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Molecular Parameters of Hyperbranched Polymers Made by Self-Condensing Vinyl Polymerization. 2. Degree of Branching[†]

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ABSTRACT: Using a modified definition, the average degree of branching, $\overline{DB}$, the fraction of branchpoints, $\overline{FB}$, as well as the fractions of various structural units are calculated as a function of conversion of double bonds for hyperbranched polymers formed by self-condensing vinyl polymerization (SCVP) of monomers (or "inimers") with the general structure AB*, where A is a vinyl group and B* is an initiating group. The results are compared to those for the polycondensation of AB_2-type monomers. At full conversion, $\overline{DB}$ is somewhat smaller for SCVP ($\overline{DB}_\infty \approx 0.465$) than for AB_2 systems ($\overline{DB}_\infty = 0.5$). There are two kinds of linear groups in SCVP whereas there is only one kind in AB_2 systems. Since there are two different active centers in SCVP, i.e., initiating B* and propagating A* centers, the effect of nonequal reactivities on $\overline{DB}$ is also discussed. At a reactivity ratio of the two kinds of active centers, $r = k_A/k_B \approx 2.59$, a maximum value of $\overline{DB}_\infty = 0.5$ is reached. For the limiting case $r << 1$, a linear polymer resembling a polycondensate will be formed whereas for $r >> 1$ a weakly branched vinyl polymer is expected. NMR experiments allow for the determination of reactivity ratio r.

Introduction

The degree of branching, DB, is one of the most important molecular parameters of hyperbranched polymers since it determines many physical properties of the polymers, such as viscosity in melt or solution. Hawker et al.[1] proposed a definition for the degree of branching of hyperbranched polymers formed in the polycondensation of AB_2-type monomers,

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

where "units" mean reacted monomer units and the "dendritic units" are the branchpoints. The "focal point" or "core" of the molecule is not taken into account; i.e., it is not counted as a unit at all. This definition has been frequently used in order to determine DB from NMR spectra of hyperbranched polymers made by polycondensation of AB_2-type monomers. Here, the monomer unit carrying the unreacted A function is regarded as the "core".

Recently, Fréchet and co-workers[2−4] reported a new way of forming hyperbranched polymers and named it self-condensing vinyl polymerization (SCVP). This reaction involves a monomer of AB* type, in which B* is a group capable of initiating the polymerization of vinyl groups, A ("inimer"). The chain initiation is the addition of an initiating B* group to the vinyl group of another monomer forming a dimer with two active sites and one double bond. Both the initiating center, B*, and the newly created propagating center, A*, can react with the vinyl group of another molecule (monomer or polymer) in the same way with rate constants k_B and k_A, respectively. The initiation step for a simple AB* monomer, i.e. *p*-(chloromethyl)styrene is shown in Scheme 1 together with a schematic representation of the further steps up to the formation of tetramers. In order to find a short representation for the various groups in the hyperbranched polymers, we use capital letters for unreacted active centers (A*, B*) and lowercase letters for reacted ones (a, b). "A" always denotes the vinyl group. It is seen that beside the unit carrying the vinyl group (A−b) there can be four different monomeric units in a polymer: terminal (T = ∿A*−B*), branched (B = ∿a−b<), and two different linear ones: one resembles a repeat unit of a polycondensate (L_c = ∿A*−b∿) and one a monomer unit of a vinyl polymer (L_v = ∿a(B*)∿). The chemical nature of these units is shown in Scheme 2 using one possible hexamer of *p*-(chloromethyl)styrene as an example.

Interestingly, only one out of the five tetrameric isomers (**4d**) is branched. A further extension of Scheme 1 shows that there are four (out of 12) branched pentamers and 16 (out of 32) branched hexamers, one hexamer having two branchpoints. In further polymerization steps the fraction of branched structures increases and finally hyperbranched polymers are generated. Ideally, all molecules possess exactly one double bond, and the number of active centers (and thus of groups which can be functionalized) is equal to the degree of polymerization. Thus, SCVP presents an attractive alternative to dendrimers, combining many functional groups in a very compact molecule with a convenient one-pot synthesis.

From Scheme 3 the following important rules of SCVP can be deduced:

1. Addition of a vinyl group to a terminal group, T = (A*B*), leads to one of the two linear units. If a B* center adds, it will lead to a condensation-type unit, L_c = (A*b) (reactions 1 and 1a); if an A* center adds, it will result a vinyl-type unit, L_v = (aB*) (reactions 2 and 2a).

2. Addition of a vinyl group to any linear unit (reactions 3 and 4) leads to a branch point, B = (ab).

3. Upon addition to any active center, the vinyl group of a polymer is always converted to an L_c = (A*b) group

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[†] Part 1. Preceding paper in this issue.

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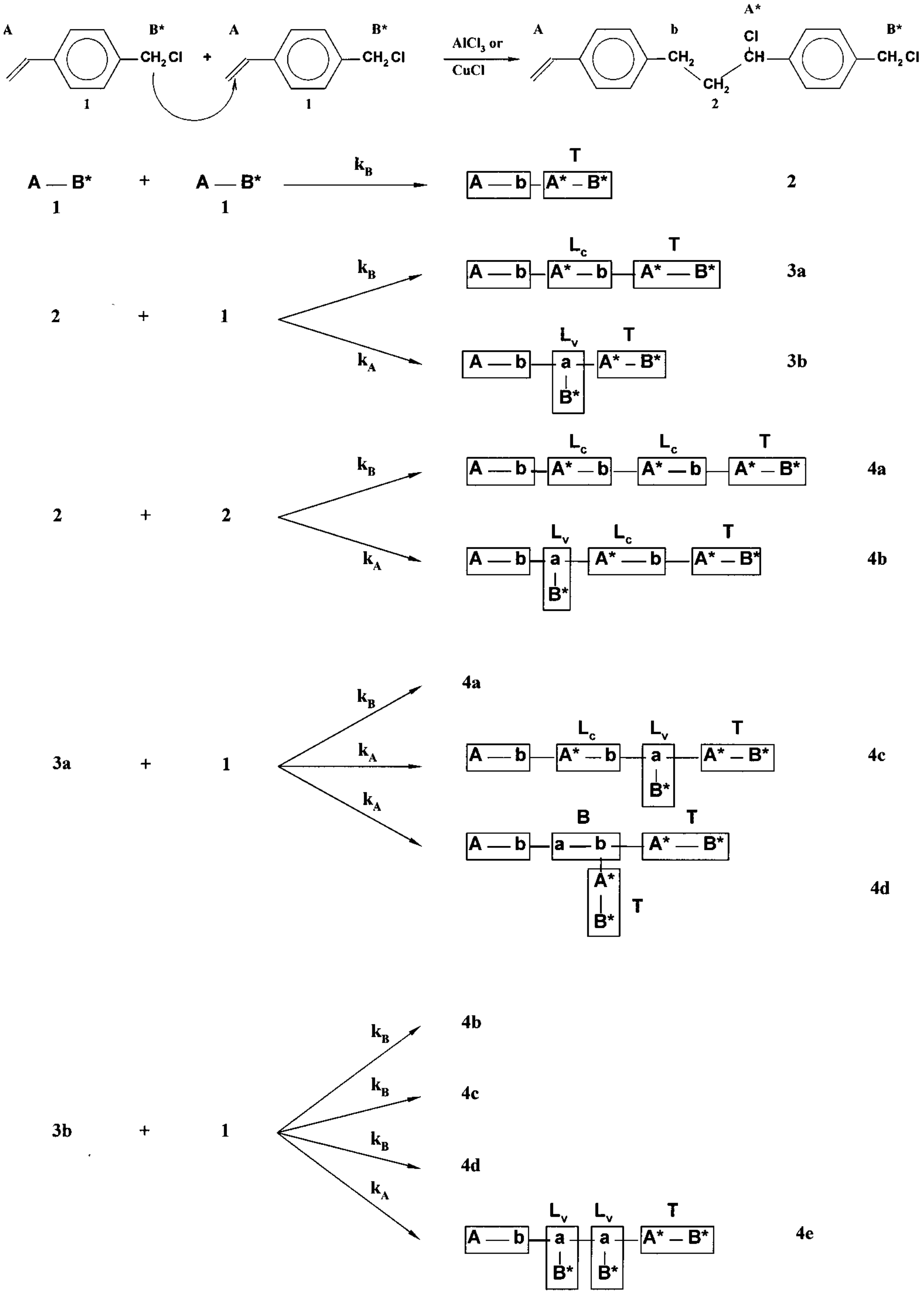
Scheme 1. Initial Steps in Self-Condensing Vinyl Polymerization



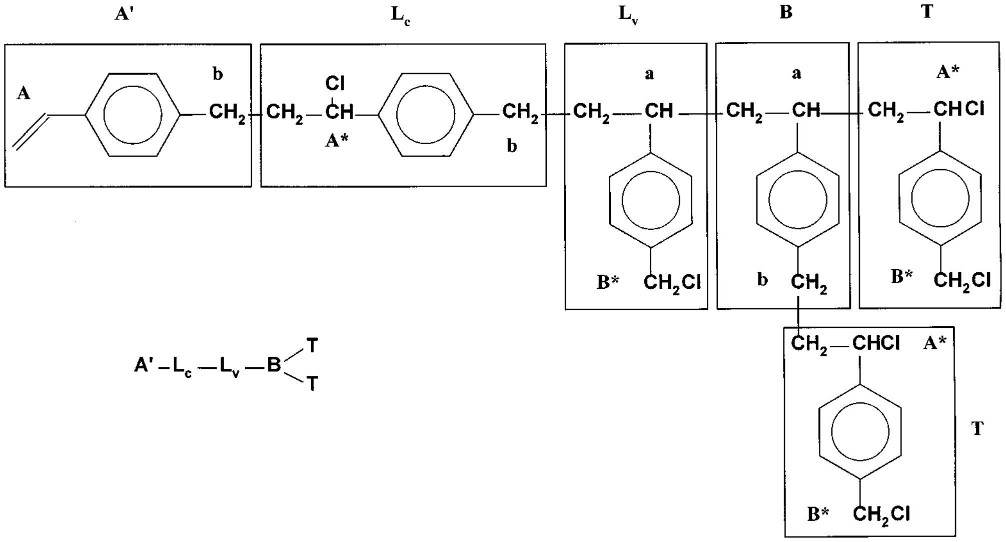
(reactions 1–4), whereas addition of a monomer, AB*, always leads to a terminal group, T = (A*B*) (reactions 1a–4a).

4. Vinyl addition converts an initiating B* center into a propagating A* center (reactions 1 and 3) whereas propagating A* centers remain unchanged (reactions 2 and 4).

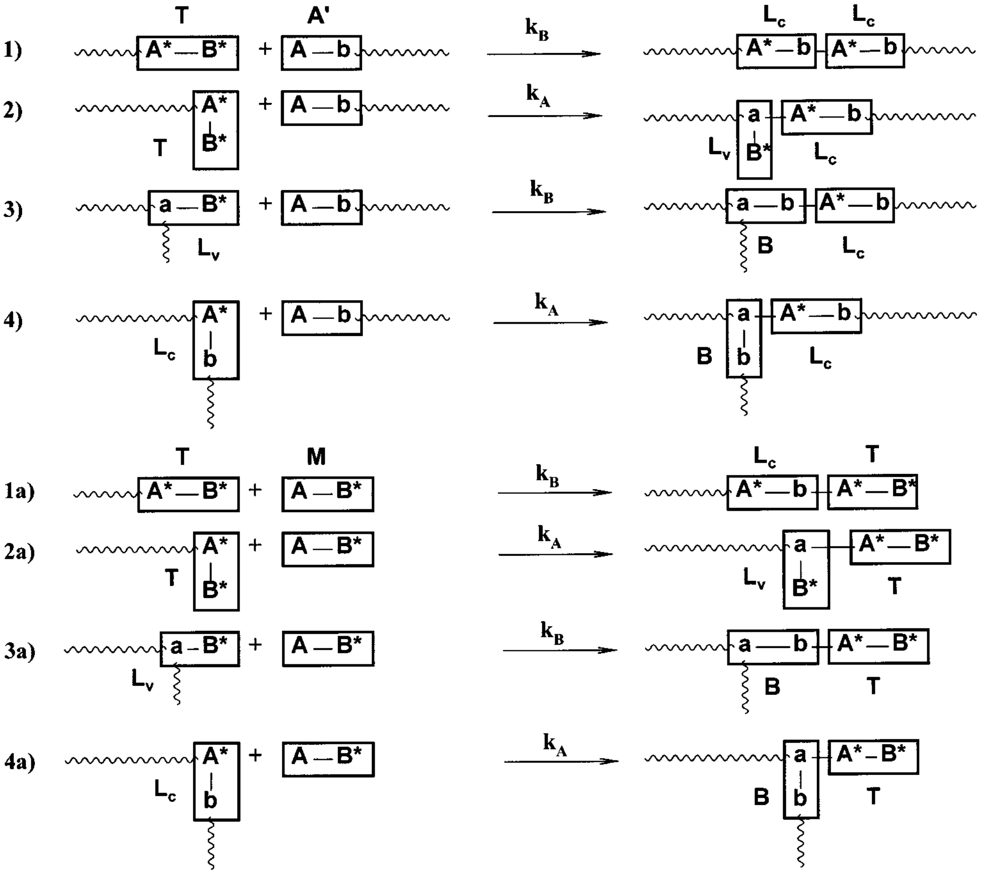
In Part 1 of this series,[5] we analyzed the general features of SCVP, especially the kinetics and the molecular weight distribution (MWD) and its moments of the polymers formed and we compared it to Flory's[6] and our own results for the polycondensation of monomers of AB_2 structure. It was found that both processes lead to different kinetics and MWD's. In this publication, we calculate DB and the fractions of various structural units of the polymers generated by both SCVP and AB_2 polycondensation as a function of conversion. Since there are two different active centers in SCVP, i.e. A* and B*, the effect of nonequal reactivities on the degree of branching will be also discussed.

Definitions of the Degree of Branching. The definition of the degree of branching given by Hawker at al.[1] does not take into account that for a linear polymer DB should be zero (it is unity for a perfect dendrimer). According to that equation all linear oligomers in Scheme 1 would have DB > 0. For example, the linear dimer **2** would have DB = 1 and the linear trimers **3** would have DB = $^1/_2$. Since a linear polymer has one initial group (or "core"; not counted) and one terminal group, this error can be avoided by subtracting one terminal group from both the numerator and the denominator[12]

Scheme 2. Example of a Branched Hexamer of *p*-(Chloromethyl)styrene



Scheme 3. Reactions Leading to Linear (1 and 2) and Branched (3 and 4) Structures



$$
\mathrm{DB} = \frac{(\text{number of branched units}) + (\text{number of terminal units}) - 1}{(\text{total number of units}) - 1}
$$

For a polymer with an *f*-functional core, *f* terminal groups should be subtracted. This equation which is valid for single molecules can be easily checked with the trimers and tetramers shown in Scheme 1. All oligomers have DB = 0, except the branched oligomer **4d** which has DB = 1. The hexamer in Scheme 2 has DB = 3/5.

From the topology of branched systems with trifunctional branchpoints, for any given molecule the number of branched units is equal to the number of terminal unit minus one[7]

$$
(\text{number of branched units}) = (\text{number of terminal units}) - 1
$$

This follows from the fact that a linear chain has one initial group (not counted) and one terminal group and addition of a new branch always adds one branchpoint and one terminal group. Again, *f* terminal groups have to be subtracted if the polymer has an *f*-functional core. Thus, eq 1 can be further simplified to

$$
\mathrm{DB} = \frac{2(\text{number of branched units})}{(\text{total number of units}) - 1} \qquad (1)
$$

Thus, DB can be regarded as the ratio of branched units in a hyperbranched polymer to those in a perfect dendrimer. Since we are interested in the average value of DB for an ensemble of *N* molecules, *N* terminal groups have to be taken into account. In order to investigate the dependence of $\overline{\mathrm{DB}}$ on conversion, it is important to exclude the residual monomer from the calculation, since we are only interested in the polymer molecules. Since the "total number of molecules" also contains the number of residual monomer molecules, we must subtract this number from the denominator. In the numerator, the monomers are neither counted as branched nor as terminal; thus, they are excluded automatically. Accordingly, we propose the following modified equation for the degree of branching (eq 1):

$$\overline{\mathrm{DB}} = \frac{2(\text{number of branched units})}{(\text{total number of units}) - (\text{number of monomers}) - N} \qquad (2)$$

Again, it should be stressed that the total number of units does not include the "core" which in SCVP is the monomer unit carrying the vinyl group (A−b). It can be argued that the degree of branching should only reflect the fraction of branched but not of terminal units. As $\overline{\mathrm{DB}}$ has already been defined in a way that it is unity for a perfect dendrimer, we define a new parameter, the fraction of branchpoints[13]

$$\overline{\mathrm{FB}} = \frac{\text{number of branched units}}{(\text{total number of units}) - (\text{number of monomers})} \qquad (3)$$

At high conversions corresponding to high degrees of polymerization, the effect of the subtracted terminal group in the denominator will be negligible. Thus, at full conversion, $\overline{\mathrm{FB}}_\infty = \overline{\mathrm{DB}}_\infty/2$, and for a perfect dendrimer, $\overline{\mathrm{FB}}_\infty = 0.5$.

Below, we derive the averages of the degree of branching and of the fraction of branchpoints for the mixture of hyperbranched polymers formed in both SCVP and AB_2 polycondensations as a function of conversion of reactive groups A.

Degree of Branching for SCVP

Structural Units in Hyperbranched Polymers. In order to determine the degree of branching we have to examine the various kinds of structural units with 0, 1, or 2 different reactive groups (see Schemes 1 and 2) and their fractions at a given conversion.

Let us use the following notation for the various structural units and their fractions in the reaction mixture (relative to the initial monomer concentration, M_0) in the hyperbranched polymer. It should be noted that the symbols *M* and *A* mean *fractions* in this article whereas they were used for *concentrations* in Part 1.[5] Fractions are derived from concentrations by dividing by the initial monomer concentration, M_0. Capital letters will be used for unreacted active centers (A*, B*) whereas lowercase letters (a, b) will be used for reacted ones.

M is the fraction of (residual) monomer.

A is a the fraction of vinyl (i.e., A∿∿) groups, including the vinyl group of the monomer, AB*. Since each molecule should have exactly one vinyl group, this is identical to the fraction of molecules present in the system, relative to the initial number of molecules

$$A = 1 - x$$

where *x* is the conversion of vinyl groups (not of monomer molecules!).

$A' = A - M$, is the fraction of vinyl groups of polymers (i.e. excluding monomer). This is identical to the fraction of polymer molecules in the system.

A^*, B^*, and $(B^*)' = B^* - M$ symbolize the fractions of *active* A* and B* groups, respectively, where only polymer molecules are counted in $(B^*)'$. Obviously

$$A^* + B^* = 1 \qquad (4)$$

a and *b* are the fractions of *reacted* A* or B* groups, i.e. they are no more active. Since a and b units are formed in reactions of A* or B* with A groups

$$a + b = 1 - A = x \qquad (5)$$

As was stated above, upon addition of a vinyl group, a B* group will form a new A* group (and an inactive b group), whereas an A* group after adding to a vinyl group will regenerate an A* group (and an inactive b group). Thus, during polymerization B^* must decrease from the initial value of unity, whereas A^* increases accordingly from the initial value zero. This leads to the relation

$$\mathrm{A}^* = \mathrm{b} \qquad (6)$$

which in conjunction with eqs 4 and 5 leads to

$$B^* = a + A \text{ and } (B^*)' = a + A' \qquad (7)$$

and, at full conversion ($A = A' = 0$)

$$B^*_\infty = (B^*)'_\infty = a_\infty \qquad (7')$$

Next we examine the four different kinds of monomer units (which always consist of two structural groups):

$L_c = (A^*b)$ is the fraction of *linear units,* ∿∿A*−b∿∿, formed by reaction 1 in Scheme 3 (i.e., addition to a terminal B* group), resembling linear polycondensates.

$L_v = (aB^*)$ is the fraction of the *linear units* with a pendant B* group, ∿∿a(B*)∿∿, formed by reaction 2 (addition to a terminal B* group), resembling linear vinyl polymers. Since they just have a *pendant* side group, these are *not* branchpoints. The existence of two different kinds of linear units is an important difference to AB_2 polycondensates.

$B = (ab)$ is the fraction of real *branchpoints,* ∿∿a−b<, formed from reaction 3 (addition to a pendant B* group) or from reaction 4 (addition to an in-chain A* group).

$T = (A^*B^*)$ is the fraction of *terminal units,* ∿∿A*−B*, formed by adding the vinyl group of the monomer to any active center (reactions 1a−4a).

The following relations hold for the fractions of the various structural units:

$$B + L_v = (ab) + (aB^*) = a \qquad (8a)$$

$$L_c + T = (A^*b) + (A^*B^*) = A^* \qquad (8b)$$

$$L_v + T + M = (aB^*) + (A^*B^*) + (AB^*) = B^* \qquad (8c)$$

Degree of Branching. In order to calculate $\overline{\mathrm{DB}}$ and $\overline{\mathrm{FB}}$, we use eqs 2 and 3. In accordance with eqs 1 and 2, we must subtract one terminal group per polymer for $\overline{\mathrm{DB}}$. Since each polymer molecule has exactly one vinyl group, this is equivalent to subtracting the fraction

Scheme 4. Kinetic Scheme for the Formation of Various Structural Units in SCVP

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

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

$$A^*B^* + A' \xrightarrow{k_B} 2A^*b \qquad \text{(reaction 1)}$$

$$A^*B^* + A' \xrightarrow{k_A} aB^* + A^*b \qquad \text{(reaction 2)}$$

$$aB^* + A' \xrightarrow{k_B} ab + A^*b \qquad \text{(reaction 3)}$$

$$A^*b + A' \xrightarrow{k_A} ab + A^*b \qquad \text{(reaction 4)}$$

$$A^*B^* + M \xrightarrow{k_B} 2A^*b \qquad \text{(reaction 1a)}$$

$$A^*B^* + M \xrightarrow{k_A} aB^* + A^*B^* \qquad \text{(reaction 2a)}$$

$$aB^* + M \xrightarrow{k_B} ab + A^*B^* \qquad \text{(reaction 3a)}$$

$$A^*b + M \xrightarrow{k_A} ab + A^*B^* \qquad \text{(reaction 4a)}$$

of vinyl groups, i.e., $A' = A - M$. Thus, the fraction of *all* units in the *polymer* is 1- $M - A' = 1 - A$. Since we do not want to consider the initial group ("core"), we have to subtract its fraction, A', another time in the denominator (this is necessary only once for $\overline{\mathrm{FB}}$). Thus, the degree of branching and the fraction of branchpoints are expressed in terms of fractions of monomer units:

$$\overline{\mathrm{DB}} = \frac{2B}{1 - M - 2A'} \tag{9}$$

$$\overline{\mathrm{FB}} = \frac{B}{1 - A} = \frac{B}{x} \tag{10}$$

Whereas M and A' have been calculated in Part 1 of this series,[5] we now have to calculate the fraction of branched units, B, and insert all into eqs 9 and 10. Since it is helpful for understanding the experimental results, we also calculate the fractions of the other structural units.

Kinetic Differential Equations. The differential equations which are necessary to calculate the fractions of all structural units are derived from the kinetic scheme (Scheme 4) which represents the reactions in Scheme 3. We first assume that A* and B* centers have equal reactivities ($k_A = k_B = k$):

$$\frac{\mathrm{d}B^*}{\mathrm{d}t} = -kM_0B^*A \tag{11}$$

$$\frac{\mathrm{d}A^*}{\mathrm{d}t} = kM_0B^*A \tag{12}$$

$$\frac{\mathrm{d}b}{\mathrm{d}t} = kM_0A^*A \tag{13}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\mathrm{d}(A^*B^*)}{\mathrm{d}t} = kM_0(M - 2AT) = kM_0[(A^*B^*) - (aB^*)] \tag{14}$$

$$\frac{\mathrm{d}L_v}{\mathrm{d}t} = \frac{\mathrm{d}(aB^*)}{\mathrm{d}t} = kM_0A(T - L_v) = kM_0A[(A^*B) - (aB^*)] \tag{15}$$

The initial conditions of eqs 11−15 are

$$B^*_0 = 1, \quad A^*_0 = T_0 = b_0 = 0, \quad M(t = 0) = A(t = 0) = 1$$

Dividing eqs 11−15 by the differential eq 16 for conversion of vinyl groups, x, given in the preceding paper[5]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM_0(1 - x) \tag{16}$$

and solving the resulting differential equations we obtain the corresponding fractions which are given in Table 1. The missing fractions are derived from eq 8. Interestingly, the fractions of the various monomer units are identical to the products of the fractions of the active or reacted centers of which they consist, e.g., $M = (AB^*) = A^* \cdot B^*$ or, $L_v = (aB^*) = a \cdot B^*$.

Substituting the expressions in Table 1 into eqs 9 and 10, one finally gains the degree of branching and the fraction of branchpoints as a function of conversion:

$$\overline{\mathrm{DB}} = \frac{2(1 - \mathrm{e}^{-x})(x - 1 + \mathrm{e}^{-x})}{1 - (1 - x)(2 - \mathrm{e}^{-x})} \tag{17}$$

$$\overline{\mathrm{FB}} = \frac{(1 - \mathrm{e}^{-x})(x - 1 + \mathrm{e}^{-x})}{1 - (1 - x)\mathrm{e}^{-x}} \tag{18}$$

At full conversion of double bonds ($x = 1$), the values of $\overline{\mathrm{DB}}$, and $\overline{\mathrm{FB}}$ are respectively

$$\overline{\mathrm{DB}}_\infty = 2\mathrm{e}^{-1}(1 - \mathrm{e}^{-1}) \approx 0.465$$

$$\overline{\mathrm{FB}}_\infty = \overline{\mathrm{DB}}_\infty/2 \approx 0.233$$

Figure 1 shows the dependences of $\overline{\mathrm{DB}}$ and $\overline{\mathrm{FB}}$ on the conversion of vinyl groups, x, in comparison to the values for AB_2 polycondensation (for derivation, see below). At conversions $x < 0.9$, the value of $\overline{\mathrm{DB}}$ is higher for SCVP than for AB_2 polycondensation, whereas at full conversion it is somewhat lower. As will be shown later, this is mainly due to the nonequal distribution of A* and B* chain ends. Under conditions where $A^*_\infty = B^*_\infty$, we find $\overline{\mathrm{DB}}_\infty = 0.5$ for SCVP.

Dependence of Fractions of Structural Units on Conversion. Figure 2 (top) shows the dependence of the fractions of monomer and of the various active and reacted centers on conversion of vinyl groups. Fractions which include monomer are shown as dotted lines. Although both A and M decrease with conversion, the fraction of polymer vinyl groups, $A' = A - M$, passes a maximum, because initially there is no polymer. The maximum value of A′ indicates that at ≈44% conversion ≈20% of all polymer units are vinyl groups which are not counted for the calculation of $\overline{\mathrm{DB}}$. Since the fraction of terminal groups which should be subtracted in the calculation of $\overline{\mathrm{DB}}$ is equal to A′, i.e. ca. 20%, neglecting this term can bring about large errors in $\overline{\mathrm{DB}}$.

As was expected above, the fraction of propagating A* centers increases and that of initiating B* centers decreases. The fraction of initiating centers in polymers, $(B^*)'$, must again increase because no polymer is present initially. The fraction of A* centers grows faster than that of B* centers because the latter are partially converted to A* centers. As a consequence, the fraction of reacted "b" groups increases faster than that of "a" groups. Finally we find a nonequal distribution of active and reacted chain ends, respectively (cf. Table 1):

$$A^*_\infty = b_\infty \approx 63\% \qquad a_\infty = B^*_\infty \approx 37\%$$

$$A^*_\infty/B^*_\infty \approx 1.72$$

Figure 2 (bottom) shows the fractions of the four different monomeric units as a function of conversion. The dependences can be understood from Schemes 2 and 3. Initially, the fraction of terminal units, $T = (A^*B^*)$,

Table 1. Structural Units and Their Fractions in Self-Condensing Vinyl Polymerization

unit	type	fraction	fraction at $x = 1$
M	monomer	$(1 - x)e^{-x} = A \cdot B^*$	0
A	vinyl group	$1 - x$	0
$A' = A - M$	vinyl group in polymer	$(1 - x)(1 - e^{-x}) = (1 - x)(1 - B^*)$	0
a	reacted A* group	$x - 1 + e^{-x} = x - b = x - A^*$	$e^{-1} = 0.368$
A^*	propagating group	$1 - e^{-x} = 1 - B^* = b$	$1 - e^{-1} = 0.632$
b	reacted B* group	$1 - e^{-x} = 1 - B^* = A^*$	$1 - e^{-1} = 0.632$
B^*	initiating group	$e^{-x} = 1 - b$	$e^{-1} = 0.368$
$(B^*)' = B^* - M$	initiating group in polymer	$x\,e^{-x} = xB^*$	$e^{-1} = 0.368$
$L_c = (A^*b)$	linear ("polyester" type)	$(1 - e^{-x})^2 = A^* \cdot b$	$(1 - e^{-1})^2 = 0.400$
$L_v = (aB^*)$	linear (vinyl type)	$e^{-x}(x - 1 + e^{-x}) = a \cdot B^*$	$e^{-2} = 0.135$
$T = (A^*B^*)$	terminal group	$e^{-x}(1 - e^{-x})\ A^* \cdot B^*$	$e^{-1}(1 - e^{-1}) = 0.233$
$B = (ab)$	branchpoint	$(x - 1 + e^{-x})(1 - e^{-x}) = a \cdot b$	$e^{-1}(1 - e^{-1}) = 0.233$

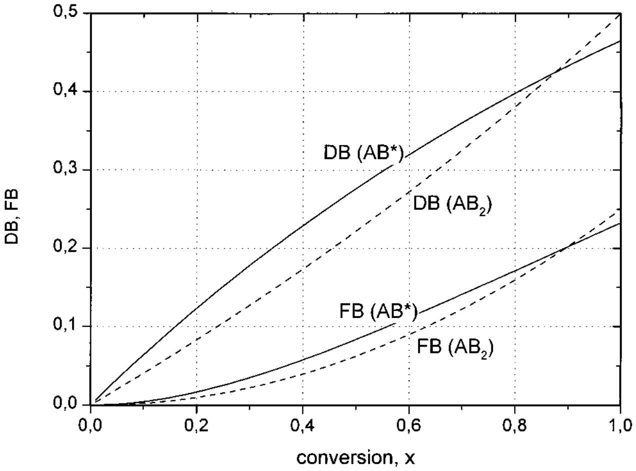


Figure 1. Dependence of the degree of branching, $\overline{\mathrm{DB}}$, and the fraction of branchpoints, $\overline{\mathrm{FB}}$, on conversion of A groups, x, for SCVP (AB*) and for polycondensation of AB_2 monomers.

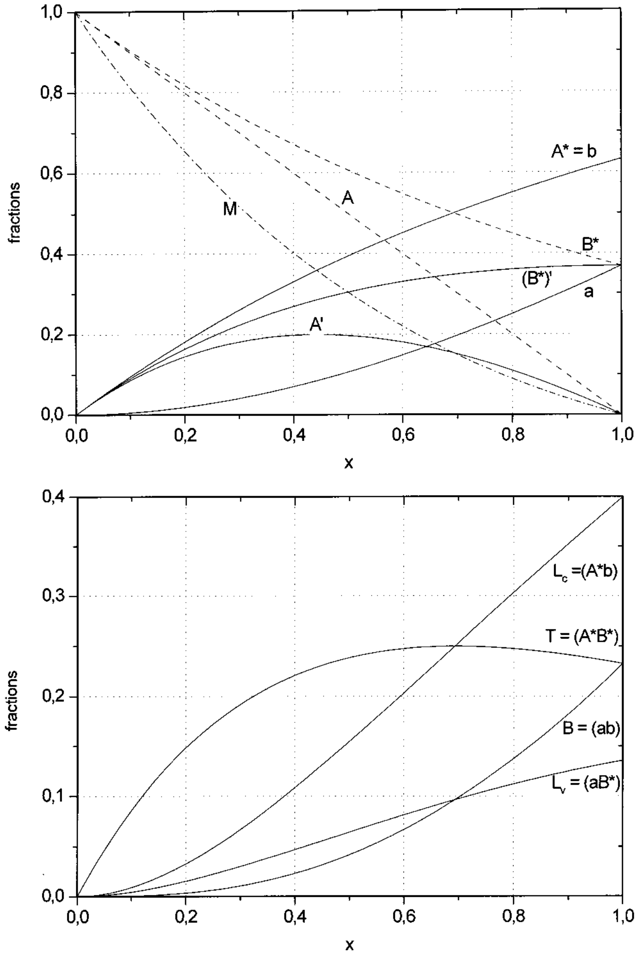


Figure 2. Dependence of the fractions of monomer and of various structural units on conversion of vinyl groups in SCVP (for details, see Table 1). Broken lines are used for fractions which include the monomer.

grows fastest since the concentration of monomer is high and reactions 1a–4a prevail. However, the final fraction is only 23%. The fraction of polycondensate-type linear units, $L_c = (A^*b)$, is second and finally becomes the largest (40%) because these units are formed in all reactions 1–4 and reaction 1a. Even two of them are formed in reaction 1. Third are linear vinyl-type units, $L_v = (aB^*)$ which finally are least (13%) and only make up 1/3 of L_c units because they are only formed in reactions 2 and 2a. The fraction of branched units, $B = (ab)$, only becomes important at higher conversions since these units are formed from both kinds of linear units, L_c and L_v, which have little importance at low conversion. Finally, $B = T = 23\%$.

Degree of Branching for AB_2 Polycondensation

Again, it is necessary to find the fractions of various structural units in the polymer mixture formed. In order to discriminate these different units, let A and B denote the unreacted groups and a and b the reacted groups, respectively. The fractions of the various units are easily derived by a probabilistic approach. The various monomeric units present in the reaction system and their fractions are listed in Table 2 and their dependence on conversion of A groups is shown in Figure 3.[14] Similar to SCVP, the maximum fraction of "core" units ($A' = AbB + Ab_2$) and consequently the fraction of one terminal unit which should be subtracted both in the numerator and in the denominator is ≈22% at ≈46% conversion.

Among the various monomeric units, $B = ab_2$ is a branchpoint, and $T = aB_2$ is a terminal unit. It is seen that there is only one kind of linear unit, i.e. $L = abB$. The focal unit is represented by AbB (half reacted) and Ab_2 (fully reacted). The degree of branching and the fraction of branchpoints are expressed by introducing their fractions into eq 2:

$$\overline{\mathrm{DB}} = \frac{2ab_2}{1 - M - 2A'} = \frac{x^3/2}{1 - (1 - x)(1 + x - x^2/4)} \qquad (20)$$

$$\overline{\mathrm{FB}} = \frac{ab_2}{x} = x^2/4 \qquad (21)$$

Figure 1 shows the degree of branching as well as the fraction of branchpoints as a function of conversion. As was stated above, the values for the polymers resulting from SCVP are slightly different. When all A groups in the reaction system are consumed ($x = 1$ or $\alpha = 0.5$), half of the monomeric units are in linear segments and

Table 2. Structural Units and Their Fractions in AB_2 Polycondensation

monomeric unit	type	probability	fraction	fraction at $x = 1$
$AB_2 = M$	monomer	$(1 - x)(1 - \alpha)^2$	$(1 - 2\alpha)(1 - \alpha)^2 = (1 - x)(1 - x/2)^2$	0
AbB	"core", partially reacted	$2(1 - x)(1 - \alpha)\alpha$	$2\alpha(1 - 2\alpha)(1 - \alpha) = x(1 - x)(1 - x/2)^2$	0
Ab_2	"core", fully reacted	$(1 - x)\alpha^2$	$(1 - 2\alpha)\alpha^2 = (1 - x)x^2/4$	0
$T = aB_2$	terminal	$x(1 - \alpha)$	$2\alpha(1 - \alpha)^2 = x(1 - x/2)^2$	0.25
L = abB	linear	$2x\alpha(1 - \alpha)$	$4\alpha^2(1 - \alpha) = x^2 (1 - x/2)$	0.5
$B = ab_2$	branched	$x\alpha^2$	$2\alpha^3 = x^3/4$	0.25
A	A groups		$AB_2 + AbB + Ab_2$	0
$A' = A - M$	"core"		$AbB + Ab_2$	0

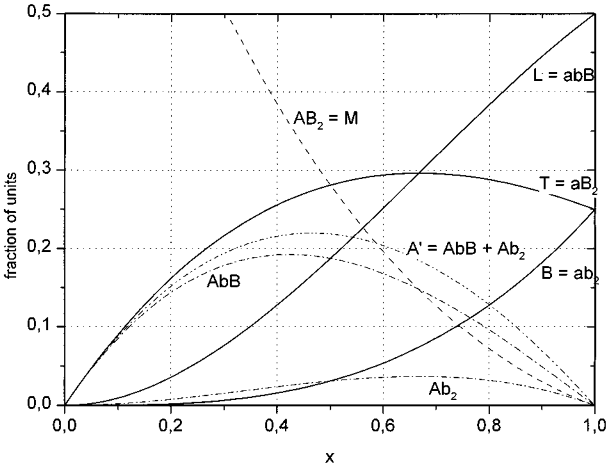


Figure 3. Dependence of the fractions of monomeric units on conversion of A groups in AB_2 polycondensation (for details, see Table 2).

one-quarter each become branchpoints and terminal units, leading to $\overline{DB}_\infty = 0.5$ and $\overline{FB}_\infty = 0.25$.[12] A "coefficient of branching" with a somewhat different definition but the same limiting value of 0.5 had already been derived by Flory.[6]

In the polycondensation of 3,5-bis(trimethylsiloxy)-benzoyl chloride, Hawker et al.[1] and Wooley et al.[7] found $\overline{DB} = 0.55-0.6$. Malström et al.[8] found $\overline{DB} = 0.7-0.8$ for hyperbranched aliphatic polyesters. These values, which were determined by NMR, are considerably higher than the maximum value, $\overline{DB}_\infty = 0.5$, predicted by theory. This deviation could stem from the neglection of one terminal unit and of unreacted monomer in Hawker's definition of the degree of branching which become significant at incomplete conversions. Also, experimental deficiencies cannot be ruled out.[15]

Degree of Branching for SCVP With Non-Equal Rate Constants

As was discussed in the preceding paper,[5] in SCVP systems the reactivities of initiating and propagating centers, A* and B*, generally are different from each other. Thus, it is important to know the effect on the degree of branching of the resulting polymers. The derivation of the following results as well as full tables and plots of the various fractions of structural units as a function of vinyl group conversion and reactivity ratio, $r = k_A/k_B$, are given as Supporting Information (Appendix 1 and 2).

Degree of Branching. Table 3 contains the expressions for the structural units necessary to calculate the degree of branching and the fractions of branchpoints using eqs 8−10. From these fractions, the degree of branching can be calculated as a function of reactivity ratio, r, and conversion, x. Figure 4 shows a monotonous increase of $\overline{DB}$ with conversion for all values of r; however, the initial slopes as well as the final values differ. At all conversions, the highest values of $\overline{DB}$ are found at $r \approx 2.59$.

The effect of ratio r on $\overline{DB}_\infty$ as well as on the fractions of the structural units at full conversion is seen in Table 3 and Figure 5. It is seen that at $r \approx 2.59$ the degree of branching has a maximum value of $\overline{DB}_\infty = 0.5$, similar to AB_2 polycondensates. A maximum is found at the same value of r for the fractions of branchpoints and terminal units, B and T, respectively, whereas the fraction of "vinyl-type" linear units, L_v, increases and that of "polycondensate-type" linear units, L_c, decreases with r. Indeed, exactly at this ratio all four structural units have equal fractions of 25% and $A^*_\infty = B^*_\infty = 50\%$. In order to understand this peculiar behavior it is necessary to investigate the effect of r on the fractions of structural units.

Dependence of Fractions of Structural Units on Reactivity Ratio, *r*. Table 3, Figure 6, and plots of the various structural units as a function of conversion and r (see Supporting Information, Appendix 2) show the following dependences.

The fraction of initiating centers, B^* (Figure 6), always decreases with conversion but the decrease is faster for lower ratios r. At $r \approx 2.59$ the final value is exactly 50% (eq 22a at $B^*_\infty = 0.5$ results $r = 1/(2 \ln 2 - 1) \approx 2.589$). Consequently, $B^*_\infty = A^*_\infty = b_\infty$ at this ratio. The fraction of initiating centers in polymers, $(B^*)'$, increases with conversion but shows a maximum for $r < 2.59$.

The fraction of vinyl-type linear units, $L_v = (aB^*)$, increases with $r = k_A/k_B$ since they are only formed via reaction 2 (with rate constant k_A), whereas the fraction of polycondensate-type linear groups, $L_c = (A^*b)$, decreases. Here, the effect of ratio r is not as strong since these units are formed from both B* and A* centers (with rate constants k_A and k_B).

The fraction of branchpoints, $B = (ab)$, increases with r in a similar way as $\overline{DB}$ (however, the slopes increase with conversion). The highest values of B are found at $r \approx 2.59$.

For the fraction of terminal groups, $T = (A^*B^*)$, there is a maximum of $T_{max} = 0.25$ at a certain conversion, x_{max} ($x_{max} \approx 0.5$ for $r = 0.025$, $x_{max} \approx 0.7$ for $r = 1$, and $x_{max} = 1$ for $r \approx 2.59$). Only for $r > 2.59$, this maximum is not reached. As was stated above, the maximum is due to the fact that terminal units are formed by addition of monomer the concentration of which decreases with conversion.

Experimental Determination of Reactivity Ratio *r*. It is possible to determine the ratio r by measuring the fractions of the active centers, A^* or B^*, with a suitable method (e.g. NMR). From Table 3 (see also eq 32 in Part 1) we see that

$$r = \frac{1 - x - e^{-z}}{1 - z - e^{-z}} = \frac{1 - x - B^*}{1 + \ln B^* - B^*} \tag{22}$$

or, at full conversion of vinyl groups that,

Table 3. Fractions of Various Species and Structural Units in SCVP and Degree of Branching, $\overline{DB}$, for Nonequal Rate Constants of Initiating and Propagating Centers[a]

		fraction at full conversion			
unit	fraction	$r = 0.025$	$r = 1$	$r = 2.59$	$r = 40$
z	value obtained by solution of eq 32, Part 1:[20] $x = 1 - r(1 - z) - (1 - r)e^{-z}$	2.980	1.000	0.692	0.208
M	$(1 - x)e^{-z}$	0	0	0	0
A	$1 - x = r(1 - z) + (1 - r)e^{-z}$	0	0	0	0
$A' = A - M$	$(1 - x)(1 - e^{-z})$	0	0	0	0
a	$x - 1 + e^{-z}$	0.051	0.368	0.5	0.812
$A^* = b$	$1 - e^{-z}$	0.949	0.632	0.5	0.188
B^*	e^{-z}	0.051	0.368	0.5	0.812
$(B^*)' = B^* - M$	xe^{-z}	0.051	0.368	0.5	0.812
$T = (A^*B^*)$	$(1 - e^{-z})e^{-z}$	0.048	0.233	0.25	0.153
$L_v = (aB^*)$	$(x - 1 + e^{-z})e^{-z}$	0.003	0.135	0.25	0.659
$L_c = (A^*b)$	$(1 - e^{-z})^2$	0.901	0.400	0.25	0.035
$B = (ab)$	$(x - 1 + e^{-z})(1 - e^{-z})$	0.048	0.233	0.25	0.153
$\overline{DB}$	see eq. 9	0.096	0.465	0.5	0.306

[a] Reactivity ratio, $r = k_A/k_B$.

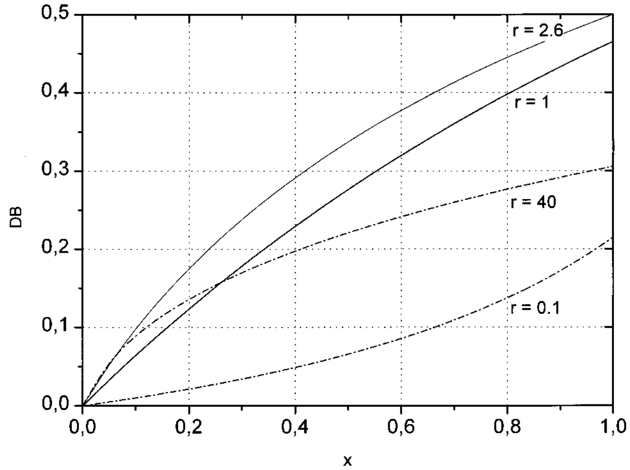


Figure 4. Dependence of the degree of branching, $\overline{DB}$, on conversion of vinyl groups for SCVP at various reactivity ratios, $r = k_A/k_B$.

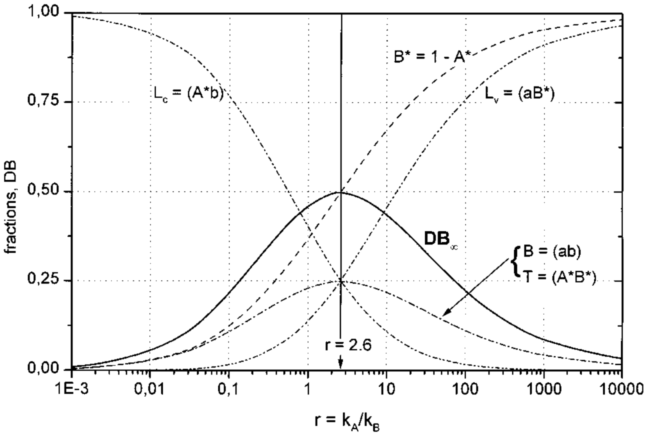


Figure 5. Fractions of structural units and degree of branching, $\overline{DB}_\infty$, as a function of $r = k_A/k_B$ for full conversion.

$$r = \frac{e^{-z_\infty}}{e^{-z_\infty} + z_\infty - 1} = \frac{B^*_\infty}{B^*_\infty - \ln B^*_\infty - 1} \qquad (22a)$$

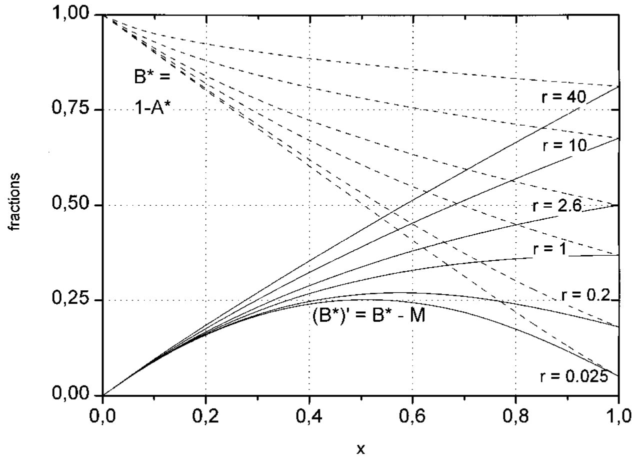


Figure 6. Fractions of active centers $B^* = 1 - A^*$ (including monomer) and $(B^*)' = B^* - M$ (polymer only) as a function of conversion for various reactivity ratios, $r = k_A/k_B$.

As an example, in the self-condensing atom transfer radical polymerization of 2-(2-bromopropionyloxy)ethyl acrylate, Matyjaszewski et al.[10c] were able to distinguish by ^{1}H NMR between $\mathbf{CH_3}$–CH(Br)COOR groups (B*, 1.85 ppm) and the reacted $\mathbf{CH_3}$–CH(COOR)(CH_2–) groups (b, 1.1–1.3 ppm). B^* was found to be larger than expected for $r = 1$ ($B^*_\infty = 0.57$ instead of 0.37), indicating $r \approx 4.3$. It is unlikely to expect such a big reactivity difference between bromine atoms on the secondary carbon atoms preceded by methyl and longer alkyl groups which are identical from the point of view of electronic effects: CH_3-CH(COOR)–Br vs ⁓CH_2-CH-(COOR)–Br. However, this process and many other new controlled polymerization processes (e.g., group transfer and cationic polymerizations) are based on the dynamic equilibration between active (radical or ionic) and dormant (covalent) species. It may happen that the deactivation process of the formed propagating centers, A*, is not fast enough and a linear growth via vinyl addition occurs several times before the deactivation takes place. Thus, the rate constants used in this article should be regarded as apparent ones. The apparent increase of A* reactivity leads to preferential formation of L_v units and enhanced proportion of B* over A* units. Thus, although chemically both A* and B* may have very similar *intrinsic* reactivities ($k_A \approx k_B$), the slow deactivation process of A* may *apparently* consume B* faster.

Figure 5 clearly demonstrates that for $r << 2.59$ or $r >> 2.59$ polymers with predominant linear units, L_c or L_v, respectively, are formed at the expense of branched and terminal ones (see next paragraph). Thus, the maximum branching is observed when $L_c = L_v$. This does not happen at $r = 1$, since $L_c = 3L_v$ due to the continuous conversion of L_v to L_c units in the reaction with end groups. At the ratio $r \approx 2.59$ this value somehow self-corrects unfavorable statistics and provides polymers with the highest degree of branching when $L_c = L_v$.[16]

It was pointed out in Part 1 that for $r = 0$ a linear polymer should be formed. However, the case $r >> 1$ is different because the number of in-chain A* centers cannot be zero. This is easily seen by looking at the addition of an A* center of a dimer onto the vinyl group of another dimer forming a new in-chain A* center (**4b** in Scheme 1) which eventually will add another vinyl group generating a branchpoint. Consequently, the degree of branching decreases slower for $r >> 1$ than for $r << 1$. Only if the rate of addition of monomer vinyl groups is much higher than that of polymer ones ($k_{\text{monomer}} >> k_{\text{polymer}}$) we will have terminal A* centers exclusively.

Limiting Cases as Linear Analogues. It is an interesting side effect that in SCVP there are two types of linear polymers conceivable as limiting structures. For $r << 1$ ($k_A << k_B$) we obtain only $L_c = (A^*b)$ units leading to a polymer of structure

$$\mathrm{Ab{-}[{-}A^*b{-}]_{\mathit{n}}{-}A^*B^*}$$

which resembles a polycondensate (see structure **4a** in Scheme 1). On the other hand, for $r >> 1$ we obtain only $L_v = (aB^*)$ units corresponding to a polymer of structure

$$\mathrm{Ab{-}[{-}a(B^*){-}]_{\mathit{n}}{-}A^*B^*}$$

which corresponds to a normal vinyl polymer with $[{-}a{-}]_n$ main chain and pendant B* groups (see structure **4e** in Scheme 1). As an example, for the monomer *p*-(chloromethyl)styrene, the former case would be a polymer with phenylene groups in the backbone and the latter would be p-chloromethyl-substituted polystyrene (see Scheme 2). The existence of two linear analogues makes it difficult to compare the properties of hyperbranched polymers with those of the corresponding linear ones.[9]

Conclusions

The degrees of branching of polymers formed by self-condensing vinyl polymerization and by AB_2 polycondensation differ. This is due in part to the existence of two kinds of linear units. The degree of branching as well as the fractions of various structural units strongly depend on the reactivity ratio of propagating and initiating centers, $r = k_A/k_B$. A maximum of the degree of branching, $\overline{\mathrm{DB}}_\infty = 0.5$, is found for $r \approx 2.59$. The fractions of the corresponding active centers, as determined by NMR, allows the determination of r. It will be shown in a subsequent paper[11] that $\overline{\mathrm{DB}}$ can be increased up to $\overline{\mathrm{DB}}_\infty = {}^2/_3$ by using multifunctional initiators and adding monomer slow enough so that the monomer molecules only add to the initiator.

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List of Symbols and Abbreviations

α	fraction of B groups reacted in AB_2 polycondensation
A	fraction of vinyl or of A groups (including monomer)
A'	$=A - M$, fraction of vinyl or A groups for polymer only
A^*	fraction of propagating centers (active A groups)
a	fraction of reacted A* groups
B^*	fraction of initiating centers (reactive B groups)
$(B^*)'$	$=B^* - M$, fraction of initiating centers for polymer only
b	fraction of reacted B* groups
$B = (ab)$	fraction of branchpoints
DB	degree of branching for one molecule
$\overline{\mathrm{DB}}$	average degree of branching
$\overline{\mathrm{DB}}_\infty$	average degree of branching at full conversion
FB	fraction of branchpoints for one molecule
$\overline{\mathrm{FB}}$	average fraction of branchpoints
$\overline{\mathrm{FB}}_\infty$	average fraction of branchpoints at full conversion
k	rate constant
k_A	rate constant of A* reacting with vinyl groups
k_B	rate constant of B* reacting with vinyl groups
$L_c = (A^*b)$	fraction of linear units (polycondensate type)
$L_v = (a^*B)$	fraction of linear units with pendant B* groups (vinyl type)
M_0	initial *concentration* of monomer
M	fraction of monomer
r	$=k_A/k_B$, reactivity ratio
$T = (A^*B^*)$	fraction of terminal units
x	conversion of A groups
z	parameter introduced for variable transformation of reaction time (see Table 1)

Supporting Information Available: Text giving the derivation of the fractions of structural units for $r \neq 1$ and the corresponding plots and tables of the fractions of monomer units and $\overline{\mathrm{DB}}$ as a function of conversion for various values of r (18 pages). Ordering and Internet access information is given on any current masthead page.

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(12) After submission of this manuscript D. Hölter, A. Burgath, and H. Frey (*Acta Polym*. **1997**, *48*, 30) published a similar consideration with regard to AB_f polycondensates and came to the same conclusion. They also calculated $\overline{DB}_\infty$ for these systems.

(13) Hölter et al.[12] defined a similar parameter and named it "average number of branches", ANB.

(14) After submission of this manuscript we learned that $\overline{DB}$ of AB_f polycondensation has been independently calculated by U. Beginn, Chr. Drohmann, and M. Möller (*Macromolecules* **1997**, *30*, 4112).

(15) In a recent paper, Malmström et al. (*PMSE Prepr. [Am. Chem. Soc., PMSE Div.]* **1997**, *77*, 151) re-evaluated their values to $\overline{DB}_\infty \approx 0.5$.

(16) In a recent paper, Hölter and Frey (*Acta Polym*. **1997**, *48*, 298) show that $\overline{DB}_\infty$ does not have a maximum for AB_2 systems but steadily approaches unity for $k_{\text{linear}}/k_{\text{terminal}} \gg 1$. This is a consequence of the fact that there is only one kind of linear unit in AB_2 polycondensation. Thus, the dependence of $\overline{DB}$ on r is another evidence for the intrinsic difference between SCVP and AB_2 polycondensation.

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