

Carbocationic polymerization: Mechanisms and kinetics of propagation reactions

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Abstract

Propagation rate constants k_p in carbocationic polymerizations can be obtained through two general methods. The first one, used for decades, calculated k_p from the polymerization rates and from the ionic species concentrations (ISC) measured or estimated in various ways. The second one, used during the last 10 years, is based on the diffusion-clock (DC) assumption, in which competitive reactions between propagation with the monomer and termination with another nucleophile N permit to calculate k_p if termination is a diffusion-controlled reaction (with e.g. $k_N = k_{diff} = 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ in CH_2Cl_2 solution).

A problem arises since the k_p obtained by this last method with, e.g. styrene and isobutylene are 10^4 to 10^5 times larger than those obtained earlier in solution by the ISC method, and the aim of this article is to try to explain this discrepancy.

The different methods of measurement of the second-order rate constants of propagation k_p^+ or k_p^\pm , respectively, on unpaired ions and ion-pairs are examined in Sections 2 and 4 and compared in Section 3 with the rate constants of model reactions.

The validity of the k_p^+ and k_p^\pm determinations by the two methods are compared (Section 6), but results are unfortunately obtained only by the DC method for styrene, *p*-chlorostyrene and *p*-methylstyrene with $k_p^\pm \sim 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, and by the ISC method for most other monomers with k_p^\pm between 10^4 and $10^5 \text{ L mol}^{-1} \text{ s}^{-1}$.

It is shown that the large difference between these two sets of values as well as that between the parameters of ionization K_i , k_i and k_{-i} of the terminal halides in living polymerizations (Section 5) cannot be explained quantitatively by the large electrophilicity of the carbocation of these poly(styrene)s. Diffusion-controlled propagation for styrene is also in contradiction with reactivity ratios and rates of copolymerization with various monomers.

The recent measurements of k_p^\pm in living polymerizations of several monomers have confirmed the validity of the k_p^\pm obtained earlier from non-living systems and based on the ionic species concentration. It is concluded that k_p^\pm for styrene should be of a similar order of magnitude.

In order to have a comprehensive view interpreting all experimental results, the hypothesis has been made of competitive termination (and possibly propagation) occurring as two-steps reactions, the first step being a complexation of the growing carbocation with the nucleophile, giving a resonance stabilized complex, and the second step a unimolecular rearrangement of the complex.

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