References and Notes

(1) Robinson, C. *Trans. Faraday Soc.* **1956,** *52,* 571.
(2) Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss. Faraday Soc.* **1958,** *25,* 29.
(3) Aviram, A. *J. Polym. Sci., Polym. Lett. Ed.* **1976,** *14,* 757.
(4) (a) Samulski, E. T.; Tobolsky, A. V. *Nature* **1967,** *216,* 997. (b) Samulski, E. T.; Tobolsky, A. V. *Macromolecules* **1968,** *1,* 555.
(5) Mori, T.; Tanaka, R.; Tanaka, T. *Polymer* **1977,** *18,* 1041.
(6) Tsutsui, T.; Tanaka, T. *J. Polym. Sci., Polym. Lett. Ed.* **1977,** *15,* 475.
(7) Tsutsui, T.; Tanaka, R. *Polymer* **1981,** *22,* 117.
(8) Okuyama, T.; Satake, K. *J. Biochem.* **1960,** *47,* 454.
(9) Toriumi, H.; Yanagi, K.; Uematsu, I.; Uematsu, Y. *Mol. Cryst. Liq. Cryst.* **1983,** *94,* 267.
(10) Sayama, N.; Kida, K.; Norisuye, T.; Teramoto, A.; Fujita, H. *Polym. J.* **1972,** *3,* 538.

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Thermodynamic Theory of Network-Forming Polymer Solutions. 1

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ABSTRACT: This paper develops a lattice theory of strongly associating polymer solutions capable of forming macronetworks. The general procedure to deduce thermodynamic properties is presented and applied to thermoreversible gels. It is demonstrated that the multiple-equilibria conditions for molecular association caused by physical cross-linking can describe, when combined with traditional solution theory, the characteristic features of the temperature–concentration phase diagram. The central problem analyzed is the interference between gelation and two-phase separation.

1. Introduction

One of the few uninvestigated important subjects of polymer solutions is the spatial organization by strongly associative forces capable of forming bonds. It is clear that consideration of strong interpolymer interaction superposed on the familiar description of statistical chains can lead to the application of polymer science in numerous systems of practical interest. These include dimerization, solvation, and network formation. The purpose of this paper is to construct a thermodynamic theory of solutions, which include polymer chains carrying reactive groups capable of pairwisely forming bonds. We assume that the binding energy of a bond is, although strong enough to form specific spatial structures, of the order of thermal energy so that the entire system can readily reach thermal equilibrium. Association caused by such interaction can be classified into the following categories:

(1) Polymer chains A associate with each other in a solvent (S). We refer to this case symbolically as A·A/S. Homopolymer networks appear in this case.

(2) Polymer chains A associate with polymer chains B in a mixture of A and B. We refer to this case as A·B. Heteropolymer networks are formed in this case.

(3) Short polymer chains B (or solvent molecules (S)) cross-link long polymer chains A by conterminous reaction (or by forming a three-dimensional complex). We refer to this case as A·B·A (or A·S·A). Network properties are controlled by the chain length of the cross-linkers.

(4) Polymer chains A and polymer chains B can associate with each other within the same species but cannot form bonds between monomers of different species. We refer to this case as A·A/B·B. Interpenetrating polymer networks (IPN) are formed in this case.

The structure of a cluster formed in each category is schematically shown in Figure 1. We develop in this paper a thermodynamic theory that can treat all of these important categories. Extensive polydispersity inherent to such associating solutions is thermally controlled and strongly dependent on the composition of the system.

In the preceding papers,[1,2] we developed a thermodynamic theory of solutions belonging to category 1 and studied the phase behavior caused by the interference between gelation and phase separation. Comparison was made with experimental observations[3,4] for atactic polystyrene in the solvent of carbon disulfide. Present theory includes this theory as its special case.

Solution properties of a system belonging to category 2 were recently studied[5,6] in relation to the cluster formation by hydrogen bonding. Our theory includes this problem as another special case.

Thermodynamics of polymer solutions[7] and statistics of chain reaction (for example, polycondensation[8]) have so far been theoretically treated separately.[9] Our theory will attempt to unify these two mainstreams in the polymer science. In section 2, we will define our problem in more specific terms. Sections 3–5 are devoted to developing the theory. Some special applications and testing of the theory are presented in sections 6 and 7.

2. Definition of the Problem

Consider a binary mixture of linear polymers A and B. We assume for simplicity that polymer chains of each species consist of statistical units of the same size, a. The numbers of the statistical units on a chain are assumed to be n_A for A chain and n_B for B chain. We also assume that each chain carries a large number of reactive groups

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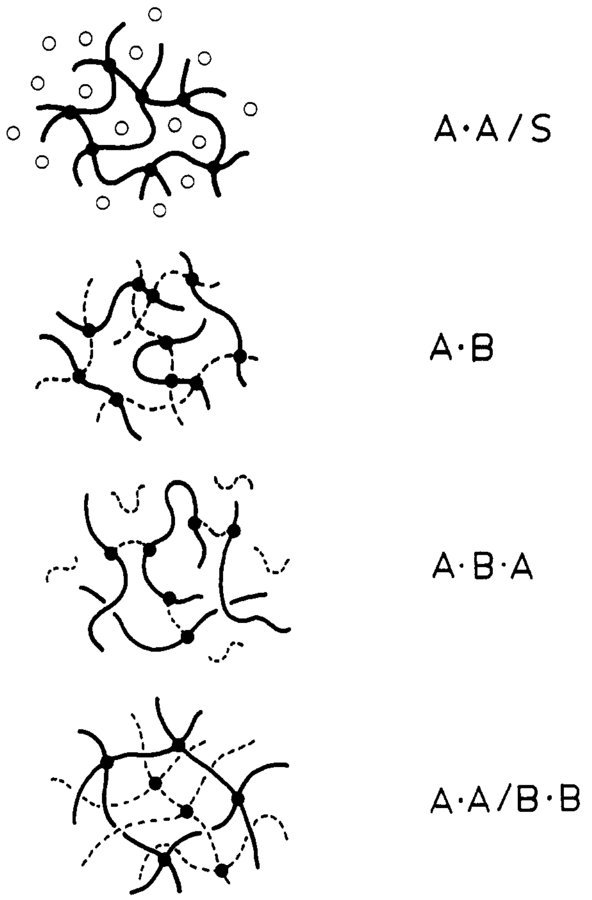

Figure 1. Four main categories of the network-forming polymer solutions are schematically drawn. Thick lines show A polymer chains, broken lines B polymer chains, and black circles cross-linked points.

capable of pairwisely forming bonds, although it is not necessary to specify the details of the interaction at this stage. In thermal equilibrium, associative interactions among specific groups on the polymer chains form intermolecular clusters with a wide spectrum of size. The system is inherently polydisperse and, in some case, contains a polymer network that has grown to macroscopic dimensions.

Let (l,m) be the symbol referring to a cluster made up of l A chains and m B chains, and let $N_{l,m}$ be the number of clusters of the type (l,m) in the system. The chains that remain isolated are then specified by the symbol (1,0) or (0,1). To avoid confusion with monomeric units, let us call them A unimer or B unimer. Let V be the total volume of the system, and let $\Omega \equiv V/a^3$ be the number of microscopic cells measured in the unit of the volume a^3 of a statistical unit. The volume fraction occupied by the total of (l,m) clusters is then given by

$$\phi_{l,m} = (ln_A + mn_B)\nu_{l,m} \tag{2.1}$$

where $\nu_{l,m} \equiv N_{l,m}/\Omega$ is the number concentration of the clusters of the (l,m) type.

To cope with the appearance of macroscopic networks (hereafter referred to as "gel"), which contain an infinite number of polymers of either the A or B species, we first specify the part of the system consisting of finite-size clusters (l,m), which will be referred to as "sol". The volume fraction of A polymers in the sol part is given by

$$\phi_A{}^S = n_A \sum_{l,m} l\nu_{l,m} \tag{2.2}$$

and similarly

$$\phi_B{}^S = n_B \sum_{l,m} m\nu_{l,m} \tag{2.3}$$

for B polymers. Here the summation is taken over all possible sets of integers (l,m) except (0,0). Infinite clusters are not included in these series. The total volume fraction of the sol part in the system is given by the sum of the two:

$$\phi^S = \phi_A{}^S + \phi_B{}^S = \sum_{l,m} \phi_{l,m} \tag{2.4}$$

This should be equal to unity when no macronetworks exist (pregel regime) but becomes smaller than unity as soon as a macronetwork appears (postgel regime). Let ϕ_i be the volume fraction of the species i (i = A, B), which can be externally controlled in the experiments. The relation

$$\phi_A + \phi_B = 1 \tag{2.5}$$

should always hold for these, because incompressibility of the system is assumed. The excess quantities

$$\phi_i{}^G \equiv \phi_i - \phi_i{}^S \qquad i = \mathrm{A, B} \tag{2.6}$$

should then be regarded as the amount of monomers of the i species that are participating in the macroscopic network. We call them the "gel volume fraction of i species". The total gel fraction is then given by

$$\phi^G = 1 - \phi^S = 1 - \sum_{l,m} \phi_{l,m} \tag{2.7}$$

The number $\nu_i{}^G$ of i chains (per lattice site) belonging to the gel part is given by

$$\nu_i{}^G = \phi_i{}^G/n_i \tag{2.8}$$

We now impose the conditions that the cluster formation–decomposition processes $l(1,0) + m(0,1) \rightleftarrows (l,m)$ are in multiple equilibria. These conditions can be expressed in a compact form

$$l\mu_A + m\mu_B = \mu_{l,m} \tag{2.9}$$

in terms of the chemical potentials for all possible sets of (l,m), as is familiar for chemical equilibria.[10] Here μ_i (i = A, B) is the chemical potential of an i unimer in the system and $\mu_{l,m}$ the chemical potential of a cluster of the (l,m) type. We have $\mu_A = \mu_{1,0}$ and $\mu_B = \mu_{0,1}$ by definition. The free energy, combined with the multiple-equilibria conditions (eq 2.9), reveals the thermodynamic properties of associating polymer mixtures. Among them we shall focus on the cluster distribution function, phase separation, and sol-to-gel transition.

3. Lattice Theory of Associating Polymer Solutions

We consider the free energy change, ΔF, to bring the system to the actual state starting from the reference state in which N_A unreacted A chains and N_B unreacted B chains are prepared separately. We first connect the chains to form clusters until their size distribution becomes exactly the same as that we have in the actual system. The free energy change, ΔF_{rea} in this step is expressed as

$$\Delta F_{rea} = \Omega\{\sum_{l,m} \mu_{l,m}{}^\circ \nu_{l,m} + \mu_A{}^{G\circ}\nu_A{}^G + \mu_B{}^{G\circ}\nu_B{}^G\} \tag{3.1}$$

where $\mu_{l,m}{}^\circ$ is the chemical potential of an (l,m) cluster in the isolated state and $\mu_i{}^{G\circ}$ (i = A, B) is the chemical potential of a single i chain that is a part of the gel network. Under a constant pressure, $\mu_{l,m}{}^{\circ}$ is equivalent to the internal free energy due to the combination and bond formation of the constitutional chains. Similarly, $\mu_i{}^{\mathrm{G}\circ}$ is the free energy change produced when an isolated i chain participates in the gel network from isolation.

We next mix thus constructed clusters to form a mixture. The free energy change in this mixing process is given by

$$\beta\Delta F_{\mathrm{mix}} = \Omega\{\sum_{l,m}\nu_{l,m}\ln\phi_{l,m} + \chi\phi_{\mathrm{A}}\phi_{\mathrm{B}}\} \tag{3.2}$$

according to the lattice theory of polymer solutions developed by Flory and Huggins,[9] where $\beta \equiv 1/kT$ is the inverse temperature and χ the Flory–Huggins χ parameter specifying the strength of the contact interaction between A monomer and B monomer. The χ parameter depends on the temperature.

Combining eqs 3.1 and 3.2, we are led to the total free energy

$$\Delta F = \Delta F_{\mathrm{rea}} + \Delta F_{\mathrm{mix}} \tag{3.3}$$

from which our theory starts. The chemical potential of each cluster in the mixture can be found from this free energy by differentiation. We find after lengthy calculation

$$\beta\mu_{l,m} = \beta(\partial\Delta F/\partial N_{l,m})_{T,N'} = \beta\mu_{l,m}{}^{\circ} + \ln\phi_{l,m} + 1 - (n_{\mathrm{A}}l + n_{\mathrm{B}}m)\nu^{\mathrm{S}} + \chi\{n_{\mathrm{A}}l\phi_{\mathrm{B}} + n_{\mathrm{B}}m\phi_{\mathrm{A}} - (n_{\mathrm{A}}l + n_{\mathrm{B}}m)\phi_{\mathrm{A}}\phi_{\mathrm{B}}\} \tag{3.4}$$

where differentiation must be taken under constant temperature and a constant number of clusters that are different from the (l,m) type. Here the total number ν^{S} of clusters in the sol part is given by

$$\nu^{\mathrm{S}} \equiv \sum_{l,m}\nu_{l,m} \tag{3.5}$$

We next introduce an averaging procedure $\langle Q\rangle$ for any quantity Q pertaining to the sol part. This is done by taking the cluster number $\nu_{l,m}$ as the probability weight. For example, we have

$$\langle l\rangle \equiv \sum_{l,m} l\nu_{l,m}/\nu^{\mathrm{S}} \tag{3.6a}$$

$$\langle m\rangle \equiv \sum_{l,m} m\nu_{l,m}/\nu^{\mathrm{S}} \tag{3.6b}$$

for the average association number for A and B molecules in the sol, respectively. By definition such an average is called the "number average".

In terms of this number average, the mean cluster number (eq 3.5) can be rewritten as

$$\nu^{\mathrm{S}} = \phi^{\mathrm{S}}/\langle n_{\mathrm{A}}l + n_{\mathrm{B}}m\rangle \tag{3.7}$$

where $\phi^{\mathrm{S}} \equiv \sum(n_{\mathrm{A}}l + n_{\mathrm{B}}m)\nu_{l,m}$ is the volume fraction of the sol part as defined in eq 2.4.

By similar differentiation of the free energy, we find

$$\beta\mu_{\mathrm{A}}{}^{\mathrm{G}} = \beta\mu_{\mathrm{A}}{}^{\mathrm{G}\circ} - n_{\mathrm{A}}\nu^{\mathrm{S}} + \chi n_{\mathrm{A}}\phi_{\mathrm{B}}{}^2 \tag{3.8a}$$

$$\beta\mu_{\mathrm{B}}{}^{\mathrm{G}} = \beta\mu_{\mathrm{B}}{}^{\mathrm{G}\circ} - n_{\mathrm{B}}\nu^{\mathrm{S}} + \chi n_{\mathrm{B}}\phi_{\mathrm{A}}{}^2 \tag{3.8b}$$

for the chemical potential of a single chain of each species belonging to the gel network.

Having obtained the chemical potentials, we now impose the multiple-equilibria conditions for the association–dissociation process. Substituting eq 3.4 into eq 2.9, we find after rearrangement

$$\phi_{l,m} = K_{l,m}x^l y^m \tag{3.9}$$

where $x \equiv \phi_{1,0}$ and $y \equiv \phi_{0,1}$ are the volume fractions of A unimer and B unimer, respectively. The association constant $K_{l,m}$ is defined by

$$K_{l,m} = \exp(l + m - 1 - \Delta_{l,m}) \tag{3.10}$$

in terms of the difference $\Delta_{l,m}$ in the dimensionless chemical potentials before and after the clustering:

$$\Delta_{l,m} \equiv \beta(\mu_{l,m}{}^{\circ} - l\mu_{\mathrm{A}}{}^{\circ} - m\mu_{\mathrm{B}}{}^{\circ}) \tag{3.11}$$

We have thus found the distribution of clusters in terms of the unimer concentration of both species. The internal free energies of the clusters affect the solution properties through the association constants. From the cluster volume fractions (eq 3.9) we find the total number of clusters, ν^{S}, in the sol and the sol volume fraction, ϕ^{S}, as a function of x and y:

$$\nu^{\mathrm{S}} = \nu^{\mathrm{S}}(x,y) = \sum_{l,m}\frac{K_{l,m}}{ln_{\mathrm{A}} + mn_{\mathrm{B}}}x^l y^m \tag{3.12}$$

$$\phi^{\mathrm{S}} = \phi^{\mathrm{S}}(x,y) = \sum_{l,m}K_{l,m}x^l y^m \tag{3.13}$$

By taking the derivatives of ν^{S}, eqs 2.2 and 2.3 are transformed into

$$\phi_{\mathrm{A}}{}^{\mathrm{S}} = n_{\mathrm{A}}x(\partial\nu^{\mathrm{S}}(x,y)/\partial x) \tag{3.14a}$$

$$\phi_{\mathrm{B}}{}^{\mathrm{S}} = n_{\mathrm{B}}y(\partial\nu^{\mathrm{S}}(x,y)/\partial y) \tag{3.14b}$$

which give the volume fraction of each species in the sol. A relation

$$(n_{\mathrm{A}}x\partial/\partial x + n_{\mathrm{B}}y\partial/\partial y)\nu^{\mathrm{S}}(x,y) = \phi^{\mathrm{S}}(x,y) \tag{3.15}$$

holds as it should.

4. Pregel Regime

To study the thermodynamic properties, we must express the unimer concentrations as a function of total concentration. In the following we take ϕ_{A} as the independent variable and write it simply as ϕ. We then have $\phi_{\mathrm{B}} = 1 - \phi$ by definition. In the pregel regime where no macronetwork exists, the infinite double power series (eq 3.13 and hence eq 3.12) converges to provide an analytical function. Because we have $\phi_{\mathrm{A}}{}^{\mathrm{S}} = \phi$ and $\phi_{\mathrm{B}}{}^{\mathrm{S}} = 1 - \phi$ in this regime, the relations 3.14a,b give the coupled equations

$$n_{\mathrm{A}}x(\partial\nu^{\mathrm{S}}(x,y)/\partial x) = \phi \tag{4.1a}$$

$$n_{\mathrm{B}}y(\partial\nu^{\mathrm{S}}(x,y)/\partial y) = 1 - \phi \tag{4.1b}$$

By these two equations we can solve the two unknown parameters x and y as a function of ϕ. Once we find x and y, we can readily express any moments of the cluster distribution function in terms of the system composition ϕ and the temperature T. For example the number-average association numbers $\langle l\rangle$ and $\langle m\rangle$ for each species are given by

$$\langle l\rangle = \partial\ln\nu^{\mathrm{S}}(x,y)/\partial\ln x \tag{4.2a}$$

$$\langle m\rangle = \partial\ln\nu^{\mathrm{S}}(x,y)/\partial\ln y \tag{4.2b}$$

The weight averages are similarly given by

$$\langle l\rangle_{\mathrm{w}} = \partial\ln\phi^{\mathrm{S}}(x,y)/\partial\ln x \tag{4.3a}$$

$$\langle m\rangle_{\mathrm{w}} = \partial\ln\phi^{\mathrm{S}}(x,y)/\partial\ln y \tag{4.3b}$$

The functional forms of $x(\phi)$ and $y(\phi)$ must be substituted after taking derivatives shown on the right-hand-side of these equations.

To study thermodynamic stability of the system, we next consider the Gibbs free energy. Gibbs–Duhem's relation gives $g = \sum \mu_{l,m}\nu_{l,m}$ for the Gibbs free energy per lattice cell, but this is equivalent to

$$g = \mu_A(\phi_A/n_A) + \mu_B(\phi_B/n_B) \qquad (4.4)$$

due to the multiple-equilibria conditions. Substituting into eq 4.4 μ_A and μ_B derived from eq 3.4 by setting $(l,m) = (1,0)$ or $(0,1)$, we find $g = g_0 + \Delta g$, where $g_0 = \mu_A{}^\circ\phi_A/n_A + \mu_B{}^\circ\phi_B/n_B$ is the free energy in the reference state, and an additional Δg defined by

$$\beta\Delta g = \phi/n_A \ln x + (1-\phi)/n_B \ln y + \phi/n_A + (1-\phi)/n_B - \nu^S(x,y) + \chi\phi(1-\phi) \qquad (4.5)$$

is due to the association and mixing. The unimer concentrations x and y in this equation should be regarded as a function of ϕ.

The spinodal line that separates the thermodynamically unstable region from the stable one on the temperature–concentration plane is given by the condition[9] $\partial^2\Delta g/\partial\phi^2 = 0$, or explicitly

$$\frac{\kappa_A(\phi)}{n_A\phi} + \frac{\kappa_B(\phi)}{n_B(1-\phi)} - 2\chi = 0 \qquad (4.6)$$

in our model, where newly appeared κ functions are defined by

$$\kappa_A(\phi) \equiv \phi\partial \ln x/\partial\phi$$

$$\kappa_B(\phi) \equiv -(1-\phi)\partial \ln y/\partial\phi \qquad (4.7)$$

The spinodal condition (eq 4.6) differs from the familiar one for a monodisperse solution[9] in that, for an associating species i, complex function κ_i appears in the numerator where there should be unity for nonassociating species. Deviation of the κ functions from unity thus gives the effect of cross-linking.

5. Sol-to-Gel Transition

We have tacitly assumed so far that the infinite double power series for ϕ^S (and hence for ν^S) converges. A point in the unit square ($0 \le x \le 1$, $0 \le y \le 1$) on the (x,y) plane gives a definite value of ϕ^S and ν^S under such convergence conditions. If we vary the total composition ϕ, the point (x,y) moves in the unit square. For a macroscopic network (l or $m = \infty$) to appear, however, ϕ^S must stick to a certain value smaller than 1 to give an excess quantity $1 - \phi^S$. This condition is satisfied if $\phi^S(x,y)$, as a function of x and y, takes a finite value smaller than 1 on a line in the unit square and diverges as soon as the point (x,y) crosses it. For a solution capable of gelling, therefore, a borderline exists and separates the square into a convergent region and a divergent region of the power series. Exactly on the boundary line, ϕ^S and ν^S take a finite value, while outside this line they diverge. Since the radius of convergence depends on the total concentration ϕ, let us express the boundary by a parametric representation $(x^*(\phi),y^*(\phi))$ for $0 \le \phi \le 1$. As ϕ varies, the sol fraction changes according to the relation $\phi^S = \phi^S(x^*(\phi),y^*(\phi))$. The gel fraction can be found by subtraction: $\phi^G = 1 - \phi^S(x^*(\phi),y^*(\phi))$. Simple examples of the boundary lines will be presented in the following section.

In the postgel regime a chain participating in the gel network is in chemical equilibrium with an isolated chain of the same species. This imposes additional conditions:

$$\mu_{1,0} = \mu_A{}^G \qquad \mu_{0,1} = \mu_B{}^G \qquad (5.1)$$

Substituting eqs 3.4 and 3.8, we find

$$\beta(\mu_A{}^\circ - \mu_A{}^{G\circ}) + \ln x^* + 1 = 0 \qquad (5.2a)$$

$$\beta(\mu_B{}^\circ - \mu_B{}^{G\circ}) + \ln y^* + 1 = 0 \qquad (5.2b)$$

Let $\delta_i \equiv \beta(\mu_i{}^{G\circ} - \mu_i{}^\circ)$ be the dimensionless free energy that an i chain gains when it is absorbed into the gel network from isolation. They depend on the total composition. The unimer concentration on the convergence line is then given by

$$x^*(\phi) = \exp\{\delta_A(\phi) - 1\} \qquad y^*(\phi) = \exp\{\delta_B(\phi) - 1\} \qquad (5.3)$$

from eqs 5.2a and b. These equations provide explicit meanings of the sol-to-gel transition boundary on the (x,y) plane in terms of the physical quantities δ_i.

We next proceed to the study of the thermodynamic properties in the postgel regime. The relation 3.14 giving the sol fraction of each species must now be replaced by

$$\phi_A{}^S = n_A x^*(\partial\nu^S/\partial x)_{x^*,y^*} \qquad (5.4a)$$

$$\phi_B{}^S = n_B y^*(\partial\nu^S/\partial y)_{x^*,y^*} \qquad (5.4b)$$

in this regime. The Gibbs free energy per lattice site in this postgel regime includes contribution from the gel:

$$g = \sum_{l,m}\mu_{l,m}\nu_{l,m} + \mu_A{}^G\nu_A{}^G + \mu_B{}^G\nu_B{}^G \qquad (5.5)$$

Multiple-equilibria conditions again lead to $g = g_0 + \Delta g$ with

$$\beta\Delta g = \phi/n_A \ln x^* + (1-\phi)/n_B \ln y^* + \phi/n_A + (1-\phi)/n_B - \nu^S(x^*,y^*) + \chi\phi(1-\phi) \qquad (5.6)$$

Taking the second derivative, we are led to the spinodal condition

$$\frac{\kappa_A{}^*(\phi)}{n_A\phi} + \frac{\kappa_B{}^*(\phi)}{n_B(1-\phi)} - 2\chi = 0 \qquad (5.7)$$

after some rearrangement, where the functions $\kappa_i{}^*$ are given by

$$\kappa_A{}^*(\phi) = \phi\frac{d}{d\phi}\left(1 + \phi_A{}^G\frac{d}{d\phi}\right)\ln x^* \qquad (5.8a)$$

$$\kappa_B{}^*(\phi) = -(1-\phi)\frac{d}{d\phi}\left(1 - \phi_B{}^G\frac{d}{d\phi}\right)\ln y^* \qquad (5.8b)$$

6. Simple Examples of the Nongelling Case

Having developed a general thermodynamic theory of associating polymer solutions, we now test it by applying it to specific systems. This will demonstrate the validity of the theory. We first focus our attention on the solutions in which polymers can form aggregates, but the size of the clusters is limited to being finite (hereafter referred to as "nongelling" case).

A. Dimer Formation. The first example is dimer formation. Consider a mixture of polymer A and polymer B, each carrying one reactive group on its chain end. Assume that a pair of reactive groups on different species can form a bond, while chains of the same species do not react with each other. A dimer A·B produced is a block copolymer. The system contains three types of molecules: (1,0), (0,1), and (1,1) in our present notation. Applying our theory, we find $K_{1,0} = K_{0,1} = 1$ and $K_{1,1} = \exp(1 - \Delta) \equiv K$ for the association constants, where $\Delta \equiv \beta(\mu_{1,1}{}^\circ - \mu_A{}^\circ - \mu_B{}^\circ)$. The incompressibility condition requires that the total volume fraction must be unity

$$\phi^S(x,y) = x + y + Kxy = 1 \qquad (6.1)$$

where x and y are the volume fractions of isolated A and B chains, respectively. The average number of clusters is similarly given by

$$\nu^{S}(x,y) = (1/n)(x/a + y/b + Kxy) \qquad (6.2)$$

with $n \equiv n_A + n_B$, $a \equiv n_A/n$, and $b \equiv n_B/n$. General procedure 4.1 leads to the relations

$$n_A x(\partial\nu^S/\partial x) = x(1 + aKy) = \phi \qquad (6.3a)$$

$$n_B y(\partial\nu^S/\partial y) = y(1 + bKx) = 1 - \phi \qquad (6.3b)$$

from which x and y can be expressed as a function of the volume fraction ϕ of A polymers. Straightforward calculation leads to the result

$$x = \phi - az \qquad y = 1 - \phi - bz \qquad (6.4)$$

where $z \equiv Kxy$ is the volume fraction of A·B chains. Substituting eq 6.4 into this definition, we find that z must be one root of a second-order algebraic equation: $z = K(\phi - az)(1 - \phi - bz)$. Taking the root with correct sign, we find

$$z(\phi) = \{a(1-\phi) + b\phi + K^{-1} + [D(\phi)]^{1/2}\}/2ab \qquad (6.5)$$

where $D(\phi) \equiv \{a(1-\phi) + b\phi + K^{-1}\}^2 - 4ab\phi(1-\phi)$. When this z function is used, the κ functions can be written as

$$\kappa_A(\phi) = \frac{1 - az'}{1 - az/\phi} \qquad \kappa_B(\phi) = \frac{1 + bz'}{1 - bz/(1-\phi)} \qquad (6.6)$$

where $z' \equiv dz/d\phi$ is the derivative of $z(\phi)$. The spinodal condition (eq 4.6) gives the limit of macroscopic stability of the system. Although it is interesting to find the miscibility gap on the temperature–concentration plane by solving this equation, there is another important factor to be considered for the case of block copolymer solutions. This is the tendency of the system to form microscopic phases.[11,12] These are spatially inhomogeneous phases including lamella structure, spherical or rodlike micelles, and so on. The novel aspect of our associating mixture is that the population of the block copolymer is automatically fixed by the equilibrium condition. Therefore, a broad possibility arises: to control microphases by changing the temperature. The competition or interference between microphase formation and macrophase separation will bring a wealth of new results, which we shall discuss in a separate paper[13] in detail.

B. Solvation. We consider another simple example of nongelling association. Consider a polymer solution in which solvent molecules can stick onto a specific group on the polymer chains. Hydrogen bonding[14] between a solvent water molecule and an oxygen atom on a water-soluble chain provides a typical example of such interaction.[15] Capture of a solvent molecule by a cavity formed between neighboring large side groups[16] is another example. Stereoregularity of the polymer plays an important role in the latter case.

Let f be the number of groups on a polymer chain that can capture a solvent molecule. In equilibrium the system contains clusters of the type (0,1), (1,0), and $(1,m)$ ($m = 1, ..., f$). We then have

$$\phi^S(x,y) = y + x\sum_{m=1}^{f} K_{1,m} y^m = 1 \qquad (6.7)$$

$$\nu^S(x,y) = y + x\sum_{m=1}^{f} \frac{K_{1,m}}{n+m} y^m \qquad (6.8)$$

The whole procedure can readily be applied to this case. Since solubility is enhanced by solvation when the temperature is decreased, we find the remarkable conclusion that the system can exhibit a closed type miscibility gap with lower critical solution temperature when certain plausible conditions are satisfied. Details will be discussed and compared with the experiments in a subsequent paper.[17]

7. An Example of the Gelling Case

We now proceed to the study of gelling systems. One of the simplest examples is a polymer solution in which polymers, each carrying f identical reactive groups, can associate each other in a solvent by forming bonds between a pair of reactive groups. The system can be symbolized as A·A/S in our notation. In a recent paper,[1,2] we studied thermodynamic properties of this system and found a variety of novel aspects in its phase behavior. These include tricriticality and three-phase equilibrium caused by the interference between gelation and phase separation. We now show that our previous theory can be derived as a special case of the present study. The clusters we have in the system consist of the types (0,1) and $(l,0)$ ($l = 1, 2, ..., \infty$). In our paper,[1] we considered the simplest model in which clusters are constructed in the form of a Cayley tree made up of chains carrying f functional groups. Internal loop formation was neglected. The association constants $K_{l,0}$ must then be proportional to the Stockmayer distribution[8] $\omega_l = (fl - l)!/l!(fl - 2l + 2)!$. We introduce a temperature shift factor $\lambda(T) \equiv f\exp(1 - \beta\Delta f_0)$, where Δf_0 is the free energy change in a single-bond formation. Concentration variables appear always with this factor. Using scaled unimer concentrations $x \equiv \lambda(T)\phi_{1,0}$ and $y \equiv \lambda(T)\phi_{0,1}$, we find

$$\lambda\phi^S(x,y) = y + f\sum_{l=1}^{\infty}\omega_l x^l \qquad (7.1)$$

and

$$\lambda\nu^S(x,y) = y + (f/n)\sum_{l=1}^{\infty}(\omega_l/l)x^l \qquad (7.2)$$

where n is the degree of polymerization of a chain. The procedure indicated by eq 4.1 leads to the result

$$fx\frac{dG_{-1}(x)}{dx} = \lambda\phi \qquad (7.3a)$$

$$fy = \lambda(1 - \phi) \qquad (7.3b)$$

where functions $G_k(x)$ for integer k are defined by the kth moment of the Stockmayer distribution:

$$G_k(x) \equiv \sum_{m=1}^{\infty} m^k \omega_m x^m \qquad (7.4)$$

Since a relation $xG_{k-1}'(x) = G_k(x)$ holds, (eq 7.3a) gives $fG_0(x) = \lambda\phi$. Inverting this relation, we find the function $\psi(\lambda\phi)$, in eq 6.11 of the ref 1. The sol-to-gel transition line is given by the radius of convergence, x^*, of the function $G_0(x)$, while the solvent concentration, y, can be arbitrary. Simple mathematical analysis gives $x^* = (f-2)^{f-2}/(f-1)^{f-1}$. The boundary line on the (x,y) plane is therefore parallel to the y axis as shown in Figure 2. Since $fG_0(x^*) = 1/(2(f - 2))$, this line corresponds to $\lambda\phi = 1/(2(f - 2))$ when mapped on the physical temperature–concentration plane. All these results are in agreement with our previous theory,[1] and we shall not repeat here the further details.

8. Conclusion and Discussion

We have developed a thermodynamic theory of associating polymer solutions. It has been demonstrated that the range of its validity is sufficiently broad so that,

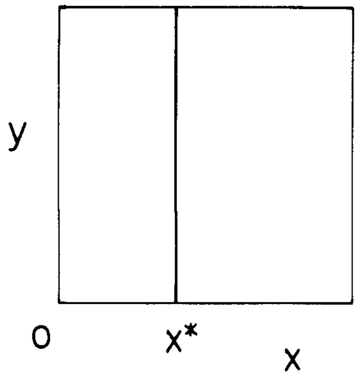

Figure 2. Sol-to-gel transition line is shown on the (x,y) plane of the unimer concentrations for a model gelling system A·A/S. The concentration x of the isolated polymers is fixed as the total concentration is changed, while the solvent concentration y is arbitrary.

as far as equilibrium properties are concerned, it can be applied to numerous systems of practical interest, including hydration, block copolymers, a large variety of gels, and an interpenetrating polymer network. Detailed studies of each specific problem will be treated in the subsequent papers. It is hoped that the study of associating polymers will provide key ideas for the understanding of other spatial and temporal structures formed by strong interactions.

Clearly, the models we discussed in this paper are crude in the sense that they are based on the classical mean-field picture. They were chosen so as to make the final calculation as simple as possible, while maintaining physical reasonableness. Since mean-field approximation does not correctly predict the nature of concentration fluctuations near the phase transition point, more sophisticated treatment of the fluctuation effects will be necessary in the next step when a new type of phase transition is predicted in our theory. The scaling theory of associating polymers developed by Cates and Witten[18] illustrates a possible approach toward this goal.

There are two major transitions in our system: gelation and phase separation, each accompanied with its own critical phenomena. In a special case where the two transitions come close to each other on the temperature–concentration plane, fluctuations of a different nature conflict. It is possible for a completely new critical phenomena to appear as a result. Comprehension of interrelations between molecular association and thermodynamic properties is an obvious prerequisite for interpretation of a wide variety of self-organization in macromolecular solutions.

References and Notes

(1) Tanaka, F. *Macromolecules* **1989**, *22*, 1988.
(2) Tanaka, F.; Matsuyama, A. *Phys. Rev. Lett.* **1989**, *62*, 2759.
(3) Tan, H. M.; Moet, A.; Hiltner, A.; Baer, E. *Macromolecules* **1983**, *16*, 28. Boyer, R. F.; Baer, E.; Hiltner, A. *Macromolecules* **1985**, *18*, 427.
(4) François, J.; Gan, J. Y. S.; Guenet, J. M. *Macromolecules* **1986**, *19*, 2755.
(5) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1989**, *22*, 570, 580, 586.
(6) Kim, H.-I.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1989**, *22*, 3374.
(7) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51; **1944**, *12*, 425. Huggins, M. L. *J. Phys. Chem.* **1942**, *46*, 151.
(8) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096. Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45; **1944**, *12*, 125.
(9) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(10) Fowler, R.; Guggenheim, E. A. *Statistical Thermodynamics*; Cambridge University Press: Cambridge, U.K., 1965; Chapter XII. Lifshitz, E. M.; Pitaevskii, L. P. *Statistical Physics*; Part 1, Pergamon Press: Oxford, U.K., 1980; Chapter X.
(11) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(12) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(13) Tanaka, F.; Matsuyama, A.; submitted for publication in *Phys. Rev. Lett.*
(14) Schuster, P. *Encyclopedia of Physical Science and Technology*; Academic Press: New York, 1987; Vol. 6, p 520.
(15) Malcolm, G. N.; Rowlinson, J. S. *Trans. Faraday Soc.* **1957**, *53*, 921. Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2053.
(16) Klein, M.; Guenet, J. M. *Macromolecules* **1989**, *22*, 3716.
(17) Matsuyama, A.; Tanaka, F., submitted for publication in *Phys. Rev. Lett.*
(18) Cates, M. E.; Witten, T. A., Jr. *Macromolecules* **1986**, *19*, 72.