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T. Tsuruta; F. Williams

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NEW CONCEPTS IN CATIONIC POLYMERIZATION

Chairman: T. Tsuruta, Tokyo, Japan
Speaker: F. Williams, Knoxville, Tennessee

Vogl: The afternoon session is concerned with cationic polymerization, and I would like to call on Professor Tsuruta to introduce the first speaker this afternoon.

T. Tsuruta, Tokyo, Japan: Ladies and gentlemen. The topic to be discussed this afternoon is, "New Concepts in Cationic Polymerization". We are very happy to have Professor Williams as the first speaker this afternoon. Dr. Williams, as you well know, is a professor in the Department of Chemistry at the University of Tennessee. He will explain how radiation chemistry is now contributing to the elucidation of the mechanism of cationic polymerization. He has 30 minutes for his talk and after his talk will be the panel discussions.

Williams: First, I should like to thank Professor Vogl and the organizing committee for the invitation to speak at this Colloquium. It is certainly a pleasure for me to talk about the radiation polymerization work that we and others have been doing over the past ten years. Incidentally, I should mention that much of my work in this field has been done with a number of collaborators from other institutions, notably with Professors Okamura and Hayashi at Kyoto University where I was a Visiting Scientist in 1965-1966. More recently I have collaborated with Professor J. P. Kennedy.

In this talk I shall try to emphasize the contribution which the study of radiation-induced polymerization has made to our general knowledge of cationic polymerization. I shall not dwell on the historical development of this field because in the early days there were many unsolved problems and artifacts that beclouded the whole subject. For many years it was thought that ionic polymerization by radiation was some kind of unusual heterogeneous reaction and a basic understanding was not achieved until much later. In fact, although the phenomenon of radiation-induced ionic polymerization was already well known more than ten years ago, there was really very little ground for optimism that anything of fundamental importance would come out. The word "mishmash" was used this morning to described the complexity of some polymerization systems. Well, if one is looking for a complex system, radiation polymerization would seem to offer a very good example because there is little or no specificity as regards the type of initiation mechanism (free radical and ionic). Nevertheless, I hope to show that the radiation technique has provided some useful information. Essentially, we find that the reason for the simplification of this complex system resides in the contrasting rate constants for the ionic and radical propagation mechanisms.

I shall begin by mentioning some experimental evidence which provides a firm foundation for believing in the existence of ions in radiation chemistry. For a long time, the idea that significant charge separation could occur in dielectric liquids exposed to high energy radiation was extremely controversial. It was not understood or appreciated how electrons could have lifetimes beyond an estimated ionic recombination time of about 10^{-13} sec in liquid systems. As the name "ionizing radiation" implies, ionization is easily measured in the gas phase but it proved to be a much more difficult problem to get definitive evidence for ions in liquids and solids. However, a variety of investigations during the 60's have provided this evidence. It comes from studies of stabilized ions and trapped electrons in glassy systems at low temperature, from chemical experiments with ionic scavengers, from pulse radiolysis studies of transient species, and from electrical conductivity measurements during irradiation. It may be helpful to mention a few specific examples of these studies. In a rigid hydrocarbon glass such as 3-methylhexane after γ-irradiation in the dark at 77°K, one can observe optical and ESR spectra which can be assigned to a trapped electron. This is physical evidence for charge separation. More recently, transient absorption spectra from trapped or solvated electrons have been observed in viscous hydrocarbon liquids following pulse radiolysis. Now, historically, the first approach to be used was that of chemical scavenging which, of course, is well known in the polymerization field -- to look for ions by means of specific chemical agents. For instance, nitrous oxide will react with electrons to give nitrogen. This reaction can be used as a measure of the number of electrons produced by radiation. We, ourselves, examined the possibility of some proton transfer reactions in aprotic media and found chemical evidence for positive ions by means of isotopic labeling experiments (ND_3 and C_2H_5OD in cyclohexane). By the choice of appropriate scavengers such as aromatic molecules (biphenyl, anthracene, etc), the pulse radiolysis technique has also been used with great advantage, because here one can identify the ionic species directly by means of its optical spectrum and, through time-resolved spectra, obtain some idea of the lifetime distribution -- the time profile, as it were, of the ions that are produced.

I should like to go on to say something about the distribution of ionic lifetimes in liquids under irradiation. Both the chemical and pulse radiolysis studies of ion scavenging have shown that in liquids of low dielectric constant - hydrocarbons and the like - most (but not all) of the ions produced by radiation combine rather quickly. This is sometimes called geminate recombination. Within about 10^{-9} sec, and certainly less than 10^{-7} sec, this fast process of geminate or cage recombination is complete due to the mutual attraction between the pair of ions. However, a small fraction of the ions drift apart by diffusion against the inter-ionic force field and become separated. And we believe that it is these free ions which are responsible for most of the polymerization that we see. Now, the electrical conductivity technique can be used to study these transient free ions during irradiation and this dovetails nicely with the polymerization studies. In fact, this work provides the firmest physical evidence for the existence of free ions. Thus, the radiation-induced conductivity varies as the square root of the dose rate, as expected for the case where the stationary state concentration of ions is determined by second order recombination between ions of opposite signs.

At this point, a question which might be asked is the following: Why is the radiation method useful since free radicals and ions are produced simultaneously? As I hinted earlier, the answer to this question lies in the relative values which emerge for the propagation rate constants for radical and cationic polymerization. Before we turn to this topic, it is useful to consider some order-of-magnitude calculations for the rates of radical and ion production in dielectric liquids during irradiation. From the studies mentioned earlier (electrical conductivity and ion scavenging), it turns out that the rate of production of these free ions is only of the order of 1/10th to 1/100th the rate of production of free radicals. To compare the stationary state concentrations of ions and radicals in a liquid system, one must also consider the termination rate constants. In each case, the stationary state concentration is given by an expression $(\underline{R}_i/\underline{k}_t)^{1/2}$ where $\underline{R}_i$ is the rate of production and $\underline{k}_t$ is the corresponding recombination or termination rate constant. Because ionic forces operate between ions at large distances in a medium of low dielectric constant (e.g., $e^2/\varepsilon r$ is equal to kT at 280 Å when $\epsilon = 2$ and $T = 300^{\circ}K$), the recombination rate constant $\underline{k}_t$ for ions, at least for species of low molecular weight, is about 100 times greater than that for neutral radicals. So, as compared to the values for radicals, the production of ions is a factor of 10 to 100 less efficient whereas the rate constant of recombination is greater by a factor of 100. The net effect is that typically the steady state concentration $(R_i/K_t)^{1/2}$ of ions is a factor of 100 lower than the steady state concentration of radicals. To give some idea of the order of magnitudes involved, calculations for hydrocarbons ($\varepsilon = 2$) show that at a dose rate of 1 Mrad/hr (which can usually be obtained with a conventional gamma radiation source), the free ion concentration is 2×10^{-10} molar whereas the free radical concentration is 1.6×10^{-8} molar. Clearly this means that radical polymerization will predominate in any system unless the propagation rate constant for ions exceeds that for radicals so as to overcome this difference of 10^2 in the relative concentrations. In other words, where the propagation rate constant for ions is lower than that for radicals, then the rate of polymerization is given solely by the $\underline{R}_p$ expression for radicals, $\underline{k}_p$ $[M\cdot][M]$, and this is what was observed in some systems at a very early date by workers such as Professor Chapiro. On the other hand, it turns out that in several monomers, the rate of ionic polymerization far surpasses that of radical polymerization showing that the propagation rate constant for ions is much more than a factor of 10^2 greater than the propagation rate constant for radicals in the same monomer system. So, in general, we find there is little ambiguity about the mechanism of polymerization under a given set of conditions and either free radical or ionic polymerization will predominate according to the $\underline{k}_p$ values for the monomer in question.

Before I go into the methods for the determination of k_p for free ions in radiation-induced polymerization, I should mention that very little can be achieved unless the monomer (and solvent, when present) system is extremely pure and free from water and other molecular species which can take up protons. In fact, this was the experimental refinement that was absolutely necessary in order to be able to observe ionic polymerization in several monomers at room temperature. The very earliest studied were concerned with those monomers which are well known to polymerize readily by cationic catalysts. These include isobutylene, α-methylstyrene, cyclopentadiene, β-pinene, and the alkyl vinyl ethers. In addition to the need to eliminate water from the system, it was demonstrated that the addition of ammonia concentrations much less than millimolar was sufficient to completely suppress the radiation-induced ionic polymerization in a dry system. These experiments provided excellent confirmation of the idea that polymerization results from a small concentration of free ions which are easily terminated by an effective scavenger. Actually, this formed the basis of our earliest attempt to obtain the propagation rate constant. We can write the general equation for the rate of polymerization,

$$R_p = \frac{k_p\,[M]\,R_i}{k_{tx}[X] + (R_i k_t)^{1/2}}$$

which includes the possibility of termination by an impurity or added scavenger X in addition to the mutual bimolecular termination between ions. Of course, a similar equation can apply in the case of radical polymerization. Essentially, the first term in the denominator can be made much larger than the second by the addition of even low concentrations of an ionic scavenger. So, we added varying concentrations of ammonia and amines to the monomer and plotted the rate (or the $\underline{G}$ (-m) value which is proportional to the kinetic chain length) as a function of the reciprocal of the amine concentration. In this way, we obtained the ratio $\underline{k}_p/\underline{k}_{tx}$ from the results and coupled with an assumption that $\underline{k}_{tx}$ is a diffusion-controlled rate constant, this allowed us to estimate the absolute value of $\underline{k}_p$. According to this kinetic analysis of amine retardation, we obtained $\underline{k}_p = 6 \times 10^8\ M^{-1}\ sec^{-1}$ for cyclopentadiene at -78° and $\underline{k}_p = 3 \times 10^6\ M^{-1}\ sec^{-1}$ for α-methylstyrene at 30°. In both of these systems, there is little or no radical polymerization so the kinetics are straightforward.

A more involved but very interesting system is styrene. Of course, it is well known that styrene is polymerized by radicals, and its radiation-induced polymerization had been interpreted very successfully in terms of radical processes, even to the extent of showing quantitative agreement with the known rate constants. For this reason, perhaps, it came as a considerable surprise that upon careful drying of styrene monomer, the rate of polymerization was enhanced by a factor of 10^2 to 10^3 depending on the efficiency with which the monomer could be dried. This finding was observed in several different laboratories and paralleled previous observations for α-methylstyrene. The dependence of the rate of polymerization on dose rate is a function of monomer purity as shown in Figure 1.

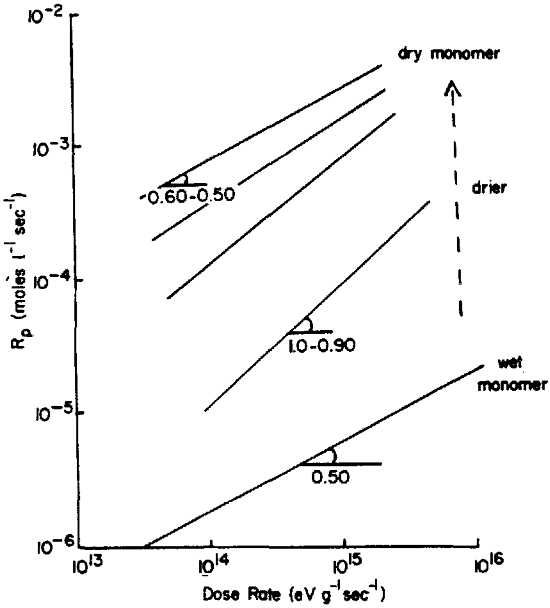


Fig. 1 (Williams). Effect of drying on radiation-induced polymerization of styrene.

For very dry monomer, the previous equation reduces to $R_p = k_p [M] (R_i/k_t)^{1/2}$ through omission of the k_{tx} [X] term and the result is a half power dependence of the rate of *ionic* polymerization on dose rate. This plot representing very high rates of polymerization corresponds to one extreme. For wet monomer, one also observes a half power relationship but the absolute rates are much lower. Thus, the two plots are parallel but displaced vertically by almost three powers of ten in R_p. As the styrene monomer is progressively dried, R_p first increases above the value for the wet monomer and the dose rate exponent changes from 0.5 to 1.0. This exponent of 1.0 corresponds to ionic polymerization with the inequality $\underline{k}_{tx}$ [X] $\gg(\underline{R}_i\underline{k}_t)^{1/2}$. Under more stringent drying, $\underline{R}_p$ increases further and according to this kinetic analysis, a limiting rate should be attained with a dose rate exponent of 0.5. To a large extent, the results obey this simple kinetic scheme. A recent paper by Potter and Metz in J. Polymer Sci. offers a critique of this kinetic formulation and, in my opinion, the agreement between theory and experiment is just about as good as can be expected. However, I think one should be careful not to push the algebra too far. For example, the effective concentration of residual water is likely to be a function of temperature on account of the strong association between water molecules in a nonpolar solvent. Hence, the anomalous temperature dependence of $\underline{R}_p$ under certain conditions of mild retardation does not invalidate the kinetic treatment. Overall, I think it's highly gratifying that this simple kinetic approach to the problem works so well.

Up to now I have not said anything specifically about the question of whether we are dealing with cationic or anionic polymerization, or a super-position of these two ionic mechanisms (this is in addition, of course, to the low rate of free radical polymerization). For styrene and α-methylstyrene, the evidence is fairly conclusive that the polymerization occurs almost exclusively by the cationic mechanism. These polymerizations are strongly retarded by low concentrations of ammonia and amines, there is considerable chain transfer to monomer which determines the molecular weight, and the reactivity ratios in copolymerization are quite characteristic of the cationic mechanism. For monomers such as isobutylene, β-pinene, cyclopentadiene, and the alkyl vinyl ethers which are known to polymerize efficiently only with cationic catalysts, confirmation of the fact that the radiation-induced polymerization of these monomers is cationic again comes from the retarding effects of Lewis bases.

Let us return now to the determination of the propagation rate constants for cationic polymerization by free ions. The $\underline{k}_p$ for styrene by free cations is found to be in the region of 3×10^6 $\underline{M}^{-1}$ $\sec^{-1}$. The precision of the data leaves something to be desired, but it is reassuring to know that there is at least qualitative agreement between the results of the amine retardation method and the "absolute" determination by the conductivity technique. In this latter method, we combined the measurements of polymerization rate with those of ionic conductivity over the same range of dose rate. Essentially, the conductivity data is used to estimate the concentration of active ionic species. The mean lifetime of the ions can be obtained directly from the specific conductivity but one also needs to know the rate of ion production. In principle, this latter quantity can be determined from a combination of conductivity and mobility data, but accurate ionic mobilities are difficult to determine experimentally. As an alternative, one can set up the expressions in terms of the ionic recombination rate constant instead of ionic mobilities, since these two quantities are related through the Nernst-Einstein relation. The advantage of this approach is that one can make a pretty good estimate of the recombination rate constant from simple theory, at least for solvents of low dielectric constant. I should also mention that we can compare the conductivity results with those found for saturated hydrocarbons and other organic liquids which have been studied in considerable detail. For further details of the method, I refer you to the papers in Trans. Faraday Soc., 63, 1478-1511, and my review article in "Fundamental Processes in Radiation Chemistry", Wiley, 1968, pp. 515-598. What I want to stress here is that we have a self-consistent picture of radiation-induced polymerization by free ions which is in accord with all the salient experimental facts. So, the main conclusion which emerges from this work is that the k_p values for the free cationic polymerization of reactive monomers (including cyclopentadiene, α-methylstyrene, styrene, isobutyl vinyl ether, and isobutylene) are in the range $10^5 - 10^9$ M^{-1} sec^{-1}. I need hardly point out at this Colloquium that these k_p values are much higher than those commonly reported in the past for the cationic polymerization of these monomers by catalysts. The significance of catalytic studies has been reviewed by Dr. Plesch in Advances in Polymer Science, 8, 137 (1971), and the only comment which I would make is that until very recently, there was no determination of k_p by chemical initiation that could be attributed to free ions. However, within the last few months, there has appeared a very detailed and significant paper by Bawn, Ledwith, and their co-workers in Polymer, 12, 119 (1971), which describes the determination of k_p by free cations in the polymerization of isobutyl vinyl ether initiated by carbonium ion salts. The authors conclude that after taking into account the effect of different solvent conditions, their results are in quite good agreement with the value obtained by radiation-induced polymerization. They regard this measure of agreement as quite remarkable considering the vastly different techniques employed, so it is most heartening to have this independent evidence which corroborates the high values of $\underline{k}_p$ for cationic polymerization by free ions. Incidentally, another paper by Ledwith and his co-workers (Polymer, 12, 509 (1971)) reports a $\underline{k}_p$ of 3×10^5 $\underline{M}^{-1}$ sec^{-1} at 0°C for N-vinylcarbazole polymerization by free cations. This value may be compared with a $\underline{k}_p$ of 6.0 M^{-1} sec^{-1} for the free radical polymerization of this monomer at +10°C. Clearly this difference in absolute reactivity parallels the findings for styrene in radiation-induced polymerization.

The latest study we have completed in this field has been concerned with isobutylene. A thorough re-investigation of the radiation-induced polymerization of this monomer seemed to be in order because it had been alleged that extremely high rates could only be obtained with added solids such as zinc oxide and, consequently, the reaction had been interpreted as a heterogeneous process. Another reason for studying isobutylene is that this monomer polymerizes only by the cationic mechanism, and the molecular weights of the polymer are generally found to be sensitive to the polymerization temperature. We disproved the heterogeneous mechanism by going to considerable trouble to purify and dry the monomer (R. B. Taylor and F. Williams, J. Amer. Chem. Soc., 91, 3728). Under proper anhydrous conditions, $\underline{R}_p$ was found to exceed the highest rates previously reported in the presence of solids and to depend on the 0.55 power of dose rate, in close agreement with the prediction of the free ion mechanism. The value of $\underline{k}_p$ at 0°C was estimated to be 1.5×10^8 $\underline{M}^{-1}$ sec^{-1} and the activation energy for propagation is quite small, probably less than 2 or 3 kcal mol^{-1}. By the way, only in the case of isobutyl vinyl ether have we found an activation energy for cationic propagation exceeding 5 kcal mol^{-1}. Now, the next stage of the isobutylene study was to examine what differences existed between the molecular weights of the polymer molecules produced by free ions and by chemical catalysis. This part of the work was done in collaboration with Dr. Kennedy. As is well known, molecular weights in cationic polymerization are frequently determined by chain transfer to monomer, a process which takes place by proton transfer in this system. Isobutylene is a good monomer to study because there are extensive data, mainly by Kennedy and his co-workers, on the dependence of the various average molecular weights on polymerization temperature for a number of different catalyst systems. The Arrhenius plots of log (mol. wt.) versus $1/\underline{T}$ show a positive slope which means that the difference between the activation energies for propagation and transfer is negative. For the BF_3, $AlEtCl_2$, and $AlCl_3$ catalyst systems, this activation energy difference expressed as the positive quantity $\underline{E}_{tr\ m} - \underline{E}_p$ is 5.9 kcal mol^{-1}. We found that a similar plot for the results of the radiation-induced polymerization gave a very similar slope corresponding to $\underline{E}_{tr\ m} - \underline{E}_p = 6.2$ kcal mol^{-1}. For all practical purposes, this activation energy difference can be regarded as identical for the catalytic and radiation-induced polymerizations. However, as shown in Figure 2, the interesting fact emerges that at any temperature, the molecular weights ($\overline{M}_v$) of the radiation-induced polymer are a factor of approximately 10 higher than those obtained in the catalytic polymerizations. Dr. Kennedy

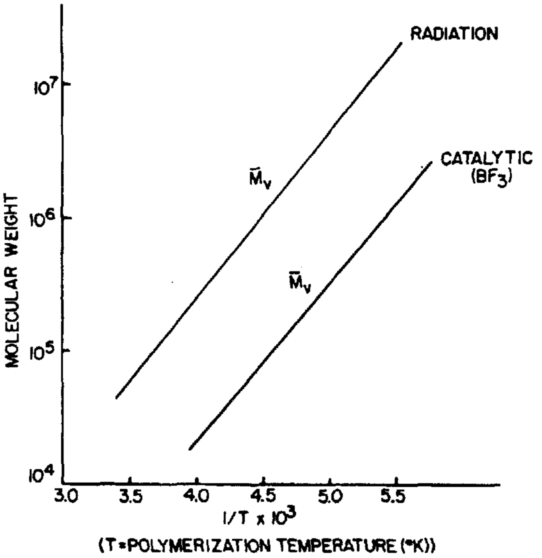


Fig. 2 (Williams). Comparison of molecular weights of polyisobutylenes produced in radiation and catalytic polymerization. T = Polymerization Temperature (°K).

may have something more to say about this in the discussion period, so I won't elaborate too much on this finding. Basically, we have interpreted this result (<u>J. Polymer Sci.</u>, <u>9</u>, 1551 (1971)) to mean that in comparison with free ion polymerization, the presence of the counter ion impedes the propagation reaction much more than the transfer reaction in ion-pair polymerization. Alternatively, the counter ion could be said to assist the transfer process whereas it impedes the propagation reaction. In more quantitative terms, $\Delta S^{\neq}_{tr\ m} - \Delta S^{\neq}_{p}$ is larger for ion-pairs (<u>ca</u>. 12 cal deg^{-1} mol^{-1}) than for free ions (9.8 cal deg^{-1} mol^{-1}) in cationic polymerization.

One implicit assumption in the kinetic treatment of radiation-induced cationic polymerization is that of fast initiation. This can be justified in some cases on the basis of mass spectrometric studies of ion-molecule reactions. For example, Volpi and his co-workers have shown (Trans. Faraday Soc., 63, 926 (1967)) that in the case of isobutylene, the $C_4H_8{}^{\cdot +}$ parent ion (i.e., the radical cation) reacts rapidly by proton transfer with a neutral molecule of isobutylene to give the t-butyl carbonium ion. Moreover, the ion distribution as a function of pressure in the mass spectrometer provides clear evidence for the first steps in the propagation chain. All these processes are very rapid under mass spectrometric conditions and the initiation reaction occurs with a rate constant of the order of 10^{-9} cm^3 $molecule^{-1}$ sec^{-1} (6 x 10^{11} $\underline{M}^{-1}$ sec^{-1}) Since proton transfer from the parent ion to an olefin is generally a fast process, I think one can assume that initiation will occur rapidly in most cases of radiation-induced cationic polymerization.

A word or two should perhaps be added about some of the problems of radiation-induced cationic polymerization. I hope I have shown that this method of determining rate constants is a most useful one but it is subject to limitations. The most serious problem is that connected with the effect of impurities. One can never be sure that negative results mean that the system is inherently incapable of polymerizing. Even if impurities are virtually eliminated before irradiation, there is always the possibility that some retarder is produced by irradiation. As in other areas of experimental chemistry, only positive results mean anything. The other limitation is that low $\underline{k}_p$ values (below 10^3 $\underline{M}^{-1}$ sec^{-1}) for cationic polymerization cannot be measured with any degree of reliability, especially in systems where rate constants for radical polymerization become at all comparable. I believe the discussion I gave earlier should have covered this point adequately.

Finally, let me say something about anionic polymerization. Surprisingly, there have been very few really clearcut demonstrations of anionic polymerization induced by high energy radiation. One such example is the bulk polymerization of nitroethylene (Trans. Faraday Soc., 63, 376 (1967)), an extremely reactive monomer in anionic polymerization. More recently, we have obtained qualitative evidence for the anionic polymerization of methyl 2-cyanoacrylate, another ultra-reactive monomer. Instead of discussing these examples, I want to mention some possible reasons why anionic polymerization seems to be less general than cationic polymerization in the radiation studies. This can be illustrated by reference to our findings for 2-vinylpyridine. Professor Szwarc has reported an anionic propagation rate constant for this monomer which is quite large, ca. 10^5 $\underline{M}^{-1}$ sec^{-1} at 25°C, and considerably larger than the rate constant for radical propagation. So, we thought this would be a good system to demonstrate anionic polymerization and, hopefully, furnish a comparison of propagation rate constants by the chemical and radiation methods. Yet, despite every effort, we have been unable to obtain any evidence for radiation-induced anionic polymerization. In fact, the only polymerization we can detect is free radical and the propagation rate constant is calculated to be $4 \times 10^{1}\ \underline{M}^{-1}\ sec^{-1}$. I think the reason why we don't observe anionic polymerization resides in the possibility of a slow initiation step which, of course, contrasts with the cationic systems discussed earlier. It must be remembered that in radiation-induced polymerization, we are dealing with transient ions whose lifetimes are on the order of 10^{-2} to 10^{-3} sec at conventional dose rates. Thus, if the initiation requires a time that is comparable to this lifetime as determined by the ion recombination mechanism, then there is little or no time available for the propagation chain to proceed before termination. These remarks only apply, of course, to liquid systems.

In this talk, I have tried to outline some of the relevant information and conclusions we have reached about cationic polymerization induced by radiation, and I leave it to the discussion to bring this work into sharper focus with the chemical studies.

Panel Discussion

Discussion Leader: V. Stannett, Raleigh

Panelists: K. Hayashi, Sapporo; J. P. Kennedy, Akron;
D. Pepper, Dublin; P. H. Plesch, Keele;
T. Saegusa, Kyoto; P. Schleyer, Princeton;
P. Sigwalt, Paris.

Tsuruta: Before we move to the panel discussion, I have the pleasure of introducing Dr. Stannett, who is a professor in the Department of Chemical Engineering, North Carolina State

University. He is a leading instigator in the radiation-induced chemistry of polymers, especially in cationic polymerization using vinyl monomers, including vinyl ether, α-methylstyrene and other related compounds. May I introduce Dr. Stannett as the discussion leader for the panel discussion.

V. Stannett, Raleigh, North Carolina: I would first like to thank Professor Vogl and Professor Lenz for inviting me to participate in this symposium. We profit greatly from Professor Bamford's experiences this morning. He started out extremely leniently and became more and more ruthless. We will try to start ruthlessly and become more and more lenient. In this way we will leave everyone with an excellent impression of the meeting.

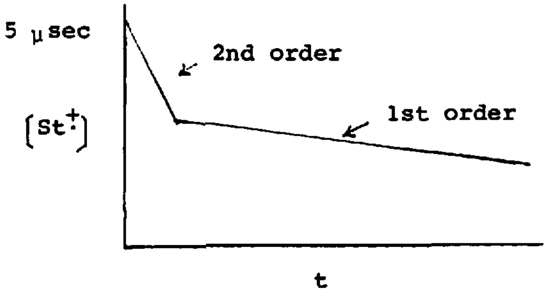
I think I will ask Professor Tsuruta to hold off a discussion on Frank Williams' paper until after Hayashi and Kennedy's contribution, as they all fit together and then this will fit rather well. After that, Professor Saegusa will talk about some hetrocyclic systems and we'll discuss these. Afterwards, we will have Pepper and Sigwalt and then Professor Plesch. Maybe we could have the discussion on these three together because they fit. Then Professor Schleyer will end up with the grand finale and correct all this appropriately. To begin with, I'd like to call on Professor Hayashi to supplement Frank Williams' remarks and add some work of his own. We're heavily weighted toward radiation at the moment.

K. Hayashi, Sapporo, Japan: Following the talk of Professor Williams, I'd like to introduce our results of a pulse radiolysis study which was made on the styrene in n-butylchloride system. We found a transient active species at the position of 350 nm having a very short lifetime of 5 microseconds. This active species might be styrene cation radical. Also, a kinetic study on the decaying behavior of this cation radical indicates the existence of two different reactions. One is a very quick second order reaction and another is a slower first order reaction. The former is a neutralization reaction of styrene cation radical with some anionic ion presumably Cl^- and the latter is a reaction with styrene monomer molecule. So, the former corresponds to a termination reaction and the latter corresponds to the first step of a free ion propagation reaction. This rate constant was determined to be on the order of 10^{10} mol/l/sec as a diffusion limited constant and on the order of 10^6 mol/l/sec. We know in the case of radiation induced ionic polymerization of styrene, the k_p constant was estimated kinetically to be on the order of 10^6. The difference might be understood by the difference of the chemical structure of styrene cation radical and growing styrene free ions. Additionally, we must consider the solvent effect. k_2 was estimated in a polar solvent and k_p was determined in the bulk, that is in a hydrocarbon system. The interesting problem of solvation effect arises for the growing free cations. However, in the case of radiation-induced polymerization in solution, we have some difficulty caused by the radiolysis product which comes from chlorinated hydrocarbon. To avoid this difficulty, we used photoinduced cationic polymerization of styrene and α-methylstyrene. α-methylstyrene, which we used more frequently, is a weak electron donor, and we photoilluminated this monomer in the presence of tetracyanobenzene (TCNB) which is electron acceptor. These compounds form a molecular complex. An absorption caused by this complex was found at 363 nm. By photo illumination at wave lengths longer than 350 nm, an excited complex was formed and transferred to a solvent separated ion pair which is equilibrated with the free ion. These ions initiated the polymerization and we obtained poly α-methylstyrene. In this system, the solvent used is dichloroethane, temperature $0^{\circ}C$ to $-78^{\circ}C$, the concentration of TCNB was in the order of 10^{2} mol/l. The polymerization mechanism was thought to be cationic, because polymerization is very sensitive to trace amounts of water and copolymer composition proves a cationic mechanism. We measured directly the behaviors of free ions by photoconductivity, and that of total ions by flash photolysis and ESR. Polymer analysis by NMR and GPC suggested the coexistence of both mechanisms of pair ion and free ions. The apparent k_p constant was estimated tentatively in the range of 10^{1} to 10^{4} mol/l/sec. Supposing 10^{4} is as the upper value for free ion and compared with k_p in bulk, it is obvious that a polar solvent reduces the k_p value at least in three orders. And I expect this concept of the solvation effect on the growing cation might be discussed with other radiation chemists.

Pulse radiolysis styrene in n BuCl

350 nm

$St^{+\cdot}$



$$\frac{-d[St^{+\cdot}]}{dt} = k_1[St^{+\cdot}][Cl^-] \qquad \text{(termination)}$$

$$+ k_2[St^{+\cdot}][St] \qquad \text{(1st propagation)}$$

k_1: 10^{10} mol/l/sec, k_2: 10^6 〃 (in n BuCl)

k_p: $10^6 \sim 10^7$ 〃 (in bulk)

Photo-induced cationic polymerization

$$\underset{(D)}{\alpha MeSt} + \underset{(A)}{TCNB} \rightleftharpoons DA$$

$$DA \xrightarrow[\text{in } C_2H_4Cl_2]{h\nu} (DA)^{*} \longrightarrow (D_s^{+\cdot} + A_s^{-\cdot}) \rightleftharpoons D_s^{+\cdot} + A_s^{-\cdot}$$

<u>Stannett</u>: I think we will combine the discussions of both Professor Williams' paper and Dr. Hayashi's remarks, and they are open for discussion now. I would like to ask Dr. Williams about this very low activation energy for isobutylene. As you may know, with the vinyl ethers, both Hayashi and ourselves find very much higher activation energies for the k_p, even though we reach the square root relationship quite

clearly. Would you have any comments why some monomers seem to give the expected very low activation energy and some much higher?

Williams: I have little to add except to agree with you that these are the facts. As compared to the other monomers we have examined, alkyl vinyl ethers do seem to have higher activation energies for cationic propagation. Incidentally, I might add that we pointed this out in 1964 (J. Polymer Sci., B 2, 143 (1964)) at a time when activation energies of this magnitude ($>$5 kcal mol^{-1}) were generally regarded as diagnostic of radical polymerization.

Stannett: Maybe it has to do with the self-solvation of the carbonium ion by the ether groups.

E. Goldberg, Webster, New York: A comment that responds to a point made by Dr. Williams. He pointed out the difference in rates of ion versus radical recombination. It would seem to me that if free ion species are important, there is another way to test this. That would be to observe the behavior of the irradiated system in an electric field which should substantially hinder the ion recombination process. Experimental information in the solid state that may relate to this concerns the behavior of organic photoconductors. They show a rather remarkable field dependent current response. Similar experiments with Dr. Williams' system might be helpful in clarifying the relative contributions of ionic and radical species.

Gaylord: Could I ask one further question before we get on? Is there any information available in solution systems regarding electric field effect?

Stannett: Yes, Professor Williams knows the Japanese work of Ise, which I suppose is the most relevant, but you perhaps remember it better.

Williams: In reply to Goldberg and Gaylord, the effect of an applied electric field on the free ion recombination rate constant would perhaps come in, but there would be other effects to consider as well. For example, the rate of free ion production should be enhanced by a field effect since the applied field would counteract (on the average) the fast geminate recombination process. Another effect might be a direct one on the propagation reaction. As Professor Stannett mentioned, Ise and his co-workers in Japan have made numerous studies on the effect of electric fields on anionic polymerization. I think they also published one or two papers on this effect in radiation-induced polymerization but, as far as I can recall, the field effect was rather small in this case. I think this is what one would expect unless the applied field strength becomes extremely large ($>10^4$ volts cm^{-1}). Recall that the field strength at a distance of 100 Å from an ion is 1.44×10^5 volts cm^{-1} in vacuo, so that one needs external fields close to 10^4 volts cm^{-1} before the recombination processes are greatly affected at a separation distance $\underline{r}_c$ of $\sim$300 Å and a dielectric constant of 2 ($\underline{r}_c$ is 280 Å as given by the relation $\underline{e}^2/\epsilon\underline{r}_c = \underline{k}\,\underline{T}$ for $\epsilon = 2$ and $\underline{T} = 300^\circ K$).

Gaylord: The question is related to the aspect of dissociation of ion pair systems of the type indicated by Dr. Hayashi in polar media. For example, in the polymerization of styrene in sulfur dioxide with a radical catalyst, the presence of polystyrene is normally attributed to the formation of the styrene cation radical which initiates styrene polymerization. We recently had occasion to study solvent effects in these reactions and discovered that in the presence of DMF you certainly do not get polystyrene. However, the molecular weight of the styrene-sulfur dioxide copolymer is higher than normal, i.e., higher than in the absence of DMF, which implies that the DMF is preventing the growing chain end from dissociating, permitting it to grow a longer distance, rather than eliminating or at least generating free ions to initiate polystyrene. We have seen this in all the alternating systems which have a tendency to shift from alternating to cationic. In other words, we have noted this with DMF, DMSO and HMP and in every case the alternating copolymer has a higher molecular weight, indicating non-dissociation rather than dissociation. I just wondered if there was any comment on that because it is completely contradictory to the effects of free ions.

Hayashi: In the case of radiation induced ionic polymerization, the formation of the cation occurs both in polar and non-polar solvents. But as I have told you, the rate of propagation of free ions is much reduced in polar solvent. However, in the case of photo-polymerization, ionic polymerization was not observed in non-polar solvent. The solvation effect by polar solvent facilitates the ion separation and initiates the polymerization. The formation of ion radicals was checked by ESR. We determined the distance between negative and positive ion radicals by the use of ESR technique of spin relaxation T2 method. And the distance was estimated on the order of 200 Å which is shorter than the critical distance 40 Å which resides in free or in pair, and this 20 Å suggests a loosely coupled ion pair.

P. Sigwalt, Paris France: I am a little surprised to see such a big difference between the reactivities of the free ion and that of such a loose ion pair, because from other results, particularly those of Szwarc and colleagues, in anionic polymerization, there was not so much difference in reactivities between a loose ion pair and a free ion. On the other hand, it is possible that in your case (chlorinated solvent solution), the fact that the propagation constant over free ions is much lower than for polymerization in bulk, might be due to cation solvation by the solvent. In that case, I don't see either how much difference there could be between the reactivities of the free ion and that of the loose ion pair because, in both cases, you would have a chlorine atom solvating the cation.

Hayashi: ESR gives information only on the radical or radical-ions. The argument which I made is related to the initiation process but not to the propagation. ESR T2 technique has some uncertainty and the 20 Å is the value to an order of magnitude. In addition, the rate constants k_p

which have been mentioned are limited values and the real values for free and pair should be closer to each other.

Schleyer: I'd like to comment on this also. The solvent is, I gather, dichloroethane, which certainly isn't a very good solvating solvent for ions. At a separation of 20 angstroms, I fail to see how you get much effect, so I'd simply like to underscore Dr. Sigwalt's comment. If I understand you, the ESR measurements which led to the 20 angstrom distance were measured under different conditions from the polymerization experiment. Is that what you're saying?

Hayashi: ESR measurement was carried out in the mixture with some viscous material such as amyl alcohol. The sample was prepared at the polymerization temperature and the measurement was made at 77°K. To use amyl alcohol facilitates the measurement because ion-radicals decayed very quickly in pure $C_2H_4Cl_2$. It seems that the distance is not markedly influenced by the temperature. On the other hand, in the case of polar solvent, the critical distance r_c is shorter and major part of ions become free ion. Consequently, strong polar solvent is not suitable to produce loosely coupled ion pairs.

Szwarc: You assume that ions in your system form pairs and that the two partners of a pair are 20 A apart. What prevents them from coming to a distance of, e.g., 10 A? After all, they attract each other!

Of course, you may have solvent separated pair. However, in such a case, you do not expect more than 2 solvent molecules in between and, hence, 20 A is much too much. Moreover, I doubt whether dichloroethane is a sufficiently powerful solvating agent to produce such a pair.

Hayashi: Molecular size of donor, acceptor and solvents are considerably large and not so many molecules exist between ion pairs as you consider.

The nature of ion pair is not the same as in the case of alkalimetal and aromatic compounds, and it is supposed that ion pairs a short distance apart neutralize quickly, maybe before or during ESR observation through tunneling effect.

ESR T2 technique gives a statistic information for the ion-radical pair but interactions between free ions are not included because their mutual distance is too long.

Szwarc: Well, what you imply is that in the whole system the average distance between the ions is 20 angstroms, but this average distance does not determine any specie. And, therefore, it will be very misleading to refer to this system as an ion pair.

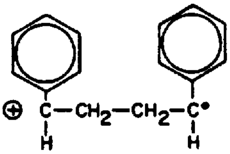
Schleyer: If I understand what you're saying, then, it may be that these ion pairs are not solvent separated at all but may be contact ion pairs and may be totally inactive. The small fraction that are separated may be just as active as the ones generated by the other procedure. I would like to ask Dr. Williams a question concerning the nature of the ions which he generates. Radical cations are being implicated in styrene. Are these the ions actually involved?

Williams: That is a very good question. We believe that in all these systems, the propagation reaction essentially involves a growing carbonium ion. So, it is necessary to explain how the parent ion (a radical cation) which is produced by the ionizing radiation reacts to give a carbonium ion. As I have discussed more fully in my written remarks, there is no problem in the case of isobutylene and other simple olefins. The reaction simply involves a fast proton transfer and this has been clearly established in the mass spectrometer.

$$\underline{\text{iso}}\text{-}C_4H_8^{+\cdot} + \underline{\text{iso}}\text{-}C_4H_8 \longrightarrow \underline{\text{tert}}\text{-}C_4H_9^{+} + C_4H_7\cdot$$

Actually, there is good reason to expect that this reaction competes more favorably with ion fragmentation processes in the liquid than under the conditions which obtain in thie high-pressure mass spectrometer.

In the case of styrene, the situation is not quite so simple. A recent study of the styrene ion-molecule reaction by ion cyclotron resonance (C. L. Wilkins and M. L. Gross, J. Amer. Chem. Soc., 93, 895 (1971)) shows no evidence for a proton transfer reaction, and the styrene radical cation was observed to react with a neutral styrene molecule to produce a complex at m/e = 208. This dimer complex is unstable in the gas phase, but it could be stabilized in the liquid. As we suggested some years ago (Trans. Faraday Soc., 63, 1478 (1967)), this dimer cation could possess a structure involving a carbonium ion at one end and a free radical at the other, viz.,



Accordingly, cationic propagation may then proceed in the usual manner from the carbonium ion end of this initiating species. I think Dr. Hayashi has proposed a similar initiation mechanism for the cationic polymerization of α -methylstyrene resulting from the photoexcitation of a charge-transfer complex.

Schleyer: Well, there are several other ways of generating a cation; one is to break a bond heterolytically and another is to add a positively charged species to an olefin.

Williams: That can be answered simply. In radiation chemistry, the primary process of ion formation occurs by the removal of an electron from the molecule. After that, there can be a variety of ion-molecule and ion fragmentation processes. Ion fragmentation occurs readily in the gas phase at low pressures, but such processes are believed to be much less important in the liquid phase because collisions can remove the excess energy before dissociation can occur. Thus, ion-molecule reactions should be favored in the liquid state.

Schleyer: So then it's a cation radical which is being produced as the typical species.

Williams: Initially, that is correct in all cases.

Chapiro: I would like to comment on this point. The ionization of a molecule by high speed electrons leads to a whole spectrum of ions, the parent ion and a series of smaller ions, resulting from dissociative ionization. The nature of these ions is known from mass spectrometer studies of the molecule, but it is questionable whether the information gained from ionization at very low pressure can be extrapolated to ionization in condensed media. This is a rather sad situation because we do not know the nature of the ions produced in liquids and there are no good methods for studying them. In the case of radiation induced polymerization, it was the fact that ionic polymerization occurred in certain systems which was considered as evidence for the existence of ionic species in irradiated liquids.

I would like to comment on another point raised by Dr. Williams, namely, on the question of anionic polymerization initiated by radiation. It is indeed true that anionic polymerizations are not as widely investigated as the cationic processes but we have obtained conclusive evidence for the anionic polymerization of acrylonitrile in various proton accepting solvents at low temperature, near the glass transition point of the mixture (L. Perec, J. Chem. Phys., 66, 1742 (1969); A. Chapiro, A. M. Jendrychowska-Bonamour and L. Perec, Adv. Chem. Ser., 82, 513 (1968)). In these systems, charge recombination is slowed down due to the very high viscosity of the medium and this leads to very favorable conditions for chain propagation.

J. P. Kennedy, Akron, Ohio: I don't want to tell you about the work I'm currently doing because in a few months you will read it in one of the unsuspecting journals anyway. As Professor Overberger pointed out, nobody can prevent us putting anything into print, if we want to. Rather, I would like to philosophize what is missing and what I would like to see happening in this area.

First, a message about nomenclature. It's more than just semantics that I am calling carbonium ions, carbenium ions; and I'd like to ask all the distinguished delegates here to pick up this proposal and to help clear a little confusion in the field of cationic polymerization. The idea behind this proposition is that the nomenclature of carbontions is inconsistent. In the literature many years ago, we had a perfectly reasonable nomenclature; we called carbenium ions the electrophitic carbons. Since about 20 years ago, incorrect terminology has been in vogue, and we use the word "carbonium ions" to denote positive carbon. So I'd like to ask all of you to re-saddle your horses and start again calling the carbonium ions--what we now call classical carbonium ions--carbenium ions. I'm, of course, joining George Olah who brought this terminology back to the attention of the field. The major argument for this proposal is this: We are using the suffix "onium" to designate situations in which the central atom has increased its valency. In other words, we term the 3-valent oxygen as oxonium ion; 3-valent sulphur, sulfonium ion; 5-valent nitrogen ammonium, 5-valent phosphorous phosphonium, etc., as we always increase the oxidation state of these elements. Consequently, the term carbonium is out of place.

Another inconsistency which I like to point out in the literature is the meaning of the word catalyst. I don't use the word catalyst, I prefer the word initiator, for obvious reasons. Another refinement, of course, is that the true initiating species is not the species like boron trifluoride but really the proton or carbenium ion source. Boron trifluoride is, in fact, a co-initiator.

Among the problems on which I would like to work, and on which I'd like my colleagues to work, are perhaps three areas--initiation, termination and transfer. The understanding of initiation, instead of getting cleared up, is getting more confused. Here I'm referring to recent work by Dr. Sigwalt and his group and the work by Czechslovak authors, particularly by Marek. It is a strong and an irrefutable fact now that we have initiation of olefins without purposely added protons, or carbenium ion, sources. What the exact initiation mechanism is, we just don't know. I carefully studied the Czech papers. In one paper they claim initiation occurs by self-dissociation of Lewis acids. In another paper a year later, this is disclaimed. And in the last paper by the Czech authors, this is a paper in Die Makromoleculare Chemie, which is a write-up of the Budapest meeting, they go on record by stating that they really don't know what's going on. But the fact remains that they are able to initiate the polymerization of isobutylene and isoprene with aluminum bromide or aluminum ethyl dichloride alone. Dr. Sigwalt published an interesting series of papers, starting about five years ago. Here I'm referring to initiation of isobutylene by titanium tetrachloride. The French workers showed that the polymerization of isobutylene can be initiated by $T:Cl_4$ <u>alone</u> if it is condensed from the vapor phase. We also are working on these problems and our thoughts will soon appear in print.

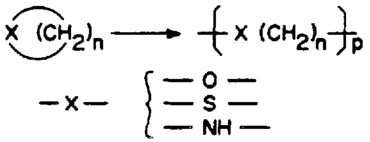
Now, in the area of propagation, the name of the game is ions and ion pairs. Here we ought to follow the lead of the anionic polymerization people who introduced this concept and very beautifully developed it. Now we have also started to scratch the surface, as you heard Dr. Williams. Free carbenium ions are more reactive, give higher rates and molecular weights and, of course, this is lovely particularly if one is interested in the preparation of useful materials.

The next two areas--termination and transfer--are the two most important areas in this whole field. These two parameters determine ultimately conversion or yield and molecular weight. As to transfer, we have models and they work very nicely. We can explain, I would say, 90% of the data with the proton expulsion re-initiation picture. The fine mechanism, whether the monomer or the counter ion is the nucleophile which extracts the proton, or whether it is a one-step/two-step process, we don't know. But at least we have a basic picture which we can use.

Termination is a sore point. We just don't know why many polymerizations stop. We have very few systems where we understand termination. And I'm referring here to Plesch's studies when he studied about 15 or 20 years ago the isobutylene titanium tetrachloride-chloroacetic acid system where he found gegan ion fragments in the polymer. We might even say that the Fontana mechanism, the generation of increasingly stable allylic ions, is a good picture to explain a few olefin terminations. Lately, I have worked with aluminum alkyls and there the termination is an alkylation process, and we have good reason to believe that this is the case with certain aluminum alkyl compounds. But why polymerization is terminating with boron trifluoride or titanium tetrachloride and all kinds of similar reactions, well, we just don't know. We propose termination by impurities. We will talk about these things more in detail next month. Mayo has a symposium on unsolved problems of polymerization. This will be the tenor of my remarks as I will present the problems in cationic polymerizations.

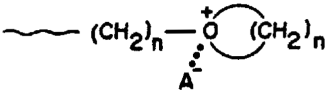
Stannett: Thank you very much. I think we will hold off the discussion until Dr. Pepper, Dr. Plesch and Dr. Sigwalt have had a chance, because it cuts right across what I hope they're going to say, and go on to Professor Saegusa's work. He's going to talk a little about hetrocyclic systems, so it will round off that part. Then we'll come back to Professor Kennedy.

T. Saegusa, Kyoto, Japan: I have been engaged in the cationic ring-opening polymerization of heterocyclic compounds, and I wish to make some comments on the characteristics of this polymerization. The ring-opening polymerization of heterocyclic compounds is expressed by a general equation (eq. (1)).



(I)

The cationic polymerization of these monomers is known to proceed through the propagating species of "cyclic onium" salt by the S_n2 mechanism. Cyclic oxonium salt (I) is the propagating species of the cyclic ether's polymerization, cyclic sulfonium salt (II) is the species of the cyclic sulfide polymerization, and cyclic ammonium salt (III) is the active species of the polymerization of ethylenimine.



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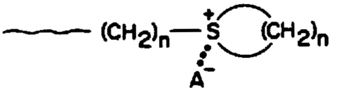

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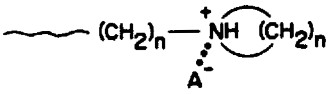
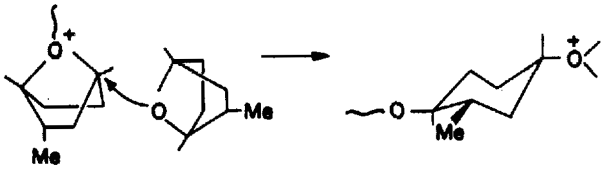
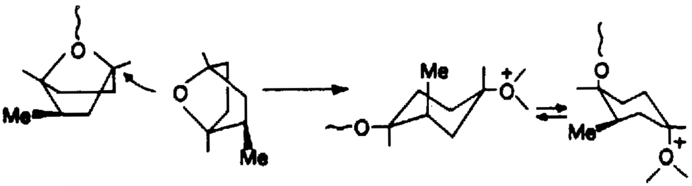


(III)

The S_n2 mechanism has been established also by the Walden inversion in the studies of stereochemistry of the polymerization of the exo and endo isomers of 2-methyl-7-oxabicyclo (2,2,1) heptane.

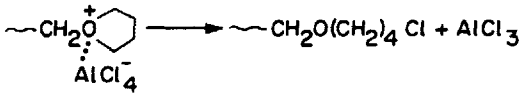


endo-Me monomer



exo – Me monomer

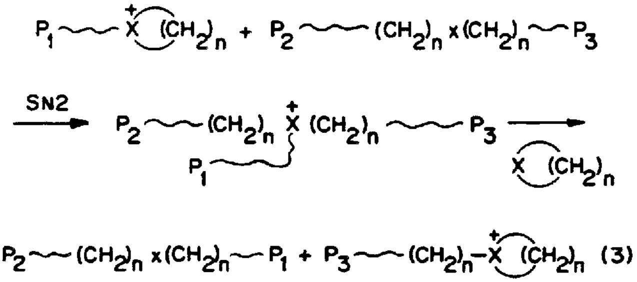
Now, I wish to talk about the synthesis of living polymer having a linear and straightforward structure. In the cationic polymerization of heterocyclics, the reactivity of the propagating species of cyclic onium structure is more moderate than that of the carbonium ion species of propagation in the cationic polymerization of olefinic monomers. Therefore, generally speaking, the polymerization of heterocyclic monomers is suitable for living polymerization. However, there are two undesirable reactions which impede the living polymerization. The first is termination. Some studies on the cyclic ether's polymerization have shown that termination consists of the attack of a nucleophile from counter anion onto the α-carbon atom of cyclic oxonium species of propagation. The termination produces a stable ring-opened alkyl halide, for example:



(2)

Termination reaction of this type is effectively prevented by using initiators which give stable and less nucleophilic counter anion. The typical examples of such counter anion are PF_6^- and SbF_6^-. The problem of termination in the tetrahydrofuran polymerization has been reviewed by Drs. P. Dreyfuss and M. P. Dreyfuss (Goodrich Co.).

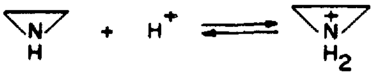
The second reaction which complicates the regular propagation is the chain transfer to polymer. The Sn2 chain transfer of cyclic onium to the hetero-atom of product polymer forms the open-chain onium and leads to the formation of dead polymer (eq. (3)).



(3)

Two Sn2 reactions of cyclic onium with polymer (chain transfer) and with monomer (regular propagation) are competitive with each other. The relative rates of the two reactions are primarily controlled by the relative nucleophilic reactivities of monomer and polymer. In the polymerization of cyclic ethers, monomers of four-membered, five-membered and seven-membered cyclic ethers are more basic and, hence, more nucleophilic than the open-chain ethers of the product polymers. Therefore, we can minimize the chain transfer to polymer ether in the cyclic ether's polymerization. In the case of cyclic sulfide, the situation is quite different. As Dr. Goehtals has pointed out, the cationic polymerization of cyclic sulfide suffers from the rapid chain transfer to the product polymer, because the open-chain sulfide is more nucleophilic than cyclic sulfide. In addition, non-cyclic sulfonium salt is of much decreased reactivity. Consequently, the chain transfer to polymer brings about the cease of polymerization.

As to the nitrogen-heterocyclic monomers, I wish to mention the cationic polymerization of ethylenimine. The secondary amine group of the product polymer is more nucleophilic than that of the ethylenimine monomer. The transfer of ammonium salt to polymer occurs readily. Furthermore, the proton transfer (eq. (6)) leads to branching.



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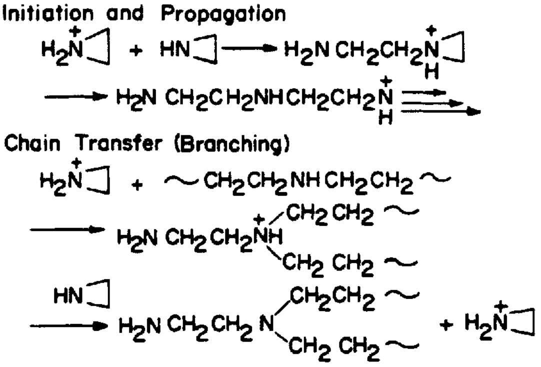
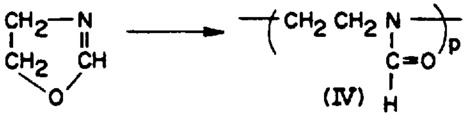


(5)

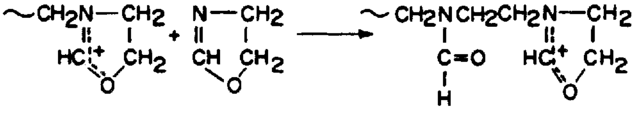
(6)

Conventional polyethylenimine prepared by the cationic polymerization of ethylenimine has a highly branched structure and, hence, it is amorphous.

In connection with polyethylenimine, I wish to tell you our new method for the preparation of linear and crystalline polyethylenimine. The starting monomer is 2-oxazoline. Recently, we succeeded in the isomerization polymerization of this monomer to produce crystalline poly (N-formylethylenimine) (IV).



(IV)



(V) (VI)

The polymerization is cationic one, and cyclic oxazolinium salts, (V) and (VI), are the propagating species. In this polymerization, the N-formyl-nitrogen of product polymer is of much decreased nucleophilic reactivity because of the formyl group. Chain transfer to the product polymer does not occur.

Alkaline hydrolysis of poly(N-formylethylenimine) gave crystalline polyethylenimine having non-branched structure. Our polyethylenimine is insoluble in cold water and soluble in hot water. This solubility property is different from that of the conventional branched one which is readily soluble in cold water.

I have talked about how to control the propagation step in the polymerization of heterocyclics. The method to keep the purity of propagation is essential for the preparation of block copolymer by means of the technique of multi-stage polymerization. For example, the living polymerization of cyclic ether was successfully applied to the synthesis of a new elastomer having a structure of three blocks.

(Poly-THF)-(Copoly THF/$_{\text{BCMO}}$)-(Poly-BCMO)

In this copolymer, an amorphous block of copolymer of THF (tetrahydrofuran) with BCMO (3,3-bis(chloromethyl)oxetane) is bound to two crystalline blocks of poly-THF and poly-BCMO. It exhibits the properties of elastomer vulcanized by crystalline part.

Goldberg: It may be of interest to note some work by Pearson and Levy in our laboratory which has not yet been published, but which indicates that a wide variety of multiblock polymers may be prepared by cross-termination of "living" difunctional anionic and cationic systems. The stable cationic species are mostly based upon oxonium ions.

Saegusa: I want to explain shortly the preparative method of our block copolymer. First, we polymerized tetrahydrofuran by BF_3-epichlorohydrin system at 0° C. This polymerization system had been shown to be an almost living one. Then, we add the second monomer of BMCO. The second polymerization is a copolymerization between unreacted THF and BCMO. Next, we cooled down the second polymerization system to -30° C and distill out the THF monomer in vacuo. Finally, we performed the third stage polymerization of BCMO.

This procedure is a multi-stage polymerization in which the nature of propagating species is cyclic oxonium throughout the block polymerization.

Mrs. M. P. Dreyfuss, Brecksville, Ohio: Did I understand correctly that you are suggesting we can control transfer in the oxonium ions by stopping at an early stage?

Saegusa: Yes.

Dreyfuss: That's fine for theoretical studies, but it doesn't do much if you want to make polymers. Can you suggest ways to actually produce the product?

Saegusa: Yes. The nucleophilic activity of the cyclic ether monomer is much higher than that of the open-chain ether. We can keep the chain transfer to a very small extent when we carry out the polymerization in the presence of fairly high concentration of monomer, i.e., in the range of not high conversions.

Dreyfuss: In our experience, we cannot control this transfer. Whenever we carry polymerizations to reasonably high conversion, we find distinct evidence for transfer in the molecular weight distributions.

Saegusa: It seems to me that the chain transfer to polymer is dependent upon the nature of counter anion, i.e., the nature of the initiator. According to our experience, we could obtain polytetrahydrofuran having a narrow distribution of molecular weight by using the initiator of the $AlEt_3$-H_2O-epichlorohydrin system. The ration of Mw/Mn was 1.04.

Dreyfuss: I'm not sure that one can use that strictly as a measure of transfer, because we have deliberately added transfer agents and find that the effect of transfer is to narrow the distribution.

Saegusa: When the concentration of open-chain ether is kept low, the degree of chain-transfer does not become high. As to the effect of chain-transfer agent, we have to consider the influential factor of its nucleophilic reactivity.

Smets: I would like to ask Professor Saegusa if the reaction mechanism for the nitrogen derivative is also valid when, instead of the group, there is hydrogen on the nitrogen. Do you also get chain transfer to polymer if there is a hydrogen on the nitrogen?

Saegusa: Do you mean the polymerization of N-phenylethylenimine?

Smets: For instance, yes.

Saegusa: We have not examined it.

Smets: As far as we know, we suppose it's not a branch of it.

Saegusa: In principle, the branching of the conventional polyethylenimine is due to the hydrogen of the secondary amine group

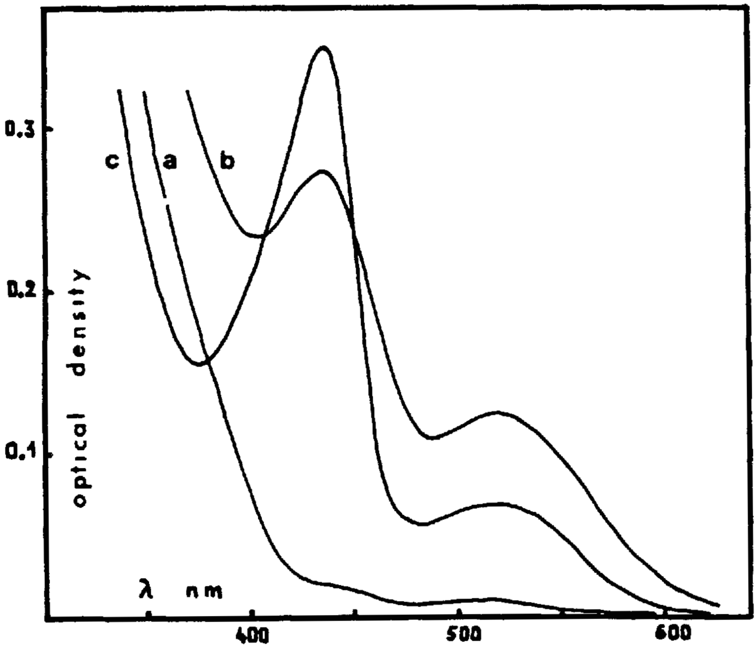


Fig. 1 (Sigwalt). Electronic absorption spectra of mixtures: 1,1-diphenylethylene (DPE), $TiCl_4$, and CH_2Cl_2 at -30°. Curve a: [DPE] = 0.318 M, [$TiCl_4$] = 2.52 X 10^{-3} M. Curve b: d° and then H_2O addition (3 X 10^{-3} M). Curve c: [DPE] = 0.029 M, [$TiCl_4$] = 2.12 X 10^{-3} M.

of the product polymer. In such a sense, the polymer of N-phenylethylenimine has no branching. However, we have still a problem from the kinetic point of view, that is the distribution of ammonium species between the two kinds of bases, the monomer and the polymer. At the present time, I have no direct data concerning the problem of distribution.

J. Sebenda, Prague, Czechoslovakia: I would like to stress only a few remarks of Dr. Kennedy. Most of our conceptions of the mechanism of reactions occurring in cationic polymerizations is derived from the kinetics of polymerization. However, sometimes we arrive at a point at which kinetic evidence is insufficient.

As an example, I would like to mention the cationic polymerization of caprolactam. In this case, a very complicated conversion curve was observed which couldn't be fit to any known mechanism. When looking more closely at the chemistry of this polymerization, it turned out that there are significant side reactions leading to the decay of the active species. As a matter of fact, the strongly acidic medium produces strong bases which destroy the catalytic species and, in addition, growth centers are consumed by these side reactions. As a result, we are dealing with a polymerization with variable concentrations of active species. After taking into account these side reactions, the peculiar conversion curve could be understood much better. I would like to stress that we have to look after such reactions destroying or producing active species also in cationic polymerizations of olefins and vinyl monomers, and that we have to be very careful in deriving reaction mechanisms from kinetic data.

Overberger: Well, I would share part of Professor Kennedy's reservations about details of the termination mechanism, but I must say that for termination of cationic systems in which you are adding aromatics of known structure, it was determined rather clearly that the rate of addition to the aromatic structure was quite similar to that order of reactivity that you would find for mercuration or nitration or bromination. In those cases, we know the rate determining step is the addition to the aromatic system and not the removal of the proton, either by the monomer or the catalyst gegen ion. At least, in that case, I think we are on relatively safe ground.

Kennedy: Charlie, you're absolutely right. However, I don't consider alkylation of an aromatic, termination. This would be chain transfer.

Schleyer: The problem of the interaction of aluminum halides with olefins was referred to, and this is another problem which gets cyclically repostulated and disposed of. Many years ago, for example, the isomerization of alkenes by aluminum chloride was postulated to involve a similar kind of process. But when heroic efforts were made in gas lines to purify the aluminum bromide and the olefins, the isomerization was not observed. I wonder whether the experiments to which you allude involved similar precautions.

Kennedy: Well, in this case, I'm very proud to say that I'm a polymer chemist because we--not I, but many of my colleagues, have worked extensively on the high vacuum line, and I would be much happier if I could state the same thing for organic chemists. Organic chemists, unfortunately, do all kinds of things with aluminum bromide which shouldn't be done. Consequently, the literature is full of peculiar things for many years until the work is repeated in high vacuum. You are entirely right--petrochemistry is full of interesting lore of aluminum chloride and aluminum bromide--what these Lewis acids do in the stirred pot. But, when you repeat the reaction under anhydrous conditions on the high vacuum line, things don't happen. Now, the problem of initiation of isomeration of olefins you are referring to has, I think, been solved. It has been shown that the presence of olefins provides the allylic site and allylic hydrogen removal starts the reaction. The concept of co-initiation truly emerged in polymer chemistry. The classical British group--Evans, Polanyi, Plesch--brought this really in focus. If you carefully look in the literature, you see tidbits of information emerging before that group (I've forgotten the names of the classic organic petrochemists who did this work) who found, for example, that one cannot alkylate with ethylene in carefully purified quartz vessels. Things like that. But these lines have not been followed up in classic organic chemistry. I think that after the concept of co-initiation was very strongly established in polymer chemistry, it also trickled over into fundamental organic chemistry.

Schleyer: The simplest mechanism for the polymerization of an olefin by aluminum bromide doesn't involve direct reaction with aluminum bromide, but the generation somehow of a proton which then adds to give a cation. Now, it's awfully difficult to eliminate all traces of water which might serve as the proton source. This is the nature of the question.

Kennedy: These problems we are very much familiar with. I think Dr. Pepper and Dr. Plesch are much more qualified to talk about the problems here because they did the work on which I broached. This question has been discussed very extensively in our literature, and I'm sure we will get back to it.

D. C. Pepper, Dublin, Ireland: The first thing that occurs to me is to draw attention to something that I am a little surprised has not been noticed so far. If you compare the titles of the two halves of this Colloquium, the first says New Phenomena in Radical Polymerization, and the second says New Concepts in Cationic Polymerization. There is a valuable point to be got out of this comparison.

This morning's list of topics was full of very striking new and complex phenomena in radical polymerization, and our task is to interpret these in terms of very well tried concepts. After all, as Professor Bamford has been able to show, the concepts of free radical reactivity and their detailed structures are really very well established.

By contrast, on the cationic field, our concepts about the reacting species are old concepts--imperfectly tested, unproved concepts, plausible perhaps, but that is their only status--they have never been decently established. What is needed in this field is not so much new concepts as some new phenomena--new experiments by which these old concepts can be properly tested and some, perhaps, eliminated.

This is perhaps not so true in the field of cationic polymerization of oxygen and sulphur heterocycles where there is, in fact, a good deal of new work (especially by Goethals) which can be clearly interpreted in terms of oxonium and sulphonium ion propagation. But in the carbonium (must I now say carbenium) field we are still, in my opinion, suffering from a surfeit of concepts and a deficit of proper information by which to test them.

I am a little out of date in saying the above, because the results Professor Hayashi has just been showing us are just what is needed--new phenomena that will help us sort out the still unestablished cationic concepts. There is a contradiction, or dilemma, in the interpretations of cationic polymerization by perchloric acid, which I was asked to talk about, and the new work by Professor Hayashi may well help to resolve some of these. My own tentative evaluation of the free cationic propagation rate constant for styrene gives a value between 10^3 and 10^4 $1\ m^{-1}s^{-1}$ (at -80° in CH_2Cl_2). This is so much less than the values $> 10^6$ found in bulk polymerization at room temperature that one has been very uncertain whether it could be valid. I know that dielectric and solvation effects should reduce the figure, but I never could quite accept that they could reduce 10^6 down to 10^3. However, the values that have been proposed by Professor Hayashi (for polymerization in butyl chloride) are down in this region, so perhaps the discrepancy is not so bad!

My values of k_p (free cation)$\sim 10^{-3} - 10^{-4}$ for styrene in CH_2Cl_2 at -80° are deduced from the observed maximum rate in the initial rapid stage coupled with an estimate of the maximum concentration of an intermediate assumed to be the polystyryl cation. Estimates at other temperatures (-70° to 0°) are in principle possible from the subsequent steady rates, if a valid interpretation can be established.

Thus, these rates are found to be first order in monomer and in initial concentration of perchloric acid ($\equiv$HA) and are partiall suppressible by tetra alkyl ammonium perchlorate salts (SA)--i.e., are reduced to a limiting value as $[SA] \to \infty$. A plausible qualitativ interpretation is that the acid has been converted (in the preceding fast initial stage) to an equivalent concentration of polystyryl perchlorate ester, PA, which then "carries" the steady rate through its ionic dissociation products (and perhaps itself, pseudocationically).

Quantitatively one may depict the dissociation to the various species, with their equilibrium concentrations and appropriate propagation rate constants:

$$\begin{array}{ccccc} \mathrm{PA} & \overset{K_1}{\rightleftharpoons} & \mathrm{P^+.\,A^-} & \overset{K_2}{\rightleftharpoons} & \mathrm{P^+ + A^-} \\ \textbf{Ester} & & \textbf{Ion pair} & & \textbf{Free ions} \\ [\mathrm{HA}]_o & & K_1[\mathrm{HA}]_o & & (K_1K_2[\mathrm{HA}]_o)^{\frac{1}{2}} \\ k_{ps} & & k_{pp} & & k_{pf} \end{array}$$

leading to an overall rate of monomer (M) consumption

$$-d[M]/dt = k_{ps}[M][HA]_o + k_{pp}[M]K_1[HA]_o + k_{pf}[M]K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}[HA]_o^{\frac{1}{2}}$$

and an apparent rate constant

$$k_p(\mathrm{app}) = k_{ps} + k_{pp}K_1 + k_{pf}K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}[HA]_o^{-\frac{1}{2}} \; \ldots\ldots\ldots \quad (1)$$

In presence of perchlorate salt, SA, dissociating with a constant K_S (K_1K_2), the common-ion effect will reduce $[P^+]$ to $K_1K_2[HA]_oK_S^{-\frac{1}{2}}[SA]_o^{-\frac{1}{2}}$ and the apparent rate constant becomes

$$k_p(\mathrm{app}) = k_{ps} + k_{pp}K_1 + k_{pf}K_1K_2.K_s^{-\frac{1}{2}}[SA]^{-\frac{1}{2}} \; \ldots\ldots \quad (2)$$

Our quantitative results only partially fit this theory, in that equation (2) does describe the "salt effect" but equation (1) does not obviously describe the behavior in "salt-free" systems (which, at a given temperature, give a constant value for k_p(app) showing no trend with $[HA]_o$ over 12-20 fold ranges).

These findings can be formally reconciled only if the third term in equation (1) is very small, which could be the case if the overall dissociation constant of the ester K_E ($\equiv K_1K_2$) is extremely small, and the free ion propagation constant, k_{pf}, not too high. Rather shaky procedures for separating K_E and k_{pf} are possible, but so far give only higher than expected values for K_E, 10^{-5} - 10^{-7} (0° and -45°) and disconcertingly low values for k_{pf}, e.g., 10 1 m s^{-1} (at 0°).

The dilemma I referred to is that the theory seems to be borne out in its <u>form</u>, but gives nonsense values for the derived constants. Perhaps the findings of Professor Hayashi give some hope that the gap to be explained is not quite as wide as nad been feared.

<u>Sigwalt</u>: To begin with, I don't want to get involved in semantics, but I must say I endorse completely the proposition of Professor Kennedy to abandon the use of "carbonium ion". But instead of "carbenium ion", I would prefer to use "carbocation" which would be more symmetrical to carbanion. But this is something that may be discussed.

I would like first to give my general impression about the status of cationic polymerization. I don't want you to get away from here with the wrong impression that something is known, in the field of the polymerization of ethylenic monomers, about the nature of the active species. I would say that very little is known about this nature in most systems. The situation is quite different from that described by Professor Saegusa in the case of the opening of heterocycles, for which very bright work had been done in recent years that has led to much success. I think the main difference is that in the case of the oxonium type polymerization, something is known of the concentration of the active centers. There have been a few techniques evolved that permit to have a good approximation of this concentration. Now the situation is quite different in cationic polymerizations of ethylenic monomers, and this is why most of the kinetic work made until now could not lead to the real values of the absolute rate constants for the reactions because the concentration of active centers is not known generally. For example, the case exemplified by Professor Pepper here, shows that it is quite difficult to find their concentration. He has made some spectrophotometric measurements that gave an indication of these values, but this is one of the rare works that has been made in this field. In many other cases, we don't know anything about the concentration; for example, in the case of initiation by Lewis acids, such as Friedel Crafts catalysts, which is probably the most interesting from an industrial point of view since it is one that gives useful polymers of high molecular weights. Well, you may be surprised perhaps to hear that the uncertainty about the concentration is sometimes by a factor of 10^4 or 10^5. My feeling is that if we are to do some progress in this field, we should concentrate on finding and studying new systems--new monomers which lead to polymerizing systems--for which the measurement of the concentration of the active species can be made preferably by direct means, that is, by a physical chemical method. And I am referring, for example, to spectrophotometric measurements or NMR measurements. But NMR may be difficult because the concentration is so low that it is not very often that results may be obtained, whereas UV spectrophotometry is possible. The interpretation of data is more controversial than NMR, naturally, but the two types of results may be correlated by independent measurements. Now, one of the problems is to measure the reactivities of the different species involved. That may be free ions, ion pairs, eventually esters or eventually also different types of ion pairs. Such type of work has begun. For example, Professor Pepper has made some work in this field by following the lines of Professor Szwarc in anionic polymerization, that is, adding a common ion electrolyte and observing the kinetics change in the process, and we are doing also some work in this field. But there remains the uncertainty of the total concentration of active species which is the main problem. Why do we know so little about this concentration? Well, it's probably because the species are extremely unstable and very reactive. Another important thing that happens in the case of the initiation by Friedel Crafts catalyst is that very little of the initiator used really gives an active center. The proportion really consumed is at most a few per cent and sometimes a few thousands and even less, that is really giving active centers. With the theory of cocatalysis when this was the only one available, it was rather easy to suppose that the catalyst is inactive by itself and the initiator is, for example, a complex of catalyst and cocatalyst. The cocatalyst may be in so small a concentration that you get at most as many active centers as co-catalyst molecules. In fact, there have been many studies in recent years that have confirmed that a cocatalytic effect occurs in many systems. That is, if you have a system that does not polymerize and if you add a certain substance, for instance a proton donor, generally polymerization occurs. This is a straightforward cocatalytic effect, and more and more systems showing such a behavior are known. But, paralleled with that, systems have also been found for which occurs a type of initiation that does not seem to involve any co-catalyst. It seems that for some systems, the two types of mechanisms may be operative simultaneously and, for others, one may be predominant. The situation may depend upon the experimental conditions and particularly upon the purity of the system, and if one succeeds in eliminating completely the co-catalyst. Now, the question that Professor Schleyer asked was, "How can you be sure that you have no co-catalyst?". This may only be shown generally by indirect reasoning, but I think it can be concluded in some cases that the polymerization may occur without being induced by a co-catalyst. The best way to show that is to give an example, because a purely theoretical reasoning may not be clear enough. I shall choose one that is not yet known by my colleagues in cationic polymerization. They have heard of other similar cases already, but I prefer to speak of a new example, the interpretation of which seems a little clearer. The reason for this is that in that case the carbocation can be seen by spectrophotometry and we may know the concentrations of the species that are formed.

The reaction we have studied recently is not a true polymerization but the dimerization of 1,1-diphenylethylene by titanium tetrachloride. We have found that by working in methylene dichloride at sufficiently low temperatures (e.g., -30° or below), the 1,1-diphenylethyl cation that is formed is indefinitely stable during the whole polymerization. This cation has been identified previously by several authors--by NMR identification of the species absorbing around 430 nm--and more recently it has been shown in Professor Szwarc's laboratory that the maximum in methylene chloride solution is at 435 nm.

One experiment may show that a cocatalyst was not present with the experimental conditions used, that is, high vacuum and baked vessels, sealed apparatus without stopcocks. If one mixes a proportion of 100 monomer molecules for 1 of $TiCl_4$, no maximum is seen in the UV spectrum between 400 and 600 nm (Figure 1, curve a). If to such a system you add a cocatalyst (such as water or hydrogen chloride), a peak is formed at 435 nm, and another one, smaller, at 520 nm (Figure 1, curve b). If more water is added, one finds that the optical density of the 435 nm peak is proportional to water concentration. The extinction coefficient of the peak may be obtained this way, based upon the water quantity and supposing that every water molecule gives birth to one carbocation, and one gets the value given for the diphenyl ethylcation obtained by different methods; for example, by mixing the carbinol with sulfuric acid. It is then possible to say that, initially, there was not in the system a significant quantity of proton donor since no peak was seen.

Let us see now the evidence for a direct initiation. I may give two different examples relative to this system. If you make the same kind of experiment, using the same $TiCl_4$ concentration, but instead of 100 parts of monomer, taking about 10 parts of monomer (relative to $TiCl_4$), one obtains a spectrum (Figure 1, curve c) that is quite similar to the one that was obtained after water has been added to the first system. This means that using less monomer has led to initiation. The first explanation would be to say that in the case of 100 parts of monomer, there was an inhibition, that did not occur when 10 parts were used, and that the inhibitor is mixed with the monomer. I don't think I can discuss this hypothesis in detail, but there are several results that are not in agreement with it. Moreover, the inhibitor hypothesis would not explain why inhibition does not occur when you add water to the first system. Another important thing should be said. The polymerization takes place in the systems when the UV maximum appears, and when there is no maximum, there is also no polymerization.

The second example I shall give is not consistent either with a possible inhibition. In that case, you also start from the same system that has no UV maximum and does not polymerize. If you distill the mixture from one part of the vessel to another part that has also been thoroughly washed and baked, the spectrum appears and polymerization takes place. This is in accordance with the results we already obtained five years ago with isobutene and that were mentioned by Dr. Kennedy. The interesting difference now is that we can measure the concentration of the cations. However, there is also a difference with isobutene. In that case, starting from a non-polymerizing mixture and condensing $TiCl_4$ from the gas phase, polymerization occurred; but with the 1-1 DPE system, addition of $TiCl_4$ in the gas phase did not lead to initiation. I think the difference is that with isobutene there is always some isobutene in the gas phase, because its vapor pressure is much higher than that of 1-1 DPE; whereas in the case of 1-1 DPE, there is no 1-1 DPE in the vapor phase. Under those conditions, if initiation occurs by $TiCl_4$ and monomer reacting in the gas phase, it does not occur with 1-1 DPE but does take place with isobutene.

<u>P. H. Plesch, Keele, United Kingdom</u>: I would like to comment on some of the points made by our colleagues. First, I want to recall a reaction reported in 1929 by Puxeddu (E. Puxeddu,

Gazetta, 59, 160 (1929)) and which has been largely ignored since then. We re-discovered it in the 1950's (W. R. Longworth, P. H. Plesch and M. Rigbi, J. Chem. Soc., 1958, 451), and I think that it may be the clue to many of the apparently irreconcilable or unintelligible phenomena which have been reported.

Puxeddu found that if a mixture of a reducible metal halide with an ether was exposed to sunlight, there was a photochemical reaction in which the metal halide was reduced. This reaction can be represented generally thus:

$$2MtX_n + RH \xrightarrow{light} 2\ MtX_{n-1} + RX + HX \qquad (1)$$

It goes with alkyl halides and hydrocarbons, and it does not need much light. I came upon this reaction when I moved from Manchester to Keele. In Manchester I worked in a dark basement, and there I could keep solutions of titanium tetrachloride in hexane for several weeks without much change. In Keele I had a south-facing laboratory and I could not keep those solutions for more than a day without a beautiful purple precipitate of titanium trichloride being formed. I think that many phenomena, such as those reported by Professor Sigwalt, may find a quite simple explanation in terms of the alkyl hallide and/or the hydrogen halide formed by a Puxeddu reaction acting as co-catalyst to the unreduced metal halide. So before we seek new explanations for new mysteries, we should make quite sure that we have made use of all our old information.

The next point on which I wish to comment is the behavior of metal halides in solution, especially their self-ionization, which I think is the clue to an understanding of their role as initiators. We found (W. R. Longworth and P. H. Plesch, J. Chem.

Soc., 1959, 1887) that titanium tetrachloride in methylene dichloride and in ethyl chloride self-ionizes, and the simplest representation of this reaction is

$$2\,TiCl_4 \rightleftarrows TiCl_3^- + TiCl_5^- \qquad (2)$$

We also concluded (Ibid) that the conductivities of aluminum halides in alkyl halide solution reported by Fairbrother and Scott (F. Fairbrother and N. Scott, J. Chem. Soc., 1955, 452) and by Jacober and Kraus (W. J. Jacober and C. A. Kraus, J. Amer. Chem. Soc., 71, 2405 (1949)) could be interpreted much more consistently and plausibly by a self-ionization of the aluminum halide

$$4AlX_3 \rightleftarrows Al_2X_5^+ + Al_2X_7^- \qquad (3)$$

We estimated the equilibrium constant of this reaction to be of the order of 10^{-18} l^2 mol^{-2} for $AlBr_3$ in EtBr at 25° C.

One of the mysteries mentioned by a previous speaker is that the catalytic, or initiating, efficiency of aluminum halides is generally extremely low, i.e., only a very small fraction of the initiator present actually initiates polymerization. This fact has of course been well known to all who are acquainted with the Butyl process and related reactions. I can see a quite plausible explanation of this in the following terms: I am satisfied that, at any rate with some monomers, aluminum halides can initiate without a co-catalyst and that even when a potentially co-catalytic solvent, such as an alkyl halide, is present, it is not necessarily involved in initiation. I have suggested (P. H. Plesch in "Progress in High Polymers, Vol. 2" Ed. J. C. Robb and F. W. Peaker, Iliffe Books, London, 1968, p. 137, chapter on "Cationic Polymerization") that in such systems the initiating species is a positive ion formed from the initiator by self-ionization, which adds to the double bond of the monomer to give a carbenium ion. In the present instance we can write this reaction as

$$Al_2X_5^+ + M \rightleftarrows AlX_2M^+ + AlX_3 \qquad (4)$$

and it is my guess that this, or something very like it, represents the initiation. The question arises: Why does reaction (4) not shift the equilibrium (3) until, say, one half of the Al atoms have participated in carbenium ion formation? This question is based on two assumptions, both of which are wrong. (i) It assumes that the self-ionization is fast and (ii) that mixing of monomer and initiator solutions does not lead to any interaction other than initiation. The assumption (i) is intuitive, but as far as I know, no one before us has studied the rate of ionization of an aluminum halide in solution. However, we have found (D. W. Grattan and P. H. Plesch, unpublished) that for $AlBr_3$ in MeBr at 0° to -80°C with $[AlBr_3]$ ca. 10^{-3} to 10^{-4}M, the ionization has a half-life ranging from ca. 10 minutes to more than 1 hour, depending on conditions. The kinetics are complicated and since we are only at the beginning of this study, I do not want to say any more at this stage, except that the MeBr does not appear to be involved in the formation of the ions. The second assumption is unfounded because it is well known that electron-deficient metal halides form fairly stable addition complexes with olefins.

In the light of these considerations, we can now understand quite simply the low initiating efficiency of the aluminum halides: When, say, a solution of $AlCl_3$ in MeCl is mixed with a solution of monomer, only the very small concentration of cations ($AlCl_2^+$

and/or $Al_2Cl_5^+$) present at the instant of mixing can initiate. The major part of the unionized $AlCl_3$ becomes complexed with monomer, and the rate of formation of more Al-cations from any residual free $AlCl_3$ is so small that, as far as the (usually very fast) polymerization is concerned, it is completely irrelevant.

I would like to emphasize that neither the initiation by addition of AlX_2^+ to olefin, nor the exact mechanism of the self-ionization of aluminum halides has been proved, though we are working on both problems; but I feel confident that my ideas about what happens in these systems point in the right direction and provide us with a picture which helps our understanding.

Also, I am sure that we must be very careful not to generalize from the halides of one metal to those of another; they all seem to have their own peculiarities.

To sum up, I think that a proper appreciation of the Puxeddu reaction and of the small extent and low rate of the self-ionization of metal halides may be of great help in understanding some of the phenomena which are puzzling us at present.

<u>Overberger</u>: I've misunderstood something here perhaps, so let met ask you some questions. You're carrying out the polymerization at -30° with titanium tetrachloride in methylene chloride--if you carefully dry everything, you get a spectrum which indicates no carbonium ion and you get no polymer, correct? Now you add water or HCl and you see the spectrum of the carbon cation ion pair and you do see polymerization. I presume the polymer is fairly low molecular weight--is it a polymer or a dimer? Now, tell me again how you deduce that you can obtain polymer without the co-catalyst.

Sigwalt: If I make another experiment just changing the monomer concentration--by keeping it low instead of having it high--the polymerization occurs.

Overberger: Do you see the spectrum of the cation?

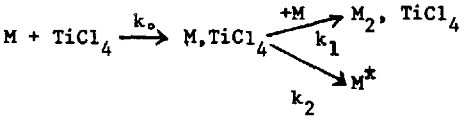
Sigwalt: Oh yes. The spectrum is about the same as the one you get with a fair quantity of water.

Overberger: So, you're saying if you reduce your monomer concentration extensively that there is some mechanism whereby you get a fully-blossomed carbanion ion pair. Now, did you make a suggestion as to the rational for this.

Sigwalt: You can always make a suggestion, even if there are arguments against it. If a direct initiation is possible, it is necessary to explain why something inhibits most of the catalyst so that it does not give the active species. And this is linked with the question of why the concentration of active species is generally so low in the case of Friedel Crafts catalysts. We are led to the conclusion that part of the catalyst is in inactive form. And the most likely inactive form I can think of is a complex between the monomer and the catalyst--an inactive complex. One may imagine that if this complex involves, for example, two monomer molecules, its formation might be competitive with a direct initiation involving only one monomer molecule and, with the right rate constants, it is possible to find a scheme explaining the results. With a big excess of monomer, most of the catalyst could be incorporated in a complex such as $TiCl_4$, 2 M, for example.

Overberger: All right, and this does not polymerize....

Sigwalt: This inactive complex has no spectrum in the region of the carbocation. One can imagine that an intermediate complex may be formed like M,$TiCl_4$:



And if $k_1 \gg k_2$, most of the $TiCl_4$ would be in an inactive form and some of it would lead to the active species M^*. About the nature of the initiation step, there are several possibilities.

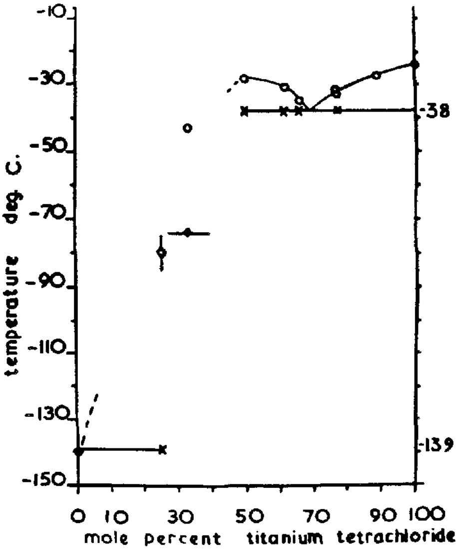


Fig. 1 (Plesch). Freezing-point phase-diagram of titanium tetrachloride and isobutene. The freezing points (O) and eutectics (X) show clearly the existence of a 1:1 complex. If the ill-characterized transition-point (◊) near -75° is a eutectic arrest, it would signify the existence of a second complex with composition $2C_4H_8{:}1TiCl_4$.

One of them was mentioned by Professor Plesch, the self-ionization of $TiCl_4$. In our case, I don't like it too much because we were able to obtain a proportion of active species relative to catalyst that were fairly high when monomer concentrations were low. The proportion could be higher than 20 per cent in some cases, and I don't think it can be easily explained by a process of self-ionizatior

I would like also to comment on the suggestion of something happening in the gas phase by photolysis. We were naturally aware of this possibility and have performed experiments in the dark, in the case of isobutene polymerization on condensation, and the results obtained were exactly the same. And in the case of 1-1 DPE, many polymerizations in solution have been made and were perfectly reproducible, initiation occurring only for the low [M]/[C] ratio, both in the dark or in daylight.

Plesch: I would like to comment on this. The existence of complexes between titanium tetrachloride and isobutene was proved by us many years ago by means of a freezing-point phase-diagram (W. R. Longworth, P. H. Plesch, and P. P. Rutherford, in "Interntl. Conf. on Co-ordination Chemistry, 1959", Chemical Society Special Publication, No. 13, p. 115). Since the actual diagram has never been published, I show it here in the Figure. One can see there evidence for certainly one, and probably a second, complex. With the techniques available at the time, it was very difficult to prevent polymerization at low temperatures and low $TiCl_4$ concentrations, and that is why the phase diagram is somewhat incomplete. It should also be noted that at least one of the complexes has a very distinctive orange-red color. This has nothing to do with carbenium ions, since the t-Bu ion does not absorb in the visible. The color is probably related to that of $TiCl_4 + C_6H_6$ mixtures, and due to a shifting of the $TiCl_4$ absorption towards the visible by complex formation.

Schleyer: I'd like just to make a brief comment. This is somewhat obvious, but I think it's a helpful viewpoint both for cationic and free radical species. We think about modifying reactivity of such species by, e.g., solvent or counterion. It may actually be more helpful to change nomenclature thus implying a different way of thinking. I think in many cases an alteration of the medium or environment actually changes the species. And I think that's probably a better way to think of the situation--as being a modified species rather than merely intermediates with modified reactivity. For example, a carbonium ion pair is really not a carbonium ion anymore. I'd prefer to think of this as a "cationoid" species, much the same was that "carbenoid" species and not free carbenes are now recognized to be involved in many reactions when carbon metal bonds are broken.

Stannett: I'd like to thank every member of the panel for initiating such a lively discussion, and everyone else who added to it in the audience. Now, I would like Professor Szwarc to offer his concluding remarks.