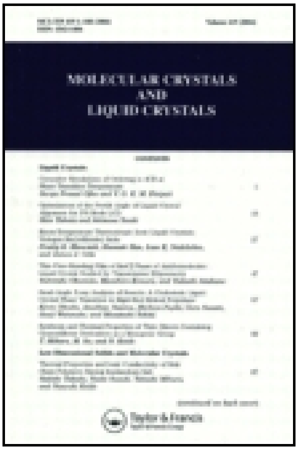

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Some Solid State Aspects of Vinyl Polymerization in Organic Cystals

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Some Solid State Aspects of Vinyl Polymerization in Organic Crystals[‡]

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Abstract—By using the polymerization of acrylamide as an example, it is shown that solid state polymerization is in general just a special case of organic solid state reactions. Insofar as the solid state aspects of the reaction are concerned, the reaction shows the expected behavior of an ordinary solid state reaction except that certain problems are exaggerated because of the large size of the product molecules involved and the large number of possible configurations the molecule may have. The reaction goes by a two phase mechanism with the polymer in general nucleating at a defect site. The product is noncrystalline because of the mismatch in geometry between the product molecule and parent lattice. The fact that the reaction mostly occurs at the interface between monomer and polymer where the reacting molecule cannot easily flip over probably also contributes to the frequent atacticity of the product. Annealing and recrystallization are factors which probably influence the over-all rate of reaction. The large molecular size of the product and the frequently disordered nature of the product phase in polymerizations allows the use of some rather simple techniques in the study of solid state polymerizations making these good model systems for the study of some solid state problems.

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Introduction

In attempting to explain the reaction mechanisms in crystalline organic solids we are confronted with some rather basic problems. Organic molecules in general do not have a highly symmetrical shape. The forces holding the crystal together are of more than one type and are usually unsymmetrically disposed about the molecule because of its shape and structure. Primary bonding forces are, of course, involved in holding the molecule together as a more or less distinct entity within the lattice. There are also the intermolecular forces that hold the molecules together in the crystals. However, these forces eminate from and act upon molecules whose configuration is not very symmetrical. To form a crystal with any degree of efficiency, the molecule must pack in a regular array which minimizes the sum total of the interaction energies resulting from these unsymmetrically disposed forces.

If a reaction occurs within the organic lattice, the product molecule and the transition state will in general have a different configuration of forces with which it interacts with its neighboring molecules. The reacting molecules must therefore act upon their neighbors and produce a configuration around themselves which is a perturbation of the normal lattice. These neighbors must in turn act upon their neighbors if the sum total of the interaction energies is to be again minimized. This process would seem to require energy which, at least in the initial stages of the reaction, ends up being stored as elastic strain or a deviation from the undisturbed lattice structure. In terms of the idealized picture of a relatively efficiently packed defect-free lattice, it would seem that this process would require enough energy to inhibit the reaction unless the lattice energies are weak enough to accommodate a good deal of distortion or else the crystal structure breaks down. Yet we know solid-state reactions do occur in which the crystal structure remains relatively intact.

Reactions like these are difficult enough to explain when the reaction takes place on the surface or, as in the case of cinnamic acid dimerization, the volume and shape of the space occupied by the product molecule, and presumably the transition state, is not greatly different from that occupied by the two reacting molecules. In solid-state polymerization the problem becomes acute. Here a large number of reactant molecules must link up to form a single large molecule that is often very very different in volume and configuration from the sum total of the original molecules that went to make it up. Saying that the molecules are precisely aligned in a fashion so as to favor reaction minimizes the problem only for the first reaction steps where local geometry is still not too greatly perturbed and does nothing about those situations in which this type of alignment does not seem to hold.

Given the properties of real rather than idealized crystals, the way out of this dilemma is often not too difficult to understand. The details of the process may vary greatly from one compound to another but some general principles seem to hold. Perhaps the best way to illustrate this is to take a solid-state reaction and try to trace its course step by step as we now understand it. For this purpose we have chosen the solid-state polymerization of acrylamide, since it is the example most familiar to us from our own work and is, hopefully, typical of many other polymerizations.

Crystal Structure and the Initiation of the Reaction

Perhaps it is best to begin with a brief description of the crystal structure of acrylamide.[1] The molecules can be considered as having an amide part and a hydrocarbon part (the double bond). The molecules are held by hydrogen bonding of the amide groups to form dimers with a centrosymmetric structure. Further hydrogen bonding ties these dimers into sheets or layers. The amide groups form the core of each layer and the hydrocarbon groups the outside. The crystal structure is made up of stacks of these layers. It is monoclinic, space group $P_{2_{1/c}}$. Figure 1 shows two views of a model we have made of this structure. In spite of the supporting wires, the layer-like arrangement is quite easily seen.[2]

It is worth noting that the weakest forces in the crystal are probably those holding the stack together and are thus between hydrocarbon end groups. The strongest forces, which are the ones involved in hydrogen bonding, are at the other end of the molecule. The molecule vibrates within the lattice and this configuration of forces makes it probable that the terminal carbon has the highest amplitude of vibration of the atoms in the molecule. There is some experimental evidence to back up this assumption. Thus the lattice forces are

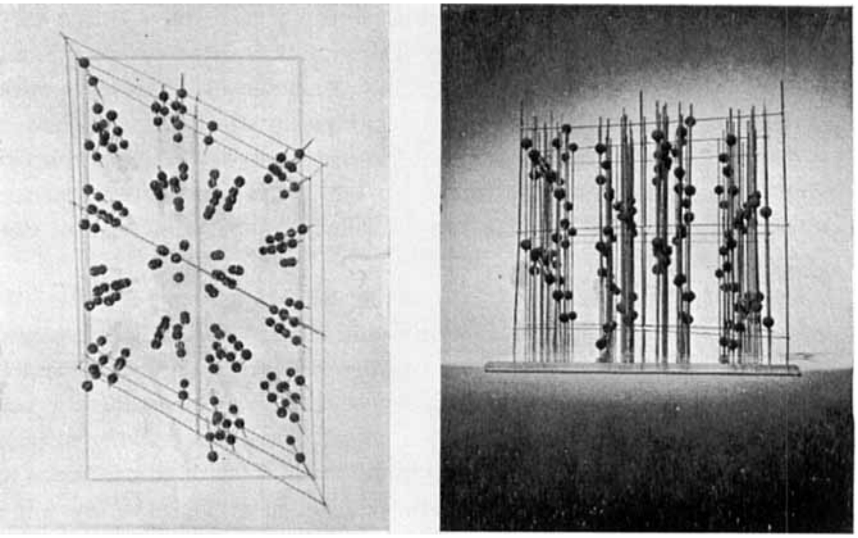
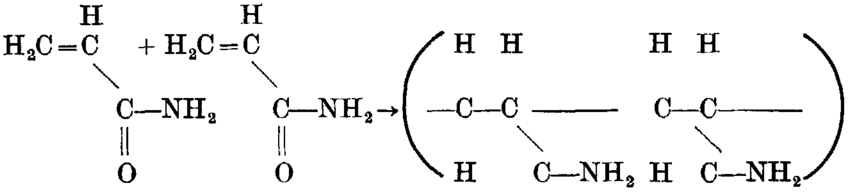


Figure 1. View of a model of the acrylamide crystal structure: (a) the hol projection; (b) view along the *c* axis.[2]

weakest and the amplitude of thermal vibration probably greatest just at those parts of the molecule most intimately connected with the reaction.[1,2]

Basically the reaction we must explain is the following:



All polymerizations must be initiated by some active species, usually a free radical or an ionic group. However, since we cannot incorporate these while growing the crystal, initiation is frequently carried out with ionizing radiation.

Among the primary effects of radiation can be listed the generation of ions, radical ions, and free radicals. In principle these can all initiate polymerization. It has been pointed out that if a radical ion is present, polymerization can initiate by either a radical or ionic mechanism[3] and since the number of free radicals would equal the number of ionic sites, the presence of an ESR spectrum would be no guarantee of a free-radical reaction. However, there has been much evidence accumulated, based on ESR and kinetic measurements, to suggest that a free radical is the initiating species.

Irradiated acrylamide shows an ESR spectrum at room temperature which is relatively stable with respect to time in a manner consistent with the reaction kinetics.[4] Oxygen is normally an efficient inhibitor of free-radical reactions. The presence of oxygen has little effect on the ESR spectrum of acrylamide, since it cannot penetrate the lattice. Under oxygen, however, the spectrum of propionamide, the saturated analog of acrylamide, is markedly changed and shows a sharply increased decay rate. Solid solutions of acrylamide and propionamide can be prepared[3] and these have the same crystal structure as acrylamide. In these solid solutions the ESR spectrum is quenched in oxygen at a rate that is dependent on the relative concentrations of the two materials. In an analogous manner, the polymerization of acrylamide is supressed by oxygen in these solid solutions.[2] The polymerization of acrylamide can also be accomplished by ultraviolet light. Here initiation at the surfaces of the crystals is favored because of the ultraviolet absorption. In this case both the rate and degree of polymerization are decreased by oxygen.[5] This parallelism between kinetic and free-radical data makes it seem fairly certain that we are dealing with a free-radical reaction.

The nature of the initiating radical is now the problem. It has been shown that the presence of acrylamide in solid solution with propionamide reduces the yields of hydrogen produced by radiolysis.[6] This suggests hydrogen scavenging by the double bond in acrylamide. This sort of scavenging is a fairly well-known phenomenon (for example, see refs. 7 and 8).

If the free radical in acrylamide is produced by hydrogen scavenging, it should have the same structure as that resulting from a loss of hydrogen by propionamide. These two compounds, at temperatures below the dimerization temperature of acrylamide, give virtually identical free-radical spectra (Fig. 2). This suggests that free radical is

$$CH_3\text{—}\dot{C}H\text{—}CONH_2.$$

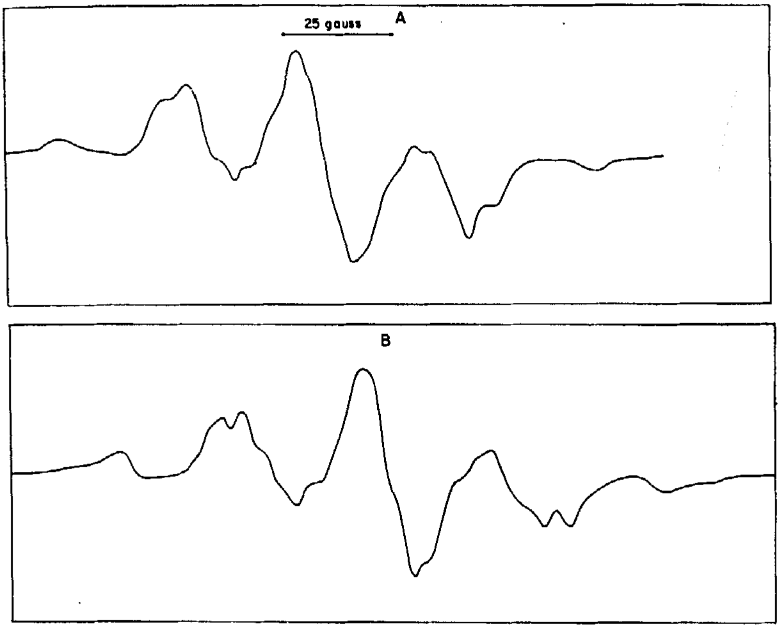
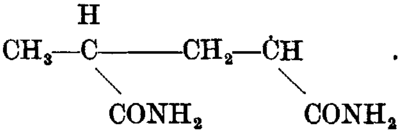


Figure 2. ESR spectra of acrylamide (*A*) and propionamide (*B*) irradiated and stored at − 196°: radiation dose, 20 Mrad[9].

This was confirmed by a single-crystal ESR study of acrylamide at low temperatures.[9] However, a great deal of what we have to say from this point on is independent of the exact nature of the initating species.

We now have an initiating radical. ESR studies of single crystals at temperatures below about − 125° indicate that this radical is oriented within the crystal lattice in a manner consistent with the crystal structure.[9] Above − 125° a subtle change begins to take place in the ESR spectra. The powder spectra begin to resemble that of the polymerizing radical at − 20 °C (Fig. 3). The single-crystal spectrum, however, still shows orientation effects at these temperatures (Fig. 4) whereas at − 20 °C the radical no longer shows orientation. Analysis suggests the new free radical is the dimer



$$CH_3-\underset{\diagdown\, CONH_2}{\overset{H}{C}}-CH_2-\underset{\diagdown\, CONH_2}{\dot{C}H} \quad .$$

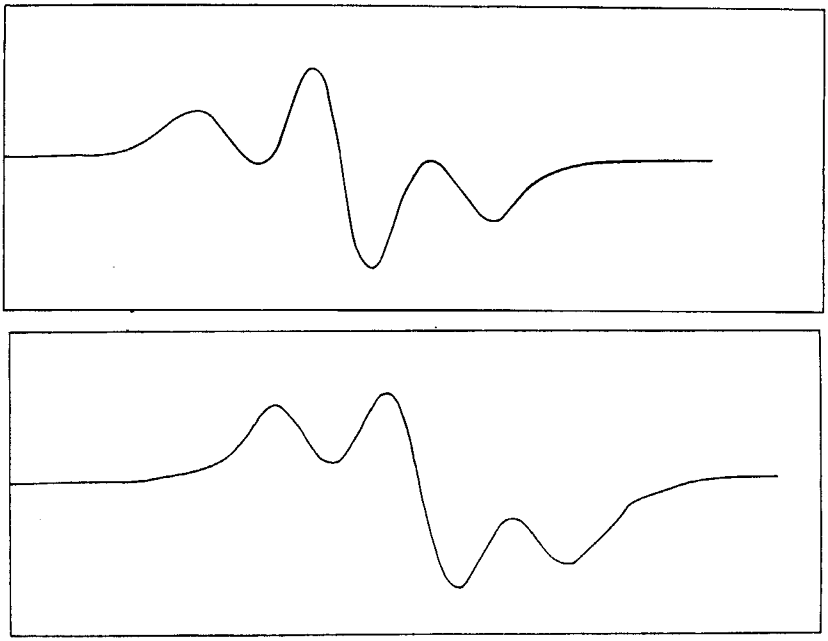


Figure 3. ESR spectra of acrylamide irradiated at − 196 °C and stored for 16 hr at (a) − 80 °C, (b) − 20 °C.[9]

This results from the addition of a single monomer unit; at these temperatures the reaction apparently goes no further. The explanation is relatively simple.

As temperature increases, so will the amplitude of the molecular vibrations. We mentioned, as you will recall, that the amplitude is greatest about the terminal carbon–carbon double bond. The shortest distance between double bonds in the intact lattice is about 4 Å along the screw axis. At some temperatures the amplitude becomes large enough so that the radical can approach its nearest neighbor in the screw-axis direction and react with it. Consideration of the crystal structure shows us that this takes place in the space between the layers where lattice forces are weakest.

If we consider the crystal structure and assume normal bond lengths and bond angles for the dimer, it is easy to show that when two molecules join through their double bonds in this fashion, there must be a net contraction in the screw axis direction of almost a third of a unit cell. This is because we have changed the van der Waals

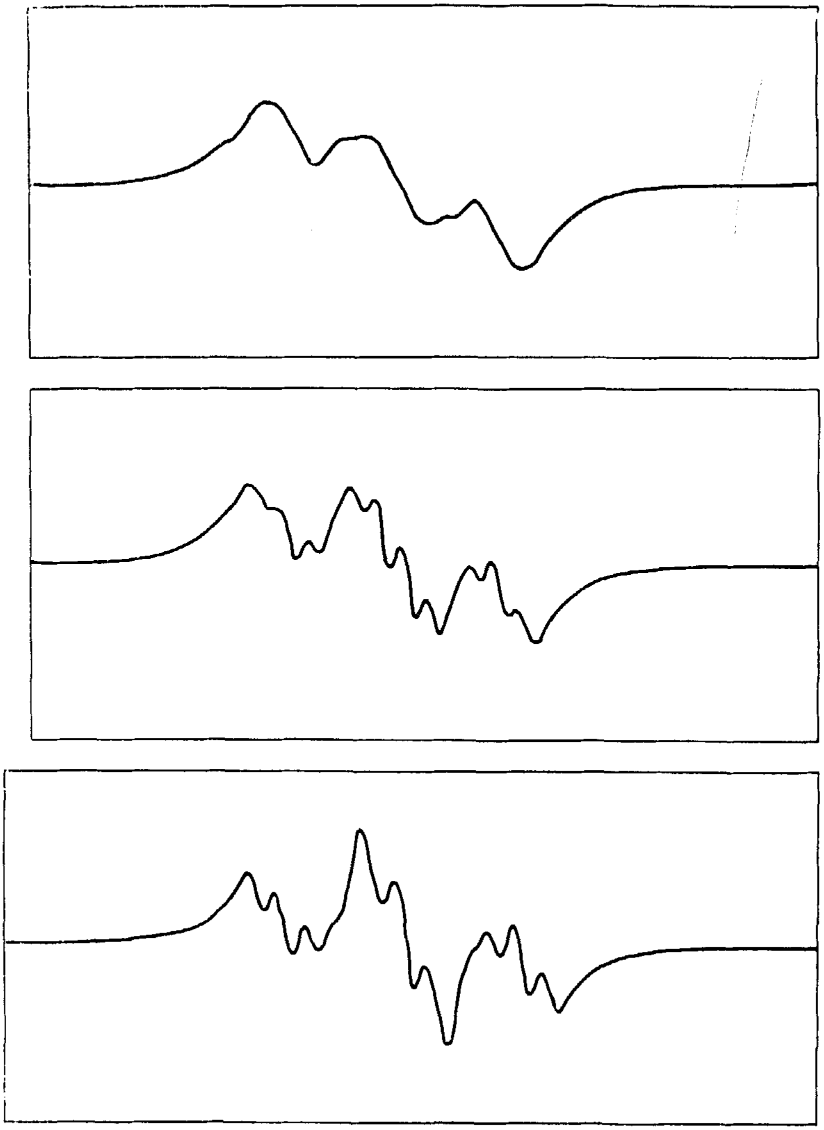


Figure 4. ESR spectrum of a single crystal of acrylamide showing the dimer spectrum. Three orientations 15° apart are shown: temperature, – 100°.[9]

distance between the two molecules to the length of a single bond, 1.54 Å. The increase in bond length from double to single bonds is not nearly enough to compensate. There may also be a small amount of spreading in the *a–c* plane. This puts the dimer radical out of step with the lattice. The next molecule in the screw-axis direction must now be far out of reach of the radical. Molecules in other directions now are closer, especially if there is some relaxation of the lattice. However, below about − 20 °C, thermal motion does not have a high enough amplitude to allow the dimer radical to twist about and react with these nearer molecules. The reaction is therefore stopped at the dimer stage. We now have a solid solution of dimer radicals in the acrylamide.

Above − 20 °C, there is a further change in the ESR spectrum. There is no longer any sign of orientation within the lattice. Polymerization has begun. Apparently at this temperature the molecular motion has become large so that the radical can now react with other molecules outside the screw-axis direction. The radical has therefore lost its orientation with respect to the lattice. We can now consider the polymer as having nucleated as a second, amorphousphase with further reaction taking place at the monomer-polymer interface.

It can thus be said that only the first reaction step takes place in a fixed direction governed by the lattice. Apparently even this is not always true. ESR experiments with solid solutions of acrylamide in propionamide seem to indicate that at polymerization temperatures, even the first reaction step need not be with its neighbor in the screw-axis direction,[9] if this position is blocked. This is also borne out by the large polymer yields and comparatively high molecular weights obtained from dilute solid solutions of acrylamide in propionamide.[10] However, it can still be said that this is still the most probable direction for the first reaction step.

We can now understand why the reaction becomes disordered with respect to the lattice and the polymer becomes amorphous. To recapitulate, the first reaction step occurs between the double bonds along the screw-axis direction both because this is where lattice forces are weakest and therefore distortion of the lattice would require the least energy, and because this is where the closest approach of the double bonds occurs. This pulls the product molecule out of line with the lattice so that it would now require too much energy and motion to join the next molecule in the screw-axis direction. It is probably far easier now to join with a molecule in some other direction. The polymer can now be treated as a second, amorphous phase, and as the polymer nucleus grows, further reaction can be thought of as taking place at the interface between amorphous polymer and crystalline monomer. In principle the reaction now takes place outside the lattice.

Two-Phase Stage of the Reaction

If the mechanism is indeed a two-phase one, it should be easy to prove by X-ray diffraction, which should show the presence of both phases.[11] Figure 5 is a rotation diagram of a partially polymerized crystal. We can see the diffuse diffraction ring due to amorphous polymer superimposed on the diffraction diagram of relatively intact monomer lattice. Some of the reflections have become a little broadened but this is due to increased strain and mosaic spread and not to any disorder.

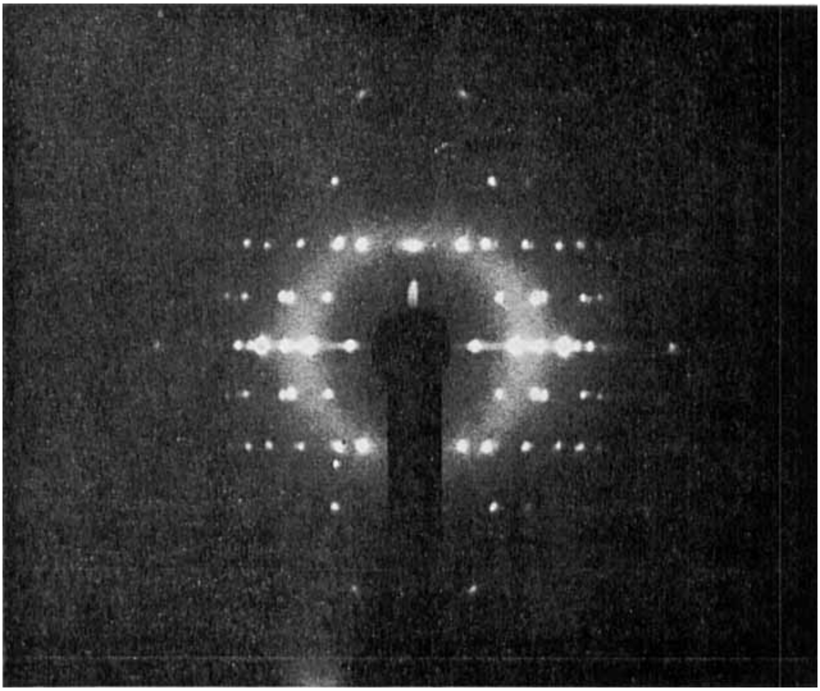


Figure 5. Rotation diagram of acrylamide crystal irradiated in a Co^{60} source, copper radiation, nickel filter.[11]

Let us look at the process again from the point of view of a real rather than an ideal crystal. A real crystal has many defects such as vacancies, edge and screw dislocations, impurity molecules, etc., each producing some amount of lattice distortion. For simplicity we will consider only the case of the edge dislocation.

An edge dislocation is a line defect that can be considered as an extra half of a lattice plane intruding into a crystal. Usually a crystal is full of them. There is a bit more free volume at the defect than there is in the intact lattice leading to somewhat freer thermal motion and diffusion. Because of this it would seem that the reaction could nucleate a bit more easily and at lower temperatures at these sites than elsewhere in the crystal. This helps explain the wide range of temperatures over which initiation (the dimerization step) occurs. Furthermore there is an interesting pattern of stress and strain about these sites (Fig. 6) consisting of both tensile and compressive components. Reaction at these sites would be favored if the strain energy is either decreased or the buildup of additional strain was minimized. Correspondingly, these sites should be favored if there is a volume change especially a decrease. The entropy change is increased at these sites especially if the polymer is amorphous. Finally, if the intruding plane lies in a certain crystallographic direction, our previous considerations as to distance of closest approach and direction of smallest lattice energy should still hold. In the case of acrylamide this would seem to be the 100 slip plane and indeed we have taken photomicrographs with polymer nuclei lying in such a plane[4] (Fig. 7).

Edge dislocations, we have said, are line defects. If these are nucleation sites for the reaction, then the result should be groups of roughly spherical, amorphous bits of polymer lying along lines. This seems to have been photographed under the electron microscope by Sella.[12] At a later stage of the reaction this can be photographed under the microscope. We have made a dark field movie of this phenomenon. Figure 8 shows two frames from this movie. It shows the polymer nuclei as light spots. These seem to lie along linear arrays and loops as is characteristic of dislocations. This can also be seen plainly in Fig. 9 which is a phase micrograph of a potassium acrylate crystal.

If the reaction does indeed nucleate at defects, it implies that the

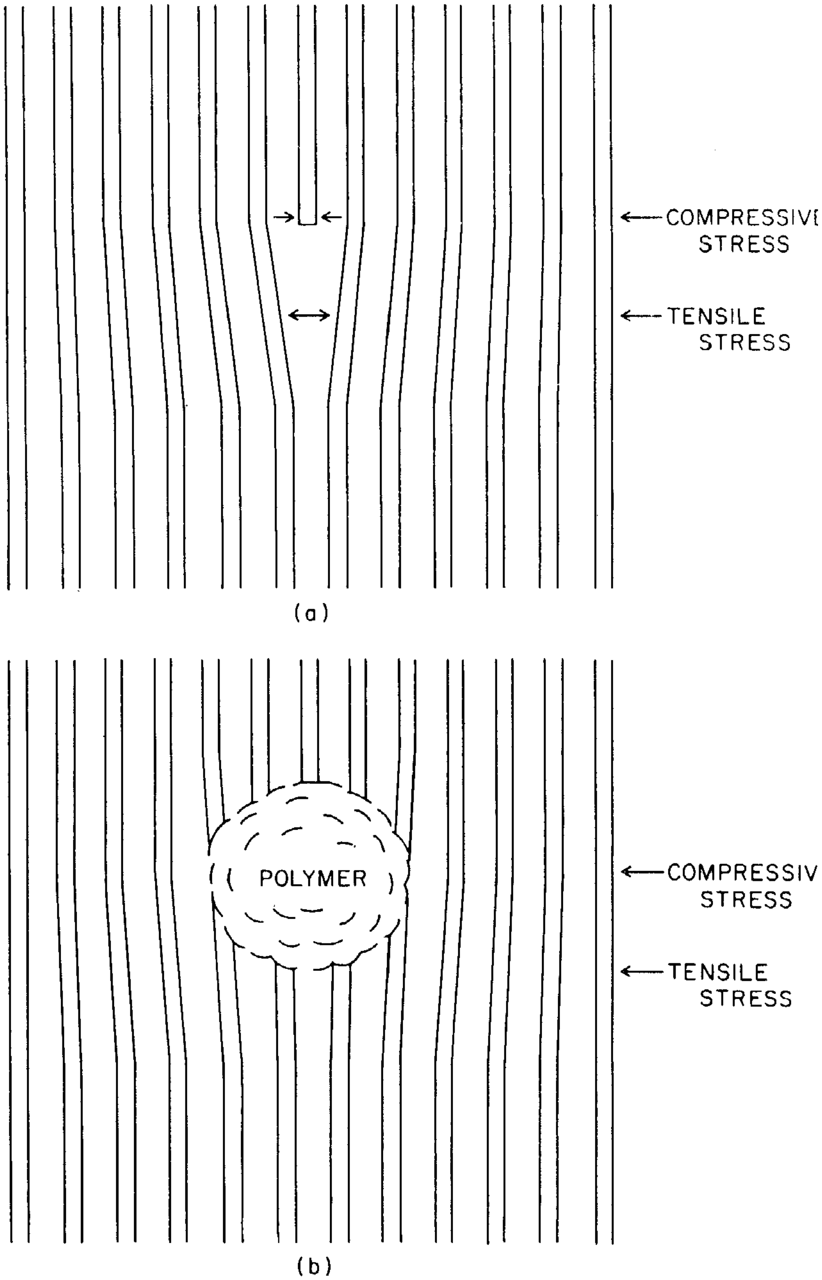


Figure 6. An edge dislocation as a nucleation site for polymer formation.

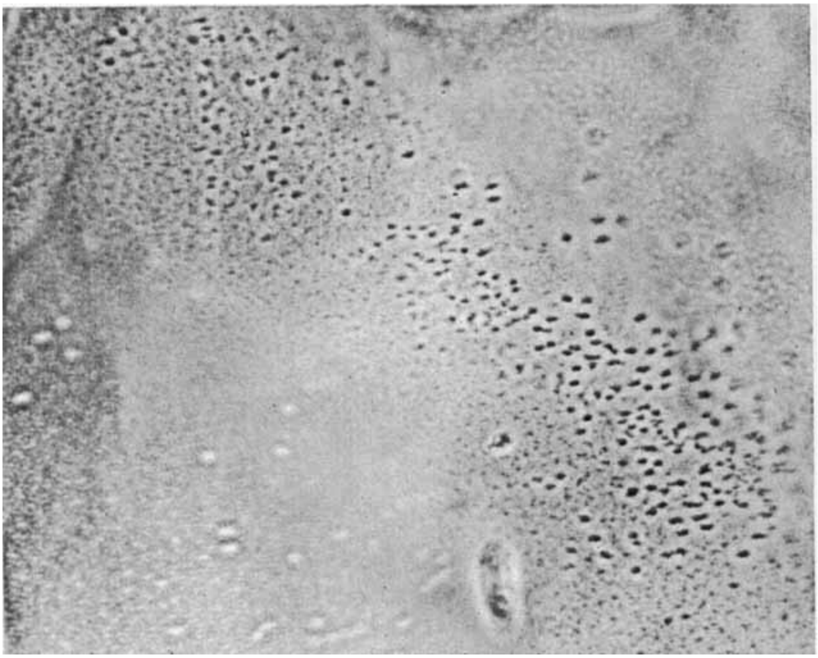


Figure 7. Acrylamide crystal given a radiation dose of 1.0 Mrad in a Co^{60} source at 500 000 rads/hr. Photographed 4 hr after irradiation. Phase contrast. Magnification, 960 ×. The polymer nuclei lie in the 100 plane which is tilted with respect to the axis of the microscope.[4]

rate of reaction would be nonuniform; that is, highest where the defect population is highest provided other processes such as annealing, recrystallization, or sublimation do not intervene too rapidly. We have taken movies under polarized light of these reactions which indicate that the reaction rate can differ by an order of magnitude from one area to another within the crystal. This is also indicated in Fig. 10 where regions of appreciable monomer content are shown in the presence of completely polymerized material. It is only when we isolate polymer from a large number of crystals and thus obtain good statistical averaging that we get reasonably reproducible kinetics.

We must now consider another factor whose importance is frequently overlooked. The change in volume and configuration on reaction must eventually cause the buildup of strain even with

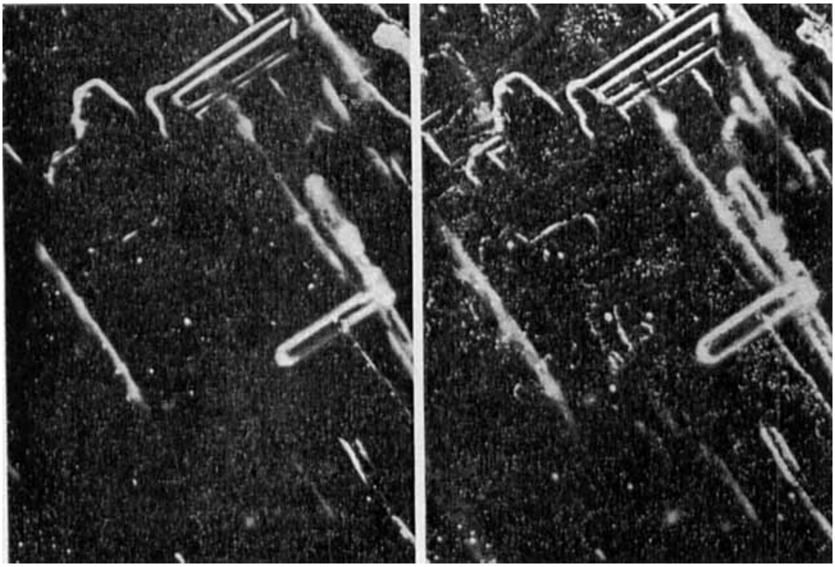


Figure 8. Acrylamide crystal given a radiation dose of 0.75 Mrad in a Co^{60} source at 650 000 rads/hr; photographed in a dark field microscope. (a) 1 hr after irradiation; (b) 46 hr after irradiation. Magnification, 480 ×. The heavy solid lines are due to steps and pits on the surface of the crystal.

initiation at defects. This strain represents a buildup of stored energy which must eventually be relieved if the reaction is not to be inhibited. This is taken care of by annealing and recrystallization within the lattice. This explains the peculiar stopping and starting of the reaction at a given crystal site that we have noted in some of our movies. The reaction rapidly builds up stress which inhibits the polymerization. Further reaction must await the relief of this stress both by annealing and by further reaction at adjacent sites.

The role of annealing has been shown in a more direct manner.[13] Solid solutions were made, in this case of methacrylamide and isobutyramide which have a limited solubility in each other. These were partially polymerized and the lattice parameters determined by X-ray diffraction. In essence, the polymerization removes the methacrylamide from the lattice. If there were no annealing, the lattice parameters of the unreacted monomer would remain essentially the same although there probably would be some line broadening. If annealing and recrystallization occurred, the lattice para-

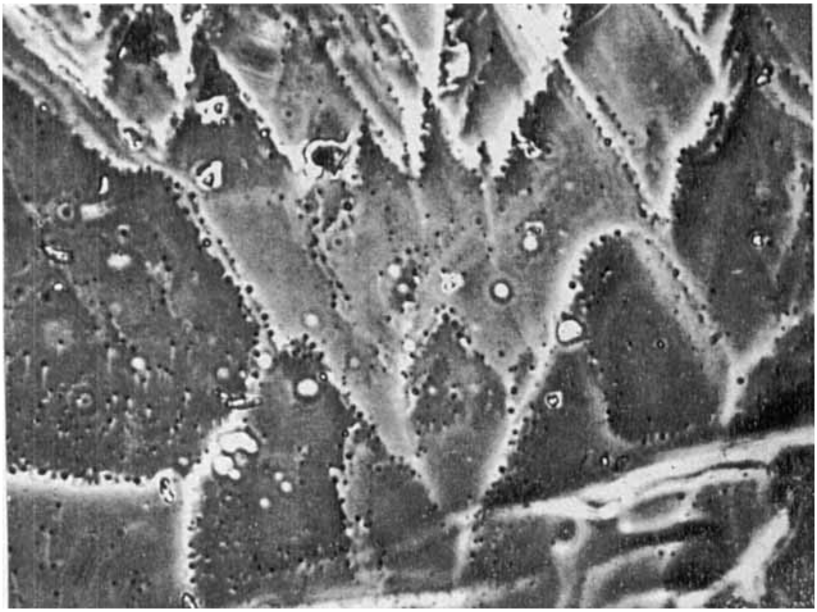


Figure 9. Potassium methacrylate given a radiation dose of 1 Mrad. Photographed under phase contrast 1 week after irradiation. Magnification, 600 ×.

meters would change so as to reflect the new composition of the unreacted phase. The latter seems to be the case.

It has been suggested that the reaction produces a disordered region of glassy or liquid-like structure around the reaction site. This is probably not true, at least in this case. Diffraction shows that there is intact monomer lattice left during the reaction. This liquid-like structure would have to exist some 50 to 100° below the melting point in the presence of a huge amount of crystal lattice. This seems to be a situation that is both thermodynamically and kinetically unstable. In addition, it could not account for the changes in lattice parameters described above. It is true that there may be a few molecules at the monomer polymer interface undergoing diffusional motion, probably by a jump mechanism. Indeed the kinetics demands this. It serves no useful purpose to label these few molecules as another phase or even to say sublimation is involved. It seems to us that these are concepts that are valid only when there is a statistically large enough number of molecules or where transfer over relatively

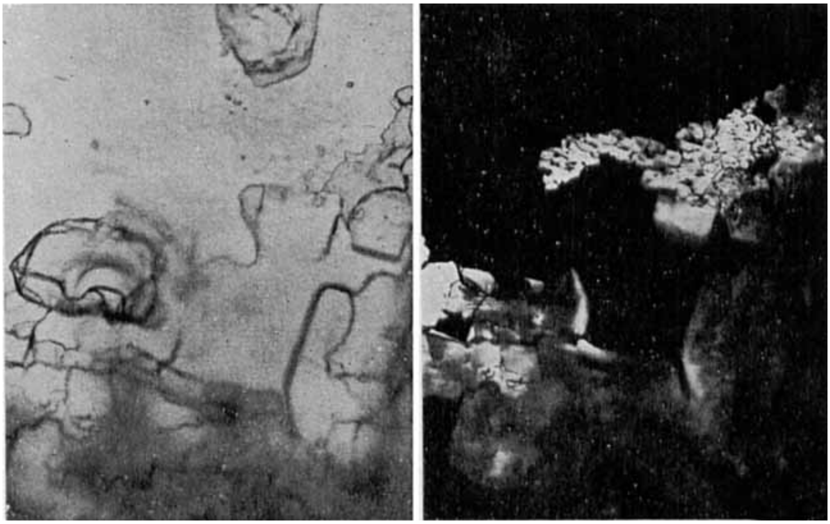
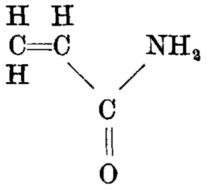


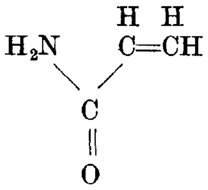
Figure 10. Acrylamide crystal given a radiation dose of 0.25 Mrad and photographed three months after irradiation: (a) bright field; (b) polarized light; magnification, 300 ×.[4]

large distances are involved. Neither appears true here. It is perhaps better to picture the process as it occurs and not to resort to labels that may be misleading. This is not to say that something like this could not be true in some cases. Indeed, a certain amount of disordered phase may exist where a material such as water is one of the products formed as is the case in some polycondensations or in the polymerization of some crystalline hydrates. However, in most cases as in acrylamide this is not likely to be true.

We are now in a position to explain another phenomenon that sometimes occurs. The tacticity (that is, the steric order along the chain) at times seems less in solid-state polymerization than in the liquid state. Reaction at the monomer-polymer interface is essentially a two-dimensional affair. In those areas where the polymer nucleus is in intimate close contact with the monomer lattice—after annealing this should correspond to crystallographic faces of relatively low Miller indices—a flat molecule-like acrylamide cannot turn over. Here there should now be two populations of acrylamide molecules, right and left hand as shown.



(a)



(b)

These two are geometrically inequivalent as long as the molecule cannot turn over. In a centrosymmetric crystal there should be an equal number of both of these present. The reactivity of both of these should be about the same; therefore, the addition would be random and the resultant polymer will be atactic or randomly structured if the same even number of diffusable molecules are available at each reaction step. If the number of molecules available for reaction at the reaction site is relatively small, reaction of one molecule of, say, the right-hand variety would leave a statistically larger number of left-hand ones if the reaction rate is not too slow compared with the rate of resupply of reactive molecules at the reaction site. This would tend to leave a statistically larger number of syndiotactic sequences of triads along the polymer chain but these would tend to be interrupted by atactic sequences. Finally, if annealing and recrystallization are relatively rapid, or if there is an appreciable amount of disordered phase due to by-product molecules such as water, regions will develop where the polymer can grow not in intimate contact with the crystal lattice. This would most likely correspond to those directions where the lattice planes would have high Miller indices. Here the molecules could flip over more readily and polymer would be freer to adopt a more isotactic configuration if this is its habit in normal polymerization. However, it would still have less isotactic polymer than is found in liquid state polymerizations. There are very little hard data available, since the necessary experiments are difficult to perform. However, instances of tacticity and its lack such as is required by these considerations seem to exist.[15,16] We are by no means stating categorically that the above is the explanation. We are merely putting it forth as a possible explanation consistent with the previously stated ideas. In liquids or where the polymer is less intimately in contact with the monomer lattice, the molecule has more freedom to flip over, and forces such as dipolar interactions should come into play and influence the order of addition. This is, of course, an oversimplification.

Kinetics of Solid-State Postpolymerization of Acrylamide

There have been a number of kinetic schemes proposed for various solid-state polymerizations in general (ref. 17 cites several examples) and acrylamide in particular.[18,3] All of these have serious shortcomings. We would like to discuss one because of the simplicity of its assumptions, which are mostly realistic.

The nucleation of polymer molecules implies that these molecules initially grow, more or less in isolation from each other. This in turn suggests that there is no true termination step in the sense employed in the usual liquid-state polymerization kinetics. This is borne out by the fact that the ESR spectrum remains almost constant in magnitude over long periods of time and by the fact that the reaction can continue for long periods of time after removal from the radiation source, the so-called postirradiation reaction.

The kinetic picture of the postirradiation reaction is greatly simplified because the over-all radical concentration is essentially constant during the course of the reaction. As we have implied above, this constancy is not due to a steady-state balance between initiation and termination, but results from the absence of any radical termination step during the postirradiation reaction. This is because the growing chain tends to run into other growing nuclei or run out of available monomer molecules with which to react. The chain ends then remain isolated.

The postirradiation rate expression can then be written as[18]

$$-\frac{dM}{dt} = K_p(M)(R_0),$$

or, in integrated form,

$$\log(M_0/M) = k_p(R_0)t/2.303,$$

where k_p is the propagation rate constant, M the monomer concentration, and R_0 the concentration of propagating chains. Therefore, a plot of log (M_0/M) versus time should give a straight line. Such a plot is given in Fig. 11 for total radiation doses of 0.25 to 2.0 Mrad. It is apparent that a straight line fits reasonably well at least at low conversions.

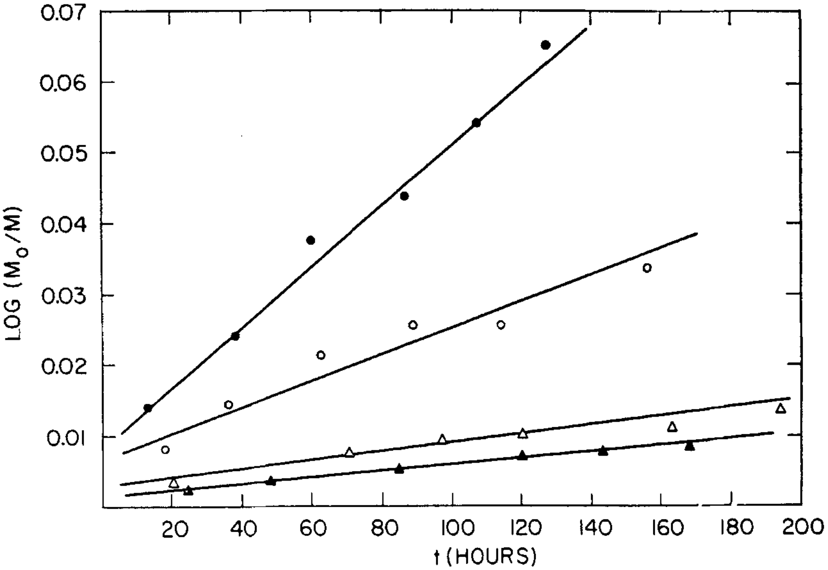


Figure 11. Postirradiation polymerization of acrylamide at 0° with different total doses: (●) 2.0 Mrad; (○) 1.0 Mrad; (△) 0.50 Mrad; (▲) 0.25 Mrad.[18]

The problem with this treatment is the meaning of the monomer concentration term in a nucleation reaction. This is a difficulty that arises in the other kinetic treatments as well.

The molecular weight distribution curves have been determined for acrylamide polymerization and are of some interest.[19] These distribution curves should give some insight into mechanism if they can be interpreted successfully.

The molecular weight distribution curves were determined for acrylamides under a series of varying conditions.[20,21] Fractionation of the polymer produced during irradiation shows a broad molecular weight distribution which is explainable by new radicals constantly being generated during the irradiation, polymerization taking place, and monomer being consumed at the same time. The fractionation results for polymer produced in the postirradiation reaction are more interesting. In Fig. 12, curve I shows the molecular weight distribution for a sample with about 18% conversion to polymer. The remarkable feature is the appearance of a large fraction with a narrow molecular weight range. When the yields are small such a fraction does not appear (conversion 5.8%, curve II). Therefore this is not explainable by a large fraction of radicals initiating at the same time and reacting at the same rate, as had been suggested early in solid-state polymerization studies.[3]

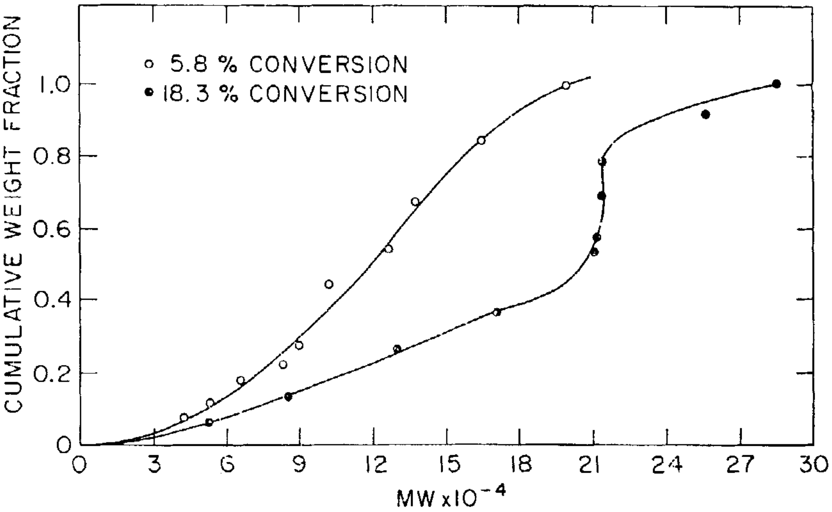


Figure 12. Cumulative weight distribution for postirradiation acrylamide polymer.[21]

We have explained these results in terms of a mechanism that postulates initiation at defects, eventual overlapping of the growing sites, and the buildup of strain which eventually anneals out. These hypotheses must be considered very tentative at present, but the point is that the peculiar distribution curves are explainable within the framework of the ideas outlined above.

Conclusion

This is as far as our present understanding of the solid-state polymerization of acrylamide goes. There are still many unsolved problems but the broad outline seems clear. To sum up, motion of some sort must occur within the crystal lattice for reaction to take place. Given a set of chemical possibilities, whether or not a reaction will occur under a given set of conditions depends, among other things, on the relationship between the reactant and the possible product structures and whether the required mode of motion is allowable by the lattice and thermal conditions. Thus we see that in acrylamide the reaction becomes disordered and the polymer amorphous because, given the structure of the reactant crystal, the possible product structures and the modes of motion required and allowed, this is the simplest way for the reaction to proceed. This interrelationship between lattice and product structures is sometimes overlooked.

Reactions frequently initiate at some type of defect because here motion, including diffusion, can be somewhat freer and modes of motion may occur which are not allowed by the intact lattice. In addition, the buildup of energy stored as strain or interfacial energy may often be minimized at these sites. The first reaction steps frequently change the local lattice conditions. As a result subsequent reaction steps may be facilitated at adjacent sites leading to nucleation of product phases. Eventually enough strain and distortion is built up in the lattice so that annealing must take place if the reaction is to proceed further. Annealing in itself implies molecular motion. Thus we see that lattice structure does have an important effect on reaction pathway but it is often subtle and indirect. These ideas seem to us to be applicable to many other solid-state polymerizations and, indeed, to other types of solid-state reactions, but the details of the process must vary in different cases. These ideas will be explored more fully and generalized in subsequent publications.

Finally, we want to end with a note of apology. We have chosen acrylamide as our example for discussion and leaned heavily on our own data simply because acrylamide has been the most thoroughly explored example, the most familiar to us personally, and we have been responsible for a major share of the total work on this compound. We believe it illustrates a number of important points. However, there have been a large number of other workers who have done equally important work. Each one of the compounds studied shows many interesting details not shown by the others. The literature is really too vast to summarize here so we have chosen one example. Meanwhile we would like to point to some recent review articles for further information.[17,22–26]

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