SOLVENT-INDUCED ASSOCIATION OF POLYMERS: CLUSTERING AND NETWORK FORMATION

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A thermodynamic treatment of a random, solvent-assisted association of polyfunctional macromolecules is developed. In the model proposed, a multiple association junction connecting m primary chains consists of m polymer functional groups with bm solvent molecules incorporated. Using Veytsman's procedure, basic thermodynamic functions and association equilibrium relations are derived. Different association characteristics are examined. When passing from a system with solvent-free junctions ($b = 0$) to our model with $b > 0$, the shape of the calculated curves changes strikingly, e.g. the relative association degree α vanishes both in the neat solvent and neat polymer points, showing a maximum near the middle of the composition range. This results in the existence of two critical points of network formation (gel points), delimitating the compositional range of the coexistence of a network with finite clusters (gel region). Using extinction probability, the quantitative parameters characterizing the cluster–network relationships are calculated and analyzed. All of them display an extreme near the middle of the gel region, and various kinds of singularities appear in the two gel points. The effect of the stoichiometric ratio b on characteristic system parameters is discussed.

Keywords: Polymer association theory; Functional group association equilibrium; Multiple chain junctions; Solvent-complexed chain junctions; Two gel points; Sol–gel relationships.

Very frequently, the association of macromolecules in solution is due to the chain heterogeneity. The association sites are constituted by chain segments that differ from the rest of the molecule in polarity, hydrophobicity, stereoregularity, chain geometry or conformation. If these sequences are long enough and uniform in length, compact monodisperse micelles can arise. This way of aggregation is highly cooperative and is called closed association[1]. On the other hand, open association occurs with molecules containing short sequences capable of aggregation into chain junctions (analogues of crosslinks in chemical gelation). Association sites of this kind will be called functional groups. If they appear at chain ends only, the associa-

tion is, according to Elias[1], molecule-related; the macromolecules join themselves into long linear superchains with improved mass uniformity. If the functional groups are interspersed along the chain, segment-related association occurs and randomly branched clusters arise showing very high mass-nonuniformity which may result in their coexistence with an infinite network structure. The random association of polyfunctional molecules will be the subject of the present work.

The dynamic and rheological behavior of an associating system depends strongly on the junction multiplicity, i.e. on the number of macromolecules that contribute to the formation of a junction. If m functional groups of different macromolecules aggregate, an m-fold junctions are formed from which $2m$ amorphous subchains radiate. While a multiple junction itself may exhibit some structural organization, the selection and combination of functional groups into a junction is random, and the same then holds for the architecture of the branched structures and the network.

Existing theories of polyfunctional polymer association are based on equilibrium statistical thermodynamics. Usually they are motivated and presented as theories of thermoreversible gelation, as the formation of physical gels is considered to be one of the most important features of this kind of association. Stockmayer was the first that took the existence of multiple junctions into consideration[2]. Tanaka analyzed different aspects of the phenomenon in numerous papers (for a review, see ref.[3]). Semenov and Rubinstein applied a different computation strategy. They extended interest to consequences of intramolecular bridging in dilute solutions, and also brought critical remarks on some papers in the field[4]. Kudlay and Erukhimovich studied specific features of phase separation, as induced by the presence of multiple junctions[5].

Experimental data indicate that arrangement of chain segments into multiple junctions often requires inclusion of solvent molecules[6]. Complexes and intercalates arise with a defined solvent–polymer ratio. The incorporation ability of a particular solvent is independent of the polarity and the contact interaction parameter occurring in polymer solution theory[7] and is determined by other factors, e.g. steric complementarity of solvent molecules with the polymer elements of the junction. The solvent participation has not been taken into account as yet in theoretical work, although it strongly affects the concentration dependence of the association degree of cluster and network parameters as well as the limits of phase instability regions. In this paper, we analyze the influence of the parameter b, defined as the ratio of the number of solvent molecules in a junction to the corre-

sponding number of polymer functional groups (i.e. to junction multiplicity).

While the Stockmayer–Tanaka theory[2] is based on a detailed mathematical description of equilibrium size distribution of association clusters, the starting point of other authors[4,5] is the equilibrium between associated and free functional groups irrespective of their appurtenance to clusters. We have preferred the latter approach. Starting from a partition function derived by Veytsman's procedure[8], we characterize the association and network formation in model systems. Another paper is in preparation, dealing with phase stability.

Basic Equations

In the Flory–Huggins model, a macromolecule is constituted by a sequence of r segments. The solution volume is divided into N segment sites, each of which can accommodate one segment of polymer A or one molecule of solvent B. A balance equation holds

$$N = rN_A + N_B. \qquad (1)$$

Weak contact interactions follow the random mixing statistics. For the Helmholtz energy of mixing we have

$$\Delta F_{inert}/k_B T = N_A \ln\varphi_A + N_B \ln\varphi_B + \chi N_B \varphi_A \qquad (2)$$

where φ_K is the volume fraction of component K (K $\equiv$ A; B). The contact-interaction parameter χ is related to one segment. The subscript "inert" means absence of association.

Now we assume that the macromolecule contains f functional groups ("stickers") different from the other elements of the chain so that they may form association junctions with other functional groups of the same character. The origin of such a junction may stipulate incorporation of solvent molecules. Following Veytsman, we shall evaluate the Helmholtz energy change accompanying the formation of junctions. Let one junction be constituted by m functional groups and bm solvent molecules ($m \geq 2$, $b \geq 0$). To produce M junctions, we have to choose mM of the total fN_A functional

groups and bmM of the total N_B solvent molecules. The number of ways of doing that is the selection factor S

$$S = \frac{(fN_A)! N_B!}{(fN_A - mM)!(mM)!(N_B - bmM)!(bmM)!} \,. \tag{3}$$

The elements chosen are to be distributed into M ordered sets, each containing m functional groups and bm solvent molecules. The corresponding combinatorial factor is

$$C = \frac{(mM)!(bmM)!}{M!} \,. \tag{4}$$

Finally we have to put down the association factor A, describing aggregation in the sets of elements constructed in the preceding step.

a) Before association, the $m + bm$ elements of a given set are essentially independent in thermal motion, so that each of them is free to visit successively each of the N segment sites. After aggregation they are bound to move jointly and the association partition function diminishes by a factor N^β, where

$$\beta = m + bm - 1 \,. \tag{5}$$

b) On association, new interactions ("bonds") arise between the elements assembled, whereby energy is released and changes in numbers of degrees of freedom of overall and intramolecular rotation occur. The Helmholtz energy change F_b pertaining to this process is a function of parameters b and m, the form of the dependence being determined by the topological structure, geometry and flexibility of the junction.

For M junctions, the association factor is

$$A = N^{-\beta M} \exp(-MF_b/k_B T) \,. \tag{6}$$

The overall contribution of the association process to the partition function is the product of three factors given by Eqs (*3*), (*4*) and (*6*). Herefrom the Helmholtz energy of association is obtained using the Stirling formula

$$F_{assoc}/k_B T = (fN_A - mM)\ln(fN_A - mM) - fN_A \ln(fN_A) + \\ + (N_B - bmM)\ln(N_B - bmM) - N_B \ln N_B + \qquad (7) \\ + M\ln M + \beta M + \beta M \ln M + MF_b/k_B T .$$

On minimizing F_{assoc} with respect to M, we find the condition of association equilibrium, which can be rearranged to

$$\ln(M/N) = -F_b/k_B T + m\ln[(fN_A - mM)/N] + bm\ln[(N_B - bmM)/N] \qquad (8a)$$

or

$$X = \eta y_A^m y_B^{bm} \qquad (8b)$$

where η is the equilibrium constant

$$\eta = m\exp(-F_b/k_B T) , \qquad (9)$$

X is the concentration of associated functional groups

$$X = mM/N \qquad (10)$$

and y_A, y_B are the concentrations of free functional groups A or molecules of B, respectively. The concentrations defined here are bound by mass balance equations

$$(f/r)\varphi_A = y_A + X \qquad (11)$$

$$\varphi_B = y_B + bX \qquad (12)$$

or, substituting from Eq. (8),

$$(f/r)\varphi_A = y_A + \eta y_A^m y_B^{bm} \qquad (13)$$

$$\varphi_B = y_B + b\eta\, y_A^m y_B^{bm}. \tag{14}$$

As it follows from the previous discussion of F_b and Eq. (*9*), η is a non-transparent function of the junction multiplicity m. For the sake of simplicity, we adhere in this work to a dependence introduced by other authors[2,5], namely

$$\eta = k^{m-1} \tag{15}$$

where k is a constant.

Substituting from Eq. (*8a*) to Eq. (*7*) and using Eqs (*10*) to (*12*), we obtain the Helmholtz energy at association equilibrium

$$F_{assoc}/k_B T = fN_A \ln\left[y_A/(f\varphi_A/r)\right] + N_B \ln(y_B/\varphi_B) + N\beta X/m. \tag{16}$$

The total change of Helmholtz energy on mixing can be obtained as the sum

$$\Delta F = \Delta F_{inert} + F_{assoc} - F_{assoc}^\circ . \tag{17}$$

Here, F_{assoc}° is F_{assoc}° for $\varphi_A = 1$ and is used to keep consistency with Eq. (*2*), where the standard state is that of the pure amorphous substance. Substituting into Eq. (*17*), we have

$$\begin{aligned}
\Delta F/k_B T = \; & N_A \ln\varphi_A + N_A f \ln[y_A/(\varphi_A y_A^\circ)] + \\
& + N_B \ln y_B + N\beta(X - \varphi_A X_A^\circ)/m + N_B \chi \varphi_A .
\end{aligned} \tag{18}$$

The concentrations y_A° and X_A° are related to the standard state.

Herefrom we obtain the chemical potentials μ_A, μ_B using the conventional formulas and respecting the functional dependence of X, y_A and y_B on φ_A:

$$\Delta\mu_A/RT = \ln\varphi_A - (r-1)\varphi_B + f\ln[y_A/(\varphi_A y_A^\circ)] + r\beta(X - X_A^\circ)/m + r\chi\varphi_B^2 \tag{19}$$

$$\Delta\mu_B/RT = \ln y_B + (1 - 1/r)\varphi_A + \beta X/m + \chi\varphi_A^2 \ . \tag{20}$$

Basic Parameters of Association

To express the relative amount of functional groups engaged in association, two quantities will be useful, namely α and z

$$\alpha = X/(f\varphi_A/r) = z(1 + z)^{-1} \tag{21}$$

$$z + X/y_A = (ky_A)^{m-1} y_B^{bm} \ . \tag{22}$$

The parameter α corresponds to the "conversion" used in chemical equilibrium thermodynamics. Here, it will be called degree of association. It expresses the probability that a given functional group participates in forming a junction.

The dependence of α on φ_A has been discussed[5] for various values of m in systems where the solvent does not enter into the junctions. In our Fig. 1, curves are shown for junctions of multiplicity 2, 4 and 6 at the same value
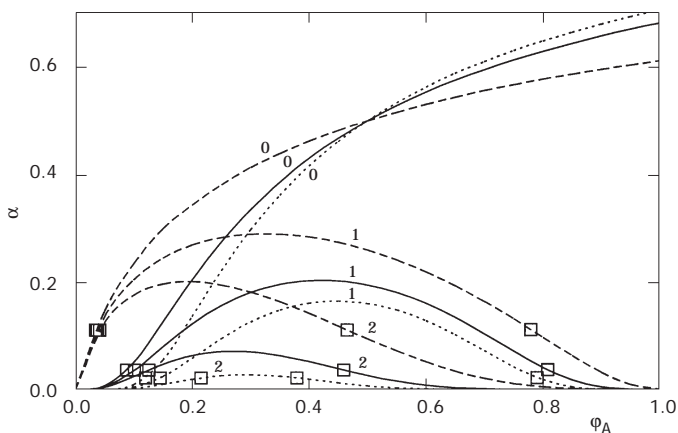

FIG. 1

The association degree α as a function of composition at various values of junction multiplicity m and solvent proportion b. $r = 100$, $f = 10$, $k = 40$. Dashed lines $m = 2$, full lines $m = 4$, dotted lines $m = 6$, □ gel points. Curves are labeled by b values

of equilibrium constant k and various values of b. The participation of solvent in junction formation affects the shape of the curves conspicuously.

In the range of small φ_A, the initial section of the curve resembles a straight line for $m = 2$, while for $m > 2$ it approaches a parabola of $(m - 1)$-th degree

$$\alpha = (kf/r)^{m-1} \varphi_A^{m-1} \ . \tag{23}$$

The higher the exponent $m - 1$, the higher concentration is necessary to achieve a certain value of α. As an asymptote, Eq. (*23*) is valid for any value of b.

If $b = 0$ (no solvent in the junctions), the association degree increases monotonically with concentration. For $b > 0$, the α–φ_A curves reach a maximum and then decrease due to lack of solvent at higher φ_A. At small φ_B, the curves assume a parabolic shape

$$\alpha = (kf/r)^{m-1} \varphi_B^{bm} \ . \tag{24}$$

Thus the degree of association approaches zero both in the left- and the right-hand periphery of the graph in Fig. 1. As we chose $b \geq 1$, the exponent of φ_B in Eq. (*24*) is higher than that of φ_A in Eq. (*23*).

The association gives rise to complex polymer–solvent clusters of general formula A_iB_j. The subscript i, giving the number of macromolecules incorporated in a particular cluster, will be called association number. In our model, for a ring-free cluster, the subscripts i and j are related to l, the number of m-fold junctions:

$$i = 1 + (m - 1)l \qquad j = bml \ . \tag{25}$$

Therefore, ring-free clusters are fully defined by their subscript i. This will find use in the form of following summations. To obtain average values of association number, we define the statistical moment function

$$I_n = \sum_{i=1} i^n \nu_i \tag{26}$$

for $n = 0, 1, 2, \ldots$. Here $\nu_i = N_i/N$ stands for the number density of clusters containing i macromolecules. In the absence of an infinite association network

$$I_0 = \sum_{i=1} \nu_i \qquad (27)$$

$$I_1 = \varphi_A/r . \qquad (28)$$

It can be shown[9] that the concentration of a finite-size cluster is given by an equilibrium relation

$$\nu_{ij} = K_{ij} p_A^i p_B^j \qquad (29)$$

where p_A and p_B are the number densities of "monomers", i.e. non-associated molecules of components A and B, respectively, and K_{ij} is the equilibrium constant of ij-cluster formation. Introducing Eq. (29) into Eq. (26), we obtain

$$I_n = \sum_{i=1} i^n K_i p_A^i p_B^j . \qquad (30)$$

Therefrom it follows

$$I_0 = \int (I_1/p_A) \, \mathrm{d}p_A \qquad [\, p_B = \text{const.}\,] \qquad (31)$$

$$I_2 = (\partial I_1/\partial \ln p_A) \qquad [\, p_B = \text{const.}\,]. \qquad (32)$$

Using these equations together with Eqs (28) and (13), we can calculate I_0 and I_2 from I_1, if we indeed know the relationship between y_A and p_A. This cannot be provided by the Veytsman procedure, which expresses the thermodynamic functions in terms of concentrations of free or associated functional groups irrespective of the cluster size. Therefore we take a similar way as given in ref.[4]

A macromolecule exists as an isolated linear entity if all of its f functional groups are free. Assuming that the functional groups are independent of each other, the probability of the event is

$$P(i = 1) = (1 - \alpha)^f = (1 + z)^{-f} . \tag{33}$$

According to Eq. (28), the number density of all macromolecules present is I_1 so that the concentration of isolated molecules is

$$p_A = I_1 (1 + z)^{-f} . \tag{34}$$

As the solvent is monofunctional ($f_B = 1$), we see immediately

$$p_B = y_B . \tag{35}$$

Following the prescription given by Eqs (31) and (32) and using Eqs (13), (22) and (34) together with their differentiated forms, we can obtain I_0 and I_2 from I_1. After all, we arrive at the relations

$$I_0 = \varphi_A/r - (m - 1)X/m \tag{36}$$

$$I_2 = I_1 = \frac{f\varphi_A/r + (m - 1)X}{f\varphi_A/r - (f - 1)(m - 1)X} . \tag{37}$$

On the right-hand side of Eq. (36), φ_A/r is the nominal number density of the polymer, while the other term expresses the decrease in number density of polymer entities (isolated molecules and clusters) if X/m junctions of multiplicity m arise in unit volume and if ring formation can be neglected. The difference of the two terms corresponds to the number density of all polymer species consistently with the definition (27).

Based on Eqs (28), (36), (37) and (21), we can express the number and mass averages of the association number as a function of the association degree

$$\langle i \rangle_n = I_1/I_0 = [1 - (m - 1)f\alpha/m]^{-1} \tag{38}$$

$$\langle i \rangle_w = I_2/I_1 = \frac{1 + (m - 1)\alpha}{1 - (f - 1)(m - 1)\alpha} . \tag{39}$$

To obtain the molar mass of a cluster i-mer, we take into consideration that for $i > 1$ every cluster contains a certain amount of solvent. The relation between stoichiometric indices i and j is given by Eq. (25); herefrom the molar mass of a cluster i-mer can be obtained

$$M_i = i(M_A + M_B') - M_B' \tag{40}$$

where M_A, M_B are nominal molar masses of the components A, B and

$$M_B' = M_B bm/(m-1) . \tag{41}$$

Neglecting the last term on the right-hand side of Eq. (40), the molar mass averages of the clusters are obtained

$$\frac{M_n}{\langle i \rangle_n} = \frac{M_w}{\langle i \rangle_w} = M_A + M_B bm/(m-1) . \tag{42}$$

The operations prescribed by Eqs (31) and (32) have been performed at constant free solvent concentration y_B, so that the ratio b does not enter explicitly into Eqs (38) and (39). Thus, the form of these equations is independent of the presence of solvent in junctions; however, α itself is dependent on the coefficient b, and the same is true for the average association number.

Condition of Existence of an Infinite Association Network

If the association degree α assumes the critical value

$$\alpha^* = \frac{1}{(f-1)(m-1)} \tag{43}$$

a singularity appears in Eq. (39) and the mass-average association number tends to infinity. This can be interpreted as inception of an infinite network structure, giving rise to a gel if the physical junctions have sufficient strength and lifetime. The network is penetrated by finite polymer clusters and the solvent. For the brevity sake, the singularity point discussed will be given the name "gel point".

Equation (43) is of the same form as the relation derived by Yamabe and Fukui[10] for a network based on multiple covalent junctions, and for $m = 2$ we have the classical gel point condition of Flory. Due to its connection

with Eq. (*39*), the critical value α^* is independent of the stoichiometric ratio *b* and is the same as in the case of solvent-free junctions. α^* indeed corresponds to a different nominal polymer volume fraction φ_A^*. This is illustrated by the points on the α–φ_A curves in Fig. 1.

Using Eqs (*21*) and (*22*), we can rewrite the condition of the gel point

$$(ky_A^*)^{m-1} y_B^{*bm} = 1/\psi \qquad (44a)$$

or

$$z^* = 1/\psi \qquad (44b)$$

where

$$\psi = fm - f - m. \qquad (45)$$

Using mass balances (*13*) and (*14*), we transform Eq. (*44a*) into

$$\left[k(f/r)\varphi_A^* \frac{\psi}{\psi+1} \right]^{m-1} \left[1 - \left(1 + \frac{bf/r}{\psi+1} \right)\varphi_A^* \right]^{bm} = 1/\psi \qquad (46)$$

which correlates φ_A^* with the system parameters immediately. In Fig. 2 the equilibrium constant calculated using Eq. (*46*) is plotted against φ_A^* to illustrate the ensuing discussion.
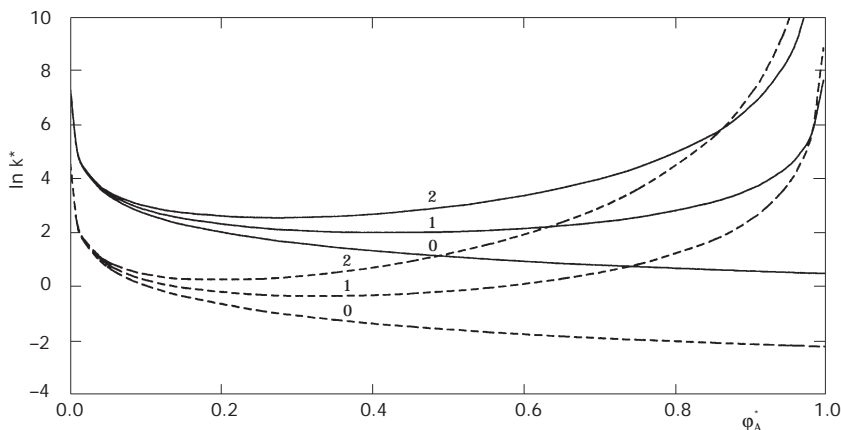

Fig. 2

The parameter k^* (i.e. gel point value of *k*) as a function of gel point composition φ_A^* at various values of junction multiplicity *m* and solvent proportion *b*. $r = 1000$, $f = 100$. Dashed lines $m = 2$, full lines $m = 4$. Curves are labeled by *b* values

Let us look first at the case $b = 0$. Then Eq. (*46*) can be to a good approximation put into the form

$$k(f/r)\varphi_A^* = [f(m-1)]^{-1/(m-1)} . \tag{47}$$

We see that the gel point concentration φ_A^* diminishes with increasing equilibrium parameter k and the density of functional groups along the chain, f/r. This result could have been expected also on the basis of the critical conversion relation Eq. (*43*) combined with Eq. (*23*), showing that φ_A^* reflects a decrease in α^* with f. On the other hand, Eq. (*47*) reads that the influence of m is opposite to that of f. This is due to the difficulty of formation of high-multiplicity junctions at smaller concentrations, as can be seen from the curves passing through the gel points in Fig. 1.

If the solvent enters into the association junctions ($b > 0$) then Eq. (*47*) holds in the range of small φ_A^* only. Otherwise we have to replace φ_A^* by a function ensuing from Eq. (*46*) for $r \gg 1$ and $f \gg 1$

$$f(\varphi_A^*) = \varphi_A^* (1 - \varphi_A^*)^{bm/(m-1)} . \tag{48}$$

This function has a maximum at

$$\varphi_{A,\max}^* = (m-1) / \beta \tag{49}$$

corresponding to a minimum of k^* in Fig. 2. Evidently, for $b > 0$ and $k^* > k^*_{\min}$, there are two solutions to Eq. (*46*), φ_{A1}^* and φ_{A2}^*. The association network can only exist in the range of volume fractions limited by these values. This range will be called gel region and its limits – the first and the second gel point. In the gel region, the moment function I_2 assumes negative values and Eqs (*38*) and (*39*) lose validity.

Now let us deal with the two gel points separately. To discuss the first gel point, we have simply to replace φ_A^* by φ_{A1}^* in Eq. (*47*) and the following section. Concerning the second gel point, we assume that φ_{A2}^* is not very far from the right-hand border of the φ_A^* range. Then Eq. (*46*) can be approximated by

$$(kf/r)^{(m-1)/bm} \, \varphi_{B2}^{*} = [f(m-1)]^{-1/bm} \qquad (50)$$

where $\varphi_{B2}^{*} = 1 - \varphi_{A2}^{*}$. A comparison with Eq. (47) indicates that the solvent content at the second gel point and the polymer content at the first gel point depend on kf/r, m and b in a similar way. However, the exponents are different; for $b \geq 1$ we always have $bm > m - 1$. It follows that the second gel point is more distant from the right-hand edge of the concentration range than the first gel point from the left edge, i.e.

$$\varphi_{B2}^{*} > \varphi_{A1}^{*} \qquad (51)$$

at the same value of equilibrium constant k. (Also, φ_{B2}^{*} increases to a larger extent than φ_{A1}^{*} if the stoichiometric ratio b increases.) Moreover, a detailed mathematical analysis has shown that at sufficiently large values of kf/r the dependence of φ_{B2}^{*} on the multiplicity m can be opposite to that of φ_{A1}^{*}. In that case, the influence of $(m - 1)$ in Eq. (43) dominates over the effect of the slow growth of conversion α with concentration. This anomaly is illustrated by the intersection of curves for different values of m at the same b in the upper right corner of Fig. 2.

If a gel point moves toward $\varphi_{A,max}^{*}$, then the slope of the function $f(\varphi_A^{*})$ (Eq. (48)) tends to zero. Therefore, the value of φ_A^{*} becomes considerably more sensitive to a change in k or f/r than it is the case at the periphery of the concentration range.

Number Density of Unassociated Molecules A and B

Before we deal with relations specific for the gel regime, we turn our attention to "monomer" concentrations p_A, p_B and their product. Our considerations will relate to the overall composition range with no principal distinction of the gel region.

According to the Flory theory of chemical gelation, the number density of the unreacted macromolecules achieves a maximum at the gel point and diminishes with increasing polymer concentration in the gel region. The same holds for the concentration of finite branched entities which are in chemical equilibrium with the unreacted molecules. Semenov and Rubinstein[4] have shown that on polymer association the sol species exhibit

the same behavior. This conclusion is valid if no solvent is incorporated into the junctions. To analyze the case of solvent cooperation ($b > 0$), we combine Eqs (28) and (30) to obtain

$$I_1(p_A, p_B) = \varphi_A/r . \tag{52}$$

We differentiate Eq. (52) and rearrange substituting from our model relations. After all we have

$$\frac{d\ln p_A}{d\varphi_A} = (rI_2)^{-1} - b\frac{fmz}{1+mz}\frac{d\ln y_B}{d\varphi_A} . \tag{53}$$

It follows from Eqs (37) and (43) that the first term on the right-hand side is zero at the gel point and negative in the gel region. The other term is positive if $b > 0$. Then the slope of $\ln p_A$ is positive at the gel point and the maximum of p_A shifts into the gel region or it disappears at all (at the 2nd gel point or even, for higher b, also at the 1st gel point).

As it is seen from Eq. (29), the clustering equilibrium depends also on the concentration of nonassociated B molecules. For finite clusters, the treatment is simplified by strict correlation of the indices i and j in the cluster formula A_iB_j due to Eq. (25). Thus we may transform Eq. (29) into the form

$$v_l = K_l q^l p_A \tag{54}$$

where l is the number of junctions in the cluster and

$$q = p_A^{m-1} p_B^{bm} . \tag{55}$$

We see that except small clusters, the equilibrium is fully determined by the variable q. Let us look at its dependence on φ_A. Substituting from Eq. (22) and using Eqs (13) and (34), we can express q in terms of z

$$q = (kf)^{-(m-1)} z(1+z)^{-(\psi+1)} . \tag{56}$$

By differentiation, we have

$$\frac{\mathrm{d}\ln q}{\mathrm{d}\varphi_A} = \frac{1-\psi z}{z(1+z)}\frac{\mathrm{d}z}{\mathrm{d}\varphi_A}. \tag{57}$$

The derivative on the left-hand side is zero: (i) in the two gel points ($z = z^*$) due to Eq. (44b); this corresponds to two maxima of q; (ii) at the point where $\mathrm{d}z/\mathrm{d}\varphi_A = 0$. This maximum of z can be found from the derivative of Eq. (22) with respect to φ_A; it results

$$\varphi_A(\text{max of } z) = (m-1)/\beta - bX. \tag{58}$$

Comparing with Eq. (49), we find a small difference in φ_A. Thus, the maximum in z, corresponding to a minimum in q, is not far from the maximum in the function $f(\varphi_A^*)$; see Eq. (48).

In Fig. 3, the relations of the free molecule concentrations, p_A and p_B, to free group concentrations, y_A and y_B, and to the parameter q are illustrated.

The dependence of the free group concentration y_A on the polymer content φ_A (curve 1) is given by the relation
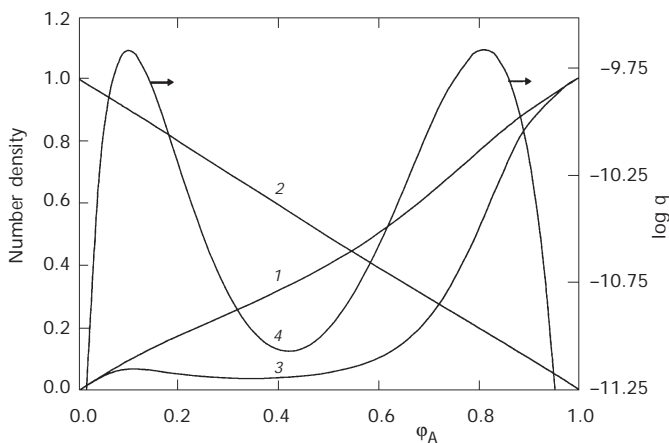

FIG. 3

Number densities of nonassociated functional groups and isolated molecules as function of composition. $r = 100$, $f = 10$, $k = 40$, $m = 4$, $b = 1$. 1 y_A, 2 $y_B = p_B$, 3 p_A, 4 log q

$$y_A(\varphi_A) = (f/r)\,\varphi_A - X(\varphi_A)\,. \tag{59}$$

The curve approaches a linear function at the edges of the concentration range but in the middle it deviates downwards, as association into junctions proceeds. Essentially similar is the behavior of the dependence of y_B on φ_B (curve *2*); however, its relative deflection in the middle is smaller (r/bf) times and hardly visible in the graph. The same curve describes p_B, see Eq. (*35*).

The relative bending in the plot of p_A vs φ_A (curve *3*), is the f-th power of the relative deflection of y_A in curve *1*, see Eq. (*34*). In this way, a maximum with a minimum may sometimes appear on the p_A-curve, as it is seen in Fig. 3.

The variable q, Eq. (*55*), is the product of powers of concentrations p_A and p_B, which have shown antagonistic trends in the preceding curves. This is reflected in the dramatic course of curve *4*, displaying q vs φ_A. As has been predicted above, one finds maxima in the two gel points and a deep minimum near the middle of the gel range.

Equation (*55*) can be used to modify the moment function relation, Eq. (*30*)

$$I_n = \sum_l [1 + (m-1)\,l]^n\,K_l\,q^l\,p_A \tag{60}$$

where the summation is performed over all finite clusters. Therefore, the characteristic features of the function $q(\varphi_A)$ must be reflected somehow in the shape of the curves $\langle i\rangle_n$ vs φ_A and $\langle i\rangle_w$ vs φ_A, as will be shown in the following graphs.

The Gel Region

Adhering to the terminology used in the covalent gelation theory, we call "sol" the ensemble of finite polymer entities embedded in the association network (gel). We proceed now to the problem of polymer partition between the sol and gel in the gel regime. An association structure may be thought to consist of two kinds of units, subchains and junctions. In the gel region, we have to distinguish units that are part of a finite cluster from those which belong to the network. To find guidance, we consider that we are passing successively from a unit to the neighboring one along the struc-

ture. Then we may find infinite continuation of a path in the network, but not in a sol particle. In the theory of covalent gelation, the probability that a bond issues no continuation to infinity is called extinction probability and is given the symbol v (see, e.g., ref.[11]). In the present model of multiple-junction association, the "bond" is understood as the passage from a functional group of molecule M_1 to that of molecule M_2, both functional groups being part of the same multiple junction J. Let us assume that this "bond" does not produce any continuation to infinity, the probability of this event being v. Now let us consider the consequences of our postulate in molecule M_2, which contains $(f-1)$ functional groups outside the junction J. None of these groups belongs to an infinite structure either. For any of them, this can be accomplished in two ways: The functional group is either unassociated (with probability $1-\alpha$), or, if incorporated into a junction of multiplicity m, it shares the junction with $m-1$ groups of other molecules with no continuation to infinity (probability αv^{m-1}). All of the $f-1$ groups of molecule M_2 have to comply with one of the two requirements declared; the probability of this complex event constitutes an alternative expression to v. Thus, using Eq. (*21*), we write

$$v = \left(\frac{1 + zv^{m-1}}{1+z} \right)^{f-1} . \tag{61}$$

This equation serves for finding v. It always has a trivial solution $v = 1$. Another root v occurs in the physical range (0;1) if $\psi z > 1$, i.e. with z in the gel region.

Using extinction probability, we can calculate interesting parameters of the sol–gel coexistence. The fraction of macromolecules contained in the sol is equal to the probability that all functional groups of a given macromolecule provide finite continuation only:

$$w^s = \left(\frac{1 + zv^{m-1}}{1+z} \right)^{f-1} \tag{62}$$

or

$$w_A^s = v^{f/(f-1)} . \tag{63}$$

Multiplying by φ_A, we obtain the respective concentration φ_A^s. In a similar way, we transform the gel fraction $w_A^g = 1 - w_A^s$ into the concentration φ_A^g.

The number density of junctions formed in the sol is equal to the overall junction number density multiplied by the probability that all the m "bonds" ascribed to the junction lack continuation to infinity:

$$X^s/m = (X/m) v^m . \qquad (64)$$

Therefrom, X^s and X^g as well as α^s and α^g can be easily calculated:

$$\alpha^s = \alpha v^{m-f/(f-1)} \qquad (65)$$

$$\alpha^g = \alpha\left(1 - v^m\right) / \left[1 - v^{f/(f-1)}\right]. \qquad (66)$$

For y_A^g (concentration of nonassociated functional groups in gel), we have

$$y_A^g = y_A - y_A^s = (f/r)\varphi_A[1 - v^{f/(f-1)}] - X(1 - v^m) . \qquad (67)$$

The fraction of solvent B absorbed in the gel junctions is

$$w_B^g = bX^g/\varphi_B . \qquad (68)$$

We have assumed that in the sol clusters no rings are formed. Therefore the consideration following Eq. (*37*) can be adapted also for the quantities related to the sol and an analogue of Eq. (*36*) can be written (see also Eq. (*27*))

$$\sum v_i^s = \varphi_A^s/ r - (m-1)X^s/ m. \qquad (69)$$

In the gel, the existence of rings must be acknowledged and the counterpart to Eq. (*69*) reads

$$0 = \varphi_A^g/ r - (m-1)X^g/ m + C^g \qquad (70)$$

where C^g is the concentration of rings in the gel. Then the relative amount of rings per functional group of gel is

$$\gamma = (m-1)\alpha^g/m - 1/f \,. \tag{71}$$

The definitions of a great majority of quantities introduced in this paragraph can be extended to the whole composition range $\varphi_A \in (0;1)$ if we put $v = 1$ outside the gel region. This is equivalent to including cluster ensembles existing in the pregel regime into the sol concept. In the conclusion we calculate the average association numbers of the sol clusters. It can be proved that the first-moment function of the sol follows a relation analogous to Eq. (28)

$$I_1^s = \varphi_A^s/r \,. \tag{72}$$

Other moment functions of the sol can be obtained using relations

$$I_0^s = \int (I_1^s/p_A)\,\mathrm{d}\,p_A \qquad [\,p_B = \mathrm{const.}\,] \tag{73}$$

$$I_2^s = (\partial I_1^s/\partial \ln p_A) \qquad [\,p_B = \mathrm{const.}\,]\,. \tag{74}$$

In a way similar to that used for systems outside the gel region we obtain

$$\langle i \rangle_n^s = \frac{1 + zv^{m-1}}{1 - (\psi/m)zv^{m-1}} \tag{75}$$

$$\langle i \rangle_w^s = \frac{1 + mzv^{m-1}}{1 - \psi zv^{m-1}} \,. \tag{76}$$

If generalized as described, the number and mass averages display singularities in the two gel points. At both of these points, the number average assumes the same value

$$\langle i \rangle_n^s = (f - 1)\, m / \psi \,. \tag{77}$$

At the gel points, the parameters mentioned above are independent of the *b*-value and therefore not influenced by the entry of solvent into junctions. The mass average association number diverges at the gel points. Both types of averages display minima for φ_A corresponding to the maximum of *z* (see Eq. (*58*)).

The concentration dependence of some sol–gel parameters, extended to the whole composition range, is depicted in Figs 4 and 5. Curve *1*, Fig. 4 displays the non-extinction probability, $1 - v$. This function assumes non-zero values in the gel region only. The position of its extreme on the φ_A-axis corresponds to that of the function $z(\varphi_A)$. Curve *1* also roughly describes the dependence of the gel fraction w_A^g, the values of which are smaller just by a few percent than those of $1 - v$.

Curve *2* shows the dependence of φ_A^s on φ_A. Outside the gel region, the curve coincides with the straight line $\varphi_A^s = \varphi_A$, while in the network region the difference between the two lines is equal to φ_A^g. The curve *3* (φ_B^s vs φ_A) can essentially be described in an analogous way; however, the curvature in the gel region is hardly observable as the amount of solvent present in the gel junctions is very small in comparison with the amount of polymer units constituting the network.
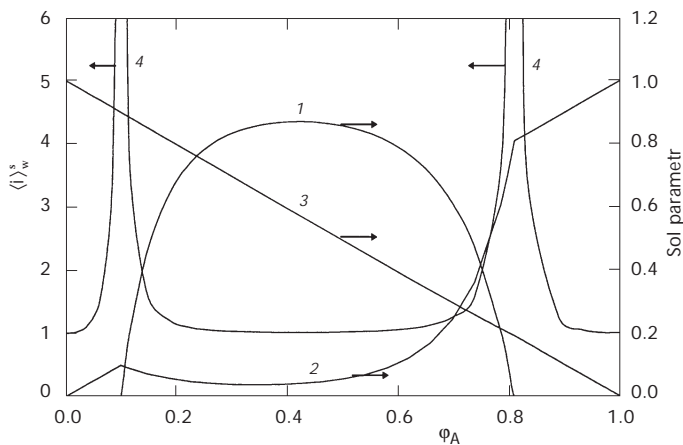

FIG. 4
Sol parameters as function of composition. $r = 100$, $f = 10$, $k = 40$, $m = 4$, $b = 1$. *1* $1 - v$, *2* φ_A^s, *3* φ_B^s, *4* $\langle i \rangle_w^s$

As has been predicted, the dependence of $\langle i \rangle_w^s$ on φ_A (curve *4*) exhibits a minimum at the same volume fraction as the dependence of *q* (see curve *4*, Fig. 3). The maxima of *q*, appearing in the two gel points are transformed by Eq. (*60*) with *n* = 2 into singularities where $\langle i \rangle_w^s$ diverges.

In Fig. 5, curve *1* depicts the dependence of the overall degree of association α on φ_A in the whole concentration range. Curves *2* and *3* allow a comparison of the association degree occurring in the sol (α^s) with that found in the gel (α^g). Both these quantities combine into the overall α (curve *1*) according to the formula

$$\alpha = w_A^s \alpha^s + w_A^g \alpha^g \ . \tag{78}$$

Curve *4* displays the population of rings in the network, as calculated from the balance equation, Eq. (*71*). Curve *5* depicts the fraction of solvent incorporated in the associated functional groups of the gel. The curve asymmetry is due to a decrease in the overall solvent content in the system with increasing polymer content.

In the next two figures the effect of the stoichiometric ratio *b* on the gelation parameters φ_A^g and $\langle i \rangle_n^s$ is shown. Figure 6 deals with φ_A^g, the concentration of the gel portion as a function of system composition (the curves are defined in the gel region only). If the junctions are solvent-free,
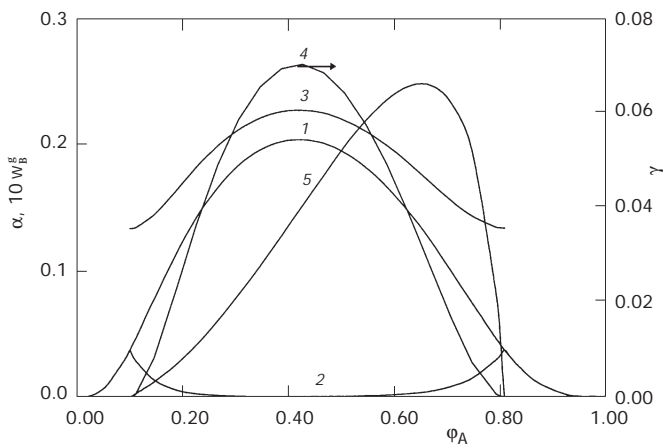

FIG. 5
Sol and gel parameters as function of composition. *r* = 100, *f* = 10, *k* = 40, *m* = 4, *b* = 1. *1* α, *2* α^s, *3* α^g, *4* γ, *5* $10 w_B^g$

there is a single gel point. Here starts φ_A^g its growth and rather early it approaches the line $\varphi_A^g = \varphi_A$, which means that nearly all macromolecules are incorporated into the gel. Moreover, from Fig. 7 we see that the average association number decreases soon to unity, which indicates that the minute amount of sol present is not associated. If the entry of solvent is unavoid-
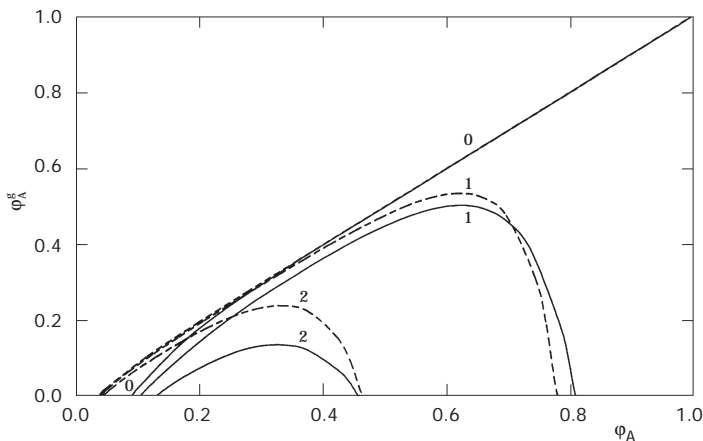

Fig. 6
Volume fraction of polymer present in the network as a function of total polymer volume fraction at various values of multiplicity m and solvent proportion b. $r = 100$, $f = 10$. Dashed lines $m = 2$, full lines $m = 4$. Curves are labeled by b values
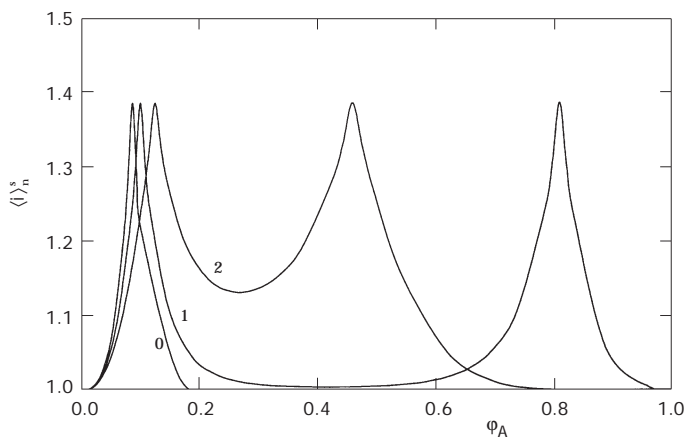

Fig. 7
Number-average association number of the sol $\langle i \rangle_n^s$ as a function of composition at various values of solvent proportion b. $r = 100$, $f = 10$, $k = 40$, $m = 4$, $b = 1$. Curves are labeled by b values

able for the junction formation ($b > 0$), lack of solvent manifests itself on increasing φ_A. Then the gel content decreases strongly until the network disappears at the second gel point. At its maximum, φ_A^g is smaller at larger b values. The content of sol increases with b and, as it is seen from Fig. 7, the same is true for its association number. In Fig. 7 we find the confirmation that in the two gelation points the number average of i is identical and independent of the b value. In these singular points, the discontinuities in the curve slope are symmetrical, i.e. the two derivative limits differ in sign, but not in the absolute value.

DISCUSSION

Remarks on the Derivation Procedure

Following Veytsman, our initial approach on derivation was focused on equilibrium between associated and free functional groups, irrespective of the cluster size and network presence. Owing to that the resulting thermodynamic mixing functions show no singularity in dependence on composition (see Eqs (*18*), (*19*) and (*20*)). This also concerns global association characteristics X, y_A and y_B and the quantities derived therefrom, like α, z, p_A, p_B and q. Quantities characterizing the sol–gel relationships and based on the extinction probability v can have their validity extended to the whole composition range, as described in the text following after Eq. (*71*). Then they exhibit singularities in the gel points: most of them are continuous, but jumps appear on the first and higher derivatives with respect to φ_A. As regards the ring population γ, jumps are not found on the first derivatives, but only on the second and higher ones. The weight-average association number $\langle i \rangle_w^s$ tends to infinity approaching from either of the two sides of a gel point.

It is remarkable that for $b = 0$, our expressions for the mean association number and for the gel point condition (see Eqs (*38*), (*39*) and (*43*)) are the same as those obtained by a procedure based on the association number distribution. In the calculation of the latter, the absence of rings from clusters was postulated, while Veytsman's approach used by us is intrinsically free of conjectures on cluster structure. The assumption of ring-free clusters has apparently been brought into our calculations later in Eq. (*33*), that expresses the probability that a given macromolecule is unassociated, and serves to calculate statistical moments of the association number (see Eqs (*31*) and (*32*)). Indeed, Eq. (*33*) is exact only if the isolated macromolecule is devoid of intramolecular association. Let us admit for a while that multi-

ple association junctions occur in some of the isolated chains, producing rings. Then the concentration p_A is the sum taken over linear and cyclic "monomer" species. If the cycling parameter c is small enough, at most one junction is expected in a molecule and Eq. (*34*) may be replaced by

$$p_A = I_1 \frac{1 + cz^m}{(1 + z)^f} . \qquad (79)$$

Then, using Eq. (*31*), an additional term in c appears on the right-hand side of Eq. (*36*). This means that in the pregel regime, rings exist in clusters, consuming part of the junctions. Thus the number density Σv_i of all polymer species is higher by a term equal to ring concentration. We may also calculate I_2 using Eq. (*32*) and we find that $\langle i \rangle_w$ is reduced due to the presence of ring formation term in the denominator of Eq. (*39*). In this way a correction is introduced into the condition Eq. (*44*) of the gel point, resulting in an increase in the critical value of z^*. We see that ignoring rings in clusters includes the use of Eq. (*33*).

Effect of the Solvent Bound in Junctions

The subject proper of this work has been the effect of the presence of solvent molecules in association junctions, as expressed by the stoichiometric ratio b. If b increases at constant f, m and k, different parameters display different trends. As regards the position of the characteristic points of the gel region, φ^*_{A1} increases with b while φ^*_{A2} decreases, until the network region disappears at a certain b. The extremes found inside the region become less pronounced and shift toward lower φ^*_A. The variable z decreases with b (cf. Eq. (*22*)). A similar behavior is then observed with quantities increasing with z; therefore X, α, w^g_A, φ^g_A, α^g decrease with b in the whole composition range, but q, $\langle i \rangle^s_n$, $\langle i \rangle^s_w$ do so outside the gel region only. On the contrary, p_A increases with b in the whole range, while q, v, w^s_A, $\langle i \rangle^s_n$, $\langle i \rangle^s_w$, φ^s_A, α^s do so inside the network region.

On comparing different systems in their gel points, we find that the influence of b is considerably limited. From Eq. (*44b*) we see that $z^* \equiv z^*(f,m)$ is independent of b and assumes the same value in the two gel points φ^*_{A1} and φ^*_{A2}. The same is found for parameters that can be expressed in terms of z^*, f and m, viz. for q^*, $\alpha^* = \alpha^{s*}$, α^{g*} and $\langle i \rangle^{s*}_n$ (cf. Figs 1 and 7). The same is valid for the derivatives of these quantities with respect to z, but not for the derivatives with respect to φ_A.

An alternative view on the influence of solvent incorporation involves finding values of equilibrium constant k necessary to achieve the same value of system property for $b = 0$, 1, 2, etc. For instance, if the property in question is the gel point composition φ_A^*, the increase in k^* with b can be visualized by drawing vertical lines in Fig. 2. The difference in k^* is small for various b-values at low gel point concentrations, but increases strongly with φ_A^*, the rates of increase being larger for smaller values of junction multiplicity.

CONCLUSIONS

We have found that the shape of the composition dependence graphs changes strikingly if solvent is present in association junctions ($b > 0$). Firstly, the function $\alpha(\varphi_A)$ is zero not only for $\varphi_A = 0$, but also for $\varphi_A = 1$, showing a maximum near the middle of the compositional range. This results in the existence of two gel points, delimitating the gel region. A maximum also appears on the composition dependence of some network-characterizing parameters, e.g. w_A^g, the proportion of the polymer constituting the gel. Minima are found for w_A^s and other parameters pertaining to the coexisting sol as well as for the constant k^*, required for having a gel point at a composition φ_A^*.

In the two gel points, the degree of association α and related parameters are independent of b, and there is no difference between their values at the first and the second gel point. On the other hand, the difference between the values found at the gel points and those observed in the maximum or minimum within the gel region decreases with b growing at constant f, m and k.

If a system has gel-like properties due to the presence of an associative network, the experimental determination of the second gel point by rheological methods may be difficult at high concentrations. This is because the effect of the network on rheology may be overlapped by other phenomena, e.g. by entanglements. This difficulty could be reduced using shorter chains for two reasons: (i) the influence of entanglements diminishes due to a decrease in chain length, and (ii) at smaller f, the second gel point is shifted toward lower polymer concentrations.

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