895. Cationic and Pseudocationic Polymerisation of Aromatic Olefins. Part I. Kinetics and Mechanism of the Pseudocationic Polymerisation of Styrene by Perchloric Acid

By A. Gandini and P. H. Plesch

The kinetics of the polymerising system styrene–perchloric acid–methylene dichloride have been studied in the temperature range +19° to −19°, by a calorimetric technique. The propagation is pseudocationic, its rate constant at 19° is $k_p = 10{\cdot}6$ l. mole^{-1} sec.$^{-1}$, and $E_p = 11{\cdot}6$ kcal. mole^{-1}. The elementary reactions are interpreted in detail by a mechanism involving an ester as chain carrier.

We have reported [1,2] that the polymerisation of styrene catalysed by perchloric acid in methylene dichloride and 1,2-dichloroethane proceeds *normally* in absence of carbonium ions (free or paired) and that the chain carriers are 1-phenylethyl perchlorate and the analogous oligomeric esters; this newly discovered kind of polymerisation we called "pseudocationic." [2] Subsequently, we investigated a series of polymerisation systems in order to ascertain whether they belong to the class of cationic polymerisations as previously suggested by other authors, *i.e.*, whether carbonium ions propagate the polymerisation, or whether they represent further examples of pseudocationic polymerisation. The present Paper is the first of a Series in which we will report on the behaviour of a wide range of polymerising systems in an attempt to map out the conditions under which cationic and pseudocationic reactions occur.

Pepper and Reilly [3] studied in detail the kinetics of the polymerisation of styrene by perchloric acid in 1,2-dichloroethane and in mixtures of 1,2-dichloroethane and carbon tetrachloride. Our investigation of the spectroscopic and conductimetric behaviour of this monomer–catalyst pair was carried out in methylene dichloride.[1] Since the evidence obtained from our work was in conflict with Pepper and Reilly's interpretation of the chemistry of the system, we decided to supplement our results by kinetic studies with methylene dichloride instead of 1,2-dichloroethane, so that mechanistic conclusions could be drawn from a self-consistent group of results, without any assumptions about the similarity of the solvents.

Experimental

Techniques.—Reactions were followed in an adiabatic calorimeter [4] according to the procedure described.[5] At the end of the polymerisations, the reaction mixture was quenched with ethanolic ammonium hydroxide and evaporated to constant weight in a vacuum oven at 40°.

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[1] A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, 1964, 240.

[2] A. Gandini and P. H. Plesch, *J. Polymer Sci., Part B, Polymer Letters*, 1965, **3**, 127.

[3] D. C. Pepper and P. J. Reilly, *J. Polymer. Sci.*, 1962, **58**, 638.

[4] R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1959, 1482.

[5] R. H. Biddulph, P. H. Plesch, and P. P. Rutherford, *J.*, 1965, 275.

Materials.—Methylene dichloride [6] and perchloric acid [7] were purified and dosed as described. Silver perchlorate (B.D.H.) was treated *in vacuo* for a few hours before use. 1-Phenylethyl bromide (Eastman–Kodak) was fractionally distilled under high vacuum and the middle fraction was collected into breakable phials; since this compound undergoes a slow decomposition, yielding hydrogen bromide and styrene, when kept in bulk, solutions of it in methylene dichloride were prepared from the original phials by the tipping technique.[7] Styrene was purified,[8] dried, and stored [9] as described. Shortly before use it was vacuum-distilled into breakable phials from a microburette.

Determination of Molecular Weight.—Owing to the very low degree of polymerisation of the polymers obtained, molecular weights ($M_{\rm n}$) were determined with a MECROLAB Vapour Pressure Osmometer, model 301 A with benzene as solvent. For values of $M_{\rm n}$ ranging between 400 and 2000 the reproducibility was ±30 units.

RESULTS

Catalysis by Perchloric Acid.—All reactions at 19, 0, and −19° were of the first order internally, up to at least 90% conversion, and all went to completion. Details are given in Tables 1—3. The first-order rate constant, k_1, is directly proportional to the acid concentration as shown by the constancy of the values of $k_{\rm p} = k_1/[{\rm HClO_4}]_0$. The Arrhenius plot for $k_{\rm p}$ gave $E_{\rm p} = 11{\cdot}6 \pm 0{\cdot}2$ kcal. mole^{-1} and $A_{\rm p} = 8{\cdot}9 \times 10^9$ l. mole^{-1} sec.$^{-1}$. Addition of further monomer at the end of the first polymerisation reaction resulted in a second polymerisation which had the same absolute rate constant (Exp. SGP11, Table 2).

TABLE 1

Reaction data for experiments at 19° ± 0·5°

Expt.	$[{\rm HClO_4}]_0$ (10^4M)	k_1 (10^3 sec.$^{-1}$)	$M_{\rm n}$	$k_{\rm p}$ (l. mole^{-1} sec.$^{-1}$)
SGP3	4·30	4·53	540	10·53
SGP4	6·72	7·17	550	10·67
SGP6 *	13·2	14·0	580	10·61
SGP8	18·0	19·3	690	10·72
SGP7 †	18·0	10·0	590	—
			Av. 590	10·63

[Styrene] = 0·334M.

* Wet solvent (vessel pumped out for only a few minutes). † The acid phial contained approximately 50% of $\rm HClO_4,H_2O$ (white crystals) and 50% $\rm HClO_4$; the actual $[{\rm HClO_4}]_0$ is therefore *ca.* 9×10^{-4}M.

TABLE 2

Reaction data for experiments at 0° ± 0·5°

Expt.	[Styrene] (M)	$[{\rm HClO_4}]_0$ (10^4M)	k_2 (10^3 sec.$^{-1}$)	$M_{\rm n}$	$k_{\rm p}$ (l. mole^{-1} sec.$^{-1}$)
SGP9	0·334	17·2	4·60	790	2·67
SGP10	,,	31·0	8·25	830	2·66
SGP11	0·134	55·5	14·7		2·65
SGP11 *	0·132	54·9	14·2	710	2·59

* Second addition of styrene.

TABLE 3

Reaction data for experiments at −19° ± 0·5°

Expt.	[Styrene] (M)	$[{\rm HClO_4}]_0$ (10^4 M)	k_1 (10^3 sec.$^{-1}$)	$M_{\rm n}$	$k_{\rm p}$ (l. mole^{-1} sec.$^{-1}$)
SGP19	0·226	23·0	1·38	1340	0·600
SGP14	0·264	73·0	4·4	1140	0·603
SGP17	0·236	91·5	5·5	1000	0·601

Water present in the monomer solution before the addition of perchloric acid did not affect the rate of polymerisation (Exp. SGP6, Table 1), but if water was added to the catalyst solution

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[6] W. R. Longworth, P. H. Plesch, and M. Rigbi, *J.*, 1958, 451.

[7] A. Gandini and P. H. Plesch, *J.*, 1965, in the press.

[8] R. O. Colclough and F. S. Dainton, *Trans. Faraday Soc.*, 1958, **54**, 886.

[9] A. Gandini and P. H. Plesch, *J.*, 1965, 4865.

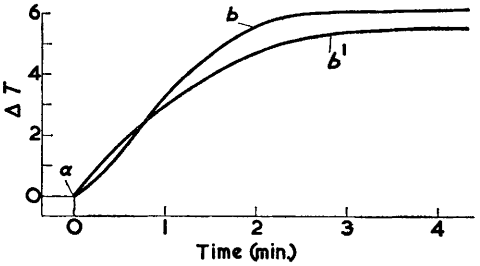
before the polymerisation, with consequent formations of $HClO_4,H_2O$, which is insoluble in methylene dichloride, only the anhydrous acid was found to be an active catalyst (Exp. SGP7, Table 1).

During virtually the whole of the polymerisation the solutions remained colourless. A yellow colour always developed towards the end of the polymerisation; its origin and phenomenology will be discussed in the next Paper of this Series. No colour formation was observed if water was present at a concentration higher than that of the perchloric acid.

DISCUSSION

Mechanism.—We have shown [1,2] that, in the polymerisation of styrene by perchloric acid under the conditions reported here, the initiation reaction does *not* produce carbonium ions and that the monomer is polymerised by non-ionic chain carriers. Since the most likely non-ionic reaction product formed from perchloric acid and styrene is the ester 1-phenylethyl perchlorate we attempted its preparation in order to try it as catalyst for the polymerisation of styrene. However, we found this ester to be unstable in methylene dichloride solution. It forms styrene oligomers, polystyryl ions, and perchloric acid, and the preparative technique and the mechanism of the reactions involved will be discussed in a Paper dealing with the spectroscopic behaviour of polymerising and polymerised systems.

Since we could not prepare a stable solution of the ester, we attempted its preparation in the styrene solution to be polymerised. Silver perchlorate was dissolved in this and the reaction was started by the crushing of a phial containing 1-phenylethyl bromide (under our conditions styrene was not polymerised by the silver perchlorate alone). The solutions became cloudy because of the formation of colloidal silver bromide, but no colour formation could be observed until the end of the polymerisation; then the solutions became yellow, very like the reaction mixtures in which perchloric acid had been used as catalyst. The ester was found to be as effective a catalyst as anhydrous perchloric acid. Equal concentrations of the ester and the acid produced very similar polymerisations as shown in the Figure; the accelerating parts of the curves obtained with the ester as catalyst are readily explained by the fact that the reaction between silver perchlorate and 1-phenylethyl bromide is not instantaneous and therefore a steady increase in catalyst concentration characterises the first part of the polymerisation.



A comparison between a perchloric acid-catalysed polymerisation (SGP11, Table 2) and one catalysed by an equivalent amount of 1-phenylethyl perchlorate (SGP21). For SGP21: $[\text{Styrene}] = 0{\cdot}158\text{M}$, $[CH_3CHPhBr] = 5{\cdot}55 \times 10^{-3}\text{M}$, $[AgClO_4] \approx 1 \times 10^{-2}\text{M}$, $T = 0°$

a indicates the crushing of the acid phial (SGP11) and of the 1-phenylethyl bromide phial (SGP21); *b* and *b'* indicate the time at which the colour appeared in the reaction mixtures.

The DP's of the polymers obtained from these experiments were the same as those of the polymers from the corresponding acid-catalysed reactions.

The above evidence strongly suggests that the pseudocationic reactions involve the ester 1-phenylethyl perchlorate and its oligomeric homologues as catalyst. It also shows that the ester is only stable when an excess of styrene is present in the reaction mixture.

Spectroscopic and conductimetric studies on the present system confirmed this interpretation and indicated that at least four molecules of styrene are required for the stabilisation of one molecule of ester. Details of the experiments carried out to investigate the stoicheiometry of ester stabilisation will be given in a later Paper. The mode of this stabilisation is not clear at present and we do not known the location of the four styrene molecules with respect to the ester.

For the system styrene–perchloric acid–methylene dichloride we can now write the following reactions on the basis of what has just been discussed and of our findings on the state of perchloric acid in methylene dichloride solutions: [9]

(i) Initiation

$$5C_8H_8 + (HClO_4)_4/4 \xrightarrow{k_i} (CH_3{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8$$

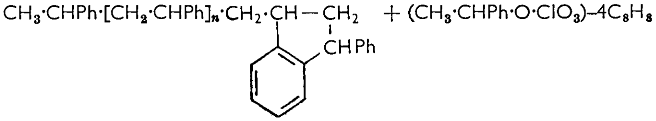
(ii) Propagation

$$(CH_3{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8 + C_8H_8 \xrightarrow{k_p} (CH_3{\cdot}CHPh{\cdot}CH_2{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8$$

The transfer reactions, undoubtedly important because of the low DP's, were not studied in detail, but both double bonds and indanyl end-groups were detected from the ultraviolet and infrared spectra of the polymers. Most probably the two types of transfer studied by Pepper and Reilly [10] are responsible for these groups: one dependent on monomer concentration, giving indanyl end-groups, and one which they termed spontaneous transfer, giving terminal double bonds. Since these authors' method could not distinguish between a truly unimolecular chain-breaking reaction and one which, though independent of monomer concentration, involved an unknown transfer agent, we prefer to call this second reaction non-committally "monomer-independent." We formulate these chain-breaking reactions as follows:

(iii) Monomer transfer

$$(CH_3{\cdot}CHPh{\cdot}[CH_2{\cdot}CHPh{\cdot}]_n{\cdot}CH_2{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8 + C_8H_8 \xrightarrow[C_8H_8]{k_{tm}}$$



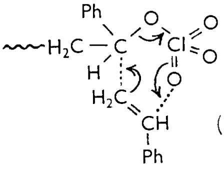
(iv) Monomer-independent transfer

$$(CH_3{\cdot}CHPh{\cdot}[CH_2CHPh]_n{\cdot}CH_2{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8 \xrightarrow[C_8H_8]{k_t}$$

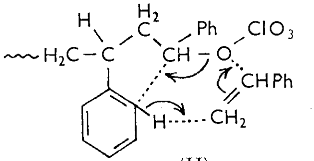
$$CH_3{\cdot}CHPh{\cdot}[CH_2{\cdot}CHPh]_n{\cdot}CH{:}CHPh + (CH_3{\cdot}CHPh{\cdot}O{\cdot}ClO_3){-}4C_8H_8$$

This mechanism applies equally well, as we have shown,[2] to the system styrene–perchloric acid–1,2-dichloroethane, studied by Pepper and Reilly [3] and therefore replaces their interpretation based on carbonium ions.

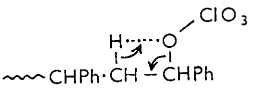
We propose to explain the mechanism of the propagation and transfer reactions in terms of even-membered cyclic transition states such as structure (I) for the propagation step (ii), structure (II) for reaction (iii), and structure (III) for reaction (iv).



(I)



(II)



(III)

An analogous structural interpretation was recently advocated by us to explain the mode of catalytic dehydration of aromatic carbinols by acids.[7]

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[10] D. C. Pepper and P. J. Reilly, *Proc. Chem. Soc.*, 1961, 460.

The Effect of Added Water.—The observation that traces of water do not influence the rate of polymerisation if the water is present in the reaction medium before the acid is added (Exp. SGP6, Table 2), indicated that: (*a*) The reaction leading to the formation of an ester is much faster than the addition of water to $HClO_4$; (*b*) the ester is fairly insensitive to quantities of water up to about 10 times its concentration,[3] *i.e.*, hydrolysis under these conditions is negligible. On the other hand, if $H_3O^+ClO_4^-$ is *already* present when the polymerisation is started, this is found to have no catalytic activity, most probably because it is insoluble in methylene dichloride (Exp. SGP7, Table 2). The destructive effect of water upon the carbonium ions formed at the end of the polymerisations will be discussed in a future Paper.

Kinetics.—The facts that (*a*) the polymerisation reactions are of the first order internally, (*b*) their first-order rate constant is directly proportional to the initial acid concentration, and (*c*) a second addition of styrene results in a second polymerisation with the same absolute rate constant of propagation, clearly suggests that we are dealing with stationary-state conditions. These facts, however, do not indicate whether this is of the First Kind (rate of initiation equal to rate of termination), or of the Second Kind (rapid and complete initiation, no termination). We have collected during the present work evidence which points unambiguously toward a stationary state of the Second Kind. Complete initiation is suggested by the twin experiments typified in the Figure; equal starting concentrations of ester and acid produce " carbon copy " polymerisations, *i.e.*, all the acid added reacts with styrene and an equivalent amount of 1-phenylethyl perchlorate is formed. After one experiment, the polymerised mixture was shaken with aqueous ammonia, and the perchlorate-ion concentration in the water layer was determined gravimetrically; 85% of the initial acid could be accounted for. Tests for chloride and chlorate ions were negative. Because of the small quantities involved (1 mmole of acid was used) and the absence of the possible degradation products, we concluded that virtually all the perchlorate ion was still present at the end of the polymerisation and that this rules out termination reactions involving destruction of the perchlorate moiety.

The kinetic equations for reactions (i)—(iv) can therefore be written as follows:

$$R_i = k_i\,[HClO_4]_0^{1/4}\,[M]^5,\ \text{fast and complete} \qquad (1)$$

$$R_p = k_p\,[HClO_4]_0\,[M] = k_1\,[M] \qquad (2)$$

$$R_t = k_t\,[HClO_4]_0 \qquad (3)$$

$$R_{tm} = k_{tm}\,[HClO_4]_0\,[M] \qquad (4)$$

where [M] indicates the styrene concentration and $[HClO_4]_0$ is both the initial acid and the stationary ester concentration.

Our kinetic results agree both qualitatively and quantitatively with Pepper and Reilly's,[3] if the comparison is made between solutions having the same dielectric constant; thus for runs at 0°, the value of k_p predicted by Pepper and Reilly for our conditions ($1/\varepsilon = 0{\cdot}117$) is 2·6 l. mole^{-1} sec.$^{-1}$ which agrees with our results in Table 2.

Since, however, we have disproved the chemical interpretation in terms of ions proposed by these authors we can conclude that the values for the rate constants and for the corresponding activation energies do *not* refer to cationic but to pseudocationic polymerisations. This distinction is most fundamental not only because of its chemical significance, but also because the two chain carriers, *i.e.*, the carbonium ions and the ester molecules, exhibit a vast difference in activity, the former giving reaction rate constants several powers of ten higher than the latter.[2] The true cationic polymerisation of styrene will receive our attention in a later Paper of this Series.

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