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Theory of gel point in real polymer solutions

K. Suematsu

Kohno Medical Institute, Tomitahama 26-14, Yokkaichi, Mie 512, Japan

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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 γ, the relative frequency φ_j of cyclization and dimension d. Applying the observed values of φ_j in linear polyesters, the theoretical result reproduces well the Wile and the Gordon-Scantlebury observations, showing the existence of a critical dilution γ_c beyond which gelation can not occur, and an asymptote γ_{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 $\varDelta$, suggesting the inequality $\varDelta \geq \frac{f\sum_j \varphi_j/2j}{g(f-g)}$, (R-A$_g$+R-B$_{f\text{-}g}$ model) which is just what polymer chemists have quested for so far, with the physical meaning having remained unknown.

PACS. 36.20.-r Macromolecules and polymer molecules

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

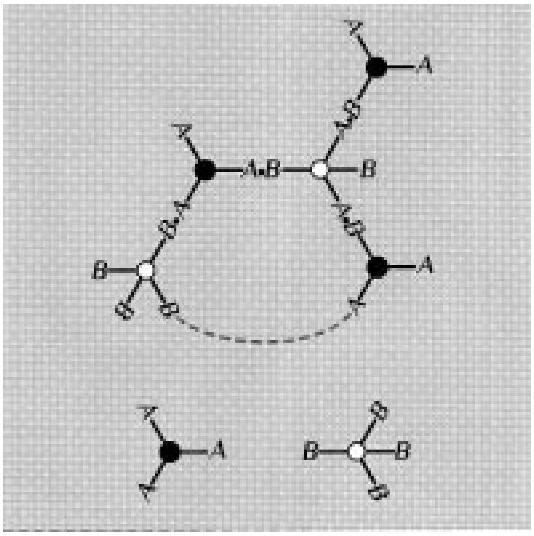

Fig. 1. Model reaction for the typical branching process of the R-A$_g$ + R-B$_{f\text{-}g}$ model. (●): A-type monomer unit;(○): B-type monomer unit. In this case, $g = 3$, $f - g = 4$, $M_0 = 4$, $N_0 = 3$ and $\kappa = 1$.

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 R-A$_g$ + R-B$_{f\text{-}g}$. This general system is defined by the statement that the type 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 R-B$_{f\text{-}g}$; the A FU can react only with the B FU and *vice versa* (see Fig. 1).

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

$$D_c = D(inter) + D(ring). \tag{1}$$

To express $D(ring)$ 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 $D(ring)$ is equivalent to the fraction of these excess bonds wasted through cyclization reaction, one has

$$D(ring) = \Gamma / g M_0$$

with Γ being the total number of rings at the gel point. Using the mole ratio of the respective FU, $\kappa = (f - g) N_0 / g M_0$, and the reciprocal γ of the initial monomer concentration, we rewrite the above equation to get:

$$D(ring) = \frac{f - (1 - \kappa) g}{g(f - g)} [\Gamma] \gamma, \tag{2}$$

with the symbol [ ] 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 $C = (M_0 + N_0)/V (\equiv 1/\gamma)$ in place of the previous definition [8] $C = M_0/V$.

Then we seek analytic expression of $D(inter)$. For this purpose, consider the general case of a mixing system with different functionalities of the types R-A$_{g_i}$ + R-B$_{(f\text{-}g)_j}$ $(i, j = 1, 2, 3, \ ...)$, each having g_i and $(f\text{-}g)_j$ FU, and M_i and N_j branching units, respectively; *e.g.*, $\{g_i\} = \{1,\ 2,\ ...\}$. 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 jth 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; $\langle g \rangle = \sum_{k=1} \chi_{g_k} g_k$ and χ_{g_k} signifies the fraction of g_k, $\chi_{g_t} = g_k M_k / \sum_k g_k M_k$. 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 $\kappa = 1$:

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

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.

2.1 Special solution: Independence model

The independence model is the most primitive paradigm which was introduced in the previous paper, giving an explicit solution, where one introduces Assumption I: *The critical extent of reaction shifts upward exactly by the number of transitions for cyclization.*

The terminology, *transition*, stands for a microscopic process in which an unreacted FU jumps to form a bond [8]. Since a branching process must develop through either intermolecular reaction or cyclization, the number of transitions for cyclization can be equated with the number of rings. Mathematically, *Assumption I* is equivalent to state that intermolecular reaction takes place independently without interference by ring formation. Hence, it follows that cyclization causes (i) the delay of the gel point, but not (ii) the change of functionality.

One way of rationalizing *Assumption I* is to take notice that cyclization reaction is subordinate to intermolecular reaction: Consider an initial stage in the R-A_g + R-$B_{f\text{-}g}$ branching reaction, then pay attention to an A-type functional unit (FU) on a randomly chosen R-A_g branching unit. The reaction must commence with intermolecular bonding, because the A FU can react only with a B FU (Fig. 1). In order for the A FU to undergo cyclization, it is essential for the FU to belong to a cluster greater than dimer; hence, the branching unit bearing the FU in question must possess more than one intermolecular bond in advance. Since, as discussed above (the 4th paragraph in Sect. 2), a ring contains only one cyclic bond (the others deriving from intermolecular reaction), the mean fraction of intermolecular bonds within a ring increases with increasing size of the ring. Cyclization reaction is thus essentially secondary in bond formation. This implies that the change of functionality is not of primary importance in respect to the shift of D_c.

Let D_{co} represent the classical gel point predicted by the ideal tree theory. *Assumption I* claims the identity $D(inter) \equiv D_{co}$, and consequently,

$$D_c = D_{co} + \frac{f[\mathit{\Gamma}]}{g(f-g)}\gamma\,. \tag{5}$$

In the following, we seek an explicit expression of equation (5).

2.1.1 R-A_g + R-$B_{f\text{-}g}$ model

The general solution of $[\mathit{\Gamma}]$ has been yet unknown, but we already know the asymptotic solution of the following:

$$[\mathit{\Gamma}]_{\gamma=0} = \sum_{j=1}^{\infty} \varphi_j [(g-1)(f-g-1)D^2]^j/2j, \tag{6}$$

with φ_j denoting the relative frequency of cyclization of j-chain to intermolecular reaction, equivalent to the ratio of the respective rate constants. This important formula was first found by Spouge [7] and later by the present author [8]. In the limit of $\gamma \to 0$, excluded volume effects should vanish rigorously, and polymer molecules become ideal. Hence, on average conformation of long chains, φ_j is expected to be Gaussian, in proportion to $j^{-d/2}$(d: dimension).

Let us confine our discussion to the case $d \geq 3$. If we are in high concentration regime, we think equation (6) is a good approximation of $[\mathit{\Gamma}]$, so we write it as a function Z of D_c

$$Z(D_c) = [\mathit{\Gamma}] \cong \sum_{j=1}^{\infty} \varphi_j [(g-1)(f-g-1)D_c^2]^j/2j. \tag{6'}$$

Note that equation (6) is physically meaningful only below $D \leq D_{co}$, since, beyond this point, the right-hand side sum diverges. So, equation (6') is a provisional equality being prepared only for mathematical convenience in the course of seeking the general solution of the gel point. With this temporary equality in mind, we expand Z with respect to $D_c = D_{co}$,

$$\begin{aligned} Z(D_c) \cong Z(D_{co}) &+ \left[\frac{\partial Z}{\partial D_c}\right]_{D_c=D_{co}} (D_c - D_{co}) \\ &+ \frac{1}{2}\left[\frac{\partial^2 Z}{\partial D_c^2}\right]_{D_c=D_{co}} (D_c - D_{co})^2 + \cdots \end{aligned}$$

The basic idea of this expansion method is to justify the equality (6') which is exact and makes sense in the limit of $D_c \to D_{co}$, or $\gamma \to 0$.

Here we note that $Z^{(n)}$ diverges in the higher order of $n \geq 2$, say, the $\sum_j \varphi_j$ term of the second derivative $Z^{(2)}$. So, we collect the leading two terms of $Z^{(0)}$ and $Z^{(1)}$; the manipulation amounts to applying the mean value theorem:

$$Z(D_c) = Z(D_{co}) + Z^{(1)}(\xi)(D_c - D_{co}),$$

in which we are now making the approximation: $Z^{(1)}(\xi) \cong Z^{(1)}(D_{co})$. Then substituting into equation (5), one has the solution

$$D_c = D_{co}\left\{\frac{1 - \frac{f}{g(f-g)D_{co}}\sum_j (1-1/2j)\varphi_j\gamma}{1 - \frac{f}{g(f-g)D_{co}}\sum_j \varphi_j\gamma}\right\}, \tag{7}$$

where we have made use of the critical relation, $(g-1)(f-g-1)D_{co}^2 = 1$. As $\gamma \to 0$, equation (7) reduces to

$$D_c = D_{co} + \frac{f\sum_j \varphi_j/2j}{g(f-g)}\gamma\,. \tag{8}$$

When we return to former definition of γ,

$$\frac{f}{f-g}\gamma \to \gamma,$$

namely, $C = (M_0 + N_0)/V \to M_0/V$, we now realize that the previous treatment [8] by the authors was actually the first approximation which took into account only the smallest ring (see Appendix):

$$\sum_{j=1}^{\infty} \varphi_j [(g-1)(f-g-1)D^2]^j/2j \to \varphi_1 (g-1)(f-g-1)D^2/2.$$

In the same way one gets for the

2.1.2 R-A_f model

$$D_c = D_{co}\left\{\frac{1-\frac{f-1}{f}\sum_j(1-1/j)\varphi_j\gamma}{1-\frac{f-1}{f}\sum_j\varphi_j\gamma}\right\}, \tag{9}$$

and for the

2.1.3 A_g-R-B_{f-g} model

$$\begin{aligned} D_c &= D_{co}\left\{\frac{1-(1/gD_{co})\sum_j(1-1/j)\varphi_j[gD_{co}]^j\omega_j\gamma}{1-(1/gD_{co})\sum_j\varphi_j[gD_{co}]^j\omega_j\gamma}\right\},\\ \omega_j &= \frac{1}{2}\left\{(1-\alpha^{1/2})^j+(1+\alpha^{1/2})^j\right\};\\ \alpha &= (g-1)(f-g-1)/g(f-g), \end{aligned} \tag{10}$$

respectively, where D represents the quantity of A FU's likewise.

Critical dilution γ_c

As the denominator decreases in equation (7), the D_c value augments. Since the extent of reaction can not exceed unity, so there must exist a critical dilution γ_c, beyond which gelation can not occur. To find the quantity, we put $D_c = 1$ to obtain the solution for the R-A_g+R-$B_{f\text{-}g}$ model:

$$\gamma_c = \frac{1-D_{co}}{\frac{f}{g(f-g)}\sum_{j=1}^{\infty}(1/D_{co}-1+1/2j)\varphi_j}\,\cdot \tag{11}$$

Asymptote γ_{asy}

Mathematically, the denominator may decrease further to approach the zero point where divergence of D_c occurs, indicating the existence of an asymptote on the γ axis. Equating the denominator of equation (7) with 0, the solution becomes

$$\gamma_{asy} = \frac{g(f-g)}{f\sum_j\varphi_j}D_{co}, \tag{12}$$

for the R-A_g+R-B_{f-g} case.

Dimensionality

It is worth mentioning the problem of dimensionality. It has been known that, for a long chain of high concentration, the end-to-end distance distribution can be well approximated by the Gaussian form [9]

$$\begin{aligned} P(r)d\vartheta = \left(\frac{d}{2\pi\langle r_j^2\rangle}\right)^{\frac{d}{2}}&\left\{1+\left(-\frac{d}{2\langle r_j^2\rangle}r^2\right)\right.\\ &\left.+\frac{1}{2}\left(-\frac{d}{2\langle r_j^2\rangle}r^2\right)^2+\cdots\right\}d\vartheta, \end{aligned}$$

which is valid for all dimensions. Cyclization probability [6] is the probability that one end of a polymer chain enters a volume ϑ around another end having a radius of a bond length ℓ. And it follows that

$$\mathcal{P}(r\le\ell) = \int_0^{\ell} S_d P(r)dr,$$

with S_d being the surface area of a d-dimensional sphere. This quantity is related to φ_j according to

$$\varphi_j = \frac{1}{\vartheta}\mathcal{P}(r\le\ell)\cdot$$

It is easy to show that because of the presence of the exponential term $\{\cdots\}$, the above integral is a rapidly decreasing function of d. If we confine our discussion to a long chain so that the inequality $\langle r_j^2\rangle \gg d$ is fulfilled, then by the relation, $dr^2/2\langle r_j^2\rangle \cong 0$, the cyclization probability $\mathcal{P}(r\le\ell)$ reduces to

$$\mathcal{P}(r\le\ell) \cong \left(\frac{d}{2\pi\langle r_j^2\rangle}\right)^{\frac{d}{2}}\vartheta,$$

resulting in the familiar expression of

$$\varphi_j = \left(\frac{d}{2\pi\langle r_j^2\rangle}\right)^{\frac{d}{2}},$$

which decreases strongly with d, because of the inequality $\langle r_j^2\rangle \gg d$.

Thus, in the regime of $\langle r_j^2\rangle \gg d$, as d increases, cyclization tends to be more suppressed, so that the gel point should approach to the classical theory [2,10]. We already know that, with increasing d, space volume renders excluded volume effects negligible [11]a. As a result, at high dimension, a branched molecule behaves as an ideal tree with no rings and no excluded volume effects, in harmony with the prediction by the percolation theory [11].

In the following section, we shall examine these theoretical results with experimentally observed data, and show that the independence model is quite successful.

3 Examination of theory with observations [12]

In his experiment on gelation of an adipic acid-pentaerythritol mixture (R-A_2+R-B_4) diluted by tetramethyleneglycol (Fig. 2), Wile [13] showed earlier that the observed gel points are extrapolated exactly to the classical gel point when plotted as against the inverse concentration $\gamma(=1/C)$. With this discovery, the ideal tree theory [2,10] has exceeded the framework of an abstract mathematical model, establishing firmly the classic status equal to the ideal gas to the real gas. In Figure 3 are plotted the observed points (◇) by Wile.

About 20 years later, Gordon and Scantlebury [14] have reexamined the concentration dependence of the gel

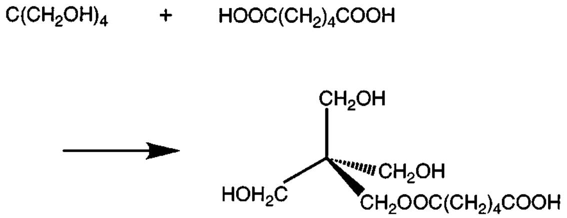

Fig. 2. Polymerization of the adipic acid-pentaerythritol mixture (R-A_2+R-B_4).

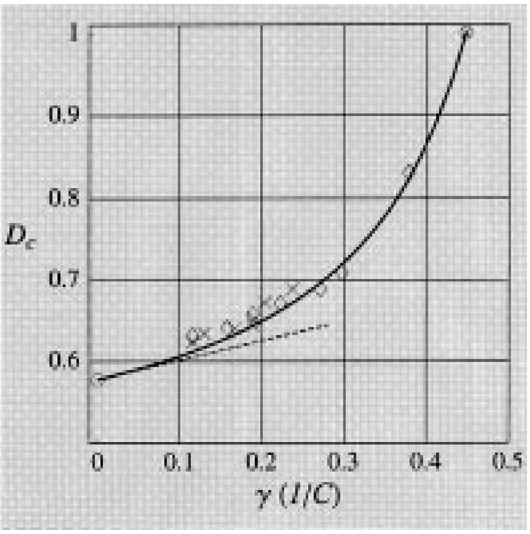

Fig. 3. D_c *vs.* γ curve. (◇): experimental points by Wile; (×): experimental points by Gordon and Scantlebury; (○): classical critical point, D_{co}; (⊗): critical dilution, γ_c; Solid line (-): theoretical line by equation (7); Dashed line (···): theoretical line by equation (8).

points for the same mixture, arriving at the same conclusion as in the Wile case. Their observed values are plotted in Figure 3 using the symbol (×).

To superimpose the present theory on the experimental points, it is needed to estimate the sums $\sum_j \varphi_j/2j$ and $\sum_j \varphi_j$. Fortunately, it has been well theorized that φ_j obeys the power law $j^{-3/2}$ for sufficiently long chains in concentrated solutions [2,9], and numerical calculation shows $\sum_j j^{-3/2} \approx 2\sum_j j^{-5/2}$. Once there was a time when much efforts have been devoted to measuring φ_j: Jones and coworkers [15] pursued ring-chain equilibria of linear aliphatic polyesters, measuring the equilibrium constant K_x which is correlated with φ_x by the relation

$$K_x = \varphi_x/2x.$$

In Table 1 are summarized the Jones and coworkers' observations, and for reference, an example of the aromatic polyester, poly(ethylene terephthalate) [16]. We see that the amounts of $\sum_x \varphi_x$ are about two times larger than are expected from the foregoing power law, which, however, can be ascribed to less production of the smaller rings of the size $x = 1$ and 2. We inspect this problem in more detail in the following.

Table 1. Observed values for the relative frequency of cyclization in linear polyesters.

Polyester	$\sum_{x=1}^{\infty} \varphi_x/2x$	$\sum_{x=1}^{\infty} \varphi_x$
Jones and coworkers[a]		
[$O(CH_2)_3OCO(CH_2)_2CO$]	0.100	0.830
[$O(CH_2)_{10}OCO(CH_2)_4CO$]	0.066	0.488
Cooper and Semlyen[b]		
[$O(CH_2)_2OCOC_6H_4.CO$]	(0.06)	(0.75)

Calculated using the experimental values for small cyclics, and applying the power law for larger cyclics; a: From reference [15]; b: From reference [16].

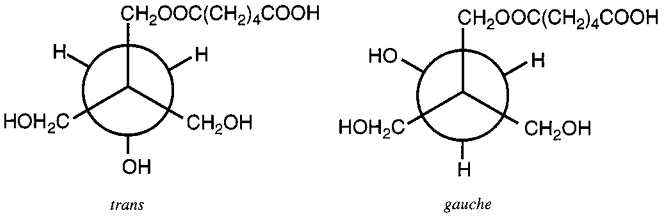

Fig. 4. Newman projection for the dimer molecule in the adipic acid-pentaerythritol mixture.

The polyesters shown in Table 1 have repeating units consisting of 9 and 18 skeletal bonds, respectively, while the adipic acid-pentaerithritol polymer has the repeating unit of 11 bonds on the same kind of aliphatic backbone, the intermediate length of the linear polyesters in Table 1. Hence, Jones and coworkers' experiment is a good measure for the present calculation. Only the both polyesters differ in one point: branched polymer has, in their own nature, large substituents, to which, in the present case, the hydroxy methyl moieties, or the ester derivatives correspond (Fig. 4).

Early in 1910's, it has been perceived by European organic chemists that some sort of substituents greatly accelerate the rate of cyclization [17]. (Azelaonitrile converts to cyclic ketone at about 30% yield according to the Thorpe-Ziegler reaction, while α, α' - dimethylazelaonitrile converts nearly exclusively to the corresponding cyclic ketone under the same reaction condition). This type of substituent effect has been called "gem-dimethyl effect" or "Thorpe-Ingold effect" after Beesley, Ingold and Thorpe, which has been comprehended as follows: In order for one end FU on a chain molecule to encounter the other end for cyclization, it is essential for the chain molecule to take *gauche* conformation, requiring some steric energy, on one hand. Since this steric effect appears most remarkably together with transannular effects in 8- to 20-membered ring formation, it is called at present "medium size ring effect", and we know that it depresses extremely in many cases the production of the corresponding rings.

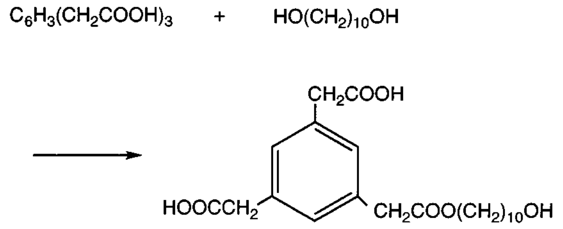

Fig. 5. Polymerization of the 1,3,5-Tri(carboxymethyl) benzene-Decamethyleneglycol mixture (R-A_2 + R-B_3).

This is the primary source of the foregoing $\sum_j \varphi_j$ anomaly (Tab. 1). Given gem-substituents, on the other hand, the energy of gauche conformation to trans conformation relatively decreases, thus raising the relative frequency of cyclization to intermolecular reaction.

On the basis of the above consideration, here we take in the trial values

$$\sum_j \varphi_j/2j = 0.32 \text{ (mol/l)}; \sum_j \varphi_j = 4 \times 0.32,$$

which amounts to estimating about 6 times higher the production of the cyclic 1-mer. This is seemingly considerably large, but likely in the light of the gem-substituents effect. Applying these values, it is found that the present theory (7) reproduces, in excellent agreement, the Wile observations, giving a critical dilution at $\gamma_c = 0.448$ and an asymptote at $\gamma_{asy} = 0.601$ (Fig. 3). Noteworthy is the fact that γ_c and γ_{asy} appear in very high concentration regime of $C \gg 1.0$ mol/l. To confirm these findings, it is essential for us to examine the present theory through a branched polymer system without the gem- substituents effect.

For this purpose, let us take up the 1,3,5-tri(carboxymethyl)benzene-decamethyleneglycol system (Fig. 5), the concentration dependence of the gel points of which has been reported by Ross-Murphy [18]. In this polymer system we expect ordinary values of $\sum_x \varphi_x/2x$ and $\sum_x \varphi_x$. The experiment for the linear polyesters in Table 1 is again a good measure. Taking an average of the observed values by Jones and coworkers, we put:

$$\sum_x \varphi_x/2x = 0.085; \sum_x \varphi_x = 8 \times 0.085.$$

Substituting these values into equation (7), we see that the theoretical curve (solid line) is in good agreement with the experimental points (◇) (Fig. 6), giving a critical dilution $\gamma_c = 0.96$, and an asymptote $\gamma_{asy} = 1.248$, greater than in the adipic acid-pentaerythritol polymer system, which arises from less production of rings in the 1,3,5-tri(carboxymethyl)benzene-decamethyleneglycol polymer system.

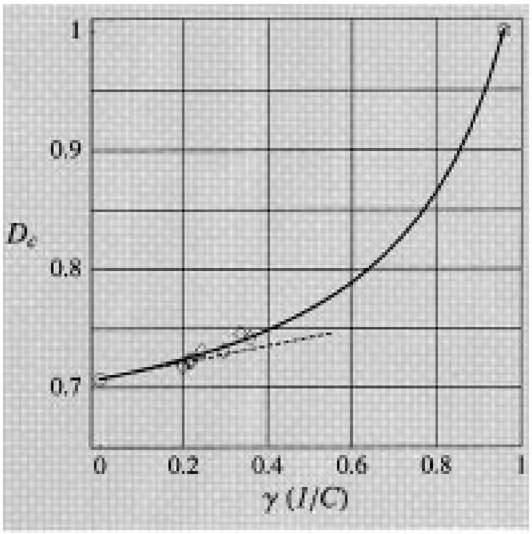

Fig. 6. D_c *vs.* γ curve. (◇): experimental points by Ross-Murphy; (○): classical critical point, D_{co}; (⊗): critical dilution, γ_c; Solid line (-): theoretical line by equation (7); Dashed line (···): theoretical line by equation (8).

Linear relationship

The straight lines in Figures 3 and 6 show tangents at $\gamma = 0$ in the D_c *vs.* γ curves. Bearing in mind the good agreement between the present model and the observed points, we attribute the observed slope as follows:

$$\varDelta \leftrightarrow \frac{f \sum_{j=1}^{\infty} \varphi_j/2j}{g(f-g)}.$$

More exactly, one must take into account the change of functionality ignored by the present model. For this purpose, expand the left-hand side term of equation (4) as a function of γ and neglect all correction terms to yield:

$$D_c = D_{co} + \left\{ \epsilon + \frac{f \sum_j \varphi_j/2j}{g(f-g)} \right\} \gamma. \tag{13}$$

ϵ signifies the first, differential coefficient for $D(inter)$, and hence represents a partial slope due to the change of functionality. Now it becomes possible to make one-to-one correspondence with the real slope $\varDelta$

$$\varDelta \equiv \epsilon + \frac{f \sum_j \varphi_j/2j}{g(f-g)}, \tag{14}$$

which is just what polymer chemists have quested for so far, with the physical meaning having remained unknown.

4 Discussion

Through the present study, we have encountered three infinities: one is the divergence of the total ring concentration, the other is that of $Z^{(n)}$ in the Taylor series, and another is that of D_c at γ_{asy}. All these are the manifestation of the essence of critical phenomena. Dodging these infinities by means of mathematical operations, we have acquired the special solutions (7, 9, 10) for the fundamental equality, based on the independence assumption.

Table 2. Theoretical results by equation (7). The observed values are shown for comparison.

	Adipic acid-Pentaerythritol polymer system				1,3,5-Tri(carboxymethyl)benzene-Decamethyleneglycol polymer system			
	$\sum_j \frac{\varphi_j}{2j}$	$\sum_j \varphi_j$	γ_c	γ_{asy}	$\sum_j \frac{\varphi_j}{2j}$	$\sum_j \varphi_j$	γ_c	γ_{asy}
Theoretical Model	0.32	4 × 0.32	0.45	0.60	0.085	8 × 0.085	0.96	1.25
Experiments:								
Linear Polyester (Jones and coworkers)	–	–	–	–	0.066 $\sim$ 0.10	0.488 $\sim$ 0.83	–	–
Branched Polyester (Wile)	–	–	$(\approx 0.4)^a$	–	–	–	–	–

a: Extrapolated to $D_c = 1$.

As we have seen in Figures 3 and 6, the theoretical result (7) is in accordance with the experimentally observed points. More importantly, it predicts, equally to the preceding theory [8], the existence of (i) a critical dilution and (ii) an asymptote.

The trial values of φ_x employed here, especially for the adipic acid-pentaerithritol polymer system, might be controversial (Tab. 2), but those are inside the permissible range in the light of the gem-substituents effect, so we think sufficiently realistic.

In spite of the striking success, the independence model ignores an essential side, the change of functionality. Certainly, intermolecular reaction must be interfered by cyclic bonds, so the change of functionality should occur, slightly raising the D_c value. Thus, the independence model underestimates the curvature of the $D_c - \gamma$ lines, say, equation (13), and accordingly tends to overestimate the concentration of rings (Tab. 2). The good agreement of the theoretical curves with the experimental data using the reasonable φ_x values, on the other hand, gives evidence that the change of functionality is not of primary importance in respect to the shift of the gel point. Probably, this is because a gelling process is generally not in equilibrium and cyclization is essentially secondary in bond formation.

Clearly there exists still another effect that the present theory ignores, in close relation with the recent work by Raphael, Gay and de Gennes [1]. The soft linkage among rings, the catenation, may occur, which is expected to work so as to shift the gel point downward, canceling out to some extent the above functionality effect.

It is important to stress that the position of the critical dilution γ_c is very susceptible to the quantity, φ_x. So, there is a hope in future that if we can devise some experimental technique to measure γ_c, then combining with the determination of the tangent at D_{co}, we would be able to gain valuable informations about occurrence of cyclization in branched polymer solutions.

In order to look at the present result from another point of view, equation (7) is plotted as a function of C (Fig. 7); experimental points are again Wile's and Gordon-Scantlebury's ones. The theoretical line is comparable to the site-bond diagram [11] in the percolation theory.

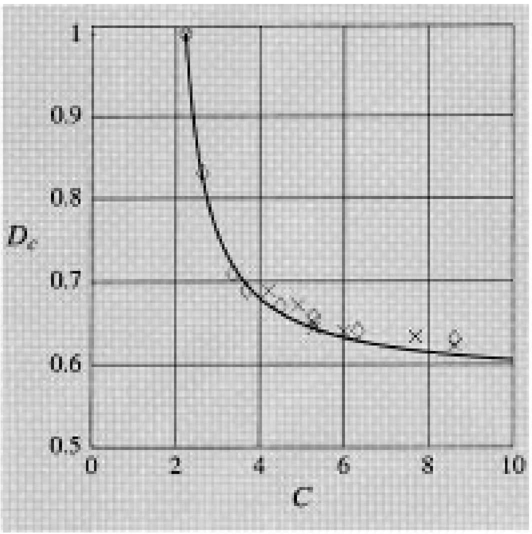

Fig. 7. D_c *vs.* C curve. ($\diamond$): experimental points by Wile; ($\times$): experimental points by Gordon and Scantlebury; ($\otimes$): critical dilution, γ_c; Solid line (-): theoretical line by equation (7).

5 Concluding remarks

The problem of finding the gel point D_c in real polymer solutions has reduced to the problem of calculating the total ring concentration and the change of functionality for intermolecular reaction at the gel point.

We have solved a special case of this problem based on the independence assumption between intermolecular reaction and cyclization: With the help of the asymptotic equality (6') of the total ring concentration and making use of the Taylor series expansion with respect to $D_c = D_{co}$, we have obtained the closed expression (7) of the gel point as a function of the inverse concentration

γ. Equally to the preceding derivation, the present theory makes prediction of the existence of a critical dilution and an asymptote.

The theoretical results have been examined in the light of the experiments in the branched polymer systems with and without the gem-substituents effect, showing good agreement with the observations. Taking into account the good predictability of the independence model, and comparing with the tangent (13), we attribute the observed slope $\varDelta$ as follows:

$$\varDelta \geq \frac{f \sum_{j=1}^{\infty} \varphi/2j}{g(f-g)}.$$

Appendix

In the previous work [8b], we have derived the tangent of the form:

$$D_c = D_{co} + \frac{c_1 D_{co}^2}{2g}(1/C). \tag{A.1}$$

Using the present definition of $1/C$, it follows that

$$D_c = D_{co} + \frac{f}{g(f-g)}(c_1/2) D_{co}^2 \gamma \tag{A.2}$$

We now compare equation (A2) with equation (8) to find the correspondence:

$$\frac{c_1}{2} D_{co}^2 \leftrightarrow \sum_j \varphi_j [(g-1)(f-g-1)D_{co}^2]^j / 2j,$$

whence we can attribute

$$c_1 = \varphi_1 (g-1)(f-g-1). \tag{A.3}$$

In reference [8b], we have employed $c_1 \approx 4.7$. With $g = 2$ and $f - g = 4$, it follows from equation (A.3) that $\varphi_1 \approx 1.6$, while, in the present case, $\sum_j \varphi_j \approx 1.3$ (see Tab. 2). These are of the same order, and consistent with each other.

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