# The Solid-State Polymerization of Hydrated Barium Methacrylate

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ABSTRACT: The dehydration of barium methacrylate monohydrate and the post-irradiation polymerization have been investigated. Dehydration *in vacuo* at 47° proceeds without loss of crystallinity and with only a minor change in lattice volume. The $^{60}$Co $\gamma$-ray initiated post-irradiated polymerization yield is dependent upon the degree of hydration. The monohydrate polymerization exhibits an induction period and a maximum conversion occurs at the "quarter hydrate" composition. The polymerization is inhibited by oxygen with maximum effect occurring at the same composition which shows maximum conversion. The role played by defects is discussed in relation to the polymerization mechanism.

In a recent report[1] on the post-irradiation polymerization of calcium acrylate dihydrate, we showed that the polymerization behavior, both *in vacuo* and in air, is profoundly affected by the degree of hydration of the salt. In the present paper we present a similar study on barium methacrylate monohydrate. This compound, which was previously reported as both a mono- and a dihydrate,[2–10] was first studied by Lando.[3] He found that, on post-irradiation polymerization in air, the "dihydrate" and anhydrous salts both polymerized to very low conversions, but the "dihydrate" exhibited an induction period after which high conversions to polymer were obtained. In recent in-source polymerization studies[9] on the "dihydrate" in air this induction period was attributed to physical trapping of short-chain propagating radicals. The nature of the radical species involved in the initiation, propagation, and termination reactions has been determined by electron spin resonance studies.[5–8]

All previous polymerization studies of hydrated barium methacrylate have been made in air and only at the two extreme limits of hydrate composition. Since the polymerization reaction occurs by a free-radical mechanism, studies in the absence of oxygen and at intermediate degrees of hydration were considered necessary for a better understanding of this solid-state polymerization process.

## Experimental Section

**Monomer Preparation and Characterization.** Barium methacrylate hydrate was prepared by slowly adding a stoichiometric amount of barium hydroxide octahydrate to a cooled, stirred aqueous solution of freshly distilled methacrylic acid, filtering, and allowing the filtrate to evaporate slowly. The monomer crystallized as large flat diamond-shaped plates. After powdering and sieving through a 40 mesh screen, the salt was stored in a desiccator over a saturated solution of calcium chloride.

The particle size distribution was determined with Canadian standard sieves, 100 and 250 mesh. The results are given as follows (weight fraction in per cent is in parentheses): $-40 + 100$ mesh, 149 $\mu$ (50); $+250$ mesh, 63 $\mu$ (25); $-250$ mesh, $<63$ $\mu$ (25).

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. *Anal.* Calcd for monohydrate: C, 29.51; H, 3.72. Found: C, 29.36 ± 0.4; H, 3.82 ± 0.05. (Calcd for dihydrate: C, 27.97; H, 4.11.) *Anal.* Calcd for anhydrate: C, 31.24; H, 3.28. Found: C, 31.06; H, 3.43.

Dehydration of the hydrate at 47° *in vacuo* yielded a weight loss of 5.7%, which is in excellent agreement with the theoretical value of 5.5% for a monohydrate composition.

Debye–Scherrer photographs were obtained with a Philips diffractometer using Ni-filtered Cu K$\alpha$ radiation.

The methods used in infrared and density measurements have been described previously.[1]

**Polymerization.** Approximately 2-g quantities of barium methacrylate monohydrate were dehydrated at 47° *in vacuo*. The extent of dehydration was controlled by the length of time of heating. The samples were cooled, pumped on for several minutes at room temperatures, and sealed under a pressure of $10^{-4}$ mm.

The experiments with oxygen were carried out by admitting dry air to the sample container just prior to sealing. The degree of hydration was calculated gravimetrically.

The monomer samples, of varying water content, were irradiated at −78° in a $^{60}$Co Gammacell 220 having an uncorrected midpoint dose rate of $4.23 \times 10^5$ rad/hr as determined by Fricke dosimetry. The net radiation dose was 0.86 Mrad and corrections were applied for sample position, electron density, dose rate decay, and 5% absorption due to the dewar and Dry Ice.

The irradiated salts were then postirradiation polymerized at 25 or 35°.

The conversion to polymer was determined by adding the powder mixture, with stirring, to distilled water containing a trace of hydroquinone. The insoluble polymer was rapidly separated from the dissolved monomer by filtration, then washed and dried to constant weight.

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TABLE I
X-RAY POWDER PATTERNS OF BARIUM METHACRYLATE

| Barium methacrylate monohydrate | | | | | Anhydrous barium methacrylate | | | |
|---|---|---|---|---|---|---|---|---|
| Intensity[a] | 2θ, deg | d spacing, Å | Miller indices | Calcd d spacing, Å | Intensity | 2θ, deg | Miller indices | d spacing, Å |
| vs | 7.60 | 11.633 | 001 | 11.500 | vs | 7.45 | 001 | 11.893 |
| w | 13.60 | 6.510 | 110 | 6.526 | | | | |
| m | 15.35 | 5.779 | 002 | 5.750 | m | 15.00 | 002 | 5.906 |
| w | 16.60 | 5.338 | 021 | 5.354 | m | 17.45 | | 5.087 |

[a] vs—very strong, m—medium, w—weak.

## Results and Discussion

The elemental analysis and weight loss data indicate a monohydrate composition, not a dihydrate as previously reported. Supporting evidence for this has been reported during the course of the present work.[10,11]

The differential scanning calorimetry (dsc) thermogram showed the maximum rate of dehydration to occur at 78 ± 3° (Figure 1) with the total water of hydration being evolved during the first heating cycle. The thermogram exhibits two overlapping endotherms, the first being due to the phase change associated with the removal of the water of hydration from its lattice site and the second corresponding to desorption of the water from the surface. When the carrier gas flow rate is very low or large crystals are used, the second endotherm occurs at temperatures over 100°. Using differential thermal analysis, O'Donnell[10] has also observed a two-peaked endotherm for the dehydration of barium methacrylate monohydrate.

Figure 2 demonstrates that the changes in the Debye–Scherrer powder photographs, as dehydration proceeds, are minor and thus it is concluded that there is no appreciable decrease in the crystallinity. A close examination of the X-ray films shows that the monohydrate pattern is gradually replaced by that of the anhydrous salt.

Table I lists the first few 2θ values and *d* spacings for the mono- and anhydrates. The Miller indices for the former, calculated from Lando's crystallographic unit cell,[3] are also included. The very strong first reflection 001 spacing increased from 11.633 Å in the monohydrate to 11.893 Å in the anhydrate. There is no significant broadening or reflections and it is concluded, therefore, that the crystalline nature is maintained and no disordering occurs.

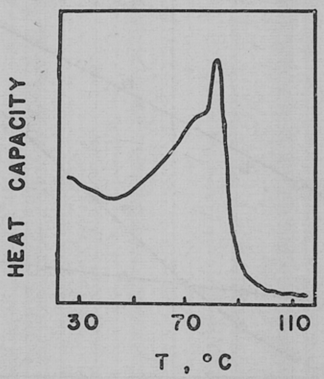

Figure 1. Differential scanning calorimetry of barium methacrylate monohydrate, 10°/min.

The density of hydrated barium methacrylate, Figure 3, is observed to decrease linearly with dehydration. The observed decrease in density results from the loss of the water of hydration and a slight increase in the lattice dimensions.

An examination of the infrared absorption revealed that the spectrum of barium methacrylate monohydrate contains a sharp strong peak at 3562 cm$^{-1}$ for the OH stretching vibration. In this hydrate, therefore, the water of crystallization experiences little or no hydrogen bonding.

From the foregoing observations, it can be concluded that the water of hydration in barium methacrylate monohydrate plays only a minor role in maintaining the crystal structure. This is in contrast to calcium acrylate dihydrate[1] where removal of the water of hydration caused collapse of the lattice to an amorphous material.

**Polymerization.** The amount of polymer formed during the irradiation at −78° is shown as a function of the degree of hydration in Figure 4. The in-source conversion is limited to rather low values (0.2–4.5%)

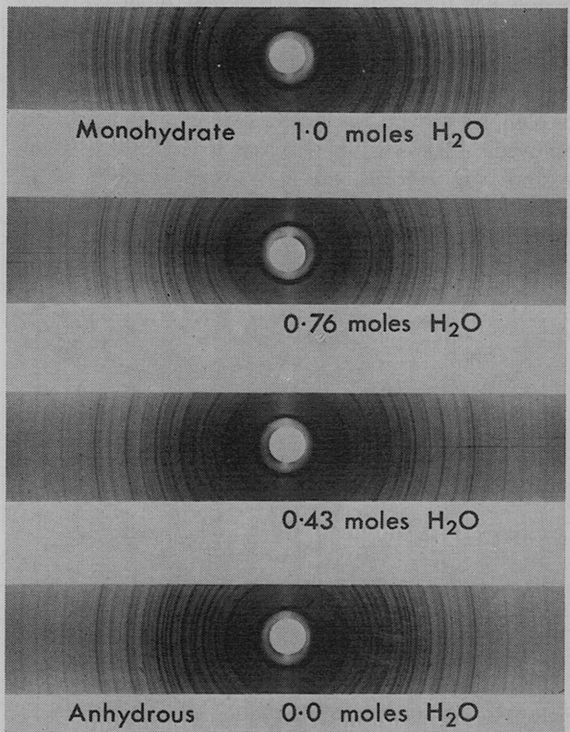

Figure 2. X-Ray diffraction of hydrated barium methacrylate.

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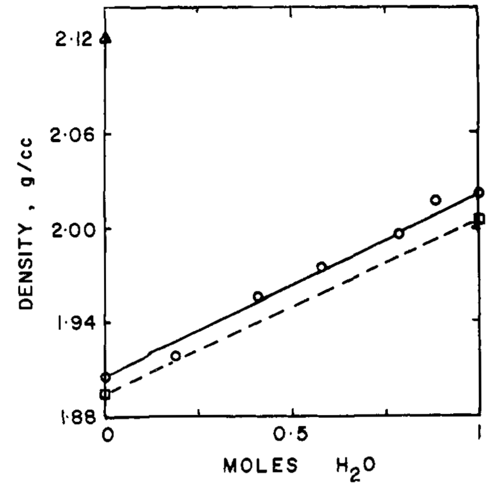

Figure 3. Density of hydrated barium methacrylate: ○, experimental; □, calculated from X-ray, no unit cell volume change; △, poly(barium methacrylate).

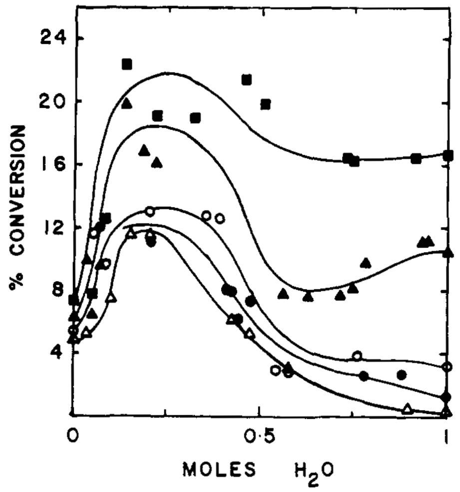

Figure 5. Post-irradiation polymerization, hydrated barium methacrylate, 35°, 0.86 Mrad at −78°: △, 0.6 days; ●, 3.0 days; ○, 7.3 days; ▲, 16.5 days; ■, 27.6 days.

and varies with the extent of hydration. Also included in Figure 4 is the conversion to polymer that occurs when samples are allowed to post-irradiation polymerize at 25° for 35.3 days. The conversion appears to be almost independent of water content at high or moderate degrees of hydration, but beyond the 50% dehydration level it shows a sharp maximum at about the quarter hydrate.

The post-irradiation polymerization at 35° for different times is shown, as a function of the degree of hydration, in Figure 5. It is evident from the figure that the initial rates of polymerization reach a maximum at partially hydrated compositions, and are the lowest for the monohydrate, and intermediate for the anhydrate. At short (0.6 days) polymerization times the conversion to polymer increases with the extent of dehydration, at first gradually, then rising more rapidly to a maximum. At longer polymerization times the rate dependence on the degree of hydration is less marked for samples in which less than half the water has been removed. However, in all cases a maximum in conversion rate is observed at approximately the 0.25 hydration level. This is precisely the same behavior observed for hydrated calcium acrylate.[1]

Figure 6 illustrates the postirradiation polymerization data at 35°, as a function of time, at three specific hydration levels. The anhydrate and "quarter-hydrate" both display an initial rapid rate of polymerization which decays to a slower, constant value after 1 day. In contrast, the monohydrate polymerizes at a very slow rate initially but then accelerates in an autocatalytic manner. Bowden, *et al.*,[9] observed a similar behavior during their in-source polymerization studies and attributed it to increased motion due to defects resulting from the γ-irradiation and from the polymerization reaction itself.

The present results, which utilized a lower radiation dose, 0.86 Mrad, are rationalized in the following way. Upon heating at 35°, the small amount of polymerization (0.2%) produced during irradiation at 78° slowly increases. This polymerization disrupts the lattice and may even cause partial dehydration in the vicinity of the monomer–polymer interface. Both processes generate defects which lead to the observed acceleration. The autocatalytic polymerization behavior of the higher hydrates, Figure 5, can also be explained on this basis. The absense of autocatalysis at lower degrees of

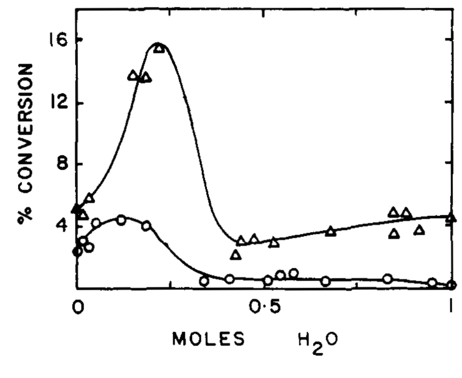

Figure 4. Solid-state polymerization of hydrated barium methacrylate: ○, "in-source" polymerization, 0.86 Mrad, −78°; post-irradiation polymerization, 25°, 35.5 days, 0.86 Mrad at −78°.

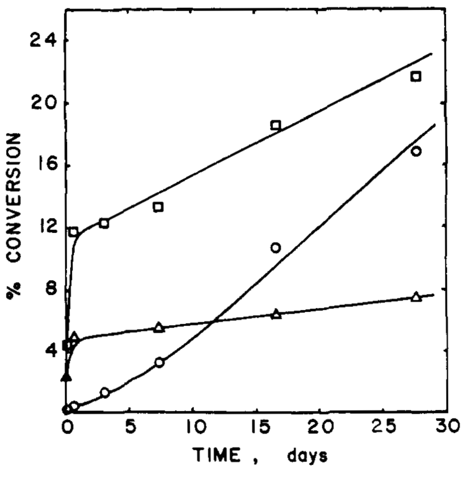

Figure 6. Post-irradiation polymerization, barium methacrylate, 35°, 0.86 Mrad at −78°: ○, monohydrate; □, maximum; △, anhydrate.

hydration, Figure 6, suggests that the number of defects generated during polymerization is small compared to that introduced by the dehydration process.

Polymerization is assumed to occur by a short-range diffusion of the monomer from the crystal lattice to the growing radical polymer chain. This hypothesis is a necessary one because the polymer has a higher density than the monomer, Figure 3. Diffusion and polymerization should thus be facilitated in the vicinity of the monohydrate–anhydrate boundary in an "open" lattice such as that possessed by the anhydrate salt. The openness of the anhydrate lattice is a consequence of the removal of the water of hydration without any collapse or contraction of the lattice.

The anhydrate polymerizability, which lies between that of the monohydrate and intermediate water contents, may be rationalized by the enhanced diffusion possible in the "open" lattice but its rate is in turn diminished, relative to the 0.25 hydrate, due to the absence of any phase boundary disorder. The monohydrate, lacking both disorder and "openness" of lattice, exhibits a very slow initial rate of polymerization.

The inhibitory effect of oxygen on the postirradiation polymerization at 35° is shown in Figure 7. This observed inhibition is the behavior expected for a radical polymerization.[5-8] Furthermore, the pattern of the inhibition–composition behavior substantiates the arguments put forward in the polymerization discussion in that the very same physical phenomena which create facile monomer diffusion can facilitate the diffusion of inhibiting $O_2$ molecules. Hence a maximum in the inhibition occurs at the identical level of hydration observed for the maximum rate of polymerization. Similar results were obtained in the case of the hydrated calcium acrylate.[1] However, one important difference is noted between the two salts. The presence of oxygen in hydrated calcium acrylate drastically inhibits the polymerization at all water contents, whereas in barium methacrylate there is only a slight suppression of polymer conversion for the mono- and anhydrates. This greater inhibition in the calcium acrylate anhydrate, relative to that for the barium methacrylate, is explained on the basis of the amorphous structure of the former. However, the fact that the crystalline calcium acrylate hydrate is so sharply inhibited relative to the crystalline barium methacrylate hydrate is surprising. We propose that this difference is due to a difference in the ease of $O_2$ diffusion in the two compounds. This, in turn, is thought to be related to the manner in which their free volumes are distributed in their respective unit cells. Inspection of the crystallographic model of calcium acrylate dihydrate[1] reveals the presence of channels parallel to the *b* axis, through which $O_2$ molecules can easily pass. In the case of the barium methacrylate monohydrate crystal,[3] however, the cations are spaced in such a manner that the presence of a channel is not apparent. Resolution of this question will only be possible, however, when the complete crystal structures are resolved.

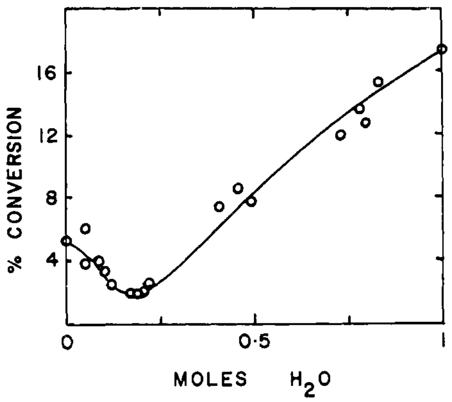

Figure 7. Post-irradiation polymerization, hydrated barium methacrylate in air, 35°, 34 days, 0.86 Mrad at −78°.

**Acknowledgments.** The authors wish to acknowledge the assistance of Drs. A. J. Frueh and R. St. John Manley in the X-ray diffraction work and the National Research Council of Canada for financial aid and for a scholarship to F. M. C.