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A Theoretical Study of the Star-Coupling Reaction of Polymer Chains

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ABSTRACT

The set of kinetic differential equations for star-coupling of polymers have been solved rigorously both with and without the effect of steric hindrance. The relations between the molecular parameters of star-branched polymers and those of prepolymers are derived. When the star-coupling reaction goes quantitatively to completion, the same theoretical result was obtained, no matter whether there is steric hindrance or not. In this case, the more arms in the star-branched polymer, the more homogeneous is the molecular weight distribution; if the number of arms is large enough, the molecular weight distribution will become very narrow and almost be independent of the polydispersity of the arms.

One of the basic methods for synthesizing star-branched polymers is a coupling reaction between prepolymer and linking agent. Some authors [1-3] have dealt statistically with this problem without considering the effect of steric hindrance. In this paper the star-coupling reaction with or without steric hindrance was studied comprehensively by solving the set of kinetic differential equations. The expressions for the molecular weight distribution function and other molecular

parameters of star polymers were derived vigorously. For better understanding, the case that neglects the effect of steric hindrance was treated first. The influence of steric hindrance on various molecular parameters of star polymers is then taken into account in Section IV.

I. KINETIC EQUATIONS AND THEIR SOLUTIONS

First of all, let us define several parameters:

N : the initial concentration of the linking agent

r : the functionality of the linking agent

P : the initial concentration of prepolymer

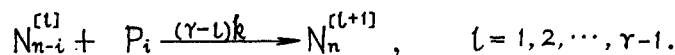
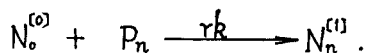
$P_n^0 = P\alpha_n$: the initial concentration of n -mer in the prepolymer, so that $\alpha_n (= P_n^0/P)$ represents the corresponding number fraction of n -mer

P_n : the residual concentration of n -mer of prepolymer

$N_n^{[\ell]}$: the concentration of star polymer with ℓ arms and n monomeric units

$N_0^{[0]}$: the residual concentration of linking agent

It had been reported that the effect of steric hindrance can be eliminated with the aid of the so-called "capping" technique [4]. During such a reaction process, the activity of every functional group of the molecule of linking agent is the same, being independent of the reaction time. Then the reaction equations are



It is evident that the following constraint or conservation conditions must hold:

$$\sum P_n = P - \sum_{i=1}^r i \sum_{n=i}^{\infty} N_n^{[i]} \quad (1)$$

$$N - N_0^{[0]} = \sum_{i=1}^r \sum_{n=i}^{\infty} N_n^{[i]} \quad (2)$$

The kinetic differential equations adapted to the reaction scheme written above are:

$$\frac{dN_0^{[0]}}{dt} = -\gamma k N_0^{[0]} \sum_n P_n. \tag{3}$$

$$\frac{dP_n}{dt} = -\gamma k N_0^{[0]} P_n - \sum_{l=1}^{\gamma} (\gamma-l) k P_n \sum_{n=l}^{\infty} N_n^{[l]}. \tag{4}$$

$$\frac{dN_n^{[1]}}{dt} = \gamma k N_0^{[0]} P_n - (\gamma-1) k N_n^{[1]} \sum_n P_n. \tag{5}$$

$$\frac{dN_n^{[l]}}{dt} = (\gamma-l-1) k \sum_{i=l}^{n-l+1} P_i N_{n-i}^{[l-1]} - (\gamma-l) k N_n^{[l]} \sum_n P_n, \quad l=2,3,\dots,\gamma. \tag{6}$$

The corresponding initial conditions are

$$N_0^{[0]}|_{t=0} = N, \quad P_n|_{t=0} = P_n^0, \quad \sum_n P_n|_{t=0} = P, \quad N_n^{[l]}|_{t=0} = 0 \quad (l=1,2,\dots,\gamma).$$

From Eq. (4) and constraint conditions, we obtain

$$\frac{dP_n}{dt} = -k P_n \left\{ \gamma N - P + \sum_n P_n \right\}. \tag{7}$$

It follows that

$$\frac{d \sum_n P_n}{dt} = -k \left\{ \gamma N - P + \sum_n P_n \right\} \sum_n P_n. \tag{8}$$

Putting

$$\lambda = \frac{P - \sum_n P_n}{P}, \tag{9}$$

namely

$$\sum_n P_n = P(1-\lambda), \tag{10}$$

substituting Eq. (10) into Eq. (8) leads to

$$\frac{d\lambda}{dt} = Pk(f-\lambda)(1-\lambda), \tag{11}$$

where

$$f = rN/P \quad (12)$$

is the equivalent ratio of linking agent to prepolymer.

Then, Eqs. (3)-(6) can be transformed into the following set of linear differential equations:

$$\frac{dN_o^{[0]}}{d\lambda} = - \frac{rN_o^{[0]}}{f-\lambda} \quad (13)$$

$$\frac{dP_n}{d\lambda} = - \frac{P_n}{1-\lambda} \quad (14)$$

$$\frac{dN_n^{[1]}}{d\lambda} = \frac{rN_o^{[0]}P_n}{P(f-\lambda)(1-\lambda)} - \frac{(r-1)N_n^{[1]}}{f-\lambda} \quad (15)$$

$$\frac{dN_n^{[l]}}{d\lambda} = \frac{(r-l+1) \sum_{i=1}^{n-l+1} P_i N_{n-i}^{[l-1]}}{P(f-\lambda)(1-\lambda)} - \frac{(r-l)N_n^{[l]}}{f-\lambda}, \quad l=2,3,\dots,r \quad (16)$$

The initial conditions of these equations transform into

$$N_o^{[0]}|_{\lambda=0} = N, \quad P_n|_{\lambda=0} = P_n^0, \quad \sum_n P_n|_{\lambda=0} = P, \quad N_n^{[l]}|_{\lambda=0} = 0 \quad (l=1,2,\dots,r).$$

Solving Eq. (13), we have

$$N_o^{[0]} = N(1-q)^r \quad (17)$$

where

$$q = \frac{\lambda}{f} = \frac{P - \sum_n P_n}{rN} \quad (18)$$

is defined as the degree of coupling, and λ as the extent of reaction of prepolymer.

From Eq. (14), the expression of P_n becomes

$$P_n = Nr \left(\frac{1}{f} - q \right) \alpha_n \quad (19)$$

It can be derived from Eq. (15) that

$$N_n^{[0]} = Nr q (1-q)^{r-1} \alpha_n \quad (20)$$

Similarly, for $\ell = 2, 3, \dots, r$, the following equation can be obtained:

$$N_n^{[\ell]} = N \binom{r}{\ell} q^{\ell} (1-q)^{r-\ell} \sum_{\sum_{k=1}^{\ell} n_k = n} \prod_{k=1}^{\ell} \alpha_{n_k} \quad (21)$$

where n_k is the degree of polymerization of the k -th arm star-branched species with ℓ arms, and α_{n_k} denotes the number fraction of n_k -mer among the prepolymer.

Equation (21) is the general expression of the molecular weight distribution function of the star polymer with ℓ arms, the factor of which,

$$\sum_{\sum_{k=1}^{\ell} n_k = n} \prod_{k=1}^{\ell} \alpha_{n_k} = \Omega(n), \quad (22)$$

can easily be calculated if the molecular weight distribution function of prepolymer has been given (see Section V below).

II. STATISTICAL MOMENTS

Since several molecular parameters of the star polymer are related to the statistical moments, it is necessary to derive the expressions for the various moments. We can obtain the following equations directly from Eq. (19):

$$\sum_n P_n = Nr \left(\frac{1}{f} - q \right). \quad (23)$$

$$\sum_n n P_n = Nr \left(\frac{1}{f} - q \right) \sum_n n \alpha_n. \quad (24)$$

$$\sum_n n^2 P_n = Nr \left(\frac{1}{f} - q \right) \sum_n n^2 \alpha_n. \quad (25)$$

For the derivation of the moments of star polymer with ℓ arms, it is convenient to solve a differential equation such as

$$\frac{d \sum_{n=1}^{\infty} n^s N_n^{[\ell]}}{d\lambda} = \frac{(r-\ell+1) \sum_{n=1}^{\infty} n^s \sum_{i=1}^{n-\ell+1} P_i N_{n-i}^{[\ell-1]}}{P(f-\lambda)(1-\lambda)} - \frac{(r-\ell) \sum_{n=1}^{\infty} n^s N_n^{[\ell]}}{f-\lambda}, \quad s=0, 1, 2; \ell=1, 2, \dots, r. \quad (26)$$

From this equation, we obtain

$$\sum_{n=l}^{\infty} N_n^{[l]} = N \binom{r}{l} f^l (1-f)^{r-l} \quad (27)$$

$$\sum_{n=l}^{\infty} n N_n^{[l]} = N l \binom{r}{l} f^l (1-f)^{r-l} \sum_n n \alpha_n \quad (28)$$

$$\sum_{n=l}^{\infty} n^2 N_n^{[l]} = N l \binom{r}{l} f^l (1-f)^{r-l} \left\{ \sum_n n^2 \alpha_n + (l-1) \left(\sum_n n \alpha_n \right)^2 \right\} \quad (29)$$

These formulas are rather simple, and a number of expressions of the molecular parameters of star polymers can be derived from them.

III. THE MOLECULAR PARAMETERS OF THE REACTION PRODUCT

Before the star-coupling reaction is quantitatively complete, there are various species in the reaction system that differ from each other in the degree of branching. Besides the species of star polymers with various numbers of arms, there are also a number of linear polymers, including the one-arm polymer, the two-arms polymer, and the residual prepolymer. Therefore, before or after the separation of linear polymer from the product of the star-coupling reaction, each molecular parameter of the product should have a different expression.

Let N_n be the molecular weight distribution function of the product; \bar{P}_n and \bar{P}_w represent the corresponding number- and weight-average of polymerization; B_l and B_{lw} denote, respectively, the number and weight fractions of the star polymer with l arms among the product; and \bar{B} be the average degree of branching. The expressions of these parameters are listed in Table 1, where \bar{P}_n^0 and \bar{P}_w^0 are defined as the number- and weight-average degrees of polymerization of prepolymer.

It is obvious that all parameters of the product vary with the reaction time. From Eqs. (11) and (18), we know that

$$\frac{df}{dt} = Pk(1-f)(1-fq) \quad (30)$$

and it follows that

$$q = \begin{cases} \frac{1 - e^{-Pkt(1-f)}}{f - e^{-Pkt(1-f)}} , & \text{when } f \neq 1. \\ \frac{Pkt}{1 + Pkt} , & \text{when } f = 1. \end{cases} \quad (31)$$

Substitution of Eq. (31) into the formulas in Table 1 gives parameters as functions of the variable t , and then their values can be computed for any stage of the star-coupling reaction.

IX. INFLUENCE OF STERIC HINDRANCE

Fetters et al. [4] had pointed out that the aspects of steric hindrance cannot be neglected when living polystyrene or living polyisoprene is used as the prepolymer in star coupling. In this case, the set of kinetic differential equations is as follows:

$$\frac{dN_0^{(0)}}{dt} = -r k_0 N_0^{(0)} \sum_n P_n \quad (32)$$

$$\frac{dP_n}{dt} = - \sum_{l=0}^r (\gamma - l) k_l P_n \sum_{n=l}^{\infty} N_n^{(l)} \quad (33)$$

$$\frac{dN_n^{(1)}}{dt} = r k_0 N_0^{(0)} P_n - (\gamma - 1) k_1 N_n^{(1)} \sum_n P_n \quad (34)$$

$$\frac{dN_n^{(l)}}{dt} = (\gamma - l + 1) k_{l-1} \sum_{i=1}^{n-l+1} P_i N_{n-i}^{(l-1)} - (\gamma - l) k_l N_n^{(l)} \sum_n P_n , \quad (35)$$

$l = 2, 3, \dots, r$

In Eq. (33), we have put:

$$r k_0 P_n N_0^{(0)} + \sum_{l=1}^r (\gamma - l) k_l P_n \sum_{n=l}^{\infty} N_n^{(l)} = \sum_{l=0}^r (\gamma - l) k_l P_n \sum_{n=l}^{\infty} N_n^{(l)}$$

The initial conditions of Eqs. (32)-(35) are the same as those mentioned in Section I. Since the values of k_0, k_1, \dots, k_{r-1} are different from one another, we manage to find a new way to settle this problem. By assuming

$$x = \int_0^t \sum_n P_n dt \quad (36)$$

TABLE 1. Expressions of Various Parameters Before and After Separating Linear Polymer from the Reaction Product

| Parameter | Before separation | After separation |
|------------------|---|---|
| N_n | $N \left\{ r \left(\frac{1}{f} - \beta \right) \alpha_n + \sum_{l=1}^y \binom{y}{l} \beta^l (1-\beta)^{y-l} \Omega^{(n)} \right\}$ | $N \sum_{l=1}^y \binom{y}{l} \beta^l (1-\beta)^{y-l} \Omega(n)$ |
| \overline{P}_n | $\frac{r}{r + f[1-r\beta - (1-\beta)^y]} \overline{P}_n^0$ | $\frac{r\beta \{1 - (1-\beta)^{y-2} [1 + (r-2)\beta]\}}{1 - (1-\beta)^{y-2} [1 + (r-2)\beta + (1-r)(1-\frac{r}{2})\beta^2]} \overline{P}_n^0$ |
| \overline{P}_w | $\overline{P}_w^0 + (r-1)f\beta^2 \overline{P}_n^0$ | $\overline{P}_w^0 + \frac{(r-1)\beta [1 - (1-\beta)^{y-2}]}{1 - (1-\beta)^{y-2} [1 + (r-2)\beta]} \overline{P}_n^0$ |
| B_t | $\frac{\binom{y}{l} \beta^l (1-\beta)^{y-l}}{1 - (1-\beta)^y + r \left(\frac{1}{f} - \beta \right)}$ | $\frac{\binom{y}{l} \beta^l (1-\beta)^{y-l}}{1 - (1-\beta)^{y-2} [1 + (r-2)\beta + (1-r)(1-\frac{r}{2})\beta^2]}$ |

$$\begin{aligned}
 \overline{B}_{uw} &= \frac{(r^{-1})f q^2 (1-q)^{r-1}}{(r^{-1})q^{r-1} (1-q)^{r-1} - (1-q)^{r-2} [1+(r-2)q]} \\
 \overline{B} &= \frac{r}{r+f(1-rq-(1-q)^r)} \\
 \overline{P}_w/\overline{P}_n &= \overline{P}_w^0/(\overline{B}\overline{P}_n^0) + \frac{r}{r+f(1-rq-(1-q)^r)} \\
 &+ \frac{\overline{P}_w^0/(\overline{B}\overline{P}_n^0) + (1-\frac{1}{r})f q^2 \{r+f[1-rq-(1-q)^r]\}}{r \{ (1-q)^{r-2} [1+(r-2)q] + (1-q)^{r-1} [1+(r-2)q + (1-q)(1-\frac{1}{2})q^2] \}}
 \end{aligned}$$

the following matrix equation can be derived from Eqs. (32), (34), and (35):

$$\begin{pmatrix} \frac{dN_0^{[0]}}{dx} \\ \frac{d\sum_n N_n^{[1]}}{dx} \\ \frac{d\sum_n N_n^{[2]}}{dx} \\ \vdots \\ \frac{d\sum_n N_n^{[L]}}{dx} \end{pmatrix} = \begin{pmatrix} -rk_0 & & & & \\ rk_0 & -(r-1)k_1 & & & \\ 0 & (r-1)k_1 & -(r-2)k_2 & & \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \vdots & \vdots & \vdots & (r-l+1)k_{l-1} & -(r-l)k_l \end{pmatrix} \begin{pmatrix} N_0^{[0]} \\ \sum_n N_n^{[1]} \\ \sum_n N_n^{[2]} \\ \vdots \\ \sum_n N_n^{[L]} \end{pmatrix} \quad (37)$$

From this set of differential equations, we obtain

$$N_0^{[0]} = N e^{-rk_0 x} \quad (38)$$

and

$$\sum_n N_n^{[L]} = N \prod_{i=0}^{L-1} (r-i)k_i \sum_{j=0}^L \prod_{i=0}^L \frac{\exp\{-(r-j)k_j x\}}{(r-i)k_i - (r-j)k_j} \quad (39)$$

where the symbol $\prod_{i=0}^L$ denotes that index i is never equal to index j in the successive product of l factors.

It is well known that the living prepolymer chains of different lengths have the same activity. Hence, the prepolymer reaction with the linking agent is completely random. In other words, the probability for each living chain of prepolymer to undergo reaction is the same, independent of its length. Consequently, $P_n / \sum_n P_n$ must be equal to P_n^0 / P , namely

$$P_n / \sum_n P_n = \alpha_n. \tag{40}$$

With Eq. (36), a transformation for Eqs. (33)-(35) can be made:

$$\frac{dP_n}{dx} = -\alpha_n \sum_{l=0}^r (\gamma-l) k_l \sum_n N_n^{[l]}. \tag{41}$$

$$\frac{dN_n^{[1]}}{dx} = \tau k_0 \alpha_n N_0^{[0]} - (\gamma-1) k_1 N_n^{[1]}. \tag{42}$$

$$\frac{dN_n^{[l]}}{dx} = (\gamma-l+1) k_{l-1} \sum_{i=1}^{n-l+1} P_i N_{n-i}^{[l-1]} / \sum_n P_n - (\gamma-l) k_l N_n^{[l]}. \tag{43}$$

From Eq. (41), it was derived that

$$P_n = \alpha_n \left[P - N \sum_{l=0}^r \prod_{j=0}^l \frac{l}{i=0} \frac{(\gamma-i)k_i}{(\gamma-i)k_i - (\gamma-j)k_j} \left\{ 1 - \exp[-(\gamma-j)k_j x] \right\} \right]. \tag{44}$$

It follows that

$$\sum_n P_n = P - N \sum_{l=0}^r \prod_{j=0}^l \frac{l}{i=0} \frac{(\gamma-i)k_i}{(\gamma-i)k_i - (\gamma-j)k_j} \left\{ 1 - \exp[-(\gamma-j)k_j x] \right\}. \tag{45}$$

Solving Eqs. (42) and (43), we have

$$N_n^{[l]} = N \prod_{i=0}^{l-1} (\gamma-i)k_i \sum_{j=0}^l \prod_{i=0}^l \frac{\exp[-(\gamma-j)k_j x]}{(\gamma-i)k_i - (\gamma-j)k_j} \Omega(n), \tag{46}$$

where the expression of $\Omega(n)$ has been given in Eq. (22). Equation (46) is the molecular weight distribution function of the star polymer with l arms formed during the coupling reaction with steric hindrance being not negligible.

According to the definitions of the degree of coupling and the extent of reaction of prepolymer given in Section I, these parameters can be expressed as

$$q = \frac{1}{\gamma} \sum_{l=0}^r l \prod_{i=0}^{l-1} (\gamma-i)k_i \sum_{j=0}^l \prod_{i=0}^l \frac{\exp[-(\gamma-j)k_j x]}{(\gamma-i)k_i - (\gamma-j)k_j} \tag{47}$$

and

$$\lambda = \frac{N}{P} \sum_{i=0}^r \sum_{j=0}^l \prod_{i=0}^l \frac{(\gamma-i)k_i}{(\gamma-i)k_i - (\gamma-j)k_j} \left\{ 1 - \exp[-(\gamma-j)k_j x] \right\}. \quad (48)$$

Substituting Eq. (21) into the left-hand sides of Eqs. (27)-(29) leads to the following equalities:

$$\sum_{n=l}^{\infty} \sum_{\substack{k=1 \\ \sum_{k=1}^l n_k = n}} \prod_{k=1}^l \alpha_{n_k} = 1. \quad (49)$$

$$\sum_{n=l}^{\infty} n \sum_{\substack{k=1 \\ \sum_{k=1}^l n_k = n}} \prod_{k=1}^l \alpha_{n_k} = l \sum_n n \alpha_n. \quad (50)$$

$$\sum_{n=l}^{\infty} n^2 \sum_{\substack{k=1 \\ \sum_{k=1}^l n_k = n}} \prod_{k=1}^l \alpha_{n_k} = l \left\{ \sum_n n^2 \alpha_n + (l-1) \left(\sum_n n \alpha_n \right)^2 \right\}. \quad (51)$$

Therefore, the first- and second-order moments of the star polymer with l arms are as follows:

$$\sum_n n N_n^{[l]} = N l \sum_n n \alpha_n \prod_{i=0}^{l-1} (\gamma-i)k_i \sum_{j=0}^l \prod_{i=0}^l \frac{\exp[-(\gamma-j)k_j x]}{(\gamma-i)k_i - (\gamma-j)k_j}. \quad (52)$$

$$\sum_n n^2 N_n^{[l]} = N l \left\{ \sum_n n^2 \alpha_n + (l-1) \left(\sum_n n \alpha_n \right)^2 \right\} \prod_{i=0}^{l-1} (\gamma-i)k_i \sum_{j=0}^l \prod_{i=0}^l \frac{\exp[-(\gamma-j)k_j x]}{(\gamma-i)k_i - (\gamma-j)k_j}. \quad (53)$$

The zeroth order moment has been given to Eq. (39).

For the case of this section, the expressions of various molecular parameters defined in Section III for the products of the star-coupling reaction, i.e., N_n , \bar{P}_n , \bar{P}_w , B_i , B_{iw} , \bar{B} , and \bar{P}_w/\bar{P}_n can easily be derived from Eqs. (39), (52), and (53) and have been omitted here.

V. CALCULATION OF $\Omega(n)$

For star coupling both with and without the effect of steric hindrance, the respective molecular weight distribution functions of the star polymers generated include the same factor, namely $\Omega(n)$. If the molecular weight distribution of the prepolymer is known, $\Omega(n)$ can be calculated, as will be shown in this section.

Supposing there are l identical series $(\alpha_1 Z + \alpha_2 Z^2 + \alpha_3 + \dots)$ multiplied by each other, we pick out one term from each bracket, that is, $\alpha_{n_1} Z^{n_1}$ from the first bracket, $\alpha_{n_2} Z^{n_2}$ from the second bracket, \dots , $\alpha_{n_k} Z^{n_k}$ from the k -th bracket, and so forth, and then multiply them together, i.e.,

$$\prod_{k=1}^l \alpha_{n_k} Z^{\sum_{k=1}^l n_k}$$

This happens to be the typical term of the expansion of $(\alpha_1 Z + \alpha_2 Z^2 + \dots + \alpha_{n_k} Z^{n_k} + \dots)^l$ before combining the similar terms. If the terms in which the exponent of variable Z equals n are gathered together, we have

$$\sum_{\sum_{k=1}^l n_k = n} \prod_{k=1}^l \alpha_{n_k} Z^n$$

It is evident that

$$\sum_{\sum_{k=1}^l n_k = n} \prod_{k=1}^l \alpha_{n_k}$$

is the coefficient of the term for Z^n in the expansion (after combining similar terms) of a generating function as follows:

$$G(Z) = (\alpha_1 Z + \alpha_2 Z^2 + \dots + \alpha_{n_k} Z^{n_k} + \dots)^l \tag{54}$$

In other words, if the generating function $G(Z)$ is expanded,

$$G(z) = \sum_n \Omega(n) z^n, \quad (55)$$

then Eq. (22) can be obtained. A few practical examples are taken into account below.

(i) The prepolymer follows a Poisson distribution:

$$\alpha_{n_k} = \frac{\tau^{n_k-1} e^{-\tau}}{(n_k-1)!}, \quad (56)$$

$$G(z) = e^{-\tau} z^t e^{\tau z} = \sum_n \frac{(\tau)^{n-t} e^{-\tau}}{(n-t)!} z^n,$$

hence

$$\Omega(n) = \frac{(\tau)^{n-t} e^{-\tau}}{(n-t)!}. \quad (57)$$

(ii) The prepolymer has the Flory (most probable or geometric) distribution:

$$\alpha_{n_k} = p^{n_k-1} (1-p), \quad (58)$$

$$\begin{aligned} G(z) &= (1-p)^t z^t (1-pz)^{-t}, \\ &= \sum_n \binom{n-1}{t-1} p^{n-t} (1-p)^t z^n, \end{aligned}$$

hence

$$\Omega(n) = \binom{n-1}{t-1} p^{n-t} (1-p)^t. \quad (59)$$

(iii) The prepolymer follows the Gold distribution [5, 6]:

$$\alpha_{n_k} = \frac{a e^{-a\tau}}{(1-a)^{n_k} (1-e^{-a\tau})} \left\{ 1 - \sum_{i=0}^{n_k-1} \frac{[(1-a)\tau]^i e^{-(1-a)\tau}}{i!} \right\}, \quad (60)$$

$$G(z) = \frac{a^t e^{-lat}}{(1-e^{-a\tau})^t} \left(\frac{z}{1-a-z} \right)^t \left\{ 1 - e^{\tau z - (1-a)\tau} \right\}^t,$$

$$\begin{aligned}
 &= \frac{a^t e^{-t a \tau}}{(1 - e^{-a \tau})^t} \sum_{k=0}^t (-1)^k \binom{t}{k} e^{-k(1-a)\tau} \left\{ \sum_{m=t}^{\infty} \binom{m-1}{t-1} \left(\frac{z}{1-a}\right)^m \right\} \left\{ \sum_{i=0}^{\infty} \frac{(k \tau z)^i}{i!} \right\}, \\
 &= \sum_{k=0}^t \frac{a^t e^{-t a \tau}}{(1-a)^k (1 - e^{-a \tau})^t} \sum_{k=0}^t (-1)^k \binom{t}{k} \sum_{i=0}^{n-t} \binom{n-i-1}{t-1} \frac{[k(1-a)\tau]^i e^{-k(1-a)\tau}}{i!} z^n,
 \end{aligned}$$

hence

$$\Omega(n) = \frac{a^t e^{-t a \tau}}{(1-a)^n (1 - e^{-a \tau})^t} \sum_{k=0}^t (-1)^k \binom{t}{k} \sum_{i=0}^{n-1} \binom{n-i-1}{t-1} \frac{[k(1-a)\tau]^i e^{-k(1-a)\tau}}{i!}. \tag{61}$$

In general, living polymers follow the Poisson or the Gold distribution; the living polymer formed in equilibrium polymerization falls within the Flory distribution [7, 8], so the examples given above are of practical importance. If the prepolymer has some other distributions, $\Omega(n)$ can be derived in a similar manner.

VI. THE CASE OF $q = 1$

During synthesis of star-branched polymers, the reaction system is always allowed to proceed for a long time to complete the coupling reaction quantitatively. Once all the functional groups of the linking agent have been consumed, i.e., $q = 1$, there is only one star species with r arms in the reactor. The excess prepolymer can be removed because its molecular weight is much smaller than that of the star polymer formed. Under the conditions discussed here, the same results are obtained no matter whether there is steric hindrance or not in the star-coupling reaction. For example, both Eqs. (21) and (46) are simplified to the following equation for $q = 1$:

$$N_n^{[r]} = N \sum_{\sum_{k=1}^r n_k = n} \prod_{k=1}^r \alpha_{n_k}. \tag{62}$$

The corresponding number- and weight-average degrees of polymerization are

$$\bar{P}_n = r \bar{P}_n^{\circ}, \tag{63}$$

$$\bar{P}_w = \bar{P}_w^{\circ} + (r-1) \bar{P}_n^{\circ}. \tag{64}$$

Then the polydispersity is

$$\bar{P}_w / \bar{P}_n = 1 + \frac{1}{r} (\bar{P}_w^{\circ} / \bar{P}_n^{\circ} - 1). \tag{65}$$

Equations (63)-(65) are identical with those derived in terms of statistics [2]. From Eqs. (57), (59), and (62), it can be concluded that the star polymer will still have a Poisson distribution if the prepolymer had the same distribution; alternatively, when the prepolymer has a Flory distribution, the star polymer formed follows the binomial distribution. It is known that the Poisson distribution may be transformed into a normal distribution if n is large enough; under those conditions, the plot of the binomial distribution becomes a continuous curve of symmetric shape, the limit of which is the curve of a normal distribution as well. That is to say, in spite of the fact that the Poisson distribution is very narrow and the Flory distribution is rather wide, the difference in the molecular weight distribution of the prepolymer has little influence on that of the resultant star polymer if r is larger.

Furthermore, from Eq. (65) we can draw the following conclusions.

- (i) The more arms the star polymer has, the more homogeneous is the molecular weight distribution.
- (ii) No matter what the polydispersity of the prepolymer is, as long as the following inequality is satisfied,

$$r > 10(\overline{P}_w/\overline{P}_n - 1), \quad (66)$$

we have

$$\overline{P}_w/\overline{P}_n < 1.1. \quad (67)$$

This means that the star polymer has the narrowest normal distribution under Condition (66). The relation between $\overline{P}_w/\overline{P}_n$ and r is shown in Fig. 1. The experimental data reported recently by Fetters et al. [9] have been treated by the equations given above, and the results obtained are listed in Table 2.

Table 2 shows that the theoretical results are in keeping with the experimental data. However, it was expected that since the prepolymer already possessed a very narrow molecular weight distribution, so did the resultant star polymer. In order to test our theory more stringently, it seems necessary to study experimentally the star-coupling reaction of a prepolymer with a broad molecular weight distribution.

TABLE 2. Molecular Weights of Decaocta-Branched Polyisoprene Stars

| Sample | Experimental data | | | | | | Theoretical value | |
|-----------|--|--|---|---|---|---|---|---|
| | \bar{M}_n (arm), 10 ⁻³ g/mol | \bar{M}_w (arm), 10 ⁻³ g/mol | \bar{M}_n (star), 10 ⁻⁵ g/mol | \bar{M}_w (star), 10 ⁻⁵ g/mol | \bar{M}_n (star), 10 ⁻⁵ g/mol | \bar{M}_w (star), 10 ⁻⁵ g/mol | \bar{M}_n (star), 10 ⁻⁵ g/mol | \bar{M}_w (star), 10 ⁻⁵ g/mol |
| 18-IAA | 18.8 | 19.7 | 3.40 | 3.44 | 3.38 ₄ | 3.39 ₃ | | |
| 18-IIAA | 12.0 | 13.1 | 2.16 | 2.18 | 2.16 | 2.17 ₃ | | |
| 18-IIIAAA | 46.0 | 49.1 | | 8.00 | 8.28 | 8.31 ₁ | | |
| 18-VIAA | 10.7 | 11.2 | 1.93 | 1.97 | 1.92 ₆ | 1.93 ₁ | | |
| 18-VIIA | 3.4 | 3.6 | 0.61 ₀ | 0.61 ₇ | 0.61 ₂ | 0.61 ₄ | | |
| 18-VIIIAA | 5.1 | 5.4 | 0.92 ₀ | 0.93 ₀ | 0.91 ₈ | 0.92 ₁ | | |

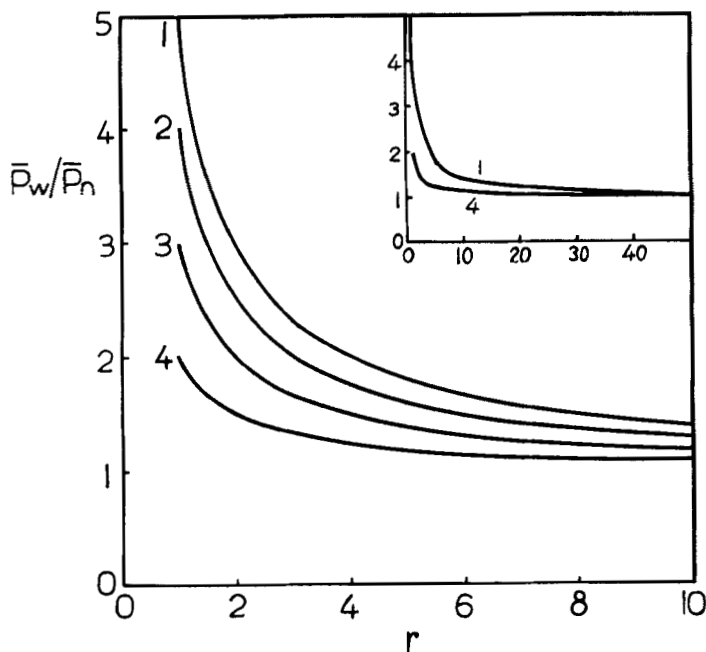


FIG. 1. Relationship between polydispersity \bar{P}_w/\bar{P}_n and degree of branching r . For curves 1, 2, 3, and 4, the respective values of the polydispersity of the prepolymer are 5, 4, 3, and 2.

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