

dichloro-1,3-butadiene, and 1,3-cyclohexadiene; polymers were isolated by extracting the thiourea. Examination of the polymers showed them to be crystalline and exclusively trans-1,4 polybutadienes. During isolation the polymers collapsed together, maintaining their orientation, to form needles. X-ray examination showed that the polymer molecules are aligned along the needle axis. The smaller monomer molecules 1,3-butadiene and vinylacetylene also polymerize in this way but produce non-stereo regular products; other similar monomers did not polymerize in the thiourea complexes under the experimental conditions employed.<sup>(94)</sup> According to Stephan *et al.*,<sup>(95)</sup> there is evidence for the presence of monocyclic structures in polymers prepared by irradiation of the 2,3-dimethyl-1,3-butadiene-thiourea complex.

Using urea complexes it is possible to produce stereoregular products from smaller monomer molecules than by use of the corresponding thiourea complexes. In this way White<sup>(96)</sup> has produced an all trans-polymer from 1,3-butadiene, an insoluble, crystalline and syndiotactic polymer from vinyl chloride and crystalline polyacrylonitrile, apparently similar to commercial polyacrylonitrile. Kiss<sup>(97)</sup> has carried out a kinetic study of polymerization in acrylonitrile-urea complexes. Polymerization of piperylene in its urea complex also produces a more stereoregular polymer than is obtained by bulk polymerization; this is attributed to an increase in trans-1,4 addition.<sup>(98)</sup>

### Reaction Mechanisms

In this section we discuss a possible reaction mechanism for the solid-state polymerization of vinyl monomers, based on the premise that reaction occurs in imperfections, and incorporating evidence and ideas which have been presented for a number of related systems. Although we cannot hope to produce a completely general mechanism, we shall attempt to obtain a picture of these reactions in which the main features of the processes involved are described, and which may be modified for different monomers as the relative importance of each factor varies.

In acrylic acid crystals at 4°C there is considerable molecular mobility,<sup>(62)</sup> and in the imperfections we may expect the mobility to be even more extensive. Under these conditions the u.v. initiated polymerization of this monomer is rapid, and e.s.r. studies on this and other monomers under similar conditions suggest that the propagating radicals are randomly orientated in the lattice. We would not, therefore, expect the orientation of the monomer molecules in the perfect lattice to control the polymerization to any significant extent at these temperatures. Yet, when polymerization is initiated with polarized u.v. radiation, the rate of polymerization in the initial stages shows a strong dependence on the angle between the plane of the electric vector of the polarized u.v. light and the crystallographic axes.<sup>(99)</sup> This result indicates that the primary act is the absorption of polarized u.v. radiation by monomer

molecules in the more perfect regions of the lattice and where the correct orientation of the molecules is retained. It is considered that the absorption of u.v. radiation produces excitons which travel through the lattice and become trapped in imperfections. Some of the excitons decay, while others, in suitable imperfections, give rise to radical formation and initiate the polymerization process. Assuming that the initiating u.v. radiation is absorbed by the vinyl groups, the observed variations in rate of polymerization described above are consistent with the known orientation of the vinyl groups in the monomer crystal,<sup>(100)</sup> with maximum absorption when the plane of the electric vector is parallel to the double bond. The e.s.r. evidence, already discussed, suggests that in polymerizations initiated by high-energy radiation the radiolytic products (e.g. hydrogen atoms) diffuse through the lattice and initiate polymerization at imperfections.

From detailed e.s.r. studies on the nature of radicals in solid monomers, we have seen that at low temperatures, when there is little or no polymerization, the radicals are subject to some degree of restriction by the lattice, either in their orientation in the lattice and/or by the adoption of a specific conformation. Since the radicals are located in imperfections we may inquire as to what factors bring about these restrictions at the lower temperatures. In the perfect lattice the molecules are held on their lattice sites by certain intermolecular forces, e.g. hydrogen bonds. In the vicinity of an imperfection, such as a dislocation or grain boundary, the molecules are displaced from their lattice sites but are still under the influence of the same intermolecular forces. Thus, some strain will be present in these regions of the lattice and there will be a certain free volume available for molecular motions. At low temperatures these motions may be frozen out, as they are in the perfect crystal, but it may be anticipated that in defects these motions may occur more easily and at lower temperatures than in the perfect lattice, as allowed by the detailed structure of the defect.

Even at  $-196^{\circ}\text{C}$  there is presumably sufficient freedom for movement in some defects to allow the addition of a hydrogen atom to the double bond of a monomer molecule and for the necessary changes in configuration of the carbon atoms to occur. The resulting radical is then firmly held in position by the intermolecular forces, and it is not surprising that such radicals are highly orientated in the lattice. At higher temperatures, when there is sufficient molecular movement in the defect, this radical will add to a nearest neighbour monomer. Accompanying this addition there will be a net shrinkage (estimated at about one-third of a unit cell along the *b*-axis for the addition of two monomers in acrylamide<sup>(60)</sup>). With the first appearance of the propagating radical no polymerization is observed and it has been suggested that propagation stops at dimer or trimer formation.<sup>(37)</sup> At this stage it is probable that substituent groups on the reacted monomers are still under the influence of the original intermolecular forces which maintain the dimer in a