

solid solutions containing low concentrations of acrylamide are inconsistent with excessive transfer to propionamide.

Adler and Reams⁽⁶⁰⁾ propose that a radical can react with any of a number of near-neighbour molecules, in a manner similar to that already discussed in relation to changes in the e.s.r. spectra. Although there is considerable mobility in the lattice it seems unlikely that acrylamide molecules can diffuse through the propionamide lattice since oxygen, which is able to diffuse through propionamide can only diffuse through acrylamide along lattice imperfections.⁽³⁰⁾ The high conversions achieved in solid solutions containing low concentrations of acrylamide are attributed to diffusion of propionamide and acrylamide at the polymer-monomer interface, thus making the monomer accessible for reaction.⁽⁶⁰⁾ It has also been suggested that in the very dilute solutions some of the acrylamide will be concentrated around dislocation lines in the propionamide lattice so that a minimum of molecular movement is required for reaction. The remaining acrylamide, in the more perfect regions of the crystals, will be unable to react, thus giving rise to limiting conversions.⁽³¹⁾

An alternative explanation for the decrease in molecular weight of the polymers obtained from solid solutions containing relatively low concentrations of propionamide has been proposed.⁽³¹⁾ This explanation, based on the mechanism outlined in the preceding section, assumes that polymerization occurs initially only at specific sites. The hydrogen atoms which initiate the γ -ray induced polymerization will diffuse throughout the sample and may add to any acrylamide molecule, but only those at suitable sites will be effective in bringing about polymer formation. In the presence of propionamide, yields of radiolytic hydrogen are much greater than in pure acrylamide,⁽⁵⁹⁾ and under such conditions the concentrations of "inactive" radicals may be higher. If the rate of polymerization is related only to the initial density of suitable sites, the rate of polymerization to high conversion may not be affected by the higher yields of radiolytic hydrogen, but at high conversion the "inactive" radicals may become capable of both initiating and terminating polymerization, and hence cause a reduction in molecular weight of the polymer.

Kaetsu *et al.*⁽¹⁰¹⁾ have discussed the influence of various additives (at concentrations of about 10 per cent) on the polymerizations of acrylic acid and acrylamide in terms of their effect on the physical structure of the binary systems. This discussion is based on estimates of interactions between additive and monomer, dislocation densities, and grain sizes. It was concluded that additives which interact strongly with the monomer (e.g. through hydrogen-bonding) have the greatest effect, and suggested that dislocations associated with grain boundaries are the most effective sites for reaction.

Methyl methacrylate polymerizes slowly in the solid state when bombarded with high energy electrons,⁽¹⁰²⁾ but it has been reported that this monomer

does not polymerize at -78°C when subjected to X- or γ -rays.⁽¹⁰³⁾ However, when the latter experiments are repeated in the presence of large concentrations of additives, such as mineral oils, polymerization to high conversion is readily achieved.⁽⁷⁵⁾ This effect is presumably physical in origin, with the additive enhancing diffusion of monomer. An equivalent result can be achieved by incorporating long side chains into the monomer; both cetyl methacrylate⁽¹⁰³⁾ and octadecyl methacrylate⁽¹⁰⁴⁾ polymerize in the solid state. It has recently been reported that γ -rays do initiate the solid-state polymerization of methyl methacrylate at -65°C , but only after a long induction period.⁽¹⁰⁵⁾

Kargin *et al.*⁽²⁷⁾ have observed, that in the presence of low concentrations of solvent, crystalline salts undergo polymerization on mechanical disintegration. It was proposed that disintegration produces lattice vacancies which act as traps for electrons which in turn initiate polymerization under suitable conditions of molecular mobility. It was also observed that a mixture of sodium acrylate and lithium or magnesium chloride crystals, in the presence of traces of solvent undergo ion exchange accompanied by polymerization.⁽²⁸⁾

Polymer Structure

An obvious feature of interest in these polymerizations is the microstructure of the polymers, especially if this differs from that obtained by liquid-phase polymerizations. To date the structures of the polymers have hardly been investigated, apart from crystallographic studies on polymers produced by the polymerization of cyclic monomers; these latter polymers have no asymmetric carbon atoms in the backbone.

Polymers resulting from the free-radical polymerization of vinyl monomers in the liquid phase are generally atactic, with a tendency for syndiotactic triads (configuration of asymmetric carbon atoms in the backbone are alternately *d*- and *l*-), as defined by Bovey and Tiers,⁽¹⁰⁶⁾ to predominate. With increasing temperature the syndiotactic content decreases and the polymers become more random. A random polymer contains 25 per cent isotactic, 50 per cent heterotactic, and 25 per cent syndiotactic triads and has a value of $\sigma = 0.5$ (the probability of consecutive asymmetric carbon atoms having the same configuration).⁽¹⁰⁶⁾ This situation holds for polymethylmethacrylate⁽¹⁰⁶⁾ and for polymethacrylic acid,⁽¹⁰⁷⁾ prepared by free-radical polymerization both of which normally contain ~ 10 per cent isotactic triads. The radiation induced solid-state polymerization of methacrylic acid at 0°C gives a polymer with a larger isotactic content (~ 20 per cent) and σ value (0.4) than the solution polymerization at 90°C ($\sigma = 0.25$, ~ 12 per cent isotactic triads).⁽¹⁰⁸⁾ It was suggested that the control of the microstructure may result from the crystal structure limiting the monomer units which may be attacked by the propagating radical.⁽¹⁰⁸⁾ Post-irradiation polymerization of crystalline barium metha-