Free Ions and Other Propagating Species in the Polymerisation of Styrene by Perchloric Acid

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The perchlorate salts $Bu^n{}_4NClO_4$ and $LiClO_4$ have been found to reduce the rates and yields in this polymerisation in methylene chloride (for definitions see preceding Communication).[1] The analogous effect in the anionic polymerisation of styrene is already known[2] and provides detailed evidence for the participation of free ions in the propagation processes. Here in the cationic polymerisation the effect is of particular importance since all previous attempts to identify carbonium ions directly, by conductivity or spectra, have proved unsuccessful.

The salt effects on the two stages of the polymerisation are quantitatively different, though both follow approximately the reciprocal square-root dependence expected for suppression of a very weak polymer perchlorate dissociation by a stronger but still weak electrolyte salt. The difference is that the Stage I conversions (X_{I}) appear to be completely suppressible by "infinite" salt concentration, *i.e.* a plot of X_{I} against $[\text{Salt}]^{-1/2}$ passes through the origin, within experimental error. On the other hand the rate constants, k, of the overall rate at 0°, or of the Stage II rates at lower temperatures, are reduced only to a limiting value

$$k = k_{(\text{lim})} + \text{constant}[\text{salt}]^{-\frac{1}{2}}$$

where $k_{(\text{lim})}$ is appreciable at all temperatures studied (down to $-77°$) amounting to about 20% of the value of k in salt-free solutions.

The simple conclusion would seem to be that Stage I of the polymerisation is carried virtually entirely by free carbonium ions, and the subsequent stage by both free ions and some "non-suppressible" propagating species, which for purposes of discussion will be regarded as an ion-pair. The following kinetic Scheme embodies this conclusion

$$\begin{tikzcd}
\text{HA} \arrow[r, "\text{M}", "1"'] & \text{HM}^+ \arrow[d, "2^{\text{a}}", "x\text{M}"'] & + \ \text{A}^- \arrow[r, shift left] & \text{HM}^+.\text{A}^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "2^{\text{b}}", "x\text{M}"'] & \text{HMA} \arrow[l, shift left] \\
& \text{P}_x^+ & + \ \text{A}^- \arrow[r, shift left, "3^{\text{a}}"] & \text{P}_x^+.\text{A}^- \arrow[l, shift left] \arrow[r, shift left, "3^{\text{b}}"] & \text{P}_x\text{A} \arrow[l, shift left]
\end{tikzcd}$$

(HA = HClO_4; M = Styrene; PA = Ester; transfer processes are omitted and the primary initiation process, 1, is left unspecified in detail.)

and those of the preceding Communication, and shows the relationships between the stages of the polymerisation and the mechanism envisaged.

Stage I is a once-for-all sequence of processes 1, 2^{a}, 3^{a}, 3^{b}. Stage II is the indefinite repetition of subsequent growth increments initiated by the re-ionization and dissociation of PA, propagated by both ionic species and terminated by ion-recombination.

The covalent ester molecules are written as "dead" chiefly for conceptual clarity, so that Stage II can be expressed as a stationary-state polymerisation with clear cut initiation and termination processes. It will be clear however ihat for certain relative values of the rate constants such a situation would be kinetically indistinguishable from one where the ester molecules themselves were capable of propagating (pseudo-cationic hypothesis of Plesch[3]).

Certain features of the polymerisation kinetics remain obscure, particularly that both Stage II rate constants and Stage I conversions have not been found to show any contribution from a 1/2 order dependence on initiator concentration that is implied by mutual termination of free ionic species. In consequence it has not yet proved possible to use the salt effect to derive absolute propagation constants for free ions and ion pairs, as in the analogous anionic case.

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[1] L. E. Darcy, W. P. Millrine, and D. C. Pepper, preceding Communication.

[2] D. H. Bhattacharyya, C. L. Lee, J. Smid, and M. Swarc, *J. Phys. Chem.*, 1965, **69**, 612.

[3] P. H. Plesch, *Pure Appl. Chem.*, 1966, **12**, 117.