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Junction Multiplicity in Thermoreversible Gelation

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ABSTRACT: A new method for analyzing the junction structure of thermoreversible gels is proposed on the basis of the recent molecular theory of gelation with multichain junctions. It is shown that a plot of the observed gelation concentration c^* on a logarithmic scale against a combined variable $10^3/T + \ln M$ (where T is the absolute temperature and M is the molecular weight of the polymer) allows simultaneous evaluation of the junction multiplicity s (the number of polymer chains combined in a single junction) and the junction length ζ (the number of statistical units along a single chain taking part in the junction). The method is applied to the experimental data reported on the gelation of polyethylene in toluene, atactic polystyrene in carbon disulfide, and poly(vinyl alcohol) in water.

I. Introduction

Most physical gels are accompanied with complex network junctions which connect polymer segments on more than two different chains. For instance, gelation by microcrystallization of chain segments, by unsaturated associating forces such as seen in ionomer solutions, and by multifunctional groups attached to the polymer chains all belong to this important category.[1−4] To treat gelation with such complex junctions, we have recently introduced the notion of *junction multiplicity*.[5,6] Junction multiplicity s is defined by the number of chains combined to a single junction. Simple pairwise cross-links, for example, therefore have multiplicity $s = 2$ whose sol/gel transition is detailed in the classical literature.[7]

For the networks which have junctions with multiplicity larger than 2, the conventional Eldridge−Ferry procedure[8] to find the heat of junction fusion, which plots the logarithm of the gel melting concentration against the temperature, or the molecular weight of polymers, fails to predict the number of statistical units taking part in a junction. To see this, let us consider a simple model junction which binds s chains via ζ sequential units per chain (see Figure 1). This model is most suitable for the description of thermoreversible gels with junctions formed by fringed-micellar crystallites, but finds application to other prevalent gels.

Now the Eldridge−Ferry method[8] gives the total enthalpy of junction fusion ΔH_0 by finding the slope of $\ln c^*$ against $1/T$ through the relation

$$\ln c^* = \Delta H_0/k_{\mathrm{B}}T + \text{constant} \tag{1.1}$$

where c^* is the gel melting concentration, T the absolute temperature, and k_{B} the Boltzmann constant. The enthalpy of junction fusion ΔH_0 is expected to be proportional to the number of segments participating in the junction. But, since the total number of segments involved in a single junction is given by ζs for the model junction described above, this equation implies the additional assumption that the sol/gel transition is independent of the junction multiplicity s, but depends only on the total number of segments ζs in a junction. This assumption, however, is obviously incorrect in the case of multiple cross-links, because gelation concentration depends explicitly on the multiplicity under the condition that the total number of segments involved in a junction and, hence, the total binding free energy are kept fixed.[5,6] It was demonstrated[6] that, for telechelic polymers carrying two functional groups, the sol/gel transition line shifts toward the high-temperature and low-concentration region as the junction multiplicity is increased under a fixed association constant.

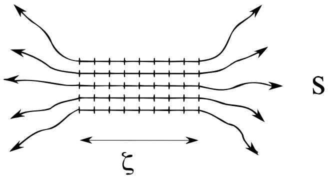

Figure 1. Model junction made up of s chains, ζ segments of each being bound together.

Another equation from which the Eldridge−Ferry method starts is a relation between the molecular weight of polymers and the gel melting temperature. It is given by

$$\ln M = \Delta H_0/mk_{\mathrm{B}}T + \text{constant} \tag{1.2}$$

where m is an integer to be adjusted to satisfy several thermodynamic requirements. (It was chosen as $m = 7$ in the original paper[8] under several assumptions.) This equation is more hypothetical than the first one and has no obvious molecular-theoretical justification.

Takahashi *et al.*[9] applied Flory's theory of melting point depression to gel-forming crystalline polymer solutions and derived the gel melting temperature as a function of the concentration. The evaluation of the junction multiplicity was, however, beyond the scope of their theory.

The purpose of this paper is to propose a new method for finding s and ζ independently from the measurement of the sol/gel transition concentration.

II. Sol/Gel Transition

In the preceding study,[5,6] we introduced a lattice-theoretical description of network-forming polymer solutions in which polymer chains of molecular weight M form clusters in a solvent by the association among functional groups they carry. As in the conventional

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lattice theory, a statistical repeat unit of a chain is assumed to represent several sequential monomeric units of the polymer. The number n of the statistical units on a single primary chain is then defined by $n \equiv M/m_0$, where m_0 is the molecular weight of a statistical unit. Using the result of generalized tree statistics,[10] we found the gelation concentration as a function of the number n of the statistical units on a chain, its functionality f (*i.e.*, the number of functional groups carried by each primary chain), and the junction multiplicity s. The result is given by

$$\lambda(T)\phi^* = nf's'/f(f's' - 1)^{s/s'} \tag{2.1}$$

where ϕ^* is the volume fraction of the polymer at gelation, $f' \equiv f - 1$ and $s' \equiv s - 1$. Here the association constant $\lambda(T)$ is given by

$$\lambda(T) = \exp(-\beta\Delta g_0) \tag{2.2}$$

where $\beta \equiv 1/k_BT$ is the reciprocal temperature and Δg_0 is the standard free energy change *per functional group*, *i.e.*, the free energy change on binding a single functional group into a junction. Because this factor $\lambda(T)$ always accompanies the polymer volume fraction, it was called the *temperature shift factor* in our preceding paper.[6] In deriving eq 2.1, it was assumed that all junctions take the same multiplicity s *(fixed multiplicity model)*. As the multiplicity is increased, with other parameters being fixed, gelation concentration changes and the sol/gel line shifts on the temperature–concentration plane. Alternative cases in which the junction multiplicity exhibits a broad distribution were also discussed, but in what follows we mainly confine our study to the case of monodisperse junctions.

When a functional group involves ζ sequential repeat units as in the model junction, we can write the standard free energy change as

$$\Delta g_0 = \zeta(\Delta h_0 - T\Delta s_0) \tag{2.3}$$

Here Δh_0 is the enthalpy of bonding and Δs_0 the entropy of bonding, both measured *per single repeat unit*. Taking the logarithm, we find an important relation

$$\ln \phi^* = \zeta\frac{\Delta h_0}{k_BT} + \ln\left[\frac{f's'n}{f(f's' - 1)^{s/s'}}\right] - \zeta\frac{\Delta s_0}{k_B} \tag{2.4}$$

from which we start our data analysis.

III. Specific Systems of Homopolymer Gelation

For the model junction introduced above, each ζ sequence of repeat units along a chain may be regarded as a functional group. A polymer chain then carries

$$f = n/\zeta \tag{3.1}$$

functional groups.

Since we have large n, and hence large f, for polymers, we can neglect unity compared to n or f. We are thus led to an equation

$$\ln c^* = \zeta\frac{\Delta h_0}{k_BT} - \frac{1}{s - 1}\ln M + \text{constant} \tag{3.2}$$

where weight concentration c^* has been substituted for the volume fraction. This equation enables us to find ζ and s independently.

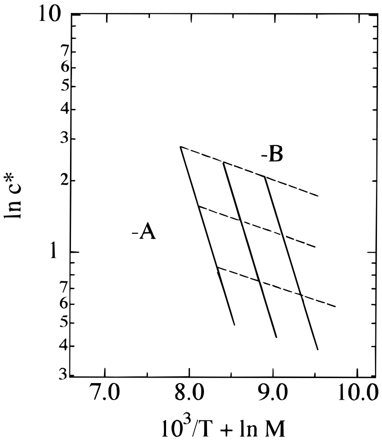

Figure 2. Schematic drawing of the modified Eldridge–Ferry plot to find the junction multiplicity s and the number ζ of repeat units in the junction per chain. The constant temperature lines (broken lines) and constant molecular weight lines (solid lines) are shown.

Let us plot $\ln c^*$ against $10^3/T + \ln M$. Then the slope $-B$ of the line at constant T gives $-1/(s - 1)$, while the slope $-A$ of the line at constant M gives

$$\zeta = \frac{10^3k_B}{|\Delta h_0|}A = \frac{10^3R}{|(\Delta h_0)_{\mathrm{mol}}|}A \tag{3.3}$$

where $(\Delta h_0)_{\mathrm{mol}}$ is the enthalpy of bonding per mole of the repeat units and R is the gas constant (10^3R = 1.9864 kcal/mol·K). This *modified Eldridge–Ferry procedure* is depicted schematically in Figure 2.

A. Polyethylene in Toluene. Let us apply the above procedure to some of the typical thermoreversible gels for which the sol/gel transition concentrations have been experimentally reported.

The first system we study is polyethylene in toluene.[11] In the case of crystallizable polymers such as polyethylene, the number ζ and multiplicity s are related to the size of the critical nucleus of microcrystallites. The binding enthalpy $|(\Delta h_0)_{\mathrm{mol}}|$ is regarded as the heat of fusion per mole of the crystalline segments. It is estimated to be 0.96 kcal/mol[12] for the bulk crystals. In this system a junction is formed by folded-chain lamellar crystallites rather than the proposed fringed micellar structure. The basic method of analysis, however, remains the same except that the free energy of chain folding at the junction surfaces must be included in the standard free energy change Δg_0. We here simply ignore this surface correction to illustrate how our fundamental idea works for a rough estimate of the junction size.

Figure 3 shows the gelation concentration reported in the paper[11] replotted against the combined variable proposed above. The molecular weight of the polymers covers the range from 3×10^3 to 6×10^6. The gelation concentration was determined by the test-tube inversion method. The data at constant temperature are connected by dotted lines, the linear fit of which gives a slope of $-B = -0.34$ for higher temperatures, though the slope fluctuates around this value for lower temperatures. From this value the average multiplicity is identified to be $s = 4.0$. Similarly, the gelation concentrations at fixed molecular weight with varied temperature are fitted by thin straight lines. They give a slope of $-A = -3.15$, hence leading to ζ = 6.25 kcal/mol/$|(\Delta h_0)_{\mathrm{mol}}|$. If we use for the heat of fusion the value in the bulk, we find $\zeta = 6.51$. Hence a junction contains

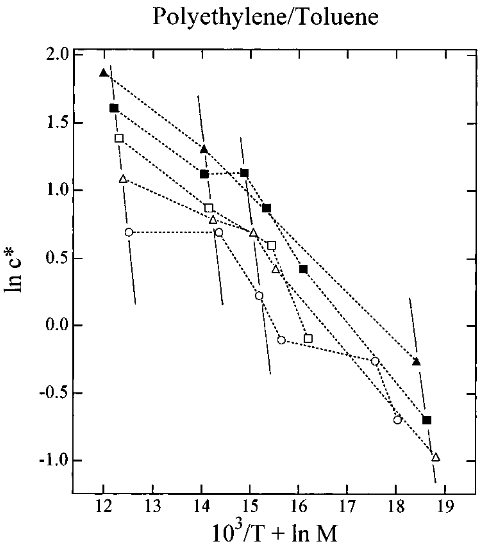

Figure 3. Modified Eldridge−Ferry plot applied to the gelation concentration of polyethylene/toluene solution. Dotted lines show the gelation concentration at constant temperature, while thin straight lines show those at constant molecular weight. (▲) 86.0 °C; (■) 60.8 °C; (□) 50.0 °C; (△) 41.3 °C; (○) 30.1 °C.

approximately $\zeta \times s = 26.0$ statistical units. This estimate is, of course, crude for several reasons. First, we neglected the free energy of chain folding. Second, we started with a hypothetical lattice cell which accommodates a statistical unit, as is in the conventional lattice theory of polymer solutions.[14] Our statistical unit (crystalline segment) of polymers must be regarded as a group consisting of several monomers. The number *z* of monomers in a statistical unit must be adjusted to produce proper solution properties.[15] The sequence number ζ must then be replaced by $z\zeta$ if we count it in terms of the number of monomers. Using the value per monomeric unit for the heat of fusion might, therefore, not be adequate. It is also to be noted that crystalline structure, and hence the heat of fusion, in microcrystalline junctions might be different from that in the bulk crystals. Finally, we neglected possible fluctuations in the multiplicity of the junctions. In spite of all these simplifications, our new method can give proper suggestion as to the structural parameters of the network junctions. More exact analysis requires detailed information on *z* and $(\Delta h)_0$, but it is beyond the scope of the present paper.

B. Polystyrene in Carbon Disulfide. The next solution we study is atactic polystyrene in carbon disulfide.[4,11,16] Polystyrene with random tacticity is chemically inactive and uncrystallizable. The mechanism of cross-linking has been the subject of a great deal of work,[4,11,16,17] but there still remains a divergence in opinions. One series of studies postulate[11] the existence of short crystallizable stereoregular segment sequences on polymer chains, even if they are atactic, which are responsible for the formation of microcrystalline junctions. Another study[4,17] reaches the conclusion that cross-linking takes place by forming stoichiometric compounds involving solvent molecules. If this complex formation is the mechanism of cross-linking, the gelation temperature is not a steadily increasing function of the polymer concentration but shows a maximum at a certain concentration,[17] so that it does not obey the Eldridge−Ferry formula. To illustrate the simplicity of our method, we here assume direct coupling between polymer segments and work with the model junction structure proposed above.

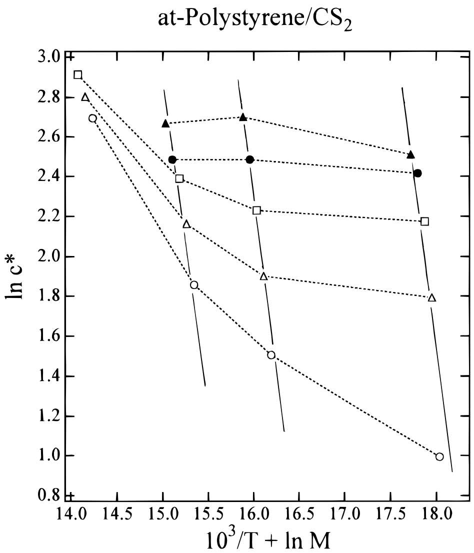

Figure 4. Same as in Figure 2 for at-polystyrene/CS_2 solution. (▲) −10 °C; (●) −15 °C; (□) −20 °C; (△) −25 °C; (○) −30 °C.

Figure 4 shows the result. The data on the gelation concentration found in ref 11 are replotted by our procedure. The slope of the curves at constant temperature varies from $-B = -0.06$ (*i.e.*, $s = 16.7$) at the highest temperature $T = -10$ °C to a larger value $-B = -0.41$ ($s = 3.4$) at the lowest temperature $T = -30$ °C. Existence of the different slopes suggests that the junction multiplicity of polystyrene gel depends on the temperature as $s = s(T)$; it becomes smaller as the temperature is lowered. In the classical theory of nucleation, the critical size of a crystallite to remain stable is proportional to $(\Delta T)^{-1}$, where ΔT is the degree of supercooling.[13] Thus cross-links with smaller junction multiplicities are preferable at lower temperatures, but they seem to remain thicker than a pairwise chain connection. In contrast, the slope of the curves at constant molecular weight (thin straight lines) gives a unique value $A = -3.84$, and hence $\zeta = 6.86$ kcal/mol/$|(\Delta h_0)_{\mathrm{mol}}|$. Use of the bulk value $|(\Delta h_0)_{\mathrm{mol}}| = 2.0$ kcal/mol for the heat of fusion of isotactic polystyrene[12] leads to a small value $\zeta = 3.43$, suggesting a short length of the crystallite. At very high supercooling the critical nucleus can be very small; thus it would be sufficient for only a very few chains to come together, which stick to form a stable nucleus with lateral dimensions still too small to create strain at the interface where chains emerge. A junction is estimated to include $\zeta \times s = 57$ (for $T = -10$ °C) and 12 (for $T = -30$ °C) statistical units in it.

C. Poly(vinyl alcohol) in Water. Poly(vinyl alcohol) (PVA) is known to be a typical crystalline polymer, but it also gels in aqueous solution under large supercooling. There are several experimental evidences that the cross-links are formed by partial crystallization of the polymer segments in which the syndiotactic sequences dominate, while subchains connecting the junctions consist mainly of atactic noncrystalline sequences on PVA chains.[18−20] The microcrystals at the junctions are supposed to be stabilized by hydrogen bonds between the hydroxy groups. In our previous work,[21] differential scanning calorimetry (DSC) and viscoelastic measurements were carried out to find the gelation temperature and gel melting temperature for PVA with different molecular weights covering the range from 2×10^4 to 8×10^5 in various concentrations. The gel melting temperature T_{m} is estimated from the temper-

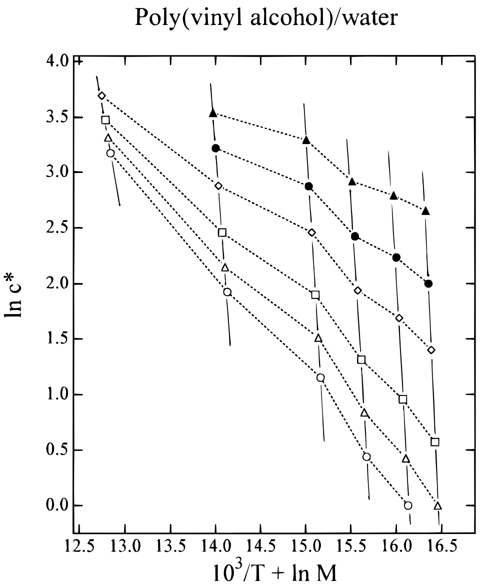

Figure 5. Same as in Figure 2 for poly(vinyl alcohol)/water solution. (▲) 91 °C; (●) 87 °C; (◇) 83 °C; (□) 78 °C; (△) 74 °C; (○) 71 °C.

ature at which the DSC heating curve shows an endotherm peak.

Figure 5 shows the result of our modified Eldridge–Ferry plot for the gel melting concentration. The slope of the solid lines with constant molecular weight gives $-A = 13.43$ almost independently of their molecular weights. Hence we find $\zeta = 26.7$ kcal/mol/$|(\Delta h_0)_{\mathrm{mol}}|$. If we use the heat of fusion $(\Delta h_0)_{\mathrm{mol}} = 1.64$ kcal/mol in the bulk crystal,[22] we find $\zeta = 16.3$. On the other hand, the slope of the dotted lines with constant temperature again depends on their temperature just as in the polystyrene solution. At the highest temperature $T = 91$ °C in the measurement, it is -0.38, while it gives a larger value -0.9 at $T = 71$ °C. The multiplicity is estimated to decrease from 3.6 for high-temperature melting to 2.1 for low-temperature melting, suggesting a very thin junction structure. From thermodynamic stability of the junctions it is only natural that a gel which melts at lower temperature has thinner junctions. The measurement of gel rigidity[18,19] and the melting temperature[20] suggested that a junction in PVA gel consists of syndiotactic sequences with 6–8 monomeric units. Our estimate gives a larger value, but, since it depends sensitively on Δh_0, further examination of the crystalline structure in the junction is necessary. There has been no report on the direct measurement of the multiplicity.

IV. Conclusions and Discussion

We have proposed a new method for the characterization of network junctions in thermoreversible gels. This method starts with a conceptual distinction between the junction size (the total number of monomers in a junction) and its multiplicity (the number of chains combined in it). It is shown that plotting the observed gelation concentration c^* on a logarithmic scale against a combined variable $10^3/T + \ln M$ enables us to evaluate the junction multiplicity and the junction length simultaneously and independently. The method is applied to the experimental data reported on the gelation of polyethylene in toluene, atactic polystyrene in carbon disulfide, and poly(vinyl alcohol) in water. For the ideal case in which polydispersity in the multiplicity is narrow, the calculations presented above encourage the expectation that our method may be broadly applicable to thermoreversible gels. When the distribution of the junction multiplicity is broad, however, eq 3.2 only gives suggestions as to structural characteristics of the network junctions. Several models to treat polydisperse junction multiplicity, for instance, the minimum junction multiplicity model or the saturating multiplicity model, were theoretically studied in our preceding paper.[6] Detailed examination of the polydispersity effect along this line will be reported elsewhere.

Another possible application of our new method is to the gelation of copolymers. For instance, crystallization of polyethylene blocks embedded in amorphous polypropylene chains leads to gelation of the copolymers whose transition concentration depends on the composition of the crystalline blocks which is proportional to the functionality f. Thus, by comparing polymers with different compositions, we can find the multiplicity from our starting equation (2.4). This can most easily be done by plotting $\ln c^*$ against $10^3/T + \ln f$. Specific examples will be reported in a forthcoming paper.

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