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Molecular Parameters of Hyperbranched Copolymers Obtained by Self-Condensing Vinyl Copolymerization. 1. Equal Rate Constants

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ABSTRACT: The kinetics, molecular weight averages and the average degree of branching, DB, are calculated analytically for the self-condensing vinyl copolymerization (SCVCP) of a vinyl monomer M with an “inimer” AB*, i.e., a molecule having a vinyl group A and an initiating group B*. MWD and DB strongly depend on the monomer/inimer ratio $\gamma = M_0/I_0$ (or the “dilution factor”, $\gamma + 1 = (M_0 + I_0)/I_0$). At low conversions, the process resembles a living polymerization of M, where the AB* inimers act as initiators only; at high conversions, the process resembles a self-condensing vinyl homopolymerization (SCVP) of AB* inimers. For a high monomer/inimer ratio ($\gamma \gg 1$), the number-average molecular weight, $\bar{M}_n$, is given by the product of the values for the SCVP of inimer and the living polymerization of monomer initiated by inimer. For a given $\bar{M}_n$ value, the polydispersity index decreases with γ. For $\gamma > 1$, DB decreases with γ, however, the DB values are 4 times higher than expected from the “dilution” of AB* molecules by M molecules. For low values of γ, DB even exceeds the values for a homo-SCVP; a maximum of DB = 0.5 is reached at $\gamma \approx 0.6$. These effects can be explained by the addition of monomer molecules to in-chain active centers (i.e., in linear segments) leading to very short branches. The trends predicted by our calculations are confirmed by preliminary experimental data.

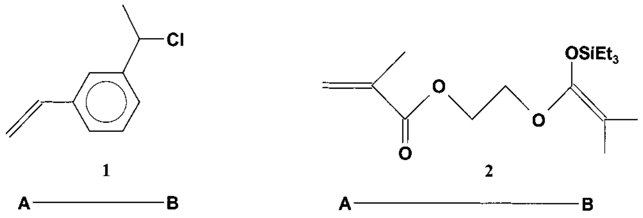
Introduction

In the past decade, highly branched topologies have become a major research interest in polymer science.[1−3] Among them, dendrimers attained much interest because of their highly ordered structure.[1,4−6] A major drawback of this class of macromolecules is their time-consuming, stepwise synthesis. As already pointed out by Flory,[7,8] an easier way to obtain highly branched structures is a one-pot polycondensation of an AB_2 monomer. The first applications of this principle were published by Baker and Walbridge[9] and by Kim and Webster.[10−12]

The recent discovery of “self-condensing vinyl polymerization” (SCVP)[13,14] made it possible to use vinyl monomers for synthesis of hyperbranched structures. In this approach, a vinyl monomer of the general structure AB is used where A is a vinyl group and B is a functional group which can be converted to an initiating group B* by an external stimulus. Thus, this species combines features of an initiator and a monomer and has therefore been named an “inimer”.[15] Chart 1 shows two examples of such inimer molecules: in **1**, activation can occur by removing the chlorine to either form a cation[14] or a radical,[16] whereas in **2**, the silylketene acetal group can be activated by nucleophilic catalysts to initiate group transfer polymerization.[17−20]

The process is initiated by the addition of the active B* group of one AB* molecule to the vinyl group A of another one forming a dimer with two active sites, A* and B* and one double bond (cf., Scheme 1). Both the initiating B* group and the newly created propagating center A* can react with the vinyl group of another monomer or dimer, etc., finally leading to hyperbranched structures. For each molecule, the number of active centers is equal to its degree of polymerization.

Chart 1. Examples for AB Inimers



Recently we calculated that the molecular weight distribution (MWD) of polymers formed by SCVP is very broad, the polydispersity index equaling the number-average degree of polymerization.[15] This can be understood by the fact that larger molecules will grow faster than small ones, because the former possess a larger number of active centers and therefore a greater probability that another molecule can be attached to them.

Besides the MWD, the degree of branching, DB, is the second key parameter for describing hyperbranched polymers.[21] DB can be regarded as the ratio of branched units in the polymer to those in a perfect dendrimer. Thus, the limiting values are DB = 0 for linear polymers and DB = 1 for a perfect dendrimer. Furthermore it has been shown recently that the statistical process of forming hyperbranched polymers leads to DB ≤ 0.5.[22−24] This means that hyperbranched polymers prepared by bulk polycondensation or polymerization contain at least 50% linear units, making this approach less efficient than the tedious synthesis of dendrimers.

Various methods have been proposed in order to narrow the MWD and to enhance the DB beyond its limiting value. They include the use of polyfunctional initiators,[25] slow monomer addition techniques,[25,26] and postsynthetic modifications.[27]

The copolycondensation of AB_2 or the copolymerization of AB* monomers with conventional monomers (AB or M) has many advantages compared with a normal

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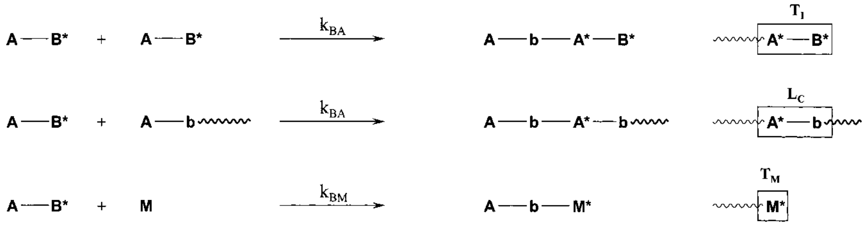
Scheme 1. Initial Steps in SCVCP



homopolymerization: (i) Conventional monomers are in most cases cheaper and easier to obtain than the corresponding AB_2 or AB* monomers, lowering the expenses of obtaining a branched polymer. (ii) Depending on the chemical nature of the comonomer, different types of functional groups can be incorporated in the polymer. (iii) The polydispersity index can be controlled by the comonomer ratio AB/AB_2 or M/AB*, and it is expected to be lower compared with hyperbranched polymers prepared by a conventional route. (iv) Copolymerization offers the possibility to control the DB. Clearly, the DB of the copolymers is expected to be lower than the DB of the corresponding homopolymers. However, the effect of the reduced DB on macroscopic quantities such as intrinsic viscosity and radius of gyration should be small, because branched polymers (above a limiting molecular weight) are self-similar objects.[28] Therefore, a copolycondensation or copolymerization is an economical approach for obtaining highly branched polymers, especially when aiming at rheology control.

Surprisingly, this approach has hardly been discussed in the literature, although the AB_2/AB copolycondensation was analyzed theoretically by Flory.[7] There are only few experimental reports on this subject. Kricheldorf et al.[29] reacted 3-trimethylbenzoyl chloride or 3-acetoxybenzoic acid with the AB_2 comonomers 3,5-bis(trimethylsiloxy)benzoyl chloride or 3,5-diacetoxybenzoic acid and yielded soluble, branched polymers.

In attempts to synthesize ω-styrylpolyisobutylene using *m*/*p*-(chloromethyl)styrene as an initiator and Al alkyls/H_2O as coinitiators, Kennedy and Frisch[30] and Nuyken et al.[31] observed the formation of soluble polymers with much higher than calculated molecular weights and broad MWD and attributed this to the formation of branched copolymers. Recently, the controlled radical copolymerization of *p*-chlorostyrene with styrene[16] and the cationic copolymerizations of 4-(1-chloroethyl)styrene with 4-methylstyrene,[32] and that of substituted styrenes with isobutylene[33,34] have been reported. However, no absolute characterization data were given.

In this paper, we will analytically calculate the kinetics of the self-condensing vinyl copolymerization (SCVCP) of an AB* inimer with a conventional vinyl polymer, M, the molecular weight distribution, and the degree of branching of the polymers obtained. We will compare these calculations to new experimental data obtained in self-condensing group transfer copolymerizations of methacrylic monomers.

General Considerations

To find a short representation for the different groups which arise in this copolymerization, we use capital letters for vinyl groups (A and M) and for active centers (A*, B*, and M*) and lowercase letters for reacted ones (a, b, and m). Compared to a normal homopolymerization of an inimer molecule, the presence of comonomer M enlarges the number of possible active centers. To rationalize the different types of reactions, we first look at the reactions of an inimer molecule AB*. This molecule can add any double bond, i.e., the double bond of another inimer AB*, that of a macromolecule A, or the double bond of comonomer M (Scheme 1). In any case, this reaction will lead to the formation of a new active species, A* or M*, respectively.

Thus, we have three different types of active centers, A*, B*, and M* which can react with double bonds A (inimer and macromolecules; each macromolecule contains strictly one double bond) and M (monomer).

Depending on the location of the active centers in the macromolecule formed, different kinds of structural units can be created by further additions. In Scheme 1, three different types of structural units can be found: the inimer terminal unit, $T_I = A^*B^*$, one type of linear unit $L_C = A^*b$, and the comonomer terminal unit $T_M = M^*$. The L_C unit is one of two possible linear units that can be formed; this structure resembles the repeat unit of a polycondensate. The other linear unit $L_V = aB^*$ arises from the reaction of an A* center with a double bond A (cf., Scheme 2) and resembles the repeat unit of a typical vinyl polymer. Linear $L_M = m$ and branched $B = ab$ units do not react with vinyl groups as they do not contain active centers.

Let us now consider all possible reactions between the different structural patterns and active centers with double bond (Scheme 2).

Generally, there are six different rate constants to be taken into account, namely,

$$A^* + A \xrightarrow{k_{AA}} A^*$$

$$B^* + A \xrightarrow{k_{BA}} A^*$$

$$M^* + A \xrightarrow{k_{MA}} A^*$$

$$A^* + M \xrightarrow{k_{AM}} M^*$$

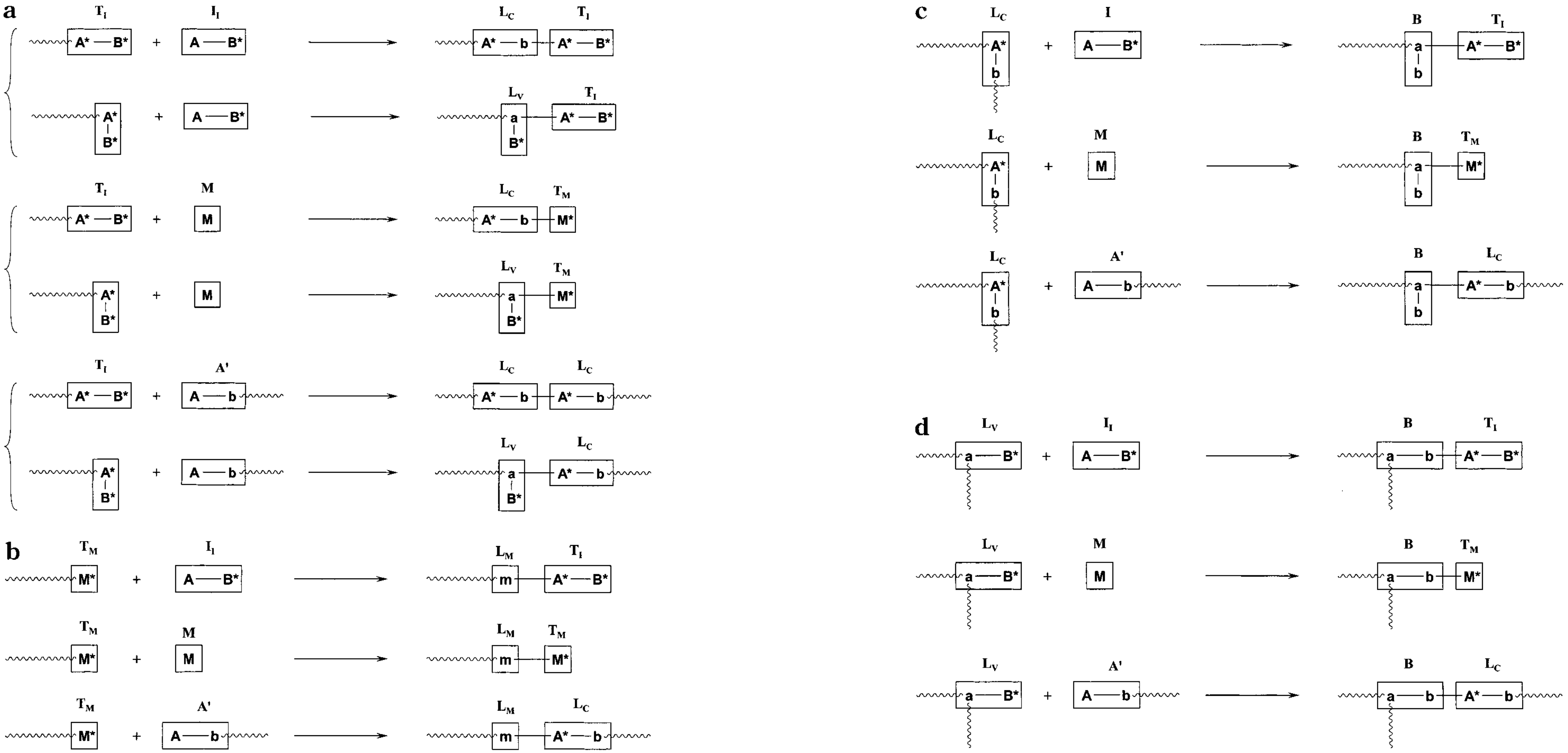
$$B^* + M \xrightarrow{k_{BM}} M^*$$

$$M^* + M \xrightarrow{k_{MM}} M^*$$

Kinetic Differential Equations

According to Scheme 2, the evolution of concentrations of active centers, comonomers, and double bonds is

Scheme 2. Reactions of Structural Units in SCVCP[a]



[a] (a) Terminal units (inimer types), (b) terminal units (monomer types), (c) linear types (polycondensate types), and (d) linear types (vinyl types).

described by the following set of differential equations:

Active Centers

$$\frac{dM^*}{dt} = k_{AM}A^*\,M + k_{BM}B^*\,M - k_{MA}M^*\,A$$

$$\frac{dA^*}{dt} = k_{BA}B^*\,A + k_{MA}M^*\,A - k_{AM}A^*\,M \qquad (1)$$

$$\frac{dB^*}{dt} = -B^*\,(k_{BA}A + k_{BM}M)$$

Comonomers

$$\frac{dM}{dt} = -M(k_{AM}A^* + k_{BM}B^* + k_{MM}M^*)$$

$$\frac{dI}{dt} = -I(k_{AA}A^* + k_{BA}B^* + k_{MA}M^* + k_{BA}A + k_{BM}M) \qquad (2)$$

Double Bonds of Inimer and Polymer

$$\frac{dA}{dt} = -A(k_{AA}A^* + k_{BA}B^* + k_{MA}M^*) \qquad (3)$$

The first three terms in the equation for inimer concentration eq 2 describe the reaction of the propagating and initiating centers (A* and B*) with the double bond of the inimer, whereas the remaining two terms are due to the reaction of an inimer's active center B* with any other double bond in the system.

The initial concentration of the active centers are

$$A^* = 0$$

$$B^* = I_0$$

$$M^* = 0$$

where I_0 is the initial concentration of inimer molecules. The total concentration of active centers is constant,

$$A^* + B^* + M^* = I_0 \qquad (4)$$

In this publication, we shall analyze the simplest case when all rate constants are equal,

$$k_{AA} = k_{BA} = k_{MA} = k_{AM} = k_{BM} = k_{MM} = k$$

As in previous derivations,[15,22] we assume rate constants to be independent of the degree of polymerization (no excluded volume effects) and an absence of cyclization reactions. The case of unequal rate constants will be described in a subsequent paper.

Kinetics and Fractions of Active Centers

From eqs 1−3, we obtain the following expressions for the conversion of monomer, x_M, with respect to time,

$$x_M = \frac{M_0 - M}{M_0} = 1 - \exp(-kI_0t) \qquad (5)$$

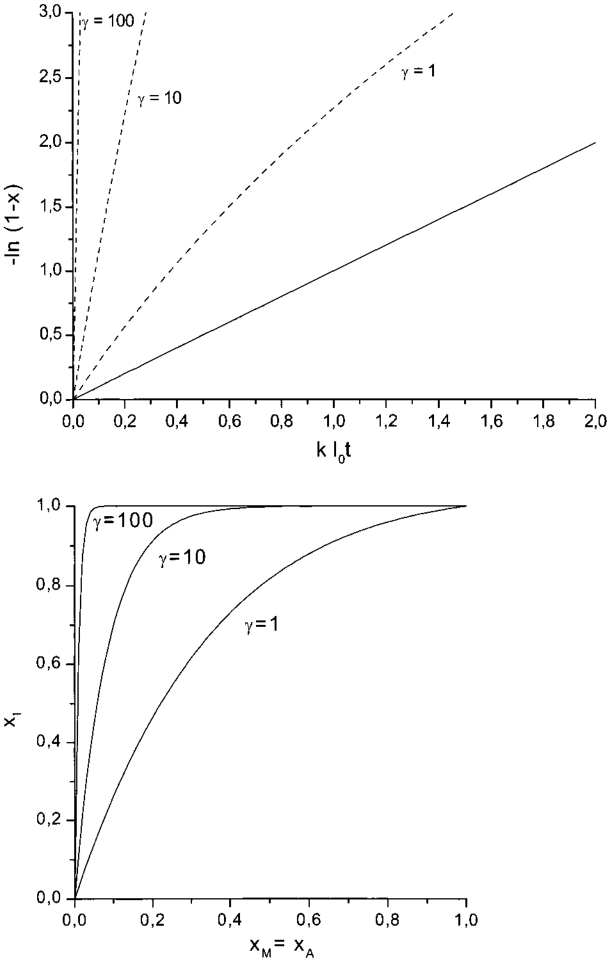


Figure 1. (a) First-order time-conversion plot for various monomer/inimer ratios, $\gamma = M_0/I_0$: solid line is for x_M and x_A and dashed lines are for x_I. (b) Conversion of inimer vs conversion of monomer and double bonds for various values of γ.

The conversion of inimer, $x_I = (I_0 - I)/I_0$, and the conversion of double bonds, $x_A = (I_0 - A)/I_0$, can be described easily in terms of monomer conversion,

$$x_I = 1 - (1 - x_M)e^{-(\gamma+1)x_M}$$

$$x_A = \frac{I_0 - A}{I_0} = x_M \qquad (6)$$

The dimensionless parameter $\gamma = M_0/I_0$ in eq 6 corresponds to the theoretical degree of homopolymerization of monomer M initiated by inimer molecules. The parameter $\gamma + 1 = (M_0 + I_0)/I_0$ can be considered a "dilution factor". The derivation of eqs 5 and 6 is given in the Supporting Information.

Let us analyze eqs 5 and 6. One can see from these equations that the dependence of monomer and double bond conversion on time is described by a first-order law as in a normal living polymerization. The dependence of inimer conversion on time cannot be expressed in such a manner. Figure 1 shows that inimer is used up much faster than monomer. At very high γ, it is consumed almost instantaneously, much like a fast initiation process in normal living polymerization. On the other hand, for low γ, the behavior resembles a slow initiation process.

The fractions of active centers, z, change with monomer conversion as

$$z_A = A^*/I_0 = \frac{1 - e^{-(\gamma+1)x_M}}{\gamma + 1}$$

$$z_B = B^*/I_0 = e^{-(\gamma+1)x_M}$$

$$z_M = M^*/I_0 = \frac{\gamma}{\gamma + 1}(1 - e^{-(\gamma+1)x_M}) \qquad (7)$$

The derivation of eq 7 is also given in the Supporting Information.

As for the fraction of active centers of different types, it follows from eq 7 that initial active centers B* disappear during copolymerization, converting into A* and M* centers. As can be seen from Figure 2, for high values of γ, already at small conversions of monomer there is no B^* left, and z_A and z_M reach their constant values very early

$$z_A = 1/(\gamma + 1) \quad z_M = \gamma/(\gamma + 1)$$

This differs from the homopolymerization of AB* where a large fraction of inimer is present in the system even at high conversion of double bonds.[15]

The concentration of macromolecules

$$N \equiv A - I = I_0(x_I - x_M)$$

first increases sharply and then decreases (Figure 3). This is explained by the fast conversion of inimer molecules into macromolecules at $x_M \ll 1$, as in a normal living polymerization, followed by linking reactions between "in-chain" active centers and double bonds of other macromolecules.

Molecular weight averages

In general, molar masses of monomer, m_M, and inimer, m_I, are different, and hence, it is of more sense to calculate average molecular weights $\bar{M}_n$ and $\bar{M}_w$ rather than average degrees of polymerization $\bar{P}_n$ and $\bar{P}_w$. Only if molar masses are equal or if $\gamma \gg 1$, where we can neglect the effect of inimer on the molecular weight, can both terms be used.

The number-average molecular weight can be calculated in a straightforward manner. According to definition, $\bar{M}_n$ is equal to the ratio of the total weight of polymer molecules, $m_M M_0 x_M + m_I I_0 x_I$, to the number of macromolecules, N,

$$\bar{M}_n = \frac{m_M \gamma x_M + m_I x_I}{(x_I - x_M)} = \frac{m_M \gamma x_M + m_I(1 - (1 - x_M)e^{-(\gamma+1)x_M})}{(1 - x_M)(1 - e^{-(\gamma+1)x_M})} \qquad (8)$$

The dependence of the number-average molecular weight on monomer conversion is shown in Figure 4 for equal molar masses. At very small conversions, $x_M \ll (\gamma + 1)^{-1}$, $\bar{M}_n$ increases linearly with conversion as it should in a normal living polymerization. However, at higher conversions the increase in $\bar{M}_n$ becomes sharper due to the linking reactions, and at $x_M \to 1$, $\bar{M}_n$ increases proportionally to $(1 - x_M)^{-1}$ similar to polycondensation or in SCVP, respectively.[15]

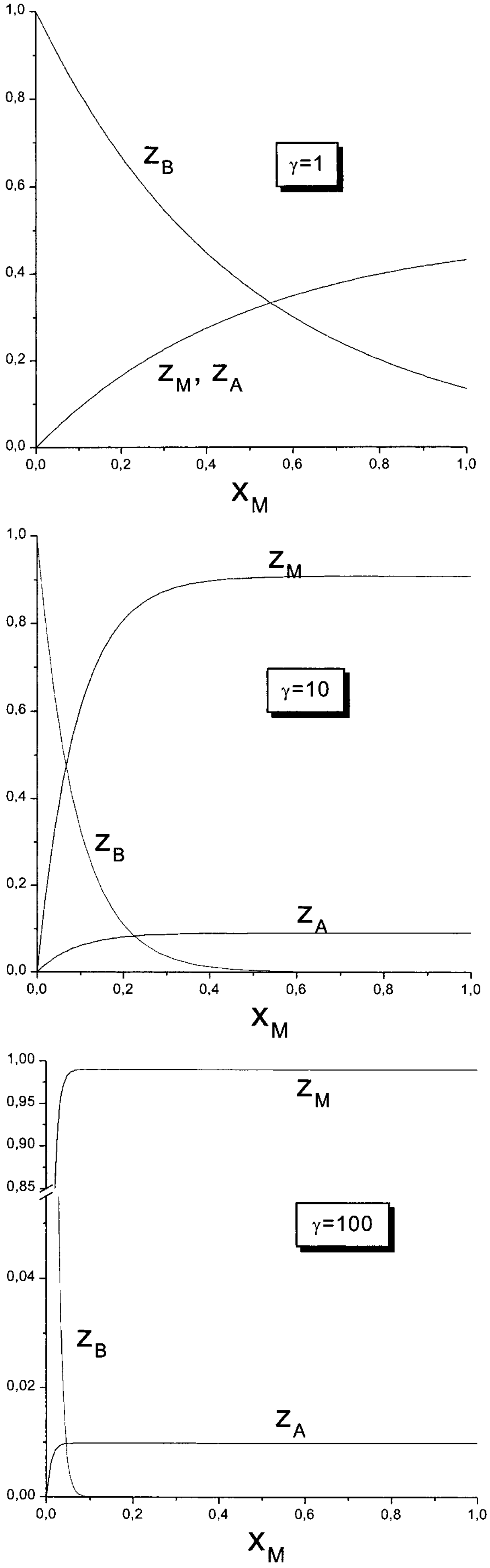


Figure 2. Evolution of fractions of active centers with monomer conversion.

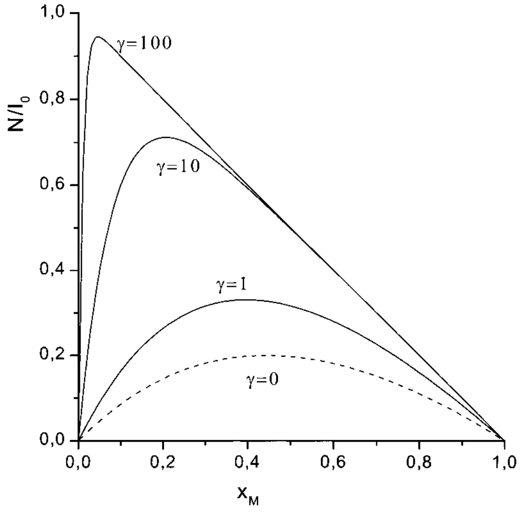


Figure 3. Dependence of the concentration of macromolecules on monomer conversion.

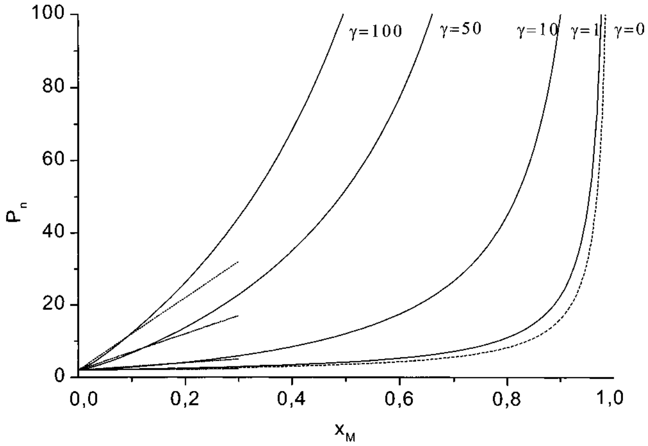


Figure 4. Dependence of the number-average degree of polymerization on conversion for various monomer/inimer ratios, γ. The straight lines correspond to a living polymerization of monomer initiated by inimer.

For a high monomer/inimer ratio ($\gamma \gg 1$), the contribution from inimer to molecular masses can be neglected, and we obtain a very simple expression

$$\bar{M}_\mathrm{n} = \frac{m_\mathrm{M}\gamma x_\mathrm{M}}{(1 - x_\mathrm{M})} \tag{9a}$$

or, correspondingly,

$$\bar{P}_\mathrm{n} = \frac{\bar{M}_\mathrm{n}}{m_\mathrm{M}} = \frac{\gamma x_\mathrm{M}}{(1 - x_\mathrm{M})} \tag{9b}$$

Thus, for high γ, $\bar{P}_\mathrm{n}$ is the product of $\bar{P}_\mathrm{n}$ generated by the living polymerization of monomer initiated by inimer,

$$\bar{P}_\mathrm{n,M} = \gamma x_\mathrm{M} = M_0 x_\mathrm{M}/I_0$$

and that of the SCVP of inimer,

$$\bar{P}_\mathrm{n,I} = (1 - x_\mathrm{M})^{-1}$$
$$\bar{P}_\mathrm{n} = \bar{P}_\mathrm{n,M}\bar{P}_\mathrm{n,I}$$

The calculation of the weight-average molecular weight is much more complex. To do so, let us introduce the variable $P_i(n)$, the concentration of polymer chains containing i units of monomer M and n active centers. It is clear that n is also equal to the number of inimer units incorporated into a polymer chain. Then, the degree of polymerization of a given molecule is $(i + n) > 1$. The changes in $P_i(n)$ occur because of the following reactions with monomers, inimers, and other polymer chains

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

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

$$P_i(n) + P_{i'}(n') \xrightarrow{k(n+n')} P_{i+i'}(n + n')$$

The kinetic differential equation for the evolution of $P_i(n)$ with respect to time is

$$\begin{aligned}\frac{1}{k}\frac{\mathrm{d}P_i(n)}{\mathrm{d}t} = {} & nM[P_{i-1}(n) - P_i(n)] + \\ & I[nP_i(n - 1) - (n + 1)P_i(n)] - \\ & P_i(n)\sum_{i',n'}(n + n')\,P_{i'}(n') + \\ & {}^1/_2 \sum_{\substack{i>i'>1\\ n>n'\geq 1}} nP_{i'}(n')P_{i-i'}(n - n') + \\ & IM\delta_{i,1}\delta_{n,1} + I^2\delta_{i,0}\delta_{n,2}\end{aligned} \tag{10}$$

for $(n + i) > 1$. The first term in the right-hand side of eq 10 describes the changes in $P_i(n)$ due to reactions with monomer, the second term with inimer, the next two are responsible for the reactions between macromolecules. The last two terms describe the formation of the two different macromolecules with DP = 2: $P_1(1)$ results from the addition of monomer M to the initiating center B* of the inimer, whereas $P_0(2)$ is formed by dimerization of two inimer molecules (cf., Scheme 1). The symbol $\delta_{i,j}$ is the Kronecker-symbol: $\delta_{i,j} = 1$ for $i = j$, and $\delta_{i,j} = 0$ for all else.

The derivation of the weight-average molecular weight, $\bar{M}_\mathrm{w}$, from eq 8 is given in Supporting Information. The following expression for $\bar{M}_\mathrm{w}$ is obtained:

$$\bar{M}_\mathrm{w} = \{m_\mathrm{M}^2\gamma x_\mathrm{M}(1 - x_\mathrm{M})^2 + \gamma x_\mathrm{M} + 2m_\mathrm{M}m_\mathrm{I}\gamma x_\mathrm{M} + m_\mathrm{I}^2[1 - (1 - x_\mathrm{M})^3 \mathrm{e}^{-(\gamma+1)x_\mathrm{M}}]\}/[(1 - x_\mathrm{M})^2(m_\mathrm{M}\gamma x_\mathrm{M} + m_\mathrm{I}x_\mathrm{I})] \tag{11}$$

For high conversions, the form of the $\bar{M}_\mathrm{w}$ dependence on x_M is governed by the denominator,

$$\bar{M}_\mathrm{w} \propto 1/(1 - x_\mathrm{M})^2$$

similar to SCVP.

For high monomer/inimer ratios ($\gamma \gg 1$), the contribution of inimer to $\bar{M}_\mathrm{w}$ can be neglected, and eq 11 simplifies to

$$\bar{M}_\mathrm{w} = m_\mathrm{M}\left[1 + \frac{\gamma x_\mathrm{M}}{(1 - x_\mathrm{M})^2}\right] \tag{11a}$$

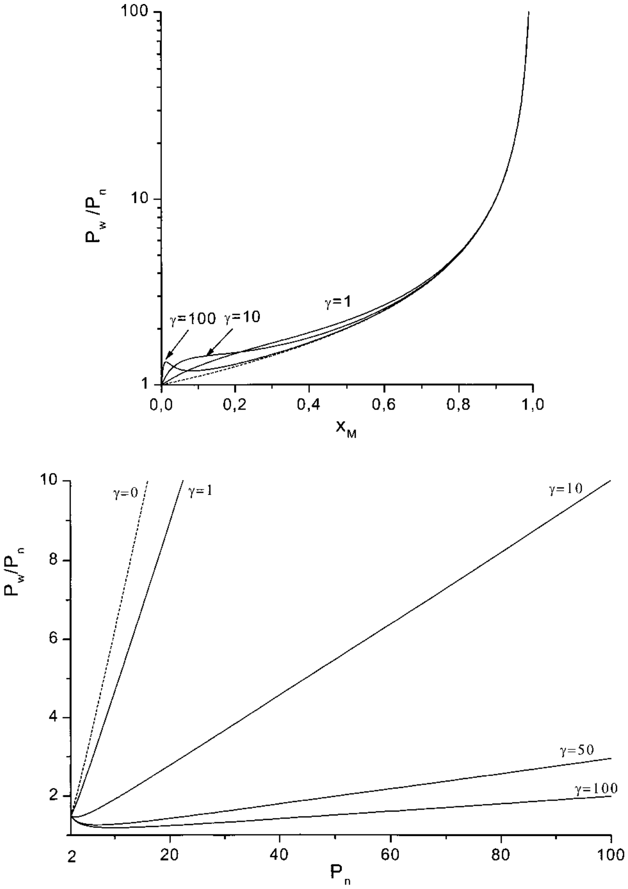


Figure 5. (a) Dependence of polydispersity on conversion and (b) the number-average degree of polymerization for various monomer/inimer ratios, γ. The dotted line is for pure inimer ($\gamma = 0$).

or

$$\bar{P}_w = \frac{\bar{M}_w}{m_M} = 1 + \frac{\gamma x_M}{(1 - x_M)^2} \tag{11b}$$

which is valid for all conversions. Hence, the polydispersity index in the limiting case of high conversion (and high γ) is

$$\bar{M}_w/\bar{M}_n = \frac{m_M}{\bar{M}_n} + \frac{1}{1 - x_M} \tag{12}$$

or

$$\bar{P}_w/\bar{P}_n = \frac{1}{\bar{P}_n} + \frac{1}{1 - x_M} \approx \frac{1}{1 - x_M} = \frac{\bar{P}_n}{\gamma x_M} \tag{12a}$$

In Figure 5a, the polydispersity index is plotted with respect to the conversion of monomer x_M. For high conversion ($x_M \approx 1$); i.e., for sufficiently high $\bar{P}_n$, the first term in eq 12 can be neglected. Then, the polydispersity index is the same as in homopolymerization by a SCVP mechanism and therefore independent of γ. However, $\bar{P}_n$ increases with γ (see eq 9b). Thus, for a given number-average degree of polymerization the polydispersity index decreases with γ (Figure 5b). Although for $\gamma = 0$ the polydispersity index $\bar{P}_w/\bar{P}_n = \bar{P}_n$, the value for high γ (and high conversions) can be expressed by

$$\bar{P}_w/\bar{P}_n = \bar{P}_n/\gamma$$

A small decrease in $\bar{P}_w/\bar{P}_n$ at low $\bar{P}_n$ is explained by the contribution from the first term in eq 12.

In conclusion, the evolution of the molecular weight averages shows that for high γ the SCVCP can be *formally* regarded as processing in two steps:

In the first step, monomer molecules add to inimer molecules, forming oligomeric species ("macroinimers") of the type $P_i(1)$. Because the concentration of monomer is much higher than the concentration of inimer, formation of $P_i(n)$ with $n \geq 2$ is not likely. Therefore, this process resembles the initiation process of a normal living polymerization, resulting in a Poisson distribution

$$\bar{P}_w/\bar{P}_n \approx 1 + 1/\gamma$$

In the second step, the growth of polymers is mainly driven by the linking reactions of the polymeric active centers with double bonds of other macromolecules P_i-(1). This process can formally be described as a normal SCVP of macroinimers leading to a broad molecular weight distribution $\bar{P}_w/\bar{P}_n = (1 - x_M)^{-1}$. Clearly, this is only a formal view of the process. In reality, both reactions occur quite simultaneously.

Degree of Branching

An important molecular parameter of branched macromolecules is the degree of branching, DB. According to earlier papers,[22,23] the DB for a given macromolecule is defined as

$$\mathrm{DB} = \frac{(\text{no. of branched units}) + (\text{no. of terminal units}) - 1}{(\text{no. of all units}) - 1}$$

$$= \frac{2\times(\text{no. of branched units})}{(\text{no. of all units}) - 1} \tag{13}$$

The focal unit (here, the vinyl group A) is not taken into consideration. According to the topology of branched systems with trifunctional branchpoints, the number of branched units is equal to the number of terminal units minus one.

Equation 13 is only valid for a single molecule. Because we are interested in the average degree of branching, $\overline{\mathrm{DB}}$, of an ensemble of N molecules, N terminal groups have to be subtracted. The concentration of *all* units in macromolecules equals $M_0x_M + I_0x_I$. Because we want to exclude the focal group (i.e., the vinyl group), we have to subtract another N units from this quantity. Thus, we finally obtain for $\overline{\mathrm{DB}}$

$$\overline{\mathrm{DB}} = \frac{2B}{M_0x_M + I_0x_I - 2N} \tag{14}$$

To calculate $\overline{\mathrm{DB}}$, we need only the concentration of branched units, B, but let us consider in more detail the formation of all structural units of different types during copolymerization. First, as a result of reactions of inimer with another inimer molecule I or with monomer M, terminal units of inimer, T_I, and monomer, T_M, types are formed, respectively (Scheme 1). In their turn, reactions of terminal groups with inimer, monomer, and double bonds of macromolecules result in the structures represented in Scheme 3.

Expressions for the various structural units are given in Table 1, and their derivation is given in Supporting

Table 1. Expressions for the Fractions of the Various Structural Units for Different Monomer/Inimer Ratios, γ

			fractions at $x_M = 1$ for particular values of γ			
unit	type	fractions = concentrations/$(I_0 + M_0)$	$\gamma = 0$	$\gamma = 0.6$	$\gamma = 10$	$\gamma \gg 1$
T_I	terminal, of inimer	$\frac{e^{-(\gamma+1)x_M}}{(\gamma+1)^2}(1 - e^{-(\gamma+1)x_M}) = \frac{z_A z_B}{\gamma+1}$	0.233	0.0625	1.38×10^{-7}	0
T_M	terminal, of monomer	$\frac{\gamma}{(\gamma+1)^2}(1 - e^{-(\gamma+1)x_M}) = \frac{z_M}{\gamma+1}$	0	0.1875	8.26×10^{-2}	$\frac{\gamma}{(\gamma+1)^2} \approx \frac{1}{\gamma}$
L_C	linear, “condensate type”, of inimer	$\left(\frac{1 - e^{-(\gamma+1)x_M}}{\gamma+1}\right)^2 = z^2_A$	0.400	0.25	8.26×10^{-3}	$\left(\frac{1}{\gamma+1}\right)^2 \approx \frac{1}{\gamma^2}$
L_V	linear, “vinyl type”, of inimer	$\frac{e^{-(\gamma+1)x_M}}{\gamma+1}\left(x_M - \frac{1 - e^{-(\gamma+1)x_M}}{\gamma+1}\right) = \frac{z_B(x_M - z_A)}{\gamma+1}$	0.135	0.0625	1.38×10^{-6}	0
L_M	linear, of monomer	$\frac{\gamma x_M - z_M}{\gamma+1}$	0	0.1875	0.826	$\left(\frac{\gamma}{\gamma+1}\right)^2 \approx 1 - \frac{2}{\gamma}$
B	branched	$\frac{(1 - e^{-(\gamma+1)x_M})}{\gamma+1}\left(x_M - \frac{1 - e^{-(\gamma+1)x_M}}{\gamma+1}\right) = z_A(x_M - z_A)$	0.233	0.25	8.26×10^{-2}	$\frac{\gamma}{(\gamma+1)^2} \approx \frac{1}{\gamma}$
$\overline{DB}_\infty$	degree of branching		0.466	0.5	0.165	$\frac{2\gamma}{(\gamma+1)^2} \approx \frac{2}{\gamma}$

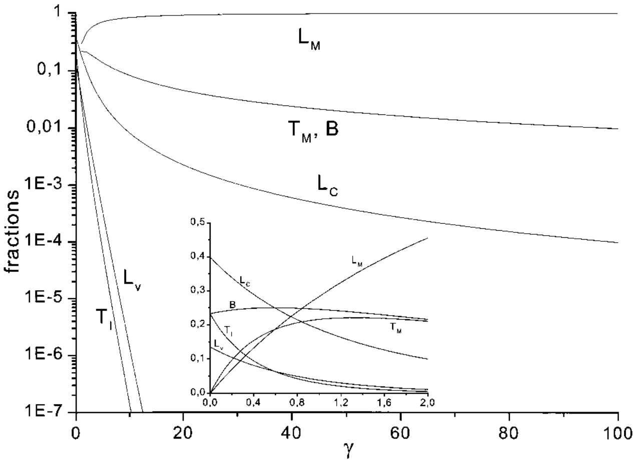
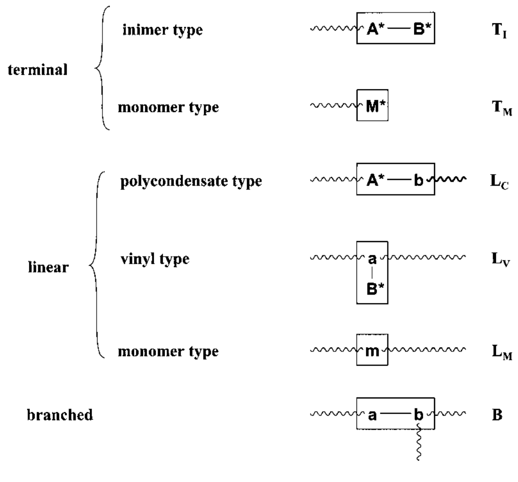


Figure 6. Dependence of degree of branching of final copolymer on the monomer/inimer ratio, γ.

Scheme 3. Set of Structural Units in SCVCP



Information. The dependences of the final fractions of structural units on the monomer/inimer ratio, γ, are shown in Figure 6 for full conversion. As can be seen, except for small values of γ, the fraction of branchpoints, B, practically coincides with the fraction of “monomer” terminal units, T_M. For high γ, the predominant fraction is obviously linear (monomer type) units, L_M.

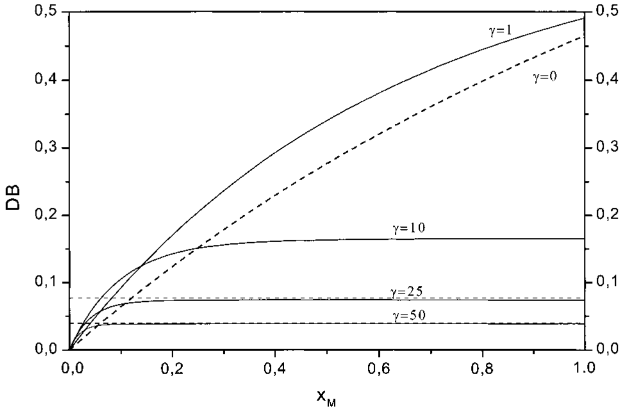


Figure 7. Dependence of degree of branching on monomer conversion for various values of γ.

For the average degree of branching, we finally obtain

$$\overline{DB} = \frac{2z_A(x_M - z_A)}{1 - (1 - x_M)(1 + z_A)} = \frac{2(1 - e^{-(\gamma+1)x_M})\left(x_M - \frac{1 - e^{-(\gamma+1)x_M}}{\gamma+1}\right)}{\gamma x_M + 1 - (1 - x_M)(2 - e^{-(\gamma+1)x_M})} \tag{15}$$

The dependence of $\overline{DB}$ on conversion for various values of γ is shown in Figure 7. It is striking that for small values of γ, $\overline{DB}$ is even higher than it is in the absence of comonomer. For small γ, $\overline{DB}$ increases monotonously with x_M, whereas for $\gamma \gg 1$, $\overline{DB}$ very quickly reaches its final value,

$$\overline{DB}_\infty \approx \frac{2}{\gamma + 1} \approx \frac{4\overline{DB}_{I,\infty}}{\gamma + 1} \tag{16}$$

where $\overline{DB}_{I,\infty} = 0.466$ is the final $\overline{DB}$ obtained in homo-SCVP.

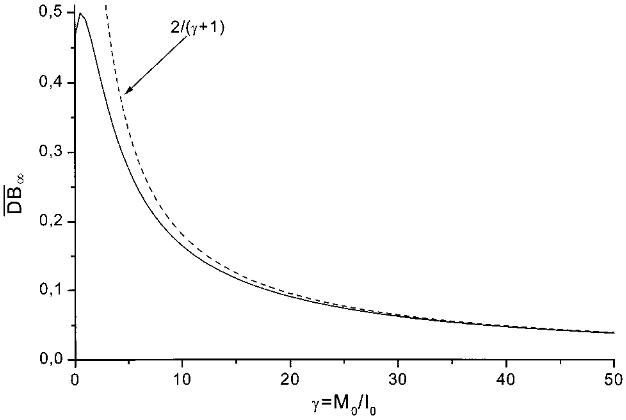


Figure 8. Dependence of degree of branching of final copolymer on γ at full conversion of monomer.

At full conversion ($x_M = 1$), eq 15 becomes

$$\overline{DB}_\infty = 2z_A(1 - z_A) = \frac{2(1 - e^{-(\gamma+1)})(\gamma + e^{-(\gamma+1)})}{(\gamma + 1)^2} \qquad (17)$$

The dependence of $\overline{DB}_\infty$ on γ is shown in Figure 8. It can be concluded from this plot that $\overline{DB}_\infty$ has a maximum value of 0.5. According to eq 17, this means that $z_A = 0.5$, which gives the following condition for the γ value necessary to obtain the maximum $\overline{DB}_\infty$:

$$2[1 - e^{-(\gamma+1)}] = \gamma + 1$$

The solution of this transcendental equation gives $\gamma \approx 0.6$ for maximum $\overline{DB}_{\infty,\max} = 0.5$.

It is quite unexpected that $\overline{DB}_\infty$ is 4 times higher than the value calculated for the pure inimer divided by the dilution factor, $\gamma + 1$. It is even more surprising that $\overline{DB}_\infty$ increases for small γ. However, this effect has a clear explanation. In a SCVP ($\gamma = 0$), at the end of the process, there still remains a large fraction of A* active centers ($z_A \approx 0.632$)[22] potentially capable of forming branch points. The addition of a small amount of monomer results in its addition to these A* centers forming short branches. For higher γ, monomer will predominantly add to M* forming linear units, thus decreasing $\overline{DB}$.

Comparison to Experimental Data

Figure 9 shows some preliminary results of the self-condensing group transfer copolymerization[35] of the inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (MTSHEMA, **2**) and methyl methacrylate (MMA) catalyzed by tetrabutylammonium bibenzoate (TBABB) in THF at room temperature at nearly complete conversion of MMA ($x_M \geq 0.98$). Experimental details are given in Supporting Information. The trends of the experimental molecular weight averages (obtained by GPC with a viscosity detector and universal calibration[36]) are in agreement with the theoretical predictions of eqs 8 and 11; i.e., $\bar{M}_n$ and $\bar{M}_w$ are proportional to γ (Fig. 9). No effect of γ on the polydispersity index is observed as predicted by eq 12. However, the absolute values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ obtained experimentally are considerably lower than the calculated ones.

This discrepancy might be attributed to the simplifications made for the calculations: (i) use of equal rate constants for the six possible propagation reactions of the different centers, (ii) neglect of excluded-volume effects, and (iii) neglect of cyclization reactions occurring between active centers and the double bond, which limits the molecular weights and narrows the distribution.[25] Nevertheless, Figure 9 shows that at least the general trends of a real system can be predicted. Detailed experimental results of the copolymerization of MTSHEMA and MMA[35] and calculations on SCVCP with nonequal rate constants[37] will be given in subsequent papers.

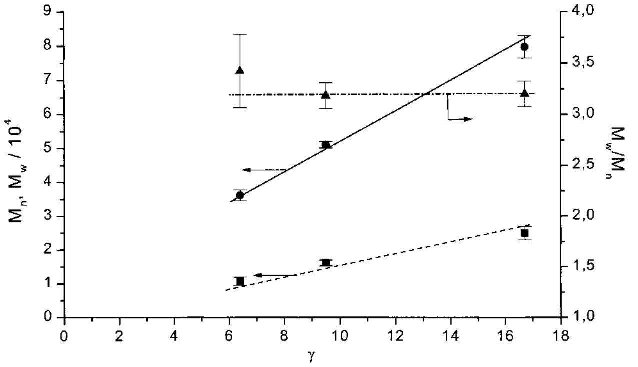


Figure 9. Dependence of molecular weight averages on γ in the self-condensing group transfer copolymerization of HEMA and MMA: (- - - ■ - - - -) = $\bar{M}_n$; (—●—) = $\bar{M}_w$; and (-·-·▲-·-·) = $\bar{M}_w/\bar{M}_n$.

Conclusions

Even a small amount of a conventional monomer affects all molecular parameters of self-condensing vinyl polymerization. Although we neglected excluded-volume effects and cyclization reactions and assumed all rate constants to be equal, the description of this idealized system is a good starting point to understand the principles of this process.

For a given molecular weight, the polydispersity index of the polymers obtained in such a copolymerization is lower than that obtained in a homo-SCVP. The degree of branching can be controlled through the incorporation of linear units of the conventional monomer. However, the effect of diluting AB* inimers by M monomers is only partially reflected in a decrease of DB, and for small monomer/inimer ratios, DB even increases.

In addition, it has been shown theoretically[28] and experimentally[35] that macroscopic properties such as intrinsic viscosity in solution only weakly depend on DB. Furthermore, the use of an appropriate comonomer allows the introduction of additional functional groups compared to a homopolymerization of an inimer. Therefore, self-condensing vinyl copolymerization is a versatile approach to highly branched structures.

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Supporting Information Available: Supporting Information Available: Text giving the calculation of conversion and fractions of active centers, calculation of the weight-average molecular weight, the calculation of the degree of branching and experimental details (5 pages). Ordering and Internet access information is given on any current masthead page.

List of Symbols and Abbreviations

γ ($= M_0/I_0$) = ratio of initial concentrations of monomer and inimer
$\delta_{i,j}$ = Kronecker symbol: $\delta_{i,j} = 1$ for $i = j$; $\delta_{i,j} = 0$ for all else
A = concentration of vinyl groups in the system (both in inimer and macromolecules)
A^* = concentration of active centers arising from vinyl group
B = concentration of branched units (ab)
B^* = concentration of initiating centers
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_{PQ} = rate constant of addition of species S to active center Q*
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 = monomer concentration
M_0 = initial monomer concentration
M^* = concentration of active centers arisen from monomer
$\bar{M}_{\mathrm{n}}$ = number-average molecular weight
$\bar{M}_{\mathrm{w}}$ = weight-average molecular weight
$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ = polydispersity index
n = number of inimer units in a macromolecule (= number of active centers)
N = concentration of macromolecules
$P_i(n)$ = concentration of macromolecules containing i monomer units and n active centers
$\bar{P}_{\mathrm{n}}$ = number-average degree of polymerization
$\bar{P}_{\mathrm{w}}$ = weight-average degree of polymerization
t = reaction time
T_{I} = concentration of terminal units (A*B*) arisen from inimer
T_{M} = concentration of terminal units (M*) arisen from monomer
x_{A} = conversion of double bonds
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*

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