European Polymer Journal, Vol. 12, pp. 1 to 4. Pergamon Press. Printed in Great Britain.

CATIONIC AND PSEUDOCATIONIC POLYMERIZATION OF AROMATIC OLEFINS—III. [1a, b]

A RE-INVESTIGATION OF THE POLYMERIZATION OF STYRENE BY PERCHLORIC ACID IN METHYLENE DICHLORIDE

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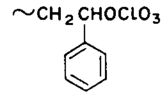
(*Received* 10 *May* 1975)

Abstract—A reinvestigation of the polymerization of styrene by perchloric acid in methylene dichloride at 0° with improved techniques has shown that the polymerizations are not of first order throughout; after the first half-life, the reaction accelerates and the electrical conductivity of the reaction mixture increases concurrently. These phenomena are ascribed to the slow ionization of the propagating polystyrylperchlorate ester to much more rapidly propagating polystyryl ions present in very low concentrations, and in equilibrium with a much larger concentration of non-propagating polystyrylindanyl ions. Our observations, together with those of other authors on the bimodal DP distribution of polystyrenes formed under similar conditions, confirm that the pseudocationic polymerization propagated by the polystyryl perchlorate ester is indeed a distinct form of reaction.

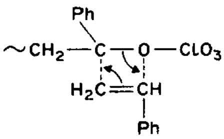
INTRODUCTION

There has been considerable argument over the mechanism of the polymerization of styrene by perchloric acid in halogenated solvents in the temperature range *ca.* 30° to *ca.* −20° [1–11]. By spectroscopic and conductance measurements, Gandini and Plesch [1] could not detect any carbenium ions during the polymerization; this and other evidence led them to conclude that the dominant propagating species is the ester, polystyryl perchlorate (I), which is stabilized by an excess of styrene.

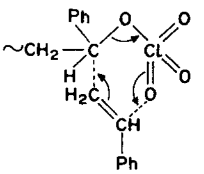


(I)

They envisaged the propagation as monomer insertion into the C–O bond of the ester via a four- or six-membered cyclic transition state (II)



(IIa)



(IIb)

The term "pseudocationic" was used to describe this mode of propagation [1d]. The arguments for pseudocationic polymerization have been set out in detail [1b, 12–14].

Most other contemporary authors have contended that the propagating species is some kind of ion-pair [2–4] or a π-complex [6, 10], although the electrochemical arguments against ion-pairs playing an important kinetic part were set out in some detail [15].

In the course of further studies of this problem, we have re-investigated this reaction in methylene dichloride at 0° using improved techniques. We found new phenomena reported here which shed fresh light on the mechanism.

EXPERIMENTAL

Materials

Styrene [16] and methylene dichloride [17,18] were purified and dosed under high vacuum; solutions of perchloric acid in methylene dichloride were prepared by standard techniques [19]. The styrene and the solutions of perchloric acid in methylene dichloride were then transferred into phials with a tipping device [19, 20].

Polymerization

The kinetics were studied by adiabatic calorimetry [18] and high vacuum isothermal dilatometry [21, 22]. The calorimeter and the dilatometers were fitted with electrodes [21] for measuring the conductivity of the reaction mixtures.

Characterization of products

The reaction products were precipitated in methanol containing 0·880 ammonia. The precipitated polymer was filtered off and dried at 50° in a vacuum oven. Evaporation of the filtrate yielded the oligomers. For molecular weight determinations, the two fractions were dissolved together in CCl_4. Molecular weights were determined with a Vapour-Pressure Osmometer.

RESULTS

A summary of the results (calorimetric and dilatometric is given in Table 1. Figure 1 shows typical

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Table 1. The polymerization of styrene by perchloric acid at 0°

Expt. No.	[Styrene] mol dm^{-3}	10^4 [HClO$_4$] mol dm^{-3}	10^3k_1 s^{-1}	DP
12C	0.331	9.90	2.76	13.8
2C	0.336	6.05	1.85	-
1C	0.335	5.15	1.67	-
27D	0.319	8.55	2.10	12.3
24D	0.326	5.50	1.31	19.0
23D	0.322	5.50	1.38	17.7
21D	0.342	5.25	1.36	17.6
225D	0.332	4.19	1.27	20.6
221D	0.346	4.18	1.16	19.9
222D	0.340	4.17	0.98	26.7
223D	0.335	3.11	0.95	22.8
224D	0.340	3.11	0.84	23.1
217D	0.336	2.33	0.61	21.5
216D	0.337	2.26	0.63	20.2
229D	0.338	2.20	0.52	17.0
230D	0.335	2.19	0.50	21.8
215D	0.342	2.07	0.61	-
220D	0.343	1.88	0.44	32.3
218D	0.354	1.31	0.32	20.2
219D	0.337	1.13	0.25	17.3
227D	0.345	0.79	0.14	20.4
228D	0.348	0.78	0.14	24.4

k_1 First-order rate-constant. C Calorimetric experiments. D Dilatometric experiments.

first-order plots (log m vs time) for the reaction at 0°. The plots are curved towards the time-axis, indicating an acceleration. This acceleration only becomes evident at, or sometime after, the first half-life. The first-order rate-constants k_1 in Table 1 correspond to the slopes of the rectilinear portion of the first-order plots. The k_1 is directly proportional to the initial concentration of the acid, as shown in Fig. 2. The slope of this plot gives the second-order rate constant k_2 in the rate expression:

$$-\mathrm{d}m/\mathrm{d}t = k_1 m = k_2[\mathrm{HClO_4}]m; \qquad (1)$$

a least squares analysis gives $k_2 = 2{\cdot}76$ dm^3 mol^{-1} s^{-1}, correlation coefficient = 0·984 (literature [1b]: 2·66 dm^3 mol^{-1} s^{-1}).

The conductivity remained constant between about 15 s after the initiation and the end of the first half life of the reactions and was approximately equal to the conductivity of the monomer solution alone (*ca.* 10^{-8} Ω^{-1} cm^{-1}) and variable from one experiment to another; the reaction mixtures were completely colourless. At or shortly after the end of the first half-life, the conductivity began to increase slowly at first; when the reaction was almost complete, it rose quickly and then became constant. At this stage the solution was yellow.

In the calorimetric studies, the kinetic acceleration only became apparent when the calorimeter was sta-

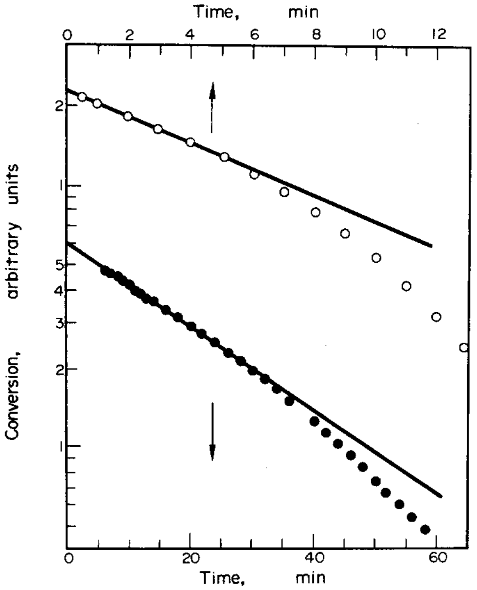


Fig. 1. First-order plots of typical calorimetric and dilatometric experiments. ○ 2C ● 217D.

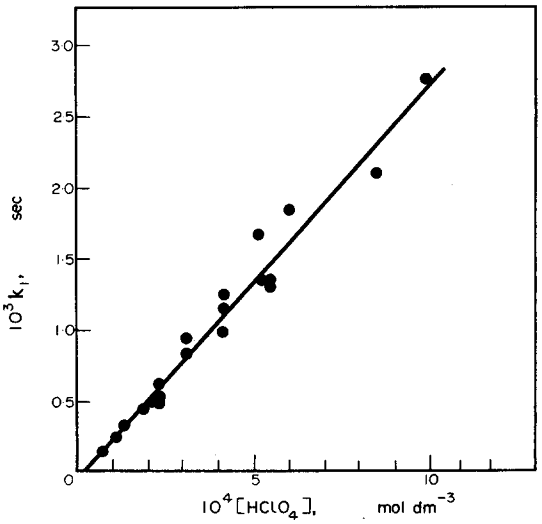
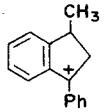


Fig. 2. The dependence of k_1 on the concentration of perchloric acid.

bilized to a constant temperature, rather than to a constant pre-cooling rate as had been the practice in the earlier work; this improvement in technique had revealed the acceleration. However, the acceleration and the corresponding increase in conductivity were also observed in the isothermal dilatometric studies so that they cannot have been caused simply by the increase in temperature during the adiabatic reactions in the calorimeter. As is well-known [1a] with this system, the degree of polymerization of the polymer increases slightly as the concentration of the initiator is lowered (Table 1).

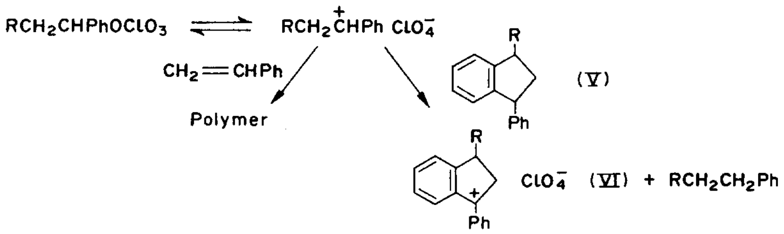
DISCUSSION

The new features shown up by this study are the increase in rate and the concurrent increase in conductivity during the greater part of the polymerizations. We attribute the increase in conductivity during the polymerization to the formation of at least two types of free ions, viz. the polystyryl ion and the polystyrylindanyl ion, the relation between which has been explained before [1b].



(III) $CH_3CH(Ph)CH_2\cdot\overset{+}{C}HPh$ (IV)

The "bistyryl" ion, viz. the 1,3-diphenyl-*n*-butyl ion (IV) and its higher homologues have been identified by Bertoli and Plesch [23]. It is known [23] that ion (IV) can abstract a hydride ion from 1,3-diphenylindane to give the 1,3-diphenylindanyl ion (III). During the polymerization of styrene by perchloric acid ion(IV) and the corresponding polystyryl carbenium ions are probably formed by the dissociation of the growing ester, oligostyryl perchlorate. They in turn can either propagate or react with polystyrylindane (V) (which is formed slowly by transfer reactions [1a, 24] to give the stable polystyrylindanyl ion (VI) analogous to (III).



Since the polystyryl carbenium ion has a very high propagation rate-constant, the slow formation of even very low concentrations of these is an adequate explanation of the acceleration; and since they are in equilibrium with a much larger concentration of the non-propagating indanyl ions (VI) the concurrent rise in conductivity follows as a corollary.

From Fig. 1 we can estimate the concentration of propagating ions, assuming simultaneous propagation by both ester and free ions. The rate equation takes the form:

$$-\mathrm{d}m/\mathrm{d}t = k'_2[\mathrm{E}]m + k''_2[\mathrm{P}_n^+]m, \qquad (2)$$

where [E] and $[\mathrm{P}_n^+]$ are the concentrations of ester and free-ions, respectively.

Hence

$$\ln m_1/m_2 = (k'_2[\mathrm{E}] + k''_2[\mathrm{P}_n^+])(t_1 - t_2). \qquad (3)$$

Towards the end of the polymerizations, the reactions tend towards first-order behaviour and thus we can make the reasonable assumption that [E] and $[\mathrm{P}_n^+]$ are constant. With the further assumptions that $[\mathrm{E}] \approx [\mathrm{HClO_4}]_0$, $K'_2 = k_2$ and $k''_2 = 10^5\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $[\mathrm{P}_n^+]$ can be calculated from the conversion curves in Fig. 1 and is found to be of the order of 10^{-8} mol dm^{-3} towards the end of the polymerizations.

This concentration is too small to account for the rise in conductivity but, as mentioned above, this is due to the much larger concentration of indanyl ions with which the propagating ions are in equilibrium.

COMPARISON WITH THE RESULTS OF OTHER WORKERS

The principal difference between these and earlier results [1–4] lies in the acceleration and the conductivity rise. Despite this, the early, non-accelerated phase of our reactions can be seen to correspond to what was observed previously because of the near identity of the rate constants, viz. 2·76 (this work) and 2·66 dm^3 mol^{-1} s^{-1}[1b].

We offer the following explanation for the acceleration.

Since the ester is relatively insensitive to water (and probably other similar impurities [1a, 2b, c]) but the propagating ions are excessively so [1b, 28] we think that in the earlier work the ions formed by the slow dissociation of the styrene-solvated ester were inactivated as quickly as they were formed; ions became evident as chain-carriers only when the depletion of monomer removed the stabilizing coordinated monomer molecules from the ester and this then ionized very rapidly, producing the final very fast "reaction-kick" observed by Gandini and Plesch [1].

The different behaviour reported here is ascribed to the much improved purity of monomer and especially solvent; consequently the ion-inactivating impurities become sufficiently depleted relatively early during the reaction so that the increasing number of surviving ions can manifest their presence kinetically.

Higashimura and co-workers have studied the polymerization of styrene in methylene dichloride initiated by acetyl perchlorate [25, 26] and by perchloric acid [26]; they found bimodal molecular weight distributions with both initiators. This important observation led Pepper [27] to carry out a systematic GPC study of the perchloric acid initiated polymerization at 0°. Over a wide range of experimental conditions the distribution was bimodal, showing two clearly defined peaks, one near molecular weight 2×10^3, insensitive to conditions of preparation, and the other at varying molecular weight in the region 2×10^3 to $1{\cdot}5 \times 10^4$. The high molecular weight peak is undoubtedly produced by an ionic propagating species, since its weight fraction is reduced in the presence of a perchlorate salt or water.

These results indicate [26, 27] simultaneous propagation by two independent species (one of which is free ions) which are not in rapid equilibrium and this is exactly what one would expect on the basis of a slow dissociation of the perchlorate ester to give free ions. The second species is certainly the ester, because ion-pairs or higher aggregates would be expected to be in rapid equilibrium with free-ions, and their effect would be to produce a broadened unimodal molecular weight distribution. Indeed, Pepper [27] concludes that the low molecular weight fraction (which contains the vast majority of chains) is formed by propagation from an ester–monomer complex, in agreement with the original postulate of Gandini and Plesch [1], and thus the reactions can be called "essentially pseudo-ionic" [27].

We conclude that the polymerization of styrene by perchloric acid in methylene dichloride at 0° involves at least two types of independent propagating species. Rate studies and conductivity measurements, in conjunction with an independent study of molecular weight distributions [26, 27], indicate that these species include the perchlorate ester and the free polystyryl carbenium ion and that the term "pseudocationic" is a very appropriate description of what is a distinctive form of organic reaction.

Acknowledgements—We thank the Science Research Council for an equipment grant.

REFERENCES

1. A. Gandini and P. H. Plesch, (a) Part I, *J. chem. Soc.* 4826 (1965); (b) Part II, *Europ. Polym. J.* **4**, 55 (1968); (c) *Proc. chem. Soc.* 240 (1964); (d) *J. Polym. Sci. Polym. Lett.* **B3**, 127 (1965).
2. P. J. Reilly and D. C. Pepper, (a) *Proc. chem. Soc.* 200 (1961); (b) *Proc. R. Soc.* A, **291**, 41 (1966); (c) *J. Polym. Sci.* **58**, 639 (1962).
3. L. E. Darcy, W. Millrine and D. C. Pepper, *Chem. Commun.* 1441 (1968).
4. B. McCarthy, W. P. Millrine and D. C. Pepper, *Chem. Commun.* 1442 (1968).
5. A. A. Zharov, V. V. Tatarintsev and N. S. Enikolopyan, *Polym. Sci. USSR* **7**, 2044 (1965), *Vysokomolek. Soedin.* 7(11), 1863 (1965).
6. S. Bywater and D. J. Worsfold, *Can. J. Chem.* **44**, 1671 (1966).
7. A. A. Zharov, A. A. Berlin and N. S. Enikolopyan, *J. Polym. Sci.* **C16**, 2313 (1967).
8. F. S. D'yachkovskii, G. A. Kazaryan and N. S. Enikolopyan, *Polym. Sci. USSR* **11**, 928 (1969).
9. T. Higashimura, N. Kanoh and S. Okamura, *J. Macromol. Sci.* **1**, 109 (1966).
10. S. D. Hamann, A. J. Murphy, D. H. Solomon and R. I. Willing, *J. Macromol. Sci. — Chem.* **A6**(4), 771 (1972).
11. A. R. Gantmakher and S. S. Medvedev, *Polym. Sci. USSR* **8**, 1052 (1966).
12. D. J. Dunn, M.Sc. Dissertation, University of Bradford (1970).
13. P. H. Plesch, *Pure appl. Chem.* **12**, 117 (1966).
14. A. Gandini and P. H. Plesch, *S.C.I. Monograph, No.* 20, *Chemistry of Polymerization Processes*. S.C.I., London (1966).
15. P. H. Plesch, *Fortschr. HochpolymForsch.* **8**, 137 (1971).
16. A. Gandini and P. H. Plesch, *J. chem. Soc.* 4765 (1965).
17. W. R. Longworth, P. H. Plesch and M. Rigbi, *J. chem. Soc.* 451 (1958).
18. R. H. Biddulph and P. H. Plesch, *Chemy Ind.* 1482 (1959).
19. P. H. Plesch and E. Mathias, *Chemy Ind.* 1043 (1971).
20. A. Gandini and P. H. Plesch, *J. chem. Soc.* 6019 (1965).
21. A. Gandini, P. Giusti, P. H. Plesch and P. H. Westermann, *Chemy Ind.* 1225 (1965).
22. M. A. Hamid, M. Nowakowska and P. H. Plesch, *Makromolek. chem.* **132**, 1 (1970).
23. V. Bertoli and P. H. Plesch, (a) *Chem. Commun.* 265 (1966); (b) *J. chem. Soc.* (B) 1500 (1968).
24. D. C. Pepper and P. J. Reilly, *Proc. R. Soc.* 460 (1961).
25. T. Masuda and T. Higashimura, *J. Polym. Sci. Polym. Lett.* **B9**, 783 (1971).
26. T. Higashimura and O. Kishiro, *J. Polym. Sci.* **12**, 967 (1974).
27. D. C. Pepper, *Makromolek. Chem.* **175**, 1077 (1974).
28. K. Hayashi, K. Hayashi and S. Okamura, *Polym. J.* 4(4), 426 (1973).