Theory of gel point in real polymer solutions

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Abstract. We develop a new theory of gelation which takes into account (i) delay of the gel point and (ii) change of functionality due to ring formation. We show that the problem of finding the gel point in real polymer solutions reduces to the problem of calculating the total ring concentration and the extent of reaction of intermolecular reaction at the gel point. In this paper, we solve a special case of this problem, on the basis of the independence assumption between intermolecular reaction and cyclization which takes into account only (i) the delay of the gel point: making use of the asymptotic equality of the total ring concentration, we acquire an approximate solution for the gel point $D_c$ as a function of the inverse concentration $\gamma$, the relative frequency $\varphi_j$ of cyclization and dimension $d$. Applying the observed values of $\varphi_j$ in linear polyesters, the theoretical result reproduces well the Wile and the Gordon-Scantlebury observations, showing the existence of a critical dilution $\gamma_c$ beyond which gelation can not occur, and an asymptote $\gamma_{asy}$. As the classical gel point is approached, the present theory reduces to the linear equation, which makes one-to-one correspondence with the real slope $\Delta$, suggesting the inequality $\Delta \geq \sum_j \varphi_j / \gamma_j (R-A_f + R-B_f, g)$ model which is just what polymer chemists have quested for so far, with the physical meaning having remained unknown.

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1 Introduction

Recently a very unique gel theory [1] appeared in statistical physics, where only rings play the role of monomer units, soft linkages (catenation) between ring molecules being formed progressively to a macroscopic cluster called Olympic gel. Making use of the power of the tree diagram, Raphael, Gay and de Gennes were able to estimate the gel point as a function of concentration. It is just this concentration dependence of the gel point that we discuss in this paper with regard to the traditional branching process where intermolecular reaction competes with cyclization.

There has not been a theory which predicts the gel point in real polymer solutions. To seek the gel point in real branching processes, it is necessary for us to take cyclization reaction into consideration which has been thought to be an essential part of the deviation [2] from the prediction of the classical theory of gelation. No one has known, however, the way of unifying the classical theories of gelation and the theories of cyclization. To overcome such situation, we here develop a new theory of gelation from a different point of view, taking into account (i) delay of the gel point, and (ii) change of functionality, due to cyclization, with the assumption of equireactivity being made for all functional units (FU’s) of the same type. We then introduce a fundamental equality of the gel point. We solve a special case of the equality, based on the independence assumption between intermolecular reaction and cyclization. The theoretical results are examined in the light of the Wile and the Gordon-Scantlebury experiments.

While it has been recognized earlier that the gel point is in close correlation with the amount of rings and the comprehension about ring formation has much progressed so far, the theoretical treatment of cyclization for multifunctional systems has been scarce. Gordon, Dusek, and coworkers [3] introduced the spanning tree approximation into the cascade process formalism [4]. Hoeve [5] generalized the Jacobson-Stockmayer treatment [6] to include rings in the R-A$_f$ polymer. Spouge [7] was the first to introduce the exact ring distribution functions into the branching process formalism. None of these approaches, however, has afforded analytic solutions of the gel point.

This paper deals with a straightforward extension of the previous work by the author [8], through the series expansion of the ring distribution functions in union with the classical picture of gelation.

2 Theory of gel point

There are conceivable two major effects, associated with cyclization reaction, which render the gel point shift. (i) One is simple delay of the gel point caused by cyclization, since branched molecules can grow only through intermolecular reaction. (ii) The other is the change
of functionality: once a functional unit (FU) on a branching unit is occupied by a cyclic bond, the functionality of the branching unit decreases exactly by the number of cyclic bonds.

We then inquire the question, “where is the gel point \( D_c \) predicted by the theory which takes into account all these effects ?” to answer this question, let us consider the branching system which has the original components of the type \( \text{R-A}_g + \text{R-B}_{(f-g)} \). This general system is defined by the statement that the type \( \text{R-A}_g \) molecules consist of \( M_0 \) monomer units bearing \( g \) functionalities, together with \( N_0 \) monomer units of \( f-g \) functionalities of the type \( \text{R-B}_{(f-g)} \); the A FU can react only with the B FU and vice versa (see Fig. 1).

Let \( D(\text{inter}) \) be the extent of reaction for A FU’s which undergo intermolecular reaction alone, and \( D(\text{ring}) \) be the corresponding quantity for cyclization. Note that the critical extent of reaction, \( D_c \), of gelation for A FU’s is separable

\[
D_c = D(\text{inter}) + D(\text{ring}).
\]

To express \( D(\text{ring}) \) analytically, we refer to the imaginary reaction in Figure 1 where three branched molecules are arranged (two monomers and one pentamer): On the largest molecule, one cyclic bond (dotted line) is formed. Including this cyclic bond, the four AB bonds compose the ring. Now cut anyone of these four bonds and the resultant molecule is simply a tree molecule without rings. It turns out that only one bond has been wasted by the cyclization, the other three bonds assisting the growth of the branching molecule. It is shown in general that only one bond is wasted every cyclization, irrespective of the size of rings. Bearing in mind that \( D(\text{ring}) \) is equivalent to the fraction of these excess bonds wasted through cyclization reaction, one has

\[
D(\text{ring}) = \frac{\Gamma}{gM_0}
\]

with \( \Gamma \) being the total number of rings at the gel point. Using the mole ratio of the respective FU, \( \kappa = (f-g) N_0/gM_0 \), and the reciprocal \( \gamma \) of the initial monomer concentration, we rewrite the above equation to get:

\[
D(\text{ring}) = \frac{f - (1 - \kappa)g}{g(f-g)}[\Gamma]\gamma,
\]

with the symbol \([ \cdot ]\) signifying the concentration, so that \([\Gamma] = \Gamma/V \) expressing the number concentration of rings. Here we have made use of the general definition of the initial monomer concentration \( C = (M_0 + N_0)/V(= 1/\gamma) \) in place of the previous definition \( C = M_0/V \).

Then we seek analytic expression of \( D(\text{inter}) \). For this purpose, consider the general case of a mixing system with different functionalities of the types \( \text{R-A}_g + \text{R-B}_{(f-g)} \) \((i, j = 1, 2, 3, \ldots)\), each having \( g_i \) and \((f-g)_j \) FU, and \( M_i \) and \( N_j \) branching units, respectively; e.g., \( \{g_i\} = \{1, 2, \ldots\} \). Here \( M_0 = \sum_i M_i \) and \( N_0 = \sum_j N_j \). A central idea is that the distribution of functionalities is caused by cyclic bonds which prevent FU’s from forming intermolecular bonds. Consider an \( m \)-tree which has \( m \) unreacted A FU’s in the first generation. Let \( N(A)_j \) be the number of A functional units in the \( j \)th generation. In equilibrium, \( N(A)_j \) may satisfy the recurrence relation of the form:

\[
N(A)_j = [(\langle g \rangle - 1)(\langle f - g \rangle - 1)D_A D_B]N(A)_{j-1}. \tag{3}
\]

where the subscripts \( A \) and \( B \) denote the quantity for the A and the B FU, respectively; \( \langle g \rangle = \sum_k \chi_{g_k} g_k \) and \( \chi_{g_k} \) signifies the fraction of \( g_k \). \( \chi_{g_i} = g_i M_i / \sum_k g_k M_k \). Thus \( \langle \cdots \rangle \) expresses the weight average of functionalities which undergo intermolecular reaction. The solution for equation (3) is \( \[8\]

\[
N(A)_j = ((\langle g \rangle - 1)(\langle f - g \rangle - 1)D_A D_B)^{j-2}N(A)_2. \tag{3'}
\]

The gel point is a point when an infinitely large cluster emerges, where the sum \( \sum_j N(A)_j \) must diverge, giving the critical condition in the mixing system of the equimolar case \( \kappa = 1 \):

\[
D(\text{inter}) = \sqrt{\frac{1}{(\langle g \rangle - 1)(\langle f - g \rangle - 1)}}.
\]

Generalizing the concept of the mixing system to include cyclization, and substituting into equation (1), we arrive at the fundamental equality:

\[
\sqrt{\frac{1}{(\langle g \rangle - 1)(\langle f - g \rangle - 1)}} = D_c - \frac{f[\Gamma]}{g(f-g)}\gamma, \tag{4}
\]

Now the problem of finding the gel point in real polymer solutions reduces to the problem of solving the equality (4). The gel point is therefore calculable by means of the weight average functionality and the total ring concentration at the gel point. In this paper, we show a special solution of this equality (4), based on the independence assumption between intermolecular reaction and cyclization.