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Polymerization of Styrene

Answer to Comments of M. Chmelir and G. V. Schulz

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The attentive reader of both my two papers and M. Chmelir's and G.V. Schulz's comments will find that there are not so many discrepancies between my interpretation and the views of Chmelir and Schulz. My experimental results can be formally described as being first-order with respect to the initial monomer concentration $[M]_0$ at low monomer concentrations but I pointed out in the discussion that the drift of the apparent rate constant k' with $[M]_0$ shows that there is no simple first order mechanism(1). The main point of disagreement is that, contrary to M. Chmelir and G.V. Schulz, I cannot see any proof of the complex hypothesis on the basis of my measurements. In my opinion Higashimura et al (2) are putting an interesting interpretation on the drift of the first order constant with $[M]_0$ which should not be dimissed before it has been thoroughly investigated. On the other hand, there is also a drift in the constants k'_k found by complex hypothesis, and the specific conductivity increases from the beginning to the end of the polymerization [(1), Fig.6], which is difficult to explain on the assumption of a monomer catalyst complex. In the following I am forced to draw a comparison between the first order plot (Fig.1) and the complex hypothesis plot (Fig.2) at $[M]_0 > 0.2$ mol·l^{-1} which I would rather have avoided. As we see from Fig.1, at higher monomer concentrations more pronounced deviations from the first order plot are found at ever lower conversions(1).

In Fig.2 we give only the experimental points. We think that from this plot one may obtain any desired complex hypothesis constant and it is not difficult to arrive at the same value. What makes this particular easy are the intercepts of the "straight lines" with the f(M)-axis, which are assumed to correspond to the conversion of the fast non-equilibrium stage of polymerization. The complex hypothesis is doubtless a valuable attempt to explain the complex phenomena in the cationic polymerization of styrene with protonic

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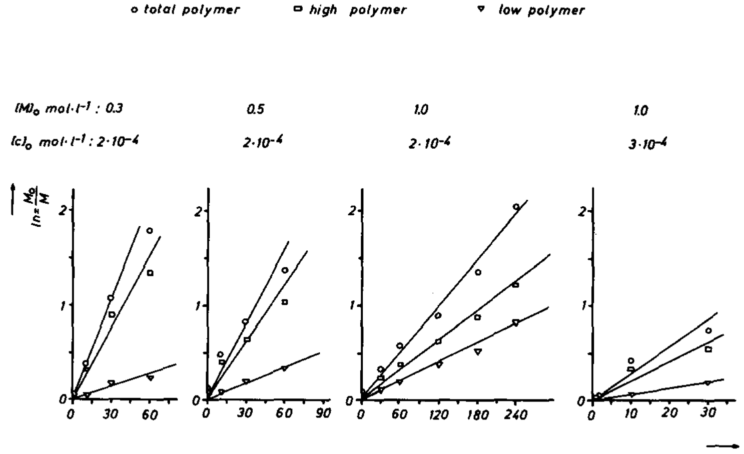

Fig.1: First-order plot for $[M]_0 > 0.2$ mol·l^{-1} at -15°C.

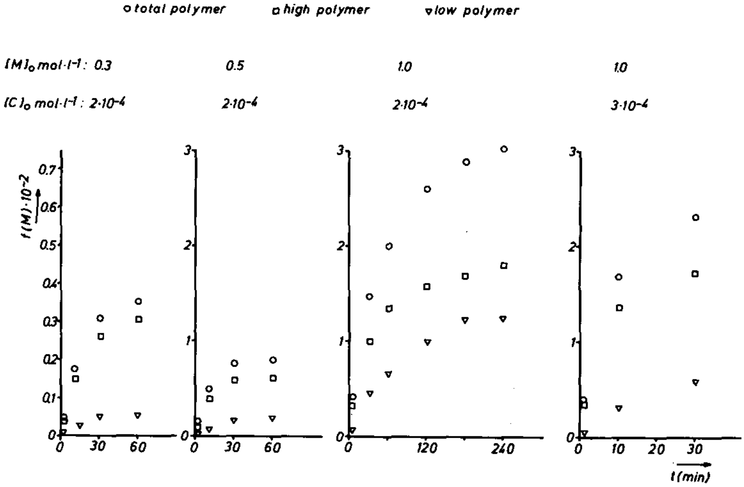

Fig.2: Complex hypothesis plot for $[M]_0 > 0.2$ mol·l^{-1} at -15°C.

acids and may be the right starting point. But unlike Chmelir we do not dare to take our experimental measurements as a proof of this complex hypothesis.

Chmelir and Schulz are right in pointing out that the activation energy found by us (3) should be a complex quantity which includes activation energies of all propagating species. We should have emphasized this fact.

(1) N. Cardona-Sütterlin: Polymer Bull. 1, 149 (1978)
(2) M. Sawamoto, T. Masuda and T. Higashimura: Makromol.Chem. 177, 2995 (1976).
(3) N. Cardona-Sütterlin: Polymer Bull. 1, 307 (1979)

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