

# Water-Dispersible Graft Copolymer Mixtures Prepared by Electron Irradiation. I. Polymerization Behavior

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## Synopsis

Highly viscous systems made up of 70 wt% epoxy resin dissolved in 30 wt% monomer mixtures of acrylic acid and styrene were irradiated with 1.5 MeV electrons to initiate graft copolymerization. The temperature measurement of the systems reveals that the polymerization reaction takes place both during and after the electron-beam exposure of about 5-sec duration. The reaction lasts about 50 sec for a low beam current of 0.6 mA, while for a high beam current of 6.0 mA it lasts merely about 20 sec. The gel permeation chromatography (GPC) measurement of obtained products demonstrates that the molecular weight distribution of ungrafted copolymer of acrylic acid and styrene becomes strikingly broader as the beam current is lowered. The GPC data suggest that the fraction of epoxy resin having a grafted branch increases with an increase in the beam current. All of these results are interpreted in terms of the mobility and the concentration of reactive species such as polymer radicals and low molecular weight free radicals.

## INTRODUCTION

Graft and block copolymers are known to have unique properties which cannot be expected from homopolymers. One of the most characteristic properties of such copolymers is its emulsifying effect due to the chemically different polymeric parts in the same macromolecule. This effect can be applied to the preparation of water-dispersible copolymers. Using free radical initiators, Woo et al. synthesized epoxy-acrylic graft copolymers which were composed of ungrafted epoxy resin, ungrafted acrylic copolymer, and epoxy-acrylic graft copolymer.<sup>1</sup> The graft copolymer mixtures were dispersed in water by the procedure involving the neutralization with base such as 2-dimethylaminoethanol.

The radiation-initiation method of polymerization has several characteristics which are not observable in the conventional chemical-initiation method.<sup>2</sup> For example, the radiation method of polymerization can be applied even to low-temperature and/or highly viscous systems. For this reason, several groups of workers have applied the radiation method to the graft copolymerization of highly viscous systems of polymers dissolved in monomers.<sup>2,3</sup> These works have been performed, in most cases, with  $\gamma$ -rays from a <sup>60</sup>Co source. Nakayama et al., however, used high-energy electrons from an accelerator to initiate the graft copolymerization of highly viscous systems of epoxy resin dissolved in acrylic monomers.<sup>4,5</sup> They found that the obtained products of

graft copolymer mixtures can be dispersed in water in the same manner as that synthesized by Woo et al. using chemical initiators.<sup>1</sup>

An important feature of the electron-beam method compared to the  $\gamma$ -ray method is that a considerably high dose rate is available for electron irradiation. At present, however, characteristics of the radiation-initiated graft copolymerization of highly viscous systems are not known in detail for high-energy electrons, although many studies have been reported for  $^{60}\text{Co}$   $\gamma$ -rays.<sup>2,3</sup> We conducted the electron-beam irradiation of highly viscous systems of epoxy resin dissolved in monomer mixtures of acrylic acid and styrene. This study revealed some characteristics of the electron-beam method of graft copolymerization. The present paper mainly describes the polymerization behavior of monomers in such highly viscous systems and the gel permeation chromatography (GPC) data for the obtained products composed of ungrafted epoxy resin, ungrafted acrylic copolymer, and epoxy-acrylic graft copolymer. A later paper of this series will describe the dispersion procedure of the graft copolymer mixtures, the particle size of obtained dispersions, and the stability of dispersions to the addition of electrolytes.<sup>6</sup>

## EXPERIMENTAL

Epoxy resin Epikoto 1009 was obtained from Yuka Shell Epoxy K. K. All the other chemicals were obtained from Tokyo Kasei or Wako Junyaku. These materials were used without further purification.

The epoxy resin was grounded to a powder by using a sample mill. A blend of this epoxy powder (350 g) with a monomer mixture of acrylic acid and styrene (150 g) was heated for 1 h at 70°C under nitrogen atmosphere with stirring. The resulting highly viscous solution was sandwiched between two polyester films, and then pressed into a 2–3-mm thick sheet by using a hot press. The sheet was placed on a conveyor, and was exposed to 1.5 MeV electrons from a Cockcroft-Walton type accelerator (Nisshin High Voltage Co., Ltd.) at room temperature. The conveyor was set to move at 3.3 m/min in the present study, so that the duration of each exposure was about 5 secs. The electron-beam current was set at 0.6, 2.0, 6.0, and 18.0 mA, so that the absorbed dose for each exposure was 3.1, 10.3, 31, and 93 kGy, respectively, as was estimated by using the CTA (cellulose triacetate) film dosimeter.<sup>7</sup>

Measurements of molecular weight distributions were carried out by using a GPC apparatus of Waters Associates, Inc. with four series-connected fractionation columns packed with styragel beads of  $10^5$ ,  $10^4$ ,  $10^3$ , and  $100 \text{ \AA}$  nominal porosities. Both a differential refractometer and a spectroflow monitor SF 770 of Schoeffel Instrument Corp. were used simultaneously in the GPC measurements. An approximately 0.5% solution of a graft copolymer mixture in tetrahydrofuran (THF) was injected into the THF mobile phase of 1 mL/min flow rate at room temperature.

## RESULTS AND DISCUSSIONS

### Conversion Versus Number of Exposures

The conversion of monomers was measured after each exposure. The effect of the monomer composition on the conversion curve was studied for the

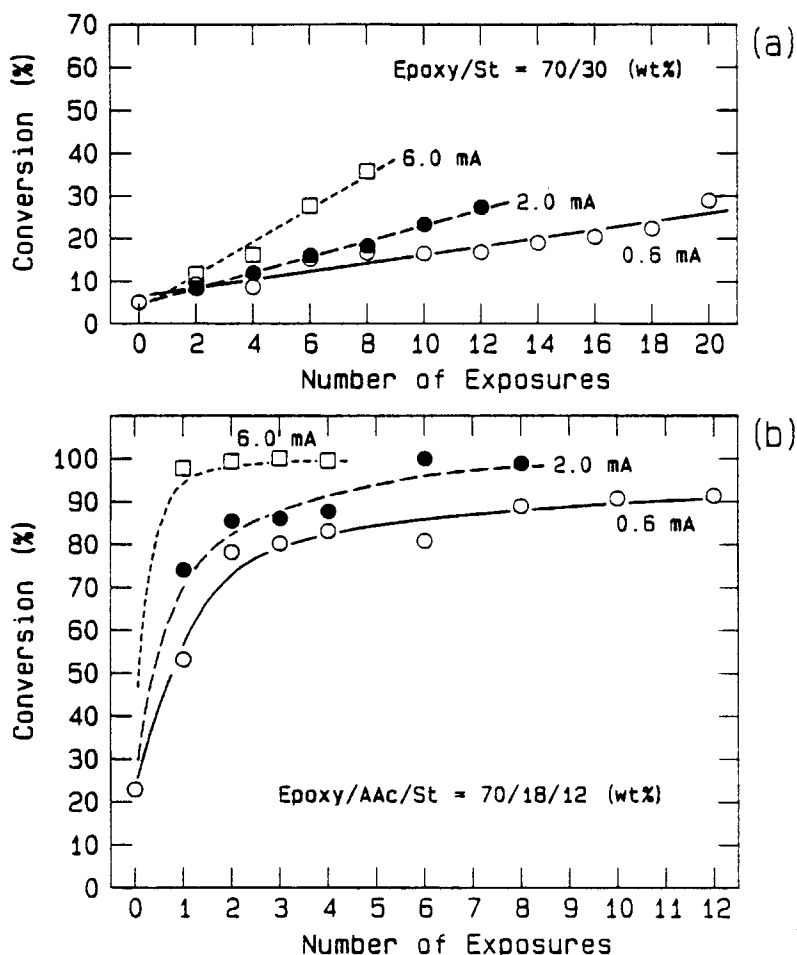


Fig. 1. Conversion of monomers as a function of the number of exposures for the formula of 70 wt% epoxy resin and 30 wt% monomer mixture of AAc and St. The AAc/St composition is (a) 0/30 and (b) 18/12 by weight.

formula of epoxy resin (70 wt%) and monomer mixtures (30 wt%) of acrylic acid (AAc) and styrene (St). The effect of the electron-beam current on the conversion curve was also studied at 0.6, 2.0, and 6.0 mA. The results are shown in Figures 1(a) and 1(b) for the AAc/St compositions of 0/30 and 18/12 by weight, respectively. In these figures, the conversion is plotted as a function of the number of exposures.

Comparison of the conversion curve between the two monomer compositions (Fig. 1) reveals that the polymerization rate is strikingly increased by the presence of acrylic acid. This effect of acrylic acid is illustrated more intelligibly in Figure 2, where the conversion after the first exposure is plotted as a function of the weight fraction of acrylic acid in the monomer mixture. Figure 2 includes also the conversion measured before the exposure. This conversion is due for the most part to the thermally initiated polymerization

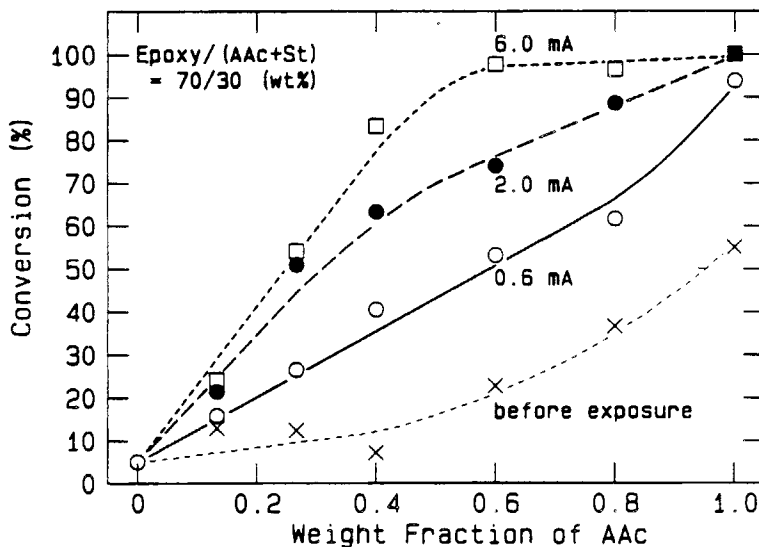


Fig. 2. Conversion of monomers before and after the first exposure as a function of the weight fraction of AAC in the AAC/St mixture for the formula of 70 wt% epoxy resin and 30 wt% monomer mixture.

during the preparation of an epoxy solution in monomers at 70°C. Then it is seen that the conversion due to the first exposure increases with an increase in the weight fraction of acrylic acid at every beam current of 0.6, 2.0, and 6.0 mA. This result appears to be associated mainly with the protective effect of styrene monomers.<sup>2</sup> In the present systems of epoxy resin dissolved in monomers, the weight fraction of epoxy is as high as 70%, and hence the total amount of energy deposition is higher in epoxy resin than in monomers. A certain amount of the energy deposited in epoxy resin is then transferred to styrene monomers, thus decreasing the number of epoxy resin radicals which initiate the polymerization of monomers. An increase in the weight fraction of acrylic acid, accordingly, will lead to a decreased efficiency of the protective effect of styrene and, consequently, to an increased conversion of monomers.

Figure 1(b) reveals that although the conversion curve for the current of 6.0 mA ( $\square$ ) approaches 100% after the first exposure, the conversion curve for the current of 0.6 mA ( $\circ$ ) reaches only about 90% even after the exposure is repeated 12 times. This result appears to be related to the temperature of the system during polymerization. A copper-constantan thermocouple inserted in the system showed that the temperature rose above 110°C for the exposure at 6.0 mA, while at 0.6 mA the temperature increased only up to about 34°C. Temperature rise above 110°C will favor the diffusion of monomers, resulting in 100% conversion. Temperatures as low as 34°C, on the other hand, will lower the diffusion rate of monomers especially when the conversion is increased by exposures, thus giving a final conversion less than 100%. Irradiation of the present systems at controlled temperatures would seem to be a fruitful area for additional work.

### Polymerization Behavior by Temperature Measurements

The temperature of the polymerization system during and after exposure was measured by using a copper-constantan thermocouple inserted in the system. Typical examples of the temperature measurement are shown in Figures 3(a) and 3(b) for the formula of epoxy resin (70 wt%), acrylic acid (18 wt%), and styrene (12 wt%) exposed at the beam currents of 0.6 and 6.0 mA, respectively. This formula is the same as that in Figure 1(b). In Figure 3, a steep rise in temperature corresponds to the exposure of about 5-sec duration which is made when the polymerization system on a conveyor passes through the electron beam.

Figure 3(a), for the current of 0.6 mA, shows that the temperature rises to

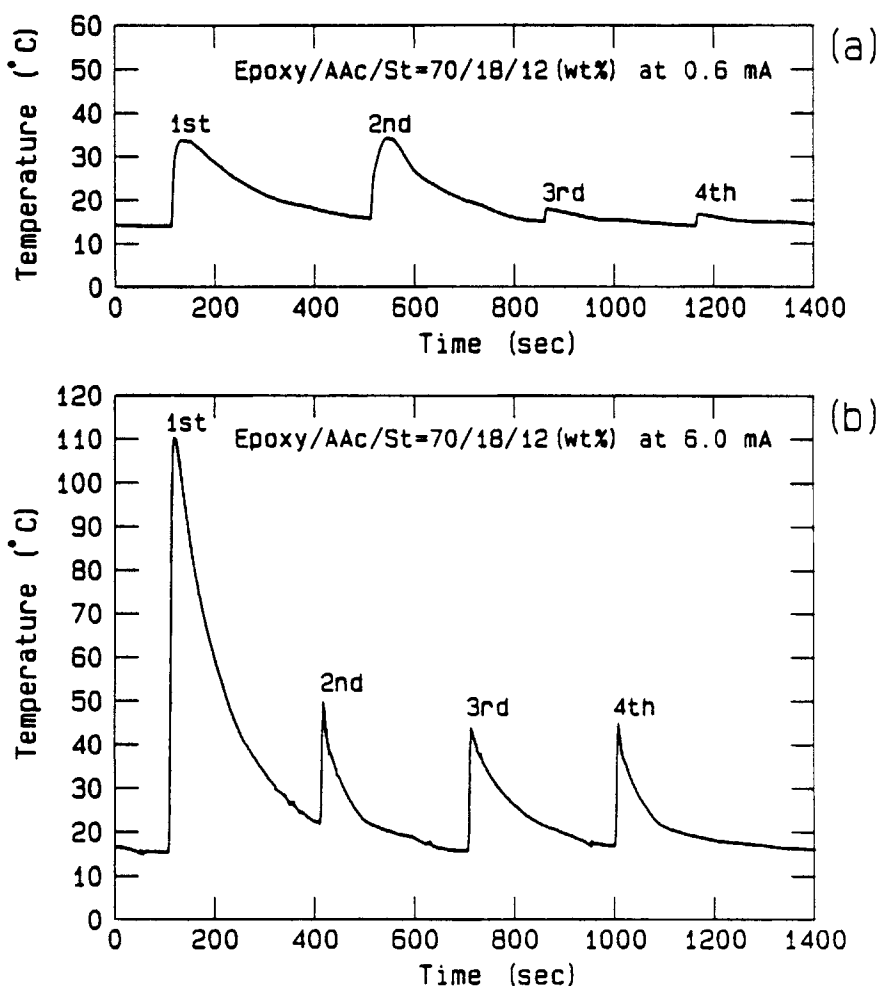


Fig. 3. Temperature of the polymerization system as a function of time for the formula of 70 wt% epoxy resin, 18 wt% AAc, and 12 wt% St exposed at the beam currents of (a) 0.6 and (b) 6.0 mA.

about 34°C in the first and second exposures, whereas in the third and fourth exposures the temperature rises only slightly above room temperature of 14°C. Figure 3(b), for the current of 6.0 mA, on the other hand, reveals that the temperature rises up to as high as 110°C in the first exposure, whereas in subsequent exposures the temperature rises only to about 45°C. Comparison of these results with the conversion data [Fig. 1(b)] suggests that the temperature increment with reference to the room temperature is correlated with the conversion increment in each exposure. For the current of 0.6 mA, for instance, the conversion increment is about 27% in the first and second exposures, whereas in the third and fourth exposures it is merely a few percentage points. It is reasonable to conclude, therefore, that the temperature increment in the first and second exposures [Fig. 3(a)] is practically due to the heat of polymerization reaction and that in the third and fourth exposures is due mainly to the heat of radiation energy deposited in the system. Similarly, the temperature increment in the first exposure at the current of 6.0 mA [Fig. 3(b)] is assigned to the heat of polymerization reaction plus radiation energy, and the temperature increments in the subsequent exposures are assigned mainly to the heat of radiation energy.

The heat generation behavior of the polymerization system was calculated from the data of temperature measurement shown in Figure 3 by using the following expression, which is derived by taking into account the heat transfer from the system to the environment.<sup>8</sup>

$$W/mc = dT/dt + K(T - T_0), \quad (1)$$

where  $W$  is the heat generation rate of the system (cal/sec),  $mc$  is the heat capacity of the system (cal/°C) ( $m$  is the mass and  $c$  is the specific heat),  $T$  and  $T_0$  are the temperatures of the system and the environment (°C), respectively,  $t$  is time (sec), and  $K$  is the heat transfer coefficient (sec<sup>-1</sup>). The value of  $K$  can be evaluated experimentally from the slope of the  $-\ln(T - T_0)$  vs. time plot in the range where  $W$  is regarded as zero. The  $W/mc$  value, when plotted against time, is considered to represent the superimposed behavior of the polymerization reaction of monomers and the radiation energy deposition in the system. The  $W/mc$  vs. time plots obtained for the temperature data in Figures 3(a) and 3(b) are shown in Figures 4 and 5, respectively. In Figure 4, for the current of 0.6 mA, the plot for the third exposure [Fig. 4(c)] virtually represents the behavior of the radiation energy deposition in the system. The plots for the first and second exposures [Figs. 4(a) and (b)], however, represent mainly the behavior of polymerization reaction of monomers. Thus it is seen that the reaction takes place both during and after each exposure, and lasts about 50 sec after the exposure of about 5 sec duration. In Figure 5, for the current of 6.0 mA, on the other hand, the  $W/mc$  vs. time plot for the second exposure [Fig. 5(b)] is attributable largely to the radiation energy deposition in the system. The plot for the first exposure [Fig. 5(a)], however, reveals that the polymerization reaction of monomers takes place mostly during the exposure and that the reaction lasts only about 20 secs.

These characteristics of the polymerization behavior should be interpreted in terms of the termination process of growing polymer chains. The termination process will be enhanced by an increase in the concentration of reactive

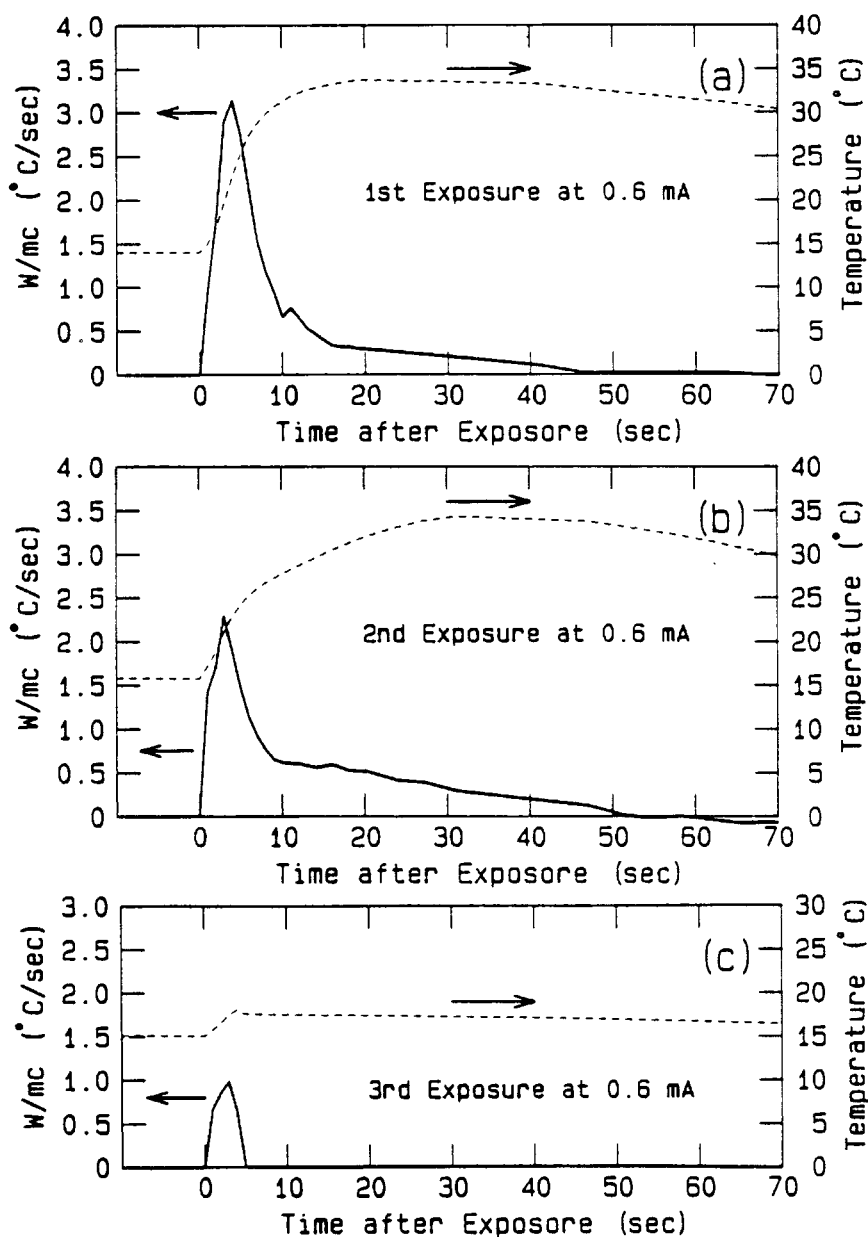


Fig. 4. Heat generation rate divided by the heat capacity of the polymerization system,  $W/mc$ , as a function of time after the (a) first, (b) second, and (c) third exposures at a beam current of 0.6 mA. This example is obtained from the temperature data shown in Fig. 3(a), which is indicated here by the dotted curve.

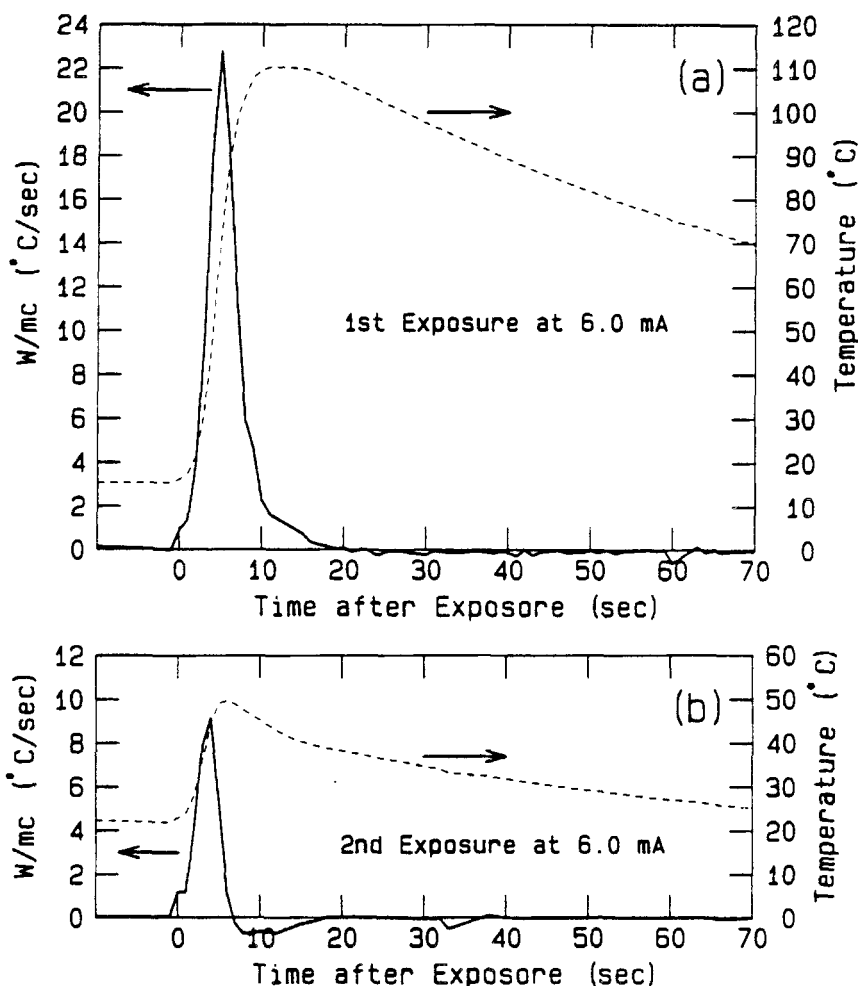


Fig. 5. Heat generation rate divided by the heat capacity of the polymerization system,  $W/mc$ , as a function of time after the (a) first and (b) second exposures at a beam current of 6.0 mA. This example is obtained from the temperature data shown in Fig. 3(b), which is indicated here by the dotted curve.

species such as polymer radicals and low molecular weight free radicals. The termination process will be further enhanced by an increase in temperature which results in an increase in the diffusion rate of such reactive species. The concentration of reactive species produced in the present system must be much higher for the exposure at 6.0 mA than at 0.6 mA, because the amount of radiation energy deposited per each exposure is directly proportional to the beam current. Furthermore, the temperature of the present system rises above 110°C for the exposure at 6.0 mA, while at 0.6 mA the temperature rises merely to 34°C (see Fig. 3). It is reasonable to conclude, therefore, that the mobility and the concentration of reactive species are responsible for the characteristic behavior of the polymerization reaction shown in Figures 4 and 5.



### Molecular Weight Distribution by GPC Measurements

In order to determine the GPC calibration curve for the epoxy resin used here, epoxy samples of narrow molecular weight distribution were obtained by fractionating Epikoto 1009 using an automatic preparative liquid chromatograph HLC-827 of Toyo Soda Co., Ltd. The molecular weight of obtained epoxy samples was measured by using a Hitachi Perkin-Elmer 115 apparatus. The GPC calibration curve thus determined for epoxy resin is shown by the solid curve in Figure 6. The broken curve in this figure is the GPC calibration curve obtained from eight standard samples of monodisperse polystyrene (Pressure Chemical Co.).

Typical examples of the GPC measurement are shown in Figures 7(a) and 7(b) for the graft copolymer mixtures obtained from the formula of epoxy resin (70 wt%), acrylic acid (12 wt%), and styrene (18 wt%) exposed at the beam currents of 0.6 and 6.0 mA, respectively. For the respective currents of 0.6 and 6.0 mA, the number of the repeated exposures was 8 and 2, and the final conversion of monomers was 93.7 and 99.8%. The solid and broken curves are the response of the ultraviolet (UV) and refractive index (RI) detectors, respectively. The dotted curve is the response of the UV detector obtained for the original Epikoto 1009 as a polymeric backbone in the graft copolymerization. The UV detector used here was set at 284 nm with the intention of detecting only the epoxy part in the graft copolymer mixture composed of ungrafted epoxy resin, ungrafted acrylic copolymer of acrylic acid and styrene, and epoxy-acrylic graft copolymer. This intention is based on the fact that although the acrylic copolymer is almost transparent at 284 nm, the epoxy resin has a strong absorption at this wavelength due to the bisphenol part, as

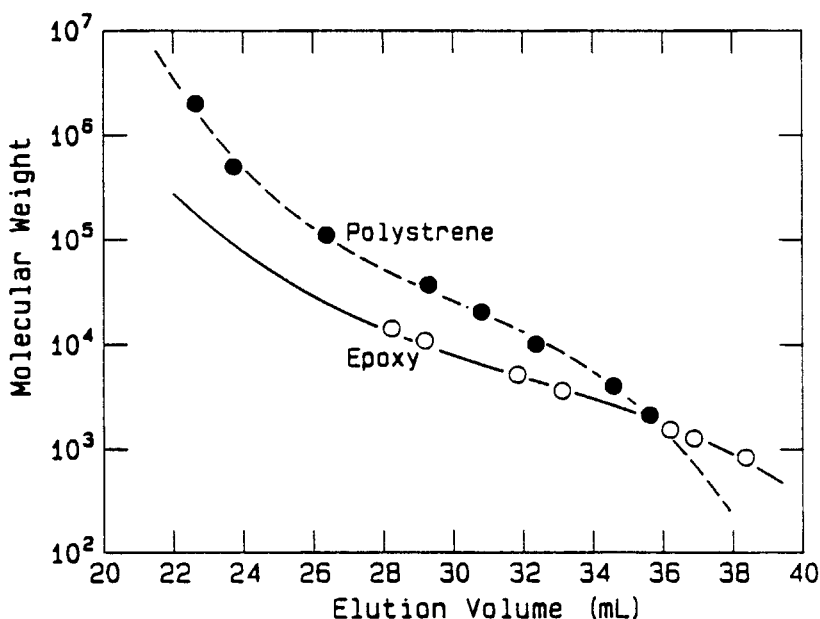


Fig. 6. GPC calibration curves of molecular weight vs. elution volume for epoxy resin (solid curve) and for polystyrene (broken curve).

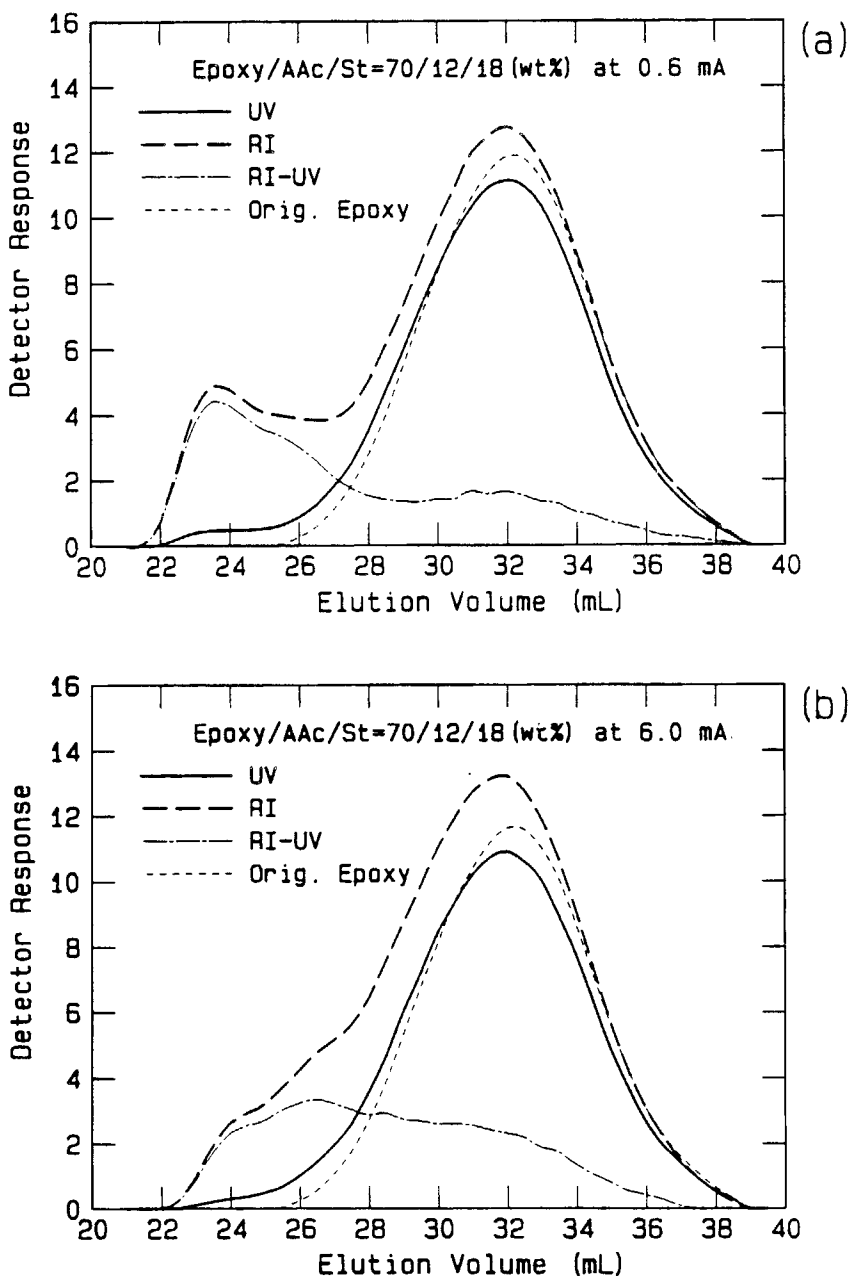


Fig. 7. GPC response curves of the ultraviolet (solid curve) and refractive index detectors (broken curve) for the graft copolymer mixtures obtained from the formula of 70 wt% epoxy resin, 12 wt% AAC, and 18 wt% St exposed at the beam currents of (a) 0.6 and (b) 6.0 mA. The dash-dot curve is a difference between the broken and solid curves at each elution volume. The dotted curve is the response of ultraviolet detector obtained for the original epoxy resin.

is inferred from the ultraviolet spectra of the analogous compounds like 2,2-bis[*p*-(allyloxy) phenol] propane.<sup>9</sup> Then, the UV curve in Figure 7 is normalized so that the area under the curve becomes the weight fraction of epoxy resin in the graft copolymer mixture (this weight fraction is 71.3 and 70.0% for the examples in Figs. 7(a) and (b), respectively). The RI curve, on the other hand, is normalized so that the area under the curve becomes 100, on the assumption that the sensitivity of the RI detector to epoxy resin and to acrylic copolymer is the same. This assumption was checked by a method similar to that described by Runyon et al.<sup>10</sup> We injected a precisely measured amount of polymer into the GPC apparatus, and integrated the RI curve over the elution volume. The integral per gram polymer was 1133 for Epikoto 1009, and was 1053 on the average for the graft copolymer mixtures studied here, thus indicating that the sensitivity of the RI detector used here does not differ appreciably for epoxy resin and acrylic copolymer.

The dash-dot curve in Figure 7 is the difference between the RI and UV curves at each elution volume. The curve thus obtained can be interpreted as the GPC chromatogram for ungrafted acrylic copolymer when the graft copolymer mixture contains no epoxy-acrylic graft copolymer. As a first approximation, this will be still true even when such a graft copolymer is contained to a certain extent. Then it is seen from the dash-dot curve in Figures 7(a) and 7(b) that the molecular weight distribution of ungrafted acrylic copolymer is appreciably broader for the exposure at 0.6 mA than at 6.0 mA. The strikingly broad distribution for the 0.6 mA exposure is perhaps related, at least in part, to the polymerization reaction which takes place both during and after exposure, and lasts as long as 50 sec after the first and second exposures [Fig. 4(a) and (b)]. For the 6.0 mA exposure, on the other hand, the reaction takes place mostly during the first exposure and lasts only about 20 sec [Fig. 5(a)], thus making the molecular weight distribution less broad compared to the 0.6 mA exposure.

In order to see the influence of the electron-beam current on the molecular weight of obtained copolymers, the number- and weight-average molecular weights of ungrafted acrylic copolymer,  $M_n^2$  and  $M_w^2$ , were tentatively calculated from the dash-dot curve in Figure 7 by using the calibration curve for polystyrene (Fig. 6). The results are shown in Table I. The log-log plot of the molecular weight vs. the beam current reveals that although the  $M_w^2$  value decreases in proportion to ca.  $-0.36$  powers of the beam current, the  $M_n^2$

TABLE I  
Effect of Electron-Beam Current on the Molecular Weights of Acrylic Copolymer and the Fraction of Grafted Epoxy ( $f$ )<sup>a</sup>

Electron-beam current (mA)	Number of exposures	Monomer conversion <sup>b</sup> (%)	Acrylic copolymer		Calculation of $f$		
			$M_n^2$	$M_w^2$	$M_{UV}$	$M_2$	$f$ (%)
0.6	8	93.7	$1.3 \times 10^4$	$3.6 \times 10^5$	$7.9 \times 10^3$	$4.9 \times 10^4$	4.7
2.0	4	98.6	$1.9 \times 10^4$	$2.7 \times 10^5$	$7.6 \times 10^3$	$4.0 \times 10^4$	4.9
6.0	2	99.8	$1.7 \times 10^4$	$1.3 \times 10^5$	$7.1 \times 10^3$	$2.4 \times 10^4$	6.5
18.0	1	93.7	$1.6 \times 10^4$	$1.2 \times 10^5$	$7.4 \times 10^3$	$2.2 \times 10^4$	8.2

<sup>a</sup> Polymerization formula: epoxy resin (70 wt%), acrylic acid (12 wt%), and styrene (18 wt%).

<sup>b</sup> Determined from a powder of the obtained solid product.

value is almost independent of the beam current. This finding may be attributable to the fact that a steady state of free radicals is not attained in the present highly viscous systems of graft copolymerization, as is seen most clearly in the polymerization behavior of monomers shown in Figures 4(a) and 4(b). At the present time, however, no clear explanation can be offered for this problem. Further studies are therefore required for a detailed discussion of this point.

Comparison of the solid and dotted curves in Figure 7(a) or 7(b) demonstrates that the UV curve for the graft copolymer mixture (solid curve) is shifted to small elution volumes compared to that for the original Epikoto 1009 (dotted curve). Such a shift is most likely due to epoxy resin whose initial molecular weight has been increased by transparent grafted branches. The shift in the UV curve shown in Figure 7, therefore, can be taken as evidence indicating that a certain amount of epoxy-acrylic graft copolymer is produced in the graft copolymer mixture prepared by the present method of electron-beam irradiation.

Taking these points into account, we tried to determine the amount of epoxy-acrylic graft copolymer from the shift in the UV curve. If the GPC calibration curves are identical for the components of ungrafted epoxy resin, ungrafted acrylic copolymer, and epoxy-acrylic graft copolymer, and furthermore, if the molecular weight distribution is monodisperse for the respective components, then the molecular weight calculated from the UV curve for the graft copolymer mixture,  $M_{UV}$ , is expressed by

$$M_{UV} = (1 - f)M_1^0 + f(M_1^0 + gM_2), \quad (2)$$

where  $f$  is the fraction of epoxy resin having on the average  $g$  grafted branches,  $M_1^0$  is the molecular weight of the original epoxy resin, and  $M_2$  is the molecular weight of the grafted branch. This equation is rewritten as

$$f = (M_{UV} - M_1^0)/gM_2 \quad (3)$$

Strictly speaking, Eq. (3) cannot be applied to the graft copolymer mixture prepared in the present work. This is because the GPC calibration curves are not identical for epoxy resin and acrylic copolymer, as is suggested by the calibration curves in Figure 6. Furthermore, the molecular weight distribution is not monodisperse for these polymers, as seen in Figure 7. In the present work, for these reasons, the weight-average molecular weights calculated by using the GPC calibration curve for epoxy resin (solid curve in Fig. 6) are tentatively used as the values of  $M_{UV}$ ,  $M_1^0$ , and  $M_2$ . The  $M_2$  value is calculated by using the dash-dot curve in Figure 7, assuming that the molecular weight distribution of grafted branches is identical with that of ungrafted acrylic copolymer. It should be pointed out, therefore, that the  $f$  value obtained here is merely a rough estimate and should be used for qualitative purposes only.

The  $f$  value thus obtained with the assumption of  $g = 1$  is shown in Table I, together with the values of  $M_{UV}$  and  $M_2$  ( $M_1^0 = 5.6 \times 10^3$ ). It is seen that the  $f$  value has a tendency to increase in the electron-beam current. This result may be attributable, at least in part, to a difference in the termination rate between a growing chain of epoxy-acrylic graft copolymer and that of

ungrafted acrylic copolymer. According to a generally accepted mechanism of radiation grafting,<sup>2,3,11</sup> a free radical is first generated on an epoxy resin, and then it initiates the polymerization of monomers, thus producing an epoxy-acrylic graft copolymer. A free radical generated on a monomer, on the other hand, leads to the formation of ungrafted acrylic copolymer. Then it is quite possible that the diffusion rate of a growing chain of epoxy-acrylic graft copolymer is lower than that of a growing chain of ungrafted acrylic copolymer. As a result, the termination process of the graft copolymer radical will be slower compared to that of the ungrafted copolymer radical, thus favoring the formation of the graft copolymer at the expense of the formation of the ungrafted copolymer. This tendency may be further enhanced by an increase in the concentration of reactive species such as polymer radicals and low molecular weight free radicals. This is because such an increase in the radical concentration will speed up the termination process of the ungrafted copolymer radical more favorably than that of the graft copolymer radical, thus increasing the yield of the graft copolymer. These considerations are, in fact, compatible with the experimental result that the fraction of epoxy resin having a grafted branch increases with an increase in the electron-beam current (Table I).

### CONCLUSIONS

The graft copolymerization of highly viscous systems of epoxy resin dissolved in monomers was carried out by using high-energy electrons from an accelerator. It was shown that the polymerization rate of monomers increases with an increase in the content of acrylic acid for the formula of 70 wt% epoxy resin and 30 wt% monomer mixture of acrylic acid and styrene. The temperature measurement of the systems revealed that the polymerization reaction takes place both during and after the electron-beam exposure of about 5-sec duration. This reaction lasted as long as about 50 sec for the exposure at 0.6 mA, whereas at 6.0 mA it lasted only about 20 sec.

The GPC measurement made for obtained products demonstrated that the molecular weight distribution of ungrafted acrylic copolymer becomes strikingly broader as the beam current is lowered. A rough estimate of the fraction of epoxy resin having a grafted branch was obtained from the GPC data, and was found to increase with an increase in the beam current. These results and the polymerization behavior described above were interpreted in terms of the mobility and the concentration of reactive species such as polymer radicals and low molecular weight free radicals.

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