

confines topotaxy to transformations "in which the majority of the atomic positions in the original and in the transformed material are substantially the same and there is accord in three dimensions between the initial and final lattices." Taking an intermediate position Dent Glassler *et al.*⁽⁸⁹⁾ state that "for true topotaxy there must be some three-dimensional correspondence between the structures of the product and its host."

It would appear unlikely that any solid-state polymerization will conform to Mackay's definition of topotaxy, and in discussing the possibilities of topotactic polymerizations it is usual to refer to the definition of Dent Glassler *et al.*⁽⁸⁹⁾ The polymerization of a vinyl monomer, of necessity, involves a change in the hybridization of the carbon atoms in the vinyl group of the monomer, and, further, non-stereoregular polymers are formed even in the solid state. It is difficult, therefore, to see how the polymerization of any vinyl monomer can be a topotactic reaction unless the crystallization of the substituent groups in the monomer controls the orientation of the product.

In an attempt to obtain a topotactic polymerization, Morosoff *et al.*⁽⁹⁰⁾ investigated the polymerization of crystalline vinyl stearate in which the vinyl groups are situated in well-separated layers. Polymerization of this monomer must almost inevitably take place in two dimensions, since an extremely high degree of mobility of the stearate residues would be required to allow sufficient diffusion for polymerization to take place in the third direction. Further, it is known that non-stereoregular polyvinyl stearate will crystallize⁽⁹¹⁾ through side-chain crystallization.

Monomeric vinyl stearate crystals are monoclinic, with the paraffinic chains in an orthorhombic sub-cell. During polymerization the stearate residues attached to the polymer retain their orientation parallel to the side chains of the monomer, but the packing changes from orthorhombic to hexagonal. This change in packing, which often occurs in long chain hydrocarbons as molecular mobility increases in the vicinity of the melting point,⁽⁹²⁾ involves an overall expansion of the sub-cell area in the plane perpendicular to the long axis of the paraffinic chains, although there is a slight contraction in one dimension. Morosoff *et al.*⁽⁹⁰⁾ followed the polymerization of this monomer by X-ray diffraction and observed that at 30 per cent conversion the presence of the normal monomer lattice could still be detected, but that at 40 per cent conversion all stearate residues were packed in the hexagonal arrangement. The polymer so formed, although more isotactic than that prepared in solution, is still non-stereoregular, and, presumably, would not pack into the crystal structures proposed for isotactic⁽⁹³⁾ and syndiotactic polymers. It was not possible to determine the manner in which the side-chains are attached to the polymer backbone and no evidence could be obtained for propagation in a preferred direction. However, the side chains do crystallize and the backbone is presumably amorphous. It would appear necessary to assume that both the backbone and a few terminal units of the

stearate chain are disordered in such a way as to allow the remainder of the stearate residue to pack in the hexagonal arrangement.

Other vinyl monomers which have been studied in this connection are *p*-acetamidostyrene and *p*-benzamidostyrene,⁽¹⁹⁾ both of which polymerize spontaneously in the solid state producing polymers less dense than the crystalline monomers. Possible crystal structures of the monomers have been proposed in which the vinyl groups are again arranged in well-separated layers. The crystal structures of these monomers must be largely determined by the strong interactions between substituent groups, and these interactions must influence the polymerization mechanism. The glass transition temperatures of poly-*p*-acetamidostyrene and poly-*p*-benzamidostyrene are 85°C and 120°C respectively. In the former case polymerizations were carried out only above the glass-transition temperature of the polymer and in the latter case both above and below it. Jakabhazy *et al.*⁽¹⁹⁾ present evidence suggesting that in both monomers, at temperatures above the glass-transition points of their respective polymers, anisotropic polymers are formed initially, subsequently relaxing to isotropic materials. In polymerizations of the benzamido-derivative below 120°C these authors report that the infra-red dichroism of the N—H stretch does not decrease below conversions of at least 80 per cent and claim that this result can only be interpreted in terms of propagation through the lattice in a specific direction.⁽¹⁹⁾ This apparently occurs as a result of an almost exact correspondence between the lattice dimensions proposed for the monomer crystal and the spacings required for the polymer to adopt a planar zigzag configuration. (It has been pointed out elsewhere that the surface topography of partially polymerized crystals suggests that dislocations are preferred sites of reaction.) As a result of the change in hybridization of the carbon atoms and the retention of the infra-red dichroism Jakabhazy *et al.*⁽¹⁹⁾ point out that it is necessary for the substituent groups to reorientate in a specific manner, with the formation of a stereoregular polymer. The polymer could be either a syndiotactic polymer of the normal head-tail structure or a regular head-head tail-tail structure; it was suggested that the latter was the more likely alternative. If this view was substantiated then polymerization of *p*-benzamidostyrene would fall into the category of a topotactic polymerization. Whatever the nature of the polymer in the above case, the retention of a property such as the infra-red dichroism must imply that the polymer is formed in such a way that the substituent groups can pack together in a fairly regular manner. It is to be expected that this will only occur in the polymerization of monomers carrying large substituent groups, preferably of the type which will interact strongly, e.g. through hydrogen bonding.

In this section mention should be made of polymerizations in urea- and thiourea-canal complexes, where propagation occurs through sequences of monomer molecules in the canals. By irradiating thiourea complexes, Brown and White⁽⁹⁴⁾ succeeded in polymerizing 2,3-dimethyl-1,3-butadiene, 2,3-