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Depleting depletion: Polymer swelling in poor solvent mixtures DEBASHISH MUKHERJI, Max-Planck-Institute for Polymer Research, CARLOS MARQUES, Institut Charles Sadron, CNRS, TORSTEN STUEHN, KURT KRE-MER, Max-Planck-Institute for Polymer Research — A polymer collapses in a solvent when the solvent particles dislike monomers more than the repulsion between monomers. This leads to an effective attraction between monomers, also referred to as depletion induced attraction. This attraction is the key factor behind standard polymer collapse in poor solvents. Strikingly, even if a polymer exhibits poor solvent condition in two different solvents, it can also swell in mixtures of these two poor solvents. This collapse-swelling-collapse scenario is displayed by poly(methyl methacrylate) (PMMA) in aqueous alcohol. Using molecular dynamics simulations of a thermodynamically consistent generic model and theoretical arguments, we unveil the microscopic origin of this phenomenon. Our analysis suggests that a subtle interplay of the bulk solution properties and the local depletion forces reduces depletion effects, thus dictating polymer swelling in poor solvent mixtures.

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