Macromolecules **1998,** *31,* 7519−7527

Analytical Functions for Molecular Weight and Branching Distributions in Star-, Comb-, and Random-Branched Polymers

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Received January 5, 1998; Revised Manuscript Received May 26, 1998

ABSTRACT: Long-chain branching has a significant effect on various polymer properties. One of the determining molecular parameters is the bivariate distribution of molecular weight and branching density. This work presents analytical distribution functions for three types of branched polymers: random, comb, and star. The primary chains are assumed to have a Schulz−Zimm distribution. It is shown that the distribution shape strongly depends on the type of branching with polydispersity in the order of star < comb < random.

Introduction

The effect of long-chain branching on certain polymer properties is known to be quite dramatic, even at a very low level of branching.[1] For example, polyethylene with a small number of branching points (fewer than one branching point per polymer molecule) shows an excellent improvement in shear thinning compared to its linear counterpart.[2,3] Branched polymers therefore offer many special functions in a wide range of applications.[4−9]

Branched polymers can be synthesized by various mechanisms. In general, a branched polymer can be viewed as an assembly of linear chains if its branching points were severed. Depending on how these primary chains are connected, the branched polymer assumes various molecular structures. A *random*-branched polymer has a structure of branches-on-branches. Such a polymer is formed if one end of each primary chain is allowed to be connected to a backbone of another chain with every monomeric unit on the backbone having an equal probability of being selected. In this case, each individual primary chain contains both reactive backbone units and one coreactive chain end. A *comb* polymer has a backbone attached with side chains. This type of branching structure is formed if the individual primary chain bears either reactive backbone units or a coreactive chain end, but not both. Thus further branching on the side chains is disallowed. A *star* polymer is a cluster of primary chains with one end of each chain bound to a common core. In this case, the individual primary chain bears only a reactive chain end but not reactive backbone units. The formation of star-, comb-, and random-branched polymers from primary chains is schematically presented in Figure 1.

An important parameter in determining the performance of a branched polymer is the bivariate distribution of molecular weight and branching density. This distribution depends on the type of branching structure. Differences between the distribution shape of star-, comb-, and random-branched polymers can be expected, even if the polymers have same average molecular weight and average branching density. Therefore, a precise description of the distribution function for different types of branched polymers is desirable and challenging.

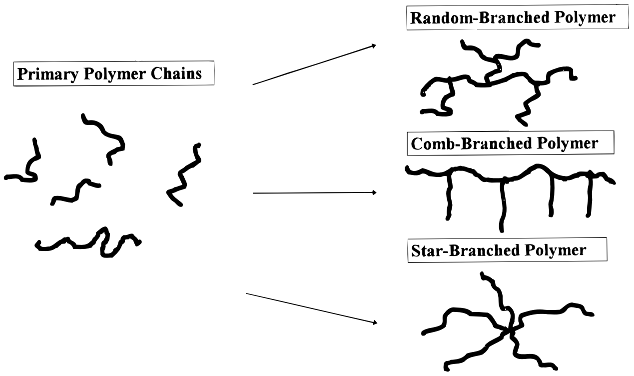

Figure 1. Schematic representation of random-, comb-, and star-branched polymers formed by connecting linear primary chains.

Modeling of the molecular weight distribution of nonlinear polymers has been studied for over half a century since the pioneering work of Flory and Stockmayer.[10,11] However, most of the work focused on determining the average molecular weight and gelation behavior of various polymerization systems. There were only a few full distribution functions reported in the literature. For example, Flory presented a model for uniform primary chains cross-linked by divinyl comonomer.[10] Stockmayer extended the model for an arbitrary primary chain distribution.[11] Beasley gave an expression for branched polymers formed by chain transfer to polymer in free radical polymerization carried out in a continuous stirred-tank reactor.[12] Bamford and Tompa dealt with the same polymerization system in a batch reactor at low monomer conversion.[13] Saito developed a rather general integrodifferential equation to describe the random coupling of primary chains.[14] Kimura and Amemiya obtained analytical solutions for the special cases of uniform and randomly distributed primary chains, respectively.[15,16] Early works in this field were summarized by Peebles.[17] Recently, Tobita used a random sampling technique and obtained an equation for homogeneously branched polymers with random primary chains.[18] Soares and Hamielec reported a distribution function for metallocene polymerization with terminal branching.[19] These models dealt exclusively with random-branched polymers having either

10.1021/ma9800055 CCC: $15.00

trifunctional (T type) or tetrafunctional (H type) branching points. Since the H-type branching leads to gel formation at a certain branching density, it is therefore excluded from further discussion in this paper.

It is difficult to control the branching structure of random-branched polymers. Synthesis of branched polymers with well-defined structures has recently received much attention due to the great potential in designing specialty commercial products. Many experimental investigations on comb- and star-branched polymers have appeared in the literature.[20−22] However, there is a lack of modeling effort particularly in developing analytical functions of the bivariate distribution of molecular weight and branching density for these polymers. For comb polymers, Stejskal et al. calculated the chemical composition distribution of polymers formed in a free-radical copolymerization with macromonomer, but they did not give the solution in closed form.[23,24] Zhu et al. derived a distribution function for a binary metallocene system with one catalyst generating polymer chains by β-hydride elimination and the other in situ propagating via terminal double bonds.[25] It was found that the comb polymer thus produced has a much narrower molecular weight distribution than a random-branched polymer with a same branching density synthesized by a single catalyst system. In subsequent publications, Zhu et al. presented two general analytical expressions: one for copolymerization of vinyl monomer with either uniform or randomly distributed macromonomer[26] and the other for graft copolymer with backbone and side chains having uniform and/or Schulz−Zimm distribution.[27]

For star polymers, Yuan et al. presented a function for the molecular weight distribution in free-radical polymerization that involves a polyfunctional chain transfer agent.[28] Tobita dealt with the same system in a more general manner.[29] The arms of the star polymer assume a random distribution. Yan investigated the influence of chain transfer on the molecular weight distribution in an anionic polymerization with multifunctional initiators using a graphical method.[30] Zhu et al. presented a general distribution function for a star polymer formed by connecting Schulz−Zimm primary chains onto a polyfunctional core.[31]

There are also some numerical investigations on the molecular weight distribution of branched polymers. However, the present paper focuses on analytical distribution functions which are often considered to be more favorable than numerical models. The objectives of this work are two-fold: The first is to integrate the distribution functions for various types of branched polymers in the literature. The approach is to develop expressions for the star-, comb-, and random-branched polymers assembled from Schulz−Zimm primary chains. Since both random and uniform distributions are just two special forms of the Schulz−Zimm distribution, the previous distribution functions are thus unified. The second objective is to compare distribution functions of the three types of branched polymers. It is of fundamental interest to know how different the molecular weight distributions for various branched polymers could be under the conditions of the same average molecular weight and branching density.

It should be pointed out that the most general case is no doubt a branched polymer system formed by primary chains having an arbitrary chain distribution. In principle, any arbitrary distribution can be deconvoluted into a series of random distributions. So far, we have not seen any solution in closed form under this condition.

General Considerations

As illustrated in Figure 1, the primary chains (P_r with the subscript r denoting the number of monomeric units) are assembled in certain manners into various types of branched polymers ($Y_{r,i}$ with r the number of monomeric units and i the number of primary chains),

$$P_r \rightarrow Y_{r,i} \tag{1}$$

where Y can be random (R), comb (C), and star (S). Obviously, the following initial conditions should be met

$$Y_{r,1} = P_r \quad \text{and} \quad Y_{r,i>1} = 0 \tag{2}$$

at $t = 0$. We define the moments as follows

$$P^{(k)} = \int_0^\infty r^k P_r \, \mathrm{d}r \quad \text{and} \quad Y^{(k)} = \sum_{i=1}^{\infty} \int_0^\infty r^k Y_{r,i} \, \mathrm{d}r \tag{3}$$

The number-average molecular weights (note that the terms of molecular weight and chain length are used interchangeably in this paper) for the primary and branched polymers are thus

$$\bar{P}_\mathrm{N} = P^{(1)}/P^{(0)} \quad \text{and} \quad \bar{Y}_\mathrm{N} = Y^{(1)}/Y^{(0)} \tag{4}$$

similarly, the weight-average molecular weights are

$$\bar{P}_\mathrm{W} = P^{(2)}/P^{(1)} \quad \text{and} \quad \bar{Y}_\mathrm{W} = Y^{(2)}/Y^{(1)} \tag{5}$$

and polydispersity indexes are

$$\mathrm{PDI}_\mathrm{P} = \bar{P}_\mathrm{W}/\bar{P}_\mathrm{N} \quad \text{and} \quad \mathrm{PDI}_\mathrm{Y} = \bar{Y}_\mathrm{W}/\bar{Y}_\mathrm{N} \tag{6}$$

The total number of monomeric units in the system should remain constant during the reaction processes, i.e.,

$$Y^{(1)} = P^{(1)} \tag{7}$$

The number-fractional distributions of the primary and branched polymers are

$$n_\mathrm{P}(r) = P_r/P^{(0)}, \quad n_\mathrm{Y}(r,i) = Y_{r,i}/Y^{(0)} \quad \text{and} \quad n_\mathrm{Y}(r) = \sum_{i=1}^{\infty} n_\mathrm{Y}(r,i) \tag{8}$$

The average branching density is defined as

$$\lambda = \sum_{i=1}^{\infty} \int_0^\infty (i-1) Y_{r,i} \, \mathrm{d}r / P^{(1)} \tag{9}$$

i.e., the number of branching points per monomeric unit (note that $\lambda = 0$ at $t = 0$ in this work). A branching point is formed when one polymer chain is connected, and therefore, the species $Y_{r,i}$ contains $i - 1$ branching points.

For simplicity, we introduce the following dimensionless variables: the reduced molecular weight of primary chains,

$$\gamma = r/\bar{P}_\mathrm{N} \tag{10}$$

and the average number of branching points per primary chain,

$$\lambda_{\mathrm{P}} = \lambda \bar{P}_{\mathrm{N}} \tag{11}$$

Correspondingly, we have the reduced molecular weight distributions

$$n_{\mathrm{P}}(\gamma) = n_{\mathrm{P}}(r)\bar{P}_{\mathrm{N}} \quad \text{and} \quad n_{\mathrm{Y}}(\gamma,i) = n_{\mathrm{Y}}(\mathrm{r},i)\bar{P}_{\mathrm{N}} \tag{12}$$

The primary chains in this work conforms to a Schulz−Zimm distribution,

$$n_{\mathrm{P}}(\gamma) = \frac{\sigma^{\sigma+1}}{\sigma!}\gamma^{\sigma-1}\mathrm{e}^{-\sigma\gamma} \tag{13}$$

with the polydispersity

$$\mathrm{PDI}_{\mathrm{P}} = (\sigma + 1)/\sigma$$

It is obvious that $\mathrm{PDI}_{\mathrm{P}}$ becomes a random distribution when $\sigma = 1$. It also approximates a uniform distribution

$$n_{\mathrm{P}}(\gamma) = \delta(\gamma - 1) \tag{14}$$

when $\sigma \rightarrow \infty$, where $\delta(\gamma - 1) = 1$, $\gamma = 1$; $\delta(\gamma - 1) = 0$, $\gamma \neq 1$. The distribution functions presented in the previous work are therefore special cases of the present study.

Random-Branched Polymer

The basic scheme to form a random-branched polymer is

$$R_{r,i} + R_{s,j} \xrightarrow{k} R_{r+s,i+j} \tag{15}$$

where k denotes the rate constant. The rate equation can be written accordingly:

$$\frac{\mathrm{d}R_{r,i}}{\mathrm{d}t} = -kR_{r,i}R^{(1)} - krR_{r,i}R^{(0)} + k\sum_{j=1}^{i-1}\int_0^r R_{r-s,i-j}sR_{s,j}\,\mathrm{d}s \tag{16}$$

The increase in branching density follows

$$\frac{\mathrm{d}\lambda}{\mathrm{d}t} = kR^{(0)} \tag{17}$$

Regardless of the detailed distribution of primary chains, the following relationships always hold:

$$R^{(0)} = P^{(0)} - \lambda P^{(1)}, \quad R^{(1)} = P^{(1)}, \quad \text{and} \quad R^{(2)} = P^{(2)}(1 - \lambda\bar{P}_{\mathrm{N}})^{-2} \tag{18}$$

and thus

$$\bar{R}_{\mathrm{N}} = \frac{\bar{P}_{\mathrm{N}}}{1 - \lambda_{\mathrm{P}}}, \quad \bar{R}_{\mathrm{W}} = \frac{\bar{P}_{\mathrm{W}}}{(1 - \lambda_{\mathrm{P}})^2}, \quad \text{and} \quad \mathrm{PDI}_{\mathrm{R}} = \frac{\mathrm{PDI}_{\mathrm{P}}}{1 - \lambda_{\mathrm{P}}} \tag{19}$$

Eliminating t in equations 16 and 17 and expressing the species concentration in terms of the number fraction as defined in equation 8 yields

$$n_{\mathrm{R}}(\gamma,i) = \mathrm{e}^{-\lambda_{\mathrm{P}}\gamma}\sum_{j=1}^{i-1}\int_0^{\lambda_{\mathrm{P}}}\left(\int_0^{\gamma} n_{\mathrm{R}}(\gamma-\varsigma,i-j)n_{\mathrm{R}}(\varsigma,j)\varsigma\,\mathrm{d}\varsigma\right)\mathrm{e}^{\lambda_{\mathrm{P}}\gamma}\,\mathrm{d}\lambda_{\mathrm{P}} \tag{20}$$

Obviously, the fraction of residue primary chains follows

$$n_{\mathrm{R}}(\gamma,1) = \mathrm{e}^{-\lambda_{\mathrm{P}}\gamma}n_{\mathrm{P}}(\gamma) \tag{21}$$

Solving equation 20 with the initial Schulz−Zimm distribution of equation 13 yields

$$n_{\mathrm{R}}(\gamma,i) = \frac{\sigma^{\sigma i+1}(\lambda_{\mathrm{P}})^{i-1}}{(\sigma i)!(i - 1)!}\gamma^{(\sigma+1)i-2}\mathrm{e}^{-(\sigma+\lambda_{\mathrm{P}})\gamma} \tag{22}$$

The total distribution is, therefore,

$$n_{\mathrm{R}}(\gamma) = \sigma^{\sigma+1}\gamma^{\sigma-1}\mathrm{e}^{-(\sigma+\lambda_{\mathrm{P}})\gamma}\sum_{i=1}^{\infty}\frac{(\sigma^{\sigma}\lambda_{\mathrm{P}}\gamma^{\sigma+1})^{i-1}}{(\sigma i)!(i - 1)!} \tag{23}$$

For the special case when the initial primary chains conform a random distribution, i.e., $\sigma = 1$, equation 23, can be simplified as[18,19,25]

$$n_{\mathrm{R}}(\gamma) = \frac{I_1(2\gamma\sqrt{\lambda_{\mathrm{P}}})}{\gamma\sqrt{\lambda_{\mathrm{P}}}}\mathrm{e}^{-(1+\lambda_{\mathrm{P}})\gamma} \tag{24}$$

where

$$I_1(z) = \sum_{i=1}^{\infty}\frac{1}{(i - 1)!i!}\left(\frac{z}{2}\right)^{2i-1}$$

is the Bessel function of the first kind of imaginary argument of the first order.

In addition, the weight fraction of branched polymers having i primary chains (equivalent to $i - 1$ branching points) can be obtained as

$$\omega_{\mathrm{R}}(i) = \int_0^{\infty}\gamma n_{\mathrm{R}}(\gamma,i)\,\mathrm{d}\gamma = \frac{[(\sigma+1)i - 1]!}{(\sigma i)!(i - 1)!}\left(\frac{\sigma}{\sigma + \lambda_{\mathrm{P}}}\right)^{\sigma i+1}\left(\frac{\lambda_{\mathrm{P}}}{\sigma + \lambda_{\mathrm{P}}}\right)^{i-1} \tag{25}$$

Substituting an initial uniform distribution of primary chains into equation 20 yields

$$n_{\mathrm{R}}(\gamma,i) = \frac{(\lambda_{\mathrm{P}}\gamma)^{i-1}\mathrm{e}^{-\lambda_{\mathrm{P}}\gamma}}{i!}\delta(\gamma - i) \tag{26}$$

Comb Polymer

To be general, we start with a comb copolymer with different backbone and side chains,

$$B_r + P_s \xrightarrow{rk} C_{r,s,2}$$

$$C_{r,s,i} + P_t \xrightarrow{rk} C_{r,s+t,i+1} \tag{27}$$

where B_r, P_s, and $C_{r,s,i}$ denote backbone, side, and comb polymers, respectively. The subscripts r, s, and i in $C_{r,s,i}$ indicate the comb polymer consisting of r monomeric units on the backbone and a total of s units on i side chains. Using a probability theory, we obtained the following expression,

$$C_{r,s,i} = B_r \frac{(\rho r)^{i-1} e^{-\rho r}}{(i-1)!} \xi_{i-1}(s) \qquad (28)$$

where ρ is the branching density of backbone chain, i.e., the number of branching point per monomeric unit of backbone chain. $\xi_x(s)$ is a function giving the combination of x side chains

$$\xi_x(s) = \int_0^s n_P(s-u) \int_0^u n_P(u-v) \ldots \int_0^y n_P(y-z) n_P(z)\, dz \ldots dv\, du \qquad (29)$$

with $x - 1$ integrals. Equation 29 has the following properties

$$\int_0^\infty \xi_x(s)\, ds = 1, \quad \int_0^\infty s\xi_x(s)\, ds = x\bar{P}_N, \quad \text{and} \quad \int_0^\infty s^2 \xi_x(s)\, ds = x\bar{P}_N[(x-1)\bar{P}_N + \bar{P}_W] \qquad (30)$$

Equation 30 is valid with an arbitrary distribution of $n_P(s)$. Substituting equations 13 and 14 into equation 29 yields

$$\xi_x(\gamma) = \begin{Bmatrix} \dfrac{\sigma^{\sigma x} \gamma^{\sigma x - 1} e^{-\sigma\gamma}}{(\sigma x - 1)!}, & \text{for Schulz−Zimm} \\ \delta(\gamma - x) & \text{for uniform} \end{Bmatrix} \qquad (31)$$

For the purposes of comparison with star- and random-branched polymers, the number of branching points per backbone chain

$$\lambda_B = \rho \bar{B}_N \qquad (32)$$

should be converted to the number of branching points per primary chain (including both backbone and side chains).

$$\lambda_P = \frac{B^{(0)}\lambda_B}{B^{(0)} + P^{(0)}} = \frac{\lambda_B}{1 + \lambda_B} \qquad (33)$$

Obviously, the number of side and backbone chains can be correlated through the number of branching points per backbone based on a stoichiometric balance:

$$P^{(0)} = B^{(0)}\lambda_B \qquad (34)$$

In this work, only those polymer chains having a backbone with the number of side chains from zero to infinity are taken into account in formulating molecular weight distributions. In other words, unreacted side chains are excluded from the distribution. Similar to equation 3, the moments of backbone and comb chains are defined as

$$B^{(k)} = \int_0^\infty r^k B_r\, dr \quad \text{and} \quad C^{(k)} = \sum_{i=1}^{\infty} \int_0^\infty \int_0^\infty (r+s)^k C_{r,s,i}\, ds\, dr \qquad (35)$$

(note that $i = 1$ indicates a unreacted backbone; see equation 27).

On the basis of equations 28−30, the following relationships can be obtained without being given any detailed information about backbone and side chain distributions

$$C^{(0)} = B^{(0)}, \quad C^{(1)} = B^{(0)}\bar{B}_N(1 + \rho\bar{P}_N), \quad \text{and} \quad C^{(2)} = B^{(0)}\bar{B}_N[(1 + \rho\bar{P}_N)^2 \bar{B}_W + \rho\bar{P}_N\bar{P}_W] \qquad (36)$$

The average molecular weights and polydispersity of the comb copolymer are thus related to those of backbone and side chains,

$$\bar{C}_N = \frac{\theta + \lambda_B}{\theta}\bar{B}_N, \quad \bar{C}_W = \frac{\theta + \lambda_B}{\theta}\bar{B}_W + \frac{\lambda_B}{\theta + \lambda_B}\bar{P}_W, \quad \text{and} \quad \mathrm{PDI}_C = \mathrm{PDI}_B + \frac{\lambda_B}{(\theta + \lambda_B)^2}\mathrm{PDI}_P \qquad (37)$$

where θ is the ratio of the number-average molecular weights of backbone and side chains,

$$\theta = \frac{\bar{B}_N}{\bar{P}_N} \qquad (38)$$

Combining equations 28 and 31 yields

$$n_C(\gamma,\varsigma,i) = \frac{\sigma^{\sigma(i-1)} \varsigma^{\sigma(i-1)-1} (\lambda_B \gamma)^{i-1}}{(i-1)![\sigma(i-1)-1]!} n_B(\gamma) e^{-(\lambda_B\gamma + \sigma\varsigma)} \qquad (39)$$

where the molecular weights and fraction are expressed in a reduced form,

$$\gamma = \frac{r}{\bar{B}_N}, \quad \varsigma = \frac{s}{\bar{P}_N}, \quad \text{and} \quad n_C(\gamma,\varsigma,i) = \frac{\bar{B}_N\bar{P}_N C_{r,s,i}}{B^{(0)}} \qquad (40)$$

Equation 39 was derived for graft copolymers where backbone and side chains have different chemical properties and thus separate molecular weights are often desirable.[27] For comb-branched homopolymers, the distribution can be expressed in terms of the total molecular weight,

$$C_{r,i} = \int_0^r C_{r-s,s,i}\, ds \qquad (41)$$

If backbone chains also conform to Schulz−Zimm distribution with κ as the parameter, then

$$n_C(\gamma,i) = \frac{(\kappa + i - 2)!\kappa^\kappa (\sigma\theta)^{\sigma(i-1)} (\lambda_B)^{i-1}}{(\kappa-1)![(\sigma+1)(i-1)+\kappa-1]!(i-1)!} \times \gamma^{(\sigma+1)(i-1)+\kappa-1} e^{-(\kappa+\lambda_B)\gamma} \times \Phi[\sigma(i-1),(\sigma+1)(i-1)+\kappa,(\kappa+\lambda_B-\sigma\theta)\gamma] \qquad (42)$$

where the reduced molecular weight and fraction are

$$\gamma = \frac{r}{\bar{B}_N} \quad \text{and} \quad n_C(\gamma,i) = \frac{\bar{B}_N C_{r,i}}{B^{(0)}} \qquad (43)$$

and Φ is a degenerate hypergeometric function,[32]

$$\Phi(m,n,z) = 1 + \frac{m}{n}\frac{z}{1!} + \frac{m(m+1)}{n(n+1)}\frac{z^2}{2!} + \frac{m(m+1)(m+2)}{n(n+1)(n+2)}\frac{z^3}{3!} + \ldots \qquad (44)$$

The weight fraction of comb polymers having i primary chains can be obtained

$$\omega_C(i) = \int_0^\infty \gamma n_C(\gamma,i)\, d\gamma = \frac{(\kappa + i - 2)!}{(\kappa - 1)!(i - 1)!}\left(\frac{\kappa}{\kappa + \lambda_B}\right)^{\kappa}\left(\frac{\lambda_B}{\kappa + \lambda_B}\right)^{i-1}\left(\frac{i - 1}{\theta} + \frac{\kappa + i - 1}{\kappa + \lambda_B}\right) \quad (45)$$

If the distribution of backbone chains is same as that of side chains, i.e., $\theta = 1$ and $\kappa = \sigma$, then

$$n_C(\gamma,i) = \frac{(\sigma + i - 2)!\sigma^{\sigma i}(\lambda_B)^{i-1}}{(\sigma - 1)![(\sigma + 1)i - 2]!(i - 1)!} \times \gamma^{(\sigma+1)i-2}e^{-(\sigma+\lambda_B)\gamma}\Phi[\sigma(i - 1),(\sigma + 1)i - 1,\lambda_B\gamma] \quad (46)$$

When the initial primary chains conform a random distribution, i.e., $\sigma = 1$, equation 42 can be simplified to the special case in ref 26.

Star Polymer

A star-branched polymer is formed by connecting primary chains onto an f-functional core,

$$A_f + P_s \xrightarrow{fk} S_{s,1}$$

$$S_{r,i} + P_s \xrightarrow{(f-i)k} S_{r+s,i+1} \quad (47)$$

$$S_{r,f-1} + P_s \xrightarrow{k} S_{r+s,f}$$

At the conversion of functional moieties ϵ, the concentration of the star polymers having r monomeric units on i branches is given by[31]

$$S_{r,i} = A_f\binom{f}{i}\epsilon^i(1 - \epsilon)^{f-i}\xi_i(r) \quad (48)$$

where

$$\binom{f}{i}\epsilon^i(1 - \epsilon)^{f-i}$$

is the probability of randomly selecting an f-functional core A_f having i functional moieties reacted, and $\xi_j(r)$ is defined by equation 29.

Similar to the comb- and random-branched polymers, the average molecular weights and polydispersity are independent of the detailed distribution of primary chains,

$$\bar{S}_N = \frac{\epsilon f \bar{P}_N}{1 - (1 - \epsilon)^f} \quad \text{and} \quad \bar{S}_W = \bar{P}_W + \epsilon(f - 1)\bar{P}_N \quad (49)$$

and

$$\mathrm{PDI}_S = \frac{[\mathrm{PDI}_P + \epsilon(f - 1)][1 - (1 - \epsilon)^f]}{\epsilon f} \quad (50)$$

Note that these averages and the following distributions are formulated on the basis of star polymers, i.e., the polymers having a core with the number of branches from 1 to f. The unreacted primary chains are excluded from the distribution formulation. To make comparisons with comb- and random-branched polymers, the parameter of branching density needs to be defined for the star polymer. The numbers of star polymers and total branches are $[1 - (1 - \epsilon)^f]A_f$ and $\epsilon f A_f$, respectively. Branching occurs when an additional primary chain is attached to a core molecule after the connection of a first chain, and thus a star polymer having i branches (often called arms) is considered to have $i - 1$ branching points. The number of branching points per primary chain can then related to the conversion ϵ and functionality f as follows:

$$\lambda_P = 1 - \frac{1 - (1 - \epsilon)^f}{\epsilon f} \quad (51)$$

Substituting equation 31 into equation 48 yields a bivariate distribution of molecular weight and branching density for star polymers[31]

$$n_S(\gamma,i) = \frac{f!\epsilon^i(1 - \epsilon)^{f-i}\sigma^{\sigma i+1}\gamma^{\sigma i-1}e^{-\sigma\gamma}}{[1 - (1 - \epsilon)^f](f - i)!(\sigma i)!(i - 1)!} \quad (52)$$

The molecular weight distribution of the total star population is then

$$n_S(\gamma) = \frac{f!e^{-\sigma\gamma}}{1 - (1 - \epsilon)^f}\sum_{i=1}^{\infty}\frac{\epsilon^i(1 - \epsilon)^{f-i}\sigma^{\sigma i+1}\gamma^{\sigma i-1}}{(f - i)!(\sigma i)!(i - 1)!} \quad (53)$$

and the weight fraction of star polymers having i branches is

$$\omega_S(i) = \int_0^\infty \gamma n_S(\gamma,i)\, d\gamma = \binom{f}{i}\frac{i\epsilon^i(1 - \epsilon)^{f-i}}{1 - (1 - \epsilon)^f} \quad (54)$$

It becomes clear that equation 52 can be simplified when $\epsilon = 1$,

$$n_S(\gamma,f) = \frac{\sigma^{\sigma f}\gamma^{\sigma f-1}e^{-\sigma\gamma}}{(\sigma f - 1)!} \quad (55)$$

which is still a Schulz–Zimm distribution with a narrower polydispersity.

Comparisons Between Star-, Comb-, and Random-Branched Polymers

The bivariate distribution of molecular weight and branching density is one of the most informative structural properties for a branched polymer. Simple analytical distribution functions are always desirable. For random-, comb-, and star-branched polymers formed from a population of Schulz–Zimm distributed primary chains as illustrated in Figure 1, equations 22, 46, and 52 give their respective bivariate distributions and they are summarized as follows:

$$n_R(\gamma,i) = \frac{\sigma^{\sigma i+1}(\lambda_P)^{i-1}}{(\sigma i)!(i - 1)!}\gamma^{(\sigma+1)i-2}e^{-(\sigma+\lambda_P)\gamma}$$

$$n_C(\gamma,i) = \frac{(\sigma + i - 2)!\sigma^{\sigma i}(\lambda_B)^{i-1}}{(\sigma - 1)![(\sigma + 1)i - 2]!(i - 1)!} \times \gamma^{(\sigma+1)i-2}e^{-(\sigma+\lambda_B)\gamma}\Phi[\sigma(i - 1),(\sigma + 1)i - 1,\lambda_B\gamma]$$

$$n_S(\gamma,i) = \frac{f!\epsilon^i(1 - \epsilon)^{f-i}\sigma^{\sigma i+1}\gamma^{\sigma i-1}e^{-\sigma\gamma}}{[1 - (1 - \epsilon)^f](f - i)!(\sigma i)!(i - 1)!}$$

where γ is the reduced molecular weight (chain length) defined by equation 10 and i is the number of primary chains constructing the branched polymers (the number

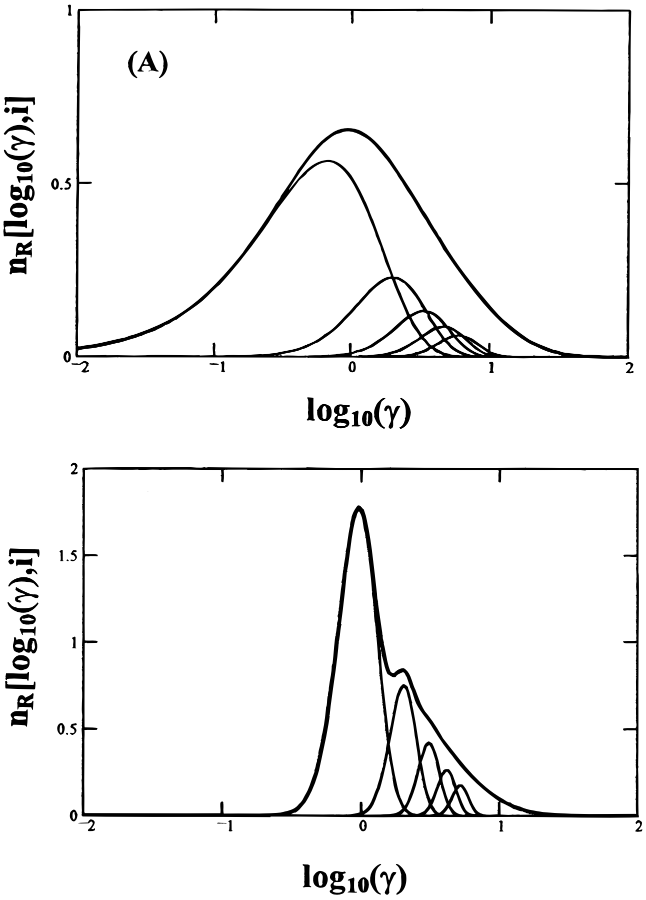

Figure 2. Molecular weight distribution of random-branched polymers having i primary chains (i = 1, 2, 3, 4, and 5) calculated using equation 22 and the total distribution accumulated from i = 1 to ∞ with $\lambda_P = 0.5$. The primary chains assume (A) a random distribution, σ =1, and (B) a narrow Schulz–Zimm distribution, σ =10.

of branching points is $i - 1$). The bivariate distribution of a branched polymer is determined by the primary chain distribution and the average branching density. A Schulz–Zimm distribution has two parameters: one is the number-average molecular weight ($\bar{P}_N$), which is hidden in the above distribution functions due to the use of a reduced form (equation 10), and the other is σ, indicating the distribution polydispersity. On the other side, the average branching density is expressed as the number of branching points per primary chain, λ_P, in the random-branched polymer formulation. The number of branching points per backbone in the comb polymer, λ_B, and the conversion of functional moieties in the star polymer, ϵ, can be converted to λ_P according to equations 33 and 51, respectively:

$$\lambda_P = \frac{\lambda_B}{1 + \lambda_B} \quad \text{and} \quad \lambda_P = 1 - \frac{1 - (1 - \epsilon)^f}{\epsilon f}$$

An additional parameter which appears in the star polymer formulation is the functionality of core molecules, f.

Figure 2 shows the molecular weight distributions of random branched polymers consisting of i (=1, 2, 3, 4, and 5) primary chains calculated using equation 22 and the total distribution resulting from summation of i from 1 to ∞ (in practice, $n_R(\gamma,i)$ becomes negligible for $i > 100$) with $\sigma = 1$, 10 and $\lambda_P = 0.5$. Note that the x-axis is a logarithmic scale and therefore the y-axis should be $n_R[\log(\gamma),i] = n_R(\gamma,i)\mathrm{d}\gamma/\mathrm{d}(\log(\gamma)) = \ln(10)\gamma n_R(\gamma,i)$. Figure 3 shows the effect of λ_P and σ on the total distribution of random-branched polymers. Figures 4 and 5 show the corresponding distributions of comb polymers using equation 46 with the same primary chain distributions and average branching density as in Figures 2 and 3, respectively. The values of λ_P = 0.5 and 0.8 are

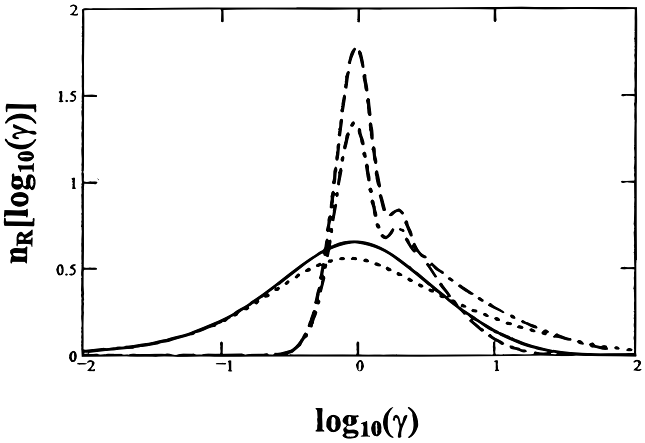

Figure 3. Total molecular weight distribution of random branched polymers: (solid) $\lambda_P = 0.5$, $\sigma = 1$; (dash) $\lambda_P = 0.5$, $\sigma = 10$; (dot) $\lambda_P = 0.8$, $\sigma = 1$; and (dash–dot) $\lambda_P = 0.8$, $\sigma = 10$.

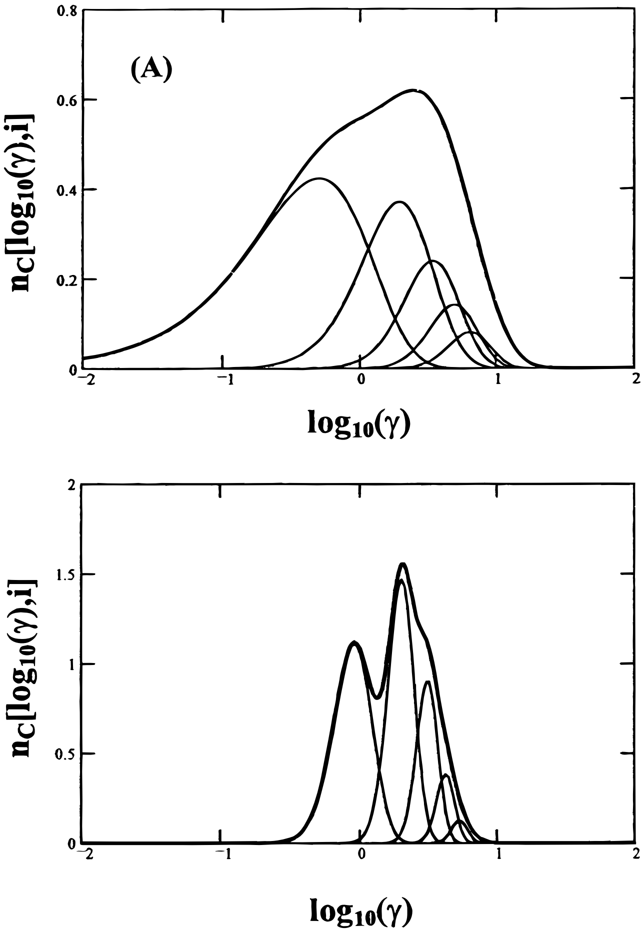

Figure 4. Molecular weight distribution of comb polymers having i primary chains (i = 1, 2, 3, 4, and 5) calculated using equation 46 and the total distribution accumulated from i = 1 to ∞ with $\lambda_P = 0.5$ (equivalent to $\lambda_B = 1$). The primary chains assume (A) a random distribution, σ =1, and (B) a narrow Schulz–Zimm distribution, σ =10.

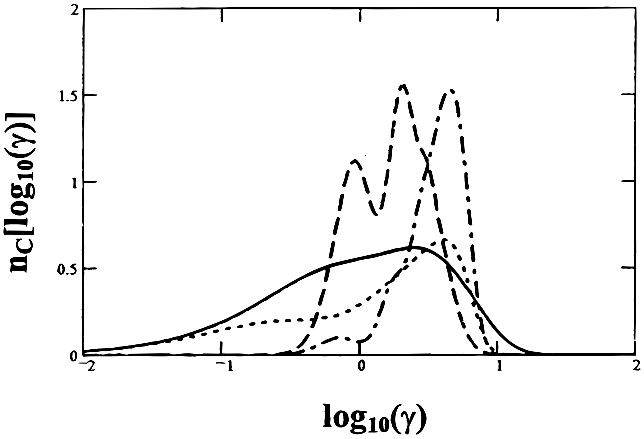

Figure 5. Total molecular weight distribution of comb polymers: (solid) $\lambda_P = 0.5$, $\sigma = 1$; (dash) $\lambda_P = 0.5$, $\sigma = 10$; (dot) $\lambda_P = 0.8$, $\sigma = 1$; and (dash−dot) $\lambda_P = 0.8$, $\sigma = 10$ ($\lambda_P = 0.5$ and 0.8 equivalent to $\lambda_B = 1$ and 4).

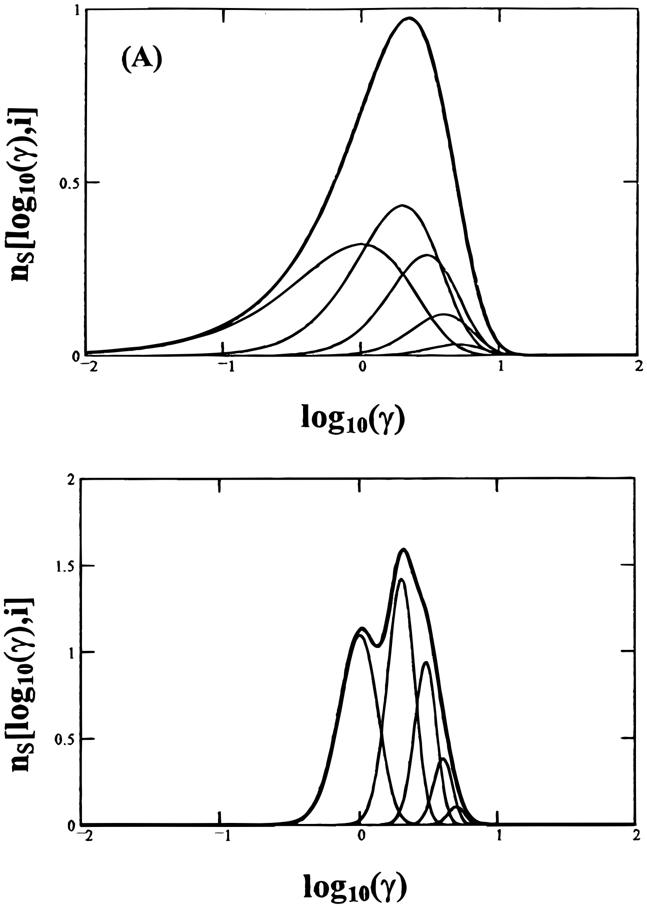

Figure 6. Molecular weight distribution of star polymers having i primary chains ($i = 1, 2, 3, 4$, and 5) calculated using equation 52 and the total distribution with $f = 10$ and $\lambda_P = 0.5$ (equivalent to $\epsilon = 0.168$). The primary chains assume (A) a random distribution, $\sigma = 1$, and (B) a narrow Schulz−Zimm distribution, $\sigma = 10$.

equivalent to $\lambda_B = 1$ and 4. Figures 6 and 7 show the distributions of star polymers using equation 52 with the same conditions as in Figures 2 and 3. The values of $\lambda_P = 0.5$ and 0.8 are equivalent to $\epsilon = 0.168$ and 0.5 with $f = 10$. In general, a narrower primary chain distribution leads to a narrower multimodal distribution for branched polymers (compare $\sigma = 10$ to $\sigma = 1$ at the same $\lambda_P = 0.5$ or 0.8 in Figures 3, 5, and 7). An increase in branching density results in a shift of distribution toward higher molecular weight (compare $\lambda_P = 0.8$ to $\lambda_P = 0.5$ at the same $\sigma = 1$ or 10 in Figure 3, 5, and 7).

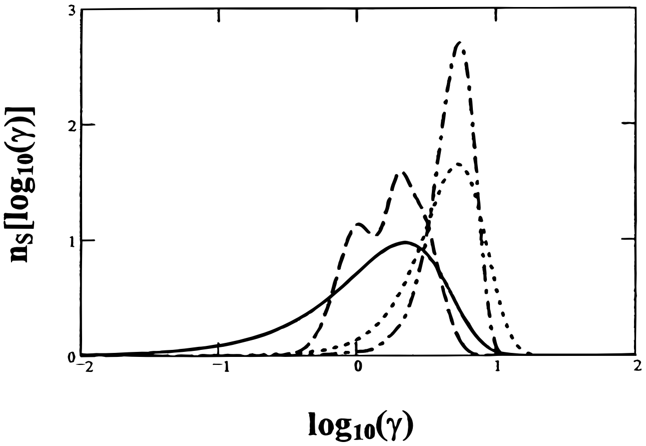

Figure 7. Total molecular weight distribution of star polymers: (solid) $\lambda_P = 0.5$, $\sigma = 1$; (dash) $\lambda_P = 0.5$, $\sigma = 10$; (dot) $\lambda_P = 0.8$, $\sigma = 1$; and (dash−dot) $\lambda_P = 0.8$, $\sigma = 10$ ($\lambda_P = 0.5$ and 0.8 with $f = 10$ equivalent to $\epsilon = 0.168$ and 0.5).

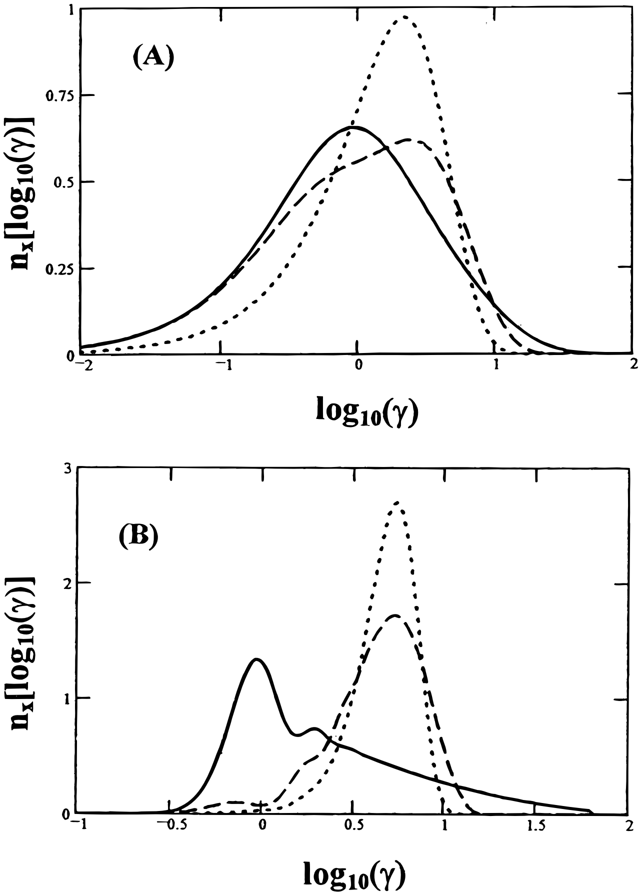

Figure 8. Comparison of total molecular weight distributions of branched polymers: (solid) random, (dash) comb, and (dot) star. The parameters are (A) $\lambda_P = 0.5$, $\sigma = 1$, and (B) $\lambda_P = 0.8$, $\sigma = 10$.

Figure 8 gives the comparison between the total molecular weight distributions of the three types of branched polymers formed from the same primary chain distribution ($\sigma = 1$ or 10) and branching density ($\lambda_P = 0.5$ or 0.8). The random-branched polymer appears to have the broadest distribution, while the star polymer has the narrowest. The former has a long skewed tail

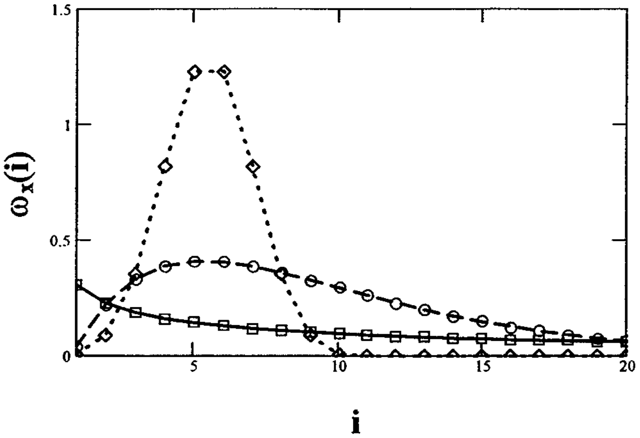

Figure 9. Weight fraction of branched polymers having i primary chains calculated using equations 25, 45, and 54 for (solid) random, (dash) comb, and (dot) star, respectively. The parameters are $\lambda_P = 0.8$, $\sigma = 1$, with the additional parameters of $\theta = 1$ and $\kappa = \sigma$ for equation 45 and $f = 10$ for equation 54.

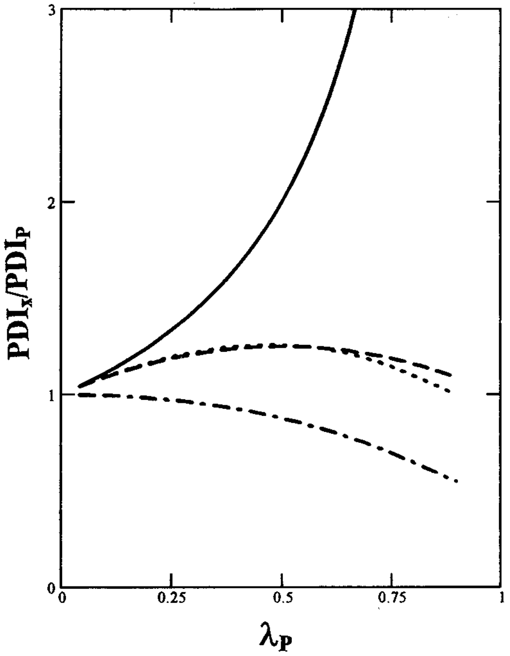

Figure 10. Development of distribution polydispersity of branched polymers calculated using equations 19, 37, and 50 for (solid) random, (dash) comb, and (dot) star, respectively. The parameters are $\theta = 1$ and $PDI_B = PDI_P$ for equation 37, and $f = 10$ and $PDI_P = 1$ (dot) and 2 (dash−dot) for equation 50.

at the high molecular weight end while the latter shows a rather sharp truncation (keep in mind the log scale of molecular weight in the distribution plots). Figure 9 shows the weight fractions as a function of the number of primary chains, i, under the conditions of $\lambda_P = 0.8$ and $\sigma = 10$ using equations 25, 45, and 54 (additional conditions are $\theta = 1$ and $\kappa = \sigma$ for equation 45 and $f = 10$ for equation 54) for random-, comb-, and star-branched polymers, respectively. The average number of primary chains in the branched polymers is five. It is evident that the maximum fractions of star and comb polymers appear in the vicinity of $i = 5$. However, in random branching, most polymers are still linear ($i = 1$) with a small fraction of high branching.

Figure 10 shows the polydispersity as a function of the branching density for different types of branched polymers. The polydispersity of a random-branched polymer always increases with the branching density, as shown in equation 19. For a comb polymer, the dependence of the polydispersity on branching density is more complex and exhibits a maximum. An examination of equation 37 under the conditions of $\theta = 1$ and $PDI_B = PDI_P$ reveals that the maximum value is $PDI_C/PDI_P = 1.25$ at $\lambda_P = 0.5$, i.e., a maximum 25% increase over the primary chain polydispersity. For a star polymer, the polydispersity is controlled not only by the branching density but also by the functionality of the core molecule. The two curves presented in Figure 10 are calculated using equation 50 with $f = 10$ and $PDI_P = 1$ and 2. The tendency of the distribution to narrow is more dramatic with broader primary chains. From our calculations using a comprehensive range of parameters, it can be concluded that the polydispersities of the three types of branched polymers are in the order of star < comb < random. It should be emphasized that this conclusion is valid for an arbitrary distribution of primary chains since equations 19, 37, and 50 were developed independent of the distribution information.

Acknowledgment. We appreciate the financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada for this research.

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MA9800055