

Studies in Radiation-Induced Polymerization of Vinyl Monomers at High Dose Rates.

II. Methyl Methacrylate

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Synopsis

The radiation-induced polymerization of methyl methacrylate was investigated with radiation sources of cobalt 60 and accelerated electrons at dose rates up to 3 Mrads/sec. Extrapolation of previous rates of polymerization at dose rates of 0.01–200 rads/sec coincided with the present results, the rates being approximately proportional to the square root of the dose rate throughout the entire set of dose rates measured. The molecular weights seemed to be independent of dose rate at the highest dose rates investigated. A combination of high polymer with a much higher molecular weight than expected was formed, together with a substantial portion of low molecular weight polymer. The reason for this behavior is not clear at this time. The $G(M\cdot)$ calculated from the molecular weights and fraction of polymer and resin was 6.0, which approaches that reported in previous investigations at low dose rates. There was no significant effect of air on the polymerization kinetics of methyl methacrylate at above 1 Mrad/sec. Nitrogen also did not influence the measured rates. Conversions to polymer were not substantially reduced by the presence of inhibitor at above 1.26×10^6 rads/sec. Water did not influence the rates of polymerization, except at the highest temperature (50°C) investigated. A large posteffect was observed in sealed degassed ampoules after 25% conversion to polymer. Only 3.4% additional polymer was formed in 24 hr after irradiation in the presence of air. The activation energy for the electron beam polymerization of methyl methacrylate was about 7.0 kcal/mole. This value, considering the complications in technique such as beam heating, did not differ from literature data enough to suggest any mechanistic difference in the polymerization at high dose rates.

INTRODUCTION

In part I of this series, the polymerization of styrene was studied¹ at dose rates up to 3.0 Mrad/sec. A substantial contribution to the polymerization from a concurrent cationic process was observed. This had the effect of increasing the rate above extrapolated values from a square-root relationship between the dose rate and rate of polymerization. In this paper, the results of a similar study with methyl methacrylate is reported. Methyl methacrylate is of interest as it has never been observed to polymerize by radiation by an ionic mechanism. In addition, the methacrylate and acrylate systems are of considerable interest as candidate coating formulations for electron curing.

The radiation polymerization of bulk methyl methacrylate has been studied at low and medium dose rates by a number of investigators. A complete account of this earlier work has been presented in detail by Chapiro.² A pronounced gel effect was observed, and the kinetics and other features of the polymerization were found to be very similar to those observed with corresponding chemically initiated systems. The effect of dose rate was studied up to 300 rad/sec. Good agreement was found among the various investigators. A square-root dependence of the rate on the dose rate was found up to about 2 rad/sec followed by a decreased dependence. The molecular weights, on the other hand, decreased roughly with the 0.26 power of the dose rate. At very high dose rates, up to about 0.1 Mrad/sec, very little polymerization was found to occur at room temperature. Significantly, however, considerable polymerization was found to take place at 65°C. The activation energy associated with the radiation-induced polymerization was found to be 4.9 kcal/mole, similar to that found with photopolymerization. The $G(\text{radical})$ value for methyl methacrylate was estimated by Chapiro² from the polymerization kinetics to be about 11.5 radicals per 100 eV. This is much larger than the value of about 4.5 found using D.P.P.H. methods. The reason for this discrepancy is not known at this time.

More recently, two additional studies of the gamma radiation-induced polymerization of methyl methacrylate were published.^{3,4} Lipscomb and Weber³ conducted studies at low temperatures (-19°C to -49°C) and at dose rates of 10.5 to 37.5 rad/sec. An activation energy of about 3.9 kcal/mole and a dose rate dependence of the polymerization rate of 0.33 were found. Palma, Busulini, and Lora⁴ used a calorimetric technique for following both the nonstationary and stationary state kinetics of gamma radiation-initiated polymerization of bulk methyl methacrylate. An overall activation energy of 3.9 kcal was found, and estimates of the propagation and termination rate constants were obtained together with their activation energies. A half-power dependence of the rate on the dose rate was found from 0.2 to 20 rad/sec between -25°C and $+55^{\circ}\text{C}$. The rates of initiation were found using D.P.P.H. and lead to a $G(\text{R}\cdot)$ value of 4.8, very similar to many other values reported in the literature. These findings will be discussed after the presentation of the results of the present study.

EXPERIMENTAL

The cobalt 60 source at North Carolina State University, the 1 MeV Van de Graaff accelerator at Duke University, and the 2.5 MeV Dynamitron at Columbia Research Corporation were used as radiation sources for this investigation. The operational characteristics and attendant limitations of these facilities are described in the preceding article.¹

Methyl methacrylate monomer inhibited with 25 ppm hydroquinone was made specially available to us by the Rohm and Haas Company. This

inhibitor is readily removed by passing through a column of Amberlyst A27 ion exchange resin. The monomer was then degassed by several freeze-thaw cycles under high vacuum and sealed in ampoules. The ampoules were kept at -78°C before use. The same metal cells described in the previous article¹ for styrene were used for the studies with the Van de Graaff accelerator. Due to the greater volatility of methyl methacrylate, there may have been some minor losses of monomer. This problem did not arise, of course, with the sealed ampoule research used for the cobalt 60 and Columbia Research Corporation studies.

The per cent conversion was determined by precipitating the polymer in methanol and weighing. The molecular weights were estimated for viscometry using the formula

$$[\eta] = 8.69 \times 10^{-5} M_n^{0.76}$$

where $[\eta]$ is the intrinsic viscosity at 30°C in benzene.⁵ In addition, molecular weights and their distribution were determined by gel permeation chromatography using a Waters Model 200 unit.

RESULTS

Since this was our first experience with the radiation-induced polymerization of this monomer, some preliminary results were obtained using the cobalt 60 source at 0.85 Mrad/hr. The first experiments were conducted using monomer which had been freed from inhibitor by washing with 2% sodium hydroxide and water and then drying over silical gel. A duplicate set of experiments were run in which the inhibitor was removed by passing over an Amberlyst 27 ion exchange column (suggested by the Rohm and Haas Company). In both cases, the monomer was then degassed by the usual freeze-thaw technique under vacuum.

The conversion-time curves are shown in Figure 1. Excellent linear plots with no induction periods were obtained, and no difference between the two methods of purification was found. These preliminary results were very gratifying after the irreproducibility and long induction periods found with methyl acrylate during preliminary investigations.

The second set of experiments were simple conversion and molecular weight measurements as a function of time at the same dose rate as before. The results are shown plotted in Figure 2 (rate data) and Figure 3 (molecular weight data). The conversion curves and molecular weight data are typical of bulk polymerizations with a marked gel effect. Even at 11.9% conversion, for example, the molecular weight had increased from 88,000 to 96,000.

Conversion curves at high dose rates using the Van de Graaff and Dynamitron electron accelerators are shown in Figures 4 and 5. The rates of polymerization and molecular weight data along with G values are tabulated in Table I. In Figure 6, the data are plotted as log rate and log molecular weight versus log dose rate together with the literature values.

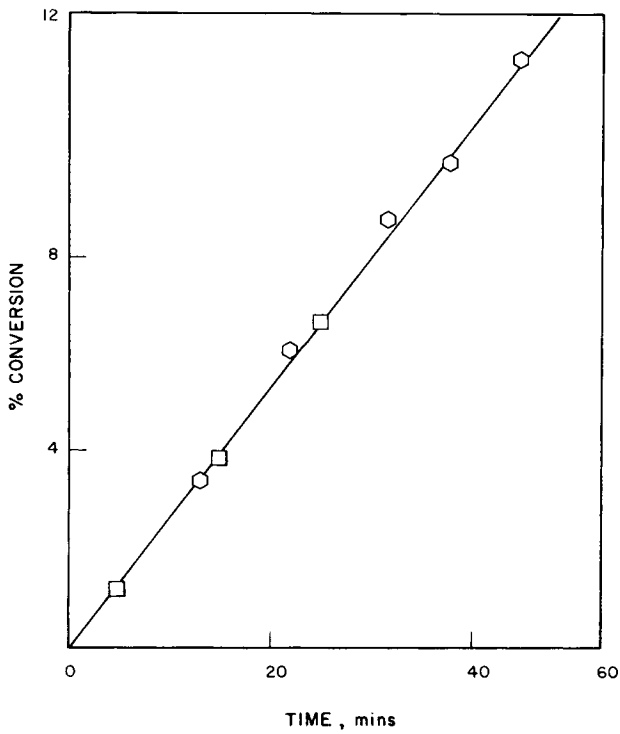


Fig. 1. Radiation-induced polymerization of methyl methacrylate at 250 rad/sec, initial conversions: (□) purified with Amberlyst A-27 column; (○) purified by sodium hydroxide wash, water wash, and drying over silica gel.

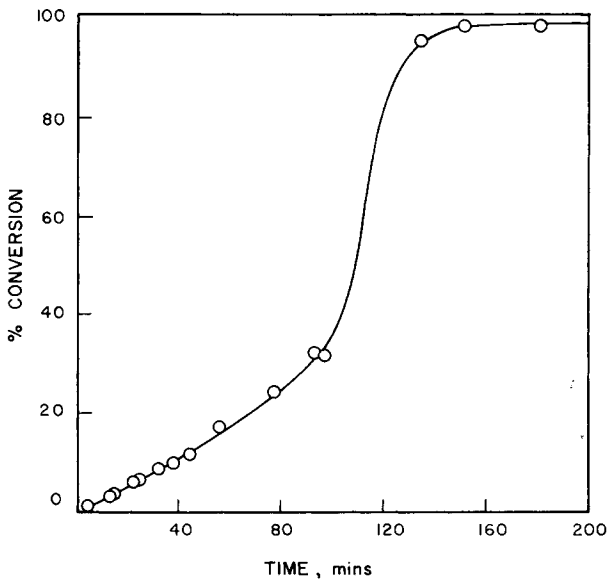


Fig. 2. Radiation-induced polymerization of methyl methacrylate at 250 rad/sec.

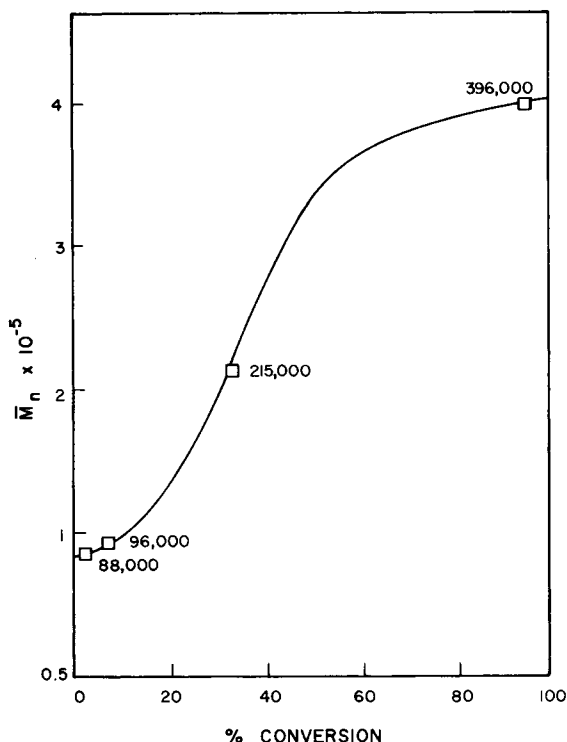


Fig. 3. Radiation-induced polymerization of methyl methacrylate, molecular weight-conversion values at 250 rad/sec.

The 250 rad/sec cobalt 60 data and the 850 rad/sec Van de Graaff data agree well with the extrapolated literature values. The higher dose rate Dynamitron data for rates of polymerization remain below the extrapolated square-root line. This is in contrast to the results obtained with styrene¹ and indicates, perhaps, that there is essentially no polymerization via an ionic mechanism. On the other hand, it is interesting that at the high dose rates the values obtained for the molecular weights tend to approach a limiting value and do not decrease catastrophically as predicted by theory at high dose rates. This suggests that the termination mechanisms must be quite different than that evoked in the simple kinetic theory.

Effect of Air and Inhibitors

Studies with the 2.5 MeV Dynamitron at the Columbia Research Corporation were made at 1 Mrad/sec in quadruplicate in air, nitrogen, and after degassing and sealing under high vacuum. The results are shown in Figure 7, and although there was a scatter of about $\pm 6\%$, it was clear that there was no effect of oxygen at the high dose rate used. As with styrene, however, the monomer layer was several millimeters thick, and the results cannot be extrapolated to thin coatings.

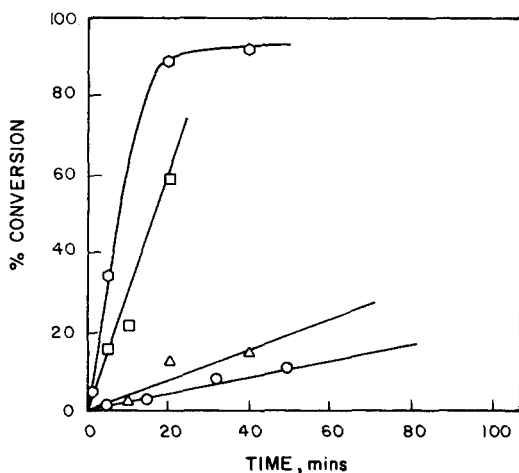


Fig. 4. Effect of dose rate on radiation-induced polymerization of methyl methacrylate: (○) 1.26×10^5 rad/sec Van de Graaff; (□) 4.20×10^4 rad/sec Van de Graaff; (△) 8.50×10^2 rad/sec Van de Graaff; (○) 2.50×10^2 rad/sec (Co 60 source).

A few experiments were conducted with and without the inhibitor at the highest Van de Graaff dose rate (1.26×10^5 rad/sec). The results are shown in Figure 8 and were somewhat scattered; it was clear, however, that the effect of the inhibitor was not large at the high dose rate used. Again, as with styrene, less than 100% conversion was reached, although as before this may very well be due to poor techniques in measuring conversion due to loss of monomer by evaporation or leakage from the brass cells.

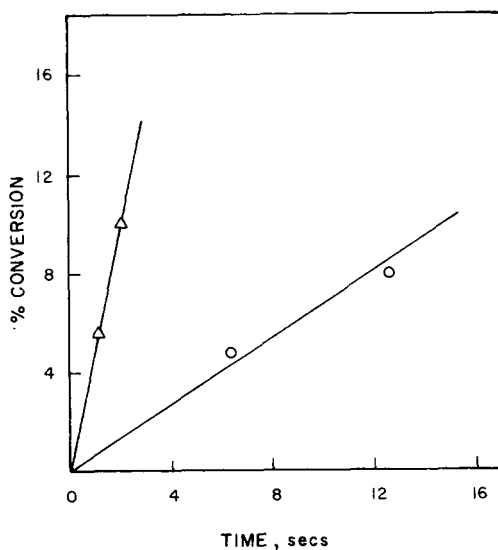


Fig. 5. Radiation-induced polymerization of methyl methacrylate at 0.33 Mrad/sec (○) and 3.0 Mrad/sec (△).

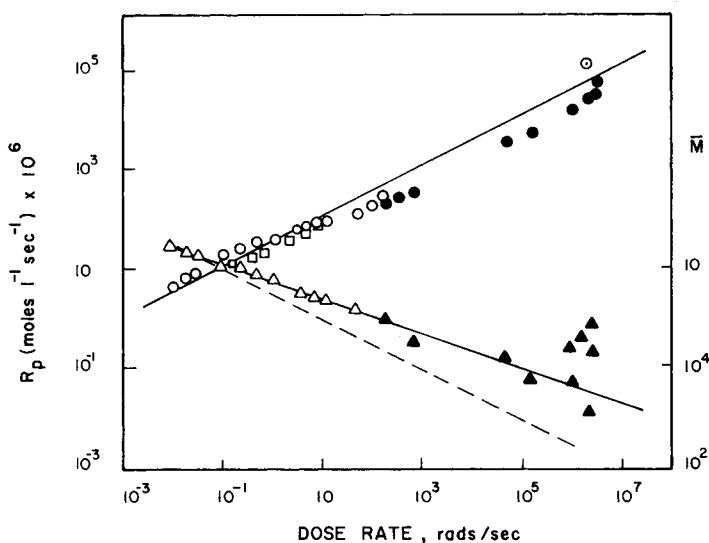


Fig. 6. Effect of dose rate on rates and molecular weights for radiation-induced polymerization of methyl methacrylate: (O) rates from literature²; (□) rates from literature⁴; (●) rates from this work; (▲) molecular weights from this work; (Δ) molecular weights from literature; (○) data corrected for methanol-soluble fraction.

With cobalt 60 irradiation in sealed tubes under vacuum, a posteffect could be clearly observed. The results are shown in Table II and are self-explanatory. The posteffect at 25.5% conversion was very large: in 24 hr, the conversion had increased to 54.5%. In the presence of air, however, i.e., on opening the tube to air, the conversion only increased from 17.0% to 20.4%, again showing the inhibiting effect of oxygen.

In general, posteffects are low at low conversions due to the high mobility of the radicals, are maximum at 50–60% conversion, and low again at high conversion due to the lack of monomer. Posteffects in the curing of coat-

TABLE I
Rate and Molecular Weight Data for Radiation-Induced
Polymerization of Methyl Methacrylate

Method	Dose rate, rad/sec	Rate R_p , moles/sec	$G(m)$	M_n	Conver- sion, %
⁶⁰ Co	2.50×10^2	1.77×10^{-4}	1543	9.60×10^4	1.20
Van de Graaff	8.50×10^2	3.13×10^{-4}	567	3.44×10^4	3.0
	4.26×10^4	3.09×10^{-3}	113	1.62×10^4	15.0
	1.26×10^6	5.55×10^{-3}	67.6	6.10×10^3	5.31
Dynamitron	3.33×10^6	4.81×10^{-2}	222.0	—	4.83
	1.00×10^6	1.25×10^{-2}	19.3	3.67×10^4	0.40
	1.00×10^6	1.23×10^{-2}	19.0	—	8.26
	1.70×10^6	2.35×10^{-2}	21.3	4.45×10^4	6.4
	3.00×10^6	4.72×10^{-2}	24.2	2.35×10^4	3.0
	3.00×10^6	5.76×10^{-2}	29.6	4.65×10^4	3.1

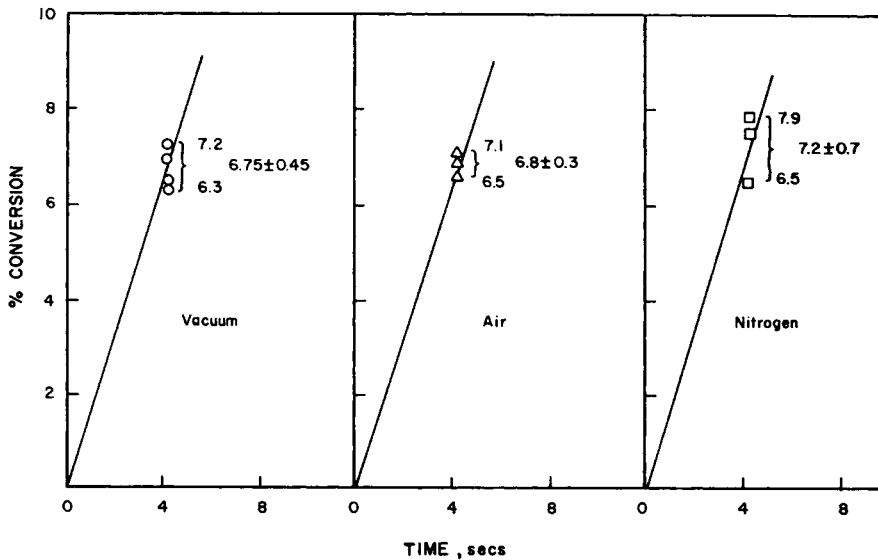


Fig. 7. Effect of air on radiation-induced polymerization of methyl methacrylate at 1.0 Mrad/sec.

ings are presumably manifested in other ways such as peroxidation and additional crosslinking or degradation since the conversions are by necessity essentially complete.

Effect of Radiolysis on the Polymer

Poly(methyl methacrylate) degrades upon irradiation. Thus, the polymer obtained at each dose has been degraded to some extent. The conversion curves are linear at the high dose rates used, and the probability of chain breakage may be considered directly proportional to the absorbed dose. Since the reciprocal of the number-average molecular weight is proportional to the number of breaks, a plot of the reciprocal of the molecular weight versus one half the absorbed dose at each conversion should

TABLE II
Posteffects During the Radiation-Induced Polymerization of
Methyl Methacrylate at 250 Rad/Sec

Condition	Conversion, %
(a) After 85 min of irradiation	
(i) tube opened immediately	25.5
(ii) tube opened after 24 hr under vacuum	54.4
(b) After 56 min of irradiation	
(i) tube opened immediately	17.0
(ii) tube opened after 24 hr to air	20.4

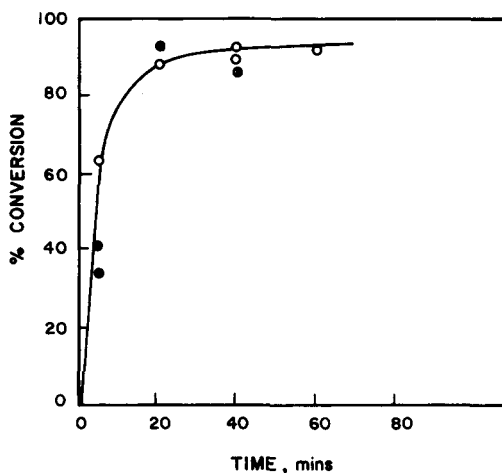


Fig. 8. Radiation-induced polymerization of methyl methacrylate, effect of inhibitor. Van de Graaff accelerator (Duke), 1.26×10^6 rad/sec: (O) without inhibitor (opened 21 hr after irradiation); (●) with inhibitor; (⊗) opened immediately after irradiation.

yield a straight line. Such a plot obtained at 2.8 Mrad/sec is shown in Figure 9. The curve is indeed linear; and from the slope, the $G(\text{breaks})$ value was calculated to be 1.86, in excellent agreement with the data summarized by Chapiro.²

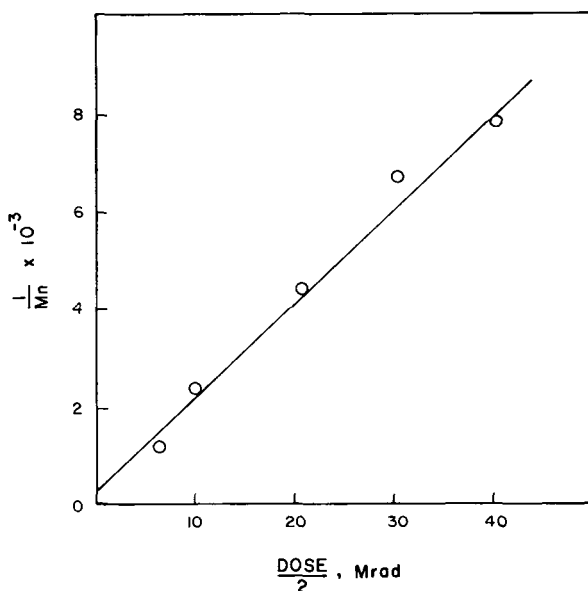


Fig. 9. Effect of dose on molecular weight of poly(methyl methacrylate) produced at high dose rates. Dose rate, 2.8 Mrad/sec.

Effect of Temperature

The effect of temperature on the polymerization kinetics of methyl methacrylate is important, particularly in methyl methacrylate-based coating formulations. Polymerization runs were carried out in sealed ampoules immersed in water to help control the temperature of the ampoule. Numerical solutions of differential equations modeling the transient temperatures in the system indicated approximately adiabatic monomer reaction conditions. Methyl methacrylate is heated approximately 4.9°C for each megarad absorbed energy, plus the temperature increases due to the reaction exotherm. The effect of these nonisothermal reaction conditions would be to increase the apparent activation energy, since the effect of temperature rise would be proportionally greater at high temperatures. Also, molecular weights would be greater than expected for isothermal polymerizations. Experimental runs were generally at doses less than 4 Mrads with associated temperature increases less than 20°C .

The activation energy for methyl methacrylate was determined to be about 7 kcal at both 1.9 and 3.2 Mrad/sec. An example of the effect of temperature is shown in Figure 10. Although these results differ slightly from the generally accepted value of 4.8 kcal, the runs were generally terminated after only a few per cent conversion. Melville⁷ reported a decrease in E_a for $K_p/K_t^{1/2}$ in chemically initiated MMA from 5.6 kcal at 0% conversion to 4.4 kcal at 10% polymer. Considering both the effect of low conversions and beam effects resulting in nonisothermal reaction conditions with the possibility of posteffects, the observed activation energies did not differ from previous work enough to suggest any basic mechanistic differences at the highest dose rates investigated.

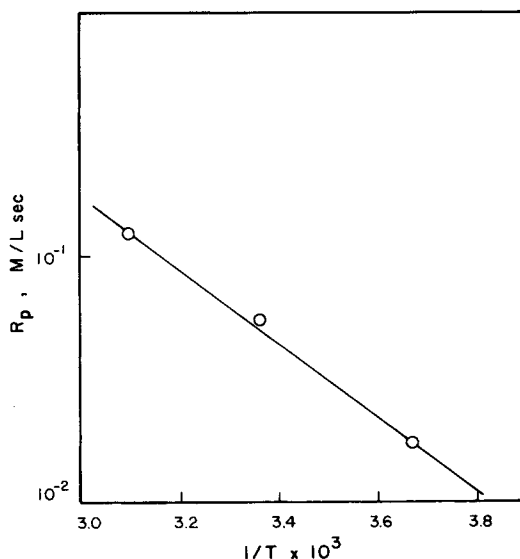


Fig. 10. Effect of temperature on rate of electron beam polymerization of methyl methacrylate. Dose rate, 3.2 Mrad/sec.

When a pass under the beam is of short duration, the effect of beam heating is reduced, but the relative contributions from posteffects is increased due to the smaller conversions achieved under irradiation. Rates at 0°C of methyl methacrylate increased from 0.008 to 0.022 M/l. sec as the irradiation time decreased from 2.1 sec to 1.05 sec at 1.9 ± 0.1 Mrad/sec. Thermal effects were expected to be more pronounced at 50°C, and the measured rates actually decreased even with increased posteffects from 0.116 to 0.093 M/l. sec as the irradiation period was reduced from 2.1 sec to 1.05 sec. The rate was not observed to show any additional decrease at irradiation times of 0.53 sec. The effect of irradiation time on the kinetics of electron beam polymerization are tabulated in Table III.

TABLE III
Effect of Irradiation Time on the Kinetics of Electron Beam Polymerization

Dose rate, Mrad/sec	Time, sec	Temp., °C	Rate, M/l. sec
3.2	0.7	50	0.117
3.2	1.4	50	0.161
1.9	2.1	50	0.116
1.9	1.05	50	0.093
1.9	0.525	50	0.093
3.2	0.7	25	0.055
3.2	1.4	25	0.078

Wet methyl methacrylate actually showed a minimum in the rates at 50°C and 1.9 Mrad/sec at irradiation times of about 1 sec. Beam heating presumably increased the rate during longer periods, and the relative contribution from posteffects was more important at runs with short times under the beam.

Autoacceleration

Methyl methacrylate was observed to autoaccelerate at approximately 20% conversion to polymer at a dose rate of 250 rad/sec (Fig. 2). This autoacceleration is the "gel effect" where the termination reaction is retarded because of polymer steric resistance to chain end diffusion. This autoacceleration is a function of the polymer molecular weight. Higher molecular weight polymer decreases the conversion necessary for the formation of "gel" and the onset of the "gel effect." Since the polymer molecular weight is greater for relatively slow rates of polymerization, the conversion at the onset of the gel effect should also be a function of the rate. Figure 11 illustrates this relationship between the onset of autoacceleration and the initial polymerization rate, where the present results with radiation initiation are compared to various chemically initiated systems. The onset point was taken as the point of departure from linearity of the conversion curve.

Methyl methacrylate autoacceleration may be prematurely introduced through the incorporation of a difunctional monomer which increases the molecular weight by crosslinking reactions. This effect will be discussed in a future publication.

Methyl methacrylate was not observed to autoaccelerate at the highest conversions obtained with electron beams in the present investigation (<20%). The incorporation of prepolymers into methyl methacrylate-based formulations would be expected to induce autoacceleration by decreasing the chain end mobility of propagating free radicals. Prepolymer solutions would also have less monomer loss through evaporation in a curing process.

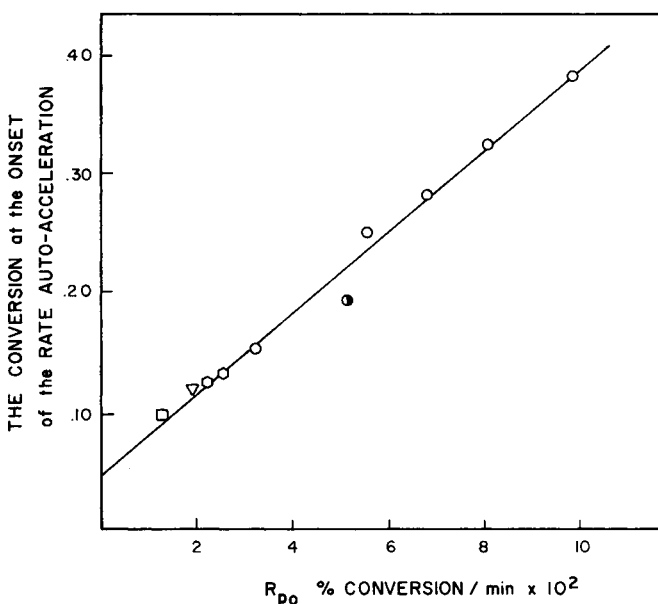


Fig. 11. Effect of initial rate on conversion at onset of rate autoacceleration: (●) present work; (□) ref. 9; (○) ref. 2; (○) ref. 10; (▽) ref. 8.

Effect of Water

A series of investigations were carried out on the polymerization of methyl methacrylate and methyl methacrylate saturated with water under equivalent conditions. Methyl methacrylate conversions to polymer at dose rates of 2.8 Mrad/sec were not significantly altered by the presence of water, as shown in Figure 12, which possibly suggests that the polymerization occurs by a predominately free-radical process, even at high dose rates. The effect of water, however, was somewhat more significant at the higher temperatures. Approximately 30% reduction in rates was observed at 50°C at 1.9 ± 0.1 Mrad/sec. The reason for this kinetic

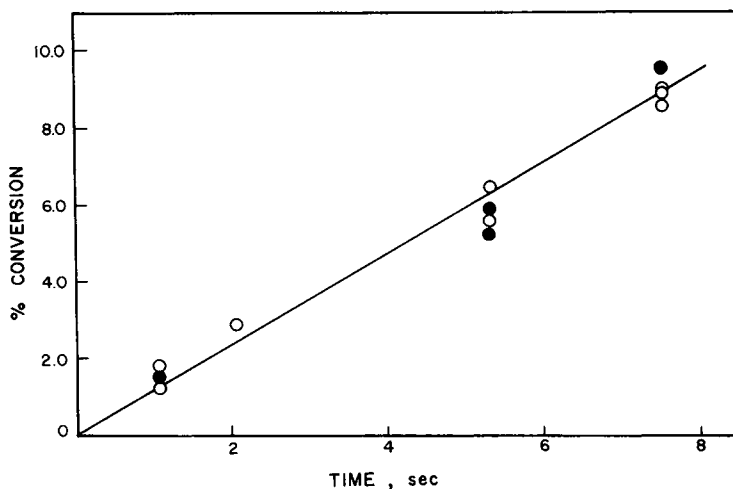


Fig. 12. Effect of water on electron beam polymerization of methyl methacrylate. Dose rate, 2.8 Mrad/sec: (○) dry; (●) wet.

retardation is not apparent at this time. The activation energy for the wet runs was approximately 5.6 kcal and 5.2 kcal for dose rates of 1.9 and 3.2 Mrad/sec, respectively.

DISCUSSION

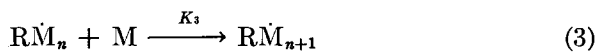
Kinetic Scheme

Theoretically, the polymerization of methyl methacrylate on the basis of a free-radical mechanism induced by radiation can be modeled in the same manner as styrene, summarized as follows:

Initiation



Propagation

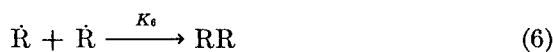


Termination



This is the conventional reaction mechanism of free-radical polymerization.

At higher dose rates, it is considered that additional termination may occur owing to the strong and fast radiolysis of the system. These reactions may be represented in the following way:



According to the usual termination, i.e., the termination step reaction (4), the rate of polymerization R_p and degree of polymerization \overline{DP}_n are deduced as

$$R_p = K_3 \frac{(K_1 I)^{1/2} (M)^{3/2}}{K_4^{1/2}} \quad (7)$$

and

$$\overline{DP}_n = \frac{2K_3 [M]^{1/2}}{[K_4 K_1 I]^{1/2}} \quad (8)$$

where I is the dose rate. It is found from the eqs. (7) and (8) that rate of propagation R_p is proportional to, and the degree of polymerization \overline{DP}_n is inversely proportional to, the square root of the dose rate.

At higher dose rates, when eq. (5) is considered, R_p and \overline{DP}_n can be derived as

$$R_p = \frac{K_3 K_2 [M]^2}{K_5} \quad (9)$$

$$\overline{DP}_n = \frac{2K_2 K_3 [M]}{K_1 K_5 I} \quad (10)$$

Unlike the former case, here the rate is independent of dose rate while the degree of polymerization is inversely proportional to the dose rate.

In the same way, as termination step (6) comes into play, the rate and molecular weight begin to drop further until only dimers and simple radiolysis products result.

Turning now to a discussion of the experimental results, it is clear that the polymerization kinetics of methyl methacrylate at high dose rates do not show the expected departure from the predicted square-root dose rate dependence of the simple kinetic theory. Previous results² seemed to indicate that the polymerization rates were approaching a limiting value at dose rates greater than 100 rad/sec. However, the rates which were measured in this investigation were well correlated with the simple kinetic scheme. Acceptable agreement was obtained with a square-root extrapolation of previous data, particularly the results of Palma.⁴

The simple kinetic scheme was not representative of the overall reaction kinetics, since the molecular weight of the polymer appeared to be approaching a limiting value at the higher dose rates investigated. The molecular weights were much higher than expected from the simple kinetic theory. This anomalous relationship between rates and molecular weights may be explained through a consideration of the mechanisms of initiation and termination coupled with an analysis of the products of radiation polymerization.

$G(M\cdot)$, the apparent number of propagating radicals produced per 100 eV of absorbed energy, may be calculated from the rate and molecular weight data. Such calculations must be corrected for the propagation of recombinations and disproportionations which take place. The average

value of 1.2 initiating radicals per chain as determined by Bevington et al.¹¹ were used and the effect of dose rate on $G(M\cdot)$ is shown in Figure 13. Low dose rate data reported by Chapiro² have also been included in the plot.

A steady decrease in the number of polymer chains produced per rad was observed, especially at high dose rates. At these high dose rates, the polymer chains did not terminate as rapidly as the simplified kinetic scheme predicted and grew much longer than expected. At relatively low molecular weights and low conversions to polymer, the termination rate constant, from steric diffusion considerations, may be expected to be less than observed for high molecular weight polymer chains.⁶

Thus, the tendency to reduce the rates of polymerization at high dose rates from a decrease in the efficiency of initiation may be offset by a decrease in the rate constant of termination.

Alternatively, the formation of localized "hot spots" in the vicinity of a propagation radical would increase both the rates and molecular weights, but these are unlikely to be formed at low viscosities. Polymerization by hot radicals in discrete volume elements has been postulated, for example, for 0.04 MeV electron irradiation of styrene polyester solutions,⁷ due to L.E.T. effects, for example. A more likely explanation may be spur overlapping, as discussed by Machi et al.¹²

To investigate the concurrent formation of low molecular weight products through the recombination of primary radicals, degassed methyl methacrylate was irradiated with electrons at a dose rate of 2 Mrad/sec and then mixed with ethanol. White poly(methyl methacrylate) precipitated from the solution. A tacky nonvolatile resin was found after evaporation of the filtered methanol solution. The relative amounts of resins separated from the high polymer were not a function of the ratio of methyl methacrylate to methanol or of the solubility parameter of the methanol-methyl methacrylate mixture in the proportions used. Table

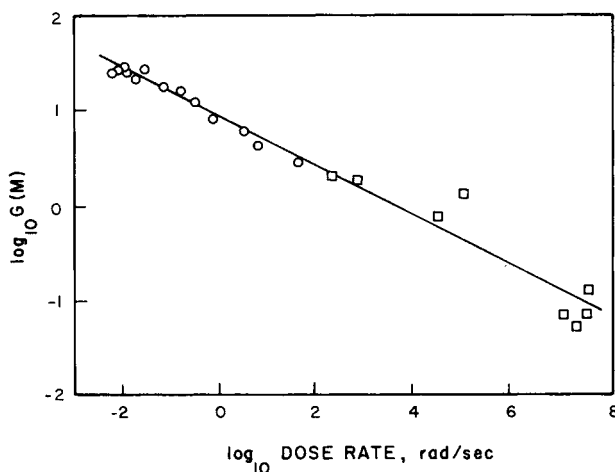


Fig. 13. Effect of dose rate on propagating free-radical yield of methyl methacrylate, $G(M\cdot)$: (□) present work; (O) ref. 2.

IV summarizes the results of the investigation of the polymer and monomer. The agreement between the four separate experiments may be considered as fair, considering the difficulties in work of this kind. The substantial amount of high polymer present could not have been formed through post-polymerization, as calculated from conventional posteffect kinetics. The monomer was quenched with hydroquinone very shortly after irradiation.

TABLE IV
Analysis of Polymers Formed at High Dose Rates^a

Run	Resin wt-%	\overline{DP}_n	Polymer wt-%	\overline{DP}_n	Resin/ polymer ratio	Rate poly- mer, (M/l. sec) 10^{+8}	Rate (total), (M/l.sec) 10^{+8}
A	3.42		4.83		0.710	6.87	11.8
B	2.92		4.51		0.648	6.43	10.6
C	3.27		4.10		0.798	5.83	10.3
D	3.41		4.98		0.686	7.1	11.9
Mean	3.25	5.23	4.60	78.5 ^b	0.707	6.55	11.15

^a Three passes at 2 Mrad/sec of duration 2.2 sec per pass. \overline{DP}_n for polymer determined by intrinsic viscosity⁵ and for the resin by vapor-phase osmometry.

^b Corrected for degradation using G (scission) = 1.86.

Since the resin was formed as a result of monomer radiolysis, the free radicals that were generated have presumably added a few monomeric units before termination and produced the resin. Since the amount of low molecular weight resin was substantial, a large fraction of the free radicals generated by radiolysis would have been used to form the resin. The number-average degree of polymerization of the methanol soluble portion was found to be 5.23 and that of the insoluble portion, 78.5, after correction for concurrent chain cleavage. These values combined with the rates give a $G(M\cdot)$ value of 10.0 assuming two radicals per chain, or 6.0 assuming 1.2 initiating species per chain. Only 8.8% of the radicals produced result in the formation of methanol insoluble high polymer.

Values for $G(R\cdot)$ for methyl methacrylate have been summarized by Chapiro² and range from about 4 to 12. The overall radical yield estimated from the overall polymer yield at 2 Mrad/sec fall within this range but is somewhat low compared with the limiting value of about 11.5 found at low dose rates. Considering, however, that volatile products probably also result from the radiolysis, there seems no reason to invoke any special behaviour with regards to the low $G(M\cdot)$ values calculated from the high polymer yields alone.

The large amount of comparatively high molecular weight product is difficult to explain without recourse to postulating some special thermal effects. The cluster of higher molecular weight points on Figure 6 at the highest dose rates tend to support the occurrence of anomalous heating effects. In addition, the dependence of the molecular weight on the reciprocal 0.3 power as shown in Figure 6, rather than the expected 0.5 power, is extremely puzzling and has already been pointed out by Chapiro²

even for the low dose rate data. The dependence of molecular weight on conversion (Fig. 3, for example) makes interpretation more difficult.

To check whether low molecular weight material was also produced at lower dose rates, a pure sample of methyl methacrylate was degassed and irradiated for 1 hr at 167 rad/sec. The polymer was isolated by pouring into an excess of methanol and filtering. The filtrate was carefully evaporated to dryness together with an exactly corresponding control. The conversion to high polymer was 15.4%, and the methanol-soluble portion including extensive washing amounted to 0.010%. Even when calculated as dimer, this only increased the $G(R\cdot)$ value from 3.42 to 4.38. This is in contrast to the results found by Machi, Silverman, and Metz,¹² who found about 11% of dimers and trimers in the case of styrene at the somewhat higher dose rate of 2.8 Mrad/hr. Their total conversion, however, was only 1.1%, and it is possible that traces of impurity could have caused the proportionately large amounts of dimers and trimers; on the other hand, dimers and trimers could have been occluded in the precipitated polymer in the present work and would have been undetected by the intrinsic viscosity method used for the molecular weight determination. Further work of the type carried out by Machi et al.¹² using gel permeation chromatography is clearly needed in studies of the liquid-phase radiation polymerization of methyl methacrylate.

Finally, although methyl methacrylate has never been observed to polymerize ionically with high-energy radiation, this possibility cannot be entirely ruled out. Experiments with superdried monomer combined with very high dose rates have not yet been made and are needed to clarify the possible role of concurrent ionic polymerization. Certainly, more work is needed before a final judgment can be made. Even a small contribution from an ionic process would be sufficient to explain the high dose rate data obtained and presented in this paper.

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