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Why Good Solvents Are Seldom All That Good S. T. MILNER, ExxonMobil, M.-D. LACASSE, ExxonMobil, W. W. GRAESSLEY — The strength of interactions between polymers and solvents is most commonly summarized in a chi parameter. Chi greater than 0.5 leads to phase separation, while a value of zero indicates an “ideal” solvent. In fact, chi values less than 0.25 are quite rare, even among so-called “good solvents” for a given polymer. Why should this be? The origin of energetic interactions between nonpolar polymers and solvents is primarily dispersive forces, which are proportional to the square of the difference in solubility parameter; hence it should be possible to choose polymer and solvent with matched solubility parameters to achieve an ideal solvent. We shall argue that there is also a generic entropic contribution to chi. One way of describing it is to say that polymer and solvent have a different propensity to explore free volume; when obliged to mix, there is an entropic penalty resulting from the necessary compromise in free volume per mer. One may also say that the solvent molecules induce a depletion attraction between chain segments, analogous to the attraction between colloidal particles induced by micellar solutions. This effect can be observed in simulations of hard-sphere chains in identical hard sphere solvent. There one finds that the radius of gyration of such chains in solvent are significantly smaller than in vacuum, though still scaling as self-avoiding walks. From this result, a chi value of about 0.3 may be inferred.

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