Molecular Weights in the Cationic Polymerisation of Styrene by Perchloric Acid

By L. E. DARCY, W. P. MILLRINE, and D. C. PEPPER*
(*Physical Chemistry Laboratory, Trinity College, Dublin*)

A DETAILED study of the number average molecular weights obtained in this polymerisation (in methylene chloride), together with the kinetics already reported in outline,[1] makes necessary a new interpretation of the general kinetic character of the polymerisation, showing it to have features in common both with the "flash" polymerisation of isobutene and the anionic "living polymerisations".

The characteristic features shown in different temperature ranges are summarised below (using the symbols M for monomer and C for initiator concentrations, X_t for the integrated first order conversion function $\equiv \ln M_0/M_t$; $\bar{M}_n$, and $\bar{M}_v$ for number and viscosity average molecular weights, $\bar{P}_n$ for degree of polymerisation $\equiv \bar{M}_n/104$, and n for the number of polymer chains formed per initiator molecule $\equiv \Delta M/\bar{P}_n.C_0$).

A. Ordinary temperatures 25° to −25°:

(i) $-\mathrm{d}M/\mathrm{d}t = kC_0M$, *i.e.* $\mathrm{d}X/\mathrm{d}t = kC_0$,

(ii) $\bar{P}_n$ falls with conversion,

(iii) $\bar{P}_n$ almost independent of C_0 (weak inverse function),

(iv) n large and increases with conversion,

(v) Distribution broad; $\bar{M}_v/\bar{M}_n \sim 7$ at 0°.

B. Low T, extreme −97°:

(i) $M_0 \rightarrow M_\mathrm{I}$ (finite) in few seconds, no further reaction,

(ii) $X_\mathrm{I} = k'C_0$; independent of M_0,

(iii) $\bar{P}_n = \Delta M/C_0$, *i.e.* $n = 1$ for all conditions,

(iv) $\bar{P}_n = M_0[1 - \exp(-k'C_0)]/C_0$, *i.e.* $\rightarrow k'M_0$ as $C_0 \rightarrow 0$,

(v) Distribution very broad; $\bar{M}_v/\bar{M}_n \sim 30$.

C. Intermediate T, −80° to −30°:

"Two stage" reaction, *i.e.*

(i) an initial "burst", Stage I, with $X_\mathrm{I} = k'C_0$ as in B,

(ii) a steady reaction, Stage II, $dX_{II}/dt = kC_0$ as in A. As T rises k' falls and k rises, (with E_{act} as in A),

(iii) $\bar{P}_n$ (I) $= \Delta M/nC_0$, *e.g.* n(I) = 1·2 at −60°,

(iv) $\bar{P}_n$ (of total product, *i.e.* I and II) increases with conversion,

(v) n(II) increases with conversion, linearly with X_{II}/C_0,

(vi) Distribution in I very broad; narrows as Stage II proceeds.

A further observation that links regions B and C is that a completed polymerisation at −97° (*i.e.* a system containing "dead" polymer and unreacted monomer) will, if raised to a higher temperature, resume polymerisation at a rate characteristic of the Stage II reaction at this temperature.

On the evidence of the "ordinary temperature" behaviour in ethylene dichloride (which is closely similar to A) the kinetic mechanism originally postulated[2] was one involving fast initiation and chain transfer but no termination. This must now be modified to include a true termination process [producing effects B(i), C(i)] which at temperatures $> -80°$ is reversible [effects C(ii), (iv), (vi)]. All the initiator must be involved in the polymerisation [effect B(iii)].

The overall reaction at −97° is then simply a "flash" polymerisation giving one chain per initiator and a correspondingly limited yield. At $T > -80°$ where the termination is reversible [C(ii)], the further reaction, Stage II, grows on to the chains already formed [C(iv), (vi)] indefinitely up to the potential limit M_0/nC_0 (where n represents the total effect of transfer in producing extra chains). This steady polymerisation is therefore similar to a "living polymerisation" except that the life of chains is intermittent not continuous. At $T > -30°$ transfer (k_{tr}) becomes dominant over termination (k_t) and the molecular weights are determined by the ratio of transfer to propagation (k_p).

On the above interpretation the molecular weight obtained under any conditions should be described by the general equation

$$\bar{P}_n = \frac{\Delta M}{C_0(1 + k_{tr}/k_t) + k_{tr}/k_p . X_{II}}$$

where the transfer is a monomer-independent process, and the two terms in the denominator then represent the number of chains started in Stages I and II respectively. Such an equation describes all $\bar{M}_n$ found, the first term dominating at very low temperatures, the second at the top of the temperature range, and both contributing in certain ranges of T and C_0. Above −20°, a monomer-dependent transfer process becomes appreciable, adding a third (constant) term to the denominator in the equation.

Two specific points have particular interest. Effect B(iv) indicates a "natural limit" of $k'M_0$ to the value of $\bar{P}_n$ in Stage I. This implies a "ceiling $\bar{M}''_n$ at −97° of 137 M_0 or *ca.* 10,000 for convenient monomer concentrations. This is very low, but is of course number average, and some chains are very much longer ($\bar{M}_v/\bar{M}_n$ *ca.* 30). The very broad distributions are also of greater interest and are believed to arise from a bimolecularity in the termination reaction, as indicated in the following Communication.

(*Received, September 10th,* 1968; *Com.* 1232.)

---

[1] L. E. Darcy and D. C. Pepper, Abstracts International Symposium on Macromolecular Chemistry, Tokyo, 1966, vol. I, p. 42.

[2] D. C. Pepper and P. J. Reilly, *Proc. Roy. Soc.*, 1966, *A*, **291**, 41.