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Effect of Autocatalytic Action of Perchloric Acid on Pseudocationic Polymerization of Styrene Initiated by the Acid

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ABSTRACT: Cationic polymerization of styrene initiated by perchloric acid shows some intriguing and unconventional features. These were attributed in the past to the formation of a hypothetical complex between perchlorate esters (the propagating species) and four molecules of styrene (the monomer). In this paper an alternative explanation is offered. An autocatalytic, perchloric acid induced decomposition of the esters is proposed and the appropriate mechanistic scheme is developed. The computer solution of the relevant differential equations shows all the interesting features claimed to be characteristic of this polymerization and provides a deeper insight into its behavior.

The kinetics of polymerization of styrene initiated in chlorinated hydrocarbons by anhydrous perchloric acid was described by Pepper and Reilly[1] and their results were confirmed by Gandini and Plesch.[2]

Both groups reported the following observations for a process proceeding at ~20 °C:

(1) Perchloric acid is consumed quantitatively and virtually instantaneously when added to a solution of styrene. In fact, its presence is undetectable during the main course of the ensuing polymerization.[3]

(2) The polymerization is first order in styrene up to ~90% conversion. The pseudo-first-order constant is proportional to the initial concentration of the added acid. The second-order rate constant is found to be ~10 M^{-1} s^{-1}. However, the consumption of styrene accelerates at ~90% conversion, and at that time the colorless and nonconducting solution suddenly discolorates and becomes conducting.

(3) After cessation of polymerization the reaction can be reinitiated by the addition of a second batch of styrene.

(4) Small amounts of water in the solvent have no influence on the course of polymerization even when its concentration exceeds the initial concentration of the acid by a factor of 3 or 4.

In his early papers[1] Pepper accounted for these observations by postulating an extremely rapid and quantitative proton transfer from the acid to the monomer, yielding carbenium ions or their ion pairs

$$HClO_4 + CH_2{=}CH(Ph) \rightarrow CH_3\overset{+}{C}H(Ph),ClO_4^-$$

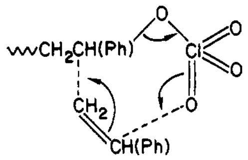
The subsequent cationic propagation was assumed to proceed without any termination, at least up to ~90% conversion, although it involves chain transfer as indicated by the low molecular weight of the product.

This mechanism was disputed by Plesch[2] since, as pointed out by him, the slowness of propagation, the inertness of the system to moisture, and the lack of conductance of the polymerizing solution are all incompatible with the supposedly ionic character of the reaction. Instead, he proposed initiation yielding a reactive perchlorate ester capable of propagating polymerization; i.e.

$$HClO_4 + CH_2{=}CH(Ph) \rightarrow CH_3CH(Ph)OClO_3$$

$$CH_3CH(Ph)OClO_3 + CH_2{=}CH(Ph) \rightarrow CH_3CH(Ph)CH_2CH(Ph)OClO_3, \text{ etc.}$$

To substantiate this mechanism, coined as a "pseudocationic polymerization", Plesch attempted a synthesis of styryl perchlorate by reacting $CH_3CH(Ph)Br$ with a solution of $AgClO_4$ in methylene chloride. However, the resulting product was unstable and decomposed. On the other hand, he reported that the same preparative method yielded an apparently stable ester when styrene was added to the solution of $AgClO_4$. The formed ester was claimed to induce polymerization of the added styrene, leading to a reaction similar in its behavior to the polymerization initiated by perchloric acid. This finding supports the pseudocationic mechanism involving the transition state of propagation:



Still two questions remained unanswered: Why is the ester unstable in the absence of styrene, and why do the polymeric esters decompose when the conversion is sufficiently high, e.g., at ~90% for $[\text{styrene}]_0$ ~0.3 M? To rationalize these phenomena, a complexation of the ester with styrene was postulated, i.e.

$$CH_3CH(Ph)OClO_3 + n(CH_2{=}CHPh) \rightleftarrows CH_3CH(Ph)OClO_3,(CH_2{=}CHPh)_n$$

presumably stabilizing the ester.

On the basis of some experimental data,[4] Plesch deduced a value of 4 for the stoichiometric coefficient *n*. Indeed, a large value of *n* is imperative if one wishes to explain the abrupt change in the behavior of polymerization as the concentration of styrene reaches some critical value. Above it the complexation equilibrium lies far to the right but, for large *n*, it shifts abruptly to the left as the styrene concentration falls below some critical value, causing then decomposition of the ester.

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The above explanation is questionable. No obvious interaction could make styrene a much more preferred agent for complexation with the ester than, say, molecules of the polar solvent. Moreover, while formation of a 1:1 complex might be plausible, it is unrealistic to suggest a complex of the ester with four molecules of styrene. Hence, an alternative hypothesis is needed to explain the abrupt change in the behavior of the system at some critical concentration of styrene and the simultaneous enhancement of polymerization.

Autocatalysis by Perchloric Acid

Consider the following mechanistic scheme governing the polymerization of styrene initiated by perchlorice acid:

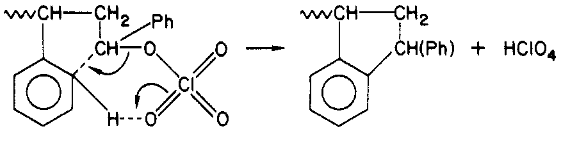
(a) $HClO_4 + CH_2{=}CH(Ph) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CH(Ph)OClO_3$

(b) $CH_3CH(Ph)OClO_3 + CH_2{=}CH(Ph) \xrightarrow{k_p} CH_3CH(Ph)CH_2CH(Ph)OClO_3$, etc.

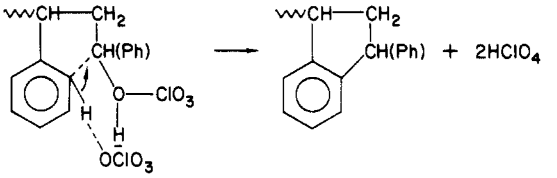
(c) $\sim\!CH_2CH(Ph)OClO_3 \xrightarrow{k_2}$ inert product + $HClO_4$

(d) $\sim\!CH_2CH(Ph)OClO_3 + HClO_4 \xrightarrow{k_3}$ inert product + $2HClO_4$

Reaction a is a reversible initiation. Reaction b, the propagation, is virtually irreversible since at the monomer–growing polymer equilibrium the concentration of styrene is exceedingly low.[5] The same propagation constant is assumed for the monomeric and polymeric ester; this simplification leaves the characteristic features of this system unaffected. Reaction c is a spontaneous decomposition of the growing polymeric ester into the acid and some inert product, e.g., as proposed by Plesch



The novel reaction d is the $HClO_4$-catalyzed decomposition shown by the scheme



The kinetics of the process above is given by four nonlinear differential equations:

$$d[HA]/dt = k_{-1}[Est] + k_2[P^*] + k_3[HA][P^*] - k_1[HA][M] \quad (1)$$

$$d[M]/dt = k_{-1}[Est] - k_1[HA][M] - k_p([Est] + [P^*])[M] \quad (2)$$

$$d[Est]/dt = k_1[HA][M] - k_{-1}[Est] - k_p[Est][M] \quad (3)$$

$$d[P^*]/dt = k_p[Est][M] - k_2[P^*] - k_3[HA][P^*] \quad (4)$$

where HA denotes the acid, M the monomer, Est the monomeric ester, and P* the growing polymeric ester. Moles of the formed polymer molecules, denoted by NP, are given by

$$d[NP]/dt = k_p[M][Est] \quad (5)$$

The numerical solution of these equations for several sets of constants k_1, k_{-1}, k_2, k_3, and k_p was obtained by computer integration (VAX 11-780) using the program developed by Gear.[6]

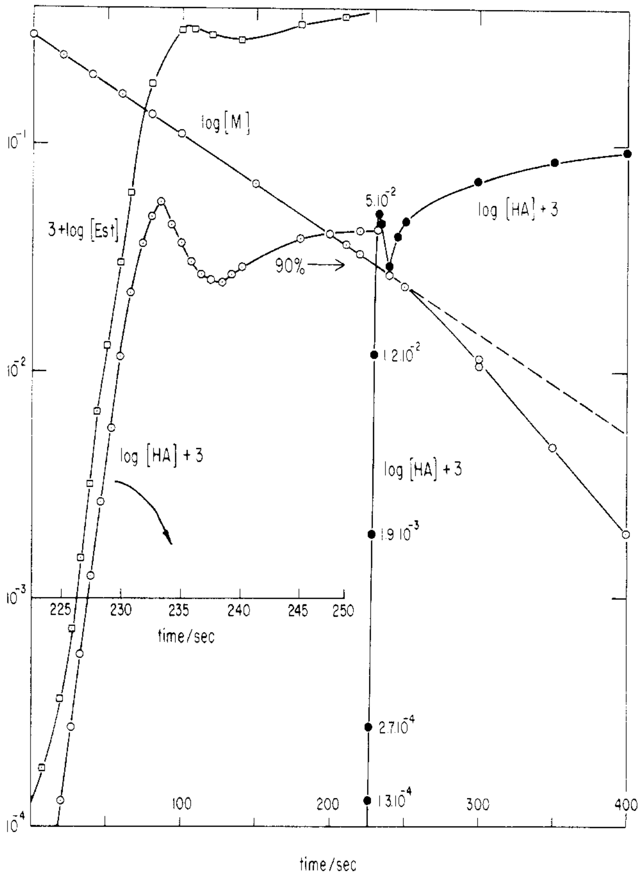


Figure 1. Plot of log [M] vs. time. Note the acceleration (a downward trend) starting at ~90% conversion. Plot of 3 + log [HA] vs. time. Note the sudden rise of log [HA] (black circles) around 225 s. The steep part of that plot is shown on the left side of the figure in an enlarged time scale, 225–250 s. In the same time scale is shown the plot of 3 + log [Est] (□) vs. time.

Numerical Results of Computation

All the computations were performed for the initial concentration $[HA]_0 = 0.001$ M and $[M]_0 = 0.3$ M, these being typical for the experiments of Pepper and of Plesch. The value of k_p was kept constant at 10 $M^{-1}\ s^{-1}$, again typical for the reported experiments, whereas the values of k_1, k_2, and k_3 were varied within reasonable limits, as shown by Table I.

For all sets of constants listed in Table I, plots of log [M] vs. time coincide, up to ~90% conversion, with a straight line having slope = $k_p[HA]_0 = 0.01\ s^{-1}$. The downward deviations of the computed lines from linearity demonstrate acceleration of polymerization in the last stages of the process. They become notable at ~200 s (~90% conversion), as shown by the data of Table I and exemplified by Figure 1. The degree of these deviations may be gauged by comparing the values of [M] computed for $t = 400$ s with the corresponding one derived through extrapolation of the linear log [M] vs. t relation. The pertinent [M]'s are listed in the last column of Table I. They show an increase of acceleration with increasing k_3 (compare runs B and E, G and H, and I and J) but its decrease on increasing k_1 (compare runs E and F).

The first effect is easily rationalized. The monomer is consumed more rapidly in the initiation than in each step of propagation. The contribution of initiation to the overall monomer consumption increases with increasing

Table I
Concentration of Styrene at 200 and 400 s after the Onset of Polymerization[a]

run	$10^{-3}k_1$, M s	k_{-1}, s	$10^{-3}k_3$, M s	k_2, M s	10^3[M], M at 200 s	10^3[M], M at 400 s
					40.6[b]	5.5[b]
A	0.1	0.001	4	0	40.4	2.0
B	0.1	0.001	4	1×10^{-5}	40.5	1.8
C	0.1	0.001	4	1×10^{-4}	40.3	1.8
D	0.1	0.001	4	1×10^{-3}	40.4	1.75
E	0.1	0.001	8	1×10^{-5}	34.0	1.1
F	0.2	0.001	8	1×10^{-5}	40.5	1.6
G	0.2	0.001	10	1×10^{-4}	39.5	1.3
H	0.2	0.001	12	1×10^{-4}	37.6	1.1
I	0.4	0.001	12	1×10^{-4}	40.4	1.8
J	0.4	0.001	20	1×10^{-4}	39.5	1.2
K	0.4	0.001	20	5×10^{-4}	39.2	1.2
L	1.0	0.001	50	5×10^{-4}	39.1	1.1
M	1.0	0.001	50	1×10^{-3}	39.0	0.97

[a] At 200 s, [M] departs only slightly from the value extrapolated from the linear dependence of log [M] upon time. The $k_p = 10\ M^{-1}\ s^{-1}$ and $[M]_0 = 0.3$ M. [b] From extrapolation of the linear dependence (slope 10).

Table II
Time Dependence of [HA], [M], [Est], and [P*] for Run B

time, s	10^3[HA], M	10^3[M], M	10^3[Est], M	10^3[P*], M	NP/$[HA]_0$
0	1.0	300	0	0	0
1	2.8×10^{-6}	296	5.7×10^{-2}	0.94	0.95
10	4.3×10^{-7}	271	4.2×10^{-6}	1.00	1.006
50	7.1×10^{-7}	181	7.8×10^{-6}	1.00	1.007
100	1.4×10^{-6}	110	1.4×10^{-5}	1.00	1.008
15	3.7×10^{-6}	66.7	3.6×10^{-5}	1.00	1.009
200	5.3×10^{-5}	40.5	4.0×10^{-4}	1.00	1.011
210	5.7×10^{-4}	36.6	3.1×10^{-3}	0.997	1.015
215	4.3×10^{-3}	34.7	1.9×10^{-2}	0.976	1.030
227.5	1.2×10^{-2}	33.9	5.4×10^{-2}	0.934	1.06
220	2.2×10^{-2}	32.9	1.2×10^{-1}	0.854	1.13
230	2.6×10^{-2}	29.2	2.3×10^{-1}	0.740	1.75
250	4.3×10^{-2}	22.4	3.9×10^{-1}	0.563	3.37
300	7.1×10^{-2}	10.5	6.7×10^{-1}	0.261	7.55
400	9.5×10^{-2}	1.8	8.6×10^{-1}	0.044	11.39
∞	1.0	0	0	0	

rate of supply of the acid produced by the autocatalytic reaction, i.e., with increasing k_3. For $k_1 \gg k_p$, the rate of HA supply, and not the value of k_1, determines the acceleration. However, an increase of k_1 leads to a decrease of [HA] at every stage of the process and hence to a decrease in the rate of HA formation through the acid-induced decomposition of the polymeric esters (reaction d). Thus, the acceleration decreases upon increasing k_1.

Concentrations of the acid and of the monomeric ester are exceedingly low during the main stage of polymerization. For example, [HA] decreases to 10^{-10}–10^{-9} M, less than 10^{-3}% of its initial value, at the end of the first second. At that time [Est] increases to ~5% of $[HA]_0$ but then rapidly decreases to less than 10^{-8} M within the next few seconds. On the other hand, the concentration of the polymeric ester rises to more than 90% of $[HA]_0$ in 1 s and remains virtually equal to $[HA]_0$ during the following 200 s, i.e., during the main stage of polymerization. These results are apparent upon inspection of Figure 1 pertaining to run A and of the data pertaining to run B collected in Table II.

The concentrations of these reagents abruptly change at ~200 s as the conversion consumes ~90% of the monomer. The most dramatic increase of [HA] is shown in Figure 1.[10] Within 8 s [HA] increases by a factor of 500, from 1×10^{-7} M at 225 s to 5×10^{-5} M (5% $[HA]_0$) at 233 s. The results of run B, given in Table II, show a 400-fold increase of [HA] within 20 s, from 5.3×10^{-8} M at 200 s to 2.2×10^{-5} M at 220 s. Similar results derived from other runs are graphically displayed in Figures 2 and 3.

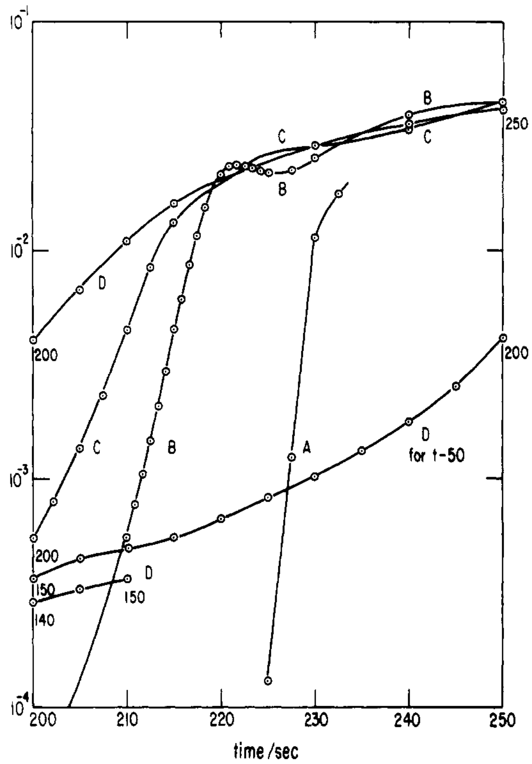


Figure 2. Plot of log [HA] vs. time for runs A, B, C, and D. The plot related to run D is shown in three segments, for t = 140–150 s, t = 150–200 s, and t = 200–250 s.

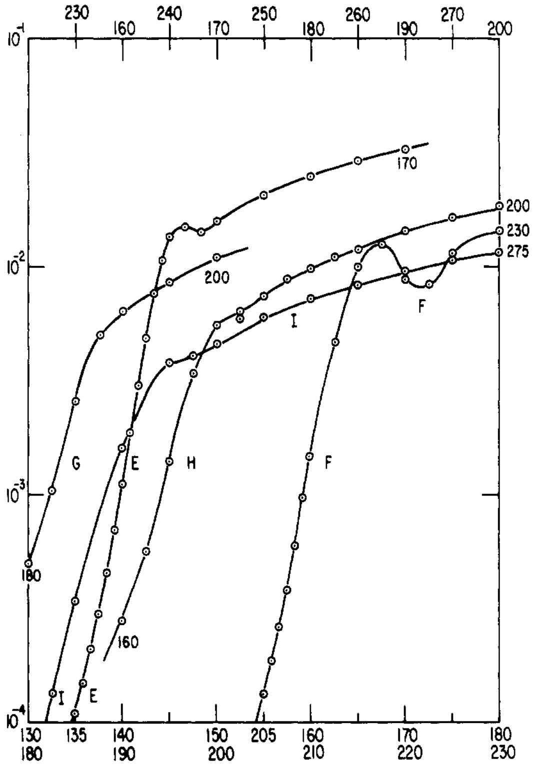


Figure 3. Plots of log [HA] vs. time for runs E, F, G, and H. The time scales are shifted: E from 135–170 s, F from 205–230 s; G from 180–200 s, H from 160–200 s, and I from 185–275 s.

The abrupt increase of [HA] is the consequence of the autocatalytic reaction d. The degree of abruptness may be gauged by the steepness of the tangents of the curves log [HA] vs. t at their inflection point. The pertinent data

Table III
Slopes of the Curves [HA] vs. Time at Their Inflection Point[a]

	run										
	A	B	C	D	E	F	G	H	I	J	K
Δt	5	9	20	40	10	8	18	9	15	14	35
k_2, s	0	1×10^{-5}	1×10^{-4}	1×10^{-3}		10^{-5}	10^{-4}				

[a] Measured by Δt, during which [HA] increases 100-fold.

are collected in Table III. Their sensitivity to the values of k_2 is remarkable; the larger k_2, the flatter the tangent. Such a dependence is readily understood. The spontaneous decomposition of the polymeric esters moderates the effect of their autocatalytic decomposition by providing a steady supply of [HA].

The abrupt increase of [HA] leads to a parallel increase of [Est] and to a precipitous decrease of [P*]. These changes explain the reported sudden onset of conductance and discoloration around 90% conversion.

Peculiarity of the Shape of the log [HA] vs. Time Curves

The peculiar shape of the curves log [HA] vs. t is most visible in Figure 1, although it is also notable in some other curves shown in figures 2 and 3. The abrupt increase of [HA] is followed by a short-lived decrease, after which [HA] gradually rises. The sequence of a maximum shortly followed by a minimum is the result of a feedback. Rapidity of the acid formation is associated with depletion of the polymeric esters which serve as a source of the acid. Concentration of the esters is replenished through reactions a and b. However, since these reactions are not instantaneous, there is a time lag during which [P*] decreases below the value anticipated for a kind of stationary state. This leads to a decrease of [HA] followed by its gradual increase as the system approaches its pseudostationary state.

Alternatively, we may account for the maximum closely followed by a minimum by considering a simplified scheme in which reaction d is the only one yielding the acid. The extremes in the [HA] vs. t function should appear when $k_1[\mathrm{M}][\mathrm{HA}] = k_3[\mathrm{P}^*][\mathrm{HA}]$. Concentration of the monomer only gradually decreases in the period of the reaction discussed here, whereas [P*] decreases rapidly. This is shown in Figure 4, where $(k_3/k_1)[\mathrm{P}^*]$ and [M] are plotted as functions of time. The intersection point of those curves corresponds to the maximum in [HA] vs. time curve. In a time comparable to the combined characteristic times of reactions a and b (approximately 1 s), the pseudostationary state is approached and thereafter [P*] very slowly decreases. In fact, in Figure 4, drawn on the basis of data of run A, a short-lasting increase of [P*] is seen. The second intersection of the curves corresponds then to a minimum in the [HA] vs. t curve.

Problem of Molecular Weight

The molecular weight of the products investigated by Plesch[2] is very low, ~600–700. The scheme discussed here predicts a relatively high molecular weight of the formed polymers. Even for the highest value of k_3 (runs L and M), the number of the formed polymeric molecules is still smaller than $20[\mathrm{HA}]_0$ when >99% of the monomer is polymerized. This leads to $\bar{M}_n > 1500$. Moreover, ~90% of the weight of the product consists of polymers having $\bar{M}_n \sim 25000$, while the remaining 10% consists of dimers and trimers formed in the last stages of the process. Hence, it is necessary to introduce a chain-transfer step into the process proposed in the earlier section of this paper.

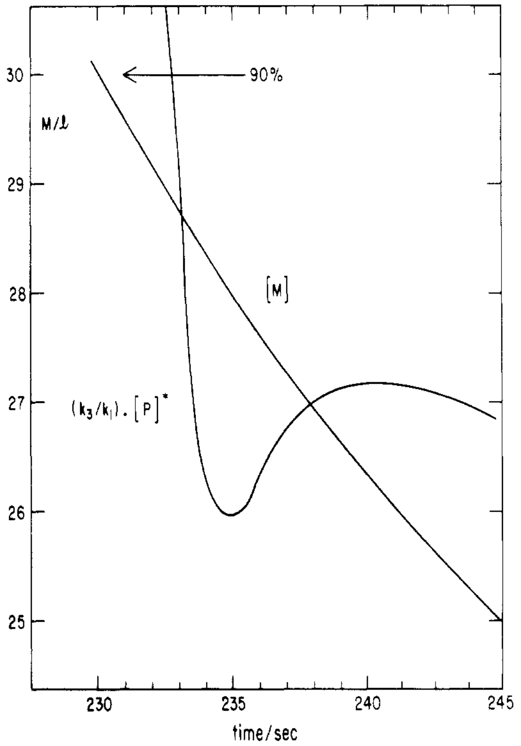


Figure 4. Plot of [M] and of $(k_3/k_1)[\mathrm{P}^*]$ vs. time. The intersections of the curves correspond to the maximum and minimum in the log [HA] vs. time curve.

Introduction of chain transfer to the monomer modifies three of our previous differential equations; namely

$$\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{-1}[\mathrm{Est}] - k_1[\mathrm{HA}][\mathrm{M}] - k_{\mathrm{p}}([\mathrm{Est}] + [\mathrm{P}^*])[\mathrm{M}] - k_{\mathrm{tr}}[\mathrm{P}^*][\mathrm{M}] \quad (2')$$

$$\mathrm{d}[\mathrm{Est}]/\mathrm{d}t = k_1[\mathrm{HA}][\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{P}^*][\mathrm{M}] - k_{-1}[\mathrm{Est}] - k_{\mathrm{p}}[\mathrm{Est}][\mathrm{M}] \quad (3')$$

$$\mathrm{d}[\mathrm{P}^*]/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{Est}][\mathrm{M}] - k_2[\mathrm{P}^*] - k_3[\mathrm{HA}][\mathrm{P}^*] - k_{\mathrm{tr}}[\mathrm{M}][\mathrm{P}^*] \quad (4')$$

Their solutions were performed for two values of k_{tr}, viz., 0.1 k_{p} and 0.2 k_{p}. The results retained the peculiar features of the scheme, viz., the abrupt increase in the concentration of the acid at some critical concentration of styrene, although the rise is slower. On the other hand, the effect of the transfer results in a higher and steady concentration of the monomeric ester and a somewhat lower but also steady concentration of the polymeric esters during the main period of polymerization.

For the sake of illustration, the computed concentrations of the monomer, acid, and the esters are shown in Figure 5, which refers to a run with the following set of constants: $k_1 = 200$ M^{-1} s^{-1}, $k_{-1} = 0.001$ s^{-1}, $k_2 = 1 \times 10^{-5}$ s^{-1}, $k_3 = 8 \times 10^3$ M^{-1} s^{-1}, $k_{\mathrm{p}} = 10$ M^{-1} s^{-1}, and $k_{\mathrm{tr}} = 2$ M^{-1} s^{-1}. As in the previous runs, the monomer disappears in a first-order fashion up to ~90% conversion, although the apparent pseudo-first-order constant is somewhat higher; viz., $(k_{\mathrm{p}} + k_{\mathrm{tr}})[\mathrm{HA}]_0 = 0.012$ s^{-1}. This is self-explanatory. The deviation from linearity takes place around 90% conversion. The concentration of acid rises slowly from 4×10^{-9}

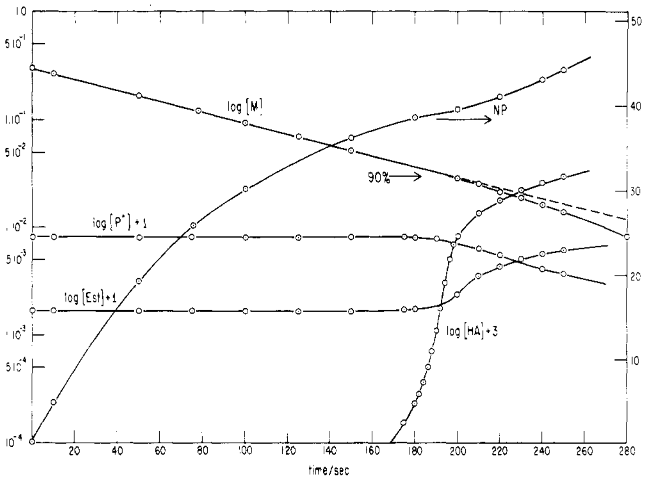


Figure 5. Plots of log [M], 3 + log [HA], 1 + log [P*], and 1 + log [Est] vs. time for the run with constants $k_1 = 200$ M^{-1} s^{-1}, $k_{-1} = 0.001$ s^{-1}, $k_2 = 1 \times 10^{-5}$ s^{-1}, $k_3 = 8 \times 10^3$ M^{-1} s^{-1}, $k_p = 10$ M^{-1} s^{-1}, and $k_{tr} = 2$ M^{-1} s^{-1}. The respective mechanism incorporates the chain transfer to monomer. The number of polymeric molecules present at *t* is shown by the plot of NP vs. time. (NP refers to the right scale.)

M at the end of the first second to 2×10^{-7} M at ~180 s, then rapidly rises to 1.3×10^{-5} M (a ~70-fold increase) in the following 30 s, and remains still below 5.5×10^{-5} M at 400 s when >99% of the monomer is polymerized. Obviously, the chain transfer moderates but does not eliminate the abrupt rise in the acid concentration. The number-average molecular weight of the polymer is ~620 at the end of 400 s and slightly higher, viz., ~720, at 200 s when ~90% of the monomer is polymerized. The increase in the number of polymeric molecules, NP, with time is shown graphically in Figure 5.

A transition state of the chain transfer to monomer was proposed by Plesch.[2] It involves closure of a five-membered ring, yielding the indan derivative with the simultaneous transfer of an aromatic H and the ClO_4 group to the monomer. Such a reaction is exothermic. The alternative, leading to a polymer terminated by a C═C bond, is less probably because it is approximately thermoneutral.

The spontaneous release of $HClO_4$ from a growing polymeric ester with formation of a C═C end group is possible. Formally it contributes to reaction c. However, this variant of the mechanism was not considered. It raises the problem of the reverse $HClO_4$ addition,[11] requires two more constants in the mathematical scheme, and, after all, does not affect the ultimate state of the system.

Instability of the Monomeric Ester

A spontaneous decomposition of the monomeric styryl perchlorate was reported by Plesch.[2] This writer suggests that such a reaction is triggered by styrene produced through equilibrium a, established within a fraction of a second.

$$\mathrm{Est} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{HA} + \mathrm{M} \qquad \text{(a)}$$

$$K_1 = k_{-1}/k_1$$

The addition of the monomer to the ester yields a growing dimer which, in turn, is decomposed autocatalytically by the acid into the inert dimeric indan derivative and more acid. Continuation of these reactions results in the decomposition of the ester and their course may be followed by utilizing the mathematical approach developed in this paper.

The computations were performed for the initial conditions: $[HA]_0 = [M]_0 = [P^*]_0 = 0$ and $[Est]_0 = 0.1$ M. The results were obtained for several sets of constants. For example, for those chosen in the last run discussed in the preceding section, i.e., $k_1 = 200$ M^{-1} s^{-1}, $k_{-1} = 1 \times 10^{-3}$ s^{-1}, $k_2 = 1 \times 10^{-5}$ s^{-1}, $k_3 = 8 \times 10^3$ M^{-1} s^{-1}, $k_p = 10$ M^{-1} s^{-1}, and $k_{tr} = 2$ M^{-1} s^{-1}, one finds 32% of the ester to be decomposed in about 15 min. The products are the acid and the corresponding amount of the dimeric indan derivative. The concentration of styrene remains very low during the decomposition, less than 10^{-3} M at the start of the reaction and ~10^{-5} M after 15 min.

The degree of the decompositon is influenced mostly by the value of K_1. For example, for $K_1 = 10^{-6}$ M ($k_1 = 1 \times 10^3$ M^{-1} s^{-1}, $k_{-1} = 1 \times 10^{-3}$ s^{-1}), 20% of the ester is decomposed in 15 min; the percentage rises to ~40% for $K_1 = 10^{-5}$ M ($k_1 = 100$ M^{-1} s^{-1}, $k_{-1} = 1 \times 10^{-3}$ s^{-1}), and it is ~80% when $K_1 = 10^{-4}$ M ($k_1 = 100$ M^{-1} s^{-1}, $k_{-1} = 0.01$ s^{-1}). For a constant K_1, variation of k_3 or introduction of the transfer step has only minor effects upon the degree of decomposition.

The statement[2] "The monomeric ester is stabilized by styrene" seems to be misleading. The presence of styrene delays the formation of the acid during polymerization. However, the addition of styrene to the ester induces polymerization, which converts the latter to dimers, trimers, etc. In fact, the mechanism proposed here predicts "stabilization" of the ester by the acid. Its addition reduces the equilibrium concentration of styrene, and it is the latter monomer that starts the chain of events leading to the formation of polymeric esters that undergo decomposition. Indeed, the decomposition is self-retarded by the acid as revealed by the computation.

Conclusions

The strange behavior of styrene polymerization induced by perchloric acid in CH_2Cl_2 or $C_2H_4Cl_2$ at ambient temperature is fully accounted for by the mechanism invoking the autocatalytic formation of the acid. It is unnecessary to invoke the improbable complexation to explain the observations.

The constants chosen in the computations are plausible. Those chosen in the run depicted in Figure 5 seem to be the best for the quantitative account of the system. However, they cannot be claimed as unique.

The question of participation of ionic and covalent species in propagation has been raised again in a most recent paper by Matyjaszwski et al.[12] The authors confirm the feasibility of pseudocationic propagation, i.e., direct monomer addition to an ester, in polymerization of THF, oxepane, etc. However, they dispute its reality in polymerization of styrene initiated by perchloric acid. Of course, one could consider a rapidly maintained equilibrium between a covalent species and its ion pair and attribute the reactivity to the latter. For example, 0.01% of ion pairs propagating with rate constant of 10^5 M^{-1} s^{-1} would account for the polymerization observed at ambient temperature, and the minute proportion of ion pairs may prevent their detection. Indeed, the participation of ion pairs, and even free ions, is evident at lower temperatures. However, the lack of influence of water on the polymerization performed at about 20 °C is the strongest argument in favor of pseudocationic polymerization.

This writer does not take sides in this controversy. He wishes only to stress that the proposed here autocatalytic process makes Plesch's mechanism more plausible by removing the necessity of postulating the highly improbable complex.

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Appendix

Some observations reported by Hamann et al.[9] call for the following suggestions. Hamann et al. investigated polymerization of styrene initiated by perchloric acid in carbon tetrachloride and found the reaction to be zero order in the monomer but its rate proportional to $[HClO_4]_0$; viz.

$$-d[M]/dt = \text{const} \times [HClO_4]_0$$

They rationalized these results by invoking again the formation of complexes between growing polymers, the acid, and monomer. However, an alternative explanation is plausible.

Participation of two or more species in ionic polymerizations are well-known and documented.[7] Consider two interchangeable polymeric species, P_1^* and P_2^*, participating in a polymerization

$$P_1^* \underset{k_b}{\overset{k_f}{\rightleftarrows}} P_2^*$$

In most systems monomer addition converts an n-meric species of one kind into an $(n + 1)$-meric of the same kind; viz.

$$P_1^* \ (n\text{-mer}) + M \xrightarrow{k_1} P_1^* \ ((n+1)\text{-mer})$$

$$P_2^* \ (n\text{-mer}) + M \xrightarrow{k_2} P_2^* \ ((n+1)\text{-mer})$$

However, reactions of the type

$$P_1^* \ (n\text{-mer}) + M \xrightarrow{k_{12}} P_2^* \ ((n+1)\text{-mer})$$

and

$$P_2^* \ (n\text{-mer}) + M \xrightarrow{k_{21}} P_1^* \ ((n+1)\text{-mer})$$

are also feasible.[8] Let us assume that a system is governed by the following rate constants:

$$k_{12} \gg k_1, \qquad k_2 = 0, \qquad k_f \ll k_{12}[M]$$

i.e., the monomer-induced conversion of P_1^* into P_2^* is faster than its propagation or its collapse into P_2^*, whereas P_2^* neither propagates nor is converted into P_1^* by the monomer, although a spontaneous conversion of P_2^* into P_1^* does take place. These relations do not violate the principle of microscopic balancing provided depropagation of any kind is sufficiently slow to be neglected. Under those conditions the rate of polymerization is

$$-d[M]/dt = k_b[P_2^*] \approx k_b[\text{polymers}]$$

when $k_f/k_b \gg 1$. Such a polymerization is therefore zero order in monomer and first order in growing polymers, i.e., in $[HClO_4]_0$.

This mechanism accounts for Hamann's findings without invoking the improbable complexes. It is premature to specify the nature of the species P_1^* and P_2^* proposed here. Tentatively one may consider P_2^*, which forms the bulk of the polymers, as a dormant, virtually inactive ester whereas P_1^* is its ion pair, which collapses into an ester on addition of the monomer.

Registry No. $HClO_4$, 7601-90-3; styrene, 100-42-5.

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(11) The reverse of reaction c yielding the indan derivative may be neglected. Such a derivative is assumed to be stable and should not generate the ester.
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Ultraviolet Analysis of Benzoyl Peroxide Initiated Styrene Polymerizations and Copolymerizations. 1

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ABSTRACT: Ultraviolet spectroscopic quantification of the end groups resulting from the decomposition of benzoyl peroxide (BPO) during the initiation of styrene polymerizations and the application of such analysis to polymerization kinetics and to the development of polymer characterization techniques are reported. As an additional example of the application of ultraviolet spectroscopy to polymer analysis, the results obtained on commercial samples of poly(n-butyl methacrylate) and poly(isobutyl methacrylate) are also presented and discussed.

Introduction

The ultraviolet analysis of styrene-containing copolymers has been, in recent years, the subject of controversy. Hypochromic effects, band shifts, etc. have been attributed to characteristics of the microstructure of the polymer molecules and to conformation effects induced by both the polymer microstructure and the thermodynamic properties of the solvents used.[1-3] The nonideal absorption behavior observed appears mainly through deviations from the line typical of single chromophores. Correlation of these deviations with microstructure characteristics such as the length of the styrene sequences has been reported and used in conjunction with size exclusion chromatography for the characterization of styrene copolymers.[2,3,5] It has been shown, however, that within the limits of experimental error, the laws of linearity and ad-

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