

syndiotactic or isotactic placements, while those in the latter group tend to yield atactic, branched polymers.

It is possible to account for the differences between the two classes if it is assumed that in order to produce a crystallizable polymer, it is necessary for each monomer unit, at the moment of addition, to retain its crystalline orientation. This in turn will only be feasible where the unit cell of the monomer crystal has similar dimensions to those of the polymer. If these conditions do not exist the successive addition of monomer units must proceed by either circumnavigating a free volume or by disruption of the monomer lattice ahead of the propagating chain, dependent on whether the polymer unit cell has a smaller or larger linear dimension than that of the monomer.

Experiments carried out with acrylamide, a monomer of the latter type, have shown that an increase in temperature, the incorporation of the non-reactive compounds within the monomer lattice, or addition of small quantities of solvent tend to enhance the rate of polymerization. In each case the treatment has the effect of disrupting or loosening the crystal lattice so that the internal stress opposing propagation is reduced. This being the case the existence or otherwise of internal stress, at least in the initial stages of a propagation reaction, may be considered to determine further the nature of a particular solid state polymerization.

Even if we assume that in all cases initiation will occur at some unique locality such as a point defect, the rate of reaction subsequent to nucleation must be governed by the magnitude of strain energy arising from the incorporation of one phase within another. Polymerization giving rise to "regular" or crystalline placements are able to propagate by rotation and translation of the monomeric crystal axes; the energy from such a transition may then add to the energy required to activate the next monomer unit, thus accounting for the low activation energy and high rate for polymerization of these monomers. Conversely, those monomers in our second category can only propagate through the movement of an interphase boundary, necessitating a large strain energy.

The application of an externally applied stress would be expected to affect the course of a solid state polymerization, favoring the propagation reaction for monomers in which the polymer is formed along a preferred crystallographic axis but reducing the rate where it tends to oppose the tensile stress exerted by, or to limit the free volume available to, the growing polymer chain.

We have studied the effect of applied pressures up to 90,000 psi (6500 atm.) on a number of radiation-induced solid state polymerizations. Presented are the results of some preliminary observations for four monomers: acrylamide and methacrylamide, both of which are believed to yield atactic polymer but show markedly different rates of reaction in the solid state,^{1,2} and some modifications of calcium acrylate and barium methacrylate. Morawetz and co-workers have extensively studied the solid state polymerization of a number of methacrylic and acrylic acid