

A THERMODYNAMIC PERSPECTIVE ON THE MEDIUM DEPENDENCE OF PROPAGATION COEFFICIENTS AND REACTIVITY RATIOS IN RADICAL POLYMERIZATION

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The thermodynamic formulation of the transition state theory is applied to interpret and compute the effect of the medium (solvent type and concentration) on the propagation rate coefficient(s) [1, 2] and reactivity ratios [3] in radical (co)polymerization. The magnitude of the medium effect is shown to be linked to the activity coefficients of the species involved in the transition state quasi-equilibrium. To validate this thermodynamic approach, the quantum chemistry-based solvation model COSMO-RS (Conductor-like Screening Model for Real Solvents) was used to estimate the activity coefficients for homo- and copolymerization systems for which literature experimental k_p and copolymer composition data is available. The comparison between measurements and predictions shows a good qualitative agreement, and, in many cases, a remarkable quantitative agreement, demonstrating the potential of this approach.

Predicted Effect of Medium on k_p and Copolymer Composition

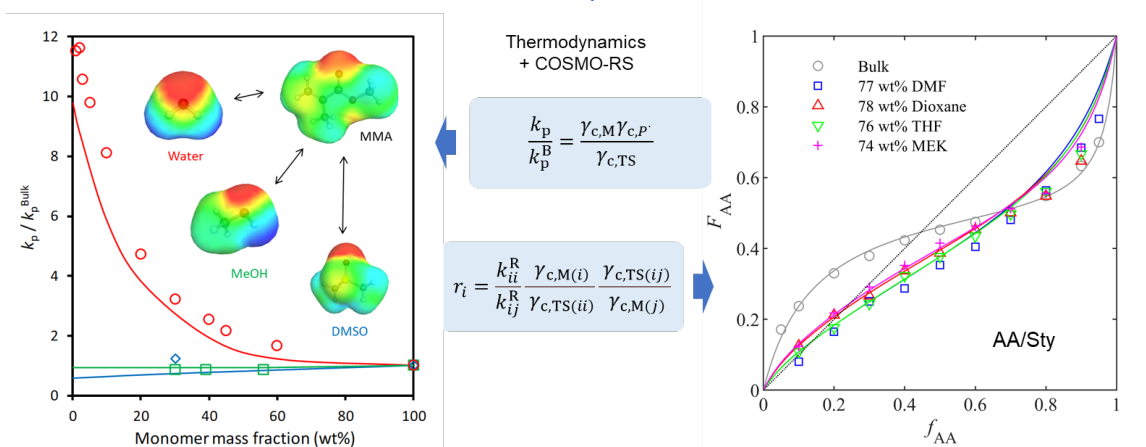


Figure 1 – Predicted influence of the medium on the k_p of the methyl methacrylate (left panel) and on the copolymer composition of the system acrylic acid / styrene (right panel).

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