

Polyelectrolyte Blends and Nontrivial Behavior in Effective Flory-Huggins Parameters

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ACS Macro Letters, 3, 698-702 (2014) DOI: 10.1021/mz500202n

Current methods to characterize heterogeneous polymer melts typically rely on the Flory-Huggins χ parameter, which determines the extent of which two or more polymer species will mix or demix. It represents the energy associated with adjacent monomers due to short-range interactions. Effective values of this χ parameter are often extracted from experiments, however it is unclear what this means in the context of charged polymers. We consider a blend of charged and uncharged polymers, and demonstrate that a random phase approximation (RPA) calculation using a recently-developed SCFT-LS theory will result in an expression for this effective χ parameter. Importantly, this expression is highly dependent on local charge structures and how they evolve upon traversing phase space. We demonstrate this in the context of homopolymer blends, and subsequently speculate on its ramifications in the characterization of heterogeneous polymer systems.

Thermodynamic information capturing local charge structures (left) leads to a correction (center) that is highly non-monotonic with volume fraction of the the charged A component of a polymer-polymer mixture. This leads to drastic deviations in the phase diagram (right) that are the direct result of small length-scale correlations.

The authors acknowledge support from NSF grant number DMR-1309027.