Pure & Appl. Chem., Vol. 53, pp. 729-731.
Pergamon Press Ltd. 1981. Printed in Great Britain.

0033/4545/81/030729-00$02.00/0

CONCLUDING REMARKS

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Professor G Smets initiated this Symposium in fine style, giving a clear explanation of the contribution that Bam has made to polymer chemistry over the past 40 years. Then like a well-behaved initiator he promptly departed from the system. Nevertheless, we were very fortunate to have Smets's contribution because it clearly identified four major themes in Bamford's work:

- alpha amino acids,
- the concept of restricted mobility,
- kinetics of free radical polymerisation,
- new free radical initiators

As the terminator of the proceedings, I do not propose to hold a wake for Bam but much more, as he would have it, to look forward to new work that we can expect in the field of Polymerisation Mechanisms. For this is an area which continues to be of extreme importance in polymer science and in material science and technology more generally.

Looking back over the Symposium one can make a broad observation. We clearly know a great deal about the qualitative aspects of Polymerisation Mechanisms, and there is also a substantial amount of quantitative data in the form of rate constants and reactivity ratios, etc. But the papers by O'Driscoll and Eastmond point to the need to have much better information on reaction kinetics, in particular, to have some precise measurements of rate constants. This is, in fact, something that Bamford himself has been advocating for the past three years. At the Molecular Division of IUPAC meeting in Warsaw in 1977 he pursuaded Commission IV.2 to set up a new project on kinetic parameters. This project envisages culling from the literature the information on rate constants that is already available, assessing its reliability, and then going on to make some measurements of some of the basic rate constants which are still not available to a reasonable degree of accuracy. These data could be extremely important from the point of view of new developments in the study of Polymerisation Mechanisms, and more particularly in the use of our knowledge of Polymerisation Mechanisms, to make polymers tailored to particular specifications. Let me be quite clear on this point, I think it is to do with molecular engineering that the need for these data arises. It is not likely to have such major impact on the chemical engineering of large plants which produce high tonnage polymers because there the engineers will always optimise that plant on parameters which are not obtained at a molecular level but rather describe the performance of the overall system. In production it is the efficiency of the plant, the quality of the product, particularly with regard to subsequent processing, and hence the morphology of the product, that is of prime importance. All of these things are not simply related back to the basic kinetic constants in the polymerisation process at the molecular level.

Confidence that there will be a continuing need to study polymerisation mechanisms arises from two basic reasons:

First, the basic understanding of polymerisation processes that lead either to synthetic or to natural materials is bound to be a subject of continuing interest, not only from a curiosity point of view, but also from what it tells us about the performance of materials and about the way in which living organisms grow.

Second, there is a need as never before for specialised materials with unique physical properties for technological applications and this generates the need for new polymer molecules and for old polymer molecules made to tighter specifications, particularly with regard to the control of structure.

If we look briefly at the situation in the field of high tonnage polymers, then it is pretty certain that in the next decade there will be no really new polymer introduced into the market. But that is not to say that there will not be continuing refinements of the existing high tonnage materials that are sold. Take, for example, Polyethylene and Polypropylene. Each polymer is really a family of products and there is fierce competition between the manufacturers and there is a continual need to refine these polymers for the general applications. Industry is continually searching for initiators that will give even higher mileage catalysts, for chlorine-free routes to their polymers, and to initiators that would allow a given plant to be used for a variety of products from the same general group of polymers, eg polyethylenes of varying densities. Solvent free processors with initiators which produce the polymer in a suitable particular form with the desired morphology is also another major target. There is much to be done and although we have a general understanding of some of the mechanistic factors involved, there is really only a very loose coupling between the actual polymerisation mechanisms and the nature of the product obtained in many of these processes.

But the particular remark I want to make in this summary applies to the lower volume, speciality polymer products which are needed for a variety of uses, eg chemical effects applications, electrical and optical applications, special films and selective membranes, biomedical applications, etc.

This conference has concentrated mainly on the Kinetic and the Chemical aspects of Polymerisation Mechanisms. Only in the papers that dealt with Template Polymerisation was there much discussion of the physical organisation of the reacting systems during the polymerisation process. For example, Kabanov and Challa's papers mentioned structural considerations before going on to a more detailed consideration of the kinetics of polymerisation. So I hope that when a symposium is next organised in honour of Bamford we will have taken a major step forward and the meeting will include a greater emphasis on the polymerisation of monomers in physically organised systems.

In one sense the paper by Eastmond touches on the physical organisation of the product but there is a growing volume of work on polymerisation mechanisms in which the monomer is ordered first before the polymerisation reaction is induced. The idea being to produce the end product with the necessary anisotropic properties through the molecular arrangements of the polymeric product.

There is, of course, a considerable amount of work already started in this field that could be cited. To take one example, the work of Ringsdorf at Mainz on polymerisation of systems containing mesogenic units giving rise to polymeric liquid crystals, in which the liquid crystal units are either in the main chain or in the side chain, according to the type of reaction. These liquid crystal units then are self-ordering to produce useful optical properties. Ringsdorf is active too in the polymerisation of diacetylenes at interfaces and also in the making of monolayers and multilayers from monomers which can be subsequently polymerised. Lando at Cleveland is doing similar work on the structure in polymerised multilayer films. Friedlander in North Carolina is looking at the control synthesis of polymers in chemisorbed complexes and in Italy, Ferina is polymerising butadiene in clathrates so that he could produce molecules that are initially not entangled. There has been considerable progress too in the polymerisation, of monomers in single crystals to form polymer crystals of controlled structures. Dr Baughman, for example, has pointed out that in such cases in order to retain steric control during polymerisation , one must find monomer crystals which have the same density as the polymer crystal which is produced as a result of initiation. Otherwise the usual change in volume which occurs destroys the selectivity of the steric control during reaction. And again in work of this kind one sees some of the ideas of template polymerisation originated many years ago by Professor Bamford emerging in a more refined and sharpened form. One has to admit, however, that many of these new polymerisation mechanisms will be a great deal more difficult to perfect than the type of mechanisms that were discussed during this symposium.

Difficult though it may be, there is no doubt that in order to achieve the anisotropic physical properties that will be demanded from specialised materials by the new emerging technologies, for example, in microelectronics, in special forms of integrated optics, and so on we will have to apply physical organisation of the starting material, principally the monomer with the perfection of the polymerisation mechanism so that one obtains the product in situ.

The very last paper by Segeusa has shown in a particularly elegant way the use of good organic chemistry introducing relatively unfamiliar elements (in this case Phosphorous) into the polymer structure. Clearly new polymers containing elements rarely found in synthetic structures could have an important impact on the search for new materials. But it does turn on an appreciation of polymerisation mechanisms and the careful selection of main chain chemical structure. Many will recall the fruitless efforts of the late 50's and 60's to produce 'Inorganic polymers.' The products often lacked hydrolytic stability and sometimes thermal stability and often this might have been expected on the basis of what was already known about the nature of some of the bonds which were intended to be incorporated as main chain bonds.

You will be aware from the way Professor Bamford has participated in this conference that he intends to remain an active research worker. That is to say, he will emulate an amorphous polymer and under go a second order rather than a first order transition. We hope that the change in activity will be barely perceptible as is often the case when polymer properties are measured in the region of a second order transition! Then he will continue to play a leading part in unravelling more mechanisms just as much as we see clearly that his work on template polymerisation and copolymer systems provides a launching pad for some of the developments I have envisaged in these closing comments. We all wish you well Bam.