

mers prepared by solid-state polymerization of trithiane⁽¹²³⁻⁴⁾ and trisele-nane,⁽¹²⁵⁾ in each case the polymer was found to grow along a preferred crystallographic direction.

On the basis of results of the type outlined above, together with certain kinetic considerations, it has been generally concluded that the monomer crystal structure plays a dominant role in determining the course of the polymerization by determining the direction of growth of the polymer chain, with polymerization occurring in perfectly ordered regions of the crystal. Recent results suggest that the crystal structure of the monomer does not play such an important role.⁽⁴⁰⁾

Among the kinetic features, which have been interpreted in terms of lattice control of polymerization, are the limiting conversions reported by a number of workers,^(39, 126-33) for both the in-source and post-irradiation reactions. It has been suggested that the limiting conversion results from aggregation of individual polymer molecules into bundles with the exclusion and disordering of residual monomer which, due to its lack of orientation, does not polymerize.⁽³⁹⁾ A kinetic expression has been developed on this basis, assuming that if a fraction x of the monomer is polymerized then a further and related fraction becomes disordered and unavailable for reaction (see also Kinetic Studies p. 6). However, there are considerable discrepancies in the reported values of maximum obtainable conversions. For example, in polymerizations of trioxan Hayashi *et al.*⁽¹³⁰⁾ observed maximum polymer yields of about 55 per cent at 55°C and 17 per cent at 50°C, while Sakamoto *et al.*⁽¹³³⁾ report a maximum conversion of 80 per cent throughout the temperature range 45°-55°C. Although limiting conversions of the order of 10 per cent have been reported for the in-source polymerization of 3,3-bis(chloromethyl)-oxetane,^(126, 128) Kagiya *et al.*⁽⁴¹⁾ find no evidence for a limiting conversion in carefully purified monomer, but report that the addition of small amounts of water and sym-dichloroacetone cause the reappearance of this effect. Kagiya *et al.*⁽¹³⁴⁾ also report that addition of additives such as phosphorus pentoxide to the unpurified monomer increase the polymer yields, presumably by removal of water. It appears, therefore, that the polymerizations are very sensitive to trace impurities.

Further evidence that trace impurities have been present in much of the previous work arises from rates of radiation-induced polymerization in the melt. In earlier papers^(126, 130) it is reported that the rates of polymerization of crystalline trioxan, β -propiolactone, diketene, and 3,3-bis(chloromethyl)-oxetane, increase with increasing temperature, reaching a maximum below the monomer melting point and falling to approximately zero in the melt. The maximum occurs at about -70°C in β -propiolactone (m.p. -33°C) and diketene (m.p. -65°C) and about 10°C below the melting point of 3,3-bis(chloromethyl)oxetane (m.p. 18°C); the actual temperature depends on radiation dosage. Similar results have been observed with other monomers,

e.g. hexamethylcyclotrisiloxane.⁽¹³⁵⁻⁶⁾ More recently, it has been pointed out that pure trioxan and 3,3-bis(chloromethyl)oxetane will polymerize in the melt,⁽¹³⁷⁾ but that the rates are very sensitive to trace impurities, e.g. water. As might be expected from the sensitivity to impurities, the observed rates and limiting conversions are dependent on conditions of crystallization of the monomer; higher limiting conversions have often been observed in monomer samples obtained by slow crystallization. Further, Rao and Ballantine⁽¹³²⁾ have been unable to obtain reproducible kinetic data even when considerable care was taken to standardize the experimental conditions.

These results suggest that impurities and lattice imperfections have a marked effect on the polymerizations, and, since crystalline polymers are obtained, it is often concluded that the effect of any imperfection is to reduce the yields and rates of polymer formation. Hayashi *et al.*⁽¹³⁰⁾ have demonstrated the effect of impurities on the post-irradiation polymerization of trioxan by direct addition of relatively large concentrations (5 per cent) of impurities such as water, methylene chloride, and methanol. A more striking result is the effect of the atmosphere on the post-polymerization of trioxan;⁽¹³⁰⁾ according to Rao and Ballantine⁽¹³²⁾ only a trace of polymer is obtained if irradiation and polymerization are carried out in vacuum. Presumably it is necessary for an atmospheric constituent to react with the products of low-temperature radiolysis in order to obtain a suitable species to initiate polymerization, or, alternatively, a reactive species diffuses out of the crystal under these conditions. In contrast, the nature of the atmosphere does not appear to affect the in-source polymerization of diketene at -78°C .⁽¹²⁶⁾ Other workers have concluded that impurities can affect radiolytic initiation, either directly or indirectly. Additives which remove carbon dioxide (which is observed on radiolysis of 3,3-bis(chloromethyl)oxetane) accelerate the polymerization.⁽¹³⁴⁾ Herz and Stannett⁽¹³⁸⁾ report that carefully purified trithiane will not polymerize in the solid, and while samples prepared by crystallization from dimethyl formamide do not polymerize, if the monomer is crystallized from chloroform polymerization does occur on radiolysis.

Rates of polymerization and limiting conversions in the solid-state are markedly temperature dependent. Thus, trioxan only polymerizes to any significant extent in the temperature range $30^{\circ}\text{--}60^{\circ}\text{C}$ (approx.),⁽¹²⁶⁾ the conversion increasing from about 2 per cent to 30 per cent with increasing temperature in this range. Results of a similar nature are observed with other monomers. Arrhenius plots often show marked changes in slope, the rates increasing more rapidly with increasing temperature (until the maximum is reached) than can be accounted for by a single activation energy. The rapid increase in rate probably parallels increasing molecular mobility; this is certainly the case in trioxan for which Komaki and Matsumoto⁽¹³⁹⁾ have carried out a broad-line n.m.r. study. The widths of the n.m.r. lines show marked decreases in second moment at about -10°C and 40°C , as new