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FLORY-STOCKMAYER DISTRIBUTION AND SCALING STUDY

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ABSTRACT

By means of the Flory-Stockmayer distribution, the critical behavior of the kth radius near the gel point is investigated. As a direct result, a scaling law associated with the kth radius is deduced.

INTRODUCTION

The curing theory of polycondensation reaction of A_a type described by Flory-Stockmayer distribution[1,2] is investigated to give a recursion formula for evaluating the kth radius. It is known that by an alternative generating function method, Gordon[3] has initiated the study of the zero, the first and the second radii. In this paper, taking advantage of the recursion formula, the critical behavior of the kth radius near the gel point is revealed in detail to reach a scaling law associated with the kth radius

$$k + 1 + \rho - \tau = \sigma\delta_k \ , \quad k = 2, 3, \ldots$$

with critical exponents

$$\rho = \frac{1}{2} \ , \quad \tau = \frac{5}{2} \ , \quad \sigma = \frac{1}{2} \ , \quad \delta_k = 2k-2 \ .$$

Note that ρ is associated with the asymptotic behavior of mean square radius of gyration due to Zimm and Stockmayer[4].

1. RECURSION FORMULA OF THE KTH RADIUS

As is well known, the equilibrium number fraction distribution P_n of a random a-functional polycondensation system has been proposed by Flory-Stockmayer[1,2]

$$P_n = \frac{a(an-n)!}{n!(an-2n+2)!} p^{n-1}(1 - p)^{an-2n+2} \qquad (1)$$

where P_n is the equilibrium number fraction distribution of n-mer, a the functionalities of the repeating units, and p the equilibrium fractional conversion.

By means of Flory-Stockmayer distribution, the kth radius of molecules $\langle R^2\rangle_k$ can be defined as

$$\langle R^2\rangle_k = \sum_n n^k R_n^2 P_n \ , \quad k = 0,\ 1,\ 2,\ \ldots \tag{2}$$

where R_n^2 is the mean square radius of gyration[3]. Gordon has presented a generating function method[3] for evaluating number average $\langle R^2\rangle_0/M_0$, weight average $\langle R^2\rangle_1/M_1$ and Z- average $\langle R^2\rangle_2/M_2$ of radius, in which the kth moment M_k is defined by

$$M_k = \sum_n n^k P_n \ , \quad k = 0,\ 1,\ 2,\ \ldots \tag{3}$$

Alternatively, the kth radius in Eq.(2) can be evaluated by means of differentiation technique. Differentiating the right and left hand sides of Eq.(2) with respect to the equilibrium fractional conversion p and considering that R_n^2 is independent of p[3] give

$$\langle R^2\rangle_{k+1} = \frac{1}{1-(a-1)p}\left[(1+p)\langle R^2\rangle_k + p(1-p)\frac{d\langle R^2\rangle_k}{dp}\right] \tag{4}$$

where we have only made use of the expression of Flory-Stockmayer distribution in Eq.(1). Eq.(4) is referred to as the recursion formula of $\langle R^2\rangle_k$, i.e. if $\langle R^2\rangle_k$ is given, $\langle R^2\rangle_{k+1}$ can be evaluated by Eq.(4). Note that in obtaining Eq.(4), we have not imposed any additional restriction upon the kth radius, and thus the recursion formula holds true for both pre-gel and post-gel.

Since $\langle R^2\rangle_0$ and $\langle R^2\rangle_1$ will not be involved in the scaling study in the next section, we limite our discussion, in this section, to the kth radius $\langle R^2\rangle_k$ for the case of $k\geqslant 2$, i.e. k=2,3,...

For pre-gel, $\langle R^2\rangle_2$ has been obtained by Gordon[3] in the form

$$\langle R^2\rangle_2 = \frac{V_2}{(p_c-p)^2} \tag{5}$$

with

$$V_2 = \frac{ab^2p}{2(a-1)^2} \tag{6}$$

where b is the average bond length in molecule and p_c is the well known Flory-Stockmayer gel point[1,2]

$$p_c = \frac{1}{a-1} \ . \tag{7}$$

This point can be regarded as the threshold of sol-gel transition.

For post-gel, if we consider the equilibrium fractional conversion in sol, p', we can obtain

$$\langle R^2\rangle_2 = \frac{T_2}{(p_c-p')^2} \tag{8}$$

with

$$T_2 = \frac{ab^2p'S}{2(a-1)^2} \tag{9}$$

where the sol fraction S and the equilibrium fractional conversion in sol p' satisfy the relation[5,6] as follows

$$S = \left(1 - p + Sp\frac{1 - p'}{1 - p}\right)^a \tag{10}$$

By taking $\langle R^2\rangle_2$ in Eqs.(5) and (8) as starting point for successive recursions, we obtain $\langle R^2\rangle_k$, from recursion formula in Eq.(4)

$$\langle R^2\rangle_k = \begin{cases} V_k/(p_c - p)^{2k-2}, & \text{for pre-gel} \\ T_k/(p - p_c)^{2k-2}, & \text{for post-gel} \end{cases} \quad k = 3, 4, \ldots \tag{11}$$

where V_k and T_k satisfy the same recursion formula

$$W_k = \frac{(2k-4)p(1-p)}{a-1}W_{k-1} + \frac{(p_c-p)}{a-1}[(1+p)W_{k-1} + p(1-p)\frac{dW_{k-1}}{dp}] \tag{12}$$

with

$$W_k = \begin{cases} V_k, & \text{for pre-gel} \\ T_k, & \text{for post-gel} \end{cases} \quad k = 3, 4, \ldots \tag{13}$$

2. SCALING STUDY OF THE SOL-GEL TRANSITION

Let us study the scaling behavior of the kth radius near the gel point $p_c(|p - p_c| \ll 1)$. It is not difficult to find, near the gel point, that $\langle R^2\rangle_2$ in Eqs.(5) and (8) can be expressed asymptotically as

$$\langle \widetilde{R^2}\rangle_2 = \frac{A_2}{|p-p_c|^2} \tag{14}$$

with

$$A_2 = V_2(p=p_c) = T_2(p=p_c) = \frac{ab^2}{2(a-1)^3}. \tag{15}$$

Taking A_2 as starting point for successive recursions, we obtain, from recursion formula in Eq.(12)

$$A_k = V_k(p=p_c) = T_k(p=p_c) = \frac{(2k-4)!!a(a-2)^{k-2}}{2(a-1)^{3k-3}}b^2. \tag{16}$$

As a direct result, we have, by means of Eq.(11)

$$\langle \widetilde{R^2}\rangle_k = \frac{A_k}{|p - p_c|^{2k-2}}, \quad k = 2, 3, \ldots \tag{17}$$

With the aid of Eq.(2), $\langle \widetilde{R^2}\rangle_k$ can be rewritten as

$$\langle \widetilde{R^2}\rangle_k = \int_0^\infty n^k \widetilde{R^2_n}\widetilde{P_n}\, dn = \frac{A_k}{|p - p_c|^{2k-2}}, \quad k = 2, 3, \ldots \tag{18}$$

It should be noted that $\widetilde{R^2_n}$ and $\widetilde{P_n}$ are defined as asymptotic forms with respect to the mean square radius of gyration R^2_n and the Flory-Stockmayer distribution P_n.

The asymptotic form of P_n

$$\widetilde{P}_n = Bn^{-\tau} \exp\left[-(k - \frac{3}{2})\frac{n}{n_\xi(k)} \right] \tag{19}$$

has been obtained by some of the present authors[5] with

$$B = a[2\pi(a-1)(a-2)]^{-1/2} \tag{20}$$

$$\tau = \frac{5}{2} \tag{21}$$

$$n_\xi(k) = \frac{(2k-3)(a-2)}{(a-1)^3}|p-p_c|^{-1/\sigma} \quad , \quad k = 2, 3, \ldots \tag{22}$$

$$\sigma = \frac{1}{2} \tag{23}$$

where B is a normalization constant, τ and σ are two different critical exponents and $n_\xi(k)$ is the generalized typical size which is a generalization of the typical size proposed by Stauffer[7]. By substituting the asymptotic form $\widetilde{P}_n$ in Eq.(18), the expression of $\langle\widetilde{R^2}\rangle_k$ becomes

$$\langle\widetilde{R^2}\rangle_k = \int_0^\infty F(n)e^{-tn}dn = f(t) \ . \tag{24}$$

This equation is a Laplace transformation of F(n) to f(t) with

$$F(n) = Bn^{k-5/2} \widetilde{R^2_n} \tag{25}$$

$$f(t) = \frac{(2k-4)!!ab^2}{2^k(a-2)}t^{1-k} \tag{26}$$

$$t = \frac{k - \frac{3}{2}}{n_\xi(k)} \tag{27}$$

It is easy to obtain F(n) by using inverse Laplace transformation

$$F(n) = \frac{1}{2\pi i}\int_{Q-i\infty}^{Q+i\infty} e^{tn}f(t)dt \tag{28}$$

to yield the asymptotic form of the mean square radius of gyration

$$\widetilde{R^2_n} = b^2\left(\frac{(a-1)}{2^3(a-2)}\right)^{\frac{1}{2}} n^\rho \tag{29}$$

with

$$\rho = \frac{1}{2} \ . \tag{30}$$

$\widetilde{R^2_n}$ is the well known formula which has been obtained by Zimm and Stockmayer[4].

By introducing the generalized typical size $n_\xi(k)$ in Eq.(22) into the right hand side in Eq.(18) and by substituting the asymptotic forms $\widetilde{P}_n$ and $\widetilde{R}_n^2$ given by Eqs.(19) and (20) into the left hand side of Eq.(18), we have

$$\frac{b^2a}{4(a-2)}\int_0^{\infty} n^{k+\rho-\tau}\exp\left[-(k-\frac{3}{2})\frac{n}{n_\xi(k)}\right]dn =$$

$$= A_k\left(\frac{(2k-2)A_k}{(2k-3)A_{k+1}}\right)^{\sigma\delta_k}\left(n_\xi(k)\right)^{\sigma\delta_k}, \quad k = 2, 3, \ldots \qquad (31)$$

with

$$\delta_k = 2k - 2 \,. \qquad (32)$$

Application of the scaling transformation T,

$$Tn_\xi(k) = Ln_\xi(k) \,, \quad \text{(L being a positive real number)} \qquad (33)$$

$$Tn = Ln \qquad (34)$$

to Eq.(31) gives immediately

$$k + 1 + \rho - \tau = \sigma\delta_k \,, \quad k = 2, 3, \ldots \qquad (35)$$

These relations, arising from the kth radius, are the scaling law which is associated with the critical exponent ρ of $\widetilde{R}_n^2$ due to Zimm and Stockmayer[4].

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