

employed, including the induced decomposition of conventional initiators⁽²¹⁾ and the action of visible light on dyes introduced into crystalline acrylamide,⁽²²⁾ which is a weak reducing agent. A difficulty associated with the introduction of sensitizers by freezing solutions in monomer is the uncertainty as to whether the sensitizer is incorporated in the crystals or if it is present only at intercrystalline boundaries. In some monomers polymerization may be induced directly by u.v. radiation of a suitable wavelength;^(23, 24) owing to the high extinction coefficients of many monomers the radiation may be completely absorbed in a thin layer of monomer. One advantage of photolytic processes is that the input of energy into the crystal may be controlled by use of different wavelengths, and there are indications that such factors are important.⁽²⁵⁾

Other techniques which have been used include the simultaneous condensation of monomer and metal vapours onto a cooled surface,⁽²⁶⁾ mechanical disintegration of certain monomers,⁽²⁷⁾ and ionic exchange processes between monomer and added salts.⁽²⁸⁾ Polymerization associated with the passage of a shock wave through monomer has also been observed.⁽²⁹⁾

In solid-state polymerizations initiated by known catalysts there is little doubt as to the nature of the propagating species. Also, it is to be expected that propagation will occur through radical intermediates in photolytically initiated reactions, although there is the possibility that in suitable cases the ionization potential of the monomer in the solid state may be sufficiently low to allow formation of ionic species. The use of high-energy radiation, however, leaves considerable doubt as to the nature of the active species, and distinction between the various modes of propagation in these systems has been the subject of considerable attention.

Sometimes chemical evidence can be used to decide between radical and ionic propagation. For example, cyclic monomers, such as trioxan, are only known to propagate through ionic intermediates in solution and it may be assumed that this also applies in the solid state. It is not to be expected that a monomer such as acrylic acid will polymerize by a cationic mechanism in the solid state and an anionic mechanism will be excluded by the presence of the acidic protons. It may, therefore, be concluded that radiolysis of this monomer will bring about a free-radical polymerization. In many of the earlier studies use was made of the techniques developed for liquid-phase polymerizations in attempts to draw a distinction between the possible modes of propagation. These latter techniques, e.g. inhibition and reactivity ratios in copolymerization, cannot normally be applied in the solid state, since it is not certain how the additive or comonomer is incorporated in the solid. Similarly, we do not know if additives are capable of diffusing through the perfect monomer lattice or along imperfection lines. Thus, a lack of inhibition by a typical free-radical inhibitor such as α, α' -diphenyl- β -picrylhydrazil does not preclude a radical mechanism. It has been demonstrated that polymerizations of acrylamide

in solid solutions with propionamide at low acrylamide concentrations are markedly retarded by oxygen which can diffuse through the propionamide lattice, whereas, in pure acrylamide oxygen has little effect since it is unable to diffuse through the lattice and can only reach reaction sites by diffusion along imperfection lines.⁽³⁰⁾ If the presence of an inhibitor does influence a reaction considerable care should be exercised in deciding whether the effect is chemical or physical, particularly if relatively high concentrations of additives are used (> 1 per cent), since, as we shall see, very small concentrations of chemically inert impurities can have a large effect on the detailed course of the reaction.⁽³¹⁾ Similar considerations apply to attempts to characterize polymerization mechanisms by copolymerization studies.

KINETIC STUDIES

The kinetics of solid-state polymerizations have been investigated both during irradiation (in-source polymerizations) and after irradiation (post-irradiation reactions). In-source polymerizations, often characterized by sigmoid conversion-time curves, may continue to complete conversion to polymer or may give rise to limiting conversions. The sigmoid curves are typical of many solid-state reactions studied previously, in which reaction is considered to start at specific sites in the crystal (i.e. imperfections) and requires the nucleation of a separate product phase in the host crystal. In such processes reaction is considered to proceed at the reactant-product interface, which increases in area in the early stages of reaction and decreases in the later stages as the product nuclei overlap. It seems likely that a number of solid-state polymerizations could show similar behaviour. Kinetic data have also been reported for a number of post-irradiation reactions when monomers are irradiated at temperatures sufficiently low to prevent significant polymerization; subsequent polymerizations at higher temperatures are usually characterized by gradually decreasing rates on prolonged heating, reaction finally ceasing at some finite conversion.

Considerable care must be exercised, in obtaining conversion-time curves, to prevent polymerization during isolation of the polymer. In some early studies polymer was extracted after melting partially polymerized monomer, but this procedure can give rise to extensive polymerization on release of trapped reactive species. This difficulty can often be overcome by dissolution of monomer at low temperatures using a solvent containing an inhibitor. A second approach is to estimate the conversion by observing changes in some physical quantity, e.g. the decrease in optical retardation with time as a birefringent monomer crystal is converted into amorphous and isotropic polymer. Techniques of this type, which measure the residual crystallinity, may not give the exact conversion at any given time if some disordering of monomer is associated with polymerization or if the polymer formed is