Can the Miscibility of Telechelic Polymer Solutions Increase with Polymer Chain Length?

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ABSTRACT: Increasing the molar mass of the polymers in blends and in solutions tends to decrease miscibility, but application of the lattice cluster theory for strongly interactiong polymer systems to telechelic polymer solutions explains why this usual trend can be inverted, a situation actually observed in some telechelic polymer solutions and blends.
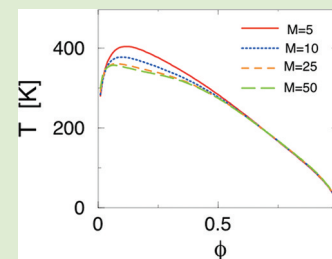
Telechelic polymers are capable of supramolecular assembly due to the presence of associative groups at the two chain ends (called "stickers"). Technological applications of telechelics range from compatibilizers or stabilizers in polymer blends and nanocomposite materials[1] to precursors of high solids coatings[2] and thermoplastic rubbers.[3] The thermodynamical description of this self-assembly process is nontrivial[4,5] because of the interplay of the strong interactions between the stickers and the van der Waals interactions between segments of all species in the system. Additional complexity arises from the chain connectivity introduced by the associative clusters as well as from the internal chemical structure of individual telechelic molecules. All these requisite ingredients for a molecular based description of self-assembly are incorporated into our recently developed lattice cluster theory (LCT).[6,7]

While prior theoretical studies[8,9] of telechelics are mostly devoted to binary blends of telechelic species, we focus on investigating the phase behavior of telechelic chain solutions, which may differ qualitatively from that for binary polymer blends. The extended lattice model[10] represents the telechelic molecules (component 1) as (completely flexible) linear chains (each composed of M united atom groups that extend over M lattice sites), and the solvent molecules (component 2) are depicted as species occupying single lattice sites, with no empty sites allowed. The segments lying at the ends of individual telechelic chains (the "stickers") interact with the strong sticky interaction energy ε_s when a pair of stickers resides on nearest neighbor lattice sites, while the remaining segments of both components interact with each other through much weaker nearest neighbor van der Waals energies $\{\varepsilon_{ij}\}$. Each sticker is permitted to participate in only one sticky bond, which implies the formation of only linear self-assembled clusters (cyclic structures are ignored). The van der Waals exchange energy ε is defined as $\varepsilon = 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}$ (with the subscripts ij labeling

the species) and provides a measure of the effective solute−solvent interactions that govern the solution's phase stability.

The Helmholtz free energy f (per lattice site) is the sum of the free energy f_o of the hypothetical reference system that is devoid of sticky interactions, that is, a system composed of the solvent and chain molecules whose segments interact only through weak Waals forces, and the free energy contribution f_s that arises from strong sticky interactions,[6,7]

$$\beta f = \beta f_o + \beta f_s \tag{1}$$

with f_s given by

$$\beta f_s = \beta f_s^{(mf)} - \sum_{i=1}^{i=4} y^i Y_i \tag{2}$$

and

$$\beta f_s^{(mf)} = -\phi x \ln \phi x + (\phi x - 2y) \ln(\phi x - 2y) + y[1 + \ln(2y/z) + \beta \varepsilon_s] \tag{3}$$

where $x = 2/M$, $\beta = 1/(k_B T)$ [with k_B being Boltzmann's constant and T designating the absolute temperature], ϕ is the volume fraction of telechelic polymers, ε_s is the sticky interaction energy (relative to the van der Waals energy ε_{11}), z is the lattice coordination number (taken as $z = 6$ for a simple cubic lattice), and Y_i ($i = 1-4$) are corrections (to the mean-field free energy $f_s^{(mf)}$) stemming from short-range correlations (involving a length scale of up to four consecutive bonds).[7]

The variable y in eqs 2 and 3 is defined as the ratio of the number (H) of sticker−sticker "bonds" in the systems to the

total number N_l of lattice sites.[7] This intrinsic quantity y in the LCT is determined by the maximum term method, that is, by applying the condition

$$\frac{\partial[\beta f_s]}{\partial y}\Big|_{N_l,T,\phi} = 0 \tag{4}$$

which can be written in terms of molecular variables as,

$$(\phi x - 2y)^2 - (2y/z)\exp\Big[\beta\varepsilon_s - \sum_{i=1}^{i=4} i y^{i-1} Y_i\Big] = 0 \tag{5}$$

Equation 5 must be solved numerically, yielding the density y^* that is substituted for y into eqs 2 and 3 to determine the free energy. This minimization of the free energy with respect to y leads to the expression,

$$\beta f = \beta f_o - \phi x \ln \phi x + (\phi x - 2y^*)\ln(\phi x - 2y^*)$$
$$+ y^*[1 + \ln(2y^*/z) + \beta\varepsilon_s] - \sum_{i=1}^{i=4}(y^*)^i Y_i \tag{6}$$

Notice that y^* depends on all molecular and thermodynamic parameters characterizing the system, that is, on T, ϕ, M, ε, and ε_s.

The specific Helmholtz free energy $f_o = F_o/N_l$ for the reference system (without sticky interactions) also emerges from the lattice cluster theory[10] as a polynomial in the volume fraction ϕ,

$$\beta f_o = (1 - \phi)\ln(1 - \phi) + (\phi/M)\ln\phi + \sum_{k=0}^{k=6} C^{(k)}\phi^k \tag{7}$$

The first two terms on the right-hand side of eq 7 represent the leading combinatorial portion of f_o, while the coefficients $C^{(k)}$ ($k = 0, 1, 2, ..., 6$) are sums of athermal limit entropy, first order energy, and second order energy contributions to the noncombinatorial portion of free energy f_o that describe non-random mixing due to correlations over distances up to the scale of four correlating bonds.[10]

Below, we demonstrate that the miscibility of telechelic chain solutions can either *decrease* or *increase* with chain length M depending on the strength of the sticky interactions. Generally, phase separation in self-assembling systems is a complex phenomenon due to the coupling between self-assembly (governed by the sticky energy ε_s) and phase separation, which is driven by the effective van der Waals solute−solvent interactions (namely, by a sufficiently large, positive exchange energy ε).[11,12] Because the telechelic solutions are assumed, for simplicity, to be incompressible, the spinodal condition for phase stability is the vanishing of the second derivative of the free energy f with respect to the system's composition ϕ

$$\frac{\partial^2(\beta f)}{\partial\phi^2}\Big|_{N_l,T} = 0 \tag{8}$$

When the second derivative of the specific Helmholz free energy f in eq 8 is evaluated from eq 6, the condition in eq 8 takes the form

$$\frac{\partial^2(\beta f_s)}{\partial\phi^2}\Big|_{N_l,T} = \frac{\partial^2(\beta f_o)}{\partial\phi^2} + \frac{2xy^*}{\phi(\phi x - 2y^*)} - \sum_{i=1}^{i=4}(y^*)^i \frac{\partial^2 Y_i}{\partial\phi^2}$$
$$- \frac{\partial y^*}{\partial\phi}\Big[\frac{2x}{\phi x - 2y^*} + \sum_{j=1}^{j=4} j(y^*)^{j-1}(\partial Y_i/\partial\phi)\Big] = 0 \tag{9}$$

where the density y^* and the derivative

$$\frac{\partial y^*}{\partial\phi} = \{2x/(\phi x - 2y^*) + \sum_{j=1}^{j=4} j(y^*)^{j-1}(\partial Y_j/\partial\phi)\}/$$
$$\{(\phi x + 2y^*)/[y^*(\phi x - 2y^*)]$$
$$- \sum_{j=2}^{j=4} j(j-1)(y^*)^{j-2} Y_j\} \tag{10}$$

are determined from eq 5 and where the derivative $\partial^2(\beta f_o)/\partial\phi^2$ simply follows from eq 7.

Illustrative examples of the spinodal curves for solutions of self-assembling telechelic solutions in Figures 1 and 2 refer to
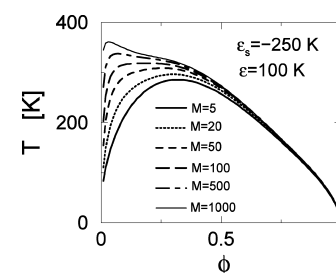

Figure 1. LCT spinodal curves for solutions of weakly interacting linear telechelic chains in solutions with single-site solvent molecules. The enegies ε_s and ε and the length M of the telechelic chains are indicated on the figure.
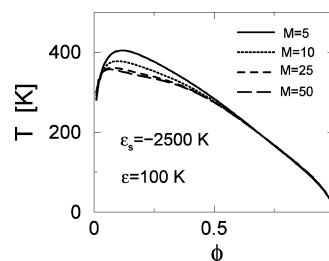

Figure 2. LCT spinodal curves for solutions of strongly interacting linear telechelic chains in solutions with single-site solvent molecules. The energies ε_s and ε and the length M of the telechelic chains are indicated on the figure.

systems with relatively weak and strong sticky energies ε_s, respectively. The spinodals in Figure 1 all correspond to the same sticky energy $\varepsilon_s = -250$ K and the same van der Waals exchange energy $\varepsilon = 100$ K but to variable lengths M of individual telechelic chains. The phase boundaries in Figure 1 conform to the well-known observation that an increase in polymer mass inevitably diminishes the solution's miscibility. This rule of thumb is perfectly consistent with the prediction of FH theory that increasing M causes a decrease of the combinatorial entropy of the system, and thereby an increase in the spinodal temperature $T_{sp}(\phi)$ and a decrease in miscibility.

The familiar trend in Figure 1 might be anticipated to be independent of the magnitude of the sticky energy ε_s, but Figure 2 demonstrates, *on the contrary*, that the system's miscibility *improves* as the chain length M increases when the sticky energy $|\varepsilon_s|$ is large relative to the exchange energy ε (for instance, $\varepsilon_s = -2500$ K). Typical hydrogen-bonding energies range from -5 to -155 kJ/mol,[13] and $\varepsilon_s = -2500$ K corresponds to about -20 kJ/mol, which lies closer to the lower than to the upper limit of this wide range.

The explanation of this unexpected behavior in Figure 2 is provided by Figures 3 and 4, which present the combinatorial
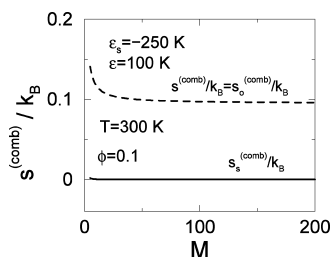

Figure 3. LCT combinatorial entropy $s^{(comb)}$ for solutions of weakly interacting linear telechelic chains in solutions with single-site solvent molecules as a function of the length M of an individual telechelic chain. Solid and dashed lines illustrate, respectively, the portions $s_s^{(comb)}$ and $s_o^{(comb)}$ of $s^{(comb)}$ that are defined in the text.

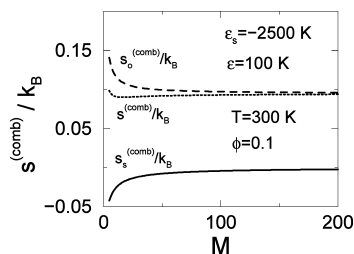**Figure 4.** Same as Figure 3, but for solutions of strongly interacting linear telechelic chains.

entropy $s^{(comb)} = s_o^{(comb)} + s_s^{(comb)}$ as a function of M for systems with relatively weak and strong sticky interactions, respectively. The quantity $s^{(comb)}$ is defined as the sum of the combinatorial entropy $s_s^{(comb)}$ arising from the sticky interactions,

$$s_s^{(comb)}/k_B = \phi x \ln \phi x - (\phi x - 2y^*)$$
$$\times \ln(\phi x - 2y^*) - y^*[1 + \ln(2y^*/z)] \quad (11)$$

and the combinatorial entropy $s_o^{(comb)}$ of the reference system (with no sticky interactions)

$$\frac{s_o^{(comb)}}{k_B} = -\frac{\phi}{M} \ln \phi - (1 - \phi) \ln(1 - \phi) \quad (12)$$

where terms linear in ϕ are excluded because these terms do not affect the system's miscibility. Thus, we retain the portion of $s_o^{(comb)}$ that corresponds to the combinatorial entropy of mixing. While both $s^{(comb)}$ and $s_o^{(comb)}$ must be positive, $s_s^{(comb)}$ can be of either sign due to the dependence of y^* on the magnitude of ε_s. When the sticky interactions are weak, $s_s^{(comb)}$ is generally positive and often much smaller than $s_o^{(comb)}$ (see Figure 3). Correspondingly, $s^{(comb)}$ either coincides with $s_o^{(comb)}$ or exceeds it somewhat. The trend of diminishing $s^{(comb)}(M)$ with increasing M is a universal characteristic of weakly associating systems, regardless of their

composition and temperature. On the other hand, when the sticky interactions are strong, the combinatorial entropy $s_s^{(comb)}$ is always *negative* and not necessarily small (see Figure 4). Consequently, the total combinatorial entropy $s^{(comb)}$ becomes smaller than $s_o^{(comb)}$ and begins *growing* slowly with M, except for a very narrow range of very small M. This upturn in the dependence of $s^{(comb)}$ on the chain length M is clearly responsible for the enhancement of the solution miscibility (see Figure 2) as M increases. The addition of the noncombinatorial entropy $s^{(ncomb)}$ to $s^{(comb)}$ in Figure 4 ensures that the entropy of mixing decreases with M over the whole range, which in turn explains why the spinodal temperatures T_{sp} in Figure 2 for $M = 10$ exceed those corresponding to $M = 5$.

The enhancement of the miscibility in Figure 2 occurs for rather short chains ($M \leq 50$), and a further increase in M does not noticeably alter the phase boundaries. The saturation of the system's miscibility as M increases is by *itself* interesting and supports the physical validity of the theory which correctly predicts that the improvement in the miscibility of the solution (driven by increasing the size of the solute) is not unbounded. The miscibility must either saturate or begin diminishing when M exceeds a critical value $M_{cr}(\varepsilon_s, \varepsilon)$. Our calculations indicate the occurrence of the former trend. Evidently, M_{cr} is a function the sticky energy ε_s and grows with $|\varepsilon_s|$. For instance, when $\varepsilon_s = -3000$ K (and $\varepsilon = 100$ K), $M_{cr} \approx 80$.

In summary, we demonstrate that unusual variations in the miscibility of self-assembling telechelic polymer solutions with the molar mass of the polymer can be explained within the framework of a statistical thermodynamic theory that incorporates a description of the molecular details of the system. These trends are expected to have implications for many applications of telechelics, and, in fact, the trends have been observed for some telechelic polymer systems. For instance, experiments for aqueous solutions of poly(N-isopropylacrylamides)[14] and poly(ethylene oxides),[15] as well as for poly-(ethylene glycol)/poly(propylene glycol) blends[16] provide evidence indicating that miscibility can increase with polymer molar mass within certain ranges of M. The former systems are lower critical solution temperature (LCST) mixtures, while the latter ones are upper critical solution temperature (UCST) binary polymer blends.

Our current theory of telechelic chain solutions has been derived only for (incompressible) telechelic solutions that phase separate upon cooling but can be extended to LCST systems as well as to compressible systems more generally.[10,17] The restriction emerges from the present modeling of the telechelic chains as linear polymer chains and the solvent molecules as occupying single lattice sites. Consequently, the positive "entropic" component of the Flory–Huggins interaction parameter χ is too small to compete effectively with a (negative) exchange energy ε to produce a LCST phase diagram,[18] a mechanism for LCST phase behavior that emerges naturally from the LCT (even for incompressible mixtures) and that has been confirmed by a large body of experimental data.[17,18] The treatment of LCST systems requires the additional nontrivial extension of the LCT for models in which solvent molecules have internal molecular structure, that is, cover several lattice sites, and the telechelic self-assembling species contain tri- or tetra-functional groups. Similar modifications of the LCT are also necessary to describe blends of two telechelic polymers with differing internal monomer structures. Nonetheless, our calculations clearly demonstrate that the miscibility trends in associating polymer systems can

depart considerably from those for non-associating polymer mixtures.

Our results suggest that the LCT is also well suited for investigating complex phase behaviors of binary mixtures of two telechelics. For instance, recent theoretical studies[9] of binary telechelic blends reveal the existence of a very rich array of miscibility patterns for these systems. However, the use of a few adjustable parameters in the merger[9] of the Coleman-Painter association model[19] and classic Flory−Huggins theory precludes obtaining a molecular interpretation of the miscibility trends and identifying the molecular factors governing the phase behavior of these systems. The application of the self-consistent field theory framework to telechelic polymer blends seems promising[8] but at the expense of heavy numerical effort. None of these issues hampers the LCT.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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