change in the geometrical disposition of the substituent groups. Although the crystal structures of most monomers are unknown it is fairly obvious, from a general consideration of organic crystal structures, that in most monomers there will be insufficient free volume available in the perfect crystal to allow these configurational changes to occur, even though the polymers are often denser than the monomers. It hardly seems reasonable, therefore, to expect polymerization to occur in the perfect regions of the crystal lattice. Consequently, it appears likely that reactions are initiated at imperfections and that polymerization takes place initially in the more imperfect regions of the monomer lattice.

In early studies of the γ-ray induced solid-state polymerization of acrylamide it was observed that amorphous polymer was produced. The crystallinity, as judged by X-ray diffraction techniques,(5, 42) decreased steadily during reaction, although it was reported that optical birefringence was retained to some extent.(42, 43) At high conversions the birefringence is completely lost and the monomer crystals are eventually converted to isotropic polymeric pseudomorphs of the original crystals.(44) Detailed X-ray studies on single crystals of acrylamide demonstrate that, as polymerization proceeds, there is a weakening of the X-ray diffraction pattern of the monomer and the gradual appearance of diffuse scattering by amorphous polymer.(45) The weakening of the monomer diffraction pattern (and the appearance of diffuse scattering) can be detected at conversions as low as 4 per cent. Even at these low conversions there is no preferential weakening of certain reflections; the original monomer diffraction pattern is still visible at 90 per cent conversion. These results suggest that throughout the polymerization amorphous polymer is produced as a separate phase in the crystal.(45)

Examination of a partially polymerized crystal by phase contrast microscopy shows the presence of spots, which are probably polymeric nuclei.(46) It was therefore suggested that polymerization is initiated at favourable sites in the crystal, i.e. at imperfections,(46, 47) and it was observed that polymerization proceeded more rapidly in the vicinity of a scratch on the crystal surface.(47) A striking proof of these ideas has been obtained by Sella and Trillat(48) and Sella and Bensasson,(49) who studied acrylamide crystals at various conversions by electron microscopy. These workers found that polymerization does not occur uniformly throughout the crystal. In the early stages of the reaction small globular particles of amorphous polymer, of the order of 20 Å diameter, appear on the surface of the crystals. These particles are distributed randomly along lines which in turn lie along a preferred crystallographic direction. As polymerization proceeds the particles retain their form but grow in diameter to about 300–400 Å. Eventually the particles coalesce to give a fibrillar structure, with the appearance of polymer fibres orientated along preferred directions in the lattice. On complete conversion the crystal is converted to a mass of globular particles.

The results obtained by electron microscopy are reminiscent of various studies of the inorganic solid state where decoration techniques allowing the direct observation of dislocations are well developed. Features similar to the globular structures mentioned above are taken to indicate the points at which dislocation lines emerge at the surfaces of the crystals. Indeed Sella and his colleagues(48, 49) suggest that dislocations are preferred sites of reaction. The original distribution of the globules suggest they lie along the slip planes of the monomer crystals.

Protruberancies have been observed on the surfaces of crystals when benzamidostyrene undergoes thermal polymerization to low conversions.(19) These protruberances also are probably sites at which dislocation lines reach the crystal surface. There is evidence that during the polymerization of this monomer some degree of crystallinity may be retained under certain conditions, a feature which is discussed elsewhere in this review.

At the present time our understanding of the detailed structure and properties of imperfections in crystals of large organic molecules is very poor in comparison with the state of knowledge in the inorganic field. Until this situation improves it is necessary to infer the properties of imperfections in molecular crystals from the established behaviour of imperfections in metallic and ionic crystals. In this way other evidence for the importance of dislocations in solid-state polymerizations has been obtained. When acrylic acid is polymerized in the solid state at 4°C by continuous u.v. irradiation the birefrigent monomer crystals are converted to isotropic polymeric pseudomorphs of the original crystals;(23) the optical retardation decreases with time in a sigmoid manner. Using thin (10–20μ) layers of single crystals it was shown that when a unidirectional pressure of about 10 atm is applied perpendicularly to the large faces of the crystals, at a conversion corresponding to about 50 per cent loss of optical retardation, reaction ceased immediately, even though irradiation was continued.(23, 24) On subsequent removal of the stress, reaction recommenced after a short induction period. The application of the same stress to methacrylic acid crystals during irradiation brought about a marked reduction in rate, but did not stop the reaction. However, the after-effect, or post-irradiation reaction, which normally occurs in this latter monomer was prevented by the applied stress, but resumed immediately when the stress was removed.(23, 24)

It is well known that dislocations can move through metallic crystals under the influence of very small stresses and pile up locally in the vicinity of obstacles such as grain boundaries,(50) and that on removal of the stress the dislocations again disperse throughout the crystal. It was suggested that a similar mechanism would explain the observed effect in the solid-state polymerization of acrylic acid, and it was concluded that radicals are produced and polymerization takes place in dislocations.(23, 24) Application of the stress is considered to move the dislocations from reaction sites, leaving the radicals