

Additions and Corrections

A New Insight into the Polymodal Molecular Mass Distributions Arising in the Wurtz Synthesis of Polysilanes

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The penultimate paragraph in our communication contained an error of reasoning. Although the overall conclusions are in no way affected by this error, we should nonetheless like to correct it. The end of the paragraph should now read as follows:

From a simplified kinetic analysis applied to those reactions of Schemes 2 and 3 that are operative at the late stages of the overall reaction, eqn. (7) can be derived. The rate constants are numbered in accordance with the reactions of Schemes 2 and 3, and M, P* and P respectively represent monomer, polymer with active chain ends (*i.e.* at the sodium surface) and polymer with chlorine chain ends (*i.e.* in solution). R_{cyc} is the rate of formation of cyclic oligomer by the back-biting reaction and R_{CE} is the rate of chain extension.

$$\frac{R_{\text{cyc}}}{R_{\text{CE}}} = \frac{k_5[\text{P}^*]}{k_2[\text{P}^*][\text{M}] + k_6[\text{P}^*][\text{P}]} = \frac{k_5}{k_2[\text{M}] + k_6[\text{P}]} \quad (7)$$

Since the concentrations of both monomer and polymer are continually decreasing, eqn. (2) shows that when $k_2[\text{M}] + k_6[\text{P}] < k_5$, a critical point is reached at which this competitive first-order reaction of active chain ends (back-biting) dominates over the combined effects of the second-order propagation and polymer-polymer reactions. It is thus essential that reaction conditions are not prolonged in the vain hope that chain extension will result. If alkali metal is used in considerable excess over monomer, such a condition will be reached at much lower degrees of polymerization.