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Structural Aspects of Polymerization in Crystalline Ionic Monomers: Comparison of Barium Methacrylate Monohydrate and Anhydrate

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Structural Aspects of Polymerization in Crystalline Ionic Monomers: Comparison of Barium Methacrylate Monohydrate and Anhydrate

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ABSTRACT

Barium methacrylate monohydrate, $\text{Ba}^{2+}[\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}^-]_2 \cdot \text{H}_2\text{O}$, may be readily polymerized in the crystalline state by γ -irradiation. However, except under special conditions, there is negligible polymer produced when anhydrous barium methacrylate is exposed to γ -irradiation. The differences in polymerizability are considered in relation to the detailed spatial arrangements of the methacrylate molecules and molecular mobility associated with development of disorder.

INTRODUCTION

Barium methacrylate provides an unusual opportunity to examine the role of the crystalline structure in determining the polymerizability of a monomer in the solid state. It may be prepared in at least two crystalline forms, the monohydrate, $\text{Ba}^{2+}[\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}^-]_2 \cdot \text{H}_2\text{O}$, $[\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}]$, and the anhydrate, $\text{Ba}(\text{MA})_2$ the crystal structures

of both forms having now been solved [1-3]. However, the x-ray powder spectrum of the dehydrated material cannot be readily indexed based on the crystal data for the compound. This suggests that although the crystal structure was determined on single crystals, the polymerization studies were carried out on a different material having the same chemical composition. Nevertheless, the two standards used in data collection, which were regularly monitored, did not vary significantly, indicating that this compound, unlike the monohydrate, did not readily polymerize when exposed to a total of 45 hr of $\text{MoK}\alpha$ x-radiation (40 kV, 20 mA). Therefore, although the polymerization studies and x-ray single crystal work were probably carried out on two different forms of barium methacrylate, neither of these compounds polymerized when exposed to x-radiation.

$\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ was one of the first monomers in which polymerization in the solid state was observed. Morawetz et al. [4-7] studied a number of methacrylate and acrylate salts and found that the rate of conversion to polymer was very dependent on the metal ion and on the crystalline form, indicating a predominant role of the solid-state structure.

Lando and Morawetz [7] found that $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ (which they believed to be a dihydrate) could be polymerized with a 55% yield of polymer, either by heating (50°C) or by γ -irradiation (-78°C , 0.8 Mrad). However, only 1% polymer was obtained when the anhydrate was exposed to these conditions. O'Donnell et al. [8-15] showed, using ESR spectra, that the polymerization proceeds by a free-radical chain mechanism. There have been reports that the anhydrate will polymerize, but at a lower rate than the monohydrate. Fydeler and Charlesby [16] obtained a 4% polymer yield (18°C , 8 Mrad of γ -irradiation) but this rose with increasing radiation dose. Costaschuk et al. [17, 18] reported an initial rate of post-irradiation polymerization greater for the anhydrate than with the monohydrate, but only with 4% yields. Parrish and Kochanny [19] stated that $\text{Ba}(\text{MA})_2$ polymerized at a "moderate" rate.

O'Donnell and Sothman [15] have found that during irradiation and post-irradiation heating negligible polymer was formed. Gravimetric analysis was carried out by extracting the residual monomer with water and weighing the residue. However, there was a substantial reduction in the number of vinyl groups in the residual monomer. Also, it was shown that: (1) low-temperature irradiation followed by residual monomer measurement, without any post-irradiation heating, produced small monomer loss; (2) infrared absorption due to $-\text{C}=\text{CH}-$ vibrations were reduced; (3) there was a considerable loss of crystallinity, which did not occur when only heat was applied. These observations could be explained in terms of dimer formation. Typical results for $\text{Ba}(\text{MA})_2$ and $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ are shown in Figures 1 and 2.

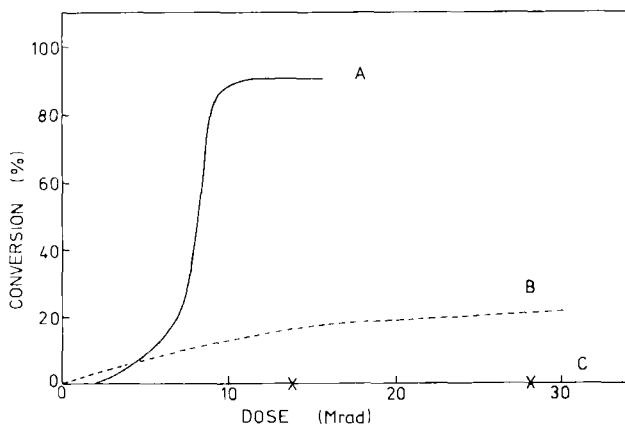


FIG. 1. Polymerization of barium methacrylate during irradiation: (A) $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$, 25°C ; (B) $\text{Ba}(\text{MA})_2$ monomer loss, 35°C ; (C) (\times) $\text{Ba}(\text{MA})_2$, high-polymer yield, 35°C .

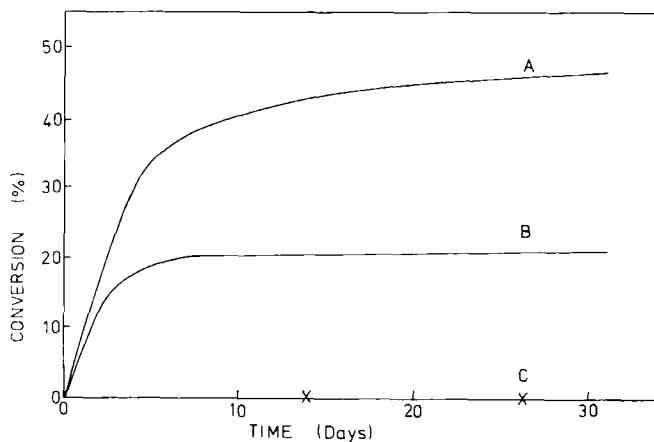


FIG. 2. Post-irradiation polymerization of barium methacrylate: (A) $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$, 50°C after 1.0 Mrad at -78°C ; (B) $\text{Ba}(\text{MA})_2$, 100°C after 10.0 Mrad at -78°C , monomer loss; (C) (\times) $\text{Ba}(\text{MA})_2$, high-polymer yield, 100°C after 10.0 Mrad at -78°C .

The topochemical control of polymerization in a crystalline monomer may occur through a variety of interrelated effects. These include: the rates of trapping of free radicals $G(R\cdot)$ and radical decay versus propagation; the heterogeneity of the initial radical distribution, which will depend on the mechanism of the radical formation; physical trapping of propagating radicals; mobility of existing and formed lattice defects and of the propagating chain and the monomer; and spatial arrangement of vinyl groups within the lattice.

Additional evidence is now available so that deductions may be made concerning the role of some of the above parameters.

RESULTS AND DISCUSSION

Crystal Structures

$Ba(MA)_2 \cdot H_2O$. The approximate arrangement of the lattice structure of $Ba(MA)_2 \cdot H_2O$ was deduced by Lando and Morawetz [7] from a determination of the barium positions. Post [1] later obtained the carbon positions, and Isaacs et al. [2] determined the complete structure from neutron diffraction data.

The unit cell is monoclinic, space group $P_{2_1/c}$ with dimensions, $a = 11.57$, $b = 12.00$, $c = 7.70 \text{ \AA}$, $\beta = 90.5^\circ$. There is a two-dimensional arrangement of barium atoms formed down the b axis. A barium atom is surrounded in a distorted arrangement by nine oxygen atoms. There are two oxygen atoms from water molecules and seven from carboxylate groups, with Ba-O distances averaging 2.84 \AA . The layers of methacrylate molecules interweave down the b axis, but the vinyl bonds are not close to one another (3.88 ; 3.85 \AA) (Fig. 3). The neutron determination enables the hydrogen atoms to be located with a high degree of certainty. The water molecules are positioned in pairs about a centre of symmetry with an intermolecular H-H distance of 2.21 \AA . There is no hydrogen bonding, and this is confirmed by the sharpness of the infrared absorption at 3500 cm^{-1} [12, 18].

$Ba(MA)_2$. The crystal structure of $Ba(MA)_2$ was determined by x-ray diffraction [3]. The unit cell is monoclinic, space group $P_{2_1/c}$ with dimensions, $a = 12.162$, $b = 8.017$, $c = 10.373 \text{ \AA}$, $\beta = 102.87^\circ$. The structure is similar to that of $Ba(MA)_2 \cdot H_2O$ in some respects. Once again there is a two-dimensional arrangement of barium atoms down one axis (c , 10.373 \AA), with each atom being surrounded by a distorted arrangement of oxygens with an average distance of Ba-O 2.80 \AA . The layers of methacrylate molecules also interweave, this time down the c axis. The minimum distance between adjacent vinyl groups is 4.09 \AA . The structure is shown in Fig. 4.

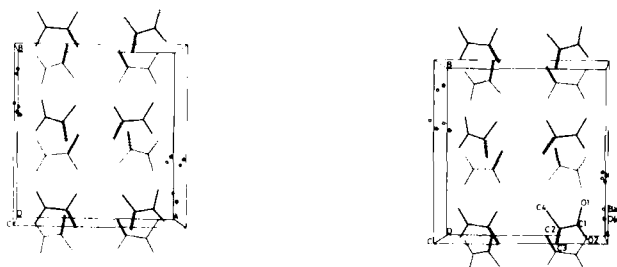


FIG. 3. Stereoscopic view of the packing of barium methacrylate hydrate in the cell viewed down the *c* axis.



FIG. 4. Stereoscopic view of the packing of barium methacrylate anhydrate in the cell viewed down the *a* axis.

Dehydration

$\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ undergoes dehydration on heating. Differential scanning calorimetry (DSC) has shown that this is a two-stage process in crystals, with endothermic transition temperatures of 74 and 104°C [20]. The x-ray powder diffraction measurements [12] indicate that the first stage corresponds to transformation to crystalline anhydrate and the second to desorption. Decomposition commences at about 230°C.

The suggested mechanism for polymerization is that the radiation breaks down one of the water molecules into H and OH radicals which may move within the crystal. This defect allows the other water molecule close to the center of the symmetry to go into that position. This rearrangement of the barium coordination sphere allows adjacent vinyl groups to interact with a free radical transfer. This is confirmed by ESR spectra which show that polymerization proceeds by a free radical mechanism and DSC studies which indicate

a two-stage dehydration on heating. A change in structure is also indicated by x-ray powder spectra studies. The x-ray powder spectra continually run on three intense reflections (100, 200, 002) confirm that there is an induction period, probably to obtain a critical concentration of free radicals, before polymerization begins. The peak width does significantly increase on exposure, indicating the possibility of increased disorder in the cell. The decrease in peak position by 1% might suggest an increase in a and c cell dimensions due to an increase in the number of defects in the cell. There are no data about the b axis.

On exposure, the (100) reflection has an initial peak at 2θ (CuK α) = 7.755° and after 31.03 hr (at 40 kV 10 mA, dose rate 556,000 rad/hr) gives a peak at 7.025°. This is at the same position as the most intense peak recorded when the material had been dehydrated at 70°C for 28 hr. This confirms that polymerization had occurred during the dehydration process.

Structure and Polymerization

In structural studies on dichlorobis(4-vinylpyridine)copper (II), Laing and Horsfield [21] found that, although adjacent vinyl groups were as close as 3.66 Å, the compound did not readily undergo polymerization. They reported some work on cobalt (II) and zinc (II) derivatives, where, in spite of the greater distance (4.35, 5.2 Å respectively), the compounds polymerized more easily. Thus, the separation of the vinyl bonds [22] is not the sole factor determining polymerizability. They found that thermal motions of the vinyl groups were very large in the last two compounds (7-11 Å²) and much smaller in the copper (II) complex (4 Å²).

This suggested an additional mechanism. Analysis of unpublished anisotropic thermal parameters for barium methacrylate showed that the B_{33} for the methyl carbon atoms were significantly greater than any thermal parameters for the other carbon atoms, and four times the values for the carboxyl carbons. However, the vinyl carbons were twice the values of the carboxyl carbons about the three principal axes. This suggested that the barium atom formed strong links with the hydrophilic oxygen atoms and any water molecules. The hydrophobic carbon atoms would stack in a way to minimize packing energy. However, this allowed some atoms to have either considerable play in packing or be disordered. Application of external excitation could increase the thermal parameters for these atoms, increasing disorder and allowing movement of the hydrophobic groups in such a way that polymerization takes place through the vinyl groups. Because the groups are stacked above each other, polymerization would occur along the c axis. Although the R for the

anhydrate was low, one C-CH₃ bond [C(31)-C(21)] was significantly long (1.52 Å) suggesting error. However, the published thermal parameters, B₃₃ and B₁₃ for C(42) are significantly higher than for all of the other thermal parameters. This suggests polymerization across a center of symmetry to a related C(42) only 4.14 Å away, to form a dimer. Because of the location of other vinyl groups, no further polymerization would take place. This is confirmed by the loss of monomer vinyl bonds when the anhydrate is irradiated.

The amount of covalent character for the barium atom will determine its directional strength for bonding. Studies on barium coordination to date [23] do not indicate any preferred coordination, with the coordination number ranging from 7 to 11, and Ba-O distances from 2.7 to 3.2 Å. Consequently there does not seem to be any significance in the differences in the coordination for the two compounds, except that the hydrate has the additional water in the barium sphere.

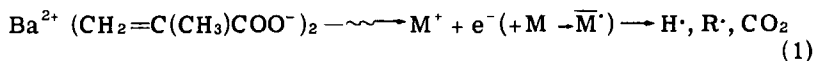
Radiolysis

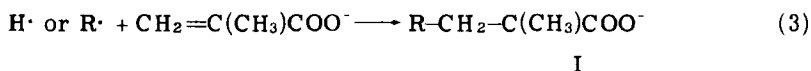
Radiolysis of aliphatic carboxylic acids [24] causes decarboxylation. With unsaturated carboxylic acids there is a lower yield of CO₂. For Ba(MA)₂·H₂O and Ba(MA)₂, values of G(CO₂) ≈ 2 have been obtained [15]. Hydrogen atoms and other radicals are mainly scavenged by C=C bonds to form methacrylate radicals which may initiate formation of dimer, oligomer or polymer chains.

Decarboxylation will have two effects: (1) disruption of the coordination around the Ba atoms and (2) development of internal stresses within the crystal. For example, 50 Mrad of irradiation with G(CO₂) = 2 will produce 1 cm³ of CO₂ at STP/cm³ of Ba(MA)₂ so that the internal pressures generated by trapped CO₂ alone will become high. This may explain the observed fragmentation of irradiated single crystals into mosaics, and the local movement of the methacrylate molecules, which would enable dimerization to occur.

Radiolysis and Polymerization

The formation of dimeric, propagating-type, methacrylate radicals according to reactions (1)-(3) is readily explained in the defect regions. This results from the radiolytic decarboxylation and subsequent local disruption of the lattice.





However, kinetic chain reactions, which normally produce high molecular weight polymer, require more extensive disintegration of the crystalline structure. This has been correlated with dehydration in $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$. Thus, the endothermic DSC peaks are replaced after irradiation by a polymerization exotherm, proportional in size to the radiation dose [13]. The crystal/crystal phase change during dehydration will be accompanied by sufficient molecular disorder and mobility to enable the vinyl double bonds to link together in chains. There has been evidence [25] by broad-line NMR measurements for molecular mobility in the temperature range where dehydration occurs. Thermal initiation, involving decomposition of peroxides, is sufficient to form a polymer in the temperature range 50-100°C without irradiation [14]. However, the molecular mobility associated with melting/decomposition in $\text{Ba}(\text{MA})_2$ at about 230°C enables it to form a polymer [13].

Polymerization may proceed via transport of monomer molecules from their lattice positions to the radical center or by movement of the propagating end of the polymer chain. The observed dependence of the ESR spectrum on the orientation of the crystal in $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ during the polymerization [8] suggests that this mechanism may be more likely. Thermal motion of the polymer chain, particularly by C-C bond rotation, in the disordered region containing the amorphous polymer phase, will assist in the detachment from the crystal lattice of the end methacrylate unit containing the radical site. A similar orientation dependence was found for propagating-type radicals in $\text{Ba}(\text{MA})_2$, a transfer reaction predominating [15].

Hydrogen-transfer reactions have been demonstrated in various systems and are apparently particularly facile in carboxylic acids [26], where a mechanistic pathway is available through the coordinated carboxylate structures. The observation that high monomer losses (up to 60%) may occur in $\text{Ba}(\text{MA})_2$ [15] during irradiation or post-irradiation heating suggests that radical-site transfer may proceed by this mechanism. The high radiation doses and high temperatures required are compatible with disruption of the lattice structure without substantial molecular mobility and are attributable to the internal stresses generated by the decarboxylation. The failure to form long-chain polymer is consistent with the absence of a dehydration reaction or similar phase change and the rigid structure of the barium-oxygen network in $\text{Ba}(\text{MA})_2$. Also the different conformation [15] of the

propagating-type radical in $\text{Ba}(\text{MA})_2$ compared with $\text{Ba}(\text{MA})_2 \cdot \text{H}_2\text{O}$ may be accounted for by the different twist of the C-C bonds in the crystal structure. It seems likely that similar high monomer losses without formation of high molecular weight polymer, may occur in other methacrylate and acrylate salts.

There has been some speculation about the role of the $\text{Ba}(\text{MA})_2$ lattice. Fydeler and Charlesby [16] obtained higher polymer yields from irradiation under 6500 atm pressure and deduced that propagation in $\text{Ba}(\text{MA})_2$ occurs "only in the perfect crystal". Costaschuk et al. [17, 18] on the other hand, attributed the apparently greater initial rate of post-irradiation polymerization in the anhydrate to "enhanced diffusion in the 'open' lattice". The crystal structure and the x-ray thermal parameters are compatible with dimer formation in the perfect crystal and polymerization associated with enhanced molecular mobility during dissolution or on melting.

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