# Chemical Compatibilization, Macro-, and Microphase Separation of Hetero-Associative Polymers

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#### Abstract

A mean-field equilibrium theory for reversible network formation due to heterotypic pairwise interactions in mixtures of associative polymers is extended via a weak inhomogeneity expansion to account for spatial fluctuations due to chemical incompatibility. We consider solutions and blends of polymers of types A and B with many associating groups per chain, and consider only A - B association between these groups. The structural correlations of the reversibly-bonded polymers are accounted for by considering the Gaussian 4-arm star-like chain conformations between cross-links, which is analogous to an affine-network assumption. Future extensions of this theory could further incorporate strand stretching from swelling or strong segregation. We show that the chemical incompatibility between A and B polymers drives a competition between associative and segregative phase separation. The addition of reversible A - B crosslinks between incompatible A and B chains compatibilizes the mixture, minimizing the propensity for macroscopic phase separation into A- and B-rich phases. Under strong binding and segregation conditions, this results in eutectic-like behavior and local microphase segregation. The crossovers from macroscopic to microscopic phase separation occur at isotropic Lifshitz points, resulting in the potential for bicontinuous microemulsions. The reactive blending of such multifunctional polymers presents the opportunity to envision novel properties, processing conditions, and applications accessible by the tunable production of supramolecular complexes, mesophases, and multicomponent polymer networks.

# Introduction

Blending polymer melts or solutions into a polymeric alloy is a straightforward and important approach for designing high-performance materials.<sup>1</sup> Polymer blends allow material properties to be optimized due to the combination of exceptional properties from multiple constituents. However, segregation effects arising from chemical incompatibility between the polymers often hinder their utility.

Polymer mixtures tend to phase separate, as their translational entropy is small for long chains, considerably amplifying the chemical mismatch between unlike monomers. Segregation occurs below a critical temperature (i.e., above a critical strength of interaction), resulting in poor-quality materials with weak interfaces and limited control over their morphology or properties.<sup>1–3</sup> Since the size and microstructure of the phase-segregated domains dictate the macroscopic properties of the material, controlling separation on prescribed length scales, however, enables tailoring of the material.

A simple approach for enhancing miscibility in a polymer blend is to prevent coarsening of the macroscopic coexisting phases. Accordingly, one method is to create bonds between different chemical species, chemically cross-linking the mixture in the one-phase region or early in the phase separation process.<sup>4–8</sup> Cross-linking reactions permit the formation of quenched domains in the range of nanometers to micrometers. Properties such as the optical transparency and mechanical behavior depend on the size of the composite domains, which can be controlled by the degree of cross-linking (i.e., distance between cross-links) and the length scale of concentration fluctuations in both the preparation and use conditions.<sup>4,6,9,10</sup>

Another approach arrests phase separation by the inclusion of an appropriate compatibilizer, often a block, random, or graft copolymer. These additives preferentially adsorb to the interfaces between A and B domains, serving to lower the interfacial tension, forming a finer dispersion, strengthening the polymer alloy and stabilizing complex morphologies.<sup>11–15</sup>

Recently, reactive blending technologies have offered an integrated approach by forming compatibilizers in situ directly at the blend interface.<sup>12,16–19</sup> Mutually reactive (A - B) polymers are blended, reactions at the interface form block copolymer "surfactants", promoting mixing and subsequently superior material properties. Interestingly, when bonding conditions are favorable, the resultant copolymers produced in the blend can form ordered mesophases that can drastically affect the overall material's structure and properties.<sup>20–23</sup>

Reactive blending relies on the binding of A chains to B chains at the interface. Typically, this is achieved by reactive sites at the chain ends, which can form covalent bonds with the other blend components. Practically, however, reversible bonds between associative groups, or "stickers", offer a more facile and tunable approach for in situ compatibilizer formation. Because the objective is selective binding between A and B chains, hetero-complementary (or heterotypic or heteroleptic) associations, in which an A reactive group binds to a Breactive group, are preferred. Such heterotypic attractive associations can include hydrogen bonding, metal-ligand, cation- $\pi$ , host-guest, or ionic interactions.<sup>24-27</sup>

The physical bonds improve the mutual miscibility between different species but also result in complex phase behavior, including macro- and microscopic phase separation, as well as gel formation. The size, morphology, and connectivity of the resultant material structures critically depend on the interplay between the strength of these physical reversible associations and the chemical incompatibility driving segregation.<sup>10,28–30</sup>

The extension of reactive blending to multifunctional polymers with many associating groups per chain creates the opportunity to envision novel properties, processing conditions, and applications accessible by the tunable production of supramolecular complexes, mesophases, and multicomponent polymer networks in these systems. Such materials should be self-healing or remendable, able to re-gain their structure and properties after failure.<sup>31–35</sup> In fact, comparable systems already exist in nature, with transient associations between proteins and nucleic acids driving sub-cellular and nuclear compartmentalization important in membraneless organelles and chromatin transcription.<sup>36–41</sup>

Clearly, there is an immense parameter space possible in associating polymer mixtures: polymer architecture and molecular weight, solvent quality, chemical incompatibility between different species, sticker density and sequence, and binding strength of the associations. The vast potential of the property space and the complexity of the design space motivate a theoretical foundation for robust design principles that link the thermodynamics, gelation, and resulting properties of these materials.<sup>28–30,34,42–54</sup> In a companion work, we developed a mean-field theory for the thermodynamics and gelation of two-component solutions of *heterotypic* or A - B-type associative polymers.<sup>46</sup> Reversible binding between hetero-complementary associating groups were found to result in branched copolymers and macroscopic percolation. Homogeneous networks are most easily stabilized near stoichiometric sticker conditions, enabling sol–gel–sol transitions as the overall composition of the mixture is altered. Good solvent conditions reduce the associations between chains, suppressing phase separation, as for *homotypic* or A - A-type sticky polymers.<sup>45</sup> However, existing mean-field theories are restricted to spatially homogeneous networks and are therefore not suitable for addressing questions of microphase segregation.

In this study, we investigate with a minimal theory the phase separation and gelation of a mixture of reversibly bonded multifunctional associating polymers of types A and B. The reversible bonding of hetero-associating groups transforms the polymer blends into macroscopic copolymer networks. Gelation proceeds when the reversible network achieves percolation across the sample, with an average of two cross-links per chain.<sup>46</sup> By extension of an equilibrium mean-field theory to account for spatial concentration fluctuations, we can furthermore describe the competition between chemical incompatibility and reversible binding that leads to macro- and microphase separation. The described polymer alloys have the advantage of thermal tuning of connectivity and segregation strength, leading to controllable phase behavior and network formation, with implications for biological condensates and polymer reprocessing.

# Theory

## Mean-Field Model

We consider a mixture of multifunctional polymers consisting of linear chains with associating groups of type i = A, B (Figure 1).<sup>46</sup> The polymers have  $N_i$  segments of size a and have ideal chain statistics described by the continuous Gaussian chain model. Each chain contains  $f_i$ stickers separated by spacers with  $s_i = N_i/(f_i - 1)$  segments. There are many stickers per chain, but significantly fewer than the number of Kuhn segments  $(1 \ll f_i \ll N_i)$  such that the spacers between stickers are long  $(s_i \gg 1)$  and the effects of sticker cooperativity can be neglected. Stickers can associate in saturable, heterotypic (i.e., heteroleptic or heterobonding, only A - B, not A - A or B - B) pairs with the energy of each bond equal to  $\epsilon k_{\rm B}T$ , where  $k_{\rm B}T$  is the thermal energy.



Figure 1: Model system of A - B associative polymers.

The monomer volume fraction of type i in solution is  $\phi_i$ , the number density of polymer chains is  $\phi_i/(a^3N_i)$ , and the number density of stickers is  $f_i\phi_i/(a^3N_i) \simeq \phi_i/(a^3s_i)$ . The degree of conversion of type  $i = A, B, p_i$ , is the fraction of stickers of type i that are associated in a bound A - B pair. The average number density of reversible bonds is

$$\rho = p_i \frac{f_i \phi_i}{a^3 N_i} \simeq p_i \frac{\phi_i}{a^3 s_i} \tag{1}$$

For convenience, we non-dimensionalize the concentrations by the segment volume  $a^3$  to de-

fine the volume fraction  $\phi = \phi_A + \phi_B$ , which is equal to unity in the limit of an incompressible melt blend.

## Weak Inhomogeneity Expansion

If the system undergoes local fluctuations,  $\phi_A$  and  $\phi_B$  become space dependent, and the resulting free energy functional becomes

$$F\{\phi_A(\mathbf{r}), \phi_B(\mathbf{r})\} = F_{\rm tr} + F_{\rm int} + F_{\rm st}$$
(2)

with the resulting formalism suitable for both homogeneous and inhomogeneous phases. The first term  $F_{\rm tr}$  accounts for the translational entropy of the chains:

$$\frac{F_{\rm tr}}{k_{\rm B}T} = \int d^3 \mathbf{r} \left[ \frac{\phi_A(\mathbf{r})}{N_A} \ln\left(\phi_A(\mathbf{r})\right) + \frac{\phi_B(\mathbf{r})}{N_B} \ln\left(\phi_B(\mathbf{r})\right) \right]$$
(3)

The second term  $F_{\text{int}}$  captures the solvent-mediated excluded volume interactions between monomers and A - B chemical incompatibility:

$$\frac{F_{\rm int}}{k_{\rm B}T} = \int d^3 \mathbf{r} \left[ \frac{v}{2} (\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}))^2 + \frac{w}{6} (\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}))^3 + \chi_{AB} \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) \right]$$
(4)

where v is the excluded volume parameter, w is the three-body interaction parameter, and  $\chi_{AB}$  is the Flory–Huggins parameter between the A and B polymers relative to the solvent. We assert in this analysis that v, w, and  $\chi_{AB}$  are not directly affected by the presence of cross-links and that the solvent is of equal quality for both A and B (i.e.,  $v_A = v_B \equiv v$  and  $w_A = w_B \equiv w$ ). Finally, the last term in eq. 2 is responsible for the enthalpy of sticker bonds and combinatorial entropy of stickers,<sup>46</sup>

$$\frac{F_{\rm st}}{k_{\rm B}T} = \int d^3 \mathbf{r} \left[ \frac{\phi_A(\mathbf{r})}{s_A} \left[ p_A(\mathbf{r}) + \ln\left(1 - p_A(\mathbf{r})\right) \right] + \frac{\phi_B(\mathbf{r})}{s_B} \ln\left(1 - p_B(\mathbf{r})\right) \right]$$
(5)

where, importantly, the degrees of conversion of stickers  $p_A(\mathbf{r})$  and  $p_B(\mathbf{r})$  are also spatiallydependent functions. The bond strength  $\epsilon$  enters this sticker energy implicitly through the degrees of conversion of A and B. Minimization of the free energy (eq. 2) with respect to the number density of sticker bonds  $\rho a^3 = p_A \phi_A / s_A = p_B \phi_B / s_B$  results in an expression for the degree of conversion of A stickers:

$$p_A(\mathbf{r}) = \frac{1}{2} + \frac{\phi_B(\mathbf{r})/s_B}{2\phi_A(\mathbf{r})/s_A} + \frac{1 - \sqrt{\left(1 + \left(\frac{\phi_A(\mathbf{r})}{s_A} + \frac{\phi_B(\mathbf{r})}{s_B}\right)\lambda\right)^2 - 4\frac{\phi_A(\mathbf{r})}{s_A}\frac{\phi_B(\mathbf{r})}{s_B}\lambda^2}{\frac{2\phi_A(\mathbf{r})}{s_A}\lambda} \tag{6}$$

where  $\lambda = (v_{\rm b}/a^3) \exp(\epsilon)$  is the attractive volume of a bond (relative to segmental volume  $a^3$ ), an exponential of the association strength. The degree of conversion of B stickers is related to the degree of conversion of A stickers by the relative concentrations of stickers of A and B:  $p_B(\mathbf{r})/p_A(\mathbf{r}) = (\phi_A(\mathbf{r})/s_A)/(\phi_B(\mathbf{r})/s_B) = r(\mathbf{r})$ , where r is the sticker stoichiometry. For spatially homogeneous systems, the gelation condition corresponds to the degrees of conversion of A and B,<sup>46</sup>

$$p_A^{\text{gel}} p_B^{\text{gel}} = r p_A^{\text{gel}^2} = \frac{1}{f_A - 1} \frac{1}{f_B - 1}$$
(7)

where the superscript "gel" refers to the critical fractional conversions at the gel point.

We can assess the stability limit of the homogeneous phase via a weak inhomogeneity expansion (the so-called random phase approximation, RPA.)<sup>55,56</sup> Thus, we consider weak spatially varying concentration perturbations of the form

$$\phi_i(\mathbf{r}) = \phi_i + \sigma \delta_i(\mathbf{r}) \tag{8}$$

where  $\phi_i$  is the mean value of the concentration given by

$$\phi_i = \frac{1}{V} \int d^3 \mathbf{r} \, \phi_i(\mathbf{r}) \tag{9}$$

and  $\sigma$  is a positive constant such that  $\sigma \ll 1$  and  $\delta_i(\mathbf{r})$  is the spatially varying part of the

concentration. Substituting the concentration perturbations (eq. 8) into the free energy functional (eq. 2) and expanding into a series of small fluctuations  $\delta_i(\mathbf{r})$ , we can decompose the free energy into mean-field and fluctuation correction contributions:

$$\frac{F}{k_{\rm B}T} = \frac{F_0}{k_{\rm B}T} + \frac{1}{2} \int d^3 \mathbf{r} \, \frac{F^{\rm fluct}}{k_{\rm B}T} (\delta_A(\mathbf{r}), \delta_B(\mathbf{r})) + \cdots$$
(10)

where the mean-field part of the free energy described by uniform (average) compositions is  $^{46}$ 

$$\frac{F_0}{k_B T} = \frac{\phi_A}{N_A} \ln(\phi_A) + \frac{\phi_B}{N_B} \ln(\phi_B) + \frac{v}{2} (\phi_A + \phi_B)^2 + \frac{w}{6} (\phi_A + \phi_B)^3 + \chi_{AB} \phi_A \phi_B + \frac{\phi_A}{s_A} [p_A + \ln(1 - p_A)] + \frac{\phi_B}{s_B} \ln(1 - p_B) \quad (11)$$

The deviation of the local monomer volume fraction from its average,  $\delta_i(\mathbf{r})$ , serves as a characteristic order parameter, which is zero in the disordered, homogeneous state and finite otherwise. It proves convenient to use Fourier transformations to provide factorization of fluctuations with different wave vectors  $\mathbf{k}$  and represent the fluctuation-induced variation of the free energy (truncated at the leading term in the  $\delta_i$  series expansion) as

$$\frac{F}{k_{\rm B}T} = \frac{F_0}{k_{\rm B}T} + \frac{1}{2} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \mathbf{S}^{-1}(\mathbf{k}) \delta_j(\mathbf{k}) \delta_l(-\mathbf{k})$$
(12)

with j, l = A, B. The kernel in eq. 12 is the inverse structure factor matrix

$$\mathbf{S}^{-1}(\mathbf{k}) = \mathbf{S}_0^{-1}(\mathbf{k}) + \mathbf{U}(\mathbf{k})$$
(13)

and in the random phase approximation can be separated into intra-chain  $\mathbf{S}_0^{-1}(\mathbf{k})$  and inter-

action  $\mathbf{U}(\mathbf{k})$  contributions.<sup>57–60</sup> The interaction matrix has components:

$$U_{AA}^{-1} = v + w(\phi_A + \phi_B) + \frac{1}{s_A^2} \left( \frac{1 + \left(\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right)\lambda}{2\frac{\phi_A}{s_A}\sqrt{1 + 2\left(\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right)\lambda + \left(\frac{\phi_A}{s_A} - \frac{\phi_B}{s_B}\right)^2\lambda^2}} - \frac{1}{2\frac{\phi_A}{s_A}} \right)$$
(14)

$$U_{BB}^{-1} = v + w(\phi_A + \phi_B) + \frac{1}{s_B^2} \left( \frac{1 + \left(\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right)\lambda}{2\frac{\phi_B}{s_B}\sqrt{1 + 2\left(\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right)\lambda + \left(\frac{\phi_A}{s_A} - \frac{\phi_B}{s_B}\right)^2\lambda^2}} - \frac{1}{2\frac{\phi_B}{s_B}} \right)$$
(15)

$$U_{AB}^{-1} = U_{BA}^{-1} = v + w(\phi_A + \phi_B) + \chi_{AB} - \frac{1}{s_A s_B} \left( \frac{\lambda}{\sqrt{1 + 2\left(\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right)\lambda + \left(\frac{\phi_A}{s_A} - \frac{\phi_B}{s_B}\right)^2 \lambda^2}} \right) (16)$$

which balance short-range repulsions with sticker-sticker attractions. The repulsions add to the excess free energy of interaction and are positive, while the attractions reduce the free energy of interaction, subtracting from  $U_{AB}^{-1}$ . The final terms of each interaction matrix component  $U_{ij}^{-1}$  representing the sticker interactions can be recast in the average degrees of conversion of A and B,  $p_A$  and  $p_B = rp_A$ , resulting in

$$U_{AA}^{-1} = v + w(\phi_A + \phi_B) + \frac{1}{\phi_A s_A} \left(\frac{p_A p_B}{1 - p_A p_B}\right)$$
(17)

$$U_{BB}^{-1} = v + w(\phi_A + \phi_B) + \frac{1}{\phi_B s_B} \left(\frac{p_A p_B}{1 - p_A p_B}\right)$$
(18)

$$U_{AB}^{-1} = U_{BA}^{-1} = v + w(\phi_A + \phi_B) + \chi_{AB} - \frac{1}{\phi_A s_B} \left(\frac{p_B}{1 - p_A p_B}\right)$$
(19)

which emphasizes the thermodynamic consequences of pairwise hetero-association, evidenced by interactions dependent on the product  $p_A p_B$ . Importantly, the sign of the sticker interaction term is positive for A - A and B - B self-interactions (i.e., repulsive), but negative and, thus attractive, for A - B cross-interactions.

Rigorously, the connectivity of each polymeric species must be accounted for explicitly in

the inverse intramolecular correlation matrix  $\mathbf{S}_0^{-1}(\mathbf{k})$ . However, unlike simpler supramolecular or telechelic models in which generating functions provide a useful approximation,<sup>61–64</sup> an unlimited number of species are formed by the association of multifunctional polymers that cannot be enumerated. In principle, this case is well suited to the use of the coherent states formalism of polymer field theory,<sup>48,65</sup> which is theoretically capable of specifying all possible reaction products, but the numerical implementation of such models is currently challenging.<sup>48</sup>

Here, we account for the Gaussian chain structure of un-associated chains of A and B and describe the associated chain configurations as an effective  $A_2B_2$  4-arm star copolymer with two arms of  $n_A A$  monomers and two arms of  $n_B B$  monomers around each reticulation site (Fig. 2).<sup>27</sup> This amounts to an affine network approximation and should be most applicable at high polymer concentration and association strength conditions. Consequently, we neglect cyclic<sup>66–68</sup> and higher-order branched species.



Figure 2: (a) Schematic illustration of reversibly bonded mixture of A and B chains. (b) Effective  $A_2B_2$  4-arm star structure of A - B associative polymers used in developing correlation functions.

Within this approximation, we write the total inverse intramolecular correlation function as

$$S_0^{-1}(k) = \frac{\mathrm{H}(n_A - N_A)}{(1 - s_A p_A)\phi_{A\mathrm{gD}}(N_A, k)} + \frac{\mathrm{H}(n_A - N_B)}{(1 - s_B p_B)\phi_{B\mathrm{gD}}(N_B, k)} + \frac{1}{2p_A \phi_A/s_A}\gamma(k)$$
(20)

where H(x) is the Heaviside step function and the bare correlation function is <sup>69,70</sup>

$$\gamma(k) = \frac{g_{\rm D}(n_A, k) + g_{\rm D}(n_B, k) + h_{\rm D}^2(n_A, k) + h_{\rm D}^2(n_B, k) + 4h_{\rm D}(n_A, k)h_{\rm D}(n_B, k)}{\left[g_{\rm D}(n_A, k) + h_{\rm D}^2(n_A, k)\right] \left[g_{\rm D}(n_B, k) + h_{\rm D}^2(n_B, k)\right] - \left[2h_{\rm D}(n_A, k)h_{\rm D}(n_B, k)\right]^2}$$
(21)

The correlations are constructed from the Debye function,

$$g_{\rm D}(n,k) = \frac{2}{(k^2 a^2/6)^2} \left[ e^{-nk^2 a^2/6} + nk^2 a^2/6 - 1 \right]$$
(22)

and a partial Debye-like function

$$h_{\rm D}(n,k) = \frac{1}{(k^2 a^2/6)} \left[ 1 - e^{-nk^2 a^2/6} \right]$$
(23)

that depend on the strand sizes  $n_A$  and  $n_B$  and wave number  $k = |\mathbf{k}|^{55}$  The first two terms in eq. 20 account for the unreacted chains, and the final term is responsible for the reacted strands. The average strand lengths are functions of the degrees of conversion of stickers:  $n_i = s_i/p_i$  reducing at complete conversion to the average number of segments between stickers  $s_i$ . In calculating the correlation functions, we have assumed that the spatial distribution of each block in a multicomponent copolymer obeys Gaussian statistics (recall the use of the Debye function in eq. 21). The assumption breaks down if the blocks are very short (i.e., the distance between cross-links is of order of the persistence length,  $s_i/p_i \gg 1$ ). Although exceptionally crude, we will see that these approximations are sufficient to qualitatively capture the physics of multifunctional associative polymer mixtures.

It is useful to compare this framework with the seminal work by de Gennes on irreversibly cross-linked blends of A and B polymers, where, in an analogy to dielectric polarization, he defined an internal rigidity constant  $\sim n^{-2}$  to capture the elastic contribution of strands of n monomers between cross-links resisting phase separation.<sup>4</sup> From the free energy functional defined above, eq. 12, a Taylor expansion in k produces an analogous  $\mathcal{O}(k^{-2})$  term, with coefficient:

$$\frac{9}{2\rho}\frac{p_A}{s_A}\frac{p_B}{s_B}\left(\frac{p_A}{s_A} + \frac{p_B}{s_B}\right) = \frac{9rp_A^2}{2s_As_B}\left(\frac{1}{\phi_A} + \frac{1}{\phi_B}\right)$$
(24)

where  $p_A$  and  $p_B$  are the average degrees of conversion of A and B stickers. This coefficient is a direct result of the bare correlation functions constructed for the "effective" star polymers constituting the network (Figure 2), which introduced k-dependence. The exact numerical prefactor is dependent on our choices regarding a 4-arm star (as compared to linear diblock or more complex architectures.)

However, we can interpret this coefficient in the same context as de Gennes' phenomenological internal rigidity constant.<sup>4</sup> It increases with decreasing concentration and is inversely proportional to the square of the number of monomers between cross-links, as predicted for the case of permanent networks.<sup>4,71–73</sup> Importantly, this internal rigidity characterizing the elasticity is also highly sensitive to the asymmetry in the concentrations of stickers A and B (directly and implicitly through  $p_A$ ), emphasizing the strong effects of sticker mismatch<sup>46</sup> and spatial inhomogeneity.<sup>74</sup> Furthermore, the elastic constant is proportional to the product of the degrees of conversion of stickers A and B, a consequence of the hetero-binding conditions.<sup>46</sup> As such, the rigidity constant depends on the fractional conversion of binding as was asserted for permanent networks.<sup>71–73</sup>

The homogeneous mixture is unstable to fluctuations when  $\mathbf{S}^{-1}(k)$  is not positive definite. The spinodal condition can then be determined by computing the zeros of the inverse scattering function,  $S^{-1}(k) = 0$ , at its minimum with respect to k while also satisfying the spatially homogeneous mean-field equations. The stability limit equivalently corresponds to a divergence in the scattering function  $S(k^*) \to \infty$  at a critical value of the wave number  $k = k^*$ . Phase separation proceeds macroscopically into two homogeneous phases if the scattering function diverges at k = 0 or into an ordered microphase with periodicity  $D^* = 2\pi/k^*$ if S(k) diverges at a finite value of  $k^*$ . The binodals for coexisting homogeneous phases are determined from the homogeneous limit of the mean-field equations, as in Ref. 46.

While the theory is applicable across the spectrum of binding energies, since heterotypic

interactions tend to be relatively strong (many  $k_{\rm B}T$ ), we focus on discussing the results at a high binding strength between A - B sticker pairs (i.e.,  $\lambda \gg 1$ ). Furthermore, we consider only the heterogeneous bonding limit, in which the stickers of A can only pair with those of B. It is straightforward to generalize the model described above to account for both selfand hetero-complementary linkages (i.e., A - A, B - B, and A - B.)

## **Results and Discussion**

In this framework, we can show that reversible associations between A and B stickers compatibilize the polymer mixture by reducing the effective chemical incompatibility (lowering the "effective"  $\chi_{AB}$  parameter) and driving a competition between associative and segregative phase separation. Associative phase separation into a sticker-poor phase in coexistence with a dense, highly associated network is favored at strong binding and low chemical incompatibility; while, segregative phase separation into A and B-rich phases is favored at weak binding and high chemical incompatibility. For both large degrees of chemical mismatch and strong binding conditions, the balance of attraction and repulsion results in microphase formation and eutectic-like behavior of the polymer alloy. Understanding the interplay of the chemical equilibrium of reversible binding and the tendency for phase separation will enable the development of a wide range of materials and applications. As such, we map out the phase diagrams, gelation conditions, and structures accessible to a solution or melt blend of multifunctional associative polymers that can be driven by molecular design, blend composition, binding interactions, or temperature.

## Competition between Segregation and Sticker Binding

We first consider the competition between repulsions due to chemical incompatibility and attractions due to sticker binding by plotting the phase diagram as a function of the Flory–Huggins interaction parameter  $\chi_{AB}$  and the association strength  $\lambda$  for a specific isopleth (line of constant composition). Figure 3 shows the gelation and phase coexistence conditions of heterotypic associating A and B chains at concentrations corresponding to a binary melt with an overall composition  $\phi_A = \phi_B = 0.5$ . In our mean-field analysis, these phase boundaries will be referred to as lines of critical points (where the spinodal and binodal curves coincide), but due to fluctuations, they are actually weakly first-order transition lines.<sup>75</sup>



Figure 3: Gelation (dashed green line) and phase coexistence conditions (blue lines) for associating polymers of type A - B with  $f_A = f_B = 20$  stickers,  $s_A = s_B = 50$  spacers,  $N_A = N_B = 1000$  degrees of polymerization, and  $\phi_A = \phi_B = 0.5$ . The solid blue line indicates spinodal decomposition at  $k^* = 0$  (macrophase separation) and the dotted blue line indicates spinodal decomposition at  $k^* > 0$  (microphase separation). The transition between macrophase and microphase separation is delineated by the dotted orange curve, which culminates at an isotropic Lifshitz point (coexistence between micro- and macrophase separation and the homogeneous one-phase) marked by an orange triangle. The quad-critical point (coexistence between sol, gel, microphases, and microphase-separated gel) is shown by a green square. Inset: zoom-in of the Lifshitz/quad critical point region.

#### Low Binding: Blend Compatibilization

Considering the phase behavior as  $\lambda$  tends to zero, there are few paired stickers, and the boundary between a homogeneous one-phase and macroscopic phase separation is delineated by a line of critical points with  $k^* = 0$  (Figure 3). At these low binding conditions, above a critical segregation strength, the polymer mixture phase separates macroscopically into Aand B-rich phases. Owing to osmotic compressibility and identical interaction parameters  $(v_A = v_B = v = 0 \text{ and } w_A = w_B = w = 1 \text{ for } \Theta$ -solvent or melt conditions), both phases have the same correlation length and overall concentration, differing only in the composition of A relative to B. The upper critical consolute point, the critical point at which raising  $\chi_{AB}$  transforms a consolute liquid (fully miscible in all compositions) into a phase-separated mixture, is at  $\chi_{AB} > 2/N$  for  $N_A = N_B = N$  and  $\phi_A = \phi_B = 1/2$  in the non-binding limit.<sup>76-79</sup>

As the bond association strength  $\lambda$  increases, the number of paired stickers grows, resulting in reversibly branched block copolymers. Thus, this line of critical points is related to the Scott line, which delineates the boundary between a disordered single-phase and macroscopic phase separation into A and B-rich phases, in A homopolymer, B homopolymer, ABblock copolymer mixtures.<sup>80,81</sup> However, importantly, in the present case, the reversibility of the heterobonding has the consequence that the structure and connectivity are annealed. For low fraction of bonds, below the overlap of attractive volumes, as  $\lambda \to 0$ ,

$$p_A \simeq \lambda \phi_B / s_B \ll 1 \tag{25}$$

and the terms in the free energy (eq. 11) related to associations take the form of pairwise attraction between stickers  $-\lambda \phi_A \phi_B / (s_A s_B)$ , reducing the  $\chi_{AB}$  parameter for A - B twobody interactions by the attractive volume fraction per monomer,  $\lambda / (s_A s_B)$ .<sup>46</sup> In this regime, corresponding to low conversion of stickers, the phase behavior can be described with the classical Flory–Huggins result for polymer blends<sup>76–78</sup> (or solutions in a non-selective solvent<sup>79,82</sup>) by replacing  $\chi_{AB}$  by

$$\chi_{AB}^{\text{eff}} = \chi_{AB} - \lambda / (s_A s_B). \tag{26}$$

This implies that the physical associations between different species improve their miscibility.

Accordingly, the boundary for phase separation shifts to higher  $\chi_{AB}$  as the strength of sticker associations increases, i.e., compatibilization (shift to lower  $1/\chi_{AB}$  in Figure 3).

It is the underlying reason why a phenomenological negative interaction parameter  $(\chi_{AB} < 0)$  is often successful at describing the interaction for associating polymers.<sup>83,84</sup> For example, blends of polystyrene/poly(xylenyl ether) (PS/PXE) are miscible in all proportions over a wide range of temperatures and molecular weights due to specific interactions between the PS phenyl rings and the PXE backbone; their phase behavior can be well described by simple solution theories using an effective interaction parameter of the form  $\chi_{AB} \sim -A + BT$  accounting for negative heat of mixing and negative local entropy of mixing.<sup>85</sup> Other miscible mixtures, including polyolefins, polycarbonates, and polyacrylates, have also been shown to require specific interactions between blend components to explain the temperature dependence of the measured negative interaction parameter.<sup>86-90</sup>

Such an approach essentially "smears" out the attractive sticker interactions over all monomers as an effective interaction parameter. It works in the limit of low degree of sticker conversion, below the overlap of attractive volumes, in which the fractional conversion increases linearly with the attractive volume fraction of stickers (eq. 25) and, accordingly, is valid for low association strengths,

$$\lambda < \left[\frac{\phi_A}{s_A} + \frac{\phi_B}{s_B}\right]^{-1}.$$
(27)

Thus, describing the system by an effective interaction parameter is ideal for homogeneous distributions of stickers with weak associations, as observed experimentally,<sup>85–90</sup> or with a smaller number of stickers that are more strongly associating, but spaced farther apart. This reinforces the balance of the excluded volume and chi interactions that occur between all monomers and the associative interactions that occur only between stickers.

#### Intermediate Binding: Micro-Ordering

With increasing  $\lambda$ , an increasing number of branched block copolymers form, becoming the dominant species. At this point, for a stoichiometric mixture of chains and stickers, there is on average one bond per chain. The chemically dissimilar segments are now joined at the reticulation site of paired stickers and can only segregate locally rather than macroscopically, resulting in the appearance of microphases. This is a special tri-critical point in the phase diagram (Figure 3), called the Lifshitz point, which corresponds to the coexistence of macrophase separation (into A and B-rich phases), microphase separation (into a locally segregated ordered mesophase), and a disordered phase.<sup>91</sup>

At the mean-field level, the appearance of Lifshitz points does not significantly affect the phase diagram (Figure 3). However, outside the theory described in Section 2, Lifshitz points are known to be unstable to strong thermal fluctuations in three dimensions and are replaced by a narrow region of bicontinuous microemulsions, a highly structured sponge-like disordered phase.  $^{16,92,93}$  Thus, it could be expected that the *A* and *B*-rich regions would contain solvent (if present) and unreacted homopolymers, but that more highly connected chains would be driven to the interface, resulting in essentially zero interfacial tension. Bicontinuous microemulsions are particularly important and interesting with regard to polymer alloys because the properties (e.g., permeability or conductivity) of one blend component are passed on to the entire material and the mechanical properties are maximized.  $^{11,93}$  The use of multifunctional associating polymers to access this phase and tune their formation conditions should be advantageous.

Although the quantitative prediction of the location of the Lifshitz point depends on our approximation of the structural correlations as an effective 4-arm star copolymer (Figure 2), we expect that this would not be appreciably altered (by a factor of order unity) by a more complete description of the chain structures. Unlike most discussed Lifshitz points in polymer blends, where a single AB block copolymer species is added to a mixture of A and B homopolymers, <sup>92,94,95</sup> at our Lifshitz point, there is an ensemble of unreacted homopolymers

with a statistical distribution of branched copolymers with two or more blocks/branches of various sizes and topologies. It would be interesting to check (experimentally with scattering or microscopy and computationally) if the inclusion of the higher order branched block copolymers affects the structure of the bicontinuous microemulsions, perhaps by stabilizing select interfacial curvatures.<sup>72,96–100</sup>

Beyond the isotropic Lifshitz point, at a higher  $\lambda$  and thus more connected copolymers (with > 1 paired stickers per chain on average), there exists a line of critical points  $(k^* \neq 0)$ that correspond to the transition from a disordered phase to an ordered microphase with increasing  $\chi_{AB}$  (Figure 3). For pure diblock copolymers, this is termed the Leibler line and occurs at  $\chi_{AB}(N_A + N_B) \simeq 10.495$  in mean-field theory.<sup>101</sup> However, in the present case, we have a mixture of differently bonded and branched copolymers (treated to first approximation as a mixture of non-bonded homopolymers and effective star block copolymers, Figure 2), with strand lengths that shorten with increased binding,  $n_i = s_i/p_i$ .

We have seen that small degrees of cross-linking can hinder macroscopic phase separation and induce microphases. On the contrary, it is well known that microphase separation is suppressed by increasing the cross-linking density.<sup>4,72,102</sup> The  $\lambda$ -dependent strand length is the primary reason for the increase in critical  $\chi_{AB}$  needed for microphase separation. For macrophase separation of a binary blend of polymers A and B with degrees of polymerization  $N_A = N_B$ , the relevant parameter is  $\chi_{AB}N_A = \chi_{AB}N_B$ . For chains of A singly paired with chains of B, the relevant parameter for microphase separation is now  $\chi_{AB}(N_A + N_B)$ . As sticker binding increases and the lengths of the strands between the cross-links decrease, the relevant parameter for phase segregation also changes:  $\chi_{AB}(n_A + n_B)$ . At complete binding, this becomes  $\chi_{AB}(s_A + s_B)$ , which corresponds to the balance of entropy and chemical incompatibility of the strands. As the number of segments joined by a single cross-link decreases from  $N_A + N_B$  to  $s_A + s_B$  (as  $\lambda$  increases and more stickers are paired), the critical  $\chi_{AB}$ necessary for microphase segregation also increases.

At a slightly higher  $\lambda$ , with a higher fraction of bonds, there are, on average, two paired

stickers per chain, signaling the onset of gelation. This results in the appearance of what has been termed a quad-critical point, in which a single-phase (sol), microphase-separated sol, homogeneous gel, and microphase-separated gel coexist. This quad-critical point is more aptly described as the gel point, as nothing special happens at the gelation threshold, since it is not thermodynamic, but rather a connectivity transition.<sup>73</sup> Below the gel point, the chains have yet to connect through the entire sample, but the elastic restoring forces between crosslinked A and B chains are still present, resulting in only local phase segregation: microphase separation takes place for  $\lambda$  both above and below the critical  $\lambda^{\text{gel}}$  for percolation (Figure 3). As we will see from the analysis of the microphase domain spacing, the domain spacing  $D^* = 2\pi/k^*$  is continuous at the gel point, diverging only at the Lifshitz point (when the mixture transitions between microphase and macrophase separation). This is in contrast to the connectivity length  $\xi_{\text{gel}}$  (i.e., the mesh size of the gel), which diverges at the gel point.

In this analysis, we find that the Lifshitz point and the quad-critical point (gel point) are remarkably close (less than a factor of 2) in phase space in both  $\chi_{AB}$  and  $\lambda$  (Figure 3). This agrees with previous work on end-linked miktoarm stars, wherein the points converge with increasing functionality of stickers from two to five,<sup>29</sup> and in the present analysis we have a 10× increase in the number of stickers per chain. Recall that the Lifshitz point corresponds to, on average, one cross-link per chain, and the gel point corresponds to, on average, two cross-links per chain. An interesting opportunity, with the gel point so close to the Lifshitz point, is the possibility for reversibly-"gelled" bicontinuous microemulsions, from which many applications could be envisaged.

#### High Binding: Connected Networks

For strong binding conditions, well above the overlap of attractive volumes, as  $\lambda \to \infty$ , the tendency is to form highly connected copolymer networks, again emphasizing the robust compatibilization effect of cross-linking the polymer blend. At high segregation strengths, these tight gels are primarily microphase separated, the structure of which is discussed

below. However, the microphase and gelation boundaries tend towards higher values of  $\lambda$  at higher  $\chi_{AB}$ . It has been suggested that this occurs because the coexisting homogeneous phases become purer, limiting the ability to associate and form a network.<sup>29,62</sup> In our current framework, at the highest association and segregation strengths, we predict macroscopic phase separation into two coexisting gel phases and ultimately into two coexisting sol phases as  $\chi_{AB}$  is increased. It is also possible that more "pure" microphases connected by sticker bonds localized to sharp interfaces are favored (relative to macrophase separation); however, the current weak inhomogeneity expansion-based theory does not account for chain stretching or sharp interfaces.

The conditions for these thermodynamic and connectivity transitions can be estimated by calculating an effective interaction parameter that describes attractive sticker interactions. In the limit of low sticker binding, as  $\lambda \to 0$ , we showed that these attractions could be described by the attractive volume per monomer  $-\lambda/(s_A s_B)$  (eq. 26). A repulsive chi parameter of the same magnitude is required to overcome the sticker pairing. Across the entire range of bonding strengths, the sticker associations that balance the chemical incompatibility, at the stability limit of the mixture, takes the form:

$$\chi_{AB} \simeq \frac{p_A}{\phi_B s_A (1 + \sqrt{r} p_A)} \simeq \frac{r p_A}{\phi_A s_B (1 + \sqrt{r} p_A)} \tag{28}$$

This simple equality is obtained from the spinodal condition at k = 0 (in the v = 0, w = 1, and  $N \to \infty$  limits). For strong binding strengths and strong segregation, where the physical behavior of the system is dominated by sticker attractions and chemical incompatibility, this should be a decent approximation of the phase boundary between homogeneous and microphase-segregated networks.

Considering  $\lambda \gg 1$  (and r = 1) such that the stickers have gone to complete conversion  $(p_A, p_B \rightarrow 1)$ , this balance of chemical incompatibility and sticker attraction becomes  $\chi_{AB} \simeq 1/(\phi_B s_A) \simeq 1/(\phi_A s_B)$ . For sticker stoichiometric mixtures, r = 1, we can further express

this condition as,

$$\chi_{AB} \simeq \frac{1}{s_A s_B} \sqrt{\frac{s_A}{\phi_A}} \sqrt{\frac{s_B}{\phi_B}}$$
(29)

which is inversely proportional to the geometric average sticker concentration  $\sqrt{(\phi_A/s_A)(\phi_B/s_B)}$  normalized by the numbers of chemically dissimilar segments per strand  $s_A$  and  $s_B$ . For segregation strengths larger than eq. 29, the chemical incompatibility between A and B segments will start to break the reversible sticker bonds and drive macrophase separation.

For even stronger segregation, the degrees of conversion of A and B will continue to decrease. Eventually, at sufficiently large  $\chi_{AB}$ , the chemical incompatibility will have driven enough bonds to break for the sample to de-percolate and transition from a gel to a sol. This condition can be estimated by considering eq. 29 as the amount of chemical incompatibility needed to break one sticker bond on average. Accordingly, to break  $\sqrt{(f_A - 1)(f_B - 1)}$ cross-links to de-percolate the reversible network, segregation strengths larger than

$$\chi_{AB} \simeq \frac{\sqrt{(f_A - 1)(f_B - 1)}}{s_A s_B} \sqrt{\frac{s_A}{\phi_A}} \sqrt{\frac{s_B}{\phi_B}} \simeq \frac{1}{s_A s_B} \sqrt{\frac{N_A}{\phi_A}} \sqrt{\frac{N_B}{\phi_B}}$$
(30)

are needed (where in the second equality we have assumed  $f_A, f_B \gg 1$ .) The transition from microphase to macrophase separation of the strongly segregated gels is expected to occur on the same order of  $\chi_{AB}$ , but intermediate to the conditions of eqs. 29-30. Full spatial calculations are likely required for accurate characterization of the microphases and phase boundary determination in such strongly segregated inhomogeneous gels.

## **Compositional Dependence**

Next, we consider the effect of the Flory–Huggins interaction parameter  $\chi_{AB}$  on the phase diagram of heterotypic associating A and B chains in a common,  $\Theta$  solvent as a function of monomeric concentrations  $\phi_A$  and  $\phi_B$  (Figure 4). Although the system is a ternary incompressible mixture (A-polymer–B-polymer–solvent), it is convenient to examine the dependence of the concentration  $\phi_A$  relative to  $\phi_B$ , with the solvent concentration  $(1 - \phi_A - \phi_B)$  implicit. Note that in Figure 3, the phase boundaries shown are lines of critical points corresponding to both spinodal and binodal conditions. However, we should note that beyond the onset of eutectic behavior (discussed below), as  $\lambda \to \infty$  and  $1/(\chi_{AB}N) \to 0$ , the isopleth spinodal may no longer be identical to the binodal condition, and should be considered approximate in Figure 3. In Figure 4, the binodal (metastable) and spinodal (unstable) conditions for phase coexistence are shown, along with representative tie lines between the co-existing compositions.



Figure 4: Phase diagram of a  $\Theta$ -solution of A - B associating polymers with  $f_A = 20$ ,  $f_B = 50$ ,  $s_A = 50$ ,  $s_B = 20$ ,  $N_A = N_B = 10^4$ , v = 0, w = 1,  $\lambda = 1000$ , and  $\chi_{AB} = 0.2$ . The binodal boundaries for the two-phase regions are shown with solid dark blue lines. The spinodal boundaries are shown with dotted dark blue lines. The dotted orange lines separate the macro- and microphase separation regions, and the dashed light blue lines are representative tie lines between coexistence points. Purple circles show the spinodal phase boundary in the absence of chemical incompatibility,  $\chi_{AB} = 0$ , for comparison. The shaded grey region is inaccessible due to incompressibility.

In the absence of chemical incompatibility ( $\chi_{AB} = 0$ , Figure 4), there is a large two-phase

region at low to intermediate monomeric concentrations. This macroscopic phase separation is caused by the associations between stickers, resulting in a dilute supernatant coexisting with a dense, more symmetric gel phase (Figure 4).<sup>46</sup> Note that the dilute coexisting phase is outside the applicability of and cannot be described by the current mean-field model, but it is expected that the concentration of this phase will be exponentially low. As the chemical incompatibility between the A and B chains increases, this region of associative phase separation shrinks (as shown for  $\chi_{AB} = 0.2$  in Figure 4) and ultimately disappears at higher  $\chi_{AB}$ .

We can understand this trade-off between repulsive chemical incompatibility interactions and attractive sticker pairing by using the effective chi parameter from eq. 28. Increasing the bare chi parameter between A and B chains transforms the interactions from dominantly attractive to balanced (and thus, overall stable) to dominantly repulsive. Balanced net interactions occur at  $\chi_{AB} \simeq p_A/[\phi_{BS_A}(1+\sqrt{r}p_A)]$  (eq. 28). At and above this condition, the effective repulsion between unlike segments (in the presence of an implicit solvent) stabilizes the polymer mixture at relatively low monomeric concentrations near the polymer overlap concentration  $\phi^* = (\phi_A + \phi_B)^*$ . This occurs by resisting condensation into a dense gel phase in which there is more A - B repulsion induced by chemical incompatibility.

However, at higher total concentrations (concentrated solutions and melts), new regions of segregative phase separation appear in previously stable compositions<sup>46</sup> with increased chemical incompatibility, driven by the repulsion of dissimilar segments (Figure 4). A standard result of the Flory–Huggins model for chemically different polymers (without associations between stickers,  $\lambda \rightarrow 0$ ) is that phase separation may occur when the interaction parameter  $\chi_{AB}$  is positive and greater than a certain critical value:<sup>76–79</sup>

$$\chi_{AB} \ge \frac{1}{2} \left[ \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B} \right] \tag{31}$$

In contrast, for hetero-binding associative polymers, we find regions of macrophase sep-

aration into an A- or B-rich gel phase in coexistence with a nearly symmetric gel (Figure 4). This lack of segregative phase separation at symmetric sticker conditions can be interpreted as compatibilization of the immiscible blend mixture. As in permanently cross-linked blends, the cross-linked system is more miscible than the non-cross-linked mixture. <sup>4,103</sup> The sticker attractions counteract the  $\chi_{AB}$  repulsions driving phase separation. The result is the stability of a dense gel network with many paired stickers. Recall the balance of  $\chi_{AB}$  and the effective attraction imposed by stickers, eq. 28, which shows that in this regime, the sticker attractions simply reduce the effective chi, stabilizing the solution. As such, the regions of symmetric gel–asymmetric sol coexistence maximize the number of bound A - B sticker pairs while also minimizing the interactions between different segments. The easiest way for the system to achieve this optimum is to create a saturated, well-connected gel network and expel excess polymers into a phase rich in one species with less penetration and connectivity of the unlike components.

However, microphase formation appears within the repulsive phase separation regions for melts and concentrated solutions with slightly off-stoichiometric stickers for A and B(Figure 4c). Unlike sticker-stoichiometric gels that tend to remain homogeneous, there is an excess of unpaired stickers and their corresponding spacer strands. In highly nonstoichiometric mixtures, the excess can be macroscopically expelled from the gel; however, for near-stoichiometric mixtures, the elastic forces resulting from the presence of cross-links resist the natural tendency for macroscopic phase separation.<sup>4,72</sup> This competition drives local microphase separation, with the appearance of microdomains alternatively rich in A and B. The microphase separation regions flank the gel region in one phase at near-stoichiometric ratios of A to B stickers, indicating that for slight differences in the number of stickers, local segregation is advantageous.

Note that the gel condition (at lower concentrations than shown in Figure 4) is unchanged in our analysis by the increase in chemical incompatibility, as we do not account for the reduced contact and interpenetration of chains as a function of chemical incompatibility.<sup>104–106</sup> In part, this is due to our RPA framework, in which the concentrations are only weakly spatially varying, which is most appropriate for weak segregation strengths. Furthermore, we do not account for the spatial variation of the solvent, which has been shown to be enriched at A - B interfaces, reducing the repulsion between A and B-rich domains.<sup>107</sup> Additionally, we have considered the case where the suspending solvent is not selective to either component of the blend. If the solvent preferentially solvates one species, it becomes consequential to account for micellar structures of the copolymers, reduction of chain interpenetration, and microdomain swelling to accurately describe the phase equilibria.<sup>79,108,109</sup>

For illustration, in Figure 4, we show the phase diagram for a mixture of chains with asymmetric numbers of stickers per chain  $f_A \neq f_B$ . In the absence of chemical incompatibility, the associative phase separation region is symmetric with respect to the sticker number densities  $\phi_A/s_A$  and  $\phi_B/s_B$ , highlighting that the sticker-sticker attractions drive phase separation.<sup>46</sup> Here, the associative phase separation region is asymmetric and tilted towards lower  $\phi_B$ , due to the higher density of stickers on *B* chains relative to *A* chains,  $s_B < s_A$ . In the non-binding limit, the regions of segregative (macro- and micro-) phase separation depend on the chain sizes  $N_A$  and  $N_B$  as well as the polymer volume fractions  $\phi_A$ and  $\phi_B$ , underscoring the importance of the balance between chemical incompatibility and translational entropy. Here, the segregative phase-separation regions resulting from the  $\chi_{AB}$ interactions are substantially asymmetric because of the relative difference in the number of stickers per chain that can compatibilize the segments of *A* and *B*.

Importantly, the  $\chi_{AB}$  repulsions act between all unlike monomers but are countered by associations that occur only between sticky monomers. This asymmetry in sticker density per chain, i.e., the size of the spacer between associative groups, leads to the strongest effects on the phase diagram and resultant physical behavior, which is why we have highlighted its effects in Figures 4-5. Collectively, these effects of various asymmetries highlight the importance of sticker mismatch in determining the phase behavior and physical properties of heterotypic associative polymers.<sup>46</sup> The chemical compatibilization at near-stoichiometric sticker conditions and the effects of sticker mismatch can be explored more fully by looking at the  $\chi_{AB}$ -dependence of the phase boundaries at a specific total concentration and varying the ratio of A to B. Figure 5 depicts the phase boundary in the coordinates of a temperature-like axis  $(\chi_{AB}N)^{-1}$  versus  $\phi_A = 1 - \phi_B$  (varying ratio of A to B in the absence of solvent). The phase envelope denotes the spinodal condition for macro- and microphase separation, with a local minimum at sticker stoichiometry:  $\phi_A/s_A = \phi_B/s_B$  (r = 1). For illustration, Figure 5 is shown for A and B chains with different spacer lengths between stickers,  $s_A \neq s_B$ . This results in an inherent asymmetry in both the compositional and temperature-like axes. The local minimum (maximum in  $\chi_{AB}$  required for phase separation) occurs at,

$$\phi_A = s_B / (s_A + s_B) \tag{32}$$

which is  $\phi_A = 0.714$  for the conditions in Figure 5, and can be described as a "eutectic point." At the eutectic composition (eq. 32), all stickers can bond, and the potential sticker attractions are at their strongest. Miscibility is substantially reduced for compositions away from the eutectic point, as unreacted stickers of the excess reactant are expelled from an otherwise highly connected network.

The eutectic miscibility increases with  $\lambda$ , and at infinite  $\lambda$  there is always a one-phase homogeneous gel at sticker stoichiometry. At finite  $\lambda$ , raising  $\chi_{AB}$  eventually induces phase separation in the eutectic composition at high enough segregation by breaking sticker bonds. Accordingly, we can use eq. 29, the chemical incompatibility necessary to break reversible bonds, to define a critical segregation strength at the eutectic point:

$$\chi_{AB}\left(\frac{s_A s_B}{s_A + s_B}\right) \simeq 10.495 \tag{33}$$

Consequently, in a metallurgical interpretation, we can define the two maxima in the spinodal as "compounds" that occur at  $\phi_A = 1 - \phi_B = 1 - N_B/(N_B + 2s_A) = 0.091$  and  $\phi_A =$ 



Figure 5: Gelation (dashed green lines) and spinodal conditions (solid and dotted blue lines) for associating polymers of type A - B in a solvent-free blend  $\phi_A + \phi_B = 1$  with  $f_A = 20$ ,  $f_B = 50$ ,  $s_A = 50$ ,  $s_B = 20$ ,  $N = N_A = N_B = 1000$  at a fixed  $\lambda = 10^4$  in the  $\chi_{AB}^{-1} - \phi_A$  plane. Lifshitz points are indicated by orange triangles.

 $N_A/(N_A + 2s_B) = 0.969$  for the conditions in Figure 5. The approximate critical segregation strength at the compounds corresponds to the product  $\chi_{AB}s_A$  for the compound at low  $\phi_A$  and  $\chi_{AB}s_B$  for the compound at low  $\phi_B$ . These compounds should correspond to the compositions of the A and B-rich domains of the microphases. Within the microphaseseparated region, altering the monomeric ratio of A to B,  $\phi_A = 1 - \phi_B$ , simply alters the relative fraction of each domain within the microstructure, which would lead to different geometrical packing such as lamellae, cylinders, and spheres. The structure factors and domain spacing of these microphase-separated gels will be discussed below.

Notably, for the melt blend conditions considered in Figure 5, most compositions result in microphase separation. Otherwise, phase separation proceeds macroscopically into coexisting A-and B-rich gels, except for high segregation strengths, in which phase separation results in nearly pure A-and B-rich sol phases. The points at which the spinodal transitions from macro- to microphase separation are isotropic Lifshitz points—tri-critical points where homogeneous two-phase, homogeneous disordered, and microphase-separated regions coexist. The Lifshitz compositions occur at  $\phi_A = 1 - \phi_B = 1 - N_B/(N_B + s_A) = 0.048$  and  $\phi_A = N_A/(N_A + s_B) = 0.980$ . For chain lengths  $N_A = N_B = 1000$  and spacer lengths  $s_A = 50$  and  $s_B = 20$ , the Lifshitz compositions are very close to those of the "compounds" in Figure 5. The Lifshitz and "compound" compositions tend towards nearly pure A and B phases as the chain lengths  $N_A$  and  $N_B$  increase or the spacer lengths  $s_A$  and  $s_B$  decrease. Conversely, the gaps between these points should widen for shorter chains with fewer stickers and longer spacers. Although our mean-field calculations do not capture the importance of fluctuations, it is known that Lifshitz compositions are accurately predicted by mean-field theory, at least for well-defined mixtures of homopolymers and diblock copolymers.<sup>16</sup> However, this might not be necessarily true in the present theory, where we approximated the associating mixture as 4-arm star copolymers and un-reacted homopolymers, particularly since the Lifshitz and "compound" compositions are close to the component overlap concentrations, and thus, the boundary for applicability of mean-field.

## Microdomain Structure and Properties

So far, we have focused on predicting the existence of microphase separation for the described reversible networks rather than on a description of the resultant structure. Various microphases can exist depending on the total concentration of the mixture and the relative composition of the polymer blend (melt or solution in a non-selective solvent). Naïvely, we would expect that near symmetric polymer volume fractions, the microphase formed should be lamellar in nature, whereas hexagonal or spherical structures would prevail for compositionally asymmetric mixtures.<sup>48,110</sup> However, we expect that for the multicomponent copolymer networks considered, random elastic forces will likely destroy long-range order, as is known for permanent networks in which orientational order and more ordered microstructures could result from anisotropic deformation.<sup>111,112</sup> In reality, Monte Carlo simulations of reversible multicomponent networks have shown topologically disordered networks with network rearrangement occurring cooperatively on scales larger than the distance between cross-links.<sup>113</sup> Further, randomly end-linked reversible copolymer networks have been shown to exhibit a wide window of co-continuous disordered phases.<sup>10</sup>

Thus, in general, we believe that the microphase separation is primarily local, where small regions alternately become more concentrated in A or B. We do not achieve a complete description of the microphase structure or symmetries, which would require much more elaborate calculations.<sup>101</sup> Stabilizing ordered phases and calculating coexistence is difficult in part because of the large distribution of unreacted homopolymers and complex branched copolymers. Homopolymers swell the microdomains of the ordered phases, whereas complex block copolymers would prefer the interfaces between A-and B-rich regions. Moreover, the stability of ordered phases at intermediate values of  $\lambda$  is possibly an artifact of the mean-field assumption, and fluctuation effects would cause the system to be disordered.<sup>55,114–116</sup>

Figure 6a-b illustrate the effects of  $\lambda$  and  $\chi_{AB}$  on the structure factor of the associating polymer mixture. S(k) has a maximum at the most probable concentration fluctuations  $k^* \neq 0$ . The peak narrows and grows in intensity with increasing  $\chi_{AB}$  (Figure 6a), and smears to a broad maximum at smaller distances (larger k) with increasing  $\lambda$ .<sup>117</sup> The scattering function diverges at the spinodal where the homogeneous melt is unstable to concentration fluctuations of wavelength  $2\pi/k^*$ , resulting in a microphase-separated structure with a domain size of  $D^* = 2\pi/k^*$ . Except for the macrophase-separating samples, in which S(k)diverges at k = 0, the structure factor tends to zero because of the absence of quenched disorder, which is a consequence of the reversible nature of the cross-links. This conveniently allows us to avoid the need for replica methods necessary in permanent networks.<sup>42</sup> The broad tail of the structure factor is indicative of networks with correlations between sticker pairs at length scales smaller than the interfacial width of the domains.<sup>112</sup>

At a specified segregation strength  $\chi_{AB} = 0.01$ , the peak in S(k) shifts to a smaller k as the strength of the sticker associations decreases from  $\lambda = 1000$  to 10, before ultimately diverging at k = 0 for low  $\lambda$  (Figure 6a), that is, macrophase separation in the limit of no sticker binding. Ignoring stretching due to strong segregation, at high  $\lambda$ , the domain size



Figure 6: (a,b) Structure factor and (c-f) characteristic length-scales for A - B associating polymers with  $\phi_A = \phi_B = 0.5$ ,  $f_A = f_B = 20$ ,  $s_A = s_B = 50$ ,  $N_A = N_B = 1000$ , v = 0, and w = 1 (unless otherwise noted) for different bonding strengths and chemical incompatibility. (a) The structure factor weakens and shifts to higher k for fixed  $\chi_{AB} = 0.01$  with increasing  $\lambda$ . (b) The structure factor intensifies for fixed  $\lambda = 10$  with increasing  $\chi_{AB}$ . (c) The domain size at fixed  $\chi_{AB} = 0.01$  is strongly dependent on  $\lambda$ . The dashed green line indicates the gel point, and the dotted orange line indicates the Lifshitz point and a discontinuous divergence in the domain size. The mesh size of the gel  $\xi_{gel}$ , the connectivity length scale, diverges at the gel point. (d) The domain size for fixed  $\lambda = 10$  is independent of the chemical incompatibility. (e) The domain size increases as the square root of the number of segments in the spacer.  $N_A = N_B = 10^5$ ,  $\lambda = 1000$ ,  $\chi_{AB} = 0.1$  (f) The domain size and mesh size of the gel decrease with increasing polymer volume fraction.  $N_A = N_B = 10^5$ ,  $\lambda = 1000$ ,  $\chi_{AB} = 0.1$ .

is minimized on the order of the Gaussian size of the spacers,  $D^* \simeq a(s_A + s_B)^{1/2}$ . Upon decreasing sticker association strength, the domain periodicity of the microphase separation increases steadily as the average number of segments in the strand between the reticulation points,  $s_A/p_A$  and  $s_B/p_B$ , increases (Figure 6c,e). Notably, this implies that the domain size can be approximated as the Gaussian size of the copolymer strands around the cross-link (recall "effective" star polymer, Figure 2):

$$D^* \simeq a \left(\frac{s_A}{p_A} + \frac{s_B}{p_B}\right)^{1/2} \tag{34}$$

until finally diverging discontinuously at the Lifshitz point. At lower  $\lambda$ , the polymers macrophase separate; at higher  $\lambda$ , the polymers microphase separate with a domain spacing of the order of the radius of gyration of a singly cross-linked A and B chain:  $D^* \simeq a(N_A + N_B)^{1/2}$ (Figure 6c). Note that nothing special occurs with the domain spacing at the gelation threshold. At high association, the domain periodicity tends towards twice the mesh size of the network, i.e., the distance between cross-links,  $\xi_{gel}$ . However, this connectivity length diverges at the gel point as the network loses percolation, while the domain spacing remains a continuous function of  $\lambda$  (Figure 6c). This is because the paired stickers have yet to percolate, but still drive a critical length scale for the copolymer to locally phase segregate.

In contrast, for a specified sticker association strength  $\lambda = 10$ , the peak in S(k) intensifies at the same wave number, and the domain size is seemingly unperturbed by an increase in the segregation strength (Figure 6b,d). While this is in good agreement with the theory and simulations of permanently cross-linked polymer blends<sup>4,73,113,117</sup> it is contrary to simulations of reversibly associating blends<sup>30</sup> and might be an artifact of our RPA approach, which is most appropriate for weak segregation. Because the cross-links are reversible, we might otherwise expect the microdomains to be better described by strong segregation theory (as for block copolymers), in which we would expect stretched domains of size  $D^* \simeq an^{2/3}\chi_{AB}^{1/6}$ , where *n* is the strand length.<sup>118,119</sup> Additionally, direct comparisons between linear diblock copolymers and star copolymers (such as the  $A_2B_2$  "effective" network strand we consider, Figure 2), have shown that the entropic penalty of junction points localized to the A - B interface increases chain stretching and domain elongation.<sup>120,121</sup> The present theory could be expanded to account for such effects.

The period of the microdomains is also a decreasing function of the concentration, owing to the reduced sticker association (Figure 6f). Recall that chain stretching due to swelling or strong segregation was not included in the current model. The scaling of the domain size with the total polymer volume fraction follows the same dependence as the gel connectivity over these conditions (away from the gel point). Thus, we can conclude that the microphase separation is dominated by the topological properties of the network, at least for weak segregation (relative to sticker association). This can be justified by the expectation that the A - B cross-links are localized at the interface between the A and B-rich domains, and that the gel connectivity dictates the accessible length scale for phase segregation. This is in agreement with recent simulations by the Jayaraman group, which demonstrated the importance of sticker placement along the chain on the resultant microdomains.<sup>30</sup> These results give additional handles on the molecular design of these materials, as the domain size can be adjusted by changing the size of the spacers between sticky groups or by the concentration of the mixture (Figure 6e,f).

# Conclusions

The physical system we have considered is a mixture of two multifunctional hetero-associating polymers A and B of different chemical nature. The aim was to study the effects of chemical incompatibility on the reversible network formation and corresponding phase behavior using an extension of the mean-field model for A - B associative polymers to account for local compositional fluctuations. Using this model, we calculated the structure factor, which allowed us to determine the microphase properties.

The central result is that reversible bonds between hetero-complementary associating groups can compatibilize immiscible polymer blends. The transient cross-links formed by the associations form branched block copolymers, which can percolate the system to create copolymer networks. These networks, both dry elastomers and gels swollen with a solvent, exhibit eutectic-like behavior. At higher degrees of chemical incompatibility, the networks assemble into microphase-separated domains because the elasticity imparted by the crosslinks resists macroscopic phase separation, establishing a microscopic domain size. The resultant microdomain structure can be tuned by adjusting the association and segregation strengths, concentration, and spacer size between stickers.

These results are the first comprehensive theoretical description of the chemical compatibilization and macro- and microphase separation of mixtures of associating polymers with numerous stickers per chain. In the limit of low chemical incompatibility, the model reduces to prior mean-field models of associative polymers.<sup>46</sup> At strong binding conditions ( $\lambda \rightarrow \infty$ ), the results are consistent with scaling model, random phase approximation, and molecular dynamics simulations predictions of permanently cross-linked polymer blends.<sup>4,71,73,117,122–124</sup> Furthermore, the results are qualitatively consistent with field-theoretic simulation predictions for reversibly end-linked tri- and tetra-functional associative polymers<sup>29,125</sup> and coarsegrained molecular dynamics simulations of regularly spaced Hydrogen bonding blends.<sup>30</sup>

We can easily extend the formalism presented here to a mixed bonding case, where A-A, A-B, and B-B cross-links all occur in the polymer mixture. In this case, hetero-bonding competes with homo-bonding, depending on the relative strength of the associations, i.e.,  $\epsilon_{AB} > \text{or} < \epsilon_{AA}, \epsilon_{BB}$ . As illustrated for the simple case of heterotypic A-B associations, the presence of hetero-bonded chains (i.e., copolymers) can stabilize mesophases that compete with homogeneous phases.

For simplicity, we considered the equilibrium conditions; however, there is a complex interplay between the kinetics of gelation and phase separation.<sup>103</sup> In particular, we have described simultaneous associations and segregation, but the order of sample processing might dictate the resultant physical properties. For example, at high  $\chi_{AB}N$ , strongly segregated mixtures can affect the ability of unlike stickers to find each other and cross-link, thereby shifting the gelation conditions. Away from equilibrium, in loosely associated systems (with the distance between entanglements smaller than the distance between cross-links), the presence of trapped entanglements would act as cross-links<sup>72,124</sup> enhancing compatibilization and favoring microphase formation rather than macroscopic phase separation.

Although we have explored the gelation and phase behavior across a range of temperatures by varying both  $\chi_{AB}$  and  $\lambda$ , we have attempted to focus on describing the limiting behaviors and identifying opportunities for further study. Accurately describing the transition from segregation-dominated to binding-dominated regimes will require more sophisticated treatment and numerical implementation of the chain statistics of all branching (and looping) reaction products. One main advantage of the current methodology is that it allows one to re-create the salient physical description of blend compatibilization, reversible gelation, and microphase formation with a minimal model that can be computed analytically.

We are keenly interested in relating our theoretical work to experiments. Although previous work demonstrated compatibilization and the transition between macro- and microphase separation for supramolecular copolymers, we are unaware of any experiments that have systematically explored the phase diagrams and structures formed by multifunctional associating polymer blends. Prediction of gelation and phase behavior can be systematically tested by preparing mixtures of associating polymers at different concentrations. In particular, eutectic behavior should be easily verifiable for a melt blend of high  $\chi_{AB}$  polymers with strongly associating hydrogen bonding or ionic groups sparsely distributed along the chains. The order–disorder transition temperature (ODT), as measured by X-ray scattering, is sticker-stoichiometry-dependent and is suppressed at matched sticker concentrations. While the entire range of binding and segregation conditions is likely not accessible within a single polymer blend, choosing systems with stickers of varied association strengths and different regions of phase space should be accessible for validation.

The physical properties of these copolymer networks are of high interest and importance,<sup>42</sup> in part, for their implications for biological condensates<sup>38,39</sup> and potential utility in polymer reprocessing.<sup>126–129</sup> For microphase-separated gels, control over domain size, by temperature, concentration, and polymer architecture enables optically and mechanically responsive materials. In particular, near the microphase and gelation transitions, optical transparency could be switchable as the domain sizes change relative to the wavelength of light.<sup>130,131</sup> For microphase formation in solution, rather than in melts, the final network will show porosity at small and adjustable length scales, which could be useful for templating separation membranes.<sup>132,133</sup> Ultimately, the mechanical properties of these networks will be highly controllable by the mesophase and network percolation, in addition to the cross-link density and lifetimes. Furthermore, for polymers with additional functionalities, such controllable connectivity and microphase formation could be utilized for confined enzymatic activity,<sup>134</sup> drug encapsulation,<sup>135,136</sup> or micro-structured conductive pathways.<sup>137–139</sup> Accordingly, our results are expected to be useful in the design and development of new reversibly bonded materials. Future work will seek to develop theoretical models to predict the mechanics and dynamics of associating polymer blends.

# Acknowledgement

This work was supported by the NSF Center for the Chemistry of Molecularly Optimized Networks (MONET), CHE-2116298. The author thanks all the members of the MONET Center for insightful discussions, as well as Michael Rubinstein and Steve Craig for assistance in preparing the manuscript.

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