Solid-State Polymerization of γ-Irradiated Hydrated Calcium Acrylate. Electron Spin Resonance Studies

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ABSTRACT: Electron spin resonance data have been obtained for γ-irradiated calcium acrylate samples of varying degrees of hydration. The results have been used to derive rate constants for the termination and propagation steps of the post-irradiation polymerization. The dependence of polymerization conversion on the degree of hydration is now explained by the different rates of propagation in the dihydrate, anhydrate, and interphase boundary regions.

We have previously reported a study of the dehydration of calcium acrylate dihydrate and the dependence of the solid state post-irradiation polymerization on the degree of hydration.[1] The polymerization rate showed a marked dependence on water content, with a maximum rate occurring at a "hemihydrate" composition. The overall rate was explained as the summation of the individual rates in the dihydrate, anhydrate, and interphase boundary regions, each weighted according to the volume fractions. In principle, the polymerization rate constant for each region is a function of its respective initiation, propagation, and termination rate constants, but our earlier studies did not provide quantitative data on the relative importance of these terms as a function of the degree of hydration. The present paper reports the results of a study of the concentration dependence of polyacrylate radicals on the degree of hydration and a kinetic analysis from the time dependence of radical concentration.

Experimental Section

The preparation of calcium acrylate dihydrate and the irradiation and polymerization methods have been described previously.[1] The same radiation dose was given as in the previous study, 0.86 Mrad, but at a dose rate of 4.12 × 10^5 rad/hr instead of 2.86 × 10^4 rad/hr. Calcium acrylate samples of differing degrees of hydration were sealed *in vacuo* in Spectrosil quartz tubes and irradiated; esr spectra were recorded at $-78°$. The samples were then thermostated at 25° and the spectra recorded as a function of time up to 52 days.

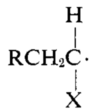
The esr spectra were obtained using a Varian V4502 spectrometer with 100-kHz modulation and very low incident power. Benzene solutions of freshly crystallized DPPH were used for calibration and sample radical concentrations were determined from the first-derivative curves by mechanical integration with a planimeter and adjusted for differences in sample tube diameter and sample packing factor.

Results and Discussion

The post-irradiation polymerization at 25° of calcium acrylate *vs.* the degree of hydration is shown in Figure 1 while the conversions, as a function of time, are compared in Figure 2 for three specific degrees of hydration.

Since the polymerization has been shown to proceed by a radical process,[1] a kinetic analysis of these data can be undertaken if one measures the numbers of radicals present throughout the polymerization period. Accordingly, radical concentration measurements were made by means of electron spin resonance.

The esr spectra, recorded at $-78°$, for irradiated calcium acrylate samples of differing degrees of hydration are shown in Figure 3a. Figures 3b, c, and d show the changes in the spectra which occur upon warming to 25° and after the samples have been maintained at this temperature for various times. The spectra are similar to those reported for other irradiated acrylic systems—acrylic acid,[2] acrylamide,[3] and acrylonitrile.[4] The spectrum arises from the polyacrylate radical



$$\mathrm{RCH_2}\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot$$

characterized by a 1:2:1 triplet caused by coupling of the unpaired electron with the α-proton and one of the β-methylene protons. The remaining β-proton interacts only to a small extent.

Only polyacrylate radicals were observed at $-78°$, Figure 3a, in agreement with previous studies that monomer addition to the initiating radical can occur at low temperatures.[5] At $-78°$ the central peak in the spectrum consists, for all degrees of hydration, of two overlapping components of approximately equal intensity, marked ○ and × in Figure 3a. For low degrees of hydration, the intensity of the ○ peak decreases rapidly with time at 25° while the intensity of the × component increases concurrently. These changes are much slower for water contents approaching the dihydrate composition. Our earlier studies[1] showed that the extent of polymerization occurring at $-78°$ was approximately 2% and was independent of the degree of hydration. The rates of post-irradiation polymerization at 25° are considerably greater for the anhydrate and low water content samples and thus the accumulation of a polymer phase within the monomer phase is much faster. It seems reasonable, therefore, to assign the ○ component of the central peak to calcium acrylate radicals of one or a few degrees of polymerization situated in an environment which is essentially unreacted monomer. The × component can then be assigned to radicals of high degrees of polymerization situated in a "polymer" phase. The different environment of the two radicals could cause slightly different conformations, resulting in the variations in esr spectra. Similar behavior has been observed for irradiated barium methacrylate.[6]

The radical concentration at $-78°$ immediately after irradi-

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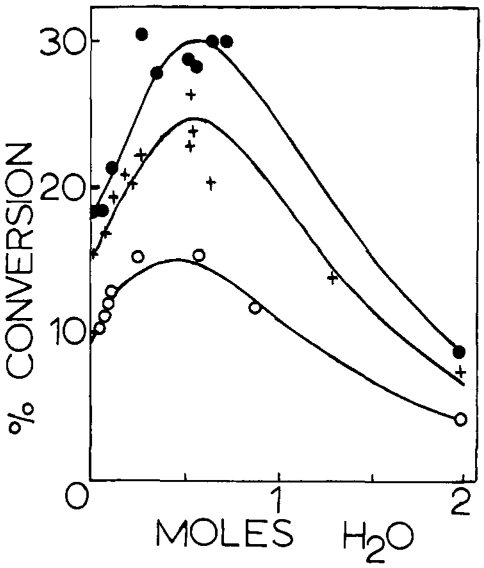
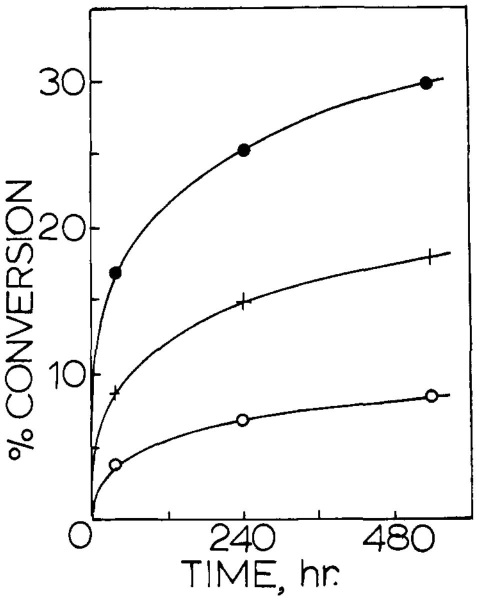


Figure 1. Post-irradiation polymerization of hydrated calcium acrylate at 25° *vs.* H_2O content, dose 0.86 Mrad at −78°: polymerization time, ○, 1.5 days; +, 10.1 days; ●, 22.2 days.



Figures 2. Rates of post-irradiation polymerization of calcium acrylate at 25°, dose 0.86 Mrad at −78°: ○, dihydrate; +, 0.5 hydrate (max); ●, anhydrous.

ation is shown, as a function of water content, in Figure 4. The concentration is linearly dependent on the degree of hydration with the highest radical yield occurring for the anhydrous material. The *G* values for polyacrylate radical production were 0.5 for the dihydrate and 3.4 for the anhydrate. There was no maximum in radical concentration at the intermediate water content which showed the maximum post-irradiation polymerization rate. The inverse dependence of radical concentration on the degree of hydration can be explained in terms of the amorphous nature of the anhydrous material. In the relatively rigid dihydrate lattice, there is less opportunity for the diffusion of the radiolytic products, both ions and radicals, away from the site of production and hence a greater rate of recombination with a resultant lower radical yield. Since γ irradiation causes radical formation throughout the bulk of the material, the total radical concentration is simply the sum of the concentrations in the dihydrate, anhydrate, and boundary phases, *i.e.*, is linearly related to the extent of crystallinity of the sample.

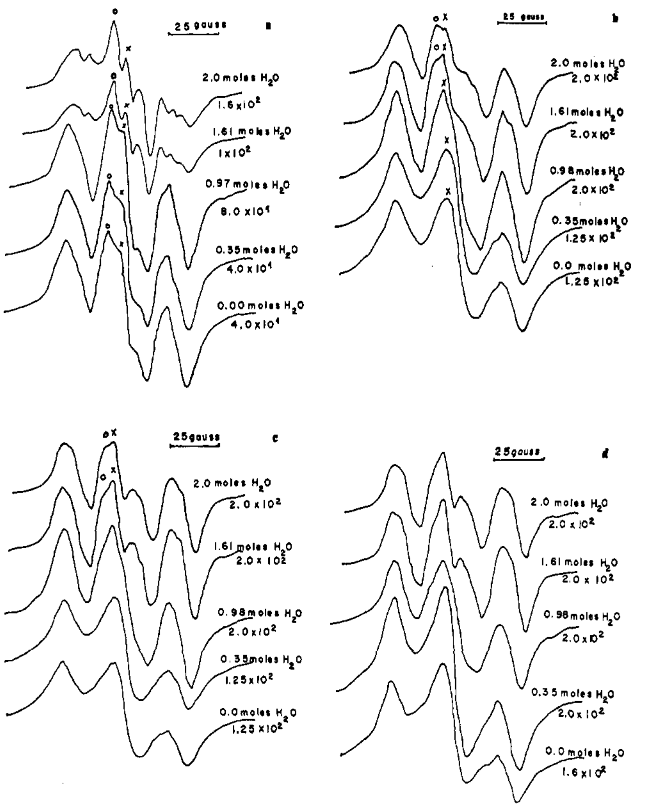


Figure 3. (a) Esr spectra of polyacrylate radicals from irradiated calcium acrylate at −78° immediately after irradiation. Numbers below the composition indicate the instrument spectrum amplitude; (b) esr spectra of polyacrylate radicals from irradiated calcium acrylate 3 hr after warming at 25°; (c) esr spectra of polyacrylate radicals from irradiated calcium acrylate, 20 hr at 25°; (d) esr spectra of polyacrylate radicals from irradiated calcium acrylate, 29.2 days at 25°

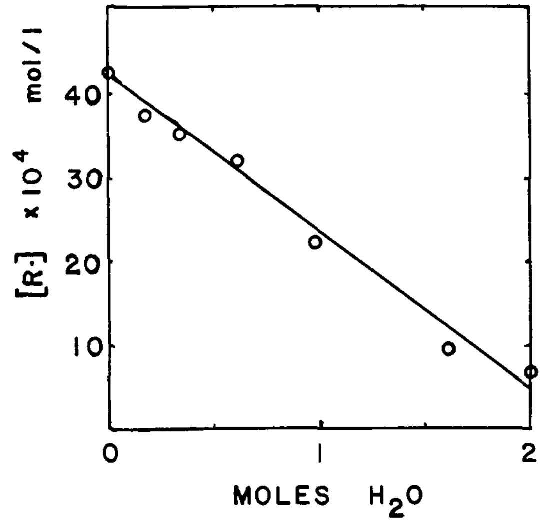


Figure 4. Concentration of polyacrylate radicals *vs.* degree of hydration of hydrated calcium acrylate at −78°, dose 0.86 Mrad at −78°.

Figure 5 contains two plots. The first shows the dependence of the radical concentration on the degree of hydration after warming to 25° while the second is a plot of the limiting radical concentrations, as a function of the degree of hydration, attained after maintaining the samples at this tempera-

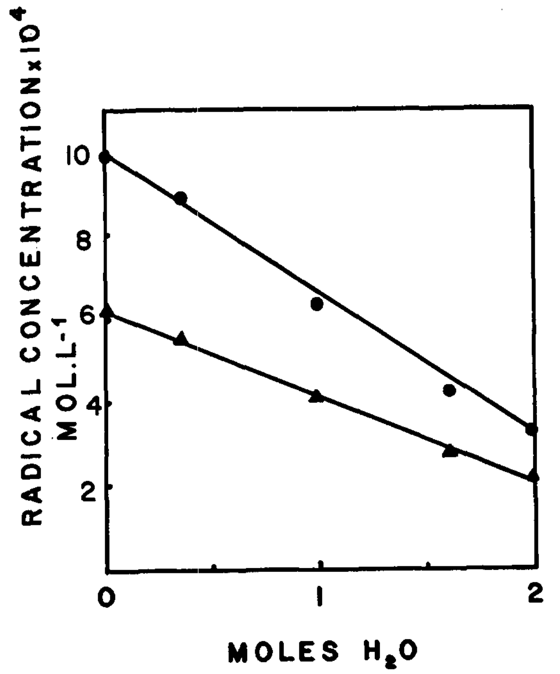


Figure 5. Concentration of polyacrylate radicals *vs.* degree of hydration of hydrated calcium acrylate, dose 0.86 Mrad at −78°: ●, upon warming to 25° from −78°; ▲, after 52 days at 25°.

ture for 52 days. Although the absolute concentrations have decreased from the values at −78°, the dependence on the degree of hydration is still evident. The time dependence of the radical concentrations is shown in Figure 6. The initial decay is fairly rapid but, after about 100 hr, almost constant values are obtained. Subtraction of the limiting radical concentrations after 52 days from the value at any given time gives the concentration of radicals which have disappeared, *i.e.*, gives the time dependence of the termination reaction, which can then be used to determine the order of the termination reaction. The data follow a second-order dependence

$$\frac{d[R\cdot]}{dt} = -k_t[R\cdot]^2 \qquad (1)$$

the rate plot for which is given in Figure 7. The slope yields a rate constant of 6.56 × 10^{-2} l. mol^{-1} sec^{-1}. It is apparent in Figure 7 that the termination is independent of the degree of hydration of the sample. However, the *fraction* of radicals which have terminated after 52 days at 25° relative to those present at −78° immediately after irradiation increases from 0.68 in the dihydrate to 0.85 in the anhydrate.

Considerable caution must be exercised in interpreting this composition-independent, second-order diminution in radical concentrations. Some speculation is, however, warranted. The picture of two polymer radicals colliding to terminate a polymerization is probably too simple an interpretation to apply. An alternative process where a radical, in a polymer phase, may combine with a small radical fragment newly freed from crystal-phase entrapment would also explain the second-order termination. The present paper, where we demonstrate the presence of radicals which exist in two different environments, lends some support to the second hypothesis, but only after a better understanding is achieved of the nature of the polymer phase as it exists *during* polymerization and not after isolation, can a well-substantiated rationale be formulated.

The radical decay pattern also strongly suggests that all radicals are not equally able to initiate polymerization. The fact that oxygen so readily inhibits polymerization[1] indicates that those radicals which do initiate are situated near grain boundaries or defects. That such should be the case has been proposed heretofore.[7]

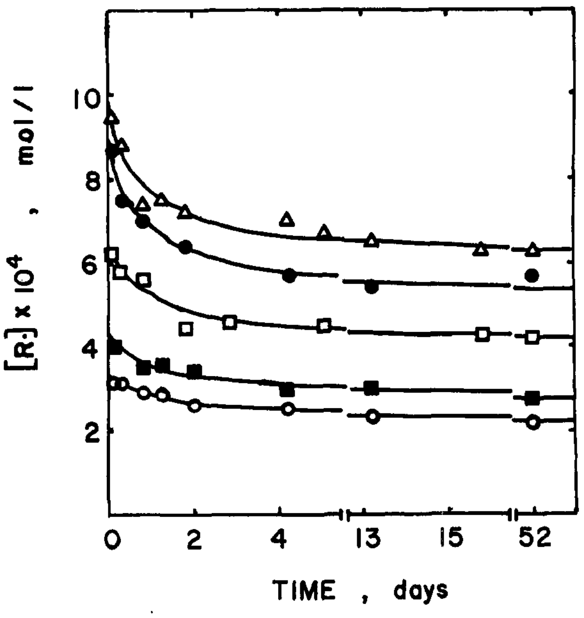


Figure 6. Rate of decay of poly(calcium acrylate) radicals at 25°, dose 0.86 Mrad at −78°: O, 2.0 mol of H_2O; ■, 1.61 mol of H_2O; □, 0.98 mol of H_2O; ●, 0.35 mol of H_2O; Δ, anhydrate.

The rates of polymerization of the calcium acrylates, R_p, can be represented by a summation of the products of the rate constants, k_j, and volume fractions, V_j

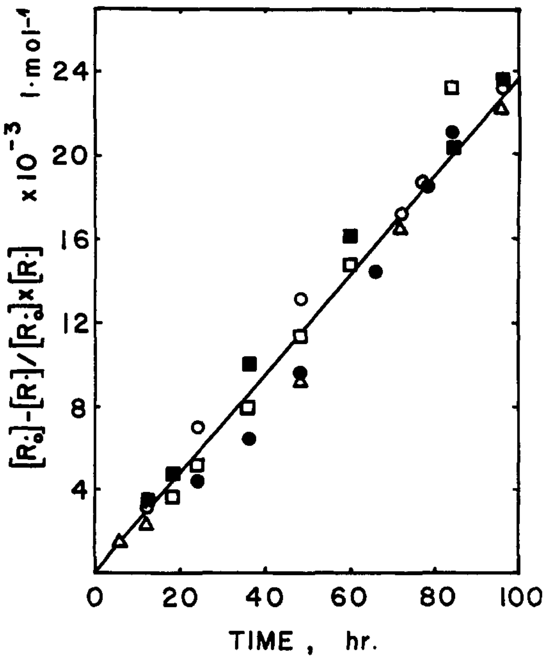


Figure 7. Second-order rate decay of poly(calcium acrylate) radicals, temperature 25°, irradiation at −78°, dose 0.86 Mrad: O, dihydrate; ■, 1.61 mol of H_2O; □, 0.98 mol of H_2O; ●,0.35 mol of H_2O; Δ, anhydrate.

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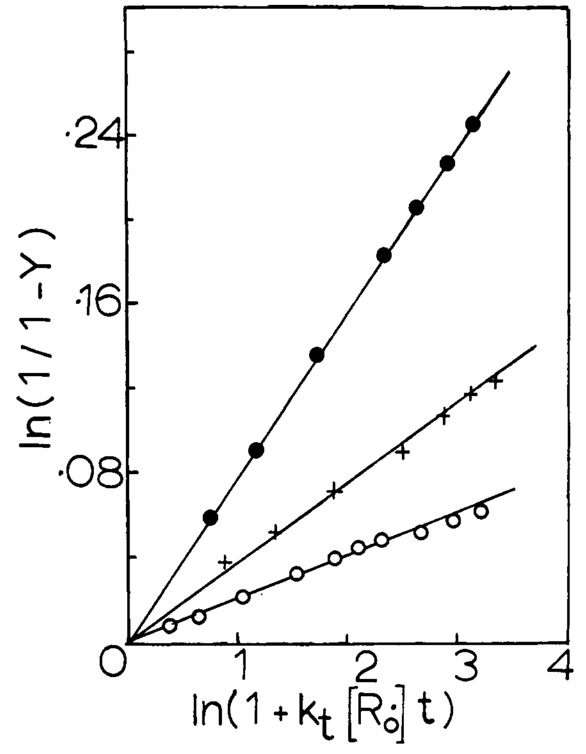

Figure 8. Kinetic plot for post-irradiation polymerization of calcium acrylate at 25°, dose 0.86 Mrad at −78°: O, dihydrate; +, anhydrate; ●, 0.5 hydrate.

$$R_p = k_1V_1 + k_2V_2 + k_3V_3 \qquad (2)$$

where subscripts 1, 2, and 3 refer to the dihydrate, anhydrate, and phase boundary, respectively. The polymerization rate constants in each case will be functions of their respective rate constants for initiation, k_i, propagation, k_p, and termination, k_t, thus

$$k_1 = f(k_{1_i} + k_{1_p} + k_{1_t}),\ \text{etc.} \qquad (3)$$

The initial radical concentration and the order and rate constants of the termination reaction have been obtained from the esr data. By combining these data with the polymerization conversion *vs.* time results, Figure 2, it is possible to determine the propagation rate constants for polymerization. Equation 1 can be integrated to give

$$[\mathrm{R}\cdot] = \frac{[\mathrm{R}\cdot_0]}{(1 + k_t[\mathrm{R}\cdot_0]t)} \qquad (4)$$

where $[\mathrm{R}\cdot_0]$ is the initial radical concentration and $[\mathrm{R}\cdot]$ is the concentration at time t. It is apparent, Figure 6, that a certain fraction of radicals do not terminate and remain trapped. The radical concentrations used in the present kinetic analysis, $[\mathrm{R}\cdot]$, refer to those which do terminate, *i.e.*, the limiting concentrations have been subtracted. The appearance of polymer is given by eq 5, where Y is the polymer yield and [M] is the monomer concentration

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_p[\mathrm{R}\cdot][\mathrm{M}] \qquad (5)$$

Equations 4 and 5 can be manipulated to give

$$\ln\left(\frac{1}{1 - Y}\right) = \frac{k_p}{k_t}\ln(1 + k_t[\mathrm{R}\cdot_0]t) \qquad (6)$$

This expression was previously derived by Morawetz and coworkers[8,9] for a polymerization terminating by a bimolecular process. All terms in eq 6 are known except k_p which can be obtained from the slope of a plot of $\ln[1/(1 - Y)]$ *vs.* $\ln(1 + k_t[\mathrm{R}\cdot_0]t)$. Figure 8 illustrates the results when this equation is applied to the polymerization behavior of the three materials referred to in Figure 2. The agreement between the data and the kinetic proposals is excellent and the k_p values for the dihydrate and anhydrate and 0.5 hydrate are 1.34×10^{-3}, 2.44×10^{-3}, and 5.05×10^{-3} l. mol^{-1} sec^{-1}, respectively. The propagation rate constant for the anhydrous material is thus almost twice that of the dihydrate and sees another doubling in the 0.5 hydrate. This latter value represents an average according to eq 2 and thus the true propagation rate constant for the interphase region must be larger than this value.

The data allow an interpretation of the different polymerization rates shown in Figure 2. The radical concentrations were shown, Figure 4, to be a function of water content, but the relationship was linear and did not follow the pattern of the R_p from Figure 2. The rate of radical disappearance was completely independent of composition, being related only to the initial radical concentration, Figure 7. Thus, of the three rate constants involved, only k_p follows the pattern of R_p. The previously observed inhibition by oxygen[1] supports the argument that k_p is diffusion dependent and that in the 0.5 hydrate the transfer of a monomer from a position on a lattice surface to the vicinity of a propagating radical is greatly facilitated relative to the same process in the two extremes of composition.

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