Aqueous phase propagation kinetics in radical polymerization

I. Lacík

Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia
igor.lacik@savba.sk

The availability of individual rate coefficients in radical polymerization is a prerequisite for understanding the polymerization kinetics and mechanism. Among all the rate coefficients, the propagation rate coefficient, k_p, is of special interest since it determines the rate of polymer chain growth, and, additionally, its availability is required to estimate termination and a transfer rate coefficients. The method of choice for determination of accurate k_p values is the pulsed-laser polymerization combined with size-exclusion chromatography, pioneered by Olaj et al. [1]. This method has been used in the last decades for determination of k_p values for a number of monomers polymerized in organic [2] and aqueous [3] solutions.

This contribution will focus on k_p behavior for various monomers in aqueous solutions, including non-ionized and ionized monomers, and sparingly water-soluble monomers. The presence of functional groups in the monomer structure gives rise to intra and intermolecular interactions that are amplified by hydrogen bonding interactions with water molecules used as a solvent.

For non-ionized monomers (i.e., acrylic acid, methacrylic acid, acrylamide, *N*-vinyl pyrrolidone), water molecules accelerate the propagation step in going from bulk polymerization to dilute systems predominantly due to lowering the barrier to the internal rotational mobility within the transition state structure for propagation. This phenomenon is generally observed for all non-ionized monomers. In case of ionized monomers (i.e, anionically charged sodium acrylate, sodium methacrylate, and cationically charged methacrylate and methacrylamide monomers), the kinetics is dominated by electrostatic interactions with k_p values being reduced compared to those for non-ionized monomers due to repulsive interactions between equally charged monomer and radical chain-end. Repulsion interactions can be shielded by counterions to the charged groups, originated either from charged monomer or from salts added to the polymerization system. The radical polymerization of sparingly water-soluble monomers (i.e., methyl acrylate, methoxyethyl acrylate, methyl methacrylate) represents an interesting situation given by a limited solubility of monomers and insolubility of formed polymers in an aqueous environment. The k_p values for these monomers significantly increase in water compared to bulk polymerization.

Keywords: PLP-SEC, propagation rate coefficient, aqueous phase polymerization

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References

[1] Olaj, O. F.; Bitai, I.; Hinkelmann, F. The laser-flash-initiated polymerization as a tool of evaluating (individual) kinetic constants of free-radical polymerization, 2. The direct determination of the rate of constant of chain propagation. *Die Makromolekulare Chemie* **1987**, *188 (7)*, 1689-1702.
[2] Beuermann, S.; Buback, M. Rate coefficients of free-radical polymerization deduced from pulsed laser experiments. *Progress in Polymer Science* **2002,** *27 (2)*, 191-254.
[3] Buback, M.; Hutchinson, R. A.; Lacík, I. Radical polymerization kinetics of water-soluble monomers. *Progress in Polymer Science* **2023,** *138*, 101645.