Modeling of Phase Behavior of Polymer Blends Containing Linear Telechelic Supramolecular Polymers

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Non-covalent "soft" interactions (e.g. hydrogen bonding, ion-ion, and ion-dipole) are used to guide the self-organization of functional polymers into well-ordered, even hierarchal structures. One especially innovative use of H-bonding has been the engineering of reversible, polymer-like chains by the end-to-end association of shorter, functionalized chains.[1-6] Recently, Meijer *et al* have used self-complementary ureidopyrimidinones[4], capable of quadruple hydrogen-bond formation, to form linear aggregates. At low temperatures, these materials can exhibit polymeric features including a well-defined glass transition and viscoelastic behavior. At elevated temperatures, aggregate chains dissociate, and the material behaves similar to a liquid or a low molecular-weight polymer melt.

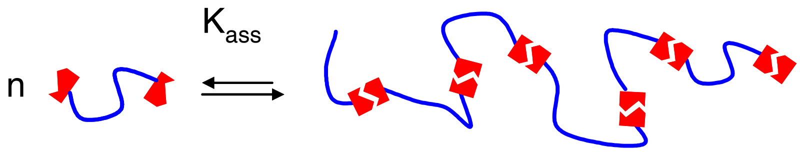

Figure 1. Cartoon depicting association of a short, macromolecular chain functionalized with two self-complementary binding site or "stickers".

Due to their inherent reversibility, materials containing supramolecular telechelic chains exhibit reversible mechanical and rheological properties, and they offer new options for improving polymer rheology and processability[7]. The present study addresses how supramolecular association affects another well-studied polymer phenomenon: polymer-polymer miscibility. While site-specific H-bonding interactions can improve the miscibility of polymers with traditionally immiscible components such as rigid-rod polymer, liquid crystals, and, to a limited extent, thermosetting polymer blends, it is unclear how binary [polymer-supramolecular polymer] blends will differ from traditional [polymer-polymer] blends.

A model was developed to predict the phase behavior of binary [polymer – supramolecular polymer blends]. The model is based on a modification of Semenov and Rubinstein's equilibrium mean-field theory on associating polymers.[8] Inputs into the model include the lengths of the unimers (N_A) and polymers (N_B), the free energy of forming supramolecular bonds (εkT), and a Flory-Huggins interaction parameter χ. The model calculates the equilibrium degree of association for a pure, supramolecular polymer and that of a mixture containing a supramolecular component and a monodisperse polymer. The free energy of mixing is calculated to determine whether the components are miscible. This exercise is repeated as a function of composition and temperature to construct phase diagrams. Resulting diagrams exhibit an upper critical solution temperature with asymmetric

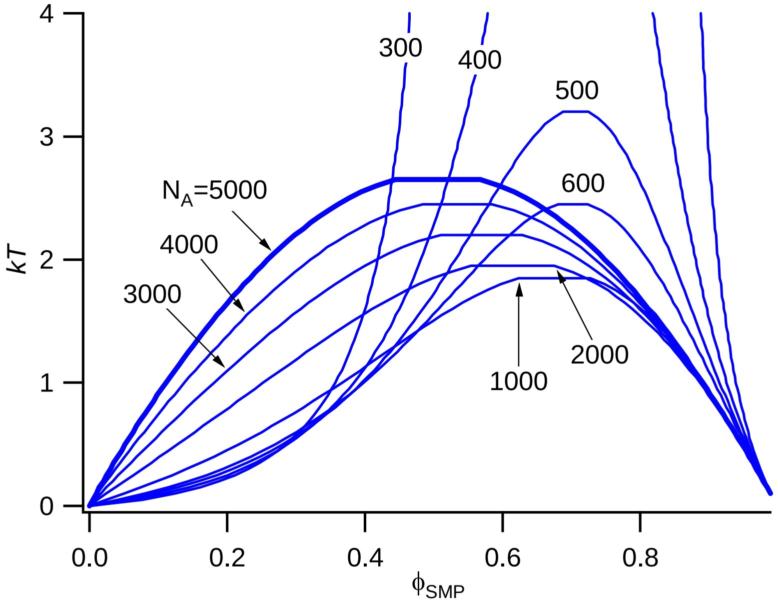

Figure 2. Predicted phase diagram for (polymer-supramolecular polymer) binary blends the using input parameters: $\varepsilon = 4$, $N_B = 5000$, and $\chi = 0.001 / kT$. Spinodal temperature curves are shown for different chain lengths of the supramolecular component (N_A) and are plotted against the volume fraction of the supramolecular component.

phase boundaries like those shown in Figure 2. At low volume fractions of the supramolecular component, the end-group concentration is diluted and the system is predicted to behave like a regular polymer-polymer blend. At higher volume fractions, the supramolecular component is highly associated, leading to phase separation at higher temperatures.

Binary blends containing monodisperse polystyrene and polybutadiene functionalized with ureidopyrimidinone groups are studied to experimentally verify model predictions. These materials are immiscible over a much wider composition range than their unfunctionalized analog. This is consistent with the model's prediction. Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research.

References

(1) Maus, C.; Fayt, R.; Jerome, R.; Teyssie, P. *Polymer* **1995**, *36*, 2083-2088.
(2) Chassenieux, C. N., T.; Tassin, J.-F.; Durand, D.; Gohy, J.-F.; Jerome, R. *2001* **2001**, *22*, 1216-1232.
(3) Binder, W. H.; Kunz, M. J.; Kluger, C.; Hayn, G.; Saf, R. *Macrmolecules* **2004**, *37*, 1749-1759.
(4) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; Joost, A. J. v. d. R.; Meijer, E. W. *Advanced Materials* **2000**, *12*, 874-878.
(5) Rowan, S. J.; Suwanmala, P.; Sivakova, S. *Journal of Polymer Science: Part A: Polymer Chemistry* **2003**, *41*, 3589-3596.
(6) Hofmeier, H.; Schmatloch, S.; Wouters, D.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 2197-2203.
(7) McKee, M. G.; Elkins, C. L.; Long, T. E. *Polymer* **2004**, *45*, 8705-8715.
(8) Semenov, A. N.; Rubinstein, M. *Macrmolecules* **1998**, *31*, 1373-1385.