

# Solid-phase Addition Polymerization

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## 1 Nature of Reaction Sites

The literature now contains many reports of the polymerization of crystalline monomers to polymers of high molecular weight. On the most naïve view, the formation of high polymers by the joining-up of suitably oriented molecules in a crystal lattice appears to be a simple process. However, a more detailed consideration reveals a number of difficulties, of which the most important is that polymer molecules cannot, in general, be fitted to the geometry of the monomer lattice. This is particularly obvious in the polymerization of vinyl derivatives when the incorporation of each monomer unit changes the hybridisation of two carbon atoms from  $sp^2$  to  $sp^3$ . Thus there is a change in intra- and inter-molecular C-C distances and in the dispositions of substituent groups. Normally the density of the polymer is different from that of the crystalline monomer. Although the geometry of a lattice may allow dimer formation (pp. 279, 298), further additions must become progressively more difficult and the formation of large polymer molecules without disruption of the lattice seems out of the question; in fact, in the vast majority of cases, this type of reaction gives amorphous polymers.<sup>1</sup> A case in which correspondence between the dimensions of the monomer lattice and the polymer molecule permits vinyl polymerization in one or two dimensions cannot be excluded, but would surely be exceptional. Ring-opening polymerization, such as that of trioxan, can lead to highly crystalline polymers with the polymer molecules oriented in specific directions with respect to the crystal axes in the solid monomer.<sup>2</sup> Here no change of hybridisation is involved since the bonds broken and formed during polymerization are of the same type, but there is a change in lattice parameters. Carazzolo *et al.*<sup>3</sup> found that polyoxymethylene formed during the solid-phase polymerization of trioxan has a helical conformation with 1.8 formaldehyde residues per turn. An expansion in a direction at right angles to the planes of the original trioxan molecules, and a lateral contraction, accompany polymerization. Even in a case of this type a simple joining-up of molecules on their lattice sites does not seem feasible without destruction of the crystal. Possible explanations of the high degree of orientation of the polymer will be discussed later.

We are thus forced to the conclusion that, in general, polymerization does not

<sup>1</sup> G. Adler and W. Reams, *J. Chem. Phys.*, 1960, **32**, 1698.

<sup>2</sup> S. Okamura, K. Hayashi, and Y. Nakamura, *Isotopes and Radiation*, 1960, **3**, 416.

<sup>3</sup> G. Carazzolo, S. Leghissa, and M. Mammi, *Makromol. Chem.*, 1963, **60**, 171.

occur in a perfect lattice, but must be associated with the presence of lattice defects. The earliest evidence for the correctness of this view was provided by the elegant X-ray studies of Adler and Reams<sup>1</sup> on the radiation-induced polymerization of acrylamide. It was clearly demonstrated that even at low conversions (4%) the polymer formed is amorphous and constitutes a separate phase within the monomer crystal. Polymerization clearly requires movement of monomer molecules from their lattice sites. Hirshfeld and Schmidt<sup>4</sup> have suggested that initiation of polymerization requires the separation of participating reactive groups in separate monomer molecules to be less than about 4 Å; this greatly exceeds the length of a normal C-C bond, so that the criterion cannot be a sufficient one for the occurrence of reaction. Any kind of defect which enhances mobility is, in principle, capable of assisting polymerization. Point defects, by facilitating monomer diffusion, may promote polymerization, particularly at high temperatures, but at low temperatures the presence of these defects alone may be insufficient to permit polymerization. In our opinion line defects, *i.e.*, dislocations, are most likely to be the sites of reaction.

The structures of dislocations in inorganic crystals have been extensively studied, and techniques for their direct observation have been developed.<sup>5,6</sup> Figure 1 shows the distortion in one plane of the crystal lattice of a metal in the

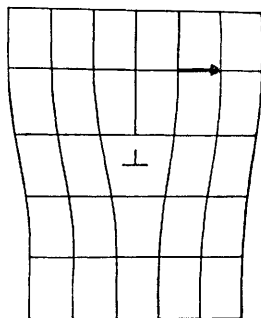


Figure 1 A simple edge dislocation; the core is represented by  $\perp$  and the Burgers vector by  $\rightarrow$ .

neighbourhood of an edge dislocation.<sup>5</sup> The core is denoted by  $\perp$  and the distortion is repeated in successive crystal planes to produce a dislocation line. In view of the relative complexity of organic crystals we may expect the dislocations to be more complicated and extensive than that in Figure 1. Until recently, however, little corresponding information was available about the organic solid state, with which this Review is mainly concerned. Within the last few years some of the techniques used for direct observation of dislocations have been extended to molecular crystals. One of the simplest of these relies on the

<sup>4</sup> F. L. Hirshfeld and G. M. J. Schmidt, *J. Polymer Sci. (A)*, 1964, 2, 2181.

<sup>5</sup> A. H. Cottrell, 'Dislocations and Plastic Flow in Crystals', Oxford Univ. Press, 1953.

<sup>6</sup> Dislocations in Solids, *Discuss. Faraday Soc.*, 1964, 38.

preferential dissolution of molecules in the vicinity of dislocation cores by a poor solvent, which produces an 'etch pit' at the point of emergence of the dislocation line. Figure 2 shows etch pits in anthracene crystals.<sup>7</sup> Evidence for the presence of dislocations in sucrose crystals has been obtained in a number of ways.<sup>8</sup> Of particular interest in the present context is the observation that, after partial thermal decomposition of sucrose crystals, protuberances ('decomposition volcanoes') may be observed on the crystal surface by replica electron microscopy (Figure 3). Thomas and Williams<sup>8</sup> suggest that decomposition occurs preferentially in dislocations, and that the protuberances may correspond to the emergence of these at the crystal surface. In agreement with this is the finding that decomposition is most rapid in regions of high dislocation density. Similar protuberances have been observed after the polymerization of p-benzamido-styrene to low conversions<sup>9</sup> (p. 289). Recent discussions of the importance of dislocations in inorganic solid-phase reactions have been given by Tompkins,<sup>10</sup> Thomas and Renshaw,<sup>11</sup> and Renshaw and Thomas.<sup>12</sup>

Sella and Trillat<sup>13</sup> and Sella and Bensasson<sup>14</sup> have published photomicrographs of the surfaces of acrylamide crystals at various stages of polymerization induced by  $\gamma$ -irradiation. These show the development of polymer 'globules', initially about 20 Å in diameter, lying randomly along lines oriented in crystallographic directions. As polymerization proceeds the diameter increases to 300–400 Å. Further polymerization gives rise to the appearance and growth of additional globules. Sella *et al.*<sup>13,14</sup> were led to the conclusion that polymerization starts in dislocations, the points of emergence of these being indicated by the surface globules. At about the same time Bamford, Eastmond, and Ward<sup>15</sup> observed that the rates of the photoinitiated polymerizations of crystalline acrylic and methacrylic acids are reduced to a remarkable extent by the application of a comparatively low stress and they inferred, from analogy with the behaviour of dislocations in inorganic crystals, that polymerization occurs preferentially in crystal dislocations. A discussion of these results is presented later.

There are therefore good reasons for believing that imperfections play a major rôle in solid-state polymerizations, as in most other reactions in the solid phase.<sup>16</sup> It is important to remember that a dislocation is not a region of complete disorder, but has a definite structure, determined by the type of dislocation, the direction of the associated Burgers vector (Figure 1), and the crystal geometry.<sup>5</sup> The course of polymerization depends on the structures of the dislocations, since these determine the local mobilities and separation of the propagating species

<sup>7</sup> J. M. Thomas and J. O. Williams, *Mol. Crystals*, in press.

<sup>8</sup> J. M. Thomas and J. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 1922.

<sup>9</sup> S. Z. Jakabhazy, H. Morawetz, and N. Morosoff, *J. Polymer Sci. (C)*, 1964, **4**, 805.

<sup>10</sup> F. C. Tompkins, I.U.P.A.C. Symposium, 'The Reactivity of Solids', Butterworths, London, 1964, 387.

<sup>11</sup> J. M. Thomas and G. D. Renshaw, *J. Chem. Soc. (A)*, 1967, 2058.

<sup>12</sup> G. D. Renshaw and J. M. Thomas, *Nature*, 1966, **209**, 1196.

<sup>13</sup> C. Sella and J. J. Trillat, *Compt. rend.*, 1961, **253**, 1511.

<sup>14</sup> C. Sella and R. Bensasson, *J. Polymer Sci.*, 1962, **56**, S1.

<sup>15</sup> C. H. Bamford, G. C. Eastmond, and J. C. Ward, *Proc. Roy. Soc.*, 1963, **A**, **271**, 357.

<sup>16</sup> 'Chemistry of the Solid State', ed. W. E. Garner, Butterworths, London, 1955.

and the monomer molecules. Thus, from suitable studies of solid-phase polymerizations it should be possible to deduce information about the nature of the organic solid state. Although many monomers have been polymerized in the solid phase, the data are often too fragmentary to permit detailed interpretation.

## 2 Practical Considerations

**A. Methods of Initiation.**—Most workers have initiated polymerization by high-energy radiation, *e.g.*,  $\gamma$ - or *X*-rays, or high-energy electrons. Two basic techniques have been employed: continuous irradiation during polymerization, or pre-irradiation at a temperature too low to permit significant polymerization, followed by warming to obtain a post-irradiation reaction. The latter procedure has the advantage of avoiding radiation damage to the reaction products. Since high-energy radiation is capable of penetrating considerable thicknesses of material, its use enables effectively uniform rates of initiation to be achieved on a macroscopic scale. On the other hand, this type of radiation produces both free radicals and ions, and there may be doubt about the nature of the initiating species.<sup>17</sup> It turns out that atomic hydrogen is often the effective initiator under these conditions.<sup>18–21</sup>

Ultraviolet initiation has been employed in a few cases<sup>15,22</sup> and allows the energy-input to be readily controlled by choice of wavelength. Although in principle it is possible for ionic products to be formed, this is not very probable in the near-ultraviolet region. A restriction on the use of the technique arises from the strong absorption of some crystalline monomers, which confines initiation to a thin layer.

Another technique of photoinitiation employs visible light with a conventional photoinitiator such as azobisisobutyronitrile<sup>23</sup> or a photosensitising dye.<sup>24</sup> Application is restricted since there is generally a lack of information about the location of the sensitiser, which may be incorporated into the crystals as a solid solution, or be situated at crystal boundaries.

A few instances of chemical initiation have been reported. Crystals of trioxan polymerize cationically when treated with boron trifluoride<sup>25–28</sup> or stannic chloride,<sup>28,29</sup> giving rise to polymers similar to those obtained by  $\gamma$ -initiation. These reactions presumably involve diffusion into the crystal of counter-ions and catalyst molecules. Inclusions of iodine have also been used to initiate the solid-

<sup>17</sup> M. Magat, *Polymer*, 1962, 3, 449.

<sup>18</sup> G. Adler and J. M. Petropoulos, *J. Phys. Chem.*, 1965, 69, 3712.

<sup>19</sup> Y. Shioji, S. I. Ohnishi, and I. Nitta, *J. Polymer Sci. (A)*, 1963, 1, 3373.

<sup>20</sup> M. Fujimoto, *J. Chem. Phys.*, 1963, 39, 846.

<sup>21</sup> J. H. O'Donnell, B. McGarvey, and H. Morawetz, *J. Amer. Chem. Soc.*, 1964, 86, 2322.

<sup>22</sup> S. Ishida and S. Saito, *J. Polymer Sci. (A1)*, 1967, 5, 689.

<sup>23</sup> C. H. Bamford, A. D. Jenkins, and J. C. Ward, *J. Polymer Sci.*, 1960, 48, 37.

<sup>24</sup> C. S. H. Chen, *J. Polymer Sci. (B)*, 1964, 2, 891.

<sup>25</sup> S. E. Jamison and H. D. Noether, *J. Polymer Sci. (B)*, 1963, 1, 51.

<sup>26</sup> M. Baccareda, E. Butta, F. Morelli, and G. Masetti, *Makromol. Chem.*, 1966, 93, 137.

<sup>27</sup> S. Okamura, E. Kobayashi, and T. Higashimura, *Makromol. Chem.*, 1966, 94, 20.

<sup>28</sup> S. Okamura, E. Kobayashi, M. Takeda, K. Tomikawa, and T. Higashimura, *J. Polymer Sci. (C)*, 1964, 4, 827.

<sup>29</sup> S. Okamura, E. Kobayashi, and T. Higashimura, *Makromol. Chem.*, 1965, 88, 1.

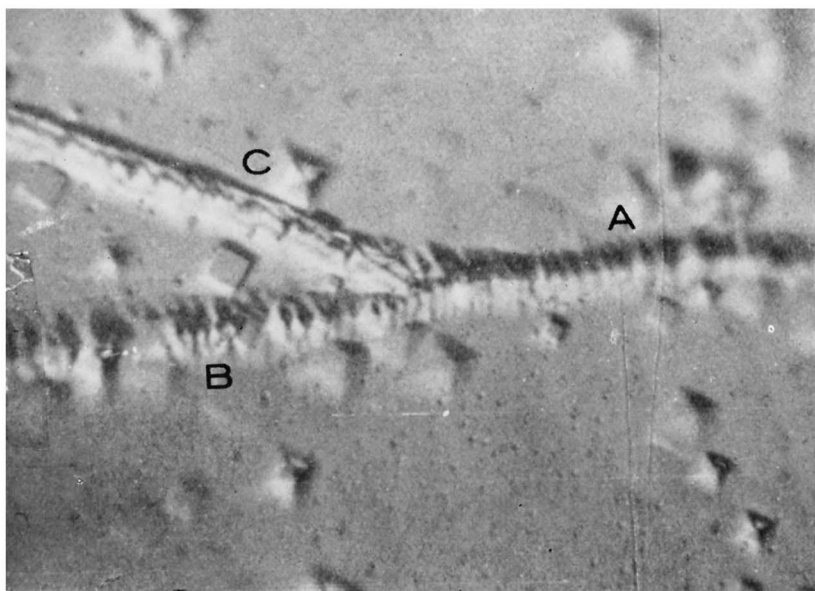


Fig 2

X 1000

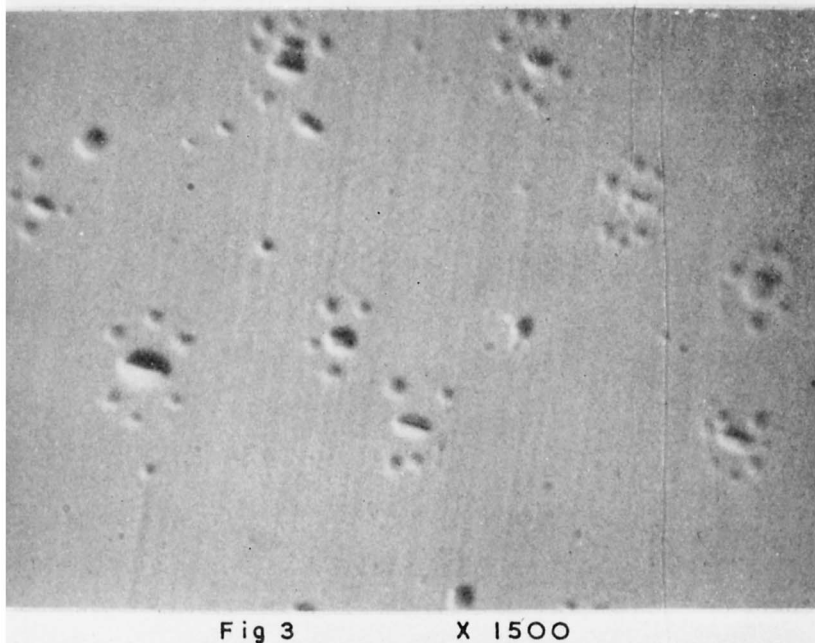


Fig 3

X 1500

**Figure 2** Etch pits on the surface of an anthracene crystal, located at the points of emergence of dislocation lines and along intersecting low-angle grain boundaries ( $\times 1000$ )  
After Thomas and Williams (ref. 7)

**Figure 3** Decomposition volcanoes on the cleavage face of a sucrose crystal after heating in a vacuum for 6 hr. at  $120^\circ$ , with satellites suggesting that further dislocations are introduced during decomposition ( $\times 1500$ )  
After Thomas and Williams (ref. 8)

phase polymerization of trioxan,<sup>30,31</sup> and crystalline itaconic anhydride has been polymerized with benzoyl peroxide as initiator.<sup>22</sup>

Some pure monomers undergo spontaneous polymerization in the solid state, e.g., acetamido- and benzamido-styrene.<sup>9</sup>

Kargin and his colleagues have used highly original methods of initiation, including the simultaneous condensation of metal (generally magnesium) vapour and monomer on a cooled surface,<sup>32</sup> mechanical disintegration of certain monomers,<sup>33</sup> and ionic exchange processes between monomer and added salts.<sup>34</sup> Polymerization induced by the passage of a shock wave has also been recorded.<sup>35</sup>

**B. Measurement of Conversion.**—The simplest procedure is to isolate the polymeric product by dissolution of residual monomer. It is important to realise that the reaction mixture will often contain active centres which may initiate further rapid polymerization when brought into contact with monomer in the liquid phase. Addition of a retarder (e.g., pyrogallol) to the solvent before dissolution is therefore necessary.

Alternatively, the conversion can be estimated by observing changes in a suitable physical property. For example, the decrease in optical retardation with time has been employed to follow the transformation of birefringent monomer into amorphous and isotropic polymer.<sup>15,22</sup> This technique measures the degree of order in the specimen and will not give the correct conversion directly if some disordering of monomer is associated with polymerization, or if there is intermediate formation of anisotropic polymer. In principle, a variety of physical methods is available of which u.v. and i.r. spectroscopy, X-ray diffraction, and calorimetric measurements<sup>36,37</sup> are potentially the most useful. Many workers have used the simple isolation technique, but the application of physical methods appears to be increasing.

**C. Associated Techniques.**—Electron spin resonance (e.s.r.) has been extensively used to measure the concentrations and structures of radical intermediates in solid-phase polymerizations. In some cases e.s.r. allows the active species to be studied during reaction under various conditions, so that it is capable of providing very detailed and useful information.

<sup>30</sup> A. A. Berlin, L. I. Kuzub, and N. S. Yenikolopyan, *Vysokomol. Soedin.*, 1966, **8**, 1200; *Polymer Sci., U.S.S.R.*, 1966, **8**, 1321.

<sup>31</sup> A. A. Berlin, L. I. Kuzub, M. A. Markvich, and N. S. Yenikolopyan, *Vysokomol. Soedin.*, 1966, **8**, 1204; *Polymer Sci., U.S.S.R.*, 1966, **8**, 1326.

<sup>32</sup> V. A. Kargin, V. A. Kabanov, and I. M. Pappisov, *J. Polymer Sci. (C)*, 1964, **4**, 767.

<sup>33</sup> V. A. Kargin, V. A. Kabanov, and N. Ya. Rapaport-Molodtsova, *Vysokomol. Soedin.*, 1961, **3**, 787; *Polymer Sci., U.S.S.R.*, 1962, **3**, 657.

<sup>34</sup> V. A. Kargin, V. A. Kabanov, and G. P. Andrianova, *Vysokomol. Soedin.*, 1959, **1**, 301; *Polymer Sci., U.S.S.R.*, 1960, **1**, 106.

<sup>35</sup> I. M. Barkalov, G. A. Adadurov, A. N. Dremin, V. I. Gol'danskii, T. N. Ignatovich, A. N. Mikhailov, V. L. Tal'roze, and P. A. Yampolskii, *J. Polymer Sci. (C)*, 1967, **16**, 2597.

<sup>36</sup> I. M. Barkalov, V. I. Gol'danskii, N. S. Yenikolopyan, S. F. Terekhova, and G. M. Trofimova, *Vysokomol. Soedin.*, 1964, **6**, 92.

<sup>37</sup> C. Chachaty, M. Magat, and L. Ter Minassian, *J. Polymer Sci.*, 1960, **48**, 139.

We have already emphasized the importance of molecular mobility in solid-phase polymerizations, and this aspect can, of course, be investigated by broad-line nuclear magnetic resonance (n.m.r.). This technique provides information about movements in the crystal lattice, but not directly about molecular mobilities in imperfect regions, which constitute only a small fraction of the crystal. Nevertheless it is likely that a correlation exists between these quantities, since the structure of the imperfections is controlled by that of the lattice.

The application of electron microscopy has already been mentioned in connection with changes in the crystal surface which accompany polymerization. Optical microscopy has also been employed in a few cases for determining the disposition of polymer in a crystal.<sup>28</sup>

**D. Nature of Chain Carriers.**—The problem of distinguishing between ionic and free-radical propagation has received considerable attention<sup>17</sup>. It arises because the conventional tests used in liquid-phase polymerization are not applicable. Thus, copolymerization and retardation studies are not helpful in general because the second component is not incorporated in the crystal lattice of the monomer. Nor can any simple kinetic law, valid in the liquid phase, be expected to hold in crystalline solids. A distinction on chemical grounds is possible with some monomers. For example, acrylic and methacrylic acids will not polymerize cationically, nor will they polymerize anionically in the presence of labile acidic protons; hence it is most likely that in the solid phase propagation takes place through radical intermediates. Conversely, trioxan is only known to polymerize ionically in solution, and it may be assumed that a similar mechanism holds in the solid state. Use of specific initiators may reveal the nature of the chain carriers or, alternatively, evidence may be adduced from a comparison of e.s.r. spectra and the course of polymerization. At the present state of knowledge, information about the chemical identity of the chain carriers, although of interest, is not the most fundamental requirement, since the major factors influencing the course of reaction, which have already been referred to, are not dependent on the presence of any particular type of species.

**E. Kinetics.**—Conventional kinetic analysis, in which the rate of reaction is expressed as a function of reactant concentrations, is not meaningful when applied to the polymerization of crystalline monomers, nor indeed to solid-phase reactions in general. The concentrations of reactants and intermediates, and the rate of reaction, are functions of position, and there may be no functional relation between the overall concentrations and the rates. Consequently the concept of order of reaction, employed in liquid and gaseous systems, has little if any application in solids. Monomer concentration can exercise an effect on the rate of polymerization if the original crystals contain more than one component in solid solution. In a solid-phase polymerization the polymer often forms a separate phase within the crystal (as with acrylamide<sup>1</sup>) and reaction occurs at the interface. In such a situation the area of the interface, and the number of

growing nuclei are important rate-controlling parameters, in addition to the local mobilities of the reacting species which have already been mentioned.

Since polymerization is normally accompanied by a volume change, nucleus formation will set up a strain in both phases, and the strain energy will contribute to the free energy of formation of the nucleus. In the perfect lattice the strain may not be readily relieved, so that the production of a nucleus may be difficult. However, in the neighbourhood of a dislocation relief of strain occurs more easily, hence dislocations are particularly favourable sites for 'germ nuclei'.

Conversion-time curves for in-source polymerizations are usually sigmoid in form,<sup>15,38</sup> and resemble corresponding plots for other types of solid-phase reaction.<sup>16</sup> Many different models for the progress of solid-phase decompositions have been advanced,<sup>39</sup> based on the growth of nuclei which may be present as germ nuclei initially, or generated as the reaction proceeds. As a result of the progress of reaction, each nucleus becomes the centre of a region of decomposition; these regions may overlap at sufficiently high conversions, or they may ingest germ nuclei from which growth has not yet started. By making assumptions about the rates of nucleation and radial growth, and allowing for overlap and ingestion, it is possible from geometrical considerations to derive equations for the rate and extent of decomposition as a function of time. The majority of equations used to describe solid-phase reactions have been obtained in this way, for example the relation (1) of Erofeev<sup>39</sup> in which  $\alpha$  is the fractional

$$\alpha = 1 - \exp[-(kt)^n] \quad (1)$$

conversion at time  $t$ ,  $k$  is a composite rate constant, and  $n$  an integer depending on the number of successive steps required to convert a germ nucleus into a growth nucleus and the number of dimensions in which growth occurs.

A number of attempts have been made to develop theoretical expressions applicable to solid-phase polymerization.<sup>39a</sup> These are based on assumptions about the geometry of chain growth (*e.g.*, that bundles of parallel chains grow linearly) and the energetics of the processes. Thus it has been assumed that a single polymer molecule may grow in a 'hot' region but becomes unstable when that region is 'cool'; such a molecule may be stabilised by annealing or be decomposed by a second exposure to radiation. With suitable choice of parameters it is then possible to predict any of the forms of kinetic curve obtained during solid-state reactions. In the opinion of the Reviewers it is more profitable at present to attempt to elucidate the nature of the individual steps than to derive overall kinetic schemes, since without this information many of the assumptions must be arbitrary.

It will become apparent in the following pages that a useful model must include (i) a branching mechanism corresponding to dislocation multiplication, (ii) a rate of radial growth which is a function of time; this is necessary to

<sup>38</sup> C. S. H. Chen and D. G. Grabar, *J. Polymer Sci. (C)*, 1964, 4, 849.

<sup>39</sup> D. A. Young, 'Decomposition of Solids', Pergamon Press, Oxford, 1966.

<sup>39a</sup> V. A. Kabanov, I. M. Papisov, and V. A. Kargin, *Vysokomol. Soedin.*, 1966, 8, 1627; I. M. Papisov, V. A. Kabanov, and V. A. Kargin, *Doklady Akad. Nauk S.S.S.R.*, 1965, 162, 136; V. A. Kargin and V. A. Kabanov, *Zhur. Vses. khim. obshch. Mendeleeva*, 1964, 9, 602.



accommodate the findings of Sella and Trillat<sup>13</sup> which show that growth effectively ceases when nuclei attains a certain size, and (iii) allowance for sites with different reactivities, which in general change during reaction.

Mechanistic deductions have frequently been made from the magnitude of overall activation energies of polymerization. However, changes in temperature affect the number and properties of sites capable of supporting reaction,<sup>18,40</sup> so that the overall activation energy would be expected to contain physical as well as chemical contributions.

### 3 Polymerization of Vinyl Monomers

**A. The Nature of the Initial Radicals and the Mechanism of Initiation.**—Free radicals are produced in a number of crystalline vinyl monomers when subjected to high-energy radiation at low temperatures ( $-196^\circ$ ). Acrylamide,<sup>18</sup> acrylic acid,<sup>19</sup> itaconic acid,<sup>20</sup> and barium methacrylate<sup>21</sup> each produce only a single chemical radical species under these conditions and e.s.r. observations show that this corresponds to the radical adduct of the monomer and a hydrogen atom, e.g.,  $\text{CH}_3\text{CHX}$  where  $\text{X} = -\text{CONH}_2$  or  $-\text{CO}_2\text{H}$ . The hydrogen atoms are produced by radiolysis of the monomer; no radical formed by removal of a hydrogen atom from a monomer molecule can, however, be seen by e.s.r.

On  $\gamma$ -irradiation at  $-196^\circ$  acrylonitrile<sup>41,42</sup> and methacrylamide<sup>41,43</sup> also produce radical species corresponding to the addition of a hydrogen atom to the monomer. Acrylonitrile gives one, and methacrylamide two, additional radicals, for which the structures  $\text{CH}_2:\dot{\text{C}}\text{CN}$ ,  $\text{H}_2\text{N}\dot{\text{C}}:\text{O}$ ,  $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)\text{-CONH}_2$  [ $\text{R} = \text{CH}_2:\text{C}(\text{CONH}_2)\text{CH}_2-$  or  $-\text{C}(\text{CH}_3):\text{CH}_2$ ] have been suggested.<sup>41,43</sup>

The additions of H and D atoms (produced in a microwave discharge) to solid monomers at  $-196^\circ$  has also been studied.<sup>44-46</sup> In all cases examined the primary radical arises from addition of the atom to the unsubstituted  $\text{CH}_2$  group in the monomer molecule.

No radical species formed by addition of a hydrogen atom to the monomer has been observed during initiation by u.v. radiation. With methacrylic acid, the first species observable by e.s.r. contains at least two monomer molecules;<sup>40</sup> detection of radicals in crystalline acrylic acid is more difficult over the temperature range investigated (down to  $-20^\circ$ ) on account of their much lower concentration, but again only the propagating species can be observed.<sup>15</sup> Broad-line n.m.r. studies on acrylic acid at  $4^\circ$ , at which temperature polymerization is rapid, show that, while most of the molecules have only restricted mobility, a fraction undergoes sufficiently extensive movements to give a poorly resolved high-resolution spectrum.<sup>46</sup> It seems likely that the molecules responsible for the narrow line are situated in crystal imperfections, probably those in which poly-

<sup>40</sup> C. H. Bamford, A. Bibby, and G. C. Eastmond, *Polymer*, 1968, 9, 629.

<sup>41</sup> R. Bensasson, A. Bernas, M. Bodard, and R. Marx, *J. Chim. phys.*, 1963, 60, 950.

<sup>42</sup> R. Bensasson, A. Dworkin, and R. Marx, *J. Polymer Sci. (C)*, 1964, 4, 881.

<sup>43</sup> H. Ueda, *J. Polymer Sci. (A)*, 1964, 2, 2207.

<sup>44</sup> C. Chachaty and M. C. Schmidt, *J. Chim. phys.*, 1964, 62, 527.

<sup>45</sup> H. C. Heller *Mol. Crystals*, in press.

<sup>46</sup> B. Arnold and G. C. Eastmond, unpublished results.

merization occurs. Therefore, with plane-polarised incident radiation we would not expect to find significant variation in the rate of initiation as the direction of the electric vector is changed with respect to the crystal axes. In fact, a strong dependence is observed, such as would be expected if the radiation absorbed by the vinyl groups in the perfect lattice were active.<sup>47</sup> From this result it was concluded that initiation occurs through an exciton mechanism, the excitons being formed by absorption of u.v. radiation by monomer molecules in their correct lattice positions. Excitons then migrate through the lattice until they become trapped in imperfections, where they may decay with simultaneous radical formation.

**B. Reactions at Low Temperatures.**—We now consider the fate of the primary radicals at temperatures too low to permit significant polymerization.

The primary radicals in acrylic acid are oriented in the crystal lattice, the  $H_3C-C$  bonds having the same directions as the double bonds in the monomer.<sup>19</sup> With acrylic acid and acrylamide at these low temperatures (about  $-100^\circ$ ) some monomer units are capable of adding to the primary radicals to form secondary radicals which give e.s.r. spectra corresponding to the propagating species in polymerization.<sup>18,19</sup> The secondary radicals in acrylamide are also oriented in the lattice.<sup>18</sup> From crystallographic considerations, Adler *et al.*<sup>18,48</sup> suggested that a primary radical in acrylamide adds to a nearest neighbour molecule in the direction of the two-fold screw axis of the monomer crystal, and they considered that reaction stops at the dimer or trimer stage, since the radical is then completely 'out-of-phase' with the crystal lattice. Further addition to a nearest neighbour can only occur in another direction, and this would cause loss of radical orientation and loss of anisotropy in the e.s.r. spectrum. In all cases studied, anisotropy disappears at higher temperatures, and only under these conditions can polymerization occur.

The species initially observable in methacrylic acid crystals after u.v. irradiation has an e.s.r. spectrum different from the conventional spectrum of methacrylate radicals in that it contains 13 lines instead of the usual 9 (see Figure 4).<sup>49</sup> Both

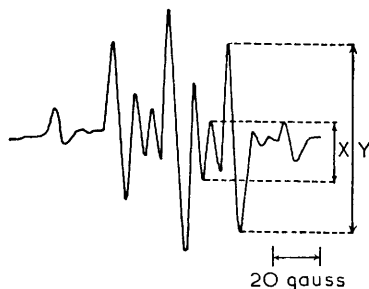


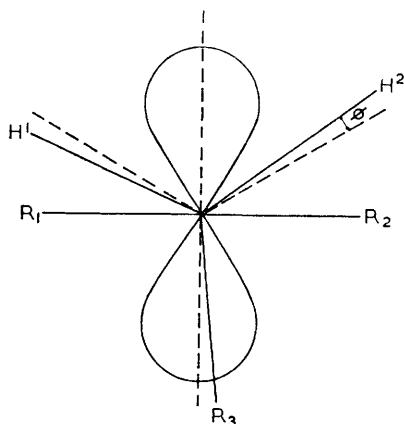
Figure 4 E.s.r. spectrum of methacrylic acid radicals obtained by ultraviolet irradiation of crystals at  $-30^\circ$ . The definitions of the parameters  $X$  and  $Y$  are shown

<sup>47</sup> G. C. Eastmond, E. Haigh, and B. Taylor, unpublished results.

<sup>48</sup> G. Adler and W. Reams, *J. Polymer Sci. (A)*, 1964, **2**, 2617.

<sup>49</sup> C. H. Bamford, G. C. Eastmond, and Y. Sakai, *Nature*, 1963, **200**, 1284.

spectra can be interpreted in terms of the same chemical species  $RCH_2\dot{C}(Me)\cdot CO_2H$ . The 13-line spectrum arises from the conformation shown in Figure 5, which represents a projection down the  $C_\alpha-C_\beta$  bond.<sup>49</sup> In this



**Figure 5** Conformations of the radical  $R^3CH_2-\dot{C}R^2$ . The figure is a projection along the  $C_\alpha-C_\beta$  axis showing the half-filled  $p$ -orbital on  $C_\alpha$ .  $H^1$ ,  $H^2$  are the methylene protons; the broken lines indicate the symmetrical conformation

conformation, the two planes through  $C_\alpha-C_\beta$  and a methylene hydrogen make angles of  $55^\circ$  and  $65^\circ$  respectively with the plane through  $C_\alpha-C_\beta$  and the axis of the half-filled  $p$ -orbital of  $C_\alpha$ . Thus the conformation is derived from the symmetrical one by a rotation  $\phi$  of  $5^\circ$  about the  $C_\alpha-C_\beta$  bond. The conventional 9-line spectrum has been considered to arise from a mixture of two conformations with  $\phi = 0$  and  $\phi = 15^\circ$ , respectively.<sup>50</sup> From studies of the propagating radicals in solution Fischer<sup>51</sup> has obtained results which support this type of interpretation; the preferred conformations are slightly different from the above and are attributable to hindered rotation around  $C_\alpha-C_\beta$ . On warming (to about  $0^\circ$ ) samples of crystalline methacrylic acid containing radicals with the 13-line spectrum, the spectrum changes gradually and irreversibly to the conventional 9-line type.<sup>49</sup> Polymerization is only observed at temperatures at which the 9-line spectrum predominates. A new 9-line e.s.r. spectrum has recently been obtained<sup>46</sup> from crystalline methacrylic acid at low temperatures ( $-160^\circ$ ) after the addition of hydrogen atoms to the monomer at  $-196^\circ$ . [The change from the initial 7-line spectrum of  $(CH_3)_2\dot{C}\cdot CO_2H$  to the new 9-line spectrum also occurs<sup>46</sup> slowly on storage at  $-196^\circ$ .] The line-widths and intensities are markedly different from those in the conventional 9-line spectrum. The new observations can be explained in terms of a further radical conformation with  $\phi = 2.5^\circ$ . On

<sup>50</sup> M. C. R. Symons, *J. Chem. Soc.*, 1963, 1186.

<sup>51</sup> H. Fischer, *Z. Naturforsch.*, 1964, 19a, 866; H. Fischer and G. Giacometti, *J. Polymer Sci. (C)*, 1967, 16, 2763.

warming the sample, the 9-line changes to the 13-line spectrum, irreversibly. It is possible that the two conformations with  $\phi = 2.5^\circ$  and  $5^\circ$  correspond to dimer and trimer, respectively. The change from 13-line to conventional 9-line spectrum is associated with an increase in molecular mobility.<sup>46</sup>

E.s.r. spectra of the radicals formed in barium methacrylate by  $\gamma$ -irradiation are anisotropic at low temperatures; the anisotropy vanishes on raising the temperature<sup>21</sup> and concurrently the spectra change from 13-line to a 9-line type in which the weak quartet has a lower intensity than in the conventional 9-line spectrum. (In ref. 21 the spectrum is considered to contain only 5 lines.) Presumably the relative populations of the various radical conformations under these conditions are different from that corresponding to the conventional spectrum. In this case also little polymerization occurs until the temperature is high enough (*ca.*  $50^\circ$ ) to produce the 9-line spectrum and n.m.r. observations show in this temperature region there is again an increase in molecular mobility.<sup>46</sup>

It follows that at low temperatures there is sufficient restriction on the movement of the radical to give rise to anisotropy and/or the existence of specific conformations. The restrictions may be attributed to the operation of intermolecular forces (*e.g.*, hydrogen bonds) and the prevailing low level of molecular mobility. On raising the temperature, the thermal energy becomes sufficient to overcome these restrictions, especially in the imperfections where the radicals are situated, since in these regions the molecular motions at a given temperature will be more extensive than in the perfect lattice. In such cases the e.s.r. technique serves as a probe for investigating the local molecular mobility in the vicinity of the radicals.

We now discuss the conformational changes in methacrylic acid radicals in more detail.<sup>40</sup> In general, the e.s.r. spectra arising from u.v. irradiation correspond to mixtures of the 13-line and conventional 9-line types; we denote the corresponding radicals T and N respectively. Examination of a spectrum enables a parameter  $X/Y$  (Figure 4) to be evaluated; this is approximately proportional to  $[T]/([T] + [N])$  and can serve as a basis for computation of the latter quantity. During irradiation of methacrylic acid at low temperatures  $X/Y$  decreases progressively and the total radical concentration  $[R\cdot]$  increases to a limiting value (Figure 6). On interrupting the irradiation there is little change in radical concentration with time, showing that conventional bimolecular termination is unimportant. It has been suggested<sup>40</sup> that, at temperatures too low for effective polymerization, the limiting values of  $[R\cdot]$  and  $X/Y$  represent a stationary state and, if this is so, the incident light must be responsible for radical destruction as well as radical formation. The limiting concentration must be determined by the number of sites suitable for reaction and corresponds to the situation in which all the effective sites contain at least one radical. The existence of the stationary radical concentration is understandable if the initial T radicals relax to N after becoming detached from the lattice, a process which may require addition of a suitably placed monomer molecule. Further initiation in the same sites produces pairs of T radicals in the vicinity of N; one of these, after relaxation to N, may undergo termination with the original N radical in the same site, leaving a T

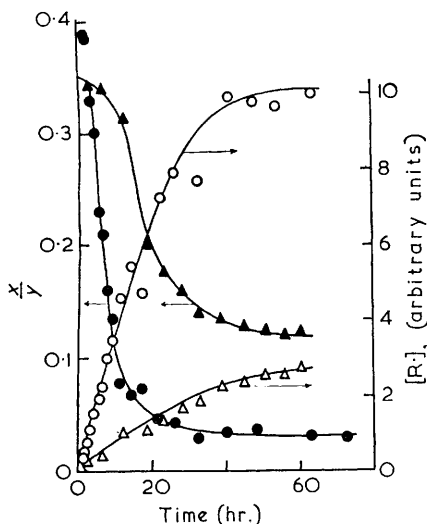


Figure 6 Values of  $X/Y$  and  $[R\cdot]$  for different periods of ultraviolet irradiation of methacrylic acid crystals

● ○  $-20^\circ$

▲ △  $-50^\circ$

From Bamford, Bibby and Eastmond (ref. 40)

radical which will subsequently relax to N. The stationary state set up in this way is summarised in Figure 7.

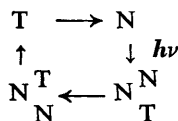


Figure 7

This hypothesis accounts for the experimental observations so far described.

For samples of methacrylic acid crystallized under the same conditions an increase in the temperature of irradiation produces an increase in the limiting value of  $[R\cdot]$  and a decrease in that of  $X/Y$ . It must therefore be supposed that, at any temperature, there exists a distribution of molecular mobility over the potential sites,<sup>40</sup> as first suggested by Adler and Petropoulos.<sup>18</sup> Assuming that the mobility in a site must exceed a certain minimum for reaction to be possible, we see that the number of effective sites will increase with increasing temperature. This accounts for the increase in the limiting value of  $[R\cdot]$  with temperature; the increase in average mobility in the sites explains the decrease in  $X/Y$ , since the rate of relaxation  $T \rightarrow N$  is determined by the mobility.<sup>40</sup>

Measurements of the kind described can clearly provide information about the number and nature of the reaction sites. It has been demonstrated that the

distribution of properties is affected by the conditions of crystallization and the presence of traces of impurities.<sup>40,52</sup> Rapid crystallization, by virtue of the increased rate of nucleation, increases the total number of sites, but decreases the average molecular mobility within them. Similarly, the addition of foreign molecules (*e.g.*, isobutyric acid) to methacrylic acid before crystallization increases both the number of sites and the average molecular mobility. The increased number of sites is reflected in higher limiting radical concentrations, and increased mobility by lower values of  $X/Y$  at short reaction times. Prolonged irradiation at low temperatures leads to values of  $X/Y$  which are independent of the nature of the specimen, showing that all reaction sites eventually acquire similar properties, at a given temperature. It is envisaged that under these conditions, reaction has progressed sufficiently to consume the more mobile monomer molecules in the cores of the imperfections, so that the local crystal structure near the reaction sites approximates to that of the perfect lattice.

So far we have discussed only the processes which lead to the formation of small radicals. We have suggested that a radical will become detached from the lattice when propagation extends beyond the dimer or trimer stage, so that in methacrylic acid  $N$  radicals are to be regarded as the propagating species. In other monomers similar considerations may apply, propagation implying a loss of restriction on the movements of the radicals. It is understandable therefore that polymerization generally occurs only at relatively high temperatures, when the thermal motions overcome the forces holding the radicals to the lattice. Occasionally, however, polymerization can be observed at low temperatures, when conditions are such as to favour high mobility. Acrylonitrile provides a well-known example (see also p. 290). This monomer exists<sup>42</sup> in two crystalline forms with a transition point close to  $-113^\circ$ . If the low-temperature form is irradiated at  $-196^\circ$  and then warmed slowly, after cutting off the radiation, polymerization occurs to about 4% conversion at  $-113^\circ$ , and not below this temperature. If the metastable high-temperature form is irradiated at  $-196^\circ$  and then warmed slowly, polymerization occurs to about 1% conversion near  $-135^\circ$ . At this temperature recrystallization to the stable low-temperature form takes place. Rapid warming of the irradiated metastable high-temperature form to temperatures above  $-113^\circ$  results in 10% conversion. Bensasson, Dworkin, and Marx<sup>42</sup> conclude from these findings that polymerization is facilitated by the phase transition at  $-113^\circ$ ; the transition is clearly associated with rearrangement of the molecules and hence with a relatively high degree of molecular mobility. These considerations also apply to the recrystallization at  $-135^\circ$ . Acrylonitrile is a fairly compact molecule with a low melting point ( $-84^\circ$ ) so that at temperatures not far above  $-113^\circ$  there is probably sufficient molecular mobility arising from thermal energy to allow polymerization.

**C. The Mechanism of Polymerization.**—When extensive polymerization occurs it becomes unrealistic to consider that reaction is confined to the volumes in the

<sup>52</sup> C. H. Bamford, A. Bibby, and G. C. Eastmond, *Polymer*, 1968, **9**, 645.

vicinity of the original imperfections. Polymerization usually results in an overall contraction, but probably produces compressive stresses in some directions, and these may give rise to dislocation multiplication. The new dislocations then become sites for further polymerization. This mechanism accounts for the auto-catalytic behaviour of the reaction under conditions of continuous irradiation,<sup>15</sup> when active species are produced continuously in the new sites. Essentially similar processes would be expected in some other types of solid-phase reaction. For example, in Figure 3, which refers to the caramelization of sucrose,<sup>8</sup> each large protuberance in the surface is seen to be surrounded by a number of satellites, which probably represent the location of dislocations arising by this mechanism. Evidence for dislocation multiplication is also provided by the experiments of Sella and Trillat.<sup>13</sup> As already mentioned, these workers observed the formation of nuclei of polyacrylamide which grow until they attain a diameter of 300—400 Å and continued polymerization was seen to be associated with the nucleation of new globules.

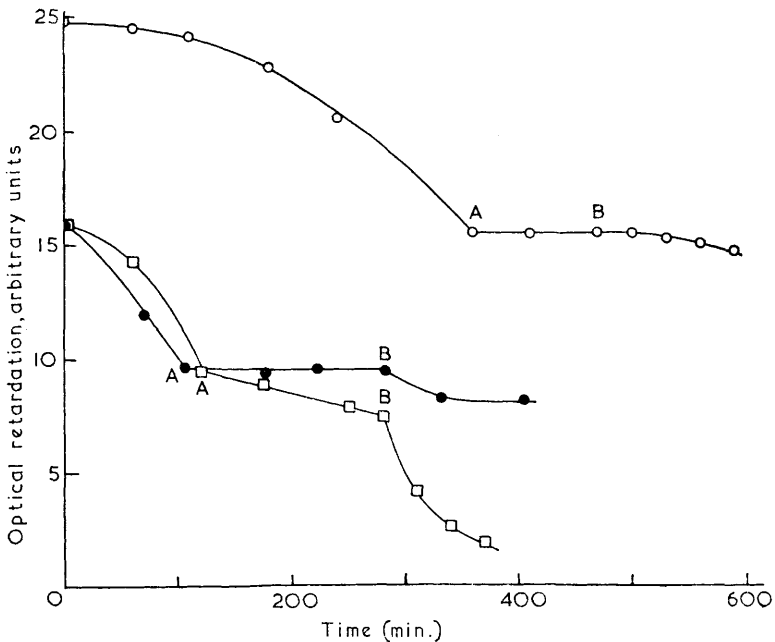
Many solid-phase polymerizations show a prolonged post-irradiation reaction ('after-effect') when the initiating radiation is cut off. The after-effect in acrylamide polymerization has been extensively studied. It might seem that a considerable kinetic simplification would be achieved under these conditions on account of the absence of the initiation reaction. Fadner and Morawetz<sup>53,54</sup> showed that the free-radical concentration remains effectively constant during the after-effect, although the rate of polymerization falls off continuously. Ultimately high yields of polymer are produced. A result of this kind can be explained in terms of the mechanism we have discussed. When irradiation is interrupted, nuclei will be present at all stages of growth; we may expect the subsequent growth to be comparatively rapid until diameters of the order 300—400 Å are attained (in acrylamide). This stage corresponds to the polymerization of monomer molecules which were initially present in the regions of the imperfections. Further propagation to yield high conversions requires additional growth of these nuclei, since no new radical can be produced; this necessitates the diffusion of monomer molecules from the lattice to the radicals in the nuclei, and would be expected to be a slow process. The post-irradiation polymerization must produce dislocation multiplication in the same way as the in-source reaction and when the growing nuclei approach these newly-formed imperfect regions growth will be temporarily facilitated.

(i) *Effects of pressure.* One of the difficulties encountered in the study of solid-phase polymerization is the lack of experimental variables of which use can be made to obtain meaningful results. Consequently it is not surprising that effects produced by application of pressure have received some attention. Bamford, Eastmond, and Ward<sup>15</sup> showed that the polymerizations of crystalline acrylic and methacrylic acids at suitable temperatures are remarkably sensitive to rather

<sup>53</sup> H. Morawetz and T. A. Fadner, *Makromol. Chem.*, 1959, **34**, 162.

<sup>54</sup> T. A. Fadner and H. Morawetz, *J. Polymer Sci.*, 1960, **45**, 475.

small compressive stresses, of the order of 150 lb. in.<sup>-2</sup> (Figure 8). The rates of polymerization under continuous irradiation are greatly reduced by such stresses, and indeed the reactions may be completely suppressed. When the stress is released, polymerization is resumed, immediately in the case of methacrylic acid, and after a short induction period with acrylic acid. It was demonstrated that these observations were not artifacts brought about by effects such as retention of polymer orientation. The polymerization of methacrylic acid shows an after-effect which may also be suppressed by stress; the normal after-effect reappears immediately on removal of the stress. The propagation reaction is thus shown to be retarded by stress.



**Figure 8** Effect of stress on the polymerization of acrylic and methacrylic acids initiated by ultraviolet radiation. Stress applied at point A and removed at B in each case

○ Acrylic acid at 4°.

□ Methacrylic acid at 7°.

● Methacrylic acid at 7°, irradiation stopped at A. This curve illustrates the suppression of the after-effect by stress.

From Bamford, Eastmond, and Ward (ref. 15)

With acrylic acid the sensitivity to stress is greatest near 4°; at high temperatures it decreases rapidly, vanishing at about 7°, a temperature close to the onset of pre-melting. The sensitivity falls off slowly with decreasing temperature below 4°. Methacrylic acid shows generally similar behaviour, the sensitivity being maximal at about 7° and gradually decreasing to zero at -14°.



These findings were among the earliest indications that dislocations probably play a part in solid-state polymerization. It is envisaged<sup>15</sup> that, when a dislocation containing a propagating radical is moved by the application of stress, the radical finds itself in a region in which the molecular mobility is so low that propagation ceases. The dislocations pile up in the vicinities of imperfections such as grain boundaries; it is impossible to say whether initiation continues in these regions since the optical resolution used was not sufficiently great. In the case of methacrylic acid, release of stress allows dislocations to return to their original positions; this is demonstrated by the immediate reappearance of the after-effect.

As the temperature of pre-melting is approached the degree of disorder in the crystals increases rapidly, to such an extent that dislocations lose their identity, and pressures of the magnitude mentioned have little effect on the rate of polymerization. At sufficiently low temperatures the dislocations become less mobile and again the effect of stress is greatly reduced.

An impurity present in a crystal tends to concentrate in the neighbourhood of imperfections such as dislocation lines in the form of Cottrell clouds,<sup>5</sup> and so might be expected to exercise a profound influence on the behaviour of the system under stress. This is found to be so in practice; with methacrylic acid crystals at 4° the sensitivity to pressure decreases as the content of isobutyric acid increases, and is barely detectable with 0.3% (v/v) of isobutyric acid.<sup>55</sup> At -14° (at which temperature pressures of 150 lb. in.<sup>-2</sup> have negligible effect) sensitivity to small stresses is quite high in crystals having isobutyric acid contents in the range 0.1—0.2%, but becomes much smaller when the acid content reaches 0.5%. In alloys, Cottrell clouds reduce the mobility of dislocations;<sup>5</sup> similar behaviour in methacrylic acid could explain the observations at 4°, but not those at -14°. The main action of the impurity is therefore to enhance the local mobility of monomer molecules; in this sense it is equivalent to a local increase in temperature. Presumably the Cottrell-cloud mechanism does not operate because the reaction temperatures employed were comparatively close to the m.p. of the crystals (16.0°).<sup>55</sup>

Many workers have studied solid-phase polymerizations under pressures in the range  $5 \times 10^3$ — $5 \times 10^6$  lb. in.<sup>-2</sup>. Generally this work has been carried out on polycrystalline materials, and the stress patterns in the specimens must have been very complex. Detailed interpretations of the results is therefore difficult, and no general picture appears to have emerged. As examples, we quote the findings of Fydeler and Charlesby<sup>56</sup> and of Tabata and Suzuki.<sup>57</sup> Both groups report that below 30° pressures of several thousand atmospheres have no effect on the initial rates of the  $\gamma$ -initiated polymerization of acrylamide. The mean rates up to specified finite conversions (*e.g.*, 20% at 28° and 60% at 18°) are decreased, but at higher conversions the rates are increased. Fydeler and Charlesby also report that pressures of  $7 \times 10^4$  lb. in.<sup>-2</sup> do not affect the initial rate of polymerization of methacrylamide, although the reaction virtually ceases

<sup>55</sup> C. H. Bamford, A. Bibby, and G. C. Eastmond, *Polymer*, 1968, 9, 653.

<sup>56</sup> P. J. Fydeler and A. Charlesby, paper presented at I.U.P.A.C. Symposium, Prague, 1965.

<sup>57</sup> Y. Tabata and T. Suzuki, *Polymer Preprints*, 1964, 5, 997.

at 0.5% conversion. Pressures of  $9.5 \times 10^4$  lb. in.<sup>-2</sup> accelerate the polymerization of crystalline and amorphous anhydrous calcium acrylate and crystalline anhydrous barium methacrylate at 18°. Fydeler and Charlesby suggested that the main influence of pressure is on propagation. The lower rates observed in the acrylamide polymerization were attributed to a reduction in the disruption of the crystals arising from polymerization, while at high conversions the applied pressure was considered to facilitate reaction by reducing the free volume produced by the reaction. For the salt this type of interpretation assumes that the crystal lattice assists propagation; we have seen that there is little evidence for this view.

(ii) *Effects of additives.* The influence of low concentrations of unreactive impurities on some polymerizations was discussed earlier. Here we consider polymerization in the presence of higher concentrations of compounds which may enter into chemical reactions.

The system acrylamide-propionamide has received most attention; these compounds form solid solutions in all proportions.<sup>54</sup> Fadner and Morawetz<sup>54</sup> observed that while the rate of the post-irradiation polymerization of acrylamide is little affected by the incorporation of up to 10% propionamide in the crystals, there is a considerable reduction in the molecular weight of the polymer. These workers therefore suggested a greatly enhanced chain-transfer activity of propionamide in the solid-phase, compared with the liquid-phase, polymerization. Adler and Reams<sup>48</sup> found that even with mixtures containing as little as 4% acrylamide by weight high conversions (60% at 4% concentration) can be obtained; the polymers isolated have number-average molecular weights greater than 9000 and Adler and Reams argued that this result is incompatible with a high chain-transfer activity of propionamide. Another mechanism for reducing the molecular weight in these systems has been suggested.<sup>52</sup> The yield of radiolytic hydrogen from propionamide is known greatly to exceed that from acrylamide under comparable conditions,<sup>58</sup> so that a greater rate of formation of primary radicals would be expected in mixtures containing propionamide. Many of these radicals may be situated in sites in which propagation cannot occur readily until polymer nuclei have grown into their vicinity. At this point some of the primary radicals will terminate growing chains, while others will initiate new chains so that the net result may be similar to that of a transfer process.

It is necessary to consider the mechanism by which very low concentrations of monomer are enabled to polymerize so extensively in the crystals. Although diffusion of acrylamide through the perfect lattice is improbable, diffusion along the interface between amorphous polymer and the lattice is more likely and was postulated by Adler and Reams.<sup>48</sup> The monomer could thus be brought into contact with radicals formed in imperfections and hence enabled to react. Another factor which might be important in systems containing extremely low concentrations of acrylamide is the concentration of monomer around the dis-

<sup>58</sup> G. Adler, D. S. Ballantine, T. Davis, and R. Ranganathan, *J. Phys. Chem.*, 1964, **68**, 2184.

location lines, in the form of Cottrell clouds.<sup>52</sup> Acrylamide molecules in these regions may have sufficient mobility to polymerize. A portion of the monomer, situated in the more perfect regions of the lattice, would be unable to react so that, as observed in systems containing less than 10% monomer, limiting conversions would be expected.

Kaetsu *et al.*<sup>59</sup> have discussed the effects of various additives, at concentrations of approximately 10% on the polymerization of acrylic acid and acrylamide in terms of the influence of the additives on the physical structure of the binary systems. From estimates of the 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. Kaetsu *et al.* suggested further that dislocations associated with grain boundaries are the most probable sites for reaction in these systems.

(iii) *Topotactic polymerization.* The term 'topotactic' implies some degree of direct control by the host lattice over the orientation of the product lattice. Several definitions, implying varying degrees of control, have been put forward.<sup>60-62</sup> Probably the most relevant definition for present purposes is that of Dent Glassler *et al.*:<sup>62</sup> 'for true topotaxy there must be some three-dimensional correspondence between the structures of the product and its host.' From the earlier discussion it will be appreciated that the polymerization of any vinyl monomer is unlikely to be truly topotactic; however, solid-phase polymerizations are known in which some direction in the monomer molecules, controlled by the lattice, appear to be retained during polymerization<sup>9,63</sup>

An example of such a reaction is the polymerization of vinyl stearate<sup>63</sup> in which the vinyl groups are situated in well-separated layers. Monomeric vinyl stearate crystals are monoclinic, with the paraffin chains in an orthorhombic sub-cell. During polymerization the stearate residues retain their orientation in the lattice, but the packing changes from orthorhombic to hexagonal. A change of this kind often occurs in long-chain hydrocarbons as the molecular mobility increases in the vicinity of the melting point;<sup>64</sup> it involves an overall expansion of the sub-cell area in the plane perpendicular to the long axis of the paraffin chains. At 30% conversion the presence of the normal monomer lattice could still be detected, but at 40% conversion all the stearate residues were packed in the hexagonal arrangement.<sup>63</sup> The polymer formed is not stereoregular and crystallinity is confined to the paraffin side-chains, the backbone being unable to crystallize.<sup>63</sup> It is known that non-stereoregular polyvinyl stearate will crystallize similarly through side-chain interaction.<sup>65</sup> No evidence has been obtained

<sup>59</sup> I. Kaetsu, N. Sagane, K. Hayashi, and S. Okamura, *J. Polymer Sci. (A1)*, 1966, **4**, 2241.

<sup>60</sup> F. K. Lotgering, *Nuclear Chemistry*, 1959, **9**, 113.

<sup>61</sup> A. L. Mackay, Proceedings 4th International Symposium on the Reactivity of Solids, Amsterdam, 1960, 571.

<sup>62</sup> L. S. Dent Glassler, F. P. Glassler, and H. F. W. Taylor, *Quart. Rev.*, 1962, **16**, 343.

<sup>63</sup> N. Morosoff, H. Morawetz, and B. Post, *J. Amer. Chem. Soc.*, 1965, **87**, 3035.

<sup>64</sup> E. R. Andrew, *J. Chem. Phys.*, 1950, **18**, 607.

<sup>65</sup> D. A. Lutz and L. P. Witnauer, *J. Polymer Sci. (B)*, 1964, **2**, 31.

which shows that propagation occurs in any preferred direction; polymerization presumably involves the disordering of a few CH<sub>2</sub> groups in the side chains near the vinyl double bonds.

*p*-Acetamido- and *p*-benzamido-styrene have been shown to polymerize thermally in the crystalline state.<sup>9</sup> The crystal structures are not known but structures have been suggested in which the vinyl groups are arranged in separated layers.<sup>9</sup> These monomers resemble vinyl stearate in possessing large and strongly interacting substituent groups which must affect the course of the reaction. When *p*-benzamido-styrene (m.p. 178°) is polymerized thermally below the glass transition temperature of the polymer (120°), the i.r. dichroism of the N-H stretching vibration does not decrease even at conversions as high as 80%. Above the glass transition the anisotropy is lost and a disoriented polymer is formed. As Jakabhazy *et al.*<sup>9</sup> remark, there must be sufficient movement of the side chains during polymerization to allow the tetrahedral requirements of the carbon atoms in the newly formed backbone to be satisfied, while the original N-H dichroism is retained. No information is available about the direction of propagation in this polymerization, although it has been suggested that polymerization effectively occurs in two dimensions, perpendicular to the long axes of the molecules, so that the growing chains link together sheets of hydrogen-bonded monomer molecules. The microstructure of the polymer is not known. Electron microscopy has revealed that during polymerization at 110° protuberances develop on the crystal surfaces,<sup>9</sup> reminiscent of those appearing on sucrose crystals during thermal decomposition<sup>8</sup> and attributed to the emergence of dislocation lines at the surface.

The most notable difference between the solid-phase polymerizations of vinyl stearate and *p*-benzamido-styrene and those of small monomers such as acrylamide lies in the retention of some crystallinity or structure during the reaction of the monomers with large side chains. The packing of the latter has a dominant effect on the crystal structures of the monomers, and presumably also on the morphology of the polymers, but, nevertheless, the side chains must allow sufficient movement of the vinyl groups to make polymerization possible.

Probably the nearest approach to a true topotactic polymerization so far achieved is the polymerization of dienes in clathrate complexes.<sup>66-70</sup> The monomer molecules are confined to channels in urea or thiourea matrices and their movements are likely to be less restricted than in a monomer lattice. The restrictions, while insufficient to prevent polymerization, suffice to give rise to controlled structures.  $\gamma$ -Ray-initiated polymerizations of 2,3-dimethyl-1,3-butadiene, 2,3-dichloro-1,3-butadiene and 1,3-cyclohexadiene in thiourea clathrates were shown by Brown and White<sup>66</sup> to lead exclusively to the *trans*-1,4

<sup>66</sup> I. F. Brown and D. M. White, *J. Amer. Chem. Soc.*, 1960, **82**, 5671.

<sup>67</sup> D. M. White, *J. Amer. Chem. Soc.*, 1960, **82**, 5678.

<sup>68</sup> V. Stephan, J. Vodehnal, I. Kössler, and N. G. Gaylord, *J. Polymer Sci. (A1)*, 1967, **5**, 503.

<sup>69</sup> L. Kiss, Paper presented at I.U.P.A.C. Symposium, Prague, 1965.

<sup>70</sup> V. S. Ivanov, T. A. Sukhikh, Yu. V. Medvedev, A. Kh. Breger, V. B. Osipov, and V. A. Gol'din, *Vysokomol. Soedin.*, 1964, **6**, 782; *Polymer Sci., U.S.S.R.*, 1964, **6**, 856.

polymers. The polymers are crystalline, and can be isolated as needles in which the chains lie along the long axis. In thiourea complexes, smaller monomers, such as 1,3-butadiene and vinylacetylene, do not give stereoregular polymers, since there is insufficient restriction to control the mode of propagation.<sup>66</sup> However, by the use of urea clathrates, it is possible to prepare an all-*trans* polymer of 1,3-butadiene and also crystalline syndiotactic poly(vinyl chloride) and crystalline polyacrylonitrile.<sup>67</sup> According to Stephan *et al.*<sup>68</sup> there is evidence for monocyclic structures in the polymer prepared from the 2,3-dimethyl-1,3-butadiene-thiourea complex.

(iv) *Effects of environment.* Morawetz and his colleagues<sup>71,72</sup> have made comparative studies of the post-polymerization of salts of acrylic and methacrylic acids following  $\gamma$ -irradiation. The rates of polymerization depend on the nature of the cation and, with calcium acrylate and barium methacrylate, on the degree of hydration. For the alkali-metal acrylates rates are in the order  $K > Li > Na$ , and for methacrylates  $K > Na$ , initially, with zero rate for the Li salt.<sup>72</sup> In all cases the polymers are amorphous. An interesting observation is that the tacticity of the polymer from barium methacrylate dihydrate changes with the extent of conversion.<sup>71</sup> At 50°, low conversions (< 10%) give a polymer containing 37% isotactic and 15% syndiotactic triads, as defined by Bovey and Tiers.<sup>73</sup> As the conversion increases to 60% the microstructure changes, finally corresponding to 21% isotactic and 33% syndiotactic triads. Since the reaction is a post-polymerization the tacticity must change with the length of the kinetic chain. In the later stages the tacticity of the newly formed polymer is similar to that in the liquid-phase reaction. Lando and Morawetz<sup>71</sup> conclude from these results that the monomer crystal structure exerts a specific influence on the course of the reaction, the progressive disruption of the lattice during polymerization accounting for the change in tacticity. Morawetz and Rubin<sup>72</sup> suggest further that the experimental observations support the view that 'the bulk of the polymer lies in an amorphous phase, but the reactive end of the growing chain is effectively anchored in the lattice of the monomer crystal and its reactivity is controlled by the geometry of the crystal lattice'. In the Reviewers' opinion much more detailed information is required, *e.g.*, on the structure of the crystals and the molecular movements in the lattice, before any precise mechanism can be advanced for the polymerization of these salts. According to any reasonable hypothesis, the crystal lattice must exert an influence on the reaction, whether direct, as apparently envisaged by Morawetz *et al.*,<sup>71,72</sup> or indirect, by control of the structure of imperfections in which the reaction occurs.

(v) *Polymerization at very low temperatures.* Several monomers are reported to polymerize under  $\gamma$ -irradiation at very low temperatures. Acrylonitrile has prob-

<sup>71</sup> J. B. Lando and H. Morawetz, *J. Polymer Sci. (C)*, 1964, 4, 789.

<sup>72</sup> H. Morawetz and I. D. Rubin, *J. Polymer Sci.*, 1962, 57, 669.

<sup>73</sup> F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, 1960, 44, 173.

ably received most attention from this point of view. We have already referred to the work of Bensasson, Dworkin, and Marx<sup>42</sup> which extended down to  $-196^{\circ}$  and established that reaction occurs particularly readily during phase transitions. Barkalov *et al.*<sup>36,74,75</sup> and Tabata and his colleagues<sup>76-78</sup> have also investigated the reaction over a similar temperature range. More recently Barkalov *et al.*<sup>79</sup> and Bruk *et al.*<sup>80</sup> have studied the polymerization at  $4.2^{\circ}\text{K}$ . It is especially important in this work to distinguish between polymerization in the solid phase during irradiation and reaction at high temperatures during melting; some workers have paid particular attention to this point, and have concluded that there is a genuine solid-phase polymerization during irradiation at low temperatures.<sup>36,76,80</sup> There appears to be general agreement that the observed activation energy of the in-source reaction at  $-196^{\circ}$  is effectively zero, while that of the post-polymerization at higher temperatures is *ca.* 3 kcal. mole<sup>-1</sup> (similar to that of the radiation-induced polymerization of the liquid monomer). No post-polymerization occurs at  $-196^{\circ}$ . Further, at high doses the conversion reaches a limiting value, which is greater at  $-196^{\circ}\text{C}$  than at  $4.2^{\circ}\text{K}$ . At the former temperature the limiting conversion is stated to increase on re-irradiation after melting and freezing.<sup>36</sup> According to Barkalov *et al.*<sup>79</sup> the rate of polymerization of acrylonitrile at  $4.2^{\circ}\text{K}$  is about half that observed at  $-196^{\circ}\text{C}$ , but the authors could not decide whether this was a result of a lower radical yield at  $4.2^{\circ}\text{K}$  or a decrease in the rate of propagation.

With hexamethylcyclotrisiloxane Barkalov *et al.*<sup>79</sup> observed higher rates at  $4.2^{\circ}\text{K}$  than at  $-196^{\circ}\text{C}$ , and Bruk *et al.*<sup>80</sup> reported that solid tetrafluoroethylene polymerizes at comparable rates at the two temperatures. Barkalov *et al.*<sup>81</sup> showed that the polymerization of crystalline vinyl acetate at temperatures down to  $-196^{\circ}$  resembles that of acrylonitrile.

The existence of polymerization processes with effectively zero activation energy would clearly raise interesting questions, since the mechanism must be different in character from that of conventional polymerization, in which propagation is activated. Semenov<sup>82</sup> has pointed out that 'preorientation' of monomer molecules, as in a crystal lattice, may create highly favourable conditions for transfer of the energy liberated in an elementary act of addition for excitation of the neighbouring monomer molecule, so that the next elementary act would not require thermal activation. In a perfect lattice both the ground state and the

<sup>74</sup> I. M. Barkalov, A. A. Berlin, V. I. Gol'danskii, and B. G. Dzantiev, *Vysokomol. Soedin.*, 1960, **2**, 1024.

<sup>75</sup> I. M. Barkalov, V. I. Gol'danskii, and V. G. Rapaport, *Doklady Akad. Nauk S.S.S.R.*, 1965, **161**, 1368.

<sup>76</sup> Y. Tabata, *Kogyo Kagaku Zasshi*, 1959, **62**, 1065.

<sup>77</sup> H. Sobue and Y. Tabata, *J. Polymer Sci.*, 1960, **43**, 459.

<sup>78</sup> Y. Tabata, S. Shu, S. Hayakawa, and K. Oshima, *Polymer Preprints*, 1964, **5**, 986.

<sup>79</sup> I. M. Barkalov, D. A. Gareyeva, V. I. Gol'danskii, N. S. Yenikolopyan, and A. A. Berlin, *Vysokomol. Soedin.*, 1966, **8**, 1140.

<sup>80</sup> M. A. Bruk, V. F. Gromov, I. V. Chernyak, P. M. Khomikovskii, and A. D. Abkin, *Vysokomol. Soedin.*, 1966, **8**, 961.

<sup>81</sup> I. M. Barkalov, V. I. Gol'danskii, N. S. Yenikolopyan, S. F. Terekhova, and G. M. Trofimova, *Vysokomol. Soedin.*, 1964, **6**, 98.

<sup>82</sup> N. N. Semenov, *J. Polymer Sci.*, 1961, **55**, 563.

excited state were considered to approximate to 'collective' levels; the energy liberated in the first act of addition (*e.g.*, to the primary radical) may excite the monomeric system containing many molecules, so that a concerted act of transformation of these to a polymer chain would occur. Adirovitch<sup>83</sup> has estimated that, according to this mechanism, a chain of 1000 links may be formed in about  $10^{-10}$  sec. A similar suggestion appears to have been advanced independently by Tabata *et al.*<sup>84</sup>

Most workers have interpreted observations made at very low temperatures in terms of a specific mechanism of this type.<sup>86,78,80</sup> However, it is important at this stage not to overlook other possible explanations of the phenomena. For example, as pointed out by Barkalov *et al.*,<sup>86</sup> the independence of rate upon the temperature of irradiation (*i.e.*, the apparent zero activation energy) could arise from limitation of the kinetic chains by structural factors such as defects. We may note that the Semenov mechanism cannot easily explain the phenomena associated with limiting conversion, nor does it seem consistent with the observation of Barkalov *et al.*<sup>81</sup> that glassy vinyl acetate at  $-196^{\circ}$  polymerizes under irradiation by 1.6 Mev electrons at least 10 times as rapidly as crystalline monomer under the same conditions. The latter observation suggests that disorder favours polymerization. A similar conclusion may be drawn from the data of Barkalov *et al.*<sup>86</sup> on the effect of repeated cycles of melting, freezing, and irradiation on the limiting conversion in the acrylonitrile polymerization.

If a mechanism of the Semenov type is not accepted it is necessary to find an alternative explanation for the occurrence of polymerization at  $4.2^{\circ}\text{K}$ , which must require effectively zero activation energy. One such explanation might be that regions of disorder in the crystal act as traps for energy packets, *e.g.*, excitons, arising from interaction of high-energy radiation with the monomer. Subsequent decay of these packets would produce 'hot' regions and so energise the molecules and promote local polymerization. Barkalov *et al.*<sup>86</sup> have considered the importance of the 'loosening' of the monomer molecules and the excitation of internal motions in the path of the primary particles and their decay products.

A reliable estimate of the life of a kinetic chain made, for example, by use of pulsed radiation, would be of great interest in assessing the validity of the Semenov mechanism.

**D. Polymer Structure.**—It is of obvious interest to compare the microstructures of polymers of the same monomer prepared by reactions in the solid and liquid phases. Free-radical polymerization in the liquid state usually produces atactic polymers, with a bias towards syndiotactic triads;<sup>78,85</sup> a random polymer contains 25% isotactic, 50% heterotactic, and 25% syndiotactic triads. As the temperature of polymerization increases the isotactic content increases and the polymers become more random. The radiation-induced solid-state polymeriza-

<sup>83</sup> E. I. Adirovitch, *Doklady Akad. Nauk S.S.S.R.*, 1961, 136, 117.

<sup>84</sup> Y. Tabata, B. Saito, H. Shibano, and K. Oshima, *Kogyo Kagaku Zasshi*, 1962, 65, 731.

<sup>85</sup> F. A. Bovey, *J. Polymer Sci. (A)*, 1963, 1, 843.

tion of methacrylic acid at 0° gives a polymer with an isotactic content (ca. 20%) higher than that of the polymer prepared in solution at 90° (ca. 12%)<sup>86</sup> and therefore with a more random structure. It has been reported that poly(methyl methacrylate) prepared by  $\gamma$ -irradiated solid state polymerization at -65° is more isotactic than the material obtained in the liquid-phase reaction at low temperatures.<sup>87</sup> Clearly in these systems, as in barium methacrylate already discussed, there is no dominating influence which would lead to a stereoregular polymer.

Tabata *et al.*<sup>78,88</sup> have pointed out that the properties of polyacrylonitrile prepared from crystalline acrylonitrile are influenced by the crystalline form of the monomer; the observed differences have been attributed to variations in the stereoregularity of the polymer. In particular, the formation of  $>C=N-$  from  $-C\equiv N$  on heating occurs more rapidly in polymers prepared at lower temperatures, suggesting that these have a higher isotactic content.<sup>89,90</sup> Similarly, poly-methacrylonitrile prepared by solid-state polymerization has been reported to contain a negligible amount of syndiotactic material.<sup>91</sup>

At present, it appears that observations on the microstructure of the products of solid-phase polymerization are too fragmentary in nature to provide any insight into the reaction mechanism, or to allow detailed interpretation.

#### 4 Polymerization of Cyclic Monomers

Considerable interest was aroused by the publications of Okamura *et al.* which demonstrated that several crystalline cyclic monomers, *e.g.*, trioxan,<sup>2</sup>  $\beta$ -propiolactone,<sup>92</sup> diketene,<sup>93</sup> and 3,3-bis(chloromethyl)oxetan,<sup>94</sup> form highly crystalline and oriented polymers when submitted to  $\gamma$ -irradiation. (It is noteworthy that in the 1930's Kohlschütter and Sprengel<sup>95</sup> observed the formation of a crystalline polymer on the surface of trioxan in the presence of formaldehyde vapour.) Early work on the polymerization of single crystals of monomers of this type appeared to establish that the fibre-axes of the polymers were oriented in specific directions with respect to the crystallographic axes of the monomer lattices. In some cases twinned structures were reported, *e.g.*, in the polymers from trioxan,<sup>8</sup> trithian,<sup>96,97</sup> and triselenan.<sup>98</sup> It seemed clear that these polymerizations in the

<sup>86</sup> H. Morawetz and I. D. Rubin, *J. Polymer Sci.*, 1962, **57**, 687.

<sup>87</sup> T. Lipscomb and E. C. Weber, *J. Polymer Sci. (A1)*, 1967, **5**, 779.

<sup>88</sup> Y. Tabata, M. Asano, and Y. Hashizume, Paper presented at I.U.P.A.C. Symposium, Prague, 1965.

<sup>89</sup> Y. Tabata, E. Oda, and H. Sobue, *J. Polymer Sci.*, 1960, **45**, 469.

<sup>90</sup> I. M. Barkalov, V. I. Gol'danskii, N. S. Enikolopyan, S. F. Terekhova, and G. M. Trofimova, *J. Polymer Sci. (C)*, 1964, **4**, 909.

<sup>91</sup> H. Sobue, T. Uryu, K. Matsuzaki, and Y. Tabata, *J. Polymer Sci. (B)*, 1963, **1**, 409.

<sup>92</sup> S. Okamura, K. Hayashi, Y. Kitanishi, and M. Nishii, *Isotopes and Radiation*, 1960, **3**, 510.

<sup>93</sup> S. Okamura, K. Hayashi, and Y. Kitanishi, *Isotopes and Radiation*, 1959, **3**, 346.

<sup>94</sup> S. Okamura, K. Hayashi, and H. Watanabe, *Isotopes and Radiation*, 1961, **4**, 73.

<sup>95</sup> H. W. Kohlschütter, *Annalen*, 1930, **482**, 75; H. W. Kohlschütter and L. Sprengel, *Z. phys. Chem.*, 1932, **B**, **16**, 284.

<sup>96</sup> J. B. Lando and V. Stannett, *J. Polymer Sci. (A)*, 1965, **3**, 2369.

<sup>97</sup> G. Carazzolo, M. Mammi, and G. Valle, *Makromol. Chem.*, 1967, **100**, 295.

<sup>98</sup> G. Carazzolo and M. Mammi, *Makromol. Chem.*, 1967, **100**, 28.



solid phase are essentially different from those of vinyl monomers in that the orientation of the monomer molecules in the perfect lattice is particularly favourable for polymerization, the conversion of monomer to oriented polymer requiring only comparatively small movements of a few atoms in each ring (see p. 271).

These conclusions received support from kinetic observations. It was reported that, with increasing temperature, the rates of polymerization of crystalline trioxan,  $\beta$ -propiolactone, diketene, and 3,3-bis(chloromethyl)oxetan increase to a maximum at a temperature below the m.p. and then rapidly decrease almost to zero above the m.p.<sup>99,100</sup> Further, in both the in-source and post-irradiation reactions, limiting conversions were observed by many workers.<sup>99,101-108</sup> This phenomenon was explained in terms of the disorientation of monomer molecules, and the inability of such molecules to polymerize.<sup>101</sup> Finally, different conditions of crystallization were found to give different rates of polymerization, and different degrees of polymer orientation. Larger crystals produced higher rates of reaction and more nearly perfect orientation.

Unfortunately the interpretation of these findings is by no means as simple as was originally envisaged. Subsequently it has been found that the values of the limiting conversion are not reproducible;<sup>99,100,108,108</sup> indeed Kagiya *et al.*<sup>109</sup> have reported that there is no limiting conversion in the in-source polymerization of 3,3-bis(chloromethyl)oxetan, provided sufficient care is taken in the purification of the crystals. Addition of small amounts of water or 1,1'-dichloroacetone caused the re-appearance of a limiting conversion. It has also been pointed out that trioxan and 3,3-bis(chloromethyl)oxetan will polymerize in the melt, but the rates are very sensitive to the presence of traces of impurities such as water.<sup>110</sup> Rao and Ballantine<sup>107</sup> have stated that they could not obtain reproducible kinetic data for the polymerization of solid trioxan, in spite of considerable care in standardizing the conditions. The same workers report that the post-irradiation reaction in crystalline trioxan is virtually non-existent if both irradiation and subsequent treatment are carried out in a vacuum.<sup>107</sup> On the other hand, the in-source reactions of diketene are unaffected by the atmosphere.<sup>99</sup> Herz and Stannett<sup>111</sup> have reported that carefully purified trithian crystals prepared from the melt or from *NN*-dimethylformamide solution will not polymerize in the solid phase while crystals from chloroform solution polymerize readily on

<sup>99</sup> S. Okamura and K. Hayashi, *J. Chim. phys.*, 1962, **59**, 429.

<sup>100</sup> K. Hayashi, H. Ochi, and S. Okamura, *J. Polymer Sci. (A)*, 1964, **2**, 2929.

<sup>101</sup> S. Okamura, K. Hayashi, and Y. Kitanishi, *J. Polymer Sci.*, 1962, **58**, 925.

<sup>102</sup> A. Chapiro and S. Penczek, *J. Chim. phys.*, 1962, **59**, 696.

<sup>103</sup> S. Nashakio, M. Kondo, H. Tsuchita, and M. Yamada, *Makromol. Chem.*, 1962, **52**, 79.

<sup>104</sup> C. David, J. Van der Paaren, F. Provost, and A. Ligotti, *Polymer*, 1963, **4**, 341.

<sup>105</sup> S. Okamura, K. Takakura, and K. Hayashi, *Pure and Appl. Chem.*, 1966, **12**, 387.

<sup>106</sup> N. S. Marans and F. A. Wessells, *J. Appl. Polymer Sci.*, 1965, **9**, 3681.

<sup>107</sup> H. Rao and D. S. Ballantine, *J. Polymer Sci (A)*, 1965, **3**, 2579.

<sup>108</sup> M. Sakamoto, I. Ishigaki, A. Shimizu, M. Kumakura, M. Nishii, H. Yamashina, T. Iwai, and A. Ito, Paper presented at I.U.P.A.C. Symposium, Japan, 1966.

<sup>109</sup> T. Kagiya, M. Izu, and K. Fukui, *J. Polymer Sci. (B)*, 1964, **2**, 93.

<sup>110</sup> K. Ueno, H. Tsukamoto, K. Hayashi, and S. Okamura, *J. Polymer Sci (B)*, 1967, **5**, 395.

<sup>111</sup> J. E. Herz and V. Stannett, *J. Polymer Sci. (B)*, 1966, **4**, 995.

$\gamma$ -irradiation. Clearly, therefore, mechanistic deductions from kinetic data must at present be regarded as speculative, in view of the sensitivity of both the liquid- and solid-phase reactions to the experimental conditions.

It is of interest to attempt to correlate the polymerization of crystalline trioxan with the occurrence of molecular mobility in the solid. Komaki and Matsumoto<sup>112</sup> have studied the broad-line n.m.r. spectrum of trioxan and have found decreases in the second moment near  $-10^\circ$  and  $40^\circ$ , corresponding to the onset of new types of molecular motion. Above  $40^\circ$  there is sufficient motion to cause the appearance of a narrow line in the n.m.r. spectrum. Komaki and Matsumoto interpret the observations at  $25^\circ$  as signifying chair-chair interconversion, occurring through a sinusoidal oscillation of proton pairs about an axis perpendicular to the pair direction. At  $45^\circ$ , rotation of the whole molecule about the three-fold axis is supposed to occur, and the narrow line is attributed to a fraction of the molecules which adopt a boat conformation and rotate. Crystalline trioxan polymerizes at a significant rate only above  $30^\circ$ ;<sup>99</sup> at these temperatures the molecules obviously have considerable mobility and, as with vinyl monomers, it appears that the existence of a comparatively high level of mobility is a prerequisite for polymerization. These results provide additional evidence against the earlier view that disorientation of molecules during reaction gives rise to a limiting conversion.

Experiments which throw new light on the mechanism of polymerization of trioxan have been reported by Adler,<sup>113</sup> who studied the post-polymerization in thin layers of single crystals by optical microscopy. Post-polymerization at  $24^\circ$  produces only small amounts of crystalline fibrous polymer having no preferred orientation with respect to the crystal axes of the monomer; indeed, some of the fibres change direction along their length. At  $46^\circ$  there is extensive post-polymerization to give fibrous bundles of crystalline polymer, which may grow across intercrystalline boundaries; the important point is that in so doing the fibres do not change direction, although the crystals may have different orientations. Thus a specific orientation of monomer crystals is not required for continued growth of crystalline polymer in a given direction. It appears, however, that growth is *initiated* along the *c*-axis of the monomer lattice, so that in single crystals the final polymer chains lie parallel to this axis. At  $54^\circ$ , the temperature at which polymerization is generally carried out, extensive recrystallization of the monomer occurs to give a small number of large crystals, and the polymer is aligned almost exclusively along the *c*-axis of the monomer crystal in which it is ultimately situated. The monomer thus appears to crystallize around the polymer, which grows in a straight line. To account for these observations it must be supposed that initiation occurs in a specific type of site. Recently Bassett<sup>114</sup> has obtained photomicrographic evidence that such sites are the  $\{00.1\}$  sub-grain boundaries.

<sup>112</sup> A. Komaki and T. Matsumoto, *J. Polymer Sci. (B)*, 1963, 1, 671.

<sup>113</sup> G. Adler, *J. Polymer Sci. (A1)*, 1966, 4, 2883.

<sup>114</sup> D. C. Bassett, *Nature*, 1967, 215, 731.

We now see that the formation of crystalline polymers is a result of the nature of the polymer, rather than of the process of polymerization. Monomers such as hexamethylcyclotrisiloxane, of which the polymers are normally rubbers, do not give crystalline polymers when polymerized in the solid state.<sup>115</sup> In trioxan the growth process presumably involves transport of monomer, by sublimation or diffusion, from the lattice to the propagating helical polymer. The mechanism of these ring-opening polymerizations therefore appears to resemble that of the vinyl monomers much more closely than was once envisaged.

## 5 The Polymerization of Aldehydes

Acetaldehyde is one of the few monomers of which the crystal structure is known.<sup>116</sup> Letort and Richard<sup>116</sup> point out that the arrangement of molecules along the direction of the *a*-axis in the crystal is well suited for polymerization to the syndiotactic polymer; the C ··· C=O and C=O ··· C angles between neighbouring molecules are close to those in the polymer, so that lateral movements of the molecules together with a small adjustment in bond directions could be sufficient for polymerization. In fact, polymerization takes place readily at the surface of the crystals on melting ( $-123^{\circ}$ ),<sup>117</sup> but the polymer formed is atactic. The process is apparently initiated by trace impurities.<sup>117</sup> The extra mobility near the surface favours polymerization, and the ordering of the molecules in the lattice may assist the process, since polymerization of liquid acetaldehyde is reported to be relatively slow. However, the nature of the polymer shows that rotation of some molecules occurs before addition. This situation recalls the earlier views on the polymerization of cyclic monomers. It appears that further work on aldehydes is necessary to establish the role played by impurities.

No polymerization takes place on  $\gamma$ -irradiation of acetaldehyde at  $-196^{\circ}$ ; subsequent warming to a temperature in the range of  $-150^{\circ}$  to  $-128^{\circ}$  is accompanied by polymerization which may be explosive<sup>118,119</sup> and is presumably initiated by active species formed during irradiation and trapped in the lattice at the low temperature. Reaction is considered to occur in the body of the crystals, possibly in disordered regions produced by the radiation. The nature of the chain-carriers is not known with certainty, but chemical considerations suggest that the polymerization is ionic in character. Charlesby<sup>120</sup> has suggested that the initiating centres are electrons produced on irradiation at  $-196^{\circ}$ ; however, the thermoluminescence in acetaldehyde which accompanies the release of trapped electrons occurs at a somewhat lower temperature (*ca.*  $-170^{\circ}$ ) than the onset of polymerization.<sup>121</sup> Polymerization may require more molecular mobility than exists at  $-170^{\circ}$ .<sup>120</sup>

<sup>115</sup> E. J. Lawton, W. T. Grubb, and J. S. Balwit, *J. Polymer Sci.*, 1956, **19**, 455; W. Burlant and C. Taylor, *ibid.*, 1959, **41**, 547.

<sup>116</sup> M. Letort and A. J. Richard, *J. Chem. Phys.*, 1960, **57**, 752.

<sup>117</sup> M. Letort and A. J. Richard, *Compt. rend.*, 1955, **240**, 86.

<sup>118</sup> C. Chachaty, Thesis, Paris, 1962.

<sup>119</sup> V. S. Pshezhetskii, V. A. Kargin, and N. A. Bach, *Vysokomol. Soedin.*, 1962, **4**, 728.

<sup>120</sup> A. Charlesby, *Reports Progr. Physics*, 1965, **28**, 463.

<sup>121</sup> A. Charlesby and R. H. Partridge, *Proc. Roy. Soc.*, 1964, **A**, **283**, 312, 329.

Solid formaldehyde polymerizes very readily on  $\gamma$ -irradiation. The polymer may be microcrystalline<sup>37</sup> or fibrous;<sup>122</sup> it has a lower degree of crystallinity than polyoxymethylene obtained by the solid-phase polymerization of trioxan. Polymerization occurs during irradiation at  $-196^\circ$  and gives rise to a temperature difference between the inside and the surface of the specimen.<sup>37</sup> If this exceeds  $5-8^\circ\text{C}$  the reaction becomes explosive, and most of the monomer is polymerized by a process which is thought to be a thermal explosion. It is reported that no explosion occurs if as little as 10% of polymer is present before irradiation.<sup>37</sup> An explosive polymerization is also obtained if the solid is given a small dose of irradiation and allowed to warm. There is no post-polymerization after irradiation at  $-196^\circ$ .

The irradiated monomer shows an e.s.r. spectrum which has been attributed to the radicals HCO and  $-\text{OCHO}-$  together with products from the irradiated polymer.<sup>119,123,124</sup> There is no agreement about the nature of the propagating species, Chachaty<sup>118</sup> favouring a radical and Tsuda<sup>122</sup> an ionic mechanism.

The measured activation energy is approximately  $2.5 \text{ kcal. mole}^{-1}$ , a value which is consistent with the occurrence of polymerization at  $-196^\circ$  especially if the ordering of molecules in the lattice leads to a high frequency factor. (The observations of Arnold and Eastmond<sup>46</sup> referred to on p. 278 show that a free-radical addition to methacrylic acid, for which the activation energy must considerably exceed  $2.5 \text{ kcal. mole}^{-1}$ , can take place slowly at  $-196^\circ$ .)

## 6 Copolymerization

The physical nature of a frozen mixture of monomers must exercise a dominating effect on the course of the solid-phase polymerization. Naturally, the likelihood of producing a copolymer is highest when the monomers are in solid solution. In the other extreme case, corresponding to separate crystallization of the monomers, there seems to be no chance of obtaining copolymers except at crystal interfaces. Systems of both types have been examined, and appear to give results consistent with the above general ideas.

Mixtures of oxetans<sup>125</sup> often form solid solutions and  $\gamma$ -irradiation of these leads to true copolymerization with apparent reactivity ratios of unity, quite different from those holding in the liquid state. The rates of copolymerization of tributylvinylphosphonium bromide and iodide in solid solution have been studied by Chen and Grabar<sup>126</sup> as a function of composition.

Acrylamide and methacrylamide form solid solutions which polymerize on  $\gamma$ -irradiation.<sup>127</sup> X-Ray observations taken during reaction suggest that the mechanism is essentially similar to that of the solid-phase polymerization of acrylamide alone.<sup>125</sup> Maleic anhydride and acenaphthene crystallize separately, and form a eutectic mixture.<sup>125</sup> In the liquid phase these monomers give an

<sup>122</sup> Y. Tsuda, *J. Polymer Sci.*, 1961, **49**, 369.

<sup>123</sup> R. Marx and C. Chachaty, *J. Chim. phys.*, 1961, **58**, 527.

<sup>124</sup> C. Chachaty and R. Marx, *J. Chim. phys.*, 1962, **59**, 792.

<sup>125</sup> K. Hayashi, M. Nishii, A. Shimizu, and S. Okamura, *Polymer Preprints*, 1964, **5**, 951.

<sup>126</sup> C. S. H. Chen and D. G. Grabar, *J. Polymer Sci. (C)*, 1964, **4**, 869.

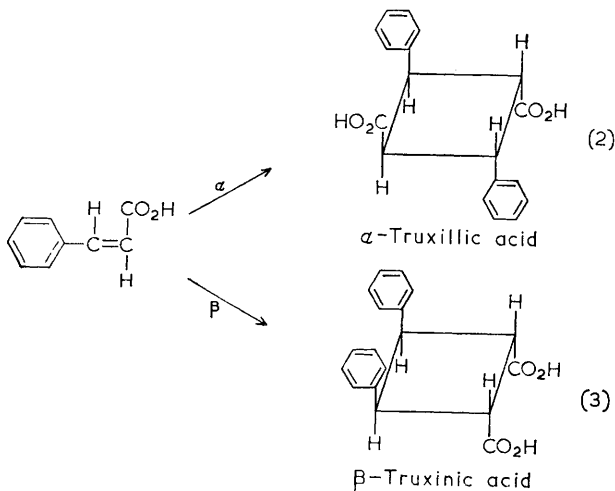
<sup>127</sup> J. Zurakowska-Orszagh, Symposium on Radiation Chemistry, Hungary, 1962.

## Solid-phase Addition Polymerization

alternating (1 : 1) copolymer, but solid-phase polymerization yields a mixture of polyacenaphthene and alternating copolymer.<sup>128</sup> The latter was considered to arise at intercrystalline boundaries near the beginning of the reaction, and also near the end when there is considerable disorder in the system. Hardy *et al.*<sup>128</sup> have investigated copolymerization in the acrylamide–acrylic acid system. Here two eutectics are formed (74.5% and 58.7% acrylic acid, respectively) and also a molecular compound containing acrylamide and acrylic acid in the ratio 1 : 2. Reactions at  $-15^{\circ}$  (at which temperature pure acrylamide does not polymerize) give copolymers of composition corresponding to the eutectics and to that of the molecular compound, together with some polyacrylic acid if the original mixture contains crystalline acrylic acid. The rates of polymerization are maximal at the eutectic compositions, and there is a minimum in the rate at the composition of the molecular compound. Chapiro and Cordier<sup>129</sup> obtained rather similar results with acrylonitrile–styrene mixtures, obtaining pure polyacrylonitrile together with a copolymer approximating to the eutectic composition. Hardy *et al.*<sup>130</sup> have examined the solid-phase polymerization of *N*-vinylsuccinimide in the presence of *N*-vinylpyrrolidone, succinimide, quinone, and phthalic anhydride (added separately). These workers point out the value of a knowledge of phase diagrams in studies of this kind, and also stress the rôle played by lattice defects.

## 7 Concluding Remarks

We have emphasized the importance of imperfect regions in monomer lattices in solid-phase polymerization. There is irrefutable evidence that in simple dimerizations the nature of the lattice exercises a dominating influence on the



<sup>128</sup> Gy. Hardy and L. Nagy, *J. Polymer Sci. (C)*, 1967, **16**, 2667.

<sup>129</sup> A. Chapiro and P. Cordier, *J. Chim. phys.*, 1967, **64**, 334.

<sup>130</sup> Gy. Hardy, J. Varga, G. Nagy, F. Cser and J. Erő, *J. Polymer Sci. (C)*, 1967, **16**, 2583

course of the reaction. Thus Cohen and Schmidt<sup>131</sup> have made an elegant study of the solid-state photodimerization of various substituted *trans*-cinnamic acids. *trans*-Cinnamic acid exists in three different crystalline forms  $\alpha$ ,  $\beta$ ,  $\gamma$ . The  $\alpha$ -modification dimerizes to  $\alpha$ -truxillic acid [equation (2)], the  $\beta$  to  $\beta$ -truxinic acid [equation (3)], while the  $\gamma$ -form is unreactive. We now wish to stress that in all cases the lattice must play an important part, but the control it exercises may be indirect, and may arise through its influence on the structure of crystal defects. To achieve anything like a complete understanding of solid-phase polymerization a much greater knowledge of defects in the monomer crystals is essential, and this will only be obtained by the use of a wide variety of techniques. At present investigations on the behaviour of active species in organic solids are furthering our knowledge of the organic solid state.

<sup>131</sup> M. D. Cohen and G. M. T. Schmidt in 'Reactivity of Solids', ed J. H. de Boer *et al.*, Elsevier Publ. Co., Amsterdam, 1961, p. 556.