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Thermoreversible Gelation via Multichain Junctions[†]

Thermoreversible gelation has been observed in a variety of polymer solutions.[1–6] In many (though not all) cases it is clearly established[5] to be due to the formation of small crystalline regions or micelles acting as cross-links. Quantitative understanding remains rather incomplete. For example, in a given polymer/solvent system at a given temperature, the critical concentration ϕ_g for gel formation depends only weakly on polymer molecular weight. Also, the onset of association prior to gelation is observable over only a small range of concentration just below ϕ_g. In this paper we rationalize these observations, modifying a treatment by Tanaka[7] with the aid of the statistical description of systems with multichain junctions due to Fukui and Yamabe.[8]

The Tanaka formalism rests on two basic assumptions:

(a) The polymer/solvent system is described by standard Flory–Huggins thermodynamics[9] with a single interaction parameter χ for all species; i.e., it is a "quasi-binary" system.

(b) The polymer chains associate through *pairwise* contacts to form an equilibrium system of branched molecules distributed according to standard tree statistics.[9,10]

These two statements are mutually consistent since, as long ago shown by Flory,[11] chemical equilibria in quasi-binary Flory–Huggins systems follow the ideal mass-action law. However, the assumption of pairwise contacts does not correspond to the multichain nature of the micellar junctions (whether microcrystalline or amorphous) in actual thermoreversible gels. Fortunately, the Fukui–Yamabe theory[8] furnishes the required relations. As far as we have been able to ascertain, these have not previously been applied to physical association and thermoreversible gelation. Here we give one simple example, leaving a more general and complete discussion to a later time.

For simplicity we take the original unassociated polymer to be monodisperse, composed of chains with a molar volume r times that of the solvent V_0. On the average,[12] a chain bears f segments each capable of taking part in a junction binding s (>2) such segments together. For a polymer of given composition, f is proportional to r. Like the original tree theories for pairwise junctions, the Fukui–Yamabe theory excludes all cyclic structures, so that the s segments forming an s-tuple junction come from s different chains. (In polymers like a-PS or PVC we can imagine these segments to be stereoregular sequences capable of crystallization.) Let the degree of association of a branched molecule be n, an integer restricted to values $n = 1 + j(s - 1)$, where j is the number of s-tuple junctions in the molecule.

The chemical potential of the solvent is given by

$$(\mu_0 - \mu_0^\circ)/RT = \ln(1 - \phi) + \phi[1 - (r\bar{n}_n)^{-1}] + \chi\phi^2 \quad (1)$$

where ϕ $(=\sum_n \phi_n)$ is the total volume fraction of polymer. The number-average degree of association is

$$\bar{n}_n = 1/[1 - f\alpha(1 - s^{-1})] \quad (2)$$

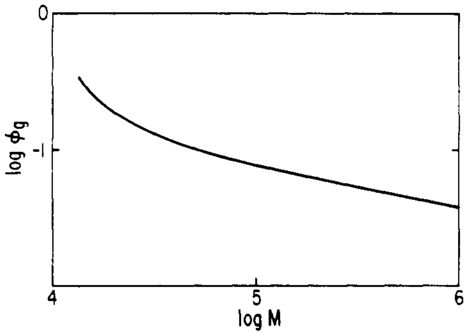

Figure 1. Double-logarithmic plot of critical gel concentration against primary molecular weight M, according to eqs 4 and 5 with $s = 6$, $f = 1.2 \times 10^{-4}$ M, $K_s = 4.49 \times 10^3$. Compare to Figure 13 of ref 5.

and the corresponding weight average is

$$\bar{n}_w = [1 + (s - 1)\alpha]/[1 - \alpha(s - 1)(f - 1)] \quad (3)$$

where α is the probability that a segment is part of a junction. It is seen that $\bar{n}_w$ diverges (i.e., gelation occurs) at

$$\alpha_g = 1/(s - 1)(f - 1) \quad (4)$$

and that Flory's classical result[13] corresponds to $s = 2$. Now it is straightforward to show that at equilibrium

$$\alpha/(1 - \alpha)^s = K_s\phi^{s-1} \quad (5)$$

where K_s is an equilibrium constant[14] independent of f. Thus we can combine eqs 4 and 5 to relate the critical concentration ϕ_g to the functionality f (and hence to the length r) of the chains. A sample result, for $s = 6$, is shown in Figure 1, which may be compared to the data of Domszy et al.[5] for various systems. Physically, the weak dependence of ϕ_g on chain length is directly due to the multiple nature of the junctions.

For low concentrations, expansions of eqs 1, 2, and 5 give the osmotic pressure:

$$\pi V_0/RT = (\phi/r) + \left(\frac{1}{2} - \chi\right)\phi^2 + \ldots - (f/r)(1 - s^{-1})K_s\phi^s \quad (6)$$

Thus, for $s > 2$, association is not evident in dilute solutions and makes no contribution to the second virial coefficient.

The detailed theory, to be presented elsewhere, involves distributions, rather than single values, of the variables r, s, and K_s. An approximate correction for the formation of rings[15,16] can be introduced, and scattering can be treated by appropriate adaptation of the random-phase approximation. Since mean-field arguments and equations are used throughout, the critical exponents at the gel point are inevitably the classical ones.

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References and Notes

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[†] Belatedly dedicated to Ron Koningsveld on his 65th birthday.

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CORRECTIONS

Wyn Brown* and Johan Fundin: Dynamical Behavior of High Molecular Weight Polystyrene in the Marginal Solvent 2-Butanone. Volume 24, Number 18, September 2, 1991, pp 5171–5178.

An incorrect version of Figure 8 was published. The correct version is as follows:

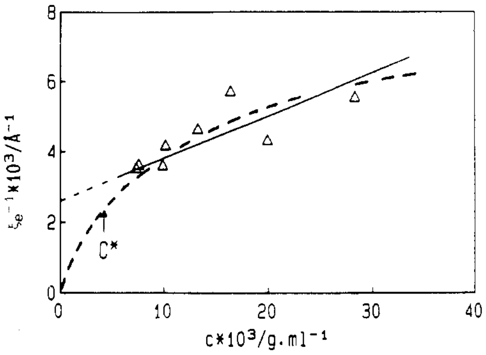

Figure 8. Plot according to eq 9 of the inverse dynamic correlation length versus concentration. The equation of the straight line is given in eq 10. The heavy dashed line is a scaling representation with exponent 0.5.