

Casting of Organic Glass by Radiation-Induced Polymerization of Glass-Forming Monomers at Low Temperature. I. Optical Strain of Thermal Stream Type

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Synopsis

It was found previously that cast articles of transparent polymer without optical strain could be obtained efficiently in a very short time by radiation-induced polymerization of glass-forming monomers at low temperature. Two types of optical strain were observed in casting of these monomers: thermal stream type and remaining (inner) stress type strain. The mechanism of thermal stream-type strain formation was investigated by following the heat and temperature change during cast polymerization in this report. It was found that the temperature difference between the upper and lower part of the sample was large and the temperature was much higher in the upper part than in the lower part under conditions of strain formation. Increase of heat removal from the sample surface decreased the temperature difference in the vertical direction and reduced the strain formation. It could be deduced that stream-type strain formed as a result of thermal stream and it was retarded in radiation casting of glass-forming monomers owing to high viscosity and low temperature.

INTRODUCTION

The authors have studied the radiation-induced polymerization of glass-forming monomers by radical mechanism and found that there were two remarkable characteristics in this polymerization. One was that polymerization rate and polymerization degree were large in the supercooled phase due to the viscosity increase of glass-forming monomers.¹ Another characteristic was that the volume shrinkage of the reaction system was small at low temperature because of the density increase of glassy monomers.²

The authors tried to apply these characteristics to cast polymerization of organic glass and found that polymer articles with no optical strain could be obtained by radiation casting in a far shorter time than by catalytic casting.² In the previous report, it was recognized that there were two types of optical strain: the eddy- or stream-form strain and the block-form strain.² In the casting of hydroxyethyl methacrylate (HEMA, typical glass-forming monomer), the former type was observed predominantly. The eddy- or stream-form strain occur mainly in casting of systems relatively rich in plasticity and relatively low in glass transition temperature, and such strain could be attributed to the result of molecular motion or orientation owing to thermal stream during polymerization.

In this report, thermal behavior of the polymerization system was studied in cast polymerization of HEMA as a model system in relation to the mechanism of optical strain formation of the eddy or stream type.

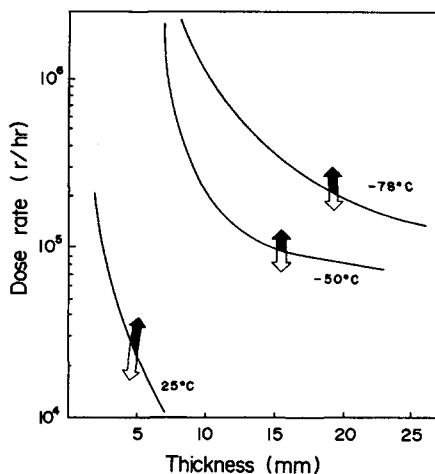


Fig. 1. Effect of thickness on optical strain formation in casting polymerization of HEMA at various temperatures: (↑) area of casting condition under which strain formed; (↓) area of casting condition under which no strain formed. Total dose 1×10^6 R, sample scale 160×80 mm.

EXPERIMENTAL

HEMA (Mitsubishi Gas Chemical Co.) was purified by distillation under reduced pressure and charged into a casting frame. Casting frames were constructed from two glass plates (100×200 mm, 5 mm thick), a silicon rubber gasket sandwiched in the plate circumference, and clamps to fasten the plate. The thickness of sample were varied by using gaskets of different diameters.

The casting frame full of monomer was kept vertically and irradiated by γ -ray from 100,000 Ci of a cobalt-60 radiation source at a determined temperature. Polymerization at low temperature was carried out by irradiating the casting frame in a reaction bath the temperature of which was regulated to a constant value by controlling the liquid nitrogen stream and the heater. After irradiation, the cast polymer was isolated from the frame and its optical strain was observed by a photoelastic strain gauge consisting of two polarization plates (polarizer), two quarter-wavelength glass plates, and a light source. The time-temperature relation during the polymerization was measured by a thermocouple, which was inserted in every part such as surface center, inner center, upper center, and lower center to detect the temperature difference and distribution.

RESULTS AND DISCUSSION

Boundary Curve of Strain Forming and Photograph of Optical Strain

In the previous paper,² it was shown that cast polymer with no optical strain could be obtained at a higher dose rate (greater polymerization rate) by super-cooled-phase polymerization using glass-forming monomers, as shown in Figure 1. The curve indicates the boundary condition of optical strain formation which was called boundary curve of strain forming. The optical strain formed in radiation casting could be classified into two types previously. One was eddy- or

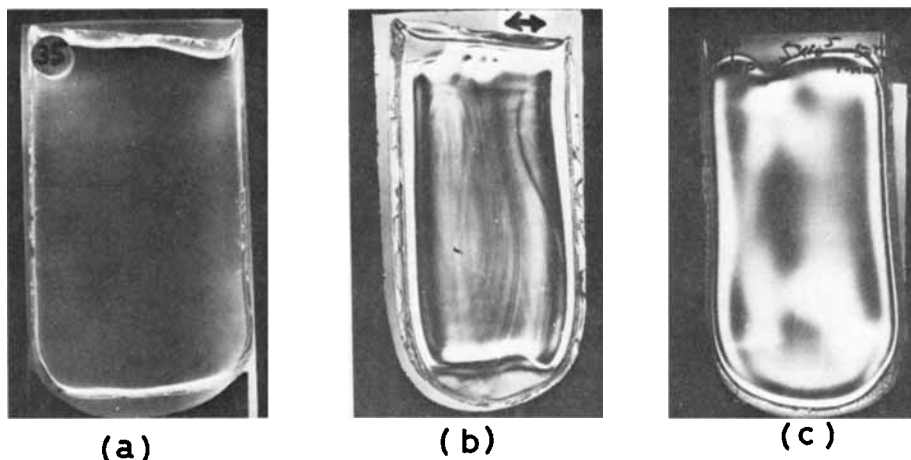


Fig. 2. Photographs of typical optical strain formed in HEMA polymer by photoelastic strain gauge: (a) sample with no strain, dose rate 1×10^5 R/hr, thickness 11 mm; (b) sample with thermal stream-type strain, dose rate 2×10^5 R/hr, thickness 15 mm; (c) sample with inner stress-type strain, dose rate 5×10^5 R/hr, thickness 11 mm. Polymerization temperature -50°C ; total dose 1×10^6 R; sample scale 160×80 mm.

stream-form strain, which was mainly studied in this work, and another was block-form strain.

Figure 2 shows both types of strains. The stream-type strain concerned in the present report is almost the same kind as the eddy strain which formed radially from the bottom part to the upper part of the sample in room-temperature cast polymerization (usual liquid phase polymerization). The eddy strain at room temperature is attributed to the result of thermal stream due to the difference in polymerization rate between the bottom and upper part of the sample. The stream-type strain in Figure 2 forms at low-temperature polymerization in the case of a relatively thicker sample. This report relates to this type of strain. As seen in Figure 2(b), other types of strain could also be observed along the circumference part of the sample which might be a kind of block-type strain, but the main optical strain in low-temperature cast polymers was the stream-type strain. Therefore, this work treats only stream strain formed in casting of HEMA monomer, and block-type strain will be studied in the next report.

Maximum Temperature in the Center of Sample

Polymerization heat was accumulated in the center of the sample with increasing of polymerization rate, and the inner temperature in the center rose and fell after reaching the maximum temperature. This maximum temperature was plotted in relation to the boundary curve of strain formation in the previous report. It was found that maximum temperature along the boundary curve decreases with increasing sample thickness and dose rate. The maximum temperature in boundary condition of strain formation almost agreed, and they ranged from about -10° to -20°C in relatively thicker samples.

In very thin samples, heat transfer from center to surface and heat removal in the surface part became easy, which might be the reason why boundary

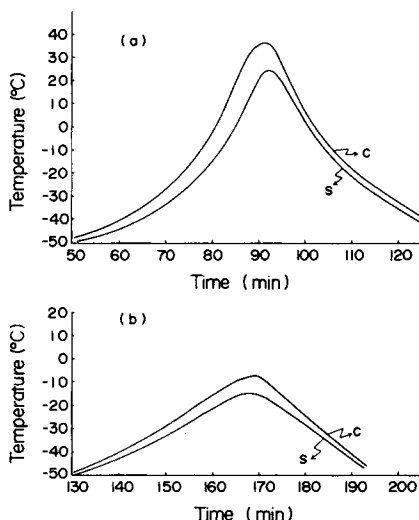


Fig. 3. Time-temperature relation curves in surface part (S) and center part (C) of sample during casting polymerization of HEMA using glass plate casting frame: (a) sample in which strain formed, dose rate 2×10^5 R/hr; (b) sample in which no strain formed, dose rate 1×10^5 R/hr; polymerization temperature -50°C ; Sample scale $160 \times 80 \times 15$ mm.

maximum temperature was high and boundary dose rate became sharply higher with decreasing sample thickness. The very sharp rise and fall of the center temperature in the time-temperature curve of thin samples suggested the same.

Temperature Difference Between Surface and Center Part

It was considered that the most important factor in stream-form strain formation were the heat transfer and heat accumulation, which could be estimated by the measurement of temperature distribution between different parts of the sample. First, temperature differences between surface and center parts of the sample were investigated under various polymerization and sample conditions.

Figure 3 shows the time-temperature curve of surface and center parts of a sample with relatively large thickness and polymerized using glass plate frames. As obvious in Figure 3, in large-thickness samples, the difference between surface and center temperature is smaller in the case forming no strain than in the case with strain formation. That is, the maximum temperature difference reached about 20°C in Figure 3(a), while the maximum difference was 7°C in Figure 3(b).

However, in relatively thin samples, the temperature difference between surface and center becomes considerably large even in case of no strain formation. It has already been clarified that the maximum temperature in the center is higher even in case of no strain formation in small-thickness samples. The temperature difference between surface and center in polymerization using aluminum frame is shown in Figure 4. As stated later, the stream-type strain formation becomes more difficult and boundary conditions of strain forming improve greatly in casting with aluminum frame. The result in Figure 4 shows

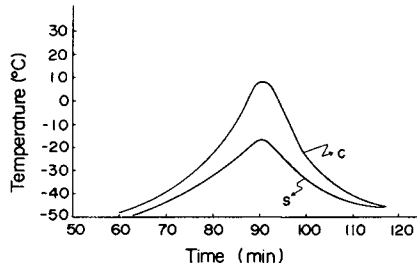


Fig. 4. Time-temperature relation curves in surface part (S) and center part (C) of sample during casting polymerization of HEMA using aluminum plate casting frame. No strain formed in this case. Polymerization temperature -50°C ; dose rate 2×10^5 R/hr; sample scale $160 \times 80 \times 5$ mm; aluminum plate thickness 0.5 mm.

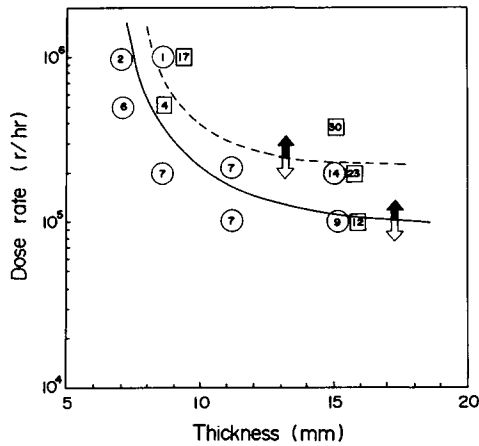


Fig. 5. Relation of boundary curve of strain formation and maximum temperature difference between surface and center part of sample in casting polymerization of HEMA using various casting frames: (O) casting using glass plate frame; (□) casting using aluminum plate frame; (1) strain formed in the conditions above this curve; (↑) no strain formed in the conditions below this curve. Polymerization temperature -50°C ; total dose 1×10^6 R; sample scale 160×80 mm.

that the temperature difference between surface and center was 24°C and the maximum temperature reached 8°C even under conditions of no strain formation.

Figure 5 shows the temperature difference between surface and center of the sample in relation to the boundary conditions of stream-type strain formation. It was remarkable that the boundary curve of strain formation was higher in the aluminum frame sample than in the glass plate sample, though the temperature difference between surface and center under boundary conditions was larger in the former than in the latter.

In the glass plate sample, stream strain formed at a temperature difference of 14°C (7 mm thickness) and 2°C (15 mm thickness), while in the aluminum plate sample, no strain was observed even at a temperature difference of 23°C (15 mm thickness). Moreover, the main strain formed in the aluminum plate sample was not stream type strain, but stress type strain, which will be studied in the next report. For example, the strain formed at a temperature difference

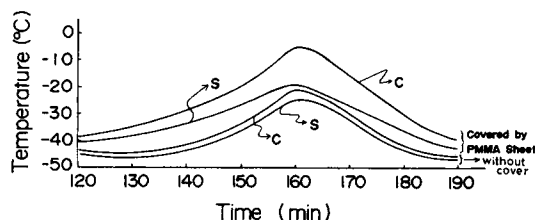


Fig. 6. Time-temperature relation curves in surface part (S) and center part (C) of sample during casting polymerization of HEMA using glass plate frame covered with PMMA sheet. Optical strain formed in this case. Polymerization temperature -50°C ; dose rate 1×10^5 R/hr; sample scale $160 \times 80 \times 11$ mm; PMMA sheet thickness 3 mm.

between surface and center as large as 30°C (15 mm thickness) was not of the stream type.

All these facts suggested that the temperature difference between surface and center is not the essential factor in stream-type strain formation, nor is the maximum temperature reached in center part of sample.

Figure 6 is the time-temperature curve in the polymerization using the glass frame covered with PMMA plate and without any cover. The temperature difference between surface and center greatly increased in the sample covered with PMMA, and strain formation occurred more easily. This was in contrast with the aluminum plate sample in which strain formation was retarded in spite of the temperature difference increase. These results suggest that temperature difference between surface and center itself could not be directly connected to stream-type strain formation, but that heat transfer from center to surface and removal of heat at the surface perhaps directly affects the strain formation. That is, in the aluminum plate sample, heat is removed and so the heat transfer is better than in the glass plate sample; the heat is then easily removed from the surface out of the sample and heat is hardly transferred in the vertical direction (to upper part) of the sample in the form of thermal stream. Good heat removal at the surface would rather accelerate the heat transfer and the temperature difference between center and surface would increase. This might be the reason why stream-type strain hardly forms in aluminum plate samples.

Temperature Difference Between Upper and Lower Part of Sample

The time-temperature relation of the upper, center, and lower parts of the sample in glass and aluminum frame was measured and is shown in Figure 7. It can be noted that there was a difference of the times to reach the temperature peak in the three parts of the sample, as in Figure 7(a), that is, the time to maximum temperature increased in the order of lower, center, and upper part. No such difference could be observed in the time-temperature curves of surface and center parts. The peak height (the maximum temperature) was large in the order of center, upper, and lower part, and the difference between lower and center part was larger than that between center and upper part. The former difference increased markedly with time and was retained after the temperature peak was reached. The latter difference was gradually enlarged with time, but it decreased after the temperature peak was attained. This fact suggested that there was

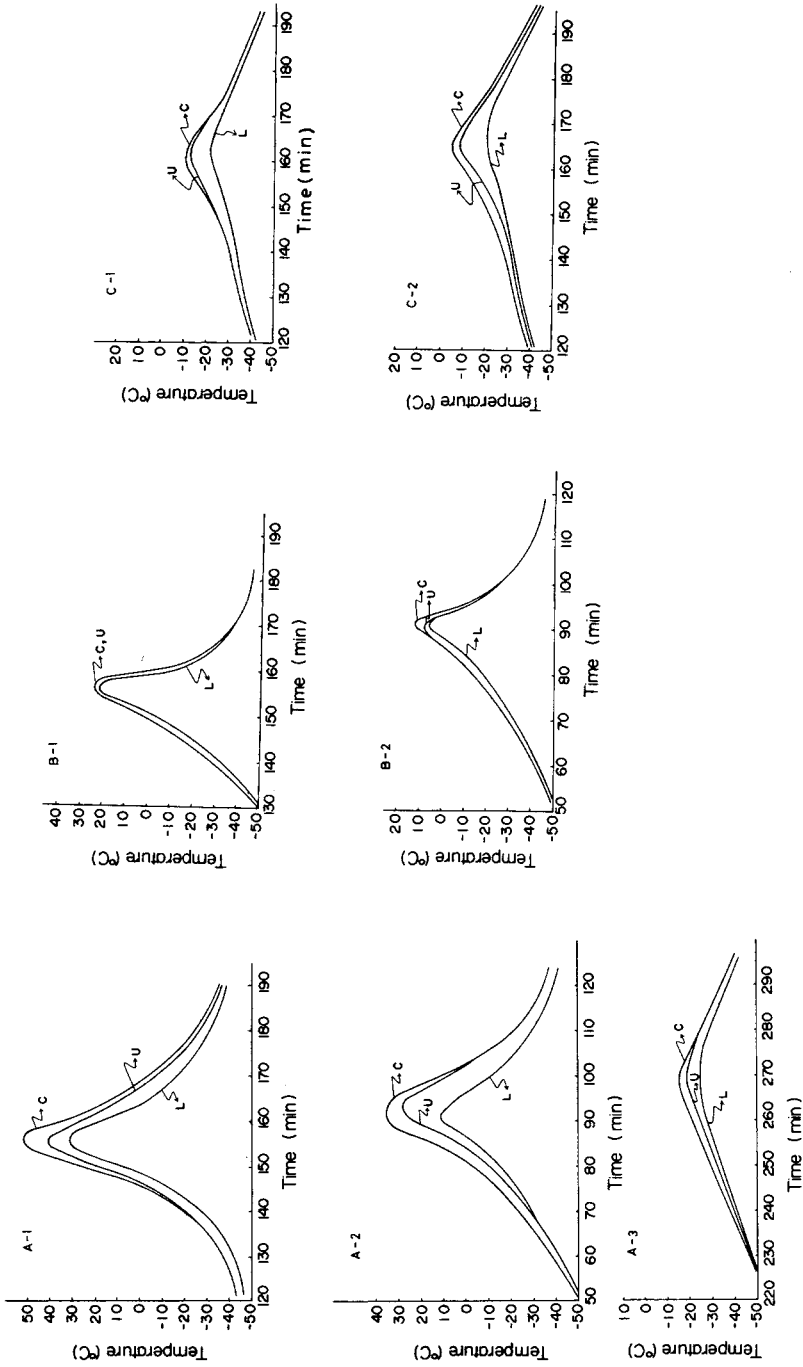


Fig. 7. Time-temperature relation curves in lower (L), middle (C), and upper (U) part of sample during casting polymerization of HEMA, (A) casting using glass plate frame: (1) sample in which stream-type strain formed, dose rate 4×10^5 R/hr; (2) of sample in which stream-type strain formed, dose rate 2×10^5 R/hr; (3) sample in which no strain formed, dose rate 5×10^4 R/hr. Polymerization temperature -50°C ; total dose 1×10^6 R; sample scale: $160 \times 80 \times 15$ mm (B) casting using aluminum plate frame: (1) sample in which stress-type strain formed, dose rate 4×10^5 R/hr; (2) sample in which no strain formed, dose rate 2×10^5 R/hr. Polymerization temperature -50°C ; total dose 1×10^6 R, sample scale $160 \times 80 \times 15$ mm. (C) casting (1) sample in which no strain formed using glass plate frame (2) sample in which stream type strain formed, using glass plate covered with PMMA sheet (3 mm thick). Polymerization temperature -50°C ; dose rate 1×10^5 R/hr; total dose 1×10^6 R; sample scale $160 \times 80 \times 11$ mm.

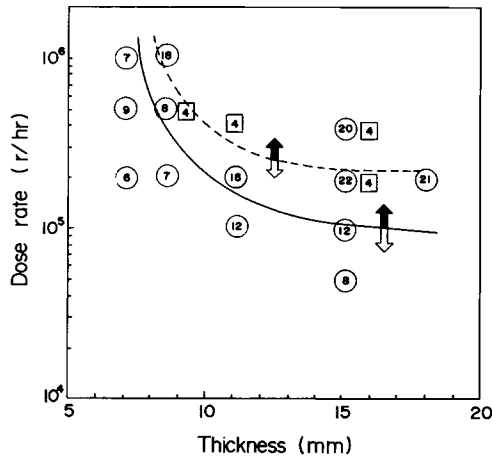


Fig. 8. Relation of boundary curve of strain formation and maximum temperature difference between lower and middle parts of sample in casting polymerization of HEMA using various frames: (O) casting using glass plate frame; (□) casting using aluminum plate frame; (↑) strain formed in the conditions above this curve; (↓) no strain formed in the conditions below this curve. Polymerization temperature -50°C ; total dose $1 \times 10^6 \text{ R}$; sample scale $160 \times 80 \text{ mm}$.

heat transfer from the lower to center part with time, and that the lower part reached the maximum temperature in the shortest time. A reason why the temperature of the center was higher than the upper part was probably that the upper part faced the atmosphere and heat dissipated out of the sample, while the center and lower parts were surrounded by the gasket which is a poor heat transfer material.

Another reason for the higher temperature of the center part than of the upper part might be the difference in polymerization rate. As the polymerization proceeded and the viscosity of the reaction system decreased with the relatively large temperature rise under severe strain-forming conditions, polymer formed sank to the lower part, accelerated the polymerization as observed at room-temperature casting, and larger polymerization heat flowed from the lower to the center part. Furthermore, the polymerization rate increased with increase in temperature at a relatively higher conversion stage, and then the center part reached the highest maximum temperature. The decrease in temperature difference between center and upper parts after the temperature peak was reached suggested the presence of heat transfer from center to the upper part during the entire polymerization.

These concepts could explain the behavior of the three parts in the time-temperature curves and support the occurrence of thermal stream due to the heat transfer. Under no strain-forming conditions [Fig. 7(a-3)] in the glass plate frame system, the difference in time to the maximum temperature in the three parts was not observed clearly, and the difference in temperature between the three parts of the samples was smaller. That is, the temperature difference between the lower and upper part was smaller than 7°C . In the aluminum plate frame sample, also the temperature difference between the perpendicular three parts was small, as in Figure 7(b), though the difference between horizontal direction (surface and center) was large. These facts suggested that the thermal transfer

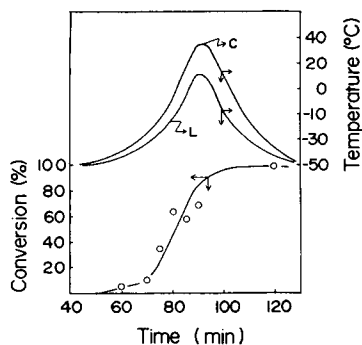


Fig. 9. Change in conversion and inner temperature with polymerization time during casting polymerization of HEMA: (C) temperature in middle part of sample; (L) temperature in lower part of sample. Polymerization temperature -50°C ; dose rate 2×10^5 R/hr; total dose 1×10^6 R; sample scale $160 \times 80 \times 15$ mm.

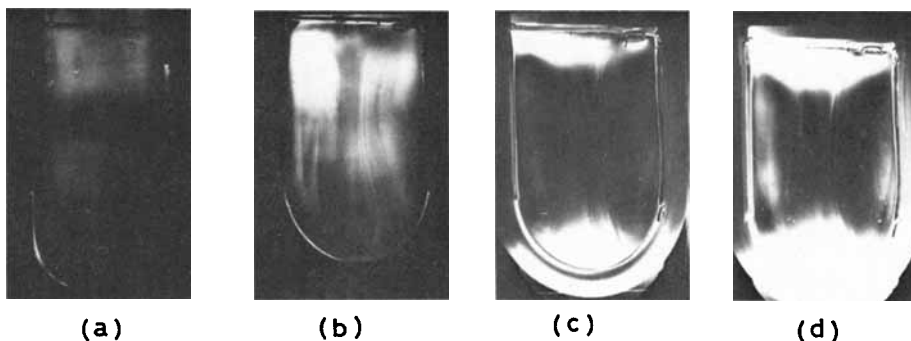


Fig. 10. Photographs of change in casting polymerization system with polymerization time observed by photoelastic strain gauge: (a) before polymerization; (b) polymerization time 90 min (conversion 68%); (c) 100 min (84%); (d) 120 min (100%). Polymerization temperature -50°C ; dose rate 2×10^5 R/hr; sample scale $160 \times 80 \times 15$ mm.

in the horizontal direction was not a necessary condition of strain formation, but the temperature difference in the perpendicular direction could be directly related to stream-type strain formation.

Figure 7(c) shows the time-temperature curves in perpendicularly different parts of a sample having the glass frame covered with PMMA plate. A rise in temperature difference between every part was evidently observed and resulted in easier strain formation.

The temperature difference between the lower and upper part was plotted in Figure 8 in relation to the boundary curve of strain formation. The temperature difference shows good correspondence with boundary conditions, that is, strain formation occurred under the condition in which the temperature difference between the lower and upper part increased more than about 12°C . In the aluminum plate frame system, the difference was small and almost always about 4°C , even under various conditions. This fact agrees with the observed result that no stream-type strain formed in aluminum frame system, but another type of strain (stress-type strain) formed.

It was deduced that stream-type optical strain formed owing to the eddy-like thermal stream which occurred owing to the heat transfer from the lower part

TABLE I
Relationship Between Thermal Behavior and Stream-Type Optical Strain Formation

		Thermal Behavior		
Frame	Sample	Maximum temperature reached in sample center	Temperature difference between surface and center parts	Temperature difference between upper, middle, and lower parts
Glass plate (stream-type strain formed)	Thick sample, more than 5 mm	Low, almost same (-10° to -20°C) in boundary condition of strain formation	Independent of boundary conditions	Small, almost same (12°C) in boundary conditions
	Thin sample, less than 5 mm	Higher, (more than $-10 \sim -20^{\circ}\text{C}$) in boundary conditions of strain formation	Independent of boundary conditions	Small, almost same ($\approx 12^{\circ}\text{C}$) in boundary conditions
Aluminum plate (stress-type strain formed)	Samples of all thickness	Independent of boundary conditions	Independent of boundary conditions	Almost same ($\approx 4^{\circ}\text{C}$) in all conditions, independent of boundary conditions

to the center and from the center to the upper part of the sample. These heat transfers occurred with the aid of an unequal polymerization rate in the lower and center parts, and also unequal heat dissipation in the center and upper parts. When the heat dissipation from the frame surface was large enough as in the aluminum plate frame system, heat transfer was carried out in the horizontal direction, and no thermal stream in the perpendicular direction occurred even when high maximum temperature was reached, because heat transfer in the perpendicular direction also hardly occurred. The stream-type optical strain could be attributed to the phenomenon of frozen molecular flow or orientation caused by the eddy-like thermal stream. The reason, in low-temperature casting, this optical strain forms with more difficulty than in the usual catalytic method might be that the viscosity of the glass-forming monomer is very large in the supercooled phase at low temperature so that molecular flow hardly occurs even under relatively large heat emission and large temperature difference. Moreover, it was also of benefit in low-temperature polymerization that the viscosity hardly decreased, even in the case of relatively large temperature rise.

Polymerization Stage of Strain Formation

The change in conversion and inner temperature of the sample with polymerization time is shown in Figure 9. As shown in this figure, the maximum temperature corresponds with a polymerization stage of about 85%–90% conversion, which is the final stage. The optical strain could be observed by a static strain gauge at 90 min (68% conversion) but not at 80 min (45% conversion). However, a kind of optical shaking wave by diffusion flow such as is usually observed in dissolving one component to another could be observed with the naked eye. From these results, it was deduced that a molecular flow owing to thermal stream already occurs at a polymerization stage earlier than 45% conversion, and it is rapidly frozen (solidified) by the rapid increase in conversion at the polymerization stage of the next 10 min. That is, the freezing of strain occurred at a stage between 45% and 85% conversion, and it occurred rapidly in a very short polymerization time. Figure 10 is a photograph of sample at these polymerization stages. The strain observed at 80 min did not increase any further after this polymerization stage.

A more detailed quantitative study of strain formation by thermal stream will be discussed in the future from the view point of thermal analysis.

CONCLUSIONS

The thermal behavior in casting polymerization of HEMA was studied in relation to the mechanism of stream-type optical strain formation in the polymer. The results could be summarized as follows:

1. The maximum inner temperature reached by the sample was almost similar to the boundary condition for stream-type strain formation in the case of relatively thick samples (more than 5 mm). This maximum temperature was -10° to -20°C . But in very thin samples, no strain formed at maximum temperatures above this value.

2. The temperature differences between the surface and the center part and

also between the upper, middle, and lower parts of the sample were investigated. Samples using glass plate frames and aluminum plate frames showed different behavior with regard to thermal property and strain formation. The results are shown in Table I.

References

1. I. Kaetsu, H. Okubo, A. Ito, and K. Hayashi, *J. Polym. Sci. A-1*, **10**, 2203 (1972).
2. I. Kaetsu, F. Yoshii, H. Okubo, and A. Ito, *Appl. Polym. Symp.*, **26**, 165 (1975).

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