

*Reprinted from*  
PROGRESS IN POLYMER SCIENCE  
Volume 2  
*Edited by*  
A. D. JENKINS  
PERGAMON PRESS - OXFORD & NEW YORK - 1970

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## SOLID-STATE POLYMERIZATION

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## INTRODUCTION

The polymerization of crystalline monomers, at first sight, appears to offer intriguing possibilities for the production of polymers with structures different from those obtained by liquid-phase polymerizations. In particular, it may be visualized that the ordered arrangement of molecules in the crystal lattice may give rise to highly crystalline or stereoregular polymers. Indeed, in the 1930s Kohlschütter and Sprengel<sup>(1)</sup> observed that, in the presence of formaldehyde vapour, a crystalline polymer formed on the surface of trioxan crystals, and that this polymer was orientated along the *c*-axis of the monomer crystal. These and other<sup>(2-4)</sup> early references to polymerizations occurring in solid monomers were "lost" in the literature until after 1954, when Mesrobian *et al.*<sup>(5)</sup> described the radiation-induced polymerization of crystalline acrylamide and the present development of this topic started. One reason for the upsurge in interest in this topic at that particular time was, no doubt, the possibility of using this technique as an alternative to the then new Ziegler-Natta catalysts. In the circumstances it seems strange that the early observations of Kohlschütter and Sprengel were forgotten, but it was not until 1960 that Okamura *et al.*<sup>(6)</sup> "rediscovered" the formation of crystalline polyoxymethylene during the solid-state polymerization of trioxan; in this case reaction was induced by high-energy radiation.

A detailed understanding of solid-state polymerization mechanisms requires consideration of factors peculiar to the solid state, including the effect of the crystal lattice, the importance of lattice imperfections, phase transitions, and molecular mobility. In order to elucidate the importance of these factors, polymerization processes in a wide range of monomers have been studied by a variety of techniques. Although this has been an active field of research for 10 years, a difficulty is still a lack of knowledge of the crystal structures of most monomers. There is also little understanding of the detailed nature of imperfections in the organic solid state. In spite of these difficulties we now have a better appreciation of the factors controlling the reactions.

An important outcome of the investigations is the information provided on the behaviour of reactive species in molecular crystals. Since most of the monomers studied are organic materials the understanding of polymerization

processes in solid monomers must inevitably have application in the general fields of organic solid-state chemistry and physics, of which this research now constitutes a large part.

During the last decade this subject has been reviewed a number of times,<sup>(7-18)</sup> and through these reviews changes in emphasis, as the subject has developed, can be traced. Most reviews have discussed the polymerization of cyclic monomers separately since they may produce highly crystalline polymers. They are also treated separately in this review, although it now appears that the sharp distinction drawn between the polymerization of these and other monomers is breaking down. The present review does not claim to be comprehensive in the sense of referring to all monomers which have been polymerized in the solid state (a recent list is given by Marans<sup>(17)</sup>) but discusses some important aspects of polymerizations in solids which were described by about the end of 1967 and, in combination, are leading to a better understanding of the principles involved in the reaction mechanisms. The results of studies on the solid-state polymerizations of aldehydes are not presented here, but have been discussed elsewhere recently.<sup>(14)</sup> Solid-state polycondensations and increases in molecular weight in polyamides and polyesters, in which diffusion of a reaction product through the lattice must play a large part, are not considered.

#### METHODS OF INITIATION

A consequence of using solid monomers is that restrictions are imposed on the methods of initiation which can be used, especially if the monomers are crystalline rather than in the form of a glass. Most workers in this field have made use of high-energy radiation, e.g.  $\gamma$ -rays, X-rays, and high-energy electrons, either by irradiating monomers at the polymerization temperature or by introducing reactive centres at low temperatures and subsequently warming the sample to obtain a post-irradiation reaction. For mechanistic investigations the latter type of study has the advantage of avoiding radiation damage to the reaction product. Further advantages of using high-energy radiation are that a range of active species may be produced so that the chances of successfully inducing a polymerization reaction are enhanced and, secondly, active centres may be produced throughout a large sample of monomer, which may not be possible with other techniques. A disadvantage is that, since both ions and radicals can be produced, there may be considerable uncertainty as to the nature of the products of radiolysis and of the propagating species. Some pure monomers undergo spontaneous thermal initiation in the solid state,<sup>(19)</sup> while others require the presence of an additive, e.g. solid vinyl carbazole polymerizes spontaneously in the presence of carbon tetrachloride.<sup>(20)</sup> In a number of cases cationic polymerizations have been induced by surface catalysis or freezing monomers in the presence of a catalyst; these reactions are referred to later. Various photolytic processes have been

employed, including the induced decomposition of conventional initiators<sup>(21)</sup> and the action of visible light on dyes introduced into crystalline acrylamide,<sup>(22)</sup> which is a weak reducing agent. A difficulty associated with the introduction of sensitizers by freezing solutions in monomer is the uncertainty as to whether the sensitizer is incorporated in the crystals or if it is present only at intercrystalline boundaries. In some monomers polymerization may be induced directly by u.v. radiation of a suitable wavelength;<sup>(23, 24)</sup> owing to the high extinction coefficients of many monomers the radiation may be completely absorbed in a thin layer of monomer. One advantage of photolytic processes is that the input of energy into the crystal may be controlled by use of different wavelengths, and there are indications that such factors are important.<sup>(25)</sup>

Other techniques which have been used include the simultaneous condensation of monomer and metal vapours onto a cooled surface,<sup>(26)</sup> mechanical disintegration of certain monomers,<sup>(27)</sup> and ionic exchange processes between monomer and added salts.<sup>(28)</sup> Polymerization associated with the passage of a shock wave through monomer has also been observed.<sup>(29)</sup>

In solid-state polymerizations initiated by known catalysts there is little doubt as to the nature of the propagating species. Also, it is to be expected that propagation will occur through radical intermediates in photolytically initiated reactions, although there is the possibility that in suitable cases the ionization potential of the monomer in the solid state may be sufficiently low to allow formation of ionic species. The use of high-energy radiation, however, leaves considerable doubt as to the nature of the active species, and distinction between the various modes of propagation in these systems has been the subject of considerable attention.

Sometimes chemical evidence can be used to decide between radical and ionic propagation. For example, cyclic monomers, such as trioxan, are only known to propagate through ionic intermediates in solution and it may be assumed that this also applies in the solid state. It is not to be expected that a monomer such as acrylic acid will polymerize by a cationic mechanism in the solid state and an anionic mechanism will be excluded by the presence of the acidic protons. It may, therefore, be concluded that radiolysis of this monomer will bring about a free-radical polymerization. In many of the earlier studies use was made of the techniques developed for liquid-phase polymerizations in attempts to draw a distinction between the possible modes of propagation. These latter techniques, e.g. inhibition and reactivity ratios in copolymerization, cannot normally be applied in the solid state, since it is not certain how the additive or comonomer is incorporated in the solid. Similarly, we do not know if additives are capable of diffusing through the perfect monomer lattice or along imperfection lines. Thus, a lack of inhibition by a typical free-radical inhibitor such as  $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazil does not preclude a radical mechanism. It has been demonstrated that polymerizations of acrylamide

in solid solutions with propionamide at low acrylamide concentrations are markedly retarded by oxygen which can diffuse through the propionamide lattice, whereas, in pure acrylamide oxygen has little effect since it is unable to diffuse through the lattice and can only reach reaction sites by diffusion along imperfection lines.<sup>(30)</sup> If the presence of an inhibitor does influence a reaction considerable care should be exercised in deciding whether the effect is chemical or physical, particularly if relatively high concentrations of additives are used (> 1 per cent), since, as we shall see, very small concentrations of chemically inert impurities can have a large effect on the detailed course of the reaction.<sup>(31)</sup> Similar considerations apply to attempts to characterize polymerization mechanisms by copolymerization studies.

#### KINETIC STUDIES

The kinetics of solid-state polymerizations have been investigated both during irradiation (in-source polymerizations) and after irradiation (post-irradiation reactions). In-source polymerizations, often characterized by sigmoid conversion-time curves, may continue to complete conversion to polymer or may give rise to limiting conversions. The sigmoid curves are typical of many solid-state reactions studied previously, in which reaction is considered to start at specific sites in the crystal (i.e. imperfections) and requires the nucleation of a separate product phase in the host crystal. In such processes reaction is considered to proceed at the reactant-product interface, which increases in area in the early stages of reaction and decreases in the later stages as the product nuclei overlap. It seems likely that a number of solid-state polymerizations could show similar behaviour. Kinetic data have also been reported for a number of post-irradiation reactions when monomers are irradiated at temperatures sufficiently low to prevent significant polymerization; subsequent polymerizations at higher temperatures are usually characterized by gradually decreasing rates on prolonged heating, reaction finally ceasing at some finite conversion.

Considerable care must be exercised, in obtaining conversion-time curves, to prevent polymerization during isolation of the polymer. In some early studies polymer was extracted after melting partially polymerized monomer, but this procedure can give rise to extensive polymerization on release of trapped reactive species. This difficulty can often be overcome by dissolution of monomer at low temperatures using a solvent containing an inhibitor. A second approach is to estimate the conversion by observing changes in some physical quantity, e.g. the decrease in optical retardation with time as a birefringent monomer crystal is converted into amorphous and isotropic polymer. Techniques of this type, which measure the residual crystallinity, may not give the exact conversion at any given time if some disordering of monomer is associated with polymerization or if the polymer formed is

ordered. Nevertheless, they provide a convenient means of studying the reaction and the use of such physical techniques (e.g. X-ray diffraction) electron microscopy, optical retardation, and infra-red and u.v. dichroism) is increasing.

A consequence of the difficulties encountered in obtaining reliable and reproducible kinetic data is that many workers simply quote experimental observations without attempting a detailed mathematical analysis of the kinetics. However, from time to time attempts have been made to produce theoretical interpretations of experimental data, or to obtain relations which predict the main features of the observed kinetic behaviour. As an example of the dangers involved in attempting to interpret the kinetics in terms of the simple reactions normally considered in polymerization reactions we may cite an early study of the kinetics of the post-irradiation polymerization of acrylamide.<sup>(32-4)</sup> It was observed that the polymer yield  $Y$  is related to the reaction time  $t$  by an equation of the form

$$Y = A \log (1 + Bt),$$

where  $A$  and  $B$  are constants. This relation is consistent with bimolecular termination of propagating radicals, and it was originally assumed that such a reaction brought about the gradual decrease in rate with reaction time. Subsequently, it was demonstrated by electron spin resonance (e.s.r.) that the radical concentration remains high while the rate of polymerization decreases to a very low value.<sup>(33, 34)</sup> Hence, it must be concluded that the decrease in rate is due to a physical rather than a chemical effect. It might be argued that the discrepancy between radical concentrations and rates of polymerization is evidence against radical propagation. On the other hand, the correlation between changes in the e.s.r. spectrum and rates of polymerization is indicative of free-radical propagation, although this does not constitute a proof. Further, ionic propagation is unlikely on chemical grounds, since anionic propagation may be expected to lead to the incorporation of  $\beta$ -alanine residues in the polymer through a proton-migration mechanism as a result of reaction through the amide group;<sup>(35)</sup> no evidence of this type has been quoted. In other solid-state polymerizations, where reaction almost certainly proceeds through radical intermediates, continuously decreasing rates in the post-irradiation reaction have been observed even though the radical concentration remains effectively constant;<sup>(23)</sup> the apparent reactivity of the radicals decrease as reaction proceeds. This is reminiscent of the occlusion of radicals in liquid-phase free-radical polymerizations when polymer precipitates during reaction, and where apparent changes in radical reactivity are due to physical effects.<sup>(36)</sup>

In view of the complex nature of these reactions, it is extremely doubtful if there is any justification, at present, for relating parameters in empirical kinetic relations to velocity coefficients for individual processes such as propagation and termination. Since it has been demonstrated that a distribution

of reaction sites with different properties may be involved,<sup>(25, 37)</sup> any such velocity coefficient must be a mean value; a situation envisaged by Adler and Petropoulos.<sup>(37)</sup> The average concentration of reactants may also be of little significance. Overall activation energies have been quoted for a large number of solid-state polymerizations, and in some cases suggestions as to the nature of the propagating species have been made from the absolute values of the activation energies. Changes in activation energy have, on occasion, been attributed to changes in mechanism. However, it is now known that many of these reactions proceed in lattice imperfections when the local molecular mobility is sufficiently great. Changes in temperature will affect the number of defects capable of supporting reaction and the overall activation energy will contain both physical and chemical contributions. In any particular case it is difficult to know how the magnitude of the activation energy should be interpreted. Pre-exponential factors should be treated with equal caution.

Attempts have also been made to analyse reaction kinetics on a statistical basis. For example, Okamura and his colleagues<sup>(38, 39)</sup> and Charlesby<sup>(14)</sup> have considered cases where the in-source polymerization leads to a limiting conversion and the polymer is highly orientated with respect to the monomer crystal axes, as in the polymerization of a number of cyclic monomers. The analyses are based on the assumption that propagation only occurs along a specific crystallographic direction, and to obtain limiting conversions it is assumed that the addition of a monomer molecule to a growing chain brings about the disorientation of other monomer molecules so that they are unavailable for reaction. In this way the general form of the kinetic curves can be satisfactorily predicted. For the polymerization of diketene at  $-78^{\circ}\text{C}$  it was calculated that 11.4 monomer units would have to become disorientated for every act of propagation to give rise to the observed limiting conversion.<sup>(14)</sup> Recent observations cast some doubt on the basic assumption that propagation can only occur along a specific crystallographic direction<sup>(40)</sup> and that limiting conversions are a genuine feature of the polymerization in pure materials.<sup>(41)</sup>

In the final analysis the actual reaction mechanism must, of course, give equations of the same form as the empirical relations. At the present time considerable care is required in interpreting these parameters, and possibly the most productive approach is to identify the factors which affect the form of the kinetic curves.

## POLYMERIZATION OF VINYL MONOMERS

### Nature of Reaction Sites

Formation of polymer from a vinyl monomer involves a change in hybridization of the olefinic carbon atoms of the monomer, which in turn requires a

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  $\gamma$ -ray induced solid-state polymerization of acrylamide it was observed that amorphous polymer was produced. The crystallinity, as judged by X-ray diffraction techniques,<sup>(5, 42)</sup> decreased steadily during reaction, although it was reported that optical birefringence was retained to some extent.<sup>(42, 43)</sup> At high conversions the birefringence is completely lost and the monomer crystals are eventually converted to isotropic polymeric pseudomorphs of the original crystals.<sup>(44)</sup> 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.<sup>(45)</sup> 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.<sup>(45)</sup>

Examination of a partially polymerized crystal by phase contrast microscopy shows the presence of spots, which are probably polymeric nuclei.<sup>(46)</sup> It was therefore suggested that polymerization is initiated at favourable sites in the crystal, i.e. at imperfections,<sup>(46, 47)</sup> and it was observed that polymerization proceeded more rapidly in the vicinity of a scratch on the crystal surface.<sup>(47)</sup> A striking proof of these ideas has been obtained by Sella and Trillat<sup>(48)</sup> and Sella and Bensasson,<sup>(49)</sup> 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<sup>(48, 49)</sup> 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.<sup>(19)</sup> 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 birefringent monomer crystals are converted to isotropic polymeric pseudomorphs of the original crystals;<sup>(23)</sup> the optical retardation decreases with time in a sigmoid manner. Using thin (10–20 $\mu$ ) 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.<sup>(23, 24)</sup> 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.<sup>(23, 24)</sup>

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,<sup>(50)</sup> 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.<sup>(23, 24)</sup> Application of the stress is considered to move the dislocations from reaction sites, leaving the radicals

in an environment where reaction cannot take place. It is then assumed that reaction does not occur in such piled up groups of dislocations, or, alternatively, it is possible that reaction in these localized regions is not observed under the experimental conditions employed. Subsequent removal of the stress allows the dislocations to become distributed throughout the lattice again and, at least in methacrylic acid, to return to their original lattice sites, where radicals are already present.<sup>(23, 24)</sup> It is not clear whether the induction period observed on removing the stress during the continued irradiation of acrylic acid is caused by dislocations taking up new sites in the monomer or by the extremely low radical concentrations present in these crystals. This type of experiment is extremely sensitive to experimental conditions and is discussed further in the section dealing with effects of pressure.

The view that dislocations are important as reaction sites in polymerizations of crystalline monomers has recently received general support from studies of lattice imperfections in sucrose. Thomas and Williams<sup>(51)</sup> have demonstrated that a detailed examination of sucrose crystals reveals various features very similar to those attributed to the presence of dislocations in metal crystals. By suitable etching techniques it has been shown that dislocations emerge at the {001} faces of cleaved sucrose crystals, and the presence of high dislocation densities along grain boundaries has been demonstrated in this way (similar etch pits have also been observed in other organic crystals).<sup>(52, 53)</sup> Further, it was demonstrated that water, liberated during the heating of sucrose crystals, is retained at the dislocation cores. Etching experiments provided evidence that dislocations in these crystals are mobile at temperatures below the decomposition temperature. Prolonged heating under vacuum, at temperatures where decomposition does occur, gives rise to decomposition volcanoes on the surface of the crystals, again probably situated at dislocation sites. Associated with these decomposition volcanoes are satellite volcanoes which suggest that dislocation multiplication occurs during decomposition. It was also noted that regions of higher imperfection density undergo preferential caramelization when sucrose crystals are heated.

Results of experiments of the types outlined above demonstrate that lattice imperfections are important as reaction sites. Further confirmatory evidence arises from the sensitivity of many of these reactions to the presence of very small concentrations of chemically inert impurities, from the general irreproducibility of reaction rates, and from the sigmoid nature of the conversion-time curves often observed during continuous irradiation at the polymerization temperature. Such additional evidence is referred to elsewhere in this review.

### Electron Spin Resonance Studies

The technique of electron spin resonance (e.s.r.) has been applied to a number of solid-state polymerizations. In some cases, the technique has been

used simply as a means of detecting the presence of radical species with a view to elucidating the mechanism of the polymerization. In others, workers have used measurements of free radical concentration in attempts to interpret reaction kinetics. Probably the most important applications of this technique result from detailed studies of changes in the spectra and radical concentrations under various experimental conditions, when information related to the mobilities of monomer molecules in the immediate vicinity of the radicals is obtained; such changes often occur gradually over a fairly wide temperature range. Free radicals are produced in a number of crystalline vinyl monomers,<sup>(64)</sup> including acrylamide,<sup>(37)</sup> methacrylamide,<sup>(65)</sup> acrylic acid,<sup>(66)</sup> itaconic acid,<sup>(67)</sup> and barium methacrylate<sup>(68)</sup> when subjected to high-energy irradiation at low temperatures (say  $-196^{\circ}\text{C}$ ); the e.s.r. spectra of the primary radicals are consistent with addition of a hydrogen atom to the unsubstituted end of the monomer. The mechanism of radical formation at these low temperatures is the capture, by monomer, of radiolytic hydrogen atoms produced by interaction of ionizing radiation with monomer. Evidence that monomers act as scavengers of hydrogen atoms is also provided from measurements of yields of radiolytic hydrogen.<sup>(69)</sup> There appears to be no evidence for the formation of other radicals (formed, for example, by loss of a hydrogen atom) which are stable in the above monomers at these low temperatures.

Studies on the orientational dependence of the e.s.r. spectra of irradiated single crystals of acrylic acid<sup>(66)</sup> and acrylamide<sup>(37)</sup> show that the primary radicals  $\text{CH}_3\dot{\text{C}}\text{HX}$  ( $\text{X} = \text{COOH}$ ,  $\text{CONH}_2$ ) are orientated along preferred directions in the crystal lattices. In each case the spectrum consists of two overlapping quartets.

Adler and Petropoulos<sup>(37)</sup> have shown that on warming crystals of acrylamide (m.p.  $86.3^{\circ}\text{C}$ ), irradiated at  $-196^{\circ}\text{C}$ , the first major change in the e.s.r. spectrum occurs at temperatures above  $-125^{\circ}\text{C}$  (e.g.  $-80^{\circ}\text{C}$ ); the original five-line spectrum changes to an anisotropic triplet. This new spectrum can be attributed to the addition of a monomer molecule to the original radical, producing a species formally identical with the propagating radical. No polymerization occurs at these low temperatures and from crystallographic considerations it has been suggested that the primary radical adds to a nearest neighbour molecule in the direction of the two-fold screw axis of the crystal.<sup>(60)</sup> Reaction probably stops at about dimer formation since the radical is then out of phase with the crystal lattice<sup>(60)</sup> and further propagation requires addition to a nearest-neighbour molecule in some other direction with consequent loss of anisotropy. Further warming to about  $-40^{\circ}\text{C}$  causes a decrease in radical concentration and a slight change in the spectrum. In the temperature range  $-30^{\circ}$  to  $-20^{\circ}\text{C}$  all anisotropy in the e.s.r. spectrum is lost. It is at this stage that the mobility of the molecules in the vicinity of the radical becomes sufficiently great to allow further propagation and, presumably, the

nucleation of polymer particles as a second phase.<sup>(67)</sup> Post-polymerization is only observed at temperatures above about  $-20^{\circ}\text{C}$ .

The occurrence of reactions which give rise to the observed changes in the e.s.r. spectrum requires a certain molecular mobility at the radical site, probably a lattice defect. At any given reaction site the mobility will be controlled by the detailed local environment and, since there is likely to be a spectrum of defects, there will be a range of local environments. Thus it is to be expected that as the temperature is raised the number of sites possessing sufficient molecular mobility to allow reaction will gradually increase; the observed change will, therefore, take place over a fairly wide temperature range.<sup>(37)</sup> Direct evidence for such a range of imperfections has been obtained in the solid-state polymerization of methacrylic acid.<sup>(25)</sup>

Irradiation of acrylamide at  $20^{\circ}\text{C}$  also leads to the formation of free radicals which exhibit the normal triplet e.s.r. spectrum. Ueda and Kuri<sup>(61)</sup> report that after low radiation doses ( $\sim 10^5$  rad) storage at  $25^{\circ}\text{C}$  causes a slight change in spectrum but no reduction in radical concentration. Subsequent heating to  $50$ – $60^{\circ}\text{C}$  produces a rapid decay in radical concentration but very little polymerization in the solid state, although melting the crystals produces significant polymerization. At higher doses ( $\sim 10^6$  rad) considerably more polymerization is observed in the crystalline state. Under the latter conditions a reduction in radical concentration accompanies polymerization, but stable radicals do remain trapped in the solid in detectable concentrations. It has previously been shown that, after irradiation at low temperatures, the radical concentration decreases to 52 per cent of its initial value after 60 hr at  $45^{\circ}\text{C}$ , but the rate of polymerization decreases by a factor of a hundred.<sup>(34)</sup>

Similar results are obtained with irradiated acrylic acid (m.p.  $12.6^{\circ}\text{C}$ ). The primary  $\text{CH}_3\dot{\text{C}}\text{H}(\text{COOH})$  radicals are orientated in the crystal in two distinct directions, corresponding to the orientations of the unreacted vinyl groups in the monomer crystal lattice.<sup>(56)</sup> The radicals, whose concentration is proportional to dose up to  $10^8$  rad, are stable at  $-196^{\circ}\text{C}$  but decay slightly on warming to  $-100^{\circ}\text{C}$ , without change in spectrum. At  $-80^{\circ}\text{C}$  there is a further reduction in radical concentration accompanied by a marked change in the e.s.r. spectrum; the anisotropic double quartet collapses into an isotropic triplet. This change corresponds to the formation of  $\sim \text{CH}_2\dot{\text{C}}\text{H}(\text{COOH})$  radicals randomly orientated in the crystal. The radical concentration decreases at about  $-50^{\circ}\text{C}$  to an undetectably low level, but polymerization does not occur until  $-25^{\circ}\text{C}$ ,<sup>(56)</sup> above which the rate of polymerization increases rapidly with temperature. Molecular motions in the crystalline monomer become detectable at about  $-30^{\circ}\text{C}$ , and increase steadily with increasing temperature; from broad-line n.m.r. data it is thought that these movements are rocking motions of hydrogen-bonded dimer units of monomer;<sup>(62)</sup> at temperatures above about  $0^{\circ}\text{C}$  more extensive motions are present.

It is also difficult to detect free radicals by e.s.r. during the u.v. initiated solid-state polymerization of this monomer.<sup>(23)</sup>

In contrast to acrylic acid, free radicals are readily observed during the solid-state polymerization of methacrylic acid at all temperatures up to the melting point (16°C).<sup>(23, 63)</sup> Ultraviolet irradiation of methacrylic acid, above about 0°C, gives rise to a 9-line e.s.r. spectrum, similar to that obtained by trapping radicals during liquid-phase polymerizations of methyl methacrylate. There has been considerable argument as to the origin of this spectrum but it now seems certain that the spectrum of the propagating radical arises from

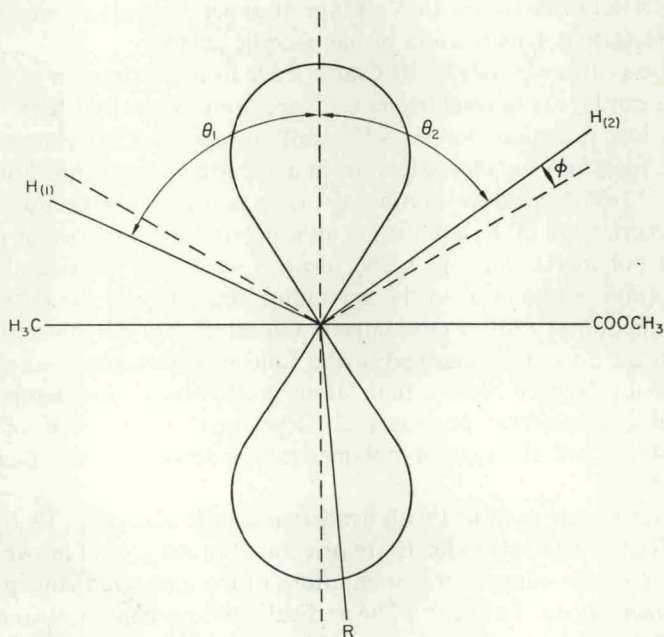


FIG. 1.

the single radical species  $\sim C_{\beta}H_2\dot{C}_{\alpha}(CH_3)COOMe$ , in which there is hindered rotation about the  $C_{\alpha}-C_{\beta}$  bond. Consequently, certain preferred conformations are adopted in which the methylene protons interact with the unpaired spin to different extents. Only the  $\alpha$ -methyl and  $\beta$ -methylene protons contribute to the hyperfine structure. Figure 1 represents a projection along the  $C_{\alpha}-C_{\beta}$  bond, where  $H_1$ ,  $H_2$  are the methylene hydrogens and R the remainder of the growing chain,  $\theta_1 + \theta_2 = 120^\circ$ .

In the symmetrical conformation  $\theta_1 = \theta_2 = 60^\circ$ ,  $\phi = 0^\circ$  and  $H_1$  and  $H_2$  are equivalent. Symons<sup>(64)</sup> proposed that the 9-line spectrum arises from two preferred conformations,  $\phi = 0^\circ$  and  $\phi = 15^\circ$ , present in different pro-

portions. This view has been confirmed by Kourim and Vacek,<sup>(65)</sup> using variously deuterated monomer, and by Fischer<sup>(66)</sup> and co-workers, who obtained highly resolved spectra of the propagating radicals in solution.

Irradiation of methacrylic acid (crystallized below about 0°C) at lower temperatures (say, about -50°C) gives rise to a 13-line e.s.r. spectrum which we attributed to the existence of a preferred conformation<sup>(63)</sup> with  $\phi = 5^\circ$  (see Fig. 1). This restricted conformation results from the lattice forces and the low molecular mobility at these lower temperatures. As the temperature of irradiation is raised to about -5°C the spectrum gradually changes from 13 to 9 lines as the molecular mobility increases<sup>(62)</sup> and the radicals relax from their restricted conformation.<sup>(63, 67)</sup> Most experimental spectra are mixtures of the 13 and 9-line spectra. Prolonged irradiation at low temperatures also causes the 13-line spectrum to change to a mixed spectrum as polymerization proceeds,<sup>(25, 63)</sup> and polymerization is more rapid under conditions where the 9-line spectrum is observed.<sup>(23, 31)</sup>

Addition of radiolytic hydrogen to itaconic acid produces the primary radical  $\text{CH}_3\dot{\text{C}}(\text{COOH})\text{CH}_2\text{COOH}$ . The e.s.r. spectrum of this radical results from the interaction of the unpaired electron with the same atoms as in the propagating methacrylic acid radical, and at room temperature the e.s.r. spectrum corresponds to a single conformation, similar to that in Fig. 1 ( $R = -\text{COOH}$ ), with  $\phi = 10^\circ$ .<sup>(57)</sup>

$\gamma$ -irradiation of barium methacrylate at -196°C gives rise to similar results;<sup>(58)</sup> the primary radical is  $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$  in which both methyl groups are rotating. O'Donnell *et al.*<sup>(58)</sup> observed that on subsequent heating to -80°C the e.s.r. spectrum changes as the primary radical is transformed into another species. From single crystal studies it has been shown that this second radical is orientated with respect to the crystal lattice and is a methacrylate radical in a restricted conformation, similar to that described for methacrylic acid, with  $\phi = 4^\circ$ . This restricted conformation is stable to temperatures about 50°C, below which polymerization is very slow. Above this temperature the spectrum changes gradually to an isotropic 5-line spectrum corresponding to a propagating radical in a preferred conformation with  $\phi = 15^\circ$ ; under these conditions polymerization is much more rapid. It has been suggested<sup>(58)</sup> that the adoption of this second preferred conformation may be due to the attachment of the propagating radical to the lattice during polymerization, with the bulk of the polymer chain existing in an amorphous phase; the lack of orientation was attributed to disintegration of the crystal during polymerization into crystallites which become disordered. Alternatively, it could be suggested that the radical is detached from the crystal lattice and therefore anisotropic, with the preferred conformation due to the presence of the barium ions which will, on average, be associated with two carboxyl groups.

Low-temperature irradiation of other monomers also leads to the formation of primary radicals corresponding to the addition of radiolytic hydrogen

atoms to monomer. With acrylonitrile<sup>(54, 68)</sup> and methacrylamide,<sup>(54, 55)</sup> however, there is evidence for the presence of other radicals stable at these low temperatures. In irradiated acrylonitrile the extra lines in the e.s.r. spectrum have been attributed to the  $\text{CH}_2 = \dot{\text{C}}\text{CN}$  radical.<sup>(54)</sup> Methacrylamide apparently gives rise to two additional radicals and it has been proposed<sup>(55)</sup> that these are  $\text{H}_2\text{N}\dot{\text{C}} = \text{O}$  and  $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)\text{CONH}_2$ , where  $\text{R}$  may be  $\text{CH}_2 = \text{C}(\text{CONH}_2)\text{CH}_2-$  or  $\text{CH}_2 = \text{C}(\text{CH}_3)-$ , formed by loss of  $\alpha$ -hydrogen or the amide group, respectively, from the monomer. In both these cases, and others, on warming to temperatures where polymerization occurs, the spectrum of the normal propagating radical appears. Both spectral changes and reductions in radical concentration in acrylonitrile samples are associated with the occurrence of solid-state transitions.<sup>(68)</sup>

Similar results have been obtained as a result of direct addition of H and D atoms (produced in a microwave discharge) to monomers.<sup>(69)</sup> Using methyl methacrylate, acrylonitrile, and styrene, the predominant species formed result from addition of H or D to the unsubstituted end of the vinyl group.

The solid-state polymerization of monomers discussed so far in this section is generally assumed to proceed by a radical mechanism. It is, however, always possible that ionic intermediates play a part in some of these polymerizations since the detection of free radicals in irradiated solids is not proof of the mechanism. Indeed, radicals have been observed in some irradiated monomers where solid-state polymerization is thought to proceed by an ionic mechanism.  $\gamma$ -irradiation of isobutene in a 3-methyl pentane glass at  $-196^\circ\text{C}$  gives rise to two superimposed e.s.r. spectra of 8 and 15 lines, both of which arise from the presence of isobutene.<sup>(10)</sup> The two spectra were attributed to different conformations of the  $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{R}$  radical, and it has been suggested that the primary species are radical cations, with propagation proceeding by a cationic mechanism.<sup>(70)</sup>

Other solid-state polymerizations of unsaturated monomers which are thought to proceed by an ionic mechanism but involve the formation of radical ions as primary species are those of conjugated dienes<sup>(71)</sup> (initiated by electron bombardment at  $-196^\circ$ ), vinyl carbazole<sup>(72)</sup> at  $20^\circ\text{C}$  (initiated by added electron acceptors which form charge-transfer complexes with the monomer), and nitroethylene<sup>(73)</sup> in a 2-methyl tetrahydrofuran glass ( $\gamma$ -irradiation at  $-196^\circ\text{C}$ ). In the first two cases it has been suggested that propagation is cationic and in the last case anionic.

### Variations in Crystal Structure

It may be anticipated that, if a monomer can exist in more than one crystalline modification, each modification will exhibit a different reactivity in the solid state. Any such change in reactivity implies that the control exercised over the reaction by the lattice varies with the crystal structure,

regardless of whether this control is a direct or indirect influence of the lattice. In this section we discuss a few studies which have been carried out on monomers in more than one crystalline form.

There is a first-order transition in crystalline acrylonitrile at  $-113^{\circ}\text{C}$ , with high- and low-temperature forms stable above and below the transition point, respectively.<sup>(68)</sup> According to Bensasson *et al.*<sup>(68)</sup> samples of the high-temperature form can be obtained at  $-196^{\circ}\text{C}$  by shock-cooling liquid monomer, and on subsequent warming this high-temperature form reverts to the stable low-temperature form at about  $-130^{\circ}\text{C}$ . After X-irradiation at  $-196^{\circ}\text{C}$ , the two forms exhibit different behaviour on warming. Samples of the low-temperature form treated in this way do not polymerize below  $-113^{\circ}\text{C}$ , at which temperature polymerization to 4 per cent conversion accompanies transformation to the high-temperature form. On warming pre-irradiated samples of the high-temperature form slowly, polymerization is first observed at  $-135^{\circ}\text{C}$ , when the unstable high-temperature form reverts to the low-temperature form with about 1 per cent conversion to polymer, whereas on rapid warming to temperatures above  $-113^{\circ}\text{C}$  about 10 per cent conversion to polymer is achieved. It was concluded that post-irradiation polymerization occurs only in the high-temperature form, or in association with a transition.<sup>(68)</sup> Barkalov *et al.*<sup>(74)</sup> have also stated that post-irradiation polymerization does not occur in acrylonitrile below  $-140^{\circ}\text{C}$ .

The existence of transitions in crystalline acrylonitrile have been referred to by other workers,<sup>(75-9)</sup> and Arrhenius plots of rates of in-source polymerizations often show a break between  $-140^{\circ}\text{C}$  and  $-110^{\circ}\text{C}$ , corresponding to different activation energies above and below the transition point. Bensasson *et al.*<sup>(68)</sup> have investigated the X-ray induced in-source polymerization of both crystal forms at temperatures above  $-174^{\circ}\text{C}$ . Below  $-140^{\circ}\text{C}$  the high-temperature form polymerizes more rapidly than the low-temperature form, but at temperatures between  $-140^{\circ}\text{C}$  and  $-113^{\circ}\text{C}$  the rates, at conversions less than 4 per cent, are approximately equal, since in this temperature range the high-temperature form reverts to the low-temperature form. Above  $-113^{\circ}\text{C}$ , where only the high-temperature form is stable, the rates are again equal reaching a maximum at  $-90^{\circ}\text{C}$ , and then falling rapidly to the melting point; at temperatures just above the melting point the rates of radiation-induced polymerization are extremely low.

A number of explanations have been put forward to account for the abrupt changes in rate of polymerization with temperature. The possibility of different reaction mechanisms, including radical<sup>(80, 81)</sup> and ionic<sup>(78, 81)</sup> propagation, collective excitation<sup>(68, 77, 79, 82)</sup> and thermal energy chains,<sup>(14)</sup> occurring in different temperature regions have been considered. It has also been suggested that the sudden onset of post-polymerization on warming irradiated monomer samples could be due to the release of a second type of active centre;<sup>(68)</sup> this is consistent with the observation of thermoluminescence



at the transition point.<sup>(14)</sup> However, according to Barkalov *et al.*<sup>(83)</sup> the increased yield in post-polymerization results from an increase in molecular weight, and is not consistent with an increase in initiation by trapped electrons. Further, it might be expected that enhanced initiation by release of trapped electrons would produce radical ions, the existence of which could be detected by changes in the e.s.r. spectrum; there is apparently no evidence for this. In view of our present knowledge that the polymerization of other vinyl monomers is largely controlled by the mobilities of molecules in the lattice, it would seem reasonable to propose that the observed differences in rates of polymerization are due to the presence of different molecular motions in the two forms of the crystalline monomer. An explanation of this type was put forward by Bensasson *et al.*<sup>(68)</sup> who proposed that the freedom for movement is greater in the high-temperature form. On this basis it would appear that there is insufficient mobility in the monomer in its low-temperature form for the post-irradiation reaction to proceed, so that post-polymerization is only observed in the high-temperature form or when the molecules move during a transition between the two forms. Chapiro and Inoue<sup>(78)</sup> suggested that the nature of the monomer crystals controls propagation rather than initiation, and according to Barkalov *et al.*<sup>(74)</sup> limiting conversions during the in-source polymerization are only observed below  $-140^{\circ}\text{C}$ . It seems possible that at least some of the polymerization, observed by various workers, at temperatures as low as  $-196^{\circ}\text{C}$  may be due to a fraction of the monomer being present in the high-temperature form, since crystallization conditions are often not quoted.

Chen and Grabar<sup>(84)</sup> obtained evidence for the existence of three polymorphic modifications of tributyl vinyl phosphonium bromide, and studied the solid-state polymerization of two forms. On X-irradiation both forms gave amorphous polymer and showed similar kinetic features; the rate of polymerization is isotropic, and conversion-time curves are sigmoid to 100 per cent conversion throughout the temperature range  $-80^{\circ}$  to  $+60^{\circ}\text{C}$ . The more unstable form polymerizes faster than the stable form by a factor of about two. No other distinguishing features between the polymerization of the two forms were observed and the difference in rates was attributed to different collisional and steric factors governed by the crystal structures. Since the packing of the molecules in the two forms is different there will be differences in the mobilities of the molecules in the lattice and in the imperfections, which will also have different structures in the two forms.

Calcium acrylate can be obtained in a number of forms, as shown by Lando and Morawetz,<sup>(85)</sup> who studied the post-irradiation polymerization of the crystalline dihydrate and monohydrate and the crystalline and "amorphous" anhydrous salts prepared from each of the hydrates, with the results summarized in Table 1. As is obvious from this table, the yields obtained vary considerably with the modification used, and these must reflect the different

TABLE I.  
POST-IRRADIATION POLYMERIZATION OF CALCIUM ACRYLATE AT 101°C

Hydrate	Form	% Yield (max.)
Dihydrate	Crystalline	52
Monohydrate	Crystalline	0
Anhydrous (ex-dihydrate)	Crystalline	53
Anhydrous (ex-monohydrate)	Crystalline	14
Anhydrous (ex-dihydrate)	"Amorphous"	90
Anhydrous (ex-monohydrate)	"Amorphous"	23

arrangements of ions and water molecules in the various forms. Apparently, only in the case of the dihydrate is there any information on the crystal structure.<sup>(85)</sup>

The number of crystalline modifications in which a monomer can be obtained is limited, but a study of the polymerization of the acrylate ion in different crystalline arrangements can be extended to include other acrylate salts. A preliminary investigation of this type has been carried out by Morawetz and Rubin<sup>(86)</sup> who studied the post-irradiation polymerization of the alkali-metal acrylates. At any given temperature the rates of polymerization vary markedly with the alkali metal, usually in the order potassium > lithium > sodium; the potassium salt polymerizes more readily at room temperature than does the lithium salt at 100°C. A similar trend is observed for degrees of polymerization. The rates of polymerization of the less reactive lithium and sodium salts are the most sensitive to temperature; in the post-irradiation reaction of lithium methacrylate an increase in temperature from 101°C to 155°C increases the polymer yield from 2 per cent to 15 per cent, in the same reaction time (the increased yield is associated with a decrease in molecular weight). X-ray studies on partially polymerized potassium acrylate show that the polymer forms a separate amorphous phase within the monomer crystal.

A few results have also been reported for methacrylate salts. In the initial stages of post-irradiation polymerizations at 152°C, potassium methacrylate polymerizes more rapidly than does the sodium salt, but polymerization of the latter monomer is autocatalytic (to a limiting yield of about 6 per cent) and at conversions greater than 1 per cent it polymerizes more rapidly than the potassium salt.<sup>(86)</sup> No post-irradiation polymerization was observed in lithium methacrylate up to 160°C.<sup>(86)</sup> Barium methacrylate dihydrate, which has a crystal structure similar to calcium acrylate dihydrate, polymerizes to about 50 per cent conversion in the temperature range 50°–120°C after irradiation at -78°C.<sup>(83)</sup> At high temperatures polymerization is accompanied by dehydration to an unreactive anhydrous salt.

In discussing reactivities of the alkali acrylates, Morawetz and Rubin<sup>(86)</sup> suggest that "the bulk of the polymer lies in an amorphous phase, but the reactive end of the growing chains is effectively anchored in the lattice of the monomer crystal, and its reactivity is controlled by the geometry of the crystal lattice." There is, at present, no information available on molecular motions in these salts but, since polymerization in many other monomers appears to require a certain minimum mobility in the lattice, it may be suggested that the different reactivities of the acrylate and methacrylate ions in the various salts arise from different molecular motions and structures of imperfections which depend on the packing of the ions and interionic forces in the individual monomers. As reaction proceeds, with formation of amorphous polymer, there must be a rearrangement of the anions, with the development of strain in the lattice, and it may be visualized that the cations in the vicinity of the polymer molecules rearrange to some extent. Reaction may then be controlled partly by the ability of the cations to move and modify the forces maintaining other anions in their lattice positions.

### Topotactic Polymerization

Considerable effort has been devoted to establishing a relation between the crystal structure of the monomer and the mechanism of polymerization. Detailed investigations of this type have largely centered on the polymerizations of cyclic monomers, which may give rise to highly crystalline polymers and were, until recently, thought to be entirely governed by the perfection of the monomer lattice. Since it has been clearly demonstrated that the polymerizations of small vinyl monomers, such as acrylamide and acrylic acid, take place in imperfections, there is a danger of completely disregarding the influence of the lattice in such polymerizations, although the lattice must control the polymerization to some extent, in that it determines the structures of the imperfections and the processes which can take place in them. The extent of this control will vary with the monomer and depend on the intermolecular forces, the packing of the molecules, the structures of the imperfections, and the geometrical rearrangements which must accompany polymerization.

Solid-state reactions in which the host lattice exercises a dominating influence over the orientation of the products are often referred to as topotactic reactions, and this phrase has been used to describe a number of solid-state polymerizations, especially those of cyclic monomers. There are at least three definitions of the term "topotactic", each of which implies a different degree of control by the host lattice in determining the orientation of the product. Lotgering<sup>(87)</sup> uses topotactic to describe "all solid-state reactions that lead to a material with crystal orientations which are correlated with the crystal orientations in the initial product." In a more stringent definition, Mackay<sup>(88)</sup>

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.*<sup>(89)</sup> 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.*<sup>(89)</sup> 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.*<sup>(90)</sup> 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<sup>(91)</sup> 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,<sup>(92)</sup> 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.*<sup>(90)</sup> 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<sup>(93)</sup> 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*-benzamidostryrene,<sup>(19)</sup> 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*-benzamidostryrene 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.*<sup>(19)</sup> 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.<sup>(19)</sup> 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.*<sup>(19)</sup> 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*-benzamidostryrene 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<sup>(94)</sup> succeeded in polymerizing 2,3-dimethyl-1,3-butadiene, 2,3-

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

preferred orientation and also cause a specific conformation to be adopted, as observed with some monomers. It may be possible from information of this type to obtain evidence on the structure of the imperfections. Under these conditions considerable strain must be developed in the vicinity of the radical.

Further propagation is apparently not possible until the thermal motions of the molecules increase sufficiently for this strain to be relieved and to allow addition of the radical to another neighbouring monomer molecule. This further addition may well not occur in a specific crystallographic direction, and the orientation of the radical with respect to the monomer crystal axes may be lost. It is at this stage that the polymer chain is likely to become detached from the monomer lattice, by breaking strained intermolecular bonds, and nucleate an amorphous polymer phase within the monomer crystal.<sup>(37)</sup> The detachment of the growing radical from the lattice allows a relaxation process to occur and the radicals to take up their preferred conformations, within any limitations imposed by the free volume available and any strong residual intermolecular or interionic forces which may still be operative (depending on the nature of the monomer); an isotropic e.s.r. spectrum of the normal propagating radical is generally observed.

At this point it is of interest to consider in detail the change from radicals under restrictions imposed by the lattice to radicals whose conformation and orientation are not controlled by the lattice. This change has been studied in some detail in the polymerization of methacrylic acid during continued u.v. irradiation,<sup>(25, 31)</sup> when the e.s.r. spectrum changes from 13 lines to 9 lines. The radicals in the restricted form ( $\phi = 5^\circ$ , Fig. 1) give the 13-line spectrum and are denoted *T*-type, while the radicals in their unrestricted form and which give the 9-line spectrum are known as *N*-type. Most experimental spectra consist of a mixture of 13- and 9-line spectra and a parameter  $X/Y$  was defined ( $X/Y = 0$  for 9 lines) which would allow estimation of the fraction of radicals in the restricted conformation. Changes in  $X/Y$  under different conditions allow the factors which control the relaxation from *T*-type to *N*-type to be identified.<sup>(25, 31)</sup> For samples crystallized at  $-196^\circ\text{C}$  and irradiated at temperatures in the range  $-50^\circ\text{C}$  to  $-20^\circ\text{C}$  (where little polymerization occurs) the value of  $X/Y$  decreases with time to a constant value characteristic of the irradiation temperature; lower values are obtained at the high temperatures. As  $X/Y$  decreases, the radical concentration increases to a stationary value; the stationary concentration increases with increasing irradiation temperature. It is concluded that at long irradiation times a stationary state is developed, radicals continuously being generated in the *T*-form in the lattice defects, relaxation from *T*-type to *N*-type (by what is believed to be a photo-assisted process<sup>(25)</sup>) and termination occurring at the same rate as initiation. Each act of initiation in u.v.-initiated polymerizations must generate two radicals in close proximity, i.e. in the same reaction site.



Initially both radicals are of the  $T$ -type. It is visualized that termination involves the relaxation of one of these radicals to a small  $N$  radical which can then react with a propagating  $N$  radical already present in the defect. Eventually the other  $T$  radical can relax to  $N$ . Thus, termination takes place during irradiation. The rate of the relaxation process must depend on the mobility of the molecules in the defect, and possibly on the energy introduced into the crystal by absorption of light, with the result that the process  $T \rightarrow N$  will occur more readily at the higher temperatures giving rise to a lower limiting value of  $X/Y$ , or  $[T]/([T] + [N])$ .

The stationary radical concentration, at long irradiation times, is taken to indicate that all defects capable of supporting reaction contain radicals.<sup>(25)</sup> Although all the samples were crystallized under the same conditions, and might be expected, on average, to contain the same number of defects, the stationary radical concentration increases with increasing temperature. This demonstrates that the crystalline monomer contains a range of imperfections, in which the monomer molecules have different mobilities. Hence, as the temperature is raised the molecular mobility in each defect increases and the number of imperfections capable of supporting reaction also increases.

Studies of the type outlined above have shown that both the number and nature of imperfections can be varied by changing crystallization conditions.<sup>(25)</sup> Samples of methacrylic acid crystallized at  $-196^\circ\text{C}$  and irradiated at  $-20^\circ\text{C}$  give a significantly higher limiting radical concentration than samples crystallized at higher temperatures, presumably as a result of a higher rate of nucleation and a higher concentration of defects. On prolonged irradiation all samples gave the same limiting value of  $X/Y$ , but in the initial stages samples crystallized at higher temperatures ( $-60^\circ\text{C}$  to  $-20^\circ\text{C}$ ) gave lower values of  $X/Y$ , indicating a higher level of molecular mobility in the defects. This higher mobility might arise from the concentration of impurities in the defects, since the presence of isobutyric acid in concentrations as low as 0.02 per cent in samples crystallized at  $-196^\circ\text{C}$  reduces the initial values of  $X/Y$  considerably.<sup>(31)</sup> In samples containing up to at least 0.1 per cent isobutyric acid the same final value of  $X/Y$  is obtained, even though this may require the ratio to increase in the initial stages. The higher molecular mobility in the presence of isobutyric acid accelerates the process  $T \rightarrow N$  initially, although ultimately the effect is lost. It may be visualized that the isobutyric acid is concentrated around dislocations in the form of a Cottrell cloud.<sup>(50)</sup> The isobutyric acid will exert its maximum influence initially, and as reaction proceeds into more perfect regions of the crystal its effect will decrease. The presence of isobutyric acid brings about a large increase in rate of polymerization at slightly high temperatures, about  $-14^\circ\text{C}$ , where polymerization is more rapid.<sup>(31)</sup>

Under conditions where the in-source polymerization is rapid and high conversions are obtained these considerations require some modification,

since the idea of reaction proceeding in a limited number of defects is unrealistic. High rates of polymerization are often associated with high molecular mobility; at 4°C broad-line n.m.r. experiments show that a fraction of the monomer molecules in acrylic acid are sufficiently mobile to allow partial resolution of the resonance peaks of the individual protons.<sup>(62)</sup> The in-source polymerizations are often characterized by sigmoid conversion-time curves, autocatalytic to high conversion. As mentioned in the discussion of reaction kinetics, the autocatalytic behaviour could be a consequence of the formation of an amorphous polymer phase in the original imperfections and reaction occurring at the monomer-polymer interface, thus causing the reaction to accelerate as the area of the interface increases. If this process continued indefinitely the results of observations on partially polymerized crystals would be expected to show the continuous growth of a relatively small number of polymeric particles. The results of Sella *et al.*<sup>(48, 49)</sup> on partially polymerized crystals of acrylamide appear to suggest that polymer particles do grow in the manner described above to diameters of the order of 300–400 Å, but they also indicate that the number of nuclei increases during polymerization. As polymerization proceeds in a dislocation, strains develop at the monomer-polymer interface and in the surrounding lattice. This strain could give rise to dislocation multiplication, and hence increase the number of reaction sites, giving autocatalytic behaviour. There is evidence of dislocation multiplication in the thermal decomposition of sucrose where reaction gives rise to “volcanoes” on the crystal surfaces, probably at the points of emergence of dislocation lines. These volcanoes are surrounded by a ring of small satellite “volcanoes” and represent the formation of new reaction sites.<sup>(51)</sup>

At the temperatures where polymerization is rapid one can still visualize that the processes described for reactions at low temperatures occur in the dislocations but at a much higher rate, so that there is no evidence of radicals in their restricted forms. It is possible that under these conditions radicals are not formed in a specific conformation. Relatively, propagation must be considerably enhanced by the increase in thermal motions in the crystals. There is also evidence that propagation is assisted by light of wavelengths too long to give rise to radical formation,<sup>(25)</sup> the mechanism for this is presumably the decay of excitons in the imperfections, effectively increasing the thermal motions. We may now speculate on the nature of the physical effect which brings about the gradually decreasing rate of polymerization during the post-irradiation reactions of many monomers. In the absence of radiation no new polymeric nuclei will be formed and extensive post-polymerization requires the continued growth of existing nuclei. The results of Sella *et al.*<sup>(48, 49)</sup> appear to show that at high conversions polymerized crystals of acrylamide contain large numbers of small nuclei. It might be suggested that the nuclei only grow readily to 300–400 Å in diameter, and this may indicate the area

around the dislocation core where monomer molecules are sufficiently displaced from their lattice positions to react readily under the reaction conditions. Further growth of these nuclei may be slow and depend on the rate at which monomer molecules can leave the more perfect regions of the lattice.

The mechanism suggested above is largely based on evidence from the polymerization of monomers carrying small substituent groups, e.g. acrylamide and acrylic and methacrylic acids. In these cases there is no evidence that the substituent groups on monomer molecules which have been incorporated into polymer play any further part in the reaction. Although the basic features of this mechanism might describe the solid-state polymerization of other monomers, in the case of monomers carrying large and strongly interacting substituent groups the details would require modification to take account of possible side-chain crystallization in the polymer and the retention of strong interactions between polymer and residual monomer.

#### Effects of Additives

The influence of additives has been studied with various objectives in view. Two types of experiment, which account for a large proportion of these studies, but not discussed in this section, are the use of known polymerization initiators to induce polymerizations in which the nature of the propagating species is known, and the use of inhibitors to determine the nature of the propagating species in radiolytically induced polymerizations. The studies described in this section are concerned with the presence of additives in concentrations greater than impurity levels; the influence of low concentrations of inert impurities has already been discussed.

Acrylamide and propionamide form solid solutions in all proportions, and the polymerization of acrylamide at 25°C in these solid solutions is the most extensively studied binary system. Fadner and Morawetz<sup>(34)</sup> found that plots of fractional conversion against time for the post-irradiation reaction of pure acrylamide and the solid solution containing 10 per cent propionamide are identical, and that for concentrations up to 50 per cent propionamide almost identical curves are obtained up to 10 per cent conversion, after which the rates of fractional conversion decrease with increasing propionamide content. Further, the molecular weights of the polymers are greatly reduced by propionamide concentrations as low as 10 per cent. These results were interpreted in terms of extensive transfer to propionamide in the solid state; the efficiency for transfer decreasing with increasing temperature.<sup>(34)</sup> However, Adler and Reams<sup>(60)</sup> obtained 100 per cent conversion of acrylamide in solid solutions containing up to 90 per cent propionamide, and up to 60 per cent conversion in solid solutions containing only 4 per cent acrylamide. Accepting that all polymers extracted are high polymers,<sup>(37)</sup> the results obtained from

solid solutions containing low concentrations of acrylamide are inconsistent with excessive transfer to propionamide.

Adler and Reams<sup>(60)</sup> propose that a radical can react with any of a number of near-neighbour molecules, in a manner similar to that already discussed in relation to changes in the e.s.r. spectra. Although there is considerable mobility in the lattice it seems unlikely that acrylamide molecules can diffuse through the propionamide lattice since oxygen, which is able to diffuse through propionamide can only diffuse through acrylamide along lattice imperfections.<sup>(30)</sup> The high conversions achieved in solid solutions containing low concentrations of acrylamide are attributed to diffusion of propionamide and acrylamide at the polymer-monomer interface, thus making the monomer accessible for reaction.<sup>(60)</sup> It has also been suggested that in the very dilute solutions some of the acrylamide will be concentrated around dislocation lines in the propionamide lattice so that a minimum of molecular movement is required for reaction. The remaining acrylamide, in the more perfect regions of the crystals, will be unable to react, thus giving rise to limiting conversions.<sup>(31)</sup>

An alternative explanation for the decrease in molecular weight of the polymers obtained from solid solutions containing relatively low concentrations of propionamide has been proposed.<sup>(31)</sup> This explanation, based on the mechanism outlined in the preceding section, assumes that polymerization occurs initially only at specific sites. The hydrogen atoms which initiate the  $\gamma$ -ray induced polymerization will diffuse throughout the sample and may add to any acrylamide molecule, but only those at suitable sites will be effective in bringing about polymer formation. In the presence of propionamide, yields of radiolytic hydrogen are much greater than in pure acrylamide,<sup>(59)</sup> and under such conditions the concentrations of "inactive" radicals may be higher. If the rate of polymerization is related only to the initial density of suitable sites, the rate of polymerization to high conversion may not be affected by the higher yields of radiolytic hydrogen, but at high conversion the "inactive" radicals may become capable of both initiating and terminating polymerization, and hence cause a reduction in molecular weight of the polymer.

Kaetsu *et al.*<sup>(101)</sup> have discussed the influence of various additives (at concentrations of about 10 per cent) on the polymerizations of acrylic acid and acrylamide in terms of their effect on the physical structure of the binary systems. This discussion is based on estimates of interactions between additive and monomer, dislocation densities, and grain sizes. It was concluded that additives which interact strongly with the monomer (e.g. through hydrogen-bonding) have the greatest effect, and suggested that dislocations associated with grain boundaries are the most effective sites for reaction.

Methyl methacrylate polymerizes slowly in the solid state when bombarded with high energy electrons,<sup>(102)</sup> but it has been reported that this monomer

does not polymerize at  $-78^{\circ}\text{C}$  when subjected to X- or  $\gamma$ -rays.<sup>(103)</sup> However, when the latter experiments are repeated in the presence of large concentrations of additives, such as mineral oils, polymerization to high conversion is readily achieved.<sup>(75)</sup> This effect is presumably physical in origin, with the additive enhancing diffusion of monomer. An equivalent result can be achieved by incorporating long side chains into the monomer; both cetyl methacrylate<sup>(103)</sup> and octadecyl methacrylate<sup>(104)</sup> polymerize in the solid state. It has recently been reported that  $\gamma$ -rays do initiate the solid-state polymerization of methyl methacrylate at  $-65^{\circ}\text{C}$ , but only after a long induction period.<sup>(105)</sup>

Kargin *et al.*<sup>(27)</sup> have observed, that in the presence of low concentrations of solvent, crystalline salts undergo polymerization on mechanical disintegration. It was proposed that disintegration produces lattice vacancies which act as traps for electrons which in turn initiate polymerization under suitable conditions of molecular mobility. It was also observed that a mixture of sodium acrylate and lithium or magnesium chloride crystals, in the presence of traces of solvent undergo ion exchange accompanied by polymerization.<sup>(28)</sup>

### Polymer Structure

An obvious feature of interest in these polymerizations is the microstructure of the polymers, especially if this differs from that obtained by liquid-phase polymerizations. To date the structures of the polymers have hardly been investigated, apart from crystallographic studies on polymers produced by the polymerization of cyclic monomers; these latter polymers have no asymmetric carbon atoms in the backbone.

Polymers resulting from the free-radical polymerization of vinyl monomers in the liquid phase are generally atactic, with a tendency for syndiotactic triads (configuration of asymmetric carbon atoms in the backbone are alternately *d*- and *l*-), as defined by Bovey and Tiers,<sup>(106)</sup> to predominate. With increasing temperature the syndiotactic content decreases and the polymers become more random. A random polymer contains 25 per cent isotactic, 50 per cent heterotactic, and 25 per cent syndiotactic triads and has a value of  $\sigma = 0.5$  (the probability of consecutive asymmetric carbon atoms having the same configuration).<sup>(106)</sup> This situation holds for polymethylmethacrylate<sup>(106)</sup> and for polymethacrylic acid,<sup>(107)</sup> prepared by free-radical polymerization both of which normally contain  $\sim 10$  per cent isotactic triads. The radiation induced solid-state polymerization of methacrylic acid at  $0^{\circ}\text{C}$  gives a polymer with a larger isotactic content ( $\sim 20$  per cent) and  $\sigma$  value (0.4) than the solution polymerization at  $90^{\circ}\text{C}$  ( $\sigma = 0.25$ ,  $\sim 12$  per cent isotactic triads).<sup>(108)</sup> It was suggested that the control of the microstructure may result from the crystal structure limiting the monomer units which may be attacked by the propagating radical.<sup>(108)</sup> Post-irradiation polymerization of crystalline barium metha-

crylate dihydrate to low conversions produces polymers in which the isotactic content is greater than the syndiotactic content.<sup>(85)</sup> As conversion of the latter monomer increases from about 10 per cent to 60 per cent (at 50°C) the isotactic content decreases from 37 per cent to 21 per cent and the syndiotactic content increases from 15 per cent to 33 per cent, i.e. as polymerization proceeds the microstructure of the polymer changes. Since this is a post-irradiation reaction, the microstructure must change along the polymer chain; in the later stages growth approximates to that observed in liquid phase. At 120°C there is an increase in isotactic content to 48 per cent at about 50 per cent conversion, with only about 8 per cent syndiotactic triads; at these temperatures dehydration to an unreactive anhydrous form accompanies polymerization.<sup>(85)</sup> Solid-state polymerization of methyl methacrylate produces a polymer containing more heterotactic and less syndiotactic triads than solution prepared polymer; the isotactic content remains approximately constant.<sup>(105)</sup>

Tabata and co-workers<sup>(77, 109)</sup> have repeatedly stated that polymers prepared from solid acrylonitrile in its various forms have different properties, e.g. thermal stability. These differences are attributed to variations in the stereoregularity of the polymers. From infra-red evidence it was shown that on heat treatment of polymers prepared at low temperatures, about -196°C,  $-\text{C} \equiv \text{N}$  groups are converted to  $>\text{C} = \text{N}$ -groups at a higher rate than in polymers prepared at higher temperatures. It was suggested that the preferential formation of  $>\text{C} = \text{N}$ -linkages is due to increased syndiotacticity in the polymers prepared at -196°C, and similar considerations were applied in the case of polymethacrylonitrile,<sup>(110)</sup> but as pointed out by Morawetz<sup>(12)</sup> the intra-molecular formation of  $>\text{C} = \text{N}$ -linkages is more favourable in isotactic polymer, in agreement with more recent n.m.r. studies in polymethacrylonitrile, when polymers prepared by solid-state polymerization were found to contain virtually no syndiotactic material.<sup>(111)</sup> Polyacrylonitrile obtained by polymerization at -196°C, initiated by vacuum u.v. radiation, was found to contain very few  $-\text{C} \equiv \text{N}$  groups, and, although treatment of polyacrylonitrile in this way is expected to cause intramolecular formation of  $>\text{C} = \text{N}$ -linkages, it was proposed that under these conditions polymerization through the vinyl group and the nitrile group occur simultaneously.<sup>(112)</sup>

X-ray diffraction patterns of polymer formed by polymerization of crystalline potassium acrylate show four diffuse rings which are not obtained from polymers prepared in solution.<sup>(86)</sup> Polyvinyl stearate prepared by polymerization in the solid phase is said to be more isotactic than that prepared in solution.<sup>(90)</sup> Infra-red studies indicate that polymerizations of *n*-butyl isocyanate in the liquid and solid phases give different polymers.<sup>(113)</sup> Polymerization of solid terephthalonitrile oxide apparently produces a polymer containing oxazoxime rings, while liquid-phase polymerization produces furoxan rings; from a consideration of the monomer crystal structure it is stated that the

formation of the former ring structure could occur with a contraction of the lattice while the latter requires an expansion.<sup>(114)</sup> Other changes in polymer structure have been referred to in the section dealing with topotactic processes.

More detailed studies are required to obtain an understanding of the way in which the stereoregularity of the polymer is controlled by the lattice, but it appears that this stems from a limitation of the types of molecular motion a monomer molecule can undergo, of the conformation of the propagating species or of the ways in which monomer can approach the reactive species, or some combination of these factors.

## POLYMERIZATION OF CYCLIC MONOMERS

### Radiation Induced

Considerable effort has been devoted to a detailed study of the polymerization of cyclic monomers since Okamura, Hayashi and their co-workers demonstrated that the radiation induced polymerization of crystalline trioxan,<sup>(6)</sup>  $\beta$ -propiolactone,<sup>(115)</sup> diketene<sup>(116)</sup> and 3,3-bis(chloromethyl)oxetane<sup>(117)</sup> can lead to the formation of crystalline and orientated polymers; propagation proceeds through a ring-opening mechanism.

This effort has been largely directed towards understanding the relationship between the crystal structure of the monomer and the direction of growth and the structure of the polymer. In an early paper on this subject Okamura *et al.*<sup>(39)</sup> published X-ray diffraction patterns and photomicrographs of polymers formed by polymerizing single crystals of the above monomers. These results demonstrate quite clearly that highly crystalline fibrous polymers are formed and that the fibres are aligned in specific orientations with respect to the crystallographic axes of the parent monomer crystal. Both trioxan and polyoxymethylene, formed by polymerization of this monomer, have hexagonal crystal structures and in partially polymerized crystals their *c*-axes are seen to be parallel.<sup>(118)</sup> Similar observations on polymers prepared by irradiation of  $\beta$ -propiolactone and 3,3-bis(chloromethyl)oxetane demonstrated that the fibres are aligned at 90° and 45° to the growth directions of the monomer crystals respectively.

Various workers have carried out partial analyses of the X-ray diffraction patterns from polyoxymethylene samples prepared by polymerization of crystalline trioxan under different conditions, and have obtained slightly different results.<sup>(119-21)</sup> Radiation induced polymerizations of single crystals of trioxan are usually carried out at 55°C and Carazzola *et al.* have performed a detailed X-ray analysis of the polymer formed under these conditions.<sup>(122)</sup> These latter workers found that the polyoxymethylene has a twinned structure, representing growth of the polymer along two directions in the monomer crystal (*viz.* along the *c*-axis of the monomer crystal and at an angle of 76°7' to this direction). Twinned structures have also been reported for poly-

mers prepared by solid-state polymerization of trithiane<sup>(123-4)</sup> and triselepane,<sup>(125)</sup> 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.<sup>(40)</sup>

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,<sup>(39, 126-33)</sup> 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.<sup>(39)</sup> 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.*<sup>(130)</sup> observed maximum polymer yields of about 55 per cent at 55°C and 17 per cent at 50°C, while Sakamoto *et al.*<sup>(133)</sup> 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,<sup>(126, 128)</sup> Kagiya *et al.*<sup>(41)</sup> 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.*<sup>(134)</sup> 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<sup>(126, 130)</sup> it is reported that the rates of polymerization of crystalline trioxan,  $\beta$ -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  $\beta$ -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.<sup>(135-6)</sup> More recently, it has been pointed out that pure trioxan and 3,3-bis(chloromethyl)oxetane will polymerize in the melt,<sup>(137)</sup> 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<sup>(132)</sup> 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.*<sup>(130)</sup> 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;<sup>(130)</sup> according to Rao and Ballantine<sup>(132)</sup> 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  $-78^{\circ}\text{C}$ .<sup>(126)</sup> 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.<sup>(134)</sup> Herz and Stannett<sup>(138)</sup> 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  $30^{\circ}$ – $60^{\circ}\text{C}$  (approx.),<sup>(126)</sup> 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<sup>(139)</sup> 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  $-10^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , as new

molecular motions become apparent. It is only above 40°C that rapid polymerization occurs, and in this temperature range a very narrow line is present in the centre of the n.m.r. spectrum, corresponding to considerable molecular motion. From theoretical calculations of second moments, Komaki and Matsumoto interpret the motions present at about 25°C as chair-chair interconversions, occurring by the proton pairs undergoing a sinusoidal oscillation about the axis perpendicular to the pair direction.<sup>(139)</sup> At about 45°C the movements are interpreted as chair-chair interconversions by rotation of the whole molecule about its  $C_3$ -axis, with the narrow line being attributed to a fraction of the molecules adopting a boat conformation and rotating about the axis perpendicular to the ring plane.<sup>(139)</sup> Obviously, there is considerable molecular movement near the melting point (trioxan is a well-known example of a plastic crystal) and it might be expected that diffusion of small molecules through the lattice could occur easily at these temperatures. It is now known that at least some of the decrease in rate of polymerization as the crystal melts is caused by the presence of impurities, and the decrease in rate as the melting point is approached could be at least partly due to diffusion of impurities (e.g. water) which terminate the polymerization, especially since polymerizations are usually carried out in the air. (The addition of water in quantities greater than 0.01 per cent does reduce rates of polymerization.<sup>(131)</sup>)

Although polymerization of these monomers by a ring opening mechanism does not require the formation of any new bond types, a certain amount of molecular rearrangement is required for polymerization. Carazzolo *et al.*<sup>(122)</sup> found that polyoxymethylene formed during the solid-state polymerization of trioxan crystallizes as a helix with 1.81—CH<sub>2</sub>—O—units per turn, whereas the monomer has 3 units per ring. The formation of polymer, therefore, requires that the ends of an open ring overlap, causing a contraction in the *a* and *b* directions and some further rearrangement in the *c* direction. These rearrangements are presumably facilitated by the high molecular mobility under the polymerization conditions.

In view of the high molecular mobility and necessary rearrangements it might be thought surprising that highly orientated polymers are formed during the polymerization of a monomer such as trioxan. Adler has demonstrated that the influence of the lattice is not as important as was first visualized by studying the post-polymerization using polycrystalline samples (in the form of thin layers of single crystals) instead of a large single crystal.<sup>(40)</sup> Irradiation of samples at 24°C and storage at the same temperature gave small amounts of crystalline fibrous polymer on the crystal surfaces; these fibres exhibited no preferred direction with respect to monomer crystal axes. Indeed, some fibres even changed direction. When the post-irradiation polymerization was carried out at 46°C there was extensive polymerization and the bundles of crystalline polymer fibres grew across intercrystalline boundaries, with little or no change in direction, although the crystals through which the

polymer forms showed different orientations. The bundles of fibres were also observed to extend beyond crystal boundaries and grow through the space between individual crystals.<sup>(40)</sup> It must be concluded from the results at these two temperatures that the growth of crystalline polymer does not require a specific orientation of monomer. As a result of post-irradiation polymerization at 54°C the polymer fibres were found to be aligned, almost exclusively, parallel to the *c*-axis of the monomer crystals. However, there had been extensive recrystallization of the samples during reaction. The monomer crystals which then surrounded the crystalline polymer were larger and fewer in number than in the original sample. These results are reconciled with the older results, where all the polymer formed during the polymerization of single crystals was aligned along preferred directions in the monomer crystal, by assuming that polymer is initially formed in a preferred direction;<sup>(40)</sup> subsequently growth is then controlled by addition of monomer to polymer which has crystallized in the form of a helix. Thus it is the crystallizability of the polymer which controls the nature of the product, rather than the crystal structure of the monomer. Adler also reports similar behaviour in the polymerization of trithiane.<sup>(40)</sup> Lando and Stannett<sup>(123)</sup> find that the n.m.r. line width in trithiane shows little change in the temperature range 25°–180°C, although post-irradiation polymerization is observed at 180°C and not at 150°C.

The fact that polymer, formed in single crystals of monomer, is always orientated along a preferred direction, suggests that polymerization is initiated at a specific type of lattice site, presumably a specific imperfection, and that it is the nature of this imperfection which determines the manner in which polymer is initially laid down in the monomer lattice. Very recently, Bassett<sup>(140)</sup> has obtained photomicrographic evidence that the {00·1} sub-grain boundaries are these specific sites at which polymerization commences.

It is notable that the only monomers which polymerize in the solid state to give crystalline polymers directly are those which give rise to readily crystallizable polymers. All the polymers which have so far been produced in a crystalline form have a symmetrical structure with no asymmetric carbon atoms in the backbone. Solid-state polymerization of hexamethyltrisiloxane gives an amorphous polymer, and it may be noted that this polymer is less easily crystallizable than those which are produced in the crystalline form.

### Nature of the Reactive Species

Free radicals have been detected in some  $\gamma$ -irradiated cyclic monomers.  $\gamma$ -irradiation of trioxan at  $-196^\circ\text{C}$  gives an anisotropic e.s.r. spectrum together with an isotropic doublet attributed to the formyl radical; subsequent exposure to u.v. radiation is reported to increase the concentration of the formyl radicals and exposure to light of wavelength  $> 2800 \text{ \AA}$  to decrease

their concentration.<sup>(142)</sup> The increase in formyl concentration on photolysis was considered to be a consequence of ionic recombination. A similar explanation was advanced to account for the increases in radical concentration observed on warming samples after irradiation at  $-196^{\circ}\text{C}$ , reaching a maximum concentration at  $-70^{\circ}\text{C}$ . It was suggested that the interaction of  $\gamma$ -rays with trioxan causes the formation of radical ions (by loss of an electron), the loss of hydrogen atoms, and ring cleavage.<sup>(142)</sup> The low-temperature ( $-196^{\circ}\text{C}$ ) irradiation of 3,3-bis(chloromethyl)oxetane yields two radicals giving 3-line and 2-line e.s.r. spectra, respectively.<sup>(141)</sup> The radical characterized by the 3-line spectrum is not thermally stable but the other radical, which gives an anisotropic e.s.r. spectrum, is stable up to about  $0^{\circ}\text{C}$ . Structures for these radicals have been proposed.<sup>(141)</sup> Radicals have also been detected on irradiation of  $\beta$ -propiolactone and diketene.<sup>(126)</sup> In all cases the e.s.r. spectrum decays as the melting point is approached and molecular mobility increases.

It is generally accepted that the radiation-induced solid-state polymerization of these cyclic monomers proceeds by a cationic mechanism, partly since only cationic polymerization is known in solution,<sup>(39)</sup> and solid-state polymerization can be induced by cationic initiators. Radiolysis of the monomer presumably produces cations or radical cations, depending on the nature of the monomer and the presence of impurities; propagation occurring by addition of monomer to the cation.

### Chemical Initiation

A number of papers have appeared which report the solid-state polymerization of trioxan initiated by surface catalysis using conventional cationic initiators, including borontrifluoride<sup>(121, 143-5)</sup> and stannic chloride,<sup>(145-6)</sup> giving rise to crystalline polymers rather similar to those obtained by radiolytic initiation. The polymerization must be controlled to some extent by the diffusion of catalyst and counterion into the crystal, and it has been reported that the solvent power of the medium in which the crystals are suspended markedly affects the molecular weights of the polymers.<sup>(144)</sup> Inclusions of iodine, formed by freezing a solution of iodine in monomer, have also been used to initiate the solid-state polymerization of trioxan.<sup>(147-8)</sup> Considerable quantities of trioxan are formed during the polymerization of crystalline tetraoxan, initiated by borontrifluoride etherate at  $30^{\circ}\text{C}$ <sup>(149)</sup> probably by the same back-biting process as occurs in the solution polymerization of this monomer; the radiation-induced polymerization at  $80^{\circ}\text{C}$  gives rise to much less trioxan.

### SOLID-STATE COPOLYMERIZATIONS

In spite of obvious limitations imposed by the solid state, a number of attempts have been made to copolymerize frozen mixtures of monomers.

The results obtained from this type of study must reflect the physical nature of the frozen binary systems. Thus, if the monomers crystallize separately it is to be expected that, apart from reaction at intercrystalline boundaries, only homopolymers will be produced. Alternatively, if the monomers form solid solutions a copolymer may be formed, the composition of which will be dictated by the nature of the solid solution rather than by the reactivity ratios which control polymerizations in the liquid phase. An example of this latter situation is the copolymerization of various binary mixtures of oxetanes, when the copolymers obtained by  $\gamma$ -irradiation of solid solutions have compositions corresponding to reactivity ratios of unity, quite different from those observed in the liquid state.<sup>(150)</sup> Other copolymerizations of solid cyclic monomers include the incorporation of ethylene oxide,<sup>(143)</sup> 1,3-dioxalane, and epichlorhydrin<sup>(151)</sup> into polyoxylmethylene formed by polymerization of trioxan; the presence of the latter two monomers increases the rate of polymerization.<sup>(151)</sup>

Tributyl phosphonium bromide and the corresponding iodide are isomorphous. The polymerization kinetics of a series of their solid solutions have been investigated in the temperature range  $-80^{\circ}\text{C}$  to  $-60^{\circ}\text{C}$  and in all cases sigmoid conversion-time curves leading to 100 per cent conversion were obtained. Chen and Grabar<sup>(152)</sup> compared the rates of reaction at various compositions from plots of the time taken to reach 50 per cent conversion against composition. On this basis both monomers and all their solid solutions reacted at the same rate at  $60^{\circ}\text{C}$ , while the rate changed monotonically with composition at  $-80^{\circ}\text{C}$ . At intermediate temperatures minimum rates were observed in solid solutions containing about 4 per cent of the iodide.

Hayashi *et al.*<sup>(150)</sup> have published phase diagrams for a number of monomer mixtures and have studied their radiation induced polymerizations. In most cases eutectics were formed and the monomers polymerized independently. Maleic anhydride and acenaphthylene, which give a 1:1 copolymer in the liquid state, produce a mixture of polyacenaphthylene and 1:1 copolymer in the solid state. As in many other binary systems, the maximum rate of polymerization occurs at the eutectic composition. Maleic anhydride is probably slightly soluble in acenaphthylene crystals, since small amounts of the anhydride were detected in the homopolymer of the latter monomer.<sup>(153)</sup> In the initial stages of reaction the 1:1 copolymer is formed preferentially, probably in the more disordered regions of intercrystalline boundaries. As reaction proceeds the acenaphthylene homopolymerizes and finally, when there is considerable disorder in the solid, there is again a preference for 1:1 copolymer formation.<sup>(153)</sup>

Polymerizations of acrylic acid-acrylamide mixtures have been studied in some detail by Hardy and Nagy<sup>(154)</sup> This mixture is characterized by two eutectics containing 74.5 per cent and 58.7 per cent acrylic acid, respectively, and a molecular compound with a composition 2:1 acrylic acid : acrylamide.

Rates of polymerization of the binary mixtures, at  $-15^{\circ}\text{C}$ , are higher than those of the pure monomers (at this temperature pure acrylamide does not polymerize), and the rates are a maximum at the eutectic compositions, with a minimum at the intermediate composition of the molecular compound. The resulting copolymers have compositions corresponding to those of the eutectics and the molecular compound; polyacrylic acid is formed under conditions where acrylic acid crystallizes from the monomer mixture. Chapiro and Cordier<sup>(155)</sup> obtained similar results in acrylonitrile-styrene mixtures polymerized at  $-94^{\circ}\text{C}$ . Styrene does not polymerize under these conditions and the polymers obtained are pure polyacrylonitrile and a copolymer containing 10-20 per cent styrene, approximately the styrene content at the eutectic point.

Copolymers of vinyl acetate and sulphure dioxide can be formed in the solid state.<sup>(156)</sup> This mixture does not polymerize when irradiated at low temperatures in the liquid state, but in the solid state the rate of polymerization increases as the temperature is decreased from the melting point ( $-120^{\circ}\text{C}$ ) to  $-150^{\circ}\text{C}$ . Below  $-150^{\circ}\text{C}$  polymerization does not occur but samples irradiated at the lower temperatures do polymerize on warming to  $-140^{\circ}\text{C}$ .

#### EFFECTS OF PRESSURE

So far, there is only a small number of references to the influence of pressure on the course of solid-state polymerizations, although this is one of the few variables available. The studies which have been carried out may be divided into two categories, the effects of very small pressures, of the order of 10 atm, studied by one group, and the effects of pressures of thousands of atmospheres reported by other workers. In the absence of further information, it would appear that a direct comparison of results obtained in the two pressure ranges may not be valid. Consequently, we shall discuss the effects separately.

##### Small Pressures

In discussing the nature of the reaction sites in the polymerization of crystalline vinyl monomers we have already described (pp. 10, 11) some of the results obtained by applying small stresses to crystals of acrylic and methacrylic acids during u.v. irradiation.<sup>(23, 24)</sup> These results have been taken to indicate that polymerization occurs in dislocations which are mobile under stresses of the order of 150 lb/in.<sup>2</sup>

The magnitudes of the effects are very sensitive to experimental conditions, and a parameter referred to as the pressure effect has been defined such that if the applied stress stops the reaction it has a value of infinity and a value of

zero if there is no effect.<sup>(157)</sup> An increase in reaction temperatures from 4°C to 7°C decreases the pressure effect in acrylic acid from infinity to zero.<sup>(23, 24)</sup> Reductions in the magnitude of the pressure effect are also observed as the temperature is lowered, although the change is much more gradual.<sup>(157)</sup> In a series of experiments using methacrylic acid as monomer, the effect decreased from 18.5 at 4°C to 2 at -10°C and zero at -14°C. This decrease in the pressure effect at lower temperatures is attributed to a general hardening of the crystals, so that movement of dislocations is more difficult.<sup>(157)</sup> The loss of the effect in acrylic acid at 7°C is considered to result from increased disorder in the monomer at this temperature. At 7°C there is considerable mobility in the crystals as judged by broad-line n.m.r.<sup>(62)</sup> and measurements of optical retardation, and probably represents the onset of premelting.<sup>(23)</sup> Under these conditions the general mobility is probably too high for the stress to have any effect.

Small impurity concentrations can have a dramatic effect.<sup>(157)</sup> The presence of 0.1 per cent isobutyric acid in methacrylic acid reduced the effect from 18.5 to 2 at 4°C, and with 0.3 per cent of the additive the effect fell to 0.5. It is conceivable that if absolutely pure monomer was available these small stresses could stop the polymerization of methacrylic acid. A pressure effect is observable at -14°C on addition of 0.1 per cent isobutyric acid but the effect is again reduced on increasing the additive concentration to 0.5 per cent.<sup>(157)</sup> The sensitivity of the pressure effect to such low concentrations of additive is further evidence that lattice imperfections play an important role in these polymerizations. In metals it is known that impurity atoms concentrate around dislocations in the form of Cottrell clouds<sup>(50)</sup> which may prevent the movement of dislocations under small stresses. This mechanism could account for the reduction of the pressure effect on addition of isobutyric acid at 4°C but would not explain the results at -14°C. It seems probable that the temperatures used in this work are too high for a Cottrell cloud mechanism to operate, since impurity clouds fail to pin down dislocations in metals at high temperatures. It is considered that addition of isobutyric acid produces an increase in mobility in the neighbourhood of the dislocations, equivalent to an increase in temperature. This view also explains the reappearance of the effect and its subsequent decrease on the addition of increasing amounts of additive at -14°C. The pressure effect is also very sensitive to the magnitude of the applied stress.<sup>(157)</sup> In view of the various observations it would appear unlikely that alternative explanations based on freezing of liquid-like regions, or squeezing liquid out of cracks could account for all the results.

### High Pressures

There are a few reports in the literature of the influence of pressures in the range  $5 \times 10^3$  to  $5 \times 10^5$  lb/in.<sup>2</sup> on the course of solid-state polymerizations.

In-source polymerizations of crystalline acrylamide have been studied by Tabata and Suzuki<sup>(158)</sup> and by Fydeler and Charlesby<sup>(159)</sup> using pressures of 5000 and about 6500 atm, respectively. At temperatures below 30°C both groups report that the application of pressure has virtually no effect on initial rates. According to the former group,<sup>(158)</sup> pressures of 5000 atm reduce the rates of polymerization at 28°C up to conversions of at least 20 per cent. At higher temperatures, up to 70°C, rates are reduced initially but increased after some finite conversion which decreases with increasing temperature from about 5 per cent at 50°C to about 1 per cent at 70°C. Using the slightly higher pressure at 18°C, Fydeler and Charlesby report that the maximum reduction in rate occurs at approximately 8 per cent conversion and that above about 60 per cent conversion rates are increased.<sup>(159)</sup> These latter workers have also reported that the applied pressure does not affect the initial rate of polymerization of methacrylamide, but after about 0.5 per cent conversion reaction virtually ceases.<sup>(159)</sup>

Prince and Hornyak have investigated the influence of high pressures (36,000 atm) on the post-irradiation polymerization of acrylamide, initiated by high-energy electrons<sup>(160)</sup> and  $\gamma$ -rays.<sup>(161)</sup> In all cases these pressures increased conversion to polymer, usually by a factor of about 2, but by considerably more at low irradiation doses. It was suggested that these pressures release trapped radicals by producing dislocations, although this presumably implies that some radicals are initially produced in the more perfect regions of the crystal. Fydeler and Charlesby found that pressures of 6500 atm did not affect the post-irradiation reaction of this monomer.<sup>(159)</sup>

Pressures of 6500 atm accelerate the rates of polymerization of crystalline and amorphous anhydrous calcium acrylate and crystalline anhydrous barium methacrylate at 18°C.<sup>(159)</sup> With crystalline anhydrous calcium acrylate the rate is increased markedly up to conversions of 50 per cent after which it decreases rapidly, while with the amorphous salt conversions approaching 100 per cent are readily achieved at low radiation doses. At low conversions (<8 per cent) the rates of polymerization of the barium salt are increased by these pressures, the acceleration increasing with conversion.

Fydeler and Charlesby have also reported some interesting preliminary results on the effects of different pressures,<sup>(159)</sup> and further results of this type must assist the interpretation of the results at present available. These workers conclude that, in all the monomers they have studied, the main influence of pressure is on propagation. It was suggested that in acrylamide the lower rates in the early stages are due to the pressure opposing disruptive stresses produced in the lattice by polymerization, but that at higher conversions the pressure reduces the free volume produced on polymerization and hence increases the rate. On the other hand, the accelerations produced in the crystalline salts are attributed to the removal of defects, which would be consistent with polymerization occurring preferentially in the perfect lattice,



in agreement with a previous suggestion that the lattice exercises a dominating influence on these polymerizations.<sup>(85)</sup>

Other reports of the effects of high pressures on the solid-state polymerizations of vinyl monomers include the in-source polymerization of methacrylonitrile (m.p.  $-35.8^{\circ}\text{C}$ ) in the temperature range  $-196^{\circ}$  to  $-43^{\circ}\text{C}$ , the rates of which are reduced by pressures of 5000 atm.<sup>(162)</sup> The polymerizations of certain fluorocarbons,<sup>(163)</sup> styrene,<sup>(164)</sup> and methyl methacrylate<sup>(164)</sup> have been studied under pressures sufficiently high to solidify the monomers at relatively high temperatures; under suitable conditions, using benzoylperoxide as initiator, styrene, and methyl methacrylate polymerized explosively.<sup>(164)</sup>

There appears to be only one reference to the effects of pressure on the polymerization of crystalline cyclic monomers. According to Rao and Ballantine,<sup>(132)</sup> application of pressures of about 36,000 atm. prior to irradiation increases the polymer yields obtained from both the in-source and post-irradiation polymerizations of trioxan. Smaller pressures applied after irradiation either reduced the extent of the post-irradiation reaction, or removed it altogether. It was proposed that the application of pressure prior to irradiation aligned the monomer molecules into positions favourable for reaction (possibly with a simultaneous reduction in rate of initiation) and that application of the pressure after irradiation caused a recombination of primary species, possibly associated with the occurrence of a phase change in the monomer.

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