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Molecular Weight Distribution of Hyperbranched Polymers Generated by Self-Condensing Vinyl Polymerization in Presence of a Multifunctional Initiator

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ABSTRACT: The molecular weight distribution (MWD) is derived for polymers generated by self-condensing vinyl polymerization (SCVP) of a monomer having a vinyl and an initiator group ("inimer") in the presence of a multifunctional initiator. If the monomer is added slowly to the initiator solution (semi-batch process), this leads to hyperbranched polymers with a multifunctional core. If monomer and initiator are mixed simultaneously (batch process), even at vinyl group conversions as high as 99%, the total MWD consists of polymers which have grown via reactions between inimer molecules (i.e., the normal SCVP process) and those which have reacted with the initiator. Consequently, the weight distribution, $w(M)$, is bimodal. However, the z-distribution, $z(M)$, equivalent to the "GPC distribution", $w(\log M)$ vs $\log M$, is unimodal.

Introduction

Recently, Fréchet and co-workers[1-3] reported on a new method for the synthesis of hyperbranched polymers based on vinyl monomers and called it "self-condensing vinyl polymerization" (SCVP). This process involves a monomer consisting of a double bond and an active site capable of chain initiation. We proposed the term "inimer" for this kind of monomer.[4,5] Various living polymerization techniques have been applied to this process: cationic polymerization,[1,2] nitroxide-mediated radical polymerization,[3] atom transfer radical polymerization,[6,7] and group transfer polymerization.[8,9] A characteristic feature of each macromolecule formed by SCVP is that it possesses exactly one vinyl group and $\bar{P}_n$ active sites which may be functionalized in various ways. Our theoretical studies[4] showed that the hyperbranched polymers generated from an SCVP possess a very wide molecular weight distribution (MWD) (polydispersity index $\bar{M}_w/\bar{M}_n \approx \bar{P}_n$, where $\bar{P}_n$ is the number-average degree of polymerization), similar to that obtained in the polycondensation of AB_2 monomers ($\bar{M}_w/\bar{M}_n \approx \bar{P}_n/2$).[10] Although the experimental determination of MWDs of branched polymers is not trivial, GPC measurements using a viscosity detector qualitatively confirm the very broad distributions.[8]

Müller and co-workers[11] suggested a process to produce hyperbranched polymers with more narrow molecular weight distribution by adding a small amount of an f-functional initiator, G_f, to the reaction system. This process can be conducted in two ways. (i) Monomer molecules can be added so slowly to the initiator solution that they can only react with the initiator molecules or to the already formed macromolecules, but not with each other (semi-batch process). Thus, each macromolecule generated in such a process will contain one initiator core but no vinyl group. The authors derived expressions of the MWD and its averages and showed that the polydispersity index is quite low and decreases with f: $\bar{M}_w/\bar{M}_n \approx 1 + 1/f$. The derived MWD is identical to that for the polycondensation of an AB_2 monomer in presence of an A_f core-forming molecule. (ii) Alternatively, initiator and monomer molecules can be mixed instantaneously (batch process). Here, the normal SCVP process and the process shown above compete and both kinds of macromolecules will be formed. For this process, only

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the equations for the molecular weight averages were derived and it was shown that the polydispersity index also decreases with f, but is higher than for the semibatch process, $\bar{M}_w/\bar{M}_n \approx \bar{P}_n/f^2$. In this publication we will derive and discuss the MWD function generated by this process. The expressions of the MWD and its averages for the star-branched polycondensation of AB monomers[12] and of the hyperbranched polycondensation of AB_2 monomers[13] in the presence of multifunctional core molecules were recently published by Yan and coworkers.

Kinetic Differential Equations. An inimer can be symbolized as AB*, in which the initiating center, B*, can initiate the polymerization of double bonds, A, of other inimer molecules forming new propagating A* centers. In the typical SCVP process, these can undergo further reactions with A groups of inimer or polymer.

If a small amount of the multifunctional initiator, G_f, is mixed with AB* monomers, two different reactions can take place which will lead to macromolecules without and with residual core moiety. Inimer molecules can react with each other or with macromolecules formed by consecutive reactions of the products (SCVP process):

$$P_i^{(0)} + P_j^{(0)} \xrightarrow{k'} P_{i+j}^{(0)} \qquad k' = (i + j)\cdot k$$

Here, $P_i^{(0)}$ denotes a molecule with i active centers (B* and A*) and one vinyl group, and $P_1^{(0)} = M$ is the monomer. These species (including monomer) at some time can react with the f-functional initiator, G_f, or with one of the unreacted functions of the core:

$$G_f + P_j^{(0)} \xrightarrow{k''} P_j^{(1)} \qquad k'' = f\cdot k$$

$$P_i^{(l)} + P_j^{(0)} \xrightarrow{k''} P_{i+j}^{(l+1)} \qquad k'' = (f + i)\cdot k; \quad l = 1, 2,..., f$$

Here, $P_i^{(l)}$ are species with $f + i$ active centers carrying an initiator fragment but no vinyl group, and l is the number of reacted initiator sites. There are $i + l$ reactive sites in the l "sectors" of a $P_i^{(l)}$ species, and $f - l$ remaining active groups of the initiator. In each of the second kind of reactions, the initiator loses one of its active sites and gains one new sector, until $l = f$.

In accordance with the nomenclature in the previous paper by Müller et al.,[11] the total concentration of polymers with $i + f$ active centers which carry an initiator fragment is

$$G_{f+i} = \sum_{l=1}^{f} P_i^{(l)}$$

As in our previous derivations we will assume that the reactivities of A* and B* centers are equal, that the intrinsic rate constant, k, does not depend on i, and that intramolecular cyclization reactions in $P_i^{(0)}$ species can be neglected. Now we can write the kinetic differential equations for this process.

$$\frac{\mathrm{d}G_f}{\mathrm{d}t} = -fkG_f \sum_{i=1}^{\infty} P_i^{(0)} \tag{1}$$

$$\begin{aligned}\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}t} &= \frac{k}{2}\sum_{j=1}^{i-1}\{jP_j^{(0)}\, P_{i-j}^{(0)} + (i - j)P_{i-j}^{(0)}\, P_j^{(0)}\} - \\ &\quad k\{iP_i^{(0)} \sum_{j=1}^{\infty} P_j^{(0)} + P_i^{(0)} \sum_{j=1}^{\infty} jP_j^{(0)}\} - fkP_i^{(0)}G_f - \\ &\quad kP_i^{(0)} \sum_{l=1}^{f}\sum_{j=1}^{\infty}(j + f)P_j^{(l)} \\ &= \frac{k}{2}\sum_{j=1}^{i-1} iP_j^{(0)}\, P_{i-j}^{(0)} - k\{iP_i^{(0)} \sum_{j=1}^{\infty} P_j^{(0)} + P_i^{(0)} \sum_{j=1}^{\infty} jP_j^{(0)}\} - \\ &\quad fkP_i^{(0)}\, G_f - kP_i^{(0)} \sum_{l=1}^{f}\sum_{j=l}^{\infty}(j + f)P_j^{(l)}\end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}t} &= fkG_fP_i^{(0)} + k \sum_{j=1}^{i-1}(j + 1)P_j^{(1)}\, P_{i-j}^{(0)} - \\ &\quad k(i + f)P_i^{(1)} \sum_{j=1}^{\infty} P_j^{(0)}\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\mathrm{d}P_i^{(l)}}{\mathrm{d}t} &= (f - l + 1)k \sum_{j=l-1}^{i-1} P_j^{(l-1)}\, P_{i-j}^{(0)} + \\ &\quad k \sum_{j=l}^{i-1}(j + 1)P_j^{(l)}\, P_{i-j}^{(0)} - k(i + f)P_i^{(l)} \sum_{j=1}^{\infty} P_j^{(0)} \\ &\quad l = 2, 3, ..., f\end{aligned} \tag{4}$$

The initial conditions of eqs 1−4 are

$$G_f|_{t=0} = G_f^0$$

$$P_i^{(0)}|_{t=0} = \delta_{i,1}M_0$$

$$P_{\mathrm{i}}^{(l)}|_{t=0} = 0$$

where G_f^0 and M_0 are the initial concentrations of the f-functional initiator and the monomer, respectively; $\delta_{i,1}$ is the Kronecker symbol. The conservation conditions are

$$G_f + \sum_{l=1}^{f}\sum_{i=l}^{\infty} P_i^{(l)} = G_f^0 \tag{5}$$

$$\sum_{i=1}^{\infty} iP_i^{(0)} + \sum_{l=1}^{f}\sum_{i=l}^{\infty} iP_i^{(l)} = M_0 \tag{6}$$

Because every molecule of $P_i^{(0)}$ carries one double bond, the conversion of double bonds is defined by:

$$x = (M_0 - \sum_{i=1}^{\infty} P_i^{(0)})/M_0 \tag{7}$$

Then,

$$\sum_{i=1}^{\infty} P_i^{(0)} = M_0(1 - x) \tag{8}$$

Differentiation of both sides of eq 8 leads to

$$\frac{\mathrm{d}\sum_{i=1}^{\infty} P_i^{(0)}}{\mathrm{d}t} = -M_0 \frac{\mathrm{d}x}{\mathrm{d}t} \tag{9}$$

From eq 2 we have

$$\frac{\mathrm{d}\sum_{i=1}^{\infty} P_i^{(0)}}{\mathrm{d}t} = -k\frac{{M_0}^2}{\alpha}(1-x) \tag{10}$$

where

$$\alpha = 1/(1 + fr) \text{ and } r = G_f^0/M_0 \tag{11}$$

Note that in the paper by Müller et al.[11] a somewhat different parameter was used, i.e., $\gamma = M_0/(fG_f^0)$. Thus, $r = 1/(f\gamma)$ and $\alpha = \gamma/(\gamma+1)$.

Comparison of eq 9 with eq 10 results in

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\frac{M_0}{\alpha}(1 - x) \tag{12}$$

Dividing eqs 1−4 by eq 12, we obtain

$$\frac{\mathrm{d}G_f}{\mathrm{d}x} = -f\alpha G_f^0 \tag{13}$$

$$\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}x} = -\left(i\alpha + \frac{1}{1-x}\right)P_i^{(0)} + \frac{i\alpha}{2M_0(1-x)}\sum_{j=1}^{i-1} P_j^{(0)}\, P_{i-j}^{(0)} \tag{14}$$

$$\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}x} = -\alpha(i + f)P_i^{(1)} + \frac{\alpha}{M_0(1-x)}\{fG_f^0\, P_i^{(0)} + \sum_{j=1}^{i-1}(j + 1)P_j^{(1)}\, P_{i-j}^{(0)}\} \tag{15}$$

$$\frac{\mathrm{d}P_i^{(l)}}{\mathrm{d}x} = -\alpha(i + f)P_i^{(l)} + \frac{\alpha}{M_0(1-x)}\{(f - l + 1) \sum_{j=l-1}^{i-1} P_j^{(l-1)}\, P_{i-j}^{(0)} + \sum_{j=l}^{i-1}(j + l)P_j^{(l)}\, P_{i-j}^{(0)}\} \qquad l = 2, 3, ..., f \tag{16}$$

The initial conditions for $x = 0$ are the same as above for $t = 0$. After making this variable transformation, we can solve the set of kinetic differential equations exactly.

MWD. The residual concentration of the multifunctional initiator can be easily derived from eq 13:

$$G_f = G_f^0 e^{-f\alpha x} \tag{17}$$

Solving eqs 14−16, we can find the molecular size distribution function of various hyperbranched species:

$$P_i^{(0)} = M_0(1 - x)\frac{(i\alpha x)^{i-1}}{i!}e^{-i\alpha x} \tag{18}$$

$$P_i^{(1)} = G_f^0\, f\frac{(i + 1)^{i-1}}{i!}(\alpha x)^i e^{-(i+f)\alpha x} \tag{19}$$

$$P_i^{(l)} = G_f^0 l\binom{f}{l}\frac{\sum_{k=0}^{l-1}\left[(-1)^k\binom{l-1}{k}(i + l - k)^{i-1}\right]}{i!} \times (\alpha x)^i e^{-(i+f)\alpha x} \qquad l = 2, 3, ..., f \tag{20}$$

The derivation procedures of eqs 18−20 are given in Appendices 1−3.

The MWD function of the total resulting hyperbranched polymer reads:

$$P_i = \sum_{l=0}^{f} P_i^{(l)} \tag{21}$$

It is of interest to calculate the moments of the MWDs of the different species. The zeroth moment of species $P_i^{(0)}$ (without initiator fragment) was expressed by eq 8

$$\mu_0^{(0)} \equiv \sum_{i=1}^{\infty} P_i^{(0)} = M_0(1 - x) \tag{8}$$

Furthermore, we can derive, respectively, the first and the second moments of $P_i^{(0)}$:

$$\mu_1^{(0)} \equiv \sum_i iP_i^{(0)} = M_0\frac{1-x}{1-\alpha x} \tag{22}$$

$$\mu_2^{(0)} \equiv \sum_i i^2P_i^{(0)} = M_0\frac{1-x}{(1-\alpha x)^3} \tag{23}$$

The derivation of eqs 22 and 23 is given in Appendix 4. Using these moments, we can calculate the average degrees of polymerization:

$$\bar{P}_n^{(0)} = \mu_1^{(0)}/\mu_0^{(0)} = 1/(1 - \alpha x)$$

$$\bar{P}_w^{(0)} = \mu_2^{(0)}/\mu_1^{(0)} = 1/(1 - \alpha x)^2$$

$$\bar{P}_w^{(0)}/\bar{P}_n^{(0)} = 1/(1 - \alpha x) = \bar{P}_n{}^{(0)}$$

Because typically $r << 1$ and thus $\alpha \approx 1$, the MWD of the species without initiator is practically identical to that obtained in the SCVP process without initiator. Note that these averages still contain unreacted monomer. If this should be excluded, P_1^0 must be subtracted from the moments. P_1^0 can be obtained from eq 18 by setting $i = 1$.

Let us calculate the moments for the polymers with initiator fragment. From the conservation conditions we have

$$\mu_0^{(G)} \equiv \sum_{l,i} P_i^{(l)} = G_f^0(1 - e^{-f\alpha x}) \tag{24}$$

Here and hereafter the double summation $\sum_{l,i}$ means $\sum_{l=1}^{f}\sum_{i=l}^{\infty}$. Further treatment gives

$$\mu_1^{(G)} \equiv \sum_{l,i} iP_i^{(l)} = M_0 \frac{(1-\alpha)x}{1-\alpha x} \qquad (25)$$

$$\mu_2^{(G)} \equiv \sum_{l,i} i^2 P_i^{(l)} = \frac{fG_f^0 \alpha x}{(1-\alpha x)^3}\,[1 + f\alpha x - f(\alpha x)^2] \qquad (26)$$

Appendix 5 shows the derivation of eqs 25 and 26. Using these moments, we can calculate the average degrees of polymerization:

$$\bar{P}_n^{(G)} = \mu_1^{(G)}/\mu_0^{(G)}, \text{ etc.}$$

Here, residual initiator may be accounted for by subtracting G_f from the moments. Consequently, various moments of the total products read

$$\mu_0 \equiv \sum_i P_i = \mu_0^{(0)} + \mu_0^{(G)} = M_0(1-x) + G_f^0(1 - e^{-f\alpha x}) \qquad (27)$$

$$\mu_1 \equiv \sum_i iP_i = \mu_1^{(0)} + \mu_1^{(G)} = M_0 \qquad (6')$$

$$\mu_2 \equiv \sum_i i^2 P_i = \mu_2^{(0)} + \mu_2^{(G)} = \frac{1}{(1-\alpha x)^3}\{M_0(1-x) + G_f^0\, f\alpha x[1 + f\alpha x - f(\alpha x)^2]\} \qquad (28)$$

Finally, we get the expressions of the number- and the weight-average degrees of polymerization:

$$\bar{P}_n = \frac{1}{1 - x + r(1 - e^{-f\alpha x})} \qquad (29)$$

$$\bar{P}_w = \frac{1-x}{(1-\alpha x)^3} + \frac{rf\alpha x}{(1-\alpha x)^3}[1 + f\alpha x - f(\alpha x)^2] \qquad (30)$$

The molecular weight averages and the polydispersity index were discussed in a previous paper[11] in detail. However, we should stress again that—in contrast to normal SCVP—the number-average degree of polymerization cannot go to infinity, but reaches a limiting value of $1/r = M_0/G_f^0$ at $x = 1$.

Numerical Results and Discussion of Distribution Curves. We are usually interested in the observation of the weight- and the *z*-distribution curves of a polymer. The normalized weight- and *z*-distribution of various hyperbranched species with different number of sectors and the total products are respectively defined by

$$W(i,l) = iP_i^{(l)} / \sum_{i=1}^{\infty} iP_i \qquad (32)$$

$$Z(i,l) = i^2 P_i^{(l)} / \sum_{i=1}^{\infty} i^2 P_i \qquad (33)$$

where $l = 0, 1, 2, ..., f$, and

$$W(i) = iP_i / \sum_{i=1}^{\infty} iP_i \qquad (34)$$

$$Z(i) = i^2 P_i / \sum_{i=1}^{\infty} i^2 P_i \qquad (35)$$

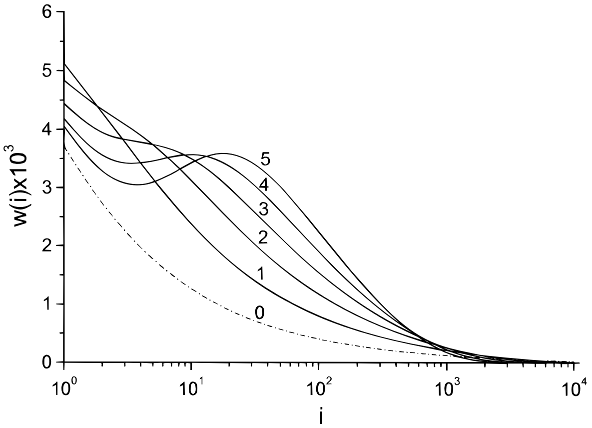

Figure 1. Weight distribution curves of hyperbranched polymers formed by self-condensing vinyl polymerization without and with various multifunctional initiators. Initiator/monomer ratio $r = G_f^0/M_0 = 0.01$; vinyl group conversion, $x = 0.99$; the numbers denote the initiator functionality, f. $f = 0$: no initiator added.

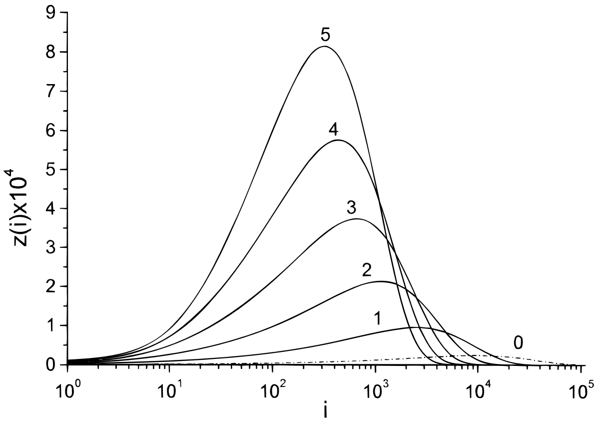

Figure 2. *z*-distribution (GPC distribution) curves of hyperbranched polymers shown in Figure 1.

It can be shown that the *z*-distribution is identical to that obtained from GPC eluograms, $z(i) = w(\log i)$. We can calculate the weight- and the *z*-distributions in terms of eqs 32–35. The weight- and the *z*-distribution curves of resulting hyperbranched polymers without and with various core moieties are given in Figures 1 and 2 for an initiator/monomer ratio $r = G_f^0/M_0 = 0.01$ and 99% vinyl group conversion. For $f = 0$ (absence of initiator), and for $f = 1$ or 2, the weight distribution monotonically decreases with increasing molecular size, but bimodal distributions can be observed if $f \geq 3$. On the other hand, every *z*-distribution curve in Figure 2 has only one peak regardless of the value of f.

Figure 3a–d show the evolution of the *z*-distribution curves of various species with different numbers of sectors as well as the total products obtained in the presence of a trifunctional core moiety at various conversions. Because the amount of the multifunctional initiator is much smaller than that of the monomer, the macromolecules without core are predominant even at $x = 0.95$, and there is still a certain amount of these species in the reaction system when $x = 0.999$, which totally disappears at the completion of the reaction, i.e., $x = 1$. As a consequence, the bimodality of the weight distribution decreases with increasing conversion. The evolution plots of various species given in this work are somewhat different from those reported for the hyperbranched species formed in the polycondensation of AB_2 type monomer with a multifunctional core moiety.[13]

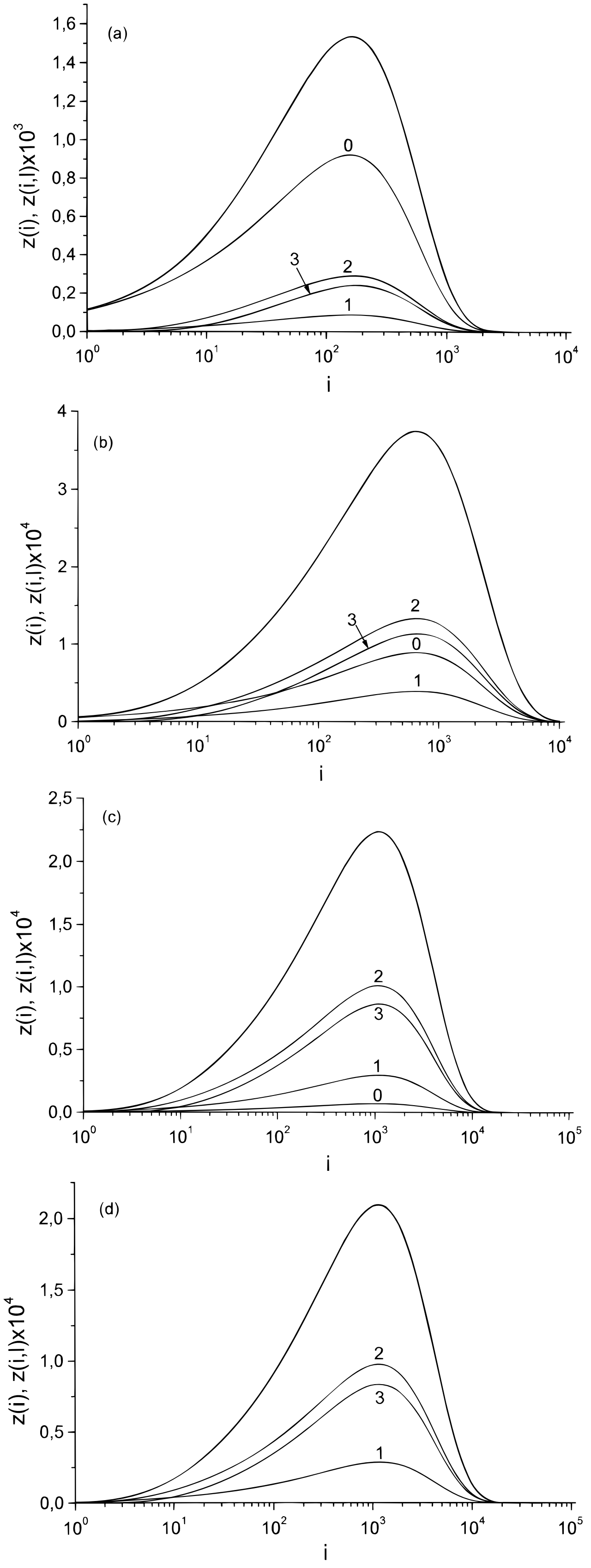

Figure 3. Evolution of z-distribution curves of various hyperbranched species and total products during self-condensing vinyl polymerization processes in the presence of a trifunctional initiator, $f = 3$; 0: $l = 0$; 1: $l = 1$; 2: $l = 2$; 3: $l = 3$; thick curve: total products. Vinyl group conversions: (a) $x = 0.95$, (b) $x = 0.99$, (c) $x = 0.999$, (d) $x = 1$.

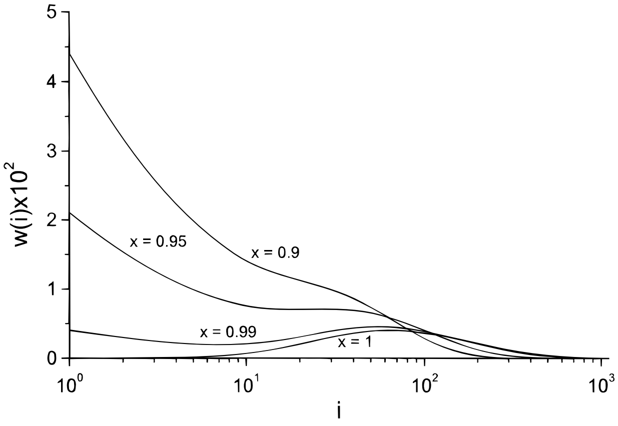

Figure 4. Evolution of the weight distribution of the total hyperbranched polymer formed in the self-condensing vinyl polymerization with a decafunctional initiator ($f = 10$); $r = 0.01$.

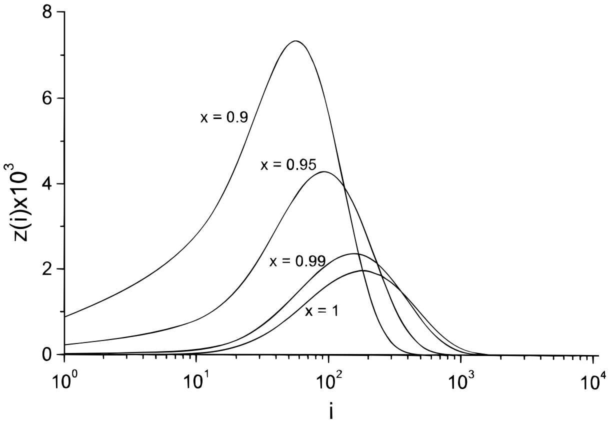

Figure 5. Evolution of the z-distribution of the hyperbranched polymer shown in Figure 4.

The evolution of the weight- and the z-distribution curves of the total resultant polymer during the self-condensing vinyl polymerization in the presence of the core moiety with $f = 10$ is given in Figures 4 and 5. The weight distributions in Figure 4 become less bimodal with increasing conversion, and the first peak only disappears at $x = 1$. In contrast, all z-distributions in Figure 5 are unimodal.

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Supporting Information Available: Text giving the derivation of eqs 18−20, 22, 23, 25, and 26 (Appendixes 1−5; 5 pages). Ordering and Internet access information is given on any current masthead page.

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