

KINETIC ANALYSIS OF CO-CONDENSATION POLYMERIZATION OF AB₂ AND AB MONOMERS*

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Abstract This work deals with the kinetics of co-condensation polymerization of AB₂ and AB monomers, giving expressions of the two-dimensional molecular weight distribution function and the number/weight average molecular weights of the resulting copolymers. The two-dimensional molecular weight distribution depends on two indices, n and l , which are the respective numbers of AB₂ and AB units in a copolymer species. The evolution of the two-dimensional weight and z distributions during the co-condensation polymerization has been evaluated systematically. Finally, the two-dimensional distribution was transformed into a one-dimensional molecular weight distribution with only one variable (the molecular weight of the products instead of the degree of polymerization). The calculated results show that the highly branched copolymer has a very broad molecular weight distribution when the co-condensation polymerization approaches completion.

Keywords Hyperbranched copolymer, Kinetic analysis, Molecular weight distribution

INTRODUCTION

Early in the 50's of the last century, Flory^[1] theoretically studied the polycondensation of AB_{*f*-1} type monomers and the co-condensation polymerization of an AB_{*f*-1} and an AB monomer by a probabilistic approach, giving the molecular size distribution function and the average degree of polymerization. A copolymer consists of two sorts of monomer units with different molecular weights. Therefore in a copolymer species with a certain degree of polymerization, there may be varieties of composition and molecular weight. The degree of polymerization and its distribution can not be directly used to describe the molecular weight and the molecular weight distribution of a copolymer. Apparently it is the molecular weight instead of the degree of polymerization that is meaningful for copolymers. As far as the co-condensation polymerization of AB_{*f*-1} and AB monomers is concerned, Flory^[1] simply assumed that the two monomers have an equal molecular weight. Apparently, this simplified assumption is unreasonable because there are few monomers with the same molecular weight. Hitherto, no effort has been made to improve the related theory. On the other hand, no attention had been paid to this kind of polymerization until Kricheldorf^[2] reported the co-condensation polymerization of AB₂ and AB monomers to prepare highly branched polyesters in 1982. It was Kim and Webster^[3-5] who synthesized a highly soluble polyphenylene from 3,5-dibromophenyl-boric acid by way of polycondensation and described it as a "hyperbranched polymer". Since then hyperbranched polymers and copolymers have attracted the attention of polymer chemists, and thousands of papers have been published to date. On a theoretical aspect, Müller and coworkers^[6] have established a kinetic theory for the polycondensation of AB₂ monomers obtaining the formulae for the degree of branching and the molecular weight distribution. In the meantime, Frey^[7-9] reported expressions for the degree of branching obtained by a statistical method for the hyperbranched polymers made from AB_{*m*} monomers and the highly branched copolymers composed of AB_{*m*} and AB monomers. The authors^[10] of this work have derived the

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Where N and L are the initial quantities of the AB_2 and $A-B$ type monomers, respectively. The constraint conditions can be written as:

$$\sum_{n+l \geq 1} nP_{n,l} = N \quad (3)$$

$$\sum_{n+l \geq 1} lP_{n,l} = L \quad (4)$$

Because there is only one A group in each of the species, the conversion of A groups is defined by:

$$x = \frac{N + L - \sum_{n,l} P_{n,l}}{N + L} \quad (5)$$

It results in

$$\sum_{n,l} P_{n,l} = (N + L)(1 - x) \quad (6)$$

Differentiating both sides of Eq. (6), one obtains:

$$\frac{d \sum_{n,l} P_{n,l}}{dt} = -(N + L) \frac{dx}{dt} \quad (7)$$

On the other hand, Eq. (1) can be written as

$$\frac{dP_{n,l}}{dt} = \frac{k}{2} \sum (n+2)P_{i,j}P_{n-i,l-j} - kP_{n,l}[(n+2)(N+L)(1-x) + N] \quad (1)'$$

Summing up the left and the right sides of Eq. (1)', respectively, over the index n and l , we find (see Appendix 1):

$$\frac{d \sum_{n,l} P_{n,l}}{dt} = -k(N+L)(1-x)[N + (N+L)(1-x)] \quad (8)$$

Comparing Eq. (7) with Eq. (8), we have

$$\frac{dx}{dt} = k(N+L)(1-x)(1+r-x) \quad (9)$$

where r is the initial fraction of the AB_2 monomer in total monomers:

$$r = \frac{N}{N+L} \quad (10)$$

The initial condition of Eq. (9) is

$$x|_{t=0} = 0 \quad (11)$$

Its solution is given as

$$x = 1 - \frac{r}{(1+r)e^{kNt} - 1} \quad (12)$$

If Eq. (1) is divided by Eq. (9), it can be transformed into a set of linear differential equations with a new variable x :

$$\frac{dP_{n,l}}{dx} = \frac{n+2}{2(N+L)} \frac{\sum_{i,j} P_{i,j} P_{n-i,l-j}}{(1-x)(r+1-x)} - \frac{(n+2)(1-x)+r}{(1-x)(r+1-x)} P_{n,l} \quad (13)$$

This equation can be solved rigorously.

MOLECULAR PARAMETERS

After a laborious derivation, we can find the solutions of Eq. (13):

$$P_{n,l} = (N+L) \cdot \frac{(l+2n)!}{l!n!(n+1)!} \cdot \frac{(1-x)(1+r-x)}{x} \cdot \left[\frac{rx(1+r-x)}{(1+r)^2} \right]^n \left(\frac{1-r}{1+r} x \right)^l \quad (14)$$

The details of derivation of Eq. (14) are given in Appendix 2. Flory derived the expression of $P_{n,l}$ by a statistical method^[1].

Equation (14) is the molecular size distribution function of the hyperbranched polymers formed during the polycondensation of an A-B type monomer with an AB₂ one. From Eq. (14) we can derive various statistical moments of various species. Besides Eq. (6) we can find the expressions of other moments of $P_{i,j}$:

$$\sum_{n,l} n^2 P_{n,l} = \frac{(N+L)r}{(1+r)^2(1-x)^2} [(1-x)^2(1+r)^2 + 2rx(2+2r-2x-rx)] \quad (15)$$

$$\sum_{n,l} l^2 P_{n,l} = \frac{(N+L)(1-r)}{(1+r)^2(1-x)^2} [(1-x)^2(1+r)^2 + 2(1-r)x(1+r-x)] \quad (16)$$

$$\sum_{n,l} nl P_{n,l} = \frac{(N+L)(1-r)rx}{(1+r)^2(1-x)^2} (3+3r-3x-rx) \quad (17)$$

The derivation procedures of Eq. (15)–(17) is given in Appendix 3. The number- and the weight-average molecular weights of the reaction system can be expressed as:

$$\overline{M}_n = \frac{\sum_{n,l} (nw_2 + lw_1) P_{n,l}}{\sum_{n,l} P_{n,l}} = \frac{w_2 r + w_1 (1-r)}{1-x} \quad (18)$$

and

$$\begin{aligned} \overline{M}_w &= \frac{\sum_{n,l} (nw_2 + lw_1)^2 P_{n,l}}{\sum_{n,l} (nw_2 + lw_1) P_{n,l}} \\ &= \{w_2^2 r [(1-x)^2(1+r)^2 + 2rx(2+2r-2x-rx)] + \\ &\quad 2w_1 w_2 r (1-r)x(3+3r-3x-rx) + \\ &\quad w_1^2 (1-r) [(1-x)^2(1+r)^2 + 2(1-r)x(1+r-x)]\} / \\ &\quad \{[w_2 r + w_1 (1-r)](1+r)^2(1-x)^2\} \end{aligned} \quad (19)$$

where w_1 and w_2 are the respective molecular weights of structural units AB and AB₂.

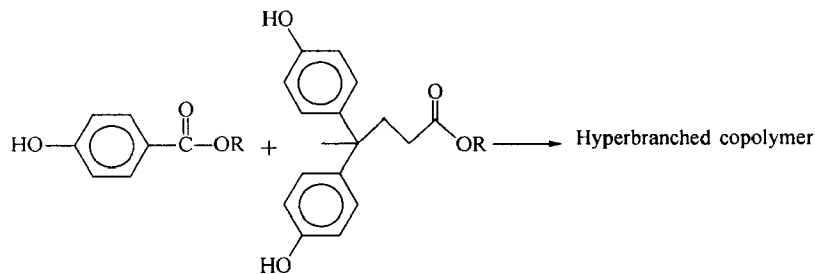
The polydispersity index is defined as:

$$D = \frac{\overline{M}_w}{\overline{M}_n} \quad (20)$$

Finally, we can predict the evolution of the molecular weight distribution and its averages for the resulting highly branched copolymer during the polycondensation.

FURTHER DISCUSSION ON AVERAGE MOLECULAR WEIGHTS

Prior to calculation of the molecular weight of a highly branched copolymer, we have to take account of varieties of the structural units in the copolymer and their molecular weights. From Scheme 1 we can find that there are two sorts of linear units (abB and ab), two sorts of terminal units (aB_2 and aB) and one kind of dendritic unit (ab_2) in the copolymer species. Besides, there is only one focus unit in every hyperbranched copolymer species, which is one of the three possible units, Ab_2 , AbB and Ab (it is the first one in Scheme 1). If we count the numbers of various units, we can further find that the number of total terminal units equals the number of dendritic units plus 2. The molecular weight of a linear unit equals the average value of the molecular weights of a terminal unit and a dendritic unit generated from the same sort of monomers. As a gross approximation, the difference in molecular weight between a linear unit and a focus unit, and between the two excess terminal units and two linear units, can be neglected because a hyperbranched copolymer species usually consists of hundreds of monomeric units. Then we can directly use Eqs. (18) and (19) to calculate the number-average and weight-average molecular weights of hyperbranched copolymers assuming the molecular weight of the ab unit is w_1 and that of the abB unit is w_2 . As an example, the following co-condensation polymerization of AB_2 and AB monomers is taken into account (see Scheme 2):



Scheme 2

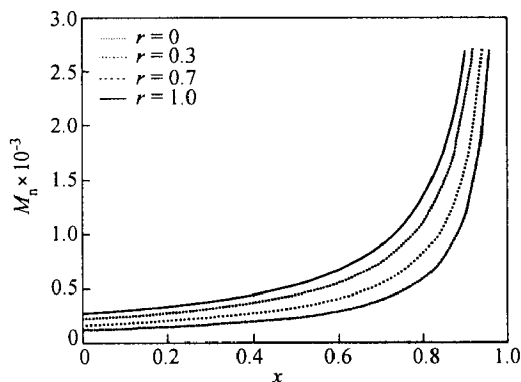


Fig. 1 Plot of number-average molecular weight versus A group conversion, $r = 0, 0.3, 0.7$ and 1.0

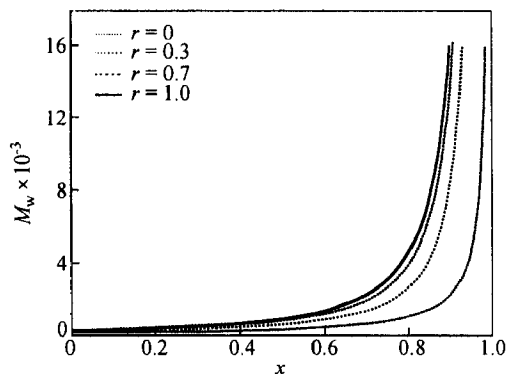


Fig. 2 Plot of weight-average molecular weight versus A group conversion, $r = 0, 0.3, 0.7$ and 1.0

For the reaction system under consideration, the molecular weight of the ab unit (w_1) is 120 g/mol, and that of the abB unit (w_2) is 268 g/mol. According to Eq. (18) and (19), the number- and the weight- average molecular weights of the resulting hyperbranched copolymer versus the A group conversion (x) are illustrated in Figs. 1 and 2, respectively, for various feed ratios of AB₂ and AB monomers. Figure 3 shows the relationship between the polydispersity index of the resulting highly branched copolymer and A group conversion. Similar to hyperbranched polymers, the molecular weight distribution of highly branched copolymers formed in the co-condensation polymerization of AB₂ and AB monomers becomes very broad when the reaction approaches completion.

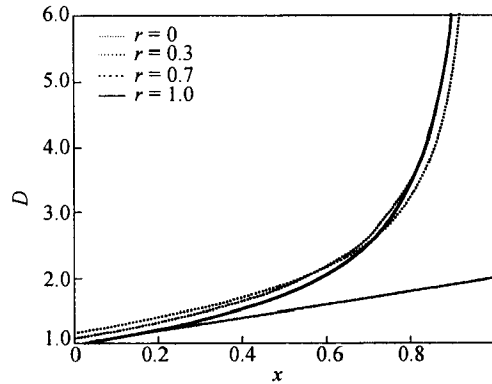


Fig. 3 Plot of polydispersity index versus A group conversion, $r = 0, 0.3, 0.7$ and 1.0

TWO-DIMENSIONAL DISTRIBUTION

The normalized number- and weight- and z-distribution functions of the resulting highly branched copolymer are defined as:

$$p(n, l) = \frac{P_{n, l}}{\sum_{n, l} P_{n, l}} = \frac{(l + 2n)!}{l! n! (n + 1)!} \cdot \frac{r^n x^{n+l-1} (1 + r - x)^{n+1} (1 - r)^l}{(1 + r)^{2n+l}} \quad (21)$$

$$\begin{aligned} w(n, l) &= \frac{(nw_2 + lw_1) P_{n, l}}{\sum_{n, l} (nw_2 + lw_1) P_{n, l}} \\ &= \frac{(l + 2n)!}{l! n! (n + 1)!} \cdot \frac{(nw_2 + lw_1)}{rw_2 + (1 - r)w_1} \cdot \frac{(1 - x)r^n x^{n+l-1} (1 + r - x)^{n+1} (1 - r)^l}{(1 + r)^{2n+l}} \end{aligned} \quad (22)$$

$$\begin{aligned} z(n, l) &= \frac{(nw_2 + lw_1)^2 P_{n, l}}{\sum_{n, l} (nw_2 + lw_1)^2 P_{n, l}} \\ &= \frac{(l + 2n)!}{l! n! (n + 1)!} \cdot \frac{(1 - x)^3 r^n x^{n+l-1} (1 + r - x)^{n+1} (1 - r)^l}{(1 + r)^{2n+l-2}} \cdot \\ &\quad \frac{(nw_2 + lw_1)^2}{\{w_2^2 r [(1 - x)^2 (1 + r)^2 + 2rx(2 + 2r - 2x - xr)] + 2w_1 w_2 r (1 - r) \cdot} \\ &\quad x(3 + 3r - 3x - rx) + w_1^2 (1 - r) [(1 - x)^2 (1 + r)^2 + 2(1 - r)x(1 + r - x)]\} \end{aligned} \quad (23)$$

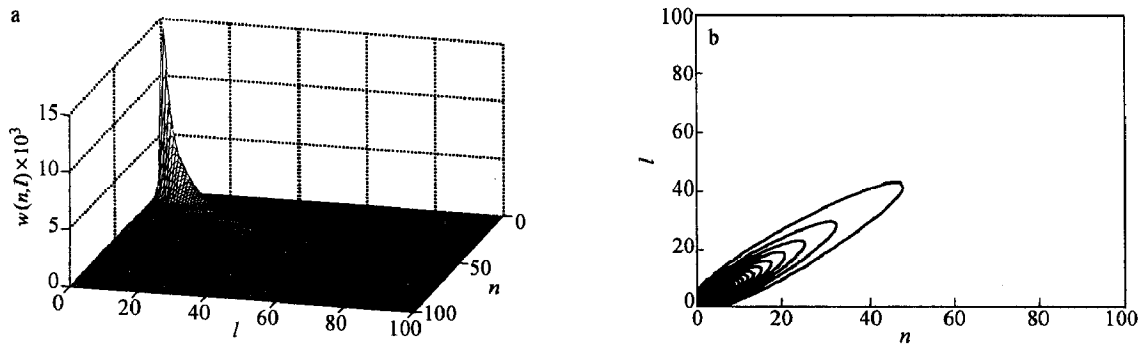


Fig. 4 Evolution of the two-dimensional molecular weight distribution and its contour map, $r = 0.5, x = 0.90$

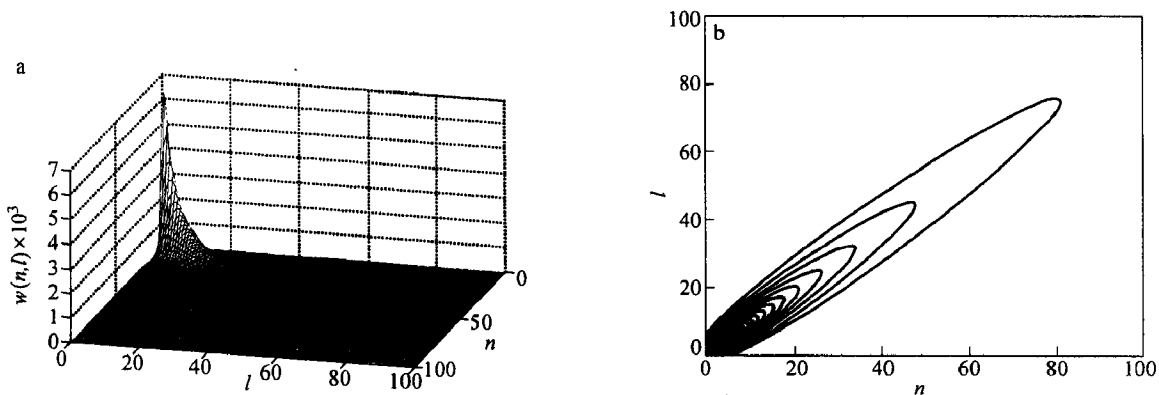


Fig. 5 Evolution of the two-dimensional molecular weight distribution and its contour map, $r = 0.5, x = 0.95$

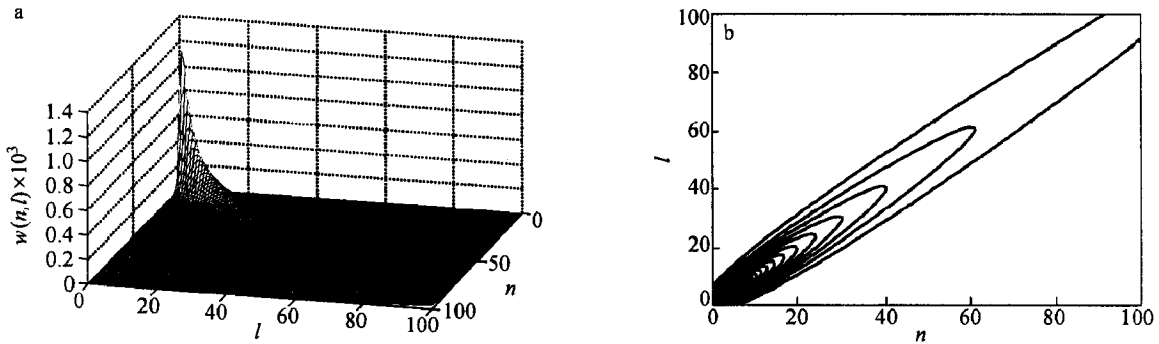


Fig. 6 Evolution of the two-dimensional molecular weight distribution and its contour map, $r = 0.5, x = 0.99$

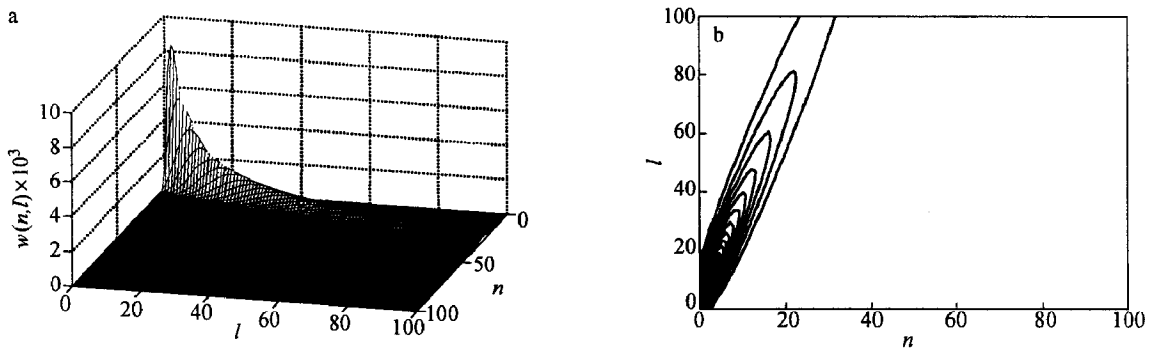


Fig. 7 Dependence of the two-dimensional molecular weight distribution and its contour map on feed ratio, $x = 0.95, r = 0.2$

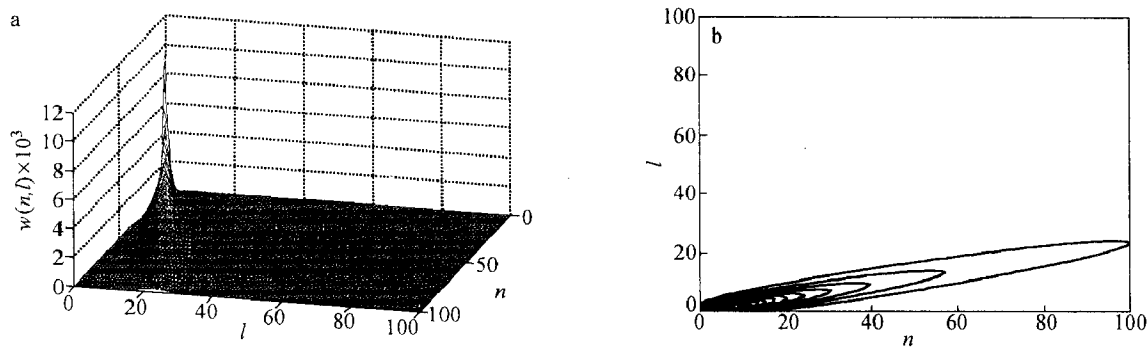


Fig. 8 Dependence of the two-dimensional molecular weight distribution and its contour map on feed ratio, $x = 0.95$, $r = 0.8$

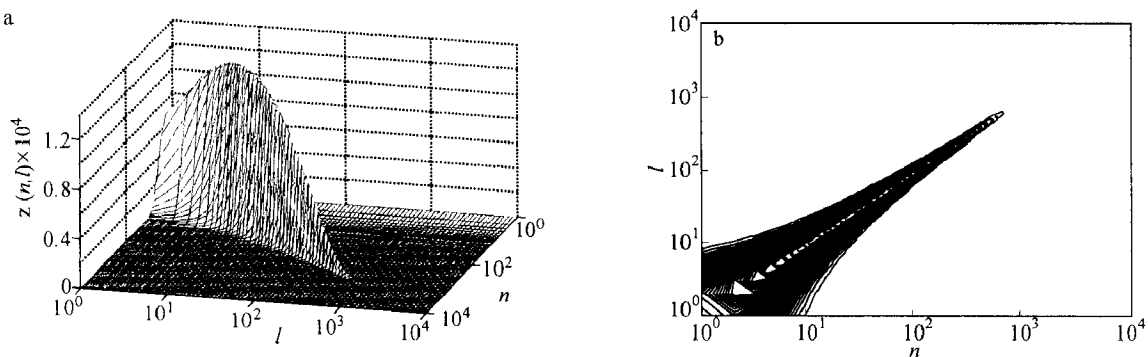


Fig. 9 Evolution of two-dimensional normalized z distribution and its contour map, $r = 0.5$, $x = 0.95$

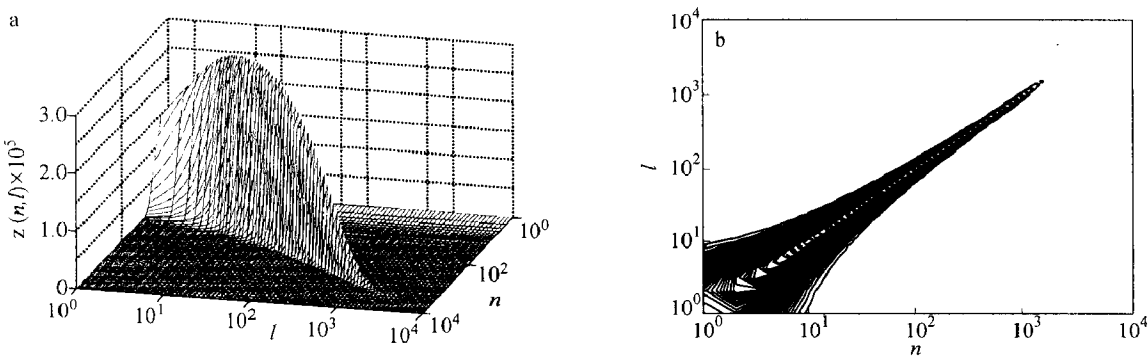


Fig. 10 Evolution of two-dimensional normalized z distribution and its contour map, $r = 0.5$, $x = 0.97$

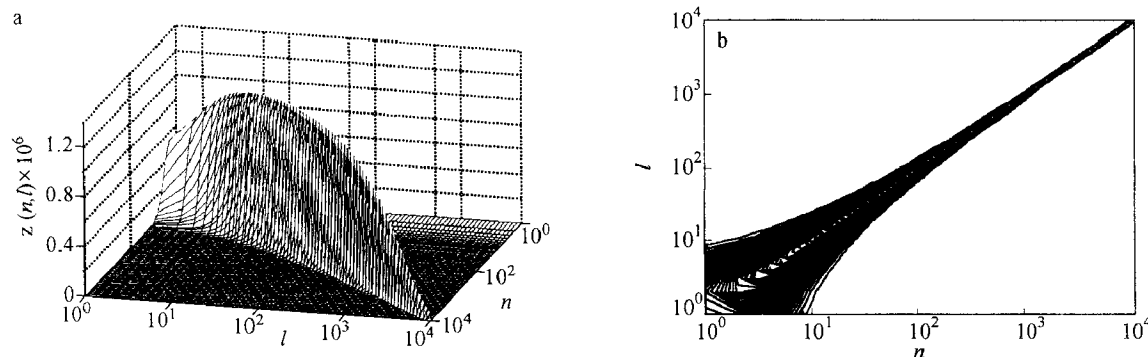


Fig. 11 Evolution of two-dimensional normalized z distribution and its contour map, $r = 0.5$, $x = 0.99$

Figures 4–6 show the normalized weight-distributions of resulting copolymers with $r = 0.5$ and various A group conversions. Fig. 4(a), Fig. 5(a) and Fig. 6(a) are the two-dimensional molecular weight distributions at $x = 0.9$, 0.95 and 0.99. For the sake of clarifying the profiles of these distribution charts, their contour maps were given in Fig. 4(b), Fig. 5(b) and Fig. 6(b), respectively. In each contour map, there are 50 contour curves with an equal interval. It is interesting that Figs. 4–6 illustrate the evolution of the weight molecular weight distribution and its contour map for the resulting copolymer with the A group conversion. Figures 7 and 8 indicate the dependence of the two-dimensional molecular weight distribution and its contour map on the feed ratio of AB_2 to AB monomer. When the feed ratio is very low, an essentially linear copolymer can be obtained, and the resulting copolymer mainly consists of AB monomer units. The content of AB_2 monomer units in the resultant copolymer increases with increasing feed ratio. If the feed ratio approaches 1, a hyperbranched polymer made of AB_2 monomer can be derived.

It is known that the z molecular weight distribution in the semilogarithmic coordinate system can better match with the SEC data^[6]. Now we take account of the two dimensional z distribution of a hyperbranched copolymer. For comparison, the evolution of the semilogarithmic z distribution and its contour map is shown in Figs. 9–11. It is evident that the molecular weight distribution of the resultant copolymer becomes wider and wider with increasing A group conversion.

ONE-DIMENSIONAL Z DISTRIBUTION

In practice most of the instruments such as GPC can not only supply one-dimensional distributions. We have to transform the two-dimensional distribution to one-dimensional one. It is hard to carry out analytically the transformation, and a numerical calculation is a better choice. For instance, we can collect the fractions of all species with the same molecular weight but different n and l in Fig. 9, and let it be a point in a new semilogarithmic coordinate system. Repeating this procedure, we can get Fig. 12. The molecular weight distribution presented in Fig. 12 is discrete, and the fractions seriously vibrate up and down. In order to abstract useful information from it, we cumulate the fractions of all points along the abscissa (MW) giving the one-dimensional integral z distribution of the hyperbranched copolymer (Fig. 13). Finally we use a phenomenological integral distribution function to fit the integral z distribution by way of a least-squares procedure. The Tung function^[11] is chosen to fit the integral data because its integral distribution expression (Eq. 24) is comparatively simple, and in the meantime its differential distribution expression (Eq. 25) can well describe the GPC distribution.

$$I(MW) = 1 - \exp(-aMW^b) \quad (24)$$

$$W(MW) = \frac{dI(MW)}{dMW} = ab \exp(-aMW^b) MW^{b-1} \quad (25)$$

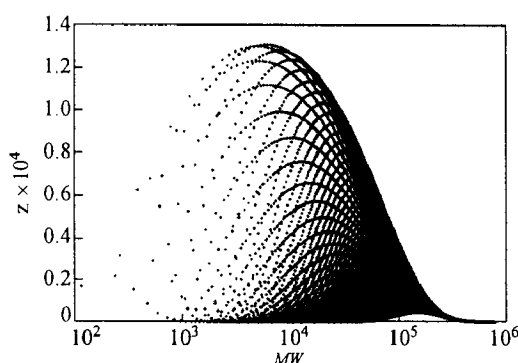


Fig. 12 Plot of merged normalized z distribution versus molecular weight, $r = 0.5$, $x = 0.95$

The fitting curve is also presented in Fig. 13. The integral z distribution and the fitting one are well in agreement with each other. Moreover, we can draw a one-dimensional differential z distribution of hyperbranched copolymers in terms of the data obtained in the fitting procedure at various x values (Fig. 14). The differential z distribution looks similar to that reported by Müller and coworkers^[6] for self-condensing vinyl polymerization.

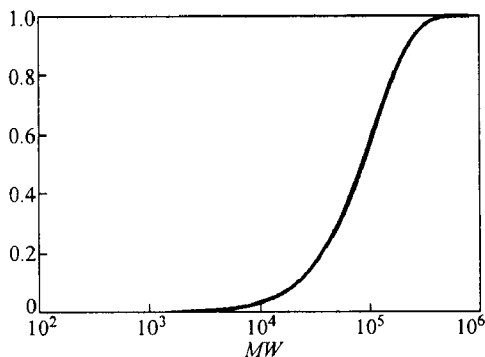


Fig. 13 Plot of integral z distribution (··) and the result curve (—) fitted by Tung function, $r = 0.5$, $x = 0.95$

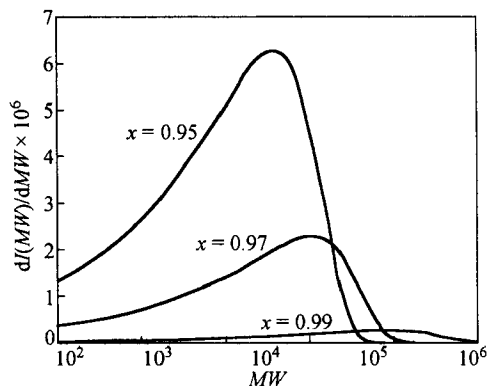


Fig. 14 Plot of the differential z distribution of Tung function at various x

Appendix 1

After summing up the left and the right sides of Eq. (1)', respectively, over the index n and l , the positive item of the right hand of Eq. (1)' becomes:

$$\text{Positive item} = \frac{k}{2} \sum_{n,l} \sum_{i,j} [(i+1) + (n-i+1)] P_{i,j} P_{n-i,l-j} \quad (\text{A1})$$

If we let $s = n - i$; $t = l - j$, then Eq. (A1) becomes:

$$\text{Positive item} = \frac{k}{2} \sum_{n,l} \sum_{i,j} [(i+1) + (s+1)] P_{i,j} P_{s,t} \quad (\text{A2})$$

Observing Eq. (A2), we can find that the subscript (i, j) and (s, t) is permutable. So $\sum_{n,l} \sum_{i,j} (i+1) P_{i,j} P_{s,t} \approx \sum_{n,l} \sum_{i,j} (s+1) P_{i,j} P_{s,t}$. Then Eq. (A2) becomes:

$$\text{Positive item} = k \sum_{n,l} \sum_{i,j} (i+1) P_{i,j} P_{s,t} \quad (\text{A3})$$

Because all the items of summation of Eq. (A3) are non-negative, and the upper limit of summation is infinite, the order of summation can be exchanged. Then Eq. (A3) can be transformed into:

$$\text{Positive item} = k \left(\sum_{i,j} (i+1) P_{i,j} \right) \left(\sum_{s,t} P_{s,t} \right) = k [N + (N+L)(1-x)] (N+L)(1-x) \quad (\text{A4})$$

The negative item of the right hand of Eq. (1)' becomes:

$$\begin{aligned}
\text{Negative item} &= k \sum_{n,l} P_{n,l} [(n+2)(N+L)(1-x) + N] \\
&= k \{ (N+L)(1-x) \sum_{n,l} n P_{n,l} + [2(N+L)(1-x) + N] \sum_{n,l} P_{n,l} \} \\
&= k \{ (N+L)(1-x)N + [2(N+L)(1-x) + N](N+L)(1-x) \} \\
&= 2k[(N+L)(1-x) + N](N+L)(1-x)
\end{aligned} \tag{A5}$$

According Eq. (A4) and (A5), we obtain:

$$\frac{d \sum_{n,l} P_{n,l}}{dt} = -k(N+L)(1-x)[N + (N+L)(1-x)] \tag{A6}$$

Appendix 2

The homogeneous equation corresponding to Eq. (13) is

$$\frac{dP_{n,l}}{dx} = -\frac{(n+2)(1-x) + r}{(1-x)(r+1-x)} P_{n,l} \tag{A7}$$

The solution of Eq. (A7) is

$$P_{n,l} = C_{n,l}(1-x)(r+1-x)^{n+1} \tag{A8}$$

where $C_{n,l}$ is a constant. Suppose the solution of Eq. (13) to be:

$$P_{n,l} = C_{n,l}(x)(1-x)(r+1-x)^{n+1} \tag{A9}$$

where $C_{n,l}(x)$ is a function to be determined. Substituting Eq. (A9) into Eq. (13), we obtain:

$$\frac{dC_{n,l}(x)}{dx} = \frac{n+2}{2(N+L)} \sum_{i,j} C_{i,j}(x) C_{n-i,l-j}(x) \tag{A10}$$

This is the equation to determine $C_{n,l}(x)$. According to the form of Eq. (A10), we assume:

$$C_{n,l}(x) = (N+L)Q_{n,l}x^{n+l-1} \tag{A11}$$

where $Q_{i,j}$ is the constant which is independent of x . Substituting Eq. (A11) into Eq. (A10), we have

$$Q_{n,l} = \frac{n+2}{2(n+l-1)} \sum_{i,j} Q_{i,j} Q_{n-i,l-i} \tag{A12}$$

Then the solution of Eq. (13) could be written as

$$P_{n,l} = (N+L)Q_{n,l}x^{n+l-1}(1-x)(r+1-x) \tag{A13}$$

From one of the initial conditions, Eq. (3), one gains:

$$P_{1,0} = N = (N+L)Q_{1,0}(r+1)^2 \tag{A14}$$

and

$$P_{0,1} = L = (N+L)Q_{0,1}(r+1) \tag{A15}$$

which result in

$$Q_{1,0} = \frac{r}{(r+1)^2} \quad (\text{A16})$$

and

$$Q_{0,1} = \frac{1-r}{r+1} \quad (\text{A17})$$

According to $Q_{1,0}$, $Q_{0,1}$ and the recurrence formula of Eq. (A12), one can obtain:

$$Q_{n,l} = \frac{(l+2n)!}{l!n!(n+1)!} \left[\frac{r}{(r+1)^2} \right]^n \left(\frac{1-r}{r+1} \right)^l \quad (\text{A18})$$

We finally get the solution of Eq. (13) as

$$P_{n,l} = \frac{(N+L)(1-x)(1+r-x)}{x} \cdot \frac{(l+2n)!}{l!n!(n+1)!} \left[\frac{rx(1+r-x)}{(r+1)^2} \right]^n \left(\frac{1-r}{r+1} x \right)^l \quad (\text{A19})$$

Appendix 3

Eq. (A19) can be written as

$$P_{n,l} = \frac{(N+L)(1-x)(1+r-x)}{x} \omega_{n,l} \lambda^n \mu^l \quad (\text{A20})$$

where

$$\omega_{n,l} = \frac{(l+2n)!}{l!n!(n+1)!}, \quad \lambda = \frac{rx(1+r-x)}{(1+r)^2}, \quad \mu = \frac{1-r}{1+r} x \quad (\text{A21})$$

Comparing Eq. (A20) with Eq. (6), we find:

$$\sum_{n,l} \omega_{n,l} \lambda^n \mu^l = \frac{x}{1+r-x} \quad (\text{A22})$$

then

$$\begin{aligned} \sum_{n,l} n^2 P_{n,l} &= \frac{(N+L)(1-x)(1+r-x)}{x} \sum_{n,l} n^2 \omega_{n,l} \lambda^n \mu^l \\ &= \frac{(N+L)(1-x)(1+r-x)}{x} \left(\lambda \frac{\partial}{\partial \lambda} \right)^2 \sum_{n,l} \omega_{n,l} \lambda^n \mu^l \\ &= \frac{(N+L)(1-x)(1+r-x)}{x} \left(\lambda \frac{\partial}{\partial \lambda} \right)^2 \left(\frac{x}{1+r-x} \right) \\ &= \frac{(N+L)r}{(1+r)^2 (1-x)^2} [(1-x)^2 (1+r)^2 + 2rx(2+2r-2x-rx)] \end{aligned} \quad (\text{A23})$$

Similarly

$$\begin{aligned}
 \sum_{n,l} l^2 P_{n,l} &= \frac{(N+L)(1-x)(1+r-x)}{x} \sum_{n,l} l^2 \omega_{n,l} \lambda^n \mu^l \\
 &= \frac{(N+L)(1-x)(1+r-x)}{x} \left(\mu \frac{\partial}{\partial \mu} \right)^2 \left(\frac{x}{1+r-x} \right) \\
 &= \frac{(N+L)(1-r)}{(1+r)^2(1-x)^2} [(1-x)^2(1+r)^2 + 2(1-r)x(1+r-x)]
 \end{aligned} \tag{A24}$$

$$\begin{aligned}
 \sum_{n,l} nl P_{n,l} &= \frac{(N+L)(1-x)(1+r-x)}{x} \sum_{n,l} nl \omega_{n,l} \lambda^n \mu^l \\
 &= \frac{(N+L)(1-x)(1+r-x)}{x} \left(\mu \frac{\partial}{\partial \mu} \right) \left(\lambda \frac{\partial}{\partial \lambda} \right) \left(\frac{x}{1+r-x} \right) \\
 &= \frac{(N+L)r(1-r)x}{(1+r)^2(1-x)^2} [3 + 3r - 3x - rx]
 \end{aligned} \tag{A25}$$

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