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

Radiation-Induced Solid-State Polymerization of Derivatives of Methacrylic Acid. VII. A Differential Scanning Calorimetric Investigation of the Dehydration and Polymerization of Barium Methacrylate

J. H. O' Donnell[a]; R. D. Sothman[a]
[a] Chemistry Department, University of Queensland, Brisbane, Australia

To cite this Article Donnell, J. H. O' and Sothman, R. D.(1972) 'Radiation-Induced Solid-State Polymerization of Derivatives of Methacrylic Acid. VII. A Differential Scanning Calorimetric Investigation of the Dehydration and Polymerization of Barium Methacrylate', Journal of Macromolecular Science, Part A, 6: 4, 745 — 760

To link to this Article: DOI: 10.1080/10601327208056872

URL: http://dx.doi.org/10.1080/10601327208056872

J. MACROMOL. SCI.—CHEM., A6(4), pp. 745-760 (1972)

Radiation-Induced Solid-State Polymerization of Derivatives of Methacrylic Acid. VII. A Differential Scanning Calorimetric Investigation of the Dehydration and Polymerization of Barium Methacrylate

J. H. O'DONNELL * and R. D. SOTHMAN

Chemistry Department
University of Queensland
Brisbane 4067
Australia

ABSTRACT

Barium methacrylate monohydrate showed two dehydration steps (at 80 and 110°C), in small crystals, but only one step (at 80°C) in fine powder. The equilibrium water vapor pressure was independent of the degree of hydration and its temperature dependence was found to be $\log_{10} p_{H_2O}$ (Torr) = 10.70 - 2858/T, giving ΔH (dehyd) = 54 ± 4 kJ mole^{-1}. Small doses of γ-irradiation at 78°C suppressed the second dehydration endotherm and shifted the first to higher temperatures. Larger radiation doses caused the endotherm to diminish and be replaced by a polymerization exotherm. The variations in position with scan rate gave E_a = 163 kJ mole^{-1}, similar to the value from isothermal polymerization rate measurements. There was no evidence of polymerization in the anhydrate except at the decomposition temperature.

---

*To whom correspondence should be addressed.

INTRODUCTION

Two crystalline forms of barium methacrylate are known, the monohydrate ($Ba(MA)_2.H_2O$), which polymerizes readily above 30°C, i.e., some 200° below the decomposition temperature, and the anhydrate, which does not polymerize beyond a few per cent up to this temperature. This difference was observed by Lando and Morawetz [1] and has been taken as an example of the importance of the spatial arrangement of the monomer molecules in the crystalline lattice in determining their polymerizability, although the detailed structure was only recently elucidated for the monohydrate [2, 3], and is still unknown for the anhydrate. However, polymerizability must also depend on molecular mobility and the possibility exists that this may be influenced by the dehydration reaction in barium methacrylate.

We have previously published the results of detailed investigations of the in-source [4] and post-irradiation [5] polymerization of $Ba(MA)_2.H_2O$. We have examined the dehydration [6] and found it to take place in the same temperature region as polymerization. Costaschuk, Gilson, and St. Pierre [7, 8] have shown that the rate of post-irradiation polymerization is greatest in the partly-dehydrated monomer.

This paper reports a further examination of the correlation between dehydration and polymerization in $Ba(MA)_2.H_2O$ by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of unirradiated and irradiated samples. Comparison can be made with the previous isothermal investigations. The possibility that neither the monohydrate nor the anhydrate structure is intrinsically polymerizable, and that polymerization only occurs 1) during the dehydration or 2) in a hemi-hydrate, is considered. The dehydration equilibrium is investigated by vapor pressure measurements.

EXPERIMENTAL

Barium methacrylate was prepared as described previously [4]. The Perkin-Elmer differential scanning calorimeter was calibrated with naphthalene, phenanthrene, and benzoic acid. Measurements were normally made at a scan rate of 8°/min with 10 mg samples contained in either unsealed or sealed cups with a constant purge of nitrogen. Different particle sizes from small crystals (10 mg) to fine powder (-200 mesh) were examined. TGA measurements were made with a Cahn microbalance and a temperature-programmed oven. The samples were irradiated with ^{60}Co γ rays at -196°C (liquid nitrogen) or -78° C (Dry Ice-acetone). For the DSC measurements they were irradiated in the aluminum cups contained in a sealed, air-filled glass tube to avoid absorption of water.

The equilibrium vapor pressure of H_2O above $Ba(MA)_2.xH_2O$ for x from 0 to 1 was measured by a static, absolute method using the apparatus shown in Fig. 1. $Ba(MA)_2.H_2O$ (2 g of -100 +200 mesh powder) was placed in Bulb A and mercury in Bulb B. The apparatus was evacuated for a period of time (1.5 to 7.5 hr) at room temperature to give a residual water content from 0.8 to 0.3 H_2O. After sealing at C the mercury was allowed to run into the Manometer D and the apparatus placed vertically in a constant temperature bath with a glass window. The pressure was read periodically on the manometer until equilibrium had been reached, (about 48 hr). The water content of the sample was determined at the conclusion of the experiment by measuring the weight loss on complete dehydration.

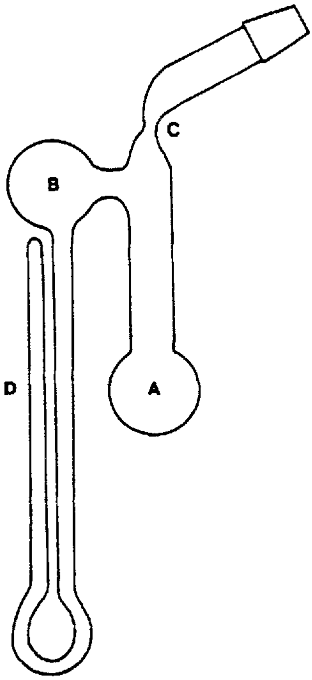

FIG. 1. Apparatus used for measurement of equilibrium vapor pressure above $Ba(MA)_2.xH_2O$. Explanation of letters in text.

RESULTS

Dehydration

The DSC traces from 35 to 450°C for $Ba(MA)_2.H_2O$ and $Ba(MA)_2$.anhyd in the form of small crystals (about 1 mg) in unsealed cups are shown in Fig. 2. Identical traces were obtained for $Ba(MA)_2$.anhyd as crystals or powder and whether obtained by dehydration of $Ba(MA)_2.H_2O$ or by crystallization from methanol. There was an endotherm at 230°C for both $Ba(MA)_2.H_2O$ and $Ba(MA)_2$.anhyd corresponding to the commencement of decomposition. No melting could be observed. Decomposition became strongly exothermic above 400°C, producing a charred brown mass. The small crystals of $Ba(MA)_2.H_2O$ showed two endotherms, at 80 and 110°C, which can be attributed to dehydration. If the sample was run from 35 to 120°C, reversed, and then re-run to 450°C, the trace was identical to the anhydrate.

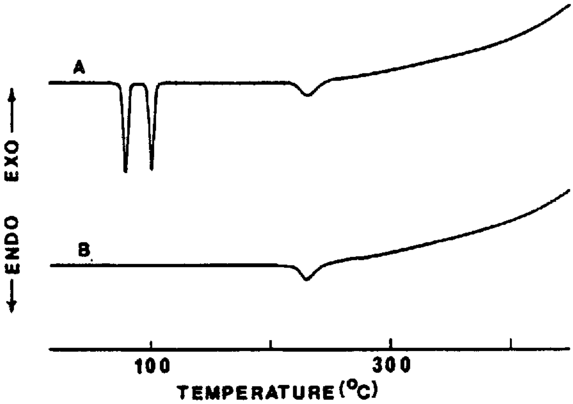

FIG. 2. DSC of (A) $Ba(MA)_2.H_2O$ and (B) $Ba(MA)_2$.anhyd in the form of small (1 mg) crystals in unsealed cups at 8° min^{-1}.

Particle Size

When the particle size of $Ba(MA)_2.H_2O$ was reduced the intensity of the second dehydration endotherm was also reduced until in fine power (-100 mesh) it was completely absent as shown in Fig. 3. The

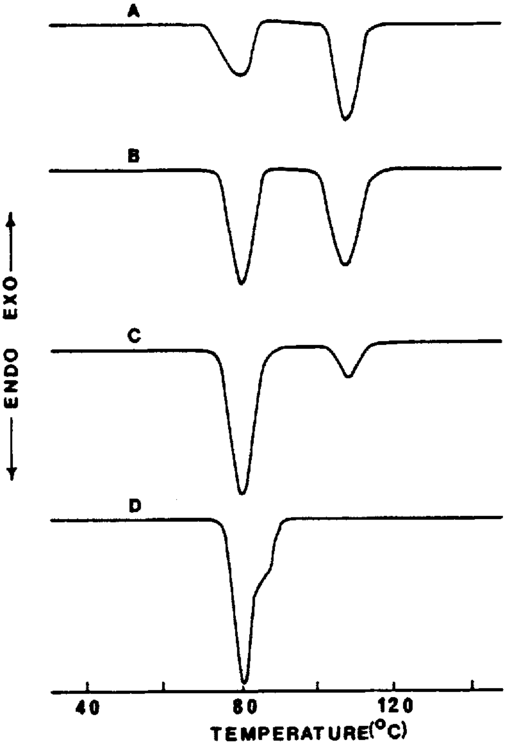

FIG. 3. Effect of particle size on the DSC of $Ba(MA)_2.H_2O$ dehydration in unsealed cups (10 mg samples) at 8° min^{-1}. (A) Single 10 mg crystal, (B) 1 mg crystals, (C) 0.3 mg crystals, (D) powder -100 mesh ≈0.01 mg.

total endothermic area remained approximately constant and the second endotherm disappeared while the first endotherm grew, i.e., there was not a progressive shift of the second endotherm towards the first. The single endotherm obtained from fine powder showed a shoulder under some DSC run conditions. The heat of dehydration, Δ H(dehyd), was estimated from the endothermic areas by comparison with the standards and a value of 48 ± 6 kJ $mole^{-1}$ was obtained.

DSC of small crystals or powder in sealed cups showed only one dehydration endotherm at 88°C between the two endotherms for unsealed cups. Retardation of dehydration is to be expected when the water vapor is prevented from escaping.

Measurements of the weight loss of the monohydrate as the temperature was raised (TGA) confirmed that the DSC endotherms were due to dehydration. For the same temperature scan rate as in the DSC measurements two separate weight loss steps were observed in the small crystals, corresponding to approximately half the water of crystallization at each step as shown in Fig. 4. These were at the same temperature as the DSC endotherms. The TGA of the powder showed that all the water was lost in one step at 80° C corresponding to the single DSC endotherm. In both cases the total weight loss was exactly equivalent to one molecule of water. Thus the dehydration can occur by a 2-step process (for large particle sizes) which is quite similar to the dehydration of zinc methacrylate dihydrate, $Zn(MA)_2.2H_2O$.

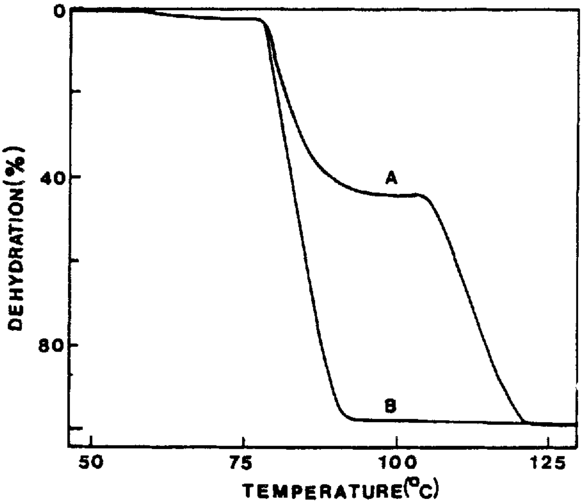

FIG. 4. TGA weight-loss curves for $Ba(MA)_2.H_2O$. (A) Small 1 mg crystals, (B) powder -100 mesh.

The DSC and TGA of $Zn(MA)_2.2H_2O$ show that the dehydration occurs in 2 steps, at 80 and 150° C, corresponding to the loss of the first and second molecules of water of crystallization, respectively. The monohydrate shows a single dehydration step at 150° C. The DTA of both hydrates and the anhydrate show a decomposition endotherm at 230° C. These results are shown in Fig. 5. The marked difference between the ease with which the first and second molecules of water can be removed is not unusual for hydrates and it confirms

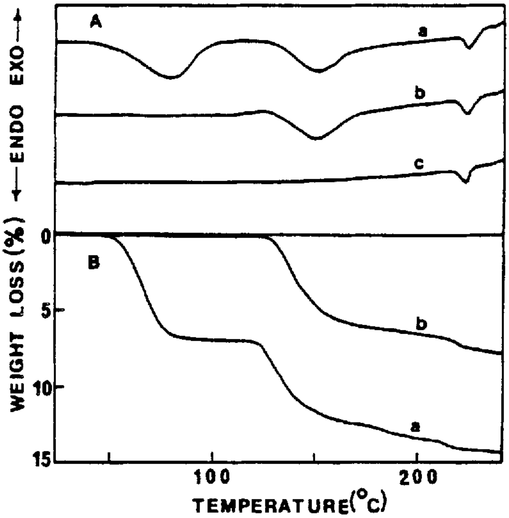

FIG. 5. (A) DSC and (B) TGA of (a) $Zn(MA)_2.2H_2O$, (b) $Zn(MA)_2.H_2O$, and (c) $Zn(MA)_2$.anhyd in unsealed cups at 8° min^{-1}.

our earlier observations [9] of the relatively high stability of $Zn(MA)_2.H_2O$. It is in marked contrast to the DSC and TGA results of Costaschuk, Gilson, and St. Pierre [10] for calcium acrylate dihydrate, where only a single dehydration step (to the amorphous anhydrate) occurred. The results for $Zn(MA)_2.2H_2O$ suggest that the two dehydration steps in $Ba(MA)_2.H_2O$ could be due to dehydration via a hemi-hydrate. This would be possible since there are two H_2O positions in the unit cell. In $Zn(MA)_2.2H_2O$ there is no difference between the DSC of small crystals and powder. When the samples are run in sealed cups the dehydration endotherms are delayed to 120 and 170°C.

Polymerization

When $Ba(MA)_2.H_2O$ was irradiated with small doses of γ-rays and then DSC runs made, two effects were observed for small crystals as shown in Fig. 6. The second dehydration endotherm was reduced after very small doses and disappeared completely by 0.02 Mrad at -78°C. The first dehydration endotherm was shifted to higher temperatures proportionately to the dose. Thus the second dehydration step was eliminated and all the dehydration occurred in the first step.

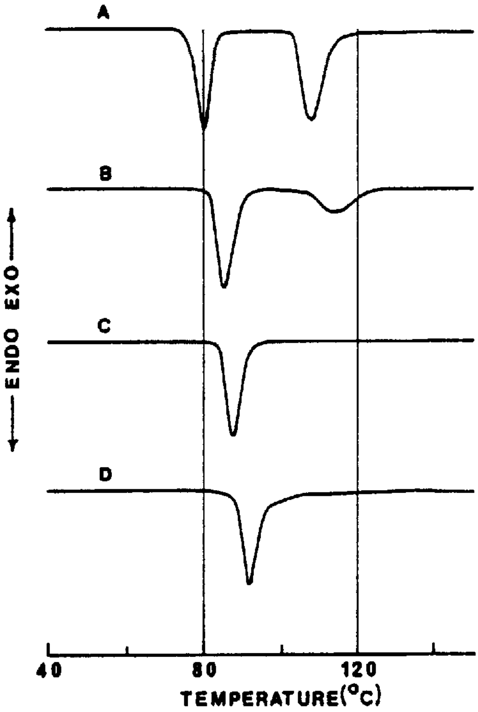

FIG. 6. DSC of small 1 mg crystals of $Ba(MA)_2.H_2O$ after (A) 0.0 Mrad, (B) 0.01 Mrad, (C) 0.025 Mrad, and (D) 0.05 Mrad of γ-radiation at -78° in unsealed cups at 8° min^{-1}.

At higher doses the magnitude of the endotherm was reduced and above 1 Mrad at -78°C was replaced by an exotherm which increased in size with increasing dose and also occurred at lower temperatures (90 → 80°C) as shown in Fig. 7. The exotherm is due to the radiation-initiated polymerization and this was confirmed by the separation of polymer. Similar results were obtained with powdered material, except that there was no second endothermic dehydration step. Also, the size of the exotherm was much smaller in each case; this must

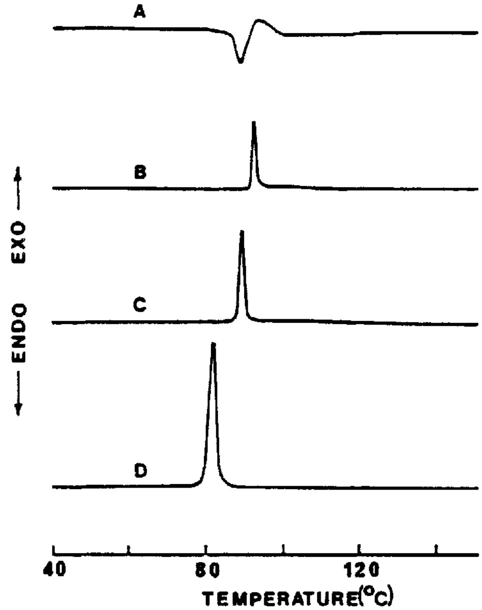

FIG. 7. DSC of small 1 mg crystals of $Ba(MA)_2.H_2O$ after (A) 1.0 Mrad, (B) 2.0 Mrads, (C) 3.0 Mrads, and (D) 5.0 Mrads of γ-radiation at -78°C in unsealed cups at 8° min^{-1}.

be due to a greater rate of dehydration in the powder, resulting in more rapid conversion to the anhydrate, which does not polymerize to any significant extent.

Irradiation at - 196°C produced smaller exotherms, i.e., less polymerization, for a given dose than irradiation at -78°C. This result is the same as that observed in isothermal post-irradiation polymerization [5] and was shown to be due to the smaller yield of trapped free radicals.

Irradiation of $Ba(MA)_2.H_2O$ in sealed cups caused the single endotherm to shift to higher temperatures until the exotherm of polymerization predominated, at which stage increasing doses shifted the exotherm to lower temperatures as in the unsealed cups. The amount of polymerization was only slightly reduced for powdered material compared with small crystals which can be attributed to the retarding effect on the dehydration of the increasing water vapor pressure in the enclosed sample.

A value for the activation energy (E_a) of the polymerization reaction can be derived from the variation in the temperature of the polymerization exotherm maximum (T_m) with the heating rate (φ) in DSC runs after a constant radiation dose using Eq. (1) [11]. A good

$$d \ln (\varphi/T_m^2)/d(1/T_m) = -E_a/R \qquad (1)$$

linear plot of ln φ/T_m^2 vs $1/T_m$ was obtained for samples of small crystals given 5.0 Mrads at -78° C and this gave E_a = 163 kJ mole^{-1} comparable with E_a = 138 kJ mole^{-1} from initial rates of isothermal post-irradiation polymerization [5].

Anhydrate

The DSC runs for the anhydrate prepared by dehydration of $Ba(MA)_2.H_2O$ and by crystallization from methanol were identical, and TGA confirmed that there was no weight loss due to occluded or incorporated methanol. The anhydrate, after 10.0 Mrads of γ-radiation at -78° C, showed no endotherm up to the decomposition temperature of 230° C. However, the normal endotherm at 230° C was not observed, but an exotherm which could be due to polymerization. We have found that polymerization does proceed at this temperature [5].

Equilibrium Vapor Pressure

The DSC and TGA measurements show that the dehydration can occur as a 2-step process. This would be consistent with the two different H_2O positions in the structure [3]. This could result in the existence of a hemi-hydrate [formally $Ba(MA)_2.\frac{1}{2}H_2O$, although there are 4 barium atoms in each unit cell], which would be confirmed by different equilibrium vapor pressures of H_2O above $Ba(MA)_2.xH_2O$ for $x < 0.5$ and > 0.5. Therefore the equilibrium vapor pressure of H_2O above barium methacrylate was measured as a function of degree of hydration. A plot of equilibrium vapor pressure vs degree of hydration at 50° C is shown in Fig. 8. There is no evidence of a lower equilibrium vapor pressure at water contents below 0.5 H_2O which would support the existence of a hemi-hydrate. Similar results were obtained for crystals and powder, although a much longer time was required to reach equilibrium in crystals, and at 25, 30, and 40° C.

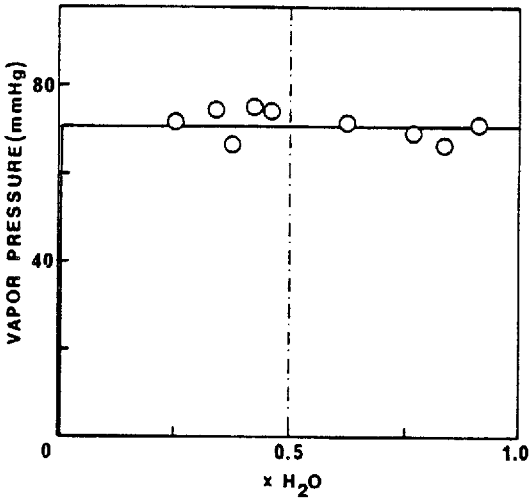

FIG. 8. Equilibrium vapor pressure above $Ba(MA)_2.xH_2O$ at 50°C.

For the dehydration reaction $Ba(MA)_2.H_2O$ (cryst) $\rightleftharpoons$ $Ba(MA)_2$(cryst) + H_2O(vap) the equilibrium partial vapor pressure (p) of H_2O should increase with temperature (T) according to Eq. (2), where ΔH^θ is the

$$\log\left[\frac{P_2}{P_1}\right] = \frac{-\Delta H^\theta}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (2)$$

heat of dehydration. The degree of dehydration of any sample in a sealed vessel can be calculated if p is known as a function of temperature, therefore the temperature dependence of p was also measured. The mean equilibrium vapor pressures determined at various temperatures are given in Table 1. The $p(H_2O)$ value of 73 Torr at 50°C can be compared with the values of 45.5 Torr for $CuSO_2.5H_2O$, 30.9 Torr for $CuSO_2.3H_2O$, and 4.5 Torr for $CuSO_2.H_2O$ at the same temperature [12].

The results in Table 1 give a good linear plot of log(p) vs 1/T from which we obtain $p(H_2O)$ Torr = 10.70 - 2858/T and ΔH(dehyd) = 54 ± 4 kJ $mole^{-1}$. An independent value for ΔH(dehyd) has been observed by comparison of the areas of the DSC dehydration endotherm in $Ba(MA)_2.H_2O$ samples with the fusion endotherms for naphthalene, phenanthrene, and benzoic acid. The value obtained was ΔH(dehyd) = 48 ± 6 kJ $mole^{-1}$ which is in satisfactory agreement with the value

TABLE 1. Equilibrium water vapor pressures above $Ba(MA)_2.H_2O$

Temperature (°C)	$p(H_2O)$ (Torr)
25	13.5
30	18.1
40	39.6
50	73.0

obtained from vapor pressure measurements considering the experimental errors in both methods.

The equilibrium water vapor pressure above barium methacrylate increases with rise in temperature more rapidly than the vapor pressure of pure water until at about 75° C they are equal. Therefore, above 75° C $Ba(MA)_2.H_2O$ will continue to dehydrate completely to the anhydrate even in a sealed vessel.

Rehydration

The anhydrate did not show any significant increase in weight when exposed to a saturated water vapor atmosphere at 25° C; under these conditions rehydration can only occur very slowly. However, when partially dehydrated $Ba(MA)_2.H_2O$ was allowed to reach its equilibrium water vapor pressure at a temperature T_1 in an evacuated, sealed vessel and then cooled and maintained at a lower temperature T_2, the equilibrium vapor pressure decreased to the lower equilibrium value for T_2, indicating that rehydration had occurred.

Partial Dehydration

The DSC of $Ba(MA)_2.H_2O$ after partial dehydration in vacuum at 50° C to $0.5H_2O$ showed a dehydration endotherm at a lower temperature (63° C) than for $Ba(MA)_2.H_2O$. Dehydration occurred more readily than was observed for a normal mixture of anhydrate and monohydrate, yet the x-ray diffraction spectrum corresponded to a mixture of monohydrate and anhydrate. The over-all structure is evidently very disrupted with many defects which act as nuclei for dehydration. When $Ba(MA)_2.H_2O$ was heated in a sealed vessel at 100° C there was no significant weight loss, but the DSC and x-ray diffraction spectrum was similar to the partly-dehydrated sample. This is readily explained by the equilibrium vapor pressure measurements which predict that the monohydrate will be thermodynamically unstable with respect to the anhydrate above 75° C.

DISCUSSION

Use of DSC

The results in this paper show how DSC can be used to follow polymerization in the solid state. It provides a rapid method of ascertaining the temperature region where polymerization proceeds and the effect of radiation dose, irradiation temperature, etc. An estimate of the activation energy for the polymerization (consistent with the value derived from the initial rates of isothermal post-irradiation polymerization) was obtained from the variation in the temperature of the polymerization isotherm with temperature scan rate. The extent of polymerization can be determined from the magnitude of the polymerization exotherm. In $Ba(MA)_2.H_2O$, polymerization has been shown to occur at the same time as dehydration. Under no circumstances could the two reactions be observed separately after irradiation.

We have previously reported that the dehydration proceeds by two steps and assigned the first step to a structural change to that of the anhydrate [6]. The present work shows that both structural change and partial dehydration occur in the first step and that the magnitude of the second step depends on the particle size of the $Ba(MA)_2.H_2O$.

Structure of $Ba(MA)_2.H_2O$

Lando and Morawetz [1] made the first investigation of the crystal structure of $Ba(MA)_2.H_2O$, reporting that it was monoclinic, space group $P2_1/a$ with cell dimensions a = 7.75 A, b = 12.1 Å, c = 11.5 Å, and $\beta = 90° 30'$, i.e., pseudo-orthorhombic, space group P_{bam}. The a and b axes were in the directions of the long and short axes, respectively, of the diamond-shaped crystals and the c axis almost perpendicular to this plane. Lando and Morawetz showed that the barium ions were effectively arranged in planes parallel to the a-b plane, four per unit cell, and postulated that the methacrylate molecules were arranged with the carboxyl groups oriented towards the barium ions so that the hydrocarbon ends of the methacrylate molecules, containing the vinyl double bonds, formed layers midway between the planes of barium ions. This structure is suggested by the easy cleavage of the crystal parallel to the a-b plane. Thus the layers containing the vinyl bonds are 11.5 Å apart in the c-axis direction and polymerization can be expected to proceed only within these layers. Unfortunately, they were unable to resolve the positions of the atoms of the methacrylate molecules. This was probably due to polymerization initiated by the x rays [13].

Singman, Spring, and Post [2] have made a detailed investigation of the structure and determined the positions of the carbon and oxygen atoms. Their results confirm that it is a monohydrate. Isaacs, Van der Zee, and Kennard [3] have used these positions to refine their neutron diffraction data to completely determine the structure, including the hydrogen positions. These results show that the spatial arrangement proposed by Lando and Morawetz is essentially correct. However, there are some interesting additional features.

Two water molecules are arranged about a center of symmetry between barium ions, oriented back-to-back with the oxygen atoms directed towards the barium ions. Therefore, there is no hydrogen bonding between the water molecules and this results in the sharp O—H ir band at 3562 cm^{-1} [7].

There are 8 carboxyl oxygen atoms forming, with 4 water oxygens, a distorted cube-octahedron about each barium ion and a two-dimensional network in the a-b plane at intervals of 11.5 Å. The hydrocarbon segments of the methacrylate molecules protrude from either side (the molecules are all oriented at about 65° to the a-b plane). The strength of this structural feature probably accounts for the relatively minor changes in the x-ray diffraction pattern on dehydration.

It is possible that the water molecules in each pair could be lost successively during dehydration and a metastable $Ba(MA)_2.H_2O$ could exist with one water molecule in an intermediate position at the center of symmetry between the two original H_2O positions. The equilibrium water vapor pressure measurements show that there is only one stable hydrate, yet a 2-step dehydration can be observed. This suggests that the second step is a kinetic feature resulting from temporary trapping of H_2O in the partly dehydrated structure.

There is a remarkable space in the a-b plane between the hydrocarbon ends of the layers of methacrylate molecules and this provides an easy cleavage plane. However, the failure of oxygen to inhibit the polymerization or affect the ESR spectrum indicates that oxygen cannot permeate this void to reach the free radicals. This is in contrast to calcium acrylate dehydrate [8] where O_2 molecules can pass through channels parallel to the b axis. Polymerization can occur and in and across these two layers of methacrylate molecules in which the vinyl groups are separated by 4.1-4.6 Å. The structural arrangement is shown in Fig. 9.

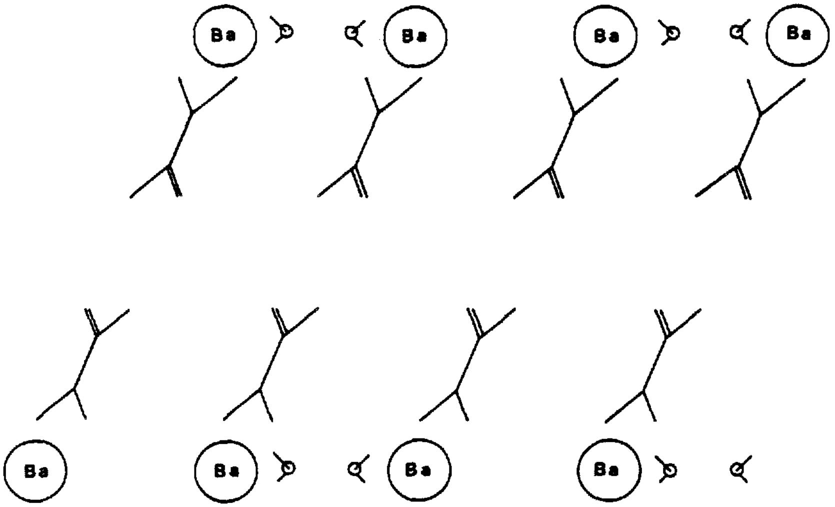

FIG. 9. An idealized projection in the a-c plane of the crystal structure of $Ba(MA)_2 . H_2O$. (Ba) = Ba ion, ≻O = H_2O, and ≻—≺ = methacrylate ion.

CONCLUSIONS

Dehydration and polymerization are intimately associated in barium methacrylate monohydrate. Partial dehydration results in a defect structure in which dehydration occurs particularly easily. Above 75°C the monohydrate is thermodynamically unstable even in sealed tubes.

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. D. F. Sangster and Mr. J. H. Bolton for provision of irradiation and DSC facilities, and Dr. H. A. J. Battaerd and I.C.I. (Australia) for use of their DSC.

REFERENCES

[1] J. B. Lando and H. Morawetz, J. Polym. Sci., Part C, 4, 789 (1964).
[2] L. Singman, M. Spring, and B. Post, Private Communication.
[3] N. Isaacs, J. Van der Zee, and C. H. L. Kennard, Private Communication.
[4] M. J. Bowden, J. H. O'Donnell, and R. D. Sothman, Makromol. Chem., 122, 186 (1969).
[5] M. J. Bowden, J. H. O'Donnell, and R. D. Sothman, Macromolecules, In Press.
[6] M. J. Bowden and J. H. O'Donnell, J. Phys. Chem., 73, 2871 (1969).
[7] F. M. Costaschuk, D. F. R. Gilson, and L. E. St. Pierre, J. Phys. Chem., 74, 2035 (1970).
[8] F. M. Costaschuk, D. F. R. Gilson and L. E. St. Pierre, Macromolecules, 4, 16 (1971).
[9] J. H. O'Donnell and R. D. Sothman, J. Polym. Sci., Part A-1, 6, 1073 (1968).
[10] F. M. Costaschuk, D. F. R. Gilson and L. E. St. Pierre, Macromolecules, 3, 393 (1970).
[11] H. E. Kissinger, Anal. Chem., 29, 1702 (1957).
[12] S. Glasstone, Textbook of Physical Chemistry, 2nd ed., MacMillan, London, 1953, p. 783.
[13] N. W. Isaacs, C. H. L. Kennard, and J. H. O'Donnell, Nature, 216, 1104 (1967).

Received for publication February 7, 1972