General Discussion

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Dr. Park (University of Wales, Cardiff, U. K.):   I should like to
take up a point about the two phase-model. It seems to me that all
the varieties of this assume something rather peculiar about the
initiation. I may be wrong. But is it true that the initiation is
assumed to be uniform throughout the whole system?
We are really interested in polymerizations that are occurring by
the decomposition of initiator, and initiator can wander around from
the liquid phase to the solid phase. Some years ago we carried out
some experiments which we were inclined to disbelieve at the time,
but perhaps they may be right. Using carbon-14-labeled initiator, we
tried to estimate the amount of benzoyl peroxide in a benzoyl peroxide-
initiated polymerization of vinyl chloride. We estimated the amount
that had gone into the polymer phase and found that at a fairly early
stage in the polymerization almost all of it had gone into that phase.
Unfortunately, we have not had the time to repeat these experi-
ments, but I suggest that it is important to do so. Those of the
audience with time available should look into it because this would
vitiate the two-phase models which have been produced so far.

Prof. Ugelstad (University of Trondheim, Norway):   According
to Talamini's model, it is extremely important where the initiator
is situated, but with my model it is of no importance, because all
radicals, whether produced from the initiator in the polymer phase
or the liquid phase or present in the particles, are from low conversion.

The reaction takes place in the particles wherever the initiator may
be. Of course, this is also true with Olaj's model, because with that
model it is stated that wherever the radical is produced it is trans-
ported at a very low conversion to the polymeric phase.

Dr. Park's observation is thus in favor of the models of Olaj or
myself–I do not know which he prefers. It is not so much in favor
of Talamini's model.

Prof. Olaj (University of Vienna, Vienna, Austria): A critical
point in our model is that the radicals, wherever they are formed,
have to contribute to the polymerization within the polymer particles.
This means that the radicals formed by the decay of initiator in the
monomer-rich phase have to be transported to the polymer particles
without any substantial loss. According to Dr. Park's, findings most
of this burden is taken from our model. If the initiator is already
preferentially in the polymer phase, the radicals which it produces
do not have to be transported there, so Dr. Park's findings add to
the reasonability of the above-mentioned critical assumption and,
accordingly, of our model as a whole.

Dr. R. R. Smith (Lancaster University, Bailrigg, Lancaster, U. K.):
We have been following the course of polymerization in some detail
over a considerable conversion range. Could we turn our attention
for a moment to polymerization at about 0.5% conversion? By that
stage we have–using Prof. Geil's phrase–a sort of nucleating precipi-
tate of about 100 Å in size, which is growing.

Do we conceive at that stage that that nucleating precipitate is
swollen with monomer and that the monomer is polymerizing within
it? We have heard from several speakers that, as the particle grows,
the inside becomes dead. I wonder when does it become dead?
Before it dies, when the monomer inside it is polymerizing–when it
becomes polymer, of course, it will attract more monomer thermo-
dynamically–we are faced with a rather interesting situation, in that
the crystallized nucleus of perhaps 100 Å is now being extended
spherically. We have found that, on stretching of PVC in this kind
of condition, a fibrillar crystallinity appears. Does this kind of
situation occur, does it then choke itself, after which further polym-
erization is on the outside of the growing particle which might have
to occur by a series of rather similar distinctive spots?

Can the panel, or perhaps Dr. Boissel comment on that?

Prof. Geil (Case Western Reserve University, Cleveland, Ohio,
U. S. A.):   I cannot comment on this. Dr. Boissel indicates to me
that he cannot either. As I think I said, this is one of the major
questions: what is happening to the molecular organization morpho-
logically inside this 1000 Å particle, beginning with the 100 Å and
from then on?

Prof. Ugelstad: Perhaps I have slightly misunderstood something
that was said. Is it correct that the reaction should take place in an
outer shell of the particle and not within the total particle? I under-
stood that this is something which happens at low pressure, not
during the polymerization itself. There is no reason why it should
take place in an outer shell. There is no thermodynamic reason
for having a shell at all, in fact, in these particles. Thus, the reaction
takes place through the whole particle, in my opinion. This shell
theory was suggested by Williams for styrene, but there it was with
water, so that there were some thermodynamic reasons for suggest-
ing a shell, that is, the loss of entropy for a polymer chain at the
interface.

In bulk polymerization, however, there is no such reason. We
must also take into account the fact that the Flory-Huggins interaction
constant is relatively high and will determine the whole situation.
This shell theory in PVC bulk polymerization is a concept in which I
do not believe.

Dr. Berens (B. F. Goodrich Co., Brecksville, Ohio, U. S. A.):
I agree that there is no obvious reason, whether from diffusion rates
or thermodynamics, why the assumption of a uniform monomer con-
centration through the particle should not be true. Yet this remains
an assumption which has not been validated experimentally to my
knowledge—that is, measurements of the actual concentration of vinyl
chloride in the PVC phase during polymerization are not published
anywhere in the literature.

Perhaps I may comment that some of our own data on the emul-
sion polymerization of vinyl chloride clearly show from measure-
ments of the conversion at which pressure drop occurs that with
increasing size of the emulsion polymerization particle there is
definitely a deficiency in monomer concentration below its equilib-
rium value. Therefore, at least in emulsion polymerization, we are
dealing with a situation in which the monomer concentration in the
particle is not at its equilibrium value. Again as Dr. Ugelstad men-
tioned, the same is apparently true in polymerizations in which
monomer is added later during the polymerization.

Dr. Boissel (Rhône-Poulenc Industries, Aubervilliers, France):
I did not say anything about a dead region in particles, or about crys-
tallinity of particles. An important point here is the problem of
observation of particles swollen with monomer. Some authors have
given us photographs of PVC particles, but what about the disappear-
ance of vinyl chloride monomer?

Dr. E. Sorvik (Polymer Group, Gothenburg, Sweden):   Ravey et al.
[J. Polym. Sci., 12, 2821 (1974)] have reported that lauroyl peroxide

was excluded by the polymer gel. This is in contradiction to what has twice been mentioned at this meeting. Could it be possible that different initiators have a different chance of entering the gel, in this way giving us different initiating situations?

Dr. Park: May I say that our experiments were confined entirely to benzoyl peroxide. I agree with the last speaker that it would be extremely interesting to investigate a number of different initiators.

Dr. Berens: The question at issue here is the monomer distribution through the phases, whether the monomer concentration is at its equilibrium value within the polymer phase. Does anyone have any further evidence on that?

Dr. Weinlich (Hoechst A. G., Gendorf, West Germany): In connection with the film shown by Dr. Berens this morning, concerning the antiparticles as defined by those holes built by double emulsions, what significance is there in this double emulsion system for primary particle kind, size, and number and also on the rheology of these products derived from these holes?

Dr. Berens: The observation that these large holes are lined with a skin gives a good explanation for their formation. I am not aware that any practical value has been demonstrated for these large hollow particles. Perhaps Dr. Collins could comment on that point too?

Dr. Collins (Goodrich Chemical Co., Avon Lake, Ohio, U. S. A.): That is a difficult question to answer, depending on what the material is being used for. It is well known that the porosity of PVC is an important property and a difficult one to measure. When we start to talk about "particle porosity" we still do not quite know how to measure it, so we always measure an average porosity. Even the interpretation of mercury porosimeter curves is difficult and questionable.

However, I would say that the larger voids, especially when they are open, can probably lead to problems or artifacts in terms of rheology, plasticizer uptake, fusion, compressibility of the particle, and so on—all these things which have an effect on particle flow, whether in the powder form or in the fusion time on the mill and so on.

Dr. Chartoff (University of Cincinnati, Cincinnati, Ohio, U. S. A.): I want to raise a couple of questions about polymer morphology in the primary "suspension" particles. I am interested in hearing anyone's ideas about the existence or nature of the film or membrane surrounding the primary particles which are together in clusters of

about six primary particles within the larger commercial suspension particles: what holds these particles together, how are they formed, and what clues they provide about the original formation of the particles themselves. In our scanning electron microscope studies we notice that there is some kind of membrane around particles which looks like a film. This seems to be holding the particles together.

Secondly, in the particle size distribution studies we have done on several commercial suspension samples there is always a very large population of extremely small particles in the system. There is some reason to believe that they are similar to emulsion particles—in fact, they may even be emulsion particles. Clearly, there is a very fine dividing line between emulsion and suspension polymerization.

We have found that on fracture surfaces of PVC extrudates (viewed with the scanning microscope), these seem to be the last particles that fuse. I wonder whether anyone else has observed this kind of behavior and what kind of comments there might be about the formation of these particles. Has anybody noticed whether such particles possibly contribute to difficulties in fusing PVC or to problems with mechanical properties of extruded rigid PVC?

Prof. Geil: To my knowledge, I am not aware of any published evidence of a film around say, the 1000 Å particles—which is what I think Dr. Chartoff is calling "primary" particles. The film that I have seen is usually around the larger, 100 μm particles. There may be a film around the 1000 Å particles; if so, the questions to ask are what is it and why is it there.

Dr. Chartoff: I think we have seen evidence of that in some of the photographs which have been presented today—at least, that is the way I interpreted the photographs.

Prof. Geil: I do not see how it could be seen by scanning electron microscopy because this looks at the surface only. Something in terms of a section is required to be able to see a film around the surface because the film is on the surface. As to what holds the primary particles together—the 1000 Å particles into rather larger agglomerates inside the 100 μm particle—from what I have heard today this is the result of some of these particles growing together. I raised the question whether they still serve as individual flow units or something like that, or whether they then act as a larger particle in subsequent processing. I presume that is what holds it together. Perhaps other people could comment.

Dr. Chartoff: We have cut some of these primary particles and looked inside them. There seems to be some kind of shell around the primary particles.

Dr. Pompon (Rhône Poulenc Polymères, Saint Auban, France):
I was extremely interested in Dr. Olaj's results on the swelling of
PVC by its monomer. Have other laboratories done any work in this
field of swelling, especially swelling during polymerization, and on
the behavior of the polymer after swelling by monomer?

Dr. Berens: Has anyone made any measurements of the degree of
swelling of polyvinyl chloride by monomer under polymerization
conditions?

Prof. Hamielec (McMaster University, Hamilton, Canada):   Our
measurements are probably indirect ones. One of the parameters
in the Talamini model is the solubility of the monomer in the polymer.
In order to fit the rate curves, this is one of the parameters for which
we search. Thus, we have solubility values at three different tem-
peratures, 30°C, 50°C, and 70°C. These values are in reasonable
agreement with your measurements. I do not think that one would
recommend this as a technique with which to measure solubility of
the monomer.

Dr. Liegeois (Université de Liège, Liège, Belgium):   In order to
apply the model I showed earlier, it was necessary to know the mono-
mer concentration in the polymer phase. We know the results from
measurements in emulsion systems made by Dr. Gerrens, who found
a fairly high value of χ in the Flory-Huggins equation (0.88). There
are also data on dry powder by Dr. Berens giving about the same
figure.
    I have made some measurements and I looked for the best fit of
the Flory-Huggins equation on 12 points, obtaining about the same
value for χ (0.91), but with a fairly large standard deviation (about
0.05). The disagreement of the experimental data with the Flory-
Huggins equation is the greatest for the lowest value of the partial
pressure of monomer. I have tried to explain this disagreement by
including an additional term to the Flory-Huggins equation, using
the Flory-Rhener theory which applied for rather crosslinked systems.
I had then as additional parameter, the average molecular weight be-
tween two crosslinks.
    I have not obtained sufficient data to know whether such model fits
better the existence of a certain number of crosslinks in the PVC,
which could arise from the slight degree of crystallinity, or something
similar. I mean that there are not sufficient data to check such a model
from a statistical point of view. Nevertheless I obtained a better fit
with the Flory-Rhener equation which contained an additional term,
than with the Flory-Huggins one, for those points at the end of the
curve. Of course, more experimental data and more precise data
would be necessary to investigate this further.

Prof. Olaj: We started this work on the swelling of PVC about eight or nine years ago. The only data available at that time were based on that high value of Gerrens. As far as I can remember, however, Gerrens never calculated this χ value for himself. It has been calculated since then from his data by other people. I think this is the reason why this χ value gives a rather good estimate because his data have been transformed into the χ value and then transformed back again. If the χ value had been measured by an independent method the result would probably have been worse.

In reply to Prof. Hamielec's question, as far as I know, at the time we started our work no direct evidence was available that anyone had tried to make measurements of swelling of PVC. The great difference of PVC as compared to other monomers is the high volatility of vinyl chloride, so that experimentally it is much more difficult to measure its swelling in the monomer form. That is the simple reason why so few data on the swelling of PVC were available then. Fortunately, more data are available now, for instance, those of Dr. Berens, which are in quite good agreement with our results. There is also quite a lot of indirect information from the pressure drop in suspension polymerization, so the problem is solved to a certain extent.

Dr. Berens: I am interested in Prof. Olaj's detection of a difference in solubility with polymerization temperature, syndiotacticity, or molecular weight, whichever is the controlling factor. In our own work, in the rubbery state above T_g and at low pressure of monomer, there was no difference among the materials covering the commercial range of molecular weight. We detected no variation with a range of polymerization temperatures from, say, about 45°C to 65°C or 70°C.

Prof. Olaj: Principally it should be possible to distinguish between the two possible reasons for the difference we observed between the two samples if samples of different molecular weight prepared at the same temperature (e.g., by using a chain transfer agent) or samples of the same molecular weight, prepared at different temperatures, are compared. In our case, the sample with a degree of polymerization of about 900 had the lower degree of swelling, while the lower molecular weight sample (degree of polymerization ca. 450) showed a significantly higher degree of swelling. At present I cannot distinguish whether this difference results from the difference in molecular weight or from the difference in the temperature of preparation, independent of molecular weight, which, of course, has been the lower one for the higher molecular weight sample.

The most important point is to investigate and to measure the swelling behavior of the samples at exactly that temperature at which

the samples have been prepared. This will give us the quantity we
are in fact concerned with in polymerization kinetics.

Prof. Hamielec: I am interested in new models published in the
literature because I should like to use the best possible model for
practical calculations. Dr. Liegeois has developed a new model for
the emulsion polymerization of vinyl chloride. I would ask him
whether, before he publishes this model, he plans to compare his
experimental results with Ugelstad's model? It needs a very careful
comparison to convince me that one is better than the other. If
Dr. Liegeois publishes his model without making such a comparison,
I would have to do this work-and I think he is more capable of doing
it than I am.

Dr. Liegeois: I have already done what Prof. Hamielec asks me
to do. I have used Prof. Ugelstad's model with my data, his model
with his own data, my model with his data, and my model with my own
data—there are four possibilities. When I apply statistical tests under
such conditions I cannot reject any model. The only aspect of Prof.
Ugelstad's model which does not satisfy me is that it is unable to give
values for the monomeric radicals concentration, and I need those
values for studying such phenomena as nucleation or copolymerization.

Of course, I am not suggesting that Prof. Ugelstad's model is wrong-
I never said that—but there are some aspects of it which do not satisfy
me in its treatment of the data. The point I have just mentioned is one
aspect; there may be others, but they are less convincing. For
instance, Prof. Ugelstad derived the steady-state equations with
respect to the number of particles containing such a number of radi-
cals. If we do not want to deal with populations of particles of differ-
ent kinds on that basis, we have to formulate the problem on another
basis. That is why I derived the steady-state equations with respect
to the actual radical concentrations. I think that is the main difference.

Prof. Ugelstad: In the preprint of Dr. Liegeois' paper it is
stated that our model does not take into account the fact that the mono-
mer radical which is formed probably has a lower reactivity than the
polymer radical. That is an incorrect statement, because we have
repeatedly drawn attention to that fact in published reports.

Secondly, using our model we have proposed and calculated par-
ticles with one monomer radical, one monomer and one polymer
radical, two polymer radicals and so on. Our model contains a term,
$(V_p/k_t)^{1/2}$, and we find that if the particle number is lowered such
that this term becomes the dominant one, we obtain the same termina-
tion constant as with bulk polymerization.

We have tried different shell models and different theories for

these shells. If we accept a shell and that its thickness is propor-
tional to the radius, it is impossible to distinguish kinetically the
shell theory from the bulk theory because there is then a constant
with which to multiply each term. Therefore the experimental re-
sults show that if there is a shell, its thickness must be proportional
to the radius of the particle. What is the shell? The shell suggested
by Williams was a thermodynamically defined shell which he calculated
on the basis of a low conformational entropy at the interface. That is,
a molecule which is at the interface will not have the freedom of all
conformations, therefore it will lose entropy.

     This leads to the formation of a shell consisting of pure monomer
which only varies little with the size of the particle. Williams'
theory was based upon results with styrene. The thermodynamic
arguments of Williams have been heavily criticized, as has also his
interpretation of the experimental results as evidence for a shell
theory. For vinyl chloride the probability of a shell of monomer
should be less than for styrene. Most probably, the reaction takes
place throughout the particles in bulk polymerization. As stated
above, neither in case of emulsion polymerization is there any need
for a shell model.

     Dr. Liegeois: It is true that there is an incorrect statement in
the preprint of my presentation, but the conclusion remains correct.
The incorrect statement is when I said that Prof. Ugelstad's model
did not consider difference of reactivity of the macroradicals and
of the monomeric radicals respectively. I agree that it does, as
reported in his second paper, but not in the first one. This second
paper was published in the British Polymer Journal (see Appendix A).

     However, as I said, the conclusion I draw from that remains true:
because we do not have the numerical value of the monomeric radi-
cals concentration, it is impossible to apply such a model to copolym-
erizations, for instance. With regard to the shell, the reason why I
considered a shell was not the same reason as that described to us
by Prof. Ugelstad in terms of Williams' theory, but comes from the
following considerations. Because initiation occurs in water, and
because the macroradicals are not soluble in the monomer—in the
particles—they will remain close to the surface. There is a type of
radical arising from the transfer but, as Prof. Ugelstad suggested—
and I agree with him—such radicals rapidly escape from the particles.
I say that they escape rapidly from the shell, but it is really the same
thing; they escape rapidly to the aqueous phase, coming back in the
particles re-initiating a polymerization chain. Since this new chain
is also insoluble in the monomer, everything remains in an outer
shell because nothing can diffuse into the inside core of the particle.

That shell is not defined thermodynamically—I agree with that—but it is related to kinetic phenomena because of which the active species appear to remain in a shell, or in a thin section outside the core of the particle. Due to kinetic considerations there is no time to migrate to the inside of the particle.

We then have to include parameters which define the geometry of the situation. I agree that this point is rather semi-empirical in nature.

Prof. Hamielec: A few years ago we investigated the emulsion polymerization of vinyl acetate in view of the core/shell model. This is an interesting system because transfer to polymer is important and there is long-chain branching. In that system, had there been a core and a shell, and the polymer been generated in the shell, the chains would have been linear. For all conditions studied we obtained very highly branched polymer, suggesting to us that polymerization must have occurred throughout the polymer phase where high concentration of polymer and long-chain branching possibilities exist. Of course, this is a different monomer system.

Prof. Olaj: It is very hard to understand why the thickness of a shell which is established by kinetic control should be proportional to the radius of the particle. Is there any reasonable explanation for this assumption?

Dr. Liegeois: That is a good question. From the point of view of answering it, I have not yet finished the work on it. The real picture of the system will probably be never known, but we need a model which satisfies enough. Two different possibilities are, first, that it is assumed that the thickness of the shell is constant and, second, it is assumed that it is proportional to the diameter. We can think of many other such assumptions which could be made. Both these two assumptions apply in this case, with respect to the statistical tests. Nevertheless I could not retain the model in which I made the thickness constant assumption because it was not possible to apply it for the nucleation processes. At the very beginning, I had a thickness of say 50 Å, greater than the particle radius itself.

Let us, therefore, consider now the second possibility; that the thickness is proportional to the diameter. The next picture I will try, which needs one more parameter, calls for a variation of the thickness of the shell. It would be initially proportional to the diameter when the dimensions of the particles are of the same order of magnitude as the macromolecule itself and then, more and more constant for larger particles. Another possibility is the thickness of the shell to be proportional to the square root of the molecular weight of the polymer molecule produced. I explain why I suggest this assumption. I have made measurements of the sulfate groups

derived from the initiator, sulfate groups which are attached to the polymer at the surface of the particles, by the method of J. W. Vanderhoff, involving washing the latex with an ion-exchange resin and titration of the monosulfuric groups. The comparison with the total amount of sulfate present in the polymer shows that 15 to 25% of the sulfate groups are located at the surface of the particles. This means that when a new chain (oligomeric) approaches a particle, the sulfate end turns backward, and the growing end toward the inside of the particle. A monomer radical coming from the transfer reaction will have to travel a distance which is proportional to the end-to-end length of the macromolecule. This is schematic, of course, but it might be interesting to apply the model to experimental data of polymerizations run in a wide range of temperatures.

I agree that the assumption that the thickness of the shell is proportional to the diameter, although it works reasonably well, does not have an actual physical significance.

Prof. Ugelstad: We could continue discussing this for a long time. But I will merely point out again that we do not have to use the shell theory, but that there is a very good model if we consider it happening throughout the whole particle. If we use a shell theory we have to take the shell proportional to the radius. This means that the different terms simply have to be multiplied by constant factors. It is not possible to make any differentiation and there is no absolute proof of the existence of the shell.

I should like to remind everyone about some of the interesting work we have heard described, for instance, Dr. Palma's work in which he found the important fact that in bulk polymerization extremely small particles are being formed, about 100 Å. There is also great interfacial energy. I have heard no one talk about the interfacial energy produced in bulk polymerization. I always think of it in connection with emulsion polymerization—as I am an emulsion polymer scientist—but it also occurs in bulk polymerization.

Another interesting phenomenon is that azobisisobutyronitrile was found to stabilize small particles. Is it really azobisisobutyronitrile, or is it a growing radical formed from that compound? Did I understand correctly that this was done by radiation polymerization with azoisobutyronitrile at such a low temperature that there was no decomposition of it, yet it was still found that this initiator had a stabilizing effect on the small particles. That is a most interesting effect.

May I also remind everyone of Dr. Park's finding that benzoyl peroxide was also present in the polymer phase after low percentage conversion. For simple thermodynamic reasons it is very unlikely that it really is in the polymer phase, but it is probably just at the

interface. It would be interesting to hear some comments on the interfacial tension that occurs in bulk polymerization; nobody has mentioned this, as far as I am aware.

Dr. Palma (Montedison, Porto Marghera, Venice, Italy): I have no further comments to make, rather I would like to hear other people's views.

Regarding our experimental evidence, it can be said that in the radiation-induced polymerization of vinyl chloride the polymer particles do not remain in a dispersed state in the monomer. They are being formed at so large a size that they undergo a rapid sedimentation on to the bottom of the container, where they cement together and are no more susceptible of dispersion. However, if some amount of azobisisobutyronitrile is added, in the polymerization carried out at 20°C, at which temperature it does not act as an initiator, there is formation of a homogeneous latticelike dispersion, lasting for some time as such, unless the system is made to undergo immediate sedimentation by agitation. Hence, we could conceivably assume that this initiator acts as a stabilizer of the dispersion and is prevalently located at the polymer particles surface. Supporting this hypothesis there are, first, that the initiator is not soluble in the polymer phase, as reported by Ravey et al. in 1974, and secondly, that it is not very soluble in the monomer either. However, we have no direct experimental evidence for this hypothesis.