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Pressure-Controlled Thermoreversible Gelation

Yukinori Okada and Fumihiko Tanaka*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

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ABSTRACT: The effect of vapor pressure on the thermoreversible gelation in polycondensation reactions is theoretically studied on the basis of the lattice theory of polymer solutions combined with the conventional Flory−Stockmayer theory of gelation. In polycondensation systems, concentration of the produced three-dimensional branched polymers in the reaction bath changes as reaction proceeds due to the byproduct of the solvent molecules, such as water, alcohol, etc., and hence it is not a controllable parameter. We calculate the polymer concentration as a function of temperature and vapor pressure of the solvent, and we study how sol/gel transition interferes with macroscopic phase separation in such reactive solutions. We find a new reentrant sol phase at high pressure that is brought by a strong backward reaction. The thermodynamic conditions to reach the gel point without phase separation are found. Gel point can be reached even for reactions in closed vessels where pressure changes under a constant volume. The pressure−temperature phase diagrams for closed systems showing sol/gel transition lines and phase separation lines are derived.

1. Introduction

In polycondensation reactions, such as polyesterification from carboxylic acids and alcohols, polyamidation from carboxylic acids and amines, water molecules split during the reaction are immediately removed to prevent backward reaction and to reach high conversion with high molecular weight linear polymers.[1,2] The condensation reaction is basically reversible, and hence, backward reaction takes place when there is excess water. Consider, for instance, a condensation reaction of the type

$$-\mathrm{A} + \mathrm{B}- \rightleftharpoons -\mathrm{AB}- + \mathrm{H_2O} \tag{1.1}$$

where A and B are functional groups. If we assume a complete reaction equilibrium, we have the condition

$$[-\mathrm{AB}-][\mathrm{H_2O}]/[-\mathrm{A}](1-\alpha_\mathrm{A})[\mathrm{B}-](1-\alpha_\mathrm{B}) = \lambda(T) \tag{1.2}$$

where $[-\mathrm{AB}-]$ is the molar concentration of the A−B bonds, $[\mathrm{H_2O}]$ is the molar concentration of water, α_A and α_B are the conversions of A and B functional groups, and $\lambda(T)$ is the equilibrium constant. For an equimolar reaction where $[-\mathrm{A}] = [\mathrm{B}-]$ holds, we have the same conversion $\alpha_\mathrm{A} = \alpha_\mathrm{B}$, which we write as α. From the equilibrium condition (1.2), the conversion α is approximately given by $\alpha \simeq 1 - 1/\sqrt{h}$, and the average degree $\langle x\rangle$ of polymerization, both number- and weight-average, is given by $\langle x\rangle \simeq 1/\sqrt{h}$, where

$$h \equiv [\mathrm{H_2O}]/\lambda(T)\psi \tag{1.3}$$

is an important dimensionless parameter to measure the effect of water.[1,2] Here, ψ is the molar concentration of the functional groups. Hence, the concentration of water must be small, or the reaction equilibrium constant must be large, to obtain long chains. The parameter h can be changed at will through experimental manipulation. Reaction is usually processed in an open vessel, and water vapor is removed by the flow of inert gases.

In contrast, in polycondensation of multifunctional monomers, reaction easily reaches the gel point because the conversion at the gel point is roughly estimated to be

$$\alpha \simeq 1/(f-1) \tag{1.4}$$

where f is the functionality of the monomer, i.e., the number of functional groups carried by a monomer.[1,3,4] For example, it is 0.33 for tetrafunctional monomers. In such a polycondensation reaction of multifunctional monomers, the water molecules should not necessarily be removed from the reaction bath, but instead, the system can be brought to the gel point by controlling the vapor pressure of water. In fact, in some extreme cases as seen in polycondensation of tetraethoxysilane (TEOS) in water and alcohol, gelation can be observed even in a closed vessel.[5] The purpose of the present paper is to theoretically study thermodynamics of multifunctional polycondensation and to find the condition to bring the system to the gel point by changing the vapor pressure of water with or without phase separation.

In the conventional statistical theories of polycondensation,[1,3,4] the effect of eliminant molecules have not been explicitly taken into consideration. The molecular weight distribution, its averages, and the condition for gelation were studied as functions of the conversion α under the condition of simple bond formation between functional groups. In a series of our preceding studies,[6−8] we have studied thermoreversible gelation of reactive solutions with the temperature and concentration as controllable parameters. In polycondensing systems in open vessels, the concentration of solute molecules is, however, not a controllable parameter because of the evaporation of water molecules. The main purpose of the present study is to find the condition for the gel point in terms of the vapor pressure, and to study the physico chemical nature of sol/gel transition interfering with the phase separation.

The formation of cross-links with simultaneous solvent evaporation is the main processes that govern quality of a majority of protective organic coating films. Thereby, the amount of evaporated solvent and increase in the conversion

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of reactive groups are interdependent. Formation of polymer films by simultaneous cross-linking and solvent evaporation was studied by combining the polymer−solvent mixing free energy with the elastic free energy of the networks due to swelling.[9] The motivation of the present study is basically the same as this literature, but we focus more on the interference between phase separation and thermoreversible gelation at reaction equilibrium, and attempt to find conditions for reaching the gel point without phase separation. We expect this problem to be important for the formation of homogeneous films. The kinetic processes with time-dependent reaction will be reported in the forthcoming paper.

2. Stoichiometric Definitions

Consider polycondensing functional molecules A dissolved in water. Let f be the number of functional groups (for example −OH) on an A molecule, and let n be the volume of an A molecule measured relative to the molecular volume a^3 of the solvent molecule (H_2O). The present theory treats only the extreme limit of complete hydrolysis. Ternary reactive system of tetraalkoxysilanes in water and alcohol, $Si(OR)_4/H_2O/ROH$, popularly used in sol−gel processing,[10] will be studied in the forthcoming paper. We mix the number N of primary A molecules (referred to as A) with the number N_0 of the solvent molecules, both in the standard reference state. The initial volume of the solution is $V_0 = (N_0 + nN)a^3$. As reaction proceeds, the volume of the solution changes if the solvent is allowed to evaporate. Let V be the volume of the solution at equilibrium under the given temperature T. In what follows, we study our reactive solutions on the basis of the lattice theory of polymer solution,[11−13] so that the volume is measured in terms of the total number Ω of the lattice cells. Hence we have $\Omega_0 = N_0 + nN$ for the initial volume, and $\Omega = V/a^3$ for the volume at final equilibrium. For reaction in a closed vessel, we have a condition $\Omega = \Omega_0$, but for reaction under a controlled pressure, the solvent molecules move between the solution phase and the gas phase, and hence the volume of the solution changes (Figure 1). The volume fraction ϕ of the polymers in the pressure-controlled system changes as a function of the pressure and the temperature, and is different from that of the initial solution $\Phi \equiv nN/\Omega_0$.

We assume the reaction equilibrium

$$lA \rightleftharpoons A_l + \Delta n_l H_2O \tag{2.1}$$

for polycondensation of A molecules, where Δn_l is the number of water molecules produced when an l-mer is formed from l primary molecules by reaction. The volume n_l of the l-mer is then given by

$$n_l = ln - \Delta n_l \tag{2.2}$$

The number Δn_l may change from the minimum $l - 1$ (tree form) to $fl/2$ (complete reaction), but here we simply consider tree forms only and neglect internal loops. We then employ the classical theory of gelation.[1,3,4] The effect of cycle formation within polymers can be taken into consideration step by step by the usual spanning-tree procedure,[14] but here we confine tree statistics. We then have $\Delta n_l = l - 1$ and

$$n_l = ln - (l - 1) \tag{2.3}$$

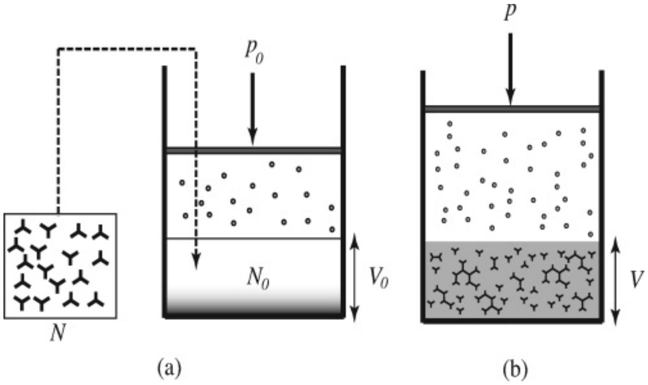

Figure 1. (a) Preparation of the polycondensing solution with the initial volume V_0 and vapor pressure p_0 immediately after mixing. (b) Final equilibrium state with a solution phase of volume V and a gas phase at pressure p.

As reaction proceeds, the average molecular weight of the connected clusters grows, and eventually becomes infinite at the gel point. Let N_l be the number of l-mers, and let N^G be the number of A molecules in the gel network, if it exists, in the final equilibrium. The volume of the solution is then given by

$$\Omega = N_0 + \sum_{l\geq 1}(l - 1)N_l + \Delta n^G N^G + \sum_{l\geq 1} n_l N_l + n^G N^G \tag{2.4}$$

where n^G is the effective volume of an A molecule in the gel network and Δn^G is the number of cross-links on it. The first three terms gives the total number

$$N_w \equiv N_0 + \sum_{l\geq 1}(l - 1)N_l + \Delta n^G N^G \tag{2.5}$$

of water molecules in the solution. The volume fraction of the polymer in the sol part is given by

$$\phi^S = \sum_{l\geq 1} n_l N_l/\Omega \tag{2.6}$$

and that in the gel part is

$$\phi^G = n^G N^G/\Omega \tag{2.7}$$

The total volume fraction of the polymer is given by $\phi = \phi^S + \phi^G$, and the volume fraction of water is

$$\phi_w \equiv N_w/\Omega = 1 - \phi \tag{2.8}$$

The gel fraction w is defined by the ratio ϕ^G/ϕ. The number of water molecules moved from the solution to the gas phase is given by

$$\Delta N_0 = \Omega_0(1 - \Phi) - \Omega(1 - \phi) \tag{2.9}$$

The total number of A molecules remains constant.

3. Free Energy of the Reactive Solutions

We apply lattice theory of associating solutions[6−8] to the present polycondensation system, and start from the free energy

$$\beta\Delta F = N_w \ln(1 - \phi) + \sum_{l\geq 1} N_l \ln\phi_l + \chi(T)\Omega\phi(1 - \phi) + \sum_{l\geq 1}\Delta_l N_l + \delta(\phi)N^G \tag{3.1}$$

where $\beta \equiv 1/k_BT$, $\chi(T)$ is Flory's interaction parameter, and

$$\Delta_l \equiv \beta(\mu_l^\circ - l\mu_1^\circ) \tag{3.2}$$

is the free energy change in forming an l-mer from the number l of separated primary molecules in the standard reference state. The volume fraction of the l-mers is given by

$$\phi_l \equiv n_l N_l/\Omega \tag{3.3}$$

and its number density is given by

$$\nu_l \equiv N_l/\Omega \tag{3.4}$$

The last term in (3.1) describes the free energy of the gel network in the postgel regime, where $\delta(\phi)$ is the free energy change per A molecule when it is connected to the gel. This term is necessary as soon as the gel point is passed (in the postgel regime), because the macroscopic number of molecules (finite fraction w of the total number of molecules) belong to the gel part. However, how the postgel free energy has to be approximated adequately is not a simple problem, and has been a matter of vivid controversies. Earlier papers by Veytsman[15] and by Panayiotou et al.[16] neglected the gel fraction and studied the hydrogen-bonding gelling polymers without the last term in the free energy. Later, Semenov and Rubinstein[17] studied gelation of polyfunctional molecules without taking into consideration the free energy of the gel fraction, and came to the conclusion such that there is no singularity associated with physical quantities. Erukhimovich et al.[18] considered the effect of excessive loop formation, and reached the conclusion that the sol/gel transition is a first-order phase transition. We showed[19] that there are several possible ways to treat the free energy from the gel fraction, and for theoretical study without ambiguity, we need at least one unknown parameter specifying the relative probability of occurrence of intra- and intermolecular reactions in the gel network.

Quite recently, we studied the thermodynamic nature of the sol/gel transition with a strong analogy to Bose–Einstein condensation.[20] If we assume that the binding free energy $\delta(\phi)$ depends on the concentration, it corresponds to the smoothed potential model of a Bose–Einstein liquid studied in the literature.[21] If it is a constant, it corresponds to the energy spectrum with a constant gap.[21] We will, however, not discuss this subtle point here, and confine the present study to the pregel regime and the gel point. Hence, in what follows, we assume $N^G = 0$ and discard the last term in the free energy.

We can find the chemical potential for each component by taking derivatives of the free energy with respect to the corresponding number of molecules. We find

$$\beta\Delta\mu_w = \phi + \ln(1-\phi) - \nu + \chi\phi^2 \tag{3.5}$$

for the water, and

$$\beta\Delta\mu_l = 1 + \Delta_l + \ln\phi_l - n_l(1-\phi+\nu) + \chi n_l(1-\phi)^2 \tag{3.6}$$

for an l-mer, where

$$\nu \equiv \sum_{l\geq 1}\nu_l \tag{3.7}$$

is the number of monomers and clusters that possess center of mass translational degree of freedom.[6-8]

4. Equilibrium Polycondensation

In the final equilibrium state, reaction 2.1 reaches a chemical equilibrium, so that we have the condition

$$l\Delta\mu_1 = \Delta\mu_l + (l-1)\Delta\mu_w \tag{4.1}$$

Substituting the chemical potentials into this equilibrium condition, we find that the volume fraction of the l-mers is given by

$$\phi_l = K_l(\phi){\phi_1}^l/{\phi_w}^{l-1} \tag{4.2}$$

where

$$K_l(\phi) \equiv \exp[-\Delta_l + (l-1)\chi(T)(1-2\phi)] \tag{4.3}$$

is the equilibrium constant of the reaction, and ϕ_1 is the volume fraction of the primary molecules that remain unreacted. In contrast to the simple association without production of the solvent molecules, the equilibrium constant depends on the concentration through the interaction term with the χ-parameter. Such concentration dependence appears from the change in the number of monomer–solvent contacts during the reaction. It renormalizes the free energy of reaction Δ_l, and leads to many interesting new features. We can now rewrite (4.2) as

$$\eta(\phi)\phi_l = K_l^\circ[\eta(\phi)\phi_1]^l \tag{4.4}$$

where $K_l^\circ \equiv \exp(-\Delta_l)$ is the "bare" (superscript °) equilibrium constant, and

$$\eta(\phi) \equiv e^{\chi(1-2\phi)}/(1-\phi) \tag{4.5}$$

is a new important factor due to water production (denominator) and to the change in the mixing enthalpy (numerator). We often encounter the same factor when we consider adsorption of molecules onto an attractive surface on which the nearest neighboring molecules interact with each other when adsorbed.[22] It leads to an Ising model type phase transition. Here, we have a new phase transition driven by the combination of water production and the contact interaction between water and the functional molecules. The conversion of functional groups becomes a nonmonotonic function of the concentration below a certain critical temperature, so that we can find three possible values of the concentration for a given value of the conversion.

The part due to the change in the number of molecular contact can be seen as follows. Consider the mixing enthalpy

$$\Delta_{\mathrm{mix}}H/k_BT \equiv \chi(T)N_w\sum_{l\geq 1}n_lN_l/\Omega \tag{4.6}$$

in the free energy (3.1), and find its change when an $(l+m)$-mer is produced as a result of the reaction between an l-mer and an m-mer. The number N_l and N_m both decrease by 1, and the number N_{l+m} increases by 1, resulting in the volume change $n_{l+m} - n_l - n_m$. The number N_w of water increases by 1. This gives the change $\Delta_{\mathrm{mix}}H/k_BT = -\chi(1-2\phi)$ per single bond, and hence the reaction free energy is renormalized from Δ_l to $\Delta_l - (l-1)\chi(1-2\phi)$ due to the contact interaction.

To find the bare part of the equilibrium constant, we now split the reaction free energy into three parts: combinatorial, conformational, and bonding terms as $\Delta_l = \Delta_l^{\mathrm{comb}} + \Delta_l^{\mathrm{conf}} + \Delta_l^{\mathrm{bond}}$. To find the combinatorial part, all clusters are assumed to take tree forms. Cycle formation within a cluster is neglected.

We consider the entropy change on combining l identical f-functional molecules to form a single Cayley tree. The classical tree statistics[4] gives $\Delta S_l^{\mathrm{comb}} = k_{\mathrm{B}}\ln[f^l\omega_l]$, where

$$\omega_l \equiv \frac{(fl-l)!}{l!(fl-2l+2)!} \tag{4.7}$$

is Stockmayer's combinatorial factor. The free energy is given by $\Delta_l^{\mathrm{comb}} = -\Delta S_l^{\mathrm{comb}}/k_{\mathrm{B}}$.

For the conformational free energy, we employ the lattice theoretical entropy of disorientation[13]

$$S_{\mathrm{dis}}(n) = k_{\mathrm{B}}\ln\left(\frac{n\zeta(\zeta-1)^{n-2}}{\sigma \mathrm{e}^{n-1}}\right) \tag{4.8}$$

for a chain consisting of n statistical units, where ζ is the lattice coordination number, σ the symmetry number of the chain. We then find

$$\Delta S_l^{\mathrm{conf}} = S_{\mathrm{dis}}(ln) - lS_{\mathrm{dis}}(n) = k_{\mathrm{B}}\ln\left[\left(\frac{\sigma(\zeta-1)^2}{\zeta \mathrm{e}n}\right)^{l-1} l\right] \tag{4.9}$$

with most probably $\sigma = 1$.

Finally, the free energy of bonding is given by

$$\Delta_l^{\mathrm{bond}} = (l-1)\beta\Delta f_0 \tag{4.10}$$

because there are $l - 1$ bonds in a tree of l molecules, where Δf_0 is the free energy change on forming a bond.

Combining all results together, we find

$$K_l^{\circ} = \frac{fn_l}{n}\omega_l\left(\frac{f\lambda(T)}{n}\right)^{l-1} \tag{4.11}$$

for the equilibrium constant, where

$$\lambda(T) \equiv [\sigma(\zeta-1)^2/\zeta \mathrm{e}]\exp(-\beta\Delta f_0) \tag{4.12}$$

is the association constant.

Collecting all results together, we find that the number ν_l of l-mers in a unit volume of the solution obeys the distribution law

$$\lambda(T)\eta(\phi)\nu_l = \omega_l x^l \tag{4.13}$$

where

$$x \equiv (f\lambda(T)/n)\eta(\phi)\phi_1 \tag{4.14}$$

is the number of functional groups on the A molecules that remain unreacted, with the renormalization factor $\eta(\phi)$ arising from solvent production during reaction. The volume fraction of the l-mers is then given by

$$\phi_l = n_l\nu_l \tag{4.15}$$

with $n_l = ln - l + 1$.

5. Reactivity and the Average Molecular Weight

Let us first consider the pregel regime where there is no infinite cluster. We take the sum of (4.13) over all sizes l, and find that the total number ν of monomers and clusters is given by

$$\lambda(T)\eta(\phi)\nu = S_0(x) \tag{5.1}$$

Similarly, the total volume fraction ϕ of the clusters at final equilibrium is given by

$$\lambda(T)\eta(\phi)\phi = (n-1)S_1(x) + S_0(x) \tag{5.2}$$

These are written in terms of the moments of Stockmayer's distribution function defined by

$$S_k(x) \equiv \sum_{l=1}^{\infty} l^k\omega_l x^l \quad (k = 0, 1, 2, ...) \tag{5.3}$$

If we define a parameter α by the equation

$$x \equiv \alpha(1-\alpha)^{f-2} \tag{5.4}$$

we can express these moments explicitly in terms of α. For instance

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

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

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

To see the physical meaning of α, let us calculate the probability for a randomly chosen functional group to be associated. Since an l-mer carries the total of fl groups, among which $2(l - 1)$ are associated, the probability of association (extent of reaction) is given by

$$2[S_1(x) - S_0(x)]/fS_1(x) \tag{5.6}$$

by using the number distribution function (4.13). This agrees with α, and hence, we find that α in fact gives the conversion, or the extent of reaction.

By using α, eq 5.2 can be written as

$$\lambda(T)\eta(\phi)\phi = \alpha(1 - f_1\alpha/2)/f_1(1-\alpha)^2 \tag{5.7}$$

where $f_1 \equiv f/n$ is the number of functional groups per monomer unit on a primary molecule. This condition connects the conversion with the polymer volume fraction. Similarly, the number of clusters is given by

$$\nu = (1 - f\alpha/2)\phi/[n(1 - f_1\alpha/2)] \tag{5.8}$$

Since an l-mer contains the number l of A molecules, the total number of A molecules in the solution is given by $\Omega\sum l\nu_l$, which must be equal to the number $N = \Phi\Omega_0/n$ of A molecules mixed when the solution is prepared. Hence we have

$$\Omega/\Omega_0 = (n - 1 + n/\bar{l}_{\mathrm{n}})\Phi/n\phi \tag{5.9}$$

where

$$\bar{l}_{\mathrm{n}} \equiv \sum l\nu_l/\sum\nu_l \tag{5.10}$$

is the nominal number-average molecular weight of the clusters. Similarly, we define

$$\bar{l}_{\mathrm{w}} \equiv \sum l^2\nu_l/\sum l\nu_l \tag{5.11}$$

for the nominal weight-average molecular weight. These are different from the true ones

$$\langle n_l \rangle_n \equiv \Sigma n_l \nu_l / \Sigma \nu_l \tag{5.12a}$$

$$\langle n_l \rangle_w \equiv \Sigma n_l^2 \nu_l / \Sigma n_l \nu_l \tag{5.12b}$$

which are observed in the experiments. Since we have $\bar{l}_n = 1/(1 - f\alpha/2)$ and $\bar{l}_w = (1 + \alpha)/[1 - (f - 1)\alpha]$ in terms of the conversion, we find

$$\Omega/\Omega_0 = (1 - f_1\alpha/2)\Phi/\phi \tag{5.13}$$

The total number (eq 2.9) of evaporated solvent molecules is given by

$$\Delta N_0/N_0 = 1 - (1 - f_1\alpha/2)\Phi(1 - \phi)/\phi(1 - \Phi) \tag{5.14}$$

For a closed system, we have a constant volume of the solution $\Omega = \Omega_0$, and hence

$$\phi = (1 - f_1\alpha/2)\Phi \tag{5.15}$$

As reaction proceeds, the volume fraction of the A molecules monotonically decreases due to the solvent production.

6. Vapor Pressure, Gel Point, and Spinodal Condition

Let us study eq 5.7, which connects the conversion with the volume fraction. It is rewritten in the form

$$\lambda(T)e^{\chi(T)(1-2\phi)} f\phi/n(1 - f_1\alpha/2) = \alpha(1 - \phi)/(1 - \alpha)^2 \tag{6.1}$$

This must be compared with conventional eq 1.2 under equilibrium condition found in the literature. Obviously, $[H_2O] = 1 - \phi$ is the number density of water molecules, but there are two differences. The first one is the volume change due to reaction. The effective volume of A molecules is reduced from n to $n(1 - f_1\alpha/2)$. The second one is the interaction between A molecules and water. It gives rise to the exponential factor, and renormalizes the reaction free energy from $\beta\Delta f_0$ to $\beta\Delta f_0 - \chi(T)(1 - 2\phi)$. The latter leads to a nonmonotonic conversion, or reverse reaction when molecular interaction $\chi(T)$ is strong compared with reaction Δf_0. By solving eq 6.1 with respect to the conversion, we find it explicitly as

$$\alpha = \{1 + c(\phi) - \sqrt{1 + (2 - f_1)c(\phi)}\}/[f_1 + c(\phi)] \tag{6.2}$$

where

$$c(\phi) \equiv 2\lambda(T)f_1\eta(\phi)\phi \tag{6.3}$$

is the scaled concentration of the functional groups.

Let us next consider reactive solutions whose vapor pressure is controlled. The vapor pressure is given by the chemical potential of water in the solution under equilibrium condition. We then find

$$\ln(p/p_0) = \beta\Delta\mu_w \tag{6.4}$$

From eq 3.5, together with ν of eq 5.8, we have

$$\ln(p/p_0) = \ln(1 - \phi) + (1 - 1/n)\phi/(1 - f_1\alpha/2) + \chi\phi^2 \tag{6.5}$$

In the usual polymer solutions without reaction, the concentration ϕ is a controllable parameter. It is fixed at the preparatory stage. But for reactive solutions treated here, the concentration is not directly controllable. Instead, we take the vapor pressure as a controlling parameter, and try to find how to bring the solution to the gel point without phase separation. We therefore solve eq 6.5 with respect to the conversion and the concentration for a given pressure and temperature, with the help of the equilibrium condition (eq 6.1).

The gel point can be found from the conventional condition for the weight-average molecular weight $\langle n_l \rangle_w$ to become infinite. It is a percolation point where the largest cluster grows to macroscopic dimensions and spans the entire solution. Simple calculation gives $\alpha = 1/(f - 1) \equiv \alpha^*$ as in the classical Flory–Stockmayer theory. We then find from eq 6.1 that the concentration ϕ^* of the solution at the gel point is given by the condition

$$\lambda(T)f_1\eta(\phi^*)\phi^* = (f - 1)[1 - f_1/2(f - 1)]/(f - 2)^2 \tag{6.6}$$

This equation must be compared with our previous result $\lambda(T)f_1\phi^* = (f - 1)/(f - 2)^2$ for simple pairwise association of polyfunctional molecules without solvent production during reaction.[6] The effect of solvent evaporation appears mainly in the factor $\eta(\phi^*)$. Since it is a nonmonotonic function of ϕ^* when $\chi > 2$, the gel phase turns back to a sol phase as the concentration increases at low temperatures (reentrant sol phase).

To study phase separation, let us derive the spinodal condition in the pregel regime. From the chemical potential (eq 3.5) for water, and eq 3.6 with $l = 1$ for a solute molecule, we find the difference between the two components is given by

$$\beta(\Delta\mu_1/n - \Delta\mu_w) = (1/n)\ln\phi_1 - \ln(1 - \phi) + \chi(1 - 2\phi) \tag{6.7}$$

By taking the derivative, we find that the spinodal condition is given by

$$\kappa(\phi)/n\phi + 1/(1 - \phi) - 2\chi = 0 \tag{6.8}$$

where a new function κ is defined by

$$\kappa(\phi) \equiv \partial(\ln\phi_1)/\partial(\ln\phi) \tag{6.9}$$

It is explicitly given by

$$\kappa(\phi) = 1 + \frac{f\phi}{1 + (1 - f_1)\alpha}\left[\frac{1}{1 - \phi} - 2\chi\phi\right]\left[\frac{1 + (f - 1)\alpha}{2n} - 1\right] \tag{6.10}$$

In the phase diagrams presented below, we draw the sol/gel transition lines and spinodal lines in the pregel regime. The spinodal lines lying inside the gel region (lines connecting the point A and B) on the phase plane are drawn by thin lines, or broken lines, only for guiding the reader's eyes.

7. Numerical Results

For numerical calculation of the temperature–pressure phase diagrams, we fix the necessary parameters in the following way. We first assume the conventional Shultz–Flory form $\chi(T) = {}^1/_2 - \psi\tau$ for the χ-parameter,[23] where $\tau \equiv 1 - \Theta/T$ is the reduced temperature deviation measured from the reference theta temperature Θ satisfying the condition $\chi(\Theta) = {}^1/_2$, and ψ is a material parameter of order unity. At the temperature Θ, the second virial coefficient of a hypothetical Flory–Huggins

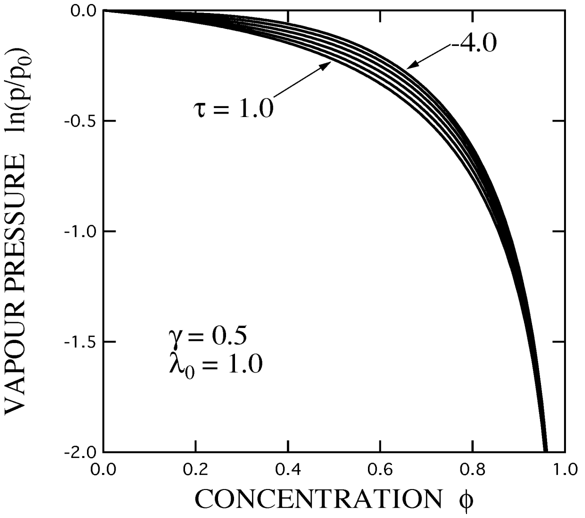

Figure 2. Polymer concentration (horizontal axis) plotted as a function of the vapor pressure (vertical axis) of the athermal solvent.

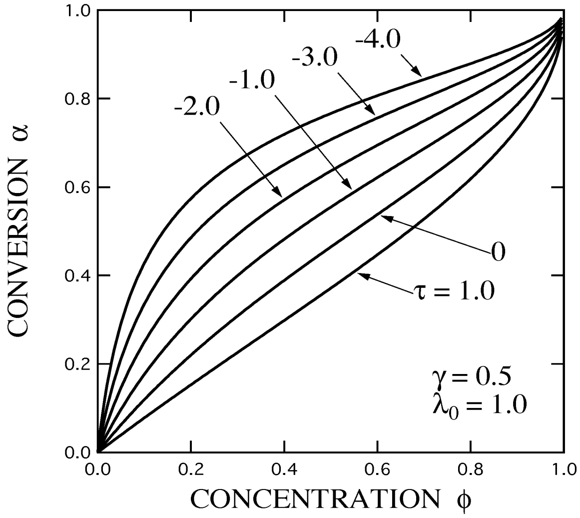

Figure 3. Conversion of the functional groups plotted against the polymer concentration produced in the solution.

solution without chemical reaction vanishes. The equilibrium constant is then expressed as $\lambda(T) = \lambda_0 \exp(|\epsilon|/k_BT) = \lambda_0 \exp[\gamma(1 - \tau)]$, where λ_0 gives the entropy part of the standard reaction free energy, and $\gamma \equiv |\epsilon|/k_B\Theta$ the reaction enthalpy in the unit of the thermal energy at the reference temperature. The reference temperature Θ is not the true theta temperature where the second virial coefficient $A_2(T)$ of the osmotic pressure vanishes. The latter lies far below Θ, because A_2 is renormalized to

$$A_2(T) = {}^1/_2 - \chi(T) - (1 - 1/n)\lambda(T)f_1^{\,2}/2 \qquad (7.1)$$

by reaction. Throughout the present numerical calculation, we fix at $\psi = 1.0$, $\lambda_0 = 1.0$, and changes the reaction enthalpy γ. For $\gamma > 1.0$, for example, the reaction enthalpy is larger than the thermal energy at the reference temperature, we call the solution "strongly reactive", and for $\gamma \ll 1.0$ we call the solution "weakly reactive". The functionality and the molecular weight of the primary molecules are fixed at $f = 4$ and $n = 5$ as a typical example in attempting to apply the present study to pressure controlled sol/gel transition in polycondensation of silicic acid $Si(OH)_4$ in water.

7.1. Athermal Solutions. We first study the simplest case of athermal solutions where there is no solvent−solute interaction. We have $\chi \equiv 0$. The only parameter we change in the calculation is the association constant $\lambda(T)$, or the free energy Δf_0 of the reaction. Even in such an ideal case, we can use a certain appropriate reference temperature Θ, and measure the temperature by the dimensionless parameter $\tau \equiv 1 - \Theta/T$. The strength of the reaction is given by the dimensionless enthalpy γ.

Figure 2 shows the concentration of the solution as a function of the vapor pressure, although the latter is taken as the vertical axis. The temperature is changed from curve to curve in the range $-4.0 \le \tau \le 1.0$. The concentration monotonically increases with decreasing pressure, i.e., by removing solvent vapor, due to the promotion of forward reaction. The conversion is plotted against the polymer concentration in Figure 3. They are monotonically increasing functions of the concentration. We first find the equilibrium concentration for a given pressure from Figure 2 and then find the conversion under the pressure from Figure 3. The conversion is uniquely found for a given pressure. By cooling the solution, the equilibrium conversion becomes larger, so that the population of the reacted functional groups relative to the total number of groups increases. This temperature effect is opposite to the reaction rate, which is accelerated by heating. The latter is decided by the height of free energy barrier lying between reacted and unreacted state of a functional group. It is modified by pH, catalysts, etc. In contrast, the equilibrium conversion is larger when the reaction free energy $|\Delta f_0|$ is larger compared to the thermal energy k_BT. Study of reaction rate is beyond the scope of the present paper.

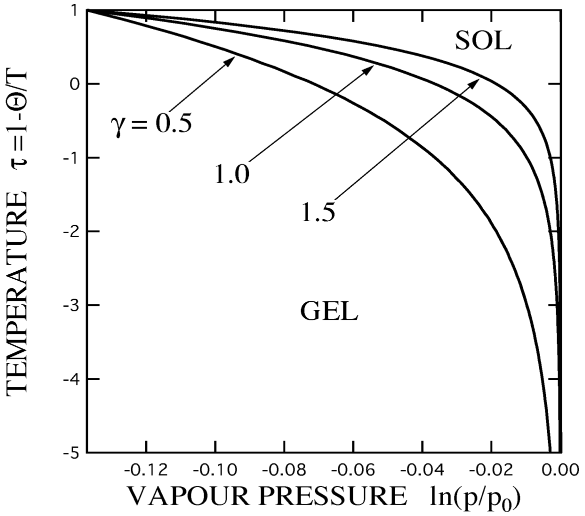

Figure 4. Sol/gel transition lines drawn on the temperature−pressure phase plane. The enthalpy of reaction is changed from curve to curve.

Figure 4 shows the sol/gel transition line on the temperature−pressure plane as a phase diagram for three different enthalpies of reaction. They are found by condition 6.6. Under a fixed temperature, for instance $\tau = -1.0$, we move from right to left as the pressure is lowered and hit the sol/gel line at $\ln(p/p_0) = -0.04$ for a weakly reactive solution $\gamma = 0.5$. Thus, we can control the sol/gel transition by pressure drop. We can also stay on the transition line by keeping the pressure. Figure 5 shows the same result shown on the temperature−concentration phase plane as usual. This phase diagram is, however, not useful because the concentration in the reaction bath cannot be controlled.

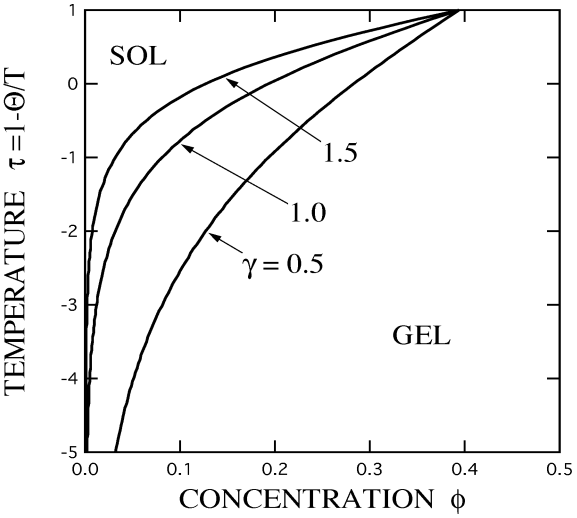

Figure 5. Sol/gel transition lines drawn on the usual temperature−concentration plane. The reaction enthalpy is changed from curve to curve.

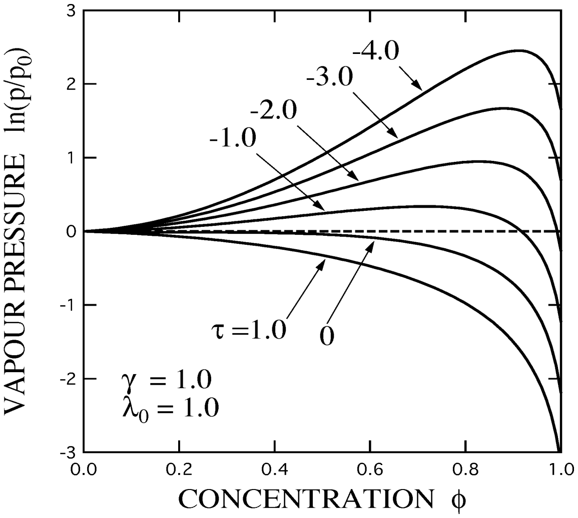

Figure 6. Polymer concentration (horizontal axis) plotted as a function of the vapor pressure (vertical axis) of the solvent for strong reaction of $\gamma = 1.0$.

7.2. Strong Reaction. We next study solutions with a finite interaction parameter. Reaction competes with phase separation. In the case of strong reaction where reaction enthalpy is larger than the mixing enthalpy, and hence the parameter γ is large, the conversion increases sharply with the concentration. Figure 6 shows the concentration as a function of the vapor pressure. At high temperatures it is a monotonic function. On cooling, however, the tendency for phase separation becomes stronger. As a result, the vapor pressure becomes larger than that of the pure solvent, and shows a maximum at a certain concentration as in the usual phase-separating polymer solutions,[13] for instance, in the case of $\gamma = 1.0$ in Figure 6. Given a pressure higher than that of the pure solvent at low temperatures, there are two concentrations giving the same pressure. If the pressure is gradually increased in the experiment by keeping equilibrium condition, the lower concentration is realized. It easily reaches $\simeq$0.5 under $\ln(p/p_0) \simeq 1.0$ for $\tau = -2.0$. Figure 7 shows the corresponding conversion as a function of the concentration. It reaches as high as 0.8 as is shown. There is a reverse reaction in the region $\phi = 0.6-0.8$ at low temperatures, but it is not strong.

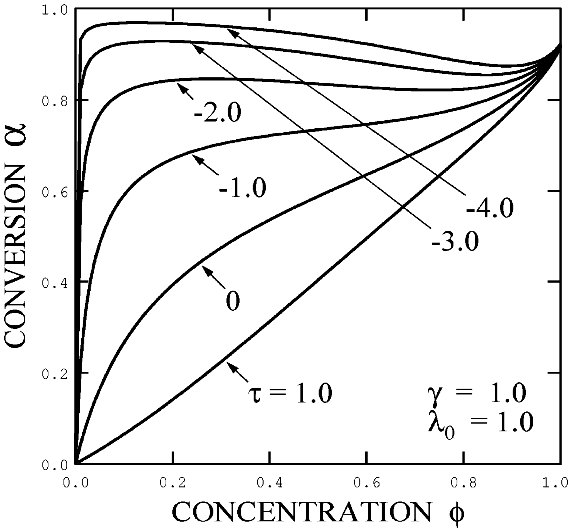

Figure 7. Conversion of the functional groups plotted against the polymer concentration produced in the solution. At low temperatures, they are not monotonically increasing functions of the concentration due to the backward reaction.

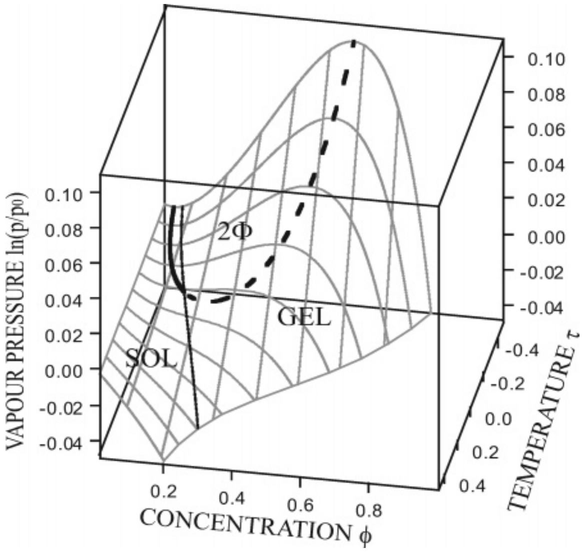

Figure 8. Three-dimensional diagram in the temperature−concentration−pressure space (Bakhuis−Rooseboom diagram) with the sol/gel transition curve (thin black line) and the spinodal lines (thick black line) for strong reaction of $\gamma = 1.0$. The vapor pressure of the solution is shown as the surface indicated by the gray thin lines. The broken line for the spinodal inside the gel region is just to guide reader's eyes. The area on the surface indicated by 2Φ is the unstable region.

In Figure 8, we show for $\gamma = 1.0$ the vapor pressure surface (thin gray lines), as a function of the reduced temperature τ and the polymer concentration, on which the sol/gel transition line (thin black line) and the spinodal line (thick black line) are drawn. (The broken line indicates the spinodal line in the postgel regime for guiding the eyes of readers.) The surface is called Bakhuis−Rooseboom space diagram in the literature.[24] We can obtain the pressure−concentration phase diagram and the temperature−concentration phase diagram by simply projecting this surface onto the corresponding plane.

The phase diagram projected onto the temperature−pressure plane is shown for three values of γ in Figure 9. Solid lines show the sol/gel transition lines. The broken lines show the stability limit (spinodal line) inside which the solution becomes thermodynamically unstable. The part connecting the point A and B lying inside the postgel regime is shown only for guiding the eyes of readers. Its precise location depends on how the

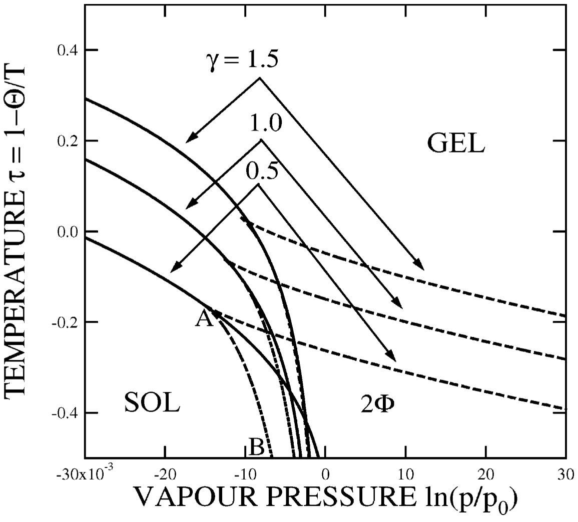

Figure 9. Sol/gel transition lines (solid lines) together with the spinodal lines (broken lines) drawn on the temperature−pressure phase plane in the case of strong reaction. The enthalpy of reaction is changed from curve to curve. The two curves (sol/gel and spinodal) cross each other at the spike point of the spinodal region indicated by 2Φ. The reaction enthalpy is changed from curve to curve.

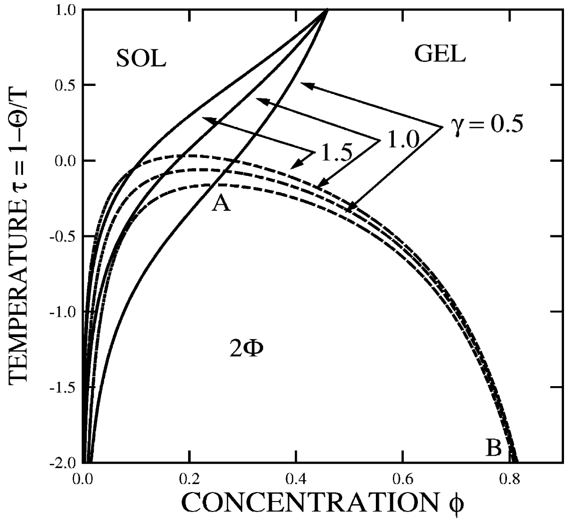

Figure 10. Sol/gel transition lines (solid lines) together with the spinodal lines (broken lines) drawn on the usual temperature−concentration plane. The two curves cross each other at the top of the spinodal region. The reaction enthalpy is changed from curve to curve.

reaction inside the gel network is treated, but nevertheless the overall structure of the spinodal boundary remains the same irrespective of the treatment. The reaction enthalpy γ is changed from curve to curve within the strong reaction regime. It has a spike at a certain temperature, like a "spinning" tool as etymological origin of spinodal line. If the solvent water is evaporated on a substrate plane below such a spike point temperature, the solution is phase separated, so that homogeneous coating of the substrate is impossible. In Figure 10, the phase diagram is mapped onto the usual temperature−concentration plane. The sol/gel transition line crosses the two-phase region indicated by the symbol 2Φ. Gelation is interfered with phase separation. The phase behavior of coexisting thermoreversible gelation and phase separation has been explored in our series of study.[6−8] For the present reactive solutions, however, the concentration is not an independent variable, but is decided by the vapor pressure.

7.3. Weak Reaction. Figures 11−15 show the results for weak reaction. The reaction enthalpy γ relative to the thermal

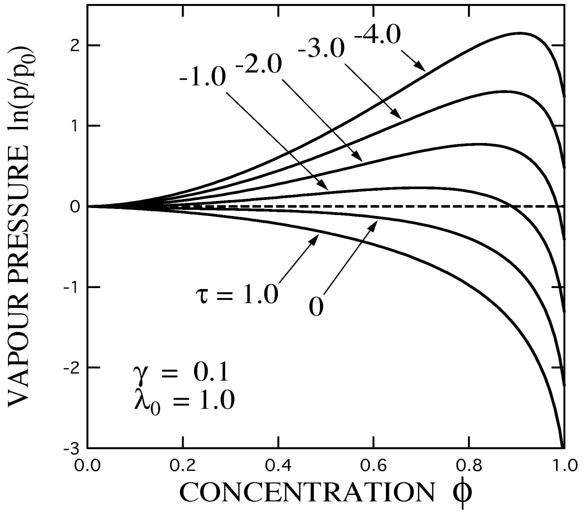

Figure 11. Polymer concentration (horizontal axis) plotted as a function of the vapor pressure (vertical axis) of the solvent for weak reaction of $\gamma = 0.1$.

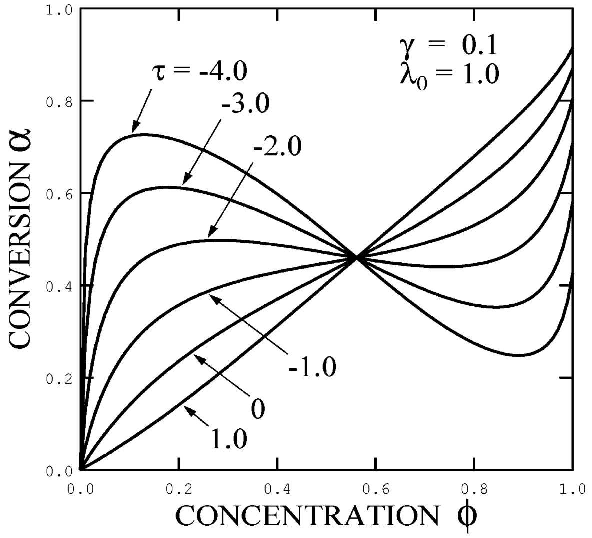

Figure 12. Conversion of the functional groups plotted against the produced polymer concentration in the case of weak reaction.

energy is assumed to take the value within the range $\gamma = 0.05-0.15$. In such weak reaction, the van der Waals type contact interaction factor $-\chi(1 - 2\phi)$ due to the change in the number of monomer−water contact is more important than the reaction enthalpy, in particular, at low temperatures. By giving pressure, the condensation reaction is easily pushed back to reduce the number of contact. The tendency to phase separation becomes stronger with lowering the temperature. As a result, a very interesting reentrant sol phase appears at high pressure, which interferes with the phase separation.

Figure 11 shows the polymer concentration (horizontal axis) plotted as a function of the vapor pressure (vertical axis) of water as before. At low temperatures, the vapor pressure shows a positive shift, reaches a maximum and the sharply decreases. Such peaks indicate strongly repulsive interaction between polymers and solvent molecules in the solution. It eventually leads to a phase separation. Figure 12 shows the conversion of the functional groups plotted against the concentration of polymers produced in the solution. At low temperatures, we notice a strong tendency to low conversion after passing a maximum with increase in the polymer concentration, or by giving high pressure. For instance, for the lowest temperature $\tau = -4.0$ in our calculation, the conversion is pushed back as

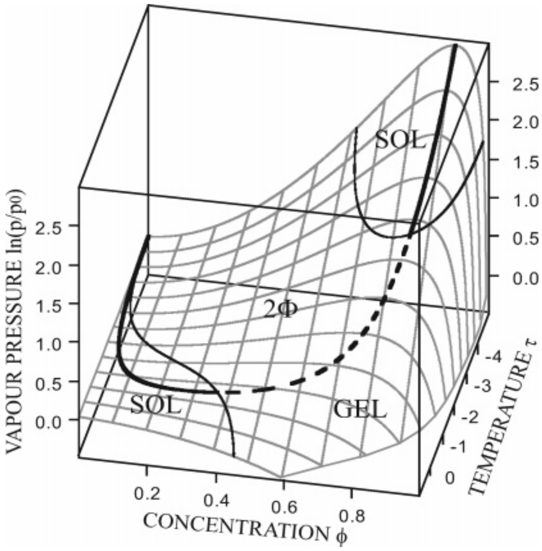

Figure 13. Same as in Figure 8, but for a weak reaction of $\gamma = 0.1$.

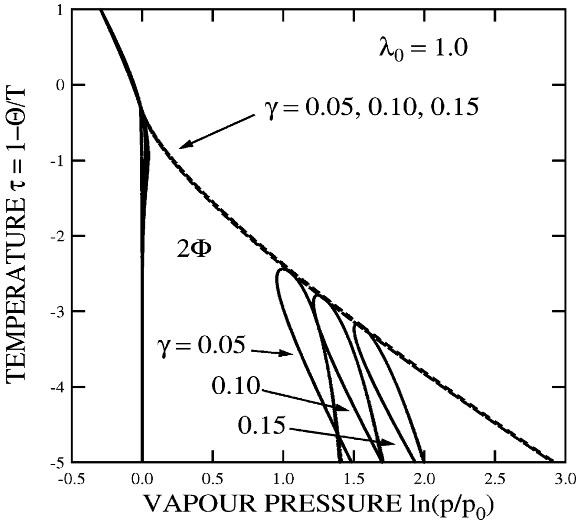

Figure 14. Sol/gel transition lines (solid lines) together with the spinodal lines (broken lines) drawn on the temperature−pressure phase plane in the case of weak reaction. The enthalpy of reaction is changed from curve to curve. The two curves (sol/gel and spinodal) cross each other at the top of the spinodal region. The reaction enthalpy is changed from curve to curve.

low as 0.25, which is lower than the gel point 0.33. The solution, thus, goes back to sol phase.

Figure 13 shows the Bakhuis−Rooseboom space diagram for the case of weak reaction. We can readily see the appearance of the reentrant sol phase at low temperature with high vapor pressure.

Projecting onto the temperature−pressure phase plane, we have similar sol/gel transition curves and the spinodal curves to those in the strong reaction case as shown in Figure 14, but there is a large difference at high pressure. (Three curves near the spinodal spike fall nearly on top of each other in this axis scale, so that their difference cannot be seen clearly in this figure.) There appears a closed loop type sol region as we can see in the figure, whose position depends on the reaction enthalpy. These are the reentrant sol phases. Figure 15 shows more clearly these reentrant sol phases on the usual temperature−concentration phase plane. We see two groups of sol/gel transition lines: one with the same shape as in the strong reaction at low concentrations (sol/gel transition), the other with dome shape at high concentrations (gel/sol transition). Such new cooperative phenomena between gelation (connection of molecules by chemical bonds) and phase separation (coexisting two different phases) by changing the vapor pressure indicate potential applications of the pressure controlled sol/gel transformation in polycondensing systems.

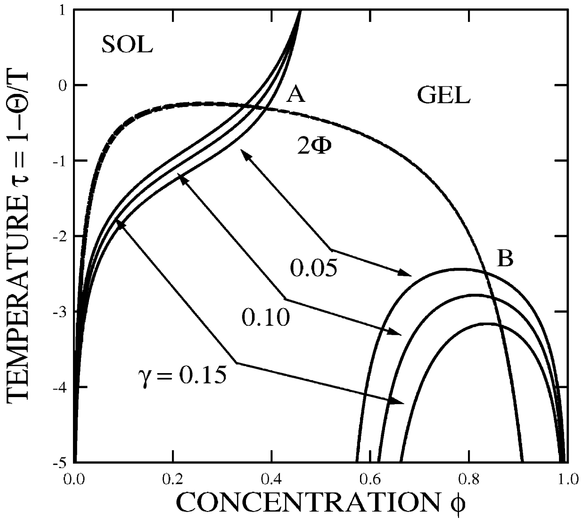

Figure 15. Sol/gel transition lines (solid lines) together with the spinodal lines (broken lines) drawn on the usual temperature−concentration plane for weak reaction. The two curves cross each other at the top of the spinodal region (phase separation region). The reaction enthalpy is changed from curve to curve.

8. Reaction in Closed Systems

When reaction takes place in a closed vessel, the volume is kept constant $\Omega = \Omega_0$, so that we have the relation 5.13. The polymer concentration is reduced by the factor $f_1\alpha/2$ as reaction proceeds due to the production of water molecules. The conversion is then found from eq 5.7 as a function of the initial concentration Φ. Explicitly, the equation for α leads to

$$2f_1\lambda\Phi(1-\alpha)^2\exp[\chi(T)(f_1\Phi\alpha + 1-2\Phi)] = [2(1-\Phi) + f_1\Phi\alpha]\alpha \quad (8.1)$$

The spinodal condition remains the same as eq 6.8, but the concentration is replaced by the closed system condition 5.13.

Figures 16 and 17 show the conversion as a function of the initial concentration for a strong and weak reaction. Temperature is varied from curve to curve. Compared to the pressure-controlled open systems, the backward reaction is enhanced due to the elevated pressure by reaction. The reentrant sol phases appear more easily.

We finally show in Figure 18 a typical phase diagram of the closed system for weak reaction. The horizontal axis is the monomer concentration in the preparation stage, so that it is now a controllable parameter. The overall structure of the phase diagram remains the same as open systems, but larger reentrant sol regions appear because of the enhanced backward reaction. Spinodal lines fall almost on top of each other, so that three curves cannot be distinguished in this axis scale.

9. Conclusions and Discussion

We have shown the advantage to bring the polycondensing systems to the gel points by controlling the vapor pressure. In a common case of primary molecules with $f = 4$ and $n = 5$, the gel point can easily be reached by depressing the vapor pressure by 1 order of magnitude. In a weak reaction, we showed that it is possible to move back to a sol from a gel by giving pressure.

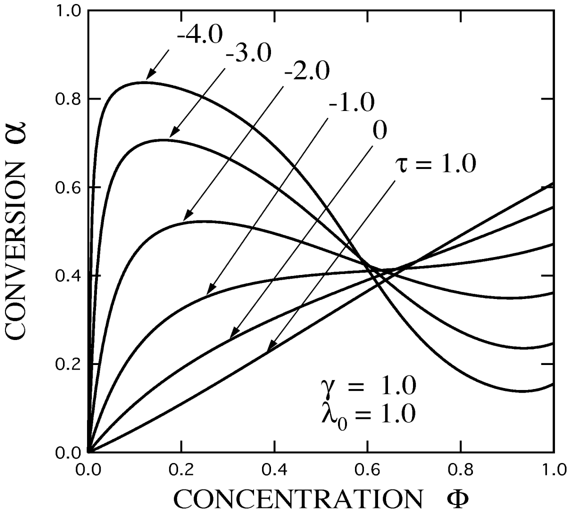

Figure 16. Conversion in closed system is plotted against the initial concentration of functional molecules in the strong reaction case. Temperature is varied from curve to curve. The strong backward reaction can be seen at high concentrations.

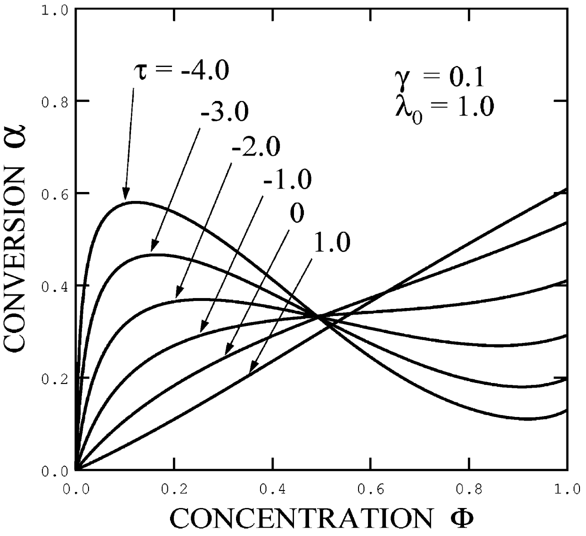

Figure 17. Same as Figure 16, but for the case of weak reaction.

The thermodynamic conditions to reach the gel point without phase separation can also be found by the theoretical consideration given in this study. Such thermodynamic description, combined with reaction kinetics, therefore turned out to be useful not only for the fundamental research but also for the practical applications.

From the theoretical point of view, the treatment of the postgel regime after the gel point is passed is important because the conversion in the gel part and that in the sol part may be different.[4,19] Historically, several consistent theoretical treatments have been proposed. The problem requires the inclusion of at least one additional unknown parameter defining the relative probability of occurrence of intra- and intermolecular reactions. We have avoided this problem, and confined the present study to the pregel regime and the gel point.

We have also treated polycondensation within the same species of functional groups such as −OH. Most of the important reactions are, however, hetero-polycondensation where different functional groups −A and B− react with the byproduct being a solvent molecule. Thermodynamic study on such hetero-polycondensation in ternary mixture will be reported in our forthcoming paper.

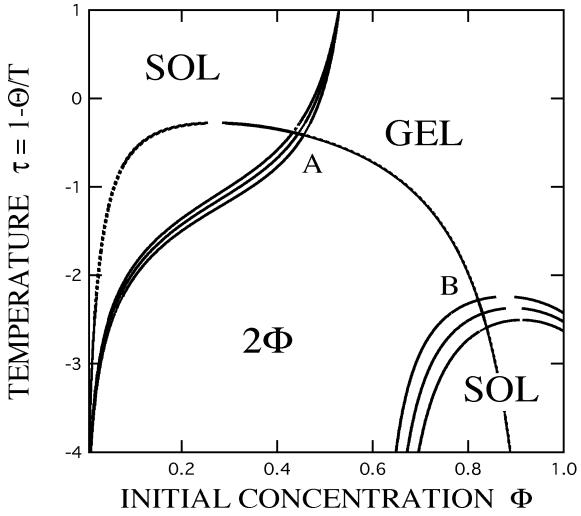

Figure 18. Typical phase diagram of a closed system with sol/gel transition lines (thick lines) and the spinodal line (thin broken lines of dome shape) drawn on the temperature and initial concentration plane. The reaction enthalpy is varied from $\gamma = 0.02$ (inner curve), $\gamma = 0.04$ (middle curve), and $\gamma = 0.02$ (outer curve). Large reentrant sol regions appear.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter IX.
(2) Vollmert, B. *Polymer Chemistry*; Springer-Verlag Inc.: New York 1973; p 207.
(3) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3091; 3096.
(4) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45. Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(5) Sakka, S.; Kozuka, H. *J. Non-Cryst. Solids* **1988**, *100*, 142.
(6) Tanaka, F. *Macromolecules* **1990**, *23*, 3784; 3790.
(7) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943.
(8) Tanaka, F. In *Molecular Gels*; Weiss, G., Terech, P., Eds.; Kluwer Academic Pub.: London, 2006; Chapter 1.
(9) Důsková-Smrčková, M.; Dušek, K. *J. Mater. Sci.*, **2002**, *37*, 4733.
(10) Brinker C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, CA, 1990; Chapter 3.
(11) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(12) Huggins, M. L. *J. Chem. Phys.* **1942**, *46*, 151.
(13) Reference 1, Chapter XII.
(14) Gordon, M.; Scantlebury, G. R. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 240.
(15) Veytsman, B. A. *J. Chem. Phys.* **1990**, *94*, 8499.
(16) Panayiotou, C.; Sanchez, I. C. *J. Chem. Phys.* **1991**, *95*, 10090. Panayiotou, C.; Sanchez, I. C. *Macromolecules* **1991**, *24*, 6231.
(17) Semenov, A. N.; Rubinstein, M. *Macromolecules* **1998**, *31*, 1373.
(18) Erukhimovich, I.; Thamm, M. V.; Ermoshkin, A. V. *Macromolecules* **2001**, *34*, 5653.
(19) Ishida, M.; Tanaka, F. *Macromolecules* **1997**, *30*, 3900.
(20) Tanaka, F. *Phys. Rev. E* **2006**, *73*, 061405.
(21) London, F. *Superfluids*; Dover Pub., Inc.: New York, 1964; Vol. II, Chapter C, Section 8.
(22) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Pub.: New York, 1986; Chapter 14.
(23) Shultz A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1963**, *75*, 3888; 5631.
(24) Koningsveld, R.; Stockmayer, W. H.; Nies, E. *Polymer Phase Diagrams*; Oxford University Press: Oxford, U.K., 2001; Part 1, Section 3.

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