

# Phase Diagram of Solutions of Associative Polymers

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**ABSTRACT:** An analytical expression for the free energy of solutions of associative polymers is obtained in the entire polymer concentration–temperature range. This expression is derived under assumption that both local intrachain loops as well as interchain associations contribute to combinatorial part of the system free energy. In a good solvent regime, theory takes into account the swelling of polymer chains and suppression of pairwise associations due to strong monomer–monomer repulsive interactions. Analysis of the general expression of the system free energy shows that associations between functional groups can lead to a collapse of a chain and phase separation even under good solvent conditions for polymer backbone. In a good solvent, changing the fraction of associative groups per chain can trigger a phase separation.

## 1. Introduction

Macromolecules with functional groups capable of forming reversible (physical) cross-links are called associative polymers.<sup>1–4</sup> These groups could be hydrophobic side chains, functional monomeric units, charged groups, etc. For example, in aqueous solutions of ethylene oxide–urethane copolymers in which hydrophobic and hydrophilic sequences alternate along the polymer backbone, the association is driven by aggregation of hydrophobic blocks. In dilute solutions, these copolymers form micelles. As polymer concentration increases micelles aggregate into clusters with different morphologies, depending on polymer composition and relative solubility of blocks. In polar solvents, charged polymers such as poly(vinyl alcohol), natural polymers (polysaccharides, DNA) associate in the presence of multivalent metallic cations or basic anions. The complexes between dissociated groups on the polymer and multivalent ions act as effective cross-links. In nonpolar solvents or in polymer melt, the counterions do not dissociate from the charged groups on the polymer backbone and stay in ionic pairs. Association of ionic pairs into multiplets leads to formation of the reversible cross-links and reinforcement of these materials. An example of such a system is sulfonated polystyrene ionomers in solvents of low polarity, such as cyclohexanone or tetrahydrofuran. Generally, formation of reversible cross-links leads to two physical phenomena:<sup>5–8</sup> (i) formation of intermolecular clusters and the gelation transition of overlapping chains into a reversible network; (ii) an increase in effective attraction between polymer chains, reducing their affinity to the solvent leading to phase separation. The formation of reversible networks has been studied in block copolymers,<sup>9–11</sup> ionomers,<sup>3,12</sup> telechelics,<sup>13–17</sup> and polyelectrolytes.<sup>18–22</sup>

In the modern approach, associative polymers are modeled by a solution of macromolecules, each carrying several functional groups (stickers). The functional groups on the chains are capable of forming reversible cross-links by association. The calculations of the phase behavior of associative polymers<sup>5,6,23–27</sup> are based on the classical ideas of gelation developed by Flory and Stockmayer<sup>28</sup> and on the lattice theory of polymer solutions proposed by Flory and Huggins<sup>28</sup> (see also for

review refs 1 and 29). In this approach, one assumes that interchain associations dominate the gelation process, neglecting intrachain associations. Thus, each polymer chain is considered to be in an effective external potential created by surrounding chains. This approximation is reasonable when the number of associative groups belonging to other chains within a volume occupied by a chain is much larger than the number of associative groups on a polymer chain, making interchain contacts more probable than intrachain ones. Unfortunately, this assumption is only correct at high polymer concentrations far above the chain overlap concentration, and it fails as polymer concentration decreases. In particular, this becomes transparent when one considers associations in dilute polymer solutions.

This approach can be improved by considering intrachain associations. The simplest way to include the intrachain associations is by taking into account formation of the shortest loops between functional groups neighboring along the polymer backbone.<sup>6</sup> Already such simple modification captures qualitative differences between intrachain and interchain associations. Only interchain associations control sol–gel transition and phase separation in solutions of associative polymers. The probability of intrachain associations is independent of the polymer concentration in a wide concentration range. However, consideration of the intrachain associations only partially solves the problem.

In dilute solutions, associations between functional groups lower polymer affinity to the solvent leading to polymer collapse. In the collapsed globule, the local chain structure resembles that of a semidilute polymer solution. The average polymer density inside a globule is determined by balancing two-body attractive interactions, if the solvent is poor for the polymer backbone, effective attractive interactions due to cross-linking of functional groups, and three-body monomer–monomer repulsive interactions. The existence of a polymer–solvent interface between dense globule and a pure solvent gives an additional contribution to the system free energy – surface energy contribution.<sup>30</sup> This contribution is absent in the original Flory–Huggins description of polymer solution, because even in a dilute solution the theory postulates a uniform polymer den-

sity profile by smearing chains over the whole volume of the system. As a result of this approximation classical Flory–Huggins theory of polymer solutions gives an incorrect coexistence curve. In reality, the difference between chemical potentials of a chain in concentrated and dilute phases in the two-phase region is equal to the surface energy of a polymer globule.<sup>30</sup> Thus, moving chains from sediment costs additional surface energy. This effect was taken into account in the scaling theory of polymer solutions (see for review, ref 30). However, to the best of my knowledge none of the papers dealing with phase separation in solutions of associative polymers addressed this question. In this paper, I will extend the model of solutions of associative polymers by explicitly including formation of intrachain cross-links and modify it to account for a surface energy contribution in dilute solutions.

The rest of the manuscript is organized as follows. In section 2, I will derive the general expression for the free energy of the solutions of associative polymers that includes formation of both intra- and interchain cross-links. Here I will obtain a crossover condition between the regimes with dominant role of intrachain and interchain associations. Section 3 shows how this model can be modified to consider reversible associations in a dilute solution. The reversible associations in good solvent conditions for the polymer backbone are treated in section 4. In section 5, I combine results obtained in sections 2, 3, and 4 to calculate phase diagrams of solutions of associative polymers.

## 2. Lattice Model of Associative Polymers

**2.1. Derivation of the Partition Function.** Consider a solution of linear polymer chains with degree of polymerization  $N$  carrying  $f$  associating groups (stickers) each. Each associating group is capable of forming a pair with association energy equal to  $-\epsilon_a$ . To describe a solution of associating polymers I will use a lattice model. The  $n$  lattice sites with coordination number  $z$  are partitioned between  $n_s$  solvent molecules and  $n_p$  polymers. Each site occupies a volume  $v$ . To place associative polymers on the lattice one can use three-stage process. First, the polymer chains are mixed with the solvent molecules, then the intrachain and interchain bonds are distributed between different chains, and finally the polymer–polymer and polymer–solvent interactions are taken into account. Thus, the partition function  $Z$  of the solution of associative polymers has three contributions

$$Z = Z_{\text{mix}} Z_{\text{bond}} Z_{\text{int}} \quad (1)$$

Such factorization of the system partition function corresponds to the three-stage process described above.

In eq 1 the first factor  $Z_{\text{mix}}$  is the number of different ways to arrange  $n_s$  solvent molecules and  $n_p$  polymers between  $n$  lattice sites with coordination number  $z$ . To calculate  $Z_{\text{mix}}$  one can for example start filling lattice sites with polymer molecules first and then fill all remaining lattice sites with the solvent molecules. The number of different ways to arrange polymer molecules is<sup>28</sup>

$$Z_{\text{mix}} = \frac{z^{n_p}(z-1)^{n_p(N-2)}}{2^{n_p} n^{n_p(N-1)}} \frac{n!}{n_s! n_p!} \quad (2)$$

The second factor  $Z_{\text{bond}}$  is due to formation of bonds

between associating groups. Let us assume that the total  $n_p m$  bonds are formed  $n_p m_1$  of which are intrachain bonds and  $n_p m_2$  of which are interchain ones. I will first calculate the contribution to the partition function due to formation of the intrachain bonds. Here I will assume that shortest loops dominate intrachain associations. The probability of forming shortest loop with number of monomers  $n_t = N/f$  is

$$P(n_t) = \frac{(z-2)}{c(z)n_t^{3/2}} \quad (3)$$

where  $c(z)$  is a numerical coefficient that depends on the coordination number  $z$  of the lattice. In the limit of large  $z$  the ratio  $z/c(z)$  approaches the value  $\sqrt{6/\pi}$  obtained for a Gaussian chain.<sup>30</sup> (The probability of forming a loop with double number of monomers,  $2n_t$ , is smaller by a factor of  $2^{3/2}$  in comparison with that of the shortest one.) In each chain, there are  $f$  associating groups, the smallest possible loop forms between adjacent associating groups, and therefore, there are  $f-1$  different ways to connect a pair of adjacent associating groups by a bond. To form the second bond, we have to distinguish between two different cases. The first case corresponds to the situation when the first bond connects any of two associating groups at the chain ends with their neighboring associating groups. In this case, there are  $f-2$  groups left, and the number of different ways to form a bond between neighboring associating groups is equal to  $f-3$ . The weight of this arrangement is equal to  $2/(f-1)$  because there are only two configurations out of the total number of  $f-1$  leading to such an arrangement of bonds. The second case corresponds to situations when the two neighboring associating groups forming the first bond can be everywhere except chain ends. Let the first associating group forming the first bond have  $k$  unassociated groups separating it from the left end of the chain, and then the second group forming this bond has  $f-2-k$  groups separating it from the other end. There are  $k-1$  possible placements of the second bond between  $k$  unassociated groups and  $f-2-k-1$  placements between  $f-2-k$  groups. The total number of locations of the second bond is equal to  $f-4$ . This number should be added to the final answer with a factor  $(f-3)/(f-1)$  because there are  $f-3$  available positions to place the first bond outside the chain ends. Summing all factors together,  $2(f-3)/(f-1) + (f-3)(f-4)/(f-1)$ , and multiplying the sum by the total number of different ways of placing the first bond,  $f-1$ , one arrives at  $(f-2)(f-3)$  possible arrangements of two bonds between  $f$  associating groups. Since bonds are indistinguishable this result has to be divided by 2. Thus, there are  $(f-2)(f-3)/2$  different ways to place two bonds connecting four neighboring associating groups out of  $f$  available associating groups. One can show by continuation of this process that the combinatorial factor counting the number of different arrangements of  $m_1$  intrachain bonds connecting  $2m_1$  nearest associating groups out of  $f$  available associating groups is identical to that of the problem of placing  $m_1$  particles of one color and  $f-2m_1$  of another color between  $f-m_1$  empty boxes. Multiplying the combinatorial factor by the probability factor due to the formation of  $m_1$  shortest loops and by the bond Boltzmann factor one arrives at the following expression

for the intrachain bond partition function

$$Z_{\text{bond}}^{\text{intra}}(m_1) = \frac{(f - m_1)!}{m_1!(f - 2m_1)!} P(n_p)^{m_1} \exp\left(\frac{m_1 \epsilon_a}{k_B T}\right) \quad (4)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. The combined contribution to the system partition function due to formation of  $m_1$  intrachain bonds on every  $n_p$  chains is equal to the product of the single chain contributions  $Z_{\text{bond}}^{\text{intra}}(m_1)^{n_p}$ .

After all  $n_p m_1$  intrachain bonds are formed  $n_p(f - 2m_1)$  associating groups remain in the system. There are  $n_p(f - 2m_1)$  different ways to select first associating group, this group is surrounded by  $z - 2$  lattice sites, assuming that associating groups are not located at the ends of the chain, each of which can be occupied by an associating group with probability  $(n_p(f - 2m_1) - 1)/n$ . Thus, the contribution to  $Z_{\text{bond}}^{\text{inter}}(n_p m_2)$  due to the formation of a single bond is equal to  $(z - 2)n_p(f - 2m_1)(n_p(f - 2m_1) - 1)/n \exp(\epsilon_a/k_B T)$ . To form a second bond, there are  $n_p(f - 2m_1) - 2$  different ways to select an associating group out of  $n_p(f - 2m_1) - 2$  remaining associating sites. The probability that at least one out of  $z - 2$  neighboring lattice sites is filled by another associating group is  $(n_p(f - 2m_1) - 3)/n$  because at this stage three associating groups have already been selected. Combining all factors one obtains that the contribution to  $Z_{\text{bond}}^{\text{inter}}(n_p m_2)$  due to the second bond is  $(z - 2)(n_p(f - 2m_1) - 2)(n_p(f - 2m_1) - 3)/n \exp(\epsilon_a/k_B T)$ . Repeating this process until  $n_p m_2$  bonds are formed, one has

$$Z_{\text{bond}}^{\text{inter}}(n_p m_2) = \frac{(z - 2)^{n_p m_2}}{n^{n_p m_2}} \times \frac{(n_p(f - 2m_1))!}{(n_p(f - 2m_1) - 2m_2)! 2^{n_p m_2} (n_p m_2)!} \exp\left(\frac{n_p m_2 \epsilon_a}{k_B T}\right) \quad (5)$$

The factor  $(n_p m_2)!$  in the denominator of eq 5 accounts for the fact that  $n_p m_2$  interchain bonds are indistinguishable and factor  $2^{n_p m_2}$  eliminates the direction of a bond. The contribution to the system partition function due to reversible bonds formation  $Z_{\text{bond}}$  is equal to the product of intra- and interchain partition functions  $Z_{\text{bond}}^{\text{intra}}(m_1)^{n_p}$  and  $Z_{\text{bond}}^{\text{inter}}(n_p m_2)$ , respectively.

Finally, the last term  $Z_{\text{int}}$  in the rhs of eq 1 describes interactions between different sites. Each polymer molecule is surrounded by

$$\pi_p = 2(z - 1) + (N - 2 - p f(z - 2) + p f(z - 3)) \approx N(z - 2) + p f \quad (6)$$

lattice sites, where  $p$  is the fraction of bonded (coupled) associating groups equal to  $(2m_1 + 2m_2)/f$  that is also known as the total degree of conversion. Each of those  $\pi_p$  lattice sites is occupied with probability  $\phi = n_p N/n$  by a monomer or with probability  $1 - \phi$  by a solvent molecule. Let us define the interaction energy between two neighboring sites occupied by polymers as  $-\epsilon_{pp}$  and that between polymer-solvent sites as  $-\epsilon_{ps}$ . The contribution to the partition function  $Z_{\text{int}}$  due to all possible arrangements of polymer and solvent molecules over  $\pi_p$  lattice sites surrounding a polymer chain is

$$Z_{\text{int}}^p = \left( \phi \exp\left(\frac{\epsilon_{pp}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right) \right)^{\pi_p} \quad (7)$$

The factor  $1/2$  is included to avoid double counting the interactions between lattice sites. Each lattice site occupied by the solvent molecule can with probability  $\phi$  interact with polymer or with probability  $1 - \phi$  with a solvent molecule. The number of lattice sites surrounding the solvent molecule is equal to the coordination number of a lattice  $z$ . The contribution to the partition function  $Z_{\text{int}}$  due to all possible arrangements of polymer and solvent molecules over  $z$  lattice sites surrounding a solvent molecule is

$$Z_{\text{int}}^s = \left( \phi \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ss}}{2k_B T}\right) \right)^z \quad (8)$$

where  $-\epsilon_{ss}$  is the interaction energy between two solvent molecules. The total interaction partition function  $Z_{\text{int}}$  is equal to the product of contributions from all individual molecules

$$Z_{\text{int}} = (Z_{\text{int}}^p)^{n_p} (Z_{\text{int}}^s)^{n_s} = \left( \phi \exp\left(\frac{\epsilon_{pp}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right) \right)^{\pi_p n_p} \left( \phi \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ss}}{2k_B T}\right) \right)^{z n_s} \quad (9)$$

**2.2. Free Energy of Solutions of Associative Polymers.** The two terms in the system partition function  $Z_{\text{mix}}$  and  $Z_{\text{int}}$  are similar to those in the solutions of ordinary polymers. Taking this fact into account, the free energy of the system of associative polymers can be separated into two different parts.<sup>6</sup> Free energy of the reference polymer system without associating bonds

$$\frac{F_{\text{pol}}}{nk_B T} = -\phi \ln\left(\frac{z - 1}{e}\right) + \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) - (z - 2)\phi \ln\left(\phi \exp\left(\frac{\epsilon_{pp}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right)\right) - z(1 - \phi) \ln\left(\phi \exp\left(\frac{\epsilon_{ps}}{2k_B T}\right) + (1 - \phi) \exp\left(\frac{\epsilon_{ss}}{2k_B T}\right)\right) \quad (10)$$

and contribution to the free energy of the system due to formation of reversible bonds

$$\frac{F_{\text{bond}}}{nk_B T} = \frac{\phi}{n_f} \left( (1 - p) \ln(1 - p) + \frac{p_1}{2} \ln\left(\frac{ep_1}{2}\right) - \frac{p_1}{2} \mu_{\text{bond}}^{\text{intra}} - \left(1 - \frac{p_1}{2}\right) \ln\left(\frac{1 - p_1/2}{e}\right) + \frac{p_2}{2} \ln\left(\frac{ep_2}{2}\right) - \frac{p_2}{2} \mu_{\text{bond}}^{\text{inter}} - 1 \right) \quad (11)$$

where I introduced a normalized chemical potential of intrachain associated bond

$$\exp(\mu_{\text{bond}}^{\text{intra}}) = \frac{(z - 2)}{c(z) n_f^{3/2}} \times \frac{\exp(\epsilon_a/k_B T)}{(\phi \exp(\epsilon_{pp}/2k_B T) + (1 - \phi) \exp(\epsilon_{ps}/2k_B T))^2} \quad (12)$$

an interchain one



$$\exp(\mu_{\text{bond}}^{\text{inter}}) = \frac{(z-2)\phi}{2n_f} \times \frac{\exp(\epsilon_a/k_B T)}{(\phi \exp(\epsilon_{pp}/2k_B T) + (1-\phi) \exp(\epsilon_{ps}/2k_B T))^2} \quad (13)$$

and degree of conversion of intra- and interchain bonds  $p_1$  and  $p_2$  ( $p = p_1 + p_2$ ). The equilibrium degree of conversion of intra- and interchain bonds is obtained by minimizing eq 11 at a given polymer volume fraction with respect to both degrees of conversion  $p_i$ . This leads to the following equations for the intrachain degree of conversion  $p_1$

$$\frac{p_1(1-p_1/2)}{(1-p)^2} = \frac{2(z-2)}{c(z)n_f^{3/2}} \times \frac{\exp(\epsilon_a/k_B T)}{(\phi \exp(\epsilon_{pp}/2k_B T) + (1-\phi) \exp(\epsilon_{ps}/2k_B T))^2} \quad (14)$$

and interchain one  $p_2$

$$\frac{p_2}{(1-p)^2} = \frac{(z-2)\phi}{n_f} \times \frac{\exp(\epsilon_a/k_B T)}{(\phi \exp(\epsilon_{pp}/2k_B T) + (1-\phi) \exp(\epsilon_{ps}/2k_B T))^2} \quad (15)$$

Equations 14 and 15 represent the mass-action law for pairwise associations. Dividing eq 14 by eq 15, one finds the relation between the degree of conversion of intra- and interchain bonds.

$$\frac{p_1(1-p_1/2)}{p_2} = \frac{2}{c(z)n_f^{1/2}\phi} \quad (16)$$

The interchain associations dominate over the intrachain ones when the polymer volume fraction  $\phi$  is higher than  $n_f^{-1/2}$ . At such high polymer concentrations, there are more associating groups belonging to other chains than to the same one within a volume  $v n_f^{3/2}$  available to an associating group. If the opposite inequality holds ( $\phi < n_f^{-1/2}$ ), the two neighboring associating groups along the polymer backbone will find each other with higher probability than associating groups belonging to the other chains.

**2.3. Gel Point.** The lattice theory of associative polymers presented in the previous sections (see also refs 6, 27, and 31) does not separate chains into ones belonging to finite clusters of chains (sol) and to an infinite cluster (gel). This is the major difference between this approach and the classical gelation theory<sup>28</sup> in which one considers separately associations between chains within sol and those within gel. By eliminating the separation into sol and gel, one simplifies the problem by imposing the equilibrium between all associated and open (available) associating groups independent of their origin. With this simplification comes a price: it is impossible in the framework of this approach to establish the location of the sol–gel point. The free energy of the system of associative polymers given by eqs 10 and 11 is continuous through the classical sol–gel point.<sup>6</sup> Thus, gelation is related to the connectivity properties of the system, manifested by appearance of the infinite cluster (gel) of associating chains above the gel point, but does not show up in the

thermodynamic properties of the system. (Another point of view on this subject was presented in ref 29, where it was argued that the gelation is the first-order phase transition. The detailed discussion of the results of the reference<sup>29</sup> is beyond the scope of this paper.)

To find the location of the sol–gel point I will use the Flory–Stockmayer gelation theory.<sup>28,32</sup> In this mean-field theory, the gelation threshold is associated with the interchain degree of conversion. In the model of associative polymers described above there are two competing process—formation of the intrachain and interchain bonds. The formation of the intrachain bonds reduces the number of associative groups available for interchain associations. After  $p_1 f$  associating groups are consumed by intrachain associations, there are  $(1-p_1)f$  associating groups left on each chain. This is a new (effective) functionality of a chain. The gelation threshold for a system of associative polymers with functionality  $(1-p_1)f$  is given by the following equation

$$p_2 = ((1-p_1)f - 1)^{-1} \quad (17)$$

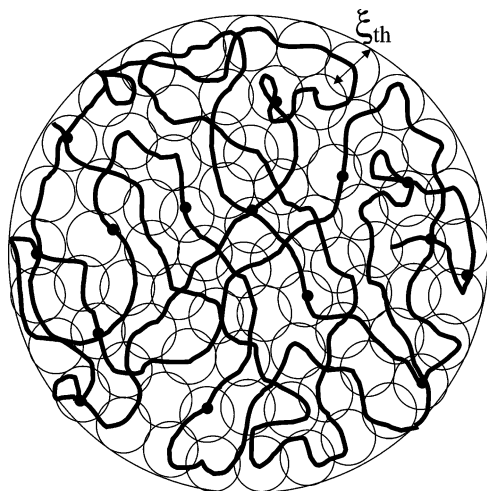
In the limit when there are no intrachain bonds ( $p_1 = 0$ ) eq 17 reduces to the classical expression for the gelation line.<sup>28</sup> However, the correction to the gelation point due to formation of the intrachain bonds is only important in dilute solutions ( $\phi < (fN)^{-1/2}$ ). This can be shown by solving eq 16 for the intrachain degree of conversion  $p_1$  and by substituting it back into eq 17. Thus, for estimation of the sol–gel point one can substitute  $p_1 = 0$  in eq 17. Equation 17 together with eqs 14 and 15 for the temperature dependence of the degree of conversion  $p_2$  on polymer volume fraction and temperature defines the gelation line in the polymer volume fraction–temperature ( $\phi$ ,  $T$ ) plane.

### 3. Lattice Model at Low Polymer Concentrations and in Dilute Solutions

**3.1. Semidilute and Concentrated Solutions.** The general expression for the free energy of the solutions of associative polymers (see eqs 10 and 11) can be simplified in the case of weak interactions ( $\epsilon_{ij}/k_B T \ll 1$ ) and at low polymer volume fractions  $\phi$ . In this case, the expression for the free energy of the system includes the virial expansion of the Flory–Huggins part of the free energy describing the mixing and interactions in the polymer–solvent system and the part describing associations between active groups on polymer chains with effective associating energy  $\tilde{\epsilon}_a = \epsilon_a - \epsilon_{ps}$ . In this approximation, the free energy of the system can be rewritten in the following form:<sup>6</sup>

$$\frac{F}{nk_B T} \approx \frac{\phi}{N} \ln \frac{\phi}{eN} + \frac{\tau}{2} \phi^2 + \frac{\phi^3}{6} + \frac{\phi}{n_f} \left( \frac{p}{2} + \ln(1-p) \right) \quad (18)$$

In writing eq 18, I have used the fact that  $p_1/2$  is smaller than unity, have omitted the terms linear in polymer volume fraction  $\phi$  and introduced the effective temperature  $\tau = 1 - 2\chi$  ( $\chi = z((\epsilon_{pp} + \epsilon_{ss})/2 - \epsilon_{ps})$  is the Flory–Huggins interaction parameter). The intra- and interchain degrees of conversion  $p_1$  and  $p_2$  satisfy the



**Figure 1.** Structure of collapsed polymer chain (globule).

following simplified equations<sup>6</sup>

$$\frac{p_1}{(1-p)^2} = \frac{4v_a(T)}{c(z)n_f^{3/2}} \quad (19)$$

$$\frac{p_2}{(1-p)^2} = \frac{2\phi v_a(T)}{n_f} \quad (20)$$

where the effective second virial coefficient of an associating group  $2v_a(T) = (z-2) \exp(\tilde{\epsilon}_a/k_B T)$  is introduced. In eq 19, I have neglected factor  $(1-p_1/2)$  which does not change qualitative description of the system presented in the next sections.

**3.2. Collapse of Polymer Chain and Dilute Solutions.** Unfortunately, the approach presented above is only correct in the case of overlapping chains,  $\phi > 1/\sqrt{N}$ , and in the range of effective temperatures  $\tau < 1/\sqrt{N}$ , where excluded volume interactions do not lead to chain swelling.

To analyze associations in dilute solutions let us consider first associations in a collapsed polymer chain (globule) with polymer volume fraction  $\phi_g$ . A chain occupies volume  $V_{ch}$  with the number of lattice sites  $n_{ch} = V_{ch}/v$ . The local structure of polymer globule shown in Figure 1 resembles that of semidilute polymer solution of polymer strands of size  $R_g \propto V_{ch}^{1/3}$  and degree of polymerization of each strand  $g_g \propto V_{ch}^{2/3}$ . In this model of a polymer globule the associations can still be separated into intrastrand associations—association between neighboring associating groups along the polymer backbone, analogue of the intrachain associations in the semidilute polymer solution—and interstrand associations—associations between groups on different strands. In this case, the parameter  $p_1$  describes the degree of conversion of intrastrand groups while  $p_2$  describes interstrand ones. The equilibrium degrees of conversions  $p_i$  are still given by eqs 19 and 20. The bulk free energy of the polymer globule with associations is

$$\frac{F_{bulk}(\phi_g)}{n_{ch}k_B T} \approx \frac{\tau}{2}\phi_g^2 + \frac{\phi_g^3}{6} + \frac{\phi_g}{n_f} \left( \frac{p}{2} + \ln(1-p) \right) \quad (21)$$

The collapsed polymer chain coexists with surrounding solution at equilibrium the osmotic pressure  $\pi^*(\phi_g) =$

$-v^{-1}\partial F_{bulk}/\partial n_{ch}$  of the polymer is equal to zero

$$\frac{\pi^*(\phi_g)v}{k_B T} = \frac{1}{2}\tau\phi_g^2 + \frac{1}{3}\phi_g^3 - \frac{\phi_g p_2}{2n_f} = 0 \quad (22)$$

This condition determines the equilibrium polymer volume fraction  $\phi_g$  within a globule and describes a coil–globule phase transition either due to the poor solvent conditions,  $\tau < 0$ , or due to formation of reversible bonds between associating groups. As one can see only non-local (interstrand) associations control the globule collapse by imposing additional constraints restricting chain conformations. The equilibrium density within a globule may be determined either by balancing the first and second terms in the rhs of eq 22, which leads to the usual linear dependence of the polymer volume fraction  $\phi_g$  on the effective temperature  $\tau$ , or by equating the second and the last terms in the rhs of eq 22. The analysis of eq 22 can be simplified by taking into account the relation between intrastrand and interstrand degrees of conversion eq 16. In this representation the last term in eq 22 has quadratic dependence on the polymer volume fraction  $\phi_g$

$$\left( \tau - \frac{c(z)p_1}{2\sqrt{n_f}} \right) \frac{\phi_g^2}{2} + \frac{\phi_g^3}{3} = 0 \quad (23)$$

because the intrastrand degree of conversion  $p_1$  depends only on the temperature in these two pure limits.

$$p_1 \approx \begin{cases} \frac{4v_a(T)}{c(z)n_f^{3/2}}, & \text{for } v_a(T) < c(z)n_f^{3/2}/4 \\ 1, & \text{for } v_a(T) > c(z)n_f^{3/2}/4 \end{cases} \quad (24)$$

The equilibrium polymer volume fraction inside the globule is equal to

$$\phi_g = \frac{3}{2}\tau_{eff} \quad (25)$$

where  $\tau_{eff}$  is the effective temperature defined as follows

$$\tau_{eff} = \frac{c(z)p_1}{2\sqrt{n_f}} - \tau \quad (26)$$

The globule can be viewed as a droplet of semidilute polymer solution of Gaussian strands with size  $R_g \propto b\tau_{eff}^{-1/3}N^{1/3}$  ( $b = v^{1/3}$  is the bond length) and the number of monomers in each strand  $g_g \approx R^2/b^2 \approx (N/\tau_{eff})^{2/3}$ . The correlation length  $\xi_{th}$  of this semidilute solution is inversely proportional to the effective temperature  $\tau_{eff}$ .

The coil–globule phase transition occurs when the polymer volume fraction  $\phi_g$  inside a globule is of the order of that within a Gaussian coil  $1/\sqrt{N}$ . The transition temperature for chain collapse is given by the following equation

$$\tau_{tr} \approx \frac{c(z)p_1}{2\sqrt{n_f}} - \frac{2}{3\sqrt{N}} \quad (27)$$

This equation shows that associations may lead to collapse of a polymer chain at temperatures well above the  $\Theta$  temperature ( $\Theta = T/2\chi$ ) for a polymer backbone. However, eq 27 has only limited applicability in the

range of positive effective temperatures,  $\tau_{tr} > 0$ . The transition temperature should be smaller than  $1/\sqrt{N}$  or  $\varphi_g > |\tau|$  where excluded volume interactions do not change the chain statistics. This requires the intrachain (intrastrand) degree of conversion  $p_1$  to be smaller than  $1/c(z)\sqrt{f}$  which is true for  $v_a(\Theta) < n_f^{3/2}f^{-1/2}$ . If the opposite inequality holds,  $v_a(\Theta) > n_f^{3/2}f^{-1/2}$ , the transition temperature  $\tau_{tr}$  moves to the good solvent regime and the expression for the free energy should be corrected by taking into account chain swelling. The collapse transition was also studied in ref 33. The results presented above can be reduced to those obtained in ref 33 in the limit  $p_1 = 0$ .

There is an additional contribution to the globular free energy associated with the variations of the polymer density through the polymer–solvent interface. These changes in polymer density occur at the length scale on the order of the correlation length  $\xi_{th}$  where the polymer volume fraction gradually varies from  $\varphi_g$  to zero. The contribution to the globule free energy due to the interfacial region of thickness  $\xi_{th}$  can be estimated as the thermal energy  $k_B T$  per each correlation blob of size  $\xi_{th}$  at the globule surface (see for details ref 30)

$$\frac{F_{surf}(\phi_g)}{k_B T} \approx C \frac{R^2}{\xi_{th}^2} \approx CN^{2/3} \tau_{eff}^{4/3} \quad (28)$$

where  $C$  is a numerical constant of the order of unity. The total free energy of the collapsed polymer chain with associating groups is

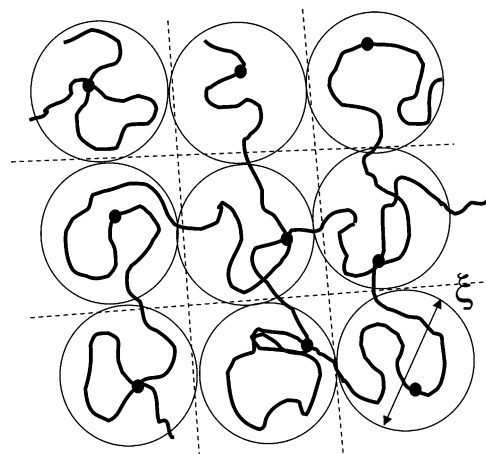
$$\frac{F_{ch}(\phi_g)}{k_B T} \approx CN^{2/3} \tau_{eff}^{4/3} + N \left( \frac{\tau}{2} \phi_g + \frac{\phi_g^2}{6} + \frac{1}{n_f} \left( \frac{p}{2} + \ln(1-p) \right) \right) \quad (29)$$

Combining together contributions from all chains and adding to them the ideal part of the chain's free energy, one obtains the total free energy of the dilute solution of associative polymers

$$\frac{F_{dilute}}{nk_B T} \approx \frac{\phi}{N} \ln \frac{\phi}{eN} + \frac{\phi}{N} \frac{F_{ch}(\phi_g)}{k_B T} \quad (30)$$

#### 4. Associative Polymers in a Good Solvent

**4.1. Crossover to a Good Solvent Regime.** As the solvent quality improves,  $\tau > 0$ , the contribution of the two-body monomer–monomer interactions,  $k_B T N \tau \phi \approx k_B T \tau \sqrt{N}$ , within the polymer coil increases. These interactions become of the order of the thermal energy  $k_B T$  at the value of the Fixman parameter,  $\tau \sqrt{N}$ , to be of the order of unity. In the range of the effective temperatures  $\tau > 1/\sqrt{N}$ , the two body monomer–monomer interactions lead to the chain swelling. In the semidilute solutions,  $\phi > 1/\sqrt{N}$ ; because of the screening of intrachain monomer–monomer interactions by surrounding polymers, the crossover into the good solvent regime takes place at higher temperatures. To estimate this temperature, I will use a blob picture of a semidilute solution.<sup>30,34</sup> In this picture, a semidilute solution is viewed as a quasi-network with a characteristic mesh size  $\xi$  – correlation blob (see Figure 2). At the length scales larger than the correlation blob  $\xi$  the interchain interactions dominate chain statistics



**Figure 2.** Schematic representation of instantaneous structure of semidilute solution of associative polymers.

while at distances smaller than  $\xi$  intrachain ones control chain behavior. Correlation blobs are space filling thus the ratio of the number of monomers  $g$  in correlation blob to the blob volume  $\xi^3$  is of the order of polymer volume fraction  $\varphi$ . In a  $\Theta$  solvent the number of monomers  $g$  in a correlation blob is proportional to  $\xi^2$ . Using this relation one can find that the number of monomers in correlation blob scales with polymer volume fraction as  $g \approx \phi^{-2}$ . The strand of the chain with  $g$  monomers starts to swell due to two-body monomer–monomer interactions when the Fixman parameter for the section of a chain with  $g$  monomers is of the order of unity,  $\tau \sqrt{g} \approx 1$ . Using the relation between number of monomers  $g$  in a correlation blob and polymer volume fraction  $\varphi$ , one can rewrite the crossover condition as  $\tau \approx \phi$ . Above this line, the two-body monomer–monomer interactions change statistics of the chain at length scales smaller than the correlation length  $\xi$ . At length scales larger than the correlation blob size  $\xi$ , the interchain interactions dominate over intrachain ones, screening them and leading to Gaussian chain statistics at these length scales. However, within a correlation blob there still exist subsections of a chain which conformations are not perturbed by monomer–monomer interactions. The number of monomers  $g_{th}$  in such subsections is given by the condition  $\tau \sqrt{g_{th}} \approx 1$ . Since the statistic of the section of a chain with  $g_{th}$  is Gaussian its size  $\xi_{th}$  is proportional to  $b\sqrt{g_{th}}$ . To summarize, in semidilute solution at good solvent conditions the statistics of a chain is Gaussian for chain subsections with  $g_s$  monomers smaller than  $\tau^{-2}$  and longer than  $g$ . While for  $\tau^{-2} < g_s < g$  it obeys a self-avoiding walk with the excluded volume parameter proportional to  $\tau$ . This leads to the following relation between the number of monomers in the correlation blob  $g$  and the blob size  $\xi$

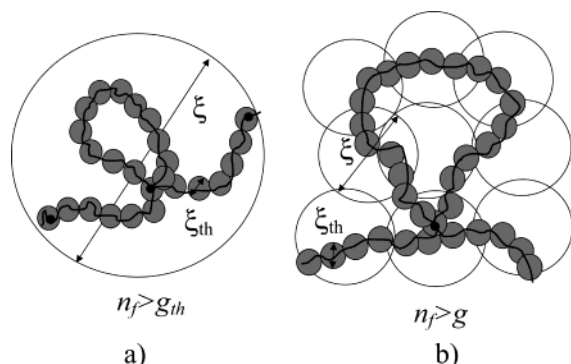
$$\xi \approx \xi_{th} \left( \frac{g}{g_{th}} \right)^\nu \approx b \tau^{1/5} g^{3/5}, \quad \text{for } g_{th} < g \quad (31)$$

where  $\nu$  is Flory's good solvent exponent,  $\nu = 3/5$ . In a good solvent regime the number of monomers in a correlation blob in a good solvent regime changes with concentration as

$$g \approx \tau^{-3/4} \varphi^{-5/4} \approx g_{th} (\tau/\varphi)^{5/4} \quad (32)$$

The energy of binary monomer–monomer interactions in a good solvent can be estimated as  $\tau k_B T$  per correla-





**Figure 3.** Schematic representation of the local chain structure in a good solvent regime used in calculation of probability of contact.

tion blob  $\xi$ . This leads to the following expression for the polymeric contribution to the free energy of the system:<sup>30,34</sup>

$$\frac{F_{\text{pol}}}{nk_B T} \approx \frac{\phi}{N} \ln \frac{\phi}{eN} + C_2 \tau^{3/4} \phi^{9/4}, \quad \text{for } \tau > \phi, \tau > N^{-1/2} \quad (33)$$

Here  $C_2$  is the numerical constant of the order of unity. The value of this constant can be defined in such a way that the interaction part of the system free energy eq 33 coincides with eq 18 at  $\tau \approx \phi$ , which leads to the value of the numerical constant  $C_2 = 2/3$ .

**4.2. Probability of Contact in a Good Solvent.** In a good solvent, strong two-body monomer–monomer interactions suppress the probability of pairwise associations in comparison with that in a  $\Theta$  solvent. In this case, the probability to find two monomers separated by  $n$  monomers along the polymer backbone within distance  $\delta_s$  from each other is proportional to<sup>35</sup>

$$P_{\text{good}} \approx \text{const} \left( \frac{\delta_s}{r(n)} \right)^{3+\theta_2} \quad (34)$$

where  $r(n)$  is the root-mean-square end-to-end distance between these two monomers in solution and  $\theta_2$  is the des Cloizeaux exponent equal to 0.78 in three dimensions. Below I will use this expression to evaluate probabilities of intra- and interchain associations in different regimes.

The monomer–monomer interactions will not lead to swelling of a polymer strand with  $n_f$  monomers as long as  $\tau \sqrt{n_f} < 1$ , or until there are many associating groups per thermal blob,  $n_f < g_{\text{th}}$ . In this temperature–concentration interval, the probability of the intrachain associations is still given by eq 3.

A section of a chain between two neighboring associative groups along the polymer backbone begins to swell when the number of monomers in the thermal blob  $g_{\text{th}}$  becomes smaller than  $n_f$ . This chain section can be viewed as a chain of effective monomers of size  $\xi_{\text{th}}$ . The root-mean-square end-to-end distance of this section of  $n_f/g_{\text{th}}$  effective monomers is equal to

$$r(n_f) \approx \xi_{\text{th}} (n_f/g_{\text{th}})^{\nu} \approx b \tau^{1/5} n_f^{3/5}, \quad \text{for } g_{\text{th}} < n_f < g \quad (35)$$

To estimate the probability of pairing between two associating groups it is useful to separate the association process into two steps (see Figure 3a). First two thermal blobs containing selected associating groups come in

contact. The probability that two thermal blobs at the ends of this chain section overlap is given by eq 34 with  $\delta_s \approx \xi_{\text{th}}$  and  $r(n) \approx r(n_f)$ . During the second step two associating groups form a pair. The probability of pairing between selected associating group and another associating group is proportional to the concentration of associating groups inside thermal blob  $\xi_{\text{th}}$ . This probability is estimated as  $g_{\text{th}}^{-3/2}$ . The total probability of intrachain pairing is equal to

$$P(n_f) \approx \left( \frac{g_{\text{th}}}{n_f} \right)^{\nu(3+\theta_2)} g_{\text{th}}^{-3/2}, \quad \text{for } g_{\text{th}} < n_f < g \quad (36)$$

The new regime starts when the number of monomers in correlation blobs becomes smaller than the number of monomers between associating groups  $n_f$  (see Figure 3b). In this regime, two correlation blobs have to be brought together first. Since the statistics of a chain at length scales larger than the correlation blob size  $\xi$  is Gaussian the probability of this process is proportional to  $(n_f/g)^{3/2}$ . Then two thermal blobs have to overlap. Before associations two thermal blobs containing associating groups can explore the whole correlation volume  $\xi^3$  independently. After association, the pair explores this volume together. Thus, the conformational energy change due to localization is similar to that during a single loop formation which probability is described by eq 34. Using eq 34 the probability of bringing two thermal blobs together can be estimated as  $(g_{\text{th}}/g)^{\nu(3+\theta_2)}$ . This probability should be multiplied by the probability of contact between two monomers inside the thermal blob,  $g_{\text{th}}^{-3/2}$ . Collecting all factors together, one obtains

$$P(n_f) \approx \left( \frac{g}{n_f} \right)^{3/2} \left( \frac{g_{\text{th}}}{g} \right)^{\nu(3+\theta_2)} g_{\text{th}}^{-3/2}, \quad \text{for } g_{\text{th}} < g < n_f \quad (37)$$

The combinatorial contribution of the intrachain associations into the system partition function is still given by eq 4 with probabilities of pairwise associations described by eqs 36 and 37.

The probability of interchain associations in a good solvent can be evaluated by viewing densely packed correlation blobs as the effective lattice sites (see Figure 2). If as before  $z$  is the lattice coordination number (average number of nearest-neighbor blobs), the number of blobs surrounding the selected one that contains chain sections belonging to other chains is equal to  $z - 2$ . Let us choose an associating group and evaluate the probability for this group to form a pair with any associating group in surrounding  $z - 2$  blobs. In the case  $n_f < g_{\text{th}}$ , there are many associating groups per each thermal blob. For two associating groups to form an interchain bond, it is necessary for two thermal blobs containing those associative groups to overlap first. The probability for any two thermal blobs belonging to two different correlation blobs to overlap is equal to  $(g_{\text{th}}/g)^{\nu(3+\theta_2)}$ . Since there are  $g/g_{\text{th}}$  thermal blobs inside each correlation blob and our selected associating group can form a pair with any associating group inside these blobs, the probability  $(g_{\text{th}}/g)^{\nu(3+\theta_2)}$  has to be multiplied by the factor  $(z - 2)g/g_{\text{th}}$ . Inside thermal blobs the probability of contact between the selected associating group and any out of  $g_{\text{th}}/n_f$  associating groups is proportional to the volume fraction of associating groups in a thermal blob,  $n_f^{-1} g_{\text{th}}^{-1/2}$ . Collecting all factors together, the probability of interchain association of a

selected associating group with any other associating group inside  $z - 2$  surrounding correlation blobs is

$$P_{\text{inter}} \approx (z - 2) \frac{g}{n_f} \left( \frac{g_{\text{th}}}{g} \right)^{\nu(3+\theta_2)} g_{\text{th}}^{-3/2} \quad (38)$$

It turns out that eq 38 has a wider scope of applicability than in the interval  $n_f < g_{\text{th}}$ . It is also true in the temperature–concentration intervals where  $g_{\text{th}} < n_f < g$  and  $g_{\text{th}} < g < n_f$ . For example, in the case  $g_{\text{th}} < n_f < g$ , the probability of interchain associations is equal to the number of associating groups in surrounding correlation blobs  $(z - 2)g/n_f$  times the probability for two thermal blobs belonging to two different correlation blobs to overlap  $(g_{\text{th}}/g)^{\nu(3+\theta_2)}$  and times the probability of contact between two associating groups inside two thermal blobs  $g_{\text{th}}^{-3/2}$ . This leads to the exactly the same expression as eq 38.

**4.3. Free Energy of Associative Polymers in Semidilute Solutions.** To complete the calculation of the interchain contribution  $Z_{\text{bond}}^{\text{inter}}(n_p m_2)$  to the bonding part of the system partition function it is necessary to evaluate the combinatorial part describing the number of different arrangements of the interchain reversible bonds. Let all  $n_p m_1$  intrachain bonds are formed and  $n_p(f - 2m_1)$  associating groups remain in the system. There are  $n_p(f - 2m_1)$  different ways to select the first associating group. The probability of this group to form a bond with any associating group in surrounding  $z - 2$  correlation blobs is equal to  $P_{\text{inter}}(n_p f(1 - p_1) - (1 - p_1)g/n_f - 1)/n_p f$ , where the factor  $(n_p f(1 - p_1) - (1 - p_1)g/n_f - 1)/n_p f$  accounts for associations only with available associating groups. The extra term  $(1 - p_1)g/n_f$  in the probability factor excludes from association the number of associating groups inside correlation blob containing selected associating group. However, this correction is small on the parameter  $g/(n_f n_p f)$  and can be safely omitted. By continuing the association process and at each step omitting terms containing parameter  $g/(n_f n_p f)$ , the interchain part  $Z_{\text{bond}}^{\text{inter}}(n_p m_2)$  of the bonding partition function is

$$Z_{\text{bond}}^{\text{inter}}(n_p m_2) = \frac{P_{\text{inter}}^{n_p m_2}}{(n_p f)^{n_p m_2}} \times \frac{(n_p(f - 2m_1))!}{(n_p(f - 2m_1 - 2m_2))! 2^{n_p m_2} (n_p m_2)!} \exp\left(\frac{n_p m_2 \tilde{\epsilon}_a}{k_B T}\right) \quad (39)$$

Combining intrachain, interchain and polymeric contributions to the system free energy, one obtains the following expression describing associative polymers in a good solvent

$$\frac{F}{nk_B T} \approx \frac{\phi}{N} \ln \frac{\phi}{eN} + C_2 \tau^{3/4} \phi^{9/4} + \frac{\phi}{n_f} \left( \frac{p}{2} + \ln(1 - p) \right), \quad \text{for } g_{\text{th}} < g < N \quad (40)$$

with intrachain degree of conversion  $p_1$  defined by the following equation

$$\frac{p_1}{(1 - p)^2} \approx 4 \frac{v_a(T)}{c(z)n_f^{3/2}} \begin{cases} 1, & \text{for } n_f < g_{\text{th}} < g \\ (g_{\text{th}}/n_f)^{\nu(3+\theta_2)-3/2}, & \text{for } g_{\text{th}} < n_f < g \\ (g_{\text{th}}/g)^{\nu(3+\theta_2)-3/2}, & \text{for } g_{\text{th}} < g < n_f \end{cases} \quad (41)$$

and the interchain one,  $p_2$ , given by

$$\frac{p_2}{(1 - p)^2} \approx 2 \frac{v_a(T)}{n_f g_{\text{th}}^{1/2}} \left( \frac{g_{\text{th}}}{g} \right)^{\nu(3+\theta_2)-1} \approx 2 v_a(T) \frac{\varphi}{n_f \tau} \left( \frac{\varphi}{\tau} \right)^\alpha \quad (42)$$

where  $\alpha = \nu\theta_2/(3\nu - 1) = 3\theta_2/4 \approx 0.6$ . The numerical constants in the two last equations were selected to match them with eqs 19 and 20 at the crossover between  $\Theta$  and good solvent regimes. Dividing eq 41 by eq 42, one can establish that intrachain associations dominate over interchain ones when there are many associating groups per correlation blob,  $n_f < g$ .

**4.4. Chain Structure in a Dilute Solution.** Consider a single chain in a good solvent for the polymer backbone with associating groups. The bulk contribution to the single chain free energy is

$$\frac{F_{\text{bulk}}(\phi)}{n_{\text{ch}} k_B T} \approx C_2 \tau^{3/4} \phi^{9/4} + \frac{\phi}{n_f} \left( \frac{p}{2} + \ln(1 - p) \right), \quad \text{for } g_{\text{th}} < g < N \quad (43)$$

The interstrand and intrastrand degrees of conversion  $p_1$  and  $p_2$  are given by eqs 41 and 42. The equilibrium polymer volume fraction within the polymer chain with associations is given by the condition for the monomeric osmotic pressure  $\pi^*(\phi) = 0$ , which in the case of good solvent is

$$\pi^*(\phi) \approx \frac{5}{4} C_2 \tau^{3/4} \phi^{9/4} - \frac{(\alpha + 1)\phi p_2}{2n_f} = 0, \quad \text{for } g_{\text{th}} < g < N \quad (44)$$

In the interval of parameters where the number of monomers in a correlation blob  $g$  is smaller than the number of monomers between associating groups  $n_f$ ,  $g < n_f$ , there is another negative contribution to the osmotic pressure due to intrastrand associations. This term is proportional to  $\delta \phi p_1/n_f$ , where  $\delta$  is the exponent of polymer volume fraction in the rhs of eq 41. However, for  $g < n_f$ , the interstrand associations dominate over intrastrand ones,  $p_2 > p_1$ , and this term can be neglected. Solving eq 44 for the interstrand degree of conversion  $p_2$ , one obtains

$$p_2 \approx \frac{n_f}{g} \approx \tau^{3/4} \phi^{5/4} n_f, \quad \text{for } g_{\text{th}} < g < N \quad (45)$$

In eq 45, I neglected all numerical coefficients. The interstrand degree of conversion  $p_2$  cannot exceed unity. This requirement is satisfied when  $\tau \leq n_f^{-4/3} \phi^{-5/3}$  or when there is at least one associating group per each correlation blob. Solving eq 45 together with eq 42, one finds

$$\frac{1}{(1 - p)^2} \approx \frac{v_a(\Theta)}{n_f^2 \tau} \left( \frac{\varphi}{\tau} \right)^{\alpha-1/4} \quad (46)$$

It is useful to rewrite eq 41 in the following form



$$\frac{p_1}{(1-p)^2} \approx \begin{cases} v_a(\Theta)/n_f^{3/2}, & \text{for } n_f < g_{th} < g \\ (\tau^*/\tau)^{\nu(6+2\theta_2)-3}, & \text{for } g_{th} < n_f < g \end{cases} \quad (47)$$

where the parameter  $\tau^*$  is

$$\tau^* \approx n_f^{-1/2} \left( \frac{v_a(\Theta)}{n_f^{3/2}} \right)^{1/(\nu(2\theta_2+6)-3)} \quad (48)$$

Consider first a case  $v_a(\Theta) < n_f^{3/2}$  and  $n_f < g_{th}$ . In this interval of parameters both intrastrand  $p_1$  and interstrand  $p_2$  degrees of conversion are smaller than unity. The combined solution of eqs 45–47 leads to the following expression for the density inside a globule

$$\varphi_g \approx \left( \frac{n_f^2}{v_a(\Theta)} \right)^{1/0.35} \tau^{1.35/0.35} \quad (49)$$

The polymer density inside globule  $\varphi_g$  should be smaller than  $\tau$  to satisfy the good solvent condition  $g_{th} < g$ . The solution given by eq 49 satisfies this condition only if the parameter  $\tau$  is smaller than  $v_a(\Theta)/n_f^2$ . However, this range of temperatures is inside a  $\Theta$  region for polymer backbone. Thus, there is no physically meaningful solution of the eqs 45–47 for  $v_a(\Theta) < n_f^{3/2}$  and  $n_f < g_{th}$ . Disappearance of the solution corresponding to a globule indicates that above the temperature

$$\tau_{tr} \approx \frac{v_a(\Theta)}{n_f^2}, \quad \text{for } n_f^{3/2} f^{-1/2} < v_a(\Theta) < n_f^{3/2} \quad (50)$$

one should search for a solution with  $\pi^*(\phi) > 0$ . In this case, eq 43 together with eqs 41 and 42 describe associations inside a swollen polymer chain. Analysis of eqs 41 and 42 shows that intrachain associations are controlled by smallest loops between neighboring along polymer backbone functional groups. Since in the interval of parameters  $v_a(\Theta) < n_f^{3/2}$ , the degree of conversion  $p_1$  is much smaller than unity a polymer chain has a conformation of a swollen chain with size  $R_{good} \propto \tau^{1/5} N^{3/5}$ . A conformation of associative polymer chain in a good solvent with only local loops was proposed by Rubinstein and Semenov.<sup>6</sup>

It follows from eqs 41–43 that the solution corresponding to a swollen chain with local loops is also exist in the interval  $\tau < \tau_{tr}$ . However, in this interval of temperatures there is also another solution corresponding to a globule with polymer density inside it given by eq 25. To select which one corresponds to a true minimum one has to compare chain free energies in both these states. Using eqs 21, 24, and 25 the bulk free energy of a globule is

$$\frac{F_g}{Nk_B T} \approx -\frac{\varphi_g^2}{6} - \frac{p_1^g}{2n_f} \quad (51)$$

where  $p_1^g$  is the intrastrand degree of conversion  $p_1$  inside a globule. The free energy of a swollen chain with functionalized groups is

$$\frac{F_{sw}}{Nk_B T} \approx -\frac{p_1^{sw}}{2n_f} \quad (52)$$

Because both degrees of conversions  $p_1^g$  and  $p_1^{sw}$  are given by the same expression, the globule has lower

free energy in the temperature interval  $\tau < \tau_{tr}$ . At  $\tau \approx \tau_{tr}$  chain abruptly swells from size  $R_g \propto N^{1/3}/\tau_{eff}^{1/3}$  to that in a good solvent  $R_{good} \propto \tau^{1/5} N^{3/5}$  by increasing in size  $(v_a(\Theta)^{1/2}/n_f^{3/2})^{8/15}$  times.

Consider now interval of parameters  $v_a(\Theta) > n_f^{3/2}$  and  $g_{th} < n_f < g$ . In this case, a solution of the eqs 45–47 exists only in the interval of temperatures below  $\tau^*$ . Here both degrees of conversions are of the same order of magnitude,  $p_1 \approx p_2 \propto 1$ . There is one associating group per each correlation blob,  $n_f \approx g$ . In this case, the polymer volume fraction inside a globule is

$$\phi_g \approx n_f^{-4/5} \tau^{-3/5}, \quad \text{for } v_a(\Theta) > n_f^{3/2}, \quad g_{th} < n_f < g \quad (53)$$

It is interesting to point out that the density inside a globule corresponds to the overlap concentration of the chain subsections with  $n_f$  monomers in a good solvent. Thus, the globule has a structure of a swollen microgel with one tetrafunctional cross-link per each correlation blob. The size of this microgel  $\tau^{1/5} N^{1/3} n_f^{4/15}$  is  $f^{4/15}$  times smaller than that of polymer chain without associating groups in a good solvent.

A transition between globular and swollen states takes place when

$$\tau_{tr} \approx \tau^*, \quad \text{for } g_{th} < g < N \quad (54)$$

At this temperature the rhs of eq 46 becomes of the order of unity which requires both degrees of conversions to be smaller than unity, which is inconsistent with eqs 45 and 47.

To establish that microgel structure is stable in the temperature interval  $\tau < \tau_{tr}$  one has to compare the chains free energies in collapsed and swollen states. For  $v_a(\Theta) > n_f^{3/2}$ , the main contributions to chains free energy are logarithmic. The free energy of a globule is

$$\frac{F_g}{Nk_B T} \approx \frac{\nu(6+2\theta_2)-3}{2n_f} \ln(\tau/\tau^*) + \frac{1}{2n_f} \ln(p_1^g), \quad \text{for } \tau \leq \tau^* \quad (55)$$

while for a swollen chain it is

$$\frac{F_{sw}}{Nk_B T} \approx \frac{\nu(6+2\theta_2)-3}{2n_f} \ln(\tau/\tau^*) + \frac{1}{2n_f} \ln(p_1^{sw}) \quad (56)$$

In both cases, the total degree of conversion  $p$  is on the order of unity. In the case of a swollen chain, it is entirely due to loop formation  $p = p_1^{sw}$ . While in the case of a globule the total degree of conversion  $p$  is equal to sum of intrastrand  $p_1^g$  and interstrand  $p_2$  one. Thus, the value  $p_1^g$  is always smaller than  $p_1^{sw}$ , and the globule has a lower free energy. Cates and Witten<sup>36</sup> have arrived at a similar conclusion about structure of a polymer chain with stickers in a good solvent. These authors argued that the compact (globule) state is more stable because of entropy gain from “stickers exchange” between each subchain and its neighbors. A transition between collapsed and swollen states takes place at  $\tau \approx \tau_{tr}$ , where chain size changes  $f^{4/15}$  times by reaching that of a swollen chain.

An abrupt transition between collapsed and swollen chain conformations is a direct consequence of value of the exponent  $\theta_2$  in the expression for the probability of contact (see eq 34). This exponent has no direct relation with the other indexes  $\nu$  and  $\gamma$  appearing in the scaling theory of polymer solutions in a good solvent. This fact

was pointed over 20 years ago in the original des Cloizeaux paper.<sup>35</sup> This indicates that the notion of contacts in polymer solutions is more complicated than widely accepted.

The scaling theory of polymer solution<sup>30</sup> implicitly assumes that there is in average one contact between monomers per correlation blob. This assumption allows a mean-field like estimation of the probability of contacts from the expression of the free energy. The second term in the rhs of eq 33 describing two-body monomer–monomer interactions can be represented as product of the number of monomers in a system  $n_p N$ , the probability of the binary contacts  $\omega$  and the contribution from each contact  $k_B T \tau$ . This leads to the following expression for probability of the binary contacts per monomer:

$$\omega \approx \tau^{-1/4} \phi^{5/4} \quad (57)$$

Since each monomer can have a contact with any out of  $g$  monomers in a correlation blob a probability of contact between two monomers is equal to  $\omega/g$ . This leads to the probability of contact to be proportional to  $g^{-2}$ . To match this result with the expression 34 the value of the exponent  $\theta_2$  should be equal to  $1/3$ . This value for the exponent is closer to one obtained by des Cloizeaux<sup>35</sup> for probability of contact between two end monomers. Let us substitute this value for the exponent and see what happens with a collapse transition. For the value  $\theta_2$  equal to  $1/3$ , the exponent  $\alpha = 1/4$  and the rhs of eq 46 does not depend on the polymer volume fraction. Solving eq 46 for the total degree of conversion  $p$ , one finds

$$p \approx 1 - \frac{n_f \sqrt{\tau}}{\sqrt{v_a(\Theta)}} \quad (58)$$

Combining eqs 58 and 36, the solution for the intra-strand degree of conversion is

$$p_1 \approx \begin{cases} n_f^{1/2} \tau, & \text{for } \tau < n_f^{-1/2} \\ 1, & \text{for } n_f^{-1/2} < \tau < n_f^{-4/3} \phi^{-5/3} \end{cases} \quad (59)$$

Now the solution for the polymer volume fraction inside a globule is

$$\phi_g \approx n_f^{-4/5} \tau^{-3/5} \left( 1 - p_1 - \frac{n_f \sqrt{\tau}}{\sqrt{v_a(\Theta)}} \right)^{4/5} \approx \phi^* f^{4/5} \left( 1 - p_1 - \frac{n_f \sqrt{\tau}}{\sqrt{v_a(\Theta)}} \right)^{4/5} \quad (60)$$

where  $\phi^*$  is the chains overlap volume fraction or polymer volume fraction inside swollen polymer chain in a good solvent

$$\phi^* \approx \tau^{-3/5} N^{-4/5} \quad (61)$$

A transition between globular and swollen states takes place when polymer volume fraction  $\phi_g$  inside a globule is on the order of  $\phi^*$ .

$$\tau_{tr} \approx (1 - p_1 - f^{-1})^2 \frac{v_a(\Theta)}{n_f^2} \approx \frac{v_a(\Theta)}{n_f^2}, \quad \text{for } \tau > \phi \quad (62)$$

Thus, as the temperature approaches the transition temperature, the polymer volume fraction inside a globule smoothly changes reaching that of a swollen chain at the transition temperature.

Unfortunately there are still no experimental data supporting existence of des Cloizeaux's index  $\theta_2$  in polymer solutions. A study of collapse transition in associative polymers may be very valuable for understanding the nature of pairwise contacts in polymer solutions.

The free energy of a single collapsed polymer chain in a good solvent for the polymer backbone with associating groups also includes the surface energy. This energy is estimated as the thermal energy  $k_B T$  per each correlation blob  $\xi$  at the globular surface. This leads to the following expression for the globule surface energy

$$\frac{F_{\text{surf}}(\phi_g)}{k_B T} \approx N^{2/3} \tau^{1/2} \phi_g^{5/6}, \quad \text{for } g_{\text{th}} < g < N \quad (63)$$

After collecting surface and bulk contributions, the single chain free energy is

$$\begin{aligned} \frac{F_{\text{ch}}(\phi_g)}{k_B T} &\approx N^{2/3} \tau^{1/2} \phi_g^{5/6} + \\ &N \left( C_2 \tau^{3/4} \phi_g^{5/4} + \frac{1}{n_f} \left( \frac{p}{2} + \ln(1 - p) \right) \right), \\ &\quad \text{for } g_{\text{th}} < g < N \end{aligned} \quad (64)$$

## 5. Phase Diagram of Solutions of Associative Polymers

Formation of the reversible bonds between associating groups may force solutions of associative polymers to phase separate into concentrated and dilute phases with polymer volume fractions  $\phi_{\text{dil}}$  and  $\phi_{\text{con}}$  respectively. At equilibrium the chains' chemical potentials and polymeric osmotic pressures should be equal in both phases.<sup>30</sup> Equating polymeric osmotic pressures, one finds

$$\frac{\phi_{\text{dil}}}{N} = \frac{\phi_{\text{con}}}{N} + \frac{\pi^*(\phi_{\text{con}})v}{k_B T} \quad (65)$$

where  $\pi^*(\phi_{\text{con}})$  is given by eqs 22 and 44. In the case of long polymer chains  $N \gg 1$ , eq 65 reduces to  $\pi^*(\phi_{\text{con}}) = 0$ . This leads to the polymer volume fraction of the concentrated phase  $\phi_{\text{con}}$  to be equal to  $\phi_g$ . To find the polymer volume fraction in a dilute phase one has to balance the chain chemical potentials. The chain's chemical potential in a dilute phase is

$$\frac{\mu_{\text{dil}}}{k_B T} = N \frac{\partial}{\partial \phi} \frac{F_{\text{dilute}}}{n k_B T} \approx \ln \frac{\phi_{\text{dil}}}{N} + \frac{F_{\text{ch}}(\phi_g)}{k_B T} \quad (66)$$

where the single chain free energy is given either by eq 29 for  $\tau < \phi_g$  or by eq 64 for  $\tau > \phi_g$ . In the concentrated phase, the chemical potential is given by the following expression

$$\frac{\mu_{\text{con}}}{k_B T} = N \frac{\partial}{\partial \phi} \frac{F}{n k_B T} \approx \ln \frac{\phi_{\text{con}}}{N} + \frac{F_{\text{bulk}}(\phi_{\text{con}})}{k_B T} \quad (67)$$

where for the bulk free energy  $F_{\text{bulk}}(\phi_{\text{con}})$  of a single chain one has to use eqs 21 and 43. In the derivation of eq 67, I used the fact that  $\pi^*(\phi_{\text{con}}) = 0$ . The two last terms in the rhs of the eqs 66 and 67 are different from

each other only by the surface energy term. At equilibrium the chain's chemical potentials given by eqs 66 and 67 are equal to each other in both phases. This leads to the following equation for the polymer volume fraction in a dilute phase

$$\phi_{\text{dil}} = \phi_g \exp(-F_{\text{surf}}(\phi_g)/k_B T) \quad (68)$$

Thus, the polymer volume fraction in a dilute phase is exponentially small in comparison with that in concentrated phase as long as the globule surface energy is much larger than the thermal energy  $k_B T$ . The polymer volume fractions are of the same order of magnitude when the surface energy is on the order of the thermal energy  $k_B T$ .

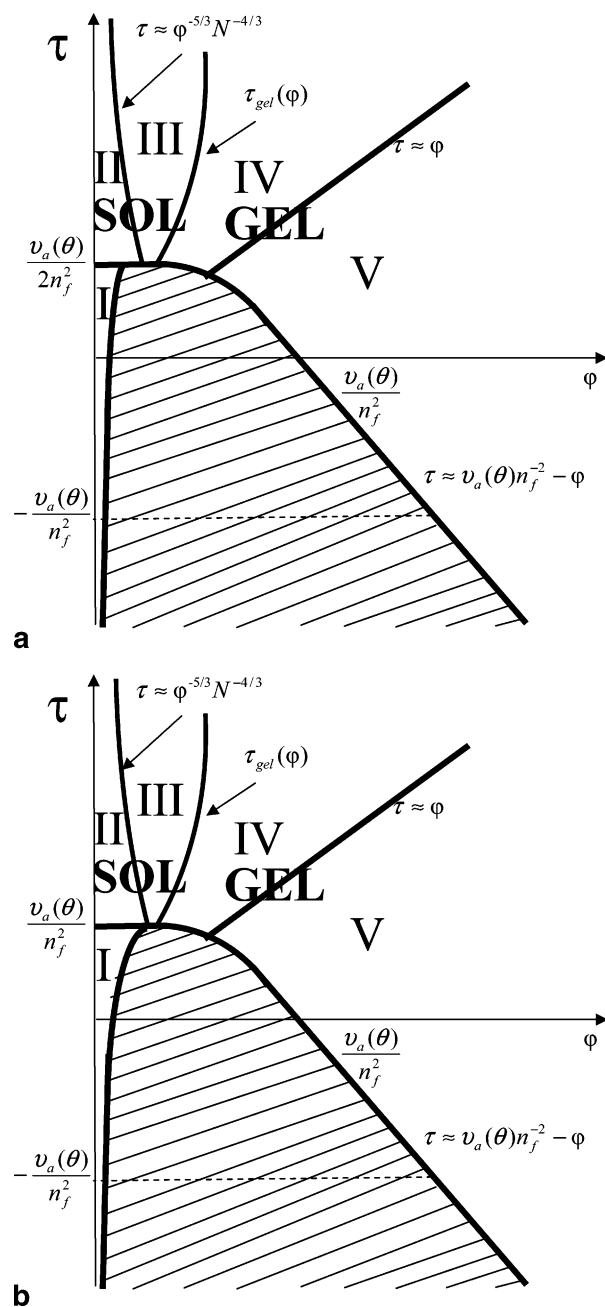
Figure 4a shows a typical diagram of states of the solutions of associating polymers at the value of the effective second virial coefficient of associating group  $n_f^{3/2} f^{-1/2} < v_a(\Theta) < n_f^{3/2}$  and for the value of the des Cloizeaux exponent  $\theta_2 = 0.78$ . (Analyses of the diagram of state for a solution of associative polymers is done on the scaling level neglecting all numerical prefactors.) The shaded area corresponds to the two-phase region that is located in the effective temperature interval below  $\tau_{\text{cr}} \approx v_a(\Theta)/n_f^2$ . Above this critical temperature the chain conformations in a dilute solution are similar to those without associating groups. Such chains begin to overlap when polymer volume fraction within a chain is of the order of the average polymer volume fraction. This takes place along the line  $\tau \approx \varphi^{-5/3} N^{-4/3}$ . This line separates dilute (regime II) and semidilute (regimes III, IV, and V) solutions. There is another line that approaches this line from the right near the critical temperature. This is the gelation line separating sol (regimes I, II, and III) and gel (regimes IV and V) regions. The equation of this line is

$$\tau_{\text{gel}}(\phi) \approx \left( \frac{f v_a(\Theta)}{n_f} \right)^{1/\alpha} \phi^{1+1/\alpha} \quad (69)$$

where  $\alpha = 0.6$  for the des Cloizeaux exponent  $\theta_2 = 0.78$  and  $\alpha = 0.25$  for the mean-field exponent  $\theta_2 = 1/3$ . This equation was obtained by substituting  $p_2 = (f - 1)^{-1}$  into eq 42.

In the two-phase region in the effective temperature range  $-(v_a(\Theta)/n_f^2) < \tau < v_a(\Theta)/2n_f^2$ , the polymer volume fraction of the concentrated phase  $\phi_g$  as well as that within individual globules in a dilute phase is of the order of  $v_a(\Theta)/n_f^2$ . However, the polymer concentration in a dilute phase is exponentially low by factor  $\exp(-C(v_a(\Theta)f^{1/2}/n_f^{3/2})^{4/3})$ . In this temperature range, the collapse of the polymer chain and phase separation are caused by formation of reversible bonds between associating groups (see section 3 equiv 25). At much lower effective temperatures  $\tau < -(v_a(\Theta)/n_f^2)$ , the two-body monomer–monomer attractive interactions play a dominant role in polymer collapse and phase behavior of the system is similar to the one observed for polymer chains in a poor solvent. Here  $\phi_g$  is proportional to  $|\tau|$ .

Figure 4b shows the diagram of state calculated for the mean-field exponent  $\theta_2 = 1/3$  and  $n_f^{3/2} f^{-1/2} < v_a(\Theta) < n_f^{3/2}$ . The different regimes in the diagram of state are similar to those shown in Figure 4a. The only difference between diagram of state shown in Figure 4a and this one is the shape of the coexistence curve near the critical point. Because of the smooth variation in the polymer volume fraction inside a globule as temperature ap-

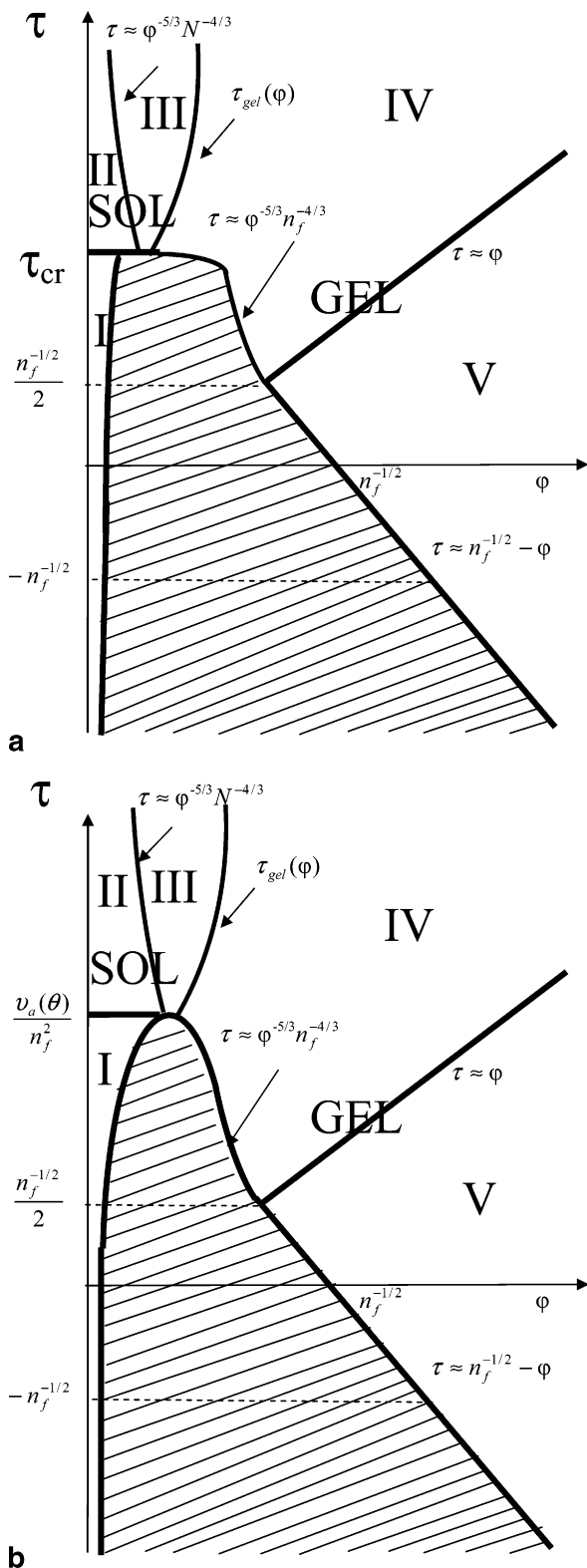


**Figure 4.** Diagram of states of a solution of associative polymers for  $n_f^{3/2} f^{-1/2} < v_a(\Theta) < n_f^{3/2}$  calculated for the value of the des Cloizeaux exponent  $\theta_2 = 0.78$  (a) and for  $\theta_2 = 1/3$  (b). Shaded area corresponds to two-phase region. Regimes I and II of the diagram of states correspond to dilute solutions of collapsed and swollen associative polymers, respectively. Regime III corresponds to the semidilute solution of associative polymers above the gelation threshold in a good solvent for polymer backbone. Regime IV corresponds to the semidilute solution of associative polymers below the gelation threshold in a good solvent for polymer backbone. Regime V corresponds to the semidilute solution of associative polymers below the gelation threshold in a  $\Theta$  solvent for polymer backbone.

proaches the transition point two branches of the coexistence curve merge at  $\varphi \approx \varphi^*$  and  $\tau \approx \tau_{\text{tr}} \approx v_a(\Theta)/n_f^2$ .

In Figure 5, I present the diagram of states of the solutions of associative polymers for  $n_f^{3/2} < v_a(\Theta)$ . The phase diagram shown in Figure 5a was calculated for the value of the des Cloizeaux exponent  $\theta_2 = 0.78$  and that in Figure 5b for the mean-field exponent  $\theta_2 = 1/3$ . In this phase diagram a significant portion of the two-





**Figure 5.** Diagram of states of a solution of associative polymers for  $n_f^{3/2} < v_a(\Theta)$  calculated for the value of the des Cloizeaux exponent  $\theta_2 = 0.78$  (a) and for  $\theta_2 = 1/3$  (b). Shaded area corresponds to two-phase region. Regimes I and II of the diagram of states correspond to dilute solutions of collapsed and swollen associative polymers, respectively. Regime III corresponds to a semidilute solution of associative polymers above the gelation threshold in a good solvent for polymer backbone. Regime IV corresponds to a semidilute solution of associative polymers below the gelation threshold in a good solvent for polymer backbone. Regime V corresponds to a semidilute solution of associative polymers below the gelation threshold in a  $\Theta$  solvent for polymer backbone.

phase region is within a good solvent regime  $n_f^{-1/2} < \tau$ . In this temperature range both intra- and interchain degrees of conversion are of the same order of magnitude and polymer volume fraction of the concentrated phase  $\varphi_g$  is equal to  $n_f^{-4/5} \tau^{-3/5}$  (see eq 42). At such high polymer volume fractions, there is on average one associating group per each correlation volume  $\xi^3$ . The two-phase region is located below the critical temperature  $\tau_{cr}$  given by eq 54. The good solvent region ends at  $\tau \approx n_f^{-1/2}$  and  $\tau \approx \varphi$ . For lower effective temperatures  $\tau < n_f^{-1/2}$ , the phase diagram is topologically similar to one shown in Figure 4.

It is interesting to point out that even in a very good solvent,  $\tau \approx 1$ , it is possible to achieve a phase separation. In this case, one can control polymer solubility by changing its chemical composition. The solution will become unstable if the number of monomers between associating groups becomes smaller than a critical value of the order of  $v_a(T)^{2/(v(2\theta_2+1)+3)}$ .

The phase behavior of the solutions of lightly sulfonated polystyrene in Decalin was studied by Chakrabarty et al.<sup>37</sup> They found that the upper critical solution temperature increases with the total acid group content on the polystyrene backbone. The increase of the sulfonation level corresponds to a decrease in the number of monomers  $n_f$  between associating groups. Thus, varying sulfonation level one effectively changes the value of the parameter  $v_a(\Theta)/n_f^{3/2}$ . With increasing sulfonation level, the experimental phase diagrams presented in ref 37 demonstrate topological transformations of the boundary of the two-phase region similar to ones shown in Figures 4b and 5b.

The phase diagram for solution of associative polymers has also been calculated by Rubinstein and Semenov.<sup>6</sup> They used a classical mean-field approach in calculation of the coexistence curve in the two-phase region by smearing out the polymer chains over the whole volume occupied by a dilute phase and equating chain chemical potential and osmotic pressure between dilute and concentrated phases. While these calculations provide a correct expression for the polymer density in a concentrated phase, they give an incorrect result for the polymer concentration in a dilute phase that is controlled by the surface energy of the globule. Further differences between results of ref 6 and ones presented here appear in a good solvent regime. Authors of ref 6 concluded that the strong monomer–monomer repulsive interactions could completely eliminate phase separation. The reason for the discrepancy between this prediction and my results lays in a qualitatively different consideration of the associations in a dilute phase. In my approach, a single polymer chain in a dilute phase was considered as a droplet of semidilute polymer solution which density and fraction of associated functional groups has to be found self-consistently by minimizing the chain free energy. This minimization leads to the structure of a collapsed polymer chain similar to that of a swollen microgel with one associating group per each correlation volume. The collapse of a single polymer chain opens a phase coexistence region in the phase diagram even in a good solvent condition for the polymer backbone. The intrachain associations were also included in the analysis presented in ref 6. However, only associations between two neighboring associating groups along the polymer backbone were taken into account. Such intrachain associations cannot lead to chain collapse and result in phase separation.

## 6. Conclusion

Using a simple model of a polymer with functional groups – stickers I have described phase behavior of the solutions of associative polymers. By separating associations into intra- and interchain ones, I have derived general expression for the free energy of the system. To describe associations within a single chain I have assumed that the local structure of a single chain resembles that of semidilute polymer solution. The derived expression for the single chain free energy was analyzed for self-consistency of the collapsed chain approximation. This model shows that associations between functional groups indeed can stabilize a globule state if the energy of pairwise associations is sufficiently large. The polymer density inside a globule is controlled by fine interplay between entropy of associations and excluded volume interactions. A globule can even be stable in a good solvent for the polymer backbone. In a good solvent the configuration of the collapsed chain can be viewed as a swollen “microgel” with  $n_f$  monomers between tetrafunctional cross-links. In addition to the bulk free energy, a collapsed polymer chain has a surface energy contribution due to well-defined polymer/solvent interface.

As the polymer concentration increases solutions of associative polymers phase separate into concentrated and dilute phases. The polymer concentration in a concentrated phase is the same as inside a polymeric globule. The partitioning of polymers between dilute and concentrated phases is governed by the surface energy of the polymer–solvent interphase. Thus, if this energy is much larger than the thermal energy  $k_B T$ , the polymer concentration in a dilute phase is exponentially low in comparison with that in the concentrated phase. The upper critical point of the two-phase region moves into high-temperature range as the number of monomers between associating groups decreases. Such high sensitivity of the upper critical point to the chemical composition allows control over polymer solubility properties by varying the number of associating groups per chain.

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