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Molecular weight distribution of comb polymers by chain polymerization with macromonomer

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A chain copolymerization of macromonomers generates branched polymers with comb structure. This work presents analytical expressions to predict the bivariate distributions of molecular weight and branching density for the comb polymers. The macromonomers are assumed to have a random or uniform distribution. The distribution functions are determined by the average number of branching points per backbone chain and the ratio of the average lengths of backbone and side chains. The model is applicable for short-chain, long-chain, and star-shaped comb branching. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Branched polymers exhibit many special functions in various applications[1,2]. Theoretical prediction of the bivariate distribution of molecular weight and branching density for branched polymers provides a great challenge for polymer scientists. Numerous theories have been derived to describe the distribution for polymers formed via various mechanisms[3–20]. However, most work focused on average molecular weights. There are only a few papers dealing with analytical distribution functions. For example, Flory presented a model for monodispersed chains cross-linked by divinyl comonomer[3]. Stockmayer generalized the model for an arbitrary chain distribution[4]. 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[5]. Bamford and Tompa dealt with the same polymerization system in a batch reactor at low monomer conversion[6]. The early works were summarized by Peebles[12]. Recently, Tobita proposed the concept of random sampling technique and obtained an analytical equation for homogeneously branched polymers with randomly distributed primary chains[21,22]. Soares and Hamielec derived a distribution function for metallocene polymerization with terminal branching[23]. These models dealt exclusively with the polymerization systems having branches generated by chain transfer to polymer and/or propagation with pendant or terminal double bonds.

Branched polymer assumes various molecular structures including dendritic, comb, and star-shaped branching. A dendritic polymer has a chain structure of branches-on-branches. A comb polymer has a backbone attached with side chains. A star polymer is a cluster of linear chains with one end of each chain chemically bound to a common central moiety. Material properties of the branched polymers depend not only on molecular weight and branching density, but also on the structure. A dendritic polymer behaves very differently from its comb and star counterparts even with a same average molecular weight and branching density. Compared to the dendritic branching on which all the aforementioned models[3–23] were based, modelling of branched polymers with comb and star structures has received less attention. In a previous paper[24], we derived a distribution function for a binary metallocene system with one catalyst generating polymer chains by β-hydride elimination and the other propagating in situ with terminal double bonds. It was found that the comb polymers thus produced give much narrower molecular weight distributions than dendritic polymers with same branching densities synthesized by a single catalyst system. The former shows a rather sharp truncation at the high molecular weight end, while the latter has a long skew tail which may cause difficulty in processing. In this work, we present a model generally applicable to various types of comb polymers synthesized via chain polymerization with macromonomers, including long-chain, short-chain and star-shaped branching as shown in *Figure 1*.

CHAIN POLYMERIZATION WITH MACROMONOMER

The polymerization system consists of initiation or activation of a reactive centre, propagation of monomers, and chain termination[25–30]. The propagation is the major step which generates a backbone bearing side chains introduced by copolymerizing macromonomers. The elementary reactions and their rate constants are as follows

$$P^*_{r,b,1} + M \xrightarrow{k_{p11}} P^*_{r+1,b,1}$$

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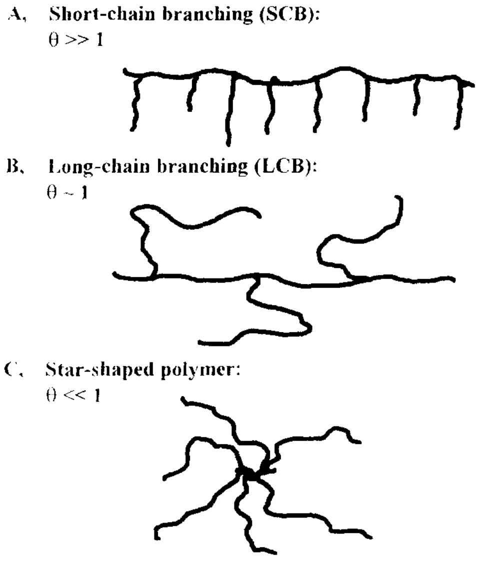

Figure 1 Schematic representation of comb-branched polymers formed by chain polymerization with macromonomer. θ is the ratio of average lengths of backbone and side (macromonomer) chains. Shown are (A) short-chain branching ($\theta >> 1$), (B) long chain branching ($\theta \sim 1$), and (C) star-shaped branching ($\theta < 1$)

$$\mathrm{P}^*_{r,b,1} + \mathrm{M}_s^= \xrightarrow{k_{p12}} \mathrm{P}_{r+s,b+1,2} \tag{1}$$

$$\mathrm{P}^*_{r,b,2} + \mathrm{M} \xrightarrow{k_{p21}} \mathrm{P}^*_{r+1,b,1}$$

$$\mathrm{P}^*_{r,b,2} + \mathrm{M}_s^= \xrightarrow{k_{p22}} \mathrm{P}_{r+s,b+1,2}$$

where $\mathrm{P}_{r,b,i}{}^*$ is the propagating polymer chain having r monomeric units and b branching points with the propagating centre indicated by the superscript * located at the monomer i (1 is the monomer M and 2 the macromonomer $\mathrm{M}_s^=$ with s monomeric units). In most cases of chain copolymerization with macromonomer, the molar concentration of macromonomer, $\Sigma_{s=1}^{\infty}\mathrm{M}_s^=$, is much lower than that of monomer M due to its high molecular weight. Also, the reactivity ratio r_2 ($= k_{p22}/k_{p21}$) is very small[25,26].

$$\sum_{s=1}^{\infty} \mathrm{M}_s^= /\mathrm{M} < < 1 \text{ and } r_2 \sim 0 \tag{2}$$

Applying a mass balance to the polymer species $\mathrm{P}_{r,b,1}{}^*$ with the steady-state hypothesis yields

$$\begin{aligned} \frac{\mathrm{dP}^*_{r,b,1}}{\mathrm{d}t} &= k_{p11}\mathrm{MP}^*_{r-1,b,1} + k_{p21}\mathrm{MP}^*_{r-1,b,2} \\ &- \left(k_{p11}\mathrm{M} + k_{p12}\sum_{s=1}^{\infty}\mathrm{M}_s^= + \tau_1\right)\mathrm{P}^*_{r,b,1} \approx 0 \end{aligned} \tag{3}$$

The first two terms on the right-hand side are the generation rates while the other with negative sign are the consumption with τ_1 representing termination (note: the bimolecular combination of polymer chains is excluded in this work). A similar equation can also be written for $\mathrm{P}_{r,b,2}{}^*$. However, with the conditions given in equation (2), the concentration of the propagating chains with active centres on macromonomer units becomes negligible. It can therefore be simplified as

$$k_{p21}\mathrm{MP}^*_{r-1,b,2} = k_{p12}\sum_{s=1}^{r-2}\mathrm{P}^*_{r-1-s,b-1,1}\mathrm{M}_s^= \tag{4}$$

For the same reason, one only needs to solve for $\mathrm{P}_{r,b,1}{}^*$.

Substituting equation (4) into equation (3) gives the following governing equation in an integral–differential form.

$$\begin{aligned} &\frac{\mathrm{d}n^*(r,b)}{\mathrm{d}r} + \left(\bar{\mathrm{P}}_{\mathrm{N,B}}^{-1} + \lambda\right)n^*(r,b) \\ &= \lambda\int_0^r n^*(r-s,b-1)n_{\mathrm{M}}(s)\,\mathrm{d}s \end{aligned} \tag{5}$$

where $n^*(r,b)$ is the number fraction of polymers having r monomeric units and b branching points, $n_{\mathrm{M}}(s)$ is the number fraction of macromonomers having s monomeric units,

$$n^*(r,b) = \mathrm{P}^*_{r,b,1}/\sum_{b=0}^{\infty}\sum_{r=1}^{\infty}P^*_{r,b,1} \text{ and } n_{\mathrm{M}}(s) = \mathrm{M}_s^=/\sum_{s=1}^{\infty}\mathrm{M}_s^= \tag{6}$$

$\bar{\mathrm{P}}_{\mathrm{N,B}}$ is the number-average length (number of monomeric units) of backbone chains, and λ is the branching density (number of branching points per monomeric unit on backbone),

$$\bar{\mathrm{P}}_{\mathrm{N,B}} = k_{p11}\mathrm{M}/\tau_1 \tag{7}$$

$$\lambda = \mathrm{d}\sum_{s=1}^{\infty}\mathrm{M}_s^=/\mathrm{dM} = \sum_{s=1}^{\infty}\mathrm{M}_s^=/(r_1\mathrm{M}) \tag{8}$$

and r_1 is the reactivity ratio k_{p11}/k_{p12}. The number of monomeric unit r in equation (5) is treated as a continuous variable due to its huge value. Another assumption is the similarity of the monomeric units on backbone and side chains. The model derived in this paper is therefore applicable to homopolymer systems. The boundary conditions are

$$n^*(0,0) = \bar{\mathrm{P}}_{\mathrm{N,B}}^{-1} \text{ and } n^*(0,b) = 0 \tag{9}$$

For polymers without branching, the right-hand side of equation (5) is zero. Solving the equation with the condition given in equation (9) yields

$$n^*(r,0) = \bar{\mathrm{P}}_{\mathrm{N,B}}^{-1}\exp\left[-\left(\bar{\mathrm{P}}_{\mathrm{N,B}}^{-1} + \lambda\right)r\right] \tag{10}$$

The backbone chains ($\lambda = 0$ in equation (10)) in this work follows Flory's most probable distribution, i.e. random distribution. The total number fraction of linear polymers is

$$\int_0^{\infty} n^*(r,0)\,\mathrm{d}r = \frac{1}{1 + \lambda\bar{\mathrm{P}}_{\mathrm{N,B}}} \tag{11}$$

The bivariate function $n^*(r,b)$ is the most informative molecular quality. Other distribution and average properties can be readily obtained. The total distributions of polymers having r monomeric units and b branching points are

$$n^*(r) = \sum_{b=0}^{\infty} n^*(r,b), \quad n^*(b) = \int_0^{\infty} n^*(r,b)\,\mathrm{d}r \tag{12}$$

The number- and weight-average molecular weights of polymers having b branching points and their total averages are

$$\bar{\mathrm{P}}_{\mathrm{N},b} = \int_0^{\infty} rn^*(r,b)\,\mathrm{d}r, \quad \bar{\mathrm{P}}_{\mathrm{W},b} = \frac{\int_0^{\infty} r^2 n^*(r,b)\,\mathrm{d}r}{\int_0^{\infty} rn^*(r,b)\,\mathrm{d}r}, \tag{13}$$

$$\mathrm{PDI}_b = \frac{\bar{\mathrm{P}}_{\mathrm{W},b}}{\bar{\mathrm{P}}_{\mathrm{N},b}}$$

$$\bar{P}_N = \int_0^\infty r n^*(r)\,dr,\quad \bar{P}_W = \frac{\int_0^\infty r^2 n^*(r)\,dr}{\int_0^\infty r n^*(r)\,dr},\quad PDI = \frac{\bar{P}_W}{\bar{P}_N} \qquad (14)$$

Note that the term of molecular weight is used for the number of monomeric units in this work interchangeably with chain length or degree of polymerization.

One advantage of using macromonomer for synthesizing of comb-branched polymers is that the side chains are well defined with a known molecular weight distribution $n_M(s)$. Most macromonomers are produced by chain polymerization mechanisms. The distribution encountered is often either random or uniform. In this work, we solve both cases of the random and uniform distributed macromonomers.

MACROMONOMER WITH RANDOM DISTRIBUTION

Equation (15) gives the random distribution of side chains,

$$n_M(s) = \bar{M}_N^{-1}\exp(-s/\bar{M}_N) \qquad (15)$$

where $\bar{M}_N$ is the number-average molecular weight of macromonomers. Substituting equation (15) into equation (5) and after some lengthy but straight-forward algebra, one obtains the following analytical solution in a series form.

$$n^*(\gamma,b) = \frac{(\lambda_B\theta)^b}{(2b)!}\gamma^{2b}e^{-(1+\lambda_B)\gamma}\Phi[b, 2b+1, (1+\lambda_B-\theta)\gamma] \qquad (16)$$

where $\Phi(m,n,z)$ is a degenerate hypergeometric function which is defined as

$$\Phi(m,n,z) = 1 + \frac{m}{n}\frac{z}{1!} + \frac{m(m+1)}{n(n+1)}\frac{z^2}{2!} + \frac{m(m+1)(m+2)}{n(n+1)(n+2)}\frac{z^3}{3!} + \dots \qquad (17)$$

θ is the length ratio of backbone over side chains, λ_B is the number of branching points per backbone, and γ is the reduced molecular weight.

$$\theta = \bar{P}_{N,B}/\bar{M}_N,\quad \lambda_B = \lambda\bar{P}_{N,b},\quad \gamma = r/\bar{P}_{N,B} \qquad (18)$$

Note that for simplicity, the distribution functions below are expressed in reduced forms, which are all normalized accordingly.

$$n^*(\gamma,b) = n^*(r,b)(dr/d\gamma) = n^*(r,b)\times\bar{P}_{N,B} \qquad (19)$$

Substituting equation (16) into equations (13) and (14) gives

$$\frac{\bar{P}_{N,b}}{\bar{P}_{N,B}} = \frac{1+(1+\beta)b}{1+\lambda_B},\quad \frac{\bar{P}_{W,b}}{\bar{P}_{N,B}} = \frac{(1+b)[2+(1+\beta)^2 b]}{(1+\lambda_B)[1+(1+\beta)b]},$$

$$PDI_b = \frac{(1+b)[2+(1+\beta)^2 b]}{[1+(1+\beta)b]^2} \qquad (20)$$

$$\frac{\bar{P}_N}{\bar{P}_{N,B}} = \frac{\theta+\lambda_B}{\theta},\quad \frac{\bar{P}_W}{\bar{P}_{N,B}} = 2\frac{\lambda_B+(\theta+\lambda_B)^2}{\theta(\theta+\lambda_B)},$$

$$PDI = 2\left[1+\frac{\lambda_B}{(\theta+\lambda_B)^2}\right] \qquad (21)$$

where

$$\beta = (1+\lambda_B)/\theta \qquad (22)$$

It should be pointed out that our calculations using a comprehensive range of parameters show that while equation (16) of this work is equivalent to equation (18) in a previous paper[24], equation (16) is much simpler in form.

It is also clear that for a special case with $\lambda_B = \theta - 1$, the degenerate hypergeometric function equals unity and equation (16) thus becomes

$$n^*(\gamma,b) = \frac{[\theta(\theta-1)]^b}{(2b)!}\gamma^{2b}\exp(-\theta\gamma) \qquad (23)$$

MACROMONOMER WITH UNIFORM DISTRIBUTION

If the side chain possesses a uniform distribution, i.e. every macromonomer has equal molecular weight,

$$n_M(s) = \delta(s-\bar{M}_N) \qquad (24)$$

equation (5) has the solution of

$$n^*(\gamma,b) = \frac{1}{b!}[\lambda_B(\gamma-b/\theta)]^b\exp[1-(1+\lambda_B)(\gamma-b/\theta)] \qquad (25)$$

Substituting equation (25) into equations (13) and (14) gives

$$\frac{\bar{P}_{N,b}}{\bar{P}_{N,B}} = \frac{1+(1+\beta)b}{1+\lambda_B},\quad \frac{\bar{P}_{W,b}}{\bar{P}_{N,B}} = \frac{1+b+[1+(1+\beta)b]^2}{(1+\lambda_B)[1+(1+\beta)b]},$$

$$PDI_b = \frac{1+b+[1+(1+\beta)b]^2}{[1+(1+\beta)b]^2} \qquad (26)$$

$$\frac{\bar{P}_N}{\bar{P}_{N,B}} = \frac{\theta+\lambda_B}{\theta},\quad \frac{\bar{P}_W}{\bar{P}_{N,B}} = \frac{\lambda_B+2(\theta+\lambda_B)^2}{\theta(\theta+\lambda_B)},$$

$$PDI = 2+\frac{\lambda_B}{(\theta+\lambda_B)^2} \qquad (27)$$

DETERMINING PARAMETERS

The distribution function in the reduced form $n^*(\gamma,b)$ is determined by two parameters: the average number of branching points per backbone chain λ_B and the ratio of the average lengths of backbone and side chains θ. For $n^*(r,b)$, the number-average molecular weight of backbone $\bar{P}_{N,B}$ is also required. However, $\bar{P}_{N,B}$ can be approximated by polymerization data without macromonomer under the same conditions of reaction temperature and concentrations of initiator, transfer agent, and monomer. With a known $\bar{M}_N$, the ratio θ is pre-determined. The branching density λ_B becomes the only variable during the copolymerization for the bivariate distribution.

POLYDISPERSITY INDEXES

Let us first examine the distribution polydisperties PDI_b and PDI. For both cases in equations (20) and (26), PDI_b is a monotonic decreasing function of b, from $PDI_b = 2$ at $b = 0$ to $PDI_b = 1$ when $b \to \infty$, as shown in *Figure 2*. At low β, i.e. the molecular weight of backbone is much higher than that of side chain, the distribution of side chains whether random or uniform does not have a significant effect on the relationship of PDI_b *versus* b. At high β values, the difference becomes obvious, since the PDI_b function of a uniform distribution of side chains decreases with increasing b much faster than that of a random distribution.

The polydispersity of the total polymer population PDI is a function of both θ and λ_B. At $\lambda_B = 0$, PDI = 2 representing

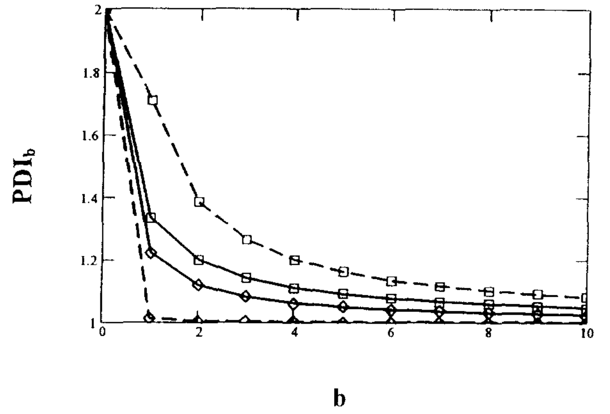

Figure 2 Polydispersity of the comb polymers having b branching points PDI$_b$ calculated using equation (20) and equation (26). Solid lines are $\beta = 1$ and dash lines $\beta = 10$. Squares are for random side chains and diamonds for uniform

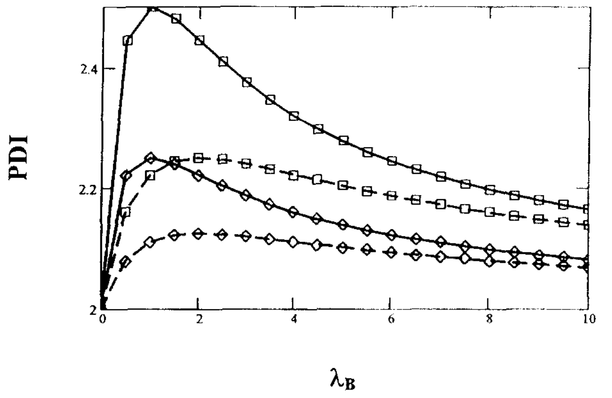

Figure 3 Polydispersity of total polymers PDI calculated using equation (21) and equation (27). Solid lines are $\theta = 1$ and dash lines $\theta = 2$. Squares are for random side chains and diamonds for uniform

the polydispersity of backbone chains. When $\lambda_B \to \infty$, i.e. highly branched polymers, the polydispersity also approaches 2 independently of the relative magnitude of molecular weights of backbone and side chains and of the distribution type of side chains. This is also the effect of the randomly distributed backbone chains. The number of branches on an individual comb polymer can be very different from each other following a random distribution. A characteristic of a PDI *versus* λ_B profile as shown in *Figure 3* is that the polydispersity increases with increasing branching density at the beginning; and after reaching a maximum value, it decreases and finally approaches 2. The maximum polydispersity is a function of θ. For both random and uniform side chains, the maximum polydispersity occurs at $\lambda_B = \theta$.

$$\mathrm{PDI}_{\max}(\lambda_B = \theta, \text{ random}) = 2 + 0.5/\theta \qquad (28)$$

$$\mathrm{PDI}_{\max}(\lambda_B = \theta, \text{ uniform}) = 2 + 0.25/\theta$$

It can be seen that the polydispersities of comb-branched polymers are rather small. Indeed, the narrow molecular weight distribution is the most remarkable feature for comb polymers. It can also be noticed in the PDI *versus* λ_B profile that comb polymers with uniformly distributed side chains are narrower than those with random side chains.

SHORT-CHAIN, LONG-CHAIN AND STAR-SHAPED BRANCHING

Depending on the magnitude of the molecular weight ratio of backbone and side chains θ, the comb polymers can be divided into three categories as shown in *Figure 1*:

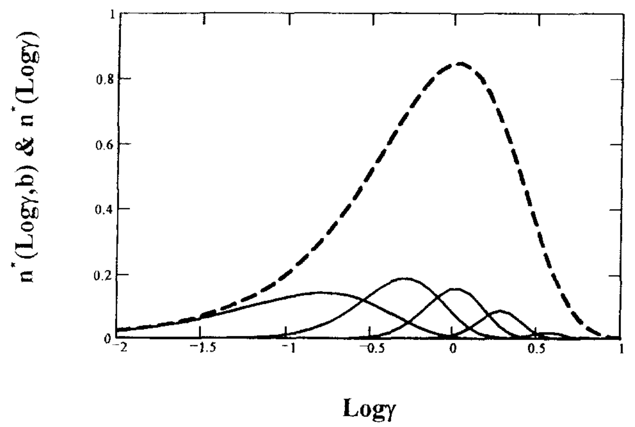

Figure 4 Molecular weight distribution of comb polymers having b branching points and the total distribution calculated using equation (16). Solid lines are $n^*(\gamma,b)$ with $b = 0, 2, 5, 10, 20, 30$ and the dash line, $n^*(\gamma)$. $\theta = 100$ and $\lambda_B = 5$

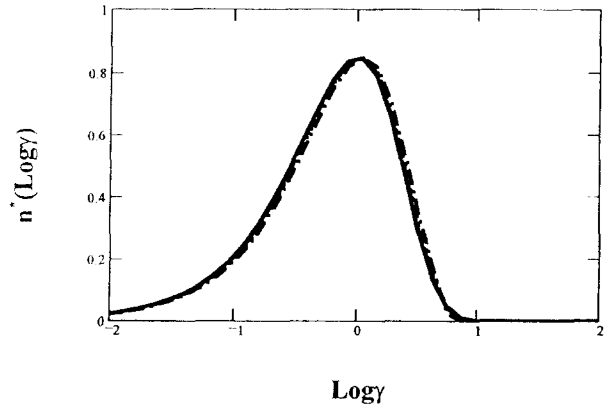

Figure 5 Development of the total molecular weight distribution of short-chain comb-branched polymer calculated using equation (16) with $\theta = 100$ and $\lambda_B = 0, 2, 5,$ and 10 (from left to right)

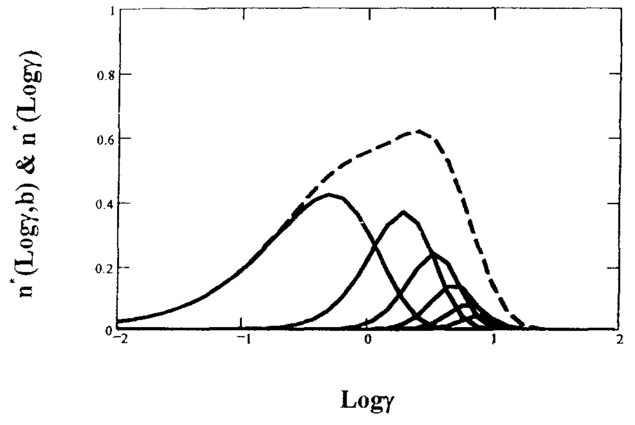

Figure 6 Molecular weight distribution of comb polymers having b branching points and the total distribution calculated using equation (16). Solid lines are $n^*(\gamma,b)$ with $b = 0, 1, 2, 3, 4, 5$ and the dash line, $n^*(\gamma)$. $\theta = 1$ and $\lambda_B = 1$

short-chain ($\theta > > 1$), long-chain ($\theta \sim 1$) and star-shaped branching ($\theta < 1$). A typical example of short-chain branching includes the copolymerization of ethylene and α-olefins. *Figure 4* shows the molecular weight distributions $n^*(\gamma,b)$ for $\theta = 100$ with the side chains having a random distribution. *Figure 5* illustrates the effect of the branching density on the total distribution $n^*(\gamma)$. Since the side chains are much smaller than the backbones, the short-chain branching does not significantly change the total molecular weight distributions. The situation can be very different in long-chain branching. *Figures 6 and 7* give the distributions for $\theta = 1$. The branched polymers exhibit a bimodal pattern.

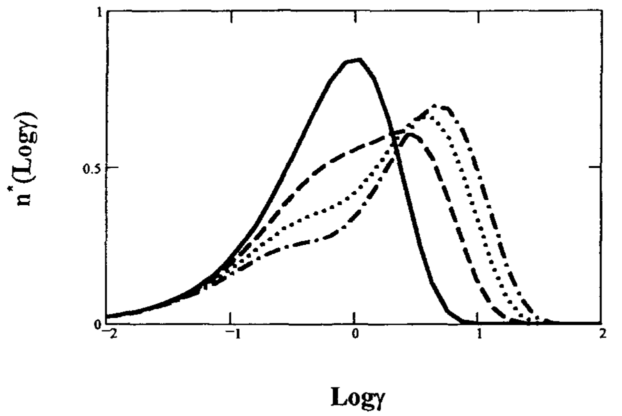

Figure 7 Development of the total molecular weight distribution of long-chain comb-branched polymer calculated using equation (16) with $\theta = 1$ and $\lambda_B = 0, 1, 2,$ and 3 (left to right)

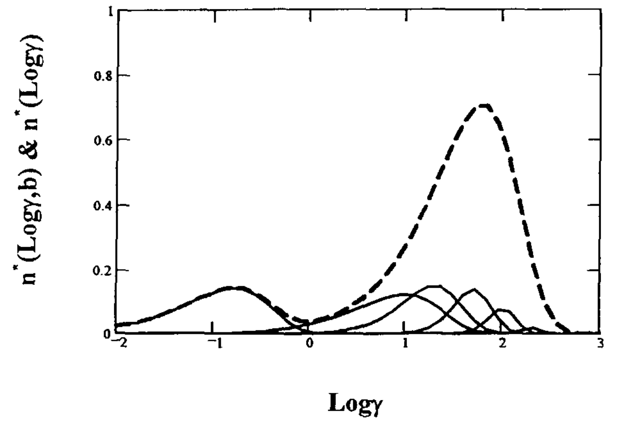

Figure 8 Molecular weight distribution of comb polymers having b branching points and the total distribution calculated using equation (16). Solid lines are $n^*(\gamma,b)$ with $b = 0, 1, 2, 5, 10, 20$ and the dash line, $n^*(\gamma)$. $\theta = 0.1$ and $\lambda_B = 5$

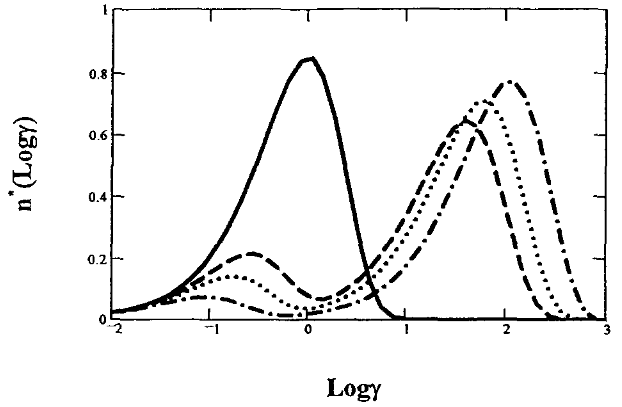

Figure 9 Development of the total molecular weight distribution of star-shaped comb-branched polymer calculated using equation (16) with $\theta = 0.1$ and $\lambda_B = 0, 3, 5,$ and 10 (left to right)

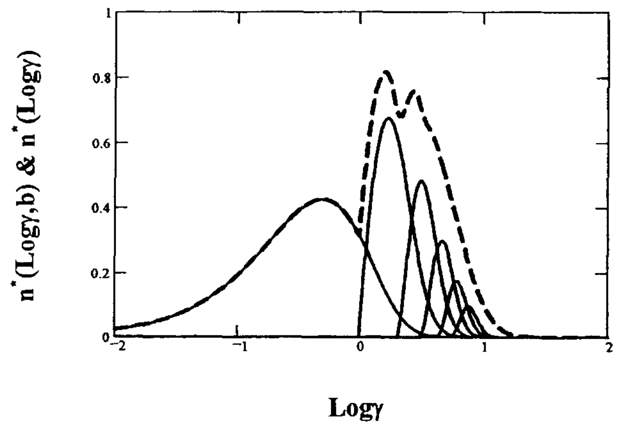

Figure 10 Molecular weight distribution of comb polymers having b branching points and the total distribution calculated using equation (25). Solid lines are $n^*(\gamma,b)$ with $b = 0, 1, 2, 3, 4, 5$ and the dash line, $n^*(\gamma)$. $\theta = 1$ and $\lambda_B = 1$

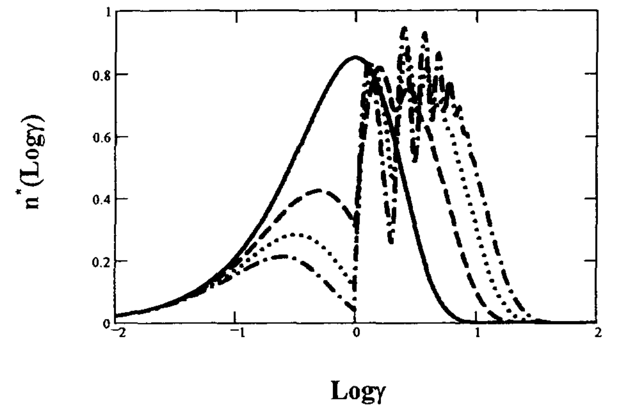

Figure 11 Development of the total molecular weight distribution of long-chain comb-branched polymer calculated using equation (25) with $\theta = 1$ and $\lambda_B = 0, 1, 2,$ and 3 (left to right)

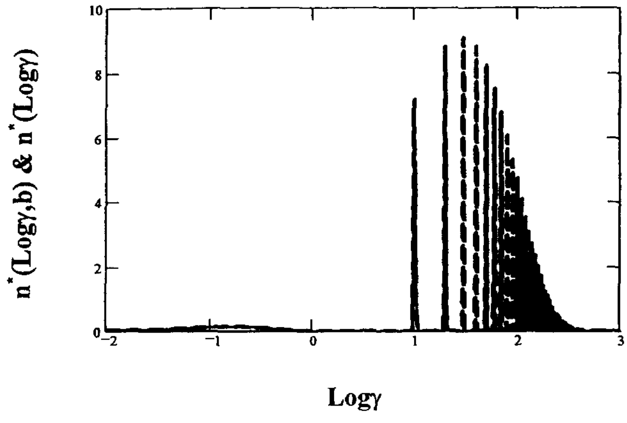

Figure 12 Molecular weight distribution of comb polymers having b branching points and the total distribution calculated using equation (25). Solid lines are $n^*(\gamma,b)$ with $b = 0, 1, 2, 5, 10, 20$ and the dash line, $n^*(\gamma)$. $\theta = 0.1$ and $\lambda_B = 5$

This pattern becomes more obvious for a star-shaped comb polymer as shown in *Figures 8 and 9* for $\theta = 0.1$, i.e. the side chain is ten times longer the backbone. Further reducing the θ value would demonstrate that the contribution of backbone chains to the comb polymer molecular weight becomes negligible.

Figure 10 presents the distributions for $\theta = 1$ with the side chains having a uniform distribution. The resolution of the polymers having different numbers of branching points improves significantly compared to the case of random distribution as shown in *Figure 6*. *Figure 11* depicts the effect of the branching density on the total distribution. The numbers of branches can be readily counted in these distribution curves. The separation of peaks becomes even more obvious for star-shaped polymers having uniform side chains as shown in *Figure 12* for $\theta = 0.1$. It should be pointed out that the use of the present model is limited by the conditions given in equation (2). These conditions could be easily satisfied in long-chain and star-shaped branching. However, for the case of short-chain branching, it is applicable only for the conditions of low comonomer levels.

Another point worth mentioning is that the distribution functions presented in this paper are for the living polymer population, i.e. the polymer chains bearing propagating centres. These are therefore instantaneous molecular weight distributions. For corresponding cumulative distributions, the following mass balance equation for the dead polymer species $\mathrm{P}_{r,b}$ applies,

$$\zeta \mathrm{P}_{r,b} + \frac{\mathrm{dP}_{r,b}}{\mathrm{d}t} = \tau_1 \mathrm{P}^*_{r,b,1} + \tau_2 \mathrm{P}^*_{r,b,2} \approx \tau_1 \mathrm{P}^*_{r,b,1} \qquad (29)$$

where ζ is the reactor mean residence time. In a steady-state continuous stirred tank reactor, the distributions of both living and dead polymers become identical, i.e.

$$n(r,b) = n^*(r,b) \qquad (30)$$

Otherwise, an accumulation in terms of polymerization time is required, particularly in a batch reactor run for high monomer conversion.

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