Molecular Weight Averages and Degree of Branching in Self-Condensing Vinyl Copolymerization in the Presence of Multifunctional Initiators

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ABSTRACT: The averages of the molecular weight distribution (MWD) and the degree of branching (DB) are calculated for hyperbranched copolymers obtained in the self-condensing vinyl copolymerization (SCVCP) of AB* initiator−monomers ("inimers") with a monomer M in the presence of an *f*-functional initiator, G*$_f$. Two cases are considered: (a) batch polymerization when all components are mixed simultaneously; (b) semibatch polymerization, i.e., slow addition of the comonomer mixture to the system. The presence of initiator leads to a considerable narrowing of the MWDs, the nonuniformity of the distribution ($U = \bar{M}_w/\bar{M}_n - 1$) decreasing with initiator functionality, *f*, similar to normal self-condensing vinyl polymerization (SCVP): U ∝ f^{-2} in the batch mode and U = f^{-1} in the semibatch mode. In the semibatch process, the presence of comonomer does not further decrease the polydispersity, as compared to the homopolymerization of AB* inimers in the presence of polyinitiator. The degree of branching is only slightly affected by the presence of polyinitiator and is mostly governed by the comonomer content. In contrast to semibatch SCVP with initiator, there is no increase in DB. The calculations are also applied to polymerizations from surface-bound initiators.

Introduction

Branched polymers have been intensively studied, both theoretically and experimentally.[1−3] Among them, dendrimers have a number of advantages such as monodispersity, and a highly ordered structure.[1,4−6] However, the synthesis of such molecules is rather troublesome and requires multistep procedures. On the other hand, hyperbranched molecules can be prepared in a one-pot synthesis, reducing cost and efforts, either using polycondensation,[7,8] or by self-condensing vinyl polymerization (SCVP) of an initiator−monomer ("inimer") AB*, i.e., a molecule having a vinyl group A and an initiating group B*.[9] Earlier, the theory of this process was elaborated.[10,11] It was shown that such a process results in polymers with a lower degree of branching, DB ≤ 0.5, and with broad molecular weight distributions, the polydispersity index, $\bar{P}_w/\bar{P}_n$, being equal to the number-average degree of polymerization, $\bar{P}_n$. Thus, the synthesis of hyperbranched polymers would be more advantageous if it would be possible to reduce the polydispersity. A way to narrow the MWD and to approach the structure to that of dendrimers was shown to be an addition of a small fraction of a multifunctional initiator, G*$_f$, to inimers.[12,13] The polydispersity of polymers obtained in such procedure drastically decreases with increasing initiator functionality *f*, the decrease was even more pronounced when inimer was slowly added to the system (semibatch polymerization).[12,14] As for the average degree of branching (DB), the presence of polyinitiator has a small effect in batch mode whereas the polymer obtained in a semibatch process is more strongly branched (DB = $^2/_3$ as compared to DB = 0.465 without initiator).

Another, more advanced procedure of obtaining hyperbranched polymers with a variety of structures is the self-condensing vinyl *co*polymerization (SCVCP) of inimers with common vinyl monomers, M.[15−18] We showed theoretically that the kinetics, the molecular weight distribution (MWD), and the average degree of branching strongly depend on the comonomer ratio, $\gamma = M_0/I_0$ and the relative reactivities of monomer and inimer.[19,20] In the ideal case, when all rate constant are equal, for high $\gamma \gg 1$ $\bar{P}_n$, is given by the product of the values for the SCVP of inimer and the living polymerization of monomer initiated by inimer, $\bar{P}_n = (\bar{P}_n)_{liv}(\bar{P}_n)_{SCVP} = \gamma x_M/(1 - x_M)$, where x_M is the monomer conversion. For a given value of $\bar{P}_n$, the polydispersity index decreases with γ as $\bar{P}_w/\bar{P}_n = \bar{P}_n/\gamma x_M$. For $\gamma > 1$, the final value of DB decreases with γ as DB = $2/(\gamma + 1)$ which is four times higher than the value expected from dilution of inimer molecules by monomers. For low values of γ ($\gamma \le 1$), DB even exceeds the values for a homo-SCVP; a maximum of DB = 0.5 is reached at $\gamma \approx 0.6$. Depending on the reactivity ratios the structure of polymer obtained can change from "macroinimers" when the monomer M is much more reactive than the vinyl groups of inimers or polymer to "hyperstars" in the opposite limiting case.

It is interesting to study the effect of multifunctional initiator on the MWD and on the structure of copolymers obtained in self-condensing vinyl copolymerization. Very recently, He et al.[21] published a Monte Carlo simulation of the batch system. However, all numerical calculations were performed only for a single set of input parameters (the ratio of total concentration of comonomers, $M_0 + I_0$, to the concentration of polyinitiator equal to 100), which does not allow us to derive quantitative conclusions. In this paper, we obtain the analytical solutions for both the batch and the semibatch process.

General Considerations

There are two ways of initiation, via inimer or polyfunctional initiator. The active B* group of an inimer can add to the double bond A of another inimer
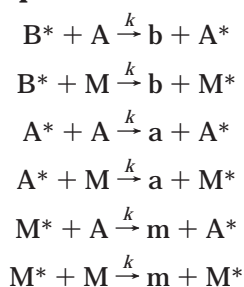
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molecule forming a dimer A−b−A*−B* with two active sites, A* and B*. Alternatively it can add to the double bond of monomer forming a dimer, A−b−M*, with the new active site M*). The dimers formed in such initiation and the polymers formed in subsequent addition steps always contain exactly one double bond. In the case of initiation via the *f*-functional initiator, the products $(B^*)_{f-1}b-A^*-B^*$ or $(B^*)_{f-1}b-M^*$ and the subsequent polymers contain no double bond. Both the initiating B* group and the newly created propagating centers A* or M* can react with the vinyl group of other molecules. Thus, we have three different types of active centers, A*, B* and M* which can react with double bonds A (inimer and macromolecules) and M (monomer) as follows from Scheme 1.

Scheme 1. Reactions between Active Centers and Vinyl Groups in SCVCP

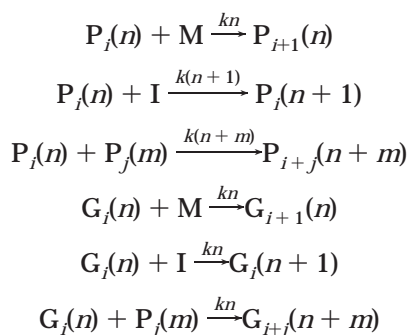$$B^* + A \xrightarrow{k} b + A^*$$

$$B^* + M \xrightarrow{k} b + M^*$$

$$A^* + A \xrightarrow{k} a + A^*$$

$$A^* + M \xrightarrow{k} a + M^*$$

$$M^* + A \xrightarrow{k} m + A^*$$

$$M^* + M \xrightarrow{k} m + M^*$$

In Scheme 1, as earlier,[10,19] we use capital letters for vinyl groups (A, M) and for active centers (A*, B*, M*) and lowercase letters for reacted ones (a, b, m).

We shall assume equal reactivities of all A*, B*, and M* centers. Of course, this is only an ideal case; in real systems, all rate constants k_{PQ} of addition of species Q to the active site P* are instead different rather than equal. The effect of different rate constants on the molecular and structural properties of the copolymers formed in the absence of polyfunctional initiator have been recently considered.[20] However, in this work, we want just to clarify the effect of polyfunctional initiator and do not want to overcomplicate the problem.

Let $P_i(n)$ be macromolecules containing *i* monomer units, *n* active centers, and a vinyl group and $G_i(n)$ be macromolecules stemming from the polyfunctional initiator, containing *i* monomer units and *n* active centers but no vinyl group. Consequently, the number of units of inimer in such molecules is *n* for $P_i(n)$ and *n* − *f* for $G_i(n)$. Parameters *i* and *n* can be varied within the range $i \geq 0$, $n \geq 1$ for $P_i(n)$ ($i + n \geq 2$) and $i \geq 0$, $n \geq f$, ($i + n > f$) for $G_i(n)$. Now we can write down the kinetic scheme for species $P_i(n)$ and $G_i(n)$

Scheme 2

$$P_i(n) + M \xrightarrow{kn} P_{i+1}(n)$$

$$P_i(n) + I \xrightarrow{k(n+1)} P_i(n+1)$$

$$P_i(n) + P_j(m) \xrightarrow{k(n+m)} P_{i+j}(n+m)$$

$$G_i(n) + M \xrightarrow{kn} G_{i+1}(n)$$

$$G_i(n) + I \xrightarrow{kn} G_i(n+1)$$

$$G_i(n) + P_j(m) \xrightarrow{kn} G_{i+j}(n+m)$$

Schemes 1 and 2 are analyzed separately for batch and semibatch polymerization.

Molecular Weight Averages

Batch Polymerization. In this process, all components: inimer, monomer, and polyfunctional initiator at initial concentrations I_0, M_0, and G_{f0}, respectively, are mixed simultaneously prior to polymerization. According to the kinetic Schemes 1 and 2, the set of differential equations for the evolution in time of the concentrations of various species can be written as follows.

Concentrations of comonomers:

$$\frac{1}{k}\frac{dM}{dt} = -MN^*$$
$$\frac{1}{k}\frac{dI}{dt} = -I(N^* + A + M) \quad (1)$$

Concentration of double bonds:

$$\frac{1}{k}\frac{dA}{dt} = -AN^* \quad (2)$$

Concentration of macromolecules containing a double bond:

$$\frac{1}{k}\frac{dP_i(n)}{dt} = nM[P_{i-1}(n) - P_i(n)] + I[nP_i(n-1) -$$
$$(n+1)P_i(n)] - P_i(n)\sum_{i',n'}(n+n')P_{i'}(n') -$$
$$P_i(n)\sum_{i',n'}n'G_{i'}(n') + \frac{1}{2}\sum_{\substack{i>i'\geq 1 \\ n>n'\geq 1}}nP_{i'}(n')P_{i-i'}(n-n') +$$
$$IM\delta_{i,1}\delta_{n,1} + I^2\delta_{i,0}\delta_{n,2} \quad (3)$$

Concentration of macromolecules without double bonds

$$\frac{1}{k}\frac{dG_i(n)}{dt} = I[(n-1)G_i(n-1) - nG_i(n)] +$$
$$M[nG_{i-1}(n) - nG_i(n)] + \sum_{\substack{i>i'>0 \\ n>n'\geq f}}n'G_{i'}(n')P_{i-i'}(n-n') -$$
$$nG_i(n)\sum_{i',n'}P_{i'}(n') \quad (4)$$

In sets 1−4, N^* is the total concentration of active centers, $N^* = A^* + B^* + M^* = I_0 + fG_{f0}$. The Kronecker symbol, $\delta_{i,j}$, in eq 3 is defined as

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

The solution of eqs 1 and 2 is

$$M/M_0 = A/I_0 = \exp(-kN^*t)$$

$$I/I_0 = \exp[-kN^*t - (\gamma + 1)(1 - e^{-kN^*t})]$$

It is convenient to express all concentrations as functions of monomer conversion, $x_M = (M_0 - M)/M_0$.

Then, we obtain

$$x_M = 1 - \exp(-kN^*t)$$

$$x_A = \frac{A_0 - A}{A_0} = x_M$$

$$x_I = \frac{I_0 - I}{I_0} = 1 - (1 - x_M)e^{-\lambda x_M}$$

where $\lambda = (\gamma + 1)/(\epsilon + 1)$ and $\epsilon = fG_{f0}/I_0$ is the ratio of concentrations of active centers in the initiator to that of inimer.

It is easy to calculate the number-average molecular weight. By definition, $\bar{M}_n$ is equal to the total weight of units incorporated into polymer chains divided to the number of macromolecules; hence

$$\bar{M}_n = \frac{m_M M_0 x_M + m_I I_0 x_I + m_G[G_{f0} - G_0(f)]}{A - I + G_{f0} - G_0(f)} \quad (5)$$

In eq 5, we do not count monomer, inimer, and initiator as polymer chains. The concentration of residual initiator, $G_0(f)$, can be found from the obvious equation

$$\frac{1}{k}\frac{dG_0(f)}{dt} = -fG_0(f)(A + M)$$

from which we obtain

$$G_0(f) = G_{f0}e^{-\lambda f x_M} \quad (6)$$

As follows from eq 6, for sufficiently high comonomer ratio, $\gamma = M_0/I_0 \gg 1$, or for high initiator functionality, f, the concentration of residual initiator can already be neglected at small conversions of double bonds. It is important for the calculation of $\bar{M}_n$ only in the homopolymerization of inimer[12] ($\gamma = 0$).

As can be seen from eq 5, at full conversion of comonomers ($x_M = x_I = x_A = 1$) the number-average molecular weight does not diverge as in SCVCP in the absence of initiator but approaches the final value

$$\bar{M}_n(x_M = 1) = \frac{m_M M_0 + m_I I_0 + m_G G_{f0}}{G_{f0}} \quad (7)$$

If all molar masses of monomer, inimer, and initiator are equal, we can define the number-average degree of polymerization, $\bar{P}_n = \bar{M}_n/m_M$, and then

$$\bar{P}_n(x_M = 1) = \frac{M_0 + I_0 + G_{f0}}{G_{f0}}$$

For a high comonomer ratio, the expression for $\bar{P}_n$ becomes even simpler

$$\bar{P}_n(x_M = 1) \approx \frac{M_0}{G_{f0}}$$

As follows from eq 7, the final value of $\bar{P}_n$ does not depend on initiator functionality f and is defined by the relationship between concentrations of monomer, inimer and initiator. The only small dependence of intermediate values of $\bar{P}_n$ on f is due to the dependence of x_I on f. Figure 1 shows the dependence of $\bar{P}_n$ on conversion for
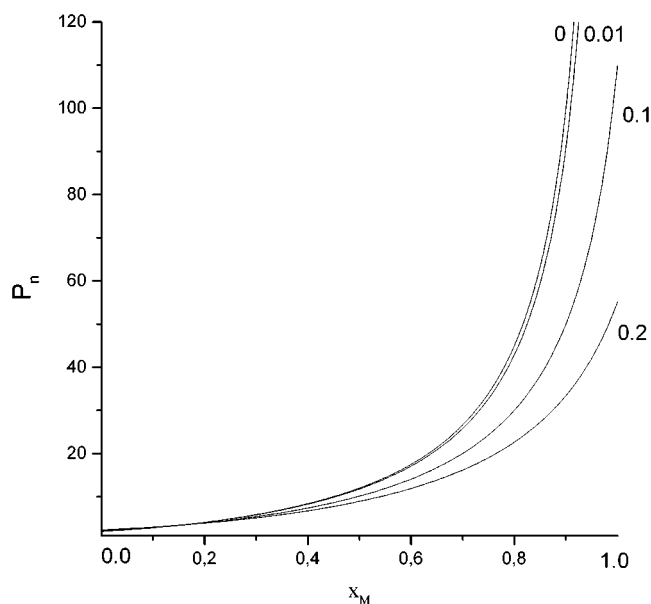
Figure 1. Dependence of the number-average degree of polymerization on monomer conversion for various ratios polyinitiator/inimer, G_{f0}/I_0. The comonomer ratio $M_0/I_0 = 10$, with no dependence on initiator functionality.

various initiator/inimer ratios G_{f0}/I_0. One can see that except for very high conversions, the effect of polyinitiator is significant only when $G_{f0}/I_0 \geq 0.01$.

To calculate the weight-average molecular weight, $\bar{M}_w$, we use the statistical moments of the MWD. The weight of macromolecule $P_i(n)$ with i monomer and n inimer units is $(m_M i + m_I n)$ and that of $G_i(n)$ is $[m_0 + m_M i + m_I(n - f)]$; hence, the lth MWD moment is

$$\mu_l = \sum_{i,n}(m_M i + m_I n)^l P_i(n) +$$
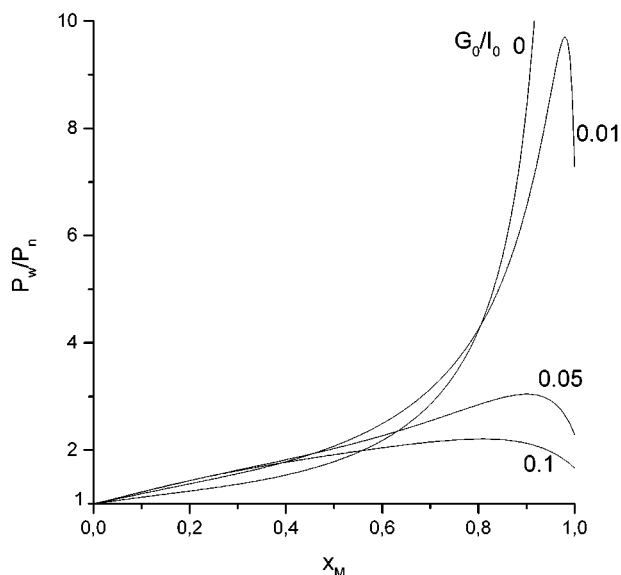$$\sum_{i,n}[m_M i + m_I(n - f) + m_G]^l G_i(n) \quad (8)$$

The weight-average molecular weight is $\bar{M}_w = \mu_2/\mu_1$. The equations for μ_l are derived from eqs 3 and 4. The derivation of expressions for $\bar{M}_w$ is given as Supporting Information.

As an example, the evolution of the polydispersity index with conversion is shown in Figure 2 for $\gamma = 10$ and $f = 4$.

Because the fraction of initiator active centers is small, at low monomer conversion chains P react predominantly with each other and the molecular weight averages are close to those obtained in the absence of initiator. The deviation of the MWD averages from those obtained without initiator becomes significant only at conversions when the number of remaining vinyl groups (i.e., the total number of macromolecules P) is comparable to the number chains formed via initiator, G_{f0}. This explains also the appearance of a maximum in the dependence of polydispersity index on conversion at high conversions (Figure 2).

At full conversion of monomer, the expression for $\bar{P}_w$ obtains the form

$$\bar{P}_w(x_M = 1) =$$
$$\frac{\gamma^2\frac{(f\epsilon + 1)}{\epsilon^2} + \gamma\left[\left(\frac{\epsilon + 1}{\epsilon}\right)^2 + 2\frac{\epsilon + f}{\epsilon}f^2\right] + \frac{(\epsilon + f)^2}{\epsilon f} + \left(\frac{\epsilon + 1}{\epsilon}\right)^2}{\gamma + 1 + \epsilon/f}$$

Figure 2. Dependence of the polydispersity index on monomer conversion for various ratios polyinitiator/inimer. The functionality of initiator is $f = 4$. The comonomer ratio $M_0/I_0 = 10$.
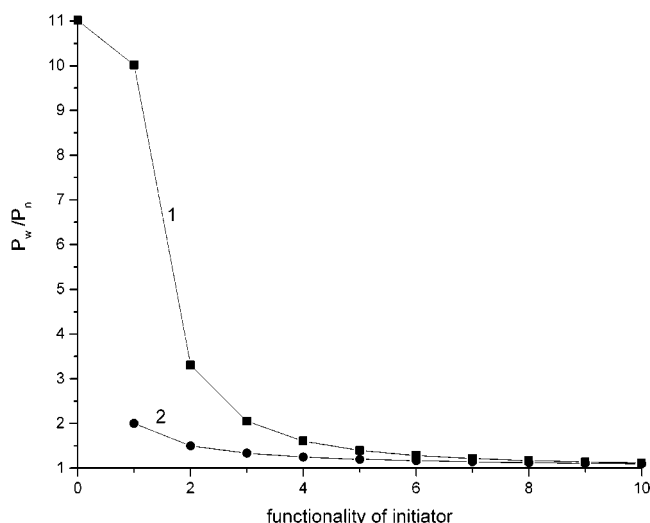
Figure 3. Dependence of the polydispersity index on the initiator functionality. $\gamma = 10$. Curve 1: batch polymerization for full conversion of double bonds and $\bar{P}_n = 100$ ($G_{f0}/I_0 = 1/9$) The point for $f = 0$ (no initiator) is calculated for 91% monomer conversion which gives $\bar{P}_n = 100$. Curve 2: semibatch polymerization.

For high monomer-inimer ratio, $\gamma \gg 1$, one obtains

$$\bar{P}_w = \gamma \frac{(f\epsilon + 1)}{\epsilon^2} = \frac{M_0(f^2 G_{f0} + I_0)}{f^2 G_{f0}{}^2} \tag{9}$$

As can be seen from eq 9, contrary to $\bar{P}_n$, the weight-average degree of polymerization does depend on initiator functionality and consequently, the polydispersity index,

$$\bar{P}_w/\bar{P}_n = \frac{1 + f\epsilon}{f\epsilon} = 1 + \frac{I_0}{f^2 G_0} = 1 + \frac{\bar{P}_n}{\gamma f^2}$$

decreases with increasing functionality as f^{-2}. This effect of functionality which was also observed in homo-SCVP,[12] is shown in Figure 3. The nonuniformity, $U = \bar{P}_w/\bar{P}_n - 1 = U_{SCVP}/\gamma$, is given by the value for SCVP,

divided by the comonomer ratio; thus, we observe the same behavior as in the absence of initiator.[19]

As can be seen from Figure 3 and as follows from eq 9, in the case of sufficiently high γ, the presence of monofunctional initiator ($f = 1$) does not drastically decrease the polydispersity index (this is not the case when γ is small or monomer is absolutely absent[12]). A bifunctional initiator, however, enables us to decrease the polydispersity index from 11 to 2.8. For example, for $\gamma = 10$, the use of an initiator with higher functionality gives one the possibility to decrease the polydispersity index by several times. Of course, at infinitely high γ, instead of highly branched copolymers one obtains star polymers with the number of branches equal to the initiator functionality and with narrow (Poisson) MWD.

Surface-Bound Initiators. It is also interesting to compare the molecular weight averages of the total polymer and those of the fraction formed from the polyinitiator (molecules of type G). A special kind of polyinitiator is a surface-grafted initiator. If initiator moieties are grafted onto a planar surface or on a large nanoparticle, the polymer bound to the surface after polymerization is easily separated from the nongrafted one. In this case it is interesting to know the MWD and DB of the grafted polymer molecules and we can regard each grafted initiator molecule as monofunctional. As an example, Mori et al.[22] investigated hyperbranched poly(methyl methacrylate) and poly(*tert*-butyl acrylate) grown from silicon surfaces and from silica nanoparticles. Under these conditions, the initial ratio of [initiator] to [monomer] + [inimer], $G_{f0}/(M_0 + I_0) = G_{f0}/(\gamma + 1)I_0$, is often very low. If small nanoparticles with only few initiator molecules are used, the whole particle can be regarded as a polyinitiator and we are interested in the MWD of the total particles. The procedure of calculation of average molecular weights of the polymer fraction grown on the multifunctional initiator is described in the Supporting Information. Of course, at very high conversions the MWD averages of the total polymer and of the fraction grown from the polyinitiator become closer and will coincide at $x_M = 1$. However, at intermediate conversions the difference may be significant (see Figure 4), especially for $f > 1$ whereas for $f = 1$ the difference is insignificant. As can be seen from Figure 4 for $f = 4$ and $G_{f0}/(\gamma + 1)I_0 \approx 10^{-3}$, $\bar{P}_n = 100$ for the total polymer is reached at $x_M \approx 0.91$ and the corresponding polydispersity index, $\bar{P}_w/\bar{P}_n \approx 6.7$. For the grafted polymer $\bar{P}_n = 100$ is reached at $x_M \approx 0.72$ and $\bar{P}_w/\bar{P}_n \approx 1.6$. Thus, it is advisable to stop the polymerization well before full conversion. In contrast, for $f = 1$ (under the same conditions), $\bar{P}_n = 100$ is reached for both total and grafted polymers at $x_M \approx 0.91$ and the difference in $\bar{P}_w/\bar{P}_n$ is negligible ($\bar{P}_w/\bar{P}_n = 10.1$ and 10.0, respectively).

Semibatch Polymerization (Slow Monomer Addition). Similar to ref 12, one can expect an even more drastic narrowing of the MWD if the mixture of monomer and inimer is slowly added to the system which initially contained only initiator. If the rate of comonomer mixture addition is low enough, the actual concentrations of monomer and inimer are negligible relative to that of the initiator. Then, the probability of initiation via inimer and, consequently, the formation of species P is negligible. Thus, we only have to take into account reactions between macromolecules $G_i(n)$ and monomeric species M and I.
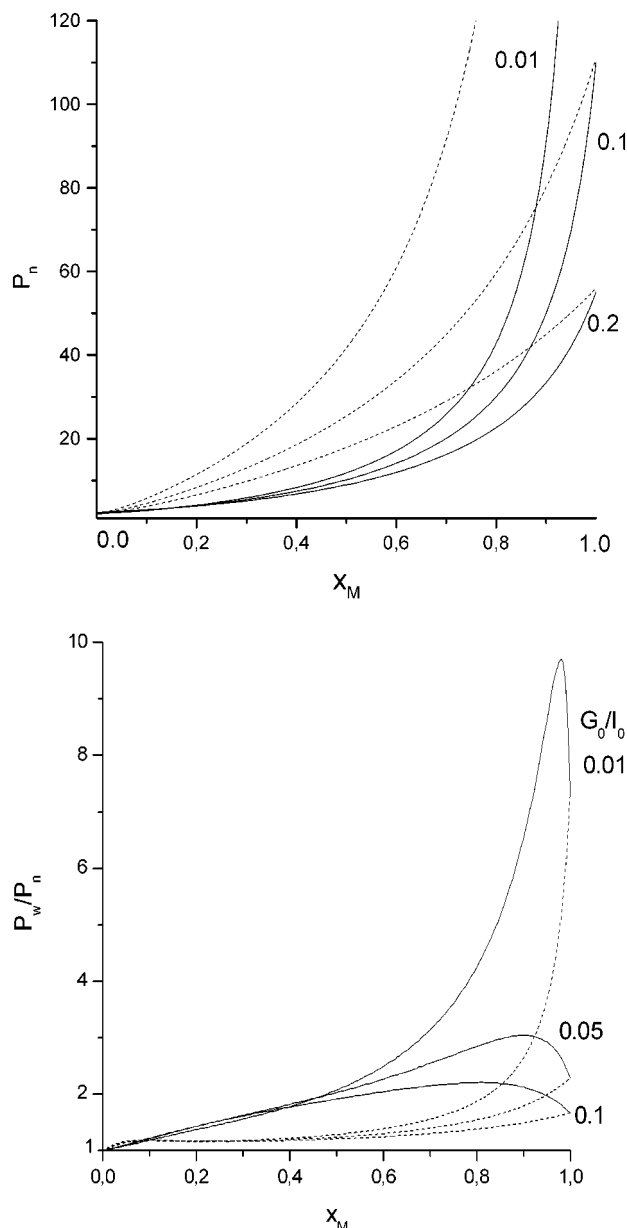
Figure 4. Comparison of molecular weight parameters of the total polymer (—) and the fraction grown on the polyinitiator (- - -) in batch copolymerization for $\gamma = 10$ and $f = 4$. Values of G_{f0}/I_0 are indicated in the figure.

Instead of sets 1−4, we now have to solve the equations

$$\frac{dM}{dt} = \frac{\gamma}{\gamma + 1}\psi - kM\sum_{i,n} nG_i(n) \qquad (10)$$

$$\frac{dI}{dt} = \frac{1}{\gamma + 1}\psi - kI\sum_{i,n} nG_i(n) \qquad (11)$$

$$\frac{1}{k}\frac{dG_i(n)}{dt} = I[(n-1)G_i(n-1) - nG_i(n)] +$$
$$M[nG_{i-1}(n) - nG_i(n)] \quad (12)$$

where ψ is the monomer flow rate, i.e., the concentration of monomer mixture introduced per time interval. Generally, ψ may be time-dependent. The parameter $\gamma = M/I$ in eqs 10 and 11 is the comonomer ratio *in the feed flow*. It follows from eqs 10 and 11 that this is also

true for the reacting mixture. However, this is not the case if rate constants are different.

The initial conditions for the set above are chosen in such a way that either there are no initial monomers in the system ($M_0 = I_0 = 0$) or $M_0, I_0 \ll G_f^0$.

The evolution of concentrations of monomer and inimer with time depends on the particular function ψ on time. In principle, we can add monomers at a constant rate or choose the dependence of ψ on time to be arbitrary. 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 $M, I \ll G_f^0$.

Similar to the procedure in ref 12, it is convenient to introduce the dimensionless time $\tau = \int_0^t kI \, dt$. Then, eq 12, rewritten in terms of τ, obtains the form

$$\frac{dG_i(n)}{d\tau} = -(\gamma + 1)nG_i(n) + \gamma nG_{i-1}(n) +$$
$$(n-1)G_i(n-1) \quad (13)$$

with the initial conditions $G_i(n)|_{\tau = 0} = G_{f0}\delta_{i,0}\delta_{n,f}$.

Equation 13 enables us to calculate average molecular weights as functions of the dimensionless time again using the MWD moments (eq 8). The derivation of corresponding expressions is given as Supporting Information. The following expressions for the average molecular weights were obtained

$$\bar{M}_n = m_G + f(m_M\gamma + m_I)(e^\tau - 1) \qquad (14)$$
$$\bar{M}_w = \frac{\mu_2}{G_{f0}\bar{M}_n}$$

where

$$\mu_2/fG_{f0} = m_M{}^2\gamma[\gamma(f+1)(e^\tau - 1)^2 - 2\gamma(\tau(e^\tau - 1) +$$
$$1) + e^\tau - 1] + 2m_M m_I\gamma e^\tau[(f+1)(e^\tau - 1) - \tau] +$$
$$m_I{}^2 e^\tau[(f+1)e^\tau - 1] - (m_G - fm_I)^2/f$$

For high dimensionless times, $\tau \gg 1$, when the degree of polymerization is high enough, we can neglect 1 in comparison to $\exp(\tau)$ and the contribution from the weight of polyinitiator, that is, m_G in the expressions for the molecular weight. In this case eq 14 yields a very simple form

$$\bar{M}_n = f(m_M\gamma + m_I)e^\tau$$
$$\bar{M}_w = (f+1)(m_M\gamma + m_I)e^\tau$$

and, consequently, the polydispersity index

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + \frac{1}{f}$$

does not depend on the comonomer ratio or on $\bar{M}_n$. Thus, it is identical to the case of homo-SCVP and we do not obtain a further narrowing of the MWD by copolymerization, as was observed in the case of copolymerization without added initiator.[19]

The dependence of the polydispersity index on initiator functionality, f, is shown in Figure 3. Comparing the polydispersity index for batch and semibatch polymerizations, we see that the latter process results in a narrower MWD especially for low functionality. Thus,

for $\bar{P}_n = 100$ and $f = 2$, $\bar{P}_w/\bar{P}_n = 2.8$ for batch polymerization and 1.5 for slow monomer addition.

Degree of Branching

Beside the width of the MWD, the core-forming initiator is expected to affect the degree of branching of the copolymer formed. For the definition of average degree of branching we use the expression derived earlier[11,12]

$$DB = \frac{2(\text{total number of branched units})}{\text{total number of units} - N_P - G_{f0}} \quad (15)$$

where $N_P = A - I$ is the total concentration of double bond-containing macromolecules. The term $N_P + G_{f0}$ in eq 15 appears in the denominator since we do not count the focal unit in our calculation and because one terminal unit has to be subtracted (even a linear chain has one "focal unit" and one terminal unit).

In the absence of common vinyl monomer ($\gamma = 0$) the polymer obtained is hyperbranched with DB ≈ 0.5 for batch polymerization and DB $= 2/3$ for semibatch.[12] For infinitely high monomer/inimer ratio, f-arm stars will be formed instead of highly branched copolymer and DB loses its meaning. It is interesting to analyze the behavior of the degree of branching for intermediate conditions.

Batch Polymerization. The analysis of the branched structure and the derivation of expressions for the concentrations of structural units are given as Supporting Information. The following expression was obtained for the fraction of branched units, B

$$B = I_0(1 - e^{-\lambda x_M})\left(x - \frac{1 - e^{-\lambda x_M}}{\lambda}\right)$$

Hence, the degree of branching is

$$DB = \frac{2B}{M_0 x_M + I_0 x_I - N_P - G_{f0}}$$

The most interesting value is the final value of DB when $x_M = x_I = 1$. For this case we obtain

$$DB_\infty = \frac{2(1 - e^{-\lambda})(\lambda - 1 + e^{-\lambda})}{\lambda(\gamma + 1 - \epsilon)} \quad (16)$$

As follows from eq 16, for high monomer/inimer ratio, $\gamma \gg 1$, DB approaches the asymptotic dependence

$$DB_\infty = \frac{2}{\gamma + 1}$$

which depends neither on initiator concentration nor its functionality; i.e., it is identical to the dependence found for the SCVCP in the absence of initiator. Figure 5 shows the dependence of the final DB on the comonomer ratio for various fractions of polyinitiator.

Semibatch Polymerization. It seems more interesting to calculate the DB of hyperbranched polymers obtained by slow monomer addition. Also the derivation of corresponding expressions is given as Supporting Information. The following dependence of B on dimensionless time was obtained

$$\frac{B}{fG_{f0}} = \frac{e^\tau - e^{-(\gamma+2)\tau}}{2\gamma + 3} - \frac{1 - e^{-2(\gamma+1)\tau}}{\gamma + 2} - \frac{\gamma(e^{-\tau} - e^{-(\gamma+1)\tau})}{\gamma + 2}$$
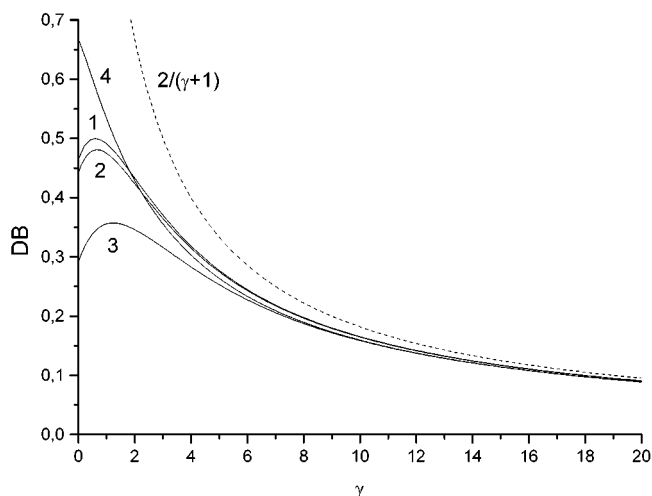
Figure 5. Dependence of degree of branching on the monomer/inimer ratio. $G_{f0}/I_0 = 0$ (curve 1), 0.01 (curve 2), and 0.1 (curve 3). Curve 4: semibatch polymerization.

For high molecular-weight polymer ($\tau \gg 1$) this expression becomes much simpler

$$\frac{B}{fG_{f0}} \approx e^\tau\left(\frac{1}{2\gamma + 3} + \frac{\gamma}{\gamma + 2}\right)$$

The total number of monomeric (monomer + inimer) units in the copolymer, $\sum G_i(n)(i + n - f) = fG_{f0}(e^\tau - 1)(\gamma + 1)$.

Finally, we obtain for DB for high τ:

$$DB = \frac{2}{\gamma + 1}\cdot\left(\frac{1}{2\gamma + 3} + \frac{\gamma}{\gamma + 2}\right) \quad (17)$$

Equation 16 gives DB $= 2/3$ for $\gamma = 0$ as was obtained earlier. DB decreases with increasing comonomer ratio, and for sufficiently high γ it approaches the asymptotic dependence[19]

$$DB \approx \frac{2}{\gamma + 1}$$

Thus, the use of a multifunctional initiator for $\gamma \gg 1$ has no advantage from the viewpoint of increasing DB. The dependence of DB on γ is shown in Figure 4.

Conclusions

The addition of a multifunctional initiator to the SCVCP strongly affects the polydispersity index. In the batch process it decreases with initiator functionality as $\bar{P}_w/\bar{P}_n \approx 1 + \bar{P}_n/f^2$, similar to the case without added initiator. The effect is even more pronounced for the semibatch process where $\bar{P}_w/\bar{P}_n \approx 1 + 1/f$. Again, this result is equal to the value obtained in homo-SCVP.

While the addition of core-forming molecules in homo-SCVP significantly enhances the degree of branching from DB $\approx 1/2$ to DB $\approx 2/3$ in the semibatch process, for high comonomer ratio the presence polyinitiator has a slight effect only on DB which decreases with increasing γ and for high γ is equal to the value obtained without initiator.

Supporting Information Available: Text giving the derivation of equations for the MWD moments and the degree of branching and a table giving expressions for the concentrations of the various structural units. This material is available free of charge via the Internet at http://pubs.acs.org.

List of Symbols and Abbreviations

A	concentration of vinyl groups of inimer and macromolecules
A^*	concentration of active centers arising from inimer addition
B	concentration of branched units (ab)
B^*	concentration of initiating centers
DB	degree of branching
f	functionality of initiator
G_f^0	initial concentrations of f-functional initiator
$G_i(n)$	concentration of macromolecules with i monomer units, n active centers, and no vinyl groups
I	concentration of inimer AB*
I_0	initial concentration of inimer = total concentration of active centers
i	number of monomer units in a macromolecule
k	propagation rate constant
L_C	concentration of linear "polycondensate type" units (A*b)
L_V	concentration of linear "vinyl type" units (aB*)
L_M	concentration of linear "monomer type" units (m)
M_M	molar mass of monomer
m_I	molar mass of inimer
m_G	molar mass of initiator
M	monomer concentration
M_0	initial monomer concentration
M^*	concentration of active centers arising from monomer
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$\bar{M}_w/\bar{M}_n$	polydispersity index
n	number of active centers in a macromolecule
$N^* = fG_{f0} + I_0$	total concentration of active centers
$P_i(n)$	concentration of macromolecules with n active centers of degree of polymerization i containing a vinyl group
$\bar{P}_n$	number-average degree of polymerization
$\bar{P}_w$	weight-average degree of polymerization
$\bar{P}_w/\bar{P}_n$	polydispersity index
t	reaction time
T_I	concentration of terminal units (A*B*) arising from inimer
T_M	concentration of terminal units (M*) arising from monomer
x_A	conversion of vinyl groups of inimer and polymer
x_I	conversion of inimer
x_M	conversion of monomer
z_A	fraction of active centers A*
z_B	fraction of active centers B*
z_M	fraction of active centers M*
$\delta_{l,m}$	Kronecker symbol: $\delta_{l,m} = 1$ for $l = m$, $\delta_{l,m} = 0$ otherwise
$\gamma = M_0/I_0$	ratio of initial concentrations of monomer and inimer
$\epsilon = fG_{f0}/I_0$	ratio of fraction of active centers in initiator and inimer
$\lambda = (\gamma + 1)/(\epsilon + 1)$	auxiliary parameter
μ_n	nth moment of the MWD
$\psi = \mathrm{d}(M + I)/\mathrm{d}t$	total flow rate of comonomers
$\tau = \int_0^t kM\,\mathrm{d}t$	dimensionless time

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