

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Concluding Remarks

M. Szwarc<sup>a</sup>

<sup>a</sup> State University of New York Syracuse,

**To cite this Article** Szwarc, M.(1972) 'Concluding Remarks', Journal of Macromolecular Science, Part A, 6: 5, 983 — 988

**To link to this Article:** DOI: 10.1080/00222337208066370

**URL:** <http://dx.doi.org/10.1080/00222337208066370>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## CONCLUDING REMARKS

M. Szwarc  
State University of New York  
Syracuse

Let me say first of all that I am much less fortunate than Professor Kennedy who was properly coached and told what he has to say. Not only that nobody coached me and told me what I should say in my final remarks, but nobody told me even that I have to make these remarks. So, in desperation, I tried to make a few notes during the meeting. I know that my secretary can read them, but I don't know if I can do it.

Let me summarize the high points of this meeting and say what I learned and what I feel should be done in the future to clarify the issues which we discussed.

We dealt with two topics: Radical polymerization and cationic polymerization. Let's start with radical polymerization. What we heard and what is relatively new is that we are now in a position to observe directly the radicals in the course of polymerization.

Such studies were pioneered by Fischer and are elegantly continued by Professor Ranby who presented here some of his recent results. We can now see free radicals by virtue of their ESR spectra; therefore, we can identify them through their pattern and determine their concentration. This in turn permits us to calculate the absolute rate constants of radical propagation. Moreover, the propagating radicals may re-arrange in the course of polymerization, and Professor Ranby's studies show us how

we can learn about these re-arrangement processes. Undoubtedly, such studies will be continued and they should shed much light on the fine details of radical polymerization.

Let me remind you that thirty years ago, when radical polymerization was intensively studied, we had no direct way to verify their existence. Nevertheless, we accepted, and correctly accepted, the indirect evidence for their presence in polymerizing systems. Now, Dr. Gaylord and other speakers postulate the existence of transient intermediates in polymerizations involving complexing agents. True, they cannot yet obtain a direct evidence for their presence, but this difficulty should not be regarded as evidence for their absence.

I talk perhaps too much in this meeting about these various complexes. Molecular complexes exist and there are numerous books and papers describing their properties. However, what we wish to know is the identity of these complexes formed in polymerizing systems and their true role in polymerization. To achieve this goal we have to look for simple systems. Consider, e.g., a system composed of some initiator, say peroxide, two or three monomers which copolymerize and some complexing agent. One may find that the polymerization is faster in the presence of the complexing agent than in its absence, that the composition of the polymer and its molecular weight are greatly changed, etc. These findings may be extremely interesting and of great practical value, but to unravel such a system and to pin down the action of the complexing agent will be at least difficult, if not impossible.

The complexing agent could affect the decomposition of the initiator which generates radicals; it could affect the primary radical and/or the propagating radical; or it could

complex with the monomer. All these reactions may proceed simultaneously and by changing the conditions, we could affect their relative contributions to a different degree. It is not surprising, therefore, that the rate of reaction, or some other property of the system that measures the changes resulting from the process, may turn out to be a complex function of concentration, or other variables determining the state of the system. Therefore, various curves with maxima or minima presented in this meeting don't surprise me, but I doubt whether any unequivocal conclusions can be drawn from studies of such systems if simpler systems (call it model systems) were not investigated. Surely, these studies will be continued, but it is highly desirable to study the "component" systems.

Another fascinating problem raised in this meeting is the problem of spacial organization of the monomer prior to its polymerization. Of course, monomer is organized in crystal lattice whenever polymerized in crystalline phase and such a "solid state" polymerization was intensively studied although not discussed here. The question arises whether some organization can be achieved in liquid phase, e.g., due to the adsorption on chains of polymers dissolved in the polymerizing medium, or due to the presence of other type of "matrix". This problem was discussed here by Dr. Gaylord and, in fact, I raised this problem about 16 years ago in my paper on "replica" polymerization. A similar problem was discussed by Dr. Bamford when he suggested "tail" effect in polymerization of Leuch's anhydrides. I feel that we do not have yet any unambiguous evidence for such a phenomenon, but I believe that one day it will be clearly demonstrated.

Finally, the problem of photochemically "excited" monomers was mentioned by one of the speakers. If I understood him correctly, he postulates participation of an excited singlet. This is highly unlikely, since the lifetime of an excited singlet is in the range  $10^{-9}$  -  $10^{-8}$  sec. Even less probable is the participation of vibrationally excited monomer (also discussed here). Recent studies of Rentzepis demonstrate that the vibrational relaxation in solution occurs within  $10^{-12}$  sec.

Let me turn now to the cationic polymerization. Here, we were faced with reports describing most unorthodox phenomena. I cannot resist the temptation of telling you a true story. One of our colleagues suggested to his student to investigate the kinetics of polymerization initiated by  $\text{TiCl}_4$  and some organo-aluminum compound. The reaction was followed dilatometrically, and the student diligently measured the movement of the meniscus in the capillary of his dilatometer. After a few weeks of studies he went to his professor and said, "It is a most unusual reaction. Whenever I go home the polymerization stops. How does the polymerization know that I went home?" Of course, his observation was correct and he told the truth, but not the whole truth. He didn't add that the dilatometer was illuminated by a bright lamp to permit him to observe the position of the meniscus and whenever he went home, he switched the light off. The reaction turned out to be photochemically initiated and thus the mystery was solved.

Now, I told you this story because I am asking the same question. Sure, some of you described a most puzzling phenomena. All that has been reported is true. But, have we been told the whole truth and I wonder what was left not reported in the

description of these experiments. I liked, therefore, the remark of Professor Plesch about the reaction of RH with halides. This type of observation may be important and have to be kept in mind.

It is also important to stress that we are clearly distinguishing now in cationic polymerization between the reactions of free ions and ion-pairs. And again, Professor Schleyer, when we talk about ion-pairs we distinguish them from free carbonium ions. Whether you wish to call the cation of such a pair carbonium-ion or to give it another name is of little importance. What matters is that the pair is different from the free ion in its chemical behavior and, therefore, also in propagation.

Now, I believe that the studies reported here by Professor Williams give us reliable rate constants of propagation of free carbonium ions in hydrocarbon media; namely, values within a range  $10^6 - 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ . The interesting photolytic studies by others led to propagation constant of about  $10^4 \text{ M}^{-1} \text{ sec}^{-1}$  when the reaction has been performed in dichloroethane. If this polymerization again involves free ions, then the results indicate enormous effect of solvation. One expects formation of a solvation shell around an ion in polar solvents; also, one expects that the formation of such a solvation shell should reduce the reactivity of an ion, but the effect seems to be rather large ( $10^2 - 10^4$ ).

Interesting block-polymers were described by Professor Saegusa. Their formation provides a clear evidence for living cationically propagating polymers. It is worth stressing the difference between this technique and a similar one briefly mentioned here by Dr. Goldberg. The conventional living polymer technique of producing block polymers requires consecutive addi-

tion of monomers--each addition producing a block. Dr. Goldberg described a technique, originally suggested by Dr. Levy, in which cationically grown living polymer endowed with two ends was added to anionically grown living polymer also endowed with two ends. Their combination produces a poly-block.

Finally, I would like to summarize what we learned about self-ionization. Self-ionization can produce ions in solvents like  $\text{TiCl}_4$ ,  $\text{SbCl}_5$ , etc., e.g.,  $2\text{SbCl}_5 \rightleftharpoons \text{SbCl}_4^+ + \text{SbCl}_6^-$ . These ions could, in principle, initiate polymerization. However, this is not the only mode of initiation possible in such systems. For example, we have shown that polymerization can be initiated by transfer of  $\text{Cl}^+$  to the monomer, e.g.,  $2\text{SbCl}_5 + \text{C}=\text{C} \rightarrow \text{SbCl}_6^- + \text{Cl}\cdot\text{C}-\text{C}^+ + \text{SbCl}_3$ .

In conclusion, I wish to thank, and I presume that I can do it in your name, the organizing committee, Dr. Vogl, Dr. Lenz and all the other people who so graciously looked after us, for organizing this meeting so efficiently, pleasantly and instructively. Thank you very much.

Vogl: Thank you, Professor Szwarc, for your concluding remarks. I wish to thank the speakers, members of the panels and the other attendees for participating in this Symposium. We are especially grateful to the companies without whose financial support this Colloquium would not have been possible.