

# Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperatures. VI. Casting Polymerization of Methyl Methacrylate Prepolymer by Irradiation

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## Synopsis

Casting of methyl methacrylate prepolymer by irradiation at relatively low temperatures was studied. It was difficult to completely glassify the methyl methacrylate monomer and prepolymer, and so the casting was carried out at temperatures above its melting point ( $-48^{\circ}\text{C}$ ). The optical strain formed in this stream remained of the stress type, and optical strain formation was reduced with increasing prepolymer concentration and decreasing temperature.

## INTRODUCTION

The authors have studied a new casting process of organic glass by radiation-induced polymerization in the supercooled phase using glass-forming monomers.<sup>1-3</sup> Remarkable characteristics were found in radiation casting. That is, the organic glass article could be polymerized without forming any optical strain in a very short casting time cycle.

Some new monomer systems for organic glass applicable to radiation casting with an excellent balance of physical properties were screened and reported in previous papers.<sup>4-6</sup> Multicomponent systems including inner-plasticizing comonomer and polyfunctional comonomer and also CR-39-modified systems having glass-forming property, good heat durability, and good impact strength were found.

These are practically useful systems. But to further enlarge the general availability of the radiation casting technique, it is important to apply it to methyl methacrylate (MMA), a most popular organic glass material, or, its modified systems. Joklik investigated casting of methyl methacrylate by irradiation more than ten years ago.<sup>7,8</sup> However, his was a preirradiation method; that is, only prepolymer syrup was prepared by radiation polymerization, and the syrup was charged into a frame to be cast thermally. The present new method is completely different from the preirradiation technique, and is distinguished by the fact that the entire strain-forming controlled stage of the polymerization is carried out

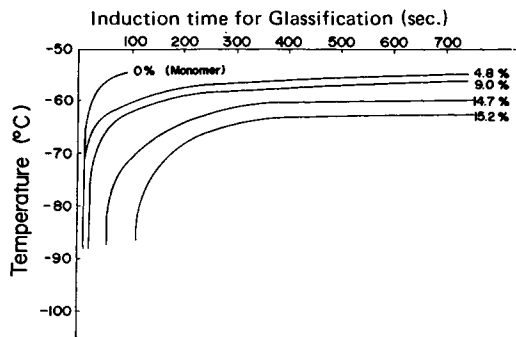


Fig. 1. Effect of prepolymer concentration on induction time for glassification of methyl methacrylate prepolymer system at various cooling temperatures. Figures in curves indicate prepolymer concentration in wt %.

by irradiation at low temperatures. It is necessary to impart a sufficient supercooling tendency and sufficient polymerizability at low temperatures to methyl methacrylate for the application of this radiation casting. This report concerns the trial and results of application of the new casting process, without strain formation, to methyl methacrylate systems.

## EXPERIMENTAL

MMA used was purified by distillation. Prepolymer was prepared by catalytic polymerization of methyl methacrylate by benzoyl peroxide (BPO). The viscosity of polymer was measured by capillary method, and its change with temperature was measured with a low-temperature viscometer (Haake Co.). The polymer molecular weight was determined by viscosity measurement of benzene solution of the polymer at 30°C. The polymerization was carried out in a glass ampoule or in a casting frame by 100,000 Ci  $\gamma$ -ray irradiation from a  $^{60}\text{Co}$  source at a definite temperature controlled by a stream of nitrogen. The polymer yield was determined by weighing. The strain formation was checked with a photoelastic strain gauge with polarized plates.

Glass-forming property was estimated by appearance at a definite temperature below the melting point. Induction time for glassification<sup>9</sup> was determined by measuring the time to the beginning of crystal precipitation at a definite temperature.

## RESULT AND DISCUSSION

### Glass-Forming Property of Methyl Methacrylate Prepolymer

Methyl methacrylate monomer is not glassified itself. Therefore, an increase in the supercooling property of methyl methacrylate by adding prepolymer was expected and tested at a relatively low temperature range. That is, the induction times for glassification at various cooling temperatures were investigated in the presence of prepolymer as a measure of the supercooling property or glass-forming property. The results are shown in Figure 1. It was found that induction time increased with increasing prepolymer concentration. However, the increased supercooling tendency was not enough to keep the supercooled

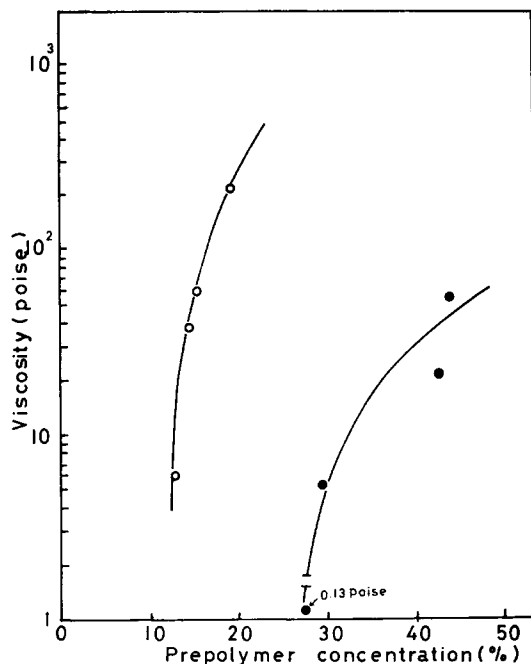


Fig. 2. Relation between viscosity and concentration of prepolymer in methyl methacrylate prepolymer of various molecular weights. Molecular weight: (O)  $4.67 \times 10^5$ ; (●)  $2.40 \times 10^4$ .

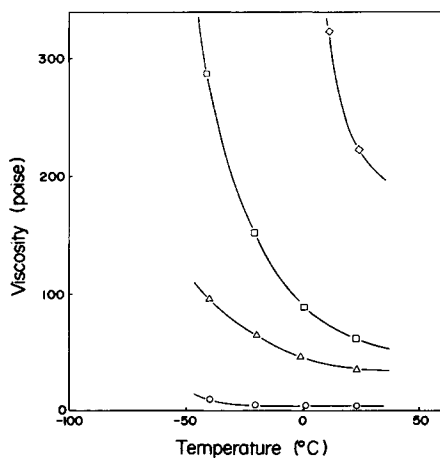


Fig. 3. Relation between viscosity and temperature in methyl methacrylate prepolymer of various concentrations: (◇) 18.7% prepolymer; (□) 15.2% prepolymer; (Δ) 14.7% prepolymer; (○) 13.2% prepolymer.

state or glassy state complete during the polymerization time, even at a prepolymer concentration of more than 15%. Consequently, it was considered that giving complete glass-forming property to methyl methacrylate by adding more prepolymer was difficult; addition of too high a concentration of prepolymer is inconvenient and troublesome because the viscosity for the casting process would be too high. Therefore, casting was carried out at temperatures above  $-48^\circ\text{C}$ , the melting point of methyl methacrylate monomer.

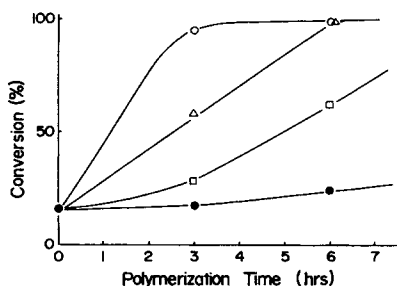


Fig. 4. Radiation-induced polymerization of methyl methacrylate prepolymer at 15.2% concentration. Prepolymer: 35 poises (viscosity at 25°C). Dose rate:  $1 \times 10^6$  R/hr in air. Polymerization temperature: (O) 25°C; ( $\Delta$ ) 0°C; ( $\square$ ) -23°C; ( $\bullet$ ) -50°C.

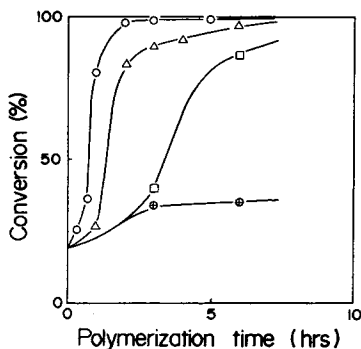


Fig. 5. Radiation-induced polymerization of methyl methacrylate prepolymer at 18.7% concentration. Prepolymer: 220 poises (viscosity at 25°C). Dose rate:  $1 \times 10^6$  R/hr in air. Polymerization temperature: (O) 25°C; ( $\Delta$ ) 0°C; ( $\square$ ) -23°C; ( $\bullet$ ) -50°C.

### Viscosity Temperature Dependence of Methyl Methacrylate Prepolymer

Viscosity of prepolymer was measured as a function of prepolymer concentration (Fig. 2), and its temperature dependence is shown in Figure 3. According to result of previous fundamental studies on the polymerization of glass-forming monomers at low temperatures, characteristic polymerizability was found at a viscosity of about 10 poises.<sup>9</sup> Apparently, the propagation reaction is retarded owing to a decrease in monomer mobility above this viscosity. Viscosities of prepolymer systems at temperatures above -48°C are comparable to or higher than those of monomer systems at lower temperatures. It was therefore expected that the cast polymerization of methyl methacrylate prepolymer above -48°C shows similar merit and effect as that of glass-forming monomer systems.

### Polymerization Rate of Methyl Methacrylate Prepolymer by Radiation

Polymerization by  $\gamma$ -irradiation was investigated at relatively low temperatures above -48°C for various concentrations of prepolymer. The results are shown in Figures 4-6. According to these results, it can be seen that the polymerization rate of the prepolymer system decreased rapidly with decreasing temperature, but that the rate increased with increase in prepolymer concen-

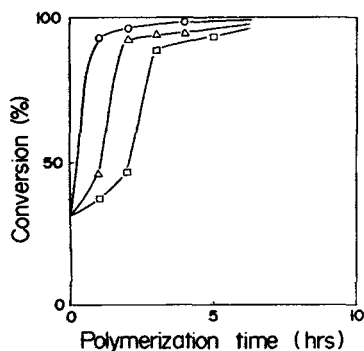


Fig. 6. Radiation-induced polymerization of methyl methacrylate prepolymer at 30.0% concentration. Prepolymer: 1360 poises (viscosity at 25°C). Dose rate:  $1 \times 10^6$  R/hr. Polymerization temperature: (O) 25°C; ( $\Delta$ ) 0°C; ( $\square$ ) -20°C.

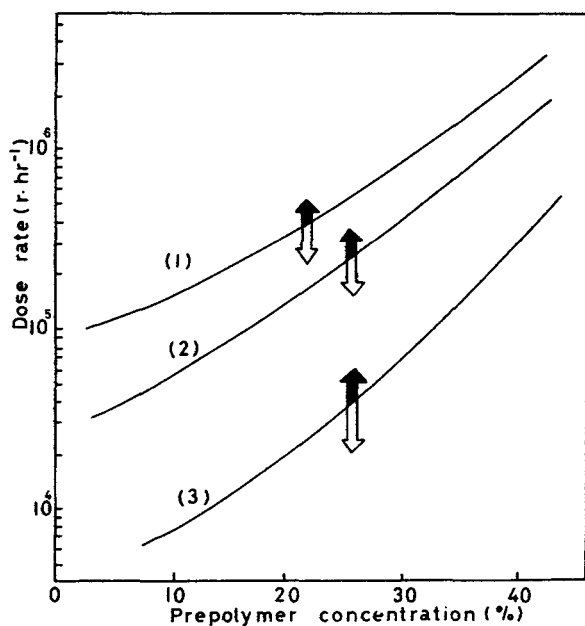


Fig. 7. Relation between dose rate, prepolymer concentration, and optical strain formation in radiation-induced cast polymerization of methyl methacrylate prepolymer system. Total dose:  $3 \times 10^6$  R. Sample scale: 20 cm  $\times$  10 cm  $\times$  5 mm thick. Polymerization temperature: (1) -20°C; (2) 0°C; (3) 25°C. — Optical strain formed in this region above the boundary condition curve. = No optical strain formed in this region below the boundary condition curve.

tration even at low temperatures, and a considerably improved polymerization rate was obtained at -20°C in the presence of 30% prepolymer. That is, about 75% conversion was reached without optical strain after irradiation of  $2.5 \times 10^6$  R at -20°C in the 30% prepolymer system. This is a sufficient rate for practical casting. Thus, it was ascertained that the addition of prepolymer was effective in increasing the polymerization rate as well as relatively increasing the supercooling tendency, as shown in Figure 1. The applicability of the prepolymer system to radiation casting at a relatively low temperature range above -48°C was then examined in the following experiments.

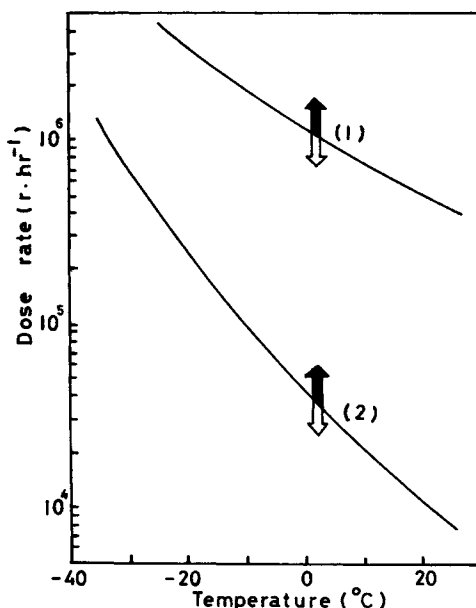


Fig. 8. Relation between dose rate, polymerization temperature, and optical strain formation in radiation-induced cast polymerization of methyl methacrylate prepolymer system. Total dose:  $3 \times 10^6$  R. Sample scale: 20 cm  $\times$  20 cm  $\times$  5 mm thick. Prepolymer concentration: (1) 42.3%; (2) 12.9%.  $\leftarrow$  Optical strain formed in this region above the boundary condition curve.  $\leftarrow$  No optical strain formed in this region below the boundary curve.

### Boundary Condition Curve of Strain Formation in Casting of Methyl Methacrylate by Radiation

Casting polymerization of prepolymer systems was investigated by irradiation at relatively low temperatures at various prepolymer concentrations. No polymer could be obtained without optical strain formation under the conditions at 0° and 25°C and at prepolymer concentrations below 23.7%. Increasing the prepolymer concentration was then tried for the purpose of decreasing volume shrinkage. It was necessary to prepare a prepolymer of lower molecular weight to increase the concentration of prepolymer. Casting polymerization was carried out using these prepolymers, and the boundary conditions of strain formation are shown in Figures 7–9 against prepolymer concentration, polymerization temperature, and polymer thickness, respectively. It is obvious that it became possible to cast MMA prepolymer without optical strain efficiently by increasing the prepolymer concentration. The boundary condition curve rose with increase in prepolymer, as shown in Figure 7, and also with decrease in temperatures.

In Figure 9, the boundary curve in the casting of hydroxyethyl methacrylate (HEMA) is shown for comparison. It can be noted that the optical strain formed in MMA monomer and prepolymer was an inner stress-type strain,<sup>3</sup> different from the thermal stream-type strain in HEMA.<sup>2</sup> The stress-type strain formation in MMA perhaps could be attributed to a relatively higher glass transition temperature (more difficult relaxation of stress) and greater volume shrinkage. It is also noted that the slope of the boundary curve of HEMA rises very sharply with decrease of thickness in the thinner-thickness region, while the slope of the

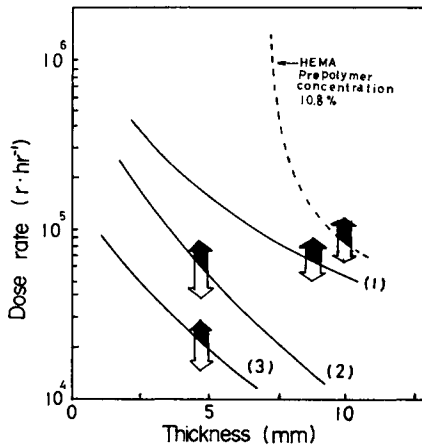


Fig. 9. Relation between dose rate, sample thickness, and optical strain formation in radiation-induced cast polymerization of methyl methacrylate prepolymer system. Temperature: 25°C. Total dose:  $3 \times 10^6$  R. Sample scale: 20 cm  $\times$  20 cm. Prepolymer concentration: (1) 42.3% ( $2.40 \times 10^4$  MW); (2) 25.7% ( $1.38 \times 10^5$  MW); (3) 12.9% ( $4.67 \times 10^5$  MW).  $\blackleftarrow$  Optical strain formed in this region above the boundary condition curve.  $\blackleftarrow$  No optical strain formed in this region below the boundary condition curve the boundary condition curve in hydroxyethyl methacrylate.

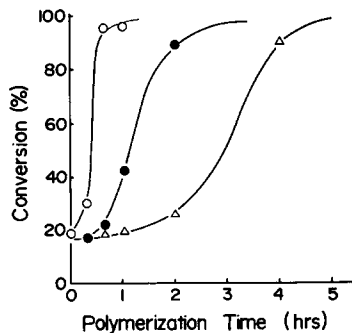


Fig. 10. Radiation-induced polymerization of methyl methacrylate prepolymer in presence of polyfunctional monomer. Polyfunctional monomer: 10% trimethylolpropane triacrylate. Prepolymer: 20% concentration. Dose rate:  $1 \times 10^6$  R/hr in air. Polymerization temperature: (O) 25°C; (●) 0°C; ( $\Delta$ ) -20°C.

boundary curve of MMA prepolymer in the thinner-thickness range, by contrast, does not show such a sharp rise with decreasing sample thickness, which could be considered a remarkable characteristic in boundary curves of stress-type strain formation.

A similar slower rise in the curve slope in the smaller-thickness region was also observed in boundary curves of monomeric systems including polyfunctional monomers. These facts suggest that thermal stream-type strain can be easily retarded by acceleration of heat removal in thinner samples, while inner stress due to volume shrinkage does not so easily relax even in thinner samples. The boundary curve itself is situated lower than that of other casting monomer and prepolymer systems previously studied. This fact can be attributed to the larger volume contraction of the methyl methacrylate system and more difficult stress relaxation due to the high glass transition temperature of its polymer. However,

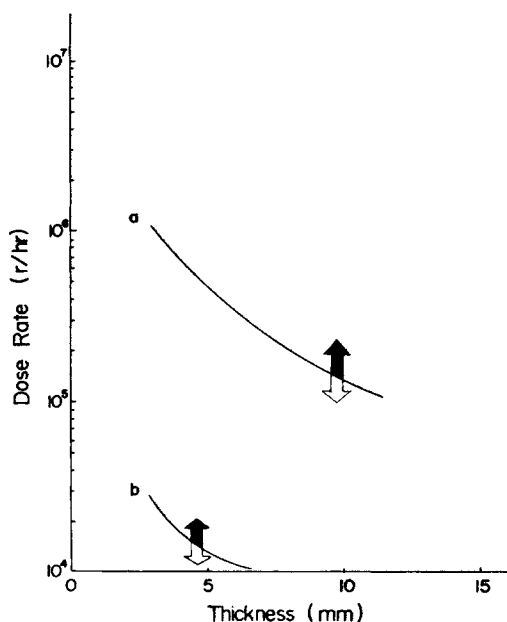


Fig. 11. Relation between dose rate, sample thickness, and optical strain formation in radiation-induced cast polymerization of methyl methacrylate–diethylene glycol diacrylate system (monomer system). Total dose:  $1 \times 10^6$  R. Sample scale: 20 cm  $\times$  10 cm. Polymerization temperature: (a)  $-50^\circ\text{C}$ ; (b)  $25^\circ\text{C}$ .  $\leftarrow$  Optical strain formed in this region above the boundary condition curve.  $\leftarrow$  No optical strain formed in this region below the boundary condition curve.

it is obvious from Figures 7–9 that the casting time cycle required to complete the polymerization without optical strain formation could be much shortened in comparison with catalytic processes.

### Polymerization and Casting of MMA–Polyfunctional Monomer Systems

It was found that the addition of polyfunctional monomers to MMA increased the polymerization rate and supercooling tendency at low temperatures. The

TABLE I  
Impact Resistance by FDA Testing Method of Methyl Methacrylate–Diethylene Glycol Diacrylate System<sup>a</sup>

Run no.	Composition, vol-%		Impact strength by FDA test, g		
	MMA	A2G	As polymerized	After treating for 16 hr at $100^\circ\text{C}$ <sup>b</sup>	After weather test for 500 hr <sup>c</sup>
1	0	100	30, 40, 40		15.8, 15.8, 15.8
2	10	90	50, 50, 50		15.8, 20, 30
3	25	75	20, 30, 30	20, 20, 30	15.8, 15.8, 20
4	50	50	20, 30, 30	30, 30	15.8, 15.8, 15.8
5	0	100	20, 20, 20	20, 30, 30	20, 20, 30
6	50	50	20, 30, 30	15.8, 15.8, 30	30, 30

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

<sup>b</sup> Heating only.

<sup>c</sup> Ultraviolet irradiation by xenon Weatherometer at  $65^\circ\text{C}$ .



time-conversion relation in MMA-trimethylolpropane trimethacrylate (TMPT) system is shown in Figure 10 as example. The polymerization rate was accelerated by addition of a relatively small quantity of TMPT even at  $-30^{\circ}\text{C}$ . The addition of diethylene glycol diacrylate (A-2G), a typical glass-forming monomer, also accelerated the polymerization rate. As pointed out in a previous report, physical properties such as impact resistance in polymers of diethylene glycol diacrylate were good.<sup>5</sup> The impact resistance as measured by FDA test in the MMA-A2G system is shown in Table I. Polymer of A2G was poor in weather resistance, but MMA-A2G (1:1) copolymer showed good impact resistance and weather durability. The boundary condition curve of strain formation in casting of MMA-A2G system is shown in Figure 11. Of course, the strain formed in this system was an inner stress-type strain. The A2G single system formed strain very easily; but with increasing addition of MMA to A2G, it became possible to cast the polymer without optical strain and a boundary curve could be obtained.

### Temperature Control Program in Casting of Methyl Methacrylate by Radiation

It has been shown that casting by radiation polymerization could be applied

TABLE II  
Radiation-Induced Casting Polymerization of Methyl Methacrylate Prepolymer Under Various Temperature Control Programs

Run no.	Sample scale, mm	Dose rate, R/hr	Temperature program Temperature, $^{\circ}\text{C}$	Time, min	Strain formation
1	$130 \times 60 \times 5t$	$1 \times 10^6$	$25^{\circ}\text{C}$ quick-cooling to $-30^{\circ}$ to $-40^{\circ}\text{C}$ warming to $25^{\circ}\text{C}$	20 30 60	slight stream type strain formed in center
2	$250 \times 230 \times 5t^a$	$1 \times 10^6$	$25^{\circ}\text{C}$ quick-cooling to $-30^{\circ}$ to $-40^{\circ}\text{C}$ $-30^{\circ}$ to $-40^{\circ}\text{C}$ warming to $25^{\circ}\text{C}$	12 15 15 68	slight stream-type strain formed in upper part
3	$300 \times 300 \times 5t$	$1 \times 10^6$	$25^{\circ}\text{C}$ quick-cooling to $-30^{\circ}$ to $-40^{\circ}\text{C}$ $-30^{\circ}$ to $-40^{\circ}\text{C}$ warming to $25^{\circ}\text{C}$	20 15 30 45	slight stream-type strain formed in upper part
4	$300 \times 300 \times 10t$	$1 \times 10^6$	$25^{\circ}\text{C}$ quick-cooling to $-35^{\circ}\text{C}$ warming to $0^{\circ}\text{C}$	5-10 50-55 60	stress-type strain
5	$300 \times 300 \times 15t$	$1 \times 10^6$	$25^{\circ}\text{C}$ quick-cooling to $-35^{\circ}\text{C}$ warming to $0^{\circ}\text{C}$	5-10 50-55 60	stress-type strain

<sup>a</sup> t = thickness.

to methyl methacrylate prepolymer and that polymers with no optical strain could be obtained effectively according to the conditions in Figures 9 and 10. However, for practical use it is more desirable to further shorten the casting time of this process, because the polymerization rate of methyl methacrylate by irradiation is not as high as that of HEMA, as seen in Figures 4–6. Temperature control was tried further to shorten the casting time of methyl methacrylate prepolymer. The polymerization was initiated quickly at relatively high temperatures such as room temperature to some conversion at first. Then the system was cooled quickly to be polymerized to considerable higher conversion at relatively low temperatures to prevent strain formation. And at last, the temperature was raised again to complete the polymerization. Of course, the strain-controlled step is the middle stage at low temperature. One merit of this method is that the strain-controlled step could be begun at relatively higher conversion (corresponding to higher prepolymer concentration) without the trouble of pouring and charging the very highly viscous prepolymer. Another merit of this method is that total casting time could be shortened by introducing two steps, first and last, at relatively higher temperatures and also by carrying out the middle, strain-controlled step at relatively higher polymer concentrations. The results are shown in Table II. The improvement can be recognized in the result.

More effective variations in temperature control programs are possible in radiation casting because radiation-induced casting can be carried out freely at any temperature. Detailed result will be reported in the future.

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