

Cast and Mold Polymerization of Organic Glass by Irradiation from Fluid and Soft Gel Prepolymers

HIROSHI OKUBO, FUMIO YOSHII, SIGERU NISHIYAMA, KENZO YOSHIDA, and ISAO KAETSU, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma, Japan*

Synopsis

Casting and mold polymerization processes were investigated by means of γ -irradiation of methyl methacrylate prepolymer systems containing some quantity of polyfunctional monomers. Some physical properties, such as supercooling tendency and temperature dependence of viscosity and relaxation time in fluid prepolymers, were measured and related to cast polymerization at low temperatures. It was found that free-state casting with no frame or mold was possible using viscous states of prepolymer in the supercooled state. Furthermore, efficient mold polymerization using soft gel prepolymer was studied. That is, plastic soft gel prepolymer was prepared conveniently by irradiation of fluid prepolymer, then molded into spherical or nonspherical curved surface shapes, and cured by reirradiation. Polymerization and gelation behavior of soft gel prepolymer and penetration degree of prepolymer as a measure of plasticity of gel were studied in relation to prepolymer composition and irradiation condition.

INTRODUCTION

The authors have studied cast polymerization of organic glass by radiation-induced polymerization at low temperatures.¹⁻⁵ It was found that organic glass plate or sheet could be prepared without forming optical strain and residual stress in markedly shortened time cycles by this casting process. This method can be applied to the casting of various optical articles such as lenses using metal molds. However, casting by metal mold is inconvenient and inefficient because construction and disassembly of heavy molds, monomer charge without foaming, and polymer release from the molds require much power and time. Obviously, mold casting from monomer or fluid prepolymer is not fit for mass production. The authors found that cast polymerization in molds could be carried out conveniently by operation at low temperature using glass-forming fluid monomer or prepolymer; in such cases completely closed molds are not necessary due to the large viscosity (almost that of a solid) of supercooled glass-forming monomer or prepolymer. Moreover, mold polymerization from soft gel prepolymer is much more simple and convenient for mold operation and preparation of optical articles. This report concerns the efficient casting of fluid prepolymer and mold polymerization from soft gel prepolymer for curved-surface organic glass articles.

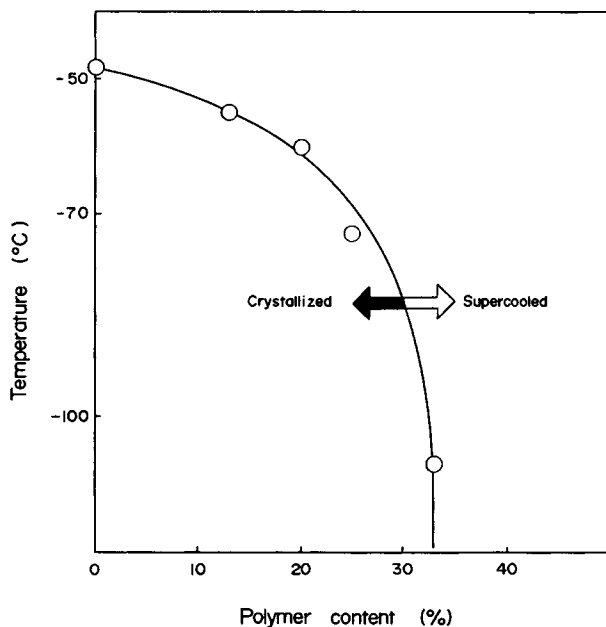


Fig. 1. Crystallization and supercooling region of methyl methacrylate prepolymer system: (O) crystallization point.

EXPERIMENTAL

All monomers used were of industrial reagent-grade quality. Fluid prepolymer for casting was obtained by dissolving poly(methyl methacrylate) (PMMA) into methyl methacrylate monomer (MMA) or into a mixture of MMA and poly-functional monomers, i.e., tetraethylene glycol diacrylate at 90°C.

Preparation of soft gel from fluid prepolymer was carried out in a frame constructed with two reinforced glass plates and gasket by γ -ray irradiation from a ^{60}Co source of 100,000 Ci at a definite temperature controlled by cooled nitrogen stream from refrigerator or liquid nitrogen tank.

The crystallization point in the crystallization supercooling boundary area of the MMA-PMMA fluid prepolymer system was determined by differential thermal analysis under cooling by liquid nitrogen using an AGNE DTA.

Measurements of the viscosity and relaxation time of fluid prepolymer or soft gel were carried out using a Haake Rotovisko rotational viscometer RV-3.

Penetration degree of soft gel was measured in accordance with ASTM D217-50 at 20°C.

RESULTS AND DISCUSSION

Viscosity of Fluid Prepolymer System at Low Temperatures

Previously, it was found that glass-forming monomeric systems can be cast conveniently into organic glass polymers by irradiation at low temperatures without optical strain.^{1,2} That is, cast polymerization in the supercooled state can be carried out with less volume shrinkage and less molecular motion of monomer by thermal stream than the hitherto reported casting process.

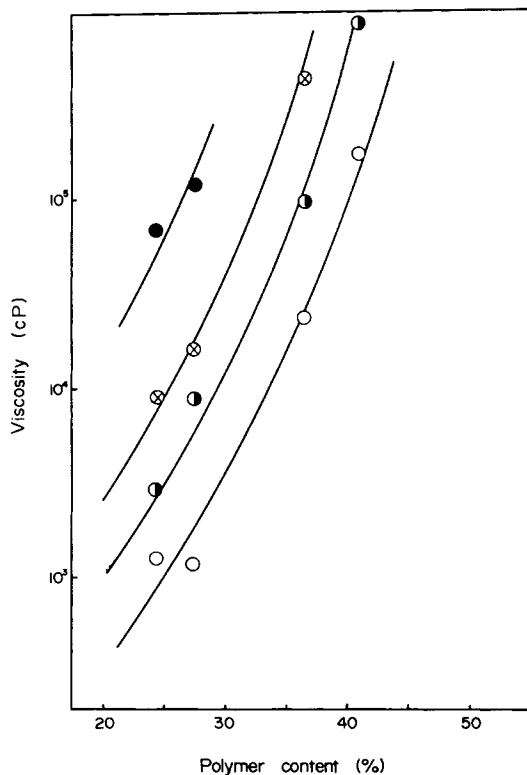


Fig. 2. Viscosity change by polymer content of methyl methacrylate prepolymer system at various temperatures containing 10% tetraethylene glycol diacrylate: (○) 20°C; (◐) 0°C; (⊗) -20°C; (●) -40°C; shear rate $D = 3.6-7.2 \text{ sec}^{-1}$.

This characteristic of a glass-forming or supercooling monomeric system can be applied advantageously to cast or mold polymerization in the free state without mold or frame. Glass-forming monomeric systems polymerized quickly by irradiation without transforming their previously given shapes and forms owing to their extremely high viscosity.

It is expected that in free-state mold polymerization a continuous molding process is possible. Moreover, formation of stress and strain in formed polymers would be reduced further than in casting with a frame, owing to the lack of competitive action between the contraction power of the polymer by polymerization and the adhesive power with the frame plane or gasket. Consequently, for free molding polymerization in the near-solid state, it is important to know the basic properties of prepolymer such as supercooling tendency and temperature dependence of viscosity.

Figure 1 shows the supercooling condition of methyl methacrylate prepolymer as a function of temperature and polymer content. According to this result, a stable supercooling or glassy state is obtained at a polymer concentration of more than 33% for every temperature tested.

The viscosity change of methyl methacrylate prepolymer containing 10% tetraethylene glycol diacrylate is shown in Figure 2 with change of temperature and polymer content. Relaxation time as a measure of rigidity or fluidity of the monomeric system is shown in Figure 3 also as a function of temperature and

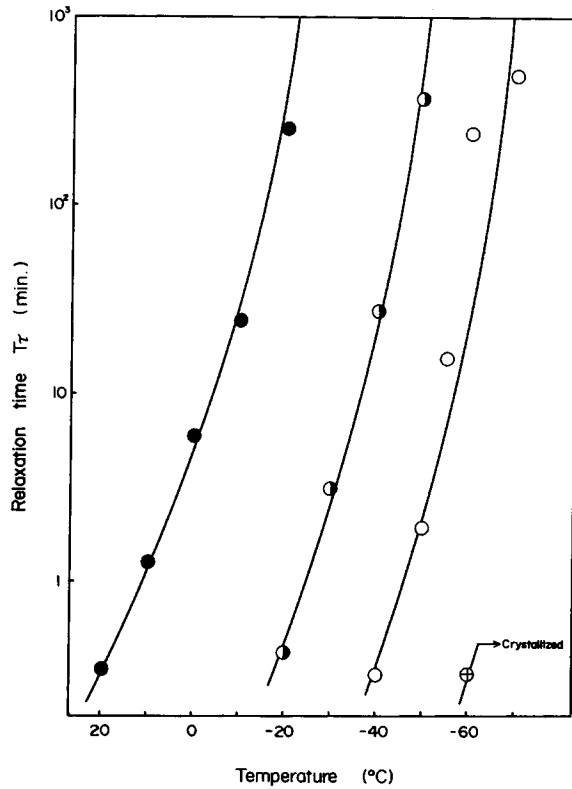


Fig. 3. Relaxation properties of methyl methacrylate prepolymer system: (⊕) PMMA:MMA:A4G = 24.4:65.6:10; (○) PMMA:MMA = 36.5:63.5; (●) PMMA:MMA:A4G = 41:49:10; (●) PMMA:MMA = 54.7:45.3; A4G, tetraethylene glycol diacrylate.

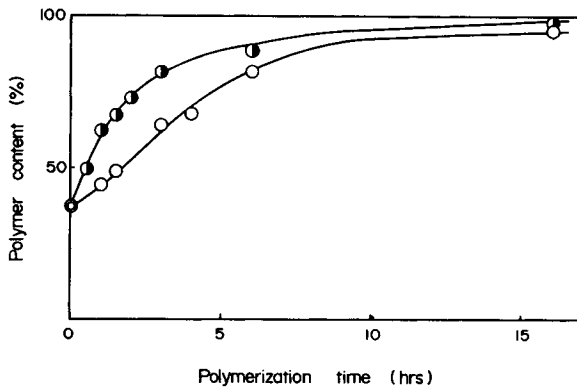


Fig. 4. Polymerization of methyl methacrylate fluid prepolymer containing 10% tetraethylene glycol diacrylate supercooled at -78°C : (○) 5×10^5 R/hr; (●) 1×10^6 R/hr.

polymer content. It is necessary to have a relaxation time of at least more than $\sim 1 \times 10^2$ min for free-state molding in order to retain a given shape or form of the monomeric system before fixing it by irradiation, though the time depends on the dose rate.

Figure 4 shows the time-conversion curve necessary for free-state curing of

methyl methacrylate prepolymer and the tetraethylene glycol diacrylate system. The polymerization shows no gel effect because of low temperature.

In order to fix the molding shape of the prepolymer, relaxation time of more than 1×10^2 min at room temperature, that is, a polymer content of 60% to 70%, is necessary, and this conversion can be attained by irradiation of $(1-2) \times 10^6$ R at -78°C .

The free-state polymerization of prepolymer sheet was then investigated at low temperatures. Two kinds of difficulty were to be solved in this process. One was the warping of the polymerized sample. This could be retarded by supporting the sample bottom with a substrate plate or by pressing the upper surface of sample with a plane weight. Another trouble was the formation of crumples in the sample surface, and this was improved by covering the sample surface with plastic film such as Mylar or by introducing nitrogen pressure on the sample surface. Some results in free-state mold polymerization are shown in Table I.

Preparation of Soft Gel Prepolymer by Irradiation and its Penetration Properties

Casting from fluid prepolymer was applied also to the preparation of curved-surface articles such as lenses in a metal mold, but large disadvantages were found in this case. As the required mold must be made from heavy metal and has a completely closed structure, the operation requires closing and opening with many bolts, and releasing the polymer from the mold is therefore very troublesome. It requires much more power and time than casting in sheet form by glass frame. These demerits often canceled out the advantage of time shortening of the casting cycle in the radiation method.

The authors have found an effective molding method to improve this problem. It was found that the mold polymerization of a curved-surface article could be

TABLE I
Free-State Polymerization of Prepolymer^a

Run No.	Sample	Irradiation	Appearance of irradiated polymer
1	fluid prepolymer (PMMA: MMA:A4G = 41:49:10)	-78°C , 1×10^6 R, completely isolated state	clear, warped, crumpled
2	same as run 1	-78°C , 1×10^6 R, supported from bottom	clear, flat sheet, crumpled
3	same as run 1	-78°C , 1×10^6 R, supported from bottom, upper surface covered	clear, flat sheet, smooth surface
4	soft gel prepolymer (original composition same as run 1, polymer content 54%)	-40°C , 2×10^5 R, completely isolated state	clear, warped, crumpled
5	same as run 4	-40°C , 2×10^5 R, upper surface pressed	clear, flat sheet, smooth surface

^a Prepolymer cooled in sheet form about 5 mm thick.

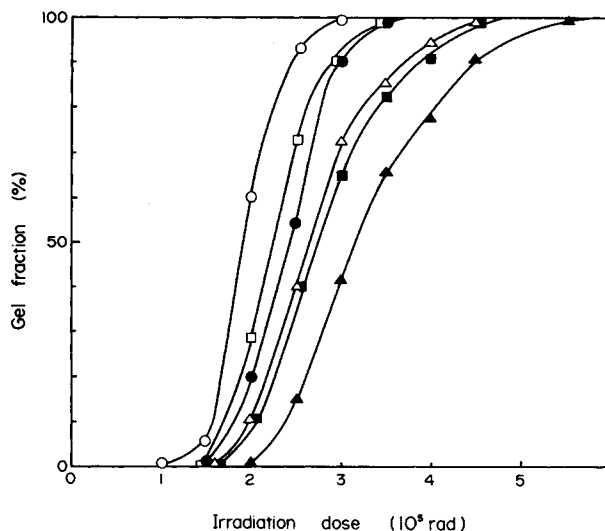


Fig. 5. Relationship between irradiation dose and gel fraction of various prepolymer systems: (\blacktriangle) PMMA:MMA:A4G = 9:81:10; (\blacksquare) PMMA:MMA:A4G = 18:72:10; (\bullet) PMMA:MMA:A4G = 27:63:10; (\triangle) PMMA:MMA:A4G = 8:72:20; (\square) PMMA:MMA:A4G = 16:64:20; (\circ) PMMA:MMA:A4G = 24:56:20; irradiation temperature 20°C.

achieved easily and conveniently first by preparing the plastic soft gel prepolymer ready to be shaped or molded into the desirable form, molding it by pressing with the curved surface of the mold only lightly, and then irradiating it to harden it. This operation eliminates construction and reconstruction of a heavy mold by bolting. Moreover, release of the gel prepolymer from the mold is very easy. Use of a whole-body of heavy mold can be avoidable in many cases because in non-closed molding of this type, only a curved mold surface is necessary and another mold surface can be substituted by lighter mold materials such as glass. Also, soft, moldable gel prepolymer could be obtained easily and conveniently by irradiation, selecting suitable monomer composition and irradiation condition.

The preparation conditions and the composition of soft gel prepolymer was studied in detail in relation to its penetration property as a measure of plasticity or moldability of gel prepolymer. Some results of the relationship between polymer conversion, gel fraction in prepolymer, and irradiation dose are shown in Figures 5 and 6. Soft gel prepolymer is obtained from compositions generally consisting of methyl methacrylate monomer or prepolymer (fluid prepolymer) and polyfunctional monomers. According to the results of Figure 6, fluid prepolymer increased the polymer conversion by irradiation, showing S-type time-conversion curves due to the gel effect at room temperature, and then reached saturated conversion. The gel fraction increased quickly after polymerization began owing to the presence of polyfunctional monomers as shown in Figure 5.

The deformation degree of soft gel was investigated by using a reconstructed penetrometer which had a flat plate 2 cm in diameter instead of a needle. Some examples of the load-deformation degree relationship are shown in Figure 7. As shown, the deformation degree of soft gel was influenced only by the degree of penetration. The penetration degrees of soft gel prepolymer are shown as functions of polymer content and irradiation dose in Figures 8, 9, and 10. Ac-

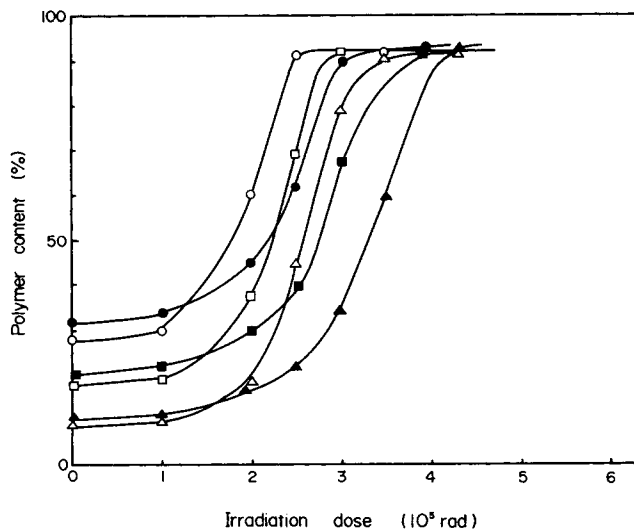


Fig. 6. Relationship between irradiation dose and polymer content of various prepolymer² systems: (▲) PMMA:MMA:A4G = 9:81:10; (■) PMMA:MMA:A4G = 18:72:10; (●) PMMA:MMA:A4G = 27:63:10; (△) PMMA:MMA:A4G = 8:72:20; (□) PMMA:MMA:A4G = 16:64:20; (○) PMMA:MMA:A4G = 24:56:20; irradiation temperature 20°C.

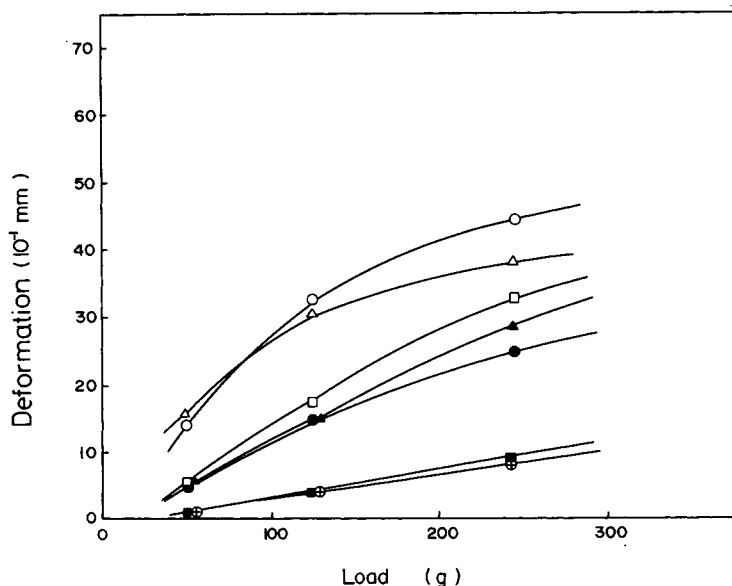


Fig. 7. Deformation test of soft gel prepolymer: (⊕) $P = 61$, containing 1% methoxytetraethylene glycolacrylate (AM4G), $R = 1.8$; (■) $P = 63$, containing 5% polypropyleneglycol dimethacrylate (P9G), $R = 2.5$; (△) $P = 185$, containing 1% trimethylolpropane trimethacrylate (TMPT), $R = 2.0$; (○) $P = 190$, containing 10% (P9G), $R = 1.35$; (□) $P = 112$, containing 5% diethylene glycol diacrylate (A2G), $R = 1.55$; (△) $P = 107$, containing 10% dipropylene glycol dimethacrylate (P2G), $R = 1.20$; (●) $P = 108$, containing 1% (P2G), $R = 1.75$; $P =$ penetration (10^{-1} mm); $R =$ dose for gel prepared ($\times 10^5$ R).

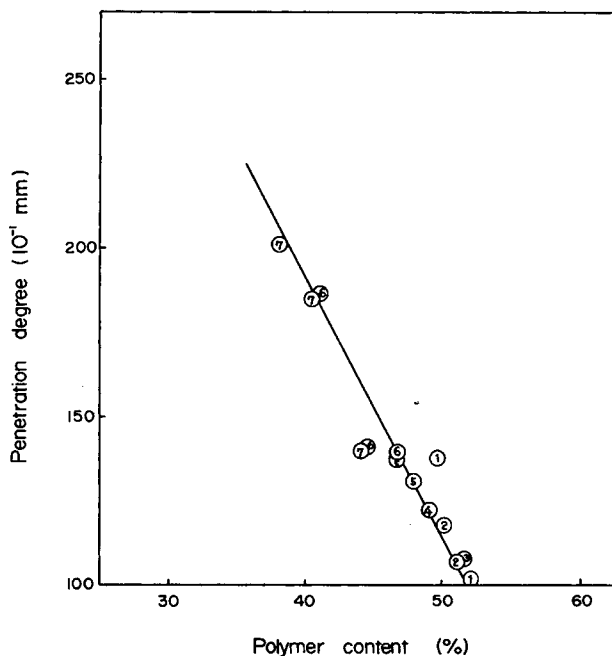


Fig. 8. Relationship between penetration degree and polymer content in soft gel prepolymer obtained from fluid prepolymer containing various kinds of polyfunctional monomers: polyfunctional monomers ① A4G; ② P9G; ③ P2G; ④ A2g; ⑤ AM4G; ⑥ TMET; ⑦ TMPT; polymerization (irradiation) temperature 20°C; irradiation dose $(1.27-1.75) \times 10^5$ R; original fluid prepolymer = 26% PMMA-74%-1% polyfunctional monomer.

According to these results, the degree of penetration decreased rapidly with increasing polymer content in every system. The slope of the decrease became larger with increasing polyfunctional monomer content such as tetraethylene glycol diacrylate.

The decrease of penetration degree (loss of plasticity) is faster with increase in polymer content (polymerization conversion) in larger monomer content systems of original fluid prepolymer. This fact suggests that penetration property or hardness (softness) of gel is essentially determined by the monomer fraction (methyl methacrylate and polyfunctional monomer) in the original prepolymer, and the poly(methyl methacrylate) fraction in the original prepolymer acts as a plasticizer. On the other hand, the decrease of penetration degree with increasing irradiation dose is faster in smaller monomer content systems of the original prepolymer. This result can be reduced to faster polymerization and gelation rates in the original prepolymer of larger polymer content as shown in Figures 5 and 6.

The suitable penetration degree of soft gel prepolymer for molding ranged between 60 and 100, although it varies with the reirradiation temperature for curing polymerization, because softness and plasticity change with temperature for further treatment. Control of plasticity is easily and conveniently accomplished by irradiation of the fluid prepolymer, choosing and adopting a very broad range for gel preparation conditions as described above. On the other hand, the usable range of preparation conditions of soft gel is very narrow in the catalytic preparation method, and control of suitable plasticity is difficult owing to rapid acceleration of polymerization and gelation at elevated temperatures.

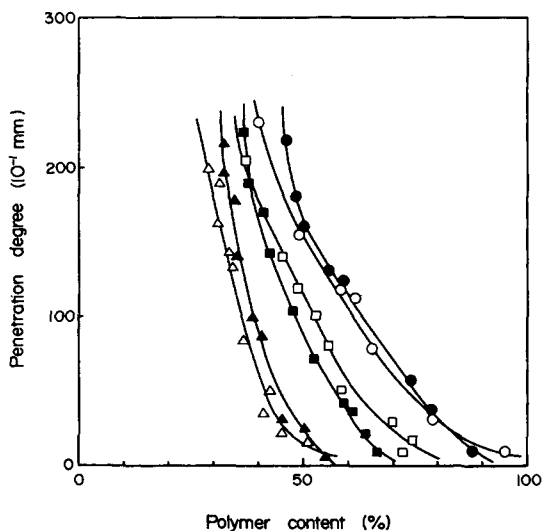


Fig. 9. Effect of prepolymer composition on relationship of penetration degree and polymer content in various soft gels including tetraethylene glycol diacrylate: (Δ) PMMA:MMA:A4G = 28:52:20; (\square) PMMA:MMA:A4G = 18:62:20; (\circ) PMMA:MMA:A4G = 10:70:20; (\blacktriangle) PMMA:MMA:A4G = 32:58:10; (\blacksquare) PMMA:MMA:A4G = 20:70:10; (\bullet) PMMA:MMA:A4G = 12:78:10; irradiation temperature 20°C.

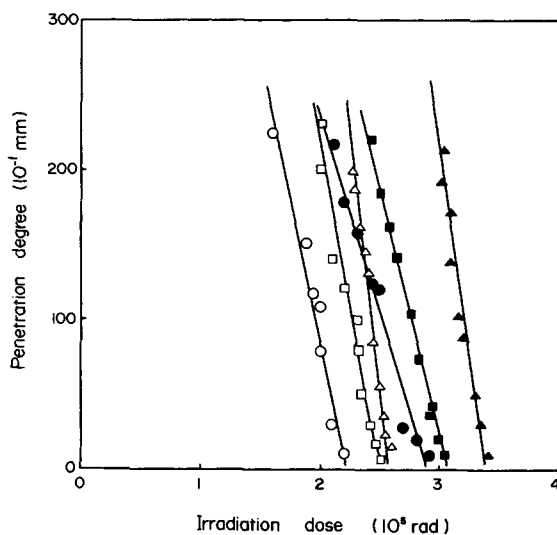


Fig. 10. Effect of prepolymer composition on relationship of penetration degree and irradiation dose in various soft gel prepolymers containing tetraethylene glycol diacrylate: (Δ) PMMA:MMA:A4G = 28:52:20; (\square) PMMA:MMA:A4G = 18:62:20; (\circ) PMMA:MMA:A4G = 10:70:20; (\blacktriangle) PMMA:MMA:A4G = 32:58:10; (\blacksquare) PMMA:MMA:A4G = 20:70:10; (\bullet) PMMA:MMA:A4G = 12:78:10; irradiation temperature 20°C.

Mold Polymerization of Soft Gel Prepolymer by Irradiation

The prepared soft gel prepolymer can be molded using a mold surface. In this case, molding is carried out conveniently by inserting and pressing lightly the gel prepolymer between the two faces of a mold with clamps. The sample is then cured to the completely polymerized hard polymer by irradiation. Curing by

TABLE II
Curing Polymerization of Soft Gel Prepolymers^a

Preparation of soft gel		Penetration degree of soft gel, 10 ⁻¹ mm	Curing of soft gel	
Dose rate, R/hr	Irrad. time required, hr		Dose rate, R/hr	Irrad. time required, hr
2 × 10 ⁵	1.0	106-108	2 × 10 ⁵	1.5
2.5 × 10 ⁵	1.0	45-50	2 × 10 ⁵	1.0
1.5 × 10 ⁵	1.5	42-45	2 × 10 ⁵	1.0
2.1 × 10 ⁵	1.0	90	2 × 10 ⁵	1.5

^a Composition of PMMA:MMA:A4G (in %) = 20:70:10.

irradiation is very convenient, in comparison with catalytic curing, because homogeneous mixing of curing catalyst with gel prepolymer is difficult.

Some results of the curing polymerizations of gel prepolymer at room temperature are shown in Table II. The operation of molding and releasing polymer was very simple and efficient by this method. This method can be applied to the production of various spherical surface lenses such as magnifier and spectacle lenses and also nonspherical lenses such as Fresnel lenses and reflection lenses.

References

1. I. Kaetsu, F. Yoshii, H. Okubo, and A. Ito, *ACS Polym. Prepr.*, **16**(1), 465 (1975).
2. F. Yoshii, H. Okubo, and I. Kaetsu, *J. Appl. Polym. Sci.*, **22**, 389 (1978).
3. H. Okubo, F. Yoshii, S. Honda, and I. Kaetsu, *J. Appl. Polym. Sci.*, **22**, 13 (1978).
4. H. Okubo, M. Kato, and I. Kaetsu, *J. Appl. Polym. Sci.*, **22**, 27 (1978).
5. H. Okubo, S. Honda, F. Yoshii, Y. Morita, and I. Kaetsu, *J. Appl. Polym. Sci.*, **22**, 43 (1978).

Received July 11, 1978

Revised November 6, 1978