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Final Report

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Title: "Controlled Polymerization of
Adsorbed Monomers"

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Historical Background for Research on Adsorption Polymerization

The original proposal on which AEC Contract No. AT(11-1)-1580 was based was written six years ago. At that time the investigation of solid-state polymerization was a subject of widespread research interest; with extensive sponsorship by AEC and comparable agencies in other countries. There had been a few studies of adsorption polymerization, but these were rather qualitative in nature.

The objectives given in the original proposal were:

1. To polymerize adsorbed molecules with known spacial relations to each other and to the adsorbing surface.
2. To determine the scope of the experimental conditions that are necessary for such a polymerization to occur.

These objectives have been accomplished, but with the inevitable changes in detailed approach that were necessary to reflect the changes in knowledge and understanding that have occurred during the past six years.

Two important new research ideas were introduced via the annual Proposed Technical Programs that were submitted. One was that Blodgett-Langmuir built-up multilayers be formed of suitable monomers and subsequently polymerized. The second was that controlled polymerization be used to form organic sheet polymers, a new form of matter that would be important in theoretical and applied polymer science if synthesis could be accomplished. A minor part of our effort went toward these objectives, but no substantial progress can be reported.

CHANGES IN KNOWLEDGE AND UNDERSTANDING, 1965-71

In this section we will describe briefly, without formal citations, the major developments from outside laboratories in the fields of solid-state polymerization and physical adsorption.

Fortunately for the proper development of our research, Mr David Richman of AEC, in telling me about the conditions of research under AEC sponsorship, encouraged visits to the AEC national laboratories in which chemical applications of nuclear radiation were being studied. These visits were all interesting, but the greatest direct value came from a visit to Dr George Adler at Brookhaven. I already knew Dr Adler, but only by visiting and seeing his marvelous motion pictures of solid state polymerization could I fully appreciate the convincingness of his explanation of the phenomenon. His work shows that, with the exception of the rather unusual case of ring-opening solid-state polymerization, the phenomenon requires the destruction of crystalline order prior to actual polymerization. Thus the paradox: Crystals polymerize only when they melt, and glasses are better materials for solid state polymerization than the crystals that were the original subject of intensive research.

Our research plans were also based on our detailed understanding of quite a different subject: the physical adsorption of gases on solids. Here the key figure is J. de Boer of Delft, Netherlands. Dr de Boer has painstakingly worked out a complete theory of physical adsorption which is almost totally at variance with the Brunauer-Emmett-Teller theory on which we based our original proposal. We accept the superiority of his theory and have two papers based on this AEC sponsored research that should help contribute to its

acceptance (references to our papers appear later in this report). The pertinent point is that the de Boer theory indicates that knowledge of molecular orientation (which was a key requirement of our original proposal) can only be obtained on homotactic surfaces. We therefore have limited our experimental work to adsorption studies on Graphon carbon black, one of the best-known homotactic adsorbents. Our own work shows that the adsorbed molecule should be rigid if the orientation is to be known, and for this reason we have used small-ring monomers only.

RESULTS. I. OBTAINING ADSORBED MONOMERS IN KNOWN SURFACE CONCENTRATIONS AND ORIENTATIONS

The adsorption of furan on Graphon carbon black has been examined in enough detail at room temperature and at -18°C to establish the monolayer point and the probable orientation (1, 2). The same methods have been used, but without as many experiments being run, to determine the monolayer point for thiophene on Graphon at room temperature and at 0°C , and for 1,4-cyclohexadiene at room temperature (2). The orientations of these two monomers have not been the subject of special study, but there is no reason to expect them to differ from the furan orientation. Finally, our experimental method coupled with de Boer's theory leads to a simple new method for finding the monolayer point in the physical adsorption of gases on solids (2).

RESULTS. II. POLYMERIZATION OF MONOMERS ADSORBED ON SOLIDS

Quantitative studies of polymerization in which the surface concentration of furan was known showed that the extent of polymerization was erratic unless the amount of furan was less than enough to form a monolayer (3). Furan undergoes some spontaneous polymerization if the monomer is not irradiated and substantially complete polymerization if it is irradiated and a

day or more allowed for post-polymerization (4). 1,4-Cyclohexadiene polymerizes spontaneously to an even greater extent than furan (4). Thiophene has less tendency than furan to polymerize spontaneously (4).

The structure of the resultant polymer has only been investigated extensively in the case of polyfuran. First, we made and published the first complete investigation of the structure of conventional (solution-polymerized) polyfuran (5). This was then extended with an experimental investigation of the structure of all types of polyfuran, including that made by adsorption polymerization (6).

All but the most recent part of this work has been summarized and placed in perspective with respect to the qualitative work of other authors (7).

We had originally thought that we might try a wide variety of monomers. Most of the commercial-type monomers would pack rather badly on the solid surface. Also, the evidence from Adler's work indicated that they would not be very different, unless we tried something like trioxane. All available evidence indicates that this would have to form a real crystal (ie, much more than a monolayer) to polymerize. For these reasons, we did not go beyond the simple disc-shaped molecules in our actual experiments. However, in the early phases of our research we did concern ourselves with the question of gases that might have zero adsorption on adsorbents such as carbon black. The possibility of zero adsorption of a gas on a solid is, for theoretical reasons, closely connected with the possibility of a 180° contact angle for a liquid on a solid. The results of our consideration of these problems show that Graphon only adsorbs water by virtue of the very small amount of inhomogeneous surface that it contains (8). This indicates that it would be a poor adsorbent for use with monomers such as formaldehyde. In the final analysis,

we decided not to attempt such adsorption polymerization for other reasons, but is interesting to note that we would have had to find and build up a background of knowledge for another adsorbent.

RESULTS. III. POLYMERIZATION IN BUILT-UP MONOLAYERS

This is an attractive idea, but for neither octadecyl methacrylate nor trans-2-octadecenoic acid did we obtain any experimental results that were any way encouraging. Discussion with others who have tried this idea or who have talked to people who have tried it indicates that no success is being had with this idea. According to the Adler concept, it would be necessary to introduce quite a bit of disorder to initiate polymerization. However, it is difficult to make disordered multilayers. Perhaps someone will succeed with multilayer polymerization one day.

RESULTS. IV. SYNTHESIS OF SHEET POLYMERS

Dr Richman was somewhat restrained in his reaction to my first suggestion that I make this a major part of our research program. Many months later, when Dr Landgrebe was visiting here, he asked for an evaluation on the importance of atomic energy in the successful commercialization of sheet polymer synthesis. I said it would be useful in scouting methods of carrying out the synthesis, but there was no reason to say that it would be essential for commercial operations. He suggested that this would mean support by the AEC would be unlikely. We have taken this advice and applied to the National Science Foundation and the Office of Naval Research for support of this research.

In our early enthusiasm for this idea, we did some research to see how controlled polymerization might lead to the synthesis of sheet polymers. We had two principal ideas. One was that molecules should be oriented at liquid-liquid interfaces. To learn more about this subject, we extended work that had been

going on at Wayne State for years - work on the interfacial tension at hydrocarbon-water interfaces - to a new class of hydrocarbons, the bicycloalkyls. We thought the possibility of a thicker layer for interfacial transition might be indicated by unusual interfacial tensions. However, the interfacial tensions were not much different from those for conventional hydrocarbons (9).

The second idea was that the mercaptan→disulfide reaction (as in the cystine→cysteine reaction that is so important in biology) might serve for one step of sheet polymerization. We had had great difficulty finding a polymerizable organic hydroxy compound that would be rigid enough for good control of orientation but still had enough hydrophobic character to orient well at an air-water interface. (Part of our enthusiasm for liquid-liquid interfaces sprang from the fact that we couldn't find a suitable monomer for use on water surfaces in air). Perhaps thiols would serve.

We found 1-octadecanethiol was not hydrophilic enough to spread at the air-water interface. However, we were able to oxidize it. Unfortunately we found that the oxidation product was an 1-octadecanesulfonate (10).

The small amount of work we did on sheet polymerization has yielded only negative information, but this negative information is being published and will be helpful to us and to others as we continue to work toward this objective.

DEGREES GRANTED FOR RESEARCH:

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PUBLICATIONS ORIGINATING FROM THIS RESEARCH

1. "The Orientation of Adsorbed Furan Molecules", H. K. Livingston and R. Senkus, J. Colloid Interface Sci., 30, 312-22 (1969).
2. "Adsorption Isotherms of Condensable Vapors on Solids: Determination of Monolayer Points from Isothermal Plots Based on the Temperature of the Vapor Source", H. K. Livingston, R. Senkus, and R. A. Spagnoli, J. Colloid Interface Sci., in press.
3. "The Effect of Surface Concentration on the Radiation Polymerization of Adsorbed Furan Molecules", H. K. Livingston and R. Senkus, J. Polym. Sci., Part B, 7, 635-41 (1969).
4. "Polymerization on Carbon Black Surfaces", H. K. Livingston, R. Senkus and J. T. T. Hsieh, ACS Div. Polym. Chem., Preprints, 11, 304 (1970).
(This is essentially an extended abstract which served as a basis for oral presentation. Thiophene data was not included. A complete paper incorporating the thiophene data will be submitted for publication soon).
5. "The Structure of Polyfuran", J. Kresta and H. K. Livingston, J. Polym. Sci., Part B, 8, 795 (1970).
6. "Branching in Furan Polymerization", H. K. Livingston and J. Kresta ACS Div. Polym. Chem., Preprints, 12, 628 (1971).
(As in ref. 4, this is an extended abstract. The complete paper will be submitted for publication later this year).

7. "Adsorption Polymerization", H. K. Livingston, Collected Plenary Lectures from the IUPAC Macromolecular Symposium in Budapest, 1969, in press. The Hungarian Academy of Sciences is publishing this collection, and proof for the articles was read and returned two months ago. However, it has never been clear exactly where it is to be published.
8. "Contact Angles in Controlled Atmospheres: Some Theoretical Considerations", H. K. Livingston and C. S. Swingley, Surface Sci. 11, 252-61 (1970).
9. "Interfacial Tensions against Water of Some C₁₀-C₁₅ Hydrocarbons with Aromatic or Cycloaliphatic Rings", J. J. Jasper, M. Nakenecnyj, C. S. Swingley, and H. K. Livingston, J. Phys. Chem., 74, 1535-9 (1970).
10. "The Oxidation of 1-Octadecanethiol at the Air-Water Interface", H. K. Livingston and C. S. Swingley, submitted to J. Colloid Interface Sci.