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Molecular Parameters of Hyperbranched Copolymers Obtained by Self-Condensing Vinyl Copolymerization, 2.[†] Non-Equal Rate Constants

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ABSTRACT: The kinetics, molecular weight averages, and the average degree of branching, DB, are calculated for the self-condensing vinyl copolymerization (SCVCP) of a vinyl monomer M with an "inimer" AB* in the case of different reactivities of active species. Emphasis is given to two limiting cases: formation of "macroinimers" occurs if the monomer M is more reactive than the vinyl groups of inimers or polymer, and "hyperstars" are formed in the opposite case. It is shown that the kinetics, the molecular weight averages, and the average degree of branching strongly depend on the relative reactivities of monomer and inimer. Comparison with experimental data shows that consistent fits of the reactivity ratios can be obtained.

Introduction

Branched polymers have been meeting increasing interest. Besides star- and comb-shaped macromolecules, hyperbranched polymers are attractive because they combine some properties of dendrimers like a self-similar structure and an exponentially increasing number of end groups with the advantage of a facile and inexpensive preparation.

Recently, Fréchet et. al.[1] showed that hyperbranched vinyl polymers are obtained using "self-condensing vinyl polymerization" (SCVP) of initiator-monomers ("inimers"[2]) having the general structure AB*, where A stands for a double bond and B* stands for an initiating group. By mixing AB* inimers with conventional monomers, M, this technique was extended to the self-condensing vinyl copolymerization (SCVCP), leading to highly branched copolymers.[3−9,21] Depending on the chemical nature of the comonomer different types of functional groups can be incorporated in the polymer. Alternatively, highly branched copolymers were prepared by SCVP of a "macroinimer", i.e., a heterotelechelic macromolecule possessing both an initiating and a polymerizable moiety.[10,11]

In the first part of this series,[7] the theory of SCVCP was elaborated for the simplest case where the rate constants of all reactions are equal. It was shown that the kinetics, the molecular weight distribution (MWD), and the average degree of branching (DB) strongly depend on the monomer/inimer ratio, $\gamma = M_0/I_0$. At low conversions, the process resembles a living polymerization of M, where the inimers act as initiators only; at high conversions the process resembles a self-condensing vinyl homopolymerization (SCVP) of AB* inimers. For high monomer/inimer ratios ($\gamma \gg 1$) the number-average degree of polymerization, $\bar{P}_n$, 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 $\bar{P}_n$ value, the polydispersity index decreases with γ as $\bar{P}_w/\bar{P}_n = \bar{P}_n/\gamma x_M$. For $\gamma \gg 1$, 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 ($\gamma \leq 1$), DB even exceeds the values for a homo-SCVP; a maximum of DB = 0.5 is reached at $\gamma \approx 0.6$. These effects were explained by the addition of monomer molecules to in-chain active centers (i.e., in linear units stemming from inimers), leading to very short branches.

The trends predicted by calculations are confirmed qualitatively by preliminary experimental data. However, the absolute values of $\bar{P}_n$ and $\bar{P}_w/\bar{P}_n$ obtained experimentally were considerably lower than the calculated ones. This discrepancy might be attributed to the simplifications made for the calculations. The most obvious one is that the rate constants used for the six possible propagation reactions of the different centers were assumed to be equal. Other reasons can be the neglect of excluded-volume effects and cyclization reactions occurring between active centers and the double bond of the same molecule which limit the molecular weights and narrow the distribution.[12−15]

This publication presents calculations on the MWD averages and DB obtained in SCVCP with nonequal rate constants, and we compare the obtained dependences with experimental data.

General Considerations

We analyze the same kinetic scheme as in part 1. The polymerization can be initiated by two ways (Scheme 1): (i) 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 and (ii) the addition of a B* group to the vinyl group of monomer M forming a dimer with one active site, M*. Both the initiating B* group and the newly

Scheme 1. Initial Steps in SCVCP (Reacted Units Are in Lower Case)
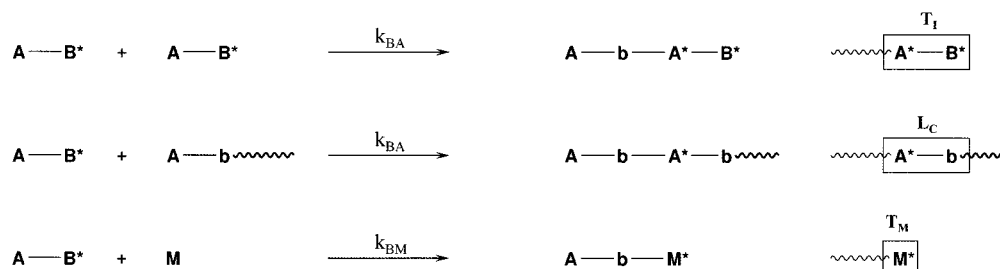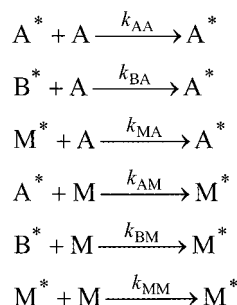

created propagating centers A* and M* can react with any other vinyl group in the system. Thus, we have three different types of active centers, A*, B*, and M* which can react with double bonds A (inimer and macromolecules; each macromolecule contains strictly one double bond) and M (monomer).

As in part 1, in our notation 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).

Let us now consider all possible reactions between the different structural patterns and active centers with double bonds of inimer and macromolecules, A, and of monomer, M (Scheme 2).

Scheme 2. Possible Reactions in SCVCP

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

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

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

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

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

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

The differential kinetic equations for the concentrations of active centers, comonomers, and vinyl groups appropriate to Scheme 2 have been already given in part 1 (eqs 1−3) and are not repeated here. As in part 1, we assume rate constants to be independent of the degree of polymerization, i.e., no excluded-volume effects and the absence of cyclization reactions.

In general, there are six different rate constants to be taken into account. The simplest case when all rate constants are equal was analyzed in part 1 and will be referred below as the ERC (equal rate constants) case. In principle, it is possible to calculate the molecular weight averages and the degree of branching for all values of the six rate constants. Obviously, this would lead to an indigestible amount of information. Thus, we restrict our calculations to certain important reactivity ratios.

For simplicity and for chemical reasons in many systems it is natural to suppose that the reactivity of A* and B* groups are the same although different from that of the M^* group i.e.,

$$k_{AA} = k_{BA} \equiv k_{IA}$$

$$k_{AM} = k_{BM} \equiv k_{IM}$$

where index I means inimer. Generally speaking, this assumption is not always true,[6,16,17] but in many cases

the difference in the reactivity between A* and B* centers is smaller than between former groups and M^* centers. Thus, we reduce the number of different rate constants from 6 to 4.

Now, similar to conventional copolymerization, let us introduce the monomer reactivity ratios

$$r_I = \frac{k_{IA}}{k_{IM}} \quad \text{and} \quad r_M = \frac{k_{MM}}{k_{MA}}$$

To further reduce the number of parameters, we first assume that $r_I r_M = 1$ (ideal copolymerization), and then we also discuss the case $r_I r_M \neq 1$.

Another important parameter is the ratio of rate constants of homopolymerization

$$a = \frac{k_{IA}}{k_{MM}}$$

Prior to calculations, two limiting cases can be distinguished.

Limiting Cases

Macroinimer Formation, $k_{IM} \gg k_{IA}$ and $k_{MM} \gg k_{MA}$ ($r_I \ll 1$ and $r_M \gg 1$). In this case the process proceeds in two steps. First, inimer will act as an ordinary initiator and add monomer until the latter is completely consumed thus forming a "macroinimer" which has one vinyl group, A, one active center, M*, and the degree of polymerization $\bar{P}_n = M_0 x_M / I_0 = \gamma x_M$

$$AB^* + M \xrightarrow{k_{IM}} A{-}b{-}M^*$$

$$AbM^* + nM \xrightarrow{k_{MM}} A{-}b{-}m_n{-}M^*$$
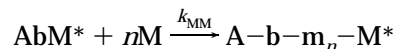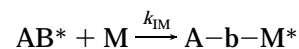
If at the same time $k_{IM} \geq k_{MM}$ (fast initiation) we shall obtain a Poisson distribution of macroinimers, $\bar{P}_w / \bar{P}_n \approx 1/\bar{P}_n$. For $k_{IM} < k_{MM}$ the process resembles slow initiation, leading to the Gold distribution[18] with $\bar{P}_w / \bar{P}_n \leq 4/3$.

Finally, for $x_M \rightarrow 1$ these macroinimers will undergo SCVP. The special case of SCVP of preformed macroinimers has been reported theoretically and experimentally.[19] It results in the following relationships between values of average parameters in this case and those of SCVP of normal inimers (index 0)

$$\bar{P}_n = (\gamma + 1)/\bar{P}_{n,0}$$

$$\bar{P}_w / \bar{P}_n = (\bar{P}_w / \bar{P}_n)_0$$

when compared at a given conversion of double bonds and

$$P_w/\bar{P}_n = (\bar{P}_w/\bar{P}_n)_0/(\gamma + 1)$$

when compared at a given $\bar{P}_n$

$$DB = \frac{DB_0}{(\gamma + 1)(1 - e^{-x})}$$

and for $x \to 1$

$$DB_\infty = \frac{0.714}{\gamma + 1}$$

Hyperstar Formation, $k_{IM} \ll k_{IA}$ and $k_{MM} \ll k_{MA}$ ($r_I \gg 1$ and $r_M \ll 1$). In this limiting case, inimer molecules will first undergo SCVP and only at very high conversions of inimer and polymer vinyl groups, $x_A \to 1$, they will add monomer leading to star-shaped polymers ("hyperstars").[3,20] This will result in high values of DP and polydispersity index already at small monomer conversion. However, because at higher conversions the polymer vinyl groups may be less accessible than those of monomer, this case is not probable if vinyl groups of inimer and monomer have the same chemical nature. It may become important if the vinyl groups of I are much more reactive than those of M.

Kinetic Differential Equations

Let us define the dimensionless time $\tau = k_{MM}I_0t$, which is the characteristic time of homopolymerization of monomer M via initiator I, conversions of different species: of monomer, $x_M = (M_0 - M)/M_0$, inimer, $x_I = (I_0 - I)/I_0$, and vinyl groups, $x_A = (I_0 - A)/I_0$; and fractions of active centers: $z_A = A^*/I_0$, $z_B = B^*/I_0$, $z_M = M^*/I_0$ and, for convenience, the total fraction of inimeric active centers, $z_I = z_A + z_B$. Then, the set of eqs 1–3 of part 1 can be rewritten in the following dimensionless form.

conversions of monomer, inimer and double bonds

$$\frac{1}{1 - x_M}\frac{dx_M}{d\tau} = \frac{a}{r_I}z_I + z_M \tag{1}$$

$$\frac{1}{1 - x_I}\frac{dx_I}{d\tau} = \frac{z_M}{r_M} + a\left(z_I + 1 - x_A + \frac{\gamma(1 - x_M)}{r_I}\right) \tag{2}$$

$$\frac{1}{1 - x_A}\frac{dx_A}{d\tau} = \frac{z_M}{r_M} + az_I \tag{3}$$

fractions of active species

$$\frac{dz_I}{d\tau} = -\frac{dz_M}{d\tau} = -\frac{a\gamma(1 - x_M)}{r_I}z_I + \frac{1 - x_A}{r_M}z_M \tag{4}$$

$$\frac{dz_B}{d\tau} = -az_B\left(1 - x_A + \frac{\gamma(1 - x_M)}{r_I}\right) \tag{5}$$

Kinetics and Fractions of Active Centers

From eqs 1 and 5, one can easily obtain the relationship between conversions of vinyl groups and inimer:

$$(1 - x_I) = (1 - x_A)z_B \tag{6}$$

Equation 6 is valid for all ratios of rate constants. Because z_B is always smaller than unity and only

decreases with time, the conversion of inimer x_I is always higher than the conversion of vinyl groups x_A.

For arbitrary values of reactivity ratios and parameters a and γ, eqs 1–5 can be solved only numerically. However, in the case $r_I r_M = 1$, dividing eq 3 by eq 1 and integrating, one obtains the relationship between conversion of monomer and double bonds:

$$(1 - x_A) = (1 - x_M)^{r_I} \tag{7}$$

Obviously, x_A as a function of x_M does not depend on the monomer/inimer ratio, γ. Unfortunately, even for $r_I r_M = 1$, eq 7 is the only analytical expression which can be derived from eqs 1–5. The other dependences have to be calculated numerically.

The dependence of the conversion of monomer M on time is affected by the reactivity ratios. Details are shown in the Supporting Information (Figure S1). For $r_I < 1$ the first-order plots look more or less linear, similar to common copolymerization. Only for $r_I > 1$ the polymerization proceeds much slower that in the ERC case. At a given value of $r_I > 1$, the deviations from the ERC curve is larger for lower values of a. For large values of r_I there is also a dependence on the procuct $r_I r_M$.

The consumption of vinyl groups A as a function of monomer conversion is shown in Figure 1. Whereas in the ERC case the conversions of vinyl groups and monomer are equal, now, for the case $r_I r_M = 1$, vinyl groups are consumed slower than monomer at $r_I < 1$ (or $r_M > 1$). At very small r_I, the conversion of vinyl groups A is very small even at x_M close to unity indicating that first macroinimers are formed which react only at high x_M. On the opposite side, if $r_I > 1$, vinyl groups are consumed faster than monomer (hyperstar case). This confirms the qualitative conclusions made earlier. At a given value of r_I, the consumption of inimer also strongly depends on the product $r_I r_M$ (Figure 1b–d).

Whereas for $r_I r_M = 1$ the conversion of vinyl groups as a function of x_M does not depend on the monomer/inimer ratio, γ, this is an important parameter affecting the inimer consumption rate. This is shown in detail in the Supporting Information (Figure S2). For sufficiently high γ, inimers disappear already at very small monomer conversions. The rate of inimer consumption increases with decreasing r_I and increasing a and also depends on the product $r_I r_M$.

Additional information on the effect of different rate constants can be obtained from Figure 2 which shows the dependence of the fraction of macromolecules, $N/I_0 \equiv (A - I)/I_0 = (x_I - x_A)$ on monomer conversion. In the ERC case already at low conversions ($x_M \sim 0.2$ for $\gamma = 10$) the formation of new macromolecules becomes slower than their disappearance due to linking reactions between "in-chain" active centers and double bonds of other macromolecules. For small r_I all macromolecules are formed very early ($x_M \approx 0.15$ for $r_I = 0.1$, $r_M = 10$, $a = 1$, and $\gamma = 10$; Figure 2a). The concentration of these primary macromolecules is comparable to I_0, which means fast initiation. During the conversion of monomer ($x_M \leq 0.95$) linking reactions are not very pronounced and only become significant at $x_M \to 1$, again confirming our earlier conclusions for the macroinimer case. On the contrary, for $r_I > 1$ most linking reactions occur at moderate conversions ($x_M < 0.3$ for $\gamma = 10$), then the
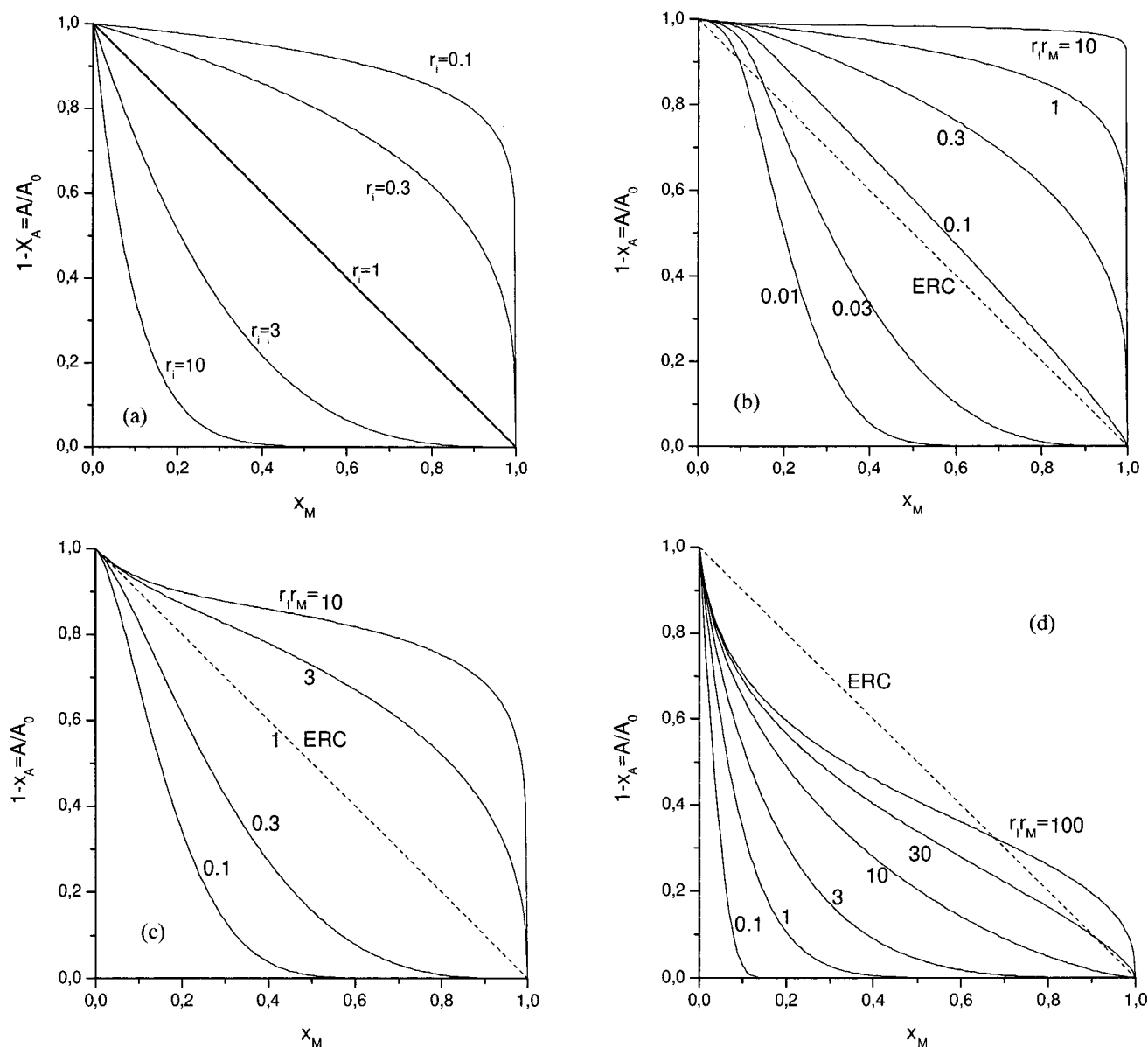
Figure 1. Conversion of inimer and polymer double bonds vs monomer conversion for various values of r_I: (a) $r_I r_M = 1$; (b) $r_I = 0.1$; (c) $r_I = 1$; (d) $r_I = 10$.
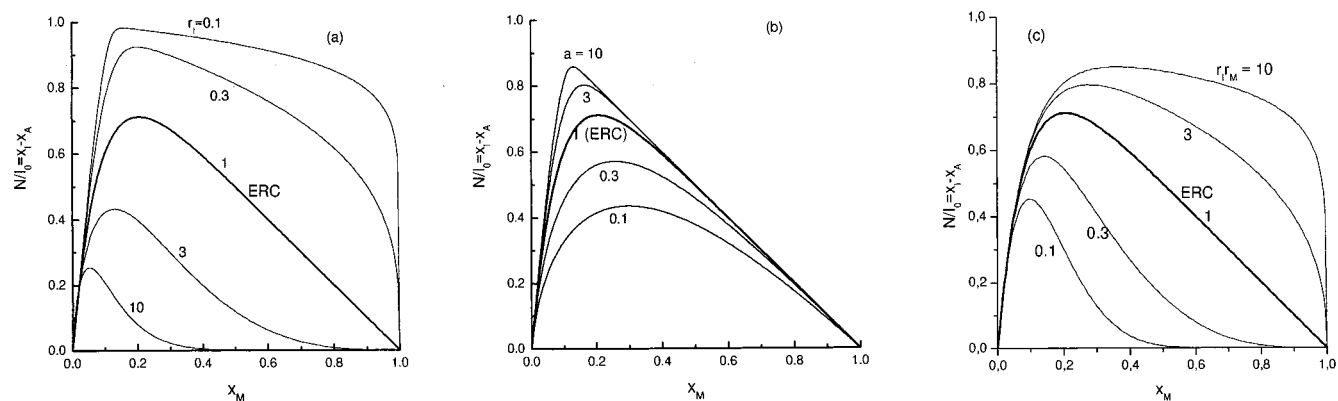

Figure 2. Dependence of the concentration of macromolecules on monomer conversion, $\gamma = 10$: (a) $r_I r_M = 1$, $a = 1$; (b) $r_I = 1$, $r_I r_M = 1$; (c) $r_I = 1$, $a = 1$.

hyperbranched polymer starts to add monomers thus forming stars. Again, this behavior is strongly affected by $r_I r_M$.

The evolution of the fractions of various active centers is discussed in the Supporting Information (Figure S3).

Molecular Weight Averages

Number-Average Molecular Weight. We shall calculate the number-average molecular weights similar to the ERC case. According to definition, $\bar{M}_n$ is equal to
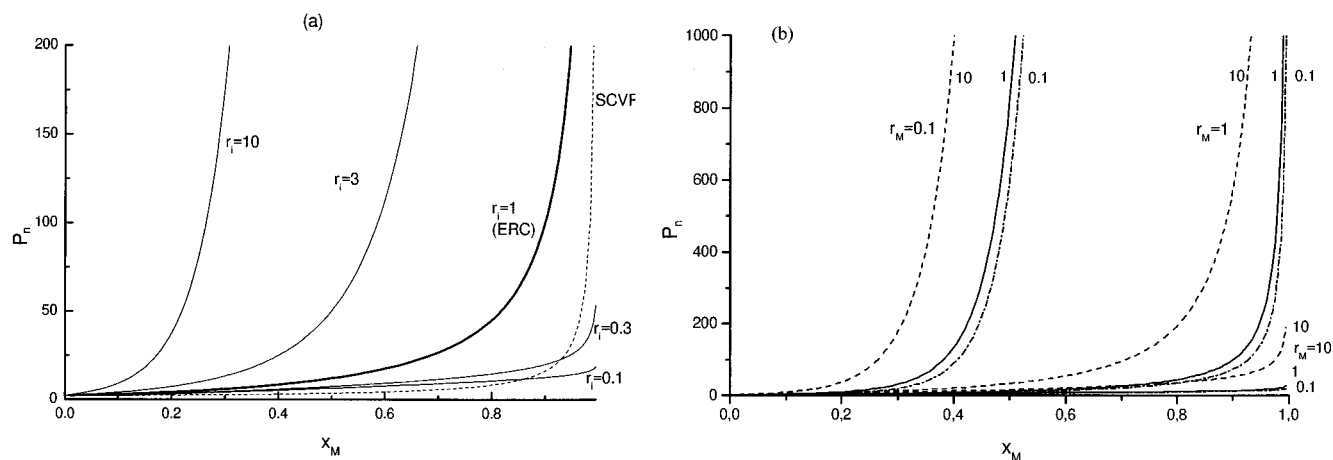
Figure 3. Dependence of the number-average degree of polymerization on monomer conversion for various reactivity ratios. γ = 10. The dotted line corresponds to the SCVP of inimer as a function of x_A: (a) $r_I r_M = 1$; (b) $r_I = 1$.
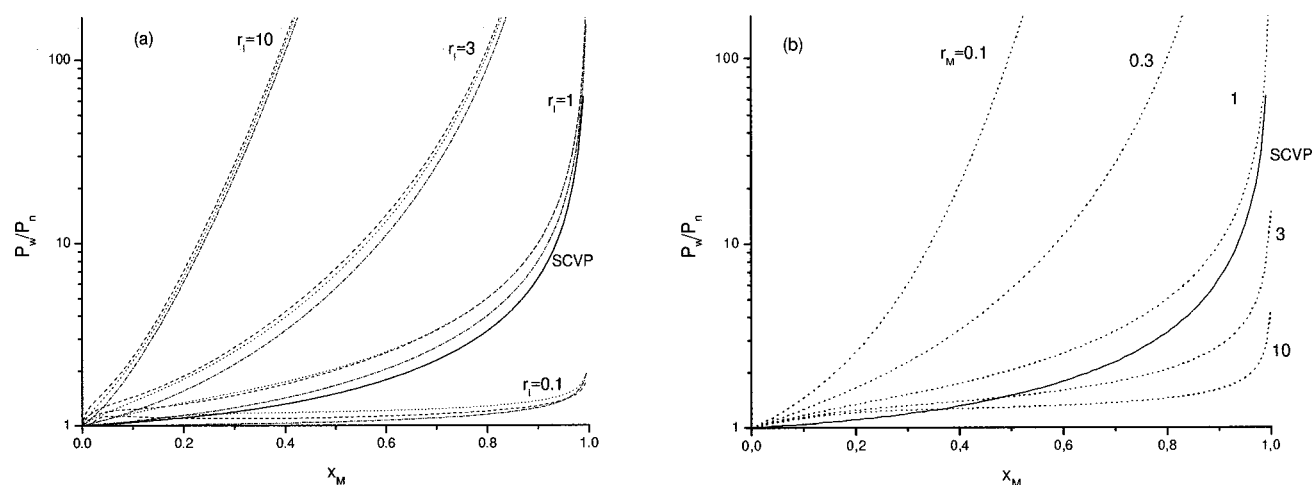

Figure 4. Dependence of polydispersity index on monomer conversion: (a) $r_I r_M = 1$ and $\gamma = 1$ ($-\cdot-\cdot$), $\gamma = 10$ ($\cdots$), and $\gamma = 50$ ($--$); ($-$) SCVP as a function of x_A; (b) at $\gamma = 10$, $r_I = 1$.

the ratio of total weight of polymer molecules, $m_M M_0 x_M + m_I I_0 x_I$, to the number of macromolecules $N = A - I = I_0(x_I - x_A)$ i.e.

$$\bar{M}_n = \frac{m_M \gamma x_M + m_I x_I}{x_I - x_A} \quad (9)$$

where m_M and m_I are molar masses of monomer and inimer, respectively. For simplification, we will only discuss the case $m_M = m_I$ which allows us to define the number-average degree of polymerization

$$\bar{P}_n = \frac{\gamma x_M + x_I}{x_I - x_A} \quad (9a)$$

The dependence of $\bar{P}_n$ on monomer conversion is shown in Figure 3. As follows from eqs 7 and 9a for $r_I r_M = 1$, $\bar{P}_n$ is almost independent of the ratio of rate constants of homopolymerization, a, (the effect of a is only through the term x_I and it is negligible for sufficiently high γ and not extremely low r_I) but depends on the value of the reactivity ratio r_I. At a given monomer/inimer ratio γ, $\bar{P}_n$ increases with r_I. At a given r_I, $\bar{P}_n$ increases almost linearly with γ, similar to the ERC case (not shown). For $r_I \ll 1$, $\bar{P}_n$ increases with conversion almost linearly up to very high monomer conversion, $x_M < 0.95$, indicating the formation of linear macroinimer. On the

contrary, for $r_I \gg 1$, $\bar{P}_n$ already shows a strong increase at low monomer conversion because inimers are consumed fast forming hyperbranched polyinimer. An even stronger effect is seen when varying r_M (Figure 3b).

Weight-Average Molecular Weight and Polydispersity Index. The calculation of the weight-average molecular weights is much more complex. The derivation of equations for the calculation of $\bar{M}_w$ is given as Supporting Information. Results of numerical calculations are presented in Figures 4 and 5 for the case of equal molar masses of inimer and monomer.

Similar to both SCVP and ERC cases, the polydispersity index monotonically increases with monomer conversion, x_M (Figure 4). At a given x_M, the effect of γ on $\bar{P}_w/\bar{P}_n$ is small as in the ERC case. The effect of ratio a is also not very pronounced and completely disappears at $\gamma \gg 1$. However, $\bar{P}_w/\bar{P}_n$ strongly depends on the reactivity ratio r_I (Figure 4a). The smaller r_I the lower the polydispersity index at a given conversion, and at $r_I \ll 1$ $\bar{P}_w/\bar{P}_n < 2$ even at $x_M = 0.995$. This corresponds to the case of normal living homopolymerization of monomer with slow initiation by I.

Figure 4b shows an even stronger effect of r_M. For $r_M > 1$ the MWD narrows and in the contrary case it broadens, indicating that the various ratios of rate constants have a significant influence on the MWD.
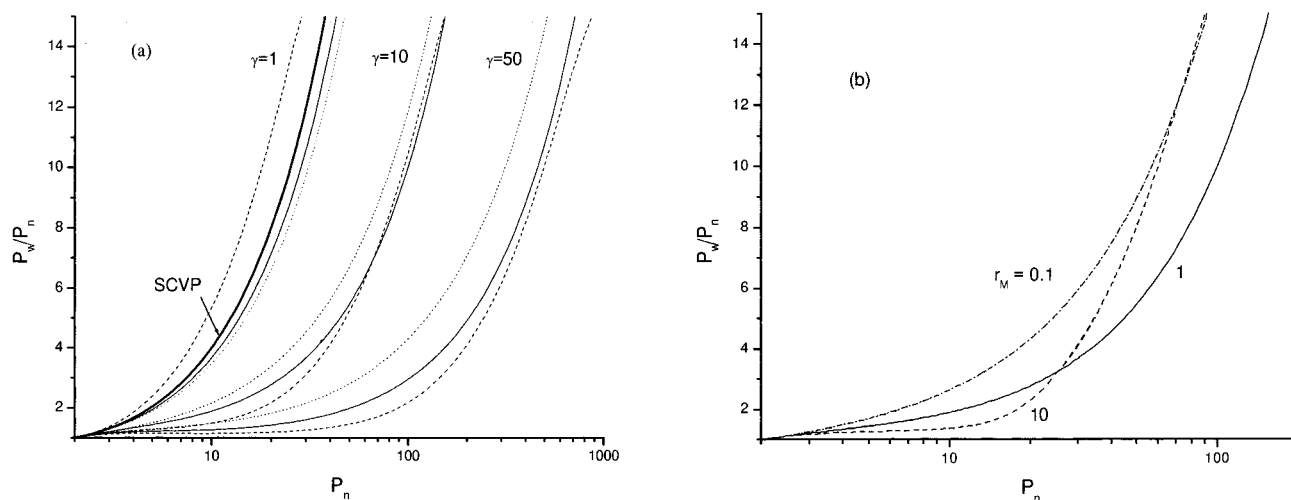
Figure 5. Dependence of polydispersity index on number-average degree of polymerization: (a) $r_I = 1$ ($\cdots$), $r_I = 0.3$ (—), $r_I = 1$ (– –), $r_I = 3$; (b) at $\gamma = 10$, $r_I = 1$.

As in part 1, it is more reasonable to discuss the polydispersity index as a function of number-average molecular weight. Figure 5a shows that $\bar{P}_w/\bar{P}_n$ increases with increasing $\bar{P}_n$ as in the ERC case. Again, the slope decreases with increasing monomer/inimer ratio. For $r_I r_M = 1$ the effect of r_I on $\bar{P}_w/\bar{P}_n$ is more complex and depends also on γ and $\bar{P}_n$. At a given $\bar{P}_n$, the polydispersity index as a function of r_I passes a minimum at sufficiently small r_I (for example, for $\bar{P}_n = 100$ the minimum is reached at $r_I \simeq 0.5$ for $\gamma = 10$ and at $r_I \simeq 0.1$ for $\gamma = 50$) and then monotonically increases. In Figure 5b the effect of r_M is also seen.

Degree of Branching

An important molecular parameter of branched macromolecules is the degree of branching, DB. We shall use the same definition of DB as in part 1

$$\overline{DB} = \frac{2B}{M_0 x_M + I_0 x_I - 2N} \quad (10)$$

Similar to part 1, we determine also concentrations of various structural units. 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 from inimer; its 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. part 1, Scheme 2) and resembles the repeat unit of a typical vinyl polymer. Clearly, the third type of linear units, $L_M = m$, and branched units, $B = ab$, do not react with vinyl groups as they do not contain active centers. The total concentration of all units is equal to the total amount of monomer and inimer incorporated into macromolecules

$$T_M + T_I + L_M + L_V + L_c + B = M_0 x_M + I_0 x_A$$

The expressions for the structural units are given in Table 1; their derivation and discussion are given as Supporting Information.

Table 1. Expressions for the Concentrations of the Various Structural Units[a]

Type	Notation	Structure	Concentration/I_0
Terminal, of monomer	T_M	M*	z_M
Terminal, of inimer	T_I	A* — B*	$z_A z_B$
Linear, "condensate type", of inimer	L_C	A* — b	$z_A(1 - z_B)$
Linear, "vinyl type", of inimer	L_V	a / B*	$z_B(x_A - z_A)$
Linear, of monomer	L_M	m	$\gamma x_M - z_M$
Branched	B	a — b	$(1 - z_B)(x_A - z_A)$

[a] Note: Fractions are given by dividing each expression from the last column by $(\gamma x_M + x_I)$.

Substituting the expression for the concentration of branched units (Table 1) into eq 10, one obtains the following expression for the degree of branching

$$DB = \frac{2(1 - z_B)(x_A - z_A)}{\gamma x_M + 1 - (1 - x_A)(2 - z_B)} \quad (11)$$

It should be noted that the definition of degree of branching does not make sense when applied to star-shaped molecules. Thus, for $r_I \gg 1$, DB becomes meaningless.

The degree of branching was calculated numerically for different reactivity ratios and different monomer/inimer ratios, γ. Figure 6 shows that DB depends on a, r_I, and $r_I r_M$. For some sets of parameters the dependence of DB on x_M can be nonmonotonic. Whereas for $a < 1$ DB monotonically increases with monomer conversion ($r_I \le 1$), for $a > 1$ it first increases at sufficiently small conversions (SCVP) and then decreases due to the addition of monomer units. Increasing r_M at a given value of r_I decreases DB. However, especially at high values of r_I, the final degree of branching is less affected.
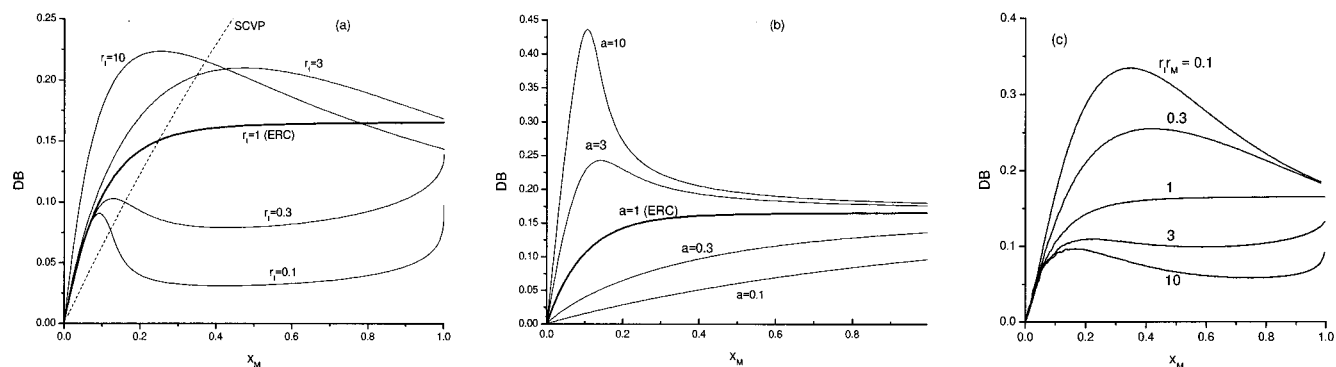
Figure 6. Dependence of degree of branching on monomer conversion at $\gamma = 10$: (a) $r_I r_M = 1$, $a = 1$; (b) $r_I r_M = 1$, $r_I = 1$; (c) $a = 1$, $r_I = 1$.
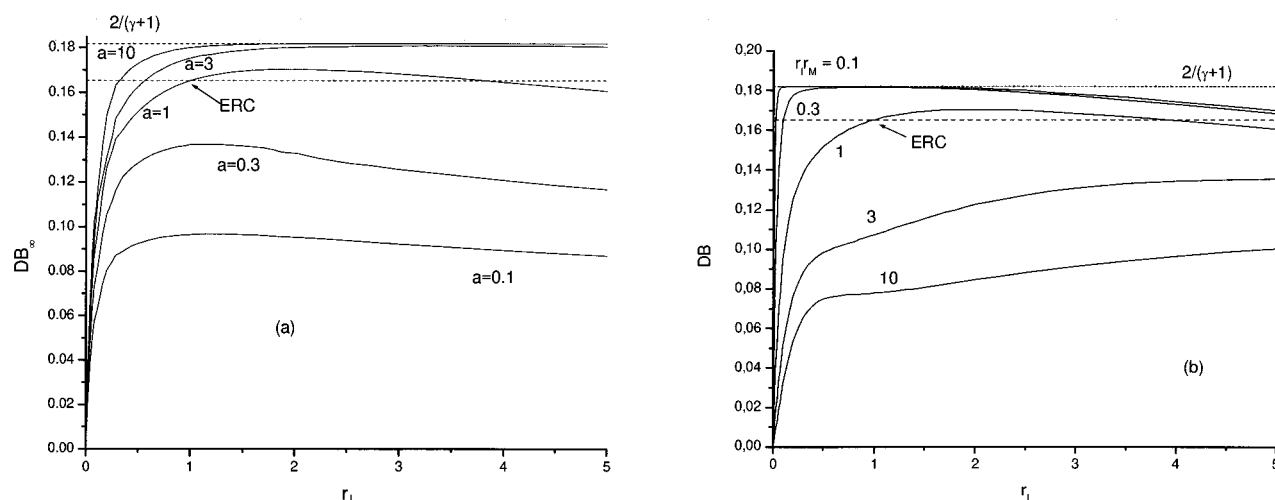

Figure 7. Dependence of final degree of branching on r_I at $\gamma = 10$: (a) $r_I r_M = 1$; (b) $a = 1$.

At full conversion of monomer and double bonds, $x_M = x_A = 1$, eq 11 obtains the form

$$DB_\infty = \frac{2(1 - z_{B,\infty})(1 - z_{A,\infty})}{\gamma + 1} \qquad (12)$$

For high γ the final values of z_B and z_A are very small, z_A, $z_B \ll 1$, and from eq 12 we obtain for DB_∞ the same asymptotic expression as in the ERC case

$$DB_\infty = \frac{2}{\gamma + 1} \qquad (13)$$

However, if γ is not very high ($\gamma \lesssim 50$) and a and r_I markedly differ from unity, the difference from the ERC case may be significant. The effect of a and r_I on the final value of DB is shown in Figure 7a for $\gamma = 10$. Figure 7b shows a similar plot for the effect of r_I and $r_I r_M$.

In the most probable case when both r_I and a are lower than unity (due to limited accessibility of A groups at high conversions), the polymer formed is less branched than in the ERC case.[7] This corresponds to the case of macroinimer. In the opposite case, $r_I > 1$ and $a > 1$, DB_∞ can exceed the corresponding value of the ERC case (this difference is marked only at not very high $\gamma \lesssim 15$). However, as was already mentioned, this case is only expected if the reactivities of vinyl groups and active centers of the inimer are higher than those of the monomer.

If one plots the dependence of DB_∞ on γ for various sets of parameters r_I and a (at $r_I r_M = 1$; Figure 8) one can see that similar to the ERC case this dependence passes a maximum at small $\gamma < 1$. The maximum value of DB_∞ is the higher the higher a (at a given r_I) or the lower r_I (at a given a).

For $r_I \gg 1$ and $\gamma \gg 1$ star polymers will be formed, and the term DB becomes meaningless. However, for $r_I \gg 1$ and $2 \geq \gamma > 0$, we will finally obtain a hyperbranched polymer and consecutively short side chains will be added to most L_C and L_V units leading to a hyperbranched polymer with high DB.

Comparison to Experiment[22]

We compare our theoretical results with experimental results obtained in the SCVCP of *p*-chloromethylstyrene (CMS) with styrene via atom transfer radical polymerization (ATRP).[4] Figure 9 shows that a consistent fit can be obtained for the molecular weight averages as a function of monomer conversion for three different molar ratios, $\gamma = [CMS]/[styrene]$, when using $a = 1$ and $r_I = 0.3$, and $r_I r_M = 1$, whereas the fit is very poor for equal rate constants. However, it must be noted that the molecular weight averages were obtained from GPC using linear polystyrene standards. Although the real values will be higher we do not expect the effect to be large enough to account for the difference between experimental and ERC values.

We do not claim that unequivocal reactivity ratios were obtained. This is not possible, since we have only
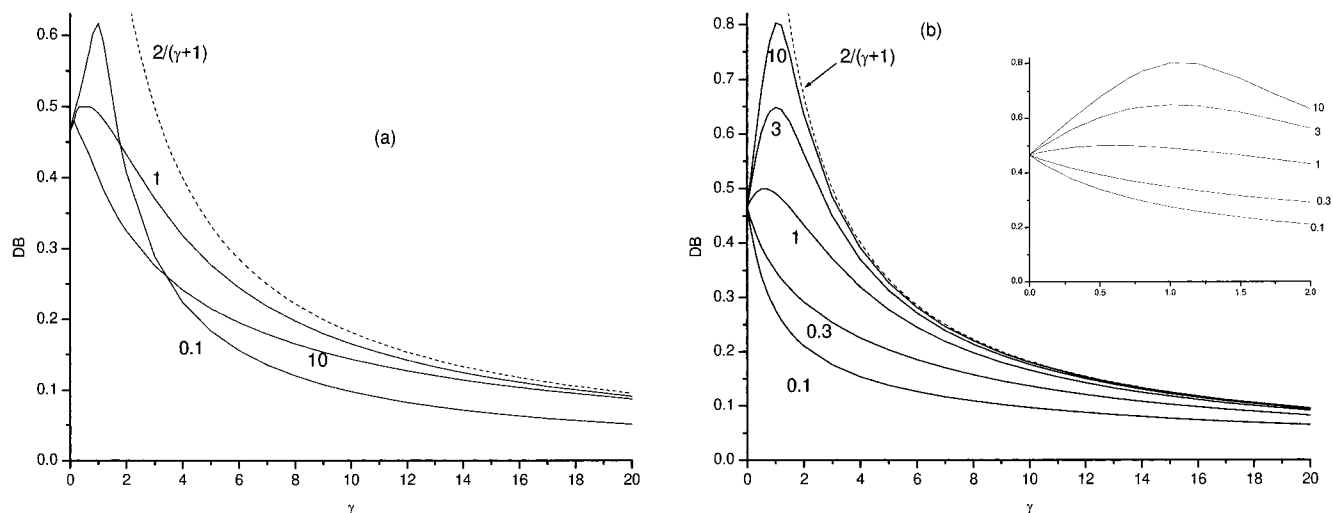
Figure 8. Dependence of final degree of branching on γ: (a) $r_I r_M = 1$, $a = 1$; (b) $r_I = 1$, $a = 1$.
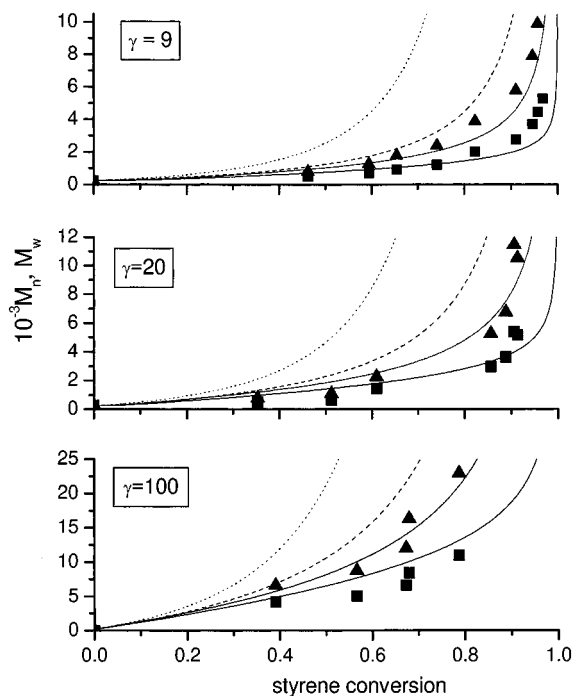

Figure 9. Dependence of (apparent) number- and weight-average molecular weights of copolymer formed in ATRP−SCVCP of p-chloromethylstyrene (CMS) with styrene on styrene conversion for various ratios of $[CMS]_0/[styrene]_0$, γ. Key: (■) $\bar{M}_n$; (▲) $\bar{M}_w$. Solid lines are calculated for $r_I = 0.3$; dashed ($\bar{M}_n$) and dotted ($\bar{M}_w$) lines are calculated for the ERC case ($r_I = 1$).

varied certain ratios of rate constants (see below). However, we have demonstrated that consistent sets of parameters can be found which lead to a satisfactory fit to the experimental data.

Conclusions

Because of the high number of parameters in this type of copolymerization, we had to restrict our calculations to certain special cases. For example, we had to assume that A* and B* centers are of equal reactivity although it was shown earlier that this is not always the case. Several examples showed that the product $r_I r_M$ also affects all interesting properties. In addition, as was argued before, intramolecular loop formation will have

a significant effect on the MWD and its averages (this is indeed true for the MTSHEMA/GTP system[9]). In real systems, we also have to take into account that apparent rate constants may depend on the size of the polymer formed. However, we still can draw some important conclusions from our calculations:

(i) The kinetics of copolymerization depends on reactivity ratios, especially for $r_I > 1$.

(ii) For higher r_I, $\bar{P}_n$ increases more rapidly with monomer conversion; it does not strongly depend on a.

(iii) At a given $\bar{P}_n$ the polydispersity index pronouncedly depends on the reactivity ratio, but not on a and γ.

(iv) The degree of branching strongly depends on r_I and a. To achieve high DB, conditions are needed where $r_I \geq 1$ ($k_{IA} \geq k_{IM}$) and $a > 1$ ($k_{IA} \geq k_{MM}$). For a given value of $r_I \geq 1$ the latter condition corresponds to $k_{IA} \geq k_{MA}$. Thus, the structure of two comonomers and the reaction conditions must be adjusted in a way that the reactivity of inimer or polymer vinyl groups is higher or equal to those of the monomer M. In addition, the centers A* and B* should be considerably more reactive than M*.

Supporting Information Available: Figures showing the dependence of kinetics on reactivity ratios, text giving the derivations of equations for the weight-average molecular weight and degree of branching, figures showing the fractions of structural units for various reactivity ratios. This material is available free of charge via the Internet at http://pubs.ac-s.org.

List of Symbols and Abbreviations

$\gamma = M_0/I_0$ ratio of initial concentrations of monomer and inimer

$a = k_{IA}/k_{MM}$ ratio of the rate constants of homopolymerizarion

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
I	concentration of inimer AB^*
I_0	initial concentration of inimer = total concentration of active centers
i	no. of monomer units in a macromolecule
k_{PQ}	rate constant of addition of species Q to active center P^*
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
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$\bar{M}_w/\bar{M}_n$	polydispersity index
N	concentration of macromolecules
$\bar{P}_n$	no.-average degree of polymerization
$\bar{P}_w$	weight-average degree of polymerization
$\bar{P}_w/\bar{P}_n$	polydispersity index
$r_I = k_{IA}/k_{IM}$	monomer reactivity ratios
r_M	k_{MM}/k_A
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 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^*

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(22) Note added in proof: After submission of our manuscript, Paulo and Puskas[21] published a paper on the cationic copolymerization of *p*-(2-methoxyisopropyl)styrene with isobutylene at high comonomer ratios ($100 \leq \gamma \leq 1000$). For this system, $r_I \approx r_M \approx 6$ ($r_I r_M \approx 33$) and $a \approx 2$ (Faust, R. Private communication). A quick numerical calculation resulted higher polydispersity indices than those given in that paper (assuming high conversions). This might be another indication of cyclization narrowing the MWD. Unfortunately, the "branching ratios" given by the authors cannot be easily correlated to DB. However, since $\gamma \gg 1$, DB is expected to be close to $2/\gamma$, i.e., $0.002 \leq DB \leq 0.02$, independent of the reactivity ratios.

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