Pseudocationic Polymerization. The End of a Controversy? 1

Michael Szwarc

Hydrocarbon Research Institute of the University of Southern California, Los Angeles, California 90089-1991

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ABSTRACT: The pseudocationic mechanism of polymerization was conceived through negative arguments; no positive evidence for its validity was ever provided. It was claimed that the ionic mechanism cannot account for the observations. It is shown here that all the observations are fully and satisfactorily accounted for by the orthodox ionic mechanism that rationalizes many facts unexplainable by the pseudocationic hypothesis. Experiments differentiating between the above two propagation mechanisms are proposed.

The concept of polymerization reaction referred to as pseudocationic[1] arose from an interpretation of the results of kinetic studies of styrene polymerization initiated in chlorinated hydrocarbons by anhydrous perchloric acid at about ambient temperatures.[1,2] While the notions of this kind of polymerization have been subsequently generalized to wider systems,[3,4] most of the experimental evidence, supposedly supporting this view, comes from that study and the investigations of similar systems. Detailed re-examination of this evidence, as well as of the other available observations, some still unpublished, shows clearly that all the features of styrene polymerization initiated by acids are accounted for satisfactorily and convincingly by the orthodox ionic mechanism. The general treatment of this subject is presented in the accompanying paper (part 2). Here I wish to examine the foundation of the pseudocationic mechanism and its merit.

Let it be stressed, to begin with, that the concept of pseudocationic polymerization has never been supported by any positive evidence. It was conceived in a negative fashion, by claiming that some of the observations reported in the early 1960s are, supposedly, incompatible with any conceivable ionic mechanism. Thus, the proponents of pseudocationic polymerization failed to observe the optical absorption and the electric conductance of the styrene solution undergoing polymerization induced by perchloric acid, while they expected them to be detectable had the reaction been ionic. The reported lack of any effect of the added water upon the rate of polymerization, which, as they believed, should destroy the carbenium ions and terminate the propagation, has been considered as the strongest evidence against participation of ionic species in the polymerization. All these facts were stressed by the proponents of the pseudocationic hypothesis as the evidence fully *disproving* the notion of ionic polymerization for this system, but no arguments whatsoever were provided to prove the capacity of the esters to propagate directly the investigated polymerization.

The above arguments are misleading. The concentration of the propagating ionic species is too low ($<10^{-7}$ M) for their detection by the instruments used in Gandini and Plesch's experiments (see part 2). In fact, the optical absorption and electric conductance of the polymerizing solutions were observed later in stopped-flow studies[5] which demonstrated unequivocally that the protonation of the monomer by the acid yields ionic species as the first products leading to the polymerization.

The lack of influence of the added water on the progress of the propagation is explained by the findings of Matyjaszewski,[6] who successfully synthesized the styryl perchlorate and showed it to be rapidly hydrolyzed by water in a reaction regenerating the acid and re-forming subsequently the esters:

$$2CH_3CHPh{-}OClO_3 + H_2O \rightarrow (CH_3CHPh)_2O + 2HClO_4 \quad (I)$$

This is contrary to the claim of Gandini and Plesch,[1b] who stated, without testing, that the hydrolysis of the ester is negligible. In view of (I) small amounts of water do not affect the polymerization since the ester is regenerated.

The negative arguments supposedly disproving the ionic nature of this polymerization are, therefore, invalid. Hence, positive evidence is needed to substantiate the pseudocationic polymerization and demonstrate the direct propagation by the ester, but regretfully none was provided.

The distinction between the ionic and pseudoionic modes of propagation was elaborated in Plesch's 1988 paper[3]: "The attack of an ion on a double bond involves a 3-center transition state, the second half of the double bond is broken whilst a new covalent bond is formed. The propagation by ester involves a cyclic transition state (6 membered) in which the simultaneous making and breaking of more than two bonds is involved." These assertions led to the controversy. Does the *covalent* ester propagate through a multicenter transition state as proposed by Gandini and Plesch,[1,3,4] or does the spontaneous ionization of the ester yield ionic species, remaining in equilibrium with the ester, which propagate the polymerization. Generation of ester end groups was never disputed; their formation in the polymerization was convincingly demonstrated by Bywater and Worsfold.[7]

To support their claims, Gandini and Plesch attempted to prepare styryl perchlorate (the ester) by metathesis of $CH_3CH(Ph)Br$ and $AgClO_4$ in CH_2Cl_2 at ambient temperature.[1c] The anticipated ester decomposed under these conditions with liberation of perchloric acid. Subsequently, they prepared the ester *in situ* in the presence of a large amount of styrene, and then the polymerization ensued. Its kinetics mimicked that induced by the equivalent amount of perchloric acid,[1c] and therefore this result was claimed to prove the validity of the pseudocationic polymerization.[1] It did

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not. It merely proved the undisputed formation of the ester in the course of polymerization induced by perchloric acid, as demonstrated by Bywater and Worsfold.[7] The question which species propagate the polymerization has been left unresolved: are they the covalent esters, or the ionic species derived from the spontaneous ionization of the ester and remaining with it in equilibrium?

The outcome of the above experiments led Gandini and Plesch to a rather implausible proposition. They attributed the stability of the ester in the presence of a large excess of styrene to the formation of a stable complex of the ester with *four* molecules of styrene, whereas the uncomplexed ester, "starved" of styrene, ionizes and decomposes, yielding acid and some ionic species. However, no conceivable interactions could be visualized that would account for the formation and stability of such an unusual complex.

Nonetheless, the above peculiar observations are correct and explained by a polymerization scheme involving an autocatlytic step (step 4) proposed by Szwarc[8] and displayed below:

$$HClO_4 + CH_2{=}CHPh \underset{k_{-1}}{\overset{k_i}{\rightleftharpoons}} CH_3.C^+HPh,^-OClO_3 \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} CH_3CHPh{-}OClO_3 \quad (1)$$

$$\sim\sim CH_2.C^+HPh,^-OClO_3 + CH_2{=}CHPh \xrightarrow{k_p} \sim\sim\sim CH_2C^+HPh,^-OClO_3, \text{ etc.} \quad (2)$$

$$\sim\sim\sim CH_2C^+HPh,^-OClO_3 \xrightarrow{k_3} \text{inert products} + HClO_4 \quad (3)$$

$$\sim\sim CH_2C^+HPh,^-OClO_3 + HClO_4 \xrightarrow{k_4} \text{inert products} + 2HClO_4 \quad (4)$$

This scheme, written originally in terms of covalent species, is rewritten here in terms of ionic species. Its computer modeling[8] with several plausible sets of rate constants reveals that the concentration of the acid falls, within a few seconds, to an extremely low value ($\sim10^{-9}$ M) at the onset of polymerization, but its concentration rises abruptly in a few seconds to $>10^{-4}$ M, as shown by Figure 1, when ~90% of the monomer is polymerized. At that instant the computed rate of monomer consumption accelerates (due to its rapid protonation) and the ester decomposes.

The decomposition of the ester, according to the proposed scheme, is induced by the traces of acid (amplified by autocatalysis), and not by the inherent lability of the ester, as assumed by Gandini and Plesch.[1c] The "stability" of the ester in the presence of styrene is not due to the formation of the implausible complex with *four* molecules of the monomer, but it results from the efficient scavenging of the acid by the rapidly protonated styrene. Again, an ionic mechanism accounts for the apparently strange observations reported by Gandini and Plesch.

Plesch admits in later papers[3,4] that both ionic and covalent species contribute to the propagation. However, he does not specify to what extent each mode contributes to the propagation. Moreover, he states[3] unequivocally: "These two species are *not* in equilibrium, on the contrary, the progressive formation of P^+ (ions) from E (esters) seems to be a frequent feature of such systems." The mechanism of ion formation from the ester was not disclosed. Are ions formed by spontaneous ionization of the esters? In such a case the polymerization is ionic, as claimed by the opponents of the pseudoionic mechanism (see part 2), and the pseudocationic hypothesis is then superfluous.

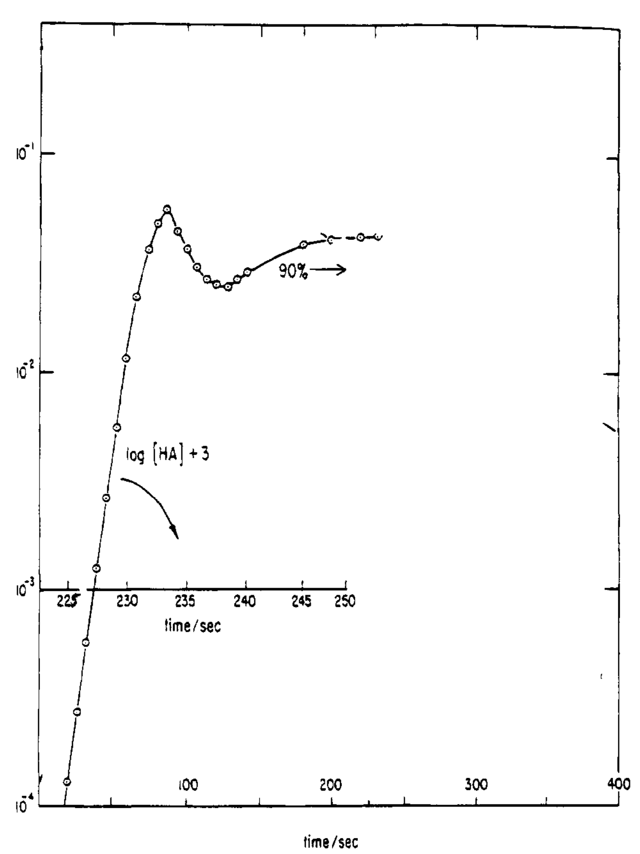

Figure 1. Rise of concentration of acid as a function of time. The "overshooting" results from the nonlinearity of the differential equations.

The puzzling assertion of Plesch claiming that the large increase in the propagation rate constant with increasing dielectric constant, ϵ, of the solvent *proves*(?) that the polymerization to be pseudocationic (see, e.g., p 15 of ref 4) calls for comments. Indeed, the observed propagation rate constant increases by four powers of ten as the ϵ of the medium rises from 2.3 to 10. Such an enormous acceleration of the rate is the strongest evidence for the ionic nature of this polymerization. It is caused by the strong enhancement of the degree of ionization of the ester, steeply increasing with the solvent's polarity. However, such an effect is not expected for the reaction of the covalent esters, or for any other pericyclic process.

Numerous observations reported in the literature, especially those pertaining to low-temperature polymerization (see part 2) or to the effects of salts on the rate of propagation and the MWD of the formed polymers, are unaccountable had the ester been the propagating species. On the other hand, they are fully and satisfactorily explained by the ionic mechanism. In fact, the restriction of the pseudocationic approach to the propagation step with disregard for its relation to the other processes proceeding in the system is the fundamental weakness of this treatment of polymerization, in contrast to the ionic approach.

The controversy between the proponents of pseudocationic polymerization and those espousing ion pairs as the propagating species is reduced, therefore, to the question whether the covalent ester propagates via a cyclic multicenter transition state or whether the propagation results from the interaction of a monomer with the ion pair, or free ion, produced by the spontaneous ionization of the esters. It is essential, therefore, to perform at least one experiment leading to the conceptual outcome different for these two modes of propagation.

As pointed out by Matyjaszewski,[9] a propagation proceeding through a cyclic transition state retains the configuration of an asymmetric ester whereas its racemization is predicted in an ionic propagation. It is crucial for the verification of the pseudocationic hypothesis to perform such an experiment to gain the first *positive* evidence of its reality. The proponents of pseudocationic polymerization are urged, therefore, to do it. Racemization of 1-phenylethyl trifluoroacetate, reported by Matyjaszewski and Lin,[9] seems to negate the pseudocationic hypothesis.

The pericyclic mechanism proposed recently by Plesch[4] to account for the living cationic polymerization may be tested in a similar way. In fact, it is disproved by the convincing NMR observations reported recently by the team of Higashimura and Sawamoto (*Macromolecules* **1992**, *25*, 2587; **1995**, *28*, 3747; *J. Phys. Org. Chem.* **1995**, *8*, 282).

In conclusion, the character of a polymerization is determined by all its steps: initiation, propagation, chain transfers, etc. The shortcomings of the pseudocationic idea is, as stated earlier, its restriction to the propagation step and to its insufficient attention to the relations of propagation with the other processes taking place in the course of polymerization. Moreover, its conclusions are contradicted by the reported observations discussed in the following paper. On the other hand, the orthodox ionic mechanism accounts satisfactorily for all the observed steps of this polymerization in spite of its sometimes puzzling complexity.

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