Change in Molecular Weight Distribution During Formation and Degradation of Star Polymers

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CHANGE IN MOLECULAR WEIGHT DISTRIBUTION DURING FORMATION AND DEGRADATION OF STAR POLYMERS

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Key Words: Modeling, Molecular Weight Distribution, Branching, Star Polymer, Degradation

ABSTRACT

A general model has been derived to describe the formation of star polymers via various polymerization mechanisms. The model gives the bivariate distributions of molecular weight and number of branches of the star polymers. Key parameters determining the distributions include the distribution of primary polymers and the branching density. Analytical distribution functions are obtained for the systems having branches of uniform, random, or Schulz-Zimm

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distributions. The distribution polydispersity of the star polymers approaches unity for sufficiently high branching densities regardless of the distribution of primary chains. The model has also been extended to give the change in the average molecular weights when star polymers undergo degradation. The scheme of disconnecting branches from star cores is considered. Polydispersity of polymer mixture shows a maximum value at an intermediate degree of degradation.

INTRODUCTION

Branched polymers exhibit special functions in many applications [1-3]. For example, branched polyolefins exhibit higher mechanical strength and at the same time better shear-thinning performance than their linear counterparts [4]. Bulk viscosities, as well as concentrated and dilute solution viscosities, can be lower for branched polymers than for a linear material of equivalent molecular weight. Branched polymethylmethacrylate is purposely added to paints and coatings to increase the solid content of the later without affecting their viscosity or spraying properties [5]. Branched polyisoprene is used as rheology modifiers in motor oils [6].

There are various types of branched polymers, mainly dendritic, comb and star-shaped. A polymer having well-defined branch-on-branch structure is called dendrimer, a comb polymer has a backbone with attached side chains, and a star polymer consists of a central core from which a given number of branches radiate. Although the polymer branching has been a matter of study for over half a century, most work has focused on randomly branched polymers made by chain transfer to polymer and/or propagation through terminal double bond via free radical mechanisms [7-12]. However, this type of branched structure is not well defined. It is difficult to control the branching distribution. Synthesis and characterization of branched polymers with well-defined chain structures have recently received much attention due to their great potential in designing specialty commercial products [1-3].

Material properties of branched polymers not only depend on the molecular weight and branching density, but also on the type of branching. The molecular weight distribution of a star polymer might be very different from that of a comb having the same average molecular weight and branching density. It is therefore essential to give a precise description of the molecular weight distribution for various types of branched polymers. Numerous models have been developed in the

literature, however, they are limited to randomly branched structures [13-15]. Modeling of star and comb polymers received much less attention.

An early work on modeling the molecular weight distribution of star polymers was by Schaefgen and Flory some fifty years ago [16]. The reaction system was the co-condensation of an AB type monomer with a multifunctional reactant of the type RA_b or RB_b. The star polymer thus formed bears b number of arms of random length. Ullisch and Burchard calculated the average molecular weight development for star polymers formed by polyfunctional chain transfer agents in free-radical polymerization [17]. Yuan et al. presented a molecular weight distribution model for the star polymer under ideal conditions [18]. Tobita dealt with the same system in a more general manner and simulated the molecular weight distribution in the presence of radical termination by combination using a Monte-Carlo method [19]. Yan investigated the influence of chain transfer on the molecular weight distribution in anionic polymerization initiated by multifunctional initiators using a graphical method [20].

Recently, the authors have presented a distribution function for a binary metallocene system with one catalyst generating polymer chains by ß-hydride elimination and the other in-situ propagating with the terminal double bonds [21]. It was found that the comb polymers thus produced give much narrower molecular weight distributions than randomly branched polymers with the same branching densities synthesized by a single catalyst system. In two subsequent papers, [22, 23] we presented comprehensive analytical theories for the bivariate distribution of molecular weight and branching density of comb polymers by chain polymerization with macromonomer and comb-branched copolymers by grafting onto, from, and through mechanisms. In this paper, we present a general model to describe the change in the molecular weight distribution of star-branched polymers during the synthesis as well as degradation processes. The model is based on random connection of a given number of linear primary chains with Schulz-Zimm length distribution onto a central core. The model is generally applicable regardless as to whether the star polymers are made by core-first or arm-first methods.
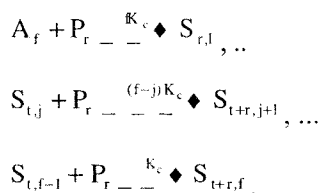
Star Formation

Arm-first and Core-first Mechanisms

There are two major approaches for synthesizing star polymers: arm-first and core-first [2,3]. In the arm-first approach, primary chains with "living" monocarbanionic ends prepared by anionic polymerization are often used as the branch material, while a multifunctional chlorosilane provides the core. The carb-

anionic centers are deactivated by the electrophile molecule and are thus connected to form a star. Since the functionality of the multifunctional electrophile can be precisely controlled, this method becomes the most favorable route of synthesizing star polymers. Divinyl monomers, such as divinyl benzene and ethylene dimeth-acrylate, have also been used to provide the core [24,25]. Copolymerization of the divinyl monomer with the carbanionic precursor yields a star-shaped structure. However, the fluctuation in the number of branches is expected due to lack of control over the size of the divinyl nodules.

The reactions involved in the arm-first methods are summarized as follows:

$$A_f + P_r \xrightarrow{\text{f} K_c} S_{r,1} , ..$$

$$S_{t,j} + P_r \xrightarrow{(f-j) K_c} S_{t+r,j+1} , ...$$

$$S_{t,f-1} + P_r \xrightarrow{K_c} S_{t+r,f} .$$

where A_f represents the molar concentration of f-functional active centers which form the cores of star polymers, and P_r is the linear primary chains having r mono-meric units. Depending on the relative concentration levels of A_f and P_r and the conversion of functional moieties, the product of the reacting system is a mixture of star polymers $S_{r,j}$ (j = 1, 2, ..., f), unreacted active centers and primary chains. The reacted primary chains become the branches (arms) of star polymers denoted as B_r. The molecular weight distribution of the star polymers is a function of the branch chains. Table 1 provides a list of the molecular weight properties of these polymer species ($S_{r,j}$, P_r, B_r). They include the number and weight fractional distributions, the number- and weight- average molecular weights, the polydispersity, and the concentrations of the polymer species. In this work, the term molecular weight indicates the number of monomeric units on polymer molecules. It is also used interchangeably with chain length and degree of polymerization. In the above reaction scheme, the reactivities of the functional moieties on active centers and primary chains are assumed to be independent of polymer molecular weight. The formation of the star polymers follows a random molecular process. The branches are randomly collected from the primary chain population, and therefore have the same molecular weight properties as the unreacted prepolymers.

In the core-first approach, multifunctional initiators, such as trimethyl-olpropane, trichloropropylbenzene and densely crosslinked polycarbanionic divinyl nodules [26-28], are employed to polymerize vinyl monomers. The initiator

TABLE 1.   Molecular Weight Properties of Various Polymer Species Involved in the Formation and Degration of Star Polymers

polymer species and symbols	j-branched star polymer, $S_{r,j}$	star polymer, $S_r = \sum_{j=1}^{f} S_{r,j}$	branch or arm, B_r	primary polymer or prepolymer, P_r
number concentration	$N_{S_j} = \sum_{r=1}^{\infty} S_{r,j}$	$N_S = \sum_{j=1}^{f} N_{S_j}$	$N_B = \sum_{r=1}^{\infty} B_r$	$N_P = \sum_{r=1}^{\infty} P_r$
weight concentration	$W_{S_j} = \sum_{r=1}^{\infty} rS_{r,j}$	$W_S = \sum_{j=1}^{f} W_{S_j}$	$W_B = \sum_{r=1}^{\infty} rB_r$	$W_P = \sum_{r=1}^{\infty} rP_r$
number fractional molecular weight distribution	$n_{S_j}(r) = S_{r,j}/N_{S_j}$ $n_S(r,j) = S_{r,j}/N_S$	$n_S(r) = \sum_{j=1}^{f} n_S(r,j)$	$n_B(r) = B_r/N_B$	$n_P(r) = P_r/N_P$
weight fractional molecular weight distribution	$w_{S_j}(r) = rS_{r,j}/W_{S_j}$ $w_S(r,j) = rS_{r,j}/W_S$	$w_S(r) = \sum_{j=1}^{f} w_S(r,j)$	$w_B(r) = rB_r/W_B$	$w_P(r) = rP_r/W_P$
number-average molecular weight	$\bar{S}_{N,j} = \int_0^{\infty} n_{S_j}(r)r\,dr$	$\bar{S}_N = \sum_{j=1}^{f} \bar{S}_{N,j}N_{S_j} \Big/ N_S$	$\bar{B}_N = \int_0^{\infty} n_B(r)r\,dr$	$\bar{P}_N = \int_0^{\infty} n_P(r)r\,dr$
weight-average molecular weight	$\bar{S}_{w,j} = \int_0^{\infty} w_{S_j}(r)r\,dr$	$\bar{S}_w = \sum_{j=1}^{f} \bar{S}_{w,j}W_{S_j} \Big/ W_S$	$\bar{B}_w = \int_0^{\infty} w_B(r)r\,dr$	$\bar{P}_w = \int_0^{\infty} w_P(r)r\,dr$
polydispersity of molecular weight distribution	$PDI_{S_j} = \bar{S}_{w,j}/\bar{S}_{N,j}$	$PDI_S = \bar{S}_w/\bar{S}_N$	$PDI_B = \bar{B}_w/\bar{B}_N$	$PDI_P = \bar{P}_w/\bar{P}_N$

propagate with monomers to form star branches. The growth of branches is halted by either termination or transfer of the propagating centers. Depending on the type of propagating center (anionic, cationic or radical), the relative rates of initiation and propagation vary. In the slow initiation/fast propagation scheme as shown in Table 2, the branches are generated successively in one-after-another manner. At any moment, a star polymer bears either zero or one propagating center. In addition to the mixture of star polymers, linear polymers are also produced in the system due to

chain transfer reactions. These polymers are equivalent to the unreacted primary chains in the arm-first scheme. However, their molecular weight properties could differ from those of the branches. It should also be pointed out that the bimolecular termination is assumed to be exclusively by disproportionation. Combination termination would potentially results in the production of three-dimensional polymer network. It is probably rather difficult to obtain well-defined star polymers by this mechanism due to the formation of star polymers having different number of branches.

Another core-first approach employs anionic polymerization as shown in Table 3. The initiation step is instantaneous, and thus the number of branches is determined, provided the initiator functionality is known. The propagation is slow with f branches growing simultaneously. In the absence of termination and transfer reactions, the branches continue to grow until all monomers are depleted. The branches have an equal molecular weight which can be estimated by dividing monomer concentration by that of initiator functional moieties. If some termination and transfer reactions occur, the branches would have different molecular weights and also primary chains are introduced. The product would be a mixture of f-functional star polymers and linear primary chains.

Controlling Parameters

The key parameters controlling the molecular weight distribution of star polymers include:

the stoichiometry between the functional moieties on active centers, fA_f^0, and the primary chains initially charged to the reactor, N_P^0

$$\alpha = \frac{fA^0}{N_P^0}$$

(1)

the ratio of the number-average molecular weight of primary chains, $\overline{P_N}$, to that of branches of star polymers, $\overline{B_N}$

$$\beta = \frac{\overline{P_N}}{\overline{B_N}},$$

(2)

the conversion of the functional moieties

$$\lambda = \frac{fA_f^0 - fA_f}{fA_f^0} = \frac{N_P^0 - N_P}{fA_f^0} = \frac{N_B}{fA_f^0}$$

(3)

TABLE 2. Elementary Reactions and Their Rate Constants in Chain Polymerization with Branching via the Core-first Mechanism —Slow Initiation and Fast Propagation

Activation/ Initiation	$A_f + M \xrightarrow{fK_i} S_{1,1}^*$
	$S_{r,j} + M \xrightarrow{(f-j)K_i} S_{r+1,j+1}^*$
	$T^* + M \xrightarrow{K_{i,T}} P_1^*$
Propagation	$S_{r,j}^* + M \xrightarrow{K_p} S_{r+1,j}^*$
	$P_r^* + M \xrightarrow{K_p} P_{r+1}^*$
Transfer	$S_{r,j}^* + T \xrightarrow{K_{tr}} S_{r,j} + T^*$
	$P_r^* + T \xrightarrow{K_{tr}} P_r + T^*$
Termination	$S_{r,j}^* \xrightarrow{\tau} S_{r,j}$
	$P_r^* \xrightarrow{\tau} P_r$

TABLE 3. Elementary Reactions and Their Rate Constants in Chain Polymerization with Branching via the Core-first Mechanism —Fast Initiation and Slow Propagation

Activation/Initiation	$A_f + M \xrightarrow{fK_i} S_{f,f}^{f*}$
	$T^* + M \xrightarrow{K_{i,T}} P_1^*$
Propagation	$S_{r,f}^{j*} + M \xrightarrow{jK_p} S_{r+1,f}^{j*}$
	$P_r^* + M \xrightarrow{K_p} P_{r+1}^*$
Transfer	$S_{r,f}^{j*} + T \xrightarrow{K_{tr}} S_{r,f}^{(j-1)*} + T^*$
	$P_r^* + T \xrightarrow{K_{tr}} P_r + T^*$
Termination	$S_{r,f}^{j*} \xrightarrow{\tau} S_{r,f}^{(j-1)*}$
	$P_r^* \xrightarrow{\tau} P_r$

where N_P and N_B are the molar concentrations of primary chains and branches, respectively, with the superscript "0" indicating the initial condition.

Note $N_B = fA_f^0 - fA_f = N_P^0 - N_P$.

Among these parameters, α is predetermined from the recipe. A stoichiometric balance between the functional moieties and primary chains is most desirable for synthesizing well-defined star polymers. In some cases, particularly when a multifunctional monomer such as divinylbenzene is used to form the core, a large fluctuation in the functionality of the active center is inevitable and thus the condition of $\alpha=1$ could be violated. As for β, it is often equal to unity. However, in the presence of a chain transfer mechanism in the core-first scheme, the chain lengths of linear by-product polymers and branches of the star could be different, particularly in a living type polymerization where the propagation of star branches is halted by chain transfer to form linear polymers with their chains continuously growing until monomer depletion. It is also possible for the star formation via the arm-first method to become chain-length dependent. Short primary chains may possess higher reactivities than their long chain counterparts due to the possible diffusion constraint imposed by the to the existing branches. In such a case, unreacted chains are often those having the highest molecular weights. The conversion of functional moiety λ is a variable reflecting the star formation kinetics. A complete conversion, $\lambda=1$, is desirable in practice. In order for the model to be general, arbitrary values of α, β and λ are considered in the derivation.

At the conversion of functional moiety, λ, the concentration of the remaining f-functional active centers, A_f, is

$$A_f = A_f^0 (1-\lambda)^f \tag{4}$$

The concentration of the star polymers having r monomeric units on j branches is given by

$$S_{r,j} = A_f^0 \binom{f}{j} \lambda^j (1-\lambda)^{f-j} \xi_j(r) \tag{5}$$

where $\binom{f}{j} \lambda^j (1-\lambda)^{f-j}$ is the probability of randomly selecting a f-functional center A_f^0 having j functional moieties reacted, and $\xi_j(r)$ is defined as:

$$\xi_j(r) = \int_0^r n_B(r-u) \int_0^u n_B(u-v) \ldots \int_0^y n_B(y-z) n_B(z) dz \ldots dv du \tag{6}$$

(with j-1 integrals) is the collection of possible combinations of primary chains for a total number of monomeric units r.

Average Molecular Weights

With an arbitrary distribution of branches, $n_B(r)$, the function $\xi_j(r)$ has the following properties:

$$\int_0^\infty r^2\xi_j(r)dr = j\overline{B}_N\left[(j-1)\overline{B}_N + \overline{B}_W\right]$$

$$\int_0^\infty \xi_j(r)dr = 1$$

$$\int_0^\infty r\xi_j(r)dr = j\overline{B}_N \tag{7}$$

The number, N_{S_j}, and weight, W_{S_j}, of j-branched star polymers are:

$$N_{S_j} = A_f^0\binom{f}{j}\lambda^j(1-\lambda)^{f-j} \text{ and } W_{S_j} = A_f^0\binom{f}{j}\lambda^j(1-\lambda)^{f-j}j\overline{B}_N \tag{8}$$

The corresponding number, $\overline{S}_{N,j}$, and weight-average, $\overline{S}_{W,j}$, molecular weights of the j-branched population are:

$$\overline{S}_{N,j} = j\overline{B}_N \text{ and } \overline{S}_{W,j} = (j-1)\overline{B}_N + \overline{B}_W \tag{9}$$

with the polydispersity, PDI_c,

$$PDI_{S_j} = 1 + \frac{PDI_B - 1}{j} \tag{10}$$

The number and weight of total star polymers (sum of j = 1, 2, ..., f) are

$$N_S = A_f^0\left[1-(1-\lambda)^f\right] \text{ and } W_S = \lambda f A_f^0\overline{B}_N \tag{11}$$

The corresponding number, $\overline{S}_N$, and weight-average, $\overline{S}_W$, molecular weights of the total star population are

$$\overline{S}_N = \frac{\lambda f\overline{B}_N}{1-(1-\lambda)^f} \text{ and } \overline{S}_W = \left[PDI_B + \lambda(f-1)\right]\overline{B}_N \tag{12}$$

with the polydispersity, PDI_S,

$$PDI_S = \frac{\left[PDI_B + \lambda(f-1)\right]\left[1 - (1-\lambda)^f\right]}{\lambda f} \tag{13}$$

The number, $\overline{M}_N$, and weight average, $\overline{M}_W$, molecular weights of the polymer mixture of star and linear polymers are

$$\overline{M}_N = \frac{\overline{S}_N N_S + \overline{P}_N N_P}{N_S + N_P} = \frac{\left[\beta + \lambda\alpha(1-\beta)\right]f\,\overline{B}_N}{f - \alpha\left[\lambda f + (1-\lambda)^f - 1\right]} \tag{14}$$

$$\overline{M}_W = \frac{\overline{S}_W W_S + \overline{P}_W W_P}{W_S + W_P} = \frac{\beta^2 PDI_P + \lambda^2\alpha(f-1) + \lambda\alpha\left(PDI_B - \beta^2 PDI_P\right)}{\beta + \lambda\alpha(1-\beta)}\overline{B}_N \tag{15}$$

and the polydispersity, PDI_M,

$$PDI_M = \frac{\overline{M}_W}{\overline{M}_N} = \frac{f - \alpha\left[\lambda f + (1-\lambda)^f - 1\right]}{f\left[\beta + \lambda\alpha(1-\beta)\right]^2}\left[\beta^2 PDI_P + \lambda^2\alpha(f-1) + \lambda\alpha\left(PDI_B - \beta^2 PDI_P\right)\right] \tag{16}$$

If the star branch and primary chain have the same molecular weight distribution, i.e., $\beta = 1$ and $PDI_B = PDI_P$, Equation (16) becomes

$$PDI_M = \frac{f - \alpha\left[\lambda f + (1-\lambda)^f - 1\right]}{f}\left[PDI_B + \lambda^2\alpha(f-1)\right] \tag{16a}$$

Equation (16a) can be further simplified, if $\lambda = 1$ in addition to $\beta = 1$ and $PDI_B = PDI_P$,

$$PDI_M = \frac{\left[f - \alpha(f-1)\right]\left[PDI_B + \alpha(f-1)\right]}{f} \tag{16b}$$

With an absolute stoichiometric balance ($\alpha = 1$), Equation (16b) becomes

$$PDI_M = 1 + \frac{PDI_B - 1}{f} \tag{16c}$$

Other molecular properties of interest are the number, n_B, and weight, w_B, fractions of branched polymers. The star polymers having one and two branches as

well as the unreacted (or newly formed) primary chains are not included in this catalogory.

$$n_B = \frac{N_S - N_{S_1} - N_{S_2}}{N_S + N_P} = \alpha \frac{1 - (1-\lambda)^f - \lambda f (1-\lambda)^{f-1} - \frac{f(f-1)}{2}\lambda^2 (1-\lambda)^{f-2}}{f + \alpha\left[1 - \lambda f - (1-\lambda)^f\right]} \quad (17)$$

$$w_B = \frac{W_S - W_{S_1} - W_{S_2}}{W_S + W_P} = \alpha\lambda \frac{1 - (1-\lambda)^{f-1} - (f-1)\lambda(1-\lambda)^{f-2}}{\beta + \lambda\alpha(1-\beta)} \quad (18)$$

It should be emphasized that the above relationships, Equations 8-18, are valid regardless of the specific type of primary chain distribution, $n_B(r)$. Figure 1 shows the star polymer polydispersity versus the functional moiety conversion calculated using Equation 13. The polydispersity of the star polymers is usually smaller than that of the branches. At the complete conversion, the polydispersity reaches $1 + (PDI_R - 1)/f$. Stars with more branches have narrower molecular weight distributions. With the monodispersed branches, the polydispersity increases at intermediate conversions because the stars with different numbers of branches coexist.
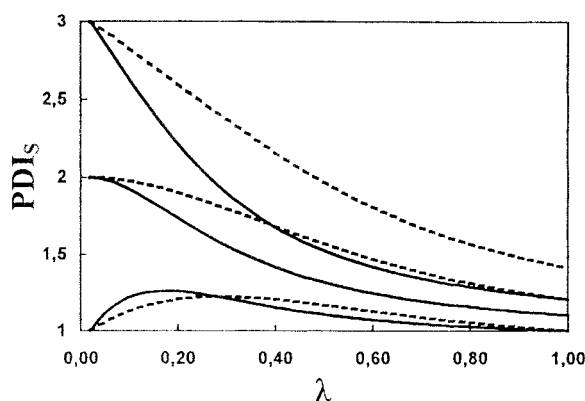
Figure 2 gives the polydispersity of polymer mixture versus the stoichiom-etry between the active centers and primary chains initially charged to the reactor. The functional moieties on active centers are assumed to be completely reacted. The results were calculated using Equation 16b. The polydispersity increases when the stoichiometric balance is deviated. This is due to the unreacted linear primary chains.

Figure 3 shows the development of number and weight fractions of branched polymers calculated using Equations 17 and 18. The star polymers with one and two branches are considered as linear polymers. The weight fraction of branched polymers develops more rapidly than the number fraction. The difference increases with the functionality.

Full Molecular Weight Distributions

The distribution function of branches, $n_B(r)$, is the prerequisite (Equation 19) for calculating the full molecular weight distribution of star polymers. Giving the branch chains have a uniform distribution, $n_B(r)$ can be expressed as:

$$n_B(r) = \delta(r - \overline{B}_N) \quad (19)$$

Figure 1. Development of the polydispersity of star polymers, calculated using Equation 13, as a function of the functional moiety conversion. f = 10 (solid) and 5 (dot). PDI_B = 1, 2, and 3.
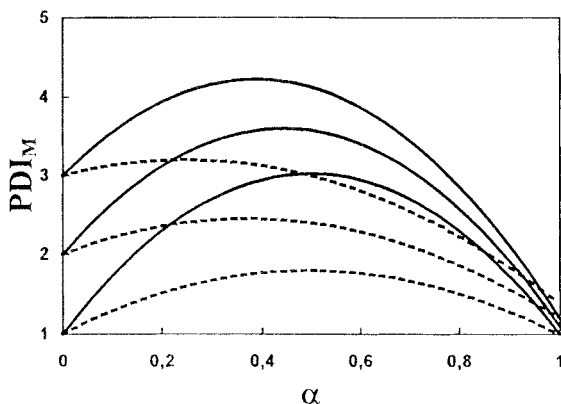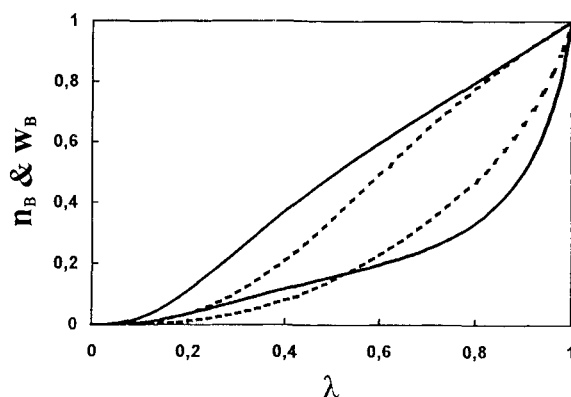

Figure 2. Polydispersity of the mixture of star polymer and primary chains, calculated using Equation 16b, as a function of the stoichiometric ratio between the functional moiety and primary chain. f = 10 (solid) and 5 (dot). PDI_B = 1, 2, and 3.

Substituting Equation 19 into Equation 6 yields:

$$\xi_j(r) = \delta\left(r - j\overline{B}_N\right) \tag{20}$$

and thus

$$S_{i,j} = A_i^0 \binom{f}{j} \lambda^j (1-\lambda)^{f-j} \delta\left(r - j\overline{B}_N\right) \tag{21}$$

Figure 3. Development of number and weight fractions of branched polymers, calculated using Equations 17 and 18, as a function of the functional moiety conversion. $\alpha = \beta = 1$ and $f = 10$ (solid) and 5 (dot).

where $\delta(x-y) = 1$, $x = y$; $\delta(x-y) = 0$, $x \neq y$. Dividing Equation 21 by Equation 11 results in the expressions for the number-, $n_s(r,j)$, and weight-fraction, $w_s(r,j)$, molecular weight distributions of the star polymers having r monomeric units on j branches:

$$n_s(r,j) = \binom{f}{j} \frac{\lambda^j (1-\lambda)^{f-j}}{1-(1-\lambda)^f} \delta\left(r - j\overline{B}_N\right) \tag{22}$$

and

$$w_s(r,j) = \binom{f-1}{j-1} \lambda^{j-1} (1-\lambda)^{f-j} \delta\left(r - j\overline{B}_N\right) \tag{23}$$

At the complete conversion of functional moieties ($\lambda = 1$), Equations 22 and 23 reduce to:

$$w_s(r,f) = n_s(r,f) = \delta\left(r - f\overline{B}_N\right) = \delta\left(r - \overline{S}_N\right) \tag{24}$$

where $\overline{S}_N = f\overline{B}_N$.

One may also assume the branch chains follow a Schulz-Zimm distribution given by:

$$n_B(r) = \frac{1}{(k-1)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{k-1} e^{-\frac{kr}{\overline{B}_N}} \tag{25}$$

where k indicates the polydispersity through $PDI_B = (k+1)/k$. Equation 24 then becomes a random distribution when $k = 1$ and a uniform distribution when $k \to \infty$. Substituting Equation 25 into Equation 6 provides:

$$\xi_j(r) = \frac{1}{(kj-1)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kj-1} e^{-\frac{kr}{\overline{B}_N}} \tag{26}$$

and thus

$$S_{r,j} = A_f^0 \binom{f}{j} \lambda^j (1-\lambda)^{f-j} \frac{1}{(kj-1)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kj-1} e^{-\frac{kr}{\overline{B}_N}} \tag{27}$$

The number-, $n_S(r,j)$, and weight-fraction, $w_S(r,j)$, molecular weight distributions of the star polymer having r units on j branches are obtained through dividing Equation 27 by Equation 11:

$$n_S(r,j) = \binom{f}{j} \frac{\lambda^j (1-\lambda)^{f-j}}{1-(1-\lambda)^f} \frac{1}{(kj-1)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kj-1} e^{-\frac{kr}{\overline{B}_N}} \tag{28}$$
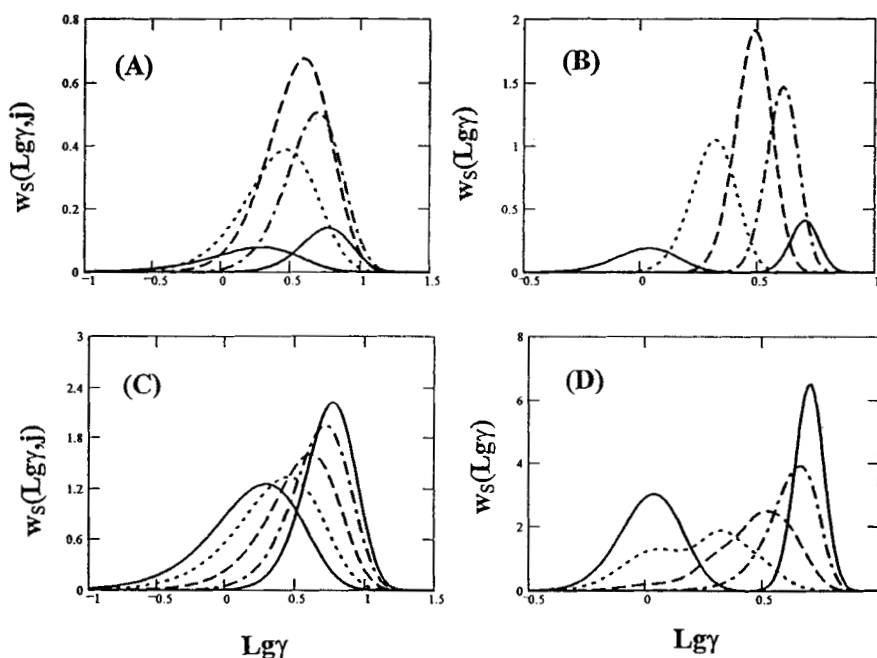
and

$$w_S(r,j) = \binom{f-1}{j-1} \frac{\lambda^{j-1}(1-\lambda)^{f-j}}{(kj)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kj} e^{-\frac{kr}{\overline{B}_N}} \tag{29}$$

At a complete functional moiety conversion ($\lambda = 1$), Equations 28 and 29 reduce to

$$n_S(r,f) = \frac{1}{(kf-1)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kf-1} e^{-\frac{kr}{\overline{B}_N}} = \frac{1}{(kf-1)!} \frac{kf}{\overline{S}_N} \left(\frac{kf}{\overline{S}_N}r\right)^{kf-1} e^{-\frac{kf}{\overline{S}_N}r} \tag{30}$$

and

$$w_S(r,f) = \frac{1}{(kf)!} \frac{k}{\overline{B}_N} \left(\frac{kr}{\overline{B}_N}\right)^{kf} e^{-\frac{kr}{\overline{B}_N}} = \frac{1}{(kf)!} \frac{kf}{\overline{S}_N} \left(\frac{kf}{\overline{S}_N}r\right)^{kf} e^{-\frac{kf}{\overline{S}_N}r} \tag{31}$$
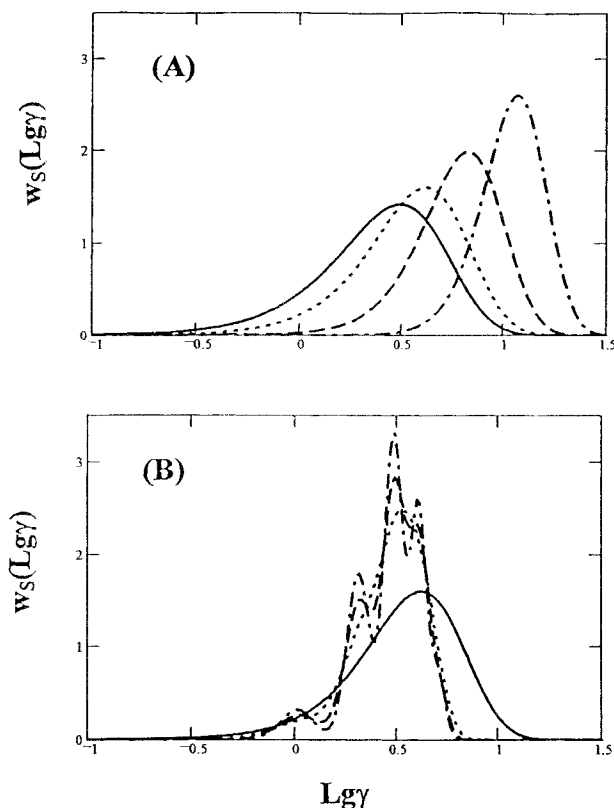
Figure 4. Molecular weight distribution of star polymers, calculated using Equation 29. f = 5.

    (A) $w_s(r,j)$: k = 1 and λ = 0.5. j = 1 (solid), 2 (dot), 3 (dash), 4 (dash-dot), 5 (solid)

    (B) $w_s(r)$: k = 1 and λ = 0 (solid), 0.2 (dot), 0.5 (dash), 0.8 (dash-dot), 1 (solid)

    (C) $w_s(r,j)$: k = 10 and λ= 0.5. j = 1 (solid), 2 (dot), 3 (dash), 4 (dash-dot), 5 (solid)

    (D) $w_s(r)$: k = 10 and λ = 0 (solid), 0.2 (dot), 0.5 (dash), 0.8 (dash-dot), 1 (solid)

It is clear from Equations 30 and 31 that, if the branches have a Schulz-Zimm distribution according to Equation 25 with the polydispersity (1+1/k), the star polymers also follow a Schulz-Zimm distribution with the polydispersity of 1+1/(kf), which is smaller than that of branches. A similar expression was derived for the case with a random branch distribution (k=1) [16, 29].

    Figure 4(A) and 4(C) show the molecular weight distributions of star polymers with various numbers of branches, calculated using Equation 29, and their

Figure 5.   Effect of f and k on molecular weight distribution of star polymers, calculated using Equation 29. $\lambda = 0.5$.

(A) $w_s(r)$: k = 1 and f = 3 (solid), 5 (dot), 10 (dash), 20 (dash-dot).

(B) $w_s(r)$: f = 5 and k = 1 (solid), 10 (dot), 20 (dash), 30 (dash-dot).

total distribution. The star branch follows a random distribution in Figure 4(A) and a narrower Schulz-Zimm distribution with the polydispersity of 1.1 in Figure 4(C). Figures 4(B) and 4(D) gives the development of the total distributions during the formation of star polymers. The distribution at the complete moiety conversion is clearly narrower than the original distribution in each case. Depending on the branch polydispersity, the distributions at the intermediate conversions could be rather broad and have multi-modal shapes resolving the number of branches on the star polymers. Figure 5(A) shows the effect of the functionality on the star distribution. Figure 5(B) shows the effect of the branch polydispersity on the star distribution.

It should be emphasized that although the model is derived based on the arm-first scheme it is also applicable to the star polymers by the core-first method provided branch chains are randomly connected onto the core. Table 4 summarizes the expressions for determining the parameters for the core-first mechanisms. In the slow initiation scheme, the rate of branching equals that of activation of functional moieties on star cores, while it always equals unity in the instantaneous initiation mechanism. The number-average molecular weights of branch chains are calculated by following the concentrations of the reacting species as listed in the table. The branch chain would have a random distribution if the chain termination and/or transfer are significant. If the chain growth is a "living" type, the uniform distribution should apply to the branches.

Star Degradation

The stability of star polymers could be an important issue, particularly, when they are used as motor oil additives subject to high shear condition [6]. There have been many theoretical investigations on the degradation of linear polymer systems [30-33]. Most notably are Saito's simple analytical equations [34]. In contrast, degradation of branched polymers received much less attention, with only a few attempts made by Monte Carlo methods [35]. Very recently, Tobita published a paper dealing with the topic [29]. Molecular weight distributions are simulated for star polymers having random and uniform branches. General expressions for the change in average molecular weights are also obtained under these conditions. However, the connection units between branches and functional moieties are assumed to have the same scission probability as the monomeric units on branches. This assumption may not be generally valid, particularly with the star polymers prepared by the electrophile deactivation of carbanionic centers. We therefore distinguish two degradation mechanisms: disconnecting branches from the star core and random scission of the branches. In the former case, each branch has an equal probability to be disconnected from the core; while in the latter, each monomeric unit has a same reactivity of chain scission regardless of its specific location on a branch. For the random scission of star branches, readers can refer to Tobita's work [29]. In the following, we consider the scheme of branch disconnection.

Disconnecting Branches from Star Cores

Let us start with a population of star polymers described by Equation 30 or 31, with the branches following Equation 25. The degree of degradation can be

TABLE 4. Calculation of Determining Parameters for Molecular Weight Distribution in Chain Polymerization with Star Branching via the Core-first Mechanism

	slow initiation	instantaneous initiation
star branch $N_B = fA_f^0 - F$ conversion of functional moiety, $\lambda = \dfrac{N_B}{fA_f^0}$	$\dfrac{dF}{dt} = -K_i MF, \quad F = fA_f^0 \text{ at } t = 0$ $\dfrac{dM}{dt} = -K_p M(S^* + P^*), \quad M = M^0 \text{ at } t = 0$ $\dfrac{dS^*}{dt} = K_i MF - (K_{tr}T + \tau)S^*, \quad S^* = 0 \text{ at } t = 0$ $\dfrac{dP^*}{dt} = K_{tr}TS^* - (K_{tr}T + \tau)P^*, \quad P^* = 0 \text{ at } t = 0$ $\tau = K_t(S^* + P^*), \text{ if bimolecular termination}$ $\dfrac{dT}{dt} = -K_{tr}T(S^* + P^*), \quad T = T^0 \text{ at } t = 0$	$N_B = fA_f^0$ $\lambda = 1$
primary chain $N_P = T^0 - T$ stoichiometry between moiety and chain $\alpha = \dfrac{fA_f^0}{N_B + N_P}$		$\dfrac{dT}{dt} = -K_{tr}T(S^* + P^*)$ $\dfrac{dS^*}{dt} = -(K_{tr}T + \tau)S^*$ $\dfrac{dP^*}{dt} = K_{tr}TS^* - (K_{tr}T + \tau)P^*$
$\beta = \dfrac{\overline{P}_N}{\overline{B}_N}$ $\overline{B}_N = \dfrac{W_B}{N_B}$ $\overline{P}_N = \dfrac{W_P}{N_P}$	$\dfrac{dW_B}{dt} = K_p MS^*, \quad W_B = 0 \text{ at } t = 0$ $\dfrac{dW_P}{dt} = K_p MP^*, \quad W_P = 0 \text{ at } t = 0$	$\dfrac{dW_B}{dt} = K_p MS^*$ $\dfrac{dW_P}{dt} = K_p MP^*$

defined as the fraction of branch chains which are disconnected from the star polymers (μ). This definition is obviously complementary to the conversion of functional moieties defined in Equation 3.

$$\mu = \frac{N_B^0 - N_B}{N_B^0}$$

(32)

where is the concentration of initial branches, and is that at the present time. The disconnected branches, referred to as primary chains, can be calculated using $N_D = N_D^0 - N_D = \mu f S_r^0$. The star polymers with branches fully disconnected (bare cores) are $S_0 = S_r^0 \mu^f$. The number of remaining star polymers are Use the same probability argument in deriving Equation (27), one obtains

$$S_{r,j} = S_r^0 \binom{f}{j}(1-\mu)^j \mu^{f-j} \frac{1}{(kj-1)!}\frac{k}{\bar{B}_N}\left(\frac{kr}{\bar{B}_N}\right)^{kj-1} e^{-\frac{kr}{\bar{B}_N}}$$

(33)

The number-, $\bar{S}_N$, and weight-average, $\bar{S}_W$, molecular weights of the star population are

$$\bar{S}_N = \frac{(1-\mu)f\bar{B}_N}{1-\mu^f} \quad \text{and} \quad \bar{S}_W = \left[\frac{k+1}{k}+(1-\mu)(f-1)\right]\bar{B}_N$$

(34)

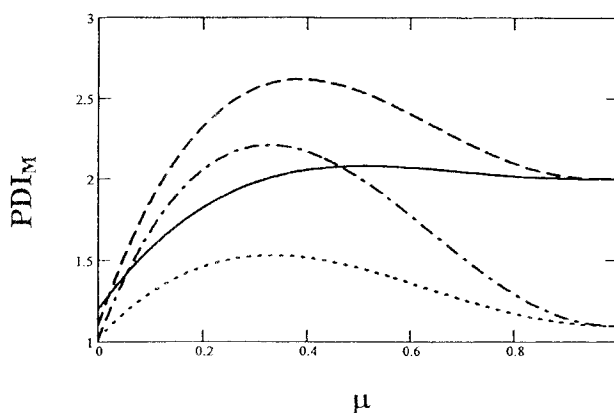with the polydispersity given by:

$$PDI_S = \frac{\left(1-\mu^f\right)\left[\frac{k+1}{k}+(1-\mu)(f-1)\right]}{(1-\mu)f}$$

(35)

Equations 34 and 35 are similar to Equations 12 and 13 with μ replaced by 1-λ. The average molecular weights and polydispersity of the mixture of star polymers and linear primary primary chains are

$$\bar{M}_N = \frac{f\bar{B}_N}{1+\mu f-\mu^f}, \quad \bar{M}_W = \left[\frac{k+1}{k}+(1-\mu)^2(f-1)\right]\bar{B}_N$$

(36)

$$PDI_M = \frac{1}{f}\left(1+\mu f-\mu^f\right)\left[\frac{k+1}{k}+(1-\mu)^2(f-1)\right]$$

(37)

Figure 6.   Change in polydispersity of star polymers undergoing degradation via the branch disconnection mechanism, calculated using Equation 37. The parameters are: (solid) f = 5, k = 1; (dot) f = 5, k = 10; (dash) f = 10, k = 1, (dash-dot) f = 10, k = 10.

It can be seen in Equations 34 or 36 that the average molecular weights decrease monotonously during degradation. Figure 6 shows the change in the polydispersity of star polymers undergoing degradation via the branch disconnection mechanism calculated using Equation 37. The polydispersity increases rapidly at the beginning from its initial value $(1+1/kf)$, reaches a maximum at an intermediate degree of degradation, and finally approaches the polydispersity of the disconnected branches $(1+1/k)$. For the same branch polydispersity (k), the maximum polydispersity increases with the functionality f.

CONCLUSIONS

Simple analytical expressions are presented to describe the molecular weight distribution of star branched polymers. The branch chains are assumed to have either uniform or Schulz-Zimm distributions. This model is based on the statistical connection of pre-formed chains onto cores. However, it is also applicable to the star polymers synthesized by core-first methods shown in Tables 2 and 3. The major parameters determining the star distribution are the branch distribution, $n_B(r)$, core functionality, f, conversion of the functional moiety, λ, as well as the branch-to-core stoichiometric ratio, α. These parameters are either predetermined or esti-

mated by following the population equations of reactants involved in the mechanism as given in Table 4. The effects of these parameters on the star distribution are illustrated in Figures 4 and 5. Presented also are the change in the average molecular weights during degradation of star polymers. The scheme of disconnecting branches from core has been taken into account.

ACKNOWLEDGMENTS

Glossary of Symbols

A_f concentration of active centers (initiator) of functionality f.

B_r concentration of branches

$\overline{B}_x$ number- (X=N) and weight- average (X=W) molecular weight of branches of star polymers

f functionality of active center (initiator)

j number of branches on $S_{r,j}$

K_x rate constant of combination (x=c), decomposition of functional group (x=d), initiation (x=i), termination (x=t), and chain transfer (x=tr)

k parameter in the Schulz-Zimm distribution function

M monomer concentration

$\overline{M}_x$ number- (X=N) and weight-average (X=W) molecular weight of polymer mixture of primary and star polymers

N_x number of branches (X=B), primary polymers or unreacted pre-polymer (X=P), star polymers (X=S), and star polymer with j branches (X=S$_j$)

n_B number fraction of branched polymers, defined in Equation (17)

$n_x(r)$ number-fractional molecular weight distribution of star branches (X=B), primary chains (X=P), star polymers (X=S), star polymers of j branched population (X=S$_j$), see Table 1.

$n_s(r,j)$ number-fractional molecular weight distribution of star polymers having j branches

PDI_X polydispersity of star branches (X=B), polymer mixture of primary and star polymers (X=M), primary chains (X=P), star polymers (X=S), star polymers of j branched population (X=S_j)

P_r concentration of primary polymers having r monomeric units

$\bar{P}_X$ number- (X=N) and weight-average (X=W) molecular weight of primary chains

r   number of monomeric units on polymers

S_r concentration of star polymers having r monomeric units

$S_{r,j}$ concentration of star polymer having r monomeric units and j branches ($1 \leq j \leq f$)

$\bar{S}_X$ number- (X=N) and weight-average (X=W) molecular weight of star polymers

$\bar{S}_{X,j}$ number- (X=N) and weight-average (X=W) molecular weight of star polymers having j branches

T   concentration of transfer agent

t   time

W_X weight of primary chains (X=P), star polymers (X=S), star polymers of j branched population (X=S_j),

w_B weight fraction of branched polymers, defined in Equation (18)

$w_X(r)$ weight-fractional molecular weight distribution of star branches (X=B), primary chains (X=P), star polymers (X=S), star polymers of j branched population (X=S_j)

$w_S(r,j)$ weight-fractional molecular weight distribution of star polymers having j branches

α stoichiometry between the functional moieties on active centers and the primary chains initially charged to the reactor, defined in Equation 1

β ratio of the number-average molecular weight of primary chains to that of branches of star polymers, defined in Equation 2

λ conversion of the functional moieties, defined in Equation 3

δ uniform function

$\xi_j(r)$ combination function of branch chains, defined in Equation 6

τ termination rate parameter

μ degree of degradation, defined in Equation 32

super 0   indicating initial condition

super *   indicating reactive center

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