Polymeric Reaction of Acrylic Polymer–Monomer System Irradiated by Low-Energy Electron Beam. II. Effect of Ester Structure of Acrylic Polymer

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Synopsis

Polymeric reactions of polyacrylate–benzyl acrylate (BzA) systems induced by a low-energy electron beam were investigated by changing the species of polyacrylates added to the system. The gel fraction, the proportion of BzA units incorporated into gel by infrared (IR) analysis, and the molecular weight and its distribution curves by gel permeation chromatography (GPC) were examined to elucidate the reaction mechanism for the polymer–monomer system. The GPC curves were detected by both ultraviolet (UV) and refractive index (RI). As the UV-detected GPC curves represent the benzyl groups of graft polymers and homo polymers, the polymerization reactions can be followed by GPC. Ester structures of acrylic polymers were varied in order to examine how much the ester group affects such individual reactions as crosslinking, graft polymerizations, and homopolymerizations. In the case of both polyisobutylacrylate–BzA and poly(isoamyl acrylate)–BzA systems, the crosslinking and graft reactions predominated, while in the case of poly(t-butyl acrylate)–BzA systems, homopolymerization was the main reaction. These results can be explained by the structure and reactivity of polymer radicals and viscosity of the system.

INTRODUCTION

With the development of a low energy type electron beam (EB) accelerator, a new manufacturing process can be developed in factories and laboratories without heavy shielding. The new process, which will have the characteristics of a solvent-free and low energy cost operation, is expected to produce the polymeric materials. Polymeric reactions induced by electron beam irradiation can be used for the *in situ* production of coatings and adhesives. It is most important for the manufacturing of coatings and adhesives in that high-molecular-weight polymer and gel are produced by starting with low-molecular-weight system with low viscosity.

The reaction and the mechanism of polymerization induced by electron beam have been investigated since about 1950, for example, in the studies of acrylate polymer,[1,2] and acrylate monomer.[3-5] Vroom and co-workers discussed the reaction mechanism and properties of the PVC–trimethylolpropane trimethacrylate system.[6-9]

In the previous paper, we reported the effects of molecular weight of polymer and polymer-to-monomer ratio on the reaction of polymer–monomer system induced by electron beam irradiation.[10] Although polybutyl acrylates with different molecular weight were used as an added polyacry-

late, there may be other factors influencing the EB-induced reactions other than the molecular weight of the added polymer. In this investigation, we report the effects of ester groups of polyacrylates on the EB-induced reaction of various polyacrylate–benzyl acrylate systems. The reaction behaviors of these systems are discussed in terms of gel fraction conversion of monomer, increasing molecular weight after irradiation, and the proportion of BzA units incorporated in the gel.

EXPERIMENTAL

Preparation of Monomer

n-Amyl, isoamyl, and neopentyl acrylates were synthesized by reacting the corresponding alcohols and acrylic chloride with amine as catalyst. The other monomers were employed by purifying commercial reagentrade products. The monomers were finally dried on CaH_2 overnight, and were distilled under vacuum.

Preparation of Polymer

n-Butyl acrylate was polymerized in ethyl acetate at 76°C for 4 h using azobisisobutyronitrile as an initiator, and t-dodecyl mercaptan as a chain transfer agent. Then, the reaction mixture was poured into a large amount of methanol–hexane. Poly(n-butyl acrylate) with weight average molecular weight (M_w) of 10×10^4 was obtained by the addition of t-dodecyl mercaptan (t-DM) in the mole ratio of [t-DM]/[BA] = 0.01. The other polyacrylates with molecular weight of about 10×10^4 were prepared by the same method.

Sample Preparation

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

Irradiation and Apparatus

A low-energy (175 keV) electron beam irradiation apparatus (Energy Sicence Inc.) which is an electrocurtain type accelerator equipped with a linear filament was used. EB irradiation was carried out at doses of 5 and 10 Mrad using currents of 10 and 20 mA, respectively, at room temperature.
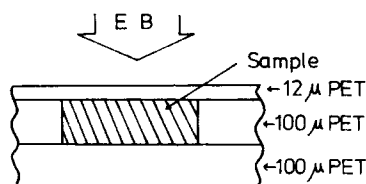

Fig. 1.   Irradiation sample.

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 fraction, which remained in the thimble, was dried for 2 h *in vacuo* and 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 standard polystyrenes. 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. The conversion of BzA was determined by weighing the polymer mixture precipitated from methanol. Proportion of BzA units incorporated in the gel was calculated by using the calibration curve obtained from the measurement of the IR absorbance ratio of the phenyl group of BzA at 700 cm^{-1} to the carbonyl group of polymers with various ester groups at 1730–1740 cm^{-1} in the mixture of polyacrylate and poly(benzyl acrylate). Poly(benzyl acrylate) was prepared by solution polymerization in ethyl acetate with AIBN as an initiator.

The molecular weight (M_w) of the added polyacrylates was approximately 10×10^4. The glass transition temperature (T_g) of polyacrylates were measured by means of differential thermal analysis (Perkin-Elmer DSC-2). The molecular weight (M_w) and glass transition temperature (T_g) of polyacrylates were shown in Table I.

The viscosities of the polymer–monomer systems were measured by a rotary viscometer (Tohki Sangyo Co., Ltd.).

RESULTS AND DISCUSSION

Reaction of Polymer System

Structural changes in polymers irradiated by electron beam of 5 Mrad were first examined in terms of gel fraction, molecular weight of soluble part, and ΔM_w [M_w (5 Mrad)/M_w (0 Mrad)]. Less than 5 Mrad irradiation,

TABLE I
Characterization of Polyacrylate and Viscosity of Polyacrylate–BzA Systems[a]

Ester group	T_g[b] (°C)	$\overline{M}_w$[c] ($\times 10^4$)	Viscosity (cps)
Ethyl	−22	11.6	6625
n-Butyl	−53	10.2	2100
n-Amyl	−60	8.9	1625
Isopropyl	−6	8.3	3400
Isobutyl	−20	11.0	8050
Isoamyl	−38	11.2	3250
t-Butyl	+43	12.5	1575
Neopentyl	+22	9.0	1800

[a] Polymer-to-monomer ratio 1 : 0.8.
[b] T_g of polyacrylate was measured by DSC.
[c] $\overline{M}_w$ of polyacrylate was measured by GPC.

reactions induced by EB did not occur enough to measure the difference in structural changes among poly(alkyl acrylate)s. Thus, EB irradiation was carried out at 5 Mrad. The gel fractions Table II in the irradiated poly-t-butyl- and poly-neopentyl acrylates were considerably lower than in the other polyacrylates. In addition, for the soluble part, the delta of molecular weight in the polyacrylates having t-butyl and neopentyl groups was much lower than that in polyacrylates having n-butyl and n-amyl ester groups.

Since crosslinking and grafting reactions may depend on the reactivity of polymer radical generated by irradiation, it was revealed that polyacrylates with t-butyl and neopentyl ester groups are less sensitive to electron beam. Their T_g's are high compared with the T_g of the other polyacrylates (Table I). Therefore, it is assumed that since the segmental motion of the polymers is suppressed at the irradiation temperature, the mobility of polymer radicals generated is low. Shultz calculated the crosslinking energy of various acrylate polymers,[2] indicating that the energy of poly(t-butyl acrylate) was higher than that of such polyacrylates as n-butyl, isobutyl, and neopentyl acrylate polymers.

Reaction of Polymer–Monomer System

Polymer–monomer mixtures which consist of polyacrylates with various ester groups as an added polymer and BzA as a monomer in the mole ratio of polymer/monomer of 1/0.8 were irradiated by electron beam. For the irradiated poly(n-butyl acrylate)–BzA, poly(isobutyl acrylate)–BzA, and poly(t-butyl acrylate)–BzA systems, GPC curves of soluble fractions separated from gels were shown in Figures 2, 3, and 4, respectively. The RI-detected GPC curves of the polyacrylate–BzA systems irradiated to 5 and 10 Mrad were broadened toward both higher and lower molecular weight ranges as the total dose increased. On the other hand, in the UV-detected GPC curves, bimodal peaks were observed when the dose was 5 Mrad. Another peak of molecular weight centered at 4×10^3 (45 counts) appeared as well as the bimodal peaks when the dose increased to 10 Mrad. This might be attributable to the occurrance of the side reaction caused by chain transfer reaction, because such a low-molecular-weight peak was not ob-

TABLE II
Reactions of Polyacrylates Irradiated at 5 Mrad

Ester group	Gel fraction (%)	$\overline{M}_w$[a] ($\times 10^4$)	$\dfrac{\overline{M}_w(5\ \text{Mrad})}{\overline{M}_w(0\ \text{Mrad})}$
Ethyl	16	15.4	1.3
n-Butyl	16	42.7	4.2
n-Amyl	18	38.9	4.4
Isopropyl	15	16.7	2.0
Isobutyl	17	21.1	1.9
Isoamyl	16	20.8	1.9
t-Butyl	9	9.2	0.7
Neopentyl	8	9.6	1.1

[a] $\overline{M}_w$ of soluble polymer after irradiation was measured by GPC.

Graft polymer

UV

30   40   50

Elution count
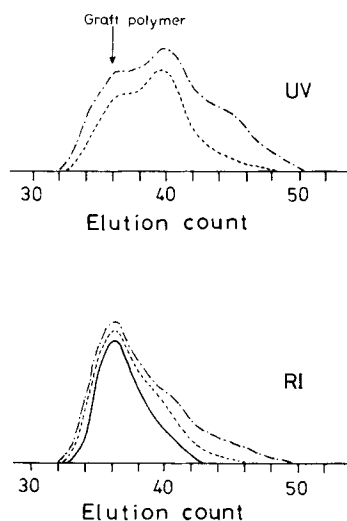
RI

30   40   50

Elution count

Fig. 2.   GPC curves of poly(n-butyl acrylate)–BzA system: (-) 0 Mrad; (- - -) 5 Mrad; (- · -) 10 Mrad.

served in the bulk polymerization of pure BzA by EB irradiation, as shown in Figure 5. The EB irradiation was carried out at 5 Mrad in the latter experiment to avoid side reactions at high doses.

The peak which appeared at a higher molecular weight range in the UV-detected curves is attributable to a graft polymer. The reasons are as follows: (1) The UV-detected peak extends further into the higher molecular weight region than the RI-detected peak observed for the original acrylate polymer; (2) the peak due to a polymer containing benzyl groups is detected by the
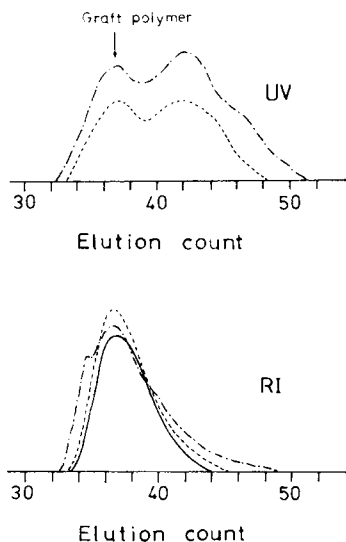
Graft polymer

UV

30   40   50

Elution   count

RI

30   40   50

Elution   count

Fig. 3.   GPC curves of poly(isobutyl acrylate)–BzA system: (-) 0 Mrad; (- - -) 5 Mrad; (- · -) 10 Mrad.
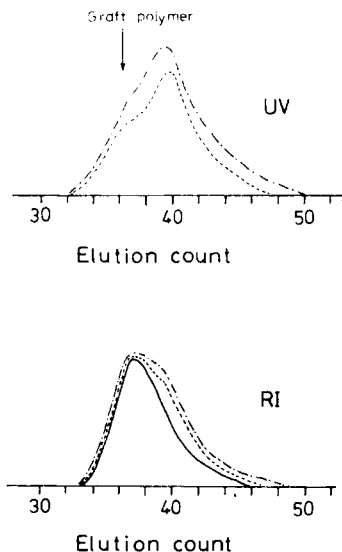
Fig. 4. GPC curves of poly(t-butyl acrylate)–BzA system: (-) 0 Mrad; (- - -) 5 Mrad; (- · -) 10 Mrad.

UV detector; (3) although no gel was obtained by EB homopolymerization of BzA, the formation of insoluble gel occurs at high doses in the polymer–monomer system. Furthermore, the UV-detected peak at a low molecular weight range can be attributed to a homopolymer of benzyl acrylate, because the molecular weight distribution curve of polybenzyl acrylate obtained by EB irradiation of the benzyl acrylate appears at the same region as the UV-detected, low-molecular-weight peak (elution count = 39–40, M_w = 3.5 × 10⁴). Comparing Figure 3 with Figure 2, the proportion of the graft polymer peak was larger in poly(isobutyl acrylate)–BzA system than in the poly(n-butyl acrylate)–BzA system. However, for poly(t-butyl acrylate)–BzA system, the proportion of the homopolymer peak was larger than that of the graft polymer peak, that is, the homopolymerization of BzA prevails over the grafting reaction.

X_g, the ratio of BzA units incorporated into graft polymers to BzA units contained in the soluble polymer, was estimated using the resolved GPC curves (Fig. 6) as follows:

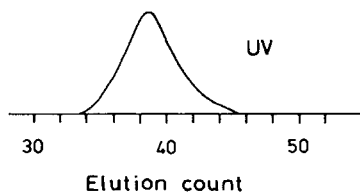$$X_g = \frac{\text{area of graft polymer peak}}{\text{area of UV-detected peak}}$$

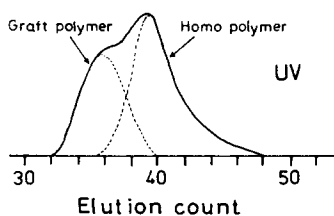Fig. 5. UV-detected GPC curves of poly(benzyl acrylate).

Fig. 6.   Resolution of UV-detected curve of PBA–BzA system.

The gel fraction, the conversion of BzA, the molecular weight, the proportion of BzA units incorporated into soluble graft polymer (X_g), and the proportion of BzA units incorporated into gel are shown in Table III.

The gel fraction and X_g in the polyisopropyl, polyisobutyl, and polyisoamyl acrylates–BzA systems were higher than in the poly(t-butyl acrylate)–BzA system. In addition, for neopentyl and isobutyl acrylates, the gel fractions were in the polymer–monomer system rather than the polymer alone.

The proportions of BzA units in the crosslinked, graftpolymers and homopolymers were calculated by the following equations, respectively:

W_c (wt % BzA units incorporated into crosslinked polymer

   in the polymer–monomer system)

   = gel fraction × wt % of BzA units into gel

(A = wt % converted BzA in the polymer–monomer system)

W_g (wt % BzA units incorporated into graft polymer

   in the polymer–monomer system)

   = $(A - W_c) \times X_g$

W_h (wt % BzA units incorporated into homopolymer

   in the polymer–monomer system)

   = $A - W_c - W_h$

A = $W_c + W_g + W_h$

   = conversion of BzA × $\dfrac{\text{monomer wt}}{\text{total wt}}$

The proportions of BzA units incorporated into crosslinked polymer, graft polymer, and homopolymer, were represented by $P_c = W_c/A$, $P_g = W_g/A$, and $P_h = W_h/A$, respectively. The estimated proportions are indicated in Table IV. In the case of linear alkyl esters, that is, polyethyl, poly-n-butyl, and poly-n-amyl acrylates–BzA systems, P_c decreased with increasing length of side chain. In the polyisopropyl, polyisobutyl, and polyisoamyl acrylates–BzA systems, P_c (39, 63, and 59%, respectively) was higher than in any systems. In the case of the poly-t-butyl and polyneopentyl acrylates–

TABLE III
Reactions of Polyacrylate–BzA Systems Irradiated at 5 Mrad[a]

Ester group	Gel (%)	Conv (%)	$\overline{M}_w$[b] ($\times 10^4$)	Increment of $\overline{M}_w$ ($\times 10^4$)	X_g[c] (%)	BzA into[d] gel (%)
Ethyl	12	23	12.1	+0.5	33	50
n-Butyl	8	24	11.3	+1.1	38	47
nAmyl	10	20	8.8	−0.1	35	24
Isopropyl	13	23	9.9	+1.6	40	36
Isobutyl	23	21	14.3	+3.3	53	29
Isoamyl	19	20	11.5	+0.3	46	30
t-Butyl	8	26	10.4	−2.1	22	12
Neopentyl	15	29	11.0	+2.0	41	14

[a] Polymer-to-monomer ratio 1 : 0.8.
[b] $\overline{M}_w$ of soluble polymer was measured by GPC.
[c] The proportion of BzA units incorporated into graft polymer to BzA units contained in the soluble polymer.
[d] Proportion of BzA units in gel was measured by IR analysis.

BzA systems, P_c was low (7 and 15%). P_g was almost independent of the difference in ester group, ranging from 17 to 35%. In the poly-t-butyl and polyneopentyl acrylates–BzA systems, P_h was higher than in any systems (73 and 50%). These results were explained considering the following factors: (1) polymer radical structure; (2) viscosity of the system: (3) T_g of polymer. The structure of polyacrylate radical generated through EB irradiation was studied with ESR by Ormerod and Charlesby.[11] They reported that the backbone radical, —CH₂—$\dot{\text{C}}$—, was observed. But the results in Table IV show that side chain radicals might also be generated by EB, since the P_c and P_h values obtained varied with difference in the ester group of added polyacrylate systems. Especially, the polyisopropyl, polyisobutyl, and polyisoamyl acrylates–BzA systems owe their high grafting efficiency to the long-lived tertiary carbon radicals formed by hydrogen abstraction. The reaction scheme shown in Figure 7 can be assumed to hold for this polymer–monomer system.

TABLE IV
Proportions of BzA Units Incorporated into Polymers in the Polyacrylate–BzA Systems (at 5 Mrad)

Ester group	P_c[a] (%)	P_g[b] (%)	P_h[c] (%)
Ethyl	47 ± 2	17 ± 2	36 ± 2
n-Butyl	32 ± 3	26 ± 2	42 ± 2
n-Amyl	25 ± 2	27 ± 1	48 ± 1
Isopropyl	39 ± 4	24 ± 3	34 ± 3
Isobutyl	63 ± 1	20 ± 1	17 ± 1
Isoamyl	59 ± 3	19 ± 3	22 ± 3
t-Butyl	7 ± 2	20 ± 1	73 ± 2
Neopentyl	15 ± 1	35 ± 1	50 ± 1

[a] Proportion of BzA units incorporated into crosslinked polymer.
[b] Proportion of BzA units in graft polymer.
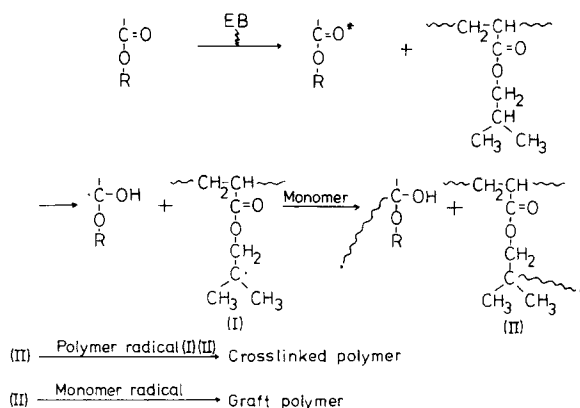[c] Proportion of BzA units in homopolymer.

Fig. 7.   Scheme for crosslinking and graft reactions by electron beam irradiation.

Since the polymer–monomer system shows very high viscosity, the reaction is considered to be diffusion-controlled. The viscosity of the systems was measured by a rotary viscometer. As shown in Table I, the viscosities of the systems to a large extent depended on the structure of polyacrylates, since the molecular weight of the polymers were almost equivalent. The highly viscous systems, such as polyisopropyl, polyisobutyl, and polyisoamyl acrylates–BzA systems (3400, 8050, and 3250 cps, respectively) gave higher P_c's. The highly viscous system is favorable for the formation of long-lived polymer radicals. A previous paper[10] showed that a highly viscous system, such as the high molecular weight polymer–monomer and the high mole ratio of polymer/monomer systems also gave high P_c. However, in the poly(ethyl acrylate)–BzA system, P_c was not high in spite of its high viscosity (6625 cps). Therefore, the reactivity should depend on both polymer radical structure and viscosity of the system.

Furthermore, the reactivity of the added polymer might be influenced by T_g of polyacrylate, since polyacrylates with high T_g's, that is, poly-t-butyl and polyneopentyl acrylates–BzA systems gave low P_c values. However, the reactivities of other polyacrylates with sufficiently low T_g's were not affected by the glass transition temperature.

CONCLUSION

The relationship between the ester structure of polyacrylate and the proportions of three kinds of reactions was studied by irradiation of polyacrylate–benzyl acrylate systems with a low energy electron beam. The conclusions of this study are as follows:

1. In the polyisopropyl, polyisobutyl, and polyisoamyl acrylates–BzA systems in which the polymer has a $—CH(CH_3)—$ group, the gel fraction was high, and crosslinking and graft reactions were dominant over homopolymerization.

2. In the poly(t-butyl acrylate)–BzA system, the gel fraction was low, and the homopolymerization is dominant.

3. The results can be satisfactorily explained by polymer radical structure and viscosity of the system.

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