Invariant Property of the Distribution of A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-Type Ideal Polymerization

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ABSTRACT: In the nonlinear polymerizations, the equilibrium number fraction distribution may have a commonly invariant property. This invariant property is revealed by taking the A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-type reaction proposed by Stockmayer as an example to yield an outcome that under the transformation between the variables for describing the total system and the variables for describing the sol, the distribution is left invariant. This invariant property may lead to the fact that the average polymer quantities for the postgel can be easily obtained from the corresponding quantities for the pregel via a simple replacement of the variables for the pregel by the sol variables for the postgel. For illustration, the kth radius of the A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-type polymerization is discussed.

Introduction

As is well-known, the theory of nonlinear polymerizations was initiated by Flory[1] and Stockmayer.[2] For the evaluation of average polymer quantities, many methods[3–12] have been proposed effectively for practical use. In polymerization, the gel point is regarded as the threshold of the sol–gel transition. The behavior of the polymer quantities for the postgel is quite different from that of the quantities for the pregel. Since theoretical methods for the evaluation of average polymer quantities have been involved only in the sol regime for both the pregel and postgel, these have made the investigators[5,7,10] aware that there might be a way to connect the quantities for the postgel with those for the pregel in order to make the evaluation much easier. It will be shown in this paper that the average polymer quantities for the postgel can be easily obtained from the corresponding quantities for the pregel via a simple replacement of the variables for the pregel by the sol variables for the postgel.

This basic result is already known to some extent. Good[5] once used a branching process analysis based on probability-generating functions to look at the statistics of the sol fraction, but he may not have made the explicit observation that the distribution of the sol fraction was the same as a pregel distribution. A general theory of gel formation of multifunctional interunit junctions was proposed by Fukui and Yamabe.[7] It is easy to find that for the A_1, ..., A_f-type reaction, the weight-average molecular size for the postgel (see eq 69 in their paper[7]) can be obtained from the weight-average molecular size for the pregel (see eq 51 in their paper[7]) via a substitution of the variables for the pregel by the sol variables for the postgel. In the calculation of molecular parameters for stepwise polyfunctional polymerization, Miller, Valles, and Macosko[10] explicitly stated that the sol fraction looks like a pregel system with the parameters adjusted appropriately. Therefore, we would like to quote a sentence from their paper[10] for treating the $A_3 + B_2$ type polymerization (p 280 of their paper[10])—"Figure 4 shows $M_{sol,w}$ (weight average molecular weight for post-gel in the sol) which can be evaluated from eq 1.26 substituting $P_{A,sol}$ (the extent of reaction in the sol fraction for post-gel) for P_A (the total extent of reaction for pre-gel) and $r_{sol}(r_{sol} = P_{A,sol}/P_{B,sol})$ for $r(r = P_A/P_B)$".

The basic result just mentioned above may arise from a commonly invariant property of the equilibrium number fraction distribution; i.e., under the transformation between the variables for describing the total system and the variables for describing the sol, the distribution is left invariant. In this paper, we take the A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-type reaction proposed by Stockmayer[3] as an example to elucidate the invariant property. Furthermore, we find that the invariant property of the distribution may arise from a set of elementary invariants. The invariant property of the distribution may lead to the fact that the average polymer quantities are invariant, since the average polymer quantities are defined theoretically by means of the distribution. The similar invariant results were obtained by examining some other kinds of polymerizations. For brevity, the details are not reported in this paper.

By means of an analysis of the relations between the numerical ranges of the variables for the postgel and those of the variables for the pregel, the invariant property of the average polymer quantities results in the simplification of the evaluation for the case of the postgel. It is shown that the average polymer quantity for the postgel can be easily obtained from the corresponding quantity for the pregel via a simple replacement of the variables for the pregel by the sol variables for the postgel. To illustrate it, the kth radius of the A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-type polymerization is discussed.

Invariant Property of Equilibrium Number Fraction Distribution

In this section, we shall take Stockmayer's A_{a_1}, ..., A_{a_s} – B_{b_1}, ..., B_{b_t}-type[3] reaction as an example to reveal the invariant property of the equilibrium number fraction distribution; i.e., under the transformation between the variables for describing the total system and the variables for describing the sol, the distribution is left invariant. The discussions and results presented in this paper are limited by the ideal network assumptions: (1) all functional groups of the same type are equally reactive; (2) all groups react independently of one another; (3) no intramolecular reactions occur in finite species. Let us consider a polymerization system[3] consisting of two species of monomers A_{a_i} (i = 1, ..., s) and B_{b_j} (j = 1, ..., t) with functionalities a_i (i = 1, ..., s) and b_j (j = 1, ..., t), respectively. In order to make our

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discussion easier, some notations are introduced: N_{a_i} (N_{b_j}) is the number of monomers of A_{a_i} (B_{b_j}) in the total system, N'_{a_i} (N'_{b_j}) is the number of monomers of A_{a_i} (B_{b_j}) in the sol, p_a (p_b) is the total equilibrium fractional conversion of species A (B), p'_a (p'_b) is the sol equilibrium fractional conversion of species A (B), X_i is the fractional functionality of species A in the total system defined as

$$X_i = \frac{a_i N_{a_i}}{\sum_{i=1}^{s} a_i N_{a_i}} \qquad i = 1, 2, ..., s \tag{1}$$

X'_i is the fractional functionality of species A in the sol defined as

$$X'_i = \frac{a_i N'_{a_i}}{\sum_{i=1}^{s} a_i N'_{a_i}} \qquad i = 1, 2, ..., s \tag{2}$$

Y_j is the fractional functionality of species B in the total system defined as

$$Y_j = \frac{b_j N_{b_j}}{\sum_{j=1}^{t} b_j N_{b_j}} \qquad j = 1, 2, ..., t \tag{3}$$

and Y'_j is the fractional functionality of species B in the sol defined as

$$Y'_j = \frac{b_j N'_{b_j}}{\sum_{j=1}^{t} b_j N'_{b_j}} \qquad j = 1, 2, ..., t \tag{4}$$

The A_{a_1}, ..., A_{a_s} − B_{b_1}, ..., B_{b_t}-type distribution of (n_1 + ... + n_s + l_1 + ... + l_t)-mer, which has been proposed by Stockmayer,[3] takes the form

$$P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = C(\{n_i\},\{l_j\})\, I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) \times \prod_{i=1}^{s}[I_a^{(i)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)]^{n_i} \prod_{j=1}^{t}[I_b^{(j)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)]^{l_j} \tag{5}$$

with

$$C(\{n_i\},\{l_j\}) = (\sum_{i=1}^{s}(a_i - 1)n_i)!(\sum_{j=1}^{t}(b_j - 1)l_j)!(\prod_{i=1}^{s}(n_i)!)^{-1}(\prod_{j=1}^{t}(l_j)!)^{-1} \times [(\sum_{i=1}^{s}(a_i - 1)n_i - \sum_{j=1}^{t}l_j + 1)!]^{-1}[(\sum_{j=1}^{t}(b_j - 1)l_j - \sum_{i=1}^{s}n_i + 1)!]^{-1} \tag{6}$$

where $\{N_{a_i}\}$ and $\{N_{b_j}\}$ are used to denote N_{a_1}, N_{a_2}, ..., N_{a_s} and N_{b_1}, N_{b_2}, ..., N_{b_t}, respectively. The $s + t + 2$ quantities I_a, I_b, $I_a^{(i)}$ (i = 1, 2, ..., s), $I_b^{(j)}$ (j = 1, 2, ..., t) defined by Stockmayer[3] in (5) can be written as

$$I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = (\sum_{i=1}^{s}a_i N_{a_i})(1 - p_a)(1 - p_b)/p_b \tag{7}$$

$$I_b(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = (\sum_{j=1}^{t}b_j N_{b_j})(1 - p_a)(1 - p_b)/p_a \tag{8}$$

$$I_a^{(i)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \frac{(a_i N_{a_i})p_b(1 - p_a)^{a_i - 1}}{(\sum_{i=1}^{s}a_i N_{a_i})(1 - p_b)} \qquad i = 1, ..., s \tag{9}$$

$$I_b^{(j)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \frac{(b_j N_{b_j})p_a(1 - p_b)^{b_j - 1}}{(\sum_{j=1}^{t}b_j N_{b_j})(1 - p_a)} \qquad j = 1, ..., t \tag{10}$$

Note that the distribution in (5) is expressed in terms of I_a, $I_a^{(i)}$ (i = 1, 2, ..., s), and $I_b^{(j)}$ (j = 1, 2, ..., t) and, equivalently, the distribution can also be expressed in terms of I_b, $I_a^{(i)}$ (i = 1, 2, ..., s), and $I_b^{(j)}$ (j = 1, 2, ..., t). It is known that the distribution (5) permits the computation of various average properties for both the pregel and postgel of ideal polymerizations. Furthermore, we emphasize that the quantities I_a, I_b, $I_a^{(i)}$, and $I_b^{(j)}$ are dependent on the total system variables N_{a_i} (i = 1, 2, ..., s), N_{b_j} (j = 1, 2, ..., t), p_a, and p_b, whereas the quantity $C(\{n_i\},\{l_j\})$ is a constant for a fixed set of $\{n_i\},\{l_j\}$. Since, for the pregel, the total system variables N_{a_i}, N_{b_j}, p_a, and p_b are identical to the sol variables N'_{a_i}, N'_{b_j}, p'_a, and p'_b, it is obvious that the quantities I_a, I_b, $I_a^{(i)}$, and $I_b^{(j)}$ are subject to $s + t + 2$ trivial invariant relations as follows:

for the pregel

$$I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_a(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \tag{11}$$

$$I_b(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \tag{12}$$

$$I_a^{(i)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_a^{(i)}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \qquad i = 1, ..., s \tag{13}$$

$$I_b^{(j)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b^{(j)}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \qquad j = 1, ..., t \tag{14}$$

These invariant relations make us realize that the same relations may be extended to the postgel regime, i.e.

for the postgel

$$I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_a(\{N'_{a_i}),\{N'_{b_j}\},p'_a,p'_b) \tag{15}$$

$$I_b(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \tag{16}$$

$$I_a^{(i)}(\{N_{a_i}),\{N_{b_j}\},p_a,p_b) = I_a^{(i)}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \qquad i = 1, ..., s \tag{17}$$

$$I_b^{(j)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b^{(j)}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \qquad j = 1, ..., t \tag{18}$$

The relations (11)−(18) show that for both the pregel and postgel, the $s + t + 2$ quantities I_a, I_b, $I_a^{(i)}$, and $I_b^{(j)}$ are left invariant under the transformation between the total system variables N_{a_i}, N_{b_j}, p_a, and p_b and the sol variables N'_{a_i}, N'_{b_j}, p'_a, and p'_b. The transformation can be written formally as

$$N_{a_i} = N_{a_i}(\{N'_{a_k}\},\{N'_{b_q}\},p'_a,p'_b) \qquad (19)$$

$$N_{b_j} = N_{b_j}(\{N'_{a_k}\},\{N'_{b_q}\},p'_a,p'_b) \qquad (20)$$

$$p_a = p_a(\{N'_{a_k}\},\{N'_{b_q}\},p'_a,p'_b) \qquad (21)$$

$$p_b = p_b(\{N'_{a_k}\},\{N'_{b_q}\},p'_a,p'_b) \qquad (22)$$

$$i, k = 1, 2, ..., s$$

$$j, q = 1, 2, ..., t$$

As a direct result of the relations in (11)–(18), we shall see that the invariant property of the distribution in (5) can be easily deduced. Thus, the $s + t + 2$ quantities I_a, I_b, $I_a^{(i)}$, and $I_b^{(j)}$ are referred to as elementary invariant quantities. Several other types of polymerizations were examined by us and it showed that the corresponding distributions did possess their elementary invariant quantities. For brevity, the details are not reported here.

Now let us deal with the invariant relations for the postgel in (15)–(18). It seems that the invariant relations for the postgel in (15)–(18) cannot be proved directly by using the transformation in (19)–(22), since the transformation equations cannot be obtained explicitly except for several special cases. Alternatively, the invariant relations for the postgel can be proved by means of the probability method without using the transformation given by (19)–(22). Let us begin to discuss the probability method. The sol fractions S_{a_i} and S_{b_j} which will be involved in the discussion are defined as

$$S_{a_i} = \frac{N'_{a_i}}{N_{a_i}} \qquad i = 1, 2, ..., s \qquad (23)$$

$$S_{b_j} = \frac{N'_{b_j}}{N_{b_j}} \qquad j = 1, 2, ..., t \qquad (24)$$

By means of the polymer statistics,[11,12] it is not difficult to find that the probability of finding, in the system, a functional group of type A which is not involved in polymerization is

$$1 - p_a \qquad (25)$$

the probability of finding a functional group of type A to react with the functional group of type B of a certain $(n_1 + ... + n_s + l_1 + l_t)$-mer in the sol is

$$p_a \sum_{j=1}^{t} Y_j S_{b_j} \frac{1 - p'_b}{1 - p_b} \qquad (26)$$

Thus, the total probability[8,9,10] of finding a functional group of type A in the sol is

$$X = 1 - p_a + p_a \sum_{j=1}^{t} Y_j S_{b_j} \frac{1 - p'_b}{1 - p_b} \qquad (27)$$

Similarly, the total probability of finding a functional group of type B in the sol is

$$Y = 1 - p_b + p_b \sum_{i=1}^{s} X_i S_{a_i} \frac{1 - p'_a}{1 - p_a} \qquad (28)$$

Since the sol fraction S_{a_i} (S_{b_j}) is the probability of finding a monomer of A_{a_i} (B_{b_j}) in the sol, it takes the form for the postgel

$$S_{a_i} = X^{a_i} \qquad i = 1, 2, ..., s \qquad (29)$$

$$S_{b_j} = Y^{b_j} \qquad j = 1, 2, ..., t \qquad (30)$$

where we have taken into account the monomers A_{a_i} and B_{b_j} which have a_i and b_j functionalities with respect to the functional groups A and B.

The probability of finding a functional group of type A, which belongs to A_{a_i}, having reacted in the sol is

$$S_{a_i} \frac{1 - p'_a}{1 - p_a} \qquad (31)$$

This probability can be evaluated by means of an alternative probability consideration. When a functional group of monomer A_{a_i} has reacted in the sol, it is obvious that there are, in the sol, $a_i - 1$ functional groups which belong to A_{a_i}. The probability of finding the $a_i - 1$ functional groups in the sol is

$$X^{a_i - 1} \qquad (32)$$

Thus, we have for the postgel

$$S_{a_i} \frac{1 - p'_a}{1 - p_a} = X^{a_i - 1} \qquad i = 1, 2, ..., s \qquad (33)$$

Similarly, we have for the postgel

$$S_{b_j} \frac{1 - p'_b}{1 - p_b} = Y^{b_j - 1} \qquad j = 1, 2, ..., t \qquad (34)$$

Combining (29) and (33) gives for the postgel

$$\frac{1 - p_a}{1 - p'_a} = 1 - p_a + p_a \frac{(1 - p'_b)(\sum_{j=1}^{t} b_j N'_{b_j})}{(1 - p_b)(\sum_{j=1}^{t} b_j N_{b_j})} \qquad (35)$$

where we have made use of (24) and (27). Similarly, we obtain, from (30) and (34) for the postgel

$$\frac{1-p_b}{1-p_b'} = 1 - p_b + p_b\frac{(1-p_a')(\sum_{i=1}^{s} a_i N_{a_i}')}{(1-p_a)(\sum_{i=1}^{s} a_i N_{a_i})} \quad (36)$$

Taking into consideration (35) together with the definition of X in (27), we have, from (29)

for the postgel

$$\frac{N_{a_i}'}{N_{a_i}} = \left(\frac{1-p_a}{1-p_a'}\right)^{a_i} \quad i = 1, ..., s \quad (37)$$

where we have made use of the definition of S_{a_i} in (23). Similarly, we have, by means of (30) and (34)

for the postgel

$$\frac{N_{b_j}'}{N_{b_j}} = \left(\frac{1-p_b}{1-p_b'}\right)^{b_j} \quad j = 1, ..., t \quad (38)$$

It should be pointed out that the $s + t + 2$ relations in (35)–(38) are independent. By a mathematical method essentially similar to that which has been introduced into the theory of the condensation of real gas by Mayer and by others and which has been applied to the theory of molecular size distribution and gel formation in branched chain polymers by Stockmayer, a general theory of gel formation of multifunctional interunit junctions was proposed by Fukui and Yamabe[7] to treat Stockmayer's A_1, ..., $A_f - B_1$, ..., B_g-type reaction to give eqs 101 and 102 on p 2060 of their paper,[7] and these two equations correspond to (37) and (38) in this paper. In this section, we shall see that by means of (35)–(38), the invariant relations of elementary invariant quantities for the postgel given by (15)–(18) can be easily proved.

It is not difficult to find that by means of the definition of I_a in (7), (36) can be rewritten as

for the postgel

$$I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_a(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad (39)$$

Similarly, we have, from (35)

for the postgel

$$I_b(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad (40)$$

Let us rewrite (37) in the form

for the postgel

$$N_{a_i}(1-p_a)^{a_i} = N_{a_i}'(1-p_a')^{a_i} \quad i = 1, 2, ..., s \quad (41)$$

Dividing the left-hand side of this equation by $I_a(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and then dividing the right-hand side by $I_a(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b')$ give

for the postgel

$$I_a^{(i)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_a^{(i)}(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad i = 1, 2, ..., s \quad (42)$$

where we have made use of (39). Similarly, we have, from (38) and (40)

for the postgel

$$I_b^{(j)}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = I_b^{(j)}(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad j = 1, 2, ..., t \quad (43)$$

The invariant relations for the postgel in (39), (40), (42), and (43) are just the relations in (15)–(18) which have been regarded as an extention of the relations in (11)–(14) for the pregel. As a direct result of the $s + t + 1$ invariant relations in (39), (42), and (43) for the elementary invariant quantities, it is easy to find that the Stockmayer distribution in (5) is left invariant under the transformation between the total system variables N_{a_i}, N_{b_j}, p_a, and p_b and the sol variables N_{a_i}', N_{b_j}', p_a', and p_b', i.e.

for the postgel

$$P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = P_{\{n_i\},\{l_j\}}(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad (44)$$

Also, we have the trivial invariant relation for the pregel

for the pregel

$$P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = P_{\{n_i\},\{l_j\}}(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad (45)$$

where we have made use of the trivial invariant relations for the pregel in (11), (13), and (14) for the elementary invariant quantities.

Invariant Property of the Average Polymer Quantities

In this section, we shall deal with the invariant property of average polymer quantities.

By means of the distribution $P_{n_i,l_j}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ in (5), an average polymer quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ which is associated with the polymer quantity $F(\{n_i\},\{l_j\})$ can be defined by writing

$$F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \sum_{\{n_i\},\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) \quad (46)$$

Notice that the polymer quantity $F(\{n_i\},\{l_j\})$ is independent of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b.

Now let us discuss first the invariant property of the average polymer quantity in (46) for the postgel. Since the distribution in (5) is an invariant quantity for the postgel (see (44)), the product of the two quantities $F(\{n_i\},\{l_j\})$ and $P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ which appear as a term in the sum in (46) is also an invariant quantity, i.e.

for the postgel

$$F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}'\},\{N_{b_j}'\},p_a',p_b') \quad (47)$$

where we have made use of the fact that the polymer quantity $F(\{n_i\},\{l_j\})$ is independent of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b and the sol variables $\{N_{a_i}'\}$, $\{N_{b_j}'\}$, p_a', and p_b'. By taking the summation with respect to the indices $\{n_i\}$ and $\{l_j\}$ on both sides of the relation in (47), we obtain

for the postgel

$$\sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (48)$$

It is obvious that this relation is an invariant relation, and it signifies that under the transformations between the total system variables and the sol variables, the quantity $\sum_{\{n_i\}\{l_j\}}F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ which keeps the expression in the summation form is left invariant. When the sums are worked out on both the left- and right-hand sides of (48), we may get two explicit expressions of the average polymer quantities which are denoted by $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$, i.e.

$$F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) \quad (49)$$

$$F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) = \sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (50)$$

We further emphasize that the explicit expressions $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ are obtained by working out the sums in (49) and in (50), respectively. It should be noted that since the numerical ranges of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b are not the same as the numerical ranges of the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b, $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ may have quite different expressions.

By using the expressions of the average polymer quantities in (49) and (50), the invariant relation in (48) becomes

for the postgel

$$F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (51)$$

This relation means that for the postgel, the numerical value of $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ or equivalently the numerical value of $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ is left invariant under the transformation between the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b and the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, p'_b.

For the pregel, it is obvious that the two expressions $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ in (49) and (50) are the same, i.e.

for the pregel

$$F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = \sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) \quad (52)$$

$$F(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) = \sum_{\{n_i\}\{l_j\}} F(\{n_i\},\{l_j\})\, P_{\{n_i\},\{l_j\}}(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (53)$$

Thus the invariant relation in (48) for the pregel can be written as

for the pregel

$$F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = F(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (54)$$

This equation is a trivial invariant relation, since, for the pregel, the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b and the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b are identical.

Relation between the Postgel and Pregel Polymer Quantities

In order to make our discussion easier, we write down again the two invariant relations in (54) and (51) which are remarked in this section as (55) and (56)

for the pregel

$$F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = F(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (55)$$

for the postgel

$$F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) = F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b) \quad (56)$$

In this section, we shall discuss the relation between the average polymer quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ on the left-hand side of (55) for the pregel and the average polymer quantity $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ on the right-hand side of (56) for the postgel. It shall be shown that the quantity $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ for the postgel can be easily obtained from the quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ for the pregel via a simple replacement of the variables for the pregel by the sol variables for the postgel. Notice that in (55), the quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ is identical with the quantity $F(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$.

Let us discuss, in the polymerization, the numerical ranges of the $s + t + 2$ total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b and the numerical ranges of the $s + t + 2$ sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b.

For the pregel, the total system variables and the sol variables are identical and their numerical ranges are given as follows

$$p_a\ (=p'_a)\colon\ 0 \rightarrow p_a^c \qquad p_b\ (=p'_b)\colon\ 0 \rightarrow p_b^c$$
$$N_{a_i}\ (=N'_{a_i}) > 0 \quad i = 1, ..., s \qquad N_{b_j}\ (=N'_{b_j}) > 0 \quad j = 1, ..., t \quad (57)$$

where the symbol c of p^c is used to denote the value of p at the gel point. (57) states that p_a ($= p'_a$) takes the values from zero to p_a^c, p_b ($= p'_b$) takes the values from zero to p_b^c, and N_{a_i} ($= N'_{a_i}$) and N_{b_j} ($= N'_{b_j}$) are positive.

For the postgel, the numerical values of the sol variables take the following ranges

$$p'_a\colon\ p_a^c \rightarrow 0 \qquad p'_b\colon\ p_b^c \rightarrow 0$$
$$N'_{a_i}\colon\ N_{a_i} \rightarrow 0 \quad i = 1, ..., s \qquad N'_{b_j}\colon\ N_{b_j} \rightarrow 0 \quad j = 1, ..., t \quad (58)$$

(58) states that p'_a takes the values from p_a^c to zero, p'_b from p_b^c to zero, N'_{a_i} from N_{a_i} to zero, and N'_{b_j} from N_{b_j} zero. Though N_{a_i} ($= N'_{a_i}$) and N_{b_j} ($= N'_{b_j}$) for the pregel (57) are fixed for a given polymerization, their values can still be changed (experimentally) at the beginning

of the reaction, and then N_{a_i} ($= N'_{a_i}$) and N_{b_j} ($= N'_{b_j}$) for the pregel can be regarded as formally changing in the manner N_{a_i} ($= N'_{a_i}$): $N_{a_i} \to 0$ and N_{b_j} ($= N'_{b_j}$): $N_{b_j} \to 0$. Thus (57) and (58) can be interpreted such that the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b for the pregel have the same numerical ranges as the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b for the postgel. These indicate that when the sum in (52) for the pregel and the sum in (50) for the postgel are worked out, the quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ for the pregel on the left-hand side of (55) and the quantity $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ for the postgel on the right-hand side of (56) will give the same explicit expression. Thus, we conclude that the quantity $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ for the postgel on the right-hand side of (56) can be easily obtained from the quantity $F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ for the pregel on the left-hand side of (55) via a simple replacement of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b for the pregel by the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b for the postgel, i.e.

$$\underset{\text{pregel}}{\{N_{a_i}\}, \{N_{b_j}\}, p_a, p_b} \to \underset{\text{postgel}}{\{N'_{a_i}\}, \{N'_{b_j}\}, p'_a, p'_b} \quad (59)$$

$$\underset{\text{pregel}}{F(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)} \to \underset{\text{postgel}}{F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)} \quad (60)$$

Now let us return to the relation in (56) satisfied by the quantities $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ and $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ for the postgel. It is known that the expression of $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ can be obtained explicitly in terms of the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b, whereas the expression of $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ cannot be, in general, obtained explicitly in terms of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b, except for some simple systems such as the $A_3 - B_2$-type,[10] $A_4 - B_2$-type, and so on. If the quantity $F_2(\{N'_{a_i}\},\{N'_{b_j}\},p'_a,p'_b)$ is given for a set of fixed values of sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b, we ask, what is the corresponding values of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b which are involved in the quantity $F_1(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$? It is easily seen that for a set of fixed values of sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b, the total system variables can be evaluated numerically by solving the transformation equations in (19)–(22) which arise from (35)–(38), but for some simple systems such as the $A_3 - B_2$-type,[10] $A_4 - B_2$-type, and so on, the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, *and* p_b can be obtained explicitly in terms of the sol variables $\{N'_{a_i}\}$, $\{N'_{b_j}\}$, p'_a, and p'_b.

The kth Radius of $A_{a_1}, ..., A_{a_s} - B_{b_1}, ..., B_{b_t}$-Type Polymerization

As an illustration of the invariant property in polymerization, the kth radius of $A_{a_1}, ..., A_{a_s} - B_{b_1}, ..., B_{b_t}$-type polymerization is taken as an example for our discussion. For brevity, we restrict our discussion to the second radius. Since the second radius is given, the other kth radius can be obtained by the recursion method which has been proposed by some of the present authors.[12]

By means of the expression of average polymer quantity defined by (46), the kth radius $\langle R^2\rangle_k$ associated with the quantity

$$F^k(\{n_i\},\{l_j\}) = \langle R^2_{\{n_i\},\{l_j\}}\rangle(\sum_i m_{a_i}n_i + \sum_j m_{b_j}l_j)^k \quad (61)$$

can be written as[12]

$$\langle R^2\rangle_k = \sum_{\{n_i\},\{l_j\}} \langle R^2_{\{n_i\},\{l_j\}}\rangle(\sum_i m_{a_i}n_i + \sum_j m_{b_j}l_j)^k \times P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b) \quad (62)$$

where $\langle R^2_{\{n_i\},\{l_j\}}\rangle$ is the $A_{a_1}, ..., A_{a_s} - B_{b_1}, ..., B_{b_t}$-type mean-square radius of gyration, and m_{a_i} (m_{bj}) is used to denote the mass of monomer A_{a_i} (B_{b_j}). In order to obtain the explicit expression of $\langle R^2_{\{n_i\},\{l_j\}}\rangle$, we shall discuss the decomposition of the combinatorial coefficient $C(\{n_i\},\{l_j\})$ given by (6).

By means of polymer chemical kinetics, the decomposition of $C(\{n_i\},\{l_j\})$ can be expressed as[12]

$$C(\{n_i\},\{l_j\}) = \frac{1}{\sum_i n_i + \sum_j l_j - 1} \sum_{\{k_i\}\{m_j\}} N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\}) \quad (63)$$

with

$$N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\}) = \frac{1}{2}[(\sum_i(a_i - 1)k_i - \sum_j m_j + 1)(\sum_j(b_j - 1)(l_j - m_j) - \sum_i(n_i - k_i) + 1) + (\sum_j(b_j - 1)m_j - \sum_i k_i + 1)(\sum_i(a_i - 1)(n_i - k_i) - \sum_j(l_j - m_j) + 1)] \times C(\{n_i - k_i\},\{l_j - m_j\})\, C(\{k_i\},\{m_j\}) \quad (64)$$

Furthermore, (63) can be rewritten as

$$\sum_{\{k_i\}\{m_j\}} \frac{N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})}{C(\{n_i\},\{l_j\})} = \sum_i n_i + \sum_j l_j - 1 \quad (65)$$

Since the term $\sum_i n_i + \sum_j l_j - 1$ on the right-hand side of (65) is the number of bonds in the $(\sum_i n_i + \sum_j l_j)$-mer, the term $N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})/C(\{n_i\},\{l_j\})$ on the left-hand side of (65) should be the number of bonds associated with an imagined split of the $(\sum_i n_i + \sum_j l_j)$-mer. From the explicit expression of $N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})$ in (64), it is not difficult to find that the term $N\{(n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})/C(\{n_i\},\{l_j\})$ is the number of bonds in the $(\sum_i n_i + \sum_j l_j)$-mer whose splitting produces two moieties of $(\sum_i k_i + \sum_j m_j)$ and $(\sum_i(n_i - k_i) + \sum_j(l_j - m_j))$ units, respectively.

By means of the decomposition of $C(\{n_i\},\{l_j\})$ in (63) together with (64), the $A_{a_1}, ..., A_{a_s} - B_{b_1}, ..., B_{b_t}$-type mean-square radius of gyration $\langle R^2_{\{n_i\},\{l_j\}}\rangle$ can be written[12] via the formulation of Gordon and Dobson[6] in the form

$$\langle R^2_{\{n_i\},\{l_j\}}\rangle = \frac{b_0^{\,2}}{(\sum_i m_{a_i} n_i + \sum_j m_{b_j} l_j)^2} \times \sum_{\{k_i\}\{m_j\}} \frac{N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})}{C(\{n_i\},\{l_j\})} [\sum_i m_{a_i}(n_i - k_i) + \sum_j m_{b_j}(l_j - m_j)][\sum_i m_{a_i} k_i + \sum_j m_{b_j} m_j] \quad (66)$$

where b_0 is the average bond length. In obtaining this expression, we have considered the meaning of the term $N(\{n_i - k_i\},\{l_j - m_j\},\{k_i\},\{m_j\})/C(\{n_i\},\{l_j\})$ in (65).

By substituting $\langle R^2_{\{n_i\},\{l_j\}}\rangle$ given by (66) and the distribution $P_{\{n_i\},\{l_j\}}(\{N_{a_i}\},\{N_{b_j}\},p_a,p_b)$ given by (5) in $\langle R^2\rangle_k$ with $k = 2$ given by (62) and then by making use of some algebraic techniques, we can obtain the second radius for the pregel

$$\langle R^2\rangle_2 = \frac{b_0^{\,2} p_b}{N_A D^2}[m_a + p_b(a_w - 1)m_b][m_b + p_a(b_w - 1)m_a] \quad (67)$$

with

$$N_A = \sum_{i=1}^{s} a_i N_{a_i} \quad (68)$$

$$D = 1 - (a_w - 1)(b_w - 1)p_a p_b \quad (69)$$

$$a_w = \sum_{i=1}^{s} a_i X_i \qquad b_w = \sum_{j=1}^{t} b_j Y_j \quad (70)$$

$$m_a = \sum_{i=1}^{s} m_{a_i} a_i N_{a_i} \qquad m_b = \sum_{j=1}^{t} m_{b_j} b_j N_{b_j} \quad (71)$$

for the postgel

$$\langle R^2\rangle_2 = \frac{b_0^{\,2} p_b'}{N_A' D'^2}[m_a' + p_b'(a_w' - 1)m_b'][m_b' + p_a'(b_w' - 1)m_a'] \quad (72)$$

with

$$N_A' = \sum_{i=1}^{s} a_i N_{a_i}' \quad (73)$$

$$D' = 1 - (a_w' - 1)(b_w' - 1)p_a' p_b' \quad (74)$$

$$a_w' = \sum_{i=1}^{s} a_i X_i' \qquad b_w' = \sum_{j=1}^{t} b_j Y_j' \quad (75)$$

$$m_a' = \sum_{i=1}^{s} m_{a_i} a_i N_{a_i}' \qquad m_b' = \sum_{j=1}^{t} m_{b_j} b_j N_{b_j}' \quad (76)$$

Notice that, in the evaluation of $\langle R^2\rangle_2$ for the postgel, we have made use of the invariant property of the distribution in (44).

It is easily seen that the second radius $\langle R^2\rangle_2$ in (72) for the postgel regime can be easily obtained from the second radius $\langle R^2\rangle_2$ for the pregel regime in (67) via a simple replacement of the total system variables $\{N_{a_i}\}$, $\{N_{b_j}\}$, p_a, and p_b for the pregel by the sol variables $\{N_{a_i}'\}$, $\{N_{b_j}'\}$, p_a', and p_b' for the postgel.

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