

in an environment where reaction cannot take place. It is then assumed that reaction does not occur in such piled up groups of dislocations, or, alternatively, it is possible that reaction in these localized regions is not observed under the experimental conditions employed. Subsequent removal of the stress allows the dislocations to become distributed throughout the lattice again and, at least in methacrylic acid, to return to their original lattice sites, where radicals are already present.^(23, 24) It is not clear whether the induction period observed on removing the stress during the continued irradiation of acrylic acid is caused by dislocations taking up new sites in the monomer or by the extremely low radical concentrations present in these crystals. This type of experiment is extremely sensitive to experimental conditions and is discussed further in the section dealing with effects of pressure.

The view that dislocations are important as reaction sites in polymerizations of crystalline monomers has recently received general support from studies of lattice imperfections in sucrose. Thomas and Williams⁽⁵¹⁾ have demonstrated that a detailed examination of sucrose crystals reveals various features very similar to those attributed to the presence of dislocations in metal crystals. By suitable etching techniques it has been shown that dislocations emerge at the {001} faces of cleaved sucrose crystals, and the presence of high dislocation densities along grain boundaries has been demonstrated in this way (similar etch pits have also been observed in other organic crystals).^(52, 53) Further, it was demonstrated that water, liberated during the heating of sucrose crystals, is retained at the dislocation cores. Etching experiments provided evidence that dislocations in these crystals are mobile at temperatures below the decomposition temperature. Prolonged heating under vacuum, at temperatures where decomposition does occur, gives rise to decomposition volcanoes on the surface of the crystals, again probably situated at dislocation sites. Associated with these decomposition volcanoes are satellite volcanoes which suggest that dislocation multiplication occurs during decomposition. It was also noted that regions of higher imperfection density undergo preferential caramelization when sucrose crystals are heated.

Results of experiments of the types outlined above demonstrate that lattice imperfections are important as reaction sites. Further confirmatory evidence arises from the sensitivity of many of these reactions to the presence of very small concentrations of chemically inert impurities, from the general irreproducibility of reaction rates, and from the sigmoid nature of the conversion-time curves often observed during continuous irradiation at the polymerization temperature. Such additional evidence is referred to elsewhere in this review.

Electron Spin Resonance Studies

The technique of electron spin resonance (e.s.r.) has been applied to a number of solid-state polymerizations. In some cases, the technique has been

used simply as a means of detecting the presence of radical species with a view to elucidating the mechanism of the polymerization. In others, workers have used measurements of free radical concentration in attempts to interpret reaction kinetics. Probably the most important applications of this technique result from detailed studies of changes in the spectra and radical concentrations under various experimental conditions, when information related to the mobilities of monomer molecules in the immediate vicinity of the radicals is obtained; such changes often occur gradually over a fairly wide temperature range. Free radicals are produced in a number of crystalline vinyl monomers,⁽⁵⁴⁾ including acrylamide,⁽³⁷⁾ methacrylamide,⁽⁵⁵⁾ acrylic acid,⁽⁵⁶⁾ itaconic acid,⁽⁵⁷⁾ and barium methacrylate⁽⁵⁸⁾ when subjected to high-energy irradiation at low temperatures (say -196°C); the e.s.r. spectra of the primary radicals are consistent with addition of a hydrogen atom to the unsubstituted end of the monomer. The mechanism of radical formation at these low temperatures is the capture, by monomer, of radiolytic hydrogen atoms produced by interaction of ionizing radiation with monomer. Evidence that monomers act as scavengers of hydrogen atoms is also provided from measurements of yields of radiolytic hydrogen.⁽⁵⁹⁾ There appears to be no evidence for the formation of other radicals (formed, for example, by loss of a hydrogen atom) which are stable in the above monomers at these low temperatures.

Studies on the orientational dependence of the e.s.r. spectra of irradiated single crystals of acrylic acid⁽⁵⁶⁾ and acrylamide⁽³⁷⁾ show that the primary radicals $\text{CH}_3\dot{\text{C}}\text{HX}$ ($\text{X} = \text{COOH}$, CONH_2) are orientated along preferred directions in the crystal lattices. In each case the spectrum consists of two overlapping quartets.

Adler and Petropoulos⁽³⁷⁾ have shown that on warming crystals of acrylamide (m.p. 86.3°C), irradiated at -196°C , the first major change in the e.s.r. spectrum occurs at temperatures above -125°C (e.g. -80°C); the original five-line spectrum changes to an anisotropic triplet. This new spectrum can be attributed to the addition of a monomer molecule to the original radical, producing a species formally identical with the propagating radical. No polymerization occurs at these low temperatures and from crystallographic considerations it has been suggested that the primary radical adds to a nearest neighbour molecule in the direction of the two-fold screw axis of the crystal.⁽⁶⁰⁾ Reaction probably stops at about dimer formation since the radical is then out of phase with the crystal lattice⁽⁶⁰⁾ and further propagation requires addition to a nearest-neighbour molecule in some other direction with consequent loss of anisotropy. Further warming to about -40°C causes a decrease in radical concentration and a slight change in the spectrum. In the temperature range -30° to -20°C all anisotropy in the e.s.r. spectrum is lost. It is at this stage that the mobility of the molecules in the vicinity of the radical becomes sufficiently great to allow further propagation and, presumably, the