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General Discussion on Thermal and Photodegradation and Stabilization

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Prof. D. A. Smith (Univeristy of London, Great Britain): My question is rather general, and although it is directed to Dr. Wirth, it is probably also directed to all authors who quote "induction periods." I am not doubting that there are induction periods when stabilizers are used. I am concerned, however, with the accurate measurement of an induction period when curves are asymptotic, or nearly so, to the time axis. It is common in chemical kinetics, where the kinetic form of reaction curves can be described accurately, to fit them to data points at higher extents of conversion, extrapolating back to the time axis in order to measure accurately an intersection point which will be a real induction period. Could Dr. Wirth say whether this is yet possible in stabilizer technology, or can anyone else comment on possible kinetic treatments?

Dr. H. O. Wirth (Ciba-Geigy, Marienberg, West Germany): There is already a small slope, but under normal conditions, dehydrochlorination during the so-called induction period is hardly detectable. We usually make a sort of an extrapolation when talking about the induction period. It is not, of course, quite correct from the standpoint of kinetics; that is, the dehydrochlorination curve actually starts at the origin of the coordinate system.

Prof. Smith: I do not want to seem academic about this, but my point is as follows. Where there is a break in the two curves you have shown, there could be real curvature through the overlap region and no induction period at all. This applies to all the experimental

points I have actually seen published by people who report induction periods. I suggest that it might be possible to fit the form of the curve higher, on the right-hand side of your sketch, and so determine what the induction period would be by measuring the intercept on the time axis. Has this been done?

Dr. Wirth: The so-called induction period is caused by the binding capacity of the stabilizer, at least to a first approximation. When the stabilizer is used up, then the PVC releases all hydrogen chloride which is chemically eliminated. And here we find in practice the starting point of the dehydrochlorination curve.

Dr. J. Millán (Instituto de Plasticos y Caucho, Madrid, Spain): It seems to me that the propagation mechanism has been less clarified than the mechanism of initiation. In this field we have found that the syndiotactic sequences give rise to much longer polyene sequences than atactic polymers. This is understandable, because in syndiotactic sequences there is such a structure that conjugated double bonds may be formed successively without the polymer chains having to adopt a special position stereochemically. This might mean that the formation of the sequences occurs before the secondary reactions, as reported by Dr. Kelen, can take place. What is the opinion of the panel, or of anyone with experience in this area?

Dr. T. Kelen (Research Institute for Chemistry, Budapest, Hungary): I agree with Dr. Millán that stereoregularity must play an important role in degradation processes. But, as was discussed by Dr. Martinez, the literature shows that more stable polymer is obtained by cold polymerization of vinyl chloride than by polymerization at higher temperatures. The stereoregularity of these polymers does not show the effects suggested by Dr. Millán. The syndiotacticity of the polymers obtained by cold polymerization is less than that of polymer obtained at higher temperature polymerization. There is no question that syndiotacticity plays a role, but perhaps in some other way.

Dr. K. B. Abbås (L. M. Eriksson Co., Stockholm, Sweden): Dr. Wirth showed us the effect of various chlorinated metal compounds on the thermal degradation. Calcium chloride and ferric chloride were not mentioned. Could you comment on the order of the catalytic effects of these compounds?

Dr. Wirth: There are so many published reports which include also iron trichloride, so I did not talk about it. For instance, Minsker et al. published a comprehensive paper, I guess in 1973, which includes studies on many metal chlorides. Since there are no stabilizers based on iron, I did not include iron trichloride in my lecture. Calcium behaves similarly as barium and lead, all of them being rather indifferent towards PVC.

Dr. Abbàs: Secondly, can Dr. Kelen tell us how he analyzed the aromatic structures formed, and what temperature was used in the experiments described?

Dr. Kelen: We analyzed only the formation of benzene. The analysis was done by means of gas chromatography. The degradation took place at 180°C or slightly higher, perhaps up to 210°C. We have not studied degradation at temperatures higher than 210°C.

Dr. M. Carrega (Rhône-Poulenc, Aubervilliers, France): What kind of polymer did Dr. Poller use for his radioactive experiment; in particular, what was its molecular weight? I understood he said that he found three reactive chlorine atoms for every 100 chains. Is that correct?

Dr. R. D. Poller (University of London, Great Britain): Suspension-polymerized polymer of about 40,000 molecular weight was used. In answer to the second question, it was three reactive chlorine atoms per 100 polymer molecules.

Dr. Carrega: Three reactive chlorine atoms per 100 polymer molecules or per 100 monomer units?

Dr. Poller: Per 100 polymer molecules. In every 100 molecules of polymer we could find three reactive chlorine atoms. This agrees with most published works, that there are very few initiation sites. There are long kinetic chains and much chain transfer in the degradation process.

Dr. Carrega: It is interesting to compare this number with the results of studies on double bonds by Dr. Michel and Dr. Guyot, in which they found approximately the same number of double bonds by ozonolysis.

Dr. Poller: We tried to confirm our results and obtained approximately the same results from experiments with ¹⁴C-labeled ethoxide ion, using conditions which we had shown with model compounds were such that only reactive chlorine atoms would react. We then applied that to the same polymer molecule and found about six reactive chlorine atoms. For polymer chemistry this is quite good agreement.

Dr. M. M. O'Mara (B. F. Goodrich, Avon Lake, Ohio, USA): In a comment to Prof. Kennedy, Dr. Wirth stated that it is known that the octyl group will not transfer to the PVC. Is Frye's work being used as the basis of the statement?

Dr. Wirth: As I have mentioned in my lecture, since Frye's work, Figger and Findeiss have carried out similar studies, using ¹⁴C-labeled alkyl groups attached to the tin. They found an extremely small amount of alkyl groups being transferred to the PVC, similar to the results of Frye.

Dr. O'Mara: Was it octyltin chloride or octyltin thioglycollate that you used?

Dr. Wirth: It was octyltin thioglycollate.

Dr. O'Mara: I think that is an inappropriate experiment because, in the first process, the thioglycollate group is transferred to the weak site. The second reaction to consider would be the transfer of the octyl group. The experiment which should be carried out is with labeled octyltin chloride to see whether there is a transfer reaction with that molecule. I think Prof. Kennedy was really asking about that in his question about the transfer reaction.

Dr. Wirth: Dr. Figger has run his experiments for long periods of heating so that we can assume a total conversion of the stabilizer into dioctyltin dichloride but he could not find a significant transfer of octyl groups to the polymer.

Dr. O'Mara: Yes, but by that stage, the weak sites are already saturated with the thioglycollate groups, so that theoretically there should be no weak sites left. In order to test Prof. Kennedy's hypothesis, we have to run the dioctyl tin dichloride experiment.

Dr. Wirth: Perhaps such an experiment would help us to have a better insight into this problem.

May I give a short comment on Dr. Poller's paper. There is some controversy between our two theories, or results. It is quite normal that in such a subject as PVC there are two different results, or meanings, with respect to one particular aspect. We have repeated the tests on the retarding effect of dialkyltin dichloride on the dehydrochlorination. Since we were not sure about the results, we finally carried out differential thermogravimetric studies. In all these experiments we found the same results: we could even prove that the increase in the activation energy of the dehydrochlorination is the same for the organotin mercaptide stabilizer and for the dioctyltin dichloride.

Dr. Poller: I entirely agree with Dr. Wirth that there are many conflicting contradictory reports. When we wrote on this area we began by saying that there are so many ways in which to make PVC, with so many variations that we should expect to get reproducible results only when the same specimens of polymer are used. However, having said that, I invite Dr. Wirth to take any two samples of PVC, put dibutyltin dichloride in one of them and nothing in the other, heat them up and he will find that the former will discolor much more rapidly than the other one.

Dr. Wirth: Maybe the discoloration gives us an explanation of the discrepancy of our results. We looked only at the dehydrochlorination.

Mr. Stapfer (Sté. Métrastat, Paris, France): In view of what Dr. Wirth implied in his slides concerning the structural aspects of stabilization, what would be his interpretation or explanation for the synergism between monoalkyltin compounds and dialkyltin compounds? He considered that dialkyltin compounds are the major stabilizers, with the mono compounds as the secondary stabilizers. Which one is the hydrochloride and which the hydrochloristat?

Dr. Wirth: This question was already raised. We can only speculate about the mechanism of the synergism, and I would prefer not to do that.

Mr. Stapfer: Could you make an educated guess?

Dr. Wirth: No, not yet. The mono compound usually influences the early color positively.

Mr. Stapfer: Why?

Dr. Wirth: I do not exactly know. Mr. Stapfer, you have worked in this area for many years and have published several interesting papers, so perhaps I could ask the same question of you: why is the mono component so active on the early color?

Mr. Stapfer: We have talked a lot about the structure of the polymer during the past few days, and it seems to me that an increasing number of people are now becoming involved with the stereospecificity of the polymer. We have heard from Dr. Poller that it is now possible to determine how many weak sites there are on these chains. Furthermore, we begin to know more about the structure of the stabilizer itself. I do not like to see organotin compounds such as the thioglycollates represented as tetracoordinated molecules. These organotin compounds are not tetrahedral. We have investigated their structure; there is a considerable intramolecular back-biting with strong contribution of the CO groups of the thioglycollate to form trigonal bipyramidal complexes. Not only that, but there are even stereoisomers of these complexes depending on the method of preparation. If we consider these steric pieces of puzzle, we find that models can be built in which either the mono or the disubstituted species fits more or less well into the weak sites of the polymer chain. This also depends upon the step of the degradation at which it is introduced; in other words, there are the antioxidative properties of these compounds on one hand, and the way in which the chlorine may be truly stabilized by coordination on the other. What the exact geometry of this coordination is remains to be established. All we know for sure is that there are great structural differences when we go from mono to di and of course to triorganotin thioglycollates.

Dr. Wirth: I am completely satisfied with that answer.

Prof. Smith: In 1965, we were interested in the effect of ferric oxide on PVC because at that time it was believed that there would be rust contamination which would destabilize the material. We studied PVC, polychloroprene, and chlorosulfonated polyethylene, obtaining essentially the same sort of results. These results were published in a Society of Chemical Industry Monograph in 1967, (Monograph 26, London, 1967, pp. 49-62). Isothermal differential thermal analysis showed that the amount of heat given out was approximately proportional to the concentration of contaminant, and so we thought that if we had a tape recorder using PVC tape heavily loaded with iron oxide, it should blow up as soon as the motor started! We then looked at the induction periods, as measured by the isothermal DTA, and found large increases with concentration. The reciprocal induction period varied with concentration according to a first-order law. At the time we explained this on the basis of stoichiometry, that if there is a little iron and large amount of chlorine it will be ferric chloride FeCl_3 , that is formed; on the other hand, if there is a lot of iron and a small amount of chlorine, it will be FeCl_2 that is formed. As is well known, the Lewis acid performance of the two compounds is quite different with respect to dehydrochlorination of PVC. This raises the question of the possible synergism of metal oxides with the stabilizers which have been discussed this morning. I wonder whether Dr. Poller or Dr. Wirth, both of whom have been involved in this field more recently, would be able to comment on the possibility of such synergism.

Dr. Poller: I have no recent experience in this field, except that there seems to be a clear correlation between Lewis acidity and prodegradant properties, which is what would be expected.

Dr. Palma (Montedison, Porto Marghera, Italy): In 1964, we published [*Materie Plastiche ed Elastomeri*, 30, 317 (1964)] some results of a work on the stabilization of PVC which were similar to those given today by Dr. Wirth. When a stabilizer is put into the PVC, the induction period is proportional to the amount of stabilizer on a stoichiometric basis. We used a mechanical mixture of stabilizer and PVC powder, since we found that any processing carried out in the preparation of the samples would bring out the destruction of some amount of the stabilizer. What was the procedure used in the work reported today?

Dr. Wirth: The way in which the stabilizer is combined with, or introduced into the PVC is very important. We have developed a special procedure in which the stabilizer is dissolved in a nonsolvent for PVC, for instance, petroleum ether. About a 10-ml portion of petroleum ether is required for 100 g of PVC, and this gives a powder which still flows. The petroleum ether is then evaporated by using a rotation evaporator. Under these conditions, reproducible results

can be obtained. Water can also be used, for instance, when metal chlorides are being investigated provided, however, that the water does not lead to a hydrolysis of the substances to be tested.

Dr. Palma: We prepared our mechanical mixtures without the use of a solvent, and yet we obtained satisfactory results.

Dr. Wirth: We did not have very reproducible results when mechanical mixing methods were used. This is why we changed to the method I have just described.

Prof. I. N. Einhorn (University of Utah, Salt Lake City, Utah, USA): I have been rather concerned by many of the reports which were made during the past few days by scientists who have studied various forms of poly(vinyl chloride) using the techniques of thermogravimetric analysis. If one calculates the amount of hydrogen chloride that could be released from the vinyl chloride monomer, they will find that this approximates 57.5% by weight. I should point out that some of the techniques that have been used, especially those involving titrimetry, are far too simplified to be used for the study of the degradation of polymeric materials. In our laboratory, we have interfaced a molecular leak valve from a combustion furnace directly into the ion source of a quadropole mass spectrometer or the ion source of a chemical ionization mass spectrometer. Using this technique, we have been able to follow and monitor single ions. In our studies of poly(vinyl chloride) polymer degradation, we have followed the 36 and 78 molecular weight ions which coincide to HCl and benzene. In these studies, we find that approximately 3.8 mole HCl is released per mole of benzene and that the appearance of HCl and benzene occurs almost simultaneously. After the reaction has passed the initial stages, we observe a gradual drop of the HCl per mole of benzene until we are just under 3 mole HCl per mole of benzene. In these studies we have, on numerous occasions, quenched the polymer with liquid nitrogen and conducted an elemental analysis on the residue. We have especially concerned ourselves with the analysis of chlorine left in the residue. These studies have clearly indicated that we do not, at high temperatures, form a polyene completely in the first period of degradation which coincides exactly with 57.5% weight loss and further corresponding to the theoretical amounts of HCl which could be generated. These results are substantiated by the fact that numerous chlorine-containing small molecules are found during the second stage of decomposition. As many as 60 or 70 different compounds may be found during the decomposition of PVC, depending on the temperature, the rate of the temperature rise employed, the sample geometry and state, and the environment to which the sample is exposed. Thus the thermal decomposition of PVC polymers is not as simple as has been reported by various people at this meeting or in the scientific literature.

I should further like to point out that we have under development at the present time a Fourier transform computer program for deconvoluting the observed thermograms and total ion spectrum. It is obvious that the HCl and benzene are selectively absorbed on the solid supports in our analytical equipment and that their absorption rates and desorption rates will differ widely. Thus the employment of Fourier transform deconvolution techniques is permitting a more accurate assessment of the rate of formation and the adsorption characteristics and desorption characteristics of each of these two compounds. Techniques employed in these studies should provide for a much better technique for analysis of the kinetics of the decomposition of polymeric materials. We have recently published several papers in the scientific literature pertaining to the pyrolysis, oxidative degradation, and flaming combustion of poly(vinyl chloride) polymers. These publications not only cover the analysis of light volatile species which are found in the gas phase, but also report on use of high-pressure liquid chromatography and other separation techniques to permit an analysis of solid particulates, polymer fragments, and liquid aerosols. If one considers the volatile components as well as the low-boiling residues and solid fragments and analyzes each of these for carbon, hydrogen, and chlorine, it is possible to obtain a mass balance which approximates 100% accounting for each of these fragments.

Dr. J. Boissel (Rhône-Poulenc, Aubervilliers, France): There seems to be some suspicion about the method of measurement of thermal stability following evolution of hydrogen chloride. The communication by Dr. Verdu showed that there is a significant diffusion of HCl through the polymer particles. As a result, some people think that evolution of HCl depends greatly on the morphology of the particles. If so, such a method of measurement would be a very bad one. Can people who have used it give an opinion on this method and whether it is a good one to use or one which should be abandoned?

Mr. Stapfer: What worries me a lot about HCl evolution is that it is slightly contrary to the principle and concept of stabilization of poly(vinyl chloride). When we say that we are stabilizing PVC we are, in fact, trying to avoid the disastrous degradation of the polymer. Once HCl is given off, all we are doing is to trap that HCl. That, in itself, is not of particular interest. We are using scavenging elements, we are trapping the HCl, but not really investigating the stabilization of the polymer against a degradation process which has taken place previously.

We constantly study the phenomena of autoxidation, induction period, and what ever else is happening before the HCl is given off. When HCl is being measured, it is not possible to see the early color development of PVC samples, be it under dynamic or static conditions.

The indications are that there is an increasing reluctance to rely on the HCl evolution as a meaningful method for the determination of the polymer stability. This is exactly what we are doing in the thermal analysis. Dr. Guyot raised the interesting question whether there is a difference in results according to the stabilizer system that is used. In fact, there is not much difference. All we investigate is what happens when the HCl is trapped, but it is too late by then, because when the HCl is given off the polymers have already undergone the unzipping reaction characterizing the dramatic decomposition of PVC.

Dr. W. Dick (L. M. Eriksson, Stockholm, Sweden): Mr. Stapfer is absolutely right. We do not measure the chemical stability of the basic PVC, but the usefulness—that is, the technological stability—of a compound. The compounds we use in the electrical industry as "stabilizers" are lead sulfate or lead carbonate, but they are not really stabilizers but trapping agents. That is quite correct.

Prof. Braun: May I thank all the participants in the discussion, and also the colleagues who presented papers in the session.