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# Unified model of association-induced lower critical solution temperature phase separation and its application to solutions of telechelic poly(ethylene oxide) and of telechelic poly(*N*-isopropylacrylamide) in water

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The authors present a model describing the coexistence of hydrophobic association and phase separation with lower critical solution temperature (LCST) in aqueous solutions of polymers carrying short hydrophobic chains at both chain ends (telechelic associating polymers). The LCST of these solutions is found to decrease along the sol/gel transition curve as a result of both end-chain association (association-induced phase separation) and direct hydrophobic interaction of the end chains with water. The authors relate the magnitude of the LCST decrease to a hydration cooperativity parameter  $\sigma$ . The LCST decreases substantially ( $\sim 100$  K) in the case of random hydration ( $\sigma=1$ ), whereas only a small shift ( $\sim 5-10$  K) occurs in the case of cooperative hydration ( $\sigma=0.3$ ). The molecular weight dependence of the LCST drop is studied in detail in each case. The results are compared with experimental observations of the cloud points of telechelic poly(ethylene oxide) solutions, in which random hydration predominates, and of telechelic poly(*N*-isopropylacrylamide) solutions, in which cooperative hydration prevails. © 2006 American Institute of Physics. [DOI: 10.1063/1.2400230]

## I. INTRODUCTION

The phase diagrams of water-soluble polymers are greatly affected by hydrogen bonding of water molecules onto the polymer chains (hydration). For instance, the phase diagram of aqueous poly(ethylene oxide) (PEO) solutions exhibits a closed-loop phase separation region (*miscibility loop*) in the intermediate temperature domain.<sup>1-3</sup> The phase boundary is highly sensitive to the molecular weight of polymers<sup>2</sup> and also to the external pressure.<sup>4</sup> As the molecular weight increases, the miscibility loop expands, and the lower critical solution temperature (LCST) decreases, approaching an inverted theta temperature in the limit of infinite molecular weight.<sup>2</sup> The first theoretical description of this peculiar phase behavior attributed it to the occurrence of hydrogen bonding between ether groups of the polymer chain and water molecules.<sup>5</sup> Later, it was shown by molecular dynamics simulation<sup>6</sup> that the PEO chain takes a loose helical conformation (11/2 helix) in aqueous solutions, and the pitch ( $\approx 1.7$  nm) of the helix fits the size of a water molecule undergoing hydrogen bonding via each hydrogen. In contrast, other water-soluble polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM), show a very flat LCST behavior. The cloud point and spinodal lines are horizontal up to polymer concentrations of 20 wt % and are almost independent of the polymer molecular weight.<sup>7-12</sup> The phase separation region resembles the bottom part of a square. We referred to it as *miscibility square* and ascribed it to the occurrence of *cooperative hydration*, i.e., hydration

with strong interaction between neighboring bound water molecules in our previous paper<sup>13</sup> (referred to as OT). There is a positive correlation in the neighboring hydrogen bonds along the polymer chain, so that sequences of contiguous bound water molecules tend to form cooperatively.

We report here a study of the association and phase behavior of telechelic and semitelechelic hydrophobically modified PEO and PNIPAM based on our previous theoretical study of water-soluble polymers. The number of hydrophobes (typically short alkyl chains) on each main chain is called the functionality  $f$  of the chain. Thus, we have  $f=1$  for one-end hydrophobized polymers and  $f=2$  for *telechelic polymers*, i.e., polymers carrying hydrophobic chains at both ends. Hydrophobic aggregation of the chain ends triggers the formation of micelles, networks, and other self-assembled structures depending upon the temperature and concentration. We will pay special attention to telechelic polymers which interact with water differently from their homopolymer counterparts in two ways:

- (1) They form micelles and networks by hydrophobic aggregation of the end chains. In the dilute region, typically solutions of concentration lower than 1 wt %, telechelic polymers form intramolecular loops, which aggregate into micelles of flowerlike shape (called *flower micelles*).<sup>14-20</sup> At higher concentrations, the chains start to form bridges between micelles, resulting in the formation of networks with micellar junctions.

- (2) The hydrophobic end chains interact directly with water, so that they drive the solutions towards liquid-liquid phase separation.

Mechanism (1) results in an apparent increase of the polymer molecular weight, compared to the homopolymers. Hence the mixing entropy decreases, inducing the polymers to demix in water. We will call this demixing enhancement tendency an *association-induced phase separation* as in the literature<sup>21,22</sup> (referred to as TS). The hydrophobe number density and the polymer volume fraction  $\phi$  are important parameters controlling this mechanism.

Mechanism (2) leads to phase separation between the end groups and water through direct hydrophobic interaction.<sup>23</sup> The tendency towards phase separation increases as the number of end groups per unit volume becomes larger. Thus, for the same volume fraction  $\phi$ , shorter telechelic polymers tend to phase separate more readily than longer ones.

Several studies<sup>18,24</sup> have shown that the LCST of aqueous telechelic PEO solutions is much lower than the LCST of solutions of PEO samples of comparable molecular weight. The magnitude of the shift in LCST can reach 100 K. The LCST of telechelic PEOs depends on the sample molecular weight: it increases with increasing molecular weight, such that the phase separation region shrinks for telechelic polymers of larger size.<sup>18,24</sup> This trend is opposite to that exhibited by aqueous solutions of PEO. In the case of aqueous telechelic PNIPAMs, the end-group induced decrease of the LCST is much weaker, on the order of 5–10 K.<sup>25,26</sup> Moreover, the transition temperature detected by microcalorimetry, which corresponds to the coil-to-globule transition of PNIPAM, is hardly affected by the end-group substituents. We present here a unified model of the LCST phase separation of aqueous hydrophobically modified telechelic polymer solutions which takes into account the nature of the water-main chain interactions through a hydration cooperativity parameter  $\sigma$ .

In aqueous solutions of hydrophobic polymers, chain association interferes with hydration with consequences on the macroscopic scale. If hydration is so strong that there are many bound water molecules near the hydrophobes, association must compete with hydration. In such a case, gelation is possible only after dehydration takes place by raising the temperature (high-temperature gelation). In our previous study,<sup>27</sup> we theoretically derived high-temperature gelation with LCST phase separation in solutions with such competing hydration and association phenomena. For telechelic polymers, however, hydration takes place along the main chain, so that it is only indirectly affected by end-chain association, except for the chain sections very close to the chain end. Dehydration and chain collapse start near the core of the flower micelles in the form of heterogeneous nucleation. In other words, hydration is decoupled from association. The solutions with such coexisting hydration and association turn into gels on cooling (low-temperature gelation) with LCST phase separation. We study here the phase diagrams of the telechelic polymer/water systems under the assumption of coexisting hydration and association. The theo-

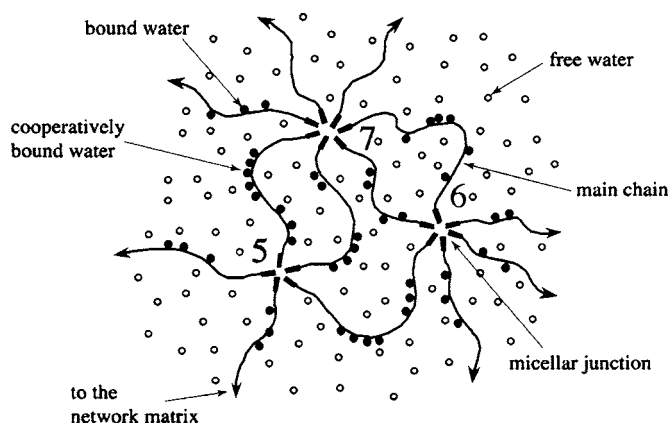


FIG. 1. Pictorial representation of a telechelic polymer network made up of hydrated polymer chains. The polymer chains are cross-linked by the micellar junctions formed by hydrophobic association of the end chains. In the case of cooperative hydration, sequences of bound water molecules are formed along the polymer chains. Chain association and hydration are expected to be independent except in the region near the junctions. The multiplicity  $k$  is indicated by the figure near a junction.

retically derived phase diagrams will be compared to experimentally established phase diagrams of telechelic PEO/water and telechelic PNIPAM/water systems.

## II. MODEL AQUEOUS SOLUTIONS OF ASSOCIATING POLYMERS

Let us consider a model solution consisting of  $N$  telechelic polymer chains having a main chain of degree of polymerization (DP)  $n$  and two end groups of DP  $n^*$ . The total DP of the polymer chains is  $n_t \equiv n + 2n^*$ . The chains are mixed with a number  $N_0$  of water molecules. We start with the lattice theoretical description of polymer solutions<sup>28,29</sup> and divide the system volume  $V$  into cells of size  $a$ , each of which can accommodate either a water molecule or a statistical repeat unit of the polymer chain. We assume incompressibility of the solution, so that the total number  $\Omega \equiv V/a^3$  of cells is given by  $\Omega = N_0 + n_t N$ . To describe the hydration of the chains by water, we follow the convention of OT, and let  $\mathbf{i} \equiv \{i_1, i_2, \dots\}$  be the index specifying the polymer chain carrying the number  $i_\zeta$  of water molecule sequences that consist of a run of  $\zeta$  consecutive hydrogen-bonded water molecules, and let  $N(\mathbf{i})$  be the number of such polymer-water complexes of type  $\mathbf{i}$  (see Fig. 1). In particular, we have  $\mathbf{i}_0 \equiv (0, 0, \dots)$  for a bare polymer chain devoid of bound water. The total number of water molecules on a chain specified by  $\mathbf{i}$  is given by  $\sum \zeta i_\zeta$ , and the DP of a complex is given by  $n(\mathbf{i}) \equiv n[1 + \theta(\mathbf{i})] + 2n^*$ , where

$$\theta(\mathbf{i}) = \sum_{\zeta=1}^n \zeta i_\zeta / n \quad (2.1)$$

is the coverage by the bound water molecules relative to the total DP of a polymer.

In thermal equilibrium, the population distribution of connected clusters formed by the end-chain association in solution is fixed by the equilibrium conditions. Following the notation used by Fukui and Yamabe,<sup>30</sup> we define a cluster as  $(\mathbf{j}; \mathbf{m})$  if it consists of  $j_k$  junctions of multiplicity

$k$  ( $k=1, 2, 3, \dots$ ) and  $\mathbf{m}(\mathbf{i})$  molecules of the hydration type  $\mathbf{i}$ . The bold letters  $\mathbf{j} \equiv \{j_1, j_2, j_3, \dots\}$  and  $\mathbf{m} \equiv \{m(\mathbf{i})\}$  denote the sets of indices. The multiplicity is here given by the number of hydrophobes in a micelle. A  $(\mathbf{j}; \mathbf{m})$  cluster is a connected cluster consisting of the number  $m(\mathbf{i})$  of hydrated chains of type  $\mathbf{i}$ . An isolated molecule of type  $\mathbf{i}$ , for instance, is indicated by the labels  $\mathbf{j}_0 \equiv \{f, 0, 0, \dots\}$  (with  $f=2$  for a telechelic chain), and  $\mathbf{m}_0(\mathbf{i}) \equiv 1$  (for the type specified by  $\mathbf{i}$ ),  $\equiv 0$  (for others).

Let  $N(\mathbf{j}; \mathbf{m})$  be the number of  $(\mathbf{j}; \mathbf{m})$  clusters in the system. Their number density is given by  $\nu(\mathbf{j}; \mathbf{m}) = N(\mathbf{j}; \mathbf{m})/\Omega$ , and their volume fraction is given by

$$\phi(\mathbf{j}; \mathbf{m}) = \tilde{n}(\mathbf{m})\nu(\mathbf{j}; \mathbf{m}), \quad (2.2)$$

where

$$\tilde{n}(\mathbf{m}) \equiv \sum_{\mathbf{i}} n(\mathbf{i})m(\mathbf{i}) \quad (2.3)$$

and  $n(\mathbf{i}) \equiv n(1 + \theta(\mathbf{i}) + 2n^*/n)$  is the total DP of a polymer-water complex of type  $\mathbf{i}$ . It is approximately given by  $n(\mathbf{i}) \approx n(1 + \theta(\mathbf{i}))$  for a polymer in which the main chain is much longer than the end groups. This gives the volume fraction of the clusters including the bound water. The total volume fraction of the polymer-water complexes is then given by  $\sum_{\mathbf{j}, \mathbf{m}} \phi(\mathbf{j}; \mathbf{m})$ .

In the postgel regime where hydrated gel networks exist, one needs to consider in addition the number,  $N(\mathbf{i})$ , of polymer chains of type  $\mathbf{i}$  involved in network formation. Their number density is given by  $\nu^G(\mathbf{i}) = N^G(\mathbf{i})/\Omega$ , and their volume fraction by  $\phi^G(\mathbf{i}) = n(\mathbf{i})\nu^G(\mathbf{i})$ .

The total number of polymer chains in solution is

$$N = \sum_{\mathbf{j}, \mathbf{m}} \left[ \sum_{\mathbf{i}} m(\mathbf{i}) \right] N(\mathbf{j}; \mathbf{m}) + \sum_{\mathbf{i}} N^G(\mathbf{i}). \quad (2.4)$$

For instance, polymer chains of hydration type  $\mathbf{i}$  that remain unassociated in solution is given by  $N(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))$ . Similarly, the number of bound water molecules is

$$N_{\text{bw}} = \sum_{\mathbf{j}, \mathbf{m}} \left[ \sum_{\mathbf{i}} n\theta(\mathbf{i})m(\mathbf{i}) \right] N(\mathbf{j}; \mathbf{m}) + \sum_{\mathbf{i}} n\theta(\mathbf{i})N^G(\mathbf{i}), \quad (2.5)$$

and the number of free water molecules is

$$N_{\text{fw}} = (1 - \phi)\Omega - N_{\text{bw}}. \quad (2.6)$$

The total volume  $\Omega \equiv N_0 + nN$  of the solution is now given by

$$\Omega = \sum_{\mathbf{j}, \mathbf{m}} \tilde{n}(\mathbf{m})N(\mathbf{j}; \mathbf{m}) + \sum_{\mathbf{i}} n(\mathbf{i})N^G(\mathbf{i}) + N_{\text{fw}}. \quad (2.7)$$

Before introducing the free energy of the solution, let us consider the number of contacts between polymers and water. Since the volume fraction of the main chain is  $\phi_c = (n/n_t)\phi$ , and that of the end chain is  $\phi_e = (2n^*/n_t)\phi$ , the number of main chain-water contacts (mw) is  $\phi_c(1 - \phi)$ , and the number of end chain-water contacts (ew) is  $\phi_e(1 - \phi)$ . We introduce the conventional  $\chi$  parameter for each contact type (mw and ew) and find that the enthalpy of polymer-water interaction per lattice cell is given by  $\bar{\chi}(T)\phi(1 - \phi)$ , where

$$\bar{\chi}(T) \equiv \chi_{\text{mw}}(T)(n/n_t) + \chi_{\text{ew}}(T)(2n^*/n_t). \quad (2.8)$$

In the case of linear alkyl chains in water near room temperature, a detailed study<sup>23</sup> of hydrophobic interaction has shown that

$$n^* \chi_{\text{ew}}(T) = 2.102n_{\text{CH}_3} + 0.884n_{\text{CH}_2}/k_B T \text{ (kcal/mol)}. \quad (2.9)$$

In particular, for the octadecyl group for which  $n_{\text{CH}_3} = 1$  and  $n_{\text{CH}_2} = 17$ , we find

$$n^* \chi_{\text{ow}}(T) = 2.102 + 0.884 \times 17/k_B T. \quad (2.10)$$

It is approximately 28.5 kcal/mol at room temperature. When we can neglect the length  $n^*$  of the end chain compared to  $n$ , the length of the main chain, the effective contact interaction parameter is given as

$$\bar{\chi}(T) \equiv \chi_{\text{mw}}(T) + \chi_1(T)/n, \quad (2.11)$$

where  $\chi_1 \equiv 2n^* \chi_{\text{ew}}$  is the effective interaction parameter between the end chain and water. The direct interaction between hydrophobic groups and water gives an  $O(1/n)$  correction, and is stronger for shorter chains.

### III. FREE ENERGY OF THE ASSOCIATING POLYMER SOLUTIONS

The free energy of the model solution has three contributions:

$$\Delta F = \Delta F_{\text{mix}} + \Delta F_{\text{hyd}} + \Delta F_{\text{assoc}}. \quad (3.1)$$

The free energy of mixing is given by

$$\beta \Delta F_{\text{mix}} = N_{\text{fw}} \ln \phi_{\text{fw}} + \sum_{\mathbf{j}, \mathbf{m}} N(\mathbf{j}; \mathbf{m}) \ln \phi(\mathbf{j}; \mathbf{m}) + \bar{\chi} \Omega \phi(1 - \phi) \quad (3.2)$$

by applying the Flory-Huggins mixing entropy for polydisperse polymer solutions.<sup>29</sup> The free energy of hydration is given by

$$\beta F_{\text{hyd}} = \sum_{\mathbf{j}, \mathbf{m}} \left[ \sum_{\mathbf{i}} \beta \Delta A(\mathbf{i})m(\mathbf{i}) \right] N(\mathbf{j}; \mathbf{m}) + \sum_{\mathbf{i}} \beta \Delta A(\mathbf{i})N^G(\mathbf{i}), \quad (3.3)$$

where  $\Delta A(\mathbf{i}) \equiv A(\mathbf{i}) - A(\mathbf{i}_0)$  is the free energy of hydration to form a complex of type  $\mathbf{i}$  starting from a bare polymer of reference conformation  $\mathbf{i}_0 \equiv \{0, 0, \dots\}$ . The free energy of hydrophobic association is given by<sup>21,22</sup>

$$\beta F_{\text{assoc}} = \sum_{\mathbf{j}, \mathbf{m}} \Delta(\mathbf{j}; \mathbf{m})N(\mathbf{j}; \mathbf{m}) + \sum_{\mathbf{i}} \delta_i(\phi)N^G(\mathbf{i}), \quad (3.4)$$

where  $\Delta(\mathbf{j}; \mathbf{m}) \equiv \beta[\mu^0(\mathbf{j}; \mathbf{m}) - \sum_{\mathbf{i}} \mu^0(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))m(\mathbf{i})]$  is the free energy change upon formation of a cluster of type  $(\mathbf{j}; \mathbf{m})$  from separated chains of type  $\mathbf{i}$ , and where  $\delta_i(\phi)$  is the dimensionless free energy gain when a polymer chain of type  $\mathbf{i}$  is connected to the network. The terms that include the number  $N^G(\mathbf{i})$  of polymer chains of type  $\mathbf{i}$  in the gel network need to be introduced only in the postgel regime.

We next derive the chemical potential for the free water and the associated complex by differentiating the free energy given above with respect to their number. We find

$$\beta\Delta\mu_{\text{fw}} = 1 + \ln \phi_{\text{fw}} - \nu^s + \bar{\chi}\phi^2 - d^G(\phi)\phi \quad (3.5)$$

for the free water, and for the associated complex of type  $(\mathbf{j}; \mathbf{m})$

$$\begin{aligned} \frac{\beta\Delta\mu(\mathbf{j}; \mathbf{m})}{\bar{n}(\mathbf{m})} &= \frac{1}{\bar{n}(\mathbf{m})} \left[ 1 + \Delta(\mathbf{j}; \mathbf{m}) + \beta \sum_{\mathbf{i}} \Delta A(\mathbf{i})m(\mathbf{i}) \right. \\ &\quad \left. + \ln \phi(\mathbf{j}; \mathbf{m}) \right] - \nu^s + \bar{\chi}[\phi^2 + r(\mathbf{m})(1 - 2\phi)] \\ &\quad + d^G(\phi)[r(\mathbf{m}) - \phi], \end{aligned} \quad (3.6)$$

where

$$\nu^s \equiv \nu_{\text{fw}} + \sum_{\mathbf{j}, \mathbf{m}} \nu(\mathbf{j}; \mathbf{m}) \quad (3.7)$$

is the total number of molecules and clusters that possess center of mass translational degree of freedom and

$$r(\mathbf{m}) \equiv (n + 2n^*) \sum_{\mathbf{i}} m(\mathbf{i}) / \sum_{\mathbf{i}} n(\mathbf{i})m(\mathbf{i}) \quad (3.8)$$

the volume of the polymer parts measured relative to the total volume of a cluster of type  $\mathbf{m}$ . In particular,  $r(\mathbf{m}_0(\mathbf{i})) \approx 1/[1 + \theta(\mathbf{i})]$  for a hydrated but unassociated polymer chain. The terms in the chemical potentials including

$$d^G(\phi) \equiv \sum_{\mathbf{i}} \delta_{\mathbf{i}}^G(\phi) \nu^G(\mathbf{i}) \quad (3.9)$$

are relevant only in the postgel regime. Finally, we have for a chain in the gel network

$$\begin{aligned} \beta\Delta\mu^G(\mathbf{i})/n(\mathbf{i}) &= \delta_{\mathbf{i}}(\phi)/n(\mathbf{i}) - \nu^s + \bar{\chi}\phi^2 \\ &\quad + r(\mathbf{m}_0(\mathbf{i}))(1 - 2\phi) + d^G(\phi)[r(\mathbf{m}_0(\mathbf{i})) - \phi]. \end{aligned} \quad (3.10)$$

#### IV. ASSOCIATION EQUILIBRIUM

In order to study equilibrium solution properties, we first impose association-dissociation equilibrium conditions on the formation of hydrophobic clusters as well as on the hydration. For the cluster formation by end-chain association, the chemical potentials should satisfy the condition

$$\Delta\mu(\mathbf{j}; \mathbf{m}) = \sum_{\mathbf{i}} \Delta\mu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))m(\mathbf{i}). \quad (4.1)$$

Similarly, for hydration we have the condition

$$\Delta\mu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = \Delta\mu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}_0)) + n\theta(\mathbf{i})\Delta\mu_{\text{fw}}. \quad (4.2)$$

Finally, for a chain of arbitrary type  $\mathbf{i}$ , the equilibrium between the free state and the network-bound state gives the relation

$$\Delta\mu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = \Delta\mu^G(\mathbf{i}). \quad (4.3)$$

The first association equilibrium (4.1) gives the volume fraction of clusters in the form

$$\phi(\mathbf{j}; \mathbf{m}) = \exp \left[ \sum_{\mathbf{i}} m(\mathbf{i}) - 1 - \Delta(\mathbf{j}; \mathbf{m}) \right] \prod_{\mathbf{i}} \phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))^{m(\mathbf{i})}. \quad (4.4)$$

The hydration equilibrium (4.2) gives

$$\phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = \exp[n\theta(\mathbf{i}) - \beta\Delta A(\mathbf{i})] \phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}_0)) \phi_{\text{fw}}^{n\theta(\mathbf{i})} \quad (4.5)$$

for the volume fraction of the unassociated chains of type  $\mathbf{i}$ . This leads to the distribution function for the number density  $\nu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))$  of the polymer chains as

$$\nu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = K_{\text{H}}(\mathbf{i}) \nu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}_0)) \phi_{\text{fw}}^{n\theta(\mathbf{i})}, \quad (4.6)$$

where

$$K_{\text{H}}(\mathbf{i}) = \exp[n\theta(\mathbf{i}) - \beta\Delta A(\mathbf{i})]/[1 + \theta(\mathbf{i})] \quad (4.7)$$

is the equilibrium constant for hydration. Upon substitution of Eq. (4.5) into Eq. (4.4), we find

$$\nu(\mathbf{j}; \mathbf{m}) = K(\mathbf{j}; \mathbf{m}) \prod_{\mathbf{i}} [K_{\text{H}}(\mathbf{i}) \nu_{\lambda} \phi_{\text{fw}}^{n\theta(\mathbf{i})}]^{m(\mathbf{i})}, \quad (4.8)$$

where we have introduced the symbol  $\nu_{\lambda} \equiv \nu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}_0))$  for the number density of unassociated bare polymers (called lambda chain) in the solution, and

$$\begin{aligned} K(\mathbf{j}; \mathbf{m}) &\equiv \frac{n^{\sum m(\mathbf{i})}}{\bar{n}(\mathbf{m})} \prod_{\mathbf{i}} [1 + \theta(\mathbf{i})]^{m(\mathbf{i})} \\ &\quad \times \exp \left[ \sum_{\mathbf{i}} m(\mathbf{i}) - 1 - \Delta(\mathbf{j}; \mathbf{m}) \right] \end{aligned} \quad (4.9)$$

is the equilibrium constant for the reversible formation of connected clusters of type  $(\mathbf{j}; \mathbf{m})$ .

In the postgel regime, we have an additional equilibrium condition (4.3) for the association of a free chain to the gel network. We are led to the result

$$\ln \phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = \delta_{\mathbf{i}}(\phi) - 1 - \beta\Delta A(\mathbf{i}). \quad (4.10)$$

The dimensionless binding free energy  $\delta_{\mathbf{i}}$  is therefore related to the volume fraction of the unassociated polymers. After taking the difference between  $\mathbf{i}$  and  $\mathbf{i}_0$ , and substituting the relation

$$\phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}))/\phi(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i}_0)) = \exp[n\theta(\mathbf{i}) - \beta\Delta A(\mathbf{i})] \phi_{\text{fw}}^{n\theta(\mathbf{i})} \quad (4.11)$$

into the result, we find

$$\delta_{\mathbf{i}}(\phi) = 1 + n\theta(\mathbf{i}) + \ln \phi_{\lambda} + n\theta(\mathbf{i}) \ln \phi_{\text{fw}}. \quad (4.12)$$

The free energy per lattice cell of the solution

$$f(\phi, T) \equiv \beta\Delta F/\Omega = \beta\Delta\mu_{\text{fw}}(1 - \phi) + \beta\Delta\mu_{\lambda}\phi/n \quad (4.13)$$

can now be decomposed into the ordinary Flory-Huggins mixing free energy  $f_{\text{FH}}$  and the free energy  $f_{\text{AW}}$  of association-hydration as  $f = f_{\text{FH}} + f_{\text{AW}}$ , where

$$f_{\text{FH}} \equiv \frac{\phi}{n} \ln \phi + (1 - \phi) \ln(1 - \phi) + \bar{\chi}\phi(1 - \phi) \quad (4.14)$$

and

$$f_{\text{AW}} \equiv \frac{\phi}{n} \ln \left( \frac{\phi_\lambda}{\phi} \right) + (1 - \phi) \ln \left( \frac{\phi_{\text{fw}}}{1 - \phi} \right) + \Delta v, \quad (4.15)$$

with

$$\Delta v \equiv 1 - \phi + \phi/n - v^S \quad (4.16)$$

being the loss in the degree of center of mass translational motion as a result of intermolecular association.

## V. OSMOTIC PRESSURE, SPINODAL CONDITION, AND OTHER SOLUTION PROPERTIES

By using the mass conservation laws for polymer and water, let us find next the two fundamental volume fractions  $\phi_\lambda$  and  $\phi_{\text{fw}}$  as functions of the volume fraction  $\phi$  of the polymers fixed in the sample preparation. Because the number  $\nu^S(\mathbf{i})$  of chains of hydration type  $\mathbf{i}$  in the sol part is given by

$$\nu^S(\mathbf{i}) = \sum_{\mathbf{j}, \mathbf{m}} m(\mathbf{i}) \nu(\mathbf{j}; \mathbf{m}), \quad (5.1)$$

and this number is given by  $\nu^G(\mathbf{i})$  in the gel parts, we find

$$\phi = n \sum_{\mathbf{i}} [\nu^S(\mathbf{i}) + \nu^G(\mathbf{i})]. \quad (5.2)$$

Similarly, we have

$$1 - \phi = \phi_{\text{fw}} + n \sum_{\mathbf{i}} \theta(\mathbf{i}) [\nu^S(\mathbf{i}) + \nu^G(\mathbf{i})] \quad (5.3)$$

for water. The chemical potentials of these two components, lambda chains and free water, are then given by

$$\beta \Delta \mu_\lambda = (1 + \ln \phi_\lambda)/n - v^S + \bar{\chi}(1 - \phi)^2 + d^G(\phi)(1 - \phi), \quad (5.4a)$$

$$\beta \Delta \mu_{\text{fw}} = 1 + \ln \phi_{\text{fw}} - v^S + \bar{\chi} \phi^2 - d^G(\phi) \phi. \quad (5.4b)$$

The osmotic pressure  $\pi$  can be found from the thermodynamic relation  $\pi a^3 = -\Delta \mu_{\text{fw}}$ . The spinodal condition is derived by differentiating the osmotic pressure once more with respect to the concentration. It can also be found by taking the derivative of the difference  $\Delta \mu_\lambda - \Delta \mu_{\text{fw}}$  between the chemical potential of the lambda chains and that of the free water. We find

$$\frac{\kappa_\lambda(\phi)}{n\phi} + \frac{\kappa_{\text{fw}}(\phi)}{1 - \phi} - 2\bar{\chi} = 0, \quad (5.5)$$

for the spinodal, where the relations

$$\kappa_\lambda(\phi) \equiv \frac{\partial}{\partial \ln \phi} \left[ 1 + \left( \sum_{\mathbf{i}} n \nu^G(\mathbf{i}) \right) \frac{\partial}{\partial \phi} \right] \ln \phi_\lambda, \quad (5.6a)$$

$$\kappa_{\text{fw}}(\phi) \equiv \frac{\partial}{\partial \ln \phi} \left[ 1 + \left( \sum_{\mathbf{i}} n \theta(\mathbf{i}) \nu^G(\mathbf{i}) \right) \frac{\partial}{\partial \phi} \right] \ln \phi_{\text{fw}} \quad (5.6b)$$

describe the effects of end-chain association and of hydration, respectively. The volume fraction  $\phi_{\text{fw}}$  of free water is assumed to be a function of the total polymer volume fraction  $\phi$  and it is substituted into these  $\kappa$  functions.

## VI. TREE STATISTICS FOR END-CHAIN ASSOCIATION

To study gelation by end-chain association, we employ the conventional tree statistics for multiple association developed by Fukui and Yamabe,<sup>30</sup> and also by TS. The multiplicity of a junction in the present situation is given by the aggregation number of the micelle. Under the tree assumption, there are two fundamental geometrical relations

$$\sum_{\mathbf{i}} m(\mathbf{i}) = \sum_{k \geq 1} (k - 1) j_k + 1, \quad (6.1a)$$

$$\sum_{k \geq 1} j_k = (f - 1) \sum_{\mathbf{i}} m(\mathbf{i}) + 1 \quad (6.1b)$$

for the number of polymer chains and junctions, where  $f$  is the functionality of the primary chain ( $f=2$  for telechelic chains).

The multiplicity of junctions is in principle determined by the equilibrium requirement for a given associative interaction. In the case of hydrophobic interaction, the chain length of the hydrophobe, the strength of water-hydrophobe interaction, and the geometric form of the aggregate determine the association constant  $\lambda(T)$  and the multiplicity of junctions.

Let  $p_k$  be the probability for a hydrophobe (end chain) to be associated into a micelle of multiplicity  $k$ , and let  $\alpha$  be the extent of association, i.e., the probability for an arbitrarily chosen hydrophobe to be associated. Then,  $p_1 = 1 - \alpha$  gives the probability for a hydrophobe to remain unassociated. In accordance with TS, we assume association-dissociation equilibrium condition for the hydrophobes forming micelles of multiplicity  $k$ , so that we have

$$p_k = K_k \psi^{k-1} p_1^k, \quad (6.2)$$

where  $K_k$  is the equilibrium constant and  $\psi \equiv f\phi/n_t$  is the total number density of hydrophobes. We may write, as in TS, the equilibrium constant in the form

$$K_k = [\lambda(T)]^{k-1} \gamma_k \quad (6.3)$$

by separating the binding free energy of a micelle into a bulk part  $\Delta g_k^0 = (k-1)\Delta g_{\text{AS}}$  and a surface part. The association constant  $\lambda(T)$  comes from the bulk part through the relation

$$\lambda(T) = \exp(-\beta \Delta g_{\text{AS}}). \quad (6.4)$$

Under these assumptions, the extent of association can be written as

$$p_1 = 1 - \alpha = 1/u(z) \quad (6.5)$$

in terms of the junction function  $u(z)$  defined by

$$u(z) \equiv \sum_{k \geq 1} \gamma_k z^{k-1}, \quad (6.6)$$

where the parameter  $z \equiv \lambda(T) \psi p_1$  is the total number density of hydrophobes that remain unassociated. The number density of unassociated polymer chains of hydration type  $\mathbf{i}$  is given by

$$\nu(\mathbf{j}_0; \mathbf{m}_0(\mathbf{i})) = p_1^f \nu^S(\mathbf{i}) \quad (6.7)$$

by definition. Upon substitution of Eqs. (6.5) and (6.6) for  $p_1$ , we find

$$\sum_{\mathbf{i}} \nu^S(\mathbf{i}) = u(z)^f \nu_{\lambda} \sum_{\mathbf{i}} K_{\text{H}}(\mathbf{i}) \phi_{\text{fw}}^{n\theta(\mathbf{i})} = u(z)^f \nu_{\lambda} g_0(\phi_{\text{fw}}), \quad (6.8)$$

where the new function  $g_0(y)$  is defined by

$$g_0(y) \equiv \sum_{\mathbf{i}} K_{\text{H}}(\mathbf{i}) y^{n\theta(\mathbf{i})}. \quad (6.9)$$

The mass conservation law (5.2) for the polymer is then expressed as

$$\phi = u(z)^f \phi_{\lambda} g_0(\phi_{\text{fw}}) + \phi^G. \quad (6.10)$$

Similarly, the conservation law (5.3) for water is transformed into

$$1 - \phi = \phi_{\text{fw}} + u(z)^f \phi_{\lambda} g_1(\phi_{\text{fw}}) + \phi_{\text{bw}}^G, \quad (6.11)$$

where  $\phi_{\text{bw}}^G$  is the volume fraction of the water molecules that are bound to the gel network. Another new function  $g_1$  is defined by

$$g_1(y) \equiv \sum_{\mathbf{i}} \theta(\mathbf{i}) K_{\text{H}}(\mathbf{i}) y^{n\theta(\mathbf{i})}. \quad (6.12)$$

The functions  $g_0$  and  $g_1$  were studied in detail in OT in the case of cooperative hydration. In the pregel regime where there is no gel network, we may simply set  $\phi^G = \phi_{\text{bw}}^G = 0$ . By solving Eq. (6.10) with respect to  $\phi_{\lambda}$ , and substituting the result into Eq. (6.11), we find

$$1 - \phi = \phi_{\text{fw}} + \phi G(\phi_{\text{fw}}), \quad (6.13)$$

where

$$G(y) \equiv g_1(y)/g_0(y) = \partial \ln g_0(y) / n \partial \ln y. \quad (6.14)$$

To summarize, we have the following set of equations:

$$\lambda(T) \psi = zu(z), \quad (6.15a)$$

$$\phi = u(z)^f \phi_{\lambda} g_0(\phi_{\text{fw}}), \quad (6.15b)$$

$$1 - \phi = \phi_{\text{fw}} + \phi G(\phi_{\text{fw}}). \quad (6.15c)$$

These should be solved for the unknowns  $z$ ,  $\phi_{\lambda}$ , and  $\phi_{\text{fw}}$  as functions of the polymer volume fraction  $\phi$  and the temperature  $T$ . If there is no hydration, we have  $g_0(z) = g_1(z) = 1$ . The equations reduce to those studied in TS for thermoreversible gelation with multiple association. If there is no hydrophobic association, on the contrary, we have  $\lambda(T) = 0 (z=0)$  and  $u(z) = 1$ . The equations reduce to those studied in OT. Hence, we here have unified theory.

The number density of molecules and clusters that possess translational degree of freedom reduces by the amount

$$\Delta \nu(\phi) = \phi G(\phi_{\text{fw}}) + \frac{1}{\lambda} \int_0^z zu'(z) dz \quad (6.16)$$

due to association and hydration.

After taking the derivatives of the mass conservation laws, we find that the  $\kappa$  functions in the spinodal condition (5.5) take the forms

$$\kappa_{\lambda}(\phi) = 1 + f[\partial \ln z / \partial \ln \phi - 1], \quad (6.17a)$$

$$\kappa_{\text{fw}}(\phi) = [1 + G(\phi_{\text{fw}})]^2 (1 - \phi) / \phi_{\text{fw}} [1 + \phi G'(\phi_{\text{fw}})] \quad (6.17b)$$

in the pregel regime.

The  $\kappa$  function for a lambda chain can be described in terms of the average multiplicity of micellar junctions. For this, we first take the logarithmic derivative of Eq. (6.15a) and find

$$\partial \ln z / \partial \ln \phi = 1 / [1 + zu'(z)/u(z)]. \quad (6.18)$$

The denominator gives the average multiplicity

$$\mu_{\text{w}} \equiv \sum_{k \geq 1} k p_k = 1 + zu'(z)/u(z), \quad (6.19)$$

and hence we have

$$\kappa_{\lambda}(\phi) = [1 - (f-1)(\mu_{\text{w}} - 1)] / \mu_{\text{w}}. \quad (6.20)$$

Because the gel point in multiple tree statistics is given by the divergence condition<sup>21,30</sup> of the weight-average multiplicity

$$(f-1)(\mu_{\text{w}} - 1) = 1, \quad (6.21)$$

we find that  $\kappa_{\lambda}$  vanishes at the gel point. This is due to the vanishing of the translational motion of the largest cluster when it grows to macroscopic dimensions.

At this stage, we realize that we can study monofunctional polymers ( $f=1$ ) and telechelic polymers ( $f=2$ ) (and also their mixtures) from the unified point of view described above. Important examples of the monofunctional case are amphiphilic diblock copolymers made up of a hydrophilic block and a hydrophobic block, such as PEO-poly(phenylene oxide) diblock copolymer, PEO-PNIPAM diblock copolymer,<sup>31</sup> etc. Another common example is that of the non-ionic surfactants  $C_i E_j$  made up of a short alkyl chain and an ethylene oxide chain.<sup>32,33</sup> The LCST phase separation depends sensitively on the number of ethylene oxide units.<sup>33</sup> The phase separation and mixing law of the end chains in the mixtures of telechelic PEO and semitelechelic hydrophobic PEO have been studied in detail in the literature.<sup>34</sup>

As for the postgel regime, there have been several different theoretical methods to treat the reaction in the sol and gel parts. One such method assumes tree structures for the gel network as well as for the sol (Stockmayer's picture),<sup>35</sup> while the other theory permits cycle formation within the network (Flory's treatment).<sup>36</sup> The difference between the two methods was examined later by Ziff and Stell<sup>37</sup> from the kinetic viewpoint, leading to a third method which bridges the two original methods. The specific form of the binding free energy  $\delta_f(\phi)$  depends on which method one chooses to treat the postgel regime. In this study, we avoid this complex problem and employ the simplest treatment of Stockmayer.<sup>35</sup>

## VII. COOPERATIVE HYDRATION

Let us next proceed to the models of hydration. If water molecules are independently and randomly hydrogen bonded onto a polymer chain, as was studied previously,<sup>5</sup> the index  $i$  can be replaced by  $m$ , the number of bound water molecules,

and  $K_H(\mathbf{i})$  is replaced by  $K_m = (1+m/n)_n C_m \lambda^m$ , where  ${}_n C_m = n!/m!(n-m)!$  is the number of different ways to choose  $m$  hydrogen-bonding sites randomly among the number  $n$  of total available sites, and  $\mu(T) \equiv \exp(-\beta \Delta f_H)$  is the hydration constant ( $\Delta f_H$  being the free energy of one hydrogen bond). The functions appearing in the thermodynamic properties are given by  $g_0(y) = (1+y)^n$ ,  $g_1(y) = y(1+y)^{n-1}$ , and  $G(y) = y/(1+y)$ , where  $y \equiv \mu(T) \phi_{fw}$  is the reduced concentration of free water. For cooperative hydration, in contrast, the equilibrium constant is most generally written as

$$K_H(\mathbf{i}) = \omega(\mathbf{i}) \prod_{\zeta=1}^n \eta_{\zeta}^{i_{\zeta}}, \quad (7.1)$$

as was shown in OT, where

$$\omega(\mathbf{i}) \equiv \left( n - \sum_{\zeta} i_{\zeta} \right)! / \left( \prod_{\zeta} i_{\zeta}! \right) \left[ n - \sum_{\zeta} (\zeta + 1) i_{\zeta} \right]! \quad (7.2)$$

is now the number of different ways to select sequences specified by  $\mathbf{i}$  from a chain, and  $\eta_{\zeta}$  is the statistical weight for a single water sequence of length  $\zeta$  formed on a chain in the reference conformation.<sup>38</sup>

Since summing up all possible types  $\mathbf{i}$  in the above functions is mathematically difficult, we replace the sum by the contribution from the most probable type  $\mathbf{i}^*$  (*one-mode approximation*). The necessary functions are then given by

$$g_0(y) = \omega(\mathbf{i}^*) \prod_{\zeta=1}^n (\eta_{\zeta} y^{\zeta})^{i_{\zeta}}, \quad (7.3)$$

$g_1(y) = \theta(\mathbf{i}^*) g_0(y)$ , and  $G(y) = \theta(\mathbf{i}^*)$ . The function  $G$  reduces to the coverage  $\theta$  by bound water molecules of type  $\mathbf{i}^*$ .

The most probable type, or sequence distribution, can be found by minimizing the free energy  $f_{AW}$  [Eq. (4.15) supplemented by Eq. (6.16)] by changing  $\mathbf{i}$ . The condition  $\partial f_{AW} / \partial i_{\zeta} = 0$  gives

$$i_{\zeta} / n = (1 - \theta) t \eta_{\zeta} q^{\zeta}, \quad (7.4)$$

for the distribution of hydrated sequences, where  $q$  is a parameter defined by the equation

$$q \equiv (1 - \phi - \theta \phi) t \exp[R(q, \phi)]. \quad (7.5)$$

Here, the function

$$R(\theta, \phi) \equiv \theta \phi / (1 - \phi - \theta \phi) \quad (7.6)$$

gives the ratio of the total number of bound water molecules to the number of free water molecules. The parameter  $t$  is defined by  $t \equiv 1 - \nu / (1 - \theta)$  as in OT. Substituting this distribution function (7.4) into the definitions of  $\theta$  and  $\nu$ , we find

$$\theta(q) = [1 - \theta(q)] t(q) V_0(q) \quad (7.7)$$

and

$$\nu(q) = [1 - \theta(q)] t(q) V_0(q), \quad (7.8)$$

and hence

$$t(q) = 1 / [1 + V_0(q)]. \quad (7.9)$$

Here two new functions  $V_0$  and  $V_1$  are defined by

$$V_0(q) \equiv \sum_{\zeta=1}^n \eta_{\zeta} q^{\zeta} \quad \text{and} \quad V_1(q) \equiv \sum_{\zeta=1}^n \zeta \eta_{\zeta} q^{\zeta}. \quad (7.10)$$

Now,  $\theta$  and  $t$  must be regarded as functions of  $q$ , so that Eq. (7.5) is an equation for the unknown variable  $q$  to be solved in terms of a given concentration  $\phi$ .

The  $\kappa_{fw}$  function in our spinodal condition (5.5) now takes the form

$$\kappa_{fw}(q; \phi) = \frac{1 + (1 - \theta) QR}{1 + (1 - \theta) QR^2} (1 + \theta)^2 (1 + R), \quad (7.11)$$

where

$$Q(q) \equiv \theta(q) - [1 - \theta(q)] \bar{\zeta}_w(q), \quad (7.12)$$

with

$$\bar{\zeta}_w(q) \equiv V_1(q) / V_0(q) \quad (7.13)$$

being the weight average length of a sequence of bound water molecules.

Our strategy is therefore as follows. We first solve Eq. (7.5) for the unknown  $q$  for a given concentration  $\phi$  and temperature  $T$ , and then find  $\theta$ ,  $\nu$ , and  $t$  as functions of them. We then substitute the result into the function  $\kappa_{fw}(q; \phi)$  to find the spinodals.

In order to carry out calculations completely, we have to specify the statistical weight  $\eta_{\zeta}$ . To do this, we employ the simplest form

$$\eta_{\zeta} = \sigma \mu(T)^{\zeta} \quad (7.14)$$

proposed by Zimm and Bragg<sup>39</sup> for the study of coil-to-helix transition of biopolymers. The front factor  $\sigma$  gives the statistical weight for the boundary between a helix and a coil (a hydrated sequence and a collapsed random coil in the present context). It is called *cooperativity parameter*. In the case of random adsorption where there is no interaction between the adsorbed water molecules, the factor is  $\sigma = 1$  and the model reduces to our previous one.<sup>5</sup> Let  $\Delta f_H \equiv \epsilon_H - T \Delta s_H$  be the free energy of a hydrogen bond, and let  $\Delta \epsilon_H$  be the interaction energy between nearest neighboring bound water molecules. The statistical weight  $\mu(T) = \exp[-\beta(\Delta f_H + \Delta \epsilon_H)]$  (called association constant) includes both the hydrogen-bonding free energy and the nearest neighbor interaction energy. The cooperativity parameter is given by  $\sigma \equiv \exp(-\beta |\Delta \epsilon_H|)$ .

Equation (7.5) to determine  $q$  now takes the form

$$q = \mu(T) [1 - \phi - \theta(q) \phi] e^{R(q, \phi)} / [1 + \sigma q w_0(q)], \quad (7.15)$$

where  $\mu(T)q$  is written as  $q$  for simplicity. The coverage  $\theta$  by bound water molecules is given by

$$\theta(q) = \sigma q w_1(q) / [1 + \sigma q w_{01}(q)]. \quad (7.16)$$

Here, the functions  $w$  are defined by

$$w_0(x) \equiv \sum_{\zeta=1}^n x^{\zeta-1} \quad \text{and} \quad w_1(x) \equiv \sum_{\zeta=1}^n \zeta x^{\zeta-1} \quad (7.17)$$

and  $w_{01}(x) \equiv w_0(x) + w_1(x)$ . The average sequence length is given by  $\bar{\zeta}_w = w_1(q) / w_0(q)$ .



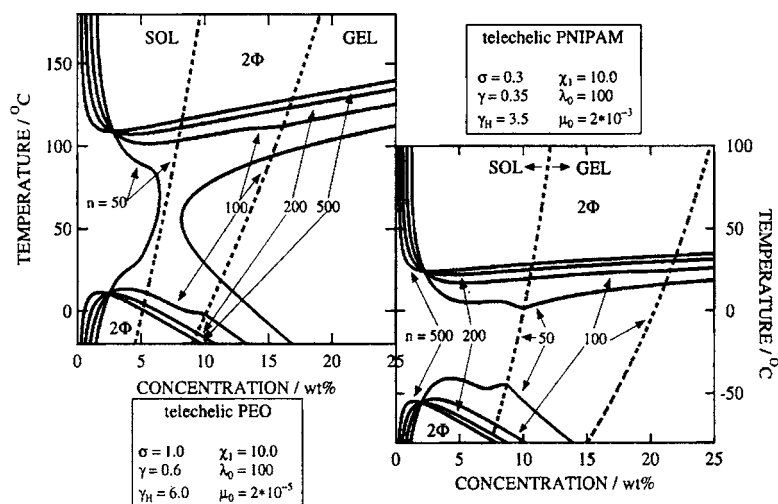


FIG. 2. Comparison of the phase diagrams of telechelic associating polymers with random hydration ( $\sigma=1.0$ , left) and with cooperative hydration ( $\sigma=0.3$ , right) over a wide concentration range. Spinodal lines (solid lines) and sol/gel transition lines (broken lines) are shown. The various curves correspond to polymers of different molecular weights.

### VIII. PHASE DIAGRAMS

For numerical calculation of the phase diagrams, we set the necessary parameters in the following way. We first assume the conventional Schultz-Flory form<sup>40</sup>  $\chi_{mw}(T)=1/2 - \psi\tau$  for the  $\chi$  parameter between monomer units of the main chains and water, where  $\tau \equiv 1 - \Theta_0/T$  is the reduced temperature deviation measured from the reference theta temperature  $\Theta_0$  satisfying the condition  $\chi_{mw}(\Theta_0)=1/2$ , and  $\psi$  is a material parameter of order unity. At the temperature  $\Theta_0$ , the second virial coefficient of a hypothetical Flory-Huggins solution without hydrophobic- and hydrogen-bonding interaction vanishes. For the interaction between the end chains and water, we have  $\chi_1 \approx 2 \times 28.5$  (kcal/mol)/ $k_B T$ . To have the sol/gel transition lines in the observed concentration range near 2%, we tried two fixed values of  $\chi_1(T)=3.0$  and 10.0. The association constant of the hydrophobic aggregation of the end chains is then given by  $\lambda(T) \equiv \exp(-\Delta g_{AS}/k_B T) = \lambda_0 \exp(\Delta \epsilon/k_B T) = \lambda_0 \exp[\gamma(1-\tau)]$  in terms of the reduced temperature, where  $\gamma \equiv \Delta \epsilon/k_B \Theta_0$  is the association energy in a unit of thermal energy at the reference temperature. We varied the numerical values of  $\lambda_0$  and  $\gamma$  to assess fits to the observed downward shift of the LCST.

Similarly, the association constant for hydration is expressed as  $\mu(T) = \mu_0 \exp(|\epsilon_H + \Delta \epsilon_H|/k_B T) = \mu_0 \exp[\gamma_H(1-\tau)]$  in terms of the reduced temperature, where  $\mu_0$  gives the entropy part of the binding free energy, and  $\gamma_H \equiv |\epsilon_H + \Delta \epsilon_H|/k_B \Theta_0$  is the dimensionless bonding energy. The reference temperature  $\Theta_0$  is not the true theta temperature  $\Theta$  at which the second virial coefficient of the osmotic pressure vanishes. The latter lies far below  $\Theta_0$  due to additional interaction. Throughout the present numerical calculation, we fix  $\psi$  at  $\psi=1.0$  and change the amplitude  $\lambda_0$ ,  $\mu_0$ , the dimensionless binding energy  $\gamma$ ,  $\gamma_H$ , and the cooperative parameter  $\sigma$ . In particular, we monitor how changes in the value of  $\sigma$  affect the LCST line. The parameters related to the strength of hydration, such as  $\mu_0$  and  $\gamma_H$ , were taken from Ref. 5 for PEO and Ref. 13 for PNIPAM. These parameters led to good fits of the experimental data in the case of the two homopolymers.

In Fig. 2 we compare the phase diagrams of aqueous solutions of telechelic associating polymers undergoing ran-

dom hydration (left figure with  $\sigma=1.0$ ) or cooperative hydration (right figure with  $\sigma=0.3$ ). (We found in OT that a value of 0.3 gave the best fit for the phase diagrams of the homopolymer PNIPAM.) The spinodal lines (solid lines) and the sol/gel transition lines (broken lines) are shown over a wide concentration range up to 25 wt%. The molecular weights of the polymers vary from  $n=50$  to 1000. The phase separation region (unstable region) shrinks, i.e., the LCST moves upwards and the upper critical solution temperature (UCST) moves downwards with increasing molecular weight for solutions of polymer concentrations higher than 2 wt%. For the solutions of concentration lower than 2 wt%, however, the opposite trend is observed; the shorter the polymer chains, the higher the spinodal temperature. In such low concentration region, intermolecular end-chain association is so limited that the average molecular weight of the aggregates of shorter chains remains smaller than that of longer chains. Hence, the tendency for phase separation is larger for longer chains as in homopolymer solutions. With increasing concentration, however, association develops to an extent such that the average molecular weight of the associated shorter chains exceeds that of the longer chains. As a result, shorter chains show a more pronounced tendency for phase separation. Such as inversion of the molecular weight effect takes place at the point on the phase plane where LCST curves for different molecular weights cross each other.

In the case of solutions of polymers undergoing random hydration, the LCST and UCST merge for polymers having a molecular weight between  $n=50$  and 100, and the phase separation region turns into hourglass shape. In cooperative hydration, the LCST curves are very flat up to high polymer concentration with only a weak molecular weight dependence.

In the left panel of Fig. 3, we present the low concentration region, up to 5 wt%, of the phase diagram of the telechelic polymer/water system for which  $\sigma=1.0$  for polymers of four different molecular weights. Note that, as a result of end-chain association, the LCST lines shift downwards, and the UCST lines shift upwards, along the sol/gel transition line. The right panel of Fig. 3 shows the same phase diagram region, but for a telechelic polymer/water system for which

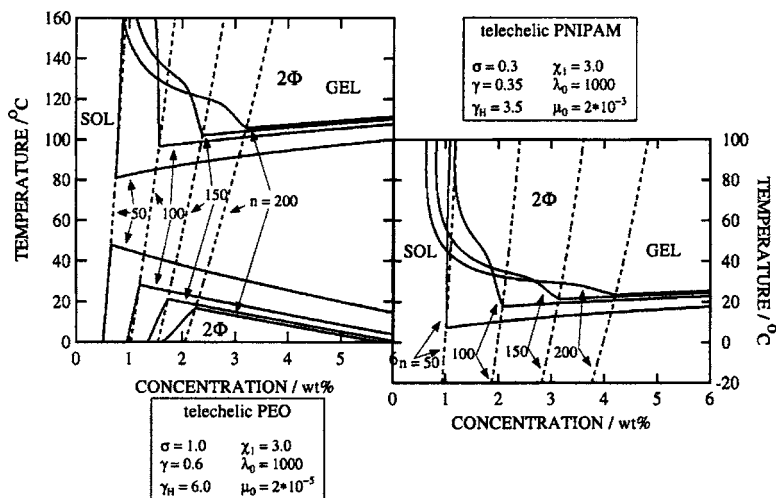


FIG. 3. (Left) Detailed representation of the phase diagram in the low concentration regime for random hydration with  $\sigma=1.0$ . The various curves correspond to polymers of different molecular weights. The LCST and UCST lines come closer to each other as the molecular weight of the polymers decreases due to end-chain association. The lines eventually merge, and the phase separation region turns into an hourglass shape. (Right) Same as the left figure, but with  $\sigma=0.3$ . The LCST remains flat almost independent of the polymer molecular weight regardless of end-chain association.

$\sigma=0.3$ . The spinodal curves for polymers of different molecular weights cross, and solutions of concentrations beyond the crossover point exhibit an inversion of the molecular weight dependence of their LCST curves. Since the critical micelle concentration is reported to be extremely small ( $c < 10^{-3}$  wt %), the spinodal curves for solutions of telechelic polymer concentration lower than 1 wt % are expected to be substantially modified due to the formation of flower micelles. Within our tree approximation, the LCST is identical to the crossing point of the spinodal curve and the sol/gel transition curve.

Experimental values of the cloud point temperature and the endotherm maximum temperature recorded by differential scanning calorimetry (DSC) for solutions of telechelic PNIPAMs of various concentrations<sup>26</sup> are presented in Fig. 4. The values recorded for solutions of the homopolymer are presented as well. For these solutions, the onset of phase separation (cloud point) coincides with the coil-to-globule transition. In contrast, in the case of telechelic PNIPAM solutions, the onset temperature of phase separation is lower than the collapse transition temperature. The shorter the

chains, the larger the temperature difference. It is as large as 10 K for the shortest chain ( $M_n=12\,000$  g/mol) measured.

Experimental cloud points of telechelic PNIPAM with  $M_w=37\,000$  g/mol recorded for solutions of various concentrations are presented in Fig. 5 together with the theoretical spinodal line. Because their spinodal lines are expected to lie above the binodal lines (cloud points), the comparison is only qualitative. The discrepancy between the binodal and spinodal becomes larger at lower concentrations, so that the fitting in the very dilute region should not be taken as a comparison.

The left panel of Fig. 6 presents the theoretical plots of the LCST and UCST of homopolymer PEO solutions as functions of the reciprocal DP. The right panel displays the corresponding phase diagrams on the conventional temperature-concentration plane. DCP is the double critical point where the LCST and UCST merge into a single critical point. HCP stands for the hypercritical point where the phase separation region of loop shape shrinks into one point. For PEO, the DCP occurs at  $n=1800$ , while HCP takes place at

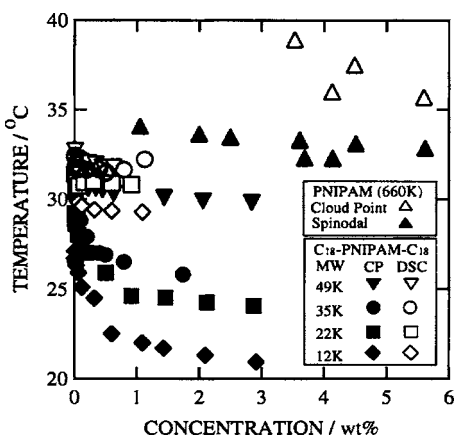


FIG. 4. Experimental cloud points (black symbols) of aqueous telechelic PNIPAM solutions determined from temperature-induced changes in the light scattering intensity of polymer solutions, and temperatures of maximum intensity (open symbols) of the endotherms recorded by DSC for aqueous solutions of telechelic PNIPAMs of four different molecular weights. The cloud points and spinodal points of PNIPAM solutions are shown for reference (Ref. 26).

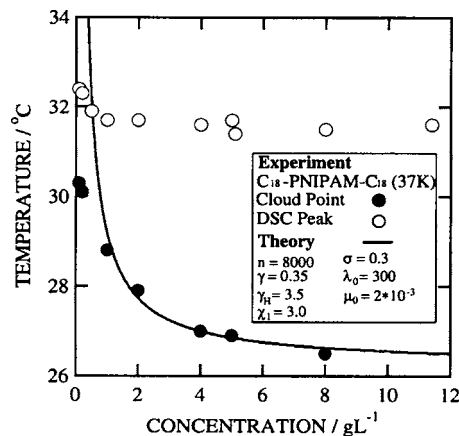


FIG. 5. Experimental cloud points (black circles) and theoretical spinodal curve (solid line) of aqueous solutions of a telechelic PNIPAM ( $M_w=37\,000$  g/mol). The coil-to-globule transition temperatures detected by DSC are also plotted (open circles). The cloud points (onset of phase separation) lie below the coil-to-globule transition temperature due to hydrophobic association. The latter temperature is almost independent of the polymer concentration because the transition is essentially related to the intramolecular conformation of each chain.

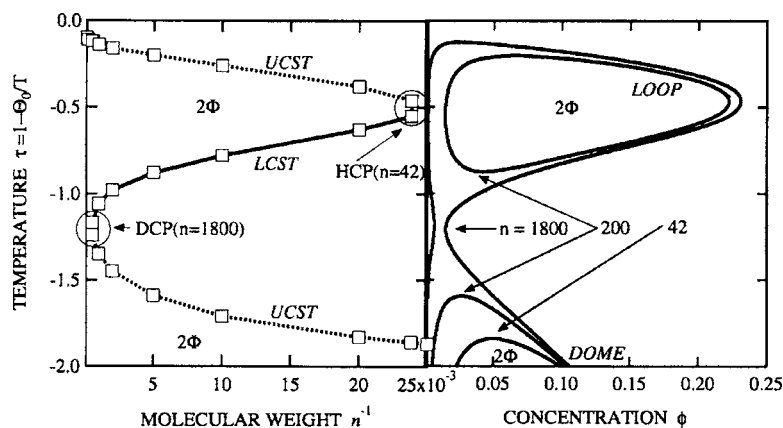


FIG. 6. UCST lines (dotted lines) and LCST lines (solid lines) of homopolymer PEO solutions as functions of  $n^{-1}$ , the reciprocal DP (left). Phase diagrams of PEO solutions (Ref. 2) on an ordinary temperature-concentration plane (right). The DP of the polymer is changed from curve to curve.

$n=42$ . The disappearance of the loop (HCP) was observed experimentally by Saeki *et al.*<sup>2</sup> in the case of polymers of lower molecular weight.

The LCST-UCST diagrams of aqueous solutions of PEO and telechelic PEO ( $\sigma=1.0$ ) are presented in Fig. 7. For chains shorter than  $n \approx 200$ , the average molecular weight of the aggregates becomes larger than that of the longer chains, and hence, the LCST decreases and the UCST increases. The two temperatures eventually merge into a DCP at a molecular weight indicated by a circle in the figure, and disappear for solutions of low DP polymers. This nonmonotonic variation of the critical points as a function of DP is a characteristic feature of associating polymer solutions. A phase separation of the hourglass type was observed in solutions of short telechelic PEO.<sup>24</sup>

The LCST-UCST diagrams of aqueous solutions of PNIPAM and telechelic PNIPAM are presented in Fig. 8 as a function of  $n^{-1}$ , the reciprocal DP, for the cooperative hydration of PNIPAM with  $\sigma=0.3$ . We note that for chains shorter than  $n \approx 200$ , the LCST decreases and the UCST follows the same trends as those of solutions of telechelic PEO, but the magnitudes of the LCST downward shift and the UCST upward shift are lower for hydrophobically modified (HM)-PNIPAMs compared to HM-PEOs. Also, the variation of the LCST values with  $n^{-1}$  is much more gradual (upper dotted

line) in the case of HM-PNIPAM. Thus, if the hydration of the polymer is cooperative, the LCST phase separation takes place within a very narrow temperature range lower than the collapse transition temperature, the latter being practically independent of the concentration because the collapse transition is caused by a sudden dehydration of each chain. A DCP cannot be seen in the diagrams drawn from calculations using the parameters shown in the right panel of Fig. 3.

## IX. CONCLUSIONS AND DISCUSSION

We have presented a theoretical framework to assess the interplay between hydration and hydrophobic association in the phase behavior of aqueous solutions of telechelic PEO and of telechelic PNIPAM. In solutions of low polymer concentration, polymers form self-loops, and loops associate into micelles of flower shape. With increasing polymer concentration, some loops turn into bridge chains connecting neighboring flowers, and the solution eventually turns into a connected network. In this study, we focused on network formation at and above the overlap concentration, and hence neglected the effect of flower micelles on the phase separation and gelation of a solution. This deficiency of the present theory may be remedied by introducing loops in equilibrium with open chains as species different from polymers, as was treated in our preceding paper.<sup>41</sup>

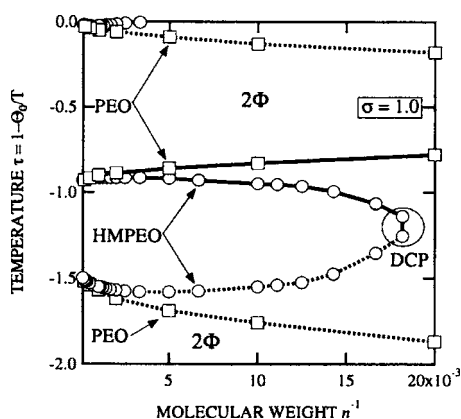


FIG. 7. LCST-UCST diagram for aqueous solutions of PEO and telechelic PEO (HM-PEO) represented as a function of the reciprocal DP. Hydrophobic modification of the polymers triggers an inversion of the molecular weight dependence of the critical points; shorter chains tend to phase separate more easily than longer chains (dotted lines). DCP appears for solutions of polymers of low molecular weights.

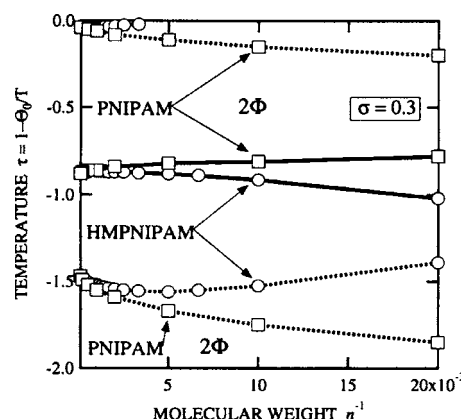


FIG. 8. LCST-UCST diagrams of aqueous solutions of PNIPAM and telechelic PNIPAM ( $\sigma=0.3$ ) are presented. LCST changes only gradually as a function of  $n^{-1}$ . DCP cannot be seen for solutions of polymers of molecular weights in the range of the graph.

In solutions of the telechelic polymers studied here, hydration (hydrogen bonding) and association (hydrophobic aggregation) are not strongly competitive, but almost decoupled from each other except for the chain parts near the end groups. In our model, we have neglected the interference between hydration and end-chain association. There is, however, experimental evidence that the dehydration starts at the core of the flower micelles, and this dehydration is followed by chain collapse, in the case of PNIPAM.<sup>42,43</sup> Upon heating a polymer solution above the phase transition temperature, end-chain association triggers dehydration and the networks start to shrink from the core of the micellar junctions. Such interference between (de)hydration and chain association remains an open problem with regard to aqueous polymer solutions.

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