Polymer Bulletin 3, 353–361 (1980)

Polymer Bulletin

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Molecular Weight Distribution in Polyrecombination Reactions

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Herrn Prof. Dr. Drs. h. c. G.V. Schulz zu seinem 75. Geburtstag gewidmet

Synopsis

It is demonstrated that the polymers obtained in batch polyrecombination reactions have a Schulz-Flory molecular weight distribution. Much wider distributions are obtained if the reaction is carried out in continuous stirred tank reactors. This article is a supplement to "Dimerisation and oligomerisation by dehydrogenation as a general synthetic principle[1]".

Introduction

In polyrecombination reactions[1,2], bifunctional molecules are converted into radicals by transferring a hydrogen atom onto primary radicals $R^{\bullet}$. The secondary radicals thus formed may combine with one another. The primary radicals are obtained by decomposition of suitable polymerisation initiators, e.g., peroxides. The reaction proceeds schematically as follows.

$$R-R \rightarrow 2R\cdot \tag{1a}$$

$$H-A-H + R\cdot \rightarrow RH + H-A\cdot \tag{1b}$$

$$2H-A\cdot \rightarrow H-A-A-H \tag{1c}$$

The larger molecules thus derived from the monomers may themselves be involved in transfer reactions and become radicals, which enter into combination reactions. Two primary radicals and a starter molecule are required for bonding two secondary radicals.

0170-0839/80/0003/0353/$01.80

1. Polymer recombinations in batch production techniques

The molecular weight distribution is governed by the reaction mechanism of polymer coupling. Since the probability is the same as that for polycondensation reactions, a Schulz-Flory distribution can be expected[3], and the distribution is derived from the reaction kinetic considerations submitted below.

Imagine that the starter is fed very slowly into a reactor containing the monomer. The number of initiator molecules and primary radicals is small compared to the number of terminal groups. Thus the probability that the secondary and primary radicals will combine is negligibly small.

In order to calculate the distribution, let us first of all consider any given conv. q with an instantaneous, unknown distribution of N_V molecules and 2 N_V unreacted terminal groups. The molar fractions γ_i for the molecules with i (i = 1,2,...) monomeric units are given by

$$\gamma_{iv} = \frac{N_{iv}}{N_v} \tag{2}$$

where N_{iv} etc. is the number of macromolecules consisting of i monomeric units.

Let us now suppose that 2a primary radicals react with the mixture in this instantaneous state and that the following two conditions apply:

$$2\,a \gg 2\,N_V \tag{3}$$

$$1 \ll 2\,a \tag{4}$$

Both conditions can always be easily satisfied.

If the plausible assumption is made that the transfer reactivity of the terminal groups does not depend on the size of the molecules, the polymer radicals formed will have the same molecular weight distribution as the polymer molecules. Under the condition expressed by Eqn. (3), the occurrence of polymer radicals is a rare event, and the occurrence of biradicals can be neglected.

The 2a radicals newly formed combine to yield new polymer molecules. The probabilities for the formation of new dimers, trimers, tetramers, etc. are w_2, w_3, w_4, etc., where

$$\sum_{i=2}^{\infty} w_i = 1 \tag{5}$$

After the reaction has proceeded through N_{in} steps, the number of molecules with i monomeric units is given by the original number of molecules minus the number of radicals formed from them and increased by the number of new molecules with i monomeric units.

It follows from Eqn. (2) that

$$\begin{aligned} N_{1n} &= N_{1v}\left(1-\frac{2a}{N_v}\right) \\ &\vdots \\ N_{in} &= N_{iv}\left(1-\frac{2a}{N_v}\right)+a.\omega_i \\ &\vdots \end{aligned} \qquad (6)$$

The following relationships apply for the probabilities w_i (see Appendix).

$$\begin{aligned} \omega_2 &= \frac{1}{N_v^2}(N_{1v})^2 \\ \omega_i &= \frac{2}{N_v^2}\left(\sum_{j=1}^{(i-1)/2} N_{jv}\cdot N_{(i-j)v}\right) ;\ i=2k+1 ;\ k=1,2,\ldots \\ \omega_i &= \frac{1}{N_v^2}\left[2\left(\sum_{j=1}^{(i/2)-1} N_{jv}\, N_{(i-j)v}\right)+\left(N_{\frac{i}{2}v}\right)^2\right] ;\ i=2k ;\ k=2,3,\ldots \end{aligned} \qquad (7)$$

N_v is the number of molecules present at a given instant. If the number of free radicals is neglected (cf. Eqn. (3)) and the total number of radicals formed by transfer is 2A, the number of terminal groups still present is given by

$$2N_v = 2N_{10} - 2A \qquad (8)$$

where N_{10} is the number of monomer molecules originally present.

It follows from Eqns. (6) to (8) that

$$\begin{aligned} \Delta N_1 &= N_{1n}-N_{1v} = -2\frac{N_{1v}}{N_{10}-A}a \\ \Delta N_2 &= N_{2n}-N_{2v} = \left(-2\frac{N_{2v}}{N_{10}-A}+\frac{N_{1v}\cdot N_{1v}}{(N_{10}-A)^2}\right)a \\ \Delta N_i &= N_{in}-N_{iv} = \left[-2\frac{N_{iv}}{N_{10}-A}+\frac{2}{(N_{10}-A)^2}\left(\sum_{j=1}^{(i-1)/2} N_{jv}\cdot N_{(i-j)v}\right)\right]a ;\ i=2k+1 ;\ k=1,2,\ldots \\ \Delta N_i &= N_{in}-N_{iv} = \left[-2\frac{N_{iv}}{N_{10}-A}+\frac{1}{(N_{10}-A)^2}\left[2\left(\sum_{j=1}^{(i/2)-1} N_{jv}\, N_{(i-j)v}\right)+\left(N_{\frac{i}{2}v}\right)^2\right]\right]a ;\ i=2k ;\ k=2,3,\ldots \end{aligned} \qquad (9)$$

The above equations (9) are now converted into differential equations. The term a is thereby considered to be the slight difference between consecutive values of A, i.e., a = dA, and N_i can be substituted for N_{iv}. The boundary conditions for integration are

$$\lim_{A\to 0} N_1 = N_{10} \qquad (10)$$

$$\lim_{A\to 0} N_{i\neq 1} = 0$$

In general,

$$N_i = (N_{10}-A)^2 \frac{A^{i-1}}{N_{10}{}^i} \qquad (11)$$

The molar fractions expressed in terms of the molecules present at a given instant are given by

$$Y_i = \frac{N_i}{N_{10}-A} = \left(1-\frac{A}{N_{10}}\right)\left(\frac{A}{N_{10}}\right)^{i-1} \qquad (12)$$

The magnitude $A/N_{10} = 2A/2N_{10}$ is the fraction q of the reactive terminal groups that have been converted. It follows that

$$Y_i = (1-q)\cdot q^{i-1} \qquad (13)$$

Eqn. (13) corresponds to the Schulz-Flory molecular weight distribution.

2. Polyrecombination in a continuous stirred tank reactor with ideal mixing

Let us consider the reactor in the stationary state. The monomer and the radical former are fed together into the reactor, and the product of the reaction is removed simultaneously. The following symbols have been adopted.

V = Volume of reactor (vol)
u = Feed rate (vol x time^{-1})
$k_{ü}$ = Absolute transfer constant for the primary radical (vol x mol^{-1} x time^{-1})
k_c = Rate constant for radical combination (vol x mol^{-1} x time^{-1})

The following set of equations applies to the polymer molecules.

$$\begin{aligned} V\cdot\frac{d[M_1]}{dt} &= u[M_1]_0 - V\cdot 2k_{ü}[R^{\cdot}][M_1] - u[M_1] = 0 \\ &\vdots \\ V\cdot\frac{d[M_i]}{dt} &= V\cdot\frac{k_c}{2}\left(\sum_{j=1}^{i-1}[M_j^{\cdot}][M_{i-j}^{\cdot}]\right) - V\cdot 2k_{ü}[R^{\cdot}][M_i] - u[M_i] = 0 \\ &\vdots \end{aligned} \qquad (14)$$

The terms containing the expression $k_{ü}$ have been multiplied by a factor of 2, because the polymer molecules have two reactive terminal groups. Products with odd indices appear twice in the expressions within parentheses, and products with even indices appear only once. The rate of a bimolecular reaction is proportional to the number of collisions between the types of molecule concerned. This number, in turn, is proportional to the probability of encounter between two molecules and thus to the possible number of linkages[4,5] (cf. the case of batch polyrecombination in the appendix).

The average residence time is given by

$$\tau = \frac{V}{u} \tag{15}$$

If it is introduced into the set of equations (14), the set of equations (16) will be obtained.

$$[M_1] = \frac{[M_1]_0}{2k_{ü}\tau[R^{\cdot}]+1} \quad ; \quad \sum_{j=1}^{i-1}[M_j][M_{i-j}] = C\cdot[M_i] \\ \vdots \qquad\qquad\qquad\qquad \vdots \tag{16}$$

These equations have been abbreviated by the introduction of the term

$$C = 2\,\frac{2k_{ü}\,\tau[R^{\cdot}]+1}{k_c\,\tau} \tag{17}$$

According to the Bodenstein principle, the following applies to the individual polymer radicals.

$$\frac{d[M_i^{\cdot}]}{dt} = 2k_{ü}[R^{\cdot}][M_i] - k_c[M_i^{\cdot}]\sum_{j=1}^{\infty}[M_j^{\cdot}] = 0 \tag{18}$$

$$[M_i^{\cdot}] = \frac{2k_{ü}[R^{\cdot}]}{k_c\sum_{j=1}^{\infty}[M_j^{\cdot}]}\,[M_i] \tag{19}$$

Eqn. (19) can be simplied by substituting B for the factor, i.e.,

$$\frac{2k_{ü}[R^{\cdot}]}{k_c\sum_{j=1}^{\infty}[M_j^{\cdot}]} = B \tag{20}$$

Inserting this in the set of equations (16) gives

$$[M_1] = \frac{[M_1]_0}{2k_{ü}\tau[R^{\cdot}]+1} \quad ; \quad [M_i] = \varphi_i\cdot\left(\frac{B^2}{C}\right)^{i-1}[M_1]^i \\ \vdots \qquad\qquad\qquad\qquad \vdots \tag{21}$$

The following[6] applies for the factor φ_i

$$\varphi_i = \sum_{s=1}^{s=i-1}\varphi_s\cdot\varphi_{i-s} = 2^{i-1}\cdot\frac{1.3.5.\ldots.(2i-3)}{i!} = \frac{(2i-2)!}{(i-1)!\,i!} \tag{22}$$

where $\varphi_1 = 1$ and $i = 2, 3, 4, \ldots \ldots$

The factor B^2/C is obtained from Eqns. (17) and (20), i.e.,

$$\frac{B^2}{C} = \left(\frac{2k_{ü}[R^{\cdot}]}{k_c\sum\limits_{i=1}^{\infty}[M_i^{\cdot}]}\right)^2 \left(\frac{1}{2}\cdot\frac{k_c\mathcal{T}}{2k_{ü}[R^{\cdot}]\mathcal{T}+1}\right) \tag{23}$$

Eqn. (19) can be rearranged to give

$$\left(\sum_{i=1}^{\infty}[M_i^{\cdot}]\right)^2 = \frac{2k_{ü}[R^{\cdot}]}{k_c}\cdot\sum_{i=1}^{\infty}[M_i] \tag{24}$$

Substituting in Eqn. (23) gives

$$\frac{B^2}{C} = \frac{1}{\sum\limits_{i=1}^{\infty}[M_i]}\cdot\frac{k_{ü}[R^{\cdot}]\mathcal{T}}{2k_{ü}[R^{\cdot}]\mathcal{T}+1} \tag{25}$$

Adding the equations in the set (14) and combining with Eqn. (15) gives

$$0 = [M_1]_0 + \frac{k_c\mathcal{T}}{2}\left(\sum_{i=1}^{\infty}[M_i^{\cdot}]\right)^2 - (2k_{ü}[R^{\cdot}]\mathcal{T}+1)\sum_{i=1}^{\infty}[M_i] \tag{26}$$

Eqn. (24) is taken to determine the sum $\sum\limits_{i=1}^{\infty} M_i$

It thus follows that

$$\sum_{i=1}^{\infty}[M_i] = \frac{[M_1]_0}{k_{ü}[R^{\cdot}]\mathcal{T}+1} \tag{27}$$

and

$$\sum_{i=1}^{\infty}[M_i^{\cdot}] = \left(2\cdot\frac{k_{ü}[R^{\cdot}]\mathcal{T}}{k_{ü}[R^{\cdot}]\mathcal{T}+1}\cdot\frac{[M_1]_0}{k_c\mathcal{T}}\right)^{0.5} \tag{28}$$

The sum of all the terminal groups $[E]$ is given by

$$[E] = 2\cdot\sum_{i=1}^{\infty}[M_i] + 1\cdot\sum_{i=1}^{\infty}[M_i^{\cdot}] \tag{29}$$

Thus the proportion q of the terminal groups that have not been converted is given by

$$q = \frac{2[M_1]_0-[E]}{2[M_1]_0} = 1-\frac{1}{k_{ü}[R^{\cdot}]\mathcal{T}+1} - \left(\frac{k_{ü}[R^{\cdot}]\mathcal{T}}{k_{ü}[R^{\cdot}]\mathcal{T}+1}\cdot\frac{1}{2k_c\mathcal{T}[M_1]_0}\right)^{0.5} \tag{30}$$

The usual order of magnitude[7] of the constants for bimolecular radical elimination reactions is 10^6 to 10^8 $1\ mol^{-1}\ sec^{-1}$. In the following estimation, similar values have been assumed for $k_c\cdot[M_1]_o$ lies within the 10 mol 1^{-1} range; and $\mathcal{T}$, in the 1 hour = 3.6×10^3 sec range. Thus the order of magnitude for the expression $k_c\mathcal{T}[M_1]_o$ is 10^{10} to 10^{11}.

The numerical value for the magnitude $k_{ü}$ was estimated in the light of the radical chain transfer constant for isopropylbenzene. At 100°C, a figure of 2.5×10^{-5} was measured during the polymerization of styrene[8] for the transfer constant $C = k_{ü}k_w^{-1}$. Since the numerical value for the growth constant[8] valid for a temperature of 100°C is $k_w = 7.42 \times 10^2$ $1\ mol^{-1}\ sec^{-1}$, it follows that the value for $k_ü$ is $k_ü = 2.1 \times 10^{-1}$. In chain transfer, the constant $k_ü$ for non-resonance-stabilized radicals, for which many starter radicals serve as an example, is greater than that for styryl radicals by a factor of 2000[9] If it is assumed that this applies to the present case, then $k_ü = 4.2 \times 10^{2}$ l mol^{-1} sec^{-1}. Even if $[R^\cdot]$ is unrealistically high, e.g., 1 mol l^{-1}, the term $k_ü[R^\cdot]\tau$ would become $10^4 - 10^5$ and would thus be less than the expression $2\, k_c \tau [M_1]_o$ by a factor of about $10^5 - 10^7$. Therefore, the last term in Eqn. (30) is negligible compared with the others. The equation is not valid for very high yields, in which case the terminal group concentration is so low that not all of the primary radicals can enter into a transfer reaction.

Neglecting the final term in Eqn. (30) gives

$$k_ü[R^\cdot]\tau = \frac{q}{1-q} \qquad (31)$$

Combining Eqns. (25), (27) and (31) yields

$$\frac{B^2}{C} = \frac{1}{[M_1]_o} \cdot \frac{q}{1-q} \cdot \frac{1}{1+q} \qquad (32)$$

Inserting Eqn. (32) in the set of equations (21) gives

$$\begin{array}{ll} [M_1] = [M_1]_o \dfrac{1-q}{1+q} \; ; & [M_i] = [M_1]_o \cdot \varphi_i \left(\dfrac{q}{(1+q)^2}\right)^{i-1} \cdot \dfrac{1-q}{1+q} \\ \vdots & \vdots \end{array} \qquad (33)$$

Combining Eqns. (27) and (31) gives

$$\sum_{i=1}^{\infty}[M_i] = [M_1]_o\,(1-q) \qquad (34)$$

Eqn. (33) applies if the yields are not too high (cf. Eqn. 30)).

The molar fractions follow from Eqns. (33) and (34), i.e.,

$$\begin{array}{ll} Y_1 = \dfrac{1}{1+q} & Y_i = \varphi_i \left(\dfrac{q}{(1+q)^2}\right)^{i-1} \cdot \dfrac{1}{1+q} \\ \vdots & \vdots \end{array} \qquad (35)$$

The molecular weight distribution obtained from the set of equations (35) is very much wider than the Schulz-Flory distribution.

3. Comparison of molecular weight distributions obtained in continuous and batch polymerisations

The number average degree of polymerisation $\bar{P}_n$ is given by Eqn. (36); the weight average $\bar{P}_w$, by Eqn. (37); and the nonuniformity U, by Eqn. 38

$$\bar{P}_n = \sum_{k=1}^{\infty} k \cdot Y_k \quad (36) \qquad \bar{P}_w = \frac{\sum_{k=1}^{\infty} k^2 \cdot Y_k}{\sum_{k=1}^{\infty} k \cdot Y_k} \quad (37) \qquad U = \frac{\bar{P}_w}{\bar{P}_n} \quad (38)$$

Eqns. (39) to (41) apply to polymers produced by batch techniques 10)

$$\bar{P}_n = \frac{1}{1-p} \tag{39}$$

$$\bar{P}_w = \frac{1+p}{1-p} \tag{40}$$

$$U = 1+p \tag{41}$$

The magnitudes $\bar{P}_n$, $\bar{P}_w$ and U for polymers produced in continuous reactions are calculated numerically with the aid of the distribution function, viz., Eqn. (35).

The results for reactions in continuous stirred tank reactors are plotted in Fig. 1.

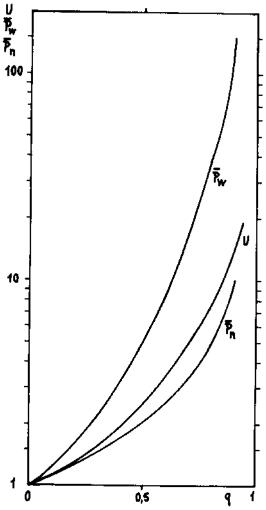

Fig. 1. Degree of polymerisation and nonuniformity for polyrecombinations in continuous stirred tank reactors

Appendix   Derivation of Eqn. (7)

The probability w_i that a molecule with i monomer units will be formed is equal to the ratio of the number of all favourable combinations to the number of all possible combinations z_m. The latter is given by

$$z_m = \binom{2a}{2} = a(2a-1) \tag{42}$$

The number of linkages that can possibly be formed by radicals of length i with similar radicals is given by Eqn. (43); and with radicals of length j, by Eqn. (44).

$$z_{ii} = \frac{1}{2} N_i (N_i - 1) \tag{43}$$

$$z_{ij} = N_i . N_j \tag{44}$$

The factor 1/2 has been introduced in Eqn. (43) in order to avoid a double count.

If n_i is the number of radicals with i monomeric units, the individual probabilities are given by

$$\omega_2 = \frac{1}{a(2a-1)} \left[\frac{1}{2} n_1 (n_1 - 1)\right] \quad \omega_i = \frac{1}{a(2a-1)} \left(\sum_{j=1}^{\frac{i-1}{2}} n_j \cdot n_{(i-j)}\right); \; i = 2k+1, \; k = 1,2,\ldots$$

$$\omega_i = \frac{1}{a(2a-1)} \left[\left(\sum_{j=1}^{\frac{i}{2}-1} n_i \, n_{(i-j)}\right) + \frac{1}{2} n_{\frac{i}{2}} (n_{\frac{i}{2}} - 1)\right]; \; i = 2k, \; k = 2,3,\ldots \tag{45}$$

The following[✦] always applies for the numbers of individual radicals n_i.

$$n_i \gg 1 \tag{46}$$

The inequalities (3), (4) and (46) allow Eqn. (45) to be simplified to give

$$\omega_2 = \frac{1}{2a^2}\left(\frac{1}{2}n_1^2\right) \qquad \omega_i = \frac{1}{2a^2}\left(\sum_{j=1}^{\frac{i-1}{2}} n_j\, n_{(i-j)}\right);\ i=2k+1,\ k=1,2,\ldots \tag{47}$$

$$\omega_i = \frac{1}{2a^2}\left[\left(\sum_{j=1}^{\frac{i}{2}-1} n_j\, n_{(i-j)}\right) + \frac{1}{2}n_{\frac{i}{2}}\left(n_{\frac{i}{2}}-1\right)\right];\ i=2k,\ k=2,4,\ldots$$

The number of radicals n_i can be obtained from the molar fraction γ_i and the total number of radicals 2a by applying Eqn. (2), i.e.,

$$n_i = 2a \cdot \gamma_i = 2a \cdot \frac{N_{iv}}{N_v} \tag{48}$$

Equation (7) follows from Eqns. (47) and (48).

+ Theoretically the inequality (46) can always be satisfied, the only condition is that 2a and thus $2N_v$ must be sufficiently large.

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Received October 18, 1980