

2nd International Symposium on PVC, Lyon, and other European Contacts, July, 1976

by - A. R. Berens

Lyon PVC Symposium

The Second International Symposium on Polyvinyl Chloride in Lyon, France, July 5-9, 1976, was organized by Prof. Guyot and CNRS and sponsored by IUPAC and GFP (Groupe Francais d'Etudes et d'Applications des Polymeres). The first such symposium was in Prague, 1970, and a third is now proposed for Cleveland in four or five years with E. A. Collins as chairman. Despite the long sessions and discomfort of record-breaking hot weather, the general feeling at the end of the week in Lyon was that the meeting was very worthwhile and successful. The general quality of the lectures and papers was high, and the discussions, both in the lecture hall and outside, were notably open and stimulating.

The symposium was truly international in scope: Attendance was about 350, representing 31 countries. Contributed papers numbered about 100 and came from 23 countries. Interestingly, about 80% of the contributed papers came from universities and institutes, and only 20% from industrial laboratories. It seems that PVC has finally become a legitimate subject of academic research. One might speculate that the PVC industry is doing less of its own basic research and supporting more academic work; yet off-the-record conversations suggest that the amount of basic research in the industry is still much greater than indicated by the relative publication figures.

The technical sessions were arranged into half-days on each of eight general topics: Polymerization, Chemical Modification, Characterization, Rheology and Viscoelasticity, Processing, Properties, Stabilization, and Combustion and Toxicity. In each session there was an invited Main Lecture, a group of contributed papers, and a panel discussion and question period. The main lectures are to be published in Pure & Applied Chemistry and the contributed papers in Journal of Macromolecular Science. The discussion periods were all tape-recorded, and Prof. Guyot, with commendable ambition, has promised to edit and publish transcripts of all questions and comments. I have a bound set of the preprints of contributed papers, and copies of a few of the main lectures and panelists' contributions, for the use of anyone interested.

The most persistent theme through the entire meeting was the importance of particle structure and morphology of PVC. From the showing of the BFG (Collins & Davidson) suspension polymerization movie on Monday morning to the closing comments on Friday, the subject of particle morphology was repeatedly brought up, especially in the sessions on polymerization, characterization, rheology, processing, and properties. Thus the importance of controlling particle structure during polymerization and its effect on subsequent behavior of PVC is now widely recognized and the subject of much research (and more speculation) in many laboratories.

In the opening session, on Polymerization, the emphasis on "nascent morphology" was the deliberate choice of the program committee. Unfortunately, Prof. Arzhakov (Moscow) did not show up to present his invited main lecture; he did send a manuscript, however (I have a copy), which contains some interesting new thoughts on the interrelation of morphology and polymerization kinetics. Contributed papers from ICI, Montedison-Bologna, and Rhone-Poulenc dealt with particle structure development in suspension and mass polymerizations. In other papers and discussion on polymerization kinetics, there seemed to be a growing awareness that polymerization may not occur uniformly throughout the polymer particles, that monomer concentration may not be at its equilibrium level in PVC during polymerization, and that the kinetics may be even more complex than considered in the best current models of Ugelstad, Olaj, Liegeois, et al.

The Chemical Modification session featured a review by Suzuki (Nippon Zeon) of reactions at unstable sites in PVC, and papers on grafting, ozonolysis, chlorination, and cross-linking of PVC. Nakamura (Iwate Univ., Japan) reported on a novel cross-linking agent and stabilizer, 2-R-4,6-dithiol-s-triazine. J. P. Kennedy (Akron U.) discussed his cationic grafts of isobutylene and styrene to PVC, emphasizing the improved stability and processability; he told me he is still most anxious to have BFG carefully evaluate the properties and economics of his products.

The main lecture on Characterization by Carrega (Rhone-Poulenc) and the contributed papers covered molecular (GPC), structural (spectroscopic), and morphological (microscopic and X-ray) investigations. Tregan (Rhone-Poulenc) discussed his quinoline "microdiffusion" method for characterizing the particle uniformity of mass and suspension PVC resins. Geil (CWRU) described work showing heterogeneity on 3 size scales in plasticized PVC; "Domains" of ~100Å, and "particulate units" in the 1000Å and few-micron range. He feels the 100Å domains represent non-uniform plasticizer distribution, but not PVC crystallites. In the discussion, the difficulty in both studying and describing (in words) the various features of particle and sub-particle morphology was apparent. Later in the week, an informal "working committee" tackled the semantic problem, and a recommendation for a consistent terminology will appear in the published proceedings.

Under the topic of Rheology, the main lecture by E. A. Collins emphasized the role of particle-flow and the shift to a more homogeneous flow mechanism at temperatures >~200°C, concepts which have become widely accepted since the Prague symposium. Munstedt and Lyngaae-Jorgensen reported studies on PVC prefused to destroy particle identity; the differences in flow behavior between PVC and polystyrene or polyethylene are attributed to a structure formed by crystalline regions, and at temperatures high enough to melt these crystallites PVC shows more "normal" flow behavior. Pezzin discussed the effect of various plasticizers on the β -relaxation process, which leads him to conclude that the β -peak is not a local relaxation, but a cooperative motion of a number of chain segments.

The main lecture in the Processing session, by Menges (Aachen), again emphasized the particle structure effects on flow and fusion; his effort to apply a capillary force treatment (a "wet-sand" model, with low molecular weight PVC and additives bridging the PVC particles) was received with some skepticism by the audience. Haaf (BASF) reported studies of composition-morphology-property relations in impact-modified PVC; he concluded that highly agglomerated rubber particles favor high impact strength, and that stress-whitening is mainly due to cavity-formation within rubber particles rather than to crazing.

In the session on Properties, attention was focussed mainly on the effects of varied thermal history and their explanation in terms of free-volume and crystallinity changes. Thermal analysis and small-molecule transport studies appear to be particularly fruitful tools in unravelling these effects. A very interesting paper by R. R. Smith (Lancaster) described the effects of brief exposure of PVC to very high temperatures in an electric furnace at 800-1000°C, followed by rapid quenching; total melting was achieved, and the samples showed reduced density, enhanced permeability, and unusual solvent-swelling behavior. Other papers dealt with fracture and stress-strain behavior and with properties of some PVC blends and graft polymers.

In the Stabilization session, the main lecture by H. O. Wirth (Ciba-Geigy) provided a well-organized and thorough review of present knowledge of PVC degradation and stabilization mechanisms. G. C. Marks (BP Chemicals) presented evidence that ATR infra-red spectroscopy may provide early indications of long-time weathering performance of rigid PVC compounds. The use of an isothermal DTA technique for comparing stability was reported by Westerberg (Sweden).

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M. O'Mara's (BFG) main lecture in the Combustion & Toxicity session emphasized the difficulties of experimental design for providing data meaningful in real fire situations; his smoke-generation data, incidentally, provided an impressive "plug" for Hi-Temp Geon. The parallel-session scheduling, unfortunately, prevented my attending a discussion of the monomer-toxicity problem; my general impression from informal comments, however, is that the excitement over this problem has greatly subsided in the past two years.

Outside the formal sessions, a number of interesting new PVC developments were mentioned in personal conversations. Those of particular interest to BFG have already been reported in an IOC from Berens, O'Mara and Collins to M. E. Roha, 7/26/76.

One further general comment seems in order: Throughout the Lyon meeting, it was quite apparent that B.F. Goodrich technical leadership in PVC is widely recognized and appreciated. BFG's performance and publication of sound basic studies has clearly been worthwhile in establishing a respected company image.

Other Contacts in Europe

While in Europe for the Lyon PVC Symposium, I visited several laboratories which are working in areas close to my interests in PVC structure and diffusion in polymers. A report of my visit to Rhone-Poulenc, Aubervilliers, France has already been issued as a BFG Chemical Co. Meeting Report, July 16, 1976. Some comments on my other visits follow:

Prof. H. F. Stoeckli, Universite de Neuchatel, Neuchatel, Switzerland. My interest in visiting Prof. Stoeckli arose from his publications on sorption of gases and vapors by PVC resin powders; he has reported variations with sample history very similar to those I have seen in my VCM sorption work. In our conversation, I learned that Stoeckli's major research interest is in the mechanism of physical adsorption, not in polymers per se; he studied PVC only as a structure which seems to contain micropores of <20Å diameter. Stoeckli and his students have done more extensive work with activated and graphitized carbons, and have related sorption isotherms and heats of sorption to pore sizes and shapes. While pore sizes above about 20Å can be determined from the hysteresis in low-temperature N₂ adsorption via the Kelvin equation, the size of smaller, micropores can so far only be estimated by the relative sorptions of various-sized probe molecules (an "exclusion" or molecular-sieve approach). Stoeckli prefers to think in terms of micropores, rather than free volume -- an apparent consequence of his background in rigid solid adsorbents, rather than organic polymers. In his experimental work, he makes extensive use of the inverse GC technique, as well as manometric and gravimetric sorption data. For the latter, he favors a new Mettler recording microbalance, over the Cahn Electrobalance, as offering greater sensitivity, capacity, stability, and convenience. He feels that comparison of static (gravimetric, equilibrium) and dynamic (inverse GC) sorption data can provide valuable information about the relative penetration of various probe molecules into the inner structure of polymers or porous adsorbents. Our discussion of the similarities and differences in our problems and approaches gave me a helpful new point of view on my current work.

Prof. Saverio Russo, Institute of Industrial Chemistry and Center for the Chemical and Physical Study of Natural and Synthetic Macromolecules, University of Genoa, Italy. Prof. Russo is part of a large and vigorous polymer research group working under the joint sponsorship of the University of Genoa (Institute) and the Italian National Research Council (Center). In addition to extensive work on membranes and diffusive separations, their current research areas include synthesis, solid-state properties

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and technology of polar polymers, photo- and bio-degradation, chain statistics and dynamics, and polypeptides and other biopolymers. Two to four senior professional people are involved in each of seven principal research projects. Russo also is a leader of the new Italian Polymer Association, a professional group formed to stimulate research and communication in polymer science and technology and to increase the international contacts of Italian polymer researchers. This group is already working toward the 1980 IUPAC Macromolecular Symposium, which will feature a special program honoring Natta and Ziegler.

The Genoa membrane group is working on the preparation and properties of a variety of structured polymer membranes, including radiation-grafted or cross-linked structures. They have developed a polyvinylidene fluoride film, grafted with a hydrophilic monomer (acrylic acid?), which effectively separates oil and water at high throughput rates. This membrane has great potential value in waste treatments, oil-spill recovery, etc. and the Institute is now seeking support for scale-up and application studies.

The most important project at Genoa now is on the preparation and study of high-modulus and extended-chain fiber-forming polymers, particularly polyamides. They have found that LiCl markedly depresses the melting point of nylon-6; anionic bulk polymerization of caprolactam in the presence of LiCl produces a product which can be melt-spun at 40-60° lower temperature than straight nylon-6. The LiCl can be extracted by hot water during or after spinning, and excellent fibers are obtained. Of even greater interest is the application of similar procedures to nylon-4, which ordinarily cannot be melt-spun as it decomposes below its melting point. LiCl depresses the melting point by 80°, allowing melt-spinning to high-modulus fibers. Its high moisture uptake suggests that nylon-4 may be the long-sought synthetic "comfort fiber", combining the desirable characteristics of synthetic fibers and cotton. CNR holds patents in this area, is presently contacting Italian companies for support, and will be making their first public disclosure of the nylon-4 results in France this fall and in the U.S. at the Spring '77 ACS meeting.

Dr. John H. Petropoulos, Democritus Nuclear Research Center, Athens, Greece. My visit to Athens was suggested by Prof. Hopfenberg, who regards Petropoulos as undoubtedly the world leader in the interpretation and theory of diffusion in polymers. The highly mathematical nature of his publications made me a little apprehensive, but I found Petropoulos very easy and interesting to talk with. We spent a full day discussing diffusion in (to me) very real and understandable terms of molecular structure, segmental motion, pore size distribution, etc.

Petropoulos' general approach is to carefully analyze theories of diffusion in porous solids and polymers, determine the detailed consequences of different theories, then analyze published data or carry out new critical experiments to ascertain the validity of the theories. He is particularly concerned about distinguishing truly non-Fickian diffusion from cases where experimental artifacts (e.g., non-uniform membranes) may produce anomalous results. He is working toward systems which display the remarkable directional or selective transport properties of biological membranes (cell walls), but even much simpler systems are still incompletely understood. Among the present theories of transport in polymers, Petropoulos feels that the Case II model (Alfrey) is only descriptive and is farther from the complex physical reality than models which consider polymer relaxations and swelling-stress-dependent transport properties.

As in my discussion with Stoeckli, the analogy between rigid, microporous materials and glassy polymers was important in Petropoulos' thinking. He feels that "free-volume" is, in effect, the small end of a continuous distribution of pore sizes, and that the determination of void size distribution is central to understanding small molecule transport in solids. In glassy polymers, the mobility of holes is an additional parameter which must be considered.

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Petropoulos was quite interested in my work with PVC powders and the possibility it offers for separating diffusion and relaxation processes. He was not surprised that I could not fit my long-time sorption data with a single relaxation time, and offered some suggestions for better ways to analyze my data.

It was quite interesting to find that Petropoulos functions with a very small group (three professionals, two technicians, no graduate students), and in a rather isolated location, yet is recognized as a world leader in his field. He apparently has adequate, if not generous, support from Greek government funds, with no obvious requirements for justifying his work on practical or military grounds. One good man, with sufficient freedom and a modest budget, still is a potent force in the world of science.



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