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Preface

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Preface

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The Third International Symposium on PVC (Case Western Reserve University, Cleveland, Ohio, August 11-15, 1980) followed those held in Prague, Czechoslovakia in 1970 and in Lyon, France in 1976. First some brief statistics. The number of registered participants increased at each successive meeting from 240 to 360 to 450, indicating in part the increased interest in the subject. The participant mix was considerably different in Cleveland, with about 175 foreign and the balance U.S. This is in contrast to only a handful of American participants at both Prague and Lyon.

In Prague, the number of papers presented was not so large, so that in addition to the main lectures published in *Pure and Applied Chemistry*, one issue of the *Journal of Applied Polymer Science* contained the remaining papers. There were no parallel sessions, and two hours were reserved each day for general discussions. In Lyon, the figure was eight special issues of the *Journal of Macromolecular Science*, four in chemistry and four in physics) in addition to the main lectures published in *Pure and Applied Chemistry*. One half-day with five parallel sessions was held and approximately one hour of general discussion was reserved for each of the eight topics. In contrast, there were 110 papers presented on seven topics in Cleveland. This large number required parallel sessions two afternoons to accommodate the large number of papers. The format was changed to include discussion at the time of each presentation. As before, the invited lectures have been published in Pure and Applied Chemistry (February 1981). Many, but not all, of the contributed papers are included in these issues of Journal of Macromolecular Science (Chemistry and Physics), with papers in the field of environmental effects, flammability, and recycling being published as a unit in Journal of Vinyl Technology.

Much like the meeting in Lyon, topics from polymerization through combustion were reviewed. Some special attention was given to PVC compounding, alloys and blends, and environmental effects. The interest in basic studies of PVC at universities has increased significantly in the last four years, probably the result of the increased attention focused on PVC at previous IUPAC meetings and the increasing importance of this commodity. The highlights and problems related to the various topics are now considered briefly.

In the field of polymerization, two new results have emerged. First is the recognition of the colloidal nature of the suspension polymerization process due to the stabilization of the primary particles by electrical charges. This new domain of investigation, opened primarily by E. L. Zichy in England, employed the very sophisticated new technique of quasi-elastic light scattering and cast a bridge between the suspension and bulk process, on the one hand, and the emulsion process on the other. Hence, the DLVO theory of particle stabilization will have to be applied. The presence of electrical charges in the suspension droplet was illustrated quite convincingly using electrophoritic techniques as shown in a film by J. A. Davidson and co-workers. A number of problems, however, still remain, such as the origin of the charges (the formation of HCl needs to be studied in more detail in that connection), the mechanism of nucleation, and the formation of the microdomains inside the primary particles.

The second important advance is the recognition of the nature of the mechanism of chain transfer to monomer. It is well known that the molecular weight of PVC is controlled by the polymerization temperature through a monomer chain transfer process. The mechanism, however, has been subject to question. The transfer constant is actually very high compared to similar monomers, such as vinyl acetate. The analysis of chain ends in low-molecular-weight fractions led to the conclusion that these, as well as the short-chain branches, were produced by a ramification of the head-to-head addition, followed by a chlorine atom shift yielding a rather unstable radical which may decompose to produce a chlorine atom radical. The latter will reinitiate polymerization to give the 1-2-chlorinated saturated endgroups rather frequently.

All consequences of this mechanism are not fully understood nor investigated. Thus the excape of this very labile chlorine radical from the polymer phase (or particles in the case of emulsion polymerization), the possible formation of HCl through abstraction of a hydrogen atom, and finally its transfer to polymer to produce long-chain branching remain to be resolved.

Some additional points concerning the polymerization are a better understanding of the formation of the internal morphology, the attention paid to the thermodynamics of the polymerization, mostly concerning the partition of the monomer, and finally the attention paid to the last stages of the polymerization process and more specifically to the polymerization under subsaturation pressure.

Numerous important advances have been made in the field of characterization, primarily of the chemical structures. These advances materialized for two main reasons: the use of more sophisticated instruments such as high-resolution proton and ^{13}C NMR and the cooperative work of the IUPAC working party on thermal stability initiated by A. Michel, CNRS, France.

In the study of chain configuration, analysis has been made up to the heptade level and led to a very important result, namely, for the whole range of commercial polymers, chain propagation obeys Bernouillian statistics; hence simple calculations can be safely applied.

Definite statements concerning short-chain branching were made and reliable methods to investigate unsaturation (both total and internal) are in hand. However, some problems remain concerning the chain ends, the long-chain branching, the labile chlorine atoms, and the tertiary chlorine atoms for which contradictory statements have been made. For the PVC area, such controversy has not been unusual. Advances concerning chain conformation have also been made using IR and Raman spectroscopy.

Crystallinity of PVC remains a problem, although evidences have been shown for different kinds of crystallites. We continue to need improved models for PVC crystallites as well as for understanding of their relationship to configuration and conformation and their contribution to the organization of the microdomains.

At the supermolecular level, it is clear that significant advances have been made concerning the morphology and its consequences for processing and ultimate properties. The need for further work in this area was a strong recommendation put forth at the Second International PVC meeting held at Lyon. First of all, it was obvious at this meeting that the nomenclature proposed by P. Geil in Lyon, after a general discussion, had been accepted by most of the authors.

Second, more and better evidence for the existence of microdomains has surfaced. The use of a suitable plasticizer has led to improved contrast between the microdomains and the amorphous phase as shown by the work of H. E. Bair et al. at Bell Laboratories. It would appear interesting to understand that strong similarities exist between the plasticizers, the processing aids, and even with compatible polymers (or copolymers) concerning their localization first between the primary particles and at a later stage of penetration between the microdomains. These kinds of studies have shown other aspects of the microheterogeneity of PVC as, for example, evidence shown for a high-temperature second T_g by the use of a small amount of a suitable plasticizer. Understanding this phenomenon, however, remains to be determined.

Several papers stressed the importance of morphology and the relationship to plasticizer adsorption—the so-called dry-up time. Some evidence that the plasticizer adsorption characteristics can be influenced by polymerization additives or techniques by their effect on the dimensions of internal solvation sites and microstructure was also reported, but here, too, much more work is necessary to understand the mechanism and reduce this to practice. There is little doubt that this is a fruitful area for future research.

Perhaps the most striking event of this symposium was attention given to morphology changes as related to processing of rigid as well as placticized systems. This was the key to understanding the different aspects of the fusion processes and also the basis for more comprehensive study of the action of lubricants, processing aids, and other compounding additives. Data presented by T. E. Fahey clearly showed that particulate breakdown does not occur in the solid bed in single-screw extrusion of rigid PVC compounds using standard geometry screws. Boundaries remain evident and only upon conversion to melt pool are these boundaries destroyed. Elastic development—a measure of fusion—was shown to occur in both the solid bed and melt pool. New light was also shed on the role of lubricants and additives on the compaction process as related to the processing mechanisms in the feed section of a screw extruder.

New insight into particulate morphology and the fusion process as affected by processing parameters and compounding additives was reported by R. J. Krzewki and co-workers. Evidence supporting different routes to the fused state depending upon the process conditions and the compounding additives was presented for the first time. A laboratory method to follow the extent of fusion was also reported and used to demonstrate the action of specific lubricants on the fusion process.

The area of copolymer blends and alloys was thoroughly reviewed by J. A. Manson of Lehigh University. His discussion reviewed the principles underlying the modification of PVC by copolymerization and blending using current examples such as copolymerization with propylene as a means of enhancing processibility and stability, use of copolymers of α-methylstyrene with acrylonitrile to increase heat distortion temperature, and the addition of semicompatible rubbery polymers such as ABS to improve impact and PVC/EVA systems that improve weathering characteristics. This set the tone for subsequent papers in this session.

In general, our understanding of polymer alloys, expecially those containing PVC, leaves much room for improvement, and this is yet another fruitful area for future research and discussion. Here the problems associated with measuring or assessing compatibility and the morphology are formidable. Some progress nonetheless has been made. In a study of blends of PVC and chlorinated PVC blended also with styrene-acrylonitrile, α-methylstyrene, and ABS, L. W. Kleiner of Diamond Shamrock reported that the mechanical properties could be related to the state of compatibility. In a separate investigation, J. R. Fried and co-workers reported that the Couchman and Fox equations could be used to evaluate the extent of miscibility. The relationship between molecular structure of blending ingredients and processing operations was also a topic of discussion.

Activities concerning the problem of degradation and stabilization have continued to be of considerable interest. However, the mechanisms of thermal degradation remain open to discussion and the prognosis is that this will probably remain so for some time to come. We have, however, made some progress since the last IUPAC meeting. We have realized that the definition of the thermal stability of PVC remains to be clarified. Two particular advances are worthy of mention. First, it has been realized that since thermal degradation is a chain process, it is necessary to consider not only the production of HCl or the development of color but also the individual contributions of the initiation and the propagation reactions. Second, the relationship between the degradation rate and the structural defects is not a good one irrespective of the defects considered and it should be necessary, as pointed out by J. Millan of Spain, to consider the possible contribution of "normal" structures with special conformation.

Once again, as was pointed out in Lyon, only a few studies have been devoted to photochemical degradation and oxidation. Work in these areas should be encouraged.

Concerning stabilization, the previous remark is especially valid for photoxidative stabilization. The basic chemical mechanism for thermal stabilization appears to have been well established, although there is still some disagreement regarding it in stabilization chemistry. More attention needs to be directed to the behavior of stabilizers during processing, following their consumption, etc. to understand why they do not react in the same way as in model experiments. Work concerning the relationship between morphology changes and thermal stabilization also remains to be done.

Special attention was given to environment-related problems. The important area of government regulations was ably summarized by J. Hechman. The VCM problem has received considerable attention so that it is now possible to produce very good resins with less than 1 ppm residual monomer. The striking aspect is that industry has used the opportunity of having to solve this problem to make real advances in the polymerization processes and in the study of the morphology; the work of A. R. Berens deserves special mention here.

On the other hand, the flammability problem remains a major one which is extremely difficult to study and resolve, primarily because the changes in the material during the combustion process are so large that we do not really know what material to work on. This area needs greater detailed investigation to get a more basic understanding of the behavior, the localization, and the structural changes of the additives as well as their synergism.

The problem of recycling of used PVC must be mentioned, and we must realize that it opens a lot of basic problems concerning the blending, processing, and stabilization processes. Very little work has been done, and again the topic may be important for the future.

In conclusion, it can be said that several very important results have surfaced during the meeting. These have enhanced our understanding of some very difficult problems; however, much still remains to be done. The remaining problems, some of which have been identified, fully justify the increasing interest in and research activity being carried out on all aspects of PVC.

It was generally agreed that a fourth international meeting should be organized in four or five years, allowing sufficient time to make significant contributions to our current state of knowledge.