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A Modified Concept for the Overall Rate in Radical Solution Polymerization Based on the Theory of Donor-Acceptor Complexes

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Summary

Experimentally observed deviations from the classical rate laws of radical polymerization in solution can be treated as solvent interactions concerning the growth step. The theory of hot radicals and the theory of donor-acceptor complexes are based on these considerations. It had been shown that the experimental data rather fit the former theory. However by a modification of the latter theory with respect to termination reactions of the different radicals a remarkable equivalence between these different views is exposed.

Introduction

In radical solution polymerization the overall rate observed often deviates from the classical rate law. Several models to explain these deviations (HENRICI-OLIVE and OLIVE,MAHABADI and O'DRISCOLL,TÜDÖS) were presented in the literature.Among the models which relate these deviations to an apparent growth constant dependent on the medium of reaction the theory of the hot radicals (TÜDÖS) rather fits experimental data than the theory of donor-acceptor complexes (HENRICI-OLIVE and OLIVE).However,if the latter theory is somehow reexamined,taking the different radical species into consideration,surprisingly some equivalence between the theory of hot radicals and the theory of donor-acceptor complexes is revealed.

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Theory

Here the concept of complexes is used in a rather kinetic way than from the aspect of equilibrium. Slightly modified kinetic schemes can be set up also to result in the principal equation summarized below. Subsequently one possible scheme is examined. M and S refer to monomer and solvent respectively. The dot behind a letter refers to a radical, a letter behind a radical indicates the respective substance attached to the radical, forming a contact pair, likewise identified as a donor-acceptor complex.

$$\mathrm{M.M} \longrightarrow \mathrm{M.} \qquad k_1 \qquad (1)$$

$$\mathrm{M.} + \mathrm{M} \longrightarrow \mathrm{M.M} \qquad k_2 \qquad (2)$$

$$\mathrm{M.} + \mathrm{S} \longrightarrow \mathrm{M.S} \qquad k_3 \qquad (3)$$

$$\mathrm{M.S} + \mathrm{M} \longrightarrow \mathrm{M.M} \qquad k_4 \qquad (4)$$

Following donor-acceptor theory only a radical-monomer pair can undergo a growth step (1). After the growth step being performed, again the radical must form a contact pair with a monomer (2) to introduce the next growth step. Erroneously a contact pair with a solvent molecule (3) may be formed. However there may occur an exchange between monomer and solvent in a contact pair (4). Assuming that a radical attached already to a monomer will react rather with this monomer than undergo a termination step, only termination reactions between free radicals and radicals attached to a solvent molecule must be taken under consideration.

$$\mathrm{M}\cdot + \mathrm{M}\cdot \longrightarrow \qquad k_{tMM} \qquad (5)$$

$$\mathrm{M}\cdot + \mathrm{M.S} \longrightarrow \qquad k_{tMS} \qquad (6)$$

$$\mathrm{M.S} + \mathrm{M.S} \longrightarrow \qquad k_{tSS} \qquad (7)$$

Setting up the stationarity equations for the different radicals and assuming that the cross termination constant is twice the geometric mean of the termination constants between like radicals, the following equation for the overall rate of polymerization is obtained:

$$- d[M]/dt = R_i^{1/2}[M]K_b(1 + A[S]/[M])(1 + B[S]/[M])^{-1}$$

R_i rate of initiation ; $K_b = k_2/(2k_{tMM})^{1/2}$;

$A = k_3/k_2$; $B = (k_3/k_4)\cdot(k_{tSS}/k_{tMM})^{1/2}$

The geometric mean assumption emerges in copolymerization kinetics and is as more real as the different species of radicals are resembling one another (SEBASTIAN and BIESENBERGER). The equation given above can be rearranged introducing the growth constant to square root of termination constant ratio for infinite dilution $K_\infty = k_4/(2k_{tSS})^{1/2}$. In this form the equation resembles closely to the expression obtained from hot radical theory.

$$- d[M]/dt = R_i^{1/2}[M]K_\infty \left\{ 1 + \frac{1}{\frac{A}{B-A} + \frac{AB}{B-A}\cdot\frac{[S]}{[M]}} \right\}$$

For comparison the expression obtained from hot radical theory is given below.

$$- d[M]/dt = R_i^{1/2}\ [M]K_\infty' \left\{ 1 + \frac{1}{\gamma + \gamma' \frac{[S]}{[M]}} \right\}$$

However there is one striking difference in the meaning of the particular constants.The hot radical theory demands a K_∞' independent on the particular solvent for a given monomer.In the present treatment,however, K_∞ <u>may</u> be equal for different solvents for a given monomer.

At the present no particular experiments are known to decide between the hot radical theory and the concept set up here.Also if correct values of the rate of initiation are known,other difficulties may arise by an eventual dependence of the termination constant on coil parameters,e.g. chain length, (MAHABADI and O'DRISCOLL),recently also confirmed by computer experiments (OLAJ et al.).Further complications for experimental investigation,under certain conditions,may arise due to several side reactions proposed in a variety of researches,e.g. primary chain termination (OLAJ),(retarded) chain tranfer (SMITH) and other specific features (POPOV and GLADISHEV) not included in the scheme.

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