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Effect of Core-Forming Molecules on Molecular Weight Distribution and Degree of Branching in the Synthesis of Hyperbranched Polymers

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ABSTRACT: The polydispersity index, the molecular weight distribution (MWD), and the degree of branching ($\overline{\text{DB}}$) are calculated for hyperbranched polymers obtained in self-condensing vinyl polymerization of AB* monomers in the presence of a core-forming molecule (i.e. a multifunctional initiator, B_f*). Two cases are considered: (a) batch polymerization, i.e., with all components mixed together; (b) semibatch polymerization, i.e., slow addition of the monomer to the core-forming molecule. The results obtained for the latter case are also valid for polycondensation of AB_2 monomers. The presence of core-forming molecules leads to a considerable narrowing of the MWD's, the polydispersity index decreasing with increasing initiator functionality, *f*. In the batch process, we find $\overline{P}_w/\overline{P}_n \approx 1 + \overline{P}_n/f^2$ and in the semibatch mode $\overline{P}_w/\overline{P}_n \approx 1 + 1/f$. The degree of branching obtained in semibatch mode approaches $\overline{\text{DB}} = {}^2/_3$, which is higher than for the synthesis using a batch process with or without initiator. The polymers resulting from semibatch mode are predicted to consist of highly branched cores, while the outer parts of the molecules contain the majority of the functional groups. Thus, they are closer to dendrimers than the polymers obtained in batch mode.

Introduction

Highly branched polymers have become an attractive field of research. Dendrimers and hyperbranched polymers are two different approaches. Dendrimers are monodisperse, and the terminal groups are located on the surface of a nearly spherical molecule.[1] Each of the repeating units in the interior is a branch unit. These well-defined structures are obtained in time-consuming and expensive syntheses. Each generation of the molecule has to be built up step by step with synthetic and purification steps. Hyperbranched molecules on the other hand can be prepared in a one-pot synthesis, reducing cost and effort. However, this simple procedure yields structures of low regularity with broad molecular weight distributions.[2−4] The functional groups are distributed throughout the molecule, and not all of them are branched. This structure is the major drawback of hyperbranched molecules as compared to dendrimers.

Two pathways have been used for the preparation of hyperbranched polymers. The first one, proposed by Flory,[2] uses a monomer of structure AB_f which has one functional group A and *f* functional groups B, where the groups A and B are capable to react with each other. The other pathway to hyperbranched polymers was recently described by Fréchet et al.[5,6] A vinyl monomer of the general structure AB* was used, where A is a vinyl group and B* is an initiating group ("inimer"). The chain initiation is the addition of an active B* group to the double bond of another monomer forming a dimer with two active sites and one double bond. Both the initiating B* group and the newly created propagating center A* can react with the vinyl group of another molecule in the same way with rate constants k_B and k_A, respectively. Since in the polymerization the vinyl groups are consumed but at the same time the polymerization shows typical behavior of a polycondensation reaction, the name self-condensing vinyl polymerization (SCVP) was created for such a kind of polymerization. Several examples of such types of polymerization have appeared in the recent literature.[5−9]

From a commercial point of view the hyperbranched route seems to be more interesting if it would be possible to reduce the polydispersity of the resulting polymer. A recent kinetic analysis of Müller et al.[3] showed that for hyperbranched polymers obtained via SCVP the polydispersity index, $\overline{P}_w/\overline{P}_n$, is equal to the number-average degree of polymerization, $\overline{P}_n$, while for the synthesis of hyperbranched polymers from AB_2 monomers the distribution is somewhat narrower ($\overline{P}_w/\overline{P}_n \approx \overline{P}_n/2$ at high conversion of A groups[2]). The degree of branching was found to approach $\overline{\text{DB}} \approx 0.465$ for SCVP[4] which is close to the value $\overline{\text{DB}} = 0.5$ expected for an AB_2 system.[2]

In their analysis the authors treated the batch process of SCVP. The extremely broad MWD can be understood on the basis that each growing chain can couple with another chain, similar to a conventional polycondensation reaction. At the same time, the rate at which a given polymer chain adds to another chain is proportional to the number of its functional groups, which again is identical to its degree of polymerization. Thus, larger molecules will grow faster than small ones, giving an additional rise in polydispersity. Therefore, it seems clear that the polydispersity could be decreased if we would be able to prevent coupling of the polymeric species itself. This can be done by introducing multifunctional core-forming molecules. In SCVP this is a multifunctional initiator, G_f, which reacts with the vinyl group of the monomer whereas in AB_f polycondensation this is a molecule of the type B_f. It will be shown that a considerable additional narrowing of the MWD can be obtained when we use conditions where the monomers can only react with the already formed core but not with each other. This can be obtained if we add

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monomer slowly enough to keep the monomer concentration very low.

In the following we will use the terminology of SCVP, although the general ideas can be used in typical AB_2 polymerizations as well. As will be shown below, the results of the special case of slow monomer addition are independent of the polymerization mechanism itself (SCVP or AB_2 polycondensation).

Molecular Weight Averages

Batch Polymerization. We shall assume equal reactivities of both A* and B* centers and of initiating group G, that is $k_A = k_B = k_G = k$. Then, the different reaction steps of a system in which an initiator is present can be schematically represented as

$$P_i + P_j \xrightarrow{k'} P_{i+j} \quad k' = (i+j)k$$

$$G_{f+i} + P_j \xrightarrow{k''} G_{f+i+j} \quad k'' = (f+i)k$$

where the symbol P_i denotes a molecule with i active centers (B* and A*) and one vinyl group, while G_{f+i} has $f + i$ active centers but no vinyl group. Therefore, $P_1 = M$ is the monomer and G_f is an ordinary initiator with f functional groups. The set of differential equations appropriate to the kinetic scheme above can be written as:

$$\frac{dP_i}{dt} = \frac{k}{2}\sum_{0<j<i}\{jP_jP_{i-j} + P_j(i-j)P_{i-j}\} - k\{iP_i\sum_j P_j + P_i\sum_j jP_j\} - kP_i\sum_{j\geq 0}(f+j)G_{f+j} \quad (1)$$

$$= \frac{k}{2}i\sum_{0<j<i}P_jP_{i-j} - kP_i\{i\sum_j P_j + \sum_j jP_j\} - kP_i\sum_{j\geq 0}(f+j)G_{f+j}$$

$$\frac{dG_{f+i}}{dt} = k(1-\delta_{i,0})\sum_{1\leq j\leq i}(f+i-j)G_{f+i-j}P_j - k(f+i)G_{f+i}\sum_{0<j}P_j \quad (2)$$

where the Kronecker symbol, $\delta_{i,j}$, is defined as

$$\delta_{i,j} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}$$

The initial conditions are

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

$$G_i(t=0) = \delta_{i,f}G_f^{\,0} \quad (3)$$

where M_0 and $G_f^{\,0}$ are the initial concentrations of monomer and of the f-functional initiator, respectively.

Since all species P_i contain one double bond, the total concentration of *all* double bonds in the system is $A = \sum_{i=1}^{\infty}P_i$. In a procedure similar to ref 3 using eqs 1 and 2 we obtain the dependence of conversion of double bonds, x, on time as

$$x = \frac{M_0 - A}{M_0} = 1 - \exp(-kI_0t)$$

where $I_0 \equiv M_0 + fG_f^{\,0}$ is the total concentration of active centers.

Using the generating functions for P_i and G_i (see Supporting Information, Appendix 1)

$$\Phi(s) = \sum_{i=0}^{\infty}G_{f+i}s^{f+i}$$

$$F(s) = \sum_{i=0}^{\infty}P_is^i$$

we can calculate the MWD moments

$$\mu_n = \sum_{i=1}i^nP_i + \sum_{i=0}i^nG_{f+i}$$

and, hence, the average degrees of polymerization.

The following expressions for the number, $\bar{P}_n$, and weight, $\bar{P}_w$, average degrees of polymerization are obtained

$$\bar{P}_n = \mu_1/\mu_0 = \frac{f\gamma}{f\gamma(1-x)+1} = \frac{M_0}{M_0(1-x)+G_f^{\,0}}$$
$$\bar{P}_w = \mu_2/\mu_1 = \frac{(\gamma+f)z^2 - 2fz + f}{\gamma} \quad (4)$$

where $\gamma = M_0/(fG_f^{\,0})$ is the ratio of active groups in the initial vinyl monomer and initiator, and the auxiliary function

$$z(x) = \frac{1+\gamma}{1+\gamma(1-x)} \equiv \bar{P}_n\frac{\gamma+1}{\gamma}$$

is used for shortening. At $x = 0$, z is unity and at full conversion of vinyl groups ($x = 1$), $z = 1 + \gamma$. If the initial concentration of initiator is much smaller than the initial concentration of monomer ($M_0/G_f^{\,0} = f\gamma \gg 1$), for all conversions except for $x \to 1$, expressions 4 transform into the corresponding expressions for SCVP without initiator

$$\bar{P}_n = \frac{1}{1-x} \qquad \bar{P}_w = \frac{1}{(1-x)^2}$$

with a polydispersity index equal to $\bar{P}_n$. However, the very important result is that in the presence of a core-forming initiator the average degrees of polymerization do not go to infinity at $x \to 1$, but approach finite values

$$\bar{P}_n(x \to 1) = f\gamma = \frac{M_0}{G_f^{\,0}} \quad (5)$$

$$\bar{P}_w(x \to 1) = f\gamma + (\gamma+1)^2 \quad (6)$$

and the polydispersity index approaches the value

$$\left.\frac{\overline{P}_{\mathrm{w}}}{\overline{P}_{\mathrm{n}}}\right|_{x\to 1} = 1 + \frac{(\gamma+1)^2}{f\gamma} = 1 + \frac{[(M_0/fG_f^{\,0}) + 1]^2}{M_0/G_f^{\,0}} = 1 + \frac{[(\overline{P}_{\mathrm{n}}/f) + 1]^2}{\overline{P}_{\mathrm{n}}} \quad (7)$$

For high values of the finite number-average degree of polymerization, eq 7 becomes even simpler

$$\overline{P}_{\mathrm{w}}/\overline{P}_{\mathrm{n}} \approx 1 + \frac{\overline{P}_{\mathrm{n}}}{f^2} \quad (7a)$$

In the experimental procedure, the low molecular weight materials, such as residual monomer and initiator are usually separated from the polymer samples by precipitation. The low molecular weight part of the products plays an important role for the polydispersity index[3]. The concentrations of unreacted monomer, $M = P_1$, and the residual initiator, G_f, are calculated in Appendix 1, eq A1-11

$$P_1 = M = M_0(1-x)\exp\left\{\frac{-\gamma x}{\gamma+1}\right\}$$

$$G_f = G_f^{\,0}\exp\left\{\frac{-f\gamma x}{\gamma+1}\right\}$$

If P_1 and G_f are excluded from the various MWD moments, the expressions for the average degrees of polymerization have the form

$$\overline{P}_{\mathrm{n}}{}' = \frac{\mu_1 - P_1}{\mu_0 - P_1 - G_f} = \frac{1-(1-x)\exp\left(-\frac{\gamma x}{\gamma+1}\right)}{(1-x)\left[1-\exp\left(-\frac{\gamma x}{\gamma+1}\right)\right] - \frac{1}{f\gamma}\left[1-\exp\left(-\frac{f\gamma x}{\gamma+1}\right)\right]}$$

$$\overline{P}_{\mathrm{w}}{}' = \frac{\mu_2 - P_1}{\mu_1 - P_1} = \frac{(\gamma+f)z^2 - 2fz + f - \gamma(1-x)\exp\left\{-\frac{\gamma x}{\gamma+1}\right\}}{\gamma\left[1-(1-x)\exp\left\{-\frac{\gamma x}{\gamma+1}\right\}\right]} \quad (4a)$$

The evolution of average molecular weights and polydispersity index with conversion is shown in Figure 1. As in the case where no initiator is added, the corrected number-average degree of polymerization, $\overline{P}_{\mathrm{n}}{}'$, is higher and the polydispersity index is lower when low molecular weight species are excluded. Since

$$G_f(x=1) = G_f^{\,0}\exp[-f\gamma/(\gamma+1)] > 0$$

the difference between average DP's obtained with and without subtraction of unreacted monomer and initiator does not vanish even at full conversion.

Because $M_0/G_f^{\,0}$ is much larger than unity, at small conversion of double bonds species P react predominantly with each other and the molecular weight averages are close to those obtained without initiator. The contribution from core-forming molecules and, hence the marked deviation of MWD averages from those in the absence of initiator becomes significant at conversions when the number of remaining vinyl groups is comparable to the number of initiator functionalities, i.e. $A \approx fG_f^{\,0}$. This explains also the appearance of a maximum in the dependence of polydispersity index on conversion at high conversions.

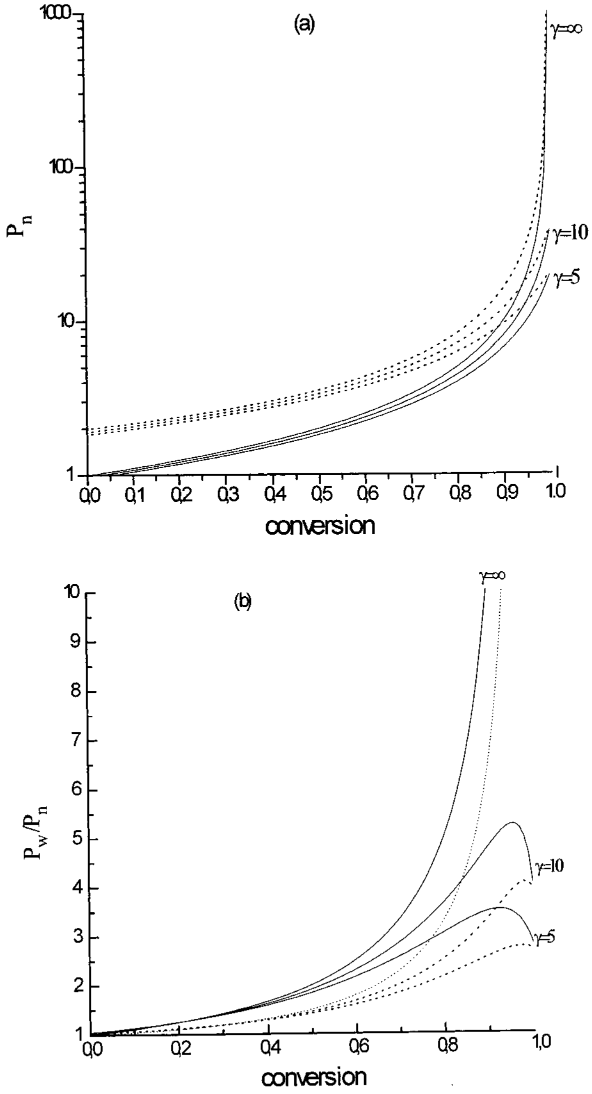


Figure 1. Dependence of the number-average degree of polymerization (a) and polydispersity index (b) on conversion of double bonds including (—) and excluding (- - -) residual monomer and initiator. The functionality of initiator is $f = 4$. $\gamma = \infty$ corresponds to the case when no initiator is added.

As follows from eq 7, even using a small fraction of monofunctional initiator ($f = 1$), for example, only 2.5% of monomer, we are able to reduce the polydispersity index at 95% conversion of double bonds from 20 to ca. 14.

As can be seen from eqs 4, the functionality of initiator has no effect on $\overline{P}_{\mathrm{n}}$, but it affects $\overline{P}_{\mathrm{w}}$ and, consequently, the polydispersity index. At a given monomer/initiator ratio, the use of an initiator with high functionality gives the possibility to decrease the polydispersity index by several times (Figure 2).

The narrowing of the MWD with increasing value of f may be explained by the fact that the convolution of f equal MWDs (one for each core functionality) will lead to a narrower MWD than the original one. For the coupling of f polymer chains with Schulz–Flory distri-

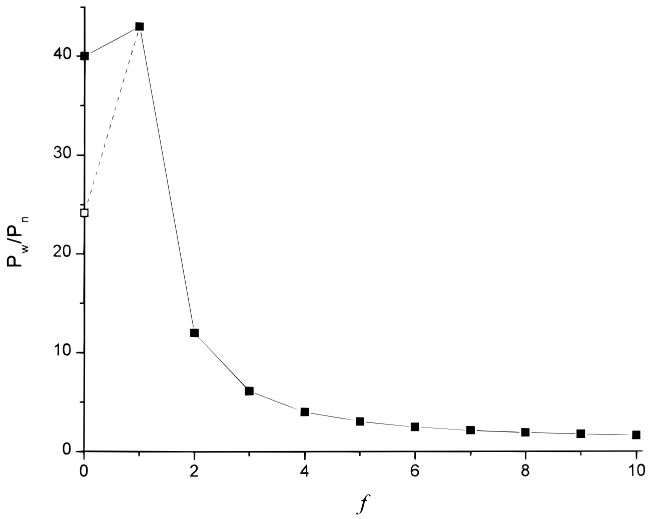


Figure 2. Dependence of the polydispersity index on the initiator functionality for full conversion of double bonds and $\overline{P}_n = f\gamma = M_0/G_f^0 = 40$. The points for $f = 0$ are calculated for 97.5% conversion which gives $\overline{P}_n = 40$ including (■) and $\overline{P}_n' \approx 60$ excluding (□) residual monomer.

bution, Schulz[10] derived that the polydispersity index decreases as $\overline{P}_w/\overline{P}_n = 1 + 1/f$. Comparison with eq 7a shows that in our case the narrowing is not proportional to $1/f$ but to $1/f^2$.

Semibatch Polymerization (Slow Monomer Addition). Thus, we see that it is quite possible to narrow the MWD of hyperbranched polymers by introducing into the system a small amount of a core-forming multifunctional initiator ($f \geq 2$). An even more drastic decrease in the MWD can be expected if monomer is added slowly enough in order to keep the actual monomer concentration, M, very low relative to G_f^0. Then, the probability of a reaction of monomer molecules with each other and formation of species P_i ($i > 1$) is negligible. For this limiting case, we only have to take into account reactions between species without vinyl group, G_{f+i}, and monomer:

$$G_{f+i} + M \xrightarrow{k''} G_{f+i+1} \qquad k'' = (f+i)k$$

This reaction scheme also describes the AB_2 case. Thus, the following derivation is valid for both SCVP and AB_2 polycondensation. Instead of eqs 1 and 2 we have to solve the equations

$$\frac{dM}{dt} = -kM\sum_{0\leq i}(f+i)G_{f+i} + \psi(t) \tag{8}$$

$$\frac{dG_{f+i}}{dt} = k(1-\delta_{i,0})(f+i-1)MG_{f+i-1} - k(f+i)MG_{f+i} \tag{9}$$

where ψ is the monomer flow rate, i.e. the concentration of monomer introduced per time interval. Generally, ψ may be time-dependent. The initial conditions (3) are chosen such that either there is no initial monomer in the system ($M_0 = 0$) or $M_0 \ll G_f^0$. The evolution of monomer concentration with time depends on the dependence of ψ on time. In principle, we can add monomer at a constant rate or choose the dependence of ψ on time such that the monomer concentration is constant. It is easy to show from eqs 8 and 9 that in order to keep monomer concentration constant, ψ should exponentially increase in time. However, as will be shown later, the particular form of ψ does not affect the polydispersity of the resulting polymer, the only requirement is that $M \ll G_f^0$.

Let us introduce the dimensionless time $\tau = \int_0^t kM\,dt$. Then, eq 9, rewritten in terms of τ, obtains the form

$$\frac{dG_{f+i}}{d\tau} = (1-\delta_{i,0})(f+i-1)G_{f+i-1} - (f+i)G_{f+i} \tag{9a}$$

and does not depend on M explicitly. Again we use the generating function for G_{f+i}

$$\Phi(s) = \sum_{i=0}^{\infty} G_{f+i}s^{f+i}$$

as it was done for batch polymerization. In this case we will calculate not only the MWD averages but also the full MWD function. The derivation of $\Phi(s)$ is given in the Supporting Information, Appendix 2. Since we have no polymeric species P, the MWD moments are $\mu_n = \sum_{i=0} i^n G_{f+i}$ or, if initiator is excluded, $\mu_n' = \sum_{i=1} i^n G_{f+i}$.

From the expression for the generating function, eq A2-3

$$\Phi(s,\tau) = G_f^0\left(1 + \frac{1-s}{s}e^{\tau}\right)^{-f}$$

we find for the MWD moments

$$\mu_0 = G_f^0 \qquad \mu_0' = G_f^0 - G_f$$

$$\mu_1 = \mu_1' = fG_f^0(e^{\tau} - 1)$$

$$\mu_2 = \mu_2' = \mu_1 + f(f+1)G_f^0(e^{\tau} - 1)^2$$

The concentration of residual initiator is

$$G_f = (\Phi/s^f)_{|s=0} = G_f^0 \exp(-f\tau) \tag{10}$$

From the moments and eq 10, we can obtain the average degrees of polymerization as

$$\overline{P}_n = \frac{\mu_1}{\mu_0} = f(e^{\tau} - 1) \qquad \overline{P}_n' = \frac{\mu_1}{\mu_0'} = f\frac{e^{\tau} - 1}{1 - e^{-f\tau}}$$
$$\overline{P}_w = \overline{P}_w' = \frac{\mu_2}{\mu_1} = 1 + (f+1)(e^{\tau} - 1) \tag{11}$$

For the polydispersity index, P_w/P_n, as a function of reduced time, τ, we finally obtain

$$\frac{\overline{P}_w}{\overline{P}_n} = \frac{1}{\overline{P}_n} + \frac{f+1}{f} \qquad \frac{\overline{P}_w'}{\overline{P}_n'} = \frac{1}{\overline{P}_n'} + \frac{f+1}{f}[1 - \exp(-f\tau)] \tag{12}$$

For sufficiently high τ ($e^{\tau} \gg 1$) and, consequently, for a

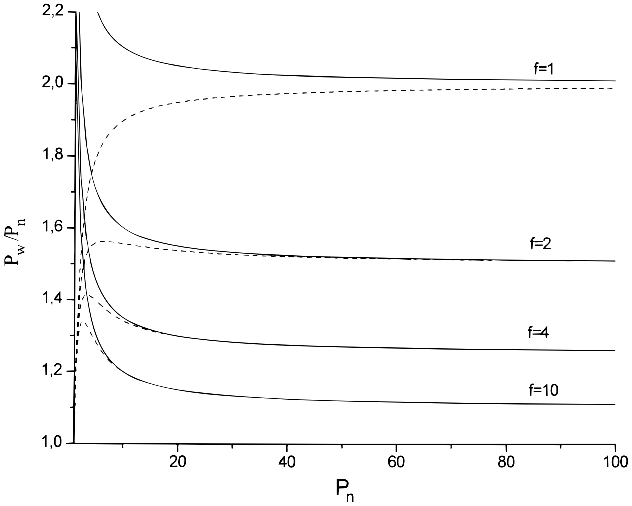


Figure 3. Dependence of the polydispersity index on the number average degree of polymerization, $\bar{P}_n$, for various initiator functionalities in semibatch mode including (—) and excluding (- - -) residual initiator from the MWD moments.

high degree of polymerization, eq 12 can be approximated by

$$\bar{P}_n \approx f e^{\tau}$$
$$\bar{P}_w \approx (f+1) e^{\tau} \tag{11a}$$

and the polydispersity index approaches the limiting value

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{\bar{P}_w'}{\bar{P}_n'} = 1 + \frac{1}{f} \tag{13}$$

The dependence of the polydispersity index on the number average degree of polymerization, $\bar{P}_n$, is shown in Figure 3 for various values of the functionality, f. Even for the lowest functionality ($f = 1$) the polydispersity is much lower than the value obtained for the batch process. Since the overall rate of monomer addition of a molecule is proportional to the number of functional groups attached, large molecules grow faster than smaller ones. In order to obtain a narrow MWD it is desirable to have similar reactivities for all species. Since the step from the pure core to the molecule with degree of polymerization $i = 1$ increases the reactivity relative to the core itself by a factor of two in the case of $f = 1$, while, e.g. for $f = 4$ and 10 the relative increase in the rate constants is $^5/_4$ and $^{11}/_{10}$, respectively. Thus, the higher functionality cores lead to similar reactivities for the first few addition steps, which means that the MWD stays rather narrow throughout the reaction and we obtain an expression for the polydispersity index which is identical to the one given by Schulz.[10] Comparing the polydispersity index for batch and semibatch polymerizations at equal number-average degree of polymerization, we see that the latter process results in a much narrower MWD. Thus, for $\bar{P}_n = 100$ and $f = 4$, $\bar{P}_w/\bar{P}_n = 7.76$ for batch polymerization (eq 7) and 1.26 for slow monomer addition (eq 12).

Molecular Weight Distribution

For the semibatch process we also calculate the full MWD function. Differentiating the generating function the corresponding number of times over s and applying $s = 0$, we obtain the concentrations G_{f+i}

$$G_{f+i} = G_f^{\,0} \frac{(f+i-1)!}{(f-1)!\,i!} (e^{\tau} - 1)^i e^{-(f+i)\tau} \tag{14}$$

Taking into account the interdependence of τ and $\bar{P}_n$ (eq 11a), we can rewrite eq 14 for large $\bar{P}_n$ in the form

$$G_{f+i} \approx G_f^{\,0} \frac{(f+i-1)!}{(f-1)!\,i!} \left(\frac{\bar{P}_n}{f}\right)^{-f} \exp\left(-\frac{if}{\bar{P}_n}\right) \tag{15}$$

Since G_{f+i} is identical to the concentration of molecules having degree of polymerization i, the normalized frequency distribution is given by $N(i) = G_{f+i}/\mu_0$, where μ_0 for large $\bar{P}_n$ is approximated by G_f^0. Thus, the normalized frequency distribution $N(i)$ for large $\bar{P}_n$ is given by

$$N(i) = \frac{(f+i-1)!}{(f-1)!\,i!} \left(\frac{\bar{P}_n}{f}\right)^{-f} \exp\left(-\frac{if}{\bar{P}_n}\right) \tag{16}$$

The normalized weight and the z-distribution, $W(i)$ and $Z(i)$ respectively, can be easily obtained as

$$W(i) = \frac{iG_{f+i}}{\mu_1} = \frac{(f+i-1)!}{f!\,(i-1)!} \left(\frac{\bar{P}_n}{f}\right)^{-(f+1)} \exp\left(-\frac{if}{\bar{P}_n}\right) \tag{17}$$

$$Z(i) = \frac{i^2 G_{f+i}}{\mu_2} = \frac{i(f+i-1)!}{(f+1)!\,(i-1)!} \left(\frac{\bar{P}_n}{f}\right)^{-(f+2)} \exp\left(-\frac{if}{\bar{P}_n}\right) \tag{18}$$

Since $Z(i) = iW(i) = W(\log i)$, the z-distribution is equivalent to the weight-distribution obtained by GPC using a logarithmic scale of molecular weight ("GPC distribution").

By using Stirling's equation for $i \gg 1$

$$i! = \sqrt{2\pi i}\,(i/e)^i$$

we can derive continuous distributions from eqs 16−18

$$N(i) = \frac{(if/\bar{P}_n)^{f-1} \exp(-if/\bar{P}_n)}{(f-1)!} \tag{16a}$$

$$W(i) = \frac{(if/\bar{P}_n)^{f} \exp(-if/\bar{P}_n)}{f!} \tag{17a}$$

$$Z(i) = \frac{(if/\bar{P}_n)^{f+1} \exp(-if/\bar{P}_n)}{(f+1)!} \tag{18a}$$

Looking at the frequency distributions $N(i)$ (Figure 4a) we observe that even at $\bar{P}_n = 50$ the predominant species is the initiator ($i = 0$) itself for $f = 1$. For $f = 2$ there still is substantial residual initiator present. This

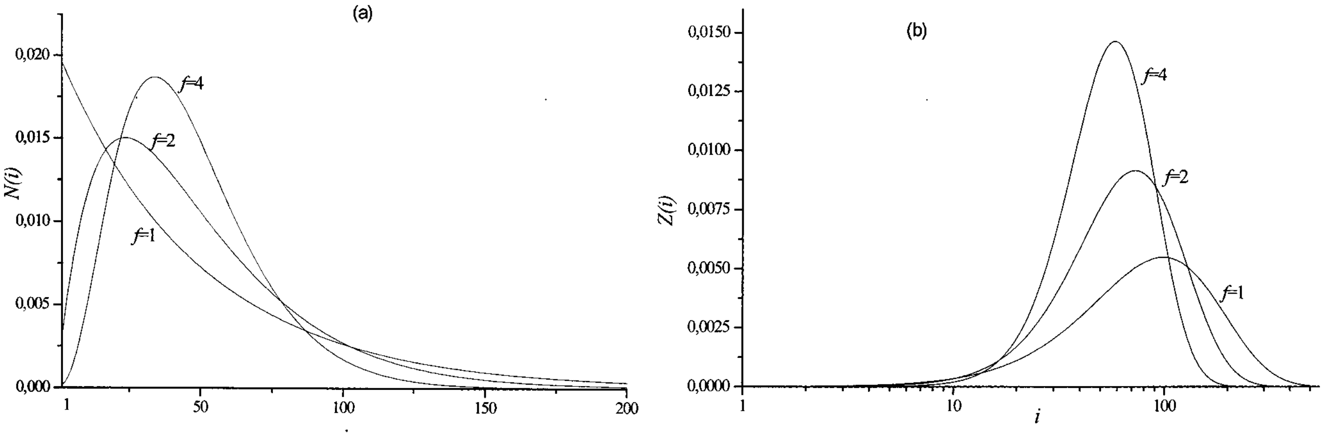


Figure 4. Frequency (a) and z-distribution (b) functions obtained in semibatch mode for various values of the initiator functionality. $\overline{P}_n = 50$.

is in agreement with the argumentation above that the larger molecules consume the monomer at the cost of the smaller molecules. Once the growth process has begun the initiator cannot compete for monomer with the larger species. In contrast to the batch process of SCVP without core-forming molecule, we can observe a maximum even in the frequency distribution function, $N(i)$, for functionalities $f > 1$. The corresponding z-distributions are given in Figure 4b.

Degree of Branching and Radial Functionality Distribution

Beside the width of the MWD, dendrimers are often preferred to hyperbranched polymers, since the placement of the functional groups is completely defined in the case of a dendrimer, while the functional groups in a hyperbranched polymer are distributed throughout the molecule. The degree of branching, DB, of a separate macromolecule constructed from an f-functional core (where all f functions have reacted) is defined in such a way that it is unity for perfect dendrimers and 0 for linear chains[4] as

$$\mathrm{DB} = \frac{(\text{number of branched units}) + (\text{number of terminal units}) - f}{\text{total number of units} - f}$$

The fraction of branchpoints (i.e. not taking into account terminal units) was defined as

$$\mathrm{FB} = \frac{\text{number of branched units}}{\text{total number of units}}$$

In the absence of a core-forming molecule these parameters were calculated[2,4] as $\overline{\mathrm{DB}} \approx 0.5$ and $\overline{\mathrm{FB}} \approx 0.25$ for the polymer mixture obtained. Therefore, is seems interesting to study the effect of a core-forming initiator on the degree of branching. Let us denote the terminal segments, which carry two functional groups, as T, the linear segments, carrying one functional group as L, and the branchpoints as B (cf. Chart 1). For simplicity we do not count the core segment as belonging to either of these types. In calculations of $\overline{\mathrm{DB}}$, equal reactivity of all functional groups, irrespective of their placement within the molecule, is again assumed.

Batch Process. It can be shown that the degree of branching for the batch process in the presence of core-forming molecules does not differ dramatically from $\overline{\mathrm{DB}}$ without them. In the discussion concerning the effect of core-forming molecules on the polydispersity index in the batch process we have found that it becomes important only at the very end of the reaction, when the number of species carrying a vinyl group, $\sum P_i$, and the number of species without vinyl groups, $\sum G_i$, become comparable. Thus, the branching statistics can be described nearly completely by the statistics of SCVP without core-forming initiator, which will lead to $\overline{\mathrm{DB}} \approx 0.5$.

Semibatch Polymerization. It seems more interesting to calculate $\overline{\mathrm{DB}}$ of hyperbranched polymers obtained by slow monomer addition. This process has some similarity with the divergent approach of dendrimer synthesis which starts with a multifunctional core ($f \geq 2$). The important difference is that in SCVP or AB_2 polycondensation the segments of a certain generation are not added simultaneously but in a statistical process. Thus, we shall frequently use the term "generation" which means the number of links between the core and the specified functional group (see Chart 1). The core itself is generation 0. The number of functional groups within a specified generation is denoted as f_G. Similarly, T_G, L_G, and B_G are the numbers of terminal, linear, and branched units in generation G.

At $t = 0$ we have only the zeroth generation, and $f_G = f\,\delta_{G,0}$. At high degrees of polymerization ($i \gg 1$), $f_0(i) \to 0$.

Since a terminal segment has two functional groups and a linear segment has one, the total number of functional groups within a generation is

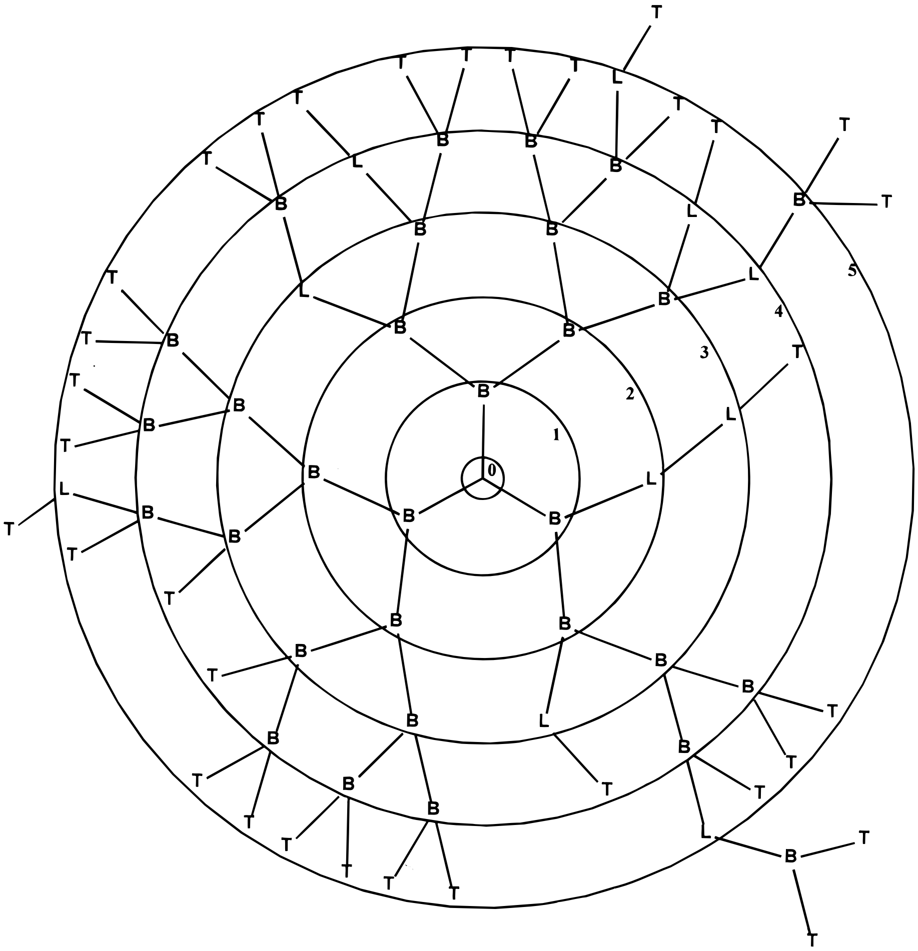
$$f_G = 2T_G + L_G$$

The total number of functional groups, of course, is equal to the initial concentration of initiator and monomer functional groups

$$\sum_{G\geq 0} f_G(i) = i + f$$

Let us calculate the number of different groups in generation G for molecules with i monomer units. If we add one monomer molecule, i.e., if we increase the

Chart 1. Hyperbranched Polymer Obtained by Growth of an AB* or AB$_2$ Monomer onto a Trifunctional Core (“Generations” 0 to 5 Numbered)



degree of polymerization by one unit, the change in f_G can be expressed as

$$f_0(i+1) - f_0(i) = -\frac{f_0(i)}{\sum\limits_{G\geq 0} f_G(i)} = -\frac{f_0(i)}{i+f}$$

$$f_G(i+1) - f_G(i) = \frac{2f_{G-1}(i) - f_G(i)}{\sum\limits_{G\geq 0} f_G(i)} = \frac{2f_{G-1}(i) - f_G(i)}{i+f} \qquad (G \geq 1) \quad (19)$$

The first term in the right-hand side of eq 19 for $G \geq 1$ describes the formation of two functional groups due to addition of the monomer to functional groups in generation $G - 1$ and the second the disappearance of a functional group in generation G due to reaction with monomer. For $G = 0$, no new groups can be formed.

Similarly, the number of the different types of segments in generation G is described by the following equations

$$T_G(i+1) - T_G(i) = \frac{2T_{G-1} + L_{G-1} - 2T_G}{i+f} = \frac{f_{G-1} - 2T_G}{i+f}$$

$$L_G(i+1) - L_G(i) = \frac{2T_G - L_G}{i+f} \quad (G \geq 1) \qquad (20)$$

$$B_G(i+1) - B_G(i) = \frac{L_G}{i+f}$$

From eq 19 we can obtain by induction for $G = 0$

$$f_0(i) = \frac{f(f-1)}{i+f-1}$$

However, it is impossible to obtain the exact solutions of eqs 19 and 20 for arbitrary i and G. Nevertheless, for large degrees of polymerization, $i \gg 1$, we can use the continuous approximation, substituting the differences like $f(i+1) - f(i)$ by the derivatives $\mathrm{d}f/\mathrm{d}i$. We then obtain the following differential equation for f_G

$$\frac{\mathrm{d}f_G}{\mathrm{d}i} = \frac{2 \cdot f_{G-1} - f_G}{i+f} \quad (G \geq 1) \qquad (19a)$$

The integration of eq 19a leads to

$$f_G = \frac{f^2 2^G}{G!(i+f)}\left(\ln\left(\frac{i+f}{f}\right)\right)^G \qquad (21)$$

Then, the fraction of functional groups in generation G can be expressed as

$$x_G = f_G/(f+i)$$

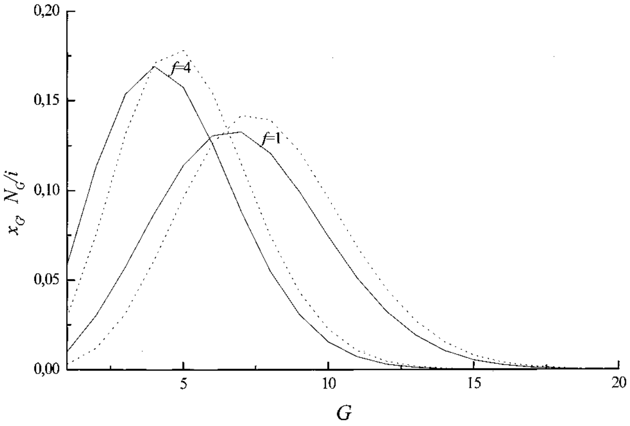


Figure 5. Fractions of functional groups, $x_G = f_G/(f + i)$ (- - -), and of total number of monomer units, N_G/i (—), as functions of generation number for various values of initiator functionality f ($i = 50$).

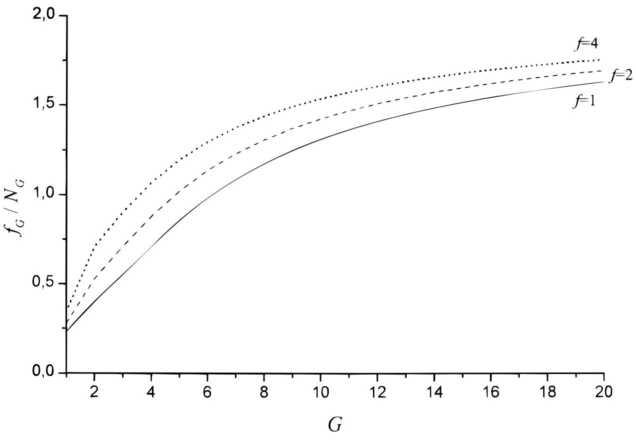


Figure 6. Density of functional groups as a function of generation ($i = 50$).

As can be seen from Figure 5, the functional groups are located apart from the center of the molecule, giving rise to a core–shell-like structure with the core virtually free of functional groups. However, it has to be taken into account that the total number of segments in a given generation

$$N_G = B_G + T_G + L_G$$

also has a maximum. This quantity is derived further below (eq 27). It is seen that the maximum of x_G is shifted to higher generations than the maximum of N_G. Thus it is natural that the "density" of functional groups that is, the number of functional groups per segment in a given generation, f_G/N_G, will monotonously increase with G, limited by the value two for terminal units (Figure 6).

In order to calculate the degree of branching, we first calculate the fractions of the various kinds of monomer units. Assuming long-chain approximation for $i \gg 1$, from eq 20 the following differential equations can be obtained for the number of terminal, $T = \sum_{G\geq 1} T_G$ and linear, $L = \sum_{G\geq 1} L_G$, segments

$$\frac{\mathrm{d}T}{\mathrm{d}i} = \frac{\sum\limits_{G\geq 1} f_{G-1} - 2T}{i = f} = 1 - \frac{2T}{i + f}$$

$$\frac{\mathrm{d}L}{\mathrm{d}i} = \frac{2T - L}{i + f}$$

The solutions are

$$T = \frac{1}{3}\left\{i + f - \frac{f^3}{(i + f)^2}\right\} \approx \frac{i + f}{3}$$

$$L = \frac{1}{3}\left\{i + f + \frac{2f^3}{(i + f)^2} - \frac{3f^2}{i + f}\right\} \approx \frac{i + f}{3} \qquad (22)$$

As follows from the topology, for one macromolecule

$$B = T - f \approx \frac{i - 2f}{3}$$

Thus, one can see that the numbers of segments are distributed in such a way that branched, linear, and terminal segments do contribute to nearly equal amounts to the whole polymer.

According to the definition given above, the degree of branching, $\overline{\mathrm{DB}}$, is

$$\overline{\mathrm{DB}} = \frac{B + T - f}{i - f} = \frac{2B}{2B + L} = \frac{2(i - 2f)}{3(i - f)} \qquad (23)$$

and for high degrees of polymerization ($i \gg 1$) we obtain[15]

$$\overline{\mathrm{DB}} \approx {}^2/_3$$

Accordingly we obtain for the fraction of branchpoints

$$\overline{\mathrm{FB}} = \frac{B}{i} = \frac{i - 2f}{3i} \approx {}^1/_3$$

These values are significantly larger than those for the batch process of SCVP and AB_2 polycondensations with or without core-forming molecule, where the number of linear units is approximately equal to the sum of branched and terminal units, while branched and terminal units contribute to equal amounts leading to a lower values of $\overline{\mathrm{DB}} \approx 1/2$ and FB $\approx 1/4$.

Now let us determine the radial distribution of different segments throughout the molecule. Integration of eqs 20 with the use of eq 21 for f_G leads to the following expression for the number of terminal segments in different generations

$$T_G = \frac{f^2 2^{G-1}}{(G-1)!(i + f)^2} \int_1^i \left(\ln\left(\frac{i' + f}{f}\right)\right)^{G-1} \mathrm{d}i' \qquad (24)$$

For high molecular weight polymers, we can replace the lower integration index by zero and the solution becomes

$$T_G = \frac{f 2^{G-1}}{(i + f)}\left\{\sum_{j=0}^{G-1}\left[\ln\left(\frac{i + f}{f}\right)\right]^{G-1-j} \frac{(-1)^j}{(G - 1 - j)!} + (-1)^G\right\} \qquad (24a)$$

Similarly

$$L_G = \frac{f^2 2^G}{G!(i + f)^2} \int_1^i \left(\ln\frac{i' + f}{f}\right)^G \mathrm{d}i' = T_{G+1} \qquad (25)$$

Summarizing eq 20, we obtain the following equation for the total number of segments in a given generation,

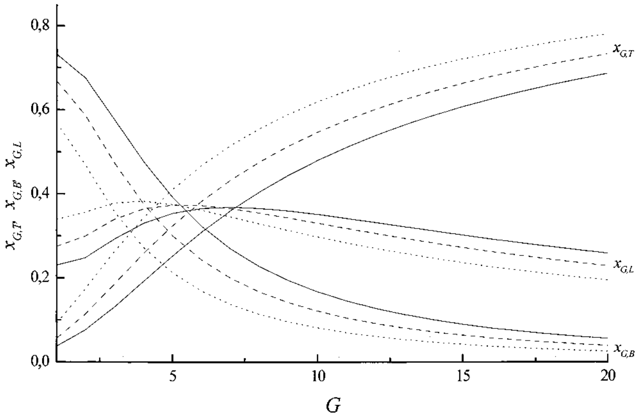


Figure 7. Fractions of branched, $x_{G,\mathrm{B}}$, linear, $x_{G,\mathrm{L}}$, and terminal, $x_{G,\mathrm{T}}$, segments as functions of generation number G ($i = 50$): (—) $f = 1$; (- - -) $f = 2$; (···) $f = 4$.

$N_G = T_G + L_G + B_G$ (total number of segments is $\sum_{G=1} N_G = i$)

$$\frac{\mathrm{d}N_G}{\mathrm{d}i} = \frac{f_{G-1}}{i + f} \tag{26}$$

The integration of eq 26 gives

$$N_G = \frac{f^2 2^{G-1}}{(G+1)!} \int_1^i \frac{1}{(i' + f)^2} \left(\ln\left(\frac{i' + f}{f}\right)\right)^{G-1} \mathrm{d}i' \approx f2^{G-1}\left\{1 - \frac{f}{f+i} \sum_{j=0}^{G-1} \left[\ln\left(\frac{f+i}{f}\right)\right]^j \Big/ j!\right\} \tag{27}$$

For perfect dendrimers, $N_G = f2^{G-1}$ for all inner generations. Thus, the second term in brackets of eq 27 shows the deviation from the case of perfect dendrimers. The typical dependence of N_G for a semibatch process was shown in Figure 5.

Using eqs 24a, 25, and 27 we can calculate the fractions of terminal, $x_{G,\mathrm{T}} = T_G/N_G$, linear, $x_{G,\mathrm{L}} = L_G/N_G$, and branched, $x_{G,\mathrm{B}} = B_G/N_G$, units in generation G. A closer look on the distribution of different segments is given in Figure 7. As can be seen, the fraction of linear segments does not show a strong dependence on generation while branched units are mainly found in lower generations, giving rise to a dense core, similar, but not identical to dendrimers where $x_{G,\mathrm{B}} = 1$ in inner generations and it the outer $x_{G,\mathrm{T}} = 1$.

Although the calculation of the distribution of linear, branched and terminal segments within a molecule was not carried out by Yan et al.,[4] it is reasonable to assume that the different segment types are distributed nearly equally throughout the molecule. This is quite different from results for slow monomer addition.

Conclusions

The addition of a core-forming molecule to the SCVP strongly affects the polydispersity index. In the batch process it decreases with initiator functionality as $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n} \approx 1 + \bar{P}_\mathrm{n}/f^2$. The effect is even more pronounced for the semibatch process where $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n} \approx 1 + 1/f$.

The results for the batch process might also explain the fact that polydispersities found in SCVP are often lower than predicted by theory.[3] The cyclization reaction (loop formation) between an initiating site and the vinyl group can lead to polymers without vinyl group, similar to the species obtained by addition of a core-forming molecule. The occurrence of such a cyclization reaction should therefore drastically reduce the polydispersity. The effect of loop formation will be discussed in detail in a subsequent publication.

While the addition of core-forming molecules shows only a slight effect on the degree of branching in the batch process, this parameter is significantly enhanced from $\overline{\mathrm{DB}} \approx 1/2$ to $\overline{\mathrm{DB}} \approx 2/3$ in the semibatch process.

The distribution of linear, branched, and terminal units in the macromolecules formed in the semibatch process is predicted to lead to a core mainly consisting of branched and linear units, while the outer portion of the molecule is dominated by linear and terminal units. Polymers obtained by slow monomer addition to a core-forming molecule will therefore closer resemble dendrimers than their analogues obtained in a batch process with respect to the distribution of the functional groups and their MWD. The gap between the perfect dendritic structure obtained by tedious synthesis and the less defined structure of a hyperbranched polymer becomes closer by a proper performance of the reaction.

It is also important to note that in the semibatch process at conditions of very slow monomer addition SCVP and AB_2 polycondensation will lead to polymers of identical structure and MWD. Thus, under the limiting conditions of slow monomer addition both processes might be given the general name “cascade polymerization”.

Experiments with slow addition of monomer to a core-forming molecule have not yet been reported. However, there are a few reports which come more or less close to this aim.

Hult and co-workers[11] used multiple additions of 2,2-bis(hydroxymethyl)propionic acid to 2-ethyl-2-(hydroxymethyl)-1,3-propanediol as a core-forming molecule. Although the single portions of monomer added at each time are too large to fulfil the requirement of slow monomer addition they reported apparent polydispersities below 2 and degrees of branching of >80%. In comparison to other similar studies in literature they concluded that the use of core-forming molecules will increase the degree of branching. Although a recent reevaluation[12] showed that the absolute $\overline{\mathrm{DB}}$ values are too high, the comparison with our calculations shows the right trend.

In another interesting approach Suzuki et al.[13] investigated the palladium-catalyzed ring-opening polymerization of a cyclic carbamate initiated by a monofunctional amine in a batch reaction. Due to the reaction mechanism, each monomer addition adds one reactive amino group to the polymer; however, the polymer molecules cannot react with each other but only with monomer. The authors named this process “multibranching polymerization”. This process should lead to the same MWD and $\overline{\mathrm{DB}}$ as slow monomer addition to a monofunctional initiator and one should expect $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n} = 2$ and $\overline{\mathrm{DB}} = 2/3$. However, the authors reported $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n} = 1.35$ and $\overline{\mathrm{DB}} = 0.44-0.52$. The deviation in the polydispersity index might be explained by the facts that the polymers had been worked up and a subsequent modification reaction had been carried out which might change the MWD. Moreover, only linear polystyrene standards were used for GPC calibration. On the other hand, there are the limitations of our approach as detailed in our earlier papers (dependence of reactivity on chain length; nonequal reactivities of initiating and propagating sites).

Very recently, Bharati and Moore[14] reported a hyperbranched polymerization of the AB_2 monomer (diiodophenyl)acetylene in presence of a diiodophenyl (B_2) initiator linked to a solid support. Although this was a batch process, the soluble polymers formed by condensation between AB_2 monomers were removed by washing and the polymers that added to the supported initiator could be recovered separately. These polymers show narrow MWD ($\overline{P}_w/\overline{P}_n = 1.1-1.5$ vs >2.5 for the soluble polymer; all data based on GPC calibrated with linear PS standards) and they also show an increase of $\overline{P}_n$ with increasing ratio of monomer over initiator. Unfortunately, no degrees of branching were determined. Although the authors attributed these effects to the presence of the solid support, we believe that this is the first real manifestation of the principle of slow monomer addition outlined above.

No experimental results have been reported yet in SCVP. However, here the rate of monomer addition is limited by the lifetime of the functional groups which may suffer from termination reactions (radical[7] or group transfer polymerization[9]) or transfer reactions (cationic polymerization[6]).

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List of Symbols and Abbreviations

$\gamma = M_0/(fG_f^0)$	initial ratio of active groups in monomer and initiator
$\delta_{l,m}$	Kronecker symbol: $\delta_{l,m} = 1$ for $l = m$; $\delta_{l,m} = 0$ else
μ_n	*n*th moment of the MWD
ψ	monomer flow rate
$\tau = \int_0^t kM\,dt$	dimensionless time
Φ	generating function for G_{f+i}
A	concentration of vinyl groups in SCVP; of A groups in AB_2 polycondensation
B	concentration of branched units
B_G	number of branched units in generation G
f	functionality of initiator
f_G	number of functional groups in generation G
G_f^0	initial concentration of f-functional initiator
G_i	concentration of macromolecules with i active centers and no vinyl groups
$I_0 \equiv M_0 + fG_f^0$	total initial concentration of active centers
i	chain length of a molecule
k	propagation rate constant
L	concentration of linear segments
L_G	number of linear units in generation G
M_0	initial concentration of monomer or double bonds
M	monomer concentration
N_G	total number of monomer units in generation G
$N(i)$	number distribution
P_i	concentration of macromolecules of degree of polymerization i which contain a vinyl group
$\overline{P}_n$	number-average degree of polymerization
$\overline{P}_w$	weight-average degree of polymerization
$\overline{P}_w/\overline{P}_n$	polydispersity index
t	reaction time
T	concentration of terminal segments
T_G	number of terminal units in generation G
x	conversion of double bonds (=A groups)
$x_{G,B}$	fraction of branched units in generation G
$x_{G,L}$	fraction of linear units in generation G
$x_{G,T}$	fraction of terminal units in generation G
$W(i)$	weight distribution
$Z(i)$	*z*-distribution

Supporting Information Available: Text giving the calculation of the average molecular weights in batch polymerization (Appendix 1) and calculation of the MWD for slow monomer addition (Appendix 2) (5 pages). Ordering and Internet access information is given on any current masthead page.

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