

since the idea of reaction proceeding in a limited number of defects is unrealistic. High rates of polymerization are often associated with high molecular mobility; at 4°C broad-line n.m.r. experiments show that a fraction of the monomer molecules in acrylic acid are sufficiently mobile to allow partial resolution of the resonance peaks of the individual protons.⁽⁶²⁾ The in-source polymerizations are often characterized by sigmoid conversion-time curves, autocatalytic to high conversion. As mentioned in the discussion of reaction kinetics, the autocatalytic behaviour could be a consequence of the formation of an amorphous polymer phase in the original imperfections and reaction occurring at the monomer-polymer interface, thus causing the reaction to accelerate as the area of the interface increases. If this process continued indefinitely the results of observations on partially polymerized crystals would be expected to show the continuous growth of a relatively small number of polymeric particles. The results of Sella *et al.*^(48, 49) on partially polymerized crystals of acrylamide appear to suggest that polymer particles do grow in the manner described above to diameters of the order of 300–400 Å, but they also indicate that the number of nuclei increases during polymerization. As polymerization proceeds in a dislocation, strains develop at the monomer-polymer interface and in the surrounding lattice. This strain could give rise to dislocation multiplication, and hence increase the number of reaction sites, giving autocatalytic behaviour. There is evidence of dislocation multiplication in the thermal decomposition of sucrose where reaction gives rise to “volcanoes” on the crystal surfaces, probably at the points of emergence of dislocation lines. These volcanoes are surrounded by a ring of small satellite “volcanoes” and represent the formation of new reaction sites.⁽⁵¹⁾

At the temperatures where polymerization is rapid one can still visualize that the processes described for reactions at low temperatures occur in the dislocations but at a much higher rate, so that there is no evidence of radicals in their restricted forms. It is possible that under these conditions radicals are not formed in a specific conformation. Relatively, propagation must be considerably enhanced by the increase in thermal motions in the crystals. There is also evidence that propagation is assisted by light of wavelengths too long to give rise to radical formation,⁽²⁵⁾ the mechanism for this is presumably the decay of excitons in the imperfections, effectively increasing the thermal motions. We may now speculate on the nature of the physical effect which brings about the gradually decreasing rate of polymerization during the post-irradiation reactions of many monomers. In the absence of radiation no new polymeric nuclei will be formed and extensive post-polymerization requires the continued growth of existing nuclei. The results of Sella *et al.*^(48, 49) appear to show that at high conversions polymerized crystals of acrylamide contain large numbers of small nuclei. It might be suggested that the nuclei only grow readily to 300–400 Å in diameter, and this may indicate the area

around the dislocation core where monomer molecules are sufficiently displaced from their lattice positions to react readily under the reaction conditions. Further growth of these nuclei may be slow and depend on the rate at which monomer molecules can leave the more perfect regions of the lattice.

The mechanism suggested above is largely based on evidence from the polymerization of monomers carrying small substituent groups, e.g. acrylamide and acrylic and methacrylic acids. In these cases there is no evidence that the substituent groups on monomer molecules which have been incorporated into polymer play any further part in the reaction. Although the basic features of this mechanism might describe the solid-state polymerization of other monomers, in the case of monomers carrying large and strongly interacting substituent groups the details would require modification to take account of possible side-chain crystallization in the polymer and the retention of strong interactions between polymer and residual monomer.

Effects of Additives

The influence of additives has been studied with various objectives in view. Two types of experiment, which account for a large proportion of these studies, but not discussed in this section, are the use of known polymerization initiators to induce polymerizations in which the nature of the propagating species is known, and the use of inhibitors to determine the nature of the propagating species in radiolytically induced polymerizations. The studies described in this section are concerned with the presence of additives in concentrations greater than impurity levels; the influence of low concentrations of inert impurities has already been discussed.

Acrylamide and propionamide form solid solutions in all proportions, and the polymerization of acrylamide at 25°C in these solid solutions is the most extensively studied binary system. Fadner and Morawetz⁽³⁴⁾ found that plots of fractional conversion against time for the post-irradiation reaction of pure acrylamide and the solid solution containing 10 per cent propionamide are identical, and that for concentrations up to 50 per cent propionamide almost identical curves are obtained up to 10 per cent conversion, after which the rates of fractional conversion decrease with increasing propionamide content. Further, the molecular weights of the polymers are greatly reduced by propionamide concentrations as low as 10 per cent. These results were interpreted in terms of extensive transfer to propionamide in the solid state; the efficiency for transfer decreasing with increasing temperature.⁽³⁴⁾ However, Adler and Reams⁽⁶⁰⁾ obtained 100 per cent conversion of acrylamide in solid solutions containing up to 90 per cent propionamide, and up to 60 per cent conversion in solid solutions containing only 4 per cent acrylamide. Accepting that all polymers extracted are high polymers,⁽³⁷⁾ the results obtained from