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Thermoreversible Gelation with Two-Component Networks

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ABSTRACT: This paper studies thermoreversible gelation in two-component polymer mixtures (A/B) in which both polymers carry associative groups capable of forming reversible pairwise bonds. The type of association is classified into the following three main categories: (i) association of polymers within the same species (AA and BB); (ii) association only between the different species (AB); (iii) all associations allowed (AA, BB and AB). On the basis of a recent theory of associating polymers, we derive possible phase diagrams for *interpenetrating networks, alternating networks, and randomly mixed networks* corresponding to each category, with special attention to the interference between gelation and macroscopic phase separation. For all types, homogeneously mixed networks are most easily stabilized near the stoichiometric concentration where the total number of A associative groups in the mixture agrees with that of B associative groups.

1. Introduction

In multicomponent polymer solutions such as biopolymers, amphiphilic synthetic polymers, polyelectrolytes, etc., thermoreversible gels are often formed by physical association between functional groups either on the same species or on different species of polymers.[1−3] Physical bonds between different species in principle improve their mutual miscibility. Nevertheless, the solutions often show complex phase behavior accompanied by competition among different phase transitions such as gelation, macro- and microscopic phase separation, and liquid crystallization.

In biological and medical science, physical gelation with mixed polymers is a very important subject. For example, it has been suggested that the repeated sol/gel transition of actin, controlled by actin-binding protein (ABP), drives motions of individual biological cells.[4] In this ternary system (actin, ABP, and water), ABP works as a cross-linker of the actin filaments. In the food industry, biopolymer mixtures in which either single or multiple ingredients form networks have many important applications, and have been the focus of intensive experimental study.[5,6] For example, Clark et al.[5] studied composite aqueous gels consisting of thermoreversible cold-setting gelling components such as agarose and gelatin by electron and optical microscopy. They reported that their micrographs appeared quite similar to those observed in a number of synthetic interpenetrating networks (referred to as IPNs), and showed phase separation into the two polymer networks with possible phase inversion at a certain mixture composition. Durrani et al.[7,8] derived a phase diagram for the ternary amylopectin−gelatin−D_2O mixture in the sol state by the use of Fourier-transformed infrared microspectroscopy.

Formation of mixed networks may also be used to modify the rheological properties of aqueous polymer solutions. For instance, quite recently it was experimentally demonstrated[9] that the viscosity of mixtures of the two species of polymers, poly(*N*-isopropylacrylamide) and hydrophobically modified poly(sodium acrylate) in aqueous solution becomes several orders of magnitude higher than is achieved without hydrophobic modification. A possible mechanism of heteropolymer cross-linking between the hydrophobes on the different species, followed by network formation by the hydrophobic aggregation of molecules, was proposed.[9]

Despite these pioneering experimental works, there seem to be only a few theoretical studies of gelation in multicomponent polymer mixtures. The main purpose of this paper is to propose a statistical-mechanical theory of network-forming multicomponent polymer mixtures, and to explore possible phase diagrams in which many phase transitions coexist. Our theory starts from the lattice theory of polymer solutions developed by Flory and Huggins[10−13] properly extended to incorporate strong associative interactions. To treat the sol/gel transition, we combine the classical gelation theory by Flory[14,15] and Stockmayer[16−18] with the lattice-theoretical free energy of polymer mixtures. Imposing multiple-equilibrium conditions on the chemical potentials derived from the free energy, we find the most probable distribution of the clusters, and from the divergence of the weight-average cluster molecular weight, we find the gel point. An outline of this study has been reported in brief articles.[19−21]

As a model system, we consider a mixture of A chains and B chains, each carrying f-functional and g-functional groups. They are assumed to form reversible pairwise bonds whose binding energies are comparable to the thermal energy. When either of the functionalities exceeds 3, a cluster grows to macroscopic dimensions as soon as a threshold in the concentration is reached.[18] Above this threshold, a network made up of the two components is formed. The strength of the bonds can

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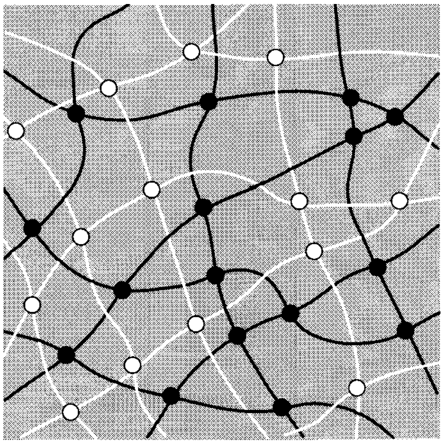

Figure 1. Schematic illustration of an interpenetrating network. The black and white lines show the A and B network. The black and white circles show A–A and B–B junctions. The networks are not connected to each other directly but are unseparable due to topological interpenetration. The matrix indicated by the shaded area includes finite clusters although not drawn explicitly.

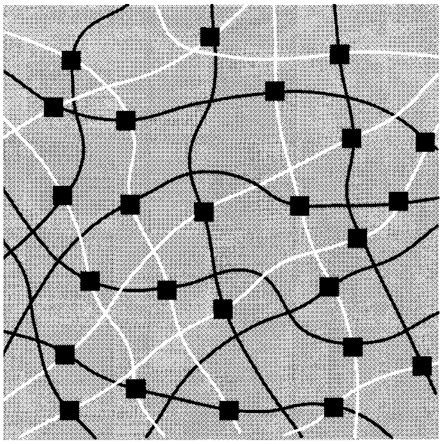

Figure 2. Schematic illustration of an alternately connected network. The black and white lines show A and B polymers in the network. The filled squares are junctions between different species of polymers.

be expressed by the three parameters

$$\lambda_{AA} = \exp(-\beta\Delta f_{AA}),\quad \lambda_{BB} = \exp(-\beta\Delta f_{BB}),\quad \lambda_{AB} = \exp(-\beta\Delta f_{AB}) \quad (1.1)$$

written in terms of the free energies $\Delta f_{\mu\nu}$ of bonding between species μ and ν, where $\beta \equiv 1/k_BT$ is the reciprocal temperature. In what follows we call these parameters *association constants*.

Let us now classify the types of association into the following fundamental three categories.

(i) *Interpenetrating networks* (IPNs): Polymer chains A and B are cross-linked within the same species, but do not form bonds between different species, i.e., $\lambda_{AB} = 0$. We refer to this case as A•A/B•B (Figure 1).

(ii) *Alternating networks* (ANs): Cross-links are allowed only between different species, i.e., $\lambda_{AA} = \lambda_{BB} = 0$. We refer to this case as A•B (Figure 2). Because the clusters (of finite or infinite size) formed are multiblock copolymers, the system may undergo microphase separation. Hence, macrophase separation, microphase separation, and gelation interfere with each other.

(iii) *Randomly mixed networks* (RMNs): If the strengths of associative forces in the three combinations AA, BB, and AB are all of the same order, cluster formation progresses randomly (Figure 3). The resultant networks can be regarded as macroscopic random block-copolymers.

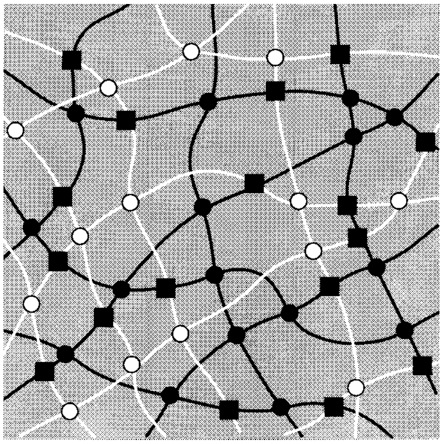

Figure 3. Schematic illustration of a randomly cross-linked two-component network. The black and white lines show A and B polymers in the network. The black circles, white circles, and filled squares show A–A, B–B, and A–B junctions, respectively.

Networks belonging to category i are defined as a nonbonded, but unseparable, combination of the two different polymer networks. As a consequence of a complex dynamic balance between the two opposite tendencies, i.e., association and phase separation, synthesis of IPNs can produce materials ranging from molecularly homogeneous to microscopically phase-separated with phase domains of various sizes, and this yields a unique method of controlling the morphology and mechanical properties. The chemistry and physics of IPNs have been extensively reviewed.[22–24] There are two main methods of synthesizing them: simultaneous IPN (sim-IPN) and sequential IPN (seq-IPN) formation. In sim-IPN formation, functional monomers (or primary chains) of both species A and B are mixed together and polymerized. In seq-IPN, a polymer network of species A is synthesized, and functional monomers B are swollen into the network and polymerized. In the present study, we consider physically cross-linked networks in which junctions are formed by noncovalent associative forces, and focus our attention on the sim-IPN. In such a weakly cross-linked IPN, polymers can reach equilibrium by the reorganization (creation and annihilation) of the network junctions in the course of phase separation, and, under certain conditions, the possibility arises that a molecularly homogeneous phase comprised of two unseparable (on a time scale shorter than the junction lifetime) networks will occur. In preceding papers,[20,21] phase diagrams have been derived theoretically and the occurrence of a stable physical IPN was pointed out on the basis of Stockmayer's treatment of the postgel regime.[16] In the present study we employ Flory's treatment[15] of the postgel regime, as well as Stockmayer's, to compare the difference in the phase behavior, specifically to examine the possibility of phase separation into two gel phases with different concentration.

Mixtures belonging to category ii form coterminously cross-linked networks when one of the components is a telechelic polymer carrying functional groups on both of its ends.[19] In the extreme case where this cross-linker is the solvent molecule itself, these networks are physical gels whose junctions are made up of complexes involving solvent molecules. It was suggested from differential scanning calorimetry data[25] that atactic polystyrene forms thermoreversible gels in the solvent carbon disulfide by forming solvent complexes at the network junctions, the sol/gel transition temperature exhibiting a peak as a function of the polymer concentration.

Associating polymers belonging to category iii form gels consisting of randomly connected two-component networks coexisting with the independent one-component pure gel networks. Typical examples studied so far are gelatin/agarose mixed gels in which the solution gels in a concentration region below the gelation concentration of each gelling component.[26]

II. Stoichiometric Definition of the Model Mixtures

We consider a mixture of the primary A chains and B chains. An A chain (B chain) consists of n_A (n_B) statistical units and carries the number f (g) of associative functional groups sparsely attached to the chain backbone. For simplicity, we assume that the volume a^3 of a statistical unit on the A chains and that on the B chains are the same, and take it as the volume of a unit cell. Let V be the total volume of the mixture, and let $\Omega \equiv V/a^3$ be the total number of the lattice cells. Let N_A (and N_B) be the total number of A chains (B chains) in the mixture. We then have

$$\phi_A = n_A N_A/\Omega, \quad \phi_B = n_B N_B/\Omega \tag{2.1}$$

for the volume fraction of each component. Throughout this paper we assume incompressibility of the mixture, so that we have $\phi_A + \phi_B = 1$. We choose ϕ_A as the independent concentration variable and write it as ϕ. We then have $\phi_B = 1 - \phi$. The total concentration of associative groups on the A chains (referred to as A groups) is given by $\psi_A \equiv f\phi/n_A$, and that on the B chains (referred to as B groups) is given by $\psi_B \equiv g(1 - \phi)/n_B$.

In equilibrium, many clusters are formed by association. Their distribution is thermally controlled. Each cluster is generally formed by the combination of subclusters that consist only of a single species (see Figure 4). To specify the types of clusters, we first introduce new notations A_i ($i = 1, 2, ...$) and B_j ($j = 1, 2, ...$) for the pure subclusters consisting of the number i of A chains and j of B chains. A cluster is then specified by the index ($\mathbf{l}$; $\mathbf{m}$), where the bold letter $\mathbf{l}$ shows the set of numbers $\mathbf{l} = \{l_1, l_2, ...\}$ indicating that it contains the number l_i of the pure A_i subclusters. Similarly, $\mathbf{m} = \{m_1, m_2, ...\}$ shows that the cluster contains the number m_j of the pure B_j subclusters.

For instance, a cluster of the type ($\mathbf{e}_i$; 0) shows a pure A subcluster of size i that is unassociated with B chains, and is referred to as A($\mathbf{e}_i$), where the bold letter $\mathbf{e}_i \equiv \{0, 0, ..., 1, 0, ...\}$ has unity at the ith position and is zero elsewhere. Similarly, (0; $\mathbf{e}_j$) shows a pure B subcluster of size j that is unassociated with A chains and is referred to as B($\mathbf{e}_j$). In particular, ($\mathbf{e}_1$; 0) and (0; $\mathbf{e}_1$) describe A chains and B chains that remain isolated in the mixture.

Let $N(\mathbf{l}; \mathbf{m})$ be the number of clusters of type ($\mathbf{l}$; $\mathbf{m}$) (referred to as AB($\mathbf{l}$; $\mathbf{m}$)) in the mixture. Their number density is then given by

$$\nu(\mathbf{l}; \mathbf{m}) = N(\mathbf{l}; \mathbf{m})/\Omega \tag{2.2}$$

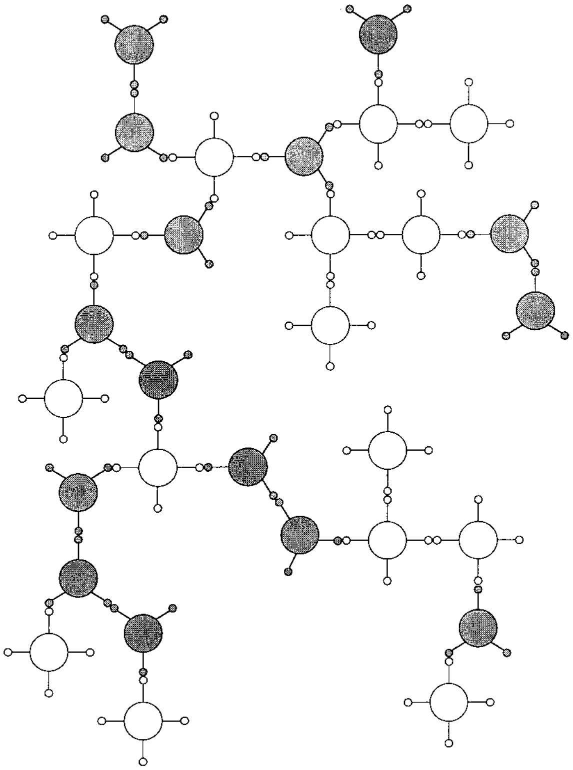

Figure 4. A typical mixed cluster made up of trifunctional A molecules and tetrafunctional B molecules. It is specified by the labels $\mathbf{l}$ = (4, 4, 1) and $\mathbf{m}$ = (7, 1, 2).

and the volume fraction occupied by them is given by

$$\phi(\mathbf{l}; \mathbf{m}) = (n_A \sum_i i l_i + n_B \sum_j j m_j)\nu(\mathbf{l}; \mathbf{m}) \tag{2.3}$$

In this paper we have to consider a solution in which sol (finite clusters) and gel (infinite cluster or network) coexist. We therefore define the volume fraction ϕ_A^S occupied by the A chains contained in the sol part as

$$\phi_A^S = n_A \sum_{\mathbf{l},\mathbf{m}} (\sum_i i l_i)\nu(\mathbf{l}; \mathbf{m}), \tag{2.4}$$

The volume fraction ϕ_A^G of the A chains connected to the gel network is then obtained by the subtraction

$$\phi_A^G = \phi_A - \phi_A^S \tag{2.5}$$

Similarly, we have

$$\phi_B^S = n_B \sum_{\mathbf{l},\mathbf{m}} (\sum_j j m_j)\nu(\mathbf{l}; \mathbf{m}) \tag{2.6}$$

and

$$\phi_B^G = \phi_B - \phi_B^S \tag{2.7}$$

for the B chains. In these equations, the first summation is taken over all possible types of clusters existing in the sol. The superscript S refers to the properties of the sol and G to those of the gel. By definition, the volume fractions ϕ_μ^S of each species are identical to the volume fractions ϕ_μ in the entire mixture in the *pregel regime*. In the *postgel regime*, however, they are smaller than ϕ_μ. The weight percentage of the gel part in each species is given by

$$w_{\mathrm{A}}^{\mathrm{G}} \equiv \phi_{\mathrm{A}}^{\mathrm{G}}/\phi_{\mathrm{A}} \quad \text{and } w_{\mathrm{B}}^{\mathrm{G}} \equiv \phi_{\mathrm{B}}^{\mathrm{G}}/\phi_{\mathrm{B}} \tag{2.8}$$

The total number of clusters in the sol part is given by

$$\nu^{\mathrm{S}} = \sum_{\mathbf{l},\mathbf{m}} \nu(\mathbf{l};\, \mathbf{m}) \tag{2.9}$$

As we will see in the following, this number appears in the chemical potentials and plays an important role.

We next consider the pure clusters. The subclusters A_i and B_j are separated from each other if the heteromolecular association is tentatively cut off. Let $\nu(A_i)$ be the total number of such A clusters consisting of the number i of primary A chains connected to each other by the bonding free energy Δf_{AA}. The number $\nu(B_j)$ is similarly defined. Note that these numbers are different from $\nu(\mathbf{e}_i;\, 0)$ or $\nu(0;\, \mathbf{e}_j)$ since A_i and B_j are to be connected to each other in the mixture.

Let us next introduce the degree of association in the mixture. The conversion α is defined as the number of A groups associated with the same A groups divided by the total number of A groups. The conversion β is similarly defined. As for heteroassociation, the probability p is defined by the probability for a randomly chosen A group is associated with a B group, and probability q is defined as that for a B group to be associated with an A group. These are basically the same as the conventional definitions in the classical theory of gelation.[12,18] (In ref 18, the symbols p_{A} and p_{B} are used for p and q.)

III. Free Energy

To study the solution properties, let us consider the free energy of the mixture. Following the general strategy,[19−21] we start from the free energy consisting of the free energy of cluster formation and the free energy of mixing them:

$$\beta\Delta F = \sum_{\mathbf{l},\mathbf{m}} N(\mathbf{l};\, \mathbf{m}) \ln \phi(\mathbf{l};\, \mathbf{m}) + \chi\Omega\phi(1-\phi) + \sum_{\mathbf{l},\mathbf{m}} \Delta(\mathbf{l};\, \mathbf{m}) N(\mathbf{l};\, \mathbf{m}) + \delta_{\mathrm{A}}(\phi) N_{\mathrm{A}}^{\mathrm{G}} + \delta_{\mathrm{B}}(\phi) N_{\mathrm{B}}^{\mathrm{G}} \tag{3.1}$$

where

$$\Delta(\mathbf{l};\, \mathbf{m}) = \beta\{\mu^{\circ}(\mathbf{l};\, \mathbf{m}) - (\textstyle\sum i l_i)\mu_{\mathrm{A}}^{\circ} - (\sum j m_j)\mu_{\mathrm{B}}^{\circ}\} \tag{3.2}$$

is the free energy required to form a single cluster of the type ($\mathbf{l}$; $\mathbf{m}$) from the primary molecules in the standard reference state in which polymers A and B are prepared separately in the hypothetical crystalline states. The (dimensionless) free energies δ_{A} and δ_{B} are the free energies required to bind a single molecule of each species into the gel network.

In order to cope with chemical equilibrium, let us first derive the chemical potentials of the clusters. The chemical potential $\Delta\mu(\mathbf{l};\, \mathbf{m})$ of an ($\mathbf{l}$; $\mathbf{m}$) cluster is given by partial differentiation of ΔF with respect to $N(\mathbf{l};\, \mathbf{m})$ with other numbers being fixed. Explicitly, we find

$$\beta\Delta\mu(\mathbf{l};\, \mathbf{m}) = 1 + \Delta(\mathbf{l};\, \mathbf{m}) + \ln \phi(\mathbf{l};\, \mathbf{m}) - (n_{\mathrm{A}}\sum_i i l_i + n_{\mathrm{B}}\sum_j j m_j)\nu^{\mathrm{S}} + \chi\{n_{\mathrm{A}}(\sum_i i l_i)(1-\phi) + n_{\mathrm{B}}(\sum_j j m_j)\phi - (n_{\mathrm{A}}\sum_i i l_i + n_{\mathrm{B}}\sum_j j m_j)\phi(1-\phi)\} + \{n_{\mathrm{A}}(\sum_i i l_i)(1-\phi) - n_{\mathrm{B}}(\sum_j j m_j)\phi\} d^{\mathrm{G}}(\phi), \tag{3.3}$$

where ν^{S} is defined by eq 2.9 and

$$d^{\mathrm{G}}(\phi) \equiv \delta'_{\mathrm{A}}(\phi)\nu_{\mathrm{A}}^{\mathrm{G}} + \delta'_{\mathrm{B}}(\phi)\nu_{\mathrm{B}}^{\mathrm{G}} \tag{3.4}$$

shows the contribution from the gel part. (The primes indicate differentiation with respect to the concentration ϕ.) Similarly, the chemical potential $\Delta\mu_{\mathrm{A}}^{\mathrm{G}}$ and $\Delta\mu_{\mathrm{B}}^{\mathrm{G}}$ are found by differentiation with respect to $N_{\mathrm{A}}^{\mathrm{G}}$ and $N_{\mathrm{B}}^{\mathrm{G}}$ as

$$\beta\Delta\mu_{\mathrm{A}}^{\mathrm{G}}/n_{\mathrm{A}} = \delta_{\mathrm{A}}/n_{\mathrm{A}} - \nu^{\mathrm{S}} + \chi(1-\phi)^2 + (1-\phi)d^{\mathrm{G}}(\phi) \tag{3.5a}$$

$$\beta\Delta\mu_{\mathrm{B}}^{\mathrm{G}}/n_{\mathrm{B}} = \delta_{\mathrm{B}}/n_{\mathrm{B}} - \nu^{\mathrm{S}} + \chi\phi^2 - \phi d^{\mathrm{G}}(\phi). \tag{3.5b}$$

IV. Cluster Distribution

To find the most probable distribution of clusters, we minimize the free energy by changing the number density of clusters, or equivalently we impose multiple equilibrium conditions on the chemical potentials.

A. Homopolymer Association. For the reaction equilibrium $i\mathrm{A}(\mathbf{e}_1) \rightleftharpoons \mathrm{A}(\mathbf{e}_i)$, we have the condition $\Delta\mu(\mathbf{e}_i;\, 0) = i\Delta\mu(\mathbf{e}_1;\, 0)$, from which we find

$$\phi(\mathbf{e}_i;\, 0) = K(\mathbf{e}_i;\, 0)\phi(\mathbf{e}_1;\, 0)^i \tag{4.1}$$

where the equilibrium reaction constant K is written in terms of the free energy of the cluster formation as

$$K(\mathbf{e}_i;\, 0) = \exp\{i - 1 - \Delta(\mathbf{e}_i;\, 0)\} \tag{4.2}$$

Similarly, we find

$$\phi(0;\, \mathbf{e}_j) = K(0;\, \mathbf{e}_j)\phi(0;\, \mathbf{e}_1)^j \tag{4.3}$$

As discussed in our preceding study,[19−21] the free energy $\Delta(\mathbf{l};\, \mathbf{m})$ includes a combinatorial factor, a conformational factor and a bonding factor. To make the combinatorial problem as simple as possible, we assume, throughout this paper, that all clusters take the Cayley tree form as in the classical theory of gelation. The effect of internal loop formation is neglected. Repeating the same consideration as in our preceding references, we find

$$\lambda_{\mathrm{AA}}\nu(\mathbf{e}_i;\, 0) = \omega_i^{(f)}(\lambda_{\mathrm{AA}} f \nu(\mathbf{e}_1;\, 0))^i \tag{4.4a}$$

$$\lambda_{\mathrm{BB}}\nu(0;\, \mathbf{e}_j) = \omega_j^{(g)}(\lambda_{\mathrm{BB}} g \nu(0;\, \mathbf{e}_1))^j \tag{4.4b}$$

where the ω's are Stockmayer's combinatorial factors:

$$\omega_i^{(f)} \equiv \frac{(fi-i)!}{i!(fi-2i+2)!} \quad \text{and } \omega_j^{(g)} \equiv \frac{(gj-j)!}{j!(gj-2j+2)!} \tag{4.5}$$

Since an A_i (B_j) cluster carries $f_i \equiv (f-2)i + 2$ ($g_j \equiv (g-2)j + 2$) groups unreacted with the groups on the same species in the tree statistics, we can rewrite these equations as

$$\lambda_{AA}\nu(A_i)(1-p)^{f_i} = \omega_i^{(f)}(\lambda_{AA}f\nu(\mathbf{e}_1;0))^i \quad (4.6a)$$

$$\lambda_{BB}\nu(B_j)(1-q)^{g_j} = \omega_j^{(g)}(\lambda_{BB}g\nu(0;\mathbf{e}_1))^j \quad (4.6b)$$

The numbers $\nu(A_i)$ and $\nu(B_j)$ of pure clusters formed before the heteroassociation is turned on were simply written as A_i and B_j in Stockmayer's study.[18]

B. Heteropolymer Association. We next proceed to find the equilibrium conditions for the formation of mixed clusters. The general reaction process can be written as $\sum_i l_i A(\mathbf{e}_i) + \sum_j m_j B(\mathbf{e}_j) \rightleftharpoons AB(\mathbf{l};\mathbf{m})$, so that we have

$$\Delta\mu(\mathbf{l};\mathbf{m}) = \sum_i l_i \Delta\mu(\mathbf{e}_i;0) + \sum_j m_j \Delta\mu(0;\mathbf{e}_j) \quad (4.7)$$

We then find that the volume fraction of the ($\mathbf{l}$; $\mathbf{m}$) clusters is given by

$$\phi(\mathbf{l};\mathbf{m}) = K(\mathbf{l};\mathbf{m})\prod_i \phi(\mathbf{e}_i;0)^{l_i}\prod_j \phi(0;\mathbf{e}_j)^{m_j} \quad (4.8)$$

where the equilibrium constant is written in terms of the free energy of cluster formation as

$$K(\mathbf{l};\mathbf{m}) = \exp[\sum l_i + \sum m_j - 1 - \Delta(\mathbf{l};\mathbf{m})] \quad (4.9)$$

Considering the three parts in Δ as before, we find

$$\lambda_{AB}\nu(\mathbf{l};\mathbf{m}) = \omega(\mathbf{l};\mathbf{m})\prod_i\left(\frac{x_i^{\,l_i}}{l_i!}\right)\prod\left(\frac{y_j^{\,m_j}}{m_j!}\right) \quad (4.10)$$

where

$$\omega(\mathbf{l};\mathbf{m}) \equiv \frac{(\sum f_i l_i - \sum l_i)!(\sum g_j m_j - \sum m_j)!}{(\sum f_i l_i - \sum l_i - \sum m_j + 1)!(\sum g_j m_j - \sum l_i - \sum m_j + 1)!} \quad (4.11)$$

is the Stockmayer's combinatorial factor for the heteropolymer gelation.[18] Here, x_i and y_j stand for

$$x_i \equiv \lambda_{AB} f_i \nu(\mathbf{e}_i;0) \quad (4.12a)$$

$$y_j \equiv \lambda_{AB} g_j \nu(0;\mathbf{e}_j) \quad (4.12b)$$

Especially for the unassociated molecules, we find

$$x_1 \equiv \lambda_{AB} f \nu(\mathbf{e}_1;0) \quad (4.13a)$$

$$y_1 \equiv \lambda_{AB} g \nu(0;\mathbf{e}_1) \quad (4.13b)$$

In what follows, for the mixture in which heteroassociation takes place (i.e. $\lambda_{AB} > 0$), we take x_1 and y_1 as the fundamental variables and write them simply as x and y. Then, the eqs. 4.4a and 4.4b are rewritten as

$$\lambda_{AA}\nu(\mathbf{e}_i;0) = \omega_i^{(f)}(\xi_A x)^i \quad (4.14a)$$

$$\lambda_{BB}\nu(0;\mathbf{e}_j) = \omega_j^{(g)}(\xi_B y)^j \quad (4.14b)$$

where $\xi_A \equiv \lambda_{AA}/\lambda_{AB}$ and $\xi_B \equiv \lambda_{BB}/\lambda_{AB}$ are the strengths of the homopolymer associations relative to the heteropolymer association.

C. Binding Free Energy of the Networks. We next consider the free energy δ to bind a single chain into the network in the postgel regime. The equilibrium conditions are given by $A(\mathbf{e}_1) \rightleftharpoons A_1^G$ and $B(\mathbf{e}_1) \rightleftharpoons B_1^G$, where the superscript G indicates the molecule attached to the network. From the conditions $\Delta\mu(\mathbf{e}_1;0) = \Delta\mu_A^G$ *etc.* for the chemical potentials 3.5a, 3.5b, we find

$$\delta_A(\phi) = \ln x + 1 + \ln(n_A/f\lambda_{AB}) \quad (4.15a)$$

$$\delta_B(\phi) = \ln y + 1 + \ln(n_B/g\lambda_{AB}) \quad (4.15b)$$

For a fixed temperature, these equations give the changes in binding free energy with polymer concentration through x and y in the postgel regime.

V. Reaction Probability and the Average Cluster Size

In order to obtain the average molecular weight as a function of thermodynamic variables such as temperature and polymer composition, we first find the conversions α and β and the reaction probabilities p and q as functions of the thermodynamic variables.

By definition the conversion α is given by

$$\alpha = \sum_i 2(i-1)\nu(A_i)/\sum fi\nu(A_i) \quad (5.1)$$

since a tree made up of i A chains has $i - 1$ pairwise bonds. On substitution of eqs 4.6a and 4.6b, this relation gives

$$\xi_A x = \alpha[(1-\alpha)(1-p)]^{f-2} \quad (5.2)$$

The factor $(1-p)^{f-2}$ appears because $f_i \equiv fi - 2(i-1)$ functional groups on the A chains must not be associated with B groups to obtain x. Another fundamental equation is derived from the relation $\phi = n_A\sum i\nu(A_i)$ for the volume fraction of A chains. On substitution of eq 4.6a again, we find

$$\lambda_{AA}\psi_A(1-p)^2 = fS_1^{(f)}(\xi_A x/(1-p)^{f-2}) \quad (5.3)$$

where $\psi_A \equiv f\phi/n_A$ is the total concentration of A groups in the mixture, and

$$S_k^{(f)}(z) \equiv \sum_{i=1}^{\infty} i^k \omega_i^{(f)} z^i \quad (5.4)$$

is the kth moment of the Stockmayer distribution for the functionality f, where $z \equiv \xi_A x/(1-p)^{f-2} = \alpha(1-\alpha)^{f-2}$. The first three moments are explicitly given by

$$S_0^{(f)}(z) = \alpha(1 - f\alpha/2)/f(1-\alpha)^2 \quad (5.5a)$$

$$S_1^{(f)}(z) = \alpha/f(1-\alpha)^2 \quad (5.5b)$$

$$S_2^{(f)}(z) = \alpha(1+\alpha)/f(1-\alpha)^2[1-(f-1)\alpha] \quad (5.5c)$$

when written in terms of the conversion α. Equation 5.3 is therefore transformed into

$$\lambda_{AA}\psi_A = \alpha/(1-\alpha)^2(1-p)^2 \quad (5.6)$$

Quite similarly, we find

$$\xi_{\mathrm{B}} y = \beta[(1-\beta)(1-q)]^{g-2} \tag{5.7}$$

and

$$\lambda_{\mathrm{BB}}\psi_{\mathrm{B}} = \beta/(1-\beta)^2(1-q)^2 \tag{5.8}$$

for B groups, where $\psi_{\mathrm{B}} \equiv g(1-\phi)/n_{\mathrm{B}}$ is the total number of B groups.

These relations can be derived in a different way by separating the association into two steps. In the first step we temporarily turn off the heteroassociation and combine polymer chains within the same species. The number

$$\Psi_{\mathrm{A}} \equiv \psi_{\mathrm{A}}(1-\alpha) = \sum f_i \nu(A_i) \tag{5.9a}$$

$$\Psi_{\mathrm{B}} \equiv \psi_{\mathrm{B}}(1-\beta) = \sum g_j \nu(B_j) \tag{5.9b}$$

of A groups (B groups) remain unassociated. Since

$$\sum f_i \nu(A_i) = \{(f-2)S_1^{(f)} + 2S_0^{(f)}\}/(1-p)^2 = \alpha/(1-\alpha)(1-p)^2 \tag{5.10}$$

we find eq 5.6. Hence we have

$$\lambda_{\mathrm{AA}}\Psi_{\mathrm{A}} = \alpha/(1-\alpha)(1-p)^2 \tag{5.11a}$$

$$\lambda_{\mathrm{BB}}\Psi_{\mathrm{B}} = \beta/(1-\beta)(1-q)^2 \tag{5.11b}$$

Before the heteropolymer association is turned on, we have the distribution of pure A and B clusters. Let us define the distribution functions w_i^{A} and w_j^{B} of the associative groups caried by the pure A clusters and pure B clusters to be connected to each other through the heteropolymer association as

$$w_i^{\mathrm{A}} \equiv f_i \nu(A_i)/\sum f_i \nu(A_i) \tag{5.12a}$$

$$w_i^{\mathrm{B}} \equiv g_j \nu(B_j)/\sum g_j \nu(B_j) \tag{5.12b}$$

On substitution of eq 4.6a,b, we find

$$w_i^{\mathrm{A}} = f_i \omega_i^{(f)}[(1-\alpha)/\alpha][\alpha(1-\alpha)^{f-2}]^i \tag{5.13a}$$

$$w_j^{\mathrm{B}} = g_j \omega_j^{(g)}[(1-\beta)/\beta][\beta(1-\beta)^{g-2}]^j \tag{5.13b}$$

Comparing these results with eq 4.12a,b, we find the general relations

$$x_i = w_i^{\mathrm{A}} q(1-p)^{f_i-1}/(1-q) \tag{5.14a}$$

$$y_j = w_j^{\mathrm{B}} p(1-q)^{g_j-1}/(1-p) \tag{5.14b}$$

The average functionalities of these clusters can be calculated as

$$f_{\mathrm{n}} \equiv \sum f_i \nu(A_i)/\sum \nu(A_i) = f(1-\alpha)/(1-f\alpha/2) \tag{5.15}$$

for the number average, and

$$f_{\mathrm{w}} \equiv \sum f_i^2 \nu(A_i)/\sum f_i \nu(A_i) = (f-2f'\alpha)/(1-f'\alpha) \tag{5.16}$$

for the weight average, where $f' \equiv f-1$. Similarly we find

$$g_n = g(1-\beta)/(1-g\beta/2) \quad \text{and} \quad g_w = (g-2g'\beta)/(1-g'\beta) \tag{5.17}$$

In the second step, we turn on the heteropolymer association. The total number ζ of A·B hetero-junctions is then given by

$$\zeta = p\Psi_{\mathrm{A}} = q\Psi_{\mathrm{B}} \tag{5.18}$$

But since this should satisfy the equilibrium condition

$$\lambda_{\mathrm{AB}}\zeta = \frac{p\Psi_{\mathrm{A}} q\Psi_{\mathrm{B}}}{\Psi_{\mathrm{A}}(1-p)\Psi_{\mathrm{B}}(1-q)} = \frac{pq}{(1-p)(1-q)} \tag{5.19}$$

we have

$$\zeta = p\Psi_{\mathrm{A}} = q\Psi_{\mathrm{B}} = pq/\lambda_{\mathrm{AB}}(1-p)(1-q) \tag{5.20}$$

By eliminating p and q from these equations, we find

$$\lambda_{\mathrm{AB}}\zeta = [1 + \lambda_{\mathrm{AB}}(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}}) - \sqrt{D}]/2 \tag{5.21}$$

where $D \equiv 1 + 2\lambda_{\mathrm{AB}}(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}}) + \lambda_{\mathrm{AB}}^2(\Psi_{\mathrm{A}} - \Psi_{\mathrm{B}})^2$.

From eq 5.11ab, we find that the conversions α and β are connected to p and q through the relations

$$\alpha/(1-\alpha) = \xi_{\mathrm{A}} q(1-p)/(1-q) \tag{5.22a}$$

$$\beta/(1-\beta) = \xi_{\mathrm{B}} p(1-q)/(1-p) \tag{5.22b}$$

Putting all the relations together we find α, β and p, q as functions of the concentration ψ_{A} and ψ_{B} of the associative groups for a given temperature. We next consider the total number ν^{S} of the clusters in the sol part. We start from the average number of pure clusters before the heteroassociation is introduced. There are Ψ_{A}/f_n A clusters and Ψ_{B}/g_n B clusters on average. Since the number of clusters reduces by one every time a new AB bond is formed, we have

$$\nu^{\mathrm{S}} \equiv \sum_{\mathbf{l},\mathbf{m}} \nu(\mathbf{l};\, \mathbf{m}) = \Psi_{\mathrm{A}}/f_{\mathrm{n}} + \Psi_{\mathrm{B}}/g_{\mathrm{n}} - \zeta \tag{5.23}$$

of clusters in the real mixture. Or, equivalently, this is given by

$$\nu^{\mathrm{S}} = \zeta(1/pf_{\mathrm{n}} + 1/qg_{\mathrm{n}} - 1) \tag{5.24}$$

This equation can be expressed in terms of the reaction probabilities α, β and p, q and hence as functions of the temperature and polymer concentration through the equations found above.

VI. Sol/Gel Transition and the Postgel Regime

When all three types of association coexist, pure A gel, pure B gel and mixed AB gel may, in principle, appear on the temperature–concentration phase diagram. The region of their appearance depends upon the relative strength of the association constants. Under the tree assumption, the conditions for the formation of pure gels are given by[15]

$$\alpha^* = 1/(f-1) \tag{6.1}$$

for the A gel and

$$\beta^* = 1/(g - 1) \tag{6.2}$$

for the B gel. (In what follows the asterisk indicates the critical values at gelation.) Upon substitution into eqs 5.6 and 5.8, we can express this condition in terms of the number of functional groups carried by (or the total volume fraction of) each species of polymer:

$$\lambda_{AA}\psi_A^* = \alpha^*/(1 - \alpha^*)^2(1 - p)^2 \tag{6.3a}$$

$$\lambda_{BB}\psi_B^* = \beta^*/(1 - \beta^*)^2(1 - q)^2 \tag{6.3b}$$

As for the mixed gel, the probabilities p and q of heteroassociation must satisfy Stockmayer's gelation condition[18]

$$1 - (f_w - 1)(g_w - 1)pq = 0 \tag{6.4}$$

at the gel point where the average functionalities f_w and g_w are those of the pure clusters to be connected by the heteroassociation. This is, however, the condition for an AB mixed gel to appear in the region of the phase plane where no pure gels are formed. A mixed network may, however, be formed in the region where either or both of the pure networks are already formed, i.e., in the postgel regime of pure A gel and/or pure B gel.

At this stage, we have to remember that there have been two different treatments of the postgel regime in the conventional theory of gelation: Stockmayer's treatment and Flory's treatment. The difference resides mainly in how to treat loop formation within the gel network.[16] Stockmayer assumed that the network should take the tree form in the limit of the infinite molecular weight of the finite tree clusters, while Flory allowed cycle formation within the gel network. In the former treatment, the conversion α' of the sol part remains at the critical value $1/(f - 1)$ and that of the gel α'' takes the infinite tree value $2/f$. The average conversion is given by

$$\alpha = \alpha' w^S + \alpha'' w^G \tag{6.5}$$

where w^S and w^G are the sol and gel fraction. In Flory's treatment,[12] the conversion α' of the sol part is first found by the condition that the quantity $\alpha(1 - \alpha)^{f-2}$, being equivalent to the volume fraction of the unassociated A-molecules in our present context, takes the same value for both the average conversion α and the conversion of the sol α'. Thus the volume fraction of the unassociated molecules is one of the invariants of the molecular distribution function. The latter treatment has recently been generalized to non-linear polycondensation by using more general invariant properties of the molecular weight distribution function holding before and after the gel point.[27] The first two invariants given in this literature are $I_a \equiv \Psi_A(1 - p)(1 - q)/q$ and $I_b \equiv \Psi_B(1 - p)(1 - q)/p$ in our notations. Obviously, they both give the association constant $1/\lambda_{AB}$, and hence remain unchanged before and after gelation. Other important invariants are $I_a^{(i)} \equiv w_i^A q(1 - p)^{f_i - 1}/(1 - q)$ and $I_b^{(j)} \equiv w_j^B p(1 - q)^{g_j - 1}/(1 - p)$, again written in our notations. These are the reduced number densities x_i and y_j (see eq 5.14a,b) of the composite pure clusters composed of the number i of A chains and j of B chains that remain unassociated to different species. Thus, we see the invariant transformation method agrees completely with Flory's postgel treatment.

The difference between Flory's and Stockmayer's treatments was later studied in detail from the kinetic-theoretical viewpoint by Ziff and Stell,[28] and a possible new treatment was suggested by them.

To cope with these complex historical situations, we have calculated phase diagrams on the basis of both Stockmayer's and Flory's treatment in this paper and have examined differences in the phase behavior in the postgel regime. For this aim we first introduce the conversions α' and β' to describe the sol part in the postgel regime of A and B polymers. These parameters are decided by the requirement that the volume fraction of the unassociated molecules should remain the same for the total average conversion α (β) and the conversion α' (β') for the sol part,[29] or, explicitly

$$\alpha(1 - \alpha)^{f-2} = \alpha'(1 - \alpha')^{f-2} \tag{6.6a}$$

$$\beta(1 - \beta)^{g-2} = \beta'(1 - \beta')^{g-2} \tag{6.6b}$$

The volume fractions ϕ_A^S and ϕ_B^S of each species, or, equivalently, the number densities of the functional groups, in the sol part are then related to the conversions of the sol part through

$$\lambda_{AA}\psi_A^S \equiv \frac{\lambda_{AA} f}{n_A}\phi_A^S = \alpha'/(1 - \alpha')^2(1 - p)^2 \tag{6.7a}$$

$$\lambda_{BB}\psi_B^S \equiv \frac{\lambda_{BB} g}{n_B}\phi_B^S = \beta'/(1 - \beta')^2(1 - q)^2 \tag{6.7b}$$

instead of eqs 5.6 and 5.8.

The gelation point of mixed AB networks in the postgel regime of A chains and/or B chains is therefore decided by the condition

$$\frac{f' g'(1 - \alpha')(1 - \beta')}{(1 - f'\alpha')(1 - g'\beta')} pq = 1 \tag{6.8}$$

Finally, let us consider the most complex situation in which all types of networks coexist, i.e., the postgel regime for A gel and B gel and mixed AB gel. To describe the postgel regime of the mixed network, we have to introduce the probabilities p' and q' for associations of different species of chains in the part where only finite clusters exist, i.e., the sol part with respect to the mixed clusters. These probabilities are obtained from the conditions

$$\alpha[(1 - \alpha)(1 - p)]^{f-2} = \alpha'[(1 - \alpha')(1 - p')]^{f-2} \tag{6.9a}$$

$$\beta[(1 - \beta)(1 - q)]^{g-2} = \beta'[(1 - \beta')(1 - q')]^{g-2} \tag{6.9b}$$

due to the Flory's postgel treatment, where α' and β' are related to p' and q' by the equations

$$\alpha'/(1 - \alpha') = \xi_A q'(1 - p')/(1 - q') \tag{6.10a}$$

$$\beta'/(1 - \beta') = \xi_B p'(1 - q')/(1 - p') \tag{6.10b}$$

as in eq 5.22a,b. The number of heterojunctions in the sol part is then given by

$$\lambda_{AB}\zeta^S = (\lambda_{AB}\Psi_A^S)p' = (\lambda_{AB}\Psi_B^S)q' = p'q'/(1 - p')(1 - q') \tag{6.11}$$

and hence there are $\zeta^G \equiv \zeta - \zeta^S$ hetero-junctions in the mixed AB network.

VII. Solution Properties and the Phase Diagrams

To study the solution properties, we start from the chemical potentials $\Delta\mu_A$ and $\Delta\mu_B$ obtained as the result of the multiple equilibrium conditions. These are two independent chemical potentials from which all equilibrium solution properties are derived. They take the form

$$\beta\Delta\mu_A = (1 + \ln x)/n_A - \nu^S + \chi(1 - \phi)^2 + (1 - \phi)d^G(\phi) \tag{7.1a}$$

$$\beta\Delta\mu_B = (1 + \ln y)/n_B - \nu^S + \chi\phi^2 - \phi d^G(\phi) \tag{7.1b}$$

The stability limit, or spinodal curve, of the mixture is then given by the condition

$$\sigma(\phi, T) \equiv \partial\beta(\Delta\mu_A - \Delta\mu_B)/\partial\phi = 0 \tag{7.2}$$

for the binary mixture where σ is defined by the concentration derivative of the chemical potential difference. Explicitly we find

$$\sigma = \frac{\kappa_A}{n_A\phi} + \frac{\kappa_B}{n_B(1 - \phi)} - 2\chi = 0 \tag{7.3}$$

where

$$\kappa_A \equiv \frac{\partial}{\partial(\ln \phi_A)}\left(1 + w_A^G\frac{\partial}{\partial(\ln \phi_A)}\right) \ln x \tag{7.4a}$$

$$\kappa_B \equiv \frac{\partial}{\partial(\ln \phi_B)}\left(1 + w_B^G\frac{\partial}{\partial(\ln \phi_B)}\right) \ln y \tag{7.4b}$$

These functions are closely related to the weight-average molecular weight P_w of the clusters. For instance, κ_A reduces to the reciprocal of the average molecular weight $P_w(\alpha)$ when there are no associations between A and B and between Bs.[19] In more general case where all types of association coexist, the average size of the mixed clusters is given by $P_w = G(\alpha,\beta,p,q)n\zeta$, where the factor G is given by

$$G(\alpha,\beta,p,q) = \frac{a^2}{(f - 2)^2p}\left(f_w - 4 + \frac{4}{f_n}\right) + \frac{b^2}{(g - 2)^2q}\left(g_w - 4 + \frac{4}{g_n}\right) + \frac{1}{1 - (f_w - 1)(g_w - 1)pq}\left[a^2q\frac{(f_w - 2)^2(g_w - 1)}{(f - 2)^2} + b^2p\frac{(g_w - 2)^2(f_w - 1)}{(g - 2)^2} + ab\frac{(f_w - 2)(g_w - 2)}{(f - 2)(g - 2)}\right] \tag{7.5}$$

with $n \equiv n_A + n_B$, $n_A \equiv na$ and $n_B \equiv nb$. This factor reduces to Stockmayer's general result[18] when appropriate replacement of the symbols is made.

The coexistence conditions (or binodal curves) for a dilute phase with the volume fraction ϕ' to be in equilibrium with a concentrated phase with the volume fraction ϕ'' are given by

$$\Delta\mu_A(\phi', T) = \Delta\mu_A(\phi'', T) \tag{7.6a}$$

$$\Delta\mu_B(\phi', T) = \Delta\mu_B(\phi'', T) \tag{7.6b}$$

For the phases lying in the postgel regime, the extent of reaction α', β' and p', q' should be used in the equations giving ν^S, x, and y in the chemical potentials.

To derive the phase diagrams, we employ the following scheme for the numerical calculation. We first introduce the reduced temperature $\tau \equiv 1 - \Theta/T$. This is the dimensionless deviation from the temperature Θ which satisfies the condition $\chi(\Theta) = {}^1/_2$. In the case where the species B is a low molecular weight molecules, this temperature reduces to the conventional Θ temperature, but we introduce it here simply as a reference temperature. Near this temperature we can assume the Schultz–Flory form

$$\chi(T) = 1/2 - \psi\tau \tag{7.7}$$

for the χ parameter. Here, ψ is a material parameter related to the entropy part of the contact (nonassociative) interaction. (This should not be confused with the number density ψ_A or ψ_B of the functional groups.) The association constants are then transformed into

$$\lambda_{\mu\nu}(T) = \lambda_{\mu\nu0} \exp[\gamma_{\mu\nu}(1 - \tau)] \tag{7.8}$$

where μ, $\nu = A, B$. Here

$$\lambda_{\mu\nu0} \equiv \exp(\Delta s_{\mu\nu}/k_B) \tag{7.9}$$

and

$$\gamma_{\mu\nu} \equiv \frac{-\Delta\epsilon_{\mu\nu}}{k_B\Theta} \quad (>0) \tag{7.10}$$

are temperature-independent constants related to the entropy change and energy change on bond formation. We have seven material parameters:

$$\psi, \lambda_{AA0}, \lambda_{BB0}, \lambda_{AB0}, \gamma_{AA}, \gamma_{BB}, \text{ and } \gamma_{AB}$$

In addition, we must specify molecular parameters such as the number n_A and n_B of the statistical units on an A chain and a B chain, and their functionalities f and g. In the following numerical calculation, we shall fix, for simplicity, the parameter ψ at $\psi = 1.0$. We take $\phi_A \equiv \phi$ as an independent concentration variable.

VIII. Interpenetrating Networks

Let us first consider the simplest case where there is no heteroassociation (i.e., $\lambda_{AB} = 0$).

The phase diagrams calculated by Stockmayer's postgel treatment were reported in our preceding paper.[20] To compare the result with Flory's treatment, we show here again in Figure 5a a typical diagram derived by Stockmayer's treatment for the symmetric mixture. The phase diagram calculated by Flory's postgel treatment is shown in Figure 5b. In both figures the molecular parameters are symmetrically fixed at $n_A = n_B = 10$, $f = g = 3$, $\lambda_{AA0} = \lambda_{BB0} = 4.0$, and $\gamma_{AA} = \gamma_{BB} = 3.0$. The sol/gel transition lines for the A gel (thick broken line) and B gel (thick dotted line), binodal (thin dashed line), and the spinodal (thin solid line) are shown. The unstable region (denoted by the letter U) is indicated

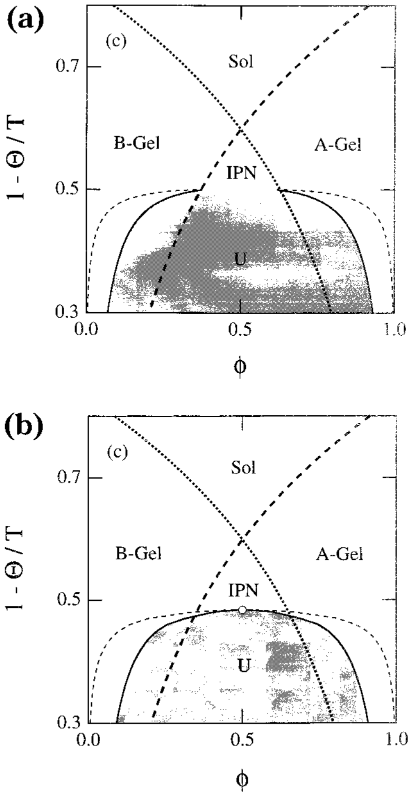

Figure 5. Phase diagrams of a simultaneous IPN in the symmetric case: $n_A = n_B = 10$, $f = g = 3$, $\lambda_{AA0} = \lambda_{BB0} = 4.0$, and $\gamma_{AA} = \gamma_{BB} = 3.0$. Key: (a) Stockmayer's postgel treatment; (b) Flory's postgel treatment. The sol/gel transition lines (thick dashed line for A gel, thick dotted line for B gel), binodal (thin dashed line), and spinodal (thin solid line) are shown. The shaded area indicated by letter U is a thermodynamically unstable region. The open circle shows a critical solution point. Although IPN region generally lies inside the unstable region, a small stable IPN region appears on the top of the miscibility dome near the stoichiometric concentration for larger values of association constant as in these figures. The critical point remains in the IPN region in Flory's treatment, so that two IPNs with different compositions may coexist in phase equilibrium.

by the shaded area. The white circle denotes the critical solution point. Generally, A gels and B gels do not mix with each other since the mixing entropy is substantially reduced as the clusters grow larger. However, as the association force becomes stronger as in these figures, with other parameters being fixed, a small region in which an IPN is thermodynamically stable appears above the miscibility dome around the stoichiometric concentration; i.e., the concentration at which the bulk concentration agrees with the relative polymer molecular composition; $n_A/n_B = \phi/(1 - \phi)$. Although Stockmayer's postgel treatment gives a flat boundary line, and therefore no spinodal line separating the stable IPN region from the unstable IPN region, Flory's treatment allows the critical point of demixing to remain in the IPN region. This is also the case for an asymmetric mixture as shown in parts a and b of Figure 6.

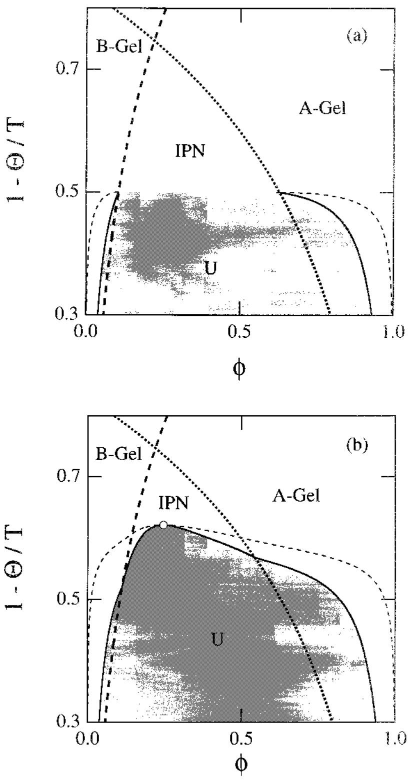

Figure 6. Phase diagrams of a simultaneous IPN with asymmetric functionalities. The functionaly is different but chain length is chosen to be the same for both species; $n_A = n_B = 10$, $f = 4$, $g = 3$, $\lambda_{AA0} = \lambda_{BB0} = 4.0$, and $\gamma_{AA} = \gamma_{BB} = 3.0$. Key: (a) Stockmayer's treatment; (b) Flory's treatment.

IX. Alternately Cross-Linked Networks

When $\lambda_{AA} = \lambda_{BB} = 0$, networks with A chains and B chains alternately cross-linked to each other are formed. Since there are no connections among molecules of the same species, the primary pure clusters are polymer chains themselves. The total number density of the unassociated groups before the heteroassociation is turned on is therefore nothing but the density ψ_μ of the groups carried by the primary μ chains. The cluster-size distribution function is given by

$$\lambda_{AB}\nu_{l,m} = \frac{(fl - l)!(gm - m)!x^l y^m}{l!m!(fl - l - m + 1)!(gm - l - m + 1)!} \tag{9.1}$$

where

$$x \equiv \lambda_{AB} f \nu(\mathbf{e}_1; 0) = \lambda_{AB}\psi_A(1 - p)^f \quad \text{and}$$
$$y \equiv \lambda_{AB} g \nu(0; \mathbf{e}_1) = \lambda_{AB}\psi_B(1 - q)^g \tag{9.2}$$

are, as in the previous definitions, the number densities of functional groups that remain unassociated in the mixture.

Also, the number density ζ of cross-links in the mixture, being equal to the number density of the reacted groups on the A and also on the B chain, is given by

$$\zeta \equiv p\psi_A = q\psi_B = pq/\lambda_{AB}(1 - p)(1 - q) \tag{9.3a}$$

$$= [1 + \lambda_{AB}(\psi_A + \psi_B) - \{1 + 2\lambda_{AB}(\psi_A + \psi_B) + \sqrt{D}\}]/2\lambda_{AB} \tag{9.3b}$$

with $D \equiv 1 + 2\lambda_{AB}(\psi_A + \psi_B) + \lambda_{AB}^2(\psi_A - \psi_B)^2$. The reduced volume fraction of the free A chain and the free B chain can then be written as

$$x = \frac{q(1 - p)^{f-1}}{1 - q} \tag{9.4}$$

and

$$y = \frac{p(1-q)^{g-1}}{1-p} \qquad (9.5)$$

respectively. The total number density ν^S of clusters belonging to the sol is given by

$$\nu^S = \phi_A^S/n_A + \phi_B^S/n_B - \zeta \qquad (9.6)$$

The threshold values p^* and q^* at which a gel begins to appear must satisfy the relation

$$p^*q^* = 1/(f-1)(g-1) \qquad (9.7)$$

Here, each p^* or q^* depends on the concentration, but the product p^*q^* is an independent constant. This critical condition can be rewritten as

$$1 + \lambda_{AB}(\psi_A^* + \psi_B^*) - \sqrt{D^*} = 2\lambda_{AB}\psi_A^*\psi_B^*/(f-1)(g-1) \qquad (9.8)$$

Solving this equation for λ_{AB}, we find the association constant λ_{AB} at gelation is given by

$$1/\lambda_{AB} = [1 + (f-1)(g-1)](\psi_A^*\psi_B^*)^{1/2}/[(f-1)(g-1)]^{1/2} - (\psi_A^* + \psi_B^*) \qquad (9.9)$$

Let ϕ_{min} and ϕ_{max} be the limiting volume fraction at which the association constant λ_{AB} goes to infinity:

$$\phi_{min} = 1/[1 + f(f-1)(g-1)n_B/gn_A] \qquad (9.10)$$

$$\phi_{max} = 1/[1 + fn_B/g(f-1)(g-1)n_A] \qquad (9.11)$$

A gel network can exist only in the region between these volume fractions. In the postgel regime, let us follow Flory's treatment[15] and postulate the condition that x and y are given by the same forms as 9.4 and 9.5, i.e.,

$$\frac{q'(1-p')^{f-1}}{1-q'} = \frac{q(1-p)^{f-1}}{1-q} \qquad (9.12a)$$

$$\frac{p'(1-q')^{g-1}}{1-p'} = \frac{p(1-q)^{g-1}}{1-p} \qquad (9.12b)$$

and ψ_A^S, ψ_B^S are found from the relations

$$\lambda_{AB}\psi_A^S = q'/(1-p')(1-q') \qquad (9.13a)$$

$$\lambda_{AB}\psi_A^S = p'/(1-p')(1-q') \qquad (9.13b)$$

Parts a and b of Figure 7 then show the calculated phase diagrams of alternately cross-linked networks in a symmetric case ($n_A = n_B = 10$, $f = g = 3$, $\lambda_0 = 1.0$). The dimensionless binding energy γ between the functional groups on A chains and B chains is changed from figure to figure. Thick solid lines show the sol/gel transition lines, thin dashed lines the binodal, thin solid lines the spinodal, and white circles the critical solution point. The gel region is indicated by the horizontal lines, and the unstable region (U) is shaded. For small γ, the gel region lies inside the unstable region, so that a stable homogeneous gel is not expected. With increase in the association energy, the gel region grows and miscibility is improved near the stoichiometric concentration ϕ = 0.5 (in the symmetric case) by the existence of mixed clusters. In Figure 7a, the population of hetero-clusters becomes so large at low temperatures that a reentrant homogeneous phase appears, and as a result, a new critical solution point appears lying on the sol/gel transition line. With further increase in the association energy, two critical solution points lying at $\phi = 0.5$ merge into a single one. Then, the unstable region splits into two separate areas as is shown in Figure 7b.

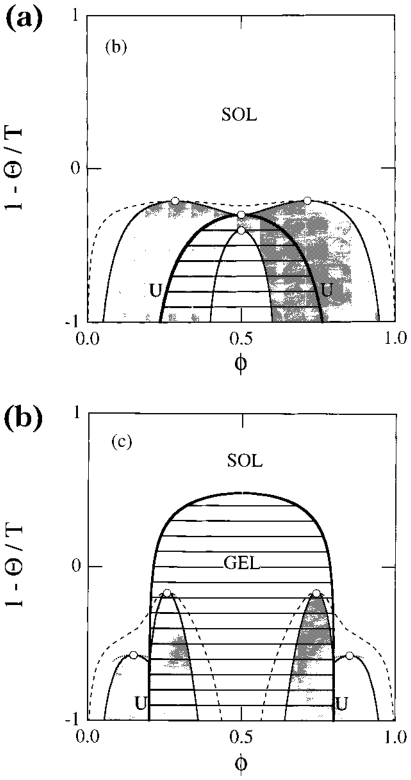

Figure 7. Phase diagrams of a alternately cross-linked network in the symmetric case (Flory's treatment); $n_A = n_B = 10$, $f = g = 3$, and $\lambda_0 = 1.0$. Association energy γ is changed from figure to figure with other parameters being fixed: (a) $\gamma = 1.9926$; (b) $\gamma = 5.0$. The sol/gel transition lines (thick solid lines), binodal (thin dashed line), and spinodal (thin solid line) are shown. The postgel region is indicated by thin horizontal lines. The shaded regions indicated by letter U, are unstable regions. The open circles show critical solution points. The gel region lies inside the spinodal for small values of association constant as in part a, but in the case of strong association as shown in part b, the miscibility gap splits into two separate pieces, and the gel region is stabilized. The alternating network works as the solvilizer in this case due to its amphiphilic nature. The critical points stay inside the gel region so that phase separation into two gels with different concentrations, and hence different cross-link density, is possible.

Figure 8 shows the theoretical phase diagrams for an asymmetric mixture ($n_A = 10$, $n_B = 5$, $f = g = 3$, $\lambda_0 = 1.0$). The overall structure of the phase diagrams remains the same as in the symmetric case. The gel region appears again near the stoichiometric concentration; now, $\phi = {}^2/_3$. For the same value of γ, however, the stable homogeneous gel region is larger compared to the symmetric case.

Let us now consider the microphase separation transition (MST) in alternately cross-linked mixtures. Although there is dynamic exchange of the primary chains between the insides and the outsides of the clusters since the cross-links are temporary, the clusters are basically block copolymers, so that the mixture can in principle undergo MST wherever the population of the

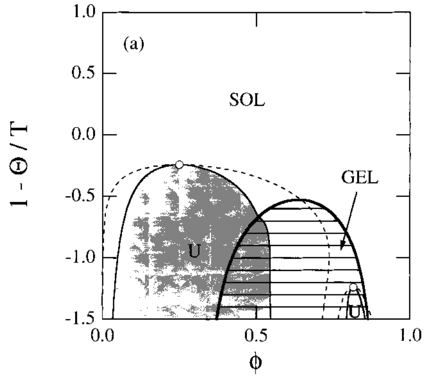

Figure 8. Phase diagrams of an alternately cross-linked network consisting of polymer chains with different molecular-weight (Flory's treatment); $n_A = 10$, $n_B = 5$, $f = g = 3$, and $\lambda_0 = 1.0$. Association energy γ is fixed at $\gamma = 1.5$. Miscibility is improved near the stoichiometric concentration as in Figure 6. For larger values of γ, the gel region expands towards higher temperature.

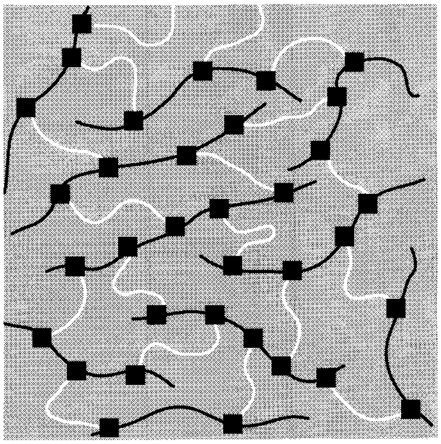

Figure 9. Schematic illustration of a coterminously cross-linked network. The black, white lines and filled squares show A and B polymers and junctions between different species of polymers. B polymers are regarded as the cross-linkers.

clusters is on average sufficiently large. The possibility of MST in physically connected diblock copolymers was first examined by Tanaka et al.[30] Quite recently the transition from a homogeneous mixture to a lamellar phase was experimentally confirmed for hydrogen bonding polymers[31] in which short chains (surfactants) carrying a single functional group are hydrogen bonded to long primary polymer chains to form comb-shaped block copolymers. A theoretical calculation of the phase diagrams, including the MST regions, for hydrogen-bonded comb polymers was reported by Tanaka and Ishida.[32] From these studies, it is highly probable that, in the stable gel regions in Figure 7b and Figure 8, networks are microphase separated near the stoichiometric concentration. To study MST in gelling mixtures, however, we have to calculate the scattering function of the networks formed by random cross-linking. A detailed result will be reported in a forthcoming paper.

Finally, we consider mixtures in which one component B is a telechelic polymer (Figure 9), i.e., a polymer carrying functional groups on both its ends. When the other component, A, carries more than three functional groups, the mixtures form polymer networks in which A chains are coterminously cross-linked by B chains.[19]

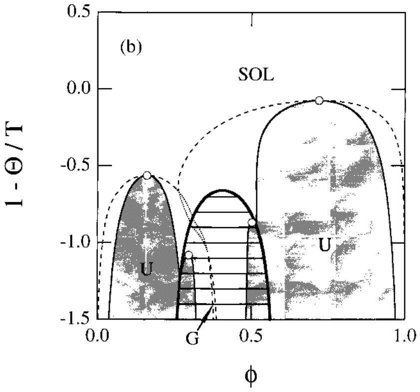

Figure 10. Phase diagrams of a coterminously cross-linked network (Flory's treatment); $n_A = n_B = 10$, $f = 3$, $g = 2$, $\lambda_0 = 1.0$, and $\gamma = 2.55$. The region indicated by letter G is a stable gel region.

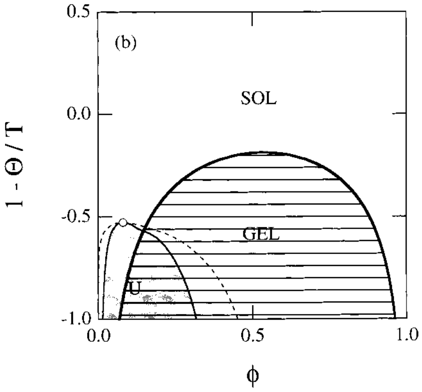

Figure 11. Phase diagrams of a network formed by solvent complexation (Flory's treatment): $n_A = 100$, $n_B = 1$, $f = 100$, $g = 2$, $\lambda_0 = 0.03$, and $\gamma = 1.5$. The gelation temperature shows a maximum near $\phi = 0.5$.

In Figure 10, a phase diagram of a coterminously cross-linked polymer network is shown. The gel region indicated by the thin horizontal lines mostly lies inside the metastable region between the binodal and the spinodal, but a narrow reentrant stable gel region indicated by the letter G appears. For larger values of λ_0, the gel region extends to the higher temperature region and is stabilized. The miscibility gap is split into two parts as in Figure 7b.

In the special limit of coterminous cross-linking, we can study the extreme case where this telechelic chain is not a polymer but a low molecular weight solvent molecule. A physical gel formed by solvent complexation[19,25,33] can be treated in this special way by fixing $n_B = 1$. We show in Figure 11 a theoretical phase diagrams for the gel formed by solvent complexation. In the case of associating polymers belonging to category ii, it was generally shown[19] that the sol/gel transition temperature has a maximum as a function of the concentration. In fact, Francois et al.[25] found a maximum temperature for a solution of atactic polystyrene in carbon disulfide. This fact led them to the conclusion that the junctions are formed by complex formation involving the solvent molecules.

Coterminous cross-linking of colloid particles, dendrimers, microemulsion droplets, *etc.* in solutions by telechelic associating polymers carrying hydrophobes at their both ends implies a very important practical application. By control of the polymer concentration, the solutions reversibly change between sol and gel states. The transition of the polymer conformation from intramolecular loop formation to more open intermolecu-

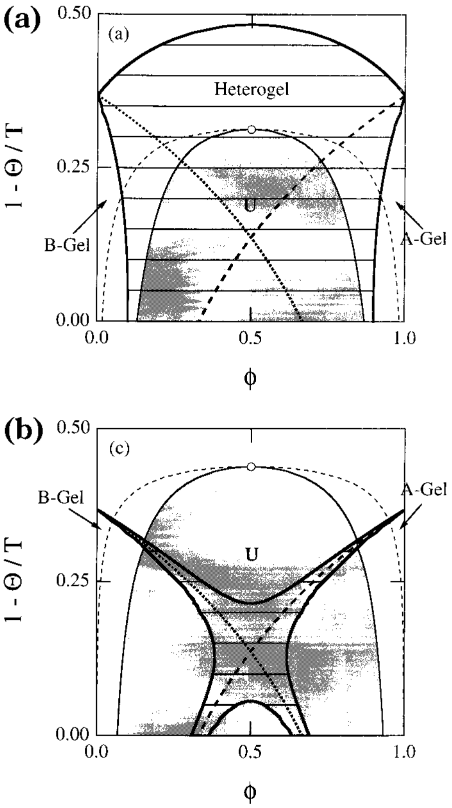

Figure 12. Phase diagrams of a randomly connected network for a symmetric case (Flory's treatment): $n_A = n_B = 10$, $f = g = 3$, $\lambda_{AA0} = \lambda_{BB0} = 1.0$, and $\gamma_{AA} = \gamma_{BB} = \gamma_{AB} = 3.0$. Association constant of the hetero-coupling is changed: (a) $\lambda_0 = 1.0$; (b) $\lambda_0 = 0.1$. The sol/gel transition lines (thick dashed line for A gel, thick dotted line for B gel, and thick solid line for heterogel), binodal (thin dashed line), and spinodal (thin solid line) are shown. Mixed gels are formed in the areas indicated by the thin horizontal lines. For large values of hetero-association constant as in part a, stable mixed gels lying outside the unstable region (U) are possible. The open circle denotes a critical solution point. In all figures pure A gel and B gel regions lie inside the mixed-gel region.

lar bridging with increase in the polymer concentration is directly correlated to gel formation. These systems may be modelled as a ternary solution of bifunctional chains A_2 and multifunctional molecules B_g in a solvent S. Thereby the loops can be regarded as the excited state of A_2 with its two functional groups joining into a single effective functional group. Our theory is directly applicable to such systems. The detailed theoretical results will be reported elsewhere.

X. Randomly Mixed Networks

In category iii, three types of gels can in principle coexist. These are pure A gel, pure B gel, and the mixed AB gel. The mixed gel exists mainly in the region where pure gels are not formed. This tendency agrees with Tolstoguzov's results.[26] Our calculations also shows that the region where all three types of gels coexist lies generally inside the thermodynamically unstable region so that the mixture separates into two phases, one containing A gel and the other B gel. This theoretical prediction agrees with the experimental results reported by Clark et al.[1]

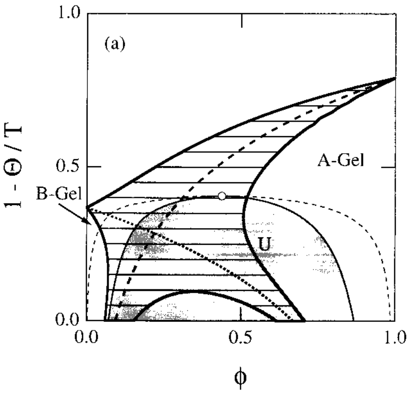

Figure 13. The same as in Figure 12 but for an asymmetric case: $n_A = n_B = 10$, $f = 4$, $g = 3$, $\lambda_{AA0} = \lambda_{BB0} = 1.0$, $\lambda_0 = 0.5$, and $\gamma_{AA} = \gamma_{BB} = \gamma_{AB} = 3.0$.

Parts a and b of Figure 12 show calculated phase diagrams for a randomly connected two-component network. The molecular parameters are fixed symmetrically at $n_A = n_B = 10$ and $f = g = 3$. In Figure 12a, the association constants are equally chosen as $\lambda_{AA0} = \lambda_{BB0} = \lambda_{AB0} = 1.0$ and $\gamma_{AA} = \gamma_{BB} = \gamma_{AB} = 3.0$, so that all associations take place with equal probability. In the figure the sol/gel transition lines of pure A gel (thick dashed line), of pure B gel (thick dotted line), and of mixed heterogel (thick solid line) are shown. The region of mixed gel is indicated by the thin horizontal lines. The binodal and the spinodal are shown by the thin dashed line and thin solid line, respectively. The unstable region, indicated by the letter U, is shaded. The open circle shows the critical solution point. For such large values of the λs, there is a large region of stable mixed gel above the critical point. If the system is quenched from the temperature in this region to the unstable region at concentration $\phi = 0.5$, for instance, it separates into two phases, one with pure B gel (low ϕ phase) and the other with pure A gel (high ϕ phase). For smaller values of the heteroassociation constant, as shown in Figure 12b in which λ_{AB0} is fixed at 0.1, the region of stable mixed gel at high temperatures shrinks, and its greatest part is included inside the unstable region.

Figure 13 shows the asymmetric case where A has larger functionality ($n_A = n_B = 10$, $f = 4$, $g = 3$). Association constants are all equal ($\lambda_{AA0} = \lambda_{BB0} = \lambda_{AB0} = 1.0$, $\gamma_{AA} = \gamma_{BB} = \gamma_{AB} = 3.0$). At high values of ϕ, the system first forms a mixed gel when the temperature is decreased, and then the mixed gel turns into a pure A gel. Switching between the two different gels is therefore possible by simply changing the temperature.

XI. Conclusions and Discussion

We have classified association in the binary mixtures into three fundamental types, each of which shows its own characteristic phase behavior. Possible new types of phase diagrams have been explored in each category. From the chemical potentials obtained to derive the phase diagrams, it is easy to study thermodynamic properties of the mixtures although detailed results are not included in this paper. The theory proposed in this paper is sufficiently general to cover a wide range of phenomena observed in binary associating polymers, such as gelation, micellization, macro- and microphase separation. Each special system can be analyzed by adjusting the molecular architecture and the association constants. However, we have not explicitly taken into account the effect of solvent. If the solvent simply dilutes the mixture without inducing any particular specific interaction, the effect can easily be incorporated into our theory. In forthcoming papers we will report a detailed study of mixtures of associating polymers in a solvent, with particular emphasis on comparison with experimental data.

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