No appreciable amount of solid product was obtained from the filtrate when it was poured in a large excess of acetone with stirring. The nmr spectra of the products of (b), (c), and (d) were identical to that of (a).

6-1 Reaction in DMF–Methanol (1:1). In 65 ml of DMF–methanol, 17.23 g (0.100 mol) of tetramethyldiaminohexane was allowed to react with 17.39 g (0.100 mol) of dibromomethane for 192 hr at room temperature. The crystals formed were filtered, washed with a small amount of the solvent (three times) and then with acetone, and dried *in vacuo* at 40°: yield 9.60 g (36.9% based on the dibromide). It was recrystallized from methanol: mp 152–152.5° (effervescence); nmr τ 4.80 (s, 4.0, 4 H, N^+–CH_2–Br), 6.44 (t, J = 6.0 Hz, 3.5, 4 H, N^+–CH_2–C), 6.74 (s, 11.9, 12 H, N^+–CH_3), 8.44 (tallest peak of the diffuse multiplet at τ 7.8–8.8, 8.7, 8 H, C–$(CH_2)_4$–C).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (hexamethylenebis(bromomethyldimethylammonium bromide)): C, 27.72; H, 5.43; Br(ionic), 30.73; Br(total), 61.46; N, 5.39. Found: C, 27.64; H, 5.51; Br(ionic), 30.66; Br(total), 61.38; N, 5.36.

The filtrate was poured into a large excess of acetone with stirring. The precipitate was filtered, washed with acetone, and dried as before, yield 4.65 g (17.9%).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$: Br(ionic), 30.73. Found: Br (ionic), 35.22.

6-2 Reaction in DMF–Methanol (1:1). Using 130 ml of methanol as solvent, 34.46 g (0.200 mol) of tetramethyldiaminohexane was allowed to react with 37.57 g (0.200 mol) of 1,2-dibromomethane for 48 hr at room temperature. The precipitated crystal was filtered, washed with a small amount of the solvent and then with acetone, and dried *in vacuo* at 40°: yield 12.35 g (22.5% based on the dibromide). It was recrystallized from methanol: mp 224.5–226.5° dec; nmr τ 6.20 (s, 8.0, 8 H, N^+–CH_2CH_2–Br), 6.56 (t, J = 6 Hz, 3.1, 4 H, N^+–CH_2–C), 6.85 (s, 11.3, 12 H, N^+–CH_3), 8.47 (strongest peak of the multiplet at 7.8–8.8, 8.1, 8 H, C–$(CH_2)_4$–C).

Anal. Calcd for $C_{14}H_{32}Br_4N_2$ (hexamethylenebis((2-bromoethyl)-dimethylammonium bromide)): C, 30.68; H, 5.89; Br(ionic), 29.16; Br(total), 58.32; N, 5.11. Found: C, 30.86; H, 5.99; Br(ionic), 29.15; Br(total), 58.23; N, 5.25.

The filtrate was treated as in the 6-1 reaction, yield 11.16 g (20.4%).

Anal. Calcd for $C_{14}H_{32}Br_4N_2$: Br(ionic), 29.16. Found: Br (ionic), 34.50.

Ionene Polymers. The *x-y* reactions yielding ionene polymers were carried out in the following way. A solution of a tetramethyldiaminoalkane was mixed thoroughly with a solution of a dibromoalkane and the mixture was left at room temperature (*ca.* 22°). The molar ratio of the diamine to the dibromide was in all cases 1:1. After a given time, the precipitated polymer was filtered; washed quickly with a small amount of the solvent, then with benzene, and finally with acetone; and dried under high vacuum at 40° (fraction I). The filtrate was poured into a large excess of acetone with stirring. The precipitated polymer was filtered, washed first with benzene and then with acetone, and dried as before (fraction II).

Acknowledgment. We wish to express our thanks to Drs. V. Hadek and H. Keyzer and Mrs. A. Kobashigawa and H. Rile for assistance with nmr and X-ray measurements. H. N. is grateful to the National Academy of Sciences-National Research Council, Washington, D. C., for the Postdoctoral Resident Research Associateship supporting this research.

Radiation-Induced Solid-State Polymerization of Derivatives of Methacrylic Acid. VIII. Postirradiation Polymerization of Barium Methacrylate

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ABSTRACT: The kinetics of polymerization of crystalline barium methacrylate monohydrate have been investigated in the temperature range 20–110° after γ irradiation at -78 and $-196°$. The initial rate was proportional to the radiation dose up to 4 Mrads and increased continuously with the polymerization temperature (E_a = 132 kJ/mol). The "limiting" polymer yields did not increase proportionately with dose or temperature. Esr spectra of the D_2O salt showed that at least 75% of the initiating radicals in the monohydrate are formed by addition of H atoms from the water of crystallization to the C=C bond. The polymerization rate was about double after irradiation at $-78°$ compared with $-196°$, and esr studies showed a proportionate difference in concentrations of trapped radicals; G(radicals) = 8.8 ± 0.5 at $-78°$ compared with 4.7 ± 0.5 at $-196°$. Less than 2% polymer was obtained from the crystalline anhydrate even after high radiation doses and prolonged heating up to 200°, although esr spectra indicated the formation of propagating radicals.

Barium methacrylate may be prepared as the monohydrate by crystallization from aqueous solution or as the anhydrate by crystallization from methanol or dehydration of the monohydrate. Lando and Morawetz (1964)[1] first reported polymerization of the monohydrate on heating after γ irradiation at $-78°$. They reported the hydrated salt to be a dihydrate, but Bowden and O'Donnell (1969),[2] who investigated the dehydration reaction, showed that it was the monohydrate, $Ba^{2+}(CH_2{=}C(CH_3)COO^-)_2 \cdot H_2O$.

Polymerization occurs sufficiently below the decomposition temperature of about 230° for there to be little likelihood of polymerization occurring in a "liquid drop" due to local melting caused by the exothermic heat of reaction.[3] It proceeds by a free-radical mechanism,[4] and esr spectra show well-resolved

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(1) J. B. Lando and H. Morawetz, *J. Polym. Sci., Part C*, No. 4, 789 (1964).

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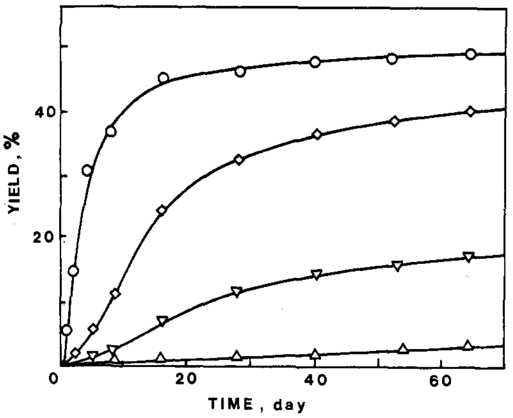

Figure 1. Effect of temperature from 20 to 50° on the polymerization of $Ba(MA)_2 \cdot H_2O$ after 1.0 Mrad at $-78°$: (○) 50°, (◇) 40°, (▽) 30°, (△) 20°.

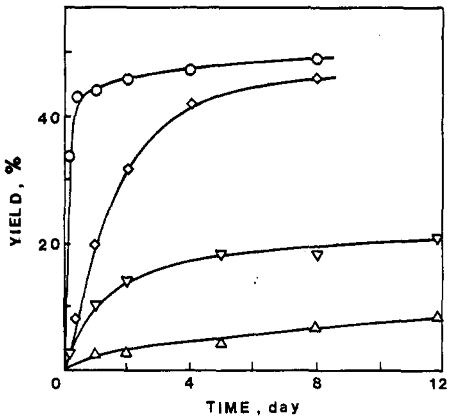

Figure 2. Effect of temperature from 65 to 100° on the polymerization of $Ba(MA)_2 \cdot H_2O$ after irradiation at $-78°$: (○) 100°, 0.5 Mrad; (◇) 65°, 0.5 Mrad; (▽) 90°, 0.1 Mrad; (△) 65°, 0.1 Mrad.

lines and high radical concentrations.[5] The spectrum at $-196°$ has been attributed to the radical formed by addition of a hydrogen atom to the C=C bond. Upon warming, the spectrum changes, and this has been correlated with monomer addition to the initial radicals to form methacrylate-propagating radicals. The propagating radicals are oriented with respect to the crystal lattice and maintain this orientation during the early stages of polymerization.[6]

We have reported a detailed investigation[7] of the polymerization of $Ba(MA)_2 \cdot H_2O$ during γ irradiation at 15–35°. The present paper gives the results of a complementary investigation of postirradiation polymerization in the temperature range 20–110° after irradiation at -196 and $-78°$. Costaschuk, Gilson, and St. Pierre[8,9] have recently reported the variation in the rate of postirradiation polymerization of barium methacrylate as a function of the degree of hydration, and some of their results can be compared with our work.

Experimental Section

Barium methacrylate was prepared by neutralization of distilled methacrylic acid (Rohm and Haas) with barium hydroxide (B. D. H. Analar) as described previously.[2] The monohydrate was obtained by crystallization from aqueous solution. The crystals were dried between filter paper and then in a desiccator over silica gel for 12 hr. They were powdered by crushing with a mortar and pestle and sieved into different particle sizes. Powder in the range -100 to $+200$ mesh (10–100 μm) was used for most of the work. The material was stored in filled, sealed bottles. $Ba(MA)_2 \cdot H_2O$ readily occludes water in the crystals and also readily dehydrates under vacuum or on heating, but the above procedure produced exact monohydrate. The water content can be accurately determined from the weight loss on complete dehydration and was 5.5%.

Samples (2 g) for γ irradiation were sealed in half-filled glass tubes (10-mm i.d., 100-mm length) in air or *in vacuo*. Small-diameter tubes are necessary to minimize the temperature rise in the sample due to the exothermic heat of polymerization.

$Ba(MA)_2 \cdot D_2O$ was prepared for esr studies by crystallization of the anhydrate from 99.5% D_2O under a stream of dry air. Barium methacrylate could not be crystallized from D_2O (or H_2O) under oxygen-free conditions, as polymer was invariably formed. Polymerization accompanying a phase change is a well-known phenomenon, and oxygen is evidently required as a chain inhibitor.[3]

$Ba(MA)_2$·anhyd was prepared by dehydration of the monohydrate in air or under vacuum. Under some conditions small amounts of polymer were formed, but not during dehydration under vacuum at 30°. The anhydrate was also prepared by crystallization from methanol.

Cobalt-60 γ irradiations were carried out in the pond facility of the Australian Atomic Energy Commission at Lucas Heights at $-196°$ (liquid nitrogen) or $-78°$ (Dry Ice-acetone) at about 0.4 Mrad/hr. Postirradiation polymerizations were carried out in constant-temperature baths with the sample tubes completely immersed to prevent distillation of water from monohydrate samples. Polymer yields were determined gravimetrically by dissolving residual monomer in distilled water at room temperature and drying the insoluble polymer to constant weight. The residual monomer was also measured by bromine titration.

Esr measurements were made on samples sealed in Spectrosil high-purity silica tubes using a Varian V4502 instrument. Radical concentrations were measured by double integration of the recorded first-differential spectra and compared with DPPH and pitch–KCl standards.

Results

Monohydrate. Polymerization Temperature 20–50°. Polymer yields for polymerization times up to 64 days after 1.0 Mrad at $-78°$ are plotted in Figure 1. The kinetic curves show slight induction periods which increase with decrease in temperature. At 50°, a limiting yield of 50% was reached after about 20 days. The rate of polymerization at 20° was very slow (3% polymer after 64 days), and a limiting value probably had not been reached. An E_a of 132 kJ mol^{-1} was calculated from the maximum slopes of the kinetic curves in Figure 1.

Polymerization Temperature 60–110°. Some of the kinetic curves after doses of 0.1 and 0.5 Mrad at $-78°$ are shown in Figure 2. The initial rates of polymerization were high and increased with temperature, but the limiting conversions did not exceed 60%. At the higher temperatures, after 0.5 Mrad, the rise in sample temperature due to the exothermic heat of polymerization must be significant. Also, above 75° the monohydrate is thermodynamically unstable[10] and dehydration is known to occur rapidly.[2,3]

Thermal Polymerization. $Ba(MA)_2 \cdot H_2O$ polymerized spontaneously when heated above 80° in air in sealed tubes,

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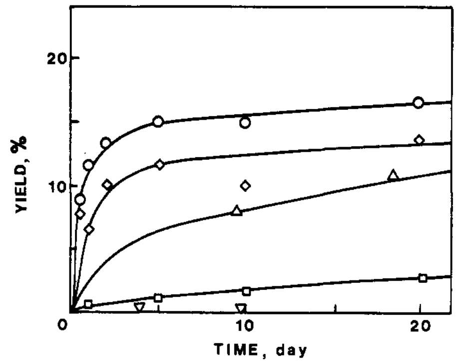

Figure 3. Thermal polymerization of $Ba(MA)_2 \cdot H_2O$: (○) −100 mesh powder in air at 100°, (◇) 1 mg of crystals in air at 100°, (□) powder *in vacuo* at 100°, (△) powder in air at 92°, (▽) powder in air at 65°.

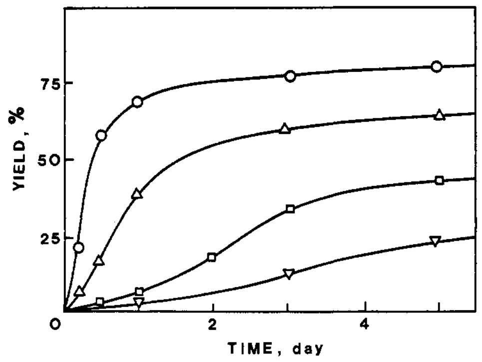

Figure 4. Effect of radiation dose at −78° on the polymerization of $Ba(MA)_2 \cdot H_2O$ at 50°: (○) 4.0 Mrads, (△) 2.0 Mrads, (□) 1.0 Mrad, (▽) 0.5 Mrad.

and the increase in rate with temperature is shown in Figure 3. Higher yields were obtained from powder than crystals. At 100° thermal polymerization must account for over half the polymer yield observed after 0.1 Mrad irradiation at −78° (see Figure 2). In evacuated tubes thermal polymerization was greatly reduced (also shown in Figure 3).

Radiation Dose. The polymerization curves at 50° after radiation doses from 0.5 to 4.0 Mrads at −78° are shown in Figure 4. The rate of polymerization increased approximately linearly with dose. An induction period was evident at low doses, but this decreased with increasing dose. The "limiting" conversion increased rapidly with dose for low doses, but less rapidly for high doses.

Crystal Size. No significant difference between large crystals and fine powder on the rate of polymerization at 50° in sealed tubes was observed, provided an adequate dissolution procedure was followed. A large effect of crystal size was evident for samples open to the air. Both the initial rate of polymerization and the limiting yield increased with increase in crystal size, as shown in Figure 5. When the polymerization was carried out in sealed tubes at 110° after 0.1 Mrad at −78° the initial rate of polymerization was eight times faster in large crystals than in powder, and the limiting yield was about 50% greater. These results provide further evidence for a relationship between polymerization and dehydration, as the rate of dehydration would be less in large crystals than powder.

Irradiation Temperature. Polymerization curves at 50° after irradiation to 1.0 Mrad at −196° and −78° are shown in Figure 6. The rate of polymerization after irradiation at −78° was approximately twice that after irradiation at −196°. This will be shown to result from a higher concentration of trapped radicals after irradiation at −78°. Dsc measurements of the postirradiation polymerization have given similar results.[10] Also, we have observed the same phenomenon for methacrylic acid.[11]

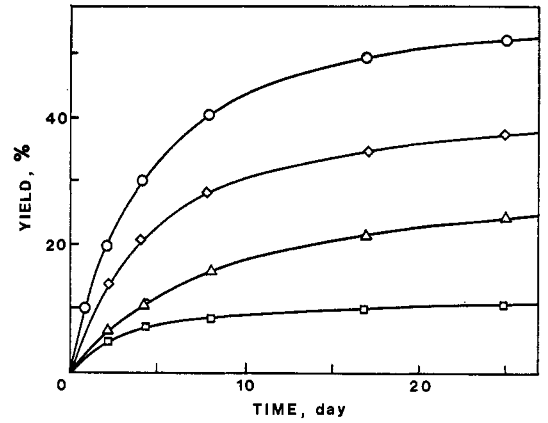

Figure 5. Effect of crystal size on the polymerization of $Ba(MA)_2 \cdot H_2O$ in open tubes at 50° after 1.0 Mrad at −78°: (○) 2 mg crystals, (◇) −30 to +36 mesh, (△) −100 to +200 mesh, (□) −200 mesh.

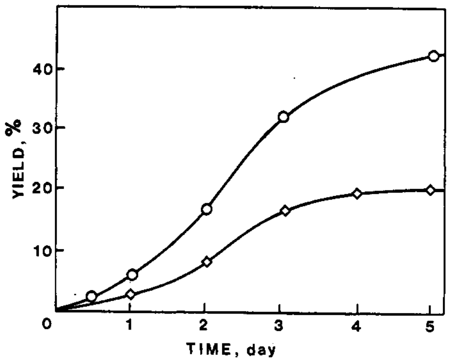

Figure 6. Effect of irradiation temperature on the polymerization of $Ba(MA)_2 \cdot H_2O$ at 30°: (○) −78°, (◇) −196°.

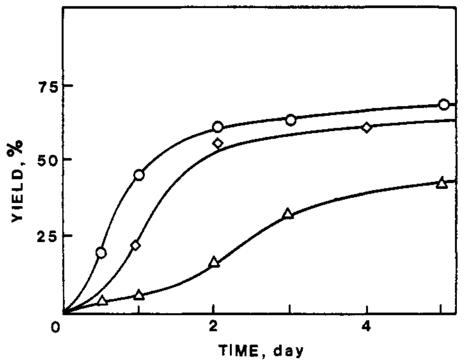

Figure 7. Effect of excess water on the polymerization of $Ba(MA)_2 \cdot H_2O$ at 50°: (△) exact monohydrate, (◇) "moist" monohydrate, (○) exact monohydrate plus 5% water.

Moisture. Barium methacrylate containing more than one molecule of water polymerized more rapidly and to higher limiting conversions than the exact monohydrate. Excess water was (a) incorporated accidentally by inadequate drying (shown by the weight loss to anhydrate) and (b) added to the

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[11] J. H. O'Donnell and R. D. Sothman, to be published.

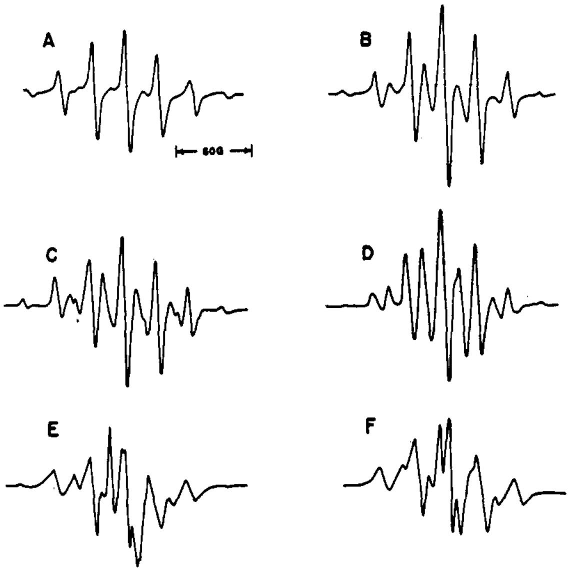

Figure 8. Esr spectra: (A) $Ba(MA)_2 \cdot H_2O$ after 1.0 Mrad at −196°, spectrum recorded at −196°; (B) $Ba(MA)_2 \cdot H_2O$ after 1.0 Mrad at −78°, spectrum recorded at −170°; (C) $Ba(MA)_2 \cdot D_2O$ after 1.0 Mrad at −196°, spectrum recorded at −196°; (D) $Ba(MA)_2 \cdot D_2O$ after 1.0 Mrad at −196°, spectrum recorded at −40°; (E) $Ba(MA)_2$·anhyd after 1.0 Mrad at −196°, spectrum recorded at −196°; (F) $Ba(MA)_2$·anhyd after 1.0 Mrad at −78°, spectrum recorded at −170°.

TABLE I

EFFECT OF TEMPERATURE, AIR, AND WATER ON POLYMERIZATION OF $Ba(MA)_2$·anhyd AFTER IRRADIATION AT −78°

Temp, °C	Dose, Mrads	Sealing condition	Time, days	Yield, %
50	10	Vacuum	1	0.4
50	10	Vacuum	8	0.5
100	10	Air	1	1.2
100	10	Air	8	1.3
200	5	Vacuum	1	1.8
200	5	Vacuum	10	1.4
250	5	Vacuum	1	2.8
250	5	Vacuum	10	2.5
50	10	Air + 5% H_2O	1	22.6
50	10	Air + 5% H_2O	8	24.3

exact monohydrate. Figure 7 shows polymerization curves for the three preparations.

Preheating. Preheating $Ba(MA)_2 \cdot H_2O$ at 100° for 6 hr in the sealed tubes before irradiation caused a substantial increase in the rate of polymerization which increased with increasing crystal size.

Air–Vacuum. Irradiations and polymerizations were normally carried out in air in sealed tubes. However, a number of measurements were made with samples sealed under vacuum and no significant differences were observed.

Anhydrate. We have examined the polymerization of the anhydrate under a variety of conditions including air and vacuum, open and sealed tubes, and temperatures from 25 to 200° after radiation doses from 1 to 10 Mrads. Under all these conditions, the polymer yield was less than 2%, provided the samples were initially polymer free and were kept free of water (Table I). Care must be taken in preparing anhydrate by dehydration of $Ba(MA)_2 \cdot H_2O$, as thermal polymerization occurs during dehydration at elevated temperatures.

Polymerization did occur in the anhydrate at 250°. This is the temperature at which decomposition commences, as indicated by a decrease in weight in the tga of unirradiated material.[2,3] There is also an endotherm in the dsc of unirradiated anhydrate at about 230° (but no melting is visually apparent) and an exotherm for irradiated samples. When 5% (w/w) water was added to the anhydrate before irradiation, the rate of polymerization was greatly increased, as shown in Table I.

Esr Spectra. $Ba(MA)_2 \cdot H_2O$. The esr spectra of $Ba(MA)_2 \cdot H_2O$ after irradiation at −196 and −78° are shown in Figure 8. The spectrum after irradiation at −196° at all doses is predominantly (90%) due to the initiating radical formed by addition of a hydrogen atom to the C=C bond, with the remainder attributable to the methacrylate-propagating radical.[5] The latter must result from a radiation-energized reaction or formation of some radicals in defects, with consequent high reactivity as no thermal monomer addition can be observed below −150°,[4] or possibly from the addition of OH radicals to C=C bonds.

After irradiation at −78°, the spectrum at −196° (or −170°) can be attributed to a mixture of initiating and propagating radicals. By comparison with simulated spectra and assuming a 58–62° conformation[5] for the propagating radical (these are the angles between the projections of the C_β–H bonds on the plane perpendicular to the C_α–C_β axis and the p_z orbital of the unpaired electron on C_α), which is appropriate if dimer but not long-chain polymer is produced, the proportions were calculated to be 40% initiating radical and 60% propagating radical after 1.0 Mrad at 0.4 Mrad/hr. After 15 Mrad, the line width had increased from 6 to 8 G, the average radical conformation had altered slightly to about 57–63°, and the proportion of propagating radicals had increased to 75%. These were values which gave the best fit between simulated and observed spectra, the computed spectrum being particularly sensitive to the conformational angle. Using the rate data for the thermal conversion of initiating to propagating radicals at −78° determined previously,[4] it can be shown that the increased proportion of propagating radicals compared to irradiation at −196° can be explained by thermal reaction proceeding at −78° during the irradiation period. This was confirmed by an increase in the proportion of propagating radicals with increase in radiation dose at a fixed rate (resulting from the nonlinearity of radical production and interradical conversion).

We have previously reported the radical yield for radiation doses up to 8 Mrads at −196°.[4] The concentration of trapped radicals dropped below linearity with dose above 2 Mrads and approached a limiting concentration of about 1.6×10^{-2} mol dm^{-3}. This could possibly have been due to saturation of the esr cavity at such high radical concentrations, and we have therefore repeated the measurements using sample tubes with two different internal diameters (2.95 and 0.84 mm). Identical values were obtained with both sets of tubes, and the results are shown in Figure 9.

The radical concentration *vs.* radiation dose relationship was determined for irradiation at −78° and is also shown in Figure 9. The radical yield was much higher, and the approach toward saturation was much slower than after irradiation at −196°. Consequently, very high radical concentrations (≈ 0.1 mol dm^{-3}) could be obtained. Identical results were obtained with sample tubes of different diameter and for samples irradiated *in vacuo* and in air. From the initial linear relationship between radical concentration and dose (up to 1 Mrad), we obtained *G*(radicals) = 8.8 ± 0.5 at −78° compared with 4.7 ± 0.5 at −196°.

$Ba(MA)_2 \cdot D_2O$. The esr spectra of irradiated $Ba(MA)_2 \cdot D_2O$ at different temperatures are shown in Figure 8. The spectrum at −196° consisted of 15 lines and can be attributed to three radical species whose stick spectra are given in Figure 10. The approximate proportions are 30% $CH_3\text{-}\dot{C}(CH_3)COO^-$, 60% $CH_2D\text{-}\dot{C}(CH_3)COO^-$, and 10% $R\text{-}CH_2\text{-}\dot{C}(CH_3)COO^-$. The radical yield in $Ba(MA)_2 \cdot D_2O$ was also determined and gave *G*(radicals) = 2.9 ± 0.5.

$Ba(MA)_2$·anhyd. The esr spectra of $Ba(MA)_2$·anhyd irradiated at −196 and −78° are shown in Figure 8. They are quite different from the corresponding spectra from $Ba(MA)_2 \cdot H_2O$. The radical concentration as a function of dose for irradiation at −196 and −78° is shown in Figure 9. From the initial slopes, *G*(radicals) = 1.4 ± 0.5 at −196° and 2.7 ± 0.5 at −78°.

Discussion

Esr. The esr studies reported in this paper confirm that polymerization in barium methacrylate proceeds by a free-radical mechanism and provide further information on the initiation step. The predominance of one radical species, identified as $CH_3\text{-}\dot{C}(CH_3)COO^-$, in $Ba(MA)_2 \cdot H_2O$ irradiated at −196° is unusual and makes the system particularly suitable for esr investigation. This radical is produced by the addition of a hydrogen atom to the C=C bond. As no complementary radical is observed, we propose that the H atoms mainly come from H-OH scission with the disappearance of the OH radicals. In alkyl methacrylates, such as octadecyl methacrylate, where there is no H_2O as a source of H atoms, the spectra are complex, indicating the presence of alkyl radicals as a result of C-H scission. *G*(radicals) in $Ba(MA)_2 \cdot D_2O$ is only 60% of the value for $Ba(MA)_2 \cdot H_2O$ and 60% of the initiating-type radicals found in $Ba(MA)_2 \cdot D_2O$ result from the addition of D to the C=C bond. These two results show the vital role of the water molecule in the formation of the initiating radical. Combination of the 40% drop in radical concentration when H_2O is replaced by D_2O and the 60% of the radicals produced in the D_2O salt attributable to D addition indicates that at least 75% of the $CH_3\text{-}\dot{C}(CH_3)COO^-$ radicals in $Ba(MA)_2 \cdot H_2O$ must come from reactions of H atoms from the H_2O.

The doubled radical yield after irradiation at −78° compared with −196°, even though chain polymerization does not occur below about 20°, makes it imperative that postirradiation polymerization rates should only be compared for the same irradiation temperature.

We have shown that during irradiation at both −196 and −78° the predominant radical initially formed is $CH_3\text{-}\dot{C}(CH_3)COO^-$, with about 10% of the propagating radical $R\text{-}CH_2\text{-}\dot{C}(CH_3)COO^-$; hence the higher *G*(radicals) is not due to production of other radicals at −78° or stabilization of initiating radicals by addition of monomer. We propose the following explanation, based on the reactions

$$H_2O \rightsquigarrow H\cdot \tag{1}$$

$$H\cdot + C{=}C \longrightarrow C{-}C\cdot \tag{2}$$

$$H\cdot + H\cdot \longrightarrow H_2 \tag{3}$$

$$H\cdot + C{-}C\cdot \longrightarrow C{-}C \tag{4}$$

$$C{-}C\cdot + C{=}C \longrightarrow R{-}C{-}C\cdot \tag{5}$$

Reaction 1 followed by reaction 2 is postulated as the sequence which produces most of the $CH_3\text{-}\dot{C}(CH_3)COO^-$ radicals. This is supported by the experiments on $Ba(MA)_2 \cdot D_2O$ described above. The complementary OH radical has not been observed. H production may also occur from C-H scission, which would be expected to be important in other methacrylates. This is a result of the ability of H atoms to move away from the site of bond fracture in the solid.

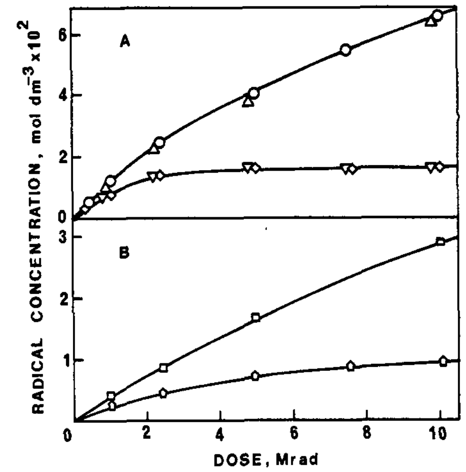

Figure 9. Radical concentration: (A) $Ba(MA)_2 \cdot H_2O$ after γ irradiation at −78° (○) 2.95-mm i.d. tubes, (△) 0.84-mm tubes, and at −196° (◇) 2.95-mm tubes, (▽) 0.84-mm tubes; (B) $Ba(MA)_2$·anhyd after γ irradiation at (□) −78° and (⌂) −196°.

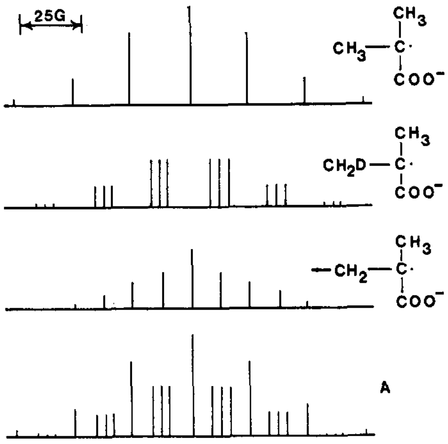

Figure 10. Stick spectra. A is the combination of the above three spectra in the calculated proportions.

Reactions 2, 3, and 4 are in competition for the H atoms. The activation energy for reaction 2 is appreciable, whereas it is effectively zero for reaction 3, but reaction 2 is favored by the high concentration of methacrylate molecules, whereas reaction 3 depends on the square of the concentration of H atoms. Consequently, both reactions occur to a significant extent. We have found H_2 to be one of the main volatile radiolysis products.[11] We postulate that the effect of the activation energy difference will be to increase reaction 2 relative to 3 as the temperature is raised from −196 to −78°, thus accounting for the increase in yield of trapped radicals. Reaction 4 will become important as the concentration of trapped radicals increases and we suggest will contribute to the falloff from linearity in the radical concentration *vs.* dose curve. At −78° this reaction would be less effective, since reaction 2 has become more important, and indeed the approach to a limiting radical concentration is much slower at −78 than −196°. We have shown that reaction 5 proceeds at −78° and accounts for the increased proportion of propagating radicals.

Polymerization. Our results show clearly that dehydration and polymerization are directly related in $Ba(MA)_2 \cdot H_2O$. Dehydration and polymerization after irradiation show a similar temperature dependence in the same temperature region. There is a strong crystal size effect on polymerization in open tubes. Thermal polymerization occurs in air above the temperature at which the monohydrate becomes thermodynamically unstable.[10]

The H_2O may only play a minor role in maintaining the crystal structure, as suggested by Costaschuk, Gilson, and St. Pierre,[9] but it has a profound influence on the rate of polymerization. We disagree with their conclusion that polymerization is facilitated in the "open" lattice of the anhydrate, as under a wide variety of conditions we were unable to obtain more than 2% polymer, provided polymer was not present from the dehydration. Polymerization did occur during decomposition, indicating the necessity for mobility and has been reported during irradiation.[12]

The increased polymerization rates which we obtained in $Ba(MA)_2 \cdot H_2O$ preheated at 100° in sealed tubes (shown to cause dehydration without water loss) confirm the higher rates observed by St. Pierre, *et al.*, in partly dehydrated barium methacrylate[9] and calcium acrylate.[13] However, our dsc measurements[10] indicate that the partly dehydrated $Ba(MA)_2 \cdot H_2O$ cannot be considered as a macroscopic mixture of monohydrate and anhydrate with some interphase material, but that the structure is disrupted throughout and dehydration occurs much more rapidly (63°) than in the monohydrate (80°).

The structure of $Ba(MA)_2 \cdot H_2O$ is now known completely[10,14] and enables a consideration of the mechanics of the polymerization. The vinyl groups are stacked on either side of a void layer like shelves on each side of a corridor and are separated by 4.1–4.6 Å in both directions. The Ba ions and O atoms form a two-dimensional network which can be considered as the walls of the corridor, and polymerization can only proceed inside each corridor.

A major question is whether (A) the monomer molecules detach themselves from the wall and migrate to the growing end of the polymer chain or (B) the polymer chain moves and attaches to the monomer molecule held in the lattice with its subsequent detachment from the lattice. St. Pierre, *et al.*,[9,13] suggest A, while we have always favored B. The coordination of carboxyl oxygen atoms around the barium ions suggests that methacrylate molecules are unlikely to readily migrate away from this point of attachment, and this is confirmed by the retention of a crystalline structure (with an X-ray pattern similar to the monohydrate structure) on dehydration in air or under vacuum. However, polymerization results in an amorphous polymer. Therefore, we envisage the polymer chain, especially when accompanied by dehydration disruption, pulling the monomer molecule out of the lattice. A molecular model of the $Ba(MA)_2 \cdot H_2O$ structure shows that a growing chain could coil around in the corridor between the barium ions and this would be assisted by the void space.

This mechanism is supported by the observation of O'Donnell, McGarvey, and Morawetz[6] that the orientation dependence of propagating radicals in $Ba(MA)_2 \cdot H_2O$ is only lost slowly during polymerization. An alternative explanation, adopted by St. Pierre, *et al.*,[15] for calcium acrylate, is that the radicals remaining trapped after polymerization are those which are not involved in polymerization. We have suggested[4] that the radicals remaining after polymerization in $Ba(MA)_2 \cdot H_2O$ are polymer radicals. This is based on (1) the high asymmetry of the radical conformation even though there is a considerable amount of monomer crystal structure remaining and (2) the complete decay of trapped radicals in similar nonpolymerizable compounds, *e.g.*, barium isobutyrate.[11] If this concept is correct, then it is not possible to subtract the concentration of radicals trapped after polymerization (assumed to be nonpolymer radicals) from the initial radical concentration and to apply a conventional kinetic treatment to this difference, taken as the concentration of polymer radicals, all of which are assumed to decay during polymerization.

Acknowledgments. We wish to thank the Australian Institute of Nuclear Science and Engineering for supporting this project, the Australian Atomic Energy Commission, and particularly Mr. J. Bolton and Mr. J. Gray for irradiation of samples, Professor L. E. Lyons for making the esr spectrometer available to us, and C.S.I.R.O. for providing a studentship for M. J. B.

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