

Radiation-Induced Polymerization of Methyl Methacrylate and Alkyl Acrylates at High Dose Rate

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Synopsis

Polymerization of methyl methacrylate and methyl, ethyl, and *n*-butyl acrylates was carried out in a wide range of dose rate, $10\text{--}10^6$ rad/s by γ -ray and electron beam irradiation. With methyl methacrylate and *n*-butyl acrylate, and steady-state kinetics in radical polymerization was maintained in an entire dose rate range at about the initial stage of the polymerization. With methyl and ethyl acrylates, the rate of polymerization increased much less markedly than expected from the square root law and the molecular weight decreased much less gradually with dose rate. In all these monomers it was found that autoacceleration of the rate of polymerization due to gel effect becomes vague at high dose rate. Two-peaked molecular weight distribution was observed for the polymers obtained at high dose rate.

INTRODUCTION

Polymerization under high dose rate radiation was first reported for styrene,¹⁻³ in which variations of the reaction rate (R_p) and molecular weight distribution (MWD) with dose rate and water content in the monomer were explained in terms of the coexistence of radical and ionic polymerization. This means that kinetic behavior at high dose rates can be essentially understood with the extrapolation of results already obtained at low dose rate with γ -rays.

In this article, polymerization of methyl methacrylate (MMA) and methyl, ethyl, and *n*-butyl acrylates (MA, EA, and BA, respectively) was studied in a wide range of dose rates. As these monomers are well known to possess high reactivity to radical but no reactivity to cation, they are excellent for the kinetic study of radical polymerization at high dose rate. Also, because of their high reactivities, they are good candidates for use in radiation processing, as coatings, in adhesion, and so on. High-dose rate polymerization of MMA was first studied by Allen et al.,⁴ but less attention was paid to the oligomeric product which was of greater importance in high-dose rate polymerization.

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EXPERIMENTAL

Monomers were washed with aqueous NaOH solution, distilled water, and dried over calcium hydride prior to distillation at reduced pressure. Two milliliters of a monomer were degassed in a stainless steel cell, inner size 90 mm in length, 26 mm in width, and 1 mm in depth, for electron beam irradiation. All irradiations were carried out at room temperature, 17–20°C. Temperature rise in MMA at 2.1×10^5 rad/s was ca. 10°C at 50 s after the onset of irradiation. Further details of the irradiation procedure were described elsewhere.⁵

After irradiation, residual monomer was removed by evaporation in a draft and then in a vacuum oven. Gel permeation chromatography (GPC) measurements were made in tetrahydrofuran (THF) solution at 40°C. All viscosity measurements were carried out in benzene solution at 30°C. Parameters, K and a in the equation, $[\eta] = KM^a$ are; 5.2×10^{-5} , 0.76 for PMMA (MW \geq 35,000),⁶ 1.95×10^{-3} , 0.41 for PMMA (MW < 35,000),⁶ 3.56×10^{-3} , 0.798 for PMA,⁷ and 2.77×10^{-2} , 0.67 for PEA.⁸

RESULTS

Time-conversion relationships in MMA at three different dose rates are shown in Figure 1. At low dose rate of γ -rays (i.e., 41 and 83 rad/s) the polymer yield increased linearly with time up to ca. 20% conversion and then autoacceleration took place. At high dose rate by electron beams, rate of polymerization R_p decreased gradually with time up to 40% conversion, then autoacceleration occurred. From these curves, it was found that at high dose rates, autoacceleration took place at higher conversion than at low dose rates.

Molecular weight distributions (MWD) of the polymers at 2.1×10^5 rad/s are shown in Figure 2. At conversion lower than 40%, a two-peaked distribution was obtained. The weight fraction of the higher MW polymer to the total polymer yield was slightly irreproducible but within $20 \pm 10\%$ in most cases. The peak MW of the high MW fraction markedly decreased with irradiation time or conversion, and at more than 60% conversion this component was merged in a tail of the main fraction. On the other hand, the peak MW of the main fraction did not change with conversion at least up to 40%.

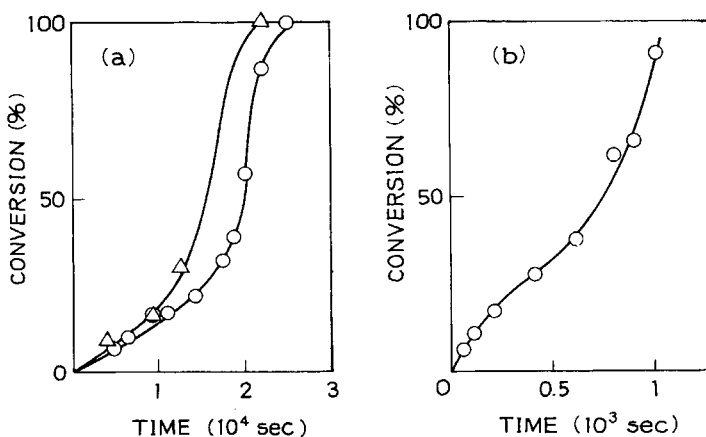


Fig. 1. Polymerization of MMA at: (a) 41 (O) and 83 (Δ), and (b) at 2.1×10^5 rad/s.

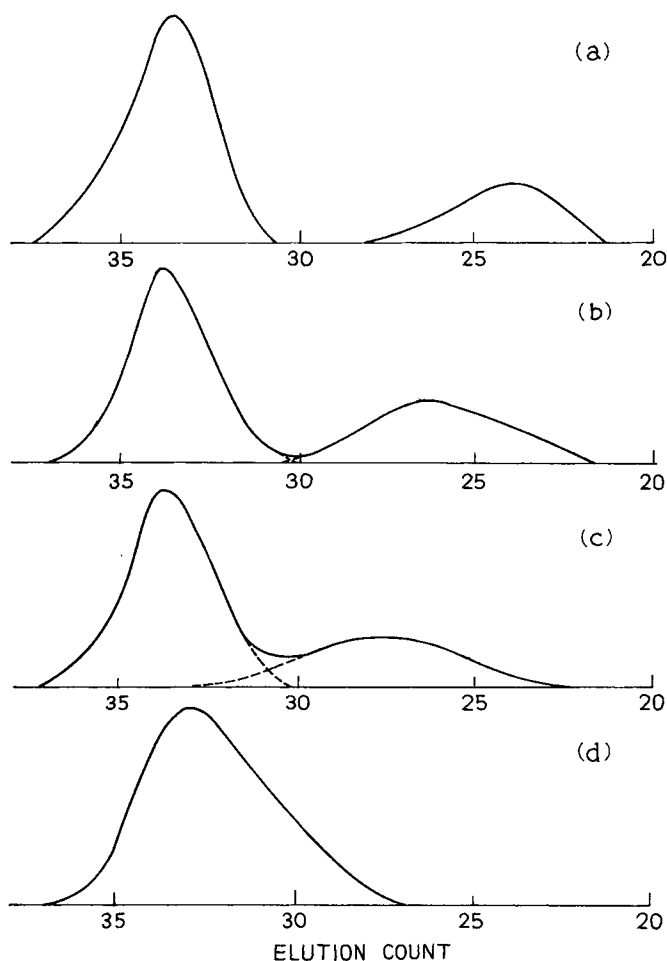


Fig. 2. MWDs of PMMA polymerized at 2.1×10^5 rad/s. Conversion: (a) 5.6%, (b) 16.8%, (c) 29.3%, 66.6%.

Number-average MW of PMMA was calculated from GPC results applying a MW-elution count relationship obtained for polystyrene. Although the obtained value, which is denoted as \bar{M}_n hereafter, is not the same as the absolute value of number-average MW of PMMA, it is enough to discuss the relative change of the MW. In Figure 3, changes in \bar{M}_n with conversion are shown. At below 40% conversion, MW of the high MW fraction was greatly reduced with conversion, though ambiguity due to graphical separation into two fractions gave considerable error in the MW, especially at above 20% conversion. On the other hand, MW of the main fraction increases slightly with conversion. The average MW of the total polymer also seems to increase slightly up to ca. 60% conversion in accordance with the MW increase of the main fraction, and then remains almost unchanged.

The MW decrease of the high MW fraction with conversion can be explained by the radiation-induced degradation of the polymer once formed. A simple calculation indicates that on bulk irradiation of PMMA,⁹ the polymer

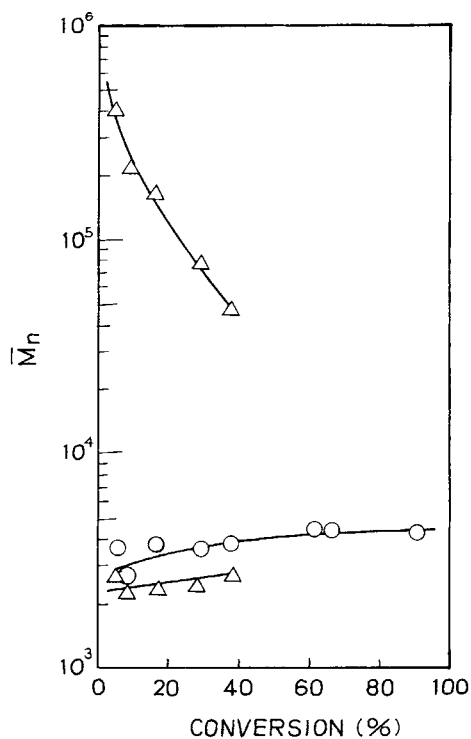


Fig. 3. MW conversion relationship in MMA at 2.1×10^5 rad/s: (Δ) the high MW and the main fraction, (\circ) total polymer.

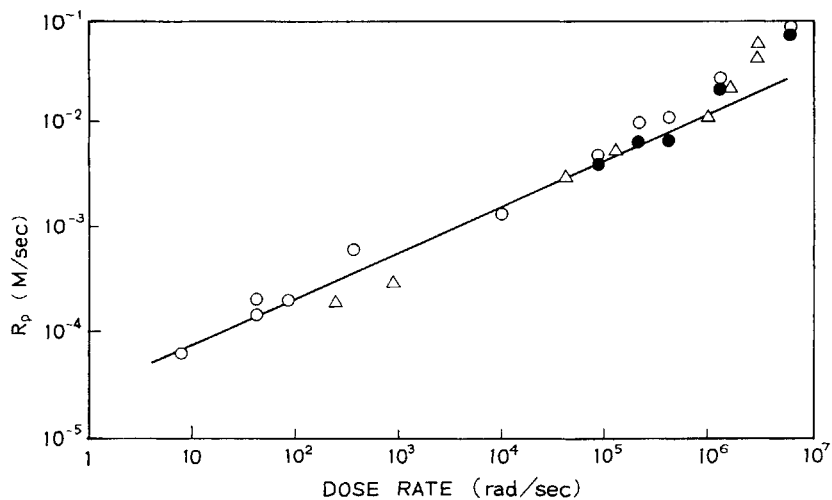


Fig. 4. Effect of dose rate on R_p in MMA: (\circ) total R_p , (\bullet) R_p for the main fraction; (Δ) rates from Ref. 4.

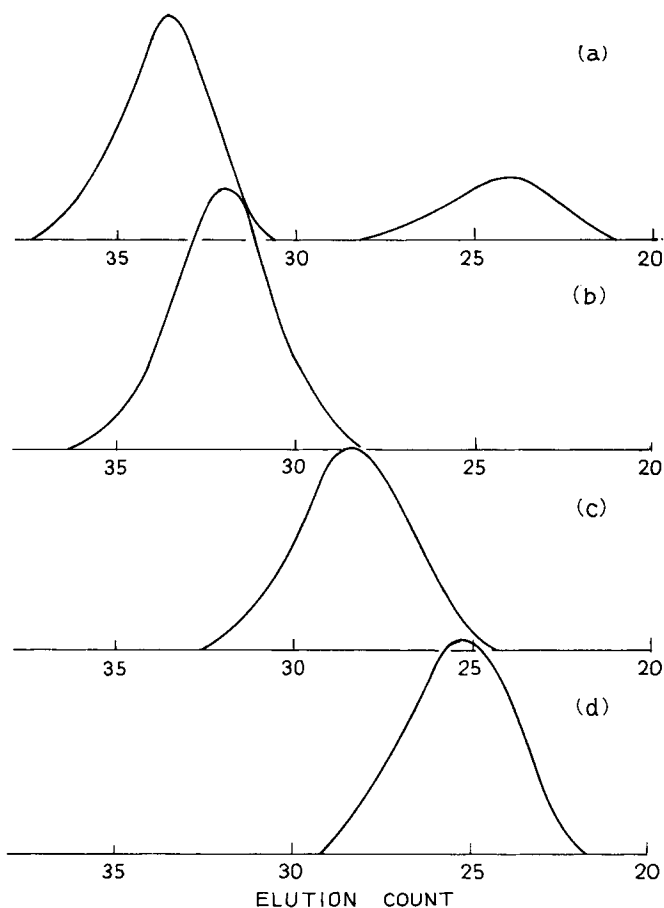


Fig. 5. Effect of dose rate on MWDs of PMMA. Dose rate and conversion: (a) 2.1×10^5 rad/s, 5.6%, (b) 1.1×10^4 rad/s, 8.6%, (c) 370 rad/s, 3.9%, (d) 7.9 rad/s, 4.2%.

degrades much more rapidly than our results even after correcting the influence of formation of new polymers. This suggests that the presence of monomer greatly protects the main chain scission of the polymer.

The R_p as a function of dose rate is shown in Figure 4. Our results fairly well agreed with those of Allen et al.⁴ The R_p 's for the main fraction are plotted with filled circles for high dose rate results in which two-peaked MWD were observed. The dose rate exponent of R_p for the main fraction at the dose rate lower than 10^6 rad/s is 0.45. It is confirmed that in MMA approximately half power dependence of R_p on dose rate is maintained in a very wide dose rate range. Positive deviation of R_p at the dose rate higher than 10^6 rad/s can be attributed to temperature rise in the cell by electron beam irradiation and heat of the reaction.

MWDs at different dose rates are shown in Figure 5. All of these curves were obtained for polymers at less than 10% conversion. The peak of the main fraction shifted to the higher MW side with lowering dose rate. At dose rate higher than 10^5 rad/s, the second peak appeared at the higher MW side of the main peak.

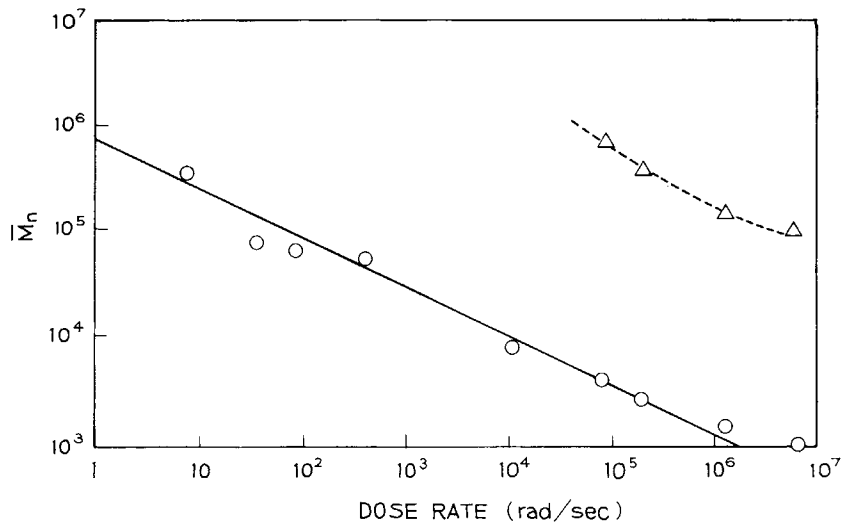


Fig. 6. Effect of dose rate on MW of PMMA: (O) the main fraction; (Δ) the second fraction.

In Figure 6, \bar{M}_n of the polymer was plotted as a function of dose rate. The \bar{M}_n was measured for the polymers at less than 10% conversion in all cases. The MW of the main fraction decreased with dose rate with an exponent of -0.47 , while Allen et al.⁴ reported the MW tends to approach a limiting value at high dose rate. This difference may be due to the fact that Allen's results were obtained on the basis of methanol-insoluble fraction. The MW of the high MW fraction decreases with dose rate in spite of its dependence on conversion since these results are taken at approximately the same conversion, ca. 5%.

Typical kinetic data at different dose rates are summarized in Table I. Since two-peaked MWD is obtained for the polymers at the dose rate higher than ca. 10^5 rad/s, the MWs for total polymer and for each fraction are given in

TABLE I
 R_p and MW Data for the Polymerization of MMA

| Source | Dose rate (rad/s) | R_p (M/s) | High MW fraction (%) | \bar{M}_n | | | \bar{M}_v | Conversion (%) |
|-------------------|----------------------|----------------------|----------------------------|------------------|------------------|---------------------|------------------------|-------------------|
| | | | | Total polymer | Main fraction | High MW fraction | | |
| ⁶⁰ Co | 7.9 | 6.4×10^{-5} | 0 | 349,000 | — | — | 712,000 | 4.1 |
| | 41 | 1.4×10^{-4} | 0 | 137,000 | — | — | — | 6.4 |
| | 83 | 2.0×10^{-4} | 0 | 67,700 | — | — | 297,000 | 8.6 |
| | 370 | 6.0×10^{-4} | 0 | 57,000 | — | — | 74,600 | 3.9 |
| Van de Graaf | 1.1×10^4 | 1.4×10^{-3} | 0 | 7,460 | — | — | 13,700 | 8.6 |
| | 8.4×10^4 | 5.1×10^{-3} | 14 | 4,840 | 4,190 | 737,000 | 1,270,000 ^a | 5.5 |
| | 2.1×10^5 | 1.1×10^{-2} | 25 | 3,630 | 2,600 | 415,000 | — | 5.6 |
| HDRA ^b | 1.3×10^6 | 2.6×10^{-2} | 25 | 1,770 | 1,340 | 167,000 | — | 1.5 |
| | 6.7×10^6 | 9.0×10^{-2} | 13 | 1,120 | 969 | 108,000 | — | 4.8 |

^a For high MW fraction.

^b High dose rate accelerator, installed in Osaka Lab., JAERI.

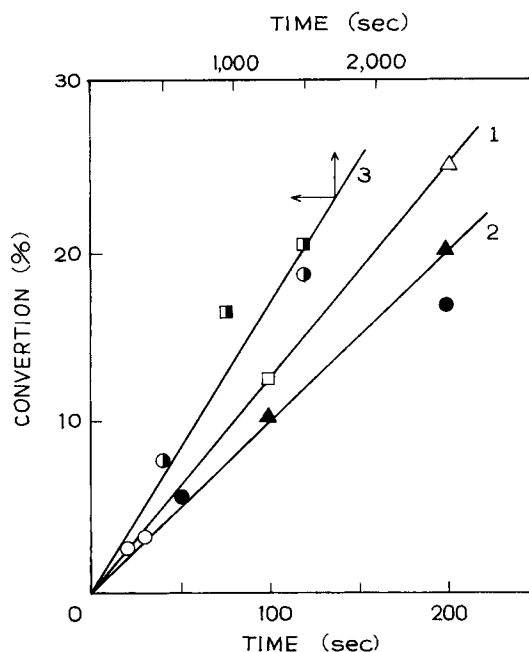


Fig. 7. Effects of air and water on the polymerization of MMA. Dose rate: (1) 4.2×10^5 rad/s; open symbols, (2) 2.1×10^5 rad/s; filled symbols, (3) 1.1×10^4 rad/s; half-filled symbols. Circles; no additives (water content, $1.4 \times 10^{-3} M$), triangles; 1 atm. air, squares; 0.81 M water.

the table. As the MW of the high MW fraction depends on conversion, the conversion of the samples for which MW were determined are also given in the last column.

Effects of water and air on R_p are summarized in Figure 7. Both additives had little influence on R_p and they all gave two-peaked MWDs which were practically the same as the MWDs of their corresponding samples without any additives.

From these results, it is clear that in MMA two different mechanisms of polymerization are taking place concurrently at high dose rate. The main fraction is certainly attributable to conventional radical polymerization. However, it is not clear what mechanisms are responsible for the high MW fraction.

An experiment with well dried monomer was carried out in order to study the reaction mechanism of the high MW fraction. MMA dried with well baked silica gel in a vacuum system was distilled into a cell and a glass ampoule for irradiations with electron beams and γ -rays, respectively. In Table II results are given to compare the kinetic data of the two monomers. Upon drying the monomer, a slight increase in R_p accompanied with MW decrease was found at both dose rates, but the fraction of the high MW polymer to the total yield did not change at high dose rate. If the increases in R_p were attributed to the promotion of ionic reaction on elimination of water, the fraction of high MW polymer should increase correspondingly.

Copolymerization with acrylonitrile (AN) was carried out in order to study whether the high MW fraction was due to an anionic mechanism. After

TABLE II
Effect of Drying on the Polymerization of MMA

| Sample | Dose rate (rad/s) | Time (s) | Conversion (%) | R_p (M/s) | High MW fraction (%) | \bar{M}_n | | | \bar{M}_v |
|----------|----------------------|-------------|-------------------|----------------------|----------------------------|---------------------------|------------------|---------------------|--|
| | | | | | | Total polymer fraction | Main fraction | High MW fraction | |
| Dry | 2.1×10^5 | 100 | 10.9 | 1.0×10^{-2} | 16 | 2,000 | 1,800 | 130,000 | — |
| Ordinary | 2.1×10^5 | 100 | 9.3 | 8.8×10^{-3} | 16 | 2,570 | 2,100 | 216,000 | 9,600 ^a 480,000 ^b |
| Dry | 7.9 | 6,910 | 4.9 | 6.6×10^{-5} | 0 | 240,000 | — | — | — |
| Ordinary | 7.9 | 6,910 | 4.1 | 5.6×10^{-5} | 0 | 350,000 | — | — | 712,000 |

^aFor high MW fraction.

^bFor the main fraction.

irradiation, the reaction mixture in THF solution was titrated with methanol to turbidity and a few more drops of methanol were added. Precipitate after an overnight storage was filtered and dried. An examination with GPC proved that by this simple procedure the high MW fraction could be well separated. AN content in polymer was determined from the nitrogen content by elementary analysis. In Figure 8, AN content in the polymer is plotted as a function of monomer composition. Comparison of the composition curves for radical and anionic copolymerization calculated on the basis of r_1 and r_2 values in the literature¹⁰ indicates that the possibility of anionic polymerization producing the high MW fraction is less likely.

Figure 9 shows results of the polymerization of MA, EA, and BA along with that of MMA at 83 rad/s. Autoacceleration of R_p due to gel effect took place in all four monomers. For MA and EA, the autoacceleration took place from the very early stage of the polymerization. For BA, the polymer yield increased almost linearly with time up to ca. 40% conversion and then R_p

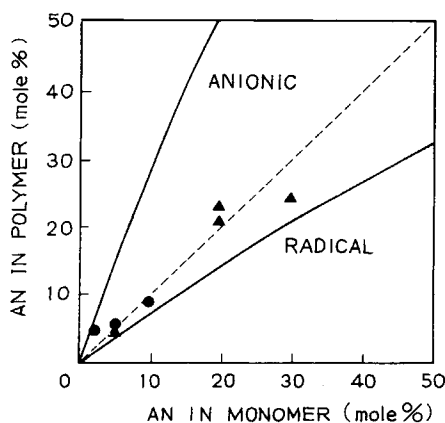


Fig. 8. Copolymerization with acrylonitrile at 0°C (●) and at room temperature (▲). Dose rate: 2.1×10^5 rad/s. Solid line curves denote polymer compositions with anionic and radical mechanism.

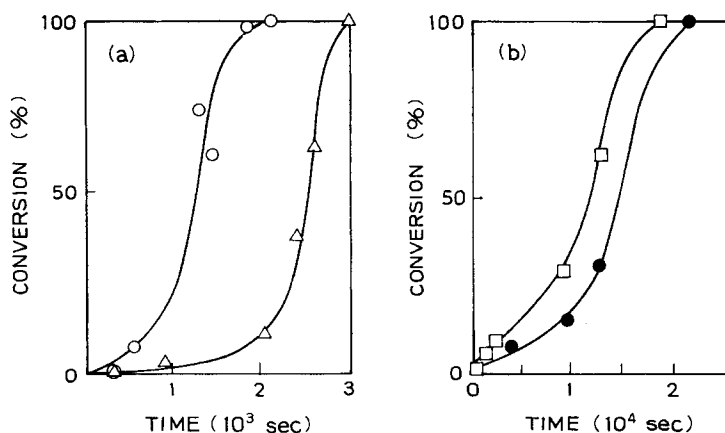


Fig. 9. Polymerizations of MA (Δ), EA (\circ), BA (\square), and MMA (\bullet) at 83 rad/s.

increased significantly. Gel product was formed at more than 50% conversion in MA and EA.

Results of the polymerization at 2.1×10^5 rad/s are shown in Figure 10. No autoacceleration was observed with EA and BA. Time-conversion curve with MA was still slightly sigmoidal and for the case of BA, R_p decreased slightly at medium conversion. Nevertheless it is clear that in all of these monomers, polymer yield increased much more linearly with the irradiation time than at 83 rad/s. This means that gel effect at high dose rate is less dominant in acrylates. In MA, the product was partly gelled at 20% conversion and completely at 50%. With EA, gel was found at 50%.

Typical MWDs of the acrylate polymers obtained at low conversion at the dose rate of 2.1×10^5 rad/s are shown in Figure 11. All are two-peaked as obtained for PMMA. MW data for these samples and R_p s are summarized in Table III along with results of MMA. It should be noted that MWs of MA and EA polymers are still substantially high at 2.1×10^5 rad/s compared with those of PMMA and PBA.

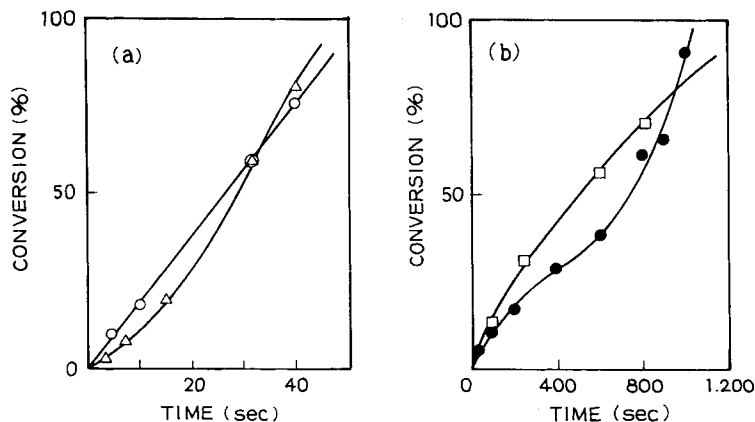


Fig. 10. Polymerization of: (a) MA (Δ), EA (\circ), (b) BA (\square) and MMA (\bullet) at 2.1×10^5 rad/s.

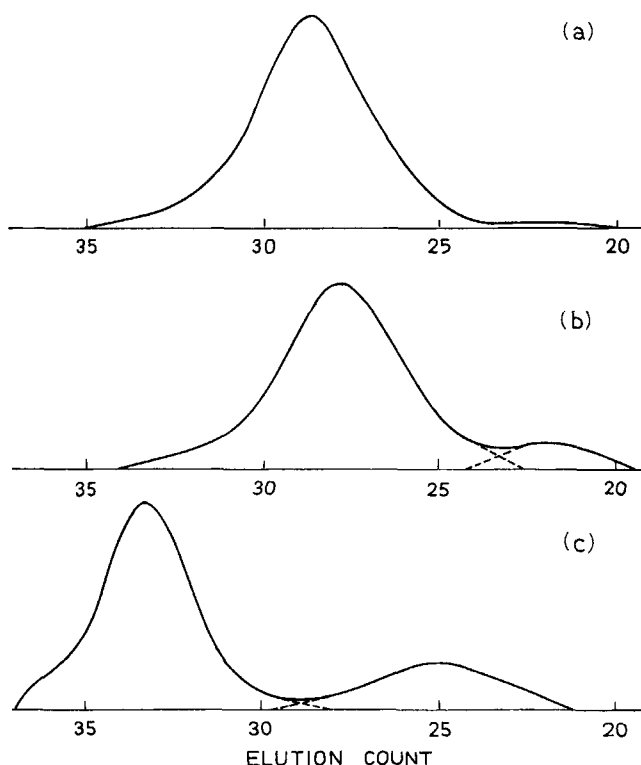


Fig. 11. MWD's of (a) PMA, (b) PEA, (c) PBA obtained at 2.1×10^5 rad/s.

R_p and MW for MA, EA, and BA as a function of dose rate are shown in Figures 12, 13, and 14, respectively. R_p s with MA and EA at low dose rate region were taken from the initial slopes of their time-conversion relationships. In most cases, MW was determined at less than 10% conversion. In MA polymerization R_p was proportional to 0.9 power of the dose rate and MW was nearly unchanged in the dose rate region studied. In EA polymerization R_p was proportional to 0.6 power of the dose rate except for the R_p at lowest dose rate, and MW decreased with increasing dose rate with an exponent of -0.24 . On the other hand, in BA polymerization the half power law was

TABLE III
Polymerization of Acrylates and MMA at 2.1×10^5 rad/s

| Monomer | R_p (M/s) | High MW fraction (%) | \bar{M}_n | | | \bar{M}_v |
|---------|----------------|----------------------------|------------------|------------------|---------------------|----------------------|
| | | | Total polymer | Main fraction | High MW fraction | |
| MA | 0.12 | 1.5 | 45,000 | 44,000 | 109,000 | 180,000 ^a |
| EA | 0.17 | 8 | 70,700 | 65,000 | 130,000 | 330,000 ^a |
| BA | 0.0088 | 24 | 3,570 | 2,700 | 230,000 | — |
| MMA | 0.0088 | 16 | 2,570 | 2,100 | 216,000 | 480,000 ^b |

^aFor total polymer.

^bFor high MW fraction.

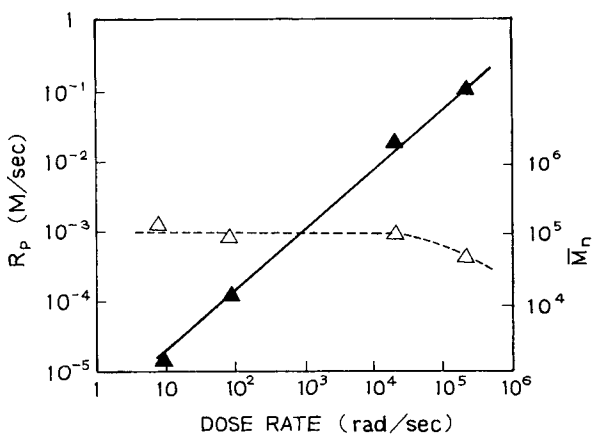


Fig. 12. Effects of dose rate on R_p (\blacktriangle) and M_n (\triangle) for MA.

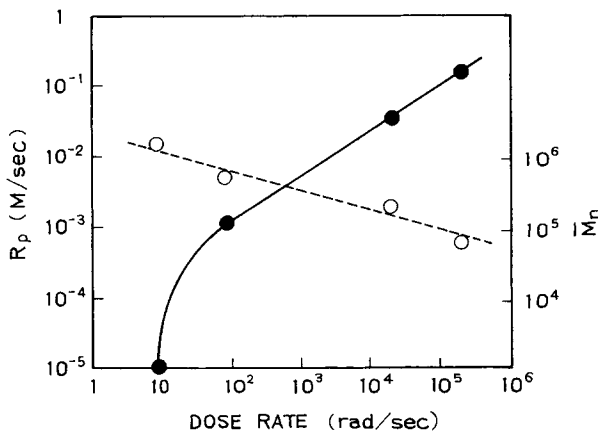


Fig. 13. Effects on dose rate on R_p (\bullet) and M_n (\circ) for EA.

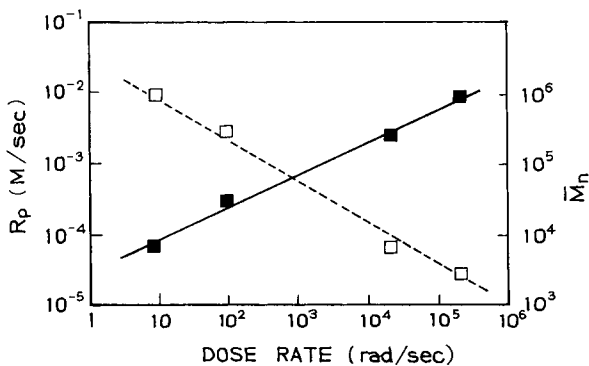


Fig. 14. Effects of dose rate on R_p (\blacksquare) and M_n (\square) for BA.

maintained for both R_p and MW. This means that in these acrylates the steady-state kinetics is maintained only with BA over the entire dose rate range studied.

DISCUSSION

It is well known that kinetic features of the gel effect are generally characterized with an acceleration of R_p in the medium stage of the polymerization and an increase of MW with increasing conversion. The whole course of the polymerization accompanied by the gel effect can be classified into three stages. In the initial stage up to a critical conversion and an abrupt increase in R_p , the polymerization proceeds smoothly at a constant rate, which follows the steady-state kinetics. At the intermediate stage, autoacceleration of R_p takes place because of the reduction in the termination rate constant due to the viscosity increase of the reaction medium¹¹ and the accumulation of radicals.¹² In the final stage, R_p is greatly decreased with conversion because of the difficulty of monomer diffusion and the polymerization ceases at a limiting conversion, leaving immobilized radicals in the system.

Our R_p and MW data were usually taken at less than 10% conversion and at the lowest dose rate, 7.9 rad/s, less than 5%. These conversion values are supposed to be substantially lower than the critical conversions of MMA at each dose rate. Therefore it is expected that the steady state is maintained at all dose rates at low polymer conversion. This is in accord with the fact that half-power dependence of R_p on dose rate is maintained with MMA over the entire dose rate range at the initial stage of the polymerization. At 2.1×10^5 rad/s, almost the same MW of the main fraction in the product for any degree of conversion indicates the absence of gel effect in the polymerization. In BA polymerization the situation must be almost the same as MMA since dose rate dependence of R_p and MW are essentially the same as those in MMA.

Kinetic results with MA and EA are much more complicated. It is well known that these monomers become highly viscous even at low conversion, giving rise to an autoacceleration almost from inception of polymerization.¹³ Actually, in Figure 9, R_p s of these monomers are very low and no region of constant R_p is observed in MA at the initial stage of irradiation. Therefore, dose rate dependence of R_p and MW for these two monomers deviate from the half-power law because practically no steady state exists at low dose rate. In EA polymerization, however, an approach to steady-state kinetics is seen in the variation of R_p and MW with dose rate.

It is clear that the gel effect is less dominant at high dose rate for all the monomers studied. This is partly due to lower MW of the polymer obtained at high dose rate. Lower viscosity of the reaction system therefore makes diffusion of radicals easier and the critical conversion is higher.

Comparing time-conversion curves in MA at 83 and 2.1×10^5 rad/s, it is evident that the gel effect appears very slightly at high dose rate, though MWs at these dose rates differ only by a factor of about 2. To account for this, some other reason than bulk viscosity change seems to be required. It is established that the gel effect is mainly attributed to the slowing down of the

segmental motion of the chain end rather than that of the translational motion of the polymer molecule.¹⁴ This implies that in MA polymerization segmental motion of the polymer is somehow retarded even at the early stage of polymerization. At high dose rate, however, the contribution of the primary radical termination becomes higher and, in consequence gel effect is less likely to occur since primary radicals find no difficulty in recombining with polymer radicals.

The possibility of an anionic mechanism as an origin of the high MW fraction is not entirely excluded at the moment. However, the lack of the influence of water on R_p and the result of copolymerization with AN greatly favor the radical mechanism. A bimodal distribution with high MW polymer can be expected in the monomer in which gel effect appears at high conversion.¹⁵ However, in our case, the high MW fraction is formed at the initial stage of polymerization.

It is not clear that the appearance of the high MW fraction is peculiar to high dose rate polymerization by electron beam irradiation, since its MWD is supposed to appear approximately in the same MW region as that of radical polymer at low dose rate. In our study, up to the present time, such a high MW fraction was obtained also in the case of water-saturated styrene³ but not with dried styrene,² α -methylstyrene,⁵ and isobutyl vinyl ether.¹⁶

As chain transfer constant to MMA monomer,¹⁷ 10^{-5} is far less than the reciprocal of the degree of polymerization of MMA. G value for initiating radical, G_R can be calculated from R_p with radical mechanism and MW data. Two different calculations were made on the basis of \bar{M}_n and \bar{M}_v values, respectively. It was shown¹⁸ that the universal calibration method was applicable to polystyrene and PMMA in THF at 35°C. Parameters required to convert MW of polystyrene to MW of PMMA basis were provided. By this calibration process the corrected \bar{M}_n value to PMMA basis was found to be 20–30% higher than the \bar{M}_n value on polystyrene basis depending on the magnitude of MW. In the calculations (Table IV), 1.2 radicals per chain was assumed¹⁹ as a correction for the competitive chain termination by disproportionation and recombination reactions.

From Table IV, we can see that the G_R value from the corrected \bar{M}_n on PMMA basis is almost constant, ca. 1.4 at high dose rate by electron beams while G_R is much higher at γ -ray region. Agreement in the two G_R values is rather poor at 7.9 rad/s, but fairly well at the other two dose rates. Our G_R

TABLE IV
Effect of Dose Rate on G Value for Free Radical Yield

| Dose rate (rad/s) | G_R calculated from the corrected \bar{M}_n | G_R calculated from \bar{M}_v |
|----------------------|--|--------------------------------------|
| 7.9 | 2.3 | 1.4 |
| 41 | 2.5 | — |
| 370 | 2.8 | 2.6 |
| 1.1×10^4 | 1.1 | 1.1 |
| 2.1×10^5 | 1.4 | — |
| 1.3×10^6 | 1.7 | — |
| 6.7×10^6 | 1.3 | — |

value at low dose rate, ca. 2.5 corresponds to the lowest limit of those collected by Chapiro.²⁰ As a possible explanation of the difference in G_R between γ -ray and electron beam polymerization, we can consider a predominance of the primary radical termination at high dose if we may assume that radical recombination somehow predominates over disproportionation. We should also consider the influence of chain scission on G_R . Since the rate of chain scission by irradiation is proportional to dose rate in contrast to square root dependence of R_p , a higher probability of chain scission during polymerization is expected with increasing dose rate. In this case, however, the calculated value for G_R should be higher at high dose rate when the influence of polymer degradation is taken into account.

Apparent G value for the initiation of the high MW fraction polymer was less than 10^{-2} . This is still lower than 0.1, which has been presumably accepted as an order of magnitude of G value for the initiation of ionic polymerization in nonpolar medium.²¹

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