

Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperatures. IV. Casting and Polymer Properties of Monomeric Systems Including Polyfunctional Monomers

H. OKUBO, F. YOSHII, S. HONDA, and I. KAETSU, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki-Shi, Gunma-ken, Japan, and Kuramoto Sangyo Company, Kawagoe-shi, Saitama-ken, Japan*

Synopsis

The applicability to radiation-induced cast polymerization of polyfunctional monomers or systems including them was studied. Most of polyfunctional monomers could be glassified and were applicable to radiation casting. The effect of tetraethylene glycol diacrylate on inner-plasticized comonomer systems was studied in detail. It was found that the glass-forming property increased by the addition of tetraethylene glycol diacrylate and that heat durability improved satisfactorily. The formation of optical strain in casting was relatively easier in polyfunctional monomers including systems due to inner stress, although the merit of radiation casting was still obvious.

INTRODUCTION

In a previous study,¹ glassifying comonomer systems were produced by adding the inner-plasticizing component in a suitable balance of impact resistance and resin hardness. However, it was desired further to improve their heat resistance or thermal durability for practical use at relatively higher temperatures such as near 100°C. The best way to improve heat resistance is to produce a cross-linked structure by using polyfunctional monomers. In this case, it is important to improve heat resistance without impairing impact strength, because a cross-linked structure often decreases the impact resistance. It was also found that the addition of some kind of polyfunctional monomer improved not only physical properties, but also polymerizability and glass-forming property. This report described the results of investigations in polymerization casting and polymer properties of glass-forming monomer systems including polyfunctional components.

EXPERIMENTAL

Monomers were used after purification of commercially available monomers by conventional methods. That is, low boiling-point components were purified

TABLE I
Physical Properties of Polyfunctional Monomers^a

Run no.	Polyfunctional monomer	Homogeneity of polymeric phase	Glass-forming property	Hardness	Impact resistance (FDA testing), g
1	Polyethylene glycol dimethacrylate	yes	yes	soft	200
2	Polypropylene glycol dimethacrylate	yes	yes	soft	100
3	Tetraethylene glycol dimethacrylate	yes	yes	hard	15.8
4	Tetraethylene glycol diacrylate	yes	yes	soft	100
5	Triethylene glycol diacrylate	yes	yes	hard	20
6	Diethylene glycol diacrylate	yes	yes	hard	30
7	Dipropylene glycol dimethacrylate	yes	yes	hard	15.8
8	Trimethylolethane trimethacrylate	yes	yes	hard	10
9	Trimethylolpropane triacrylate	yes	yes	hard	10
10	Trimethylolpropane trimethacrylate	yes	yes	hard	10
11	Neopentyl glycol dimethacrylate	yes	unstable	hard	10
12	Neopentyl glycol diacrylate	yes	unstable	hard	20
13	1,3-Butylene glycol dimethacrylate	yes	unstable	hard	10

^a Impact resistance by FDA testing 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. 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.

by distillation and high boiling-point component such as polyfunctional monomers, by passing them through columns filled with ion exchange resin for hydroquinone removal. Hexanediol monoacrylate (HDMA) was prepared by reacting hexanediol with acrylic acid.

Glass-forming property was tested by the appearance of glassification of the sample in a cooling bath kept at a definite temperature. Glass transition temperature (T_g) was determined by differential thermal analysis.

Polymerization was carried out by 100,000 Ci irradiation of γ -rays from a ⁶⁰Co

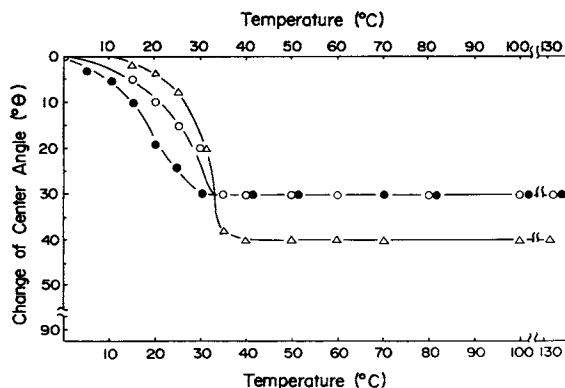


Fig. 1. Heat durability of new organic glass materials including tetraethylene glycol diacrylate (TEGDA): (O) no. 42 composition 50 vol%-TEGDA 50 vol-%; (●) no. 43 composition 70 vol%-TEGDA 30 vol-%; (Δ) no. 29 composition 70 vol%-TEGDA 30 vol-%; sample: polymer obtained at 25°C by irradiation of 1×10^6 R.

source in a reaction bath kept at a definite temperature using a casting frame constructed in the same manner as described in previous reports.^{2,3}

Optical strain of polymer was observed by a photoelastic strain gauge including polarization plates. Impact strength was estimated by the FDA test method and the JIS impact resistance method.¹

Heat durability was estimated by reading the change in the center angle of the sample during weighing and heating in equipment in which the sample was gripped at one end and loaded by a weight at the other end.

Bending strength and stretch strength were measured by the JIS-K6911 method.

The weather durability was estimated by change in appearance such as coloring and crack formation and by impact resistance after sunshine exposure and the xenon Weatherometer test.¹

RESULTS AND DISCUSSION

Properties of Polyfunctional Monomer Single Systems

To improve heat resistance of inner-plasticized systems without decreasing impact resistance, individual properties of polyfunctional components were investigated. The properties were shown in Table I. It should be noted that most polyfunctional monomers were stable glass-forming monomers because of their bulky molecular structure and that, conveniently, the addition of polyfunctional monomer increased the stability of the glass-forming property. It was found that polyethylene glycol difunctional monomers such as tetraethylene glycol dimethacrylate (diacrylate), triethylene glycol dimethacrylate (diacrylate), and diethylene glycol dimethacrylate (diacrylate) were relatively good in impact strength. A suitable length of oxyethylene unit was necessary to be consistent in having both polymer hardness and impact resistance in homopolymer of polyfunctional monomers. Suitable length was also required in the case of adding to inner-plasticized systems in order to be compatible in increasing heat resistance and in keeping impact resistance. The above-mentioned polyfunctional monomers satisfied this condition.

Addition Effect of Polyfunctional Monomer to Inner-Plasticized System

The effect of addition of various polyfunctional monomers to inner-plasticized systems¹ such as no. 29, no. 42, and no. 43 are summarized in Table II. It was ascertained that the addition of di-, tri- or tetraethylene glycol diacrylate was effective in improving the heat resistance and reaching a balance between the impact resistance and heat resistance. The final selected system consisted of inner-plasticized composition 70% and tetraethyleneglycol diacrylate (A4G) 30%. The results of impact resistance, heat durability, and weather durability in finally selected systems are shown in Figure 1 and Tables III, IV, and V. The general physical properties of the best system are summarized in Table VI.

It is concluded that newly found organic glass is superior to poly(methyl methacrylate) in impact resistance and heat durability, especially at temperatures above 100°C and almost equivalent to CR-39 resin in heat resistance.

TABLE II
Effect of Addition of Polyfunctional Monomers to Inner-Plasticized Systems^a

Run no.	Monomer system	Appearance of polymer	Impact resistance by FDA test, g	Heat durability by change of center angle, deg
1	No. 29 90-TMPT 10	hard, elastic	20-50	8
2	No. 29 80-TMPT 20	hard, brittle	15.8-20	
3	No. 29 90-TMET 10	hard, elastic	40	25
4	No. 29 80-TMET	hard, elastic	15.8	
5	No. 29 90-ATMPT 10	hard, elastic	30	15
6	No. 29 80-ATMPT 20	hard, elastic	30	4
7	No. 29 90-NPG 10	hard, elastic	30-50	35
8	No. 29 80-NPG 20	hard, elastic	15.8-40	12.5
9	No. 29 90-ANPG 10	soft	30-100	35
10	No. 29 80-ANPG 20	hard, elastic	15.8-40	16
11	No. 29 90-BG 10	hard, elastic	100-200	30
12	No. 29 80-BG 20	hard, elastic	30-50	0
13	No. 29 90-P2G	soft	15.8	
14	No. 29 80-P2G 20	hard, elastic	15.8	
15	No. 29 90-A3G 10	soft	200	
16	No. 29 50-A3G 50	hard, elastic	20-30	4
17	No. 29 90-P9G	soft	100-200	
18	No. 29 50-P9G 50	soft	200	
19	No. 42 90-TMPT 10	hard, elastic	15.8	
20	No. 42 80-TMPT 20	hard, elastic	15.8	
21	No. 42 90-TMET 10	hard, brittle	20	
22	No. 42 80-TMET 20	hard, brittle	15.8	15
23	No. 42 90-ATMPT 10	hard, elastic	15.8-30	
24	No. 42 80-ATMPT 20	hard, elastic	15.8	

25	No. 42 90-NPG 10	hard, elastic	15.8	
26	No. 42 80-NPG 20	hard, brittle	15.8	
27	No. 42 90-ANPG 10	soft	20-40	15
28	No. 42 80-ANPG 20	hard, elastic	15.8-20	
29	No. 42 90-BG 10	hard, elastic	40-100	15
30	No. 42 80-BG 20	hard, elastic	15.8-20	
31	No. 42 50-P2G 50	hard, elastic	15.8-30	
32	No. 42 90-A3G 10	hard, brittle	15.8	
33	No. 42 50-A3G 50	hard, elastic	30	
34	No. 43 90-TMPT 10	hard, elastic	15.8	
35	No. 43 80-TMPT 20	hard, brittle	15.8	
36	No. 43 90-TMET 10	hard, elastic	15.8	
37	No. 43 80-TMET 20	hard, brittle	15.8	
38	No. 43 90-ATMPT 10	hard, elastic	15.8	
39	No. 43 80-ATMPT 20	hard, brittle	15.8	
40	No. 43 90-NPG 10	hard, elastic	20-30	6
41	No. 43 80-NPG 20	hard, elastic	15.8	
42	No. 43 90-ANPG 10	hard, elastic	15.8	
43	No. 43 80-ANPG 20	hard, elastic	15.8	
44	No. 43 90-BG 10	hard, elastic	15.8	
45	No. 43 80-BG 20	hard, elastic	15.8	
46	No. 43 90-P2G	hard, elastic	20	23
47	No. 43 50-P2G 50	hard, brittle	15.8	
48	No. 43 90-A3G 10	hard, elastic	30-40	
49	No. 43 50-A3G 50	hard, elastic	15.8-40	5

^a TMPT: Trimethylolpropane trimethacrylate; TMET: trimethylolthane trimethacrylate; A-TMPT: trimethylolpropane triacrylate; NPG: neopentyl glycol dimethacrylate; A-NPG: neopentyl glycol diacrylate; BG: 1,3-butylene glycol dimethacrylate; P2G: dipropylene glycol dimethacrylate; A3G: triethylene glycol diacrylate; P9G: polypropylene glycol dimethacrylate; no. 29: butyl acrylate-methyl methacrylate-glycidyl methacrylate (35-35-30 vol-%); no. 42: methyl methacrylate-hexanediol monoacrylate-hexanediol diacrylate-hexanediol (60-31-8.7-4.4 vol-%); no. 43: hydroxyethyl methacrylate-methyl methacrylate-hexanediol monomethacrylate-hexanediol diacrylate-hexanediol (35-30-26.6-17.9-4.7 vol-%).

TABLE III
Impact Resistance by FDA Testing Method and Heat Durability of Inner-Plasticized Composition^a

Run no.	Material	Impact resistance by FDA test after heat treatment, g			No heating	No heating	Heat durability by center angle change, deg		
		100°C, 5 hr	100°C, 10 hr	100°C, 16 hr			100°C, 2.5 hr	100°C, 10 hr	100°C, 16 hr
1	no. 29 90-4G 10	30-50	30-40	30	37	26	24	25	
2	no. 29 80-4G 20	15.8-30	15.8-30	15.8-30	21	25	24	24	
3	no. 29 75-4G 25	30-100	15.8-40	15.8-30	12	15	9	12	
4	no. 29 70-4G 30	30-50	10-20	15.8-30	6	4	6	7	
5	no. 29 50-4G 50	30	15.8-30	15.8-30	3	4	5	7	
6	no. 29 80-A4G20	40-100	15.8-30	15.8-100	12	14	14	13	
7	no. 29 75-A4G 25	40-300	20-100	30-50	4	10	10	9	
8	no. 29 70-A4G 30	50-200	15.8-40	40-50	4	4	4	6	
9	no. 29 50-A4G 50	40-100	20-100	20-30	5	5	5	5	
10	no. 42 80-40	30	10-30	10-30	10	9	10	10	
11	no. 42 75-4G 25	20-40	20-30	15.8-20	11	8	9	9	
12	no. 42 70-4G 30	20-40	10-15.8	15.8-20	6	6	10	10	
13	no. 42 75-A4G 25	20-50	15.8-30	15.8-100	77	12	12	8	
14	no. 42 70-A4G 30	40-50	20	30-50	3	7	7	2	
15	no. 43 75-4G 25	15.8-40	20-30	15.8-30	2	8	7	4	
16	no. 43 70-4G 30	15.8-40	20-30	15.8-30	5	3	6	4	
17	no. 43 50-4G 50	15.8-20	15.8	15.8-40	3	6	5	7	
18	no. 43 75-A4G 25	15.8-40	15.8-40	20-30	2	6	5	6	
19	no. 43 50-A4G 50	20-40	30	20-30	30	6	6	3	

^a Tetraethylene glycol dimethacrylate (4G) and diacrylate (A4G) systems after heat treatment and no heat treatment.

Bending and stretching strengths are inferior to those of poly(methyl methacrylate) and near to those of CR-39 resin. The physical properties are predominantly affected by monomer composition, and difference in polymerization temperature did not have an essential effect. In Figure 2, bending strength and Young's modulus in polymers obtained at 25° and -50°C are compared. A slight difference was observed. The result of copolymer analysis of residual monomer composition by gas chromatography showed that copolymer composition at any polymerization stage did not seriously differ between 25° and -50°C.

Glass-Forming Property of Systems Including Polyfunctional Monomer

The change in glass-forming property by addition of polyfunctional monomer was investigated. As shown in Figure 3, for example, the glass-forming

TABLE IV
Impact Resistance by JIS K 6718 Method of Inner-Plasticized Composition^a

Materials composition vol-%	Sample thickness, mm	Impact resistance by JIS-K-6718 method											
		200 g ^b				300 g				500 g			
		0.7 ^c	1.0	1.4	2.0	0.7	1.0	1.4	2.0	0.7	1.0	1.4	2.0
Before Weather Test													
No. 29-A4G	4.95	○	○	x									
70-30	5.00	○	○	○	○	○	○	○	○	○	○	x	
	5.10	○	○	○	○	○	○	○	○	○	○	○	○
	5.20	○	○	○	○	○	○	○	○	○	○	○	x
No. 42-A4G	4.60	○	○	○	x								
70-30	4.60	○	○	○	x								
	4.60	○	○	○	x								
	4.60	○	○	○	○	○	○	○	○	○	x		
No. 43-A4G	4.60	○	○	○	○	○	○	○	○	○	○	x	
70-30	4.70	○	○	○	○	○	○	○	○	○	x		
	4.70	○	○	○	○	○	○	○	○	○	○	x	
	4.80	○	○	○	○	○	○	○	○	○	○	○	x
PMMA	5.00	○	○	○	x								
	5.00	○	○	○	x								
	5.00	○	○	○	x								
	5.00	○	○	○	x								
After Weather Test (1046 hr)													
No. 29-A4G	4.50	○	○	○	○	○	○	○	○	○	○	○	x
70-30	4.70	○	○	x									
	4.80	○	○	○	○	x							
	5.40	○	○	○	○	○	○	○	○	○	○	x	
No. 42-A4G	5.00	○	○	○	○	x							
70-30	5.00	○	○	○	○	x							
	5.00	○	○	○	○	○	○	○	○	○	○	x	
	5.10	○	○	○	○	○	○	○	○	○	○	x	
No. 43-A4G	4.70	○	○	○	○	○	○	x					
70-30	4.75	○	○	○	x								
	4.75	○	○	○	x								
	4.75	○	○	x									

^a Tetraethylene glycol diacrylate (A4G) systems before and after weathering test; ○ = not destroyed; x = destroyed.

^b Ball weight.

^c Falling height, in meters.

property of inner-plasticized system greatly increased, and the glass-forming composition range was much enlarged by the addition of a polyfunctional component because most polyfunctional monomers were very stable glass-forming monomers. Consequently, the addition of polyfunctional monomer was beneficial for radiation casting as well as for improving the physical properties.

Volume Shrinkage in Systems Including Polyfunctional Monomer

The volume shrinkage accompanying the polymerization was investigated. For example, the results in the no. 29-A4G system is shown in Figure 4. Volume shrinkage decreased with increasing A4G composition, because the volume change of A4G was smaller than that of no. 29. However, the polymerization rate and gel formation rate by crosslinking was much higher in the A4G-including system than in the original no. 29, and as a result the optical strain formation due to contraction stress increased in the A4G-including system, as stated later.

Polymerization Rate of Systems Including Polyfunctional Monomer

The initial polymerization rates of A4G-including systems were plotted against polymerization temperature in Figure 5. The temperature dependence of the initial rate has a maximum at low temperature above the glass transition temperature (T_g) as generally observed in radical polymerization of glass-forming monomers. This maximum rate temperatures T_p were about -75° and -85°C

TABLE V
Impact Resistance by FDA Testing Method of Inner-Plasticized Composition^a

Run no.	Material composition	Impact resistance by FDA testing	
		Before weather test	After weather test
1	no. 29 90-4G 10	30	15.8
2	no. 29 70-4G 30	15.8-20	15.8
3	no. 29 80-A4G 20	40-100	15.8
4	no. 29 70-A4G 30	15.8-40	10-15.8
5	no. 29 25-A4G 75	30-100	15.8-20
6	no. 42 80-4G 20	15.8-20	10-15.8
7	no. 42 70-4G 30	10-20	15.8
8	no. 42 80-A4G 20	30	15.8-20
9	no. 42 75-A4G 25	20-100	20-40
10	no. 42 70-A4G 30	30-100	20-50
11	no. 42 50-A4G 50	40-50	30-50
12	no. 42 25-A4G 75	15.8-30	cracking
13	no. 43 70-4G 30	15.8-40	15.8
14	no. 43 75-A4G 25	30-50	15.8-50
15	no. 43 70-A4G 30	30	30-40
16	no. 43 50-A4G 50	15.8-30	cracking
17	CR-39	40-50	40-50
18	PMMA	15.8	15.8

^a Tetraethyleneglycol dimethacrylate (4G) and diacrylate (A4G) systems before and after weathering test by xenon Weatherometer for 1046 hr.

TABLE VI
Physical Properties of Best Composition in Inner-Plasticized Composition^a

Properties	No. 29-A4G 70-30 vol-%	No. 42-A4G 70-30 vol-%	No. 43-A4G 70-30 vol-%	PMMA	CR-39 resin
Impact resistance FDA method, g	30-100	20-50	20-30	15.8	40
JIS K 6718 method, g, m	500 g, 2 m	500 g, 2 m	400 g, 2 m	200 g, 2 m	
Izod method JIS K 6911, kg-cm/cm ²	32.0	18.5	15.7	18.7	18.4
Heat durability by change of center angle, deg					
100°C, 20 min, 20 g	40	30	30	10	<10
150°C, 20 min, 20 g	40	30	30	90	<10
H-value after falling sand method, %	29	22	22	25	56
Pencil hardness	HB	HB	HB	5H	2H
Stretching strength by JIS 6911, kg/cm ²	1.3	1.7	1.9	5.3	2.5
Bending strength by JIS 6911, Kg/cm ²		2.9	2.7	10.5	17.6
Burning rate by JIS 6911, cm/min		1.80	1.46	3.3	
Light transmittance by ASTM D 1003, %	91	93	92	93	93
Refraction index by ASTM D 542	1.495	1.497	1.500	1.49	1.498

^a Tetraethyleneglycol diacrylate (A4G) system.

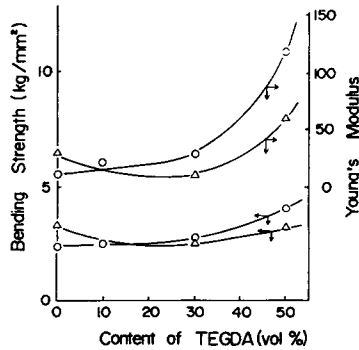


Fig. 2. Effect of tetraethylene glycol diacrylate addition on bending strength and Young's modulus of new organic glass materials: (O) polymer obtained at -50°C polymerization; (Δ) polymer obtained at 25°C polymerization; total dose: 1×10^6 R.

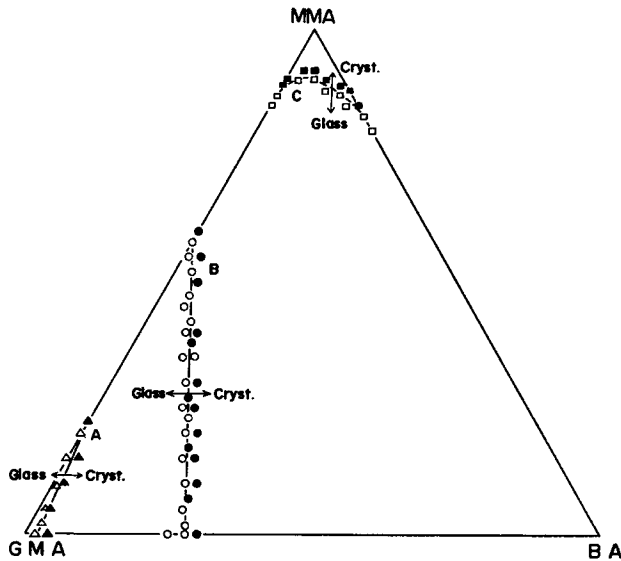


Fig. 3. Glassifying property of monomeric systems for new organic glass materials. (a) boundary condition curve of crystallization and glassification at cooling temperature -78°C in No. 29 composition system: (Δ) glassified; (∇) crystallized. (b) Boundary condition curve of crystallization and glassification at cooling temperature -196°C in no. 29 composition system: (O) glassified; (\bullet) crystallized. (c) Boundary condition curve of crystallization and glassification at cooling temperature -78°C in no. 29 composition-tetraethylene glycol diacrylate system. Content of tetraethylene glycol diacrylate is 30 vol-% of total monomer composition. The composition of the 70% of the other three monomers is shown in the three-component map: (\square) glassified; (\blacksquare) crystallized.

for the two systems. Glass transition temperatures were found to be about -105° and -115°C , respectively, for the two systems.

The time-conversion curve in the polymerization of the no. 29-A4G system is shown in Figure 6. Relation between the gel fraction of polymer and the polymerization time is shown in Figure 7. From these results, it is obvious that the polymerization rate increased greatly with increase in A4G content and the gel formation was also much accelerated by the addition of A4G. The reason may be that the polymerization rate increased because of the polyfunctionality

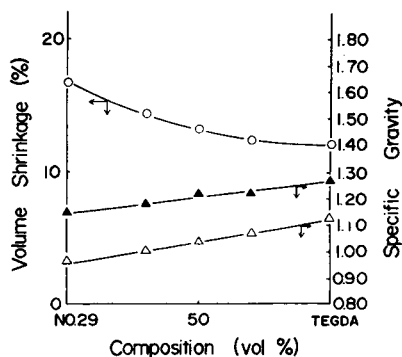


Fig. 4. Relation between volume shrinkage, specific gravity, and composition in no. 29-tetraethylene glycol diacrylate system: (O) volume shrinkage accompanied by polymerization at -50°C ; (Δ) specific gravity of monomer system at -50°C ; (\blacktriangle) specific gravity of polymerized system at -50°C .

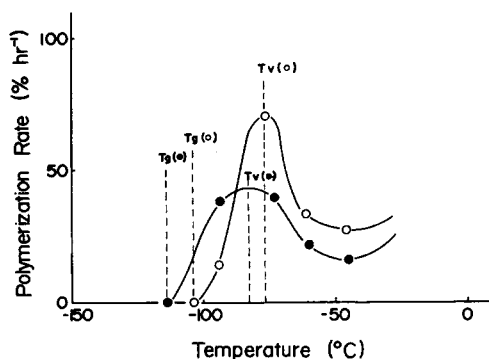


Fig. 5. Effect of polymerization temperature on initial polymerization rate of No. 29 composition-tetraethylene glycol diacrylate system and no. 43 composition-tetraethylene glycol diacrylate system: (O) no. 43 composition 70 vol-%-A4G 30 vol-%; (\bullet) no. 29 composition 70 vol-%-TEGDA 30 vol-% dose rate: T_g : glass transition temperature; T_v : temperature of apparent maximal polymerization rate.

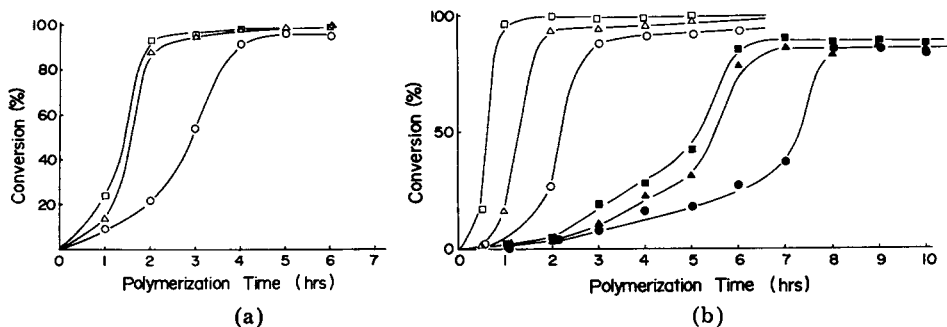


Fig. 6. Relation between conversion and polymerization time in no. 29 composition-tetraethylene glycol diacrylate (A4G) system. (a) Time-conversion curve at 25°C : (O) no. 29 composition; (Δ) no. 29 composition 95 vol-%-A4G 5 vol-%; (\square) no. 29 composition 90 vol-%-A4G 10 vol-%; dose rate: 2×10^5 R/hr under vacuum. (b) Time-conversion curve at -50°C : (\bullet) no. 29 composition; (\blacktriangle) no. 29 composition 95 vol-%-A4G 5 vol-%; (\blacksquare) no. 29 composition 90 vol-%-A4G 10 vol-%; (O) no. 29 composition 80 vol-%-A4G 20 vol-%; (Δ) no. 29 composition 70 vol-%-A4G 30 vol-%; (\square) no. 29 composition 50 vol-%-A4G 50 vol-%; dose rate: 1×10^6 R/hr under vacuum.

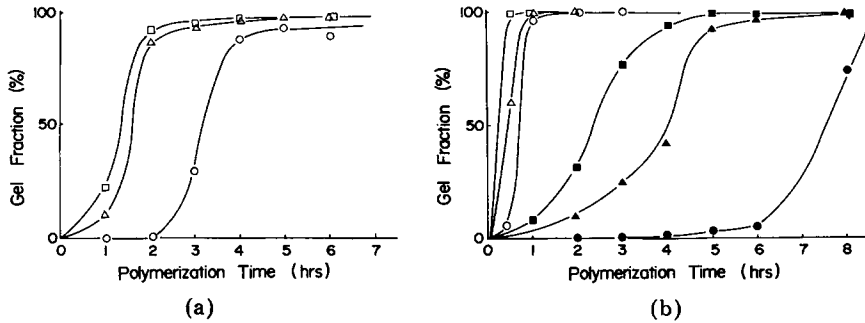


Fig. 7. Relation between gel fraction of polymer and polymerization time in no. 29 composition-tetraethylene glycol diacrylate (A4G) system. (a) Time-gel fraction curve at 25°C: (O) no. 29 composition; (Δ) no. 29 composition 95 vol-%-A4G 5 vol-%; (\square) no. 29 composition 90 vol-%-A4G 10 vol-%; dose rate: 2×10^5 R/hr under vacuum. (b) Time-gel fraction curve at -50°C: (\bullet) no. 29 composition; (\blacktriangle) no. 29 composition 95 vol-%-A4G 5 vol-%; (\blacksquare) no. 29 composition 90 vol-%-A4G 10 vol-%; (O) no. 29 composition 80 vol-%-A4G 20 vol-%; (\triangle) no. 29 composition 70 vol-%-A4G 30 vol-%; (\square) no. 29 composition 50 vol-%-A4G 50 vol-%; dose rate: 1×10^6 R/hr under vacuum.

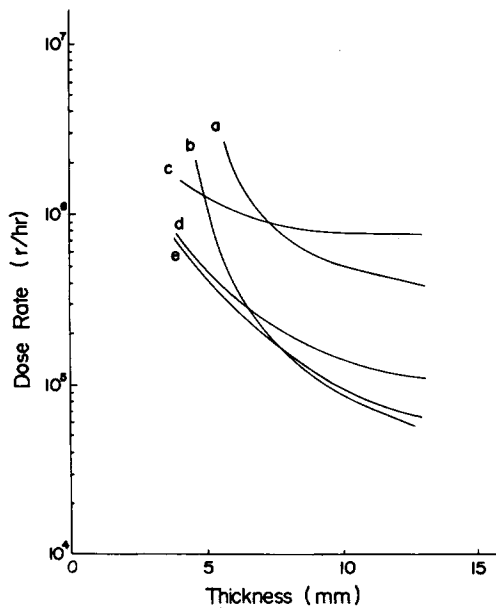


Fig. 8. Effect of dose rate and sample thickness on optical strain formation in casting of new organic glass systems at -50°C. The condition in the region above the curves gave the optical strain in cast polymer, and the condition in the region below the curves gave no optical strain in polymer: (a) no. 43 composition; (b) no. 43 composition 70 vol-%-A4G 30 vol-%; (c) no. 29 composition; (d) no. 42 composition 50 vol-%-A4G 50 vol-%; (e) no. 29 composition 70 vol-%-A4G 30 vol-%; total dose: 1×10^6 R; sample scale: 20 cm \times 10 cm.

of the monomer and also because of a decrease in termination rate by formation of crosslinking.

The gel formation also occurred in the absence of A4G at a much slower rate, and it could be attributed to the vinyl crosslinking by radical recombination of main chain radicals formed in the irradiated no. 29 copolymer. The great acceleration of polymerization rate by polyfunctional monomer is very convenient for practical casting at low temperatures.

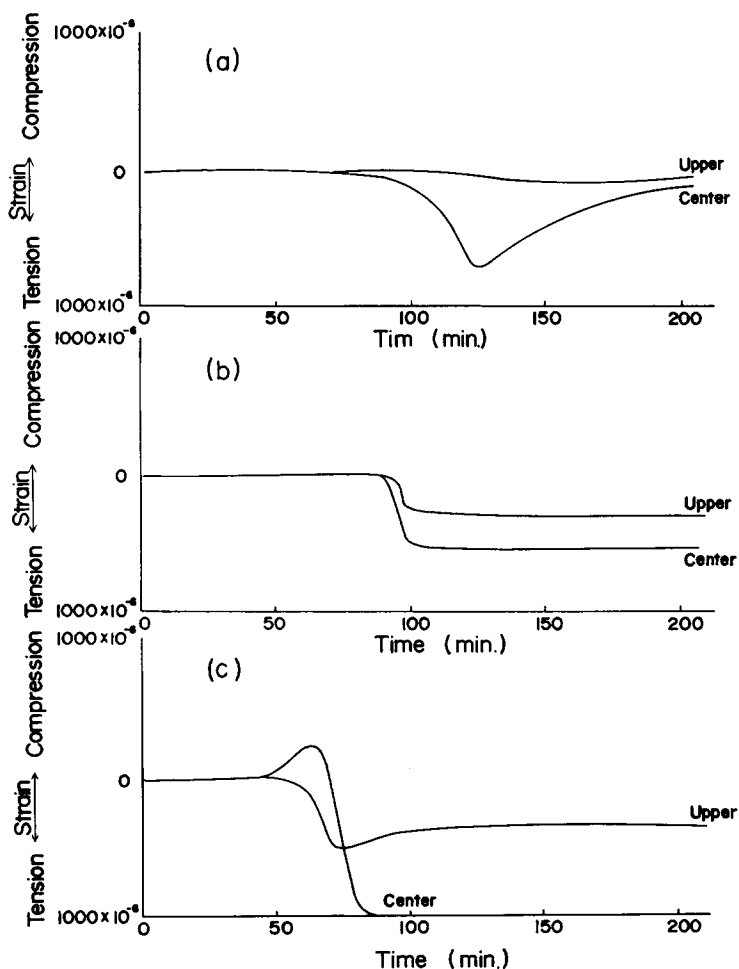


Fig. 9. Relation between stress and polymerization time in dynamic strain gauge in casting of new organic glass systems at 25°C: (a) time-stress curve in no. 29 composition 90 vol-%-A4G 10 vol-%; (b) time-stress curve in no. 29 composition 70 vol-%-A4G 30 vol-%; (c) time-stress curve in no. 29 composition 50 vol-%-A4G 50 vol-%; dose rate: 2×10^5 R/hr; sample scale: 20 cm \times 10 cm \times 5 mm thick.

Casting of Systems Including Polyfunctional Monomer

The casting of polyfunctional monomer-including systems was studied in sheet plate by radiation polymerization. In the previous reports,²⁻⁴ the authors pointed out that two types of optical strain could be distinguished, that is, the thermal stream-type strain and the inner stress-type strain. It was found that inner stress-type strain formed predominantly without exception in the casting of monomer systems including a polyfunctional component. In Figure 8, the boundary condition curves of optical strain formation in casting of monomeric systems including A4G were plotted. The boundary curves were obtained at low temperatures, but at room temperature, all conditions at dose rates higher than 1×10^4 R/hr gave strain formation. The merit of casting at relatively low temperatures is obvious. It is also obvious that boundary curves were lowered

with increasing A4G content. The addition of A4G accelerated the strain formation to some degree. The formed strain was an inner stress-type strain⁴ generally present in polyfunctional monomer-including systems.

Figure 9 shows the change of strain gauge signal with the time in casting of the no. 29-A4G system. The stress formed with the initiation of polymerization gradually relaxed with time in the no. 29-10%A4G system, but it did not relax with time and was not removed even by thermal annealing in the no. 29-50%A4G system. Inner stress-type strain formed even in samples of small thickness, and the slope of the boundary curve of this strain was relatively smaller than in the original no. 29 system, as seen in Figure 8. These results suggest that strain in polyfunctional systems forms as a result of poor relaxation of inner stress caused by volume shrinkage, perhaps due to the formation of crosslinked structure in the polymer. More detailed analysis of inner stress-type strain formation will be forthcoming articles.

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