

nucleation of polymer particles as a second phase.⁽⁶⁷⁾ Post-polymerization is only observed at temperatures above about -20°C .

The occurrence of reactions which give rise to the observed changes in the e.s.r. spectrum requires a certain molecular mobility at the radical site, probably a lattice defect. At any given reaction site the mobility will be controlled by the detailed local environment and, since there is likely to be a spectrum of defects, there will be a range of local environments. Thus it is to be expected that as the temperature is raised the number of sites possessing sufficient molecular mobility to allow reaction will gradually increase; the observed change will, therefore, take place over a fairly wide temperature range.⁽³⁷⁾ Direct evidence for such a range of imperfections has been obtained in the solid-state polymerization of methacrylic acid.⁽²⁵⁾

Irradiation of acrylamide at 20°C also leads to the formation of free radicals which exhibit the normal triplet e.s.r. spectrum. Ueda and Kuri⁽⁶¹⁾ report that after low radiation doses ($\sim 10^5$ rad) storage at 25°C causes a slight change in spectrum but no reduction in radical concentration. Subsequent heating to 50 – 60°C produces a rapid decay in radical concentration but very little polymerization in the solid state, although melting the crystals produces significant polymerization. At higher doses ($\sim 10^6$ rad) considerably more polymerization is observed in the crystalline state. Under the latter conditions a reduction in radical concentration accompanies polymerization, but stable radicals do remain trapped in the solid in detectable concentrations. It has previously been shown that, after irradiation at low temperatures, the radical concentration decreases to 52 per cent of its initial value after 60 hr at 45°C , but the rate of polymerization decreases by a factor of a hundred.⁽³⁴⁾

Similar results are obtained with irradiated acrylic acid (m.p. 12.6°C). The primary $\text{CH}_3\dot{\text{C}}\text{H}(\text{COOH})$ radicals are orientated in the crystal in two distinct directions, corresponding to the orientations of the unreacted vinyl groups in the monomer crystal lattice.⁽⁵⁶⁾ The radicals, whose concentration is proportional to dose up to 10^8 rad, are stable at -196°C but decay slightly on warming to -100°C , without change in spectrum. At -80°C there is a further reduction in radical concentration accompanied by a marked change in the e.s.r. spectrum; the anisotropic double quartet collapses into an isotropic triplet. This change corresponds to the formation of $\sim \text{CH}_2\dot{\text{C}}\text{H}(\text{COOH})$ radicals randomly orientated in the crystal. The radical concentration decreases at about -50°C to an undetectably low level, but polymerization does not occur until -25°C ,⁽⁵⁶⁾ above which the rate of polymerization increases rapidly with temperature. Molecular motions in the crystalline monomer become detectable at about -30°C , and increase steadily with increasing temperature; from broad-line n.m.r. data it is thought that these movements are rocking motions of hydrogen-bonded dimer units of monomer;⁽⁶²⁾ at temperatures above about 0°C more extensive motions are present.

It is also difficult to detect free radicals by e.s.r. during the u.v. initiated solid-state polymerization of this monomer.⁽²³⁾

In contrast to acrylic acid, free radicals are readily observed during the solid-state polymerization of methacrylic acid at all temperatures up to the melting point (16°C).^(23, 63) Ultraviolet irradiation of methacrylic acid, above about 0°C, gives rise to a 9-line e.s.r. spectrum, similar to that obtained by trapping radicals during liquid-phase polymerizations of methyl methacrylate. There has been considerable argument as to the origin of this spectrum but it now seems certain that the spectrum of the propagating radical arises from

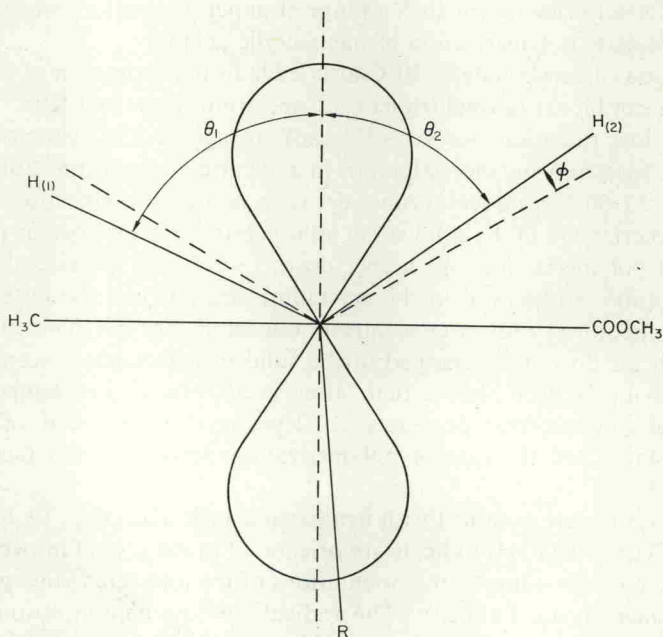


FIG. 1.

the single radical species $\sim C_{\beta}H_2\dot{C}_{\alpha}(CH_3)COOMe$, in which there is hindered rotation about the $C_{\alpha}-C_{\beta}$ bond. Consequently, certain preferred conformations are adopted in which the methylene protons interact with the unpaired spin to different extents. Only the α -methyl and β -methylene protons contribute to the hyperfine structure. Figure 1 represents a projection along the $C_{\alpha}-C_{\beta}$ bond, where H_1 , H_2 are the methylene hydrogens and R the remainder of the growing chain, $\theta_1 + \theta_2 = 120^\circ$.

In the symmetrical conformation $\theta_1 = \theta_2 = 60^\circ$, $\phi = 0^\circ$ and H_1 and H_2 are equivalent. Symons⁽⁶⁴⁾ proposed that the 9-line spectrum arises from two preferred conformations, $\phi = 0^\circ$ and $\phi = 15^\circ$, present in different pro-