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Molecular Parameters of Hyperbranched Polymers Made by Self-Condensing Vinyl Polymerization. 1. Molecular Weight Distribution

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ABSTRACT: The molecular weight distribution (MWD) and its moments are calculated for hyperbranched polymers formed by self-condensing vinyl polymerization (SCVP) of monomers ("inimers") with the general structure AB*, where A is a vinyl group and B* is an initiating group. The calculated MWD is extremely broad, the polydispersity index (PDI) being equal to the number-average degree of polymerization: $\bar{P}_w/\bar{P}_n = \bar{P}_n$. It is twice as broad as that for the polycondensation of AB_2 type monomers. If the fraction of unreacted monomer is not taken into account, the MWD becomes somewhat narrower, $\bar{P}'_w/\bar{P}'_n \approx 0.40\bar{P}'_n$. The kinetics of the polymerization process are first order with respect to the concentration of vinyl groups; $\bar{P}_n$, $\bar{P}_w$, and PDI increase exponentially with time. Comparison of the theoretical results with experimental data indicates that the rate constant of addition of an active center to a vinyl group decreases with increasing degree of polymerization. Since there are two different active centers in SCVP, namely initiating ones, B*, and propagating ones, A*, nonequal reactivities of the two centers ($k_A \neq k_B$) have a strong effect on kinetics and MWD. The MWD narrows down to $\bar{P}_w/\bar{P}_n = 2$ for $k_A \ll k_B$ (corresponding to the common polycondensation of AB monomers) but broadens for $k_B > k_A$. Several deviations from ideal behavior are discussed.

Introduction

As early as 1952, Flory[1] pointed out that the polycondensation of AB_f-type monomers will result in soluble "highly branched" polymers and calculated the molecular weight distribution (MWD) and its averages using a statistical derivation. Ill-defined branched polycondensates had been known even before.[2,3] In 1982 Kricheldorf *et al.*[4] published the cocondensation of AB and AB_2 monomers to form branched polyesters. However, only after Kim and Webster[5] published the synthesis of pure "hyperbranched" polyarylenes from an AB_2 monomer in 1988, this class of polymers became a topic of intensive research of many groups. A multitude of hyperbranched polymers synthesized via polycondensation of AB_2 monomers have been reported,[6−12] and reviews were published recently.[13] The interest in hyperbranched polymers arises from the fact that they combine structural features of dendrimers (e.g. low viscosity, high functionality) with a much simpler synthesis.

In attempts to synthesize ω-styrylpolyisobutylene using *m*-/*p*-(chloromethyl)styrene as an initiator and aluminum alkyls/H_2O as co-initiators, Kennedy and Frisch[14a] found significantly less than 100% of vinyl groups in the product. They concluded that copolymerization of the vinyl group of the "initiator" with isobutylene occurred as a "deleterious side reaction". In a similar experiment, Nuyken *et al.*[14b] 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. On the other hand, copolymerizations of isobutylene with *p*-(chloromethyl)styrene or *p*-(chloromethyl)-α-methylstyrene initiated with boron trifluoride or $EtAlCl_2$ were reported earlier.[15] All these results indicate that *p*-(chloromethyl)styrene acts both as a cationic *ini*tiator

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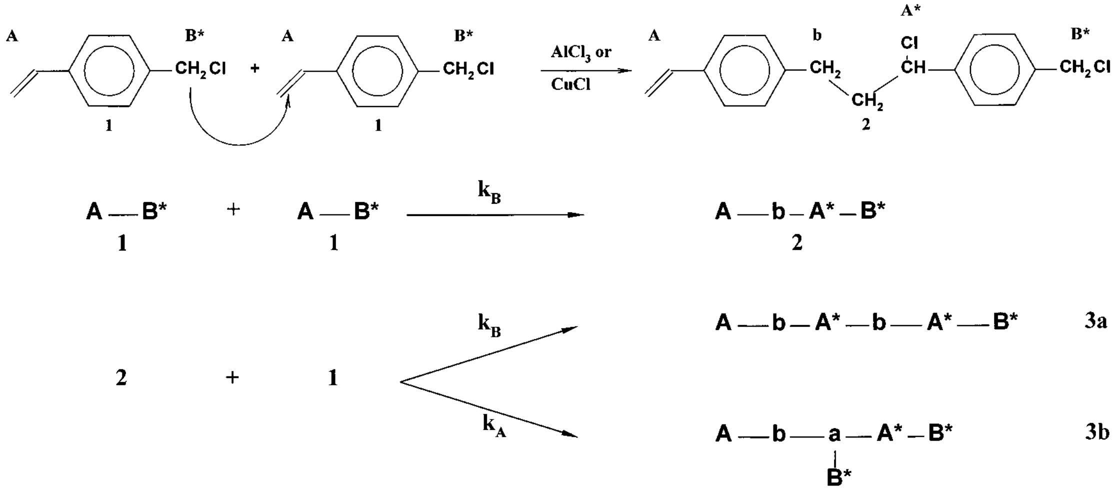
Scheme 1. Initial Steps in Self-Condensing Vinyl Polymerization



and as a mono*mer* (we are tempted to coin the word "*inimer*" for such a molecule).

Recently, Fréchet and co-workers[16-18] reported the homopolymerization of such molecules as a new way of forming pure 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. A simple example is *p*-(chloromethyl)-styrene where chlorine can be abstracted heterolytically or homolytically to form the corresponding carbocation or radical, respectively. The chain initiation is the addition of the active B* group to the double bond of another monomer (cf. Scheme 1). The double bond, A, of the second monomer is thus converted into a new active center, A*. The dimer formed has two active sites and one double bond. Both the initiating B* group and the newly created propagating center, A*, can react with the vinyl group of any other molecule (monomer or polymer) in the same way with rate constants k_A and k_B, respectively. The initial steps up to the formation of trimers are shown in Scheme 1. The addition of a vinyl group to a *terminal* A* or B* center leads to a linear linkage, whereas the addition of a double bond to a *side group* B* (e.g., **3b**) or an A* center *within the polymer* (e.g., center of **3a**) leads to a branch point. 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 sites is equal to the number of monomer units.

Living cationic,[16,17] nitroxide-mediated radical,[18] atom transfer radical,[19] and group transfer[20] polymerizations have been applied to the synthesis of hyperbranched polymers by SCVP. The molecular weight distribution of the products is very wide, and the polydispersity index increases as the polymerization proceeds. In order to gain insight into the reaction process of a self-condensing vinyl polymerization, it is necessary to analyze the kinetics of this reaction. The kinetics, the molecular weight distribution (MWD), and the average molecular weights of the hyperbranched polymers generated are derived in this article. The results are compared to experimental data and to the MWD obtained by the polycondensation of AB_2 type monomers. The effect of nonequal reactivities of initiating B* and propagating A* centers on the MWD averages will be also dealt with. The degree of branching of the hyperbranched polymers is discussed in detail in the subsequent article in this issue.[21]

Kinetic Differential Equation and Dependence of Conversion on Time

From the architecture of a hyperbranched polymer formed in a self-condensing vinyl polymerization, we can derive the following rules (possible deviations in reality are discussed at the end of this paper).

1. There is only one double bond per molecule in the system.
2. There are *i* active sites of A* and/or B* centers in every *i*-mer. Thus, the reactivity of a molecule is proportional to its degree of polymerization, *i*.

We first assume equal intrinsic reactivities of A* and B* groups ($k_A = k_B = k$; the case $k_A \neq k_B$ will be dealt with further below) and neglect intramolecular reactions (this and other deviations from ideal behavior will be discussed below). Then we can set up the following simple reaction scheme for the reaction between two molecules:

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

P_i is a molecule with the degree of polymerization i and k' denotes the effective rate constant of the reaction of the whole molecules P_i and P_j. As will be shown later, k' has a different expression for AB_2 polycondensation which will finally lead to a different MWD.

The reaction scheme above leads to the kinetic differential equation

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

$$= \frac{k}{2} i \sum_{0<j<i} P_jP_{i-j} - kP_i\{i\sum_j P_j + \sum_j jP_j\} \qquad (1)$$

where P_i denotes the concentration of an *i*-mer. The first term of eq 1 is related to the formation of the *i*-mer from smaller species, and the second term represents the consumption of the *i*-mer during the reaction process. The initial condition of eq 1 is

$$P_i(t=0) = \delta_{i,1}M_0, \quad \delta_{i,1} = \begin{cases} 1, & \text{if } i = 1 \\ 0, & \text{if } i \neq 1 \end{cases}$$

where P_1 ($\equiv M$) is the concentration of residual monomer and M_0 is its initial concentration. If A is the concentration of residual double bonds in the reaction system, since there is only one double bond per molecule, the zeroth moment, μ_0, of the molecular weight distribution (MWD) reads

$$\mu_0 = \sum_i P_i = A \tag{2}$$

From the material balance condition we know the first moment, μ_1, of the MWD:

$$\mu_1 = \sum_i iP_i = M_0 \tag{3}$$

The conversion of double bonds (not of monomer molecules!) is defined as

$$x = \frac{M_0 - A}{M_0} \tag{4}$$

i.e.,

$$\mu_0 = A = M_0(1 - x) \tag{4'}$$

Summation of both sides of eq 1 over index i results in

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_i P_i = -kM_0\sum_i P_i = -kM_0A \tag{5}$$

Combining eq 4′ with eq 5, we get

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kM_0^2(1 - x) \tag{5'}$$

On the other hand, differentiation of both sides of eq 4′ leads to

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -M_0\frac{\mathrm{d}x}{\mathrm{d}t} \tag{5''}$$

Comparing eq 5′ with eq 5″, we have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM_0(1 - x) \tag{6}$$

From eq 6 we find the first-order relationship between double bond conversion, x, and reaction time, t

$$-\ln(1 - x) = kM_0t = \tau$$

or

$$x = 1 - \mathrm{e}^{-\tau} \tag{7}$$

where

$$\tau = kM_0t \tag{8}$$

is a reduced time. Dividing eq 1 by eq 6, we obtain

$$\frac{\mathrm{d}P_i}{\mathrm{d}x} = \frac{i\sum_{0<j<i} P_jP_{i-j}}{2M_0(1 - x)} - \left(i + \frac{1}{1 - x}\right)P_i \tag{9}$$

with the initial condition

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

Equation 9 can be solved rigorously (cf. Supporting Information, Appendix 1).

MWD and Average Molecular Weights

From eq 9 we can derive the concentrations of the i-mers:

$$P_i = M_0(1 - x)\frac{(ix)^{i-1}e^{-ix}}{i!} \tag{10}$$

The zeroth and the first moments of MWD were expressed by eqs 2 and 3, respectively, and the second moment reads

$$\mu_2 = \sum_i i^2P_i = \frac{M_0}{(1 - x)^2} \tag{11}$$

The derivation of eq 11 is given as Supporting Information (Appendix 2). Now we can give the expressions of the number-, the weight- and the z-distribution functions of the hyperbranched polymer, respectively:

$$N(i) = \frac{P_i}{\sum_i P_i} = \frac{(ix)^{i-1}\,\mathrm{e}^{-ix}}{i!} \tag{12}$$

$$W(i) = \frac{iP_i}{\sum_i iP_i} = (1 - x)\frac{(ix)^{i-1}\,\mathrm{e}^{-ix}}{(i - 1)!} \tag{13}$$

$$Z(i) = \frac{i^2P_i}{\sum_i i^2P_i} = \frac{(1 - x)^3(ix)^i\,\mathrm{e}^{-ix}}{x(i - 1)!} \tag{14}$$

Since $Z(i) = i\mathrm{W}(i) = W(\log i)$, the z-distribution is equivalent to the weight-distribution obtained by GPC using a logarithmic scale of molecular weight (“GPC distribution”). Figure 1 shows the GPC distributions for various conversions of the vinyl group, x.

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

$$i! \approx (i/\mathrm{e})^i\sqrt{2\pi i}$$

we can derive continuous distributions from eqs 12–14:

$$N(i) = \frac{x^{i-1}e^{i(1-x)}}{\sqrt{2\pi}}i^{-3/2} \tag{15}$$

$$W(i) = (1 - x)\frac{x^{i-1}e^{i(1-x)}}{\sqrt{2\pi}}i^{-1/2} \tag{16}$$

$$Z(i) = (1 - x)^3\,\frac{x^{i-1}e^{i(1-x)}}{\sqrt{2\pi}}i^{1/2} \tag{17}$$

Figure 2 compares the number-, weight-, and z-distributions for two different conversions of the vinyl group, x, in a bilogarithmic way (using the exact expressions in eqs 12–14). It is seen that only the z-distributions show a maximum whereas the others decrease monotonously with i.

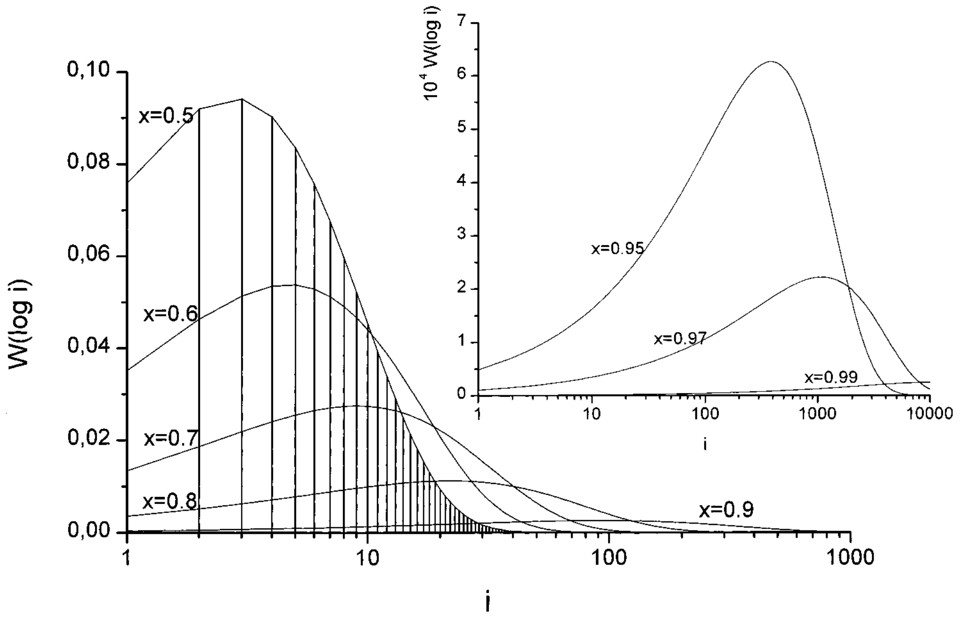


Figure 1. Semilogarithmic molecular weight distribution (GPC distribution) of hyperbranched polymers generated from self-condensing vinyl polymerization at various conversions of vinyl groups, *x*.

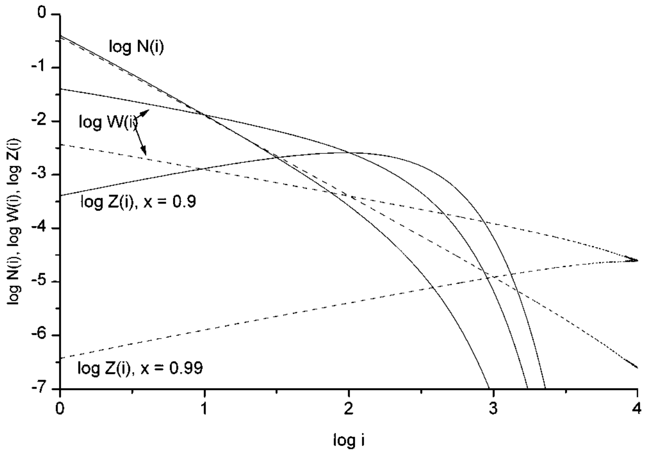


Figure 2. Bilogarithmic plot of the number-, weight- and *z*-distributions for conversion of vinyl groups, $x = 0.9$ (—) and $x = 0.99$ (- - -).

For high conversions of vinyl groups, the following simple power laws are valid up to a limiting value of *i*:

$$\lim_{x\to 1} N(i) = \frac{1}{\sqrt{2\pi}} i^{-3/2} = 0.399 i^{-1.5} \tag{18}$$

$$\lim_{x\to 1} W(i) = \frac{1-x}{\sqrt{2\pi}} i^{-1/2} \tag{19}$$

$$\lim_{x\to 1} Z(i) = \frac{(1-x)^3}{\sqrt{2\pi}} i^{1/2} \tag{20}$$

A similar power law, $N(i) \propto i^{-5/2}$, was proposed and experimentally observed for gelation processes of polymers before the gel point is reached.[23] Even Smoluchowski's kinetic differential equation for the cluster size distribution in coagulation processes[24] set up in 1916 strongly resembles eq 1. In fact, the formation of hyperbranched polymers has a certain similarity with gelation processes where physical or chemical bonds are formed between polymer chains. The main difference is that in gelation all monomer units of both chains can take part in the reaction whereas in SCVP one of the two chains can only react with its vinyl group, i.e., one chain segment. This possibly explains the difference in the exponent of the power laws.

The number- and the weight-average degrees of polymerization, and the polydispersity index read:

$$\bar{P}_{\mathrm{n}} = \frac{\mu_1}{\mu_0} = \frac{1}{1-x} = \mathrm{e}^{\tau} \tag{21}$$

$$\bar{P}_{\mathrm{w}} = \frac{\mu_2}{\mu_1} = \frac{1}{(1-x)^2} = \mathrm{e}^{2\tau} \tag{22}$$

$$\frac{\bar{P}_{\mathrm{w}}}{\bar{P}_{\mathrm{n}}} = \frac{1}{1-x} = \mathrm{e}^{\tau} = \bar{P}_{\mathrm{n}} \tag{23}$$

From eq 23 we see that the molecular weight distribution of the hyperbranched polymer formed by SCVP is extremely broad, roughly twice as broad than in the polycondensation of an AB_2 type monomer (see below), and the polydispersity index increases exponentially with reaction time.

In experimental procedure, the low molecular weight materials, such as residual monomer etc., are usually separated from the polymer samples by precipitation, and the low molecular weight part of the products plays an important role for the polydispersity index.[22] If the contribution of unreacted monomer, *M*, is excluded from the various moments, the expressions of number- and weight-average degrees of polymerization can be written as

$$\bar{P}'_{\mathrm{n}} = \frac{\mu_1 - M}{\mu_0 - M} = \frac{1 - M/M_0}{1 - x - M/M_0} = \frac{1-(1-x)\mathrm{e}^{-x}}{(1-x)(1-\mathrm{e}^{-x})} \tag{21'}$$

$$\bar{P}'_{\mathrm{w}} = \frac{\mu_2 - M}{\mu_1 - M} = \frac{1-(1-x)^2 M/M_0}{(1-x)^2(1-M/M_0)} = \frac{1-(1-x)^3\mathrm{e}^{-x}}{(1-x)^2[1-(1-x)\mathrm{e}^{-x}]} \tag{22'}$$

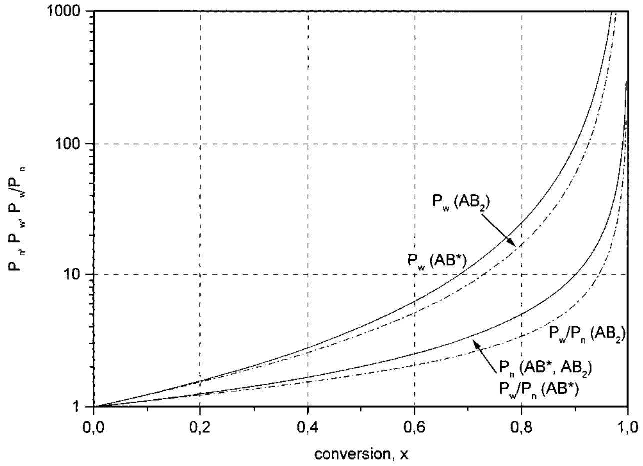


Figure 3. Dependence of MWD averages and polydispersity index on conversion of A groups, x, for SCVP (AB*) and for polycondensation of AB$_2$ monomers.

where the fraction of residual monomer is

$$M/M_0 = (1 - x)\mathrm{e}^{-x} \tag{24}$$

(cf. eq 10 for $i = 1$). Then the expression of polydispersity index becomes

$$\frac{\bar{P}'_{\mathrm{w}}}{\bar{P}'_{\mathrm{n}}} = \frac{(1 - x - M/M_0)[1 - (1 - x)^2 M/M_0]}{(1 - x)^2(1 - M/M_0)^2} = \frac{(1 - \mathrm{e}^{-x})[1 - (1 - x)^3\mathrm{e}^{-x}]}{(1 - x)[1 - (1 - x)\mathrm{e}^{-x}]^2} \tag{23$'$}$$

Figures 3 and 4 show the molecular parameters as functions of monomer conversion and reaction time, respectively. Figure 4 shows that $\bar{P}'_{\mathrm{n}}$ is considerably larger than $\bar{P}_{\mathrm{n}}$, even at high conversion. This is due to the fact that there is a large fraction of monomer present in the system even at high conversion. In fact, for $x \to 1$ the ratio of monomer over total vinyl groups, $M/A = \mathrm{e}^{-x}$ becomes $\mathrm{e}^{-1} = 0.368$. This leads to $\bar{P}'_{\mathrm{n}}/\bar{P}_{\mathrm{n}} = 1/(1 - \mathrm{e}^{-1}) = 1.58$. Of course, for $x = 1$ there is only one molecule left and $M = A = 0$. Since $\bar{P}'_{\mathrm{w}}$ does not differ very much from $\bar{P}_{\mathrm{w}}$ at higher conversions, the corrected polydispersity index decreases to $\bar{P}'_{\mathrm{w}}/\bar{P}'_{\mathrm{n}} = (1 - \mathrm{e}^{-1})^2\bar{P}'_{\mathrm{n}} = 0.40\bar{P}'_{\mathrm{n}}$.

Figure 5 shows that the experimental data for the cationic SCVP of m-(1-chloroethyl)styrene[16] fit well to the straight line expected from eq 22 in a semilogarithmic plot. The slopes correspond to the product kM_0, where k is an apparent rate constant, depending on the fraction of activated species (the mechanistic consequences of the equilibrium between dormant and active species are discussed further below). However, the intercept is larger than expected. If an accidental fractionation of the polymer by precipitation and systematic errors due to GPC calibration with linear standards can be excluded, this effect is congruent with Fréchet's observation that the condensation occurs faster in the initial stage ($i < 10$). This may be due to a lower accessibility of reactive centers at the inside of larger branched molecules. It will lead to a narrower MWD than the expression given above. This problem will be discussed in more detail in the final section.

Kinetic Analysis of the Polycondensation of AB$_2$ Type Monomers

In order to compare the hyperbranched polymer obtained from a self-condensing vinyl polymerization with that produced in a polycondensation of AB$_2$ type monomer, we make a brief analysis for the latter reaction system using a kinetic approach.

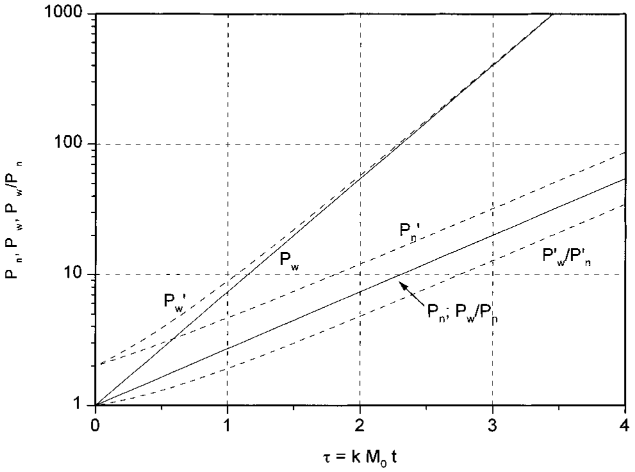


Figure 4. Dependence of MWD averages and polydispersity index on reduced time, τ, for SCVP including (—) and excluding (- - -) residual monomer.

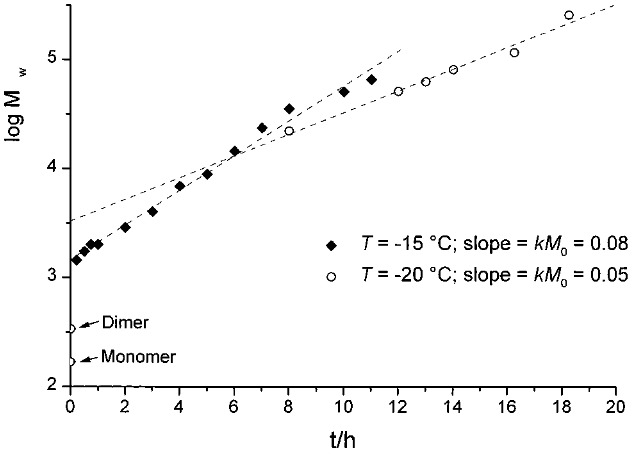


Figure 5. Comparison of calculated and experimental weight average molecular weights of hyperbranched poly[m-(1-chloroethyl)styrene]. Data taken from Figure 1 of ref 16.

If we count the numbers of the unreacted A and B groups in an arbitrary i-mer formed, we can find that there is only one residual A site per molecule, and there are i+1 free B groups in a i-mer. Thus, the reaction between two molecules is represented by

$$P_i + P_j \xrightarrow{k'} P_{i+j}; \quad k' = (i+j+2)k$$

The different definition of k' leads to a somewhat different kinetic differential equation

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \frac{k}{2}\sum_{0<j<i}\{(j + 1)P_jP_{i-j} + (i - j + 1)P_{i-j}P_j\} - k\{(i + 1)P_i\sum_j P_j + P_i\sum_j (j + 1)P_j\}$$
$$= \frac{k}{2}\sum_{0<j<i}(i + 2)P_jP_{i-j} - kP_i\{(i + 2)\sum_j P_j + \sum_j jP_j\} \tag{25}$$

The initial condition of eq 25 is identical with that of eq 1, and the material balance condition is the same as eq 3. From eq 25 one can derive by summation

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_i P_i = -k\{M_0\sum_i P_i + (\sum_i P_i)^2\} \tag{25a}$$

This equation differs from eq 5 for SCVP in the additional quadratic term. Now we define α and x as the fraction of the B and A groups, respectively, which have condensed. The expression of x is identical with eq 4, and evidently, $\alpha = x/2$.

By a similar approach used previously, one obtains an expression for the kinetics of the process[29]

$$\alpha = \frac{1 - e^{-\tau}}{2 - e^{-\tau}} \quad \text{or} \quad x = 2\frac{1 - e^{-\tau}}{2 - e^{-\tau}} \tag{26}$$

where τ is the reduced time, and has the same expression as given below eq 8. Equation 26 shows that AB_2 polycondensation is not a first-order process, in contrast to SCVP (cf. eq 7). Figure 6 shows that it initially proceeds somewhat faster than SCVP, due to the second term in eq 25a.

The solution of differential eq 25 is

$$\begin{aligned} P_i &= M_0\frac{(2i)!}{i!(i+1)!}\alpha^{i-1}(1-\alpha)^{i+1}(1-2\alpha) \\ &= M_0\frac{(2i)!}{i!(i+1)!}\left(\frac{x}{2}\right)^{i-1}\left(1-\frac{x}{2}\right)^{i+1}(1-x) \end{aligned} \tag{27}$$

From the molecular weight distribution function, eq 27, the number- and the weight-average degrees of polymerization and the polydispersity index are derived leading to the same expressions as those derived by Flory[1] using a statistical approach:

$$\bar{P}_n = \frac{1}{1-2\alpha} = \frac{1}{1-x} \tag{28}$$

$$\bar{P}_w = \frac{1-2\alpha^2}{(1-2\alpha)^2} = \frac{1-x^2/2}{(1-x)^2} \tag{29}$$

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{1-2\alpha^2}{1-2\alpha} = \frac{1-x^2/2}{1-x} = \frac{\bar{P}_n^{\,2} + 2\bar{P}_n - 1}{2\bar{P}_n} \approx \bar{P}_n/2 \quad (\text{for } \bar{P}_n \gg 1) \tag{30}$$

Comparison of eqs 28–30 with eqs 21–23 respectively shows that the molecular weight distribution of the products of self-condensing vinyl polymerization is twice as broad as that of the polymer formed in polycondensation of AB_2 type monomers; however, $\bar{P}_n$ is the same (see Figure 3).

Again, we can calculate the fraction of monomer from eq 27 by setting $i = 1$

$$M/M_0 = (1-\alpha)^2(1-2\alpha) = (1-x/2)^2(1-x)$$

Subtracting the residual monomer from the various moments, similar to eqs 21′–23′, we will again find that the polydispersity index becomes smaller.

Analysis of SCVP with Nonequal Rate Constants

Generally, in SCVP systems, the reactivities of initiating B* and propagating A* groups can be different from each other. All self-condensing vinyl polymerizations reported so far involve living polymerizations with reversible termination. In fact, most of the active centers are present as dormant species which are only shortly activated, add to a vinyl group, and then become dormant again. Activation can occur by Lewis acids in cationic polymerization, by nucleophiles in group transfer polymerization (GTP), by thermal dissociation in nitroxide-mediated radical polymerization, or by a transition metal halide in atom transfer radical polymerization (ATRP). Thus, the measured rate constants are only apparent ones, being given as the product of the true rate constant of monomer addition and the concentration of activated centers.[22,25]

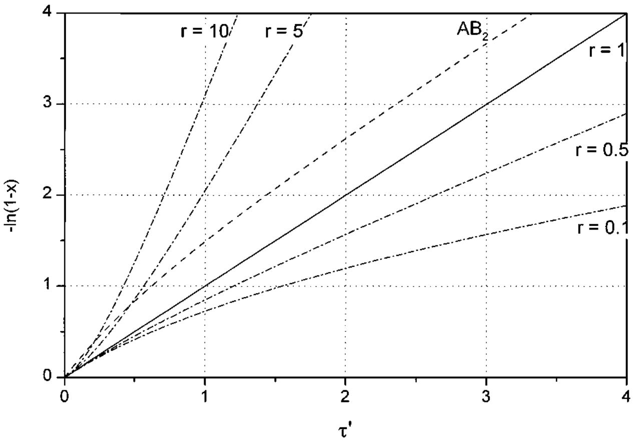


Figure 6. First-order plot of conversion of A groups, x, vs reduced time, $\tau' = k_B M_0 t$, for SCVP (AB*) with various reactivity ratios, $r = k_A/k_B$. Dotted line: polycondensation of AB_2 monomers.

For example, in cationic polymerization of *p*-(chloromethyl)styrene, the initiating center B* is a primary cation and the propagating center A* a secondary one after activation by a Lewis acid. This has two consequences: (i) the equilibrium of ionization is shifted more toward the ionized species for secondary cations, and (ii) secondary cations are less reactive than primary ones. Usually, the former effect is predominant over the latter, making primary centers less reactive than secondary ones in cationic polymerization. In anionic or group transfer polymerizations, this effect may be reversed whereas in radical polymerization it will be less important.

In all polymerization steps there are new propagating A* centers formed, either by addition of vinyl groups to initiating B* or to A* centers. If now deactivation is slow compared to propagation, the A* centers formed will have a longer lifetime than just one monomer addition. Then, multiple monomer additions to A* centers will occur before a B* center can be activated. Consequently, the apparent rate constant of propagating A* centers will be higher than that of initiating B* centers, even if they are chemically equivalent (e.g., in controlled radical polymerization).[19c,21] This may have consequences for kinetics, MWD, and the degree of branching.

The kinetic treatment of such a problem is extremely complicated, and to our knowledge it is impossible to find the analytical solutions of the MWD function and the weight-average molecular weight. However, the kinetics and the number-average molecular weight can be derived. The weight-average molecular weight and the polydispersity index are calculated numerically. The degree of branching can be calculated analytically; it is given in the subsequent paper.[21]

If $P_i = P_{n,m}$ represents a molecule with n A* and m B* units, so that $n + m = i$, the reaction between two molecules is represented by the following two reactions:

$$P_{n,m} + P_{s,r} \xrightarrow{k'_{A}} P_{n+s,m+r};\quad k'_{A} = (n+s)k_{A}$$

$$P_{n,m} + P_{s,r} \xrightarrow{k'_{B}} P_{n+s+1,m+r-1};\quad k'_{B} = (m+r)k_{B}$$

The second equation takes into account that by reaction of a B* unit with a vinyl group an A* unit is formed. The kinetic differential equation and the derivation of the following results are given as Supporting Information (Appendix 3). After introducing the variable transformation

$$z = k_{B}\int_0^t A\,\mathrm{d}t$$

$$\text{i.e.,}\quad \frac{\mathrm{d}z}{\mathrm{d}t} = k_{B}A \tag{31}$$

and the reactivity ratio of A* and B* centers,

$$r = k_{A}/k_{B}$$

we can derive the conversion of vinyl groups as a function of z.

$$x = 1 - r(1 - z) - (1 - r)e^{-z} \tag{32}$$

The relationship between z and x is important because we can determine the value of z from the conversion of vinyl groups, x, in terms of eq 32, and then calculate the concentration of monomer:

$$M = M_0(1 - x)e^{-z} \tag{33}$$

The expression for $\bar{P}_n$

$$\bar{P}_n = \frac{M_0}{A} = \frac{1}{1 - x} \tag{34}$$

is unchanged and thus independent of r.

The relationship between variable z and reaction time, t, is

$$t = \frac{1}{k_{B}M_0}\int_0^z \frac{\mathrm{d}u}{r(1-u) + (1-r)e^{-u}} \tag{35}$$

This equation, together with eq 32 gives a relation between the conversion of vinyl groups, x, and a modified reduced time, τ'

$$\tau' = k_{B}M_0 t = \int_0^z \frac{\mathrm{d}u}{r(1-u) + (1-r)e^{-u}} \tag{35'}$$

It is shown in Figure 6 in a semilogarithmic plot, indicating that the kinetics deviate from first order for $r \neq 1$. For $r > 1$ ($k_A > k_B$) induction periods are observed due to the fact that A* groups are only formed in the course of the polymerization process. This effect is similar to slow initiation in living polymerization ($k_p > k_i$). The opposite occurs for $r < 1$ since here the fraction of more reactive B* groups steadily decreases. A plot of $\bar{P}_n$ vs τ' (Figure 7) shows that the dependence of $\bar{P}_n$ on reaction time is a function of r.

In order to calculate $\bar{P}'_n$ (where monomer is excluded), the fraction of residual monomer, M, has to be subtracted from the first and zeroth moments, according to eq 21. A plot of $\bar{P}'_n$ vs conversion for various values of r is given in Appendix 3 (Supporting Information).

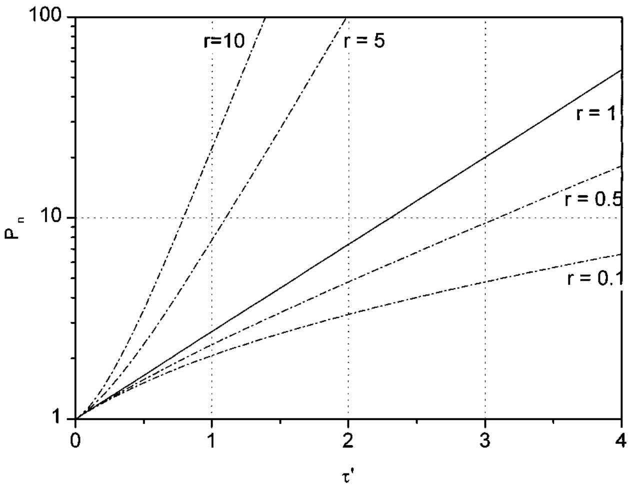


Figure 7. Dependence of number-average of polymerization, $\bar{P}_n$, on reduced time, $\tau' = k_B M_0 t$, for SCVP at various ratios of rate constants, $r = k_A/k_B$.

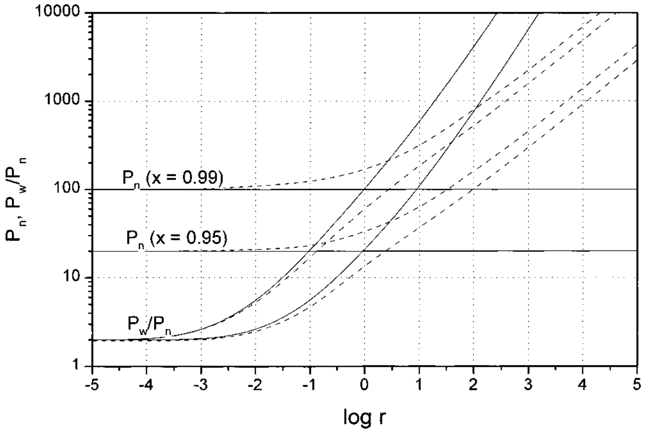


Figure 8. Dependence of number-average degree of polymerization, $\bar{P}_n$, and polydispersity index, $\bar{P}_w/\bar{P}_n$, on reactivity ratio $r = k_A/k_B$, for SCVP at given conversions of double bonds. Data with dotted lines are calculated without taking the residual monomer into account.

Figure 8 shows that, at a given conversion and for $r > 1$, $\bar{P}'_n \gg \bar{P}_n$. This is due to the fact that with increasing values of r an increasingly large fraction of molecules in fact is monomer.

Unfortunately, the weight-average degree of polymerization and the polydispersity index cannot be calculated analytically. However, for $r = 0$ (i.e., $k_A = 0$) SCVP degenerates into a normal polycondensation of linear polymers with a B* end group and unreactive A* groups in the chain, leading to a Schulz–Flory distribution with polydispersity index, $\bar{P}_w/\bar{P}_n = 1 + x$.

For other values of r, the differential equations for the MWD moments were derived and solved numerically. The MWD function was calculated using the program package Predici which employs the adaptive *Rothe* method for time discretization and the discrete *Galerkin h–p* method for the representation of chain length distributions.[27] The details of the numerical calculations are given as Supporting Information (Appendix 4). Appendix 4 also shows figures of the polydispersity index vs conversion and vs $\bar{P}'_n$ as a function of r. It is seen that at a given conversion a given $\bar{P}'_n$ both $\bar{P}_w/\bar{P}_n$ and $\bar{P}'_w/\bar{P}'_n$ increase with increasing ratio r. Moreover, $\bar{P}'_w/\bar{P}'_n$ is a linear function of $\bar{P}'_n$ whereas $\bar{P}_w/\bar{P}_n$ depends on $\bar{P}'_n$ in a nonlinear way.

The numerical analysis reveals that the polydispersity index at high conversions increases from $\bar{P}_w/\bar{P}_n = 2$ for

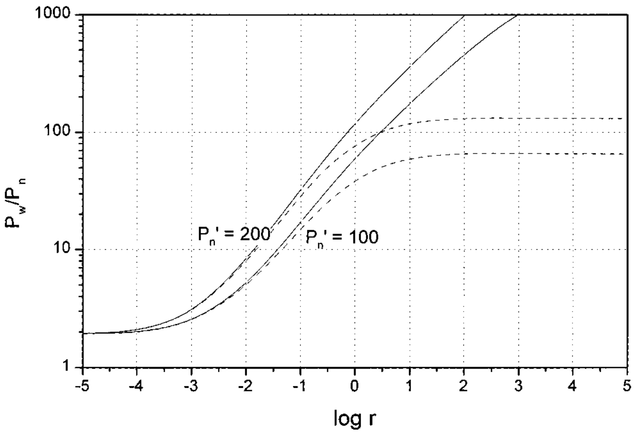


Figure 9. Dependence of polydispersity index, $\bar{P}_w/\bar{P}_n$, on reactivity ratio $r = k_A/k_B$, for SCVP at a given values of the number-average degree of polymerization (without monomer), $\bar{P}'_n$. Data with dotted lines are calculated without taking residual monomer into account.

$r = 0$ (corresponding to a polycondensation of linear molecules) to very large values, $\bar{P}_w/\bar{P}_n > \bar{P}_n$ for $r > 1$. When the large fraction of residual monomer molecules is not taken into account, the polydispersity index also increases with *r*, but not as strongly. Figure 9 shows that for $r >> 1$ the polydispersity index (excluding monomer) becomes proportional to the degree of polymerization with a limiting value, $\bar{P}'_w/\bar{P}'_n \approx 0.63\bar{P}'_n$.

This is surprising since, for $r >> 1$, nearly linear polymers with a terminal A* group, few in-chain A* groups, but mostly pendant B* groups, are expected. However, this case is different from the case $r = 0$. Since the monomer only has a (nearly unreactive) B* center we now have a very slow initial phase where active A* centers are formed (see Figure 6). In contrast to the case where $r = 0$, 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 (cf. Scheme 1). Consequently, we will always have a dependence of reactivity on $\bar{P}_n$.

Deviations From Ideal Behavior

All calculations are based on ideal conditions which may not be fulfilled in reality. Thus, certain deviations are to be expected. These are briefly discussed below.

Steric Hindrance in Larger Molecules. When comparing the calculated to the experimental M_w's, it was already pointed out that the average rate constant of a single addition may decrease with increasing size and degree of branching of the polymers. Since the vinyl groups and the active centers at the surface of the globular molecules are more easily accessible then those inside we may assume that the effective rate constant of a given molecule is not proportional to its degree of polymerization, *i*, (roughly corresponding to its volume), i.e., $k' \propto i$, but rather to its outer part (proportional to the surface), i.e., $k' \propto i^{2/3}$. Since the very broad MWD's calculated can be understood on basis of the linear increase of reactivity with $\bar{P}_n$, we can assume that a less than linear increase of reactivity will lead to somewhat narrower distributions. This problem will be treated numerically in a later publication.

Intramolecular Loop Formation. Addition of an A* or B* center to the vinyl group of its own molecule will lead to a partial of full loss of vinyl groups. This will lead to smaller degrees of polymerization at full conversion of double bonds and eventually stop the condensation process prematurely. In fact, in the self-condensing GTP of methacrylates, Simon[26] could not detect any vinyl groups in the polymers by NMR after longer reaction times. The kinetic scheme for this unimolecular reaction is

$$P_i \xrightarrow{k''} P_i^d$$

This problem is difficult to assess quantitatively because the rate constant of loop formation, k'', may depend on the degree of polymerization and on the degree of branching in a complicated way. We assume that k'' will increase to a maximum value because the density of accessible active centers around the vinyl group will not increase after a certain degree of polymerization is reached. Such a problem can only be treated numerically. However, it will be shown in a subsequent publication[28] that initial addition of an *f*-functional initiator will lead to a considerable decrease of PDI, $\bar{P}_w/\bar{P}_n \approx 1 + \bar{P}_n/f^2$. Since loop formation also results in a multifunctional initiator during polymerization, it is expected that the PDI decreases.

Chemical Side Reactions. These may occur in real systems. Thus, in living cationic polymerization spontaneous or monomer transfer may occur leading to more than one vinyl group in some molecules and subsequent cross-linking. In living radical polymerization, termination via recombination or disproportionation is to be expected. If recombination occurs intermolecularly, more than one vinyl group per chain can occur, which may lead to gelation. For intramolecular termination (which may be more probable) the number of active sites will decrease and their distribution will be affected. In anionic or group transfer polymerization of (meth)acrylic monomers it is possible that attack of the anion onto the ester groups of the own polymer molecule ("backbiting") will even remove whole branches from the polymer, thus decreasing the molecular weight considerably.[20]

Conclusions

It is shown that self-condensing vinyl polymerization leads to different kinetics and MWD than AB_2 polycondensation, the polydispersity index being equal to the number-average degree of polymerization. Most of the published data[11,19,20] give significantly lower polydispersity indices than calculated for the ideal case with equal rate constants of propagating and initiating centers ($r = k_A/k_B = 1$). This may indicate that $r < 1$ ($k_A < k_B$). However, with additional information (i.e. the fractions of A* and B* centers observed by NMR[19c,21]) this is less likely for some systems. It may rather be due to one of the other deviations discussed above, especially loop formation. No absolute MWD data have been published so far, taking into consideration that GPC calibration with linear standards fails for branched systems. In part 2 of this series,[21] it will be shown in detail that the degree of branching also differs for the two mechanisms and that this molecular parameter as well as the fractions of the various structural units are strongly affected by the reactivity ratio *r*.

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List of Symbols and Abbreviations

α	fraction of B groups reacted in AB_2 polycondensation
$\delta_{l,m}$	Kronecker symbol: $\delta_{l,m} = 1$ for $l = m$; $\delta_{l,m} = 0$ else
μ_n	nth moment of the MWD
τ	$=kM_0t$, reduced time
τ'	$=k_BM_0t$, reduced time
A	concentration of vinyl groups in SCVP; of A groups in AB_2 polycondensation (including monomer)
A^*	concentration of propagating groups
B^*	concentration of initiating groups
k	rate constant
k_A	rate constant of A* reacting with vinyl groups
k_B	rate constant of B* reacting with vinyl groups
M_0	initial concentration of monomer or double bonds
M	monomer concentration
$N(i)$	number distribution
r	k_A/k_B, reactivity ratio
P_i	concentration of polymer chains of degree of polymerization i
$\bar{P}_n$	number-average degree of polymerization
$\bar{P}_w$	weight-average degree of polymerization
$\bar{P}_w/\bar{P}_n$	polydispersity index
t	reaction time
x	conversion of vinyl groups (=A groups)
$W(i)$	weight distribution
$Z(i)$	z-distribution
z	parameter introduced for variable transformation of reaction time

Supporting Information Available: Text giving derivations of eqs 9 and 11 and derivation of the kinetics, $\bar{P}_n$, and $\bar{P}_w$ for $r \neq 1$ and plots of $\bar{P}_n$, $\bar{P}_w$, and $\bar{P}_w/\bar{P}_n$ vs conversion as a function of r (11 pages). Ordering information is given on any current masthead page.

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