

to effective catalysis by the side chains. Then if allowance is made for the fact that the chromophore is confined to a polyelectrolyte coil, the remainder of the reasoning used for the P176 case in the other pH regions indicates that tethered dye in P94 behaves like that of free dye in the *cis* → *trans* isomerization.

### Bound Dye Systems

Completion of the trilogy of dye systems requires mention of the case for bound dyes. Since these systems are more complicated than the free and tethered dye systems, details will be covered separately.<sup>33</sup>

For the moment, we note that in general the *cis* → *trans* return rates of bound photochromic dye are much more rapid over the whole pH range, when polycarboxylic acids are employed, than for either of the other two types of systems.

This stems from two main factors: (1) Adsorption bound dye may be in a different sort of environment

(33) Preliminary report; ref. 1, p. 68C.

than is tethered dye. Perhaps it is not even distributed evenly throughout the macromolecular domain. (2) There are two paths for isomerization of bound dye: (a) it may isomerize while bound; (b) it may unbind, isomerize out in solution, and rebind.

Besides these factors, the rate at which binding processes occur may enter, and the binding equilibrium constants for both isomers certainly do. Rates at which the macromolecule undergoes conformation changes are perhaps superimposed.

From the data in Table II, it is obvious that both polycarboxylic acids should act as effective catalysts; this is in fact the case, but with a pH dependency which reflects the broadened titration curve of a macroion.

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## Polymerization in the Crystalline State. VI. Electron Spin Resonance Study of the Propagating Species in a Polymerizing Single Crystal of Barium Methacrylate Dihydrate<sup>1a</sup>

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Single crystals of barium methacrylate dihydrate were irradiated at  $-196^\circ$  with  $\gamma$ -rays from a  $\text{Co}^{60}$  source. The e.s.r. spectrum recorded at the irradiation temperature was isotropic and consisted of seven lines spaced at 23 gauss. This spectrum was assigned to the species  $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$  formed by the addition of a hydrogen to the double bond of a methacrylate ion. On warming to  $20^\circ$  a new and anisotropic spectrum appeared which had 9 lines when observed with the magnetic field parallel to the *a*- or *b*-axis of the pseudo-orthorhombic monomer crystal but 13 lines when the magnetic field was parallel to the *c*-axis. This spectrum was attributed to the propagating radical  $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)\text{COO}^-$ . The anisotropy of the e.s.r. spectrum of this species proves that a preferred orientation of the propagating radical in a crystallographic direction of the parent monomer is retained with at least one monomer unit added to the primary radical. When polymerization is carried to high conversion at  $50^\circ$ , the anisotropic spectrum gradually disappears, leaving an isotropic 5-line spectrum. This transformation is believed to be due to a conformational transition to a form in which one of the methylene hydrogens becomes magnetically equivalent to the hydrogen of the  $\alpha$ -methyl group, while interaction of the unpaired electron with the other methylene hydrogen becomes negligible.

### Introduction

It is a surprising fact that a variety of organic reactions may proceed in the crystalline state in spite of the restricted mobility of the reagent molecules within the crystal structure.<sup>2</sup> It is then of particular interest to determine the extent to which the geometrical arrangement of the molecules within the crystal structure of the reagent determines the characteristics of the reaction. Such "topochemical" effects may be deduced in several ways: (1) Chemically similar substances may react at very different rates in the solid state, although no corresponding differences would be expected in the liquid state.<sup>3-5</sup> (2) Different crystalline modi-

fications of the same reagent may be characterized by different reactivities.<sup>6</sup> (3) A comparison of the rates of similar reactions in the glassy and crystalline states may show that the chemical process may be either favored or hindered by the molecular arrangement in the crystal.<sup>7</sup> (4) If the reaction can proceed in alternative directions, the nature of the reaction product obtained in the solid state process may be determined by crystallographical factors<sup>8</sup> and be different from the product obtained if the reaction proceeds in the liquid state.<sup>8,9</sup> (5) The molecules of a crystalline reaction product may have a definite orientation with respect to the crystallographic directions of the reagent crystal (topotaxy).<sup>10</sup>

(1) (a) We are indebted for financial support of this study to the U. S. Atomic Energy Commission, Contract AT(30-1)-1715; (b) to whom inquiries should be addressed.

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A research program in this laboratory has been concerned particularly with evidence of topochemical phenomena in the solid state addition polymerization of crystalline vinyl and vinylidene derivatives.<sup>11-15</sup> The most convincing indications that the disposition of the reactive double bonds in the monomer crystal plays a crucial role in the polymerization process came from the wide differences in the reactivities of different acrylic and methacrylic acid salts<sup>13,14</sup> or different crystalline modifications of the same salt,<sup>14</sup> differences in the stereoregularity of poly(methacrylic acid) prepared in the crystalline and disordered phase,<sup>13,14</sup> and the retention of the infrared dichroism of *p*-benzamidostyrene crystals, if their polymerization is carried out below the glass transition temperature of the polymer.<sup>10,15</sup> On the other hand, X-ray diffraction studies indicate<sup>12,16</sup> that in typical solid state polymerization processes the polymer formed is amorphous; *i.e.*, the molecular chains seem to retain no trace of the long-range order of the monomer crystals from which they originated.

Electron spin resonance spectroscopy offers a powerful tool for the study of the extent to which the restraints of the crystal structure determine the direction of radical chain propagation. A number of investigators have found that the irradiation of single crystals of various organic compounds leads to the production of long-lived radicals with an e.s.r. spectrum depending on the crystal orientation in the magnetic field.<sup>17</sup> This shows that these radicals are highly oriented with respect to the crystallographic axes of the crystal in which they originated. The question then arises whether such a preferred orientation can be maintained during the propagation of a polymeric chain radical and the present investigation of polymerizing single crystals of barium methacrylate dihydrate was undertaken principally to throw light on this problem. However, since e.s.r. spectra obtained from radicals imbedded in single crystals tend to be much sharper than spectra obtained from radicals in an amorphous phase, the results of this study serve also to furnish additional information about the nature of the e.s.r. spectra of polymethacrylate radicals, which has been for some time a subject of controversy.

### Results and Discussion

Barium methacrylate dihydrate has been shown previously<sup>14</sup> to be monoclinic, space group  $P2_1/a$ ,  $a = 7.75 \text{ \AA}$ ,  $b = 12.1 \text{ \AA}$ ,  $c = 11.5 \text{ \AA}$ ,  $\beta = 90.5^\circ$  with four molecules per unit cell. Since  $\beta$  deviates only slightly from  $90^\circ$ , the crystal may be described as pseudo-orthorhombic, space group Pbam. Although the complete structure has not been solved, it is known that the barium ions lie in sheets perpendicular to the *c*-axis.

Single crystals of barium methacrylate dihydrate were irradiated under vacuum with 0.5 Mrad of  $\gamma$ -

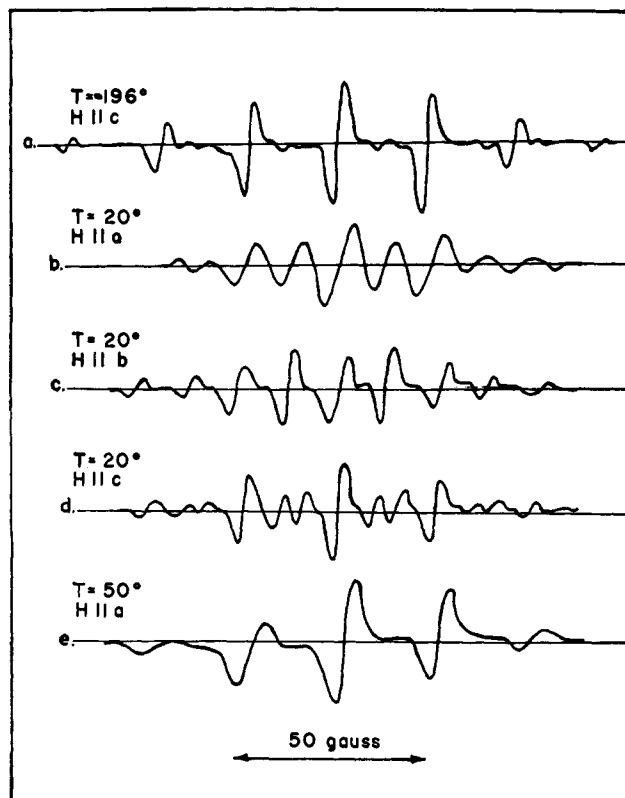
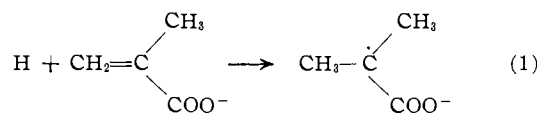


Fig. 1.—Electron spin resonance spectra of single crystals of barium methacrylate dihydrate. Spectra b, c, and d were taken after warming the sample for 2 hr. to room temperature. Spectrum e was taken after 200 hr. at  $50^\circ$ .

radiation from a  $\text{Co}^{60}$  source at  $-196^\circ$ . If the e.s.r. spectrum of the irradiated crystal was recorded at  $-196^\circ$ , a pattern of seven equally spaced lines with a binomial intensity distribution and a hyperfine splitting of 23 gauss was observed (Fig. 1a). This spectrum was almost independent of the orientation of the crystal in the magnetic field. It suggests the interaction of six equivalent protons with the unpaired electron so that the primary radical appears to be formed by the addition of a hydrogen atom to the monomer



Similar additions of a hydrogen atom to ethylenic double bonds seem to be the normal manner by which the primary radicals are formed in radiation-induced solid state polymerizations of vinyl or vinylidene derivatives.<sup>18,19</sup> The radicals formed by the loss of a hydrogen from the monomer or the water of hydration disappear apparently too fast to be detected by the usual experimental methods. It may be noted that e.s.r. spectra similar to that shown in Fig. 1a were reported also for irradiated isobutyric acid salts<sup>20</sup> and aminobutyric acid<sup>17e</sup> and were assigned in both cases to the species  $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$ . The absence of any significant anisotropy of this spectrum in our case does, apparently, not exclude the possibility of a high degree of orientation of the radical, since the hyperfine splitting

(18) R. Bensasson, A. Bernas, M. Bodard, and R. Marx. *J. chim. phys.*, **60**, 950 (1963).

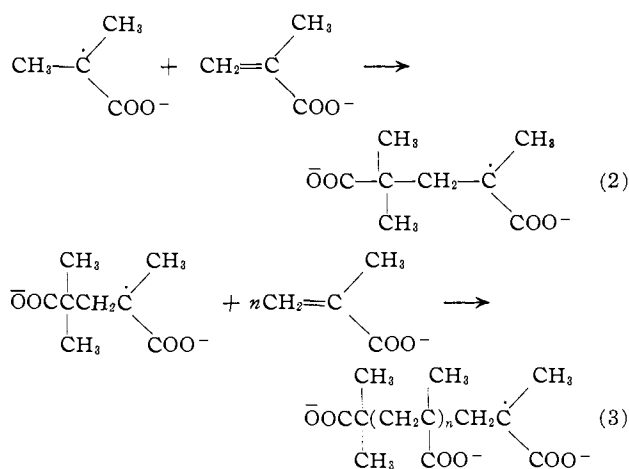
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due to the interaction of unpaired electrons with  $\beta$ -hydrogens has generally a very small anisotropic component.<sup>17c,f</sup>

When the irradiated barium methacrylate dihydrate crystals were warmed to about  $-80^\circ$ , the spectrum was observed to change slowly into that of another species. This transformation was studied in detail at  $20^\circ$ , where it was completed in about 2 hr. The new spectrum was strongly anisotropic with nine lines at a uniform spacing of 11.5 gauss when the  $a$ - or  $b$ -axis was parallel to the magnetic field. When the magnetic field was parallel to the  $c$ -axis, the spectrum was found to consist of thirteen lines. It could be described as a system of five lines 23 gauss apart containing a doublet with a spacing of 5.5 gauss centered in each of the four intervals. Typical examples of these spectra are shown in Fig. 1b, 1c, and 1d. Since irradiated crystals of barium methacrylate dihydrate have been observed to polymerize in the solid state,<sup>14</sup> the new spectrum may be presumed to be due to the propagating chain radical represented by



The unpaired electron will then interact with three equivalent hydrogen atoms of the methyl group and two hydrogen atoms of the methylene, which will exert an effect depending on the molecular conformation. According to Heller and McConnell,<sup>17c</sup> the isotropic component of the hyperfine splitting is given by

$$Q(\theta) = B \cos^2 \theta \quad (4)$$

where the constant  $B$  has a value of about 46 gauss and  $\theta$  is the angle between the  $\text{C}_\beta\text{-H}$  bond and the symmetry axis of the  $p_z$ -orbital, both projected onto a plane perpendicular to the  $\text{C}_\alpha\text{-C}_\beta$  bond. If the propagating chain radical has a conformation such as to maximize the distance between the bulky substituent of the methylene group from the methyl and carboxylate groups attached to the  $\text{C}_\alpha$  atom (Fig. 2a) then  $\theta = 60^\circ$  for both methylene hydrogens. The hyperfine splitting due to the methylene hydrogens will then be exactly half of that due to the hydrogens in the freely rotating methyl group and a 9-line spectrum such as shown in Fig. 1b and 1c would be expected.<sup>21</sup> On the other hand, a 13-line spectrum similar to that in Fig. 1d would correspond to a conformation in which the methylene group is rotated through a small angle so as to lead to different values of  $\theta$  for the two hydrogen

atoms ( $\theta_1 = 56^\circ$ ,  $\theta_2 = 64^\circ$ ). We are then led to the conclusion that the methylene hydrogens are nonequivalent and that the anisotropic component of the hyperfine coupling tensor is responsible for the coalescence of the 13-line spectrum into the 9-line pattern in certain crystal orientations. In any case, the results lead to the striking conclusion that the primary radical may add at least one monomer unit to produce a radical which is highly oriented with respect to the crystallographic directions of the monomer crystal. This is a remarkable result considering the highly exothermic nature of the reaction and the large bulk of both interacting species. It is in sharp contrast to the result obtained with irradiated single crystals of acrylic acid, when the e.s.r. spectrum became isotropic as soon as the primary radical was converted to the propagating chain radical.<sup>19</sup>

Previous studies have shown<sup>14</sup> that the solid state polymerization of irradiated barium methacrylate dihydrate is a very slow process at room temperature, leading to a yield of 3% polymer after 670 hr. at  $25^\circ$ . The reaction becomes, however, much more rapid at  $50^\circ$ , where a conversion of 58% was obtained after 162 hr.<sup>14</sup> It was, therefore, of interest to observe the changes in the e.s.r. pattern if polymerization was allowed to proceed to high conversion at that temperature. When the irradiated crystal was heated to  $50^\circ$ , the intermediate lines in each 23-gauss interval gradually disappeared until only a 5-line spectrum as shown in Fig. 1e remained. It should be noted that the anisotropy of the spectrum was observable as long as the intermediate lines were visible and the process had, therefore, the appearance of a reaction in which a highly oriented species is transformed into a new radical with a random orientation. The species with the 5-line e.s.r. spectrum may be represented tentatively by the conformation shown in Fig. 2b where one methylene hydrogen is characterized by  $\theta_1 = 45^\circ$ , thus becoming magnetically equivalent to the hydrogens in the freely rotating methyl group. The other methylene hydrogen, with  $\theta_2 = 75^\circ$ , would lead to a hyperfine splitting of only 3 gauss which may possibly not be resolved.

It is interesting to speculate about the possible causes of such a conformational transition in the propagating chain radical. One possibility is that the first monomer units adds to the primary radical much more easily than successive monomer molecules, so that we may observe at  $20^\circ$  predominantly the dimer radical, which is transformed to the longer chain radicals at a significant rate only at  $50^\circ$ . It is not unreasonable to assume that these two species are characterized by different con-

formations. If we represent them by  $\text{RCH}_2\dot{\text{C}}\begin{array}{l} \text{CH}_3 \\ \text{COO}^- \end{array}$  then it may be seen by inspection of eq. 2 and 3 that the R group has a plane of symmetry in the dimer, but not in the longer chain radicals, which contain an asymmetric carbon next to the methylene residue. It might then be expected that the C-R bond would be eclipsed with respect to the  $p_z$ -orbital in the dimer radical, while in the longer chain radicals it would be twisted to one side or the other. It is also possible that the conformational transition is due to the cumulative effect of steric restrictions involving a number of monomer units. Evidence for such a phenomenon has

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been found from high resolution n.m.r. studies of polystyrene, which undergoes a characteristic conformational change as the chains are extended from about ten to about twenty monomer units.<sup>22</sup> There is, however, a disturbing discrepancy between our results and the 9-line e.s.r. spectra observed in experiments in which long chain polymethacrylate radicals were trapped in a gel.<sup>23,24</sup> The significance of this difference is at present unknown.

Like other vinyl-type monomers polymerizing in the solid state,<sup>12,16</sup> crystalline barium methacrylate dihydrate is transformed to a polymer which appears amorphous by the criterion of its X-ray diffraction pattern. It was suggested that evidence of the topochemical control<sup>25</sup> of solid state polymerization reactions may be reconciled with the formation of amorphous polymer if it is assumed that the active end of the propagating chain is attached to the surface of monomer crystallites, while the bulk of the chain lies in a separate amorphous phase.<sup>11,12</sup> This concept is consistent with the interpretation of the present investigation as outlined above since the monomer crystal breaks up in the course of the polymerization process into small crystallites which become increasingly disordered with respect to each other as the reaction attains a high degree of conversion.

### Experimental

Barium methacrylate was prepared by neutralization of an aqueous solution of freshly distilled methacrylic acid (Rohm and Haas). Crystals of the dihydrate were grown from a filtered aqueous solution by slow evaporation at 20°. The crystals were diamond-shaped platelets whose long and short diagonals were found to be parallel to the *b*- and *a*-axes, respectively, of the unit cell as described in the preceding section. Single crystals of barium methacrylate dihydrate were enclosed in Spectrosil tubes sealed under vacuum. They were exposed at -196° to 0.5 Mrad of  $\gamma$ -radiation from a Co<sup>60</sup> source.

The e.s.r. spectra of the irradiated crystals were recorded on a

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(25) A term introduced by Kohlschütter (*Z. anorg. Chem.*, **105**, 1 (1918)) to describe the dependence of a reaction on the geometrical arrangement of the reagent molecule in its crystal structure.

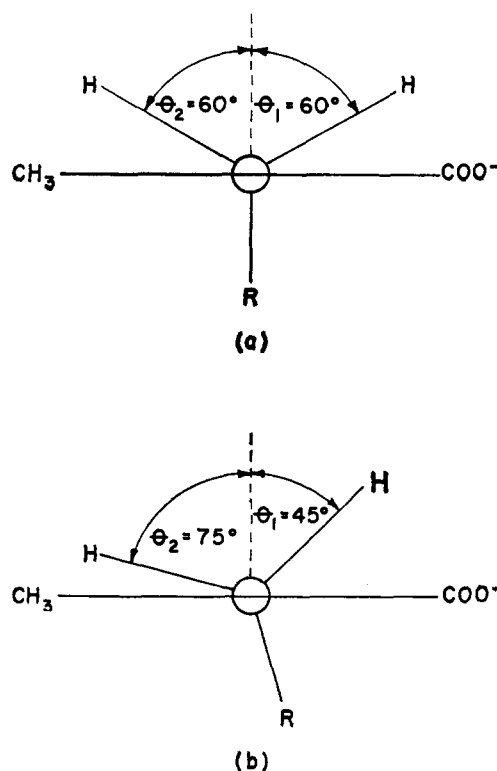


Fig. 2.—Conformation of the radical  $RCH_2\dot{C}\begin{matrix} CH_3 \\ \diagup \\ COO^- \end{matrix}$  with equivalent methylene hydrogens (a) and with one of the methylene hydrogens equivalent to the hydrogens in a freely rotating methyl group (b).

Varian Model V-4500-10A spectrometer in the X-band region using a 100-kc. sweep frequency. The low temperature spectra were taken with the sample enclosed in the Spectrosil tube and only crystal orientations in which the *b*-axis was perpendicular to the magnetic field could be studied under these conditions. At room temperature the spectra were found to be unaffected by exposure of the crystals to the atmosphere, apparently due to negligibly slow diffusion of oxygen through the crystals. Under these conditions the crystals could be removed from the tube, facilitating their orientation relative to the magnetic field. It was necessary to operate at a very low microwave power level, since there was a marked tendency for the resonance to saturate, so that additional lines appeared in the spectrum at higher microwave power, presumably due to species present in very low concentration.

[CONTRIBUTION FROM THE DIVISION OF APPLIED CHEMISTRY (N.R.C. No. 7956), NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA]

## Electron Spin Resonance in Irradiated Glycine Crystals

BY J. R. MORTON

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Irradiated glycine crystals enriched with 55%  $NH_3^+C^{13}H_2CO_2^-$  have been studied by electron spin resonance. The two radicals which are formed both exhibit  $C^{13}$  hyperfine interaction and are shown to be  $NH_3^+CHCO_2^-$  and  $CH_2CO_2^-$ . The methylene group in  $CH_2CO_2^-$  is apparently undergoing hindered rotation about the C-C bond.

### Introduction

The interpretation of the electron spin resonance spectra of radiation-damaged glycine ( $NH_3^+CH_2CO_2^-$ ) has been the subject of some conjecture since the first experiments<sup>1</sup> in 1955. The spectrum of irradiated powdered glycine is a broad triplet variously assigned<sup>1-3</sup>

(1) W. Gordy, W. B. Ard, and H. Shields, *Proc. Natl. Acad. Sci. U. S.*, **41**, 983 (1955).

to the radicals  $CH_2NH_3^+$ ,  $CH_2CO_2^-$ , and  $NH_2$ . Uebersfeld and Erb<sup>4</sup> obtained spectra from irradiated single crystals of glycine and concluded that two radicals were present. Ghosh and Whiffen<sup>3,5</sup> analyzed the single

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