more reasonable to assume that He-type molecules do occur in normal serum, but in quantitatively much smaller amounts than Le-type molecules. This at least is the implication of the statistical finding that only 4 out of 58 γA-myeloma proteins belonged to subclass He (*7*).

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31 May 1966

Acrylonitrile Polymerization in a Miniaturized High-Pressure Optical Cell

Abstract. *A miniaturized high-pressure optical cell has been used to investigate the feasibility of carrying out high-pressure polymerization, wherein the process can be observed both spectroscopically and optically while the polymerization process is occurring. The method has been illustrated by a novel polymerization of acrylonitrile.*

Recently some results have been reported on the high-pressure effect in radical heterogeneous polymerization of acrylonitrile at 50°C (*1*). The pressure effect is unusual in comparison with that of homogeneous radical polymerizations and the heterogeneous radical polymerization of α-methylacrolein (*2*). It seemed interesting to investigate the behavior of acrylonitrile in a miniaturized high-pressure optical cell (*3*), which was shown to be a very useful tool for studying many phenomena at high pressures (*4*).

Mallinckrodt acrylonitrile was used without further purification. Molybdenum foil of 1 mil (0.0254 mm) thickness was used as the gasket material in the diamond cell with a smaller diamond surface of about 0.058 mm^2, as measured by making use of its photomicrograph (250×). The technique for liquid sampling is similar to that described recently (*5*). Infrared spectra of samples in the diamond cell were taken with a Perkin-Elmer 421 infrared spectrometer with a double beam condensing unit. All the experiments were carried out at room temperature (~ 26°C), with the sampling area being viewed through a Leitz microscope supplied with an arrangement for taking photomicrographs.

The pressure "zero-point" was estimated with the melting points of carbon tetrachloride and benzene. With this diamond cell, pressures up to 36 to 40 kb could readily be achieved.

In most runs the pressure was increased and decreased at a speed of about 7 kb per 10 minutes. Under these conditions the crystallization of acrylonitrile in the form of "needles" (phase I) occurs at 28 to 32 kb. At this pressure a new crystalline form (phase II, "plates") starts to grow in a short time, gradually covering all of the field (Fig. 1). A decrease of pressure down to 6 kb does not result in any change. The crystalline form II was viewed through a microscope. At 6 kb the transition II–I occurs (Fig. 2), and at about 5 kb melting takes place. Further decrease of pressure gives rise to the polymerization (Fig. 3), and in about one-half of an hour all of the viewed area is covered by the polymer phase. The polymerization usually starts in a region near 2 to 3 kb.

The great difference in crystallization and melting of acrylonitrile seems to be due to the "superpressing" phenomenon similar to the "supercooling" one. The spectra of liquid acrylonitrile, crystalline form II, and polymer in the region of 2600 to 3300 cm^{-1} are shown in Fig. 4. (The spectrum of crystalline form I looks similar to that of crystal-

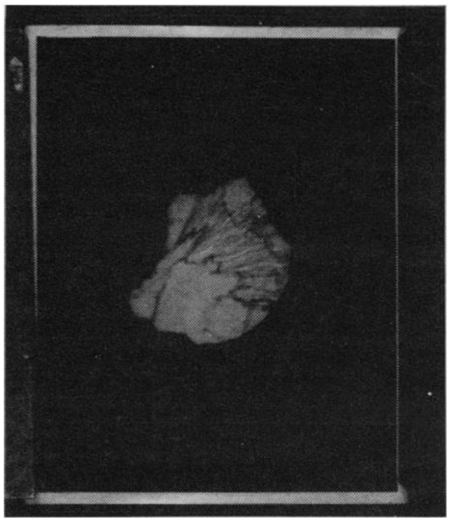

Fig. 1. Crystalline acrylonitrile at about 30 kb and room temperature. Two phases are present; the transition I–II is occurring.

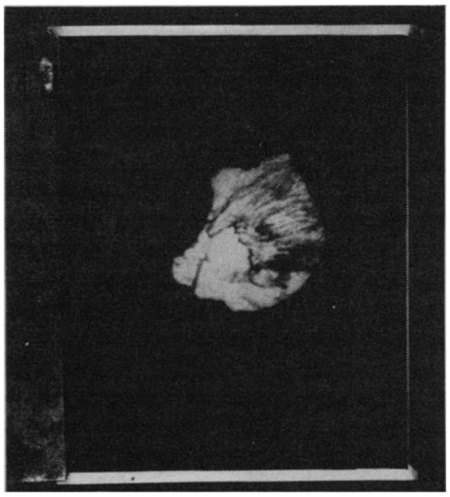

Fig. 2. Crystalline acrylonitrile at about 6 kb. Two phases are present; the transition II–I is occurring.

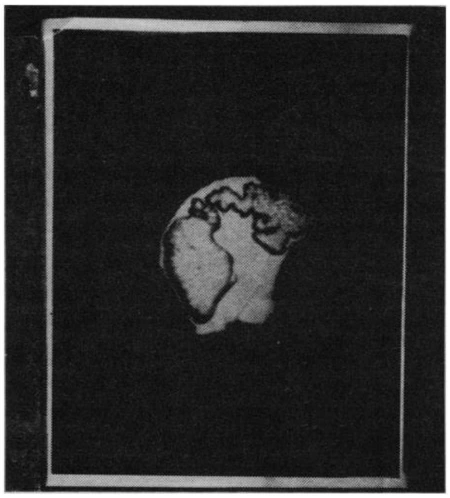

Fig. 3. Polymerization of acrylonitrile in the liquid phase at about 2 kb.

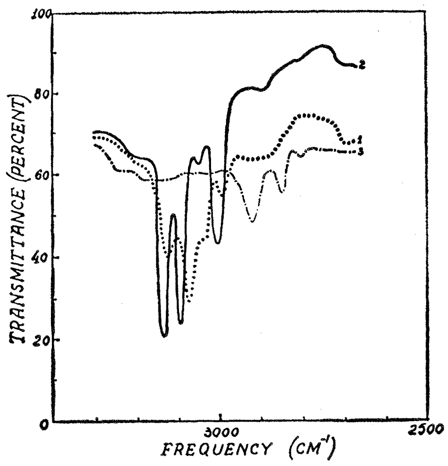

Fig. 4. Infrared spectra at 20 kb; curve 1 (dotted), liquid acrylonitrile; curve 2 (solid), solid acrylonitrile (phase II); curve 3 (dot-dash), polyacrylonitrile.

line form II.) The spectra were taken by the following procedure. Initially, pressure was increased up to 20 kb, and the sample was allowed to stand overnight. No crystallization occurred. The spectrum of this liquid acrylonitrile is shown in Fig. 4 (curve 1). The pressure was then increased up to 36 kb, at which pressure the crystalline modification II formed. The spectrum of this form was recorded after releasing the pressure to 20 kb (Fig. 4, curve 2). The pressure was then decreased until the polymerization took place; after that, it was increased to 20 kb, and the spectrum of the polymer was recorded (Fig. 4, curve 3).

The band positions of the liquid acrylonitrile under pressure, which are shown in Fig. 4, are in satisfactory agreement with those reported for liquid acrylonitrile at atmospheric pressure (*6*). In the region of frequencies presented, bands were found at 2990, 3033, 3068, and 3125 cm^{-1}. We have found the bands at 2992, 3035, 3075, and 3125 cm^{-1}. The corresponding bands of crystalline acrylonitrile are more intense and shifted slightly to higher frequencies (about 15 cm^{-1}). The spectrum of the same sample in which polymerization has taken place shows no absorption at frequencies higher than 3000 cm^{-1}. There are two bands at 2850 and 2925 cm^{-1}. Liang and Krimm have observed bands at 2870 and 2940 cm^{-1} for polyacrylonitrile (*7*). These bands were assigned to the symmetric and asymmetric stretching C—H vibrations in the CH_2 group. It seems reasonable to give the same assignment to the bands found here, in spite of some difference in the frequencies.

Polymerization of acrylonitrile proceeds below the pressure at which melting occurs. The reaction usually starts at one or two points and is developed from these points by "jumps" to cover all the viewed area. The beginning of the process was observed when the pressure was increased. If the polymer phase is allowed to cover only a part of the field, an increase of pressure stops further growth of the phase. The data on radical heterogeneous polymerization of acrylonitrile show that increasing the pressure up to 6 kb gives rise to an explosion which should be considered a result of the great rise in the polymerization rate (*1*). On this account the polymerization of the acrylonitrile in the diamond cell may not be a radical polymerization. However, the lack of an uncontrollable reaction in this case may be due in part to better temperature control because of the relatively large surface-to-volume ratio of the sample. The monomer crystallization does not seem necessary for the polymerization to occur. We have observed some polymerization without preliminary crystallization by decreasing the pressure from 20 kb.

The polymerization process discovered in this work shows rather interesting features and deserves to be investigated in more detail.

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Inheritance of Reactivity to Experimental Manipulation in Mice

Abstract. *The mode of inheritance of open-field defecation was found to differ according to earlier treatment of the mice. Activity of hybrids, however, was closer to that of the less active parent for all conditions of pretreatment. These results suggest that adequate sampling not only of gene pools, but also of both pretest and test environments, is necessary before statements concerning effects of prior treatment, or mode of inheritance of specific behavior, are valid.*

The value of genetic studies in determining the evolutionary significance of certain behaviors has been proposed (*1*). An implicit assumption in such quantitative studies is that either no environment-gene interaction exists or that environmental conditions have been adequately sampled (*2*). Most investigators using designs adequate for analyzing genetic effects have, however, limited their studies to naive animals reared under one fairly restricted environmental condition. Since there is evidence that pure strains differ greatly in reactivity to experimental manipulation (*3*) and that buffering effects may occur in interstrain hybrids (*2*), the neglect of gene-environment interactions is extremely precarious with regard to behavioral traits. Unfortunately, most investigators interested in combined genetic and environmental effects have limited their studies to pure strains only, so that genetic effects cannot be analyzed in detail as by Broadhurst (*4*) and Bruell (*5*).

I have investigated genetic influences on reactivity to various amounts of environmental stimulation, with a diallel mating system; this report describes only the mode of inheritance of defecation and exploratory activity in an open field under three different conditions of prior treatment (*6*).

A total of 1440 C57B1/10 J, DBA/1 J, C3H J, and Balb/C J mice and their