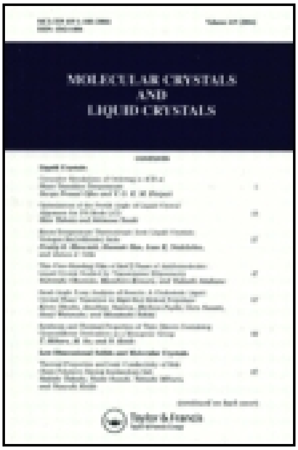

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The Growth of Organic Solid State Chemistry: A Personal Perspective

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THE GROWTH OF ORGANIC SOLID STATE CHEMISTRY: A PERSONAL PERSPECTIVE

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ABSTRACT: Some aspects of the development of organic solid state chemistry are described from the point of view of one of the participants.

I have been asked to make this presentation on organic solid state chemistry from a historical point of view, I presume, because I am one of the oldest here, having survived at this game a long time, and because there is little else that a retired chemist can do at these meetings. It is easiest for me to present this little discourse from a personal perspective, for which I hope you will forgive me. Personal perspective means, of course, that I won't have to read all the literature again, mainly my own stuff. That is punishment enough.

I first stumbled upon this line of work in the early 1950's. Compared to our knowledge today organic solid state chemistry was in a primitive state. Large scale computer facilities were not yet widely available. Doing a structure determination by diffraction even on a rather small organic molecule was still a significant task, often done with a mechanical calculator and Beevers-Lipson strips(1). Published studies on organic solid state reactions were few and far between and dealt mostly with the chemical aspects (2). Kitaigorodski and his group had begun their work on organic crystal chemistry (3). Studies on spectroscopy and energy transfer in solids had begun to be more frequent, fueled largely by the development of better instrumentation and an interest in organic scintillators and photography. Since World War II there had been an increase in interest in the effects of radiation on organic materials. This was further enhanced upon discovery of the Van Allen radiation belts and concern for the organic components of satellites such as electrical insulation. However, published studies on the mechanism of organic solid state reactions and the effect of the crystalline environment on them were few and far between.

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In the early 50's systematic studies of organic solid state reactions received an impetus from two rather disparate lines of research. One was the classic work of Gerhard Schmidt and his group on the anils, the chalcones and, particularly, on the solid state dimerization of cinnamic acid and related substances (4). The results of this study reinforced the belief that the course of reaction and the nature and orientation of the product molecules would be governed by and reflect the position, nature and orientation of the reactant molecules in the initial crystal, a reaction course we now call topochemical. That idea stems from the premise that molecules are closely packed and more or less rigidly held in the lattice and that large deviations from of the geometry of the parent crystal would be inhibited. This led to the conclusion that the reactive centers should be close together, no more than a certain maximum distance apart, and properly oriented if the reaction is to be favored in the solid. Thus the amount of atomic motion and distortion of the lattice required by the reaction would be minimized. These ideas have a certain elegant logic and intuitive appeal. This approach has been and continues to be extremely useful and has led to much important work.

The second line of research dealing with reaction mechanisms, which developed independently, had solid state polymerization as its theme. It was initiated for a rather curious reason. Nuclear power reactors were beginning to be important at that time. Reactors produce radioactive fission products. Something had to be done with these. One proposal was to put all that radioactivity to work in industrial processing, possibly as an initiator for chemical reactions. Unfortunately, when all the necessary costs were accounted for, including the required shielding and protection for personnel, it proved to be an expensive proposition. However, if a chain reaction could be initiated, then a little radiation could go a long way. Thus polymerization suggests itself.

Unfortunately even this approach had problems. Though polymerization could be easily achieved, the polymers produced in the fluid phases generally had no better properties than those resulting from the usual cheaper initiators. However, if polymerization could be initiated in a crystalline monomer, the thought was that the polymer itself would be crystalline due to a topochemical reaction mechanism and would thus have superior physical properties. Initiation in crystalline solids is difficult to achieve by ordinary means. On the other hand, with penetrating radiation it was a simple matter to create free radicals. If these would initiate polymerization within the crystal, the result might be a superior product perhaps worth the cost.

One of the early extensively studied crystalline monomers was acrylamide. Several papers had been published on the kinetics and presumed polymerization mechanism of this and a few other monomers. The mechanism was thought to be well enough understood so that, reasoning backwards from a presumed topotactic mechanism, a crystal structure for acrylamide was proposed but never published.

It was at this point I blundered into the problem. I was offered the job of cleaning up the problem by actually determining the crystal structure of acrylamide. This was considered to be relatively short term project and I was to go on afterwards to other matters. Since at the time I needed a job, I accepted even though it did not seem a very promising career.

Soon after I started two observations were made that radically changed our perspective. In the radiation induced reactions then known, the primary chemical processes were believed to be essentially over in a matter of milliseconds at most. Acrylamide was the first of a long list of solids we found in which the reaction could keep on going for months, perhaps even years, after removal of the material from the radiation field (5). This became known as the post irradiation effect. It created some interest, particularly among radiation and polymer people. It also threw into question much of previously determined kinetic data on solid state polymerization. For me it meant that I could observe the reaction closely without becoming part of the radiation experiment myself. It allowed the use of standard techniques without the need for specially designed equipment.

The second observation was perhaps more interesting. When the polymerization of acrylamide was complete, what was left was a bit of polymer roughly the same size and shape as the original crystal. Strangely, it was completely amorphous. Every monomer of the dozen or so we tried, including ionic compounds, yielded amorphous polymer. The only polymerizing ring compound I knew of at the time, hexamethyl-cyclotrioxane (6), also yielded a non-crystalline polymer. It seemed to be a general phenomenion (5). I learned later that in the case of acrylamide this had been previously reported by R. B. Mesrobian, P. Ander, et al., (7). Unfortunately little attention was paid to this.

There were now two extreme types of reaction, one the epitome of a topochemical process and the other seemed to be as far from topochemical as it was possible to get. An interesting problem now arose. How does it go from a rigid, well ordered crystal to a completely disoriented structure without disrupting the crystal during the process? To make the puzzle more acute, I first met Gerhard Schmidt at this time and we became aware of each other's work, work which seemed to produce such strangely disparate results.

To shorten the story, the explanation eventually arrived at was that of the reaction product tended to nucleate as a separate phase, preferentially at defect sites such as dislocations (8). This was demonstrated by several techniques. The initiating radicals were found to be oriented in the crystal in a manner consistent with the crystal structure. The reaction, which involved going from the Van der Waals distance between molecules to the much shorter single bond length, would cause considerable net shrinkage, especially in the reaction direction. As each monomer unit was added to the growing polymer molecule the reactive chain end became more and more out of step with the surrounding lattice until the nearest neighbor to the active chain end was no longer in the originally preferred direction. Also, the amorphous polymer is less dense than the crystalline and therefore minimizes the build up of strain which could inhibit the process. The result was disorder and nucleation as a second phase. According to these ideas, the surroundings of the active site, even at defects, would still influence the reaction, largely by affecting the extent and type of motion possible. Furthermore, once reaction occurred at a given site, the environment at the site became altered to some extent and this would influence further reaction resulting in nucleation of a new phase. In this view, the difference between our polymerization results and the results of Schmidt's and other groups working with non-polymerization reactions was due to the fact that their reaction product was a particular small molecule which could fit more easily into the lattice and would normally be crystalline. With polymer, on the other hand, each reaction step increased the mismatch with the surrounding lattice. In that sense, the effect was additive.

The reason I bring up this ancient history is because these results proved so unexpected that it stirred up some controversy. For a while the approaches were considered by some workers to be complementary and by others to be competitive. This was fortunate for it helped stimulate interest in the field and led to much important work. A sizeable fraction of this work was fueled by the interest stirred up by the amorphous character of the polymer and its interpretation. I, for one, am grateful for the controversy because it kept me working in a fascinating field I might otherwise have left. A sizeable volume of valuable work from laboratories around the world, notably including our hosts at this meeting, appeared at this time some of which had a distinctly applied slant. In the United States, besides myself, for lack of space and time I will mention only the group led by Herbert Morawetz (9) which produced significant polymerization results. I should add that neither Gerhard Schmidt nor I saw any real conflict. I felt that we were working at the opposite ends of a whole spectrum of possibilities. Gerhard put it more elegantly, saying we were looking at the opposite poles of the axis around which the field revolved.

Meanwhile the other aspects of organic solid state chemistry were far from being neglected. John Sherwood was producing some interesting results on diffusion in crystals (10). John Thomas published fascinating electron microscopic studies on crystals and their defects as well as studies of some reaction mechanisms (11). And, of course, the group at the Weizmann Institute expanded their work and kept on getting beautiful results consonant with their original ideas.

Some of the ideas on mechanism led naturally to the concept of reaction in a cavity whose size and shape was defined by the surrounding molecules whether at a defect site or in the intact lattice. I had sometimes pictured it as reaction in a cage with slightly elastic walls and with limited free space. I believe this to be a development of the older concept of the cage reaction which had been used to explain certain aspects of radiation and photochemistry. These ideas were made more explicit by Mendel Cohen (12) and given a more quantitative form by Gavezzotti (13). McBride, at Yale, began to produce his beautiful studies defining the motion required and the role of strain development in the course of some of the reactions (14).

Just when it was beginning to look as if no truly special polymer would ever be produced by solid state polymerization, along came the work of Gerhard Wegner and others on the diacetylenes (15). Not only were the polymers beautifully crystalline, they seemed to fit well within the parent lattice. They also had fascinating electronic properties. Somewhat prior to this, the first of the highly conducting charge transfer complexes were found (16). These literally opened up a whole new horizon in solid state chemistry and physics and brought about an explosion of theoretical and experimental work. In addition, it opened up the possibility of many new applications in the electronic, photo-copying and similar fields. This work grew rapidly, an expansion that is still continuing and producing surprises. This field alone grew large enough for its own specialized meetings.

At the same time the older lines of research on solid state reaction mechanisms continued to develop. From the embryonic stage of the 50's we have come far and fast. The advances in instrumentation, theory, diffraction techniques and computer facilities have enabled us to do things we could only dream of back then. I believe we now have reasonably secure foundations on which to start building comprehensive theories of reactivity and electronic properties. We have come far enough so that we can even speak of crystal engineering and actually have it mean something. Possible applications to industry, biomedical research and special synthetic methods have appeared and continue to appear. Organic solid state chemistry began to acquire more of an interdisciplinary nature.

Back in 1965, I visited Schimidt in Israel. In my discussions with him, he brought up the idea of holding an international conference on the organic solid state. We knew of no previous meetings devoted to the organic solid state except for a group of annual one day seminars organized at the Franklin Institute by Mort Labes. I agreed to the idea provided that the meeting encompass the whole spectrum of organic solid state work and that it be limited in size so that the participants from the various disciplines could get to know each other. We did not want a large meeting with parallel sessions which would only defeat our purposes. The first meeting was held in 1968 at Brookhaven National Laboratory under the joint sponsorship of the laboratory and the State University of New York at Stony Brook. I had the honor of being both the chairman and the editor of the proceedings of that meeting (17). The results seemed promising enough to warrant further meetings. We are now at the eighth of the series with the promise of more to come. I believe they have had considerable value in promoting the field.

It seems to me that organic solid state chemistry is a discipline that has yet to reach full maturity. Although important groundwork has been laid, the field is still open. As this conference shows new discoveries are constantly being reported. Our understanding of reaction mechanisms has grown enormously. Studies relevant to electronics, biology and medicine, synthetic organic chemistry, continue to appear. Having watched the growth of this field for over about 35 years, I feel confident that we can look forward to an interesting future.

There are many aspects of organic solid state chemistry I haven't mentioned and many workers in this field I should have. It wasn't for lapse of memory despite my age. Time and space forbade it. Had I done so, this little discourse would have been twice as long and three times as boring. I can only apologize to those I haven't mentioned and who made so many important contributions to the subject.

When I first started out in this field, I had a laboratory next to that of some more traditional solid state physicists. I was politely informed that I was wasting my time on the organic solids. They were too complicated, too unsymmetrical, too difficult for useful theory or calculations. I would be better off, I was told, sticking to simple solids such as germanium or sodium chloride where there was at least a chance of doing something useful. No one has presumed to make such a statement to me for many years. Organic solid state chemistry has become a well recognized important field. It is still a developing field with even greater promise for the future. I am proud to have been a part of it and to have made whatever contribution I could. Now that I am retired and can look back at it, I can say it has been a rewarding career after all.

REFERENCES

(Note: Where feasible, the references are to review papers by the authors cited. This was done in the belief that these would be more valuable to the general reader. Anyone interested in the primary references can find them cited in the reviews.)

1. H. Lipson, W. Cochran; The Determination of Crystal Structures, first edition; G. Bell & Sons, publishers, (1953).

2. H. S. A. Gilmour; "The Photochemistry of the Organic Solid State" in the Physics and Chemistry of the Organic Solid State, Volume 1; D. Fox, M. M. Labes, A. Weisberger, editors; Interscience publishers, (1963).

3. a) A. I. Kitaigorodski; Organic Chemical Crystallogrpahy, English edition; Consultants Bureau, publisher, (1961).
   b) A. I. Kitaigorodski; Molecular Crystals and Molecules; Academic Press, (1973).

4. a) M. D. Cohen, G. M. J. Schmidt; "Structure Sensitive Reactions of Organic Crystals;" Reactivity of Solids, Proceedings of the Fourth International Symposium on the Reactivity of Solids; J. H. de Boer, editor; Elsevier, (1961).
   b) G. M. J. Schmidt; "The Photochemistry of the Solid State;" Reactivity of the Photoexcited Organic Molecule, Proceedings of the 13th Conference on Chemistry at the University of Brussels; Interscience, publisher, (1965).
   c) M. D. Cohen, G. M. J. Schmidt; Topochemistry, Part 1; J. Chem. Soc. 1996, (1964) and subsequent papers in this series.
   d) G. M. J. Schmidt; Pure and App. Chem., 27, 647 (1971).

5. G. Adler; J. Chem. Phys., 31, 848 (1959).

6. G. Peyronel; Rend. Acad. Naz. Lincei., Serie VIII, 15, 402 (1953).

7. R. B. Mesrobian, P. Ander, D. S. Ballantine, G. J. Dienes, J. Chem. Phys., 22, 565 (1954).

8. a) G. Adler, D. S. Ballantine, B. Baysal; J. Polymer Sci., 48, 195 (1960).
   b) G. Adler, Molec. Cryst. Liq. Cryst., 9, 361 (1969).
   c) G. Adler, Trans. Am. Cryst. Soc., 7, 55 (1971).

9. a) H. Morawetz; J. Polymer Sci., 48, 195 (1960).
   b) H. Morawetz; Science, 152, 705 (1987).

10. a) J. M. Sherwood, D. J. White; Phil. Mag. 15, 345 (1967).
    b) J. M. Shwerwood, D. J. White; Phil. Mag. 16, 975 (1967).

11. a) C. Roscoe, J. M. Thomas, Proc. Roy. Soc. A, 297, 397 (1967).
    b) J. M. Thomas, Endeavour, XXIX, 149, (Sept. 1970).
    c) J. M. Thomas, J. O. Williams; Progress in Solid State Chemistry, Volume 6, H. Reis; J. O. McCaldin, editors; Pergamon Press (1971).
    d) J. M. Thomas, Phil. Trans., Roy. Soc. London, 227, 251 (1974).

12. a) M. D. Cohen; Angew. Chem., Internat. Edit; 14, 386 (1975).
    b) M. D. Cohen; Molec. Cryst. Liq. Cryst., 50, 1 (1979).

13. a) A. Gavezzotti; M. Simonetta; Chem. Rev., 82, 1 (1982).
    b) A. Gavezotti; J. Am. Chem. Soc., 105, 5220 (1983).
    c) A. Gavezotti; J. Am. Chem. Soc., 107, 962 (1985).
    d) A. Gavezotti; Molec. Cryst. Liq. Cryst., 93, 113, (1983).

14. a) J. M. McBride, B. E. Segmuller, M. D. Hollingsworth, D. E. Mills, B. A. Weber; Science, 234, 830 (1986).
    b) J. M. McBride; Molec. Cryst. Liq. Cryst., 96, 19 (1983).
    c) J. M. McBride; Acc. Chem. Research, 16, 304 (1983).

15. a) G. Wegner; Faraday Discussions, Chem. Soc., 68, 494 (1964).
c) G. Wegner; Angew. Chem., Internat. Ed. Engl., 20, 361 (1981).

16. a) A. Garito, A. J. Heeger; Acc. Chem. Soc., 68, 494 (1964).
b) P. Delhaes; Molec. Cryst. Liq. Cryst., 96, 229 (1983).

17. The proceedings of these meetings in print are:
a) Molec. Cryst. Liq. Cryst., 9, (1969).
b) Molec. Cryst. Liq. Cryst., 32, (1976), abstracts only.
c) Molec. Cryst. Liq. Cryst., Part A, 50, (1979).
Molec. Cryst. Liq. Cryst., Part B, 52, (1979).
d) Molec. Cryst. Liq. Cryst., Part A, 93, (1983).
Molec. Cryst. Liq. Cryst., Part B, 96, (1983).
e) Molec. Cryst. Liq. Cryst., Part A, 134, (1986).
Molec. Cryst. Liq. Cryst., Part A, 136, (1986).
and the present volumes.

18. a) I. C. Paul, D. Y. Curtin; Science, 187, 19 (1975).
b) E. Hadjoudis; Molec. Cryst. Liq. Cryst. 134, 237 (1986).

19. a) B. S. Green, M. Lahav, G. M. J. Schmidt; Mol. Cryst. Liq. Cryst. 29, 187 (1975).
b) K. Penzian, G. M. J. Schmidt, Angew. Chem., Internat. Edit. Engl., 8, 608 (1969).

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