Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article O'donnell, J. H. and Sothman, R. D.(1980) 'Radiation-Induced, Solid-State Polymerization of Derivatives of Methacrylic Acid. XI. Aspects of the Polymerization of Methacrylic Acid by γ-Irradiation', Journal of Macromolecular Science, Part A, 14: 6, 879 — 898

To link to this Article: DOI: 10.1080/00222338008068118

URL: http://dx.doi.org/10.1080/00222338008068118

J. MACROMOL. SCI.–CHEM., A14(6), pp. 879-898 (1980)

Radiation-Induced, Solid-State Polymerization of Derivatives of Methacrylic Acid. XI. Aspects of the Polymerization of Methacrylic Acid by γ-Irradiation

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ABSTRACT

Aspects of the radiation-induced polymerization of methacrylic acid in the crystalline state have been investigated and utilized to evaluate the mechanism of polymerization. In particular, results for post-irradiation polymerization at 0°C after radiation doses of 0.1 to 2.0 Mrad support the concepts of Lando and Semen that chain initiation essentially all commences at the same time, that chain propagation continues without termination, and that termination of nonpropagating radicals proceeds simultaneously.

INTRODUCTION

The solid-state polymerization of methacrylic acid is of particular interest because this compound is the basic member of a whole series of methacrylic acid salts and esters in which polymerization in the solid state has been investigated [1-5].

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Initial experiments by Morawetz and co-workers showed that polymerization occurred during γ-irradiation [6] at -18°C and during post-irradiation heating [7] at 0°C with an indication that the polymer was much less syndiotactic than when prepared by polymerization in the liquid phase. Bamford and co-workers have published studies on the solid-state polymerization of methacrylic acid initiated by ultraviolet light, x-rays, and high frequency electric discharge [8-16]. Initiation occurred at the surface, and the polymerization characteristics may be expected to differ from the more uniform initiation by γ-radiation. Sakai [17-19], Lando and Semen [20], and Chachaty et al. [21] have examined the polymerization of methacrylic acid under selected conditions.

In this paper we report our results for the effect of various parameters on the in-source and post-irradiation polymerization rates, conversions, and molecular weights of methacrylic acid in the solid state initiated by γ-radiation and assess their compatibility with the measurements and interpretations of the above authors.

EXPERIMENTAL

Methacrylic acid (MAA, Rohm and Haas) was distilled at 60°C under 10 Torr (1.3×10^3 Pa) of nitrogen, ferrous sulfate being used to decompose peroxides and cuprous chloride to inhibit polymerization during distillation. Samples of MAA were degassed by freeze-thaw cycling and sealed under vacuum ($< 10^{-2}$ Pa) by using 5-7 g in Pyrex tubes for polymerization measurements and ca. 0.2 g in Spectrosil tubes for ESR. Irradiations were carried out by using a constant-low-temperature bath unit [22] modified to use stainless-steel Dewar vessels, a circulating water/glycol unit, liquid nitrogen (-196°), Dry Ice/acetone (-78°C), or crushed ice/H_2O (0°C) in the cobalt-60 γ-irradiation pond facility of the Australian Atomic Energy Commission Research Establishment. ESR measurements were made with a Varian V-4502 spectrometer and a variable temperature cavity.

Polymer yields were determined by crushing the samples into powder at -196°C by using a stainless steel piston-in-cylinder device and then transferring the powder to a high speed blender containing 500 ml of hexane, which is a good solvent for MAA but is a non-solvent for the polymer. The insoluble polymer was filtered and dried to constant weight in a vacuum oven at 30°C. Unreacted monomer was determined by titration of the double bonds by use of an aqueous brominating agent [23]; it was necessary to use water in the blender in this case.

Molecular weights ($\overline{M}_v$) were obtained by dilute solution viscosity measurements in methanol at 25°C in a Ubbelohde viscometer and taking [24] $[\eta] = 0.242\ \overline{M}_v^{0.51}$ g/cm^3.

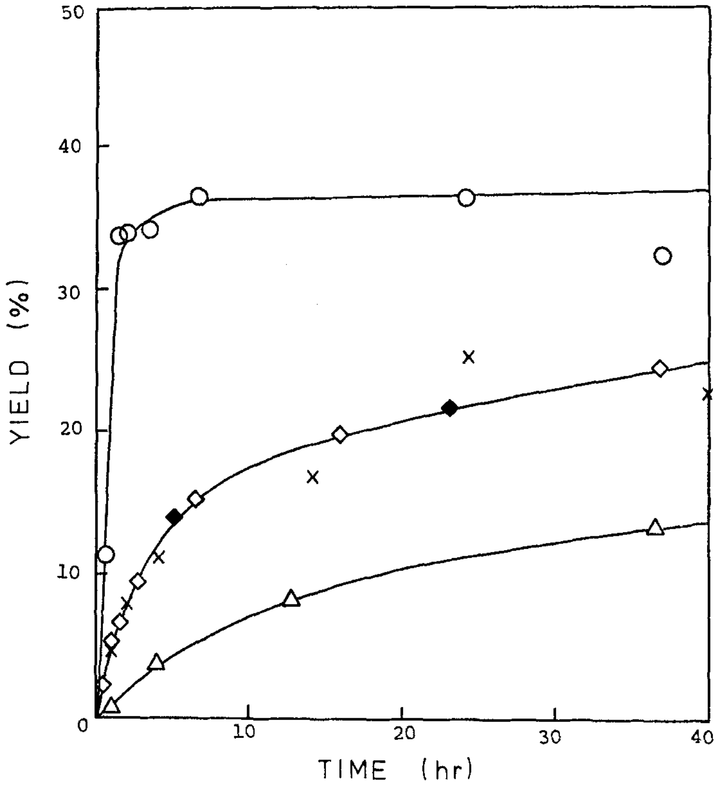


FIG. 1. Post-irradiation polymerization of MAA with 0.5 Mrad at -196°C: (○) +10°C; (◇) 0°C; (△) -10°C; (◆) volumetric results at 0°C; (X) results of Lando and Semen [20] at 0°C after 0.23 Mrad at -78°C.

RESULTS

Post-Irradiation Polymerization

Polymerization Temperature. The kinetic curves for post-irradiation polymerization at -10, 0, and +10°C after 0.5 Mrad at -196°C are shown in Fig. 1. The melting point of the monomer was 15.5°C. The initial rate increased with temperature, being very fast at +10°C, and in all cases decreased with time to a very low value approaching a "limiting" conversion below 50%.

Radiation Dose. The initial rate of polymerization increased with radiation dose as shown in Fig. 2 for polymerization at 0°C after

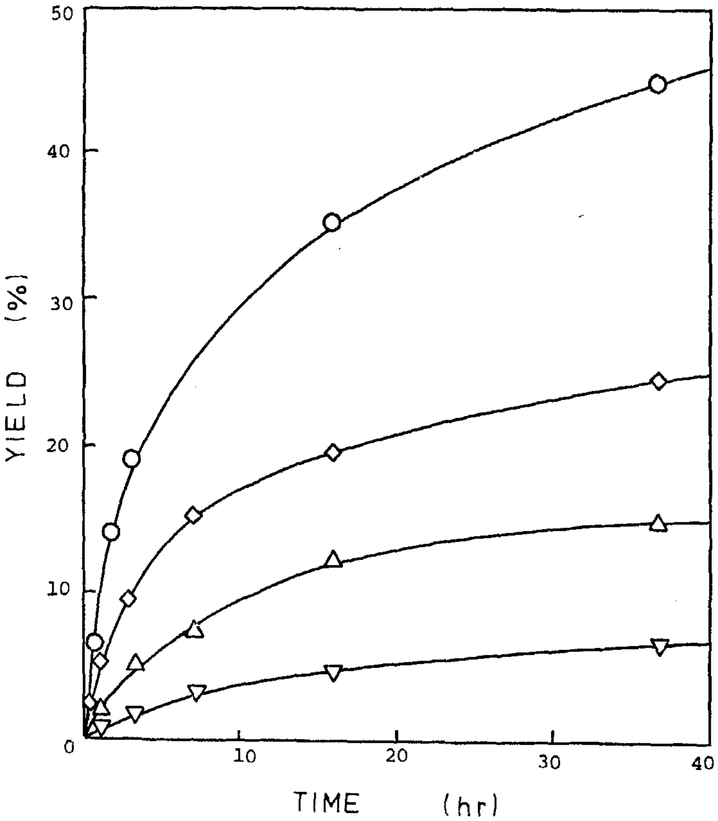


FIG. 2. Dose dependence of post-irradiation polymerization in MAA with doses of: (○) 1.0 Mrad; (◇) 0.5 Mrad; (△) 0.25 Mrad; (▽) 0.1 Mrad. Irradiation at -196°C; polymerization at 0°C.

irradiation at -196°C; these results show an adequate fit to a first-order dependence on dose. The "limiting" conversion also increased with dose.

Oxygen. The initial rates of polymerization and the "limiting" yields of polymer were reduced by a factor of two for samples sealed in tubes containing 1 atm of air instead of under vacuum.

Irradiation Temperature. Irradiation at -78°C resulted in slightly more than twice the polymer yields for post-irradiation polymerization at a given temperature compared with the same dose at -196°C. Typical results are shown in Fig. 3 for polymerization at 0°C after a dose of 0.5 Mrad.

Molecular Weights. Molecular weights above 10^5 were obtained from post-irradiation polymerization. They increased with

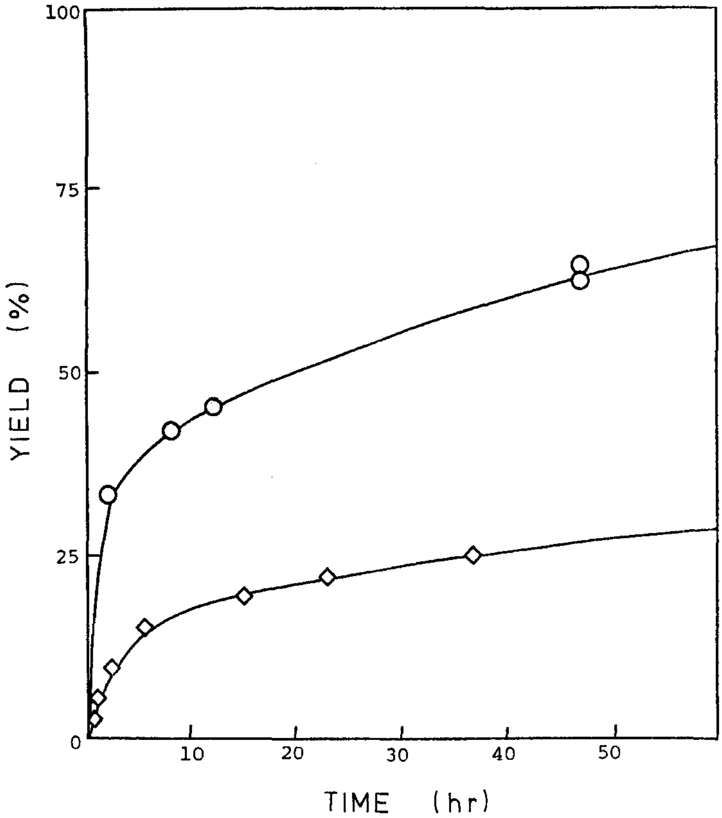


FIG. 3. Effect of irradiation temperature on the post-irradiation polymerization of MAA: (○) -78° C, (◇) -196° C, Radiation dose; 0.5 Mrad; polymerization at 0° C.

polymerization time (conversion) and polymerization temperature as shown in Fig. 4.

In-Source Polymerization

Temperature. Sigmoidal polymerization curves were obtained for irradiation at -10, 0, and +10° C, giving polymer yields approaching complete conversion and with a marked positive temperature dependence as shown in Fig. 5. Good agreement was observed between gravimetric measurements of polymer formation and volumetric measurements of residual monomer.

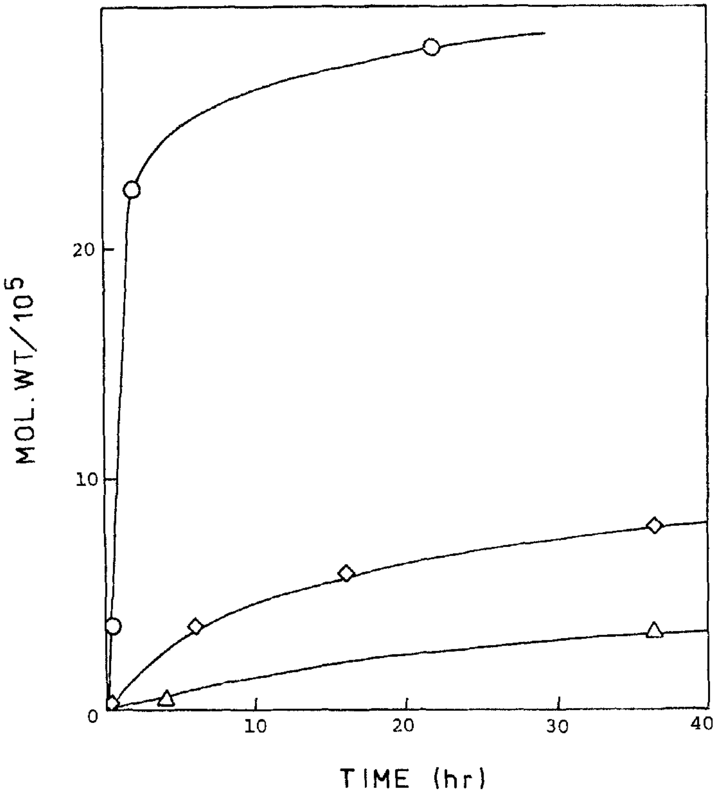


FIG. 4. Variation of molecular weight ($\overline{M}_v$) with post-irradiation polymerization time: (○) +10°C; (◇) 0°C; (△) -10°C.

Dose Rate. The polymerization rate increased approximately linearly with radiation dose-rate from 8.8 to 100 krad/hr at 0°C and less rapidly at higher dose rates, although the polymerization rates were then too high for satisfactory measurements. Typical results are shown in Fig. 6.

Molecular Weight. The molecular weight initially increased with irradiation time similarly to conversion but beyond the inflection point in the sigmoidal yield/dose relationship at high conversion decreased markedly, indicating radiolytic chain scission of the polymer, as shown in Fig. 7.

ESR Spectra

The ESR spectrum at -196°C was predominantly 7 lines, attributable to initiating radicals I, but also containing intermediate lines.

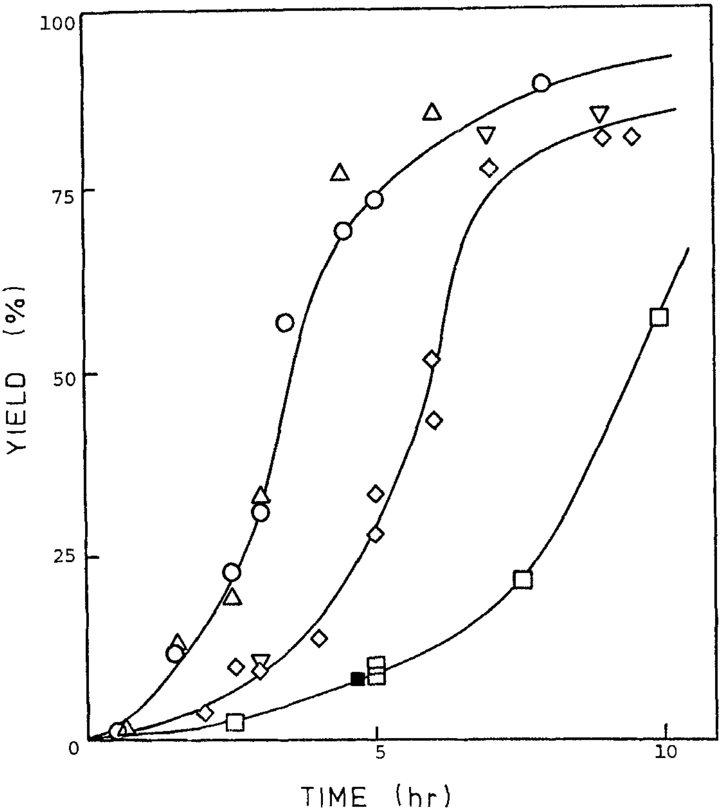


FIG. 5. In-source polymerization of MAA. Gravimetric polymer yields: (○) +10°C, (◇) 0°C, (□) -10°C; volumetric yields: (△) +10°C, (▽) 0°C, (■) -10°C. Dose rate, 36 krad/hr.

On warming to -150°C the intermediate lines developed and the outer lines of I decreased. Evidently the addition of monomer molecules to I to form dimeric propagating radicals II occurs below -150°C. Further warming caused splitting of the alternate peaks into doublets and in the temperature range of post-irradiation polymerization a slow decrease in intensity of the intermediate peaks occurred. Irradiation at 0°C produced the spectrum of the propagating radical with doublet intermediate peaks at low doses which changed progressively with increasing dose to the spectrum with highly alternating line intensities attributable to long-chain propagating radicals. Typical spectra are shown in Fig. 8.

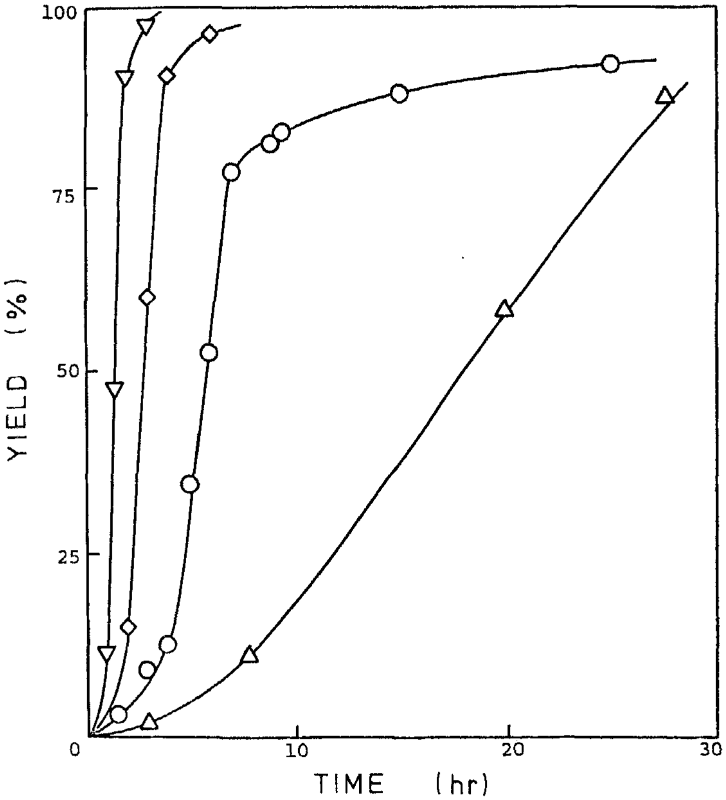
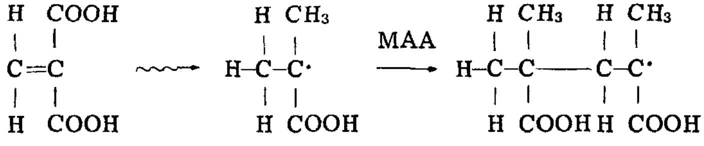


FIG. 6. Dose-rate dependence of in-source polymerization of MAA at various dose rates: (▽) 204 krad/hr; (◇) 76 krad/hr; (○) 36 krad/hr; (△) 8.8 krad/hr. Temperature: 0°C.



$$\begin{array}{cc}\mathrm{H} & \mathrm{COOH}\\ | & |\\ \mathrm{C} & \!\!=\!\!\mathrm{C}\\ | & |\\ \mathrm{H} & \mathrm{COOH}\end{array} \rightsquigarrow \begin{array}{ccc} & \mathrm{H} & \mathrm{CH_3}\\ & | & |\\ \mathrm{H}- & \mathrm{C}- & \mathrm{C}^{\bullet}\\ & | & |\\ & \mathrm{H} & \mathrm{COOH}\end{array} \xrightarrow{\mathrm{MAA}} \begin{array}{ccccc} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3}\\ & | & | & | & |\\ \mathrm{H}- & \mathrm{C}- & \mathrm{C}- & -\mathrm{C}- & \mathrm{C}^{\bullet}\\ & | & | & | & |\\ & \mathrm{H} & \mathrm{COOH} & \mathrm{H} & \mathrm{COOH}\end{array}$$

I II

Radical Concentrations. The concentration of trapped radicals increased linearly with dose from 0.05 to 2.0 Mrad for irradiation at -196°C as shown in Fig. 9 and gave G(R·) = 0.6. This value was not significantly affected by the crystallization conditions. No effect of dose

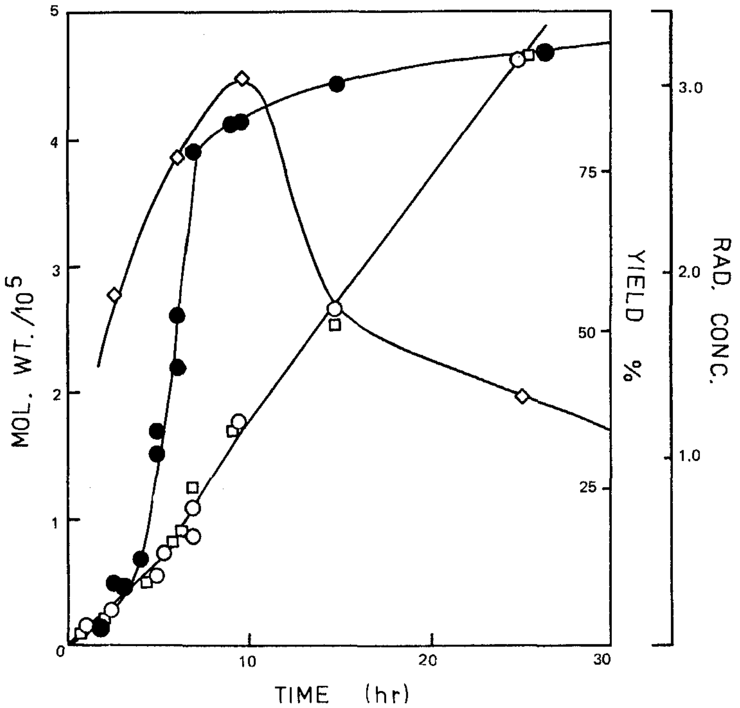


FIG. 7. In-source polymerization of MAA at 0°C: (●) polymer yield, (◇) molecular weight ($\overline{M}_v$), (○, □) radical concentration [R·]. Dose rate, 36 krad/hr.

rate was observed between 144 and 705 krad/hr. Measurements at -150°C after irradiation at -78°C gave G(R·) = 1.2.

Radical Decay. The radical decay at 0°C following various doses at -196° is shown in Fig. 10. The initial radical concentrations $[R\cdot]_0$ were proportional to the radiation dose, but the decay rates were higher for higher doses suggesting that the kinetics are higher than first order. The radical concentrations did not decay to zero, but to "limiting" values $[R\cdot]_\infty$ which increased with dose; however $[R\cdot]_\infty/[R\cdot]_0$ was not constant but decreased with dose as shown in Fig. 9. $[R\cdot]_\infty$ values were stable for long periods e. g., 100 hr.

Radical decay rates increased with temperature in the range -10 to +14°C as shown in Fig. 11, but in all cases the radical concentration approached a limiting value which decreased with increasing temperature as shown in Fig. 12.

Irradiation in air did not significantly affect the initial concentration of trapped radicals but the decay rate in the post-irradiation polymerization temperature range was rapid and the decay was

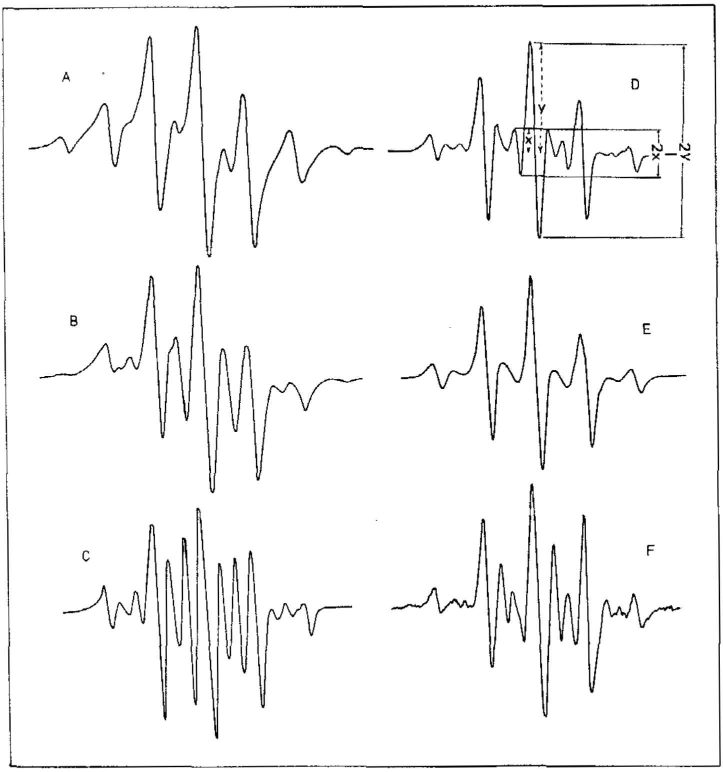


FIG. 8. ESR spectra of irradiated MAA: (A) -196°C; (B) -150°C; (C) -30°C; (D) 1 hr at 0°C; (E) 44 hr at 0°C (similar spectrum obtained after 15 hr irradiation at 0°C at 36 krad/hr); (F) spectrum at -150°C after 36 krad at 0°C (dose rate, 36 krad/hr).

complete as shown in Fig. 11, although the shape of the spectrum was unaltered.

During irradiation at 0°C the total concentration of trapped radicals increased approximately linearly with dose during the polymerization period, with G(R·) = 1.9, and then more rapidly, with G(R·) = 2.9, when the radicals were being produced by irradiation of the amorphous polymer as shown in Fig. 7.

DISCUSSION

Polymerization Yields

There are two aspects of the measurement of yields in solid-state polymerization which must always be carefully evaluated and there

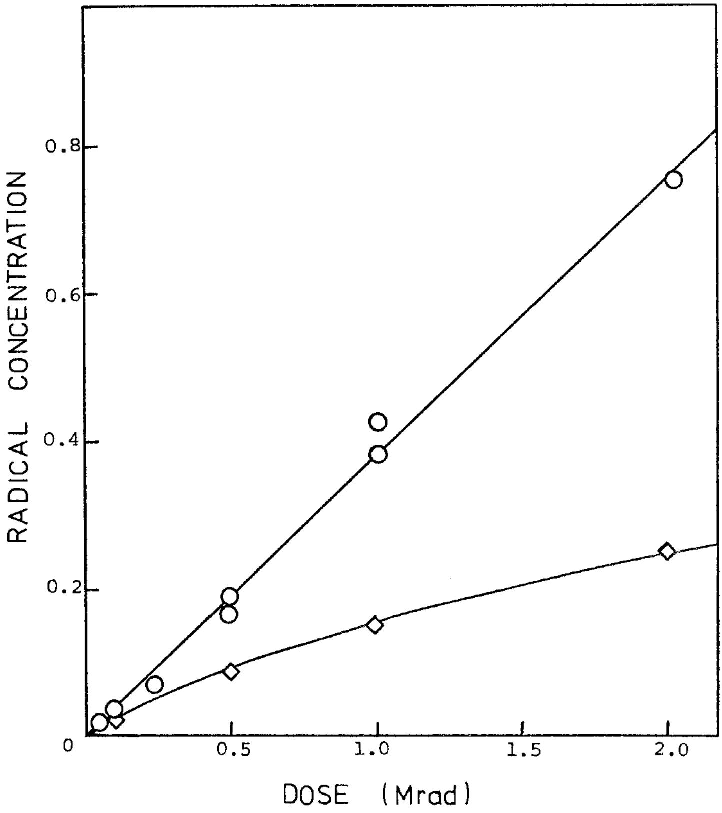


FIG. 9. Radical concentrations in MAA: (○) "initial" values from measurement at -150°C after irradiation at -196°C; (◇) "limiting" values after decay at 0°C.

are many examples in the literature where this has not been done. Firstly, the partly polymerized solid monomer is dissolved (usually in a solvent for the monomer, which is a nonsolvent for the polymer). This must be done rapidly to avoid post-irradiation polymerization occurring as the temperature approaches that of the solvent, during the dissolution procedure, or in solution. An inhibitor is frequently added to the solvent, but this will only prevent post-irradiation polymerization in solution. A more effective technique is to use finely divided monomer and high-speed stirring, preferably with the use of cold solvent. Slow dissolution of large lumps of monomer, or particularly melting of the monomer, can give greatly inflated polymerization yields. Zero yields after zero periods of post-irradiation heating following the maximum radiation dose is a test of the procedure, but may not be applicable to partially polymerized samples where

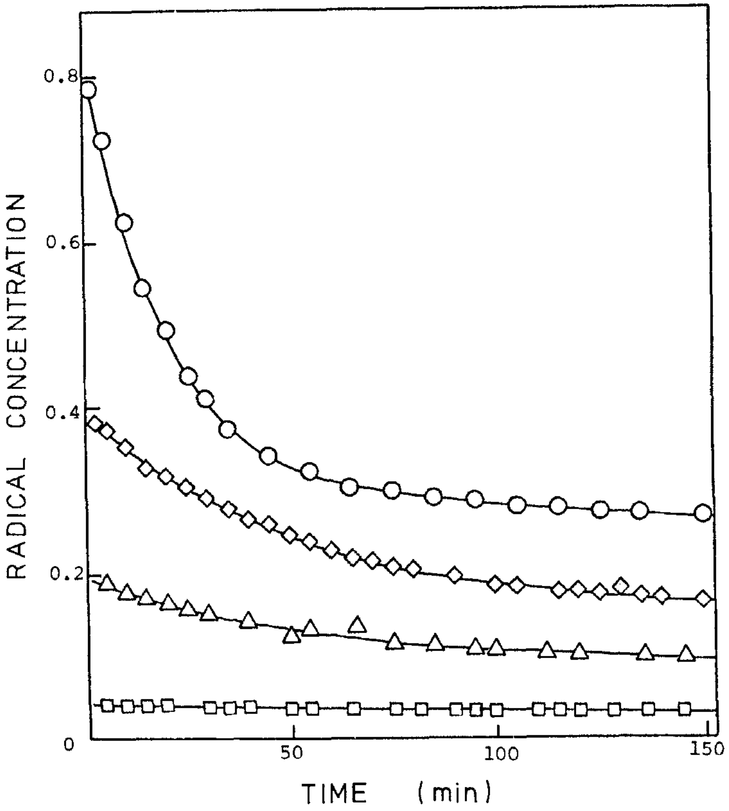


FIG. 10. Dose dependence of radical decay in MAA at 0°C at various radiation doses at -196°C: (○) 2 Mrad; (◇) 1 Mrad; (△) 0.5 Mrad; (□) 0.1 Mrad.

monomer trapped in regions of polymer will be more difficult to dissolve. Secondly, the yield of polymer and the loss of monomer should always be separately measured for some samples and compared. Formation of dimers or soluble, low molecular weight polymer can cause quite misleading results for conversions based on gravimetric separation of polymer.

Polymerization Parameters

The shapes of the post-irradiation polymerization curves were similar to those observed previously in methacrylate salts [5, 25] and esters [26] and in MAA [19, 20], with no induction period and a

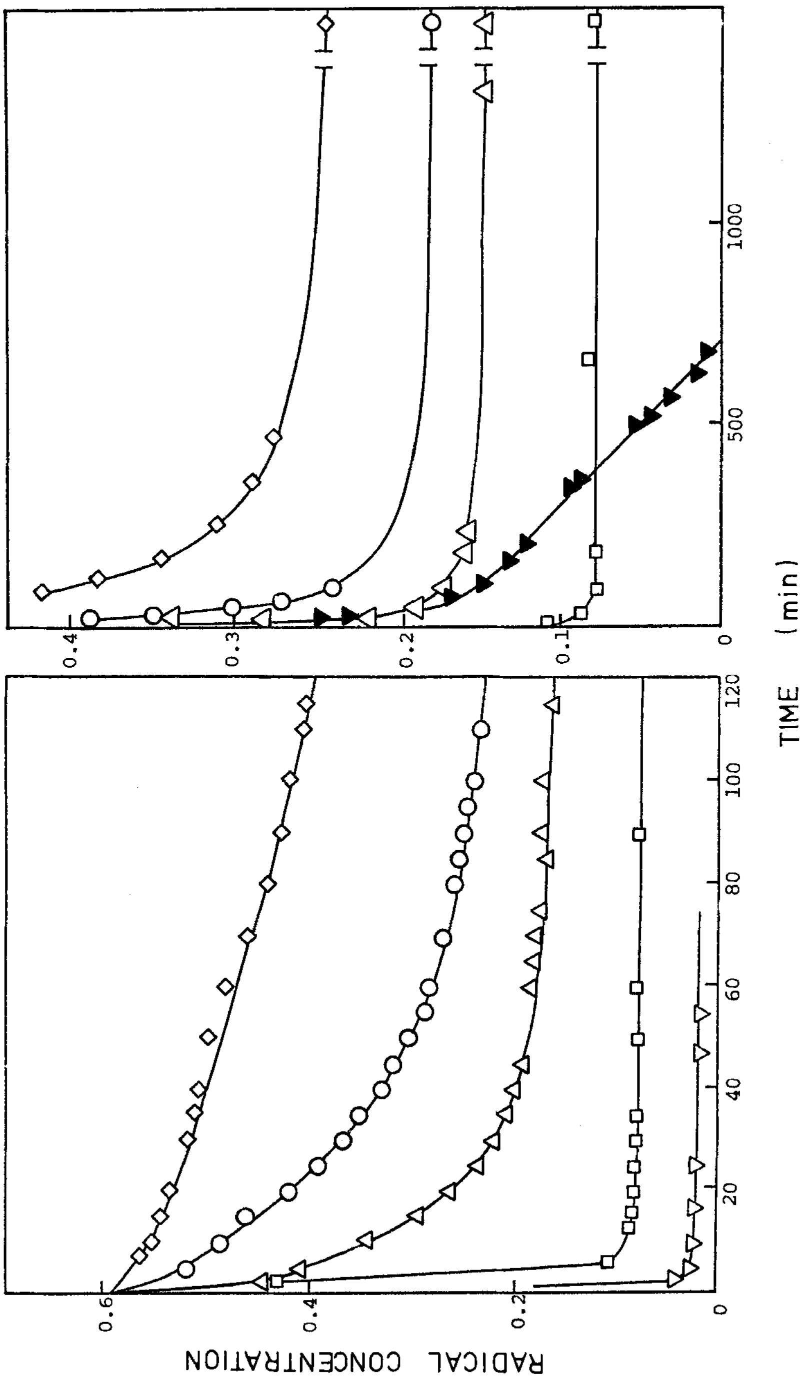


FIG. 11. Temperature dependence of radical decay in MAA: (◇) -10°C, (○) 0°C, (△) +5°C, (□) +10°C, (▽) +14°C, (▼) 0°C in air. Radiation dose, 0.5 Mrad at -78°C.

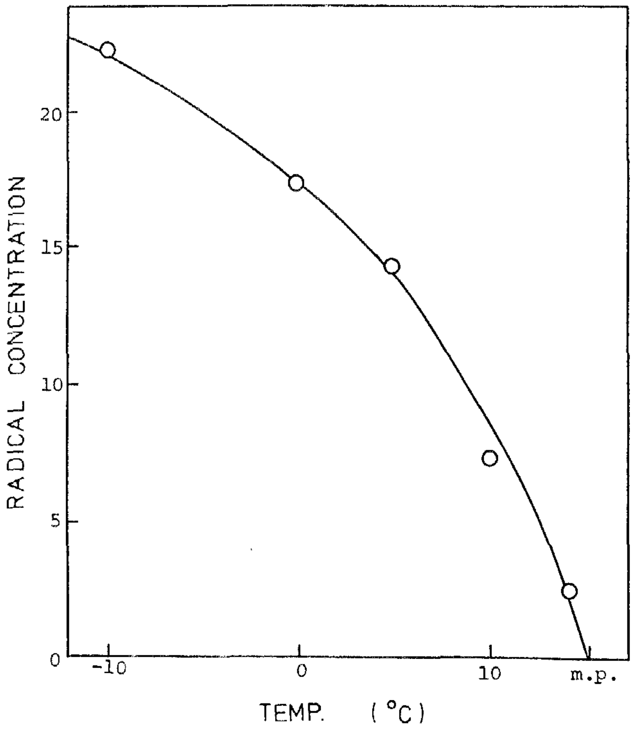


FIG. 12. "Limiting" radical concentrations for post-irradiation polymerization of MAA at various temperatures. Radiation dose, 0.5 Mrad at -78°C.

very marked decrease in rate well below complete conversion even at relatively high temperatures.

An Arrhenius plot of the initial rates of post-irradiation polymerization gave an apparent activation energy of 88 kJ/mole, and although its significance is uncertain since it is not derived from values of a rate constant, it can be compared with values of 42 kJ/mole for anhydrous zinc methacrylate [25], 71 kJ/mole for potassium acrylate [2], and 84 kJ/mole for octadecyl methacrylate [26] obtained in the same way.

The increased post-irradiation polymerization rates after irradiation at -78°C compared with -196°C (a factor of two) can be related to the difference in trapped radical concentrations. Thus we found G(R·) = 1.2 at -78°C and 0.6 at -196°C. This is quantitatively similar to our results for barium methacrylate monohydrate [5] and confirms the importance of the irradiation temperature, although no long-chain polymerization occurs at either -196°C or -78°C. However the trapped radicals are all dimeric propagating species (II) at -78°C, whereas several types of radical, including particularly the initiating radical I, are observed at -196°C. The proportion of trapped radicals which decay without initiating polymerizing chains would be expected to be greater at -196°C and could explain the observation that the relative polymerization rate at -78° is somewhat greater than the ratio of initial trapped radical concentrations at the two temperatures. This is supported by the higher ratio of "limiting" trapped radical concentrations (see Fig. 3).

On this basis we would expect that the post-irradiation polymerization yields of Lando and Semen [20] at 0°C after 0.23 Mrad of γ-irradiation at -78°C would be similar to our results for polymerization at 0°C after 0.5 Mrad at -196°C. Quite good agreement is observed, as shown in Fig. 1. This suggests that the crystallization conditions may not be important in this case.

The marked decrease in molecular weight of the PMAA obtained from in-source polymerization with increasing radiation dose at high conversions (Fig. 7) clearly shows that G(scission) is high for PMAA. The polymer was always completely soluble, hence $G(S) > 4G(X)$. These scission and crosslinking sensitivities would be expected from the behavior of poly(methyl methacrylate), provided that the carboxylic acid substituent does not cause specific, radiation-induced reactions producing crosslinking.

ESR Spectra

The seven main lines in the ESR spectrum at -196°C (Fig. 8) are attributed to radical I, formed by addition of radiolytically produced H atoms to monomer molecules, and the subsidiary lines can be accounted for by the reaction of "hot" radicals with monomer [3]. Methacrylic acid behaves similarly to barium methacrylate monohydrate [3], in that the conformation of the propagating radical varies with the degree of polymerization and the extent of conversion, but differs in showing doublet intermediate peaks, giving a 13-line spectrum (Fig. 8C) corresponding to a greater asymmetrical twist of the dihedral angle.

The relaxation of the radical conformation was followed during post-irradiation polymerization, and the decrease in the ratio X/Y (defined in Fig. 8D) with time is shown in Fig. 13. It was faster at higher temperatures and decreased to approximately zero after ca. 20% conversion to polymer.

During in-source polymerization (irradiation at -10 to +10°C) the ESR spectrum was similar to that shown in Fig. 8C at low doses, but with increasing irradiation times and hence increasing conversion to polymer was transformed into the spectrum of Fig. 8E with an alternating intensity distribution.

The extremely rapid decay of trapped radicals at 10°C must indicate a high degree of molecular mobility in the crystal lattice 5° from the

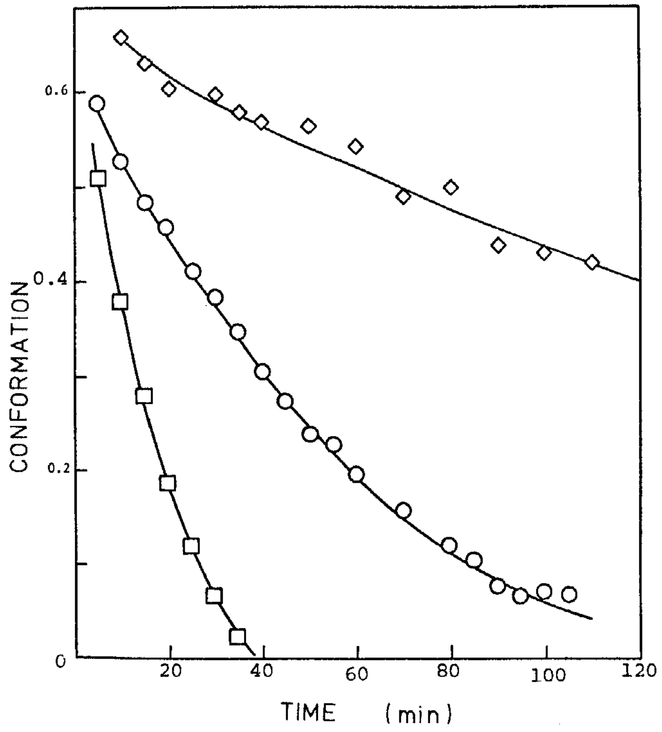


FIG. 13. Conformational changes in MAA during post-irradiation polymerization: (◇) -10°C; (○) 0°C; (□) +5°C. Radiation dose, 0.5 Mrad at -78°C. The conformation is represented by the ratio X/Y in Fig. 8.

melting point. This is undoubtedly enhanced by the radiation-induced defects and the high rate of polymerization, which through the exothermic heat of polymerization may be anticipated to produce local melting in the vicinity of propagating radicals.

The correlation between the sharp drop-off in polymerization rate and the substantial decrease in radical concentration at +10°C, suggests that a significant proportion of the trapped radicals decay. This may be associated with the local liquid regions and will therefore be less likely at lower temperatures. It is confirmed by the high $\overline{M}_v$ (Fig. 4).

Our ESR results differ from those of Chachaty et al. [21], in that we find that the value of $[R\cdot]_\infty/[R\cdot]_0$ decreases with radiation dose (Fig. 9). Moreover, the value of $[R\cdot]_\infty$ decreased markedly with increasing temperature over the range -10 to +13°C for a particular

TABLE 1. Radical Production and Decay in MAA at 0°C

Dose (Mrad)	$[R\cdot_0]$	$[R\cdot_\infty]$	$[R\cdot_\infty]/[R\cdot_0]$
0.1	8	5	0.63
0.25	17	9.5	0.56
0.5	34	16	0.47
1.0	69	27	0.39
2.0	140	46	0.33

radiation dose at -196 or -78°C as shown in Fig. 12. Our measurements of radical decay rates after different radiation doses at the same temperature (0°C) give values of $[R\cdot]_\infty/[R\cdot]_0$ which decrease with increasing dose as shown in Table 1; however we do obtain a value of 0.4 after 1 Mrad at -196°C similar to that reported by Chachaty et al.

The effect of dose rate on the total radical concentration in MAA irradiated to the same total dose at -196°C was investigated. For dose rates of 144, 328, and 705 krad/hr the relative radical concentrations at -150°C were 0.169, 0.170, and 0.169, respectively, showing that there was no effect in this range.

Molecular Weight

The molecular weight ($\overline{M}_v$) of the polymer produced by post-irradiation polymerization at 0°C increased linearly with polymer yield, similar to the results of Lando and Semen [20]. We obtained these results for four radiation doses from 0.1 to 1.0 Mrad, and if they are normalized to polymer yield/radiation dose on the x-axis, all the lines lie close together. Since we need to normalize the results to a constant concentration of propagating chains the radiation doses should be adjusted for the variation in the proportion of propagating to initially trapped radicals $[R\cdot]_\infty/[R\cdot]_0$. By using data from Fig. 9 the appropriate corrections are given in Table 1. The resultant plots lie very closely on a single straight line through the origin (except for 0.1 Mrad) as shown in Fig. 14. This provides strong evidence for the consistency of the data and the suitability of the treatment. It strongly supports the proposal of Lando and Semen that chain initiation essentially all begins at the same time and that propagation continues uniformly without chain transfer or termination.

If we accept the mechanism for post-irradiation polymerization proposed by Lando and Semen and supported by our present work, then $[R\cdot]_\infty$ represents the concentration of nonterminating, propagating

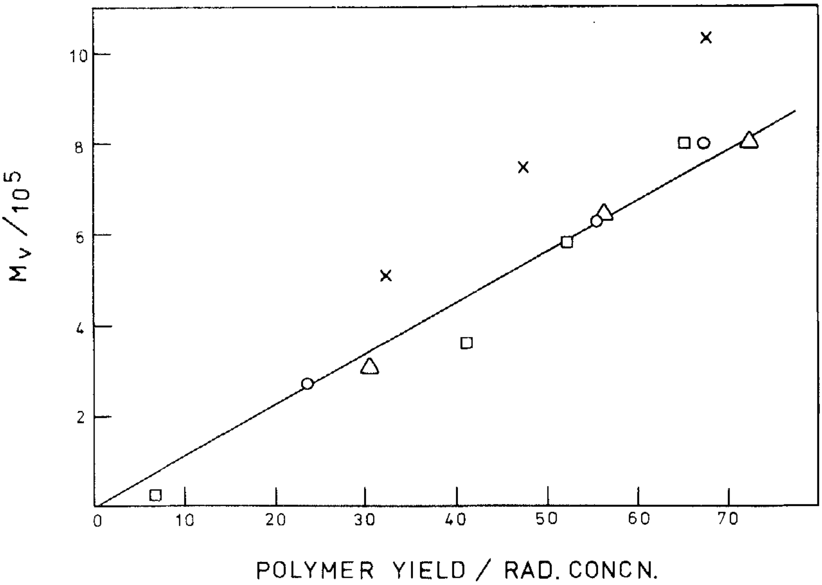


FIG. 14. Molecular weight ($\overline{M}_V$) of polymer from post-irradiation polymerization at 0°C after various radiation doses at -196°C vs. conversion normalized to a constant concentration of propagating radicals using the data in Table 1. Radiation dose: (×) 0.1 Mrad; (○) 0.25 Mrad; (□) 0.5 Mrad; (△) 1.0 Mrad.

radicals (although they may be physically "terminated" after long polymerization times), and $[R\cdot]_t - [R\cdot]_\infty$ represents the concentration of radicals which can undergo termination in the sense that the radical site is destroyed and the intensity of the ESR spectrum appropriately reduced. It is therefore appropriate to study decay kinetics of $[R\cdot]_t - [R\cdot]_\infty$. We have found good first-order plots for the decay at 0°C for different radiation doses, whereas the second-order plots are markedly curved.

When the data for radical decay rates at 0°C for radiation doses in the range 0.1 to 2.0 Mrad (Fig. 10) are converted to $[R\cdot]_t - [R\cdot]_\infty$ and normalized to the same initial radical concentration, the first-order kinetic decay plots for 0.5 and 1.0 Mrad are effectively coincident, and although the first-order rate constant for 0.1 Mrad is a little lower and for 2.0 Mrad somewhat higher, the variation is very much smaller than the dose range. Thus, the evidence at 0°C supports a predominantly first-order decay of nonpropagating radicals.

ACKNOWLEDGMENTS

We wish to thank the Australian Institute of Nuclear Science and Engineering for support, the Australian Atomic Energy Commission for irradiation facilities, and Dr. P. J. Pomery for assistance with the ESR measurements.

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Accepted by editor April 19, 1979
Received for publication May 14, 1979