other polymer systems,[15] the *p*-phenylene polymers (VP to VIIP) exhibit somewhat better weight retention than the *p*-phenylene ether polymer (IP to IVP) after aging at 400° in air. This general trend is in agreement with recent reports[9,16] that the oxidative stability of polyquinoxalines containing diphenyl ether moieties is less than that of polyquinoxalines containing other moieties (*e.g.*, diphenyl sulfone, benzophenone, *p*-phenylene).

Acknowledgment. The authors would like to express their appreciation to Dr. J. M. Augl of Naval Ordnance Laboratory, Silver Spring, Md., for T_g determinations and to Mr. W. Wrasidlo for helpful discussions.

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(16) W. Wrasidlo, *ibid.*, in press.

Solid-State Polymerization of Hydrated Calcium Acrylate

F. M. Costaschuk, D. F. R. Gilson, and L. E. St. Pierre

Department of Chemistry, McGill University, Montreal, Canada.

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ABSTRACT: The dehydration of calcium acrylate dihydrate at 60° *in vacuo* involves a dihydrate → anhydrous transition with a significant loss of crystallinity. The ^{60}Co γ-ray initiated postirradition polymerization at 25 and 50° was strongly dependent on the degree of hydration. A marked inhibition of the postirradiation polymerization by oxygen was observed with maximum inhibition occurring at the hydrate composition for which maximum conversion was observed for polymerization *in vacuo*. The rate of polymerization is dependent on the short-range diffusion of monomer which, in turn, is dependent upon defects introduced during the dehydration process.

The solid-state polymerizations of various acrylate and methacrylate salts have been studied by Morawetz and coworkers.[1,2] These salts provided an excellent system for the study of solid-state postirradiation polymerization since their melting points are at much higher temperatures than that at which polymerization occurs, *i.e.*, premelting phenomena do not complicate the process. Postirradiation polymerizations were effected at 50 and at 101° with concurrent dehydration of the hydrated salts at the higher temperature. Markedly different yields were observed on postirradiation polymerization of different crystalline and amorphous modifications of calcium acrylate hydrate and anhydrate and of barium methacrylate hydrate and anhydrate. The polymerizations were, however, carried out in the presence of air and any possible effects of oxygen were ignored.

It seemed probable to us that a carefully controlled method of dehydration of the hydrated salts would permit a control of the extent of lattice defects and allow a study of the role of defects in the mechanism of postirradiation polymerization. Of the various factors which affect the kinetics and mechanisms of solid-state polymerization reactions, evidence is accumulating that such defects play a dominant role.[3-5] Indeed, Bamford and Eastmond state that, in general, polymerization will not occur in a perfect lattice.[6]

The present paper describes a study of the dehydration process in calcium acrylate dihydrate and the effect of intermediate degrees of hydration on the polymerization conversion *in vacuo* and in air.

Experimental Section

Monomer Preparation and Characterization. Calcium acrylate dihydrate was prepared by gradually adding a stoichiometric quantity of calcium hydroxide to a stirred, cooled aqueous solution (3 *N*) of freshly distilled acrylic acid, filtering, and allowing the filtrate to evaporate slowly. The monomer, obtained as long thin needles, was powdered in a mortar, sieved through a 40-mesh screen, and stored in a desiccator over a saturated solution of calcium chloride.

The work reported here was conducted on powdered material from several separately prepared batches, and the reproducibility of data between batches was excellent. The particle size distribution of the monomer powder was analyzed with Canadian standard sieves, 100 and 250 mesh. The distribution of particle sizes is shown as follows (the weight fraction is given in per cent): −40 + 100 mesh (149 μ), 20%; +250 mesh (63 μ), 20%; −250 mesh (<63 μ), 60%.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The results for the dihydrate were C, 33.04 ± 0.2; H, 4.62 ± 0.1 (calcd C, 33.02; H, 4.62). For the anhydrous material, C, 39.41; H, 3.62 (calcd C, 39.55; H, 3.32).

Dehydration experiments on the dihydrate were conducted by heating *in vacuo* at 60° using a Cahn electrobalance, Model RG. The extent of dehydration at any time could thus be controlled. The total weight loss was 16.5%, in excellent agreement with the theoretical value. These conditions of dehydration yield an amorphous product rather than the crystalline material derived from slow dehydration.[2]

The differential scanning calorimetry (dsc) studies were performed with a Perkin-Elmer dsc-1, using a 5°/min heating rate and a sample weight of 3–5 mg.

Infrared spectra in KBr pellets and as mulls in hexachloro-

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(1) (a) T. A. Fadner, I. D. Rubin, and H. Morawetz, *J. Polym. Sci.*, **37**, 549 (1959); (b) H. Morawetz and I. D. Rubin, *ibid.*, **57**, 669 (1962).

(2) J. B. Lando and H. Morawetz, *ibid., Part C*, **4**, 789 (1964).

(3) V. A. Kargin, V. A. Kabanov, and G. P. Andrianova, *Polym. Sci. USSR*, **1**, 106 (1960).

(4) V. A. Kargin, V. A. Kabanov, and N. Ya. Rapaport-Molodtsova, *ibid.*, **3**, 657 (1962).

(5) I. Kaetsu, N. Sagane, K. Hayashi, and S. Okamura, *J. Polym. Sci., Part A-1*, **4**, 2241 (1966).

(6) C. H. Bamford and G. C. Eastmond, *Quart. Rev., Chem. Soc.*, **23**, 271 (1969).

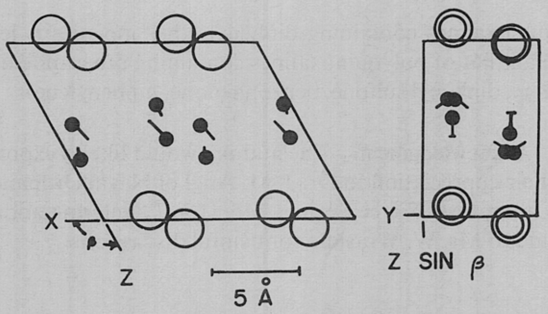

Figure 1. Calcium acrylate dihydrate unit cell: monoclinic, space group $P2/_1a$: $a = 14.36$ Å, $b = 6.59$ Å, $c = 11.62$ Å, $\beta = 118.9°$, $Z = 4$, density = 1.506 g/cc; ○, calcium ion; ●—, acrylate ion; ——, vinyl group.

butadiene and Nujol were obtained with a Perkin-Elmer spectrometer, Model 337.

Calcium acrylates of various water contents were prepared as described above for Debye–Scherrer powder diagrams. The photographs were obtained with a Phillips X-ray diffractometer using Cu Kα radiation and Ni as a filter.

The density determinations of the monomer prepared in the above manner were conducted pycnometrically, utilizing a deaerated mixture of the monomer in a paraffin oil of known density.

Polymerization. Samples of 1–2 g of calcium acrylate dihydrate were placed in 10-ml round-bottomed containers and sealed under vacuum. In cases where water removal was desired, the salts were dehydrated at 60° *in vacuo* for times ranging from 5 min to 6 hr. Following the heat treatment, the sample was pumped on for 5–10 min at room temperature, cooled, and then sealed under a pressure of 10^{-4} mm. Polymerizations in the presence of oxygen were carried out by admitting dry air at atmospheric pressure to the sample container just prior to sealing.

Samples were irradiated at −78° in a ^{60}Co Gammacell 220 with an uncorrected midpoint dose rate of 2.86×10^4 rad/hr as measured by Fricke dosimetry. The net radiation dose was either 0.86 or 0.23 Mrad with corrections made for sample position in the cell chamber, electron density of the salt, dose rate decay, and a 5% absorption due to the dewar and Dry Ice.

The samples were then postirradiation polymerized at temperatures of −78, 25, or 50°.

The extent of conversion to polymer was determined by adding the powder mixture with stirring to distilled water containing a trace of hydroquinone. Within minutes the insoluble polymer was separated from the dissolved monomer, washed, and dried to constant weight *in vacuo* at 90–100°.

For the postirradiation polymerizations *in vacuo* at 50° any dehydration loss during the time of polymerization was considered insignificant. Assuming a high vapor pressure of the hydrate of 0.5 atm, the calculated water loss is 3 mg for a 10-ml volume. Since the initial amount of water is approximately 200 mg, this amount of loss is not considered serious.

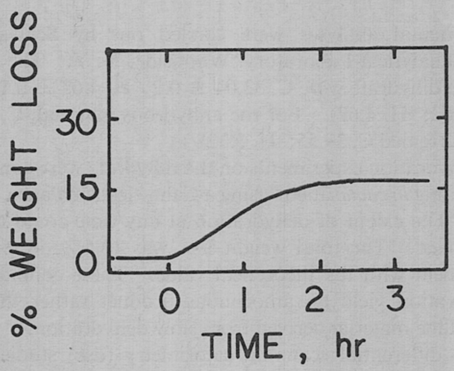

Figure 2. Thermogravimetric analysis of calcium acrylate dihydrate at 60° *in vacuo*.

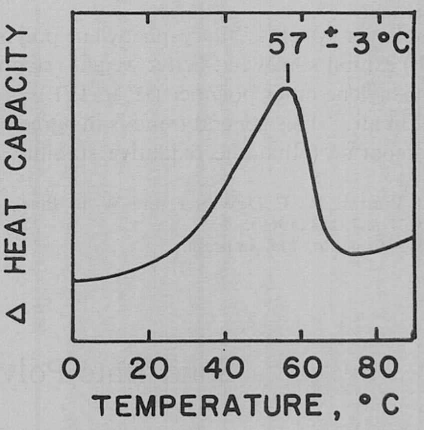

Figure 3. Differential scanning calorimetry of calcium acrylate dihydrate at 5°/min.

Molecular Model. The crystallographic analysis of Lando[7] was used as a basis for a molecular model of the unit cell of calcium acrylate dihydrate, Figure 1.

Results and Discussion

Dehydration. Prior to any discussion of the polymerization behavior of calcium acrylate at its various

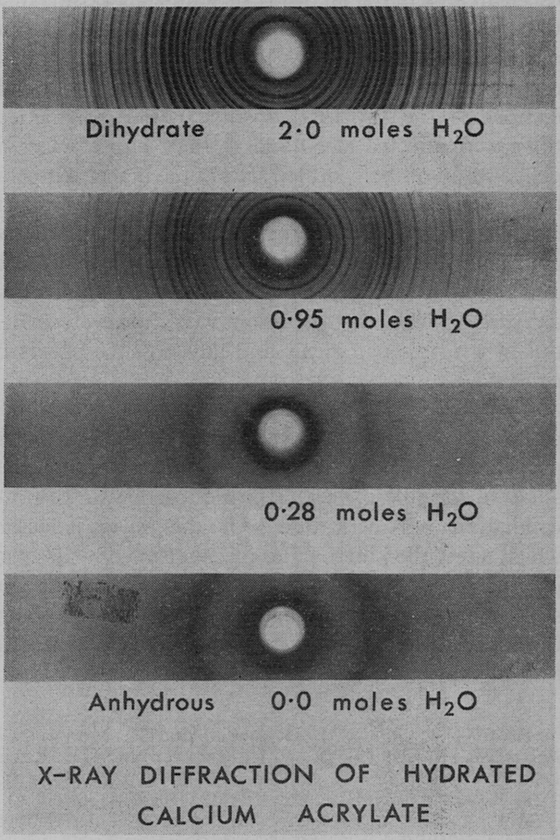

Figure 4. X-Ray diffraction of hydrated calcium acrylate.

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(7) J. B. Lando, Ph.D. Thesis, Polytechnic Institute of Brooklyn, June 1963.

TABLE I
X-RAY POWDER PATTERNS OF CALCIUM ACRYLATE

Calcium acrylate dihydrate					Anhydrous calcium acrylate		
Intensity	2θ, deg	d spacing, Å	Miller indices	d(calcd), Å	Intensity[a]	2θ, deg	d spacing, Å
VS	8.50	10.402	001	10.173	S (broad)	8.3	10.612
S	12.48	7.095	$\bar{2}01$	7.097			
M	14.08	6.290	200	6.286	M (halo)	23	3.84
S	15.93	5.566	011	5.531	W (halo)	30	2.93
			$\bar{1}11$	5.638			
S	18.35	4.836	$\bar{2}11$	4.829			
M	19.70	4.506	201	4.468	VW (halo)	42	2.15
			210	4.549			

[a] VS—very strong, S—strong, M—medium, W—weak, VW—very weak.

states of dehydration, it is desirable that some understanding of the nature of the salts be reached. To begin with let us consider the dehydration process.

Figure 2 is a weight loss *vs.* time plot from thermogravimetry. It indicates the dehydration to be a smooth single process involving a rapid initial weight loss, followed by a decaying rate of dehydration until the anhydrous composition is reached.

The dsc thermogram, Figure 3, shows the dehydration as one endotherm with its maximum at 57 ± 3°. Upon reheating the dehydrated sample, only the smooth base line is observed, indicating that the loss of both water molecules is contained within the single endotherm.

The Debye–Scherrer powder photographs as a function of water content are shown in Figure 4. It can be seen that a substantial decrease in the crystallinity occurs during the dehydration process. The dihydrate pattern of approximately 40 lines gradually decreased in intensity with a simultaneous increase in the intensities of the four halos of the anhydrous pattern, but the dihydrate pattern is visible even at the lowest degree of hydration studied of 0.28 mol of H_2O. With the present method of dehydration (60° *in vacuo*) no distinct compounds of intermediate composition appear to be present. Table I lists the first six 2θ values observed for the dihydrate, the d spacings, and their Miller indices based on Lando's crystallographic unit cell. Similar data for the anhydrate are also presented. The dihydrate and anhydrous patterns are in excellent agreement with the reported results of Lando and Morawetz,[2] although their "amorphous" anhydrous salt was prepared by room temperature vacuum dehydration. From Figure 4 the 001 reflection is observed to broaden progressively as well as increase slightly in spacing. Nevertheless, it can be concluded that any changes in the *c* crystallographic direction are minimal.

The relationship between density and degree of hydration is illustrated in Figure 5. The density is seen to decrease slightly, in a smooth linear manner, as the water is removed, but it does not approach the value calculated from the X-ray density[7] for the equivalent dihydrate unit cell volume with the water molecules absent. Since the observed density decreases by only a fraction of this calculated reduction, the lattice must be contracting or collapsing as the water is withdrawn.

From these data it is evident that the water of crystallization is essential to the dihydrate structure, with the crystallinity diminishing as the dehydration proceeds. Spectroscopic analysis shows that the OH absorption band in the infrared spectrum of calcium acrylate dihydrate covers a very broad range, 3750–2800 cm^{-1}, with maximum absorption at 3382 cm^{-1}. This behavior may be taken as evidence of extensive hydrogen bonding of the water of hydration which in turn is in agreement with the structure analysis of Lando.[7]

An examination of the spatial arrangements of the vinyl groups in calcium acrylate dihydrate, Figure 1, shows that they are situated near the center of the unit cell as two closely spaced pairs and such that a chain of vinyl groups is formed through successive unit cells parallel to the *b* axis of the crystal. The separation of vinyl groups along this direction is about 2–3 Å, *i.e.*, almost in contact. The separations along the *a* and *c* axes are 4–5 and 9–10 Å, respectively. The density measurements revealed that the lattice volume was reduced by 15% on dehydration, and the X-ray results showed that this contraction occurred along the *a* and/or *b* axes but not the *c* direction. Hirschfeld and Schmidt[8] have suggested that a necessary condition for polymerization is that the reactive groups of the monomer molecules should be within about 4 Å of each other.

Polymerization. The conversion of monomer to

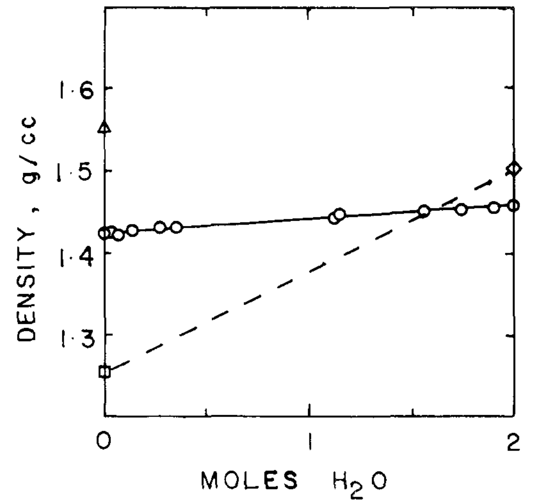

Figure 5. Density of hydrated calcium acrylate: ——, experimental; -----, calculated for H_2O removal with no volume change in unit cell; Δ, poly(calcium acrylate), experimental.

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(8) F. L. Hirshfeld and G. M. J. Schmidt, *J. Polym. Sci., Part A*, 2, 2181 (1964).

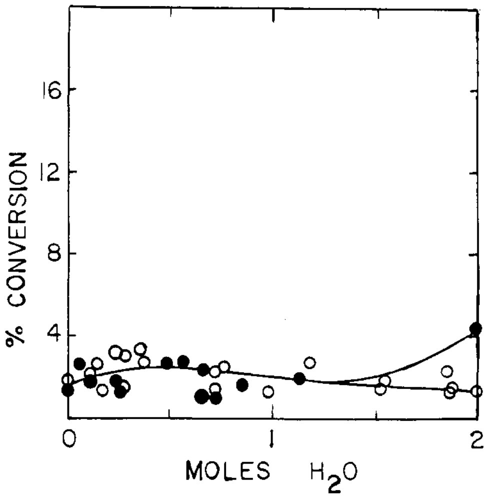

Figure 6. Solid-state polymerization of hydrated calcium acrylate at −78°: dose, 0.86 Mrad; dose rate, 2.86 × 10^4 rad/hr; ●, 10.3 days postpolymerization; ○, 0.0 days.

polymer as a function of water content at −78° is shown in Figure 6. The amount of polymerization that occurs during the low-temperature irradiation is seen to be quite small (2–4%) and very little additional polymer formation is observed when samples are allowed to postirradiation polymerize for 10.3 days outside of the radiation source. Thus at −78° hydrated calcium acrylate will polymerize slowly in source but does not undergo postirradiation polymerization.

Upon increasing the postirradiation polymerization temperature to 50°, Figure 7, a great increase in the rate of polymerization is observed. Furthermore, the observed rates are strongly dependent on irradiation dose and on the degree of hydration. The polymerization rate is seen to pass through a maximum at approximately the "hemihydrate" composition.

Figure 8 shows the postirradiation polymerization at 25° and constant dose, for time intervals from 0.5 to 41.4 days, and again the same behavior is observed. These data have been replotted at three specific degrees of hydration as a function of time in Figure 9. This latter figure illustrates that the postirradiation polymerization has no induction period and that the rapid initial polymerization rates decay to very low values. The plots follow a general pattern in which the rate diminishes with decreasing concentration of monomer. The falloff in rate is, however, clearly not associated in any simple way with this diminution in reactant concentrations. It appears, on the other hand, that some radius of activity is available which, in turn, is dependent upon the degree of hydration and that with the exhaustion of monomer in this region the polymerization stops.

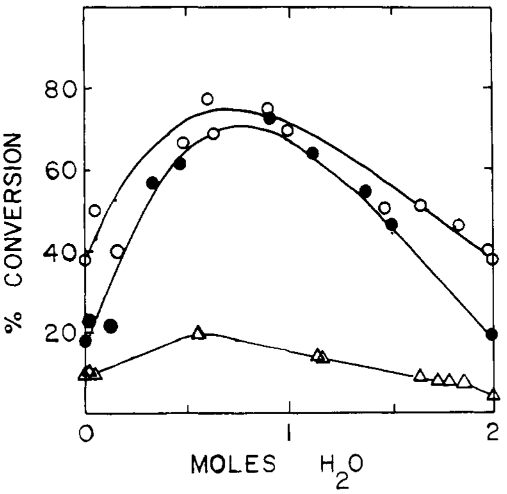

Figure 7. Postirradiation polymerization of hydrated calcium acrylate at 50°, irradiated at −78°: △, 0.23 Mrad, polymerization time 48 hr; ○, 0.86 Mrad, 48 hr; ●, 0.86 Mrad, 25 hr.

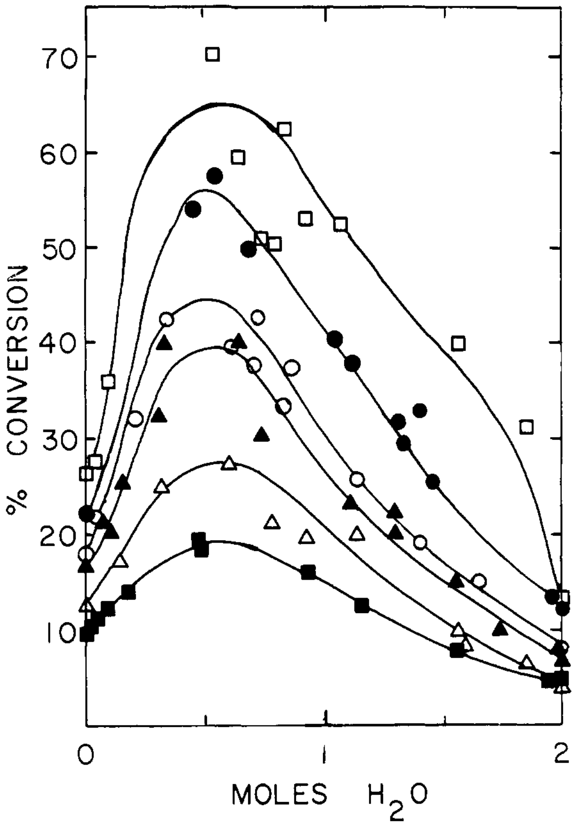

Figure 8. Postirradiation polymerization of hydrated calcium acrylate at 25°, 0.86 Mrad: ■, 0.5 days; △, 1.5 days; ▲, 6.0 days; ○, 10.1 days; ●, 22.2 days; □, 41 days.

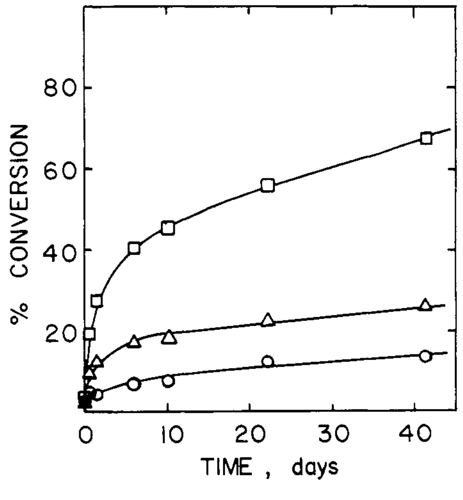

Figure 9. Postirradiation polymerization at 25°, 0.86 Mrad: ○, dihydrate; △, anhydrous; □, maximum (hemihydrate).

This radius of activity, or reaction volume concept in the case of vinyl monomers, is related to the number of monomer units which leave the crystal lattice to add to the reacting radical. In the present case, where the polymer is more dense than the monomer, a diffusion step will be required with the distance of the diffusion gradually increasing as the conversion rises. At some point termination will occur caused either by the usual coupling or other types of radical reaction, or when a reactive end group becomes buried in polymer.

The observation that the rate of polymerization of the anhydrous salt is faster than that of the dihydrate, Figure 9, can be explained by the relatively small extent of short-range diffusion which is possible in the crystalline regions. In the anhydrous form, in which most of the crystallinity or lattice order has been lost, the resulting defect structure affords increased capability for diffusion and thus a higher rate of polymerization. In addition, the reactive groups are in closer contact along the *a* and *b* directions in the anhydrous salt. That a diffusion mechanism is operative is strongly supported by the data in Figure 10, which show that, in the presence of oxygen, the polymerization rate is diminished for all compositions but a minimum conversion rate is observed at exactly the composition where the rate maximum occurs in the vacuum polymerization. These results lead to the conclusion that maximum diffusion of monomer, and therefore fast polymerization, occurs at this composition, but that in air the diffusion of oxygen is also facilitated, giving ready access to radicals and resulting in maximum inhibition by oxygen. The conversion *vs.* hydrate composition curve is thus inverted. It is further evident from Figures 7 and 10 that the extent of inhibition is greater in the amorphous anhydrate than in the crystalline dihydrate. A similar observation involving a rapid diffusion of O_2 molecules has been reported for the mixed crystal case of acrylamide–propionamide.[9] Since all diffusion in the crystalline state would probably be confined to boundaries, this lesser oxygen effect upon the dihydrate is to be expected.

If the intermediate hydrate compositions consisted of a simple two-phase (dihydrate plus anhydrate) system, it might be expected that the polymerization rates would be a simple additive function of the rates of the two phases and their relative concentrations, *i.e.*, the plot of conversion *vs.* water content, would be a straight line. Figures 7, 8, and 10 show that this is not the case. To explain the results it is therefore necessary to include the effects due to an interphase boundary within each partially dehydrated monomer particle. This highly reactive interfacial region will be characterized by dislocation lines and planes, and possibly cleavages, plus a certain amount of strain due to the lattice volume difference between the two phases. A high degree of disorder is expected in this region. Since the chain propagation occurs by small scale diffusion of the monomer to the growing radical chain, these successive diffusion steps will be strongly hindered in a perfect crystal but enhanced in a disordered and strained network, especially along dislocations and cleavages. This thesis is supported by the values of the apparent activation energies, calculated from an Arrhenius plot for the initial rates at 25 and 50° of 20, 9, and 1 kcal mol^{-1} for the dihydrate, 0.5 hydrate, and anhydrate, respectively. Since polymerization is controlled by monomer mobility, a high activation energy for lattice diffusion in the crystalline material results in a higher activation energy for polymerization. The presence of a maximum indicates that the rate in the interphase volume is much greater than the rates in either of the two extreme compositions. The position of the maximum on the rate–composition curves will be a function of the rate constants and the respective volumes, with the volume of the intermediate phase being a function of the degree of hydration. This particular topic will be the subject of a publication in the near future.

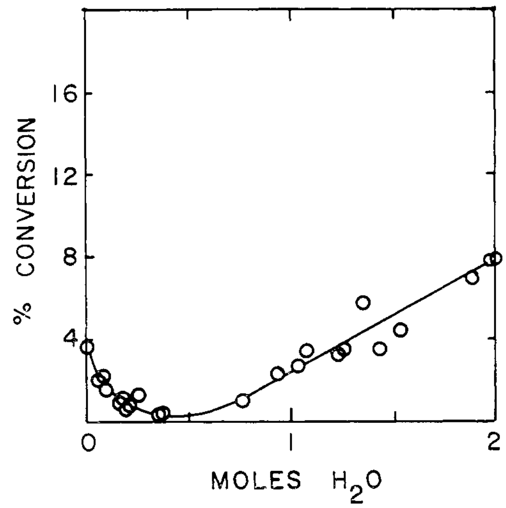

Figure 10. Postirradiation polymerization of hydrated calcium acrylate in air at 50°, 0.86 Mrad; 4 days polymerization time.

Summary

The dehydration process of calcium acrylate dihydrate at 60° *in vacuo* has been shown to be a dihydrate → anhydrous transition with a significant loss of crystallinity, a 15% contraction in the lattice volume, and that this reduction is at the expense of the *a* and/or *b* crystallographic axes.

The polymerizability of hydrated calcium acrylate has been shown to possess a marked dependence on the degree of hydration, both *in vacuo* and in air. The polymerizabilities in decreasing order are interphase boundary > anhydrate > dihydrate. The reaction is inhibited in the presence of oxygen.

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