portions. This view has been confirmed by Kourim and Vacek,[65] using variously deuterated monomer, and by Fischer[66] and co-workers, who obtained highly resolved spectra of the propagating radicals in solution.

Irradiation of methacrylic acid (crystallized below about 0°C) at lower temperatures (say, about $-50°C$) gives rise to a 13-line e.s.r. spectrum which we attributed to the existence of a preferred conformation[63] with $\phi = 5°$ (see Fig. 1). This restricted conformation results from the lattice forces and the low molecular mobility at these lower temperatures. As the temperature of irradiation is raised to about $-5°C$ the spectrum gradually changes from 13 to 9 lines as the molecular mobility increases[62] and the radicals relax from their restricted conformation.[63, 67] Most experimental spectra are mixtures of the 13 and 9-line spectra. Prolonged irradiation at low temperatures also causes the 13-line spectrum to change to a mixed spectrum as polymerization proceeds,[25, 63] and polymerization is more rapid under conditions where the 9-line spectrum is observed.[23, 31]

Addition of radiolytic hydrogen to itaconic acid produces the primary radical $CH_3\dot{C}(COOH)CH_2COOH$. The e.s.r. spectrum of this radical results from the interaction of the unpaired electron with the same atoms as in the propagating methacrylic acid radical, and at room temperature the e.s.r. spectrum corresponds to a single conformation, similar to that in Fig. 1 ($R = -COOH$), with $\phi = 10°$.[57]

γ-irradiation of barium methacrylate at $-196°C$ gives rise to similar results;[58] the primary radical is $(CH_3)_2\dot{C}COO^-$ in which both methyl groups are rotating. O'Donnell et al.[58] observed that on subsequent heating to $-80°C$ the e.s.r. spectrum changes as the primary radical is transformed into another species. From single crystal studies it has been shown that this second radical is orientated with respect to the crystal lattice and is a methacrylate radical in a restricted conformation, similar to that described for methacrylic acid, with $\phi = 4°$. This restricted conformation is stable to temperatures about 50°C, below which polymerization is very slow. Above this temperature the spectrum changes gradually to an isotropic 5-line spectrum corresponding to a propagating radical in a preferred conformation with $\phi = 15°C$; under these conditions polymerization is much more rapid. It has been suggested[58] that the adoption of this second preferred conformation may be due to the attachment of the propagating radical to the lattice during polymerization, with the bulk of the polymer chain existing in an amorphous phase; the lack of orientation was attributed to disintegration of the crystal during polymerization into crystallites which become disordered. Alternatively, it could be suggested that the radical is detached from the crystal lattice and therefore anisotropic, with the preferred conformation due to the presence of the barium ions which will, on average, be associated with two carboxyl groups.

Low-temperature irradiation of other monomers also leads to the formation of primary radicals corresponding to the addition of radiolytic hydrogen

atoms to monomer. With acrylonitrile[54, 68] and methacrylamide,[54, 55] however, there is evidence for the presence of other radicals stable at these low temperatures. In irradiated acrylonitrile the extra lines in the e.s.r. spectrum have been attributed to the $CH_2 = \dot{C}CN$ radical.[54] Methacrylamide apparently gives rise to two additional radicals and it has been proposed[55] that these are $H_2N\dot{C} = O$ and $RCH_2\dot{C}(CH_3)CONH_2$, where R may be $CH_2 = C(CONH_2)CH_2$— or $CH_2 = C(CH_3)$—, formed by loss of α-hydrogen or the amide group, respectively, from the monomer. In both these cases, and others, on warming to temperatures where polymerization occurs, the spectrum of the normal propagating radical appears. Both spectral changes and reductions in radical concentration in acrylonitrile samples are associated with the occurrence of solid-state transitions.[68]

Similar results have been obtained as a result of direct addition of H and D atoms (produced in a microwave discharge) to monomers.[69] Using methyl methacrylate, acrylonitrile, and styrene, the predominant species formed result from addition of H or D to the unsubstituted end of the vinyl group.

The solid-state polymerization of monomers discussed so far in this section is generally assumed to proceed by a radical mechanism. It is, however, always possible that ionic intermediates play a part in some of these polymerizations since the detection of free radicals in irradiated solids is not proof of the mechanism. Indeed, radicals have been observed in some irradiated monomers where solid-state polymerization is thought to proceed by an ionic mechanism. γ-irradiation of isobutene in a 3-methyl pentane glass at $-196°C$ gives rise to two superimposed e.s.r. spectra of 8 and 15 lines, both of which arise from the presence of isobutene.[10] The two spectra were attributed to different conformations of the $(CH_3)_2\dot{C}CH_2R$ radical, and it has been suggested that the primary species are radical cations, with propagation proceeding by a cationic mechanism.[70]

Other solid-state polymerizations of unsaturated monomers which are thought to proceed by an ionic mechanism but involve the formation of radical ions as primary species are those of conjugated dienes[71] (initiated by electron bombardment at $-196°$), vinyl carbazole[72] at 20°C (initiated by added electron acceptors which form charge-transfer complexes with the monomer), and nitroethylene[73] in a 2-methyl tetrahydrofuran glass (γ-irradiation at $-196°C$). In the first two cases it has been suggested that propagation is cationic and in the last case anionic.

Variations in Crystal Structure

It may be anticipated that, if a monomer can exist in more than one crystalline modification, each modification will exhibit a different reactivity in the solid state. Any such change in reactivity implies that the control exercised over the reaction by the lattice varies with the crystal structure,