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Dr. Berens (B. F. Goodrich Co., Brecksville, Ohio, U. S.): I will ask Dr. Geil to start the discussion because his area of expertise is polymer morphology. A suitable subject on which to start is the relationship between morphology, as formed during polymerization, and some of the morphological features observed in solid PVC during and after processing.

Dr. Geil: In terms of the general subject of PVC, since I first became interested several years ago in PVC morphology, both in the nascent state and after processing, there have been two features of concern and interest to me in addition to the morphology itself. The first is the number of papers, including my own, which start by saying that despite years of work little is know of this or that having to do with PVC. My own research proposals began like that, saying that despite the commercial interest and value of PVC little is known about its morphology.

Secondly, of interest and concern, is the vast number of terms used to describe the morphology of PVC and all its facets in the nascent state. I am thinking here in terms of such aspects as primary particles, polymerization particles, granules, aggregates, grains, subparticles, microgranules, macrogranules. For someone coming into this field it is almost impossible to sort it all out and to work out what we are talking about. If nothing else happens as a result of this symposium other than that we come to some agreement on how to define the various particles one sees in PVC, by electron microscopy or other means, this in itself would be a great gain for anyone beginning to work in this area. I do not know exactly how we can solve the latter problem. Even in what I have to say I shall be oscillating from one term to another. But it will be an advantage if we can do it.

With respect to the papers presented at this session the combination of the film and papers goes a long way towards clarifying the development and organization of what I will call the large-scale structure of PVC in its polymerized state—at least in suspension, and to some extent bulk polymerization. While I am certain that the chemistry of the polymerization will continue to be argued in various forms, the morphological techniques for investigating what I call the large-scale structure are well developed. In fact, as pointed out by Tregan some years ago [1], the grains of PVC have a number of forms, depending on how they have been formed.

Tregan's findings are shown on Fig. 1. In the present session of this symposium we have seen a number of ways of following the formation of the grains.

I will pick out a few features of interest related to this point, in terms of the papers we have heard so far and in relation to comments I wish to make later. For instance, Dr. Zichy has shown techniques of following growth from particles about 1000 Å in size to larger sizes. This resulted in his suggestion about a cause of aggregation related to the amount and type of surface active material. He suggested the definition of what I will call the primary particle, that is, the particle sized between about 1000 Å and 10000 Å, becomes progressively blurred as the particle grows. Is this true internally as well as externally, or are the boundaries still present in these particles to play a role in subsequent flow processes? We do not know this yet, at least in terms of what we have heard today.

Also, in the plot Dr. Zichy showed of the logarithm of the coagulation rate versus the diameter he suggested that there is a stable size in the vicinity of about 10 Å to 100 Å—that is between 10^{-3} and 10^{-2} μm—but there was no direct evidence in the paper for this, in terms of electron microscopy. However, I think it is well accepted that a particle of such a size would be expected.

Dr. Boissel also suggested an original 100 Å granule (microdomain), as he defined it, which then grows until a more critical size is reached. The point I am making is that this 100 Å-sized particle is a particle which in both those papers, appears—as the authors suggest—to grow until a larger, 1000 Å or 10000 Å particle is reached, but we hear nothing about the structure inside the 1000 Å particle. It is this which will be of concern to me.

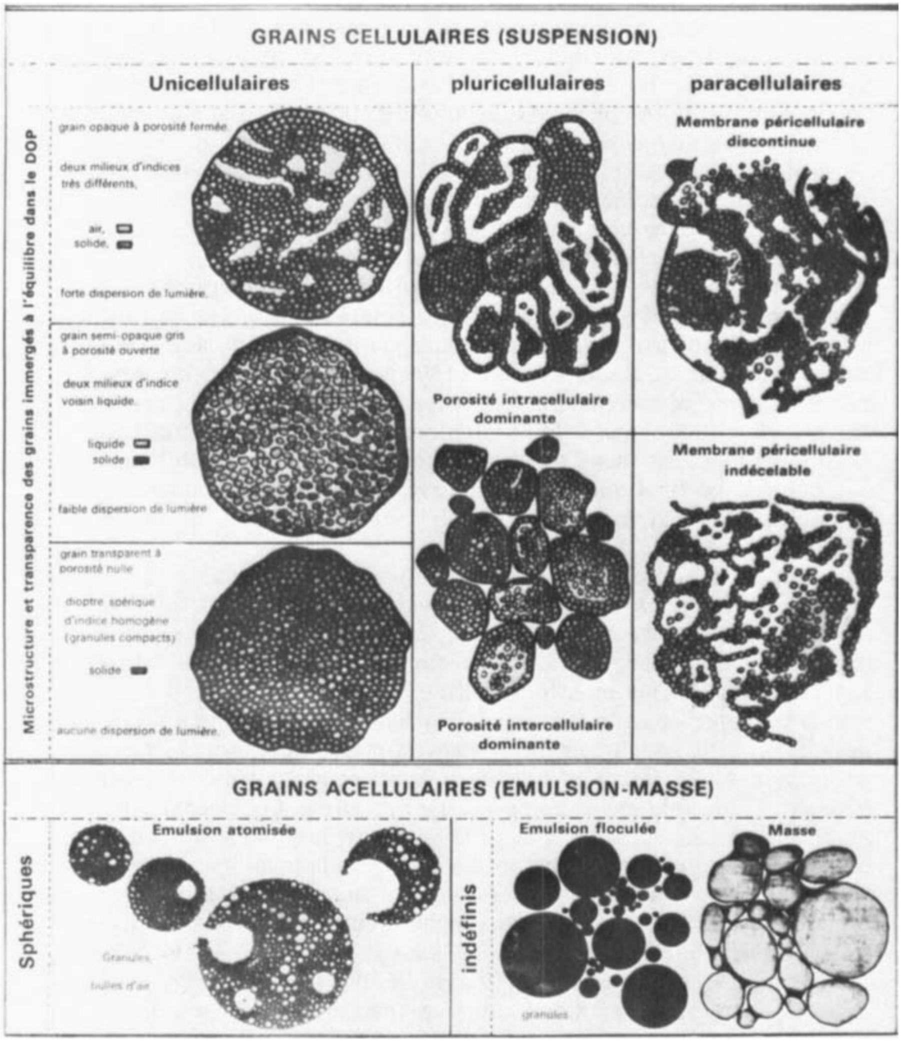

FIG. 1. Different types of grains of PVC as described by Tregan and Bonnemayre [1].

Also, in Dr. Allsopp's and Dr. Palma's papers we were able to follow the growth and merging of the suspension particles, by indirect means in the first case and by electron microscopy in Dr. Palma's paper. Of particular interest to me was Dr. Allsopp's suggestion that growth after the pressure drop is detrimental to surface area, as well as his suggestion that there is a morphological difference between PVC produced by initiator in the free monomer and that absorbed on the surface. Desirable, and probably possible now in terms of the techniques available, would be direct observation of the type of thing suggested by Dr. Allsopp.

As I pointed out previously, I believe that the techniques for following the morphology, in industrially related processes as well as what one might call more fundamental type research, are now available for looking at structures on a 1000 Å size scale and larger. We can think here of optical microscopy, scanning electron microscopy, and swelling techniques. In particular, I should like to emphasize such techniques as those of freeze-fracture and freeze-etching which are being used for biological samples, but which should also be adaptable to studying polymerization primary particles as they are being polymerized.

I want to describe briefly what I believe to be the basic morphological problem that is remaining, one which has not been touched on so far in the papers. Fortunately, Dr. Carrega gave me a copy of the paper he will present in a later section of this symposium. As he will discuss, PVC is most crystalline as first polymerized. It is still a polymer of very low crystallinity, in terms of the kind of polymers with which I normally work for polymer morphology—polyethylene, for instance—but there is supposedly some crystallinity present. This feature of being most crystalline as originally polymerized is common also to a number of other polymers—we can think of branched polyethylene, polytetrafluoroethylene and so on.

The question to ask is what is the morphology of this original primary particle or subparticle—about 1000 Å to 10000 Å in size? In Dr. Tregan's diagrams (Fig. 1), what is the morphology inside the little spheres which he has inside the big spheres? This, as I said, is something which has not even been mentioned in today's papers. In fact, it was only in the last paper that we saw any evidence that the electron microscope beam was getting through the particle because we saw nothing other than what was more or less a solid black sphere.

That is the problem: where are the crystals, if there are any, in these particles? I emphasize the phrase, "if there are any." What is their size, their perfection? Are they fringe micelle-type crystals, or some other form of crystal? Is the particle we see—the 1000 Å

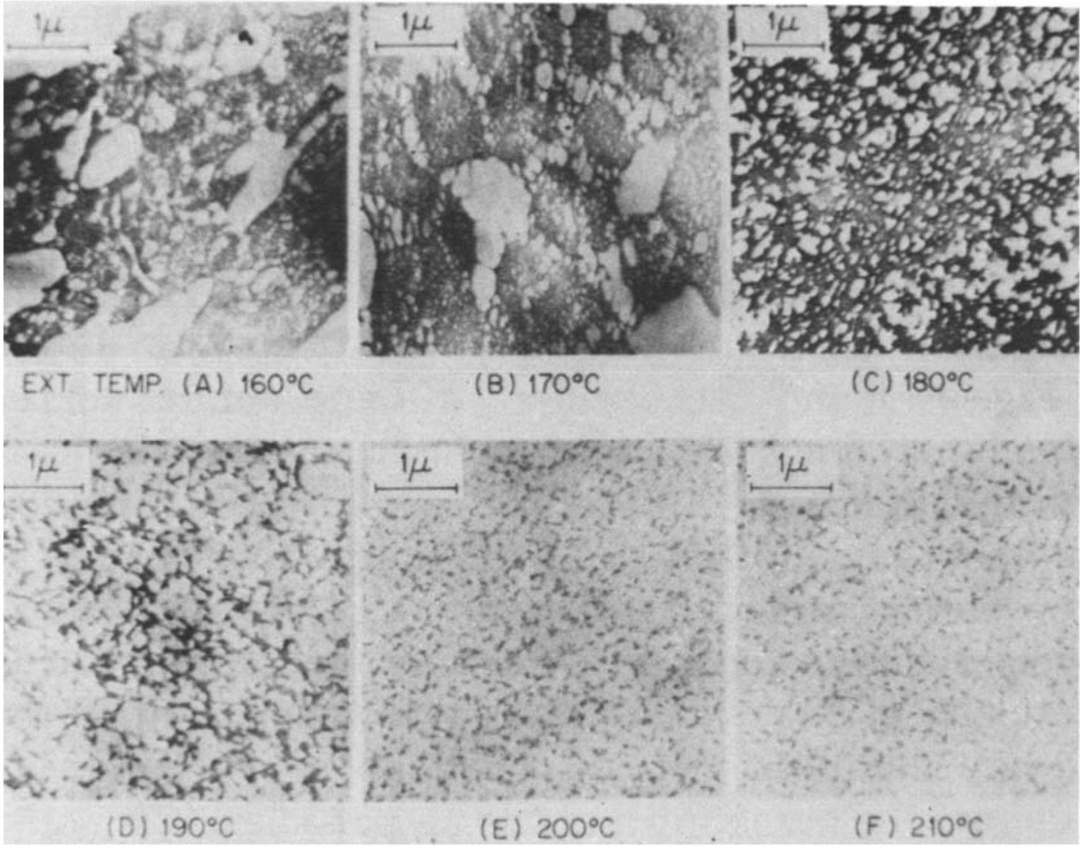

FIG. 2. Copy of a figure from Hattori et al. [2] showing electron micrographs of sections of PVC extrudates with different extruder exit temperatures. The samples were embedded in methyl methacrylate, which was polymerized before sectioning.

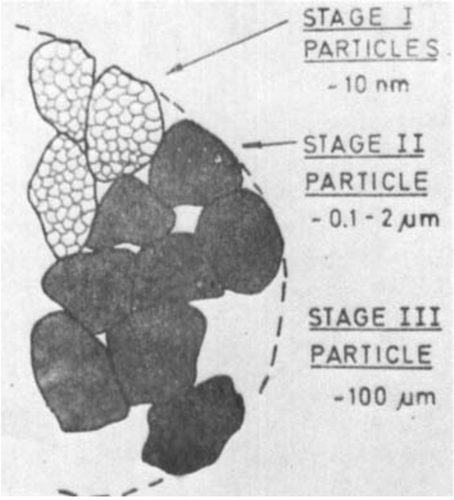

FIG. 3. Diagram of proposed substructure of a PVC grain [4].

particle—homogeneous in terms of density and segmental orientation within it, as well as such aspects as branching and molecular weight? Is it homogeneous on this scale, or not? We have heard nothing about these questions today, yet they are the fundamental problems remaining in this area.

There are several published papers—a paper by Hattori et al. [2] from Japan, also Dr. Behrens' recently published paper [3]—which suggest that there is a 100 Å substructure inside the 1000 Å particle. Unfortunately, in all the published papers except one that I have seen so far the reproduction of the micrographs is so poor that the reader cannot tell whether what the author states is correct.

An example of this is shown in Fig. 2 from a copy of one of Dr. Hattori's figures. On the bottom right-hand side we are supposed to see a 100 Å fibrillar structure present in the sample. I do not question that he sees something like this, but it is very difficult for the reader of his paper—perhaps because of the way in which the journals are produced at present—to see what the author is trying to describe.

However, I think that the evidence for a fibrillar structure in these particles is even less than that for some form of domain structure on a 100-Å scale.

The result of observations like that is a model such as that shown in Fig. 3, taken from a paper by Dr. Faulkner [4] but similar to the one described by Dr. Hattori. Three sizes of particles are shown here. There is the large polymerization particle (grain), the 100 μm diameter particle which Hattori describes as stage III. (Another way of labeling the particles is in terms of three stages). Stage II is the 0.1-2 μm primary particle. Stage I, with which I am particularly concerned, is the 100 Å particle (microdomain). In Dr. Hattori's paper the little spheres in Fig. 3 were more or less drawn as fibers. Other than that, the two figures are essentially identical.

What is the structure of what is labeled here as a stage I-type particle? Probably the best picture I know to describe this sort of thing is one published by Dr. Cobbold and Dr. Mendelson of ICI, in a paper [5] discussing the "value of sectioning polymers" for electron microscopy rather than a paper discussing PCV.

Figure 4 is a micrograph of a section of PVC particles showing

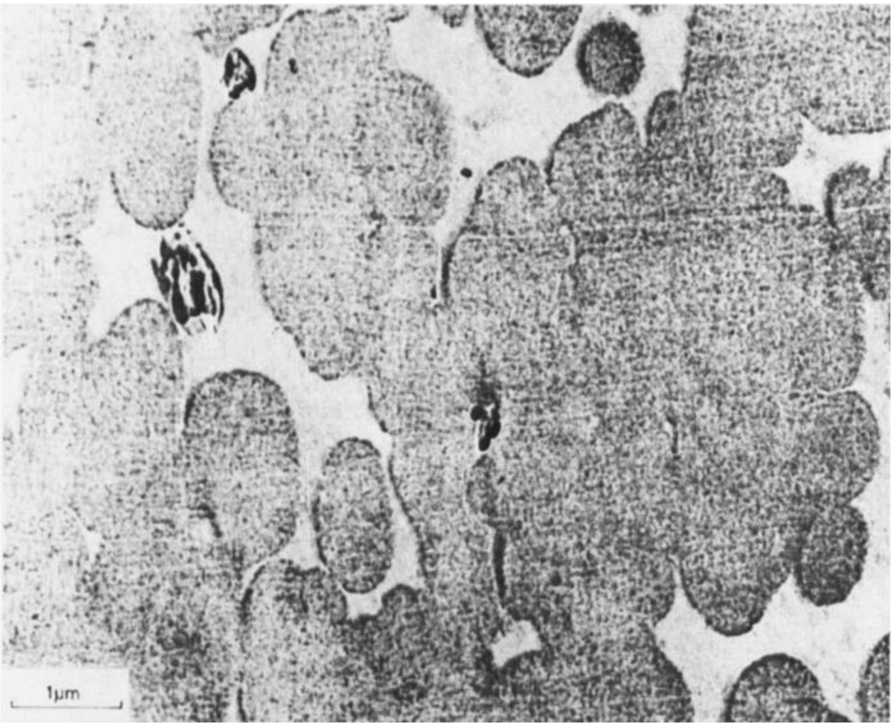

FIG. 4. Electron micrograph of a sectioned PVC grain as described by Cobbold and Mendelson [5].

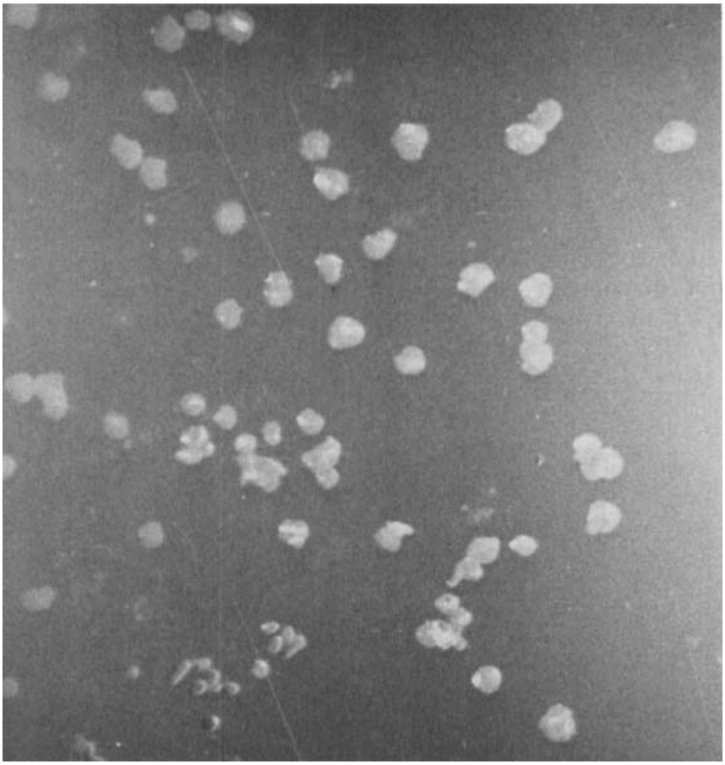

FIG. 5. Dark-field electron micrograph of polytetrafluoroethylene (PTFE) emulsion particles. The bright areas in each particle correspond to PTFE crystals properly oriented to diffract at the selected angle.

some form of domain structure. At least, there is some variation in density within the individual particles themselves, which is more or less on the 100 Å scale.

I came across this early in our work on plasticized PVC, in which there is clear evidence of a 100-Å domain structure, both by microscopy and small-angle x-ray diffraction. When I wrote to Dr. Cobbold to obtain a copy of his paper in order to see the original figure, his reply contained something which has concerned me ever since. He suggested in his note that it is well-known that there is a 100 Å domain structure in as-polymerized PVC and that this is accepted by everybody. Ever since then I have been trying to find any other evidence for this 100 Å domain structure and I must admit that I have not been able to find it. I wish that Dr. Cobbold were here because he might be able to contribute to the discussion on this matter.

However, even if a 100 Å domain structure is present, this still does not clarify the structure of these 100 Å domains or their relationships to each other or to the larger-scale structure. I believe that this is the morphologically interesting, fundamental problem remaining at the present time. I want to note that these are within the 1000 Å particles and that it is not a problem of their growing to the 1000 Å particles. I am talking about internal structure within the 1000 Å particles. What can we do about it; what is the problem of direct observations on this scale for poly(vinyl chloride)? The particles with which we normally deal are about 1000 Å in size, and, since poly(vinyl chloride) has a high scattering power for electrons, with the normal electron microscopes it is difficult to take a 1000 Å particle and see through it. I think, though, that techniques are available to do this–thinking, in particular, of the new scanning transmission electron microscopes which can get through samples of this thickness. I look forward too to the application, for instance, of dark-field microscopy to some of these particles, of cold-stage techniques, and others, that are now available to look at structure of polymers in the sort of situation we are discussing.

I look forward especially to looking at PVC in the same way as we look in Fig. 5 at polytetrafluoroethylene emulsion particles. This is a dark field micrograph of polytetrafluoroethylene. Fortunately, it is a sample which is highly crystalline. We are looking at it by dark-field microscopy so that the bright regions are the individual crystals of polytetrafluoroethylene inside the emulsion particle of the PTFE. If we can do this for PVC–and the possibilities are now available, in terms of equipment–this will go a long way towards solving what I regard as the fundamental problem in understanding the polymerization process of PVC, how the molecules are getting together within the 1000 Å size particle. We are beginning to try to do it ourselves, and I suggest to people here, both those in industry and in academia, that they also begin to try to do it.

Dr. Berens: Turning to the relations between the morphology and the polymerization kinetics, Dr. Ugelstad has considered this point and will comment on the mathematical models for polymerization particularly attempting to relate this to particle formation in polymerization.

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