

Study of Photopolymers. IX. Synthesis and Rates of Photocrosslinking of Epoxy Acrylates

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Synopsis

Epoxy acrylates such as bisphenol type (I-A), propylene glycol type (II-A), and phthalic acid ester type (III-A) were prepared from addition reaction between each epoxy resin and acrylic acid. These reactions were carried out in the absence of solvent and in the presence of quaternary ammonium salt. The rate of addition reaction between glycidyl ether-type epoxide and acrylic acid obeyed first order. The rates of addition reaction between glycidyl ester-type epoxide and acrylic acid obeyed first order at 80°C, but obeyed second order rather than first order at 90°C and above. The rates of photocrosslinking of epoxy acrylates were measured by IR spectrophotometry. Epoxy acrylates with benzoin ethyl ether (1 wt-%) were irradiated with a high-pressure mercury lamp in oxygen-free atmosphere. The rates of photocrosslinking of epoxy acrylates II-A, III-A, and I-A decrease in that order.

INTRODUCTION

A photopolymer such as poly(vinyl cinnamate)¹ has been used widely as a photoresist in electrical industries and as a printing plate in the printing industry. This polymer is soluble in some solvents before irradiation by light and become insoluble in any solvents after the irradiation.

Recently, some photocurable polymers have been reported. They are liquids before the irradiation by light and are cured after the irradiation. They are used as a photocurable coatings² and a quick-drying printing inks.^{3,4}

Although many patents⁵⁻¹⁶ have been published on photocurable polymers, detailed investigation of these polymers have not been reported.

In this paper, addition reaction between epoxy resins and acrylic acid and the rates of photocrosslinking of epoxy acrylates obtained were investigated.

EXPERIMENTAL

Materials

Technical-grade epoxy resins such as bisphenol type (I) (Dow Chemical; DER-331), propylene glycol type (II) (Dow Chemical; DER-736), and

phthalic acid ester type (III) (Showa Denco; Syodyne-508) were used. The epoxide equivalents of these resins were about 190. Reagent-grade acrylic acid, styrene, triethylbenzylammonium chloride (TEBAC) as a reaction catalyst, monomethoxy hydroquinone (MQ) as a thermopolymerization inhibitor, and benzoin ethyl ether as a photopolymerization initiator were further used.

Synthesis of Epoxy Acrylate of Bisphenol Type (I-A)

Epoxy acrylate I-A was prepared as follows: Epoxy resin I (95 g, 0.5 mole), acrylic acid (36 g, 0.5 mole), TEBAC (2 g), and MQ (0.05 g) were stirred for 2 hr at 100–110°C. The reaction mixture was cooled to room temperature and analyzed (degree of esterification, 99.9 mole-%).

Synthesis of Epoxy Acrylate of Propylene Glycol Type (II-A)

Epoxy acrylate II-A was prepared from Epoxy resin II (95 g, 0.5 mole), acrylic acid (36 g, 0.5 mole), TEBAC (2 g) and MQ (0.05 g) under the same conditions as epoxy acrylate I-A (degree of esterification, 99.4 mole-%).

Synthesis of Epoxy Acrylate of Phthalic Acid Ester Type (III-A)

Epoxy acrylate III-A was prepared from epoxy resin III (95 g, 0.5 mole), acrylic acid (36 g, 0.5 mole), TEBAC (2 g) and MQ (0.05 g) under the same conditions as epoxy acrylate I-A (degree of esterification, 95.3 mole-%).

Measurement of Molecular Weight and Hydroxyl Number

Molecular weight of epoxy acrylate, reducing to standard polystyrene (Pressure Chemical's reagents), was measured in tetrahydrofuran by gel permeation chromatography (TOYOSODA, Model HLC-801). The hydroxyl number was measured by the usual method.¹⁷

Measurement of Rates of Addition Reaction Between Epoxy Resins and Acrylic Acid

Additional reactions between epoxy resins and acrylic acid were carried out at 80°, 90°, 100°, and 110°C as follows: The mixture of epoxy resin (95 g, 0.5 mole), acrylic acid (36 g, 0.5 mole), and MQ (0.05 g) was heated to reaction temperature, and TEBAC (2 g) was added to the mixture with stirring. After a certain time, the sample (0.1–2 g) of the reaction mixture was removed from the flask and titrated with a 0.1*N* alcoholic KOH solution in dioxane (20 ml). Acid titration was carried out as for the starting acids.

Measurement of Rates of Photocrosslinking and After-Polymerization

The rates of photocrosslinking were measured as follows: Benzoin ethyl ether (1 wt-%) was added to the epoxy acrylates and the mixtures. The photocurable polymers were applied on KRS plates, and the polymers were irradiated in oxygen-free atmosphere by a high-pressure mercury lamp (manufactured by Ushio Electric Co., Model USH-500D) at a distance of

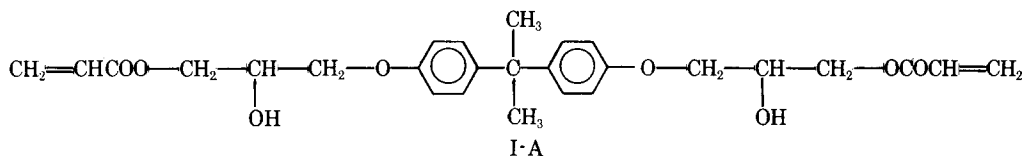
30 cm. The decrease in the absorbance of the >C=C< bond at 1640 cm^{-1} was measured by IR spectrophotometry (Hitachi, Model EP-1-G2). The degree of conversion of photocrosslinking was estimated from the IR spectra obtained.

In the same manner, afterpolymerization of these polymers were measured as follows: The photocurable polymers were applied on KRS plates and the polymers were irradiated for 0.2 sec under the same conditions as the measurement of the rates of photocrosslinking. The irradiated polymers were protected from light. After a certain time, the decrease in the absorbance of the >C=C< bond at 1640 cm^{-1} was measured by IR spectrophotometry. The absorbances were measured as the absorbances after irradiation for 0.2 sec.

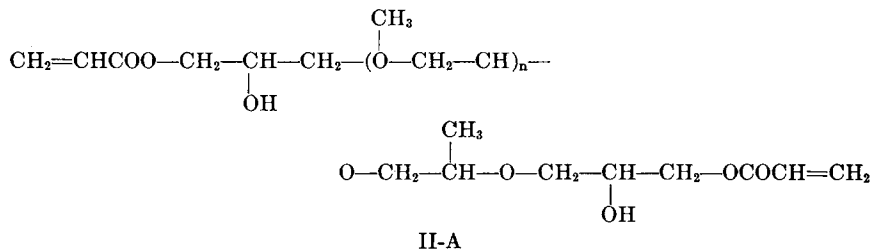
RESULTS AND DISCUSSION

Synthesis of Epoxy Acrylate

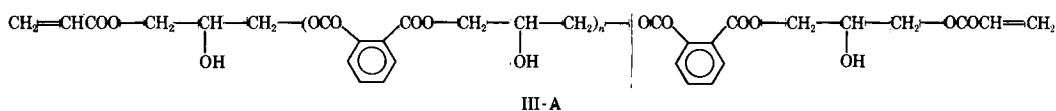
Epoxy acrylate I-A is obtained by addition reaction between epoxy resin I and acrylic acid. This epoxy acrylate is a high-viscosity liquid, with a viscosity of 12400 poises at 25°C . This epoxy acrylate is soluble in acetone, ethyl acetate, methanol, and dioxane, but insoluble in water:



Epoxy acrylate II-A is obtained by addition reaction between epoxy resin II and acrylic acid. The viscosity of this epoxy acrylate is 13 poises at 25°C . It is soluble in acetone, ethyl acetate, methanol, dioxane, and water:

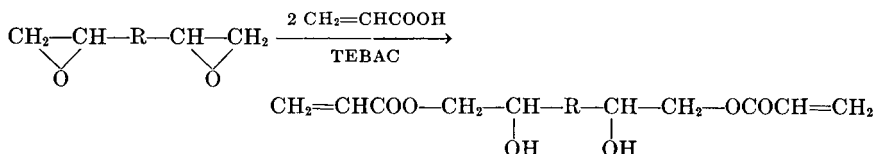


Epoxy acrylate III-A is obtained by addition reaction between epoxy



resin III and acrylic acid. The viscosity of this epoxy acrylate is 1367 poises at 25°C. It is soluble in acetone, ethyl acetate, methanol, dioxane, and water:

From acid titration of free acrylic acid, NMR spectra of protons and IR spectra of the disappearance of the absorption as carboxylic groups at 1680 cm^{-1} , and epoxide groups at 950 cm^{-1} , and of the appearance of hydroxyl groups at 3480 cm^{-1} and ester groups at 1730 cm^{-1} , it was confirmed that any side reaction, such as esterification, etherification, transesterification,



hydrolysis, and hydration, have not occurred under these conditions. This is also reported by Alvey,¹⁸ Sakai et al.,¹⁹ and Kakiuhi and Tanaka.²⁰

Rates of Addition Reaction Between Epoxy Resins and Acrylic Acid

The reactions between epoxide and carboxylic acid in some solvents have been studied by many investigators.¹⁸⁻²² In this paper, the addition reactions between epoxy resins and acrylic acid are discussed. These reactions were carried out in the absence of any solvents and in the presence of quaternary ammonium salt. In Figure 1, epoxy acrylate I-A is obtained

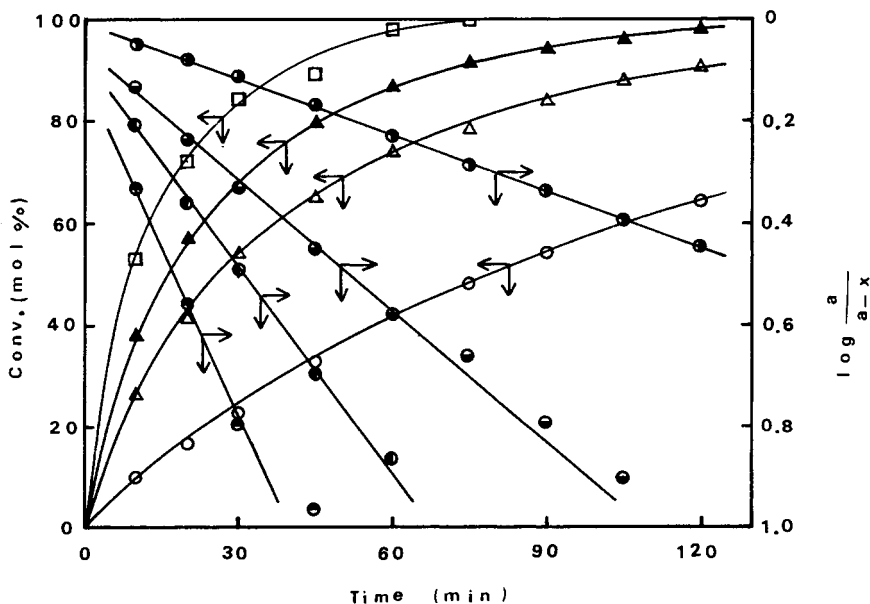


Fig. 1. Reaction between epoxy resin I and acrylic acid (epoxy resin, 95 g (0.5 mole); acrylic acid, 36 g (0.5 mole), TEBAC, 2 g; MQ, 0.05 g). Temp.: °C (○, ●) 80°C; (△, ▲) 90°C; (●, ▲) 100°C; (●, □) 110°C.

quantitatively by addition reaction between epoxy resin I and acrylic acid at from 100°C to 110°C. The decrease of the acrylic acid concentration obeyed a good first-order rate. The rate constants (k_1) at each reaction temperature were found to be: $3.65 \times 10^{-3} \text{ min}^{-1}$ (80°C), $8.58 \times 10^{-3} \text{ min}^{-1}$ (90°C), $13.76 \times 10^{-3} \text{ min}^{-1}$ (100°C), and $22.54 \times 10^{-3} \text{ min}^{-1}$ (110°C), respectively. Activation energy calculated for this reaction from the Arrhenius plot was 16.55 kcal/mole.

In Figure 2, epoxy acrylate II-A is obtained quantitatively by addition reaction between epoxy resin II and acrylic acid at from 100°C to 110°C. The decrease of the acrylic acid concentration obeyed a good first order rate. The rate constants (k_1) at each reaction temperature were found to be: $2.66 \times 10^{-3} \text{ min}^{-1}$ (80°C), $4.10 \times 10^{-3} \text{ min}^{-1}$ (90°C), $9.90 \times 10^{-3} \text{ min}^{-1}$ (100°C), and $16.64 \times 10^{-3} \text{ min}^{-1}$ (110°C), respectively. The activation energy calculated for this reaction from the Arrhenius plot was 16.72 kcal/mole. In Figure 3, at the initial stage, the rate of addition reaction between epoxy resin III and acrylic acid was much faster than those between other epoxy resins and acrylic acid. But at the last stage, addition reaction became slow and could not go to completion. In Figure 4, at the initial stage of reaction between epoxy resin III and acrylic acid, the decrease of the acrylic acid concentration obeyed a good first-order rate, but at the last stage, it was not obeyed at 80°C. At 90°C and above, the decrease of the acrylic acid concentration obeyed second-order rather than first-order rate. The rate constant (k_1) of this reaction at 80°C, which was

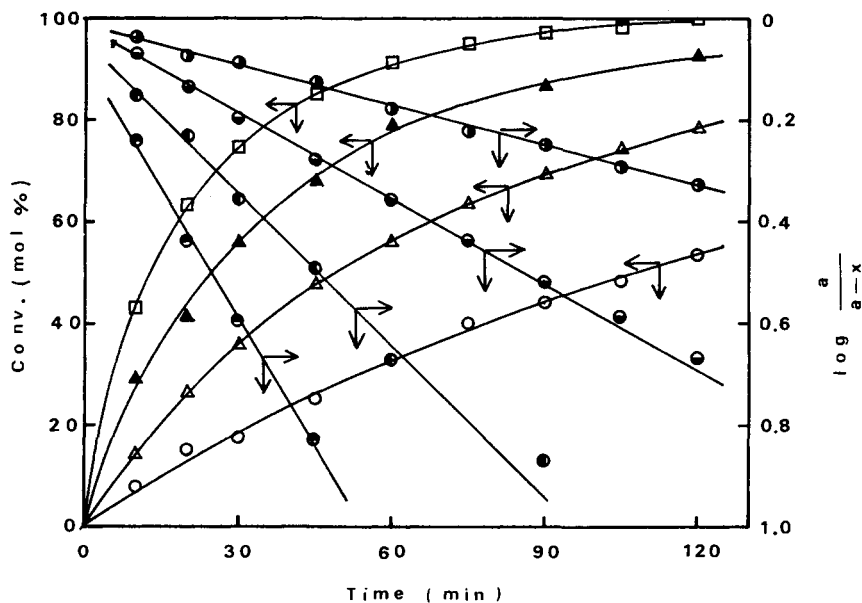


Fig. 2. Reaction between epoxy resin II and acrylic acid (epoxy resin, 95 g (0.5 mol); acrylic acid, 36 g (0.5 mol), TEAC, 2 g; MG, 0.05 g). Temp.: (O, ●) 80°C; (○, △) 90°C; (●, ▲) 100°C; (●, □) 110°C.

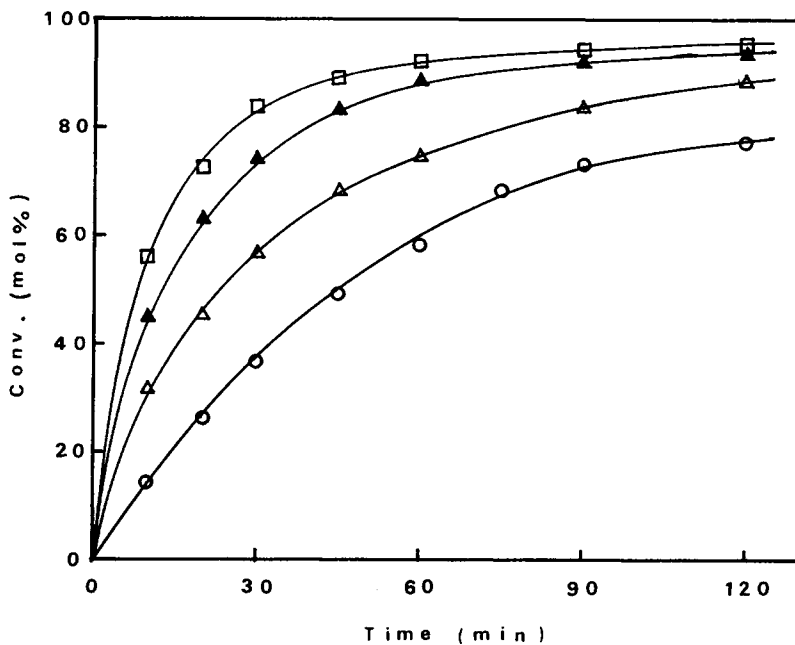


Fig. 3. Reaction between epoxy resin III and Acrylic acid (epoxy resin, 95 g (0.5 mole); acrylic acid, 36 g (0.5 mole); TEBAC, 2 g; MQ, 0.05 g). Temp.: (○) 80°C; (△) 90°C; (▲) 100°C; (□) 110°C.

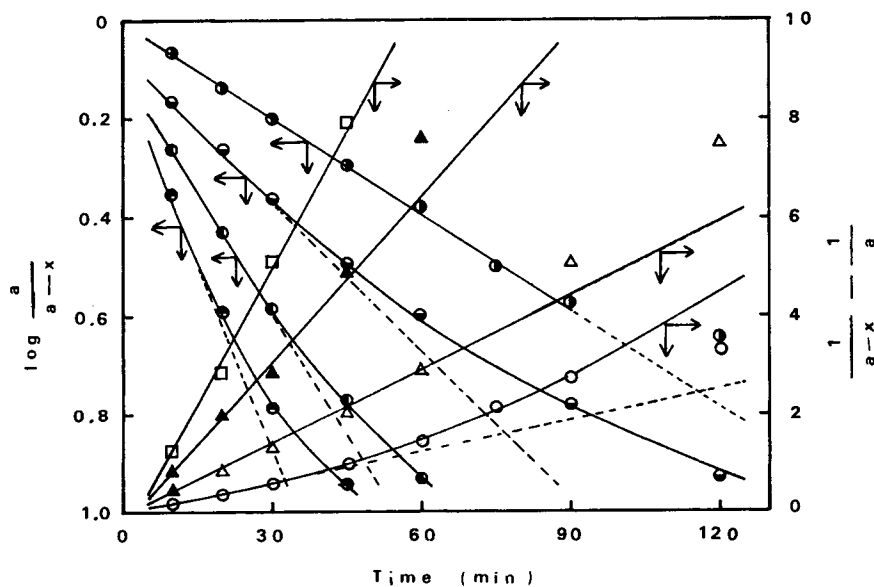


Fig. 4. Rate of addition reaction between epoxy resin III and acrylic acid (epoxy resin, 95 g (0.5 mole); acrylic acid, 36 g (0.5 mole); TEBAC, 2 g; MQ, 0.05 g). Temp.: (○, ⊙) 80°C; (⊖, △) 90°C; (⊙, ▲) 100°C; (⊖, □) 110°C.

first order, was found to be $4.53 \times 10^{-3} \text{ min}^{-1}$. The rate constants (k_2) which were second order were found to be: $5.08 \times 10^{-2} \text{ mole}^{-1} \cdot \text{min}^{-1}$ (90°C), $11.02 \times 10^{-2} \text{ mole}^{-1} \cdot \text{min}^{-1}$ (100°C), and $18.34 \times 10^{-2} \text{ mole}^{-1} \cdot \text{min}^{-1}$ (110°C), respectively.

From these results, the rate of the addition reaction between glycidyl ether-type epoxide and acrylic acid was first order. On the other hand, the rate of the addition reaction between glycidyl ester-type epoxide and acrylic acid at a lower temperature was different from that at higher temperature. It was suggested that the reaction obeyed a different mechanism at a lower temperature than at a higher temperature.

Rates of Photocrosslinking of Epoxy Acrylates

The rates and conversions of photocrosslinking were measured by the IR-spectrophotometric method.^{23,24} The relationships between degree of conversion of photocrosslinking and time for each epoxy acrylate and its mixture are shown in Figure 5.

At the initial stage, the rate of photocrosslinking of epoxy acrylates II-A, III-A, and I-A decreases in that order. The viscosity of epoxy acrylate II-A, III-A, and I-A was 13, 1367, and 12400 poises, respectively at 25°C . After 2 sec of irradiation time, the conversion of photocross-

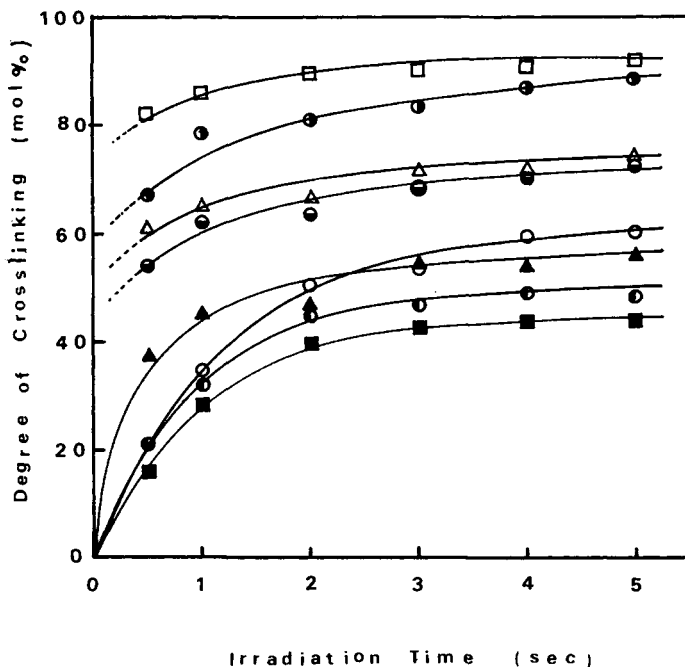


Fig. 5. Degree of conversion of photocrosslinking (light source, 500-W high-pressure mercury lamp): (○) I-A; (△) II-A; (□) III-A; (●) I-A (50 wt-%)-II-A (50 wt-%); (⊙) I-A (25 wt-%)-II-A (75 wt-%); (▲) I-A (90 wt %)-styrene (10 wt-%); (⊖) I-A (80 wt-%)-styrene (20 wt-%); (■) I-A (70 wt-%)-styrene (30 wt-%).

linking of epoxy acrylates II-A, III-A, and I-A was about 90, 70, and 50 mole-%, respectively. When epoxy acrylate II-A, having a low viscosity, was added to epoxy acrylate I-A, having a high viscosity, the rate of photocrosslinking of the mixture became higher than that of epoxy acrylate I-A and tended to increase with increasing the addition amount. On the other hand, when styrene (10 wt-%) was added to epoxy acrylate I-A, the rate of photocrosslinking of the mixture increased until 2 sec of irradiation time, but decreased thereafter. The rates of photocrosslinking of the mixtures tended to decrease with increasing the addition amount of styrene. The rate of polymerization of styrene²⁵ is slower than that of acrylate.

The relationships between degree of conversion of photocrosslinking and time for each epoxy acrylate and its mixture at the last stage are shown in Figure 6. The conversion of photocrosslinking of epoxy acrylate II-A was around 100 mole-% completely after 30 sec of irradiation time, whereas the conversions of photocrosslinking of epoxy acrylate III-A and I-A were 97 and 80 mole-%, respectively after the same irradiation time. On the other hand, when styrene was added to epoxy acrylate I-A, the conversions of photocrosslinking of the mixture of I-A (90 wt-%) and styrene (10 wt-%) and the mixture of I-A (70 wt-%) and styrene (30 wt-%) were about 97 and 85 mole-%, respectively, after 120 sec of irradiation time. When the photocurable polymers applied on glass plates were irradiated, epoxy acrylates II-A, III-A, and I-A became insoluble in acetone after 0.1, 0.2, and

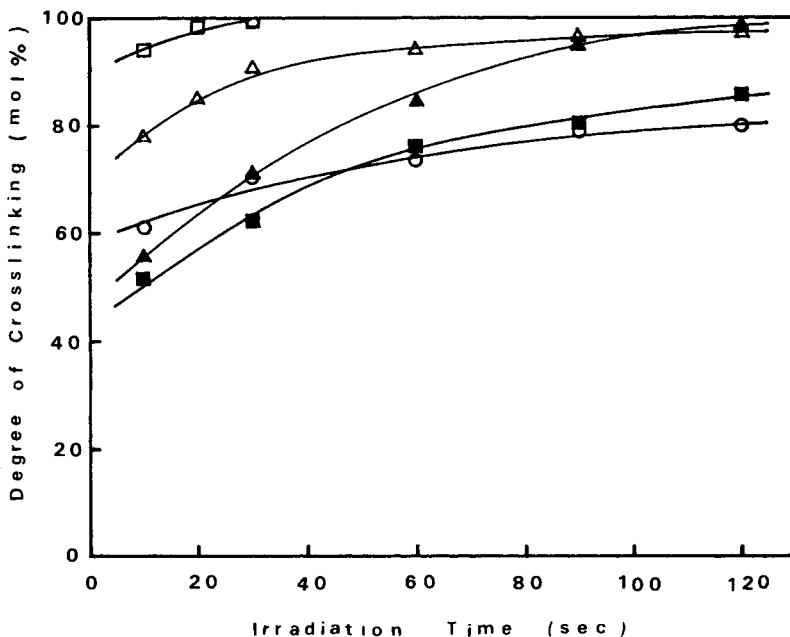


Fig. 6. Degree of conversion of photocrosslinking (light source, 500-W high-pressure mercury lamp): (O) I-A; (□) II-A; (Δ) III-A; (▲) I-A (90-wt%)-styrene (10 wt-%); (■) I-A (70 wt-%)-styrene (30 wt-%).

0.5 sec of irradiation time, respectively. This sequence agreed with the sequence of the rate of photocrosslinking by IR spectrophotometry.

From these results, when the rates of photocrosslinking of epoxy acrylates having the same degree of molecular weight are compared (Table I), the following can be concluded. The rates of photocrosslinking of epoxy acrylates at the initial stage were controlled by the molecular mobility, and the rate of photocrosslinking of epoxy acrylates having lower viscosity was higher than that of those having higher viscosity; whereas the rates of photocrosslinking of epoxy acrylates at the last stage were influenced by the glass transition temperature^{26,27} of the crosslinking epoxy acrylates. The molecular mobility of epoxy acrylate at the initial stage and the glass transition temperature of the crosslinking epoxy acrylate at the last stage were controlled by the molecular structure of the epoxy acrylate.

TABLE I
Molecular Weights and Hydroxyl Numbers of Epoxy Acrylates

Epoxy acrylate	Number-average mol wt \bar{M}_n	Weight-average mol wt \bar{M}_w	\bar{M}_w/\bar{M}_n	Hydroxyl number
I-A	809	871	1.07	235.1
II-A	692	749	1.08	207.6
III-A	662	753	1.13	230.1

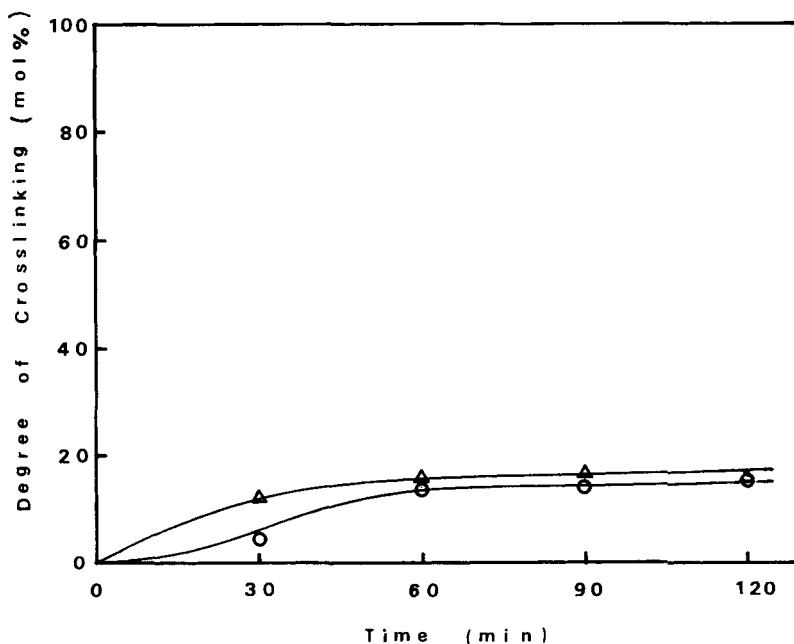


Fig. 7. Afterpolymerization (light source, 500-W high-pressure mercury lamp). Irradiation conditions: 0.2 sec at a distance of 30 cm; (O) I-A; (Δ) III-A.

Afterpolymerizations of Epoxy Acrylates

In Figure 7, afterpolymerization of epoxy acrylate II-A did not proceed, whereas afterpolymerizations of epoxy acrylates I-A and III-A did proceed, about 15–17 mole-% for 2 hr.

It is uncertain whether this is caused by the density of polymerizable double bonds remaining or by the influence of viscosity hindering the diffusion of oxygen into the epoxy acrylates.

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