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### New Phenomena in Radical Polymerization

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NEW PHENOMENA IN RADICAL POLYMERIZATION

Chairman: G. Smets, Louvain, Belgium

Speaker: V. Zubov, Moscow, U.S.S.R.

G. Smets, Louvain, Belgium: Gentlemen, as Professor Vogl already said, Professor Zubov will present today the paper which should have been presented by our colleague, Professor Kabanov. Each of us knows very well the very active research directed by Professor Kabanov at the Lomonosov University of Moscow. We do regret very sincerely his absence. May I now ask, please, Professor Zubov to take the chair.

V. Zubov, Moscow, U.S.S.R.: The purpose of today's talk is to discuss some of the new developments in the field of radical polymerization. The properties of the free radicals and the rates of the radical reactions, if not controlled by diffusion, are relatively not much dependent on the characteristic of the reaction medium, for example, of its polarity. In the case of radical polymerization at certain temperatures, the set of the rate constants of the elementary steps is mainly determined by the nature of the monomer. One of the disadvantages of common radical polymerization arises from this fact, namely from the difficulties to control the chain propagation step which affects the total rate of the reaction and determines the microtacticity of the macromolecules as well as the composition and sequence distribution in the copolymerization products. At the present

time, a number of nonradical polymerizations are known in which the propagation step can be controlled rather successfully. It should be stressed that in all cases such control is brought about by the interaction of the propagating chain ends with the complementary species such as counterions or components of the coordination complexes and so on. In common radical polymerization systems there are no similar particles present in the vicinity of the active center. There are free propagating radicals and chain propagation occurs during the independent successive addition of the monomer molecules to the radical.

The basic ideas of the mentioned "classical" mechanism of radical polymerization had been formulated on systems where the kinetic parameters of the chain propagation are ruled mostly by the intermolecular interaction of the unpaired electron of the radical or double bond of the monomer with a substituent in the radical and the monomer. Thus the nature of radical and the corresponding monomer determines all the kinetic behavior of the system, and variation of the solvents and other reaction conditions have very little effect on the process. But at the same time, during the last few years it has been shown that a situation which is rather similar to the ionic or coordination ionic polymerization could also be achieved in the free radical polymerizations. Two kinds of the radical polymerizations where similar effects can be successfully used will be discussed. The first is the polymerization of the ionizable monomers, which have a salt-like or acidic functional group. The second group is made up of the systems where various complexing agents are introduced in the reaction medium which, in fact, may produce similar results.

Let us start with the polymerization of the ionizable monomers. As it is well known from the physical chemistry, the state of the ion-pairs and ion associates could be easily regulated by varying of the reaction media, its polarity, solvation power, ionic strength and so on. Usually, in the case of conventional ionic or coordination ionic polymerization, one of the ions is in fact the terminal atom of the propagating chain, and the active center is easily destroyed by the introduction of protons or hydroxyl groups into the system. But in the case of the radical polymerization, the active center (free radical) itself is inert to the solvents like water, alcohols and so on. Therefore, it is possible to vary the nature of the reaction media to a very wide extent starting from non-polar solvents and coming to the aqueous media without destroying the active centers. Thus one can vary the mode of interaction of the ion and counterions which are not by themselves the reacting species as in ionic polymerization but are situated in close vicinity to the reactive sites such as unpaired electron or double bond. Thus one can induce at least two kinds of effects. The first one is the variation of the electronic structure of the reactive species, e.g., change of the polarization in the monomer and in the radical by changing of the ionic state of the substituent. The second may be called an intermolecular effect of the ionic substituent that is a variation of the intermolecular interaction between the monomer and the radical due to electrostatic repulsions at variation of the ionic state of the ion pairs. I want to demonstrate some of these effects by means of the few rather arbitrarily chosen examples, most of them based on the results obtained in

the Moscow State University and in the Topchiev Petrochemical Institute (Moscow).

Let us consider the polymerization of methacrylic and acrylic acid in aqueous medium. If one plots the relative polymerization rate of acrylic or methacrylic acids at different pH, the typical picture is like this. At first the increase of pH from 2 to 7 is accompanied by a sharp decrease of polymerization rate which is due to the appearance of the molecules of ionized acrylic or methacrylic acids. Then further increase of pH up to 10 brings about a rather sharp increase of polymerization rate. The detailed analysis of the phenomenon showed that the increased polymerization rate is due to the rising of ion aggregates in the transition state. At the beginning of this region (pH 7-8), the propagating radical and the monomer are both ionized, and the increase of the polymerization rate with further increase of pH value is due to the formation of the ion aggregates on the end of the propagating radicals which release the electrostatic repulsion in the transition state so the propagation reaction proceeds in a much easier way. The proof of this mechanism comes from the effects of neutral salts like NaCl. Addition of NaCl increases the rate in the alkaline region and does not affect it in the pH range 1-7. The actual measurements of the propagation and termination constant at different pH values and the data on copolymerization of the methacrylic and acrylic acids with various monomers like N-vinyl pyrrolidone or acrylamide at various pH values quantitatively confirm the proposed mechanism. Actually, if methacrylic acid is  $M_1$ ,  $r_1$  values increased to the same extent as the value

of the homopropagation constant  $k$  (V.A. Zubov, Lecture at Boston Congress of IUPAC, 1971. Pure and Applied Chem., 8, 69, 1971). So it seems to be quite certain that formation of the ion pairs at the end of the propagating radical could be used as a means of the regulation of the propagation in polymerization of the ionizable monomers. Another example is polymerization of the salt of the vinylpyridine (1,2 dimethyl((5-vinylpyridine)methyl)).

In polymerization of this monomer, the reaction media (actually the polarity of the reaction media), shows a very high effect on the polymerization behavior. When coming from absolute methanol as a solvent to its mixtures with water, the total polymerization rate slightly decreases (by about 2 times) attaining a limiting value at a 50 per cent mixture. Much more drastic effects are observed in the case of copolymerization of this salt monomer with its starting analog 2-methyl-5 vinylpyridine. In this case, when coming from pure methanol to the aqueous methanol, there is a very drastic change in the copolymerization behavior. Actually, there is nearly complete alternation of the monomer units in copolymer obtained in aqueous methanol instead of the unilateral enrichment of the copolymer with the vinyl pyridinium and the salt monomer units in methanol. In order to find out what are the actual reasons for such behavior, the rate constants had been determined and the main results are as follows, which I think are quite characteristic: If coming from methanol to the aqueous methanol, the propagation constant is somewhat decreased (about 5 times). The termination is decreased even more, but still the decrease of propagation overwhelms the decrease of termination, and there is reason for the two-fold decrease of

the total polymerization rate. But, at the same time, transition to the more ionizing medium causes a sharp increase of the cross-propagation constant in copolymerization with 2-methyl-5-vinylpyridine. In pure methanol, both constants ( $k_{11}$  and  $k_{12}$ ) are nearly equal, and the corresponding copolymerization constant ( $r_1$ ) is close to 1. But when we are coming to the ionizing media, in parallel with decrease of the homopropagation constant, the cross-propagation additionally increased by about 20 times. It means that polarization in the propagating radical is drastically changed by variation of the reaction media, so the character of the interaction of the ion and the counterion in the propagating radical actually governs the polarity, or e character, of the propagating radical. There are also quite a number of other examples of strong effects of the nature of the ions in the ion associates, giving wide possibilities to regulate radical polymerization which I don't have time to develop on further.

I also want to discuss some possibilities of stereochemical control in the radical polymerization of the ionizable monomers. Let us consider one example. If one uses different kinds of neutralizing agents in the polymerization of methacrylic acids, for example, ammonia or sodium hydroxide, it turns out that the content of triads in the polymethacrylic acid formed in polymerization will be considerably changed with pH in the way specific to the nature and amount of the neutralizing agent or the corresponding counterion. Actually, in the case of ammonia neutralized methacrylic acid, practically pure syndiotactic polymer is formed at room or lower temperatures. A very high content of syndiotacticity was achieved in polymerization of acrylic

acid as well, and it also increased with the pH value of the reaction medium. So there are quite wide possibilities of stereoregulation and it is characteristic that this effect seems to be quite specific and very selective.

In conclusion, I briefly dwell upon the other approaches in the field of regulation of radical polymerization, namely on the regulation of radical polymerization by introducing different complexing agents into polymerizable systems. As I said in my lecture in the Boston Symposium, by introducing the complexing agents like halides or alkylhalides of metals of I-III groups, it is possible to vary to a very wide extent the behavior of the radically polymerizable systems. It relates to the homopolymerization of the polar vinyl monomers and to copolymerization of polar vinyl monomers with various other monomers. In fact, depending on the nature of the monomer or comonomer and the coordinating complexing agent, it is possible to prepare different kinds of copolymers and to regulate the rates of the polymerization and molecular weights of the polymers. Not dwelling upon the mechanism of the effects of the complexing agents on the propagation reactions, I only want to draw attention to the fact, which is very unusual for radical polymerization, and is closely connected with the mechanism of polymerization in the presence of the complexing agent. We found that introduction of the complexing agents can decrease termination rate constant to a very high extent even if the system remains homogeneous. Binding of the propagating radical containing the functional groups in the monomer units with the complexing agents causes changes in the conformational behavior of the



propagating radical in such a way that in some cases we observed no bimolecular termination of the system. Using post polymerization techniques, namely the post polymerization priorly gamma irradiated (at  $-196^{\circ}\text{C}$ ) samples, it is possible to carry out polymerization by the mechanism of "living" chains. The typical example is polymerization of complexes of methacrylic esters with  $\text{ZnCl}_2$ . As a result, one can observe that exact correlation between molecular weight calculated by dividing amount of the polymerized monomers on the concentration of the radicals determined by ESR and the experimental value of molecular weight holds. The molecular weight of the polymer is so determined by the initial dose and conversion. The polymers thus obtained have a molecular weight distribution which is actually very narrow, e.g., for polymers with molecular weight some several millions the ratio of the  $M_z$  average weight and  $M_w$  average molecular weights would be like 1.03. As far as I know, polymerization by the "living" chain mechanism was hitherto known only in the ionic polymerization. Application of the complexing agents into radically polymerizable systems can widen to a large extent the scope of the "living" chain mechanism in the polymerization processes.

#### Panel Discussion

Discussion Leader: C. H. Bamford, Liverpool, U.K.

Panelists: J. Furukawa, Kyoto; N. G. Gaylord, Newark,  
G. Manecke, Berlin; N. Platé, Moscow;  
B. Ranby, Stockholm; M. Szwarc, Syracuse;  
F. Tudos, Budapest

G. Smets: I shall now ask Professor Bamford, who is the discussion leader of this morning's session, to take the

chair. I will only add that I think the choice of the Colloquium chairman today was exceptionally good, and that Professor Bamford's authority in polymerization kinetics is the best guarantee of the success of our discussions today.

C. H. Bamford, Liverpool, U.K: Ladies and gentlemen. It is a great pleasure for me to be here today. May I first say how much I appreciate Professor Smets' generous remarks. I now have to present our distinguished panelists; it is not necessary to introduce them because they will all be well known to you, so I will just mention their names: Professor Furukawa (Kyoto), Professor Ranby (Stockholm), Professor Tudos (Budapest), Dr. Gaylord (Newark, N.J.), Professor Manecke (Berlin), Professor Szwarc (Syracuse, N.Y.), and Professor Platé (Moscow). Unfortunately, Dr. Lazar (Bratislava) is not able to be with us today.

After listening to Professor Zubov's interesting talk and recalling last week's IUPAC meetings and the volume of recent publications, I think there is little doubt that interest in polymerizations involving complexed radicals and/or monomers will persist for a considerable time in the future. The concept of such complexes is by no means new; indeed the formation of complexes between polyacrylonitrile radicals and ions was invoked by Jenkins, Johnston and myself in 1957 to account for some kinetic phenomena observed in the polymerization of acrylonitrile in the presence of lithium chloride. However, the concept has lain dormant until recent years. I was interested in Professor Overberger's reference to the statements one hears from time to time that certain areas of macromolecular

science are completely worked out. I well remember hearing remarks of this kind (about polymerization mechanisms) just before the possibility of stereoregulation broke upon us. It is only to be expected that activity in any given field will show phases of stagnation and rapid growth; we are probably now witnessing the latter aspect in free-radical polymerization involving complexed species. A great deal of new information is appearing and it is often difficult to see the wood for the trees.

Our main task this morning is to look at the subject broadly in order to establish important general features, and to identify and encourage what appear to be profitable lines of development rather than to debate at length over details. I know no one better able to separate out dormant from living species than Professor Michael Szwarc, so I am going to ask him to start our discussion by making some general remarks about the properties of free-radicals. Before asking him to take the floor, may I point out that our time is probably limited to 80 minutes, so that if only the panelists speak (and I hope this will not be the case), we have an average time of less than fifteen minutes per speaker. I hope, therefore, that everyone will keep their remarks as brief as is consistent with intelligibility. Michael, this is in no way directed at you specifically!

M. Szwarc, Syracuse: Recently numerous strange observations have been reported, and continue to be reported, in the field of radical chemistry. Hence, following Dean Appley, who drew our attention to strange students, I wish to focus your attention on these strange phenomena.

It would be interesting to summarize first our past activities in radical chemistry before discussing the new problems. In the past we were mainly concerned with three types of radical reactions: (1) the addition of free radicals to suitable reactive centers, mostly to C=C double bonds. Such a reaction is exemplified by initiation or propagation step of vinyl, or vinylidene, polymerization; (2) the abstraction of an atom, or even a group of atoms by a free radical. These reactions involve usually hydrogen atoms and they are exemplified in polymerization processes by chain transfer; (3) finally, the destruction of free radicals resulting from their combination or disproportionation; the termination of radical polymerization illustrates this process. Hence, whenever we dealt with the concept of reactivity of free radicals, we kept in mind one or the other of these three elementary processes.

I would like to stress now two characteristic properties of free radicals which become important when we try to understand some of the recent observations disclosed in the polymer literature. Free radicals have low ionization potentials and high electron affinities, and these properties come into play when they react with suitable electron donors or electron acceptors. Such interactions may lead to the formation of various complexes and that affects the reactivity of free radical in every meaning of this word. It modifies the rates of their reactions, the stereochemistry of their addition, their preference for a substrate when two or more substrates compete for a radical, etc. Thus, the formation of such complexes may affect the rate of propagation and termination and, therefore, the molecular weight of the resulting polymer, the

modification of stereochemistry of addition affects the tacticity of the resulting product, and by changing the preference for a substrate, one may modify the composition of copolymers through formation of suitable complexes.

Therefore, we have to keep in mind how the modification of structure of radicals, and also of monomer, affects their ionization potential and electron affinity.

The ability of a radical to gain or to lose electrons allows us to convert it into an ion, carbanion or carbonium ion. Thus, by using a suitable electron donor or acceptor, we may convert a radical polymerization into an ionic polymerization and, hence, the border line between radical and ionic polymerization becomes fuzzy when a radical polymerization proceeds in presence of such agents.

The transition from radical to ionic polymerization can be gradual because the complexing of a radical with a donor or acceptor need not lead to a complete electron-transfer but may involve a partial transfer only as, e.g., in the formation of a charge-transfer complex. Thus, we may observe a whole spectrum of behaviors and cationic and anionic polymerizations are then the extreme cases. The choice of the complexing agent permits us, therefore, to shift the character of radical polymerization in either direction and to any desired degree.

What I said is not really new. Waters, who was the first to fully recognize the significance of free radicals in various solution reactions, pointed out many years ago that free radicals can be oxidized to carbonium ions or re-

duced to carbanions and thus bridged the chemistry of free radicals with the chemistry of ionic reactions.

Any transformation of a free radical into an ionic species is accompanied by the formation of an oppositely charged species, namely a counter-ion. In low dielectric constant solvents, the two oppositely charged species combine and form a unit which, on one extreme, may be treated as an electrostatically bonded ion-pair or, in the other, as a covalently bonded molecule. It has been shown recently by Kochi that a change from one extreme to the other may be attained in oxidation of radicals by cupric salts.

Finally, let us recall that in the chemistry of ionic species, a chemistry that was developed long before we started to explore the chemistry of free radicals, we are used to the concept of solvation and solvation shell. The variation of the solvation shell affects the reactivities, and generally all the properties, of the respective ions. It is not surprising, therefore, that being acquainted with these concepts we tried to apply them to free radicals. Thus, we tried to rationalize some observations in the chemistry of free radicals by postulating a variable degree of their solvation by the molecules of the surrounding medium. Studies of Russell provide a good example of such strategems. Hence, we may treat the complexes between radicals and some complexing species as solvation complexes in which a radical is "solvated" by the other molecule. It may be that this is only a play of words, but I would prefer to think about such a complex as an aggregate in which the complexing molecule is solvated by a

radical. This is really a play of words because whenever A interacts with B, B interacts with A. Nevertheless, it seems to me that it is easier to treat a radical as a solvating agent than the other way around.

P. Schleyer, Princeton: I wonder if you'd clarify your remark about the ionization of radicals. What you have said is true in a relative sense, but not in an absolute sense. The ionization potentials of radicals in the gas on the order of 10 electron volts, are prohibitively high and are certainly not appreciably different from that of olefins, for example. The ionization process is facilitated in a complex by providing some place for the radical to go, but then you can't really call the resulting product a carbonium ion anymore. The species so produced is a complex and I'm not exactly clear what kind of complex you meant.

Szwarc: Yes, the ionization potential of radicals is lower than ionization potential of olefins. For example, ionization potential of ethyl radical is 8.8 V while of ethylene 10.5 V, of allyl radical 8.2 V, whereas of butadiene 9.1 V, of benzyl radical 7.8 V as compared with 8.5 of styrene. Thus, the differences are usually more than 20 kcal/mole. Moreover, the energy requirement for an electron transfer is reduced by the electron affinity of the acceptor and further reduced by the appreciable solvation energy of the resulting ions when the reaction takes place in a polar solvent.

However, you are perfectly right that a complete electron transfer with the formation of proper carbonium ion is an ex-

treme case. Indeed, I pointed out that we observe a whole spectrum of complexes varying from those in which the electrons are shared to those leading to the formation of ion-pairs.

Schleyer: The point I'm trying to make is that the ionization potentials, on the order of 200 kilocalories, are way out of sight. What I'm really questioning is the actual nature of the species produced when you've transferred an electron from or to a free radical under the reaction conditions. I don't believe that you really should call these species "carbonium ions" or "carbanions" because they really are tight complexes-- new species in themselves. They have to be in order to be able to carry out the electron transfer. In other words, the orbital energies have to be more or less equal in order to have the interactions to permit this kind of transfer. The absolute transfer (absolute ionization) of an electron from a radical is just unobtainable under normal circumstances. I'm trying to establish by this line of questioning what you really mean by the complexes postulated.

Szwarc: I don't know whether I should answer this question and continue this discussion. We are talking about the same thing, Paul. All that I am trying to say is that radical can be reduced or oxidized and that these processes are relatively facile because the ionization potential of a radical is relatively low and its electron affinity relatively high. It may be that I confused the audience by giving the values in Volts instead of kcal/mole. The figures are therefore low -- 1 Volt is, after all, 23 kcal/mole. But all that matters is that the



ionization potential of radicals is lower than that of the corresponding olefin.

Bamford: It seems to me that Professor Szwarc has been discussing complex formation involving the actual radical centers. However, complexation of radicals and monomers may also involve substituent groups if these are sufficiently polar (e.g.,  $-C\equiv N$ ), and I believe there is evidence that complexes formed in this way play an important part in the polymerizations we are considering. Szwarc's considerations are probably relevant to differences in complexing power shown by monomers and their derived radicals.

F. Williams, Univ. of Tenn: I should like to make a brief comment on the subject of radical complexes. Recently we observed in the solid state the product of electron capture by methyl bromide (J. Chem. Phys., 54, 5425 (1971)). The ESR spectrum can be interpreted in terms of a methyl radical complexed to a bromide anion. The magnitude of the hyperfine splittings suggests that there is a transfer of about 10% of the spin density from the methyl radical to a 4p orbital of the bromide ion. This complex was produced by  $\gamma$ -irradiation of methyl bromide in a crystalline acetonitrile matrix at low temperature. When the sample was warmed, the complex dissociated irreversibly, and we were then able to observe the ESR spectrum of the free methyl radical. Therefore, the binding energy of the methyl radical-bromide ion pair must be small, and it would seem unlikely that a complex of this type could exist in solution. However, this experiment does show that

even weak complexing can reduce the spin density in the p-orbital of the radical.

Bamford: What temperature was that done at, please?

Williams: The complex was produced at  $77^{\circ}\text{K}$  and it dissociated thermally at ca.  $175^{\circ}\text{K}$ .

Bamford: Perhaps we should leave this subject at this point because we have quite a lot of work to do. I'd like to ask Professor Furukawa if he would make some remarks. I know he has quite a few ideas on this subject.

J. Furukawa, Kyoto: I have two comments on so-called alternating copolymerization which seems to be very interesting in the field of polymerization. It affords polymers of high degree of alternation, which enables crystallization of polymers on stretching. These comments concern with the mechanism proposed by Kabanov and Zubov. In general, the alternating copolymerization is explained in two ways; one is the so-called Markovian model and the other is the Bernoullian one. Acrylic monomers can undergo alternating copolymerization with olefins and diolefins in the presence of Lewis acid, such as  $\text{EtAlCl}_2$  found by Dr. Hirooka. This is accounted for by the formation of a donor-acceptor monomer complex prior to or in situ polymerization, but it is also explainable in terms of the alternating addition of monomers with enhanced polarity by the complexing agent. The distinction between them is under question, and I propose two methods.

One is the investigation of the effect of monomer composition on the polymerization rate. In ordinary case, a maximum rate is achieved at the 1:1-monomer composition. This fact is compatible with a mechanism involving a donor-acceptor monomer complex but is not generally valid for the alternating addition mechanism, since in the latter case the monomer ratio  $M_1/M_2$  for a maximum rate is given by  $(k_{12}/k_{21})^{1/2}$ ,  $k_{12}$  and  $k_{21}$  being rate constants for the additions of  $M_1$  to  $M_2$  and  $M_2$  to  $M_1$ , respectively (J. Furukawa, Chemistry (Japanese), 25, 133 (1970)). Figure 1 illustrates the existence of a maximum rate at the 1:1 monomer composition for the alternating copolymerization of butadiene and acrylonitrile in the presence of  $\text{EtAlCl}_2$  and  $\text{VOCl}_3$  (J. Furukawa, E. Kobayashi, K. Haga and Y. Iseda, Polymer J., 2, 475 (1971)).

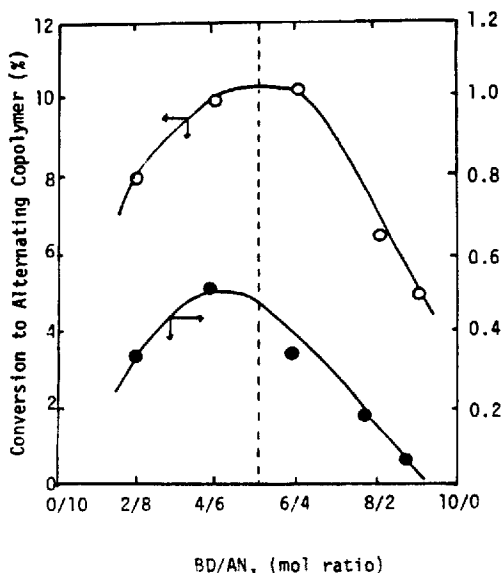


Figure 1 (Furukawa). Effects of butadiene-acrylonitrile ratio in the monomer feed on the rate of the alternating copolymerization.

The second method for distinction is made by a high resolution NMR analysis, which gives information not only about the polymer composition but also the distribution of diads or triads. In a Markovian mode, there exists the following relation among diad fractions,

$$F_{11} \cdot F_{22} = (r_1 r_2 F_{12} \cdot 2F_{21})^2 \quad (1)$$

In fact, equation (1) was found to be valid for the ordinary radical copolymerization of butadiene and acrylonitrile, but is not for the alternating copolymerization of those in the presence of  $\text{EtAlCl}_2$  and  $\text{VOCl}_3$  as shown in Figure 2 (Furukawa, loc. cit.).

The second comment is concerned with the activated state for donor-acceptor complex polymerizations. According to a simple molecular orbital consideration, a donor-acceptor complex is formed by the electron transfer from the highest occupied level of butadiene to the lowest vacant level of acrylonitrile, where the orbital symmetry of the former is (+,+,-,-) and that of the latter is (+,-) and these

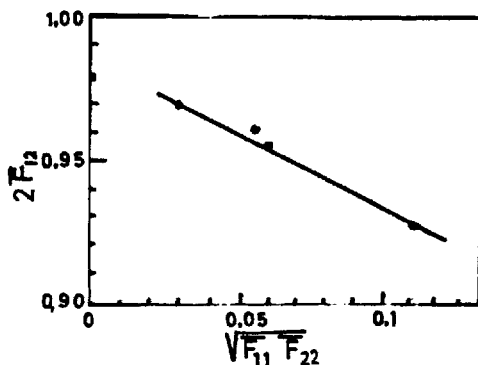


Figure 2 (Furukawa). A non-proportional relationship between  $2F_{12}$  and  $\sqrt{F_{11} F_{22}}$  for the conventional radical copolymerization of butadiene and acrylonitrile.

symmetries are favorable to the formation of a six-membered ring or the Diels-Alder reaction. I found that the alternating copolymerization takes place when the complex is activated by a co-catalyst such as  $\text{VOCl}_3$  or by UV-irradiation (J. Furukawa, Report from Japan Chemical Fiber Institute (Japanese), 27, 83 (1970)). The trans-structure of butadiene unit in the alternating copolymer suggests that the complex is activated to the excited state whose orbital symmetry of butadiene is (+,-,-,+) (Figure 3) (Furukawa, loc. cit.)

Figure 4 shows the Arrhenius plots for the UV-irradiated alternating copolymerization and for the Diels-Alder reaction (Furukawa, loc. cit.). The former requires no activation energy in contrast to a large one for the latter reaction. We also attempted a terpolymerization of butadiene, acrylonitrile and methyl methacrylate (MMA) (J. Furukawa, E. Kobayashi, Y. Iseda and Y. Arai, J. Polymer Sci., B9, 179 (1971)). It was observed that there exists some difference in polymer composition influenced by photoirradiation.\*

Bamford: Professor Furukawa, before you leave, just to make specific what you're talking about, could you tell us what systems give this behavior?

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\*However, the further study done after the colloquium showed that there occurs the formation of a considerable amount of Diels-Alder reaction product in the dark especially at elevated temperature. Therefore, there is some possibility that the difference in the copolymer composition will come from the different rate of Diels-Alder reaction in the dark and in UV-light. We only point out the effect of UV-light on the activated state of the monomer.

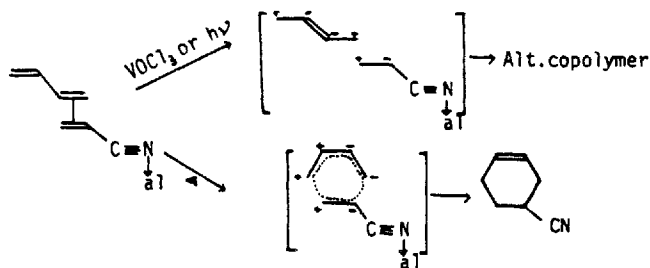


Figure 3 (Furukawa). Different activated states proposed for the Diels-Alder reaction and the alternating copolymerization of butadiene and acrylonitrile.

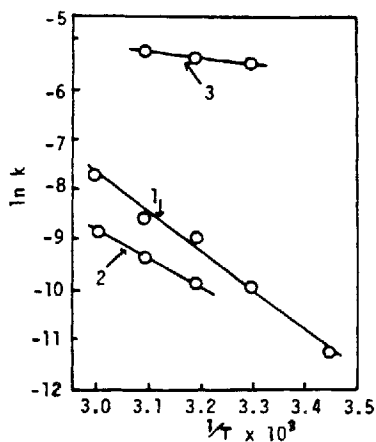


Figure 4 (Furukawa). Arrhenius plots for Diels-Alder reaction (1) accompanied by alternating copolymerization (2) in the dark and the alternating copolymerization in the UV light (3). Zinc chloride is used as a complexation agent for both cases.

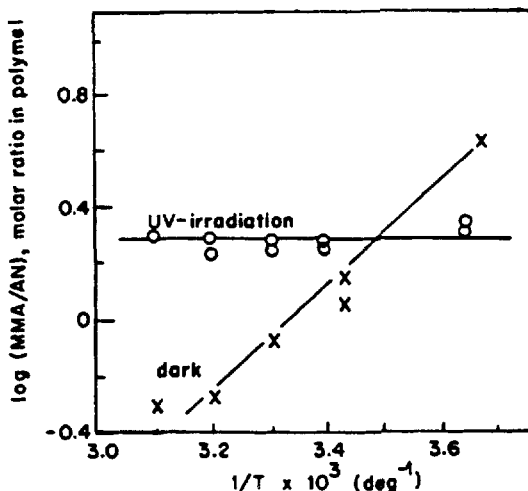


Figure 5 (Furukawa). Terpolymerization of BD, MMA and AN by  $\text{EtAlCl}_2$   
 BD: 0.12 mole, MMA: 0.04 mole  
 AN: 0.04 mole,  $\text{EtAlCl}_2$ : 4 m mole

Furukawa: The copolymerization of styrene-maleic anhydride (Maleic anhydride-thiophen system: A. Cardon and E. J. Goethals, XXIII IUPAC, Macromolecular Preprint, Vol. 1, 359 (1971)), or that of butadiene-acrylonitrile together with  $\text{EtAlCl}_2$  is the case, in which the maximum rate is achieved at the 1:1 monomer composition.

Bamford: Professor Furukawa has raised some very interesting points. Do we have any comments now, please, and I don't wish to exclude the panelists.

N. G. Gaylord, Newark: Basically, the real question as I see it, is whether the three particular items that Professor Szwarc mentioned have really exhausted the possibilities as to the nature of the reactions of free radicals. When you look at the systems in the presence of complexing agents, or in the

case of monomers which tend to form alternating copolymers in the absence of complexing agents, such as styrene-maleic anhydride, vinyl ether-maleic anhydride, etc., we find a number of very unusual characteristics. Although much of our discussions have to do with propagation steps, the initiation step has not been given enough examination. In all of these systems, there is one interesting characteristic, that is, on polymerizing a system such as styrene-maleic anhydride or vinyl ether-maleic anhydride in the presence of a radical catalyst, no catalyst residues are found in the polymer although a radical catalyst is used. Further, when these systems are run in the presence of halocarbons, such as chloroform and carbon tetrachloride, it is discovered that there is no chain transfer, as far as influencing the molecular weight is concerned, and there is no halogen in the polymer. You might reply that it is obvious that a good electron acceptor monomer such as maleic anhydride may not have a tendency to pull hydrogen or chlorine from chloroform or carbon tetrachloride, respectively. However, another problem that arises is that when this is done in the presence of a free radical catalyst of the conventional type, such as a peroxide, which certainly should pull hydrogen from chloroform and carbon tetrachloride, the resulting products should be initiating species. They should become incorporated into the polymer. Nevertheless, they do not become part of the polymer as a terminal group. Therefore, we must conclude not only that the growing chain end is not capable of undergoing chain transfer reactions in the conventional sense but also that, whatever the nature of the initiation step, it does not involve anything of the conventional addition type. Tsuchida



in Japan has found that in the styrene-maleic anhydride system, there is one catalyst residue for every 90 polymer chains. He assumes tremendous chain transfer to maleic anhydride which is inconsistent with the 5-10,000,000 molecular weight that can be obtained in this system. Similarly, he finds that the chlorine content of a copolymer produced in chloroform or carbon tetrachloride is one chlorine for every 300 polymer chains, indicating that these are not major participants in the reaction scheme. Thus, we have to consider the fact that in these radical initiated systems the propagating chains participate in reactions other than those with which we are accustomed.

A new aspect has recently entered radical chemistry. Over the last few years a number of reactions have been found which are carried out by radical catalysts under unusual conditions. One reaction involves the now readily polymerizable maleic anhydride. Up until a few years ago, maleic anhydride could not be polymerized very readily. We now find that it is one of the easiest monomers to polymerize and it can be polymerized by any radical catalyst under the right conditions. Although much of the polymerization work has involved radiation, radical catalysts are also effective at concentrations of 5% or higher. However, this is not the only factor because you can also polymerize maleic anhydride using radical catalysts at concentrations of 0.1% if the reaction is carried out under conditions where the catalyst half-life is about 10 minutes or less.

This raises the question whether we have changed the nature of the species which arises from the radical precursor simply by changing the temperature of decomposition. This

shows up very clearly in the polymerization of butadiene and maleic anhydride wherein radical catalysts under normal conditions yields the Diels-Alder adduct rather than the copolymer. When the catalyst is used under short half-life conditions, the copolymer is obtained.

This leads to another very interesting question, namely, the polymerization of ethylene under high pressure and high temperatures. Those who are familiar with the field are aware that (1) ethylene polymerization can be initiated with oxygen and (2) catalysts that would normally be used at 30-50°C are used at temperatures of 200°C. In Raff's book on "Crystalline Olefin Polymers", there is a table from a Monsanto patent showing useful catalysts and the temperatures at which they have a half life of 1 minute. We are obviously dealing with species from this type of decomposition which will initiate reactions which otherwise could not be initiated.

This brings us to the point that Professor Furukawa has just mentioned, namely, the question whether the species which is polymerizing is an activated or excited species versus a ground state species. In other words, even if you get donor-acceptor interaction, is this all that is required? Recently, we found on the polymer horizon the concept of chemically induced dynamic nuclear polarization which indicated that radicals are not necessarily radicals - that they are excited species under many circumstances. They have emission spectra as well as absorption spectra and they are excited species which are capable of transferring their excitation energy to other species in the system. Working with the butadiene-maleic anhydride system, which up to a few years ago was not

known to polymerize at all, it has been possible to produce polymers by radical precursors as well as under ultraviolet light. Several years ago a paper was entitled "Photochemistry Without Light" and described reactions resulting from the generation of active species from radical precursors - I do not call them radical species - which species behave in a manner which we normally associate only with excited states.

What Professor Furukawa has pointed out and to which I would like to add some data, is that in the butadiene-acrylonitrile-methyl methacrylate system it would be anticipated that the two comonomer complexes, i.e., butadiene-acrylonitrile and butadiene-methyl methacrylate, in the organoaluminum halide-containing system, would be present in relative concentrations depending upon the temperature due to the differences in their equilibrium constants. Actually, although the butadiene-acrylonitrile system has a higher rate of polymerization, there is less acrylonitrile and more methyl methacrylate in the terpolymer. As the temperature is changed, one would expect differences in complex concentrations and, if that was the only factor involved, differences in terpolymer composition with temperature would be expected. This is actually observed as a function of temperature. However, when the system is exposed at various temperatures to light, the terpolymer has the same composition independent of temperature, despite the fact that we have not changed the dependence of complex concentration on temperature. If the only polymerizable species was the complex, then the composition should vary. The only constant factor in this ternary system when you change the temperature is the initial monomer concen-

tration. The complex concentration per se is varying with temperature. It must be concluded that light is exciting monomers, not just complexes, to generate a certain relative concentration of polymerizable species independent of temperature.

In our own work we have examined the styrene-acrylonitrile-methyl methacrylate system which has some unusual characteristics. The copolymer composition from styrene-acrylonitrile in the presence of ethyl aluminum sesquichloride changes from an alternating copolymer to a free radical copolymer above  $60^{\circ}\text{C}$ , obviously a temperature dependent system. The styrene-methyl methacrylate system does not change until  $120^{\circ}\text{C}$ . Therefore, when temperature effects are studied, changes in composition relating to this break would be expected. When these reactions are carried out spontaneously, i.e., if there is a high enough EASC content, the reactions proceed without any catalyst and there is a variation in terpolymer composition with temperature, similar to the case reported by Professor Furukawa. If the reactions are conducted under light, the rates of polymerization are five times higher and the terpolymer compositions become much closer together. The most interesting phenomena occur when a radical catalyst is added to the dark systems, namely, the products obtained from the radical system are more similar to those produced under light than to those produced in the dark. The radicals, apparently, under the right conditions are capable to exciting monomers to change their reactivity or rather their nature.

I have propounded the view that complexes do not copolymerize with monomers but that excited species can copolymerize. Conse-

quently, when non-equimolar compositions are obtained, these are the results of the reaction of excited species.

A well-known reaction of charge transfer systems is the deactivation of an excited donor-acceptor pair to generate a ground state donor and an excited acceptor. The excited acceptor is capable of copolymerizing with an excited complex. This is the basis for the formation of terpolymer compositions in which the concentration of one component in the terpolymer is dependent upon the concentration of another component in the charge without the concentration of the latter in the terpolymer changing. Thus, Iwatsuki has reported in the anethole-maleic anhydride-acrylonitrile system that the anethole-maleic anhydride ratio in the terpolymer is always 1:1 but the more anethole in the charge the more acrylonitrile in the terpolymer. The anethole-acrylonitrile complex apparently generates excited acrylonitrile which can copolymerize with the excited anethole-maleic anhydride complex. Excitation is obviously a new factor appearing in radical chemistry.

Another new factor involves the question of whether hydrogen transfer is necessarily a chain transfer reaction. It now appears that hydrogen transfer may be an intermediate step in the propagation stage in a number of monomer systems. A specific example is the cyclopolymerization reactions reported by Professor Butler wherein the products are now recognized as possessing five-membered rings rather than six-membered rings. Until now, the driving force of the reaction was considered to be the strong tendency to form a six-membered ring. Actually, it would appear that the driving force is the tend-

ency to form a six-membered transition state which yields a five-membered ring as a result of hydrogen transfer.

Bamford: Can we discuss these points? First of all, does anyone wish to dispute any of these findings?

Audience: I'd like to make a comment. When you talk about excited species, would you please clarify what you mean by excited species?

Gaylord: Due to the character of these reactions, we feel that the excited species are singlets because they are not inhibited by oxygen and do not have the other characteristics of triplets. Also, they do not add to excess monomers which are present in the system, which a triplet would do to yield a cyclopropane ring. Therefore, we think they are excited singlets.

Audience: So they have a very short lifetime.

Gaylord: Their lifetime only has to be the time of contact. According to Millikan, the charge transfer complex and the excited charge transfer complex need not have any longer existence.

Audience: Most of the charge transfer complexes in the excited state have a lifetime between nonaseconds and less. Would that be sufficient lifetime?

Gaylord: I think so according to the mechanism in which I propose that the complexes are aligned in a matrix. They do not have to have a very long lifetime. They can become ex-

cited and then immediately react with the next member of the matrix. Once the complexes are pre-aligned in the ground state, they do not have to have too much excited state lifetime to react. They do not wander around looking for a chain end as an excited species.

Audience: Why should they be aligned?

Gaylord: Due to the changes in polarity of the donor and acceptor as a result of complexation and interaction, the complexes are aligned due to electrostatic interaction:

+--+--+--+--+  
 .....:.....

Audience: This might be the case in some situations.

Gaylord: Professor Zubov's data indicates that the propagation rate may be reduced as a result of interaction but the alternating tendency is increased. It is very difficult to explain why so many of these reactions have energies of activation of 1 and 2, as compared to the normal energy of activation of between 15 and 22 for a radical reaction. These reactions are explosive and if we consider a selective reaction in which only a monomer of the opposite polarity reacts, this cannot explain the tremendous rates of these reactions. In Ziegler-Natta polymerizations when you put in an additive to control the stereoregularity, the non-selective, more reactive sites are removed and the reactions are slowed. Yet, in the complex cases we are speeding up the reactions explosively.

Audience: Are you sure that you are radiating certain species or the complex itself, or are you radiating the monomer?

Gaylord: We do not know. We feel, however, that you may be exciting one monomer. The point is well taken.

Audience: Because you are using broad UV light.

Gaylord: No. While some of these effects are noted under ambient light, they are particularly notable at specific wave lengths. In addition, you cannot polymerize butadiene-maleic anhydride in the presence of a photosensitizer that has a triplet energy below that of maleic anhydride. Just as you prepare the benzene-maleic anhydride photochemical adduct with a sensitizer with a triplet energy above 70, the same occurs in the copolymerization. The copolymer cannot be prepared in the presence of acetone which has a triplet energy of 60. Therefore, it is possible that you are exciting maleic anhydride which then collapses into the excited butadiene-maleic anhydride complex, or excites a butadiene-maleic anhydride complex. We do not know anymore about the actual path than is known about the benzene-maleic anhydride system.

Zubov: I want to make some comments on the statements made by Professor Furukawa and Dr. Gaylord. I think that before discussing the detail mechanism explaining these unusual phenomena to radical polymerization, the first basic principal has to be to find out what the actual propagation is. As can be seen and was shown by Professor Furukawa and Dr. Gaylord, there is no basic difference in alternation radical copolymerization in the systems like maleic anhydride and vinyl-ether or like systems, and in systems acrylonitrile, aluminum alkyl halides plus hydrocarbon monomers. In other words, the ac-



ceptability of the polar monomer, like acrylonitrile or methacrylate, is increased by introducing the complexing agent to an extent which is sufficient to produce the same effect as is achieved by the maleic anhydride by itself.

The actual steps of the chain propagation can be observed directly by the ESR technique. The first, and very nice work in this way, has been done by Professor Ranby. By using a flow technique for ESR measurements, he managed to observe the successive steps of propagation in the alternating copolymerization of the maleic and fumaric acids with vinylacetate. It was shown that normal monoradicals appeared one after another in an alternative way. Initiation starts with an OH radical, then the addition of the double bonds occurs in proportion to the activities of the monomers (vinylacetate is more active), etc. We managed to observe similar phenomena in copolymerization of the complex species as well as in copolymerization of maleic anhydride by applying low temperature technique in combination with ESR measurements. So, if we take these results as a proof of the succession of the elementary acts of the chain propagation, we can see that there is "normal" radical propagation starting with monoradicals of initiator and further proceeding by addition of single monomer molecules in an alternative way, and not by addition of the binary monomer complexes. Now there are a number of questions to answer. Why the reaction proceeds in such a way, unusual to the random copolymerization? One has also to answer some of the questions which had been suggested by Dr. Gaylord and Professor Furukawa, such as the maximum copolymerization rate at 1:1 monomeric ratio and some other phenomena. As can be easily seen, that maximum copoly-

merization rate at this ratio can be achieved if the cross propagation constants  $k_{12}$  and  $k_{21}$  are heightened not much different from each other. So, considering that the propagation proceeds as the "normal" addition of monomer molecules, we can easily observe this rate dependence. Then, there is no or very little chain transfer to carbontetrachloride. If the radical is a very strong acceptor, like maleic anhydride or complexed acrylic radical, it could be complexed with the donor species, e.g., donor molecules of the other monomer. It is a well-known fact that the activity of the radical is very much decreased by formation of the  $\pi$ -complexes. In this case, we can expect practically no chain transfer because radicals are actually complexed with the unlike monomer. If they are complexed, they can add the unlike monomer and not the like monomer. I think I might finish like this. Actually, there are no facts in consideration which could not be explained by applying normal radical scheme.

Gaylord: How about the rates of reaction and the energies of activation?

Zubov: If the rate of the cross propagation is very high, the total rate has also to be very high.

Gaylord: Even when there is a ninefold excess of the other monomer?

Zubov: Yes. It's easy to show by quantumchemical calculations that if the donor-acceptor interaction is strong enough, e.g., the lower vacant energy level of reacting particle, e.g., radical, is close in value to the upper occupied energy level

of the other particle (monomer), the activation energy of the reaction could be close to zero. This, in fact, had been shown by the simple molecular orbital calculations of the complexed acrylic and hydrocarbon monomers. Initiation in these systems can also proceed without any sufficient activation energy or by irradiation with diffused light, which was observed by us. These phenomena may account for fast "spontaneous" reactions resulting in alternating copolymers.

Bamford: Thank you, Professor Zubov. I think we must be very careful here about generalizing; we're dealing with a wide variety of systems. The common factor, to me, seems to be the formulation of an alternating polymer. There may well be many different reactions and we shall get ourselves into a terrible tangle, I think, if we try to push everything into one mechanism.

Szwarc: We are talking here about three different problems. One is concerned with the modification of the monomer. Complexing of a monomer or converting a monomeric acid like acrylic acid into its salt produces a new species. Surely its chemistry is expected to be different from that of the unmodified monomer. To make my point strong, consider HCl and NaCl. Surely they behave differently. Why, therefore, should anybody expect the polymerization of acrylic acid to be similar to polymerization of sodium acrylate?

Another problem is encountered in a copolymerizing system when the two copolymerizing monomers, say A and B, may form a complex, say AB. In such a system, a new monomer AB is present and this may exclusively polymerize giving an

alternating copolymer or copolymerize with one or both of the original monomers. As far as I know, this idea was first suggested by Barb.

Bamford: I think that's disputed, is it not? I think that's not the only explanation of Barb's results.

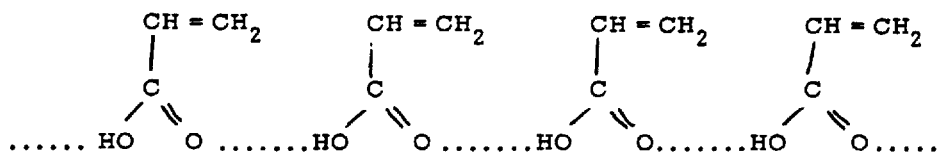
Szwarc: It is possible that Barb's explanation is incorrectly accounting for his own findings. But this is not important as far as our present discussion is concerned. People can introduce interesting and basically useful ideas to account for some observations. Later it turns out that these ideas do not apply to the observations for which they were invented but, nevertheless, they are in principle valid and, subsequently, observations which confirm them are found. This happens not seldom and Barb's ideas certainly are an example of such a situation. I do not doubt that complexes between two monomers are important in some copolymerizing systems.

Now, the third problem arises when we modify the growing radical by complexing. Hence, what we need is to examine carefully each case and to see which of these factors are really important, and we may make progress by choosing systems in which only one of these factors is dominant and by studying them to prepare ground for understanding of systems in which two or more of these phenomena simultaneously participate.

A. Chapiro, Bellevue, France: I would like to comment on some of the points which were raised by the last few speakers. I believe that many of the conflicting views on the subject arise because we are dealing with very complicated phenomena which cannot be explained by conventional concepts. Therefore, various

assumptions are proposed concerning "complexed" systems in which the "complexing" action either involves growing chains, or the activated state or the monomer or monomer pairs. We should be aware of the fact that merely the word "complex" is a sign of our ignorance and since we do not know what sort of complexes we are dealing with in most systems, we should not be satisfied by explaining the observed effects with the word "complex". I would like to introduce another concept which is based on recent experimental evidence and which has not been referred to so far, except perhaps by Norman Gaylord in his lecture at the IUPAC Meeting in Boston. The point I would like to make concerns the bulk structure of the liquid itself. We have recently studied a number of very simple polymerizing systems without the presence of any so-called "complexing agent" and found a number of effects which are related to the points raised in this discussion.

The first system on which I would like to comment is acrylic acid. The polymerization of this monomer in bulk at room temperature proceeds with an extremely high rate and leads to a syndiotactic polymer which readily crystallizes (A. Chapiro and T. Sommerlatte in Europ. Polym. J., 1969, 5, 705-745). Our present explanation for this unusual behavior is that the molecules of acrylic acid are aggregated by hydrogen bonds and do not only form the well-known dimers as all carboxylic acid but also form linear structures of significant length:



The best experimental evidence we have so far for the existence of such aggregates is the high viscosity of acrylic acid monomer which cannot be caused by dimers. We also found that the addition of polar solvents (methanol, water, dioxane) to the monomer does not alter the high viscosity nor the unusual kinetic features of its polymerization, whereas toluene, n-hexane or chloroform reduce at the same time the viscosity of acrylic acid and its rate of polymerization and lead to atactic polymer. High viscosity is also observed when zinc chloride is dissolved in styrene plus methyl methacrylate solutions and here, again, this increase in viscosity cannot be accounted for by a molecular complex involving one monomer molecule and, therefore, suggests the formation of plurimolecular aggregates. This idea of "Swarms" or linear organized structures has also been proposed by Gaylord, and this could indeed account for some of the observations. If an initiation process occurs somewhere along such structures, a "zip" propagation can be envisaged, involving a large number of monomer molecules of the aggregate, and such a reaction would indeed scarcely be affected by the presence of free radical inhibitors or transfer agents.

Another simple system in which we have met unusual results is the solution of styrene plus methyl methacrylate in dimethylformamide. Here we have obtained without any further additive an alternating copolymer at room temperature. At lower temperatures ( $-78^{\circ}\text{C}$ ), styrene or methyl methacrylate readily polymerize in dimethylformamide solution by a free radical mechanism, but the addition of a few per cents of one monomer to the other produces complete inhibition. In aniline solution the same monomer pair readily copolymerizes at  $-78^{\circ}\text{C}$  giving an alter-

nating copolymer. The rate of copolymerization exhibits a minimum at the stoichiometric composition of both monomers. When the temperature is raised to 20°C, a normal random copolymer is formed in the same mixtures. This behavior indicates the formation of a "complex" between styrene, methyl methacrylate and the solvent. With dimethylformamide, this complex is still stable at room temperature, whereas in aniline it only persists at low temperatures. It should be noted that these mixtures do not crystallize but form glasses when cooled to very low temperatures, which again indicates a high viscosity and, consequently, the formation of plurimolecular aggregates.

To conclude, I would like to stress that Professor Bamford was right in saying that we are probably dealing with a large number of different systems which cannot be confined into a single framework. A number of factors are responsible for the "complex" behavior, but the structure of the bulk liquid undoubtedly plays a role in certain cases. This can, fortunately, be studied with conventional physical chemical techniques.

Bamford: Thank you, Professor Chapiro. I think it is gradually becoming clear (as emphasized by the remarks of the last three speakers) that what we need is more precise physical chemical investigation; for example, observation of the effects of initiation by monochromatic radiation for a range of wavelengths, or physio-chemical evidence for the existence of complexes.

I believe some workers assume the existence during polymerization of complexes in relatively high concentration;

if this is correct, it should be possible to detect such species by available techniques. Dr. Hirooka, in his IUPAC lecture, presented evidence which appeared to show that in some systems forming alternating copolymers monomer-monomer complexes are not formed.

Furukawa: I think that Dr. Hirooka will propose a new idea in which he claimed that the donor-acceptor monomer complex will not exist under the normal condition, but the complex may be formed in the presence of free radicals of the growing polymer chains. It is a very interesting idea to solve many problems under discussion. But we need the evidence for the complex formation enhanced by free radicals.

Bamford: Yes, we need experimental evidence. We have a theory and experimental evidence which seems to refute it.

Gaylord: Is this not really a question of the validity of negative evidence? In one of my papers, I quoted the fact that complexes had not been detected but I proposed that they were there. I later had to add a note in proof that they were detected while the paper was in press. I do not really think that negative evidence has too much significance unless one can detect the presence of another material. The fact that you cannot detect something does not mean that much.

Bamford: I cannot agree with that. You assume the presence of a relatively large concentration of an oriented phase in the form of micelles or liquid crystals which surely should influence the physical properties of the system. If you have to assume further that these aggregates have no ob-



servable properties except that they give rise to alternating polymers, your argument is greatly weakened.

Gaylord: I think that liquid crystals or materials of that type are relevant. We might be able to detect them, for example, by magnetic field or electric field effects. These are the methods that are really necessary to break up such aggregates.

Overberger: Just a remark and a question. If you don't consider any excited states, I've written down seven mechanisms. If you consider excited states, then there are at least seven more. Now a question related to monomer complexing with Lewis acids that have been used in most of this work--what data is available in the literature at the present time that these Lewis acids complex with the monomer that they do not homopolymerize--for example, in the copolymerization of acrylonitrile and styrene?

Gaylord: There is one such piece of evidence. One group of Japanese workers has found that the tacticity of the styrene-methyl methacrylate copolymer is dependent upon the nature of the metal halide. Their interpretation is that tin can complex with the carbonyl group of methyl methacrylate as well as the benzene ring of styrene, thereby modifying the tacticity, whereas aluminum complexes only with the methyl methacrylate. At high concentrations of the metal compound, you are apt to get cationic polymerization of the donor as well as copolymerization with the acceptor. We have demonstrated that at low concentrations of the metal halide radical, polymers are obtained.

Overberger: If you take the monomer that doesn't give you a cationic polymerization, let us say, acrylonitrile, can you measure the extent of the complexing?

Gaylord: Hirooka's data demonstrates 100% complexation. It is not an equilibrium. The metal complexes 100% with the acceptor monomer to the extent that the metal is present.

Overberger: It is complexed 100%?

Gaylord: Yes, and Furukawa's cryoscopic data indicates similar results. The complex concentration is in direct proportion to the amount of metal added. There is a change in the number of molecules.

Overberger: It is a 1:1 complex?

Gaylord: Right, although there are also 2:1 complexes. Both complexed molecules are acceptors, such as in the case of acrylonitrile. There is an acrylonitrile-acrylonitrile-aluminum complex although there is generally a 1:1 methyl methacrylate-aluminum complex.

Overberger: So the donors can't be studied because they polymerize. You only know that you have one monomer complexed.

Gaylord: Professor Furukawa has found by NMR that there is an indication that benzene can complex with methyl methacrylate-aluminum. By cryoscopy, he says that he can detect three component complexes.

F. Tudos, Budapest, Hungary: I want to add a few words about the charge-transfer complexes in solution which are very dif-

ferent from those in the solid state. In solution, there is the possibility of formation of not only the 1:1 complexes but also 2:1 and 1:2 complexes, especially in the case of the inhibited polymerization of styrene with chloroquinones. We can demonstrate that in this case there are numerous complexes of two styrene molecules and one acceptor molecule. Another characteristic of charge-transfer complexes in solution is that there are complexes for which the force of interaction is in the order of two to three kcal or a little more, so that these complexes are very loose and their equilibrium distance will vary with temperature.

B. Ranby, Stockholm, Sweden: I would first like to comment on the previous discussion. I think there are good possibilities to establish, using ESR measurements, whether singlet states do occur in the monomer complex formation. It is even possible that ESR studies can contribute to the problems of charge transfer complexes, we previously discussed. Singlet oxygen absorptions to double bonds give very clear shifts in the UV spectra as recently shown by Tsuji et al. in Japan. At this time, I would like to report on our recent ESR work on allyl monomer reactions, which has not been presented and discussed before. If it is all right with the chairman, I will present our new data on allyl monomer initiation in free radical polymerization, obtained in cooperation with Dr. Z. Izumi, a visiting scientist in our laboratories.

It is correct as mentioned by Professor Zubov, that just before the meeting we published data from our laboratories describing ESR spectra of various radicals consecutively

formed during initiation, propagation, and copolymerization (Takakura, K. and Ranby, B., J. Polymer Sci., C 22, 939 (1969) and A-1, 8, 77 (1970)). These studies should have been brought up at the IUPAC Meeting in Boston, but they were not known in time. The papers were published rather late. What we are working on now is allyl monomers, preferentially because their reaction offer many interesting problems which are particularly suitable for ESR studies (Doi, Y. and Ranby, B., J. Polymer Sci., C 31, 231 (1970)). We have studied initiation of allyl alcohol, allyl amine, allyl acetate, allyl sulfonate, and their copolymerization with other monomers. We have also studied the corresponding methyl-allyl compounds, e.g., acetate, alcohol, sulfonate, and amine and their copolymerization with other monomers. There are some data I'd like to present here to show the usefulness of these physico-chemical measurements as a basis for discussion of the reactions. The initiation has been made with three redox systems, giving hydroxyl radicals, amine radicals and methyl radicals, respectively, which are basically very different in their affinity to these monomers.

A good monomer to use as a reference is acrylonitrile (AN) because it gives a beautiful and well resolved ESR spectrum (Figure 1). Every main line is split into three equal components due to the coupling to the nitrogen nuclei with the spin (-1,0, +1). Acrylonitrile is of interest also because some of the allyl monomers are now being used as comonomers with AN. This is the ESR spectrum of the monomer radical of acrylonitrile in aqueous solution (Figure 1) obtained using the flow technique, which I presume most of you know. Figure 2 shows the ESR spectrum of allyl alcohol initiated by HO $\cdot$  radicals.

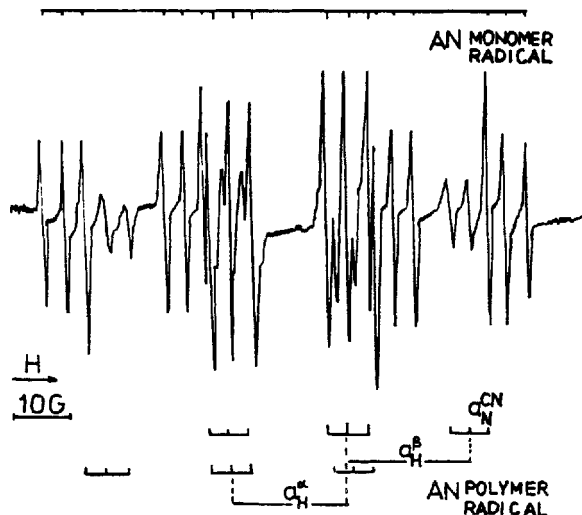


Figure 1 (Ranby). ESR spectrum of acrylonitrile (AN) monomer radicals, initiated with  $\text{HO}\cdot$  radicals from the redox system  $\text{TiCl}_3 + \text{H}_2\text{O}_2$  in aqueous solution.

It can be observed directly in the spectrum that three different radical components are formed in the initiation reaction. The main spectrum (about 90% of the intensity) is due to a species which we call head radicals (I), formed by addition of  $\text{HO}\cdot$  radicals to the tail end of the monomer. The stick spectrum at the top indicates where the lines of (I) occur, and it is clear that they are the strongest lines in the recorded spectrum. The sextet spectrum of (1) is interpreted as due to coupling to the five  $\alpha$  and  $\beta$  hydrogens which are sufficiently equivalent to give just one set of lines in this resolution. A weaker spectral component (5 to 7%) is due to radical (II) which we call tail radicals. They are formed by  $\text{HO}\cdot$  radical addition at the head of the monomer. There is finally a third very weak spectral component due to allylic radicals (III), formed by abstraction of a hydrogen from the original allyl alcohol. As shown in Figure 2, one ESR spectrum can

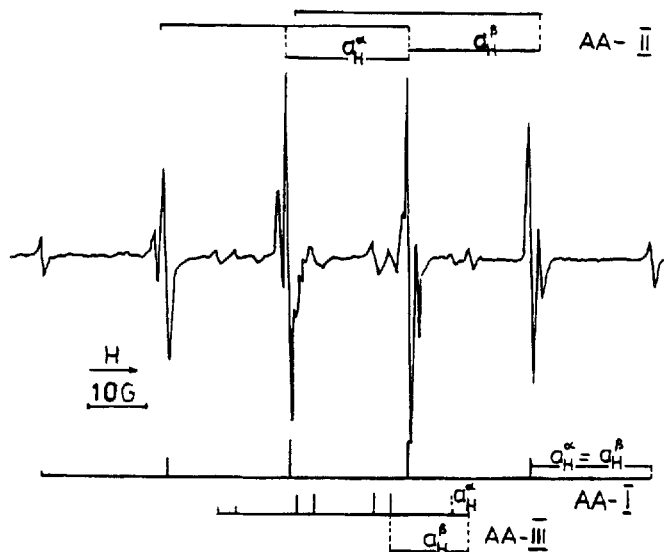


Figure 2 (Ranby). ESR spectrum of allyl alcohol ( $\overline{AA}$ ) monomer radicals, initiated with  $\text{HO}\cdot$  radicals.  $[\overline{AA}] = 5.5 \times 10^{-2}$   $[\text{H}_2\text{O}_2] = 1.1 \times 10^{-1}$  and  $[\text{TiCl}_3] = 7 \times 10^{-3}$  mole/l.

give information of the structure and the amount of three different radicals formed, in this case after initiation with  $\text{HO}\cdot$  radicals in a flow system with aqueous solutions. Turning to another allyl monomer like allyl acetate, the ESR spectrum looks more complex but can be resolved in an analogous way (Figure 3). Head radicals (I) are the main part of the spectrum. The tail radical spectrum (II) shown at the top, is much weaker. The allyl radical spectrum (III) is very weak indeed, and the location of its lines is indicated by the arrows. The position of the spectral lines are known from previous work. Otherwise, the spectrum (III) would probably have been overlooked. Allylic radicals are formed in much lower amounts from allyl acetate than with allyl alcohol. The ESR spectrum of allyl acetate in a system initiated with amine radicals from hydroxyl amine is quite different (Figure 4). It

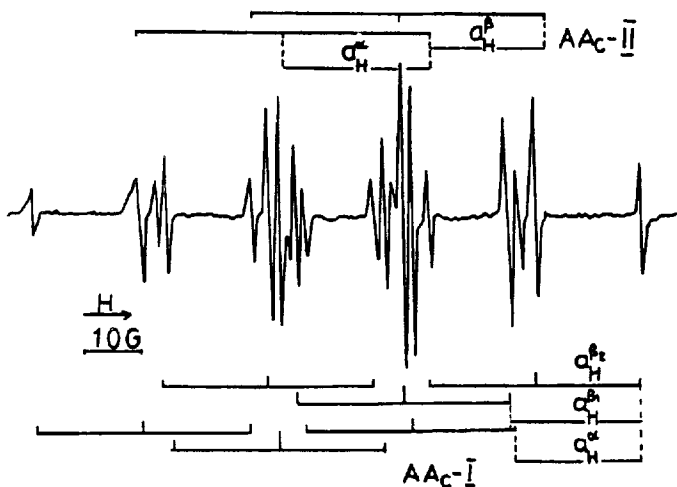


Figure 3 (Ranby). ESR spectrum of allyl acetate (AAC) monomer radicals, initiated as in Figure 2.

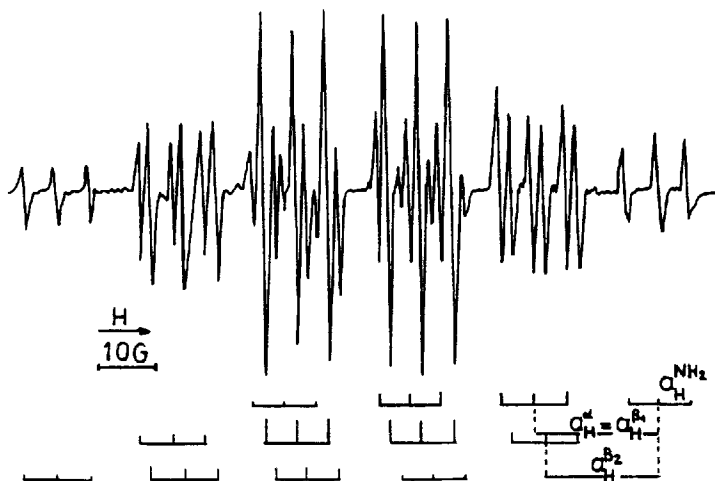


Figure 4 (Ranby). ESR spectrum of allyl acetate monomer radicals, initiated with  $\text{H}_2\text{N}\cdot$  radicals from the redox system  $\text{NH}_2\text{OH} - \text{TiCl}_3$ .  $[\text{AAC}] = 5.5 \times 10^{-2}$   
 $[\text{NH}_2\text{OH}] = 2.5 \times 10^{-2}$  and  $[\text{TiCl}_3] = 7 \times 10^{-3}$  mole/l.

shows only one radical (I), interpreted as a head radical, formed by addition of an amine radical at the tail of the monomer. No other radical can be identified in this spectrum. Amine radicals add apparently very preferentially to the tail end of AAC.

Figure 5 shows an ESR spectrum obtained from copolymerization of allyl alcohol with AN. The spectrum can be resolved into five different components. That is what Dr. Zubov indicated in the discussion. We see the allyl alcohol spectra (I), (II), and (III) given at the top of Figure 5. In addition, the acrylonitrile spectrum with its triplets is indicated as AN• and the

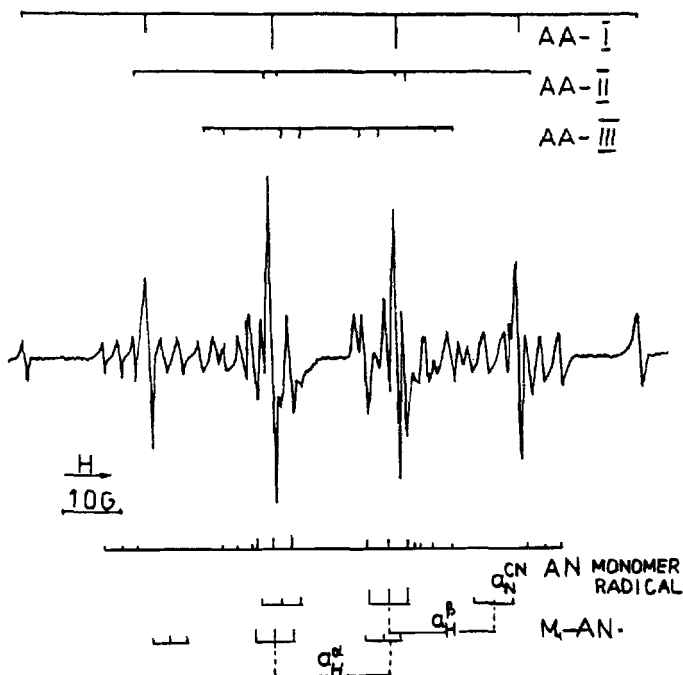


Figure 5 (Ranby). ESR spectrum of copolymerizing system of AA and AN in aqueous solution, initiated as in Figure 2.  $[AA] = 5.5 \times 10^{-2}$  and  $[AN] = 2.0 \times 10^{-2}$  mole/l.



copolymer radical AA - AN $\cdot$  (allyl alcohol plus acrylonitrile) which are identified with good evidence. The AA - AN $\cdot$  spectrum resembles the AN radical spectrum, but it is more narrow (lower coupling constant for  $\beta$ -hydrogen) due to the steric hindrance in the rotation between the AA and the AN monomer units in the dimer.

The interpretation of Figure 5 is an example that we can handle directly an ESR spectrum of five different radicals, identify them, and measure their concentration. I think these results will please our chairman, Professor Bamford, who was a pioneer in this field some 15 years ago (Bamford, C.H. et al., Nature, 175, 894 (1955)). In one study, he measured the ESR spectra for acrylic radicals during polymerization in gel phase where the radicals build up to rather high concentrations due to low termination rates.

The chart in Figure 6 shows the radical concentrations when allyl alcohol is copolymerized with increasing amounts of acrylonitrile as comonomer after initiation with HO $\cdot$  radicals. The allyl alcohol concentration is constant. Addition of acrylonitrile in increasing amounts first of all decreases the concentration of allyl alcohol (I) radicals (head radicals). It also decreases the concentration of allyl alcohol (II) radicals (tail radicals). Both (I) and (II) seem to react with AN monomer. But the amount of allylic radicals (AA III) actually increases a little when AN is added, which could mean that they do not take part in the reaction with AN. Also acrylonitrile radicals (AN $\cdot$ ) are increasing at higher AN monomer concentration

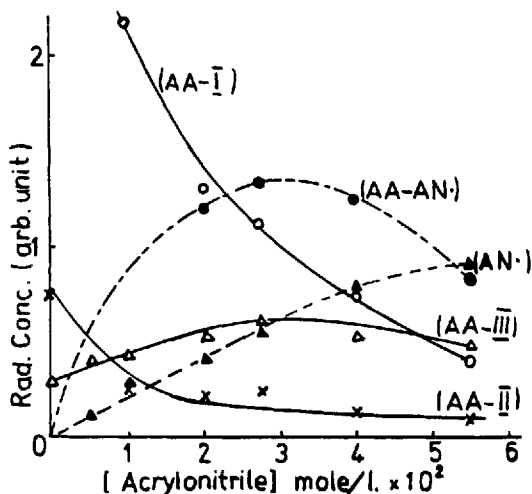


Figure 6 (Ranby). Concentration of different radicals (arbitrary units) measured from ESR spectra during copolymerization of AA with AN at different molar concentrations of AN in the AA-AN system, initiated with  $\text{HO}\cdot$  radicals.

(AA-I $\cdot$ ) ; head radical

(AA-II $\cdot$ ) ; tail radical

(AA-III $\cdot$ ); allylic radical

(AN $\cdot$ ) ; AN monomer radical

(AA-AN $\cdot$ ) ; AA-AN copolymer radical

[AA] =  $5.5 \times 10^{-2}$  mole/l.

as expected. The copolymer radical AA - AN $\cdot$  shows a maximum concentration at (AN)  $\approx 3 \times 10^{-2}$  mole/lit. From another type of graph (Figure 7) you can directly derive the reactivity of allyl alcohol and allyl acetate radicals towards a certain

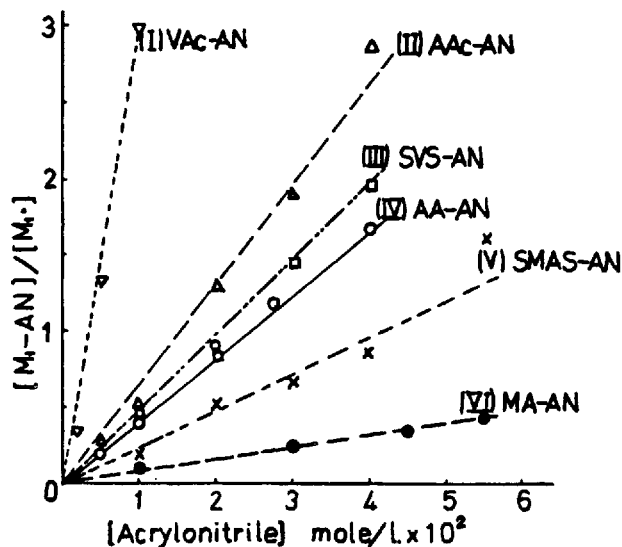


Figure 7 (Ranby). Plots of concentration ratio  $M_1\text{-AN}\cdot / M_1\cdot$  versus concentration of AN for the systems:

(I)  $\nabla$ Ac-AN; (II) AAc-AN; (III) SVS-AN; (IV) AA-AN;  
 (V) SMAS-AN; (VI) MA-AN; initiated with  $\text{HO}\cdot$  radicals.

$[M_1] = 5.5 \times 10^{-2}$  mole/l (constant).

monomer, acrylonitrile in this case. For comparison, data for vinyl acetate (VAc), sodium vinyl sulfonate (SVS), sodium methallyl sulfonate (SMAS) and maleic anhydride (MA), are plotted in the same graph (Figure 7), the VAc radicals, being very reactive, show a very high slope. Maleic anhydride radicals having a rather low reactivity, show the lowest slope. The other monomer radicals have intermediate reactivity, decreasing in the order AAc, SVS, AA and SMAS. Due to the time limit, I cannot continue further. I hope these results have shown that ESR measurements are a very useful technique for radical polymerization studies. And I will just sum up by presenting a few general results from our work.

Allylic radicals in measurable amounts are formed only from allyl alcohol and allyl ethers and not from allyl esters. This means that there should be some other explanation than formation of allylic radicals for the transfer reactions and the termination of polymerization with the allyl monomers mentioned.

Methallyl acetate gives only  $\alpha$ -methylene radicals with the double bond retained. No other radicals are found.

Allyl monomers need very active initiation species because they are not reactive as monomers. Hydroxyl radicals can give both head and tail radicals, but with amine radicals, we can only get tail addition, i.e., head radicals of allyl monomers.

Bamford: Thank you very much, Professor Ranby for your very interesting results. Now, I'd like to ask Professor Platé if he will speak to us.

N. Platé, Moscow, U.S.S.R: I would like to emphasize that our topic today is new phenomena in radical polymerization. In my viewpoint, this area is not limited to the problem of complex formation during the radical polymerization although this particular field, of course, is of great interest and of great practical importance and can really inspire new life into classical area.

Usually, and our present discussion confirms this, people are paying quite a bit of attention to the particular chemical mechanism of the propagation step. The nature of active species, the structure of the transition state, etc., are being studied in detail and sometimes elegant hypothesis are proposed. But we forget very often that macroradicals in the polymerization

system are material substances and not ideal spiritual species and their conformation and perhaps supermolecular characteristics may play a very important role in the kinetics and mechanism of the reaction. To look on radicals as real physical particles is now a tendency in the field of radical polymerization, and this approach is one of the new sides of the old field.

Two examples of the role of the physics of the macroradicals follow. One is the system of radical photopolymerization of methyl methacrylate studied by Professor N. Enikolopyan in the Institute of Chemical Physics in Moscow. Polymerization of MMA in bulk is initiated by flash-photolysis with the UV-source during a time of  $10^{-3}$  sec. This time is enough to produce a very low concentration of radicals of the order of  $10^{-9}$  mole/l. After the reaction with impurities, this concentration is decreased ten times and the concentration of radicals,  $10^{-10}$  mole/l, is a stationary concentration practically without recombination. This system is very convenient for studying the kinetics of the propagation rate because the lifetime of the growing radicals is high enough, such as in the "living" polymerization systems.

Using the technique of light scattering, the polymerization rate and the molecular weight were followed and it was found that the degree of polymerization is a function of reaction time. At first it is a linear relationship but, finally, there exists an acceleration phenomenon. The apparent molecular weight of PMMA measured by light scattering reaches some millions. Taking into consideration that this cannot exist in reality (chain transfer to the monomer limits the highest possible molecular weight of MMA), the reason of the phenomena ob-

served is not the change of  $K_p$  on the course of polymerization. The explanation is that growing macroradicals penetrate one into another or into the dead chain in such a way that you have finally the big coil consisted of interpenetrated chains of PMMA. What is interesting is the fact that you cannot succeed to achieve such dense interpenetration by mixing of individual dead PMMA macromolecules. On the contrary, they are separated easily from the system produced during the reaction. It means that you have a very specific interaction of growing macroradicals and that they possess a high interpermeability which depends on the particular conformational behavior of the growing species.

The other example is the polymerization of acrylates and methacrylates with long aliphatic ester groups, cetyl methacrylate, octadecyl acrylate, etc., studied in our laboratory in the Moscow State University. Polymerization in bulk or in solution easily produces high molecular weight samples approximately  $10^6$ . The presence of classical chain transfer agents like chloroform and carbon tetrachloride practically does not change the polymerization degree. This system is close to emulsion polymerization in micelles when the side branchings in growing macroradical can form a separate phase. The propagation proceeds in the sterically hindered conditions in the self-organized system. The termination step for such macroradicals becomes difficult and the reaction medium is nothing else than a set of microphases. It should be added that the electron microscopic photos show the existence of individual globular structures, the sizes of which correspond to the molecular weight of the individual macromolecule with

the X-ray diffraction order with interplanar distance of  $4,2 \text{ \AA}$ -- typical for the liquid crystalline packing of side chains in the comb-like polymer.

Bamford: Thank you, Professor Platé. I would like to ask Professor Manecke to speak now.

G. Manecke, Berlin, Germany: We investigated the influence of substituents on the polymerizability of different styrene and other vinyl derivatives. We have synthesized quite a number of such different substituted derivatives and found that very slight differences in the constitution effect dramatically the polymerization ability of these monomers. We thought that maybe the differences in polymerizability can be explained by NMR spectra, as we had a suspicion that some of the substituents have pulled the vinyl group out of the plain of the benzene ring. Actually, most of these derivatives have shown the same chemical shifts for the vinyl group and also the same coupling constants, so that the different polymerization abilities cannot be explained by NMR spectra. It is known that many substitution reactions in organic chemistry can be predicted by estimating the activation enthalpy of a reaction. H. LÜssi has tried to make predictions for the reaction of copolymerization couples by means of a model, which enables the calculation of the activation enthalpy for the radical chain propagation reaction of styrene and other vinyl derivatives.

In this model, the activation energy is proposed to be proportional to the sum of the perturbation energies of the radical on the monomer, which arise during the approach of these two reacting species. This, actually, is the model of

isolated molecules, and in many cases in organic chemistry one is able to predict by means of this model the possibility of some reactions (e.g., substitution reactions).

Therefore, we (E. Anders at our Institute) have applied the Lüssi-model to calculate the activation enthalpy of the radical chain propagation reaction in order to get an explanation for our experimental results. One has to calculate (LCAO-HMO-method) the perturbation energies in terms of bond orders and  $\bar{n}$ -electron charges of the attached centers. Actually, one gets by this method for nearly all styrene derivatives the same values for the activation enthalpy. Maybe the LCAO-HMO-method and/or the Lüssi-model are too rough for these calculations. Therefore, there should be found a way to consider in these calculations also the reciprocal interaction of the not nearest neighbors. Also the stereochemistry, the chain transfer, and other possible reactions should be considered. All this would be a further refinement.

Bamford: Professor Tudos, may we have your remarks, please.

Tudos: I will try in two minutes to say something about hot radicals. There is a very general phenomena of the stoichiometry in radical polymerization. If we take a classic inhibitor for radical polymerization as, for example, a quinone, we do not observe a simple stoichiometry for inhibition, that is two radicals being deactivated by one inhibitor molecule. Instead, for example, for the parabenzoquinone inhibitor in the polymerization of styrene, the stoichiometry is 1.23, and for vinyl acetate polymerization is 0.33. This means that only a portion of the inhibitor is consumed as such and some side reaction also



takes place. We can explain this stoichiometric analysis if we assume that when the growing radical reacts with the inhibitor molecule and the heat of reaction is liberated, we get excited radicals as products. This species can then react, without substantial activation energy with monomer, and in this way we get back a growing polymer radical. So we get no inhibition but only inhibitor consumption. In other cases, we can have deactivation of the inhibitor radical by collision with the monomer or with solvent molecules, and in this way we would get cold radicals that are able to react further in their combination with other growing chains to form inactive products. This then is a real inhibition step in which two radicals are deactivated by one inhibitor molecule. In this case, the experimental stoichiometry would be a value of two, but generally it is much lower than the theoretical one. An analogous consideration can also be applied to chain propagation.

Bamford: Thank you, Professor Tüdös. Ladies and gentlemen, we shall now have to close this session. I do not think we could hope to reach many very specific conclusions this morning about the wide range of complicated phenomena which we have heard about. Nevertheless, I believe the discussion has served a useful purpose, not only by indicating the kind of information which is required for an understanding of the mechanisms of the polymerizations we have been considering, but also by suggesting possible techniques for obtaining such data. Observations which fall into Professor Overgerger's category of refined measurements are clearly necessary before much progress can be made. May I conclude by thanking all the panelists and all the members of the audience who contributed.