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A new gelation theory

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Summary

Based on an infinite network gel model, using Graph theory and Probability as investigative tools, first of all, advanced a new theory about predicting the gel point P_C .The critical state equations of gelation for three kinds of non-linear polymerization have been derived. The P_c obtained by these equations lies between the results from Carothers equation and Statistical theory, and is in good agreement with experimental results.

Introduction

The conception of gelation was first put forward by Carothers. He took $\overline{X_n} \rightarrow \infty$ as a gel model and derived a useful relationship between the extent of reaction at gel point and the average functionality, $\bar{f}$, that is, Carothers equation $P_c = 2/\bar{f}$.(1)
Flory and Stockmayer laid out the basic relations of the statistical theory of non-linear polymerization(2,3). Later on, many theoretical works such as Combinatorial arguments(4), Stochastic branching process, Recursive technique(5), and Resolving kinetic equation(6) et al. were developed. These theories all belonged in the statistical category. The gel model that statistical theory was based on was that the weight-average degree of polymerization approached infinity ($\overline{X_w} \rightarrow \infty$).
In contrast to the experimental results, the Pc given by Carothers equation ($\overline{X_n} \rightarrow \infty$) was consistently higher, the Pc from the statistical theory ($\overline{X_w} \rightarrow \infty$) conversely was lower(1). It is said that the appearance of this regular deviation was due to the hypotheses for simplifying derivation (no intra-molecular cyclization and equal reactivity of functional groups), and people had implemented several revisions to reduce the deviation(7,8). But,

authors of this paper consider that the main reason for appearing above deviation is not from the hypotheses, but from the inappropriateness of the gel model. For neither Carothers model ($\overline{X}_n \rightarrow \infty$) nor the statistical model ($\overline{X}_w \rightarrow \infty$) represent the real structure of a gel.

In view of the above mentioned facts, this paper, on the gel model of an infinite network and with Graph theory and Probability as mathematical tools, firstly presented a new theory for predicting the gel point P_c.

General Principle

1. *Contents of Graph theory(9)*

Let us consider a graph with n vertices, m edges and ρ connected components, its cyclomatic number $\gamma_{(G)}$ equals

$$\gamma_{(G)} = m - n + \rho \qquad (1)$$

e. g., in H graph, m=18, n=12, ρ=2, the substitution of m, n and ρ in Eq(1) yields

$$\gamma_{(G)} = 18 - 12 + 2 = 8$$

that is, the H graph contains 8 independent cycles (or loops).

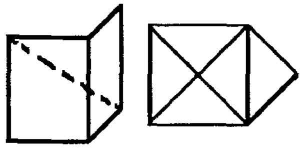


Figure 1 H Graph

2. *Network and cross-linking reaction*

The most typical structural feature of a gel is that it contains a number of network circuits. The network only come from the intra-molecular cross-linking reaction, instead of inter-molecular reaction. As contrasted with the inter-molecular reaction which only results in the combination of two molecules, each step intra-molecular reaction exactly results in forming a loop.Therefore the cross-linking reaction extent may be expressed quantitatively by the number of the network circuits formed. Here, we took A_3 (—<) self condensation system as example to elucidate this relationship.

Provided that the system with N_A functional groups has gelled and has ρ independent components with the reaction extent P_A , In terms of definition of vertex and edge, the number of the edges should be the total number N_A of A functional groups, while the number of vertices should be the sum of three, two and single dimensional vertices,therefore

$$\gamma_{(G)} = N_A - [N_A/3 + N_A P_A/2 + N_A(1 - P_A)] + \rho \qquad (2)$$

$$= N_A/2(P_A - 2/3 + 2/3\overline{X}_n)$$

where, $\overline{X}_n = N_A/3\rho$ is the average polymerization degree of gel units. Eq(2) means that beside the molecular weight and molecular weight distribution, the structure of the cross-linked gel also be characterized by the reaction extent P_A according to the Eq(2).

3. *Gel point and its physical meaning*

In terms of Eq(2), $\gamma_{(G)}$ will increase as P_A approaches to 1, when $P_A = 1$,$\gamma_{(G)}$ reaches the maximum (to see Fig.2). When P_A decreases, $\gamma_{(G)}$ will slope down with it. $\gamma_{(G)} = 0$ means that the system has no the network circuits, therefore it is in a critical state of gel and ungel; this reaction extent P_A at this time is the gel point P_{AC} and the function:

$$G(f_i, r_j, p_k) = 0 \qquad (3)$$

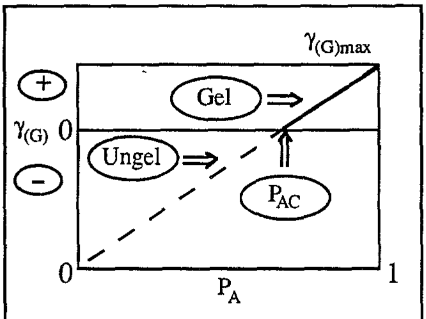
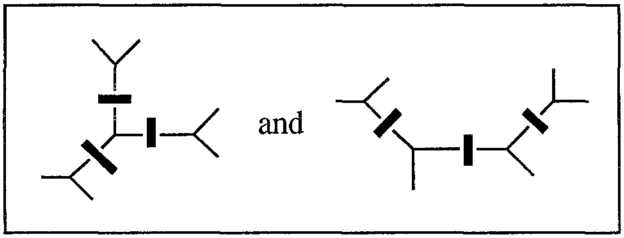


Figure 2 Physical meaning of the gel point

may be termed the general equation of the critical state of gelation. Where, f_i, r_j and p_k represents the variable functional degree, molar ratio and reaction extent respectively. To A_3 system mentioned above, a solution

$$P_{AC} = 2/3 - (2/3\,\overline{X}_n) = 2/3\,(1 - 1/\overline{X}_n) \qquad (4)$$

may be obtained. From Eu(4), it can be seen that Carothers's result ($P_{AC} = 2/3$) and Flory 's result ($P_{AC} = 1/2$), in fact, represent two limited values: the former –the maximum ($\overline{X}_{nc} \to \infty$) means that each branched macromolecule has reached infinite before the cross-linked; while the latter ($\overline{X}_n = 4$) responds to the following two structures which are impossible to gel,



and hence it expresses another limit– the minimum .

In the following, we are going to take some common non-linear condensation polymerization systems as examples to illustrate in detail the principle and method needed to derive the critical state equation of gelation.

The Critical state Equations of Three Common Non-linear Condensation Polymerization

1.A_2-B_3 (A–A $\text{B}\!-\!\!<\!\begin{smallmatrix}\text{B}\\ \text{B}\end{smallmatrix}$) *system*

To a system in which the initial molecular number of A_2 and B_3 are N_A and N_B, suppose the total system has gelled and has ρ independent units; the reaction extent of A and B functional groups are P_A and P_B respectively; then, the probability of an A group taking part in the reaction is P_A, $(1\text{-}P_A)$ is the unreacted probability of A group and so forth , P_B and $(1\text{-}P_B)$ may express the probability of B group, reacted, and unreacted, respectively. Heretofore, the random state and statistical amount of A_2 , B_3 molecules in the gelled system can be listed in Table 1

Table 1 The state and statistical amount of various molecules of A_2--B_3 system

Symbol	N_{A2}	N_{A1}	N_{A0}	N_{B3}	N_{B3}	N_{B1}
State	--BA-AB---	--BA-A	A-A	$\text{--AB}\!-\!\!<\!\begin{smallmatrix}\text{BA--}\\ \text{BA--}\end{smallmatrix}$	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{BA--}\\ \text{BA--}\end{smallmatrix}$	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{BA--}\\ \text{B}\end{smallmatrix}$
Amount	$N_AP_A^2$	$2N_AP_A(1\text{-}P_A)$	$N_A(1\text{-}P_A)^2$	$N_BP_B^3$	$3N_BP_B^2(1\text{-}P_B)$	$3N_BP_B(1\text{-}P_B)^2$

Symbol	N_{B0}	N_{B30}	N_{B20}	N_{B21}	N_{B31}
State	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{B}\\ \text{B}\end{smallmatrix}$	$\text{A-AB}\!-\!\!<\!\begin{smallmatrix}\text{BA–A}\\ \text{BA–A}\end{smallmatrix}$	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{BA–A}\\ \text{BA–A}\end{smallmatrix}$	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{BA–A}\\ \text{BA--}\end{smallmatrix}$	$\text{B}\!-\!\!<\!\begin{smallmatrix}\text{BA–A}\\ \text{BA--}\end{smallmatrix}$
Amount	$N_B(1\text{-}P_B)^3$	$N_BP_B^3(1\text{-}P_A)^3$	$3N_B(1\text{-}P_B)$ $(1\text{-}P_A)^2P_B^2$	$6N_BP_B^2P_A$ $(1\text{-}P_B)(1\text{-}P_A)$	$3N_BP_B^3P_A$ $(1\text{-}P_A)^2$

If we take A_2 molecules combined into gel as edges, and B_3 molecules combined into gel as vertices, according to Eq(1), the following equation can be obtained:

$$\gamma_{(G)}=N_A'-N_B'+\rho \quad (5)$$

Where N_A' is the effective molecular number of A_2 molecules, two groups of which have all reacted, N_B' is the effective molecular number of B_3 molecules, and at least two groups of three B groups have reacted.

For example, in Fig. 3, $N_A' = 5$, $N_B' = 4$ and $\rho = 1$,put them in Eq(5), yield $\gamma_{(G)} =5-4+1=2$, i.e., the network shown in Fig.3 contains two circuits that correspond to the two step cross-linking reactions.

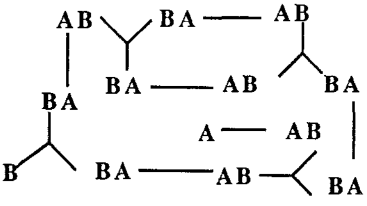


Figure 3 Cross-linking model of A_2-B_3 system

It can be seen from Table 1 that N_{A2} in fact, contains yet invalid N_{B1} that is not combined into the gelled network. Therefore, the effective molecular number N_A' should equal:

$$N_A' = N_{A2}- N_{B1} P_A \quad (6)$$

(P_A is the fraction of N_{A2} in N_{A2} and N_{A1})

The same principle is used in defining effective number of nodes---N_B':

$$N_B' = N_{B3} - N_{B30} - 1/6\, N_{B31} + N_{B2} - N_{B20} -1/4\, N_{B21} \quad (7)$$

Where 1/6 and 1/4 are the combination coefficients of A_2 molecule in N_{B31} and N_{B21} respectively.

Placing the statistical amounts of various state molecules in Table 1 in Eq (6) and (7), after arranging, yields

$$N_A'= N_A P_A^2 - 3N_B (1-P_B)^2 P_B P_A \quad (8)$$

$$N_B'= N_B P_B^3(P_A^3/2 - 2P_A^2 + 5/2\, P_A) + 3 N_B P_B^2(1-P_B)(3/2\, P_A - P_A^2 /2) \quad (9)$$

According to Eq(3), when the polymerization system is in the critical gel state, $\gamma_{(G)} = 0$ then

$$\gamma_{(G)}=N_A'-N_B'+\rho =0 \quad (10)$$

$$N_A'=N_B'-\rho \approx N_B' \quad (11)$$

Placing Eq. (8) and (9) in Eq(11), we may obtain:

$$N_AP_{AC}^2 = N_BP_{BC}^3\,(P_{AC}^3/2 - 2P_{AC}^2 + 5/2\,P_{AC}) + 3\,N_B\,P_{BC}^2 \\ (1-P_{BC})(3/2\,P_{AC} - P_{AC}^2/2) + 3\,N_BP_{BC}P_{AC}(1-P_{BC})^2 \qquad (12)$$

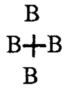
By taking in $r = 2N_A/3N_B$ and $P_B = r\,P_A$, Eq(12) becomes

$$r^2\,P_{AC}^4 - r^2P_{AC}^3 + (2r^2 - 3r)\,P_{AC}^2 - 3rP_{AC} + 3 = 0 \qquad (13)$$

Eq(13) is the critical state equation of gelation of A_2-B_3 polymerization system. Putting different r values in Eq(13), we can get correspondent P_{AC} by trial and error approach methods. Some results are listed in Table 2. Under the same component and system, the results from Carothers Eq. and the statistical theory also are tabulated in Table 2 for comparison. It is evident that the values assaied by Eq(13) are situated between the results of two theories mentioned.

Table 2. Gel point P_{AC} of A_2-B_3 System

	P_{AC}		
r	Flory	Authors	Carothers
0.8	0.791	0.873	0.917
1.0	0.707	0.768	0.833
1.2	0.646	0.696	0.778
1.4	0.598	0.642	0.738
1.6	0.559	0.602	0.708



2 A_2-B_4 (A–A, $B\overset{B}{\underset{B}{+}}B$) *system*

In comparison with A_2– B_3, the effective molecular number of vertices of the A_2-B_4 system should include N_{B4} and N_{B3} as well as N_{B2}.The state and statistical amount of monomers in this system are similar to that of A_2– B_3.

Using a similar method, we may derive the critical state equation of gelation of A_2-B_4 system:

$$r^3P_{AC}^6 - r^3\,P_{AC}^5 - (4r^2 + r^3)\,P_{AC}^4 + (4r^2 + 3r^3)\,P_{AC}^3 \\ + (6r - 8r^2)\,P_{AC}^2 + 6r\,P_{AC} - 4 = 0 \qquad (14)$$

The P_{AC} corresponding to different r values are tabulated in Table 3. It can be seen that the P_{AC} values determined by Eq(14) are situated between the results from Carothers Eq. and the statistical theory.

Table 3. Gel point P_{AC} of A_2-B_4 system

r	P_{AC}		
	Flory	Authors	Carothers
0.8	0.654	0.725	0.813
1.0	0.577	0.643	0.750
1.2	0.527	0.585	0.708
1.4	0.488	0.542	0.607
1.6	0.456	0.508	0.563

3 A_2-B_2-C (A–A, B–B, $\mathrm{B}\!-\!\!\left<\begin{matrix}\mathrm{B}\\ \\ \mathrm{B}\end{matrix}\right.$) *system*

There are three kinds of monomers in the system of A_2-B_2-C . According to analogous principle and methods, if we take B monomer as vertices, A molecules as edges, then, in the critical state of gelation, there is the following relation:

$$N_A\,[P_{AC}^2\,\rho^2 + P_{AC}^2\,\rho\,(1-\rho)] = N_C\,[P_{BC}^3\,(\,P_{AC}^3/2 - 2P_{AC}^2 + 5P_{AC}/2\,) + 3P_{BC}^2(1-P_{BC})(3P_{AC}/2 - P_{AC}^2/2) + 3P_{AC}P_{BC}(1-P_{BC})^2] + N_B P_{AC} P_{BC}(1-P_{BC}) \quad (15)$$

put $\rho = 3N_C/(3N_C + 2N_B)$, $r = 2N_A/(3N_C + 2N_B)$ and $P_B = r\,P_A$ in Eq(15), we can get the critical state equation of A_2-B_2-C system as follows:

$$3 - 3(1-\rho)/\,\rho(1-rP_{AC}) = r^2P_{AC}^4 - r^2P_{AC}^3 + (2r^2-3r)P_{AC}^2 - 3rP_{AC} + 6 \qquad (16)$$

Appointing a set of r and ρ values, we would evaluate the corresponding P_{AC} by Eq(16). Table 4 lists some results (r = 1), which are in agreement with that of the above two systems.

Table 4. Gel point P_{AC} of A_2-B_2-C system (r = 1)

ρ	P_{AC}		
	Flory	Authors	Carothers
1.0	0.707	0.768	0.833
0.8	0.745	0.801	0.867
0.6	0.791	0.839	0.900
0.4	0.845	0.885	0.933
0.3	0.877	0.910	0.950
0.2	0,913	0.938	0.967
0.1	0.953	0.968	0.983
0.0	1.000	1.000	1.000

In order to simplifying derivation, we, in addition to retaining the assumption that the same functional group is of equal reactivity, have appointed ρ to be zero. This additional assumption would undoubtedly produce some deviations; but, because the present theory has delineated the most essential feature of gelation (the cross-linking reaction of the branching macromolecule), its results are closer to the experimental ones in comparison with Carothers's and the statistical theories (see Table 5)(10).

Table 5. Gel point determinations for a few systems

Monomers	$r = \frac{COOH}{OH}$	ρ	P_C			
			Observed	Flory	Authors	Carothers
1,2,3, Propanetriol + Dicarboxylic acid	1.000	1.000	0.765	0.707	0.768	0.833
Pentaerythritol + Dicarboxylic acid	1.000	1.000	0.630	0.577	0.643	0.750
Tricarboxylic Acid + DG + Adipic acid	1.000	0.293	0.911	0.879	0.917	0.951
Dicarboxylic succinic acid + DG + Acid	1.000	0.194	0.939	0.916	0.943	0.968

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