

Solvent Effect on the Kinetics, Tacticity and Composition in Free Radical Polymerization Reactions: A Computational Study

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It is known that the nature of the solvent influences the rate of free radical mediated polymerization of vinylic and acrylic monomers. Fast polymerization in water is attributed to hydrogen bonds between monomers and water, the conformation of polymer coils, the hydrophobic interactions as well as the local monomer concentration.¹⁻² For example, although EMA and EHMA resemble each other in structure, EHMA propagates faster in bulk due to the presence of intermolecular hydrogen bonds, which tend to facilitate the approach of the propagating species. This falls in contrast with the experimentally observed lower propagation rates of EHMA in ethanol compared to toluene; calculations show that this is caused by the polar protic solvent's disruptive effect on the intermolecular hydrogen bonds between propagating species.³ Tacticity strongly influences the physical properties of polymers because it is a measure of stereoregularity of a polymer chain and many of the polymer properties such as tensile strength, melting point, and solubility depend on it. Recently, N-Isopropylacrylamide (NIPAM) has attracted great attention because its polymer, Poly(N-Isopropylacrylamide) (PNIPAM) has a lower critical solution temperature around human body temperature (LCST=32°C).⁴ The solvent dependence of free-radical polymerization kinetics of the ST/HEMA system has been investigated through a combination of quantum-mechanical tools with the incorporation of solvation methods. This presentation will focus on the usage of quantum mechanics and molecular dynamics to understand and clarify the solvent effect on the kinetics, the tacticity and the composition of vinylic and acrylic monomers.⁵

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