

Some Remarks on Solid State Polymerization

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One of Professor Baysal's long time interests has been solid state polymerization, particularly the ones that yield amorphous polymer. Though it has not produced viable commercial product, the work has been valuable nevertheless. It helped stimulate interest in organic crystalline solids and has led to a better understanding of chemical processes in solids. Because the starting material is anisotropic and the product is isotropic, it permitted the use of simple techniques to follow the reaction. For example, by using polarizing microscopy, the course of the reaction could be followed visually¹. Once the refractive indices of the crystal were known, it became possible to determine conversion at individual sites on a single crystal by observing the polarization color. These studies helped to arouse interest in the physics and chemistry of organic solids resulting in promising research on materials with unusual electronic and optical properties. Several reviews of the topic have been published, at least two with Prof. Baysal as an author^{2,3}. I will describe here some of the research in which he played a significant part.

Molecules in a crystal are normally as tightly packed, precisely positioned and oriented with respect to each other's molecular forces, geometry and thermal vibrations will allow. This results in highly regular long range ordered structures which fill space as efficiently as is feasible. One could reasonably expect that the mechanism and kinetics of any chemical processes occurring inside a crystal would then be directly influenced by these conditions. If disturbance of the lattice is to be minimized, this would seem to suggest that the nature and orientation of the reaction product would reflect the structure of the parent crystal in some direct fashion. Furthermore, reaction implies the making and breaking of chemical bonds. This implies movement of the groups of atoms or molecules involved. The molecular arrangement at the reaction site should be such that the requisite motion is feasible with minimal disturbance of the local environment, otherwise excessive temporary displacement of neighboring molecules in a tightly packed structure would be necessary, a process requiring considerable energy. There are many examples of reactions which appear to fit such a pattern. Elegant examples are the photodimerizations in the solid state of cinnamic acid⁴ and of anthracene and several of its derivatives⁵.

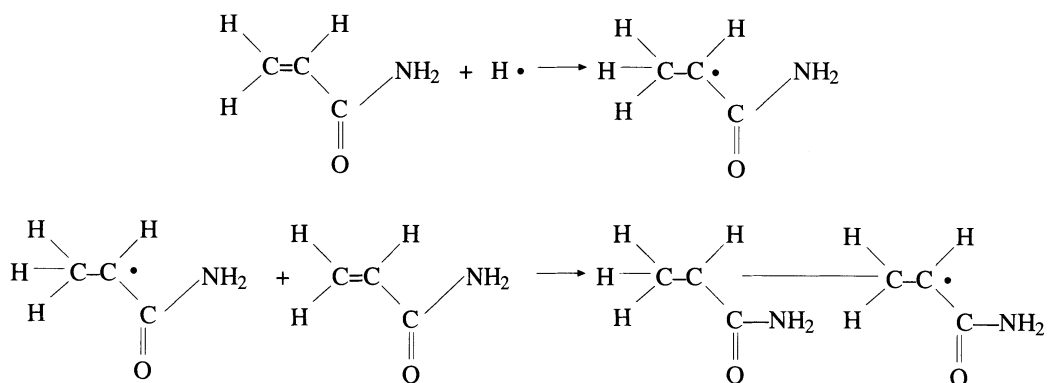
Many of the reactions studied involved photo or radiation initiation since, under proper conditions, the reaction could be initiated within the crystal without involving thermal or chemical initiation which might perturb the lattice. The intermediate reaction steps were often rather difficult to observe. An important part of such studies therefore consisted of the determination the structure of the parent crystal and of the product, then inferring the mechanism from that.

When it was discovered that polymerization could be initiated with radiation in many crystalline monomers, the hope arose that such techniques could lead to the synthesis of well ordered polymeric structures^{6,7,8,9}. It came as a surprise when it was shown that acrylamide yielded completely amorphous

polymer^{6,7,8,9}. It was soon found that the other crystalline vinyl type monomers tried did the same. It became evident that this occurred in many solid state polymerizations. A further surprise came when it was shown that acrylamide, as well as many other monomers, would keep on reacting long after the material was removed from the radiation source⁸. These appeared to be entirely solid state reactions. No evidence of local melting was found under microscopic examination in any of the relevant compounds if the experiment was conducted under proper conditions. Further evidence came from some crystalline acrylate salts^{2,10}. These are crystals with ionic bonds. They either have high melting points or else decompose before melting. They yielded amorphous polymer but showed no evidence of melting or decomposition.

Acrylamide and the other solid state polymerizations we tried proved to be a rather slow process. Some of the intermediate steps could be easily monitored. The acrylamide single crystal retained its apparent shape except for some shrinkage but lost all signs of crystalline order. This raised some interesting questions. The reaction occurred within well ordered monoclinic crystal containing strictly oriented, tightly packed, relatively unsymmetrical molecules. The amorphous nature of the product implied that extensive motion, both rotation and translation, had to take place within the crystal. How was this possible within such a well organized structure? Why did the material become amorphous? During the polymerization many individual molecules, separated by Van der Waals distances, had to join to form one large molecule with the units held together by shorter covalent bonds. This resulted in a shrinkage of the overall system causing buildup of strain as the reaction proceeded. This should eventually either inhibit further reaction or cause the crystal to break up. Yet neither happened. How could this occur without showing evidence of excessive strain? Finally, how could a reaction, presumably initiated by highly reactive free radicals or ions, continue for long periods after removal from the radiation source? It was at this point Prof. Baysal came to Brookhaven National Laboratory and began a long collaboration that helped to answer some of these questions. We concentrated on acrylamide since it was easy to grow large crystals, react at convenient temperatures and its behavior appeared to be typical.

Acrylamide readily polymerizes when exposed to radiation at temperatures above about -20°C. If irradiated at low enough temperatures polymerization is inhibited though abundant free radicals are present. Polymerization resumes upon warming, apparently without any phase change occurring. The reactions involved are the following:



When exposed to gamma radiation, acrylamide yields hydrogen as a primary product¹¹. Hydrogen atoms are therefore available during irradiation. ESR powder spectra taken at low temperatures showed five peaks whose relative sizes indicate that the observed radical was generated by scavenging hydrogen atoms and adding them to the double bond¹². Propionamide, the saturated analog of acrylamide, was shown to have a crystal structure similar to acrylamide but with a slightly larger unit cell¹³. When irradiated, propionamide also yielded a five peak ESR spectrum¹⁴ very similar to acrylamide. This was formed by

loss of a hydrogen atom from the molecule. This suggested that both substances yielded identical radicals. It was shown by Fadner and Morawetz¹⁵ that two substances could form solid solutions over a range of concentrations. In solid solutions of the two, acrylamide could be extensively polymerized even if present as a minor constituent. Apparently the propionamide radical can also initiate polymerization¹⁶.

In general free radicals react avidly with oxygen. In propionamide and other linear amide crystals, the radicals quickly reacted and disappeared upon such exposure¹⁷. In methacrylamide, the oxygen inhibited the post irradiation polymerization¹⁸. In acrylamide the radicals persisted^{6,19} and polymerization continued. However, in solid solutions where propionamide was the major component, acrylamide radicals rapidly disappeared and polymerization ceased¹⁹. Apparently oxygen was unable to diffuse into acrylamide but could into propionamide. This reinforced the idea that the radical seen by ESR in acrylamide was the initiator. Since propionamide lacked the polarizable double bond conjugated with the amide group, the intermolecular forces around the terminal carbons were probably weaker than in acrylamide. In addition, the unit cell volume in propionamide is somewhat larger. These effects allowed oxygen diffusion more easily into that crystal.

Single crystal ESR spectra indicated that the acrylamide radicals were highly oriented in a manner that fit precisely with the parent lattice¹². At temperatures of about -40°C the five peak powder spectrum changed to one consisting of three broad peaks. Single crystal data showed that this was due to a radical which was still oriented but not in quite as precise a fashion as the original. For several reasons this was attributed to a dimer radical formed by adding an acrylamide molecule to the original radical. Upon warming to temperatures at which the polymerization takes place, approximately above -30°C , the spectrum showed the same three peaks but with a complete loss of orientation. There was little decay of the spectrum with time although the reaction continued to progress. Exposing part of a large acrylamide crystal to a collimated radiation beam showed that the polymerized region did not extend beyond the area directly exposed (Figure 1). These observations suggested a free radical reaction in which the radicals were neither trapped nor underwent extensive termination reactions. Evidently the radicals had enough mobility to bring about reaction within the crystal but the mobility was still low.



Figure 1. Acrylamide crystal irradiated by a collimated X-ray beam showing the edge of the irradiated region. Magnification 50X

Single crystal x-ray diffraction diagrams taken during the course of the reaction showed sharp Bragg reflections plus a diffuse ring due to polymer¹. As the reaction proceeded, this ring, though absent at initiation, grew more intense as the crystalline reflections grew weaker and finally disappeared. Laue diagrams taken at the early stages with nickel filtered Cu radiation showed increasing diffuse scattering suggesting increasing disorder (Figure 2). These observations showed that amorphous polymer nucleated as a separate phase at an early stage. The polymerization could thus be considered as a two phase reaction, probably with the bulk of the process after initiation taking place at the interface between monomer and polymer.

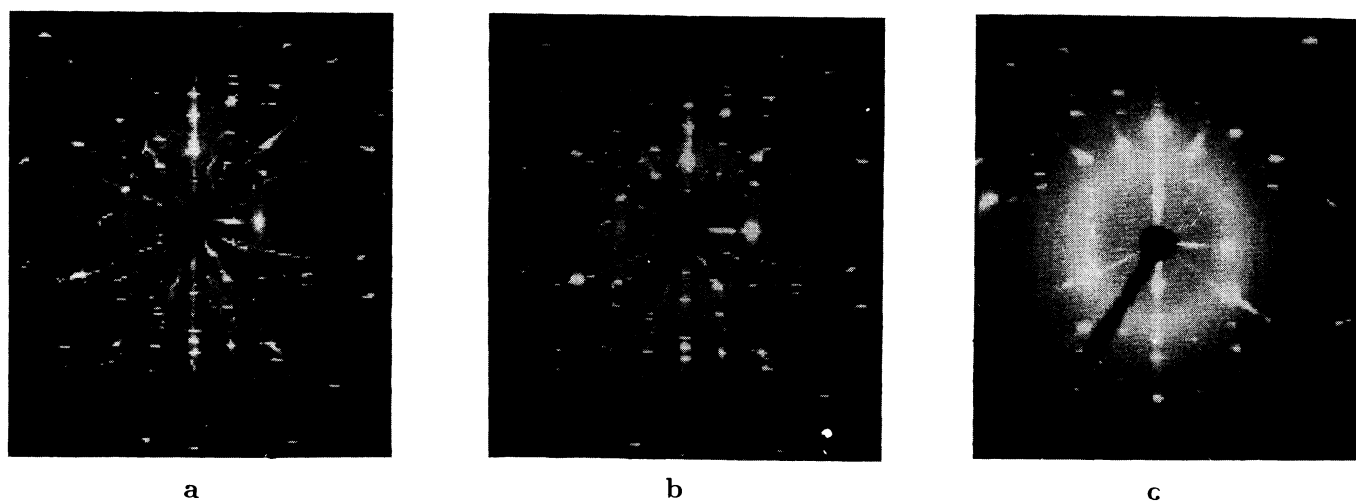


Figure 2. Laue diagram of acrylamide irradiated at 24°C, K_{α} radiation used with nickel filter used to emphasize diffuse scattering.

a) After 6 hours in X-ray beam.

b) After 2.5×10^5 Rad exposure to Co^{60} showing of Bragg reflections and diffuse ring due to polymerization.

c) After 5×10^5 Rad exposure.

Polarized light photomicrographs and time lapses microcinematography showed that the reaction did not take place at a uniform rate throughout the crystal¹. Instead, it was more rapid in some sites than others. Reactions at a given site would proceed for some time, then would slow down or stop while an adjacent site would start reacting. This suggested to us some role for the buildup of strain. Dark field and phase micrographs taken at low polymer conversion showed the distribution of reaction sites more clearly^{3,8} (see figure 3). These suggested that the reaction tended to initiate at crystal defects such as edge dislocations and similar sites. This was also consistent with electron micrographs taken by Sella²⁰.

Prof. Baysal developed kinetic equations describing the overall polymerization rates based on extensive kinetic data, both for polymerization while exposed to radiation and for polymerization after exposure. Based on the lack of decay of the ESR spectra, he made the innovative assumption that radical termination did not readily occur. This was further justified when acrylamide crystals, immersed in styrene long after irradiation, initiated polymerization²¹ presumably yielding a diblock copolymer. The equations fit the data rather well²². Morawetz and his group took rate data on the post-irradiation reaction for material irradiated at liquid nitrogen temperatures then warmed up. Their equation also fit their data well¹⁵. However, their equations were based, in part, on a radical termination step. Several other kinetic equations have been proposed. These may be useful for predicting conversion rates in powdered material.

However, as Prof. Baysal noted, in view of the other data indicating non uniform distribution of reaction rates and sites, they should be used with caution when trying to assess reaction mechanisms. Prof. Baysal's equations did demonstrate that a radical termination step need not be invoked in this type of reaction.

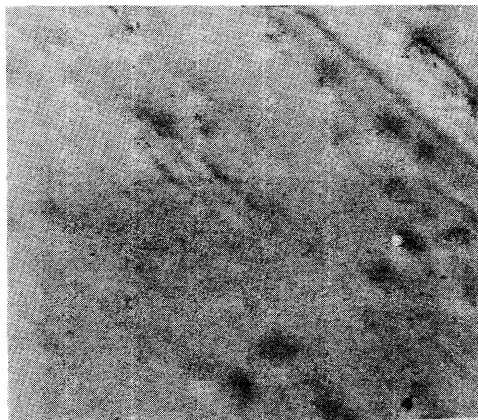


Figure 3. Acrylamide showing nucleation of polymer. Radiation dose 7.5×10^5 Rad, 24° C 24 hours after irradiation. Magnification 200 X

The crystal structures of acrylamide²³ and propionamide^{23,24} were determined by Isakov and by Prof. Usanmaz at Brookhaven. His results for acrylamide is shown plotted in figure 4. The structure of propionamide is almost identical except for the saturation of the carbon-carbon bond and slightly larger unit cell parameters. For discussion purposes the acrylamide molecule can be considered as having two parts; the head or amide end and the tail or hydrocarbon end. The molecules are bound into dimers by hydrogen bonding. Further hydrogen bonding ties the molecules into layers. Two layers placed back to back form a sort of bilayer. The crystal structure consists of stacks of these bilayers resulting in a head to head, tail to tail arrangement. Thus the reactive hydrocarbon ends lie adjacent to each other. This is a structural theme common to fatty amides²³, fatty acids and similar materials^{24,25,26,27}. During the solid state polymerization investigations, it was discovered that in many substances with a similar structural motif, the packing of the hydrocarbon ends when they face each other is such that there is enough free space to provide a passage for diffusion of oxygen and other gases¹⁷.

Based on the observations cited above and other supporting data, a mechanism for the polymerization of acrylamide and similar substances was proposed. It relied on the known existence of surfaces, dislocations and similar crystal defects. An edge dislocation, for example, may be pictured as the intrusion of a lattice plane partially into the crystal. This is shown schematically in figure 6 of reference 3. At the edge of the intrusion there is an increase of local free volume. This would tend to favor reaction by allowing more space for motion necessary to the reaction. Furthermore, there also exists a pattern of stress and strain surrounding this edge. The stress and the accompanying strain would tend to be compressive at the edge and tensile just beyond it. Any reaction giving a transition state or products occupying less volume than the reactant molecules would tend to be favored by the compressive strain by an amount dependent on energy stored in the strain pattern at the site. Thus some of the strain would be relieved, or, if the reaction increases the strain, its further buildup would be minimized. Similar reasoning holds where a volume increase is involved. This suggests that radicals trapped at defects are likely to be favored as reaction initiation sites over those trapped at the close packed sites some distance from defects. As mentioned above, the free radical

in irradiated acrylamide and other double bonded substances, is formed by scavenging radiolytic hydrogen atoms drifting through the lattice. The direction of drift may be biased in favor of line defects since they offer an easier path for diffusion. Since the hydrogen addition results in an increase in molecular volume, this also might require slightly less energy at such sites. Therefore there may be a somewhat higher concentration of free radicals at defects than in the intact lattice. This suggests defects are the sites where reactions are most likely to be initiated. This would explain the distribution of reaction sites seen under the microscope and much other data.

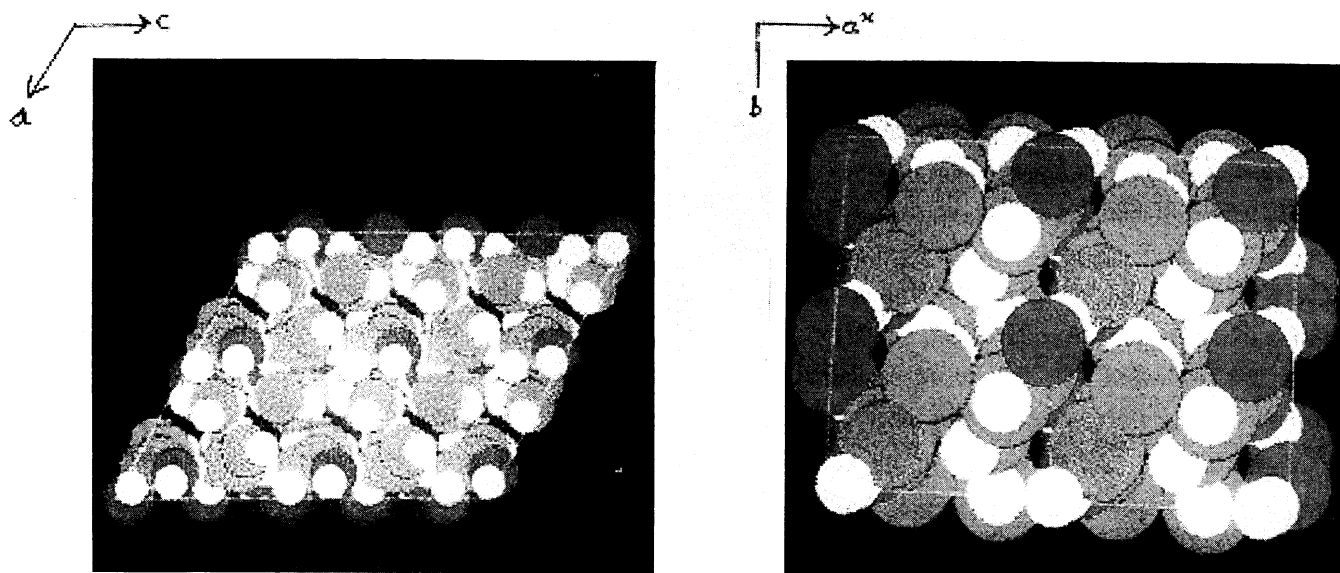


Figure 4. The structure of acrylamide plotted as $4 \times 4 \times 4$ unit cells using the parameter from reference 23b and standard atomic diameters.

Colors: Orange - Carbon
 Green - Oxygen
 Blue - Nitrogen
 White - Hydrogen

The initial reaction in this system consists of the addition of an acrylamide molecule to the radical to form a dimer radical, as shown in equation 1. In the case of acrylamide, this first step takes place principally in the direction of the b axis. This is shown by some of the ESR data mentioned above¹² and the observation that the relevant Bragg reflections broaden and weaken more rapidly in this direction than in the others. This changes the local geometry at the site. In particular, it changes the geometric constraints upon reaction that the nearest neighbor molecules experience. In the type of polymerizations discussed here, the dimer occupies less volume than the two molecules from which it was formed. This suggests there should be more free volume with somewhat different geometrical constraints at that site. There should also occur some relaxation of the lattice surrounding the site to accommodate any changes in the strain pattern. These effects could facilitate the next reaction step. Furthermore, the dimer, in some sense, still remains attached to the lattice through hydrogen bonding and other intermolecular forces. This would explain the retention of orientation by the dimer radical.

In forming the dimer radical, two molecules must move from a Van der Waals distance to a single bond length of about 1.54 Angstrom. This is a considerable shrinkage in molecular terms and must put the radical function out of step with the rest of the lattice. As implied in figure (12), reference²⁷ this should facilitate the addition of the next molecule from some other direction than the b axis. The material can now be considered as having nucleated as a second, amorphous, phase.

This can be viewed from another perspective. The reaction results in a net shrinkage of volume, approximately 12 for acrylamide. This suggests a buildup of strain during the reaction. Calculation shows that if the molecule were to follow the lattice geometry and become crystalline, the volume shrinkage would have to be considerably larger. Thus, by becoming amorphous, the buildup of strain likely to be reduced though not entirely eliminated. Strain will continue to build up as the reaction continues. As a result, one of three things is likely to happen. The strain could build up until the crystal shatters. For example, a collimated x-ray beam has been known to drill a hole in a cinnamic acid crystal (G. M.J. Schmidt, private communication), most likely due to this effect. Another possibility is that the strain continues to build up until the gain in energy from the reaction is less than that required for the strain increase from the next reaction step. The reaction then stops. This has been noted in some solid state polymerizations, for example, polymerization of N-tert-butylacrylamide. The reaction can often be restarted by heating the crystal so annealing removes some of the strain. It then proceeds until the sufficient strain is again built up. However, if the crystal is at temperatures at which it can anneal rapidly enough, episodic periods of annealing could occur and the reaction temperature, the reaction will proceed until nearly complete conversion. Apparently this is what occurs in the case of acrylamide. It has been observed that, during exposure to x-rays, the diffraction reflections decrease in intensity and then often increase slightly before resuming the decline (G. Adler, unpublished data), suggesting annealing. This annealing effect was also demonstrated in polymerizations in solid solutions of methacrylamide in isobutyramide²³.

One other aspect of strain might be considered. It is known that, in some materials at least, strain can cause a multiplication of defects in a crystal³⁰. It is conceivable that, under appropriate conditions, this could also occur in organic crystals. If so, there would be an increase in the number of dislocations in the vicinity of the initial reaction site. These most likely would occur at a site at which free radicals are trapped in the nearby lattice. Such an effect would at least partially explain the acceleration of reaction rate after initiation.

Molecular weight distributions of acrylamide polymer were determined under various reaction conditions¹¹. One peculiarity was noticed in post-irradiation polymerization. The molecular weight distribution curve was about as would be expected except for a large fraction with a narrow molecular weight distribution seen where conversion was carried far enough. This has been attributed to the overlapping of reacting polymer molecules. Two other mechanisms seem possible. If dislocation multiplication occurs as postulated above, the sharp fraction might reflect the molecular weight at which sufficient strain has built up locally. Perhaps defect multiplication occurs by something like the Frank-Read process^{29,30} at close by sites where polymerization has started. Another possibility is that it occurs when the strain builds up enough so that annealing begins. Annealing requires some sort of motion of the molecules this would likely result in a spurt of more rapid polymerization. In those cases in which a phase change can occur, as in solid solutions for example, such a spurt could also ensue²¹.

We would like to explain one more thing, the lack of a radical termination step. It has been noticed that in propionamide, at room temperature under vacuum, the radicals decay slowly, after an initial stage, by a second order process. This apparently common in aliphatic amides with saturated hydrocarbon chains¹². This does not happen in acrylamide.

For radicals to disappear, two of them must encounter each other and react. In propionamide the radical, produced by loss of a hydrogen atom by radiolysis, can drift about in the crystal by mechanisms such as abstraction of a hydrogen atom from a neighboring molecule. Thus the radical function will eventually encounter another radical and terminate each other by recombination or disproportionation. ESR, under vacuum, thus shows slow decay of the radical spectrum. A similar mechanism has been invoked in other

situations. Acrylamide, on the other hand, forms the radical by gaining a hydrogen at the double bond. In doing so it generates a terminal methyl group which is bulkier than the original configuration. Also, once the polymerization has started, the radical has become too big to be able to diffuse easily. Both effects would tend to inhibit the radical decay.

We believe that the above mechanism is a reasonable way of explaining some of the phenomena seen in acrylamide and a number of other polymerizations. The final question is then, how general is such a mechanism? As far as we knew then, every vinyl type solid state polymerization gave some evidence of such a mechanism, at least to the extent of showing nucleation and yielding amorphous polymer³². But what about non-vinyl polymerizations?

It had been shown that trioxane, a ring compound, could be polymerized in the solid state to yield highly crystalline polymer oriented along the *c* axis of the parent crystal as might be expected from the known crystal structure³³. This could have been taken as an indication of a simple direct "topotactic" mechanism. However, careful consideration suggested a problem³⁴. The polymer had a helical conformation. It might have been expected that one turn of the helix would have the same number of monomer units as one ring molecule. Instead there was an odd fractional relationship between the two. Polymerization carried out at a somewhat lower temperature than the usual showed that the polymer chain could grow at odd, non-crystallographic angles to the parent lattice. This was reminiscent of the phase change of paradichlorobenzene in which the two phases were not crystallographically aligned³⁵. X-ray diffraction of trioxane showed considerable diffuse scattering, a characteristic of 'plastic' crystals. The material was found to have a relatively large vapor pressure and to sublime easily. This and some other relevant data led to the suggestion that the observed orientation correlation of polymer with the *c* axis was due to an epitaxial overgrowth of the growing polymer on the trioxane, a process subsequent to the actual polymerization step in which transfer through the vapor phase was probably involved. The polymer tends to be crystalline no matter how it is synthesized. It is interesting to note that hexamethylcyclo trisiloxane, another ring compound, yields amorphous polymer no matter how it is polymerized^{36,38} again suggesting that the polyoxmethylenes from trioxane was crystalline due to a secondary process. This implies that caution may be needed when suggesting a mechanism based the alignment of reactant and product phases.

Another non-vinyl solid state polymerization extensively studied was the diacetylenes discovered by Wegner³⁷. These gave beautifully crystalline, metallic looking crystals. These apparently showed less volume shrinkage upon polymerization than did acrylamide, thus mitigating some of the conditions that caused acrylamide to become amorphous. In considering these reactions, it should be noted that both the monomer and the polymer have stiff backbones greatly elongated along one axis. For the polymer to become amorphous, the molecule would have to be able to rotate about an axis perpendicular to the long axis. This would require considerable energy even at defect sites. In addition the shrinkage upon dimerization, for example, would be a smaller percentage of the molecular and lattice dimensions than is the case in acrylamide. As a result, if the reaction is to proceed, it must result in highly oriented, polymer. It is interesting to note that the reaction often yielded highly twinned polymer crystals, suggesting some misorientation can occur in directions other than the long axis.

Conclusion

Prof. Baysal helped pioneer the studies on acrylamide and its analogues mentioned above. This yielded a plausible mechanism for a whole class of solid state reactions. Some of the aspects of this are also common to other fields. For example, strain has become an important consideration in inorganic solid state reactions³¹.

Furthermore, these studies helped considerably in arousing interest in organic solid state chemistry which has since become an important area of research.

As well as Prof. Baysal's important contribution, the author wishes to acknowledge the aid of his other collaborators in this project, notably John Petropoulos, Walter Reams and Antonio Faucitano, Ali Usanmaz. The photomicrography was done by R.F. Smith. Thanks are also due to Brookhaven National Laboratory and Middle East Technical University for providing the facilities where much of the work described above was initiated.

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