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General Discussion on Chemical Modifications

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Prof. O. F. Olaj (University of Vienna, Vienna, Austria): What are Professor Kennedy's ideas about the number and the length of the grafts in these large-scale graft copolymers which were the subject of his talk?

Prof. Kennedy: The best answer that I can give is reference to Fig. 3 of my presentation [J. Macromol. Sci.–Chem., A12, 197 (1978)], in which the molecular weights were shown. Our estimation was about 1 or 1.5 branches per backbone. The molecular weight of the grafts is low. We estimate them to be about 10,000 to 15,000 on the average.

Prof. Olaj: How is the content of the copolymer chains changed? Is it by increasing the number of grafts or their length?

Prof. Kennedy: By both means, and depending on the conditions of grafting. While these graft syntheses are not optimized, the main variables that we have changed were the time and the amount of Et_2AlCl used. Both reactions go hand in hand; in other words, the chains might grow and the less active sites might start to initiate.

Dr. A. Guyot (CNRS, Villeurbanne, France): I question the exact meaning of the improvement of the thermal stability as determined by dehydrochlorination rate under static conditions. In practice, PVC is used under dynamic conditions, so that the strains on the chains may break them, producing free radicals which may initiate dehydrochlorination. Chemical modification cannot prevent this, although it may affect the surface of the grains. This may be important because it might improve the internal lubrication of the polymer. It is possible that a large part of the improvement in the thermal stability may come more from this than from chemical modification.

Prof. Kennedy: That question ought to be answered by someone who did what Dr. Guyot asked. None of us, on the panel, as I understand it, has really examined heat stability under dynamic conditions. I am sure that people in the audience have studied the heat stability under dynamic conditions.

Prof. Y. Nakamura (Iwate University, Japan): I studied the thermal stability of PVC sheets blended with a calender roll under test-tube conditions only, so I know nothing about it under dynamic conditions.

Dr. Guyot: Dr. Nakamura showed us some slides with color changes that had occurred during milling of PVC on a roll mill. This is a thermal stability test done under dynamic conditions.

Mr. A. Shakoor (Iraq): In neiter of Dr. Nakamura's studies was there a stabilizer of PVC present. All he has is some compounds which look like typical antioxidants of a nitrogen-containing type. He ought to study the stabilizing effect in an inert atmosphere and also in an atmosphere of oxygen. The role of antioxidants here is to destroy chromophores which discolor poly(vinyl chloride).

Prof. Nakamura: I think that the antioxidant properties of 2-anilino-4,6-dithiol-s-triazine in the papers are so weak that the stabilizing activity of 2,4,6-trianilino-s-triazine disappears.

Prof. B. Rånby (Royal Institute of Technology, Stockholm): We cannot be sure that the increased thermal stability is due to the introduction of crosslinks or grafts. In addition, there has also been the removal of impurities, emulsifier residues, metal organic impurities from the autoclave, etc. The PVC has to be treated in the same way as during grafting or crosslinking, except that neither grafting nor crosslinking should be carried out. We know that these residues are photochemically active and we can be misled about the effect of the chemical reactions.

Prof. Kennedy: The grafting reactions which we carried out were done under exactly the conditions Prof. Rånby asks for. Our "control" underwent exactly the same treatment given to the grafts. Sometimes, we even used two, three or four kinds of controls. Dr. Suzuki quoted our results and showed a slide of one of our studies in which one control was the native, or untreated material, a second was washed, a third control was washed and precipitated, undergoing exactly the same history as the grafting.

Dr. I. Suzuki (Nippon Zeon, Japan): I have some experimental data on this. In suspension polymers, I think that the main impurities are the dispersants and the radical initiator. Such compounds do not seem to affect the thermal stability of PVC. We were able to ascertain that repetition of the purification and precipitation procedure did not cause a change in the thermal stability of PVC. Thus I think that impurities present in suspension polymers do not affect the thermal stability markedly, but we cannot say the same for emulsion polymers. Indeed, an emulsifier such as sodium alkylbenzene sulfonate, affects the thermal stability of PVC.

What's more, I think impurities in the monomer, for example, butadiene, chlorobutadiene, and other chloride compounds, are more important with regard to the thermal stability of PVC, and we cannot completely exclude such impurites from the monomer before carrying out a polymerization experiment. Such compounds are more important than impurities in the suspension polymers.

Prof. Kennedy: Before progressing with the discussion, we should deal with the question raised by Dr. Guyot: that is, the dynamic heat stability question. I should like to go perhaps one step further in the direction that Dr. Guyot is leading us and ask the audience to try to consider when giving their answer to his question whether there is a test which is the meaningful test to use to study the heat stability of PVC. Perhaps the audience can come up with a recommendation.

Dr. E. A. Collins (B. F. Goodrich, Brecksville, Ohio, USA): We have done a lot of work on the relationship between steady-state or oven-type stability—static stability—versus dynamic stability. One dynamic thermal stability test is the Brabender plastograph. While this is an instrument which is very difficult to analyze, it is simple to use and in many ways simulates processing operations. Using techniques published by other, we have been able to obtain an extremely good correlation between static and dynamic measurements. The static measurements are made by using the Instron capillary rheometer, recording thermal stability as a function of time under a constant shear rate. This work was published recently [Polym. Eng. Sci., 16, 240 (1976)].

In one of the mechanisms described, Dr. Suzuki stated that there was an improvement in stability by a factor of three—that is, three times the stability of the control. He added that this was not near the theoretical possibility of stability. In his estimation, what is possible: 10×, 100× or what?

Dr. Suzuki: This is a difficult question, which indeed I cannot really answer properly. As far as using chemical modification after polymerization, we cannot obtain the theoretical value of poly(vinyl chloride) because the stabilized structure of some unstable structure is always more unstable than the normal structure. If we can obtain the theoretical value of thermal stability, we should use an ionic polymerization method. Of course, it should be noted that our theoretical values are only for static evaluation.

Prof. Kennedy: May we now continue the discussion on the dynamic versus heat stability tests?

Mr. Stapfer (Société Metrastat, Paris): I think it is a fairly important question. Indeed, when several compounds and several additives are put into PVC, we are dealing with the delicate subject of synergism, so it becomes a matter of determining what does what and when under what conditions. For instance, it is possible to stabilize rigid PVC with organic structures which act as peroxide decomposers–I am thinking of aminocrotonic esters, thiolauric anhydride, and so on. Although dehydrohalogenation does occur, the product can be extruded fairly well, so it looks fairly good dynamically. But the extruded product is orange. What has happened is that the crosslinking of the PVC has been hindered. However, if we look at the static stability, we will dismiss this type of stabilizer altogether. Conversely, it will be necessary to eliminate that orange color and we have to go to costabilizers which improve the early color. Thus, what is being done in a twin system, or in a ternary system is to add the properties of one stabilizer to those of the other. Therefore, we have to look at both the static, or the residual stability of the final compound and the dynamic stability. With respect to an ideal test, there does not seem to be one. We have to combine both. We have developed an oven system which allows a continuous determination of thermal stability at a constant temperature and a constant speed. The advantage of this is that it is possible to determine the thermal stability of the starting material, the dry blend, and then to consider what this dry blend does in an extruder, for instance, we can begin to correlate what is happening between the moment these additives are mixed and the formation of the end-product.

Prof. Kennedy: I think that Dr. Collins might want to rebuff Mr. Stapfer because he was of the view that the dynamic and static testing were reinforcing each other.

Dr. Collins: I have to state that one of the conclusions reached from the dynamic and static-type measurements was that the temperature is the all-important criterion. There is the effect of the mixing, but it is not so much an effect of the degradation of the molecule as perhaps the mastication of the additives and their dispersion. It is the time and the temperature in a dynamic situation which are of most importance. Of course, it is difficult to predict how the material will behave because the shear rate, the time, and the shear-induced heating are not known. If such things were known, it would be possible to predict how stable the material would be in dynamic conditions, as in an extruder or on a mill.

Mr. Stapfer: The major difficulty is that it is almost impossible to correlate what happens on the Brabender, on a single-screw extruder, on a two-roll mill, on a twin-screw extruder, and so on. In static tests there is at least a point of reference, although I admit that one procedure is by no means exclusive from the other.

Prof. Braun (Deutsches Kunststoff Institut, Darmstadt): In addition to impurities and abnormal structure in PVC, we ought to take into consideration the fact that normally our samples are not measured under the same physical conditions. All the copolymers, the chemically modified or plasticized polymers, are in a different physical state. This may contribute to the overall thermal stability. Which of these chemical modifications or copolymers which have been mentioned are commercially available?

Prof. Kennedy: Dr. Nakamura mentioned that one of his procedures is commercially available. Perhaps he could amplify that statement?

Prof. Nakamura: I already studied modified PVC, using other thiols, such as ethane dithiol or thiokol. It was not suitable for industry to use ethylenediamine as accelerator because a large volume of water was required to wash the product. The present study is of modification of PVC on the mixing roll under the usual blending conditions. For this purpose, a crosslinking agent with a strongly acidic thiol such as dithiol-s-triazine, is very suitable. I am now studying the mixing of 100 parts of PVC and 200 parts of 2,4,6-trithiol-s-triazine. When this has been done successfully, such a blend when heated at 180° PVC with branching thiol groups may be obtained, which might show a strong adhesion to metal surface. The process of the modification of PVC with thiol triazine would be done on the blend or the injection molding, I think.

Mr. Shakoor: Can Dr. Caraculacu tell me which kinds of catalytic agents have been used in the phenolysis of PVC and whether their kinetics were studied? I have carried out similar work in an attempt to hydrolyze poly(vinyl chloride) to poly(vinyl alcohol) but I could not get positive results. This may be because of the high stability of chlorine atoms to substitution by another functional group.

Dr. A. Caraculacu (Romanian Academy of Sciences, Jassy, Romania): The reaction with phenol is carried out without catalyst, and only labile chlorine atoms will react. We have also measured the kinetics of this process. This work has been published [J. Polym. Sci. A-1, 4, 1839 (1966)]. Phenolysis is a process like alcoholysis. From kinetic measurements, we have found that the mechanism is not identical, however. We have measured the Hammett function, and a large difference was found between the values of the constants for phenolysis and alcoholysis. If phenol is not reacted with PVC but with a copolymer of vinyl chloride with isopropylene chloride, it is possible to obtain a polyphenol without using a catalyst. This is soluble in alkali and water, which means that it can be used as a polyelectrolyte. This work was published some years ago.

Mr. Jungk (Metall Gesellschaft, Frankfurt, Germany): I was greatly impressed by Dr. Suzuki and Prof. Nakamura in the crosslinking of PVC and stabilizing it with a triazine. What progress has been made so far in improving PVC heat deflection temperature by chemical modifications by crosslinking or grafting?

Dr. Suzuki: When we try to stabilize some PVC which is a copolymer by chemical modification, the mechanical properties do not change. This is because the extent of modification is very small, probably 0.01 per cent on average. By conducting such a reaction the mechanical properties, for example heat deflection temperature, are not changed.

Prof. Nakamura: The effect of crosslinking appears particularly on PVC with lower degree of polymerization. For the material mentioned in my paper the degree of polymerization is about 700. Such a PVC is very suitable for chemical crosslinking, as the tensile strength and creep behavior at a high temperature are extremely improved.

Mr. Jungk: I really asked my question of the whole panel, or even to the audience, from the practical point of view of how much progress has been made in improving the heat deformation temperature of PVC. I used Dr. Suzuki's paper as a motive for asking the question.

Prof. Kennedy: Is there anyone in the audience who would care to comment on Mr. Jungk's question?

Prof. G. Pezzin (Instituto Chimico G. Ciamician, Bologna, Italy): I think everyone knows that the only ways in which it is possible so far to substantially increase heat deflection temperature of PVC are, first, post-chlorination or, second, low temperature polymerization. In both cases the heat softening point has been raised by a few degrees, perhaps 10 degrees.

Dr. Smith (University of Lancaster, Great Britain): The conditions for crosslinking used by Dr. Suzuki and Prof. Nakamura were about 30 min at 180°C. Can either of them tell me whether there is any upper temperature limit which the triazine would impose on the system? Would it be possible, for example, to go to 220 or 230°C for a shorter time if degradation of the PVC could be avoided?

Prof. Nakamura: The temperature for the crosslinking is over about 150°C. Above 190°C the PVC becomes colored, so the suitable condition is 180°C.

Dr. Smith: That is not quite the answer I had hoped for, perhaps. I could make myself a little clearer. In conventional techniques using as Prof. Nakamura has done, compression molding, there are quite serious time limits because heat is getting in by conduction. But there are other methods of heating which allow much shorter times. If short-time heating to higher temperatures could be used, would the method work?

Prof. Nakamura: The problem is the degree of desired crosslinking which is desired. The gel fraction of crosslinked PVC is 100% if the conditions are severe. To improve the mechanical properties it is not necessary to crosslink the product completely, and about 80% crosslinking is satisfactory. Such a product can be obtained in about 5 min at 180°C. If a less reactive crosslinking agent is required, then the substituent R in 2-R-4,6-dithiol-s-triazine can be weaker, for instance, of the anilino type. As the decomposition point of 2-dibutylamino-4,6-dithiol-s-triazine (DB) is about 210°C, it may be impossible to crosslink over 200°C. The sodium, calcium, and magnesium salts of DB, however, can be used on PVC crosslinking of high temperature over 200°C without decomposition.

Prof. Kennedy: Perhaps Prof. Nakamura and Prof. Smith could discuss the point after the meeting to clarify it. I do not think that the question has been answered.

Dr. Guyot: When, for whatever reason, we make some chemical modification in PVC, we have to consider the reactivity of the newly formed bond to hydrochloric acid. Can Prof. Nakamura tell us what is the reactivity of the sulfur to carbon bond he obtains to hydrochloric acid? What is the reactivity of the new bond obtained with triazine crosslinking? Is the bond definitely stable to hydrochloric acid, or is it broken by that acid?

Prof. Nakamura: A decomposition temperature of an S-substituted thioltriazine as tributyltrithiocyanurate is about 250°C. But on thiocyanurate in the crosslinkage, the basic substrate R is supposed to accelerate the degradation of PVC, so that in order to make a thermally stable PVC, it is necessary to use a small amount of a crosslinking agent. If a lot of crosslinking agent is used, the color stability of the crosslinked product becomes lower. Trialkyltrithiocyanurate was reported to undergo acid-catalyzed hydrolysis. Therefore, an acid acceptor such as MgO is necessarily used on PVC crosslinking with thioltriazine.

Mr. Shakoor: Can Prof. Kennedy tell me what are the important parameters which we ought to study to distinguish between a grafted structure and a physical mixture?

Prof. Kennedy: There are many ways of making this distinction. One of the most important ways, is by fractionation. The solubility characteristics of the graft are usually somewhere between those of the homopolymers. Classical methods have been developed, e. g., fractional elution, fractional precipitation, or fractional dissolution–all kinds of fractional solvent and solution manipulations. Another method is GPC. This method gives an idea whether there is a multicomponent system or a single component system. Very often films of sequential copolymers give a clue whether there is a composite or a homogeneous material. We have found, for example, that the temperature effect on the intrinsic viscosity is an interesting way of proving the existence of sequential copolymers. In every one of the sequential copolymers studied we have observed discontinuities. One of the most important quantitative proofs of the existence of grafts is a comparison between the calculated and found molecular weights. If the composition of the graft is known, the theoretical molecular weight can be calculated. Can anybody else add anything?

Dr. Olaj: There is also the possibility of measuring light scattering in isorefractive solvent so that only the grafts can be measured, giving the molecular weight of the isolated graft.

Prof. Kennedy: Not quite, because we have to be absolutely sure that the system is a graft and not a mixture of homopolymers.

Dr. Semancik (Diamond Shamrock, USA): Has the panel addressed itself to the morphological implications of the reactions of PVC? Are these specific morphologic entities that might be preferential sites for reaction? Specifically, are we reacting within the 100 Å-sized particle, or are we getting surface effects? Secondly, might the reactions be due more to the types of structures formed at various conversion levels throughout the polymerization?

Prof. Kennedy: My understanding of most of the work reported here was that it was in solution, except the contribution I gave this afternoon on suspension grafting. Are you interested in it?

Dr. Semancik: Specifically in the suspension grafting.

Prof. Kennedy: I could not answer the question because the problem is extremely complicated. The only answer I can give is to say that the grafting probably occurs in the least crystalline, the most exposed and swollen areas, probably not in what we call aggregates, crystalline or syndiotactic areas. This problem, at least in our laboratories, has not been examined at all.

Dr. Nettesheim (Wacker Chemie, West Germany): I have some questions for Prof. Kennedy about the grafting of the isobutylene on PVC in suspension. First, is it necessary to use fractionated precipitation to obtain pure PVC grafts with polyisobutylene? Secondly, can he give us some details about the reaction conditions and the scale used?

Prof. Kennedy: In answer to the first question, we have to remove the homopolymer formed if we are interested in the physical properties of the pure material. We were able to obtain grafting efficiencies up to 75 or 80%. There was 20% homopolyisobutylene formed. The physical properties of the pure material were investigated. However, if I did not inform you that there was 20% homopolyisobutylene in the material, no one would know it was there. It would not be known by its film-forming or stress-strain properties because the 20% of polyisobutylene is so intimately compatible with the graft that we have to search for it to find it.

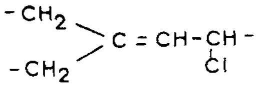
Dr. Nettesheim: What was the scale of the reactions, and may we have some details about the reaction conditions?

Prof. Kennedy: The general scale used for our physical properties measurements was from 50 to 100 g. The conditions of the grafting can be very simple. Those who are interested in the ionic polymerization will agree with me, but those more used to the general conditions used in radical polymerization might find our procedure rather more cumbersome. This is because we usually have to work at lower temperature and water cannot be used. The exact conditions will be published soon by D. L. Davidson and myself.

Mr. Stapfer: Since only a limited amount of the product was prepared, is Prof. Kennedy able to make any comment about the mechanical and physical properties of the grafted isobutylene PVC?

Prof. Kennedy: Yes, but I did not bring the results with me. We have extensive results on the mechanical properties; again, these will soon appear in a book the title of which is Cationic Graft Copolymerization, a book of about 200 pages, 50 pages of which will deal with the poly(vinyl chloride)-polyisobutylene system. The publisher is Wiley.

Dr. M. Kolínský (Institute of Macromolecular Chemistry, Prague): I have a comment to the main lecture of Dr. Suzuki. An ideal structure of PVC chain is represented by chlorine atoms in the 1,3 positions. This can be demonstrated, for example, with respect to the stability of 2,4,6-trichloroheptane by modeling an ideal PVC chain. This compound is not damaged, even when heated to its boiling temperature (240°C); even when held for several hours at this temperature, there is no perceptible decomposition, in contrast to conventionally produced PVC which is visibly decomposed by heating for a short time at 170°C. Similar differences can also be observed between other models and the corresponding conventionally produced polymers. We have prepared different model compounds, e. g., 2,4-dichloropentane, 2,4,6-trichloroheptane, different pentanes with chlorine atoms in position 3 or 4, chlorinated heptenes, and heptadienes. Kinetic parameters obtained in the thermal decomposition of these models were used under several simplifications in extrapolation to processes which proceed in the polymer. The results obtained in thermal decomposition of model compounds were used to corroborate the following conclusions when applied to PVC: (1) the increasing length of polymeric chain above is not the reason for suppressed thermal stability of the chain; (2) an unsaturated structure of the type CHCl=CH–CHCl at the end of the chain is not the labile site of PVC chain of the first importance; (3) the most labile among the possible structures present in PVC the internal double bonds of cis configuration and branched structures of the type:

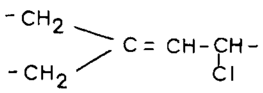


At 200° C, the models of such structures split off hydrogen chloride at a velocity higher by four orders of magnitude than the models of regular structure and higher by about two orders of magnitude than the models of structures with an internal double bond of the trans configuration.

Dr. Suzuki: It is very important for us that the superior thermal stability of 2,4,6-trichloroheptane (P_3) in comparison with that of real PVC suggests the possibility of improving the thermal stability to a large extent. Of course it should not be considered that the thermal stability of P_3 is completely equal to that of the normal structure in real PVC. An experiment with low molecular model compounds might be insufficient for getting the theoretical maximum value of the improvement.

To clarify the theoretical level of the improvement, other components such as the mechanochemical thermal stability of the long chain normal structure during the processing conditions should be combined with the model compounds experiment. It should be recognized that the internal allylic chloride structure is far more thermally unstable than the chain and allylic chloride structure based on the model compounds experiment. However, both allylic chloride structures are far more unstable than the normal structure. Therefore, it cannot be said that the chain end of the allylic chloride structure is not the initiation point of the PVC thermal degradation during processing. Furthermore, when the solvolytic displacement reactions are applied to the model compounds of the allylic chloride structure, 3-chloro-pentene-1 could be considered as the model compound of both internal and chain end allylic chloride structures. The reason is dependent on the fact that the S_N1 substitution reaction is not strongly influenced by the steric hindrance.

If the structure



exists in real PVC, the structure should be a typical initiation point of the degradation. But the presence of this structure in PVC is quite questionable. 3-Chloro-3-ethylenepentane is thermally stable in vinyl chloride at 80° C. If tertiary chloride structures occur as branch points in PVC during the polymerization, the structure should remain after the polymerization.

Prof. J. L. Garnett (University of New South Wales, Australia): Can Dr. Barton tell me the degree to which homopolymer formation occurs using this complex technique? With methyl methacrylate homopolymer formation may be a problem depending upon the copolymerization conditions used. Thus we have found marked homopolymer formation in radiation grafting of this monomer and related acrylates [S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phuoc, J. Polym. Sci. C, 37, 57 (1972)]. I wondered whether analogous problems occurred in your system. Secondly, we have recently developed a technique termed secondary electron capture negative ion (SECNI) mass spectrometry (I. W. Fraser, J. L. Garnett, and I. K. Gregar, Talanta, in press) which we feel is an elegant method for the characterization of complexes such as Dr. Barton uses for his present reactions. I suggest that Dr. Barton may wish to consider the use of this SECNI technique if he encounters problems of characterization of his complexes.

Dr. J. Barton (Institute of Polymers, Bratislava): In reply to Prof. Garnett's question, the grafting efficiency was about 75%. With regard to the characterization technique, we are also studying reactions of these complexes. We use primarily electron spin resonance spectroscopy because practically all this species is paramagnetic. After changing the paramagnetism we can study whether or not there is any reaction.

It is also possible to study the reaction products by techniques such as chromatography and so on. It would certainly be useful to use mass spectrometry too, and of course it is possible to use such a method in this way.

Prof. Kennedy: The problem of homopolymerization or by-product formation in grafting and block copolymerization, of course, is an extremely difficult one. I should like to make a challenging statement and say that I know no grafting method for PVC, except one–which I will describe later–which gives 100% grafting efficiency. In other words, the grafts which we call graft copolymers and block copolymers are really mixtures. We go through an elaborate separation technique, as we have just heard from Dr. Barton, but are really working with mixtures and studying physical properties of mixtures. I think Dr. Pillot's statement agrees with that too. The paper I presented at this symposium states the same: unless the homopolymer components have been carefully removed, we are always dealing with a mixture. Does anyone know of any grafting or blocking method on PVC with 100% grafting efficiency?

Prof. Garnett: We believe that we have such a system in rapid curve radiation grafting (C. H. Ang, N. P. Davis, J. L. Garnett and N. T. Yen, Proc. 1st Int. Meeting Rad. Processing, Puerto Rico 1976, in press), but unfortunately the process is being patented because of possible commercial utilization and we make no further comment here at this time. We have yet to carry out extensive fractionation on this system, but preliminary experiments are promising. We have used these rapid cure polymers for both enzyme immobilization and metal complex heterogenization and during all of our treatments, we have no data that suggest we have been working with mixtures. This very interesting point by Prof. Kennedy also raises the question as to whether the preirradiation grafting techniques can accomplish 100% grafting efficiency on PVC. Work by Stannett, Chapiro, and ourselves using the preirradiation method (i. e., radicals are formed in the PVC by radiation prior to copolymerization) suggest that initially 100% grafting efficiency could be achieved by this method.

Prof. Kennedy: I agree with Prof. Garnett that it is tantalizing to be unable to divulge information which is known. I look forward to at least the patent number being revealed, or some kind of disclosure in the future. I should like to describe briefly the process which we believe gives 100% grafting efficiency. Some time ago we discovered that poly(vinyl chloride) is an excellent initiator of THF polymerization. Polymerization of THF can be effected excellently with silver triflate, for example. Certain silver salts in conjunction with poly(vinyl chloride) initiate the polymerization of THF or other cyclic ethers. The THF polymerization is a "living" polymerization, i. e., a living polymerization can be initiated from PVC. Consequently, no homopolymerization occurs. Details are given in our publication [P. Dreyfuss and J. P. Kennedy, J. Polym. Sci. Polym. Letters Ed., 14, 139 (1976)].

Dr. Barton: That means you are stating that it is possible to initiate polymerization of tetrahydrofuran in the presence of poly(vinyl chloride) alone, not in connection with this salt?

Prof. Kennedy: The first step of the reaction is the formation of the poly(vinyl chloride) triflate ester and the removal of silver chloride. The fundamentals of the process can be followed by gravimetrically measuring the formation of silver chloride.

Dr. Guyot: Has Prof. Garnett made any comparisons between the metal complexes fixed by his method and those fixed by Haag's method (W. D. Haag and D. D. Whitehurst, Proc. Int. Cong. Catalysis 5th 1972, Vol. 1, North Holland, 1973, p. 465).

Prof. Garnett: No, we have not, for several reasons. Firstly, we feel that there is a limitation to the latter ("chemical") technique used by Haag, because of data reported when heterogenization experiments were carried out on styrene-divinylbenzene as polymer. Similar conclusions also appear to be valid when PVC is used instead of styrene-divinylbenzene. We have summarized in detail what we consider to be the advantages of our present radiation technique when compared with chemical methods elsewhere, e. g., for enzyme immobilization (J. L. Garnett, R. S. Kenyon, and M. J. Liddy, J. Chem. Soc. Chem. Commun., 1974, 735] and metal complex heterogenization (H. Barker, J. L. Garnett, R. S. Kenyon, R. Levot, M. J. Liddy, and M. A. Long, Proc. 6th Int. Cong. Catalysis, London, 1976, in press). Thus in brief, the copolymer from the radiation technique appears to be more uniform with the active groups available for attachment essentially on the surface of the copolymer. The radiation technique, when compared with the chemical method, also seems to be more versatile and flexible, in that a wide range of novel copolymers potentially useful for insolubilization can be readily prepared in a one-step process. Thus, using chemical methods, I am not sure that it would be possible easily to graft the vinyl phosphorus derivatives used for the present experiments nor would I expect to be able to copolymerize the same variety of derivatives of use in heterogenization as can be obtained by the radiation grafting process.

Dr. Guyot: I will restate my question. Haag and Whitehurst have treated PVC with lithium diphenylphosphine in order to get supported catalysts. Has Prof. Garnett made any direct comparisons between PVC covered by graft modified polymers and PVC covered directly by a phosphine group attached by chemical modification?

Prof. Garnett: Yes, I understood the question, however the confusion may have arisen because I used styrene-divinylbenzene as my original polymer example. Haag, as well as Manassen, Pitkethly, Pittman, and related groups, originally used styrenedivinylbenzene for this purpose, then PVC was subsequently studied. The limitations to the use of styrene-divinylbenzene for heterogenization by these earlier workers also appear to be applicable to PVC, since with both polymers "chemical" methods were used for attachment purposes. We have not used the chemically prepared PVC copolymers because we feel that they possess limitations with respect to the type and uniformity of surface graft capable of being achieved. From our experience a surface graft is needed. Grafting within the bead does not appear to us to be necessary, although other workers have discussed possible advantages of such a copolymerization. We feel that there is a critical distance from the surface for attachment to occur, such that the enzyme or the complex can react with maximum efficiency.

Dr. Guyot: Of course, I agree, but surface treatment can also be done in a solvent medium which is not a solvent for the polymer and which would give modification only on the surface.

Prof. Garnett: There is no doubt that a surface graft can be achieved by chemical means; however, from comments made at the 1974 Rideal Conference on the chemical technique and from our own experience with the radiation process, we feel that a more uniform surface copolymer can be prepared by the radiation method. An important and attractive feature that we have stressed in the development of the radiation technique for insolubilization is its versatility. The principle is generally applicable to all types of catalysts, whether they be enzymes or metal complexes. For a specific enzyme or metal complex there may be unique difficulties with the attachment process. Thus steric effects will certainly influence such reactivity but again these problems will be relevant to both catalytic systems. We consider the radiation grafting method as a general concept and in this respect we would prefer not to differentiate between the two catalytic systems.

Prof. Kennedy: I am not familiar with Prof. Garnett's expression, "Trommsdorff peak." Can he tell us something about it? Also how does he explain the ascending and descending parts of his curves in which grafting is shown as a function of styrene in the medium?

Prof. Garnett: This is an important question, in that it accentuates the fact that our present paper utilizes work in three fields, namely radiation chemistry, catalysis, and polymerization. The Trommsdorff effect has previously been observed in conventional polymerization reactions. In the present context it is a function of radiation dose and dose rate, type of monomer, and solvent, also the concentration of monomer in solvent. If we consider a radiation grafting reaction such as the present one involving PVC or even polyethylene (Fig. 1), we may plot per cent graft versus per cent

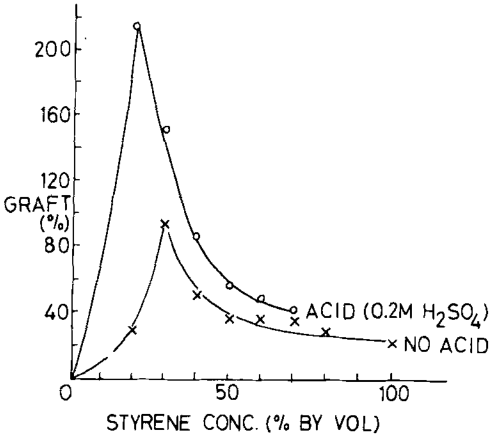


FIG. 1. Extent of grafting vs. styrene concentration.

monomer (styrene) in solvent (methanol), and a Trommsdorff or gel peak is observed in the grafting reaction. Odian and Silverman have studied this effect in the styrene-methanol-polyethylene system and have concluded that the phenomenon is a function of concentration of occluded styrene in the polyethylene and the viscosity of the amorphous region of the polyethylene which is swollen by styrene. Thus the presence of methanol reduces the concentration of occluded styrene in the polyethylene, and since methanol does not swell polyethylene the viscosity of the grafting medium increases. At low styrene concentrations, the initiation and propagation rates are low because of the high viscosity of the medium. At high styrene concentrations, the propagation rate tends to decrease but termination also increases due to the decreased viscosity of the swollen polymer. Between these two extremes there is a styrene concentration where the grafting rate is a maximum. We [J. L. Garnett and N. T. Yen, J. Polym. Sci. Polym. Letters Ed., 12, 225 (1974)] have also found in the radiation-initiated process that hydrogen atom formation influences the formation of the Trommsdorff peak. In methanol, the radiolytic yield G(H) of hydrogen atoms, is significant, and these hydrogen atoms appear capable of affecting the intensity of the gel effect. If mineral acid is added to the system, then the intensity of the peak is markedly increased and is due to reactions such as

$$H^+ + e \longrightarrow H$$

Thus in the present radiation grafting system the complete explanation for the Trommsdorff effect appears to be due to contributions from Odian, Silverman, and ourselves.

Prof. Kennedy: The Trommsdorff effect is a function of molecular weight and conversion. The molecular weight rises sharply at high conversions because of the termination by combination. I did not realize that the molecular weight comes down again, so my question was what makes it go up and come down. I am more puzzled, in fact, about the reason for the coming down. What is being plotted? Is it percentage of graft? To put the question more precisely: how is it that there is less graft at higher styrene percents? I understand the ascending part of the curve, but the descending part is puzzling.

Prof. Garnett: This is an extremely interesting question and has been raised a number of times at recent grafting conferences. We have carried out further work on this aspect of the styrene-methanol-polyethylene radiation grafting system (J. L. Garnett, G. Fletcher, and N. T. Yen, J. Polym. Sci., in press) and have concluded that an additional parameter which influences the formation of a Trommsdorff peak (i. e., both the ascending and descending parts of the curve) is the stability of styrene-methanol intermediates (MR.) in both low and high styrene concentrations. Thus the descending part of the curve can be expalined just as readily as the ascending part by considering a kinetic treatment of the stability of MR under different styrene concentrations. This analysis is treated in detail in the above reference.