Low Temperature Stopped Flow Studies of the Stage I Polymerisation of Styrene and Derivatives by $HClO_4$ in CH_2Cl_2

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Summary A transient intermediate (λ_{max} 340 nm), detected during the fast polymerizaton of styrene by $HClO_4$ in CH_2Cl_2 at −80°, is tentatively interpreted as the polystyryl carbenium ion, and apparent rate constants derived.

STOPPED-FLOW studies of the rapid non-stationary phase (Stage I) of styrene polymerisations by $HClO_4$ at −80° indicate its overall kinetic features and reveal a transient intermediate, absorbing at 340 nm. Assuming this to be the reactive chain carrier, polystyryl carbenium ion, leads to estimates of the propagation rate constant, 2200 ± 1400 l mol^{-1} s^{-1} at −80° (and very low styrene concentrations, 0·02—0·1 M).

The stopped-flow apparatus was conventional in principle, but designed to operate at −80° with provision for protection of the moisture sensitive reactants (by N_2 blankets). All experiments were performed in the solvent CH_2Cl_2, with concentrations of anhydrous $HClO_4$, C_0, in the range 2—10 × 10^{-3}M, and of styrene, M_0, 0·02—0·2M (limited by the high extinction coefficient). A few semiquantitative observations were made with four substituted styrene monomers.

Oscilloscope traces of the styrene transmittance (at λ 290 nm) revealed the form and duration of the non-stationary, terminated polymerisation, showing it to be faster, and shorter, the higher the monomer concentration (<50 s at $M_0 = 0{\cdot}02$; < 5 s at $M_0 = 0{\cdot}2$). The yields decreased with M_0 and increased sharply with C_0, but were approximately proportional to C_0^2. The form and time-scale appeared independent of C_0. Bu_4NClO_4 and Pr_4NClO_4 reduced the yields without affecting the time-scale.

The polymerising solutions showed transient absorptions at 340 nm (but nowhere else in the region λ 300—440 nm). Absorbances (OD_{340}) rose to a peak at 0·2—2 s (according to M_0) and declined 'in phase' with the polymerisation, *i.e.* correlated well with the reduced rates $1/([M]d[M]/dt)$ at corresponding times.

Assuming an extinction coefficient of 10^4 (as for polystyryl anions) the peak OD_{340} values correspond to concentrations of intermediates, $[P^+]$ *ca.* 1—10 × 10^{-5}M (according to conditions), *i.e. ca.* 1% of C_0. This finding excludes an earlier hypothesis[1] that initiation could be taken as effectively instantaneous, leaving the kinetics of Stage I to be determined only by those of propagation and termination. It is now clear that initiation is not fast enough to permit such a simple non-stationary situation, nor slow enough to allow a classical stationary state. The polymerisation yields cannot therefore be expected to be simple algebraic functions of the reagent concentrations.

The instantaneous rate should, however, be capable of analysis to give the propagation rate constant, k_p, in $-d[M]/dt = k_p[M][P^+]$ (where rate and $[M]$ are derived from the styrene traces, and $[P^+] = OD_{340}/800$; optical path, 0·8 mm and $\epsilon = 10^4$). From 7 sets of results, in which rate varied 10-fold, $[M]$ 4-fold, and $[P^+]$ 7-fold the derived k_p values scattered between 1300 and 3600 l mol^{-1} s^{-1} with no obvious trends. Less precise results at the highest $[M]_0$ 0·2M indicated k_p 5000 — 15,000 l mol^{-1} s^{-1}.

These values lie far below those deduced for free cationic propagation constants in bulk styrene at room temperature (*ca.* 10^6 l mol^{-1} s^{-1}, from radiation-induced polymerisation[2]). Subsequent conductivity measurements have, however, indicated that the optically absorbing species are predominantly free ions. Some proportion of ion pairs is not excluded, but the resolution of the apparent k_p into components from free and paired ions is not yet possible.

With various substituted styrenes polymerised by $HClO_4$, transient absorptions could also be seen at −80°. That with *p*-chlorostyrene (at 325 nm) appeared to be 'in phase' with the polymerisation, but with the other monomers α-methylstyrene (350 nm), *p*-methoxystyrene (340 nm) and 2,4,6-trimethylstyrene (325 nm) appeared to be product species of variable life-time. Firm identification of these species will not be easy since they are likely to be highly unstable (*e.g.* solutions from *p*-methoxystyrene polymerisations on warming develop a succession of visible colours, green → bronze → purple, reminiscent of the changes in the u.v. spectra of a $HClO_4$ polymerised styrene solution seen by Bertoli and Plesch.[3])

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