog.
NPG	Heterog.	Heterog.	Slightly heterog.	Homog.
A-NPG	Slightly heterog.	Slightly heterog.	Slightly heterog.	Homog.
BG	Heterog.	Heterog.	Slightly heterog.	Homog.
M-4G	Homog.	Homog.	Homog.	Homog.
AM-4G	Homog.	Homog.	Homog.	Homog.
A-4G	Homog.	Homog.	Homog.	Homog.
4G	Slightly	Slightly heterog.	Homog. heterog.	Homog.
P-2G	Heterog.	Heterog.	Slightly heterog.	Homog.
A-3G	Slightly heterog.	Slightly heterog.	Homog.	Homog.
M-9G	Homog.	Homog.	Homog.	Homog.
AP-9G	Homog.	Homog.	Homog.	Homog.
A-9G	Homog.	Homog.	Homog.	Homog.
P-9G	Slightly heterog.	Slightly heterog.	Slightly heterog.	Homog.
9G	Slightly heterog.	Slightly heterog.	Homog.	Homog.

<sup>a</sup> TMET: Trimethylolethane trimethacrylate; TMPT: trimethylolpropane trimethacrylate; A-TMET: trimethylolethane triacrylate; A-TMPT: trimethylpropane triacrylate; A-TMM-3: tetramethylolmethane triacrylate; NPG: neopentyl glycol dimethacrylate; A-NPG: neopentyl glycol diacrylate; BG: 1,3-butylene glycol dimethacrylate; M4G: methoxytetraethylene glycol methacrylate; AM4G: methoxytetraethylene glycol acrylate; A4G: tetraethylene glycol diacrylate; 4G: tetraethylene glycol dimethacrylate; P2G: dipropylene glycol dimethacrylate; A3G: triethylene glycol diacrylate; M9G: methoxypolyethylene glycol dimethacrylate; AP9G: polypropylene glycol diacrylate; A9G: polyethylene glycol diacrylate; P9G: polypropylene glycol dimethacrylate; 9G: polyethylene glycol dimethacrylate; homog.: homogeneous phase; heterog.: heterogeneous phase.

<sup>b</sup> Concentration of polyfunctional monomer.

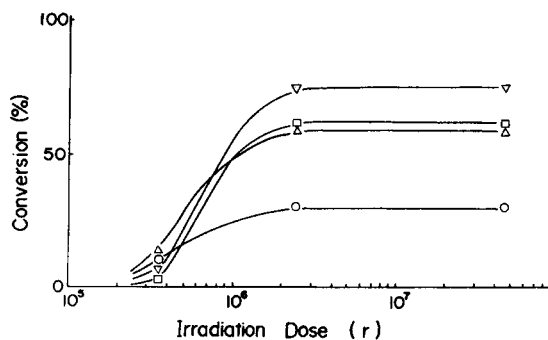


Fig. 3. Radiation-induced polymerization of CR-39-MMA system: ( $\nabla$ ) CR-39 40 vol-%-MMA 60 vol-%; ( $\square$ ) CR-39 50 vol-%-MMA 50 vol-%; ( $\Delta$ ) CR-39 60 vol-%-MMA 40 vol-%; ( $\circ$ ) CR-39 80 vol-%-MMA 20 vol-%; dose rate:  $6 \times 10^5$  R/hr; temperature:  $25^\circ\text{C}$ .

by irradiation, and the polymerization of CR-39-MMA system was not complete by mere irradiation, as shown in Figure 3. According to Figure 2, IPP (isopropylperoxy carbonate) can complete the catalytic polymerization of CR-39, while BPO (benzoyl peroxide) cannot complete the catalytic polymerization. The polymerization rates of MMA-rich compositions were higher than those of MMA-poor compositions in radiation-induced and BPO-induced polymerizations, while the rate of CR-39-rich compositions was higher than that of CR-

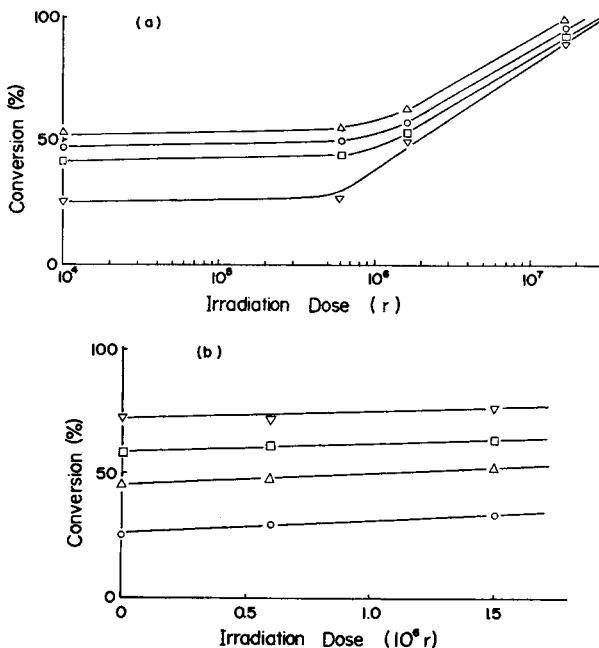


Fig. 4. Two-step polymerization of CR-39-MMA system. Precatalytic polymerization-postirradiation method. (a) Precatalytic polymerization by isopropylperoxy carbonate at  $60^\circ\text{C}$  for 20 min: ( $\nabla$ ) CR-39 40 vol-%-MMA 60 vol-%; ( $\square$ ) CR-39 50 vol-%-MMA 50 vol-%; ( $\Delta$ ) CR-39 60 vol-%-MMA 40 vol-%; ( $\circ$ ) CR-39 80 vol-%-MMA 20 vol-%; dose rate:  $6 \times 10^5$  R/hr; temperature:  $25^\circ\text{C}$ . (b) Precatalytic polymerization by benzoyl peroxide at  $60^\circ\text{C}$  for 4 hr: ( $\Delta$ ) CR-39 40 vol-%-MMA 60 vol-%; ( $\square$ ) CR-39 50 vol-%-MMA 50 vol-%; ( $\Delta$ ) CR 39 60 vol-%-MMA 40 vol-%; ( $\circ$ ) CR-39 80 vol-%-MMA 20 vol-%; dose rate:  $6 \times 10^5$  R/hr; temperature:  $25^\circ\text{C}$ .

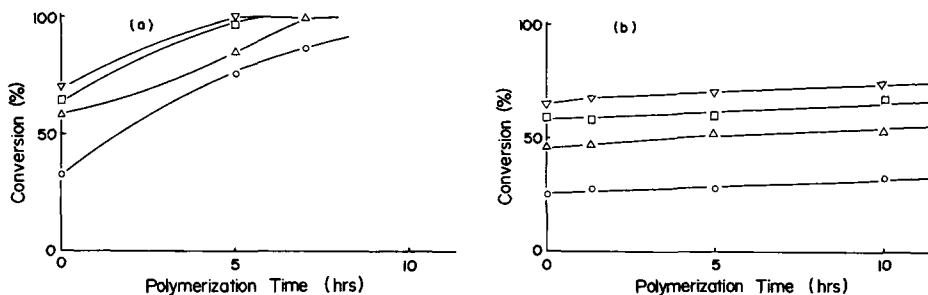


Fig. 5. Two-step polymerization of CR-39-MMA system. Preirradiation-postcatalytic polymerization method. (a) Postcatalytic polymerization by isopropylperoxy carbonate at 80°C: (▽) CR-39 40 vol-%-MMA 60 vol-%; (□) CR-39 50 vol-%-MMA 50 vol-%; (Δ) CR-39 60 vol-%-MMA 40 vol-%; (○) CR-39 80 vol-%-MMA 20 vol-%; preirradiation:  $2 \times 10^6$  R at 25°C. (b) Postcatalytic polymerization by benzoyl peroxide at 80°C: (▽) CR-39 40 vol-%-MMA 60 vol-%; (□) CR-39 50 vol-%-MMA 50 vol-%; (Δ) CR-39 60 vol-%-MMA 40 vol-%; (○) CR-39 80 vol-%-MMA 20 vol-%; preirradiation:  $2 \times 10^6$  R at 25°C.

TABLE III  
Physical Properties of CR-39-Polyfunctional Monomer Systems<sup>a</sup>

Run	Monomer composition and concentrations, vol-%	Polymer appearance	Impact strength by FDA falling test, g	Heat durability by change in center angle, deg			
				100°C	120°C	140°C	160°C
1	CR-39 80-TMET 20	Nontransparent	15.8-20	1	1.5	1.5	2
2	CR-39 80-A-TMMT 20	Half-transparent	15.8-30	0	0	1	1
3	CR-39 80-A-TMM-3 20	Half-transparent	15.8	0	0	1	1.5
4	CR-39 80-A-TMPT 20	Transparent	15.8-30	0	1.5	1.5	1.5
5	CR-39 80-BG 20	Transparent	20	0.5	1	1	1
6	CR-39 80-NPG 20	Transparent	15.8-20	0	1	1	1
7	CR-39 80-A-NPG 20	Transparent	15.8	1	2	2	2
8	CR-39 80-4G 20	Transparent	20-40	3	4	—	—
9	CR-39 60-4G40	Transparent	20-30	2	3	3	3
10	CR-39 80-P2G 20	Transparent	20	1	1	—	—

<sup>a</sup> Impact resistance by FDA falling test is expressed by the weight of a steel ball which destroys a sample 5 cm × 5 cm × 2.1 mm thick when dropping from a height of 127 cm.

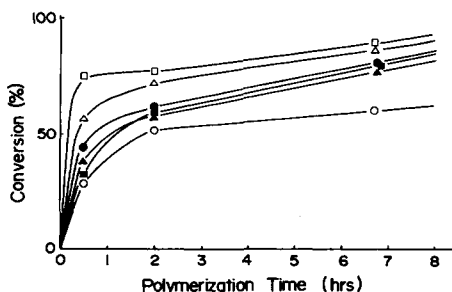


Fig. 6. Catalytic polymerization of CR-39-polyfunctional monomer system. Catalyst, isopropylperoxy carbonate (IPP), 2%: (□) CR-39 60 vol-%-AM4G 40 vol-%; (Δ) CR-39 60 vol-%-M4G 40 vol-%; (●) CR-39 80 vol-%-AM4G 20 vol-%; (▲) CR-39 80 vol-%-M4G 20 vol-%; (■) CR-39 80 vol-%-M9G 20 vol-%; (○) CR-39 60 vol-%-M9G 40 vol-%.

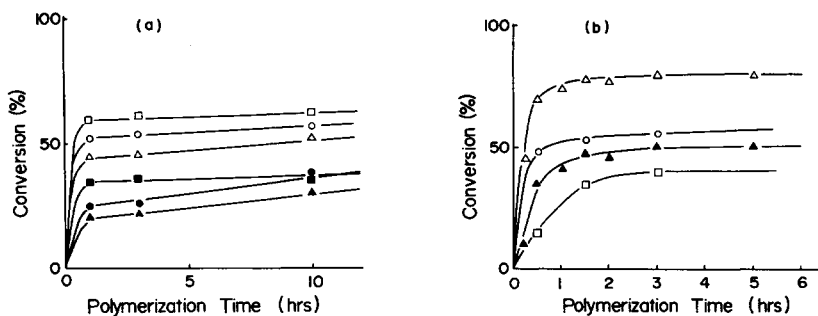


Fig. 7. Radiation-induced polymerization of (a) CR-39-polyfunctional monomer system: ( $\square$ ) CR-39 60 vol-%-AM4G 40 vol-%; ( $\circ$ ) CR-39 60 vol-%-M9G 40 vol-%; ( $\Delta$ ) CR-39 60 vol-%-M4G 40 vol-%; ( $\blacksquare$ ) CR-39 80 vol-%-AM4G 20 vol-%; ( $\bullet$ ) CR-39 80 vol-%-M9G 20 vol-%; ( $\blacktriangle$ ) CR-39 80 vol-%-M4G 20 vol-%. (b) CR-39-tetraethylene glycol dimethacrylate (69-40 vol-%) system: ( $\Delta$ ) 25°C; ( $\circ$ ) 0°C; ( $\blacktriangle$ ) -48°C; ( $\square$ ) -78°C. Dose rate:  $1 \times 10^6$  R/hr.

39-poor compositions in IPP-induced polymerization. This fact suggests that radicals formed by radiation or BPO easily induce degradative chain transfer to CR-39 monomer, while radicals by IPP are reactive for monomer addition of CR-39.

It was necessary to adopt a two-step polymerization consisting of radiation and catalytic steps to obtain complete, polymerized polymer. A postirradiation method after precatalytic polymerization was tried at first, as shown in Figure 4. The results indicated that a relatively large irradiation dose was necessary to complete the polymerization, and this does not satisfy the purpose of the present study to provide an efficient casting process. Postcatalytic polymerization after preirradiating polymerization was then tried and found most effective to complete the polymerization as quickly as possible, as shown in Fig-

TABLE IV  
Appearance of Cast Polymer Obtained by Radiation-Induced Polymerization of CR-39-Tetraethylene Glycol Dimethacrylate (60-40 vol-%) System

Polymerization Dose, roentgens	Temperature, °C	Appearance of polymer after irradiation	Appearance of polymer after curing
$2.5 \times 10^5$	-78	Colorless, transparent	Yellow, transparent
	-48	White, half-transparent	Yellow, transparent
	-24	White, half-transparent	Yellow half-transparent
	0	White, half-transparent	Yellow half-transparent
	25	White, turbid	Yellow, turbid
$5.0 \times 10^5$	-78	Colorless, transparent	Slightly yellow, transparent
	-48	Colorless, transparent	Slightly yellow, transparent
	-24	White, half-transparent	Slightly yellow, transparent
	0	White, half-transparent	Yellow, half-transparent
	25	White, turbid	Yellowish white, half-transparent
$1 \times 10^6$	-78	Colorless, transparent	Slightly yellow, transparent
	-48	Colorless, transparent	Slightly yellow, transparent
	-24	Colorless, transparent	Slightly yellow, transparent
	0	White, half-transparent	Yellow, transparent
	25	White, half-transparent	Yellow, transparent

TABLE V  
Physical Properties of CR-39-methyl methacrylate-Polyfunctional Monomer Systems<sup>a</sup>

24 Run no.	Monomer composition and concentration, vol-%	Polymer appearance	Impact strength by FDA falling test, g	Heat durability by change in center angle, deg			
				100°C	120°C	140°C	160°C
1	CR-39-MMA-A-TMPT (48-32-20)	Slightly brown, transparent	15.8-20	2	2	2	2
2	CR-39-MMA-A-TMPT (32-48-20)	Slightly brown, transparent	15.8-20	0	1	1	1
3	CR-39-MMA-A-TMM-3 (48-32-20)	Slightly brown, transparent	15.8-20	0	0	0	0
4	CR-39-MMA-A-TMM-3 (32-48-20)	Slightly brown, transparent	15.8-20	1	1.5	1	1
5	CR-39-MMA-A-NPG (48-32-20)	Colorless, transparent	15.8-20	2.5	3	3	3
6	CR-39-MMA-A-NPG (32-48-20)	Colorless, transparent	15.8-20	0	2	2	2
7	CR-39-MMA-NPG (48-32-20)	Slightly brown, transparent	15.8-20	0	0	0	0
8	CR-39-MMA-NPG (32-48-20)	Slightly brown, transparent	15.8	1.5	3	3	4
9	CR-39-MMA-BG (48-32-20)	Slightly brown, transparent	15.8-30	0	1	2	2
10	CR-39-MMA-BG (32-48-20)	Slightly brown, transparent	15.8-30	0	0	1.5	1.5
11	CR-39-MMA-4G (48-32-20)	Colorless, transparent	30	4	5	5	5
12	CR-39-MMA-4G (32-48-20)	Colorless, transparent	15.8-20	9	11	11.5	11.5
13	CR-39-MMA-4G (36-24-40)	Slightly brown, transparent	20-30	1	2	2	2
14	CR-39-MMA-4G (24-36-40)	Slightly brown, transparent	15.8-20	3	4	5	5

<sup>a</sup> The results of FDA test are expressed in the same way as in Table III.



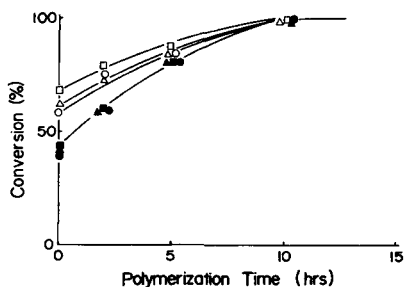


Fig. 8. two-step polymerization of CR-39-polyfunctional monomer system. Preirradiation-postcatalytic polymerization method: (□) CR-39 60 vol-%-AM4G 40 vol-%; (Δ) CR-39 60 vol-%-M4G 40 vol-%; (○) CR-39 60 vol-%-M9G 40 vol-%; (■) CR-39 60 vol-%-M4G 20 vol-%; (▲) CR-39 80 vol-%-M9G 20 vol-%; (●) CR-39 80 vol-%-M4G 20 vol-%; preirradiation:  $2 \times 10^6$  R at  $25^\circ\text{C}$  in the presence of 2% IPP; postcatalytic polymerization (curing):  $60^\circ\text{C}$ .

ure 5. In the precatalytic method, CR-39 was consumed predominantly, and the MMA unit entered the copolymer by the irradiation stage; while in the preirradiation method, MMA reacted more easily and then CR-39 entered the copolymer to form effective crosslinking. The latter type of reaction is more desirable for homogeneity of polymerization phase and uniform physical properties. The effect of various catalysts on the monomer reactivity ratio and physical properties in precatalytic and postirradiation methods may be one of future interesting problems. The polymerization of the CR-39-MMA-GMA system could be carried out effectively in a way similar to precatalytic and preirradiation polymerization methods. However, the heat durability of all these systems was not satisfactory in comparison with CR-39 resin. The polymerization and properties of CR-39-polyfunctional monomer systems were then investigated in the following section.

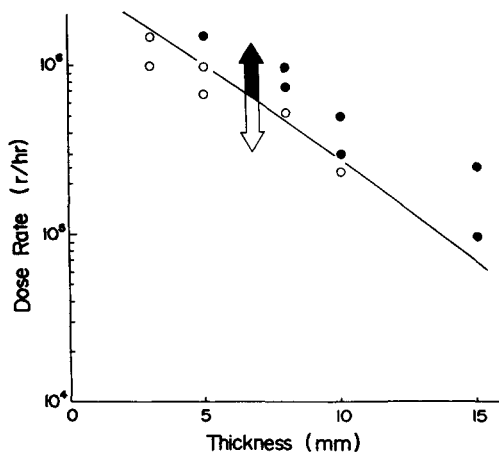


Fig. 9. Relation between dose rate, sample thickness, and optical strain formation in radiation-induced cast polymerization of CR-39-tetraethylene glycol dimethacrylate (60-40 vol-%) system:  $\blacktriangle$  optical strain formed in this region above the boundary condition curve;  $\circ$  no optical strain formed in this region below the boundary condition curve; total dose:  $1.5 \times 10^6$  R; temperature:  $-48^\circ\text{C}$ .

### Polymerization and Physical Properties of CR-39-Polyfunctional Monomer Systems

Screening of CR-39-polyfunctional monomer systems was carried out. Most polyfunctional monomers have a relatively large supercooling tendency, and almost all CR-39-polyfunctional monomer binary systems form fairly stable glassy state in polyfunctional monomer-richer compositions. The homogeneity of the polymerization phase varied with the monomer system, as shown in Table II. But it was noted that in many systems, including CR-39 and polyfunctional monomer, the polymerization at room temperature proceeded in the heterogeneous phase (precipitated state) while the polymerization phase was kept homogeneous (transparent state) at low temperatures. This is the great merit of low-temperature casting. The impact resistance by FDA standard test was better than that of poly(methyl methacrylate) in CR-39-polyfunctional monomer systems such as tetraethylene glycol dimethacrylate (diacrylate), triethylene glycol dimethacrylate (diacrylate), diethylene glycol dimethacrylate (diacrylate), and butanediol dimethacrylate (diacrylate).

Heat durability was excellent and satisfactory in most systems. The CR-39-tetraethylene glycol dimethacrylate (diacrylate) system was selected as the best system for a balanced level of properties.

The polymerization of CR-39-polyfunctional monomer systems was investigated as shown in Figures 6-8. The polymerizability was similar to that of

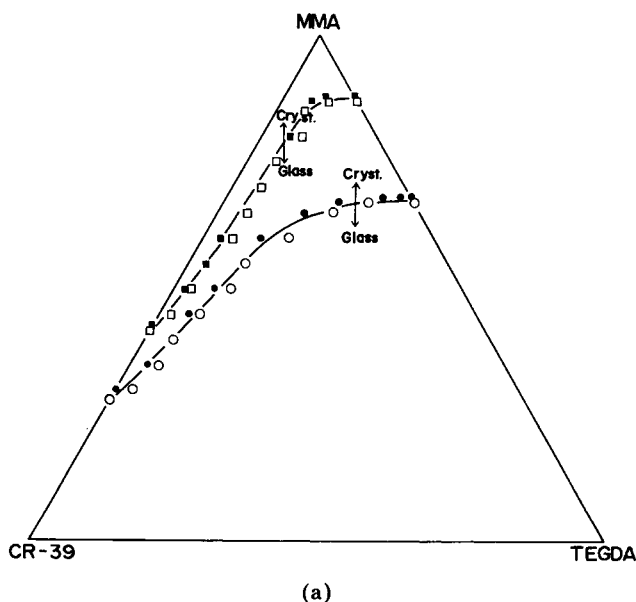
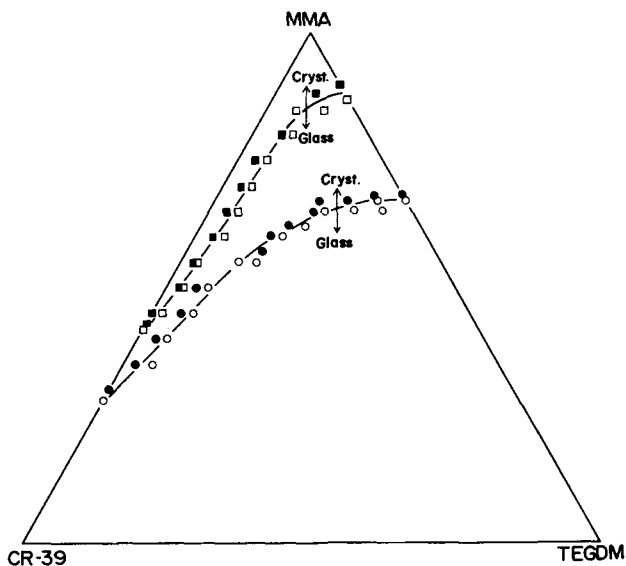
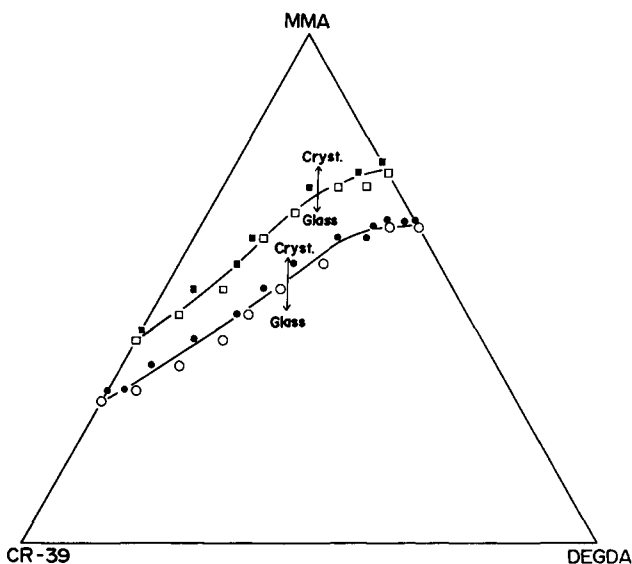


Fig. 10. Composition diagrams of glassification and crystallization in CR-39-MMA-polyfunctional monomer systems. (a) Diagram of CR-39-MMA-tetraethylene glycol diacrylate (A4G) system: (■) crystallized at  $-196^{\circ}\text{C}$ ; (□) glassified at  $-196^{\circ}\text{C}$ ; (●) crystallized at  $-78^{\circ}\text{C}$ ; (○) glassified at  $-78^{\circ}\text{C}$ . (b) Diagram of CR-39-MMA-tetraethylene glycol dimethacrylate (4G) system: (■) crystallized at  $-196^{\circ}\text{C}$ ; (□) glassified at  $-196^{\circ}\text{C}$ ; (●) crystallized at  $-78^{\circ}\text{C}$ ; (○) glassified at  $-78^{\circ}\text{C}$ . (c) Diagram of CR-39-MMA-diethylene glycol diacrylate (A2G) system: (■) crystallized at  $-196^{\circ}\text{C}$ ; (□) glassified at  $-196^{\circ}\text{C}$ ; (●) crystallized at  $-78^{\circ}\text{C}$ ; (○) glassified at  $-78^{\circ}\text{C}$ .



(b)



(c)

(continued from previous page)

CR-39-monomer systems, and two-step polymerization was necessary to complete the polymerization.

The casting of the CR-39-tetraethylene glycol dimethacrylate system was carried out, and the boundary condition curve of optical strain formation in the preirradiation step is shown in Figure 9. As shown, casting under polymerization conditions in regions above the boundary curve resulted in inner stress-type optical strain formation in the polymer. According to Figure 9, the casting 5-mm-thick samples, use of a dose rate of 1 megaroentgen (1 MR) per hr is possible,

TABLE VI  
Impact Resistance by JIS.K.6718 Method of CR-39-Methyl Methacrylate-Tetraethylene Glycol Dimethacrylate (36-24-40 vol-%) System<sup>a</sup>

Run no.	Material	Sample thickness, mm	JIS impact resistance										Izod value, kg-cm/cm <sup>2</sup>		
			200 g <sup>b</sup>					300 g							
			1.2 m <sup>c</sup>	1.4 m	1.6 m	1.8 m	2.0 m	1.2 m	1.4 m	1.6 m					
1	1.5 × 10 <sup>6</sup> R irradiated polymer	4.75	○	○	x										
2		4.75	○	○	○	○	○			○		x			11.4
3		4.80	○	○	○	x									
4		4.83	○	○	○	○	○			○		○		x	
5		4.60	○	○	○	○	x								
6	11.2 × 10 <sup>6</sup> R irradiated polymer	4.80	○	○	x										19.0
7		4.95	○	○	x										
8		5.00	○	○	x										
9		4.80	○	○	○	x				x					
10	CR-39 resin	4.90	○	○	○	○			○		x				18.5
11		4.92	○	○	○	○			○		○		x		
12		4.95	○	○○	○	○			x						

<sup>a</sup> X = Destroyed; O = not destroyed.

<sup>b</sup> Weight of ball.

<sup>c</sup> Falling height.

and so 2 hr of irradiation with 2 MR is enough for the preirradiation step. As the rate-determining step to polymerize without strain formation is the preirradiation step, the postcatalytic step can be carried out quickly without fear of strain formation at more elevated temperatures. The merit of radiation casting is thus clear in these CR-39-modified systems, because the catalytic casting process of CR-39 is well known as a less efficient process due to the very long

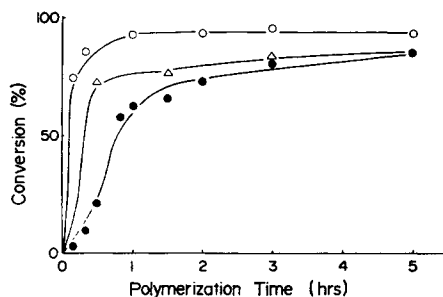


Fig. 11. Radiation-induced polymerization of CR-39-MMA-tetraethylene glycol dimethacrylate (TEGDM) system. Irradiation temperature: (O) 25°C; (Δ) 0°C; (●) -48°C; dose rate:  $1 \times 10^6$  R/hr.

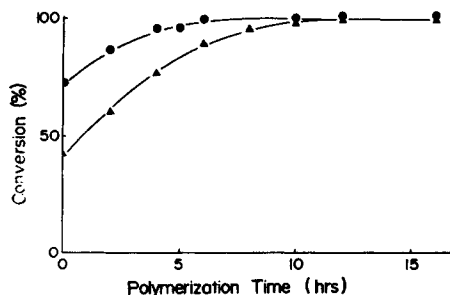


Fig. 12. Two-step polymerization of CR-39-tetraethylene glycol dimethacrylate (4G) (60-40 vol-%) system and CR-39-MMA-4G (36-24-40 vol-%) system. Preirradiation:  $1.5 \times 10^6$  R at 25°C in the presence of 2% IPP. Postcuring (catalytic polymerization) at 90°C: (●) CR-39-MMA-TEGDM; (▲) CR-39-TEGDM.

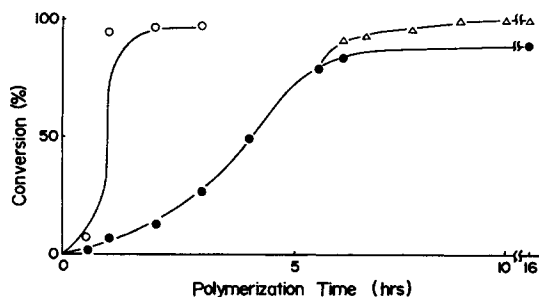


Fig. 13. Radiation-induced polymerization and two-step polymerization of CR-39-MMA-diethylene glycol diacrylate (A2G) (20-60-20 vol-%) system: (O) radiation-induced polymerization at 25°C, dose rate:  $1 \times 10^6$  R/hr; (●) radiation-induced polymerization at -48°C, dose rate:  $1 \times 10^6$  R/hr; (Δ) two-step polymerization, preirradiation:  $6 \times 10^6$  R at -48°C, postcuring: at 90°C.

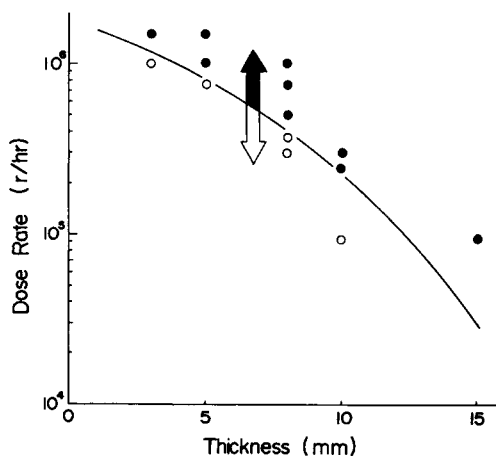


Fig. 14. Relation between dose rate, sample thickness, and optical strain formation in radiation-induced cast polymerization of CR-39-MMA-tetraethylene glycol dimethacrylate (36-24-40 vol-%) system: ● optical strain formed in this region above the boundary condition curve; ○ no optical strain formed in this region below the boundary condition curve; total dose:  $6 \times 10^6$  R; temperature:  $-48^\circ\text{C}$ .

casting time cycle required to obtain an article without defect and strain. The slope of the boundary curve in Figure 9 is lower than that in the casting of hydroxyethyl methacrylate in the small thickness region, and the type of strain formed in CR-39-modified systems is inner stress-type strain,<sup>3</sup> which is different from the thermal stream-type strain<sup>2</sup> in hydroxyethyl methacrylate. This fact suggests that stress relaxation is important even in thinner samples as for the inner stress-type strain formation caused by a crosslinking structure, while thermal stream-type strain formation becomes negligible in thinner samples.

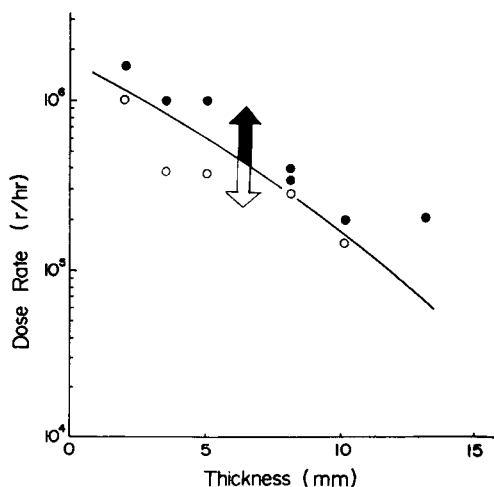


Fig. 15. Relation between dose rate, sample thickness and optical strain formation in radiation-induced cast polymerization of CR-39-MMA-diethylen glycol diacrylate (20-60-20vol-%). ● optical strain formed in this region above the boundary curve; ○ no optical strain formed in this region below the boundary condition curve; total dose:  $6 \times 10^6$  R; temperature:  $-48^\circ\text{C}$ .

### Polymerization and Physical Properties of CR-39-MMA-Polyfunctional Monomer Systems

It was expected that the three-component system would further increase glass-forming property in the larger-composition range, and therefore polyfunctional monomers which showed homogeneity of the polymerization phase with CR-39 were chosen. As shown in Figure 10, three-component systems had a more stable glassy phase over a wide composition range. These systems did not crystallize at low temperatures nor during the course of the temperature rise after supercooling.

As shown in Table III, for a example, it should be noted that heterogeneous precipitation of white, turbid polymer occurred at room-temperature polymerization as recognized in the case of binary systems, which did not become homogeneous even after heating. On the other hand, in the polymerization at low temperature, a homogeneous polymerization phase was maintained during the entire polymerization stage (Table IV).

The difference in phase homogeneity perhaps resulted from the difference in the reactivity of the crosslinking monomer. That is, it is possible that at the room-temperature early polymerization stage, the crosslinking monomer predominantly formed an enriched crosslinking structure and precipitated in the relatively early relatively uniformly perhaps because of the large viscosity and reduced mobility of the glass-forming system. The impact resistances of the systems are shown in Table V; CR-39-MMA-polyfunctional monomers such as tetraethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, and butanediol dimethacrylate were found to be excellent in FDA standard tests.

The Izod impact test and the JIS drop impact resistance test were done for the CR-39-MMA-4G system, and the results are shown in Table VI. Impact resistance was almost the same or superior to that of poly(methyl methacrylate). Heat durability was good and satisfactory in comparison with CR-39 resin and poly(methyl methacrylate). The results of the polymerization are shown in Figures 11-13. The two-step polymerization was necessary as in all systems including CR-39, and the system could be completely polymerized by quick postheating with IPP, whatever preirradiation dose or temperature was used or whatever conversion had been attained in the preirradiation polymerization stage. Figures 14 and 15 show the results of casting polymerization of the CR-39-MMA-4G system, and CR-39 MMA-A2G system. These results are similar to those of the CR-39-4G system, and the merit of radiation casting at low temperature is obvious.

It can be concluded that the application of the new radiation casting technique to CR-39-modified systems produces physical properties such as impact resistance and heat durability which are superior or equal to those of poly(methyl methacrylate) and CR-39 resin. These polymer articles could be cast without optical strain in a much shorter time cycle than with any conventional catalytic method.

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