

Polymeric Reaction of Acrylic Polymer-Monomer System Irradiated by Low Energy Electron Beam. I. Effects of Molecular Weight of Polymer and Polymer-to-Monomer Ratio

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Synopsis

Polymeric reaction of the poly(*n*-butyl acrylate) (PBA)-benzyl acrylate (BzA) system induced by a low-energy electron beam was investigated. In order to elucidate the reaction behavior of the PBA-BzA system, the gel fraction, molecular weight of soluble part, and molecular weight distributions were examined by means of gel permeation chromatography (GPC) equipped with both ultraviolet (UV) and refractive index (RI) detectors. RI-detected GPC curves represented the molecular weights and their distributions of the total polymers, graft polymer, homopolymer, and unreacted PBA, while UV-detected curves only corresponded to the benzyl groups of graft polymer and homopolymer. Thus, the reaction behavior of the system was able to be followed by GPC. The molecular weight of added PBA and the mole ratio of PBA/BzA were varied. The crosslinking, the graft reaction and the homopolymerization of BzA proceeded competitively during the polymeric reaction. The proportions of BzA unit incorporated into the crosslinked, graft and homo polymers were estimated by combining of measurement of gel fraction, UV-detected GPC curves, and infrared (IR) spectrum of gel. It was revealed that in the system containing PBA with high molecular weight, the grafting, and the crosslinking reactions predominated. The main reaction was the grafting in the system with a high mole ratio of PBA/BzA, while it was the homopolymerization in the systems with the low mole ratio of PBA/BzA. The reaction mechanism is discussed on the basis of reactivity and mobility of polymer radicals.

INTRODUCTION

Polymeric reactions induced by electron beam irradiation have been used for the curing of polyethylene by a high energy type accelerator in the electric cable industry. Recently, with the development of a low energy type accelerator, the polymeric reaction induced by the electron beam process has been applied to manufacturing coatings and adhesives, because of minimization of the apparatus and of speeding up of the reaction due to high current. The low energy electron beam is expected to produce a new manufacturing process for polymeric materials which will be characteristic of a solvent-free system and low energy cost. For the coatings and adhesives to be synthesized by this process, it is the most important that high molecular weight of the polymer be achieved by starting from the low molecular weight system which has low viscosity suited for coating. There are two possible types of the materials used in this system. One is a prepolymer

with multifunctional group system. The other is a polymer–monomer system.

Reaction mechanism of the polymerization induced by electron beam has been investigated since about 1950, for example, in the studies of acrylate polymer^{1,2} and acrylate monomer.³⁻⁵ The mechanical properties of the coatings were studied on epoxyacrylate polymer–monomer system.^{6,7} Few studies were reported on the polymerization of acrylate polymer–monomer systems. Vroom and co-workers discussed the reaction mechanism of PVC–trimethylolpropane trimethacrylate system.⁸⁻¹⁰

Our study aims to find polymeric materials which can be manufactured by irradiating to the polymer–monomer system with an electron beam and can be used for adhesives and other thin products. For example, in order to produce adhesives with high adhesive strengths, it has been found that they must be of high molecular weight. Thus, it is important to find a method which gives high molecular weight polymer by irradiation of an electron beam in the polymer–monomer system. In the first step, acrylate polymer–monomer system was selected to examine the reaction mechanism of the system. Benzyl acrylate is used as a monomer in our system. The advantages of this monomer include that (1) use of a monomer and its polymer which absorb UV light facilitates monitoring of the reaction, (2) the low reactivity of the monomer causes the formation of low gel fraction, which makes it easy to analyze the reaction products of the polymer–monomer system, and (3) IR spectrum of gel shows the proportion of BzA unit incorporated into it. Poly(*n*-butyl acrylate) (PBA) is used as a polymer because of its moderate reactivity.

The reaction behavior is discussed in terms of the gel fraction which was separated from soluble part by Soxhlet extraction method, the conversion of monomer, and the molecular weight which was measured by gel permeation chromatography equipped with both UV and RI detectors, and the proportions of BzA unit incorporated into gel.

EXPERIMENTAL

Preparation of Monomer

Benzyl acrylate (BzA), *n*-butyl acrylate (BA), and acrylic acid (AA) were dried on CaH₂ overnight, and were distilled under vacuum.

Preparation of Polymer (PBA)

n-Butyl acrylate was polymerized in ethyl acetate at 76°C for 4 h using azobisisobutyronitrile as initiator, and *t*-dodecyl mercaptan as chain transfer agent. Then, the reaction mixture was poured into a large excess of methanol–hexane. Poly(*n*-butyl acrylate) with weight-average molecular weights of 1×10^4 , 10×10^4 , and 40×10^4 , were obtained by the addition of *t*-dodecyl mercaptan (*t*-DM) in the mole ratio of $[t\text{-DM}]/[\text{BA}] = 0.04$, 0.01, and 0.001, respectively.

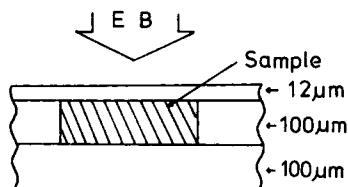


Fig. 1. Irradiation sample.

Sample Preparation

PBA which is a liquid with extremely high viscosity was mixed with BzA under nitrogen to give highly viscous liquid. The liquid was sandwiched between 12 and 100 μm polyester films to give a liquid membrane about 100 μm in thickness (Fig. 1).

Irradiation and Apparatus

A low energy (175 KV) electron beam irradiation apparatus (Energy Science Inc.) which is an electrocurtain type accelerator equipped with linear filament was used. Radiation doses ranged from 0.25 Mrad to 10 Mrad using currents of 1–20 mA, with the irradiation carried out at room temperature.

Gel Fraction, GPC, and IR Analysis

The soluble fraction was extracted by means of a Soxhlet extractor. An irradiated sample (1–2 g) was placed in a weighed cellulose thimble and extracted with refluxing ethyl acetate for 24 h. The insoluble part remaining after drying for 2 h *in vacuo* was defined as the gel fraction. The molecular weight characteristics of the soluble part were measured using gel permeation chromatography (GPC) equipped with both ultraviolet (UV) and refractive index (RI) detectors. The molecular weight was calculated by using the calibration curve obtained with standard samples of monodisperse polystyrene. The GPC measurement was performed on polymer solution in tetrahydrofuran by means of a Toyo Soda HLC-802UR using four styragel columns, that is, G-2000H, G-2000H, G-3000H, and G-4000H.

Typical chromatograms before and after irradiation were shown in Figure 2. Before irradiation, the PBA peak was only detected by RI, while after

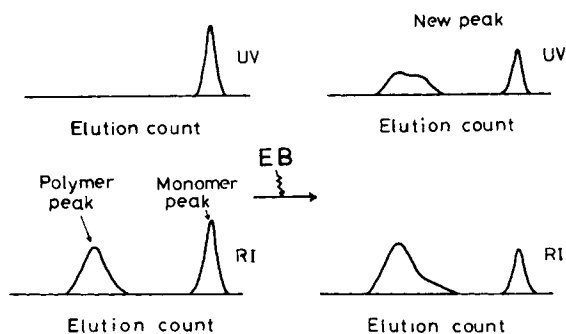


Fig. 2. GPC curves of PBA-BzA system.

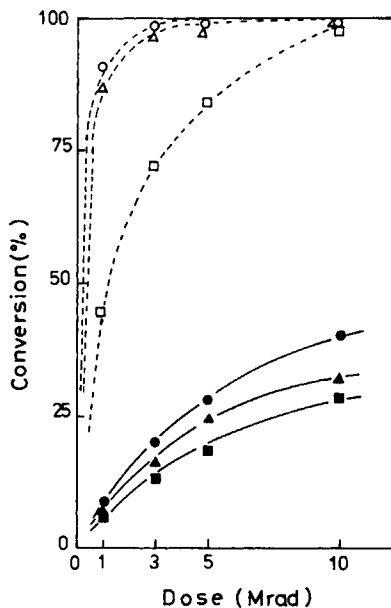


Fig. 3. Percent conversion as function of dose: (○) PBA ($\bar{M}_w = 1 \times 10^4$)-AA; (△) PBA ($\bar{M}_w = 10 \times 10^4$)-AA; (□) PBA ($\bar{M}_w = 40 \times 10^4$)-AA; (●) PBA ($\bar{M}_w = 1 \times 10^4$)-BzA; (▲) PBA ($\bar{M}_w = 10 \times 10^4$)-BzA; (■) PBA ($\bar{M}_w = 40 \times 10^4$)-BzA.

irradiation, the polymer peaks were detected by both RI and UV. The polymer peaks detected by UV were attributable to benzyl groups in the polymer. The conversion of BzA was determined by weighing the polymer mixture precipitated from methanol.

The proportion of BzA unit incorporated into gel was calculated by using the calibration curve, which was obtained with the measurement of the IR absorbance ratio of phenyl group of BzA at 700 cm^{-1} /carbonyl group of PBA at 1733 cm^{-1} in the mixtures of PBA and poly(benzyl acrylate) (PBzA).

RESULTS AND DISCUSSION

Effects of Molecular Weight of Polymer

Polymer-monomer mixtures which consist of PBA with \bar{M}_w of 1×10^4 , 10×10^4 , 40×10^4 as polymer and BzA or AA as monomer in the mole ratio of PBA/monomer of 1/0.7 were irradiated by electron beam. As shown in Figure 3, the conversion of both monomers increased with increasing dose. AA gave polymer in a high conversion by EB irradiation for short time, while BzA showed a low conversion. However, it was found that the conversions of both monomers decreased as the molecular weight of PBA increased.

On the other hand, as shown in Figure 4, the gel fraction depended on the molecular weight of the PBA and the kind of monomer. In the presence of PBA with $\bar{M}_w = 1 \times 10^4$, the gel fraction was low in both polymer-monomer systems than in the presence of PBA with higher molecular

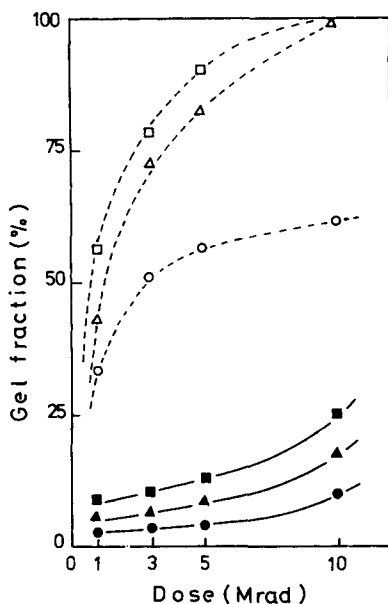


Fig. 4. Gel fraction as function of dose: (○) PBA ($\bar{M}_w = 1 \times 10^4$)-AA; (△) PBA ($\bar{M}_w = 10 \times 10^4$)-AA; (□) PBA ($\bar{M}_w = 40 \times 10^4$)-AA; (●) PBA ($\bar{M}_w = 1 \times 10^4$)-BzA; (▲) PBA ($\bar{M}_w = 10 \times 10^4$)-BzA; (■) PBA ($\bar{M}_w = 40 \times 10^4$)-BzA.

weights. Nevertheless, in the case of AA, high gel fractions over 50% were obtained by irradiation at 3 Mrad, while BzA gave a small amount of gel.

In the first place, the influences of molecular weight of the added polymer on the soluble part were examined. As shown in Figure 5, the RI-detected GPC curves of the PBA ($\bar{M}_w = 10 \times 10^4$)-BzA systems irradiated at 5 and 10 Mrad broadened toward both higher and lower molecular weight ranges as the total dose increased. On the other hand, in the UV-detected GPC

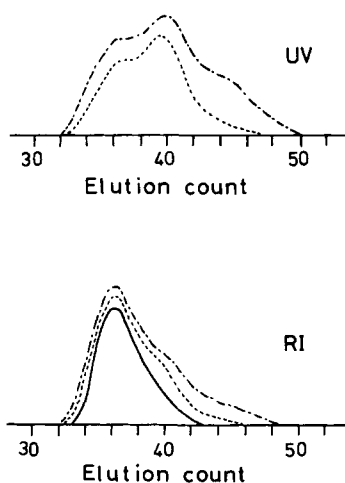


Fig. 5. GPC curves of PBA-BzA system irradiated at various doses: (—) 0 Mrad; (---) 5 Mrad; (- · -) 10 Mrad.

curves, bimodal peaks were observed when the dose was 5 Mrad. Another peak of molecular weight of 4×10^4 (45 counts) appeared as well as the bimodal peaks when the dose was increased to 10 Mrad. This might be attributable to the occurrence of the side reaction caused by chain transfer since such low molecular weight peak was not observed in the bulk polymerization of pure BzA by EB irradiation as shown in Figure 6. The conversion of BzA increased and the weight-average molecular weight of poly(benzyl acrylate) decreased with increasing dose and the unimodal GPC curve was observed. The EB irradiation was carried out at 5 Mrad in the later experiment in order to avoid such side reactions at higher doses.

The peak which appeared at a higher molecular weight range in the UV-detected curves is presumably attributable to a graft polymer. The reasons are as follows: (1) The UV trace extends further into the higher molecular weight region than the RI trace for the original PBA; (2) the peak due to a polymer containing benzyl groups is detected by UV; (3) the GPC curves using CHCl_3 instead of tetrahydrofuran as a solvent also provides the same pattern; (4) the formation of insoluble gels occurs as the reaction progresses. The peak which appeared at a low molecular weight range possibly showed a homopolymer of benzyl acrylate. Therefore, three kinds of reactions, that is, crosslinking, graft polymerization, and homopolymerization, occur in the polymer-monomer system.

As shown in Figure 7, the GPC curves of soluble part in the PBA ($\bar{M}_w = 1 \times 10^4$, 10×10^4 , and 40×10^4)-BzA systems which were irradiated at 5 Mrad, showed bimodal peaks composed of both graft polymer and homopolymer. The molecular weights of graft polymer and homopolymer, the gel fraction, the conversion of BzA, the graft efficiency, and the proportion of BzA unit incorporated into gel by IR analysis were determined as shown

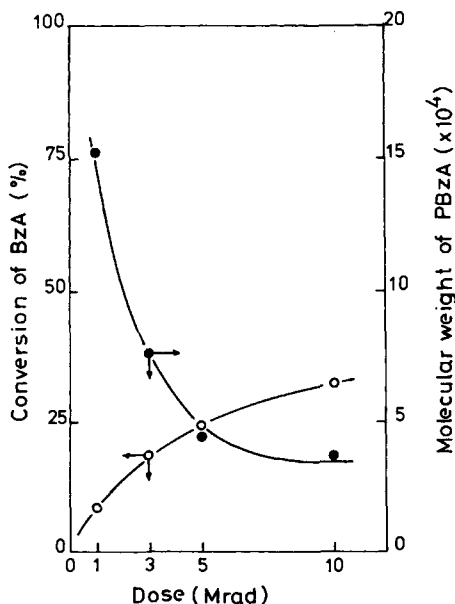


Fig. 6. Molecular weight of poly(benzyl acrylate) and conversion of BzA as function of dose.

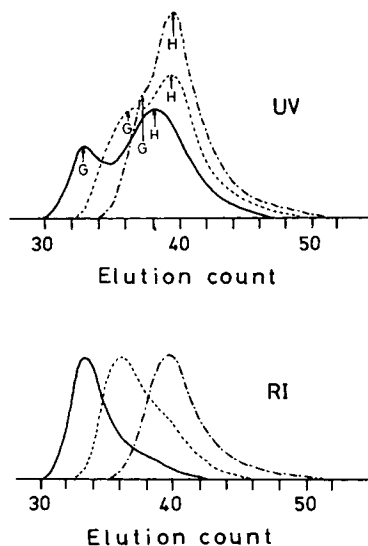


Fig. 7. GPC curves of PBA-BzA system irradiated at 5 Mrad. (— · —) PBA ($\bar{M}_w = 1 \times 10^4$)-BzA; (—) PBA ($\bar{M}_w = 10 \times 10^4$)-BzA; (—) PBA ($\bar{M}_w = 40 \times 10^4$)-BzA; G = graft polymer; H = homopolymer.

in Table I. Graft efficiency of soluble part was estimated using the GPC curve as followed:

$$\begin{aligned} \text{Graft efficiency} &= \frac{\text{monomer incorporated into graft polymer}}{\text{monomer incorporated into soluble polymer}} \\ &= \frac{\text{area of graft polymer peak}}{\text{area of UV-detected peak}} \end{aligned}$$

As shown in Figure 8, The areas of graft and homo polymers were calculated by resolved curves.

It is noteworthy that as the molecular weight of PBA increased, higher gel formation, higher molecular weights of both graft polymer and homopolymer, but lower conversion of BzA were obtained. The graft efficiency of soluble part was the highest in the presence of PBA with \bar{M}_w of 10×10^4 system. The polymerization behaviors that were observed in the polymer-monomer system at the dose of 5 Mrad are summarized in Table II. When the low molecular weight ($\bar{M}_w = 1.0 \times 10^4$) polymer was added to

TABLE I
Relationship between Molecular Weight and Reactivity of Polymer-Monomer System^a

Trunk polymer $\bar{M}_w (\times 10^4)$	Graft polymer $\bar{M}_w (\times 10^4)$	Homo polymer $\bar{M}_w \times 10^4$	Gel (%)	Conv. (%)	Graft efficiency (%)	BzA ^b into gel (%)
1.0	3.3	1.0	3	26	30.0	49
10.0	14.0	2.1	8	24	38.1	47
40.2	83.0	3.9	13	14	26.2	35

^a Mole ratio of PBA/BzA is 1/0.7; \bar{M}_w was measured by GPC.

^b Proportion of BzA unit incorporated into gel was calculated in IR spectrum.

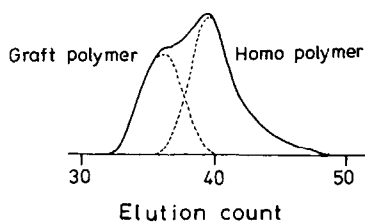


Fig. 8. Resolution of UV-detected GPC curve.

the system, graft polymer, and homopolymer with molecular weights of 3.3×10^4 and 1.0×10^4 were formed, respectively. On the other hand, the addition of high molecular weight polymer ($\bar{M}_w = 40.2 \times 10^4$) provided the graft polymer with very high \bar{M}_w of 83.0×10^4 and the homopolymer with fairly high \bar{M}_w of 3.9×10^4 . In addition, the gel fraction (13%) was also higher on the addition of high molecular weight polymer than that on the addition of low molecular weight polymers. This fact reveals that the presence of high molecular weight polymer gave rise to the formation of high molecular weight polymer. The proportions of BzA unit into the crosslinked, graft, and homo polymers were calculated by following equations:

$$W_c \text{ (wt \% BzA unit incorporated into crosslinked polymer)} \\ = \text{gel fraction} \times \text{BzA unit into gel}$$

$$W_g \text{ (wt \% of BzA unit incorporated into graft polymer)} \\ = (A - W_c) \times \text{graft efficiency of soluble part}$$

$$W_h \text{ (wt \% of BzA unit incorporated into homopolymer)} \\ = A - W_c - W_g$$

$$A = W_c + W_g + W_h = \text{conversion} \times \frac{\text{monomer weight}}{\text{total weight}}$$

The proportions of BzA unit incorporated into crosslinked polymer, P_c , graft polymer, P_g , homopolymer, P_h were represented by W_c/A , W_g/A , W_h/A , respectively, as shown in Table III. When the low molecular weight ($\bar{M}_w = 1 \times 10^4$) polymer was added to the system, the proportion of BzA unit incorporated into homopolymer was high (62%). On the other hand, the addition of high molecular weight PBA ($\bar{M}_w = 40.2 \times 10^4$) increased the proportion of BzA unit incorporated into crosslinked polymer with increas-

TABLE II
Effects of Molecular Weight of BA

	High \bar{M}_w PBA system ($\bar{M}_w = 40 \times 10^4$)	Low \bar{M}_w PBA system ($\bar{M}_w = 1 \times 10^4$)
Conversion of BzA	Low	High
Gel fraction	High	Low
\bar{M}_w of graft polymer	High	Low
\bar{M}_w of homopolymer	High	Low
Graft efficiency ^a	Low	Low

^a Graft efficiency of soluble part was the highest in the PBA ($\bar{M}_w = 10 \times 10^4$) system.

TABLE III
Proportions of BzA Unit Incorporated into Polymers in the System Containing PBA with Various Molecular Weight

\bar{M}_w of PBA ($\times 10^4$)	P_c^a (%)	P_g^b (%)	P_h^c (%)
1.0	11	27	62
10.0	32	26	42
40.2	66	9	26

^a P_c = proportion of BzA unit into crosslinked polymer.

^b P_g = proportion of BzA unit into graft polymer.

^c P_h = proportion of BzA unit into homopolymer.

ing gel fraction and decreased the proportions of BzA unit incorporated into graft and homo polymers. The fact revealed that the high molecular weight graft and homo polymers caused by irradiation were incorporated into gel as a crosslinked polymer.

The polymeric reactions which occurred in the polymer-monomer system might be explained as follows: The crosslinking is caused by the reaction between polymer radicals, the grafting results from the reaction between polymer radical and monomer or between the polymer radical and propagating radical from monomer, and the homopolymerization occurs between the propagating radical and monomer or between the propagating radicals. For the above three reactions, the reaction rates of reactions can be expressed by the following equations:

$$R \text{ (crosslinking)} = k_{t1}[\text{P}\cdot]^2 \quad (1)$$

$$R \text{ (grafting)} = k_{p2}[\text{P}\cdot][\text{M}] + k_{t2}[\text{M}_n\cdot][\text{P}\cdot] \quad (2)$$

$$R \text{ (homopolymerization)} = k_{p3}[\text{M}_n\cdot][\text{M}] + k_{t3}[\text{M}_n\cdot]^2 \quad (3)$$

where $[\text{P}\cdot]$ = concentration of polymer radical, $[\text{M}_n\cdot]$ = concentration of propagating radical from monomer, $[\text{M}]$ = concentration of monomer, k_{t1} , k_{t2} , k_{t3} = termination rate constants, and k_{p2} , k_{p3} = propagation rate constants. Initiation and chain transfer reactions were not considered here. The results of Tables II and III can be explained using eqs. (1)–(3).

In the case of diffusion-controlled polymerization, the termination rate constant k_t is related to diffusion constant according to Robertson¹¹:

$$k_t = \frac{A \exp(-E/RT)}{1 + [B \exp(-E/RT)/(D_1 + D_2)]}$$

where A and B are constants, E activation energy, D_1 and D_2 diffusion constants of the two particles, T absolute temperature, and R ideal gas constant.

The termination rate constant decreases as the diffusion of polymer molecule decreases, while the dependence of the propagation rate constant on the viscosity might be much smaller than that of the termination rate constant, because the former is mainly related to monomer mobility.

Since in highly viscous PBA system containing high molecular weight polymer, the termination rate constant is lowered by the high viscosity, the following relation might hold:

$$k_{p2}, k_{p3} \gg k_{t1}, k_{t2}, k_{t3}$$

Thus, it is considered that the grafting and homopolymerization reactions predominate. The low conversion of BzA is attributable to the slow diffusion rate of the polymer radical, propagating radical, and monomer. The high gel fraction could be caused by crosslinking of PBA and graft polymer, since the PBA and graft polymer with higher molecular weights must have tendency to become insoluble by crosslinking. Since the graft polymer could also be incorporated into gels, the graft efficiency decreased.

Effect of Polymer/Monomer Ratio

As the crosslinking, graft, and homo polymerization were found to be controlled to some extent by the viscosity of the system, the effects of mole ratio of PBA/BzA on the polymerization behaviors were examined. For the mole ratios of PBA ($\bar{M}_w = 10 \times 10^4$)/BzA of 1/1.3, 1/1, 1/0.7, and 1/0.25, the polymer-monomer system was irradiated at 5 Mrad. The results are shown in Table IV. The GPC curves of two kinds of polymer/monomer ratio are illustrated in Figure 9, indicating that the fractions of graft polymer and homopolymer depended to a large extent on the mole ratio of PBA/BzA. It was seen that the molecular weight and graft efficiency increased, but the gel fraction and conversion of monomer decreased with the increasing mole ratio. The proportion of BzA unit incorporated into gel decreased with the increasing mole ratio. The tendency of polymerization is summarized in Table V. The proportions of BzA unit incorporated into crosslinked, graft and homo polymers were shown in Table VI. In the low mole ratio of PBA/BzA the proportion of BzA unit into crosslinked polymer increased while in the high mole ratio of PBA/BzA the proportion of BzA unit into graft polymer increased and the proportion of BzA unit into homopolymer was constant with various mole ratio of PBA/BzA.

The results of Tables V and VI can also be explained using eqs. (1)–(3). Since the higher viscosity caused the slow diffusion rates of the polymer radical and monomer in the system having higher mole ratios, the following relation might hold:

TABLE IV
Relationship between Mole Ratio of Polymer/Monomer and Reactivity

Mole ratio of PBA/BzA	Gel (%)	\bar{M}_w (RI) ^a ($\times 10$)	Conv. (%)	Graft ^b efficiency (%)	BzA into ^c gel (%)
1/1.3	10	10.0	35	28.6	58
1/1	10	10.2	30	31.0	52
1/0.7	8	11.3	24	38.1	47
1/0.25	2	12.4	19	52.1	20

^a \bar{M}_w was measured by GPC (RI).

^b Graft efficiency of soluble part was calculated by UV-detected GPC curves.

^c Proportion of BzA unit incorporated into gel was calculated by IR spectrum of gel.

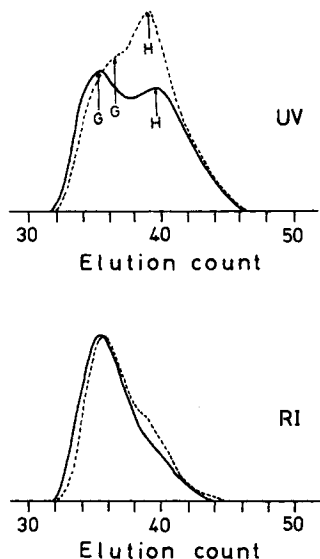


Fig. 9. GPC curves of the 1:1 PBA/BzA system (—) and the 1:0.25 system (---) irradiated at 5 Mrad. G = graft polymer; H = homopolymer.

$$k_{p2}, k_{p3} \gg k_{t1}, k_{t2}, k_{t3} \text{ and } [P \cdot] > [M_n \cdot]$$

Thus, the graft polymerization presumably prevailed over the other reaction, resulting in the low gel fraction, the high molecular weight of the soluble part, and the high proportion of BzA unit incorporated into graft polymer. Moreover, the low conversion should be attributable to the slow diffusion rate of the polymer radical and propagating radical from monomer.

On the other hand, in the case of lower mole ratios, it was observed that the high gel fraction, low molecular weight of soluble part, and the low proportion of BzA unit incorporated into graft polymer were obtained. Since in the system with lower mole ratios, the lower viscosity causes the more rapid diffusion rates of the polymer radical and monomer, the following relation might hold:

$$k_{p2}, k_{p3} > k_{t1}, k_{t2}, k_{t3} \text{ and } [M_n \cdot] > [P \cdot]$$

TABLE V
Effects of Mole Ratio of PBA/BzA

	High mole ratio system (PBA/BzA = 1/0.25)	Low mole ratio system (PBA/BzA = 1/1)
Conversion of BzA	Low	High
Gel fraction	Low	High
\bar{M}_w of soluble part	High	Low
Graft efficiency	High	Low

TABLE VI
Proportion of BzA Unit Incorporated into Polymers in the System with Various Mole Ratios of PBA/BzA

Mole ratio of PBA/BzA	P_c^a (%)	P_g^b (%)	P_h^c (%)
1/1.3	33	17	50
1/1	30	22	48
1/0.7	32	26	42
1/0.25	9	48	43

^a P_c = proportion of BzA unit into crosslinked polymer.

^b P_g = proportion of BzA unit into graft polymer.

^c P_h = proportion of BzA unit into homopolymer.

Vroom et al. suggested that the reaction behavior should depend on the polymer/monomer ratio and that grafting can be predominant in the system with the higher ratio of polymer/monomer, while the homopolymerization of the trifunctional monomer can be predominant in the system with the lower ratio of polymer/monomer.

Though the materials in our system were different from that of Vroom's system, the reaction of the PBA-BzA system presumably proceeds through similar reaction types. The reaction mechanism can be assumed using these results, as shown in Figure 10. When the carbonyl groups of polymer and/or monomer can be excited by irradiation of electron beam, the polymer radical may be formed by the abstraction of H· from polymer. The reaction between the polymer radical and the monomer causes the grafting. When the radical is generated from the carbonyl group of the monomer, the homopolymerization can proceed.

The structure of polyacrylate radical after irradiation has been studied by ESR since about 1950. The radicals, $-\text{CH}_2-\dot{\text{C}}\text{H}-$ generated from decarboxylation of acrylate polymer and, $-\text{CH}_2-\dot{\text{C}}-\text{COOR}$ formed abstraction of a hydrogen atom of the of main chain were assumed.^{12,13}

It is considered that the reaction behaviors in the polymer-monomer system are influenced by the stability of polymer radical which depends on the structure and mobility of polymer radical. Since the mobility of polymer radical is lowered by the high viscosity of the system, the addition of higher molecular weight polymers in the system and higher mole ratios of polymer/

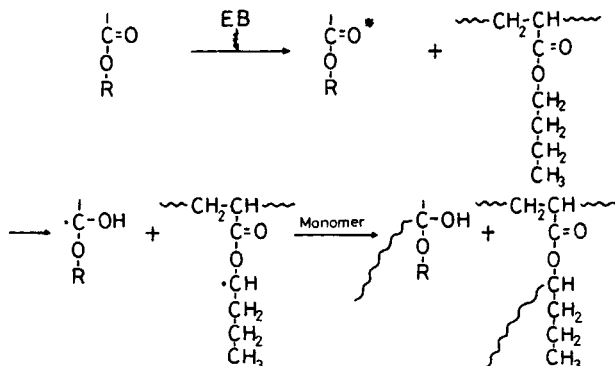


Fig. 10. Scheme for graft polymerization by electron beam irradiation.

monomer might make the polymer radical more stable than in low viscosity system, which causes higher extents of the crosslinking and grafting.

CONCLUSION

The relationships between the molecular weight of added PBA and reaction mechanism and between the mole ratio of PBA/BzA and reaction mechanism were studied by irradiation of low energy electron beam. The conclusions of this study are as follows:

1. The higher the molecular weight of added PBA was, the higher the molecular weight of soluble part and the higher the gel fraction in the polymer-monomer system.
2. The higher the mole ratio of PBA/BzA in the system was, the higher the molecular weight of soluble part produced. The lower the mole ratio of PBA/BzA in the system was, the higher the gel fraction formed.
3. Three reactions, that is, crosslinking, grafting, and homopolymerization, presumably proceeded competitively in the polymer-monomer system. The crosslinking and grafting may be predominant in the system with the higher molecular weight of added PBA and the grafting may be predominant with the higher mole ratio of PBA/BzA.

References

1. F. A. Bovey, *The Effects of Ionizing Radiation on Natural and Synthetic High Polymer*, Interscience, New York, 1958, p. 183.
2. A. R. Shultz and F. A. Bovey, *J. Polym. Sci.*, **22**, 485 (1954).
3. S. S. Labana, *J. Polym. Sci.*, **8**, 176 (1970).
4. J. Seto, T. Noguchi, T. Nagai, and S. Arakawa, *Kobunshi Ronbunshu*, **40**, 9 (1983).
5. W. Oraby and W. Walsh, *J. Appl. Polym. Sci.*, **23**, 3227 (1979).
6. M. Gotoda, *Japan Atomic Energy Research Institute Rep.*, **5029**, 105 (1974).
7. M. Gotoda, *Japan Atomic Energy Research Institute Rep.*, **5029**, 114 (1974).
8. G. N. Taylor, M. Y. Hellman, and T. N. Bowmer, *Macromolecules*, **16**, 34 (1983).
9. W. I. Vroom, D. D. Davis, T. K. Kwei, and T. N. Bowmer, *J. Appl. Polym. Sci.*, **26**, 3669 (1981).
10. W. I. Vroom, M. Y. Hellman, and T. N. Bowmer, *J. Appl. Polym. Sci.*, **28**, 2083 (1983).
11. E. R. Robertson, *Trans. Faraday Soc.*, **52**, 426 (1956).
12. M. G. Ormerod and A. Charlesby, *Polymer*, **5**, 67 (1964).
13. P. Hesse and H. Heusinger, *Eur. Polym. J.*, **9**, 581 (1973).

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