7312 *Macromolecules* **1995,** *28,* 7312−7314

Pseudocationic Polymerization. The End of a Controversy? 2

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Received March 24, 1995; Revised Manuscript Received August 21, 1995[⊗]

ABSTRACT: The behavior of the polymerization of styrene induced by perchloric acid is examined, emphasizing its kinetics and the molecular weight distribution (MWD) of the resulting polymers. The chain transfer to monomer explains the behavior of this reaction near ambient temperature. The results of low-temperature experiments provide a deep insight into the nature of the propagating species, proving their ionic structure, whereas they are incompatible with the postulated propagation by the esters assumed to be the active species by the proponents of the pseudocationic hypothesis. The results of stopped-flow experiments, the effects of the added salts, and the MWD of the produced polymers all point to the ionic character of this polymerization and to the important role of ion pairs.

The extensively investigated cationic polymerization of styrene initiated by perchloric acid provides a deep insight into the mechanism of this kind of reaction. In spite of its high reproducibility, insensitivity to traces of water, and the apparent simplicity,[1,2] this polymerization is, in fact, quite complex. Let us summarize, therefore, the reported findings.

Mixing styrene solution in chlorinated hydrocarbons (CH_2Cl_2 or CH_2ClCH_2Cl) with a solution of perchloric acid (HA) near ambient temperature leads to a fast reaction consuming all the acid within a few seconds[3] and simultaneously yielding the oligomeric esters, $\sim\sim\sim CH_2CHPh{-}OClO_3$. The propagation induced by these oligomers seems to be simple. The rate of monomer consumption is first order in styrene up to ~90% conversion, and the pseudo-first-order rate constant, $-d\ln[M]/dt$, is approximately proportional to the initial concentration of the acid;[1,2] i.e., for a reasonable range of the acid concentration

$$-d\ln[\text{styrene}]/dt \sim k_{ex}[HA]_0$$

However, and most significantly, the experimental bimolecular rate constant of propagation, k_{ex}, is strongly affected by the dielectric constant, ϵ, of the medium in which the reaction takes place.[1] As ϵ rises from 2.3 to 10, the rate constant k_{ex} increases by 4 powers of 10, an observation undeniably proving the ionic character of this polymerization. A reaction proagated by the covalent nonionic ester (the so-called pseudocationic polymerization) could not be affected by the solvent's polarity to such a large degree.

After exhausting the initially provided monomer, the polymerization resumes when fresh monomer is supplied.[1] The subsequent propagation proceeds with the same rate as the previous one, and the DP_n of the produced polymers remains the same as before (~10). Its independence of the monomer concentration and the degree of conversion implies the participation of a chain transfer to monomer in the overall process.

The resumption of the polymerization on addition of fresh monomer shortly before the previously provided one was consumed indicates that the agent inducing the polymerization, whatever its nature, is regenerated in the process. The number of polymeric molecules formed by each molecule of the acid may be calculated by knowing their experimentally determined DP_n. Its value depends on the temperature of the polymerizing solution, being about 100−200 around ambient temperature.

Although the acid is consumed within a few seconds, the ensuing stationary polymerization continues for many minutes. Hence this process has to be governed by the propagation and chain-transfer steps only:

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$$

$$P_n^* + M \xrightarrow{k_{tr}} P_n + P_1^*$$

Here P* denotes a growing polymer and P a terminated one.

The nature of P* needs consideration. The pseudoionic hypothesis assumes them to be the esters. Alternatively, they could be ion pairs formed by the ionization of the esters, or free cations resulting from dissociation of ion pairs, or perhaps still other species, e.g., acid-activated esters, etc., and most probably mixtures of some of them. In the latter case, the composition of the mixture had to be determined by the pertinent equilibria to account for the stationary character of the ensuing propagation and the constancy of k_{ex} in each run. This conclusion contradicts the explicit statement of Plesch,[3] who asserts lack of equilibrium in these systems.

Careful studies of the molecular weight distribution (MWD) of the polymers formed at ambient temperature reveal their bimodal nature under a variety of conditions. The bimodality of polystyrene prepared by initiating its polymerization by acetyl perchlorate was reported previously by Higashimura,[5] who concluded that the bimodality manifests the participation of two or more species in the polymerization. The higher peak of the molecular mass distribution is suppressed by the addition of perchlorte salts (e.g., NBu_4^+, ClO_4^-) but not by the salts of the other anions[4] (e.g., not by $NR_4^+SbF_6^-$). Hence, the suppression demonstrates the participation of free carbocations in the polymerization process, since their concentration is expected to be reduced by the common salt effect. However, other modes of salt action are also possible; e.g., the interaction of a salt (A^-,Cat^+) with an ion pair $\sim\sim\sim Sty^+$, ClO_4^- might facilitate the dissociation of the latter caused by the reaction

$$\sim\sim\sim Sty^+,ClO_4^- + A^-,Cat^+ \rightarrow \sim\sim\sim Sty^+ + A^-,Cat^+,ClO_4^-$$

(a known mode of triple ion formation). This reaction

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

0024-9297/95/2228-7312$09.00/0

might account for the *increase* of the apparent propagation constant resulting from the salt addition, reported by Lorimer and Pepper[6] (see p 563 of their paper).

The free carbocations are expected to contribute to the population of the polymers of higher molecular mass due to their faster growth or longer lifetime than those of ion pairs. Two problems call, therefore, for consideration: (1) how to account for the bimodality of the produced polymers and (2) how to reconcile the *substantial* contribution of the free cations to the polymer growth (see Figures 2–4 of ref 4) with the approximate proportionality of the propagation rate constant with the initial concentration of the acid.

Let us consider the second problem first. The propagation rate of a polymerization involving ion pairs and free ions is given by

$$k_{\pm}K_i[\mathrm{HA}]_0 + k_{+}(k_iK_{dis})^{1/2}[\mathrm{HA}]_0^{\;1/2}$$

where k's denote the respective propagation rate constants, K_i is the ionization constant of the ester, and K_{diss} is the dissociation constant of the resulting ion pairs. The k_{ex} computed from the above expression is approximately proportional with the $[\mathrm{HA}]_0$ for a sufficiently small K_{diss} and not too wide a range of $[\mathrm{HA}]_0$. For example, for $K_{\mathrm{i}} = 10^{-3}$, $K_{\mathrm{diss}} = 10^{-7}$ M, and $k_+/k_\pm = 2$, the following relative values of k_{ex} are computed for $[\mathrm{HA}]_0$'s varying from 2 to 10 mM:

$[\mathrm{HA}]_0$/mM	2	4	6	8	10
k_{ex}/(M s)	2.9	5.3	7.5	9.8	12
% polymer resulting from the free ions	31	32	25	22	20

The low value of K_{diss} may be justified by substantial contribution of a covalent structure to the ionic $\mathrm{C^+{-}OClO_3^-}$ bond.

Let us pass now to the problem of bimodal distribution. Treatments of the MWD of living polymers invoke the exchange process between the species growing with different rates.[7] It seems that the exchange between free ions and their ion pairs is fast enough to prevent the bimodality of MWD. However, in the system under consideration, frequent chain transfer takes place. A fast chain transfer (the lifetime of the growing polymers limited by the chain transfer seems less than 1 ms) terminates the growing polymers before they have a chance to exchange. This explanation, proposed by Pepper,[12] accounts for the observed bimodality.

The study of polymerization proceeding around ambient temperature does not provide sufficient information to allow further inquiry about the nature of the propagating species. On the other hand, a deep insight into the mechanism of this kind of polymerization is gained from studies of its conduct at low temperatures.

As reported earlier,[4] a burst of rapid polymerization completed in seconds but consuming only a fraction of the available monomer is observed at −97 °C. The weight of the formed polymers is proportional to the initial concentration of the acid. Moreover, their number, computed from the experimentally determined $\mathrm{DP_n}$, reveals that each acid molecule produces only one polymer molecule; i.e., chain transfer is negligible at this low temperature, but the ensuing polymerization is terminated by some irrevocable process. Stopped-flow experiments[6] demonstrate the formation of the carbocations (free or paired) as the first products of styrene protonation by the acid. These species seem to propagate a fast but limited polymerization, observed at −97 °C, before collapsing into the unreactive esters. Hence, the collapse of the ionic species into the esters is the irrevocable termination step of this reaction. Since the esters are unreactive at this very low temperature, the observed "burst" of polymerization cannot be explained by the pseudoionic hypothesis. It fails here entirely.

Interestingly, the MWD of the polymers formed in the burst polymerization (stage I) at −97 °C indicates the presence of many short oligomers and relatively few polymers of higher $\mathrm{DP_n}$. It seems that ion pairs are the first species formed by the protonation; they grow relatively slowly, and their lifetime is short because they collapse into the unreactive esters. However, few of them have the chance to dissociate into free cations, and the latter grow faster and live longer since they have to recombine into ion pairs before collapsing into the unreactive esters. Hence, the free ions seem to generate polymers of higher $\mathrm{DP_n}$.

The proposed above sequence of events is confirmed by the effect of the added perchlorate salt. The yield $Y = \Delta M/M_0$ of the polymer formation is reduced by the salt addition but not entirely as shown by the intercept of the linear plot of $X = -\ln(1 - Y)$ vs $1/[\mathrm{ClO_4^-}]$ depicted in Figure 4 of ref 4. This has to be expected. The addition of salt reduces the concentration of the free cations but not of the ion pairs, which still grow for a while before collapsing into the esters unreactive at −97 °C.

The above observations demonstrate (1) that ion pairs are the first products of protonation, (2) that some ion pairs dissociate into free ions which yield polymers of higher $\mathrm{DP_n}$, (3) that ion pairs ultimately collapse into unreactive esters, and (4) that the pseudocationic hypothesis has to be discarded since it cannot account for such a behavior of the polymerization.

The quiescent solution of the apparently unreactive polymers formed at −97 °C in the nonstationary stage I of the reaction becomes reactive when warmed to −60 °C.[4] Significantly, the $\mathrm{DP_n}$ of the previously dormant polymers increases then with conversion. Hence, the polymers produced in the nonstationary stage I of the polymerization continue their growth in the stationary stage II of the process. The rate of ionization of the esters, too low at −97 °C to allow for their reionization, becomes sufficiently high at −60 °C to induce a propagation observed in the stationary stage II of the process.

The formation and decay of the transient, identified as the styryl cation, is clearly revealed in stopped-flow experiments. The experiments performed at −80 °C with $\mathrm{HClO_4}$ as the protonating acid show the transient disappearing while the monomer is still available. Apparently, the acid was consumed and the ion pairs collapsed before all the monomer was polymerized. A different behavior is observed in the polymerization induced by triflic acid. As shown by Vairon[13] and by Kunitake and Takarabe,[14] the transient persists even when all the monomer is consumed and ultimately it slowly decays. The triflate ion pairs do not collapse into the corresponding esters. Indeed, Matyjaszewski and Sigwalt,[15] who attempted to prepare it, concluded that such an ester is not formed even at −78 °C. Hence, the polymerization induced by triflic acid could not be propagated by the nonexisting ester but by the ion pairs or free ions. The growth of polymers is terminted by deprotonation, and the regenerated acid initiates then a new carbenium ion. The process continues until the monomer is exhausted, and thereafter a slow deprotonation destroys the transient.

The different behavior of perchloric acid and triflic acid reflects the higher nucleophilicity but lower basicity of the former compared with the latter.

The behavior of the polymerization induced by triflic acid demonstrates again the failure of the pseudocationic idea. The polymerization proceeds although esters are not formed. The ion pairs, as well as the free cations, are the propagating species, and not the nonexisting esters.

Could the esters be the propagating species in the stationary polymerization induced at ambient temperature? Such a presumption is superfluous; the participation of the ion pairs and free ions in the polymerization is undeniable, and it accounts for all the observations. There is no need, therefore, to postulate the esters as another propagating species. Nothing is gained by this assumption, for which no evidence has ever been provided.

The quantitative treatment of this polymerization discussed in terms of ionic species has been outlined previously by Pepper.[12] His treatment of chain transfer, especially illuminating, shows the operation of spontaneous chain transfer at lower temperatures and the increasing importance of chain transfer to monomer at higher temperatures, the latter becoming dominant above −25 °C.

Acknowledgment. I had an active cooperation with Professor David H. Pepper during the preparation of these two papers. He kindly provided me with a copy of his latest paper, still in press at that time, and with numerous and most valuable unpublished data. I am also grateful for his many suggestions and advice.

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MA950399P