LINEAR VERSUS THREE-ARM STAR POLYBUTADIENE: EFFECTS OF POLYMER ARCHITECTURE ON THE THERMODYNAMIC SOLUTION BEHAVIOR

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ABSTRACT

In contrast to expectations based on current theories, even minute changes in the polymer architecture influence the thermodynamic solution behavior markedly. This lecture presents data for the interaction of linear and of three-arm star polybutadiene (PB) with THF and models them on the basis of an approach[1] accounting for chain connectivity and conformational relaxation of the components.

Information for dilute solution rests on light scattering experiments; Flory-Huggins interaction parameter χ stem from vapor pressure measurements as a function of φ, the volume fraction of polymer. Despite the minute divergence in the architecture, the second osmotic virial coefficients of the two polybutadienes differ noticeably. The present work demonstrates that these disparities become much more pronounced as φ increases; furthermore they depend strongly on temperature. Fig. 1 shows the results for χ_o (vanishing polymer concentration) and for χ_∞ (vanishing solvent concentration) as a function of temperature.

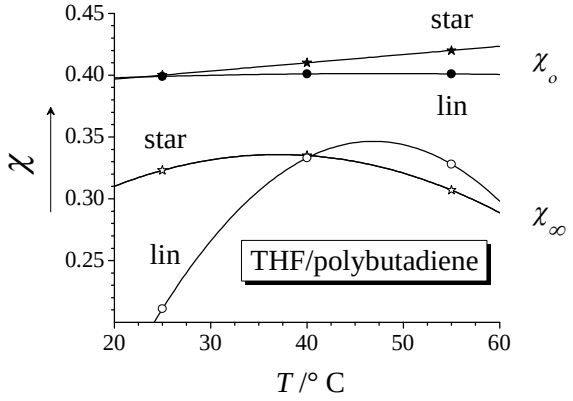

Fig. 1: Temperature dependence of the Flory-Huggins interaction parameter χ for the polymer of different molecular architecture in the limit of vanishing polymer concentration (χ_o) and vanishing solvent concentration (χ_∞)

The above-mentioned approach[1] enables a rationalization of the experimentally observed complex dependencies χ (φ, T), which are related to the dissimilar free volumes of the polymers of dissimilar molecular architecture.

Reference:

[1] Wolf, B.A. *Advances in Polymer Science* **2011**, *238*, 1.