(6) Makarewicz, P. J.; Wilkes, G. L. *J. Appl. Polym. Sci.* **1978**, *22*, 3347.
(7) Ouchi, I.; Hosoi, M.; Shimotsuma, S. *J. Appl. Polym. Sci.* **1977**, *21*, 3456.
(8) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 445.
(9) Cheng, S. Z. D.; Cao, M.-Y.; Wunderlich, B. *Macromolecules* **1986**, *19*, 1868.
(10) Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1987**, *20*, 1630.
(11) Cheng, S. Z. D.; Wu, Z. Q.; Wunderlich, B. *Macromolecules* **1987**, *20*, 2082.
(12) Wunderlich, B. *Macromolecular Physics, Crystal Melting*; Academic: New York, 1980; Vol. III.
(13) Wunderlich, B.; Bopp, R. C. *J. Thermal Anal.* **1974**, *6*, 335. See Also: Mehta, A.; Bopp, R. C.; Gaur, U.; Wunderlich, B. *J. Thermal Anal.* **1978**, *13*, 197.
(14) Ginnings, D. C.; Furukawa, G. T. *J. Am. Chem. Soc.* **1953**, *75*, 522.
(15) Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 577, 595.
(16) Bu, H. S.; Cheng, S. Z. D.; Wunderlich, B., in preparation.
(17) Cheng, S. Z. D.; Bu, H. S.; Pan, R.; Wunderlich, B., to be submitted for publication in *Makromol. Chem.*
(18) Cheng, S. Z. D.; Wunderlich, B.; Wu, Z. Q.; Li, W. H., in preparation.
(19) See, for example: Wunderlich, B.; Baur, H. *Adv. Polym. Sci.* **1970**, *7*, 151.
(20) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(21) Blundell, D. J.; Buckingham, K. A. *Polymer* **1985**, *26*, 1623.
(22) Wunderlich, B. *J. Phys. Chem.* **1960**, *64*, 1052. Gaur, U.; Wunderlich, B. *Polym. Prpr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20*, 429.
(23) Wunderlich, B.; Bodily, D. M.; Kaplan, M. H. *J. Appl. Phys.* **1964**, *35*, 95.
(24) Unpublished observation in our ATHAS Laboratory.
(25) Menczel, J.; Wunderlich, B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 261.
(26) Wolpert, S. M.; Weitz, A.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* 1971, *9*, 1887.

On the Curing Theory and the Scaling Study of the Polycondensation Reaction of $A_{a_1}...A_{a_s}$–$B_{b_1}...B_{b_t}$ Type

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ABSTRACT: For the polycondensation reaction of $A_{a_1}...A_{a_s}$–$B_{b_1}...B_{b_t}$ type, the sol fraction above the gel point is investigated in detail by taking Stockmayer's gelation condition as a criterion. Furthermore, the scaling behavior near the gel point is revealed to reach an asymptopic form of Stockmayer's equilibrium number distribution from which a generalized scaling law is deduced.

Introduction

As is well-known, the polycondensation reaction of $A_{a_1}...A_{a_s}$–$B_{b_1}...B_{b_t}$ type has been initiated by Stockmayer.[1-5] In this paper, above the gel point, which is regarded as the threshold of the sol–gel transision,[3,5-10] the behavior of the sol fraction involving the total, sol, and gel equilibrium fractional conversions is investigated in detail by taking Stockmayer's gelation condition[3] as a criterion. With limitation of procedure approached from above the gel point, three equivalent forms of the gel point are obtained.

It is known that in the theory of branching processes, the probability generating function with differentiation technique proposed by Gordon[8,11] can be used for evaluation of polymer moments. In this paper, based on Stockmayer's equilibrium number distribution of $A_{a_1}...A_{a_s}$–$B_{b_1}...B_{b_t}$ type,[3] a direct differentiation method with some mathematical techniques is presented to obtain the recursion formula of polymer moments in the form

$$M_{k+1} = D\left[EM_k + Fp_a\left[(1-p_a)\frac{\partial M_k}{\partial p_a} + \partial_x M_k\right] + Ip_b\left[(1-p_b)\frac{\partial M_k}{\partial p_b} + \partial_y M_k\right]\right] \quad (1)$$

This formula is suitable for both above and below the gel point, and especially, it is useful in approaching the scaling study near the gel point.[12-14]

For revealing the critical behavior of a sol–gel transition, a reasonable approach without using the Stirling approximation[12] is proposed to reach an asymptopic form of Stockmayer's equilibrium number distribution

$$\tilde{P}(n_1,...,n_s,l_1,...l_t) = B(s+t-1)!(n_1+...+n_s+l_1+...+l_t)^{-(s+t+(3/2))} \times \exp\left[-\left(k-\frac{3}{2}\right)\frac{(n_1+...+n_s+l_1+...+l_t)}{n\xi(k)}\right] \quad (2)$$

with

$$\tilde{P}_n = \int_0^n \mathrm{d}m_{s+t-1} \int_0^{m_{s+t-1}} \mathrm{d}m_{s+t-2} \cdots \int_0^{m_2} \mathrm{d}m_1 \times \tilde{P}(m_1, m_2-m_1, ..., m_{s+t-1}-m_{s+t-2}, n-m_{s+t-1})$$

$$\tilde{P}_n = Bn^{-5/2}\exp\left[-\left(k-\frac{3}{2}\right)\frac{n}{n\xi(k)}\right] \quad (3)$$

where B is a normalization constant

$$B = (2\pi J)^{-1/2}E(p_a{}^c, p_b{}^c) \quad (4)$$

and where the generalized typical size[14] $n\xi(k)$ is defined as

$$n\xi(k) = (p_b{}^c/2)^2(2k-3)J|p_b - p_b{}^c|^{-2} \quad (5)$$

Consequently, a generalized scaling law[13,14]

$$\tau - 2 = \sigma\beta \quad (6)$$

$$k + 1 - \tau = \sigma\gamma_k \qquad k = 2, 3, ... \quad (7)$$

is deduced.

Sol Fraction above the Gel Point with Stockmayer's Gelation Condition as a Criterion

Let us consider a polycondensation system consisting of two species of monomers A_{a_i} and B_{b_j} with functionalities

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a_i ($i = 1, 2, ..., s$) and b_j ($j = 1, 2, ..., t$). In order to make our discussion easier, some notations are in prior introduced: N_{a_i} (N_{b_j}), the number of monomers of A_{a_i} (B_{b_j}); p_a (p_b), the total equilibrium fractional conversion of species A (B); p'_a (p'_b), the sol equilibrium fractional conversion of species A (B); p''_a (p''_b), the gel equilibrium fractional conversion of species A (B); S_{a_i} (S_{b_j}), the sol fraction of A_{a_i} (B_{b_j}); x_i, the fraction functionality of species A defined as

$$x_i = a_i N_{a_i} / N_A{}^0 \tag{8}$$

with

$$N_A{}^0 = \sum_{i=1}^{s} a_i N_{a_i} \tag{9}$$

y_j, the fractional functionality of species B defined as

$$y_j = b_j N_{b_j} / N_B{}^0 \tag{10}$$

with

$$N_B{}^0 = \sum_{j=1}^{t} b_j N_{b_j} \tag{11}$$

Let us discuss the sol fraction above the gol point[3,5–10] with Stockmayer's gelation condition as a criterion.[3]

Under the assumptions of equireactivity and of no intramolecular reaction between A–B groups in the sol, we have, by means of polymer statistics,[5]

$$S_{a_i} = \left(1 - p_a + p_a \sum_{j=1}^{t} y_j S_{b_j} \frac{1 - p'_b}{1 - p_b}\right)^{a_i} \tag{12}$$

$$S_{a_i}(1 - p'_a) = (1 - p_a)\left(1 - p_a + p_a \sum_{j=1}^{t} y_j S_{b_j} \frac{1 - p'_b}{1 - p_b}\right)^{a_i - 1} \tag{13}$$

to give, by combining eq 12 and 13,

$$\frac{1 - p'_a}{1 - p_a} = S_{a_i}{}^{-1/a_i} \qquad i = 1, 2, ..., s \tag{14}$$

Similarly, we obtain

$$S_{b_j} = \left(1 - p_b + p_b \sum_{i=1}^{s} x_i S_{a_i} \frac{1 - p'_a}{1 - p_a}\right)^{b_j} \tag{15}$$

$$S_{b_j}(1 - p'_b) = (1 - p_b)\left(1 - p_b + p_b \sum_{i=1}^{s} x_i S_{a_i} \frac{1 - p'_a}{1 - p_a}\right)^{b_j - 1} \tag{16}$$

$$\frac{1 - p'_b}{1 - p_b} = S_{b_j}{}^{-1/b_j} \qquad j = 1, 2, ..., t \tag{17}$$

When eq 17 is substituted in eq 12, we have

$$P_a = (1 - S_{a_l}{}^{1/a_l})\left(1 - \sum_{j=1}^{t} y_j S_{b_j}{}^{(b_j - 1)/b_j}\right)^{-1} \tag{18}$$

Application of S_{b_j} in eq 15 together with the relation

$$S_{a_i}{}^{1/a_i} = S_{a_l}{}^{1/a_l} \qquad i, l = 1, 2, ..., s \tag{19}$$

to eq 18 yields

$$p_a = \frac{1 - S_{a_l}{}^{1/a_l}}{1 - \sum_{j=1}^{t} y_j (1 - p_b + p_b \sum_{i=1}^{s} x_i S_{a_l}{}^{(a_i - 1)/a_l})^{b_j - 1}} \tag{20}$$

Similarly, as we have just done for obtaining p_a, it is easy to find that

$$p_b = (1 - S_{b_l}{}^{1/b_l})(1 - \sum_{i=1}^{s} x_i S_{a_i}{}^{(a_i - 1)/a_i})^{-1} \tag{21}$$

and

$$p_b = \frac{1 - S_{b_l}{}^{1/b_l}}{1 - \sum_{i=1}^{s} x_i (1 - p_a + p_a \sum_{j=1}^{t} y_j S_{b_l}{}^{(b_j - 1)/b_l})^{a_i - 1}} \tag{22}$$

Let us discuss Stockmayer's gelation condition[3] as a criterion of eq 12, 13, 15, and 16 from which eq 20 and 22 stem. When $S_{a_1} = 1$ ($S_{b_1} = 1$), eq 20 (eq 22) becomes indefinite, i.e., 0/0, and then application of the L'Hospital's rule to eq 20 (eq 22) leads us to the gelation condition

$$1 - \sum_{i=1}^{s} (a_i - 1) x_i \sum_{j=1}^{t} (b_j - 1) y_j (p_a)_c (p_b)_c = 0 \tag{23}$$

This equation involving the gel point $(p_a)_c$ and $(p_b)_c$ can be further reformulated in terms of the weight average of functionalities

$$a_w = \sum_{i=1}^{s} a_i x_i \tag{24}$$

and

$$b_w = \sum_{j=1}^{t} b_j y_j \tag{25}$$

to give

$$1 - (a_w - 1)(b_w - 1)(p_a)_c (p_b)_c = 0 \tag{26}$$

This relation is in accordance with the form that has been proposed by Stockmayer.[3,9]

It is clear that p_a and p_b in eq 18 and 21 are subject to the relation

$$p_a = r_b p_b \tag{27}$$

with

$$r_b = N_B{}^0 / N_A{}^0 \tag{28}$$

r_b being the stoichiometric ratio.

In the polycondensation reaction, there are $s + t$ sol fractions S_{a_i} ($i = 1, 2, ..., s$) and S_{b_j} ($j = 1, 2, ..., t$), but only one of them can be taken as an independent variable. Indeed, by means of eq 18, 21, and 27, we come to know that the $s + t$ sol fractions are subject to st simultaneous equations

$$(1 - S_{a_l}{}^{1/a_l})(1 - \sum_{i=1}^{s} x_i S_{a_i}{}^{(a_i - 1)/a_i}) = r_b\left(1 - S_{b_j}{}^{1/b_j}\right)\left(1 - \sum_{j=1}^{t} y_j S_{b_j}{}^{(b_j - 1)/b_j}\right) \tag{29}$$

$$l = 1, 2, ..., s; \qquad j = 1, 2, ..., t$$

Since

$$S_{a_1}{}^{1/a_1} = S_{a_2}{}^{1/a_2} = ... = S_{a_s}{}^{1/a_s}$$
$$S_{b_1}{}^{1/b_1} = S_{b_2}{}^{1/b_2} = ... = S_{b_t}{}^{1/b_t} \tag{30}$$

it is easily seen that only one of the st equations is independent. For illustration, we take the independent one as an example

$$(1 - S_{a_1}{}^{1/a_1})(1 - \sum_{i=1}^{s} x_i S_{a_1}{}^{(a_i - 1)/a_1}) = r_b(1 - S_{b_1}{}^{1/b_1})(1 - \sum_{j=1}^{t} y_j S_{b_1}{}^{(b_j - 1)/b_1}) \tag{31}$$

in which two sol fractions S_{a_1} and S_{b_1} are involved. As a direct result of eq 29 and 30, only one of the $s + t$ sol fractions can be taken as an independent invariable. When one of the $s + t$ sol fractions is taken from experiment, the remaining $s + t - 1$ ones can be evaluated by means of eq 30 and 31.

Now let us begin to deal with the three equivalent forms of the gel point. For the total fractional conversions p_a and p_b, the gel points $(p_a)_c$ and $(p_b)_c$ can be easily deduced from the gelation condition in eq 26 to give, with the aid of eq 27,

$$(p_a)_c = \left[\frac{r_b}{(a_w - 1)(b_w - 1)}\right]^{1/2} \tag{32}$$

$$(p_b)_c = \left[\frac{1}{r_b(a_w - 1)(b_w - 1)}\right]^{1/2} \tag{33}$$

When eq 12 is substituted in eq 13, we obtain

$$p'_a = 1 - (1 - p_a)S_{a_1}^{-1/a_1} \tag{34}$$

Similarly, we have, from eq 15 and 16

$$p'_b = 1 - (1 - p_b)S_{b_1}^{-1/b_1} \tag{35}$$

For the sol fractional conversions p'_a and p'_b, when $S_{a_1} = 1$ and $S_{b_1} = 1$ are substituted in eq 34 and 35, we get immediately

$$(p'_a)_c = (p_a)_c \tag{36}$$

and

$$(p'_b)_c = (p_b)_c \tag{37}$$

Furthermore, by means of the conventional polymer statistics,[5] it is not difficult to find

$$\sum_{i=1}^{s} x_i S_{a_i}(1 - p'_a) + \sum_{i=1}^{s} x_i(1 - S_{a_i})(1 - p''_a) = 1 - p_a \tag{38}$$

Multiplying both sides of this equation by $(1 - p_a)^{-1}$ and then taking into consideration eq 14 give

$$\sum_{i=1}^{s} x_i S_{a_1}^{(a_i-1)/a_1} + \sum_{i=1}^{s} x_i(1 - S_{a_i})\frac{1 - p''_a}{1 - p_a} = 1 \tag{39}$$

to yield

$$p''_a = 1 - (1 - p_a)\frac{1 - \sum_{i=1}^{s} x_i S_{a_1}^{(a_i-1)/a_1}}{1 - \sum_{i=1}^{s} x_i S_{a_1}^{a_i/a_1}} \tag{40}$$

where we have made use of eq 30.

A parallel procedures as we have just done leads us to the result

$$p''_b = 1 - (1 - p_b)\frac{1 - \sum_{j=1}^{t} y_j S_{b_1}^{(b_j-1)/b_1}}{1 - \sum_{j=1}^{t} y_j S_{b_1}^{b_j/b_1}} \tag{41}$$

For the gel fractional conversions p''_a and p''_b, we obtain, from eq 40 and 41,

$$(p''_a)_c = \frac{1}{a_w} + \frac{a_w - 1}{a_w}(p_a)_c \tag{42}$$

and

$$(p''_b)_c = \frac{1}{b_w} + \frac{b_w - 1}{b_w}(p_b)_c \tag{43}$$

where the L'Hospital's rule has been used in treating the indefinite form, 0/0.

It is obvious that with any one of the equilibrium fractional conversions p_a (p_b), p'_a (p'_b), and p''_a (p''_b), the discussion of curing theory will go through without difficulty. But in order to make the scaling study in this paper easier, we shall choose the total equilibrium fractional conversion p_a (p_b) to proceed with our discussion.

Polymer Moments of Stockmayer's Number Distribution

In this section, we shall take advantage of differentiation technique to evaluate the polymer moments.

For the $A_{a_1}...A_{a_s}$–$B_{b_1}...B_{b_t}$ polycondensation associated with n_i-mers of A_{a_i} ($i = 1, 2, ..., s$) and l_j-mers of B_{b_j} ($j = 1, 2, ..., t$), Stockmayer's number fractional distribution $P(n_1,...,n_s,l_1,...,l_t)$ of $(n_1 + n_2 + ... + n_s + l_1 + l_2 + ... + l_t)$-mers takes the form[3-5]

$$\begin{aligned} P(n_1,...,n_s,l_1,...,l_t) = {} & UC(n_1,...,n_s,l_1,...,l_t)(\prod_i x_i^{n_i})(\prod_j y_j^{l_j}) \times \\ & (p_a)^{\sum_{j=1}^{t} l_j}(p_b)^{\sum_{i=1}^{s} n_i}(1 - p_a)^{\sum_{i=1}^{s}(a_i-1)n_i - \sum_{j=1}^{t} l_j + 1} \times \\ & (1 - p_b)^{\sum_{j=1}^{t}(b_j-1)l_j - \sum_{i=1}^{s} n_i + 1} \end{aligned} \tag{44}$$

with

$$\begin{aligned} U &= N_A^0[p_b(\sum_{i=1}^{s} N_{a_i} + \sum_{j=1}^{t} N_{b_j})]^{-1} \\ &= (p_b\sum_{i=1}^{s} x_i/a_i + p_a\sum_{j=1}^{t} y_j/b_j)^{-1} \end{aligned} \tag{45}$$

and

$$\begin{aligned} C(n_1,...,n_s,l_1,...,l_t) = {} \\ & (\sum_{i=1}^{s}(a_i - 1)n_i)!(\sum_{j=1}^{t}(b_j - 1)l_j)!(\prod_i n_i!)^{-1}(\prod_j l_j!)^{-1} \times \\ & [(\sum_{i=1}^{s}(a_i - 1)n_i - \sum_{j=1}^{t} l_j + 1)!]^{-1}[(\sum_{j=1}^{t}(b_j - 1)l_j - \\ & \sum_{i=1}^{s} n_i + 1)!]^{-1} \end{aligned} \tag{46}$$

Note that this distribution is defined in the postgel region where it becomes an improper distribution with total mass equal to S, the sol fraction.

It is known that the kth polymer moment M_k can be evaluated by means of the distribution in eq 44 such that

$$M_k = \sum_{\substack{n_1,...,n_s \\ l_1,...,l_t}} (\sum_{i=1}^{s} n_i + \sum_{j=1}^{t} l_j)^k P(n_1,...,n_s,l_1,...,l_t) \qquad k = 1, 2, ... \tag{47}$$

Furthermore, it is easy to find that

$$M_{k+1} = \sum_{i=1}^{s} R_i(k) + \sum_{j=1}^{t} T_j(k) \tag{48}$$

with

$$R_i(k) = \sum_{\substack{n_1,...,n_s \\ l_1,...,l_t}} (\sum_{i=1}^{s} n_i + \sum_{j=1}^{t} l_j)^k n_i P(n_1,...,n_s,l_1,...,l_t) \tag{49}$$

and

$$T_j(k) = \sum_{\substack{n_1,...,n_s \\ l_1,...,l_t}} (\sum_{i=1}^{s} n_i + \sum_{j=1}^{t} l_j)^k l_j P(n_1,...,n_s,l_1,...,l_t) \tag{50}$$

As $R_i(k)$ ($i = 1, 2, ..., s$) and $T_j(k)$ ($j = 1, 2, ..., t$) are independent, eq 48 shows that M_{k+1} ($k = 0, 1, 2, ...$) is dependent on $s + t$ independent quantities. Thus, $s + t$

independent quantities $x_2, x_3, ..., x_s, y_2, y_3, ..., y_t, p_a, p_b$ involved in $P(n_1,...,n_s,l_1,...,l_t)$ can be taken as partial differentiation variables to perform the differentiation with respect to the both sides of eq 47 to give

$$x_1R_i(k) - x_iR_1(k) = x_a^0\left(\frac{1}{a_i} - \frac{1}{a_1}\right)x_1x_iM_k + x_1x_i\frac{\partial M_k}{\partial x_i} \qquad i = 2, 3, ..., s \quad (51)$$

$$y_1T_j(k) - y_jT_1(k) = x_b^0\left(\frac{1}{b_j} - \frac{1}{b_1}\right)y_1y_jM_k + y_1y_j\frac{\partial M_k}{\partial y_j} \qquad j = 2, 3, ..., t \quad (52)$$

$$\sum_{i=1}^{s}R_i(k) - p_b\sum_{j=1}^{t}(b_j - 1)T_j(k) = (x_a + x_bp_b)M_k + p_b(1 - p_b)\frac{\partial M_k}{\partial p_b} \quad (53)$$

$$\sum_{j=1}^{t}T_j(k) - p_a\sum_{i=1}^{s}(a_i - 1)R_i(k) = (x_b + x_ap_a)M_k + p_a(1 - p_a)\frac{\partial M_k}{\partial p_a} \quad (54)$$

where

$$x_a^0 = \frac{N_A^0}{N_A + N_B} \qquad x_b^0 = \frac{N_B^0}{N_A + N_B} \qquad x_a = \frac{N_A}{N_A + N_B}$$

$$x_b = \frac{N_A}{N_A + N_B} \qquad N_A = \sum_{i=1}^{s}N_{a_i} \qquad N_B = \sum_{j=1}^{t}N_{b_j} \quad (55)$$

By summing $s - 1$ equations in eq 51, we have

$$\sum_{i=1}^{s}x_1R_i(k) - R_1(k) = x_1\sum_{i=2}^{s}x_i\frac{\partial M_k}{\partial x_i} + x_a^0x_1\left(\sum_{i=1}^{s}\frac{x_i}{a_i} - \frac{1}{a_1}\right)M_k \quad (56)$$

Multiplying both sides of eq 51 by a_i and then summing the corresponding $s - 1$ equations give

$$\sum_{i=1}^{s}x_1a_iR_i(k) - a_wR_1(k) = x_1\sum_{i=2}^{s}a_ix_i\frac{\partial M_k}{\partial x_i} + x_a^0x_1\left(1 - \frac{a_w}{a_1}\right)M_k \quad (57)$$

It is straightforward to eliminate $R_1(k)$ from eq 56 and 57 to give

$$a_w\sum_{i=1}^{s}R_i(k) - \sum_{i=1}^{s}a_iR_i(k) = \partial_xM_k + (x_a - x_a^0)M_k \quad (58)$$

where the symbol ∂_x is used to denote

$$\partial_x = \sum_{i=2}^{s}(a_w - a_i)x_i\frac{\partial}{\partial x_i} \quad (59)$$

A parallel procedure as we have just performed yields, from eq 52,

$$b_w\sum_{j=1}^{t}T_j(k) - \sum_{j=1}^{t}b_jT_j(k) = \partial_yM_k + (x_b - x_b^0)M_k \quad (60)$$

with

$$\partial_y = \sum_{j=2}^{t}(b_w - b_j)y_j\frac{\partial}{\partial y_j} \quad (61)$$

Note that in eq 58 and 60, a_w and b_w are the weight-average functionalities defined by eq 24 and 25.

By solving simultaneously the five equations (48), (53), (54), (58), and (60), it is not difficult to obtain the solutions of the five quantities M_{k+1}, $\sum_{i=1}^{s}R_i(k)$, $\sum_{j=1}^{t}T_j(k)$, $\sum_{i=1}^{s}a_iR_i(k)$, and $\sum_{j=1}^{t}b_jT_j(k)$. For simplicity, only the result of M_{k+1} is given as follows

$$M_{k+1} = D\left[EM_k + Fp_a\left[(1 - p_a)\frac{\partial M_k}{\partial p_a} + \partial_xM_k\right] + Ip_b\left[(1 - p_b)\frac{\partial M_k}{\partial p_b} + \partial_yM_k\right]\right] \quad (62)$$

with

$$D = \frac{1}{1 - (a_w - 1)(b_w - 1)p_ap_b} \quad (63)$$

$$E = F[x_b - x_a(a_w - 1)p_a + x_a^0p_a] + I[x_a - x_b(b_w - 1)p_b + x_b^0p_b] \quad (64)$$

$$F = 1 + (b_w - 1)p_b \quad (65)$$

$$I = 1 + (a_w - 1)p_a \quad (66)$$

The recursion formula in eq 62 shows that when the kth moment M_k is given, the $(k + 1)$th moment M_{k+1} can be evaluated. For simplicity, the first moment M_1,[4,5]

$$\begin{aligned} M_1 &= \sum_{\substack{n_1,...,n_s\\ l_1,...,l_t}}\left(\sum_{i=1}^{s}n_i + \sum_{j=1}^{t}l_j\right)P(n_1,...,n_s,l_1,...,l_t) \\ &= 1, \qquad \text{for } p_b \leqslant (p_b)_c \\ &= S, \qquad \text{for } p_b \geqslant (p_b)_c \end{aligned} \quad (67)$$

is chosen as the starting point for evaluating the second moment M_2. Note that the total sol fraction S in eq 67 takes the form

$$S = \sum_{i=1}^{s}x_{a_i}S_{a_i} + \sum_{j=1}^{t}x_{b_j}S_{b_j} = U\left(p_b\sum_{i=1}^{s}S_{a_i}\frac{x_i}{a_i} + p_a\sum_{j=1}^{t}S_{b_j}\frac{y_j}{b_j}\right) \quad (68)$$

with

$$x_{a_i} = \frac{N_{a_i}}{N_A + N_B} \qquad x_{b_j} = \frac{N_{b_j}}{N_A + N_B} \quad (69)$$

The total sol fraction S varies from 1 to 0. In order to simplify our notations, we shall use p_a^c and p_b^c to replace $(p_a)_c$ and $(p_b)_c$.

It is clear that by use of the recursion formula in eq 62 together with the expression of M_1 in eq 67, we obtain

$$\begin{aligned} M_2 &= DW_2(p_a,p_b), \qquad \text{for } p_b \leqslant p_b^c \\ &= (-D)V_2(p_a,p_b), \qquad \text{for } p_b \geqslant p_b^c \end{aligned} \quad (70)$$

with

$$W_2(p_a,p_b) = E \quad (71)$$

$$V_2(p_a,p_b) = -\left[ES + p_aF\left[(1 - p_a)\frac{\partial S}{\partial p_a} + \partial_xS\right] + p_bI\left[(1 - p_b)\frac{\partial S}{\partial p_b} + \partial_yS\right]\right] \quad (72)$$

where D, E, F, and I, which are closely related with p_a and p_b, have been given by eq 63–66. It should be noted that when $p_b = p_b^c$, the quantity D becomes divergent.

Taking M_2 in eq 70 as the starting point for recursion, one can find, by repeated application of the recursion formula (62), to reach the kth moment with $k \geqslant 3$,

$$\begin{aligned} M_k &= D^{2k-3}W_k(p_a,p_b), \qquad \text{for } p_b \leqslant p_b{}^c \\ &= (-D)^{2k-3}V_k(p_a,p_b), \qquad \text{for } p_b \geqslant p_b{}^c, \qquad k = 3, 4, \ldots \end{aligned} \tag{73}$$

where $W_k(p_a,p_b)$ and $V_k(p_a,p_b)$ are subject to the same recursion formula

$$\begin{aligned} H_k = {} & (2k-5)p_ap_b[[\mathrm{F}(1-p_a) + I(1-p_b)](a_\mathrm{w}-1) \times (b_\mathrm{w}-1) + Fp_a(a_\mathrm{v} - a_\mathrm{w}{}^2) + Ip_b(b_\mathrm{v} - b_\mathrm{w}{}^2)]H_{k-1} + {} \\ & \frac{1}{D}\left[EH_{k-1} + Fp_a\left[(1-p_a)\frac{\partial H_{k-1}}{\partial p_a} + \partial_x H_{k-1}\right] + Ip_b\left[(1-p_b)\frac{\partial H_{k-1}}{\partial p_b} + \partial_y H_{k-1}\right]\right] \end{aligned} \tag{74}$$

with

$$a_\mathrm{v} = \sum_{i=1}^{s} a_i{}^2 x_i \qquad b_\mathrm{v} = \sum_{i=1}^{t} b_j{}^2 y_j \tag{75}$$

In eq 74, H_k is used to denote $W_k(p_a,p_b)$ or $V_k(p_a,p_b)$.

Scaling Study of the Sol-Gel Transition

In this section, we shall deal with the polymer moments near the gel point $p_b{}^c$,[12-14] i.e., $|p_b - p_b{}^c| \ll 1$.

Let us consider first the first moment M_1 near the gel point. From eq 67, we have

$$\begin{aligned} M_1 &= 1, \qquad \text{for } p_b \leqslant p_b{}^c \\ &= S, \qquad \text{for } p_b \geqslant p_b{}^c \end{aligned} \tag{76}$$

where the total sol fraction S takes the form

$$S = 1 + (\mathrm{d}S/\mathrm{d}p_b)_{p_b{}^c}(p_b - p_b{}^c) = 1 - A_1(p_b - p_b{}^c), \qquad \text{for } p_b \geqslant p_b{}^c \tag{77}$$

with

$$A_1 = \frac{4(a_\mathrm{w}-1)(b_\mathrm{w}-1)}{(b_\mathrm{w}-1)(a_\mathrm{v} - 3a_\mathrm{w} + 2) + (a_\mathrm{w}-1)^2(b_\mathrm{v} - 3b_\mathrm{w} + 2)p_b{}^c} \times \left[\frac{x_a{}^0}{p_b{}^c} + x_b{}^0(a_\mathrm{w} - 1)\right] \tag{78}$$

In eq 77, the differentiation of the total sol fraction S in eq 68 with respect to p_b, $\mathrm{d}S/\mathrm{d}p_b$, has been performed by use of the relations[5]

$$\sum_{i=1}^{s} x_i\left(\frac{1-p_a}{1-p'_a}\right)^{a_i-1} = \frac{p'_b(1-p_b)}{p_b(1-p'_b)}$$

and

$$\sum_{j=1}^{t} y_j\left(\frac{1-p_b}{1-p'_b}\right)^{b_j-1} = \frac{p'_a(1-p_a)}{p_a(1-p'_a)}$$

For simplicity, the details are omitted.

Alternatively, the total sol fraction S near the gel point can be expressed in the form

$$\begin{aligned} S &= 1, \qquad \text{for } p_b \leqslant p_b{}^c \\ &= 1 - A_1(p_b - p_b{}^c), \qquad \text{for } p_b \geqslant p_b{}^c \end{aligned} \tag{79}$$

As the sol fraction S and the gel fraction G are subject to the relation

$$S + G = 1 \tag{80}$$

we have, from eq 79

$$\begin{aligned} G &= 0, \qquad \text{for } p_b \leqslant p_b{}^c \\ &= A_1(p_b - p_b{}^c), \qquad \text{for } p_b \geqslant p_b{}^c \end{aligned} \tag{81}$$

Furthermore, the second moment M_2 near the gel point can be obtained, by use of eq 70

$$\begin{aligned} M_2 &= \int_0^\infty \ldots \int_0^\infty \mathrm{d}n_1 \ldots \mathrm{d}n_s\, \mathrm{d}l_1 \ldots \mathrm{d}l_t \times (n_1 + \ldots + n_s + l_1 + \ldots + l_t)^2 \tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t) \\ &= \frac{p_b{}^c W_2(p_a{}^c,p_b{}^c)}{2(p_b{}^c - p_b)}, \qquad \text{for } p_b \leqslant p_b{}^c \\ &= \frac{p_b{}^c V_2(p_a{}^c,p_b{}^c)}{2(p_b - p_b{}^c)}, \qquad \text{for } p_b \geqslant p_b{}^c \end{aligned} \tag{82}$$

It should be noted that $\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t)$ is defined as the asymptopic form of Stockmayer's distribution near the gel point. Through a lengthy calculation, we obtain

$$W_2(p_a{}^c,p_b{}^c) = V_2(p_a{}^c,p_b{}^c) = E(p_a{}^c,p_b{}^c)$$

to give, from eq 82

$$\begin{aligned} M_2 &= \int_0^\infty \ldots \int_0^\infty \mathrm{d}n_1 \ldots \mathrm{d}n_s\, \mathrm{d}l_1 \ldots \mathrm{d}l_t \times (n_1 + \ldots + n_s + l_1 + \ldots + l_t)^2 \tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t) \\ M_2 &= \frac{A_2}{|p_b - p_b{}^c|} \end{aligned} \tag{83}$$

with

$$A_2 = \frac{p_b{}^c}{2}W_2(p_a{}^c,p_b{}^c) = \frac{p_b{}^c}{2}V_2(p_a{}^c,p_b{}^c) = \frac{p_b{}^c}{2}E(p_a{}^c,p_b{}^c) \tag{84}$$

The symbol $E(p_a{}^c,p_b{}^c)$ means that p_a and p_b involved in the quantity E in eq 64 are replaced by $p_a{}^c$ and $p_b{}^c$, respectively.

Taking A_2 as the starting point for recursion, we can make use of the recursion formula (74) repeatedly to reach

$$A_k = (p_b{}^c/2)^{2k-3}(2k-5)!!J^{k-2}E(p_a{}^c,p_b{}^c) \qquad k = 3, 4, \ldots \tag{85}$$

with

$$\begin{aligned} J = {} & (1-p_a{}^c)F(p_a{}^c,p_b{}^c) + (1-p_b{}^c)I(p_a{}^c,p_b{}^c) + {} \\ & p_a{}^c p_b{}^c[p_a{}^c(a_\mathrm{v} - a_\mathrm{w}{}^2)F(p_a{}^c,p_b{}^c) + p_b{}^c(b_\mathrm{v} - b_\mathrm{w}{}^2)I(p_a{}^c,p_b{}^c)] \end{aligned} \tag{86}$$

The symbols $F(p_a{}^c,p_b{}^c)$ and $I(p_a{}^c,p_b{}^c)$ mean that p_a and p_b involved in the quantities F and I in eq 65 and 66 are replaced by $p_a{}^c$ and $p_b{}^c$.

From eq 73 and 83, we obtain immediately the kth moment near the gel point

$$\begin{aligned} M_k &= \int_0^\infty \ldots \int_0^\infty \mathrm{d}n_1 \ldots \mathrm{d}n_s\, \mathrm{d}l_1 \ldots \mathrm{d}l_t \times (n_1 + \ldots + n_s + l_1 + \ldots + l_t)^k \tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t) \\ M_k &= \frac{A_k}{|p_b - p_b{}^c|^{2k-3}}, \qquad k = 2, 3, \ldots \end{aligned} \tag{87}$$

where A_k with $k = 2, 3, \ldots$ are defined by eq 84 and 85.

The kth moment in eq 87 can be reformulated in terms of $\tilde{P}_n$ in the form

$$M_k = \int_0^\infty n^k \tilde{P}_n\, \mathrm{d}n = \frac{A_k}{|p_b - p_b{}^c|^{2k-3}}, \qquad k = 2, 3, \ldots \tag{88}$$

with

$$\tilde{P}_n = \int_0^n \mathrm{d}m_{s+t-1} \int_0^{m_{s+t-1}} \mathrm{d}m_{s+t-2} \ldots \int_0^{m_2} \mathrm{d}m_1 \times \tilde{P}(m_1,m_2 - m_1,\ldots,m_{s+t-1} - m_{s+t-2},n - m_{s+t-1}) \tag{89}$$

where we have made use of the substitutions

$$n_1 = m_1, \qquad n_2 = m_2 - m_1, \ldots, n_s = m_s - m_{s-1}$$
$$l_1 = m_{s+1} - m_s, \ldots, l_{t-1} = m_{s+t-1} - m_{s+t-2}$$
$$l_t = n - m_{s+t-1}$$

It is obvious that $n = n_1 + \ldots + n_s + l_1 + \ldots + l_t$.

Now let us deal with the asymptopic form $\tilde{P}_n$ in eq 89. From eq 88, we introduce

$$X_k = \frac{\int_0^\infty n^k \tilde{P}_n \, \mathrm{d}n}{\int_0^\infty n^{k+1} \tilde{P}_n \, \mathrm{d}n} = \frac{A_k}{A_{k+1}} |p_b - p_b^c|^2, \qquad k = 2, 3, \ldots \tag{90}$$

to recast the kth moment as well as the $(k + 1)$th one in eq 88 into the forms

$$\int_0^\infty n^k \tilde{P}_n \, \mathrm{d}n = \frac{(A_k)^{k-(1/2)}}{(A_{k+1})^{k-(3/2)}} X_k^{(3/2)-k} \tag{91}$$

and

$$\int_0^\infty n^{k+1} \tilde{P}_n \, \mathrm{d}n = \frac{(A_k)^{k-(1/2)}}{(A_{k+1})^{k-(3/2)}} X_k^{(1/2)-k} \tag{92}$$

Taking X_k as variable to differentiate both sides of eq 91 and then using eq 92 yield

$$\int_0^\infty n^k \left[\frac{\mathrm{d}\tilde{P}_n}{\mathrm{d}X_k} + \left(k - \frac{3}{2} \right) n \tilde{P}_n \right] \mathrm{d}n = 0, \qquad k = 2, 3, \ldots \tag{93}$$

to give

$$\frac{\mathrm{d}\tilde{P}_n}{\mathrm{d}X_k} + \left(k - \frac{3}{2} \right) n \tilde{P}_n = 0 \tag{94}$$

It is easy to solve this equation to obtain

$$\tilde{P}_n = C(n,k) \exp[-(k - (3/2)) n X_k], \qquad k = 2, 3, \ldots \tag{95}$$

Hence the integration constant $C(n,k)$ can be determined by means of eq 91 such that

$$\int_0^\infty y^k C(y X_k^{-1}, k) \exp\left[-\left(k - \frac{3}{2} \right) y \right] \mathrm{d}y = \frac{(A_k)^{k-(1/2)}}{(A_{k+1})^{k-(3/2)}} X_k^{5/2} \tag{96}$$

Note that we have made use of the substitution

$$n X_k = y \tag{97}$$

As a direct result, a partial differential equation can be deduced from eq 96

$$\frac{\partial C(y X_k^{-1}, k)}{\partial X_k} = \frac{5}{2} \frac{C(y X_k^{-1}, k)}{X_k} \tag{98}$$

with the solution

$$C(y X_k^{-1}, k) = g(y,k) X_k^{5/2} \tag{99}$$

By means of the substitution given in eq 97, the form of $C(yX_k^{-1},k)$ can be rewritten as

$$C(n,k) = g(n X_k, k) X_k^{5/2} \tag{100}$$

As n and X_k in $g(nX_k,k)$ take the form of nX_k and $C(n,k)$ is independent of X_k, $g(nX_k,k)$ should have to take the form

$$g(n X_k, k) = B_k (n X_k)^{-5/2} \tag{101}$$

to give

$$C(n,k) = B_k n^{-5/2} \tag{102}$$

By using eq 96 and the expressions of A_k in eq 84 and 85, the constant B_k can be determined by writing

$$B = B_k = (2\pi J)^{-1/2} E(p_a^c, p_b^c) \tag{103}$$

The symbol B means that the constant B_k is independent of k. Thus, the asymptopic form $\tilde{P}_n$ in eq 95 can be written explicitly as

$$\tilde{P}_n = B n^{-5/2} \exp[-(k - (3/2)) n X_k], \qquad k = 2, 3, \ldots \tag{104}$$

where we have not made use of Stirling's approximation to obtain the exponent 5/2.[12,14]

Let us further introduce a generalized typical size $n\xi(k)$, which is a generalization of the typical size with $k = 2$,[14] as

$$n\xi(k) = X_k^{-1} = (p_b^c/2)^2 (2k - 3) J |p_b - p_b^c|^{-1/\sigma} \qquad k = 2, 3, \ldots \tag{105}$$

with

$$\sigma = 1/2 \tag{106}$$

to reformulate $\tilde{P}_n$ in the form

$$\tilde{P}_n = B n^{-\tau} \exp\left[-\left(k - \frac{3}{2} \right) \frac{n}{n\xi(k)} \right], \qquad k = 2, 3, \ldots \tag{107}$$

with

$$\tau = 5/2 \tag{108}$$

By taking the relation in eq 89 and the distribution $\tilde{P}_n$ in eq 107 as boundary conditions, the distribution $\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t)$ can be obtained by a similar procedure as we have performed in obtaining $\tilde{P}_n$. For brevity, we only state without proof that

$$\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t) = B(s + t - 1)!(n_1 + \ldots + n_s + l_1 + \ldots + l_t)^{-\tau'} \exp\left[-\left(k - \frac{3}{2} \right) \frac{(n_1 + \ldots + n_s + l_1 + \ldots + l_t)}{n\xi(k)} \right] \tag{109}$$

with

$$\tau' = (3/2) + s + t \tag{110}$$

When $\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t)$ is substituted in eq 89, we have

$$\tilde{P}_n = \int_0^n \mathrm{d}m_{s+t-1} \int_0^{m_{s+t-1}} \mathrm{d}m_{s+t-2} \ldots \int_0^{m_2} \mathrm{d}m_1 \times \tilde{P}(m_1, m_2 - m_1, \ldots, m_{s+t-1} - m_{s+t-2}, n - m_{s+t-1})$$

$$\tilde{P}_n = B n^{-\tau} \exp\left[-\left(k - \frac{3}{2} \right) \frac{n}{n\xi(k)} \right] \tag{111}$$

As both $\tilde{P}_n$ and $\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t)$ are characterized by the generalized typical size $n\xi(k)$, we can evaluate the kth moment M_k by means of $\tilde{P}_n$ or $\tilde{P}(n_1,\ldots,n_s,l_1,\ldots,l_t)$ with a definite k' (in formal) such that

$$M_k = B(s + t - 1)! \int_0^\infty \ldots \int_0^\infty \mathrm{d}n_1 \ldots \mathrm{d}n_s \, \mathrm{d}l_1 \ldots \mathrm{d}l_t \times (n_1 + \ldots + n_s + l_1 + \ldots + l_t)^{k-\tau'} \exp\left[-\left(k' - \frac{3}{2} \right) \frac{(n_1 + \ldots + n_s + l_1 + \ldots + l_t)}{n\xi(k')} \right]$$

$$M_k = B \int_0^\infty n^{k-\tau} \exp\left[-\left(k' - \frac{3}{2} \right) \frac{n}{n\xi(k')} \right] \mathrm{d}n$$

$$M_k = B \lambda^{-(k-(3/2))} \int_0^\infty t^{k-(5/2)} e^{-t} \, \mathrm{d}t$$

$$M_k = B \lambda^{-(k-(3/2))} \Gamma(k - (3/2)) \tag{112}$$

with

$$\lambda = \left(k' - \frac{3}{2}\right)\frac{1}{n\xi(k')} \tag{113}$$

where $\Gamma(k - (3/2))$ is the conventional Γ function.

For $k \geqslant 2$, we have from eq 112

$$M_k = B(s + t - 1)!\int_0^\infty ... \int_0^\infty \mathrm{d}n_1 ... \mathrm{d}n_s\, \mathrm{d}l_1 ... \mathrm{d}l_t \times (n_1 + ... + n_s + l_1 + ... + l_t)^{k-\tau'} \times \exp\left[-\left(k' - \frac{3}{2}\right)\frac{(n_1 + ... + n_s + l_1 + ... + l_t)}{n\xi(k')}\right]$$

$$M_k = B\int_0^\infty n^{k-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n\xi(k')}\right] \mathrm{d}n$$

$$M_k = A_k|p_b - p_b^c|^{-\gamma_k}, \qquad k, k' = 2, 3, ... \tag{114}$$

with

$$\gamma_k = 2k - 3 \tag{115}$$

Though we have made use of the distributions $\tilde{P}_n$ and $\tilde{P}(n_1,...,n_s,l_1,...,l_t)$ with a definite k' (in formal) in evaluating the kth moment, the result in eq 114 is independent of k' and it is in accordance with eq 87 and 88.

When $k = 1$, eq 112 becomes

$$M_1 = B\lambda^{1/2}\int_0^\infty t^{-3/2}e^{-t}\, \mathrm{d}t = B'\lambda^{1/2}\frac{\Gamma(-1/2)}{\Gamma(1/2)} \tag{116}$$

with

$$B' = \pi^{1/2}B = \frac{E(p_a^c,p_b^c)}{(2J)^{1/2}}$$

Note that the integrand $t^{-3/2}e^{-t}$ is divergent at the point of $t = 0$. In order to overcome this difficulty, we extend the expression of M_k in eq 112 to the complex form

$$M(Z) = B\lambda^{-z}\int_0^\infty t^{z-1}e^{-t}\, \mathrm{d}t = B\lambda^{-z}\Gamma(Z) \tag{117}$$

where Z is a complex parameter and the Gamma function $\Gamma(Z)$ satisfies the relation

$$\Gamma(1 - Z) = -Z\Gamma(-Z) \tag{118}$$

It is clear that

$$M_k = M(ReZ) \tag{119}$$

and

$$\Gamma(1 - ReZ) = -ReZ\Gamma(-ReZ) \tag{120}$$

with

$$ReZ = k - 3/2 \tag{121}$$

When $k = 2$ and $ReZ = 1/2$, eq 119 and 120 can be written as

$$M_2 = B\lambda^{-1/2}\int_0^\infty t^{-1/2}e^{-t}\, \mathrm{d}t = A_2|p_b - p_b^c|^{-1} \tag{122}$$

and

$$\Gamma(-1/2) = -2\Gamma(1/2) \tag{123}$$

The relation in eq 123 is not useful in evaluating the second moment M_2 in eq 122, but it is useful in treating the divergent behavior of the first moment M_1 in eq 116. When eq 123 is substituted in eq 116 and the divergent behavior is removed, we obtain

$$M_1 = B\lambda^{1/2}\int_0^\infty t^{-3/e-t}\, \mathrm{d}t = QA_1(p_b - p_b^c) \tag{124}$$

with

$$Q = 2(p_b^c JA_1)^{-1}E(p_a^c,p_b^c) \tag{125}$$

where we have made use of $|p_b - p_b^c| = \pm(p_b - p_b^c)$ and taken the one with a negative sign, $-(p_b - p_b^c)$.

Since the distribution $\tilde{P}(n_1,...,n_s,l_1,...,l_t)$ and $\tilde{P}_n$ have been obtained only by use of eq 87 and 88, which hold true for the kth moment M_k with $k \geqslant 2$, without involving the expression of M_1 in eq 76, the first moment M_1 defined by eq 112 with $k = 1$ may not be exact to meet the correct expression in eq 76 unless a constant N is introduced in eq 124, i.e.,

$$\begin{aligned} M_1 &= NB\lambda^{1/2}\int_0^\infty t^{-3/i}e^{-t}\, \mathrm{d}t = NQA_1(p_b - p_b^c) \\ &= 1, \qquad \text{for } p_b \leqslant p_b^c \\ &= 1 - A_1(p_b - p_b^c), \qquad \text{for } p_b \geqslant p_b^c \end{aligned} \tag{126}$$

This equation acts as a boundary condition, to which the constant N is subject, to give

$$N = \frac{1}{QA_1(p_b - p_b^c)} - \delta \tag{127}$$

with

$$\begin{aligned} \delta &= 0, \qquad \text{for } p_b \leqslant p_b^c \\ &= 1/Q, \qquad \text{for } p_b \geqslant p_b^c \end{aligned} \tag{128}$$

As a direct consequence, we obtain, by use of eq 76, 77, and 81,

$$G = \delta B(s + t - 1)!\int_0^\infty ... \int_0^\infty \mathrm{d}n_1 ... \mathrm{d}n_s\, \mathrm{d}l_1 ... \mathrm{d}l_t \times (n_1 + ... + n_s + l_1 + ... + l_t)^{1-\tau'} \times \exp\left[-\left(k' - \frac{3}{2}\right)\frac{(n_1 + ... + n_s + l_1 + ... + l_t)}{n\xi(k')}\right]$$

$$G = \delta B\int_0^\infty n^{1-\tau} \exp\left[-\left(k' - \frac{3}{2}\right)\frac{n}{n\xi(k')}\right] \mathrm{d}n$$

$$\begin{aligned} G &= 0, \qquad \text{for } p_b \leqslant p_b^c \\ &= A_1(p_b - p_b^c), \qquad \text{for } p_b \geqslant p_b^c \end{aligned} \tag{129}$$

Alternatively, a direct way of obtaining the expression of gel fraction G in eq 129 for $p_b \geqslant p_b^c$ is available by means of a direct comparison of eq 124 and 81.

The Scaling Law

Let us have a brief discussion of the generalized scaling law.[14]

By means of the generalized typical size $n\xi(k)$, eq 114 and 129 can be rewritten as

$$B(s + t - 1)!\int_0^\infty ... \int_0^\infty \mathrm{d}n_1 ... \mathrm{d}n_s\, \mathrm{d}l_1 ... \mathrm{d}l_t \times (n_1 + ... + n_s + l_1 + ... + l_t)^{1-\tau'} \times \exp\left[-\left(k' - \frac{3}{2}\right)\frac{(n_1 + ... + n_s + l_1 + ... + l_t)}{n\xi(k')}\right] = QA_1\left(\frac{A_{k+1}}{A_k}\right)^{\sigma\beta} n\xi(k)^{-\sigma\beta} \qquad \text{for } p_b \geqslant p_b^c \tag{130}$$

$$B(s + t - 1)!\int_0^\infty ... \int_0^\infty \mathrm{d}n_1 ... \mathrm{d}n_s\, \mathrm{d}l_1 ... \mathrm{d}l_t \times (n_1 + ... + n_s + l_1 + ... + l_t)^{k-\tau'} \times \exp\left[-\left(k' - \frac{3}{2}\right)\frac{(n_1 + ... + n_s + l_1 + ... + l_t)}{n\xi(k')}\right] = A_k\left(\frac{A_k}{A_{k+1}}\right)^{\sigma\gamma_k} n\xi(k)^{\sigma\gamma_k} \qquad k = 2, 3, ... \tag{131}$$

and

$$B\int_0^\infty n^{1-\tau}\exp\left[-\left(k'-\frac{3}{2}\right)\frac{n}{n\xi(k')}\right]dn = QA_1\left(\frac{A_{k+1}}{A_k}\right)^{\sigma\beta} n\xi(k)^{-\sigma\beta} \qquad \text{for } p_b \geqslant p_b^{\,c} \quad (132)$$

$$B\int_0^\infty n^{k-\tau}\exp\left[-\left(k'-\frac{3}{2}\right)\frac{n}{n\xi(k')}\right]dn = A_k\left(\frac{A_k}{A_{k+1}}\right)^{\sigma\gamma_k} n\xi(k)^{\sigma\gamma_k} \qquad k = 2, 3, \ldots \quad (133)$$

Application of the scaling transformation T associated with a positive real number L

$$Tn = Ln, \qquad Tn\xi = Ln\xi$$
$$Tn_i = Ln_i, \qquad i = 1, 2, \ldots, s$$
$$Tl_j = Ll_j, \qquad j = 1, 2, \ldots, t \qquad (134)$$

to eq 130–133 gives immediately

$$\tau' - s - t - 1 = \sigma\beta$$
$$k + s + t - \tau' = \sigma\gamma_k, \qquad k = 2, 3, \ldots \qquad (135)$$

and

$$\tau - 2 = \sigma\beta$$
$$k + 1 - \tau = \sigma\gamma_k, \qquad k = 2, 3, \ldots \qquad (136)$$

with

$$\tau' = \tau + s + t - 1 \qquad (137)$$

These relations characterized by the generalized typical size $n\xi(k)$ are a generalization of the scaling law with $k = 2$.[14]

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(2) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(3) Stockmayer, W. H. *J. Polym. Sci.* **1952**, *9*, 69; **1953**, *11*, 424.
(4) Tang, A.-c.; Kiang, Y.-s. *Sci. Sin. (Engl. Ed.)* **1963**, *12*, 997.
(5) Tang, A.-c. *The Statistical Theory of Polymeric Reactions (Chinese)*; Science Press: Beijing, China, 1981; Chapter 2.
(6) Kiang, Y.-s. *Acta Sci. Nat. (Chinese)* **1962**, *1*, 135.
(7) Flory, P. J. *J. Am. Chem. Soc.* **1947**, *68*, 30.
(8) Gordon, M. *Proc. R. Soc. London, A* **1962**, *268*, 240.
(9) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(10) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(11) Dusek, K.; Ilavsky, M.; Lunak, S. *J. Polym. Sci., Polym. Symp.* **1975**, *52*, 29.
(12) Peniche-Covas, C. A. L.; Dev, S. B.; Gordon, M.; Judd, M.; Kajiwara, *Faraday Discuss. Chem. Soc.* **1974**, *57*, 165.
(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979; Chapter 5.
(14) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* 1982, *44*, 103.

Study of Viscoelastic Relaxation in Amorphous Polypropylene near T_g by Dynamic Light Scattering and Shear Creep

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ABSTRACT: Polarized photon correlation measurements of completely amorphous polypropylene at temperatures between 268 and 293 K are reported. The time correlation functions of density fluctuation caused by local segmental motion have been represented by the Kohlrausch–Williams–Watts functions. The theory of Wang and Fischer enables us to compute the longitudinal compliance from the time correlation of the density fluctuation. The retardation spectra $L(\log \tau)$ are calculated also formally. Mechanical measurements of the longitudinal or bulk compliances are not available for comparison. However, shear creep measurements have been made by Plazek and Plazek. We find the Kohlrausch exponent of longitudinal compliance from dynamic light scattering agrees rather well with that determined from the local segmental mode contribution to the shear creep. The strong temperature dependence of the effective relaxation time was found to be experimentally identical with that observed for the shift factor of the local segmental mode and the softening transition obtained from shear creep measurements. Thus in the absence of bulk viscoelastic data we may use shear creep measurements to make comparison with dynamic light scattering data. Plazek and Plazek have found the softening dispersion has a different temperature dependence of time scale shift ($a_{T\alpha}$) from that of the terminal dispersion or the viscosity ($a_{T\eta}$) in the temperature range of −4.8 to −7.0 °C. The light scattering data have extended this temperature range up to 13 °C in which both these two different shift factors are actually measured and they continue to be different. The combined light scattering and mechanical data are examined in the light of the coupling model of relaxation. The predictions of the model account for the time correlation function observed by light scattering and the time dependence of the creep compliance obtained by mechanical measurements. More importantly the extra prediction of the model can explain the occurrence of two shift factors and relate them quantitatively, in agreement with experimental data.

Introduction

Photon correlation spectroscopy (PCS) is a potential tool in the study of slow thermal density fluctuations in polymer melts near the glass transition temperature (T_g).[1] The density time correlation function measured by PCS has been identified to be related[2] to the time-dependent bulk longitudinal compliance $N(t)$,[3] which otherwise cannot be easily obtained. The first experimental verification of this relation was subsequently carried out in the case of poly(vinyl acetate) (PVAc).[4,5]

The bulk longitudinal stress relaxation modulus $M(t)$ is given by[6] the combination $K + (4/3)G$ of the bulk modulus K and the shear modulus G. It was argued[4,5] that bulk effects predominate in $M(t)$, $K(t) \gg G(t)$ applies, and $M(t)$ is indistinguishable from the bulk modulus. Hence $N(t)$ is also well approximated by the bulk (compressional)