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Random Degradation of Chain Polymers Accompanied by Partial Dissolution of the Degraded Material*

D. MEJZLER, *Institute for Fibres and Forest Products Research, State of Israel, Ministry of Commerce and Industry, Jerusalem, Israel*

Synopsis

Some processes of random degradation of chain polymers in suspension are accompanied by the dissolution of the part of the degraded material having the shortest chain lengths. The molecular weight determinations are then usually made not on the total degraded material, but only on its undissolved part. It is shown that if any two of the following three experimentally determinable values are known: (1) weight fraction of undissolved degraded material, (2) number-average DP of undissolved degraded material, (3) weight-average DP of undissolved degraded material, the following parameters may be calculated: (1) the third experimental value; (2) the extent of degradation of the total degraded material and, therefore, the true values of the number-average and weight-average DP of the total material; (3) the maximum chain length of the degraded material in solution; (4) the number-average and the weight-average DP of the dissolved part of the degraded material; (5) the respective number fractions of the dissolved and undissolved chains in the degraded material. The calculations are carried out for the two conventional models of random degradation, that of Kuhn and that of Montroll-Simha. For the former model, simple approximate formulas are also given, which yield solutions with a satisfactory accuracy.

Introduction

Cases are known in polymer chemistry, where random degradation of a chain polymer is accompanied by partial dissolution of the degraded material, fragments of the lowest molecular weight passing into solution. Oxidative and acid degradation of cellulose, starch, and starch components may serve as an example.

In such cases, as a rule, certain parameters, including the distribution of molecular weights, can be determined on the undissolved part of the degraded material, such determinations cannot be carried out on the dissolved fractions, owing to great experimental difficulties.

It is the purpose of this paper to show that, as far as chain polymers are concerned, full information on the state of the dissolved fraction may be obtained from the experimental data available for the undissolved part alone; the assumptions on which the demonstration is based have been accepted in polymer chemistry for a long time.

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The fundamental assumption is that the dissolved fraction consists of the shortest chains present. In other words, we shall assume that if the dissolved part of the material contains molecules of chain length n, the undissolved part will not contain molecules of a chain length shorter than n.

The degraded chain polymer may be regarded as a system $\{n_k\}$ composed of n_1 monomeric, n_2 dimeric, . . ., n_k k-meric, . . . molecules.

Let n be the degree of polymerization (DP) of the longest molecules still in solution. If p is the weight fraction of the undissolved material (calculated on the total amount of material), then

$$p = \left(\sum_{k=n+1}^{\infty} kn_k \right) \Big/ \sum_{k=1}^{\infty} kn_k \tag{1}$$

and the weight fraction of the dissolved material q will be

$$q = 1 - p = \left(\sum_{k=1}^{n} kn_k \right) \Big/ \sum_{k=1}^{\infty} kn_k \tag{2}$$

We also assume a perfectly random degradation from the initial DP distribution $\{n_k^0\}$ to the final distribution $\{n_k\}$. The latter is then known to be fully determined by the initial state $\{n_k^0\}$ and by the extent of degradation α defined by

$$\alpha = \frac{\text{number of bonds broken}}{\text{total number of bonds}}$$

or

$$\alpha = 1 - \left[\sum_{k=1}^{\infty} (k-1)n_k \right] \Big/ \sum_{k=1}^{\infty} (k-1)n_k^0 \tag{3}$$

We shall discuss here two mathematical models of random degradation: (*1*) that of W. Kuhn,[1] where the starting, undegraded, material consists of one single infinitely long molecule; (*2*) that of Montroll and Simha,[2] where the undegraded starting material consists of an infinitely large number of chains, all having the same DP equal to N_0 (For a discussion of these models see also Mejzler et al.[3])

The extent of degradation α may be calculated from the experimentally determined average DP of the degraded product. This may be either the number-average DP N, defined as

$$N = \left(\sum_{k=1}^{\infty} kn_k \right) \Big/ \sum_{k=1}^{\infty} n_k \tag{4}$$

or the weight-average DP N_w defined as

$$N_w = \left(\sum_{k=1}^{\infty} k^2 n_k \right) \Big/ \sum_{k=1}^{\infty} kn_k \tag{5}$$

(Other average DP's, such as Z-average or viscosity-average DP, will not be considered here.)

When a part of the degraded material has passed into solution, the number-average and/or weight-average DP is determined on the undissolved part only and not on the entire material. That is, the experimentally determined values M and M_w are

$$M = \left(\sum_{k=n+1}^{\infty} kn_k \right) \Big/ \sum_{k=n+1}^{\infty} n_k$$

and

$$M_w = \left(\sum_{k=n+1}^{\infty} k^2 n_k \right) \Big/ \sum_{k=n+1}^{\infty} kn_k \tag{6}$$

Obviously, if the proportion of the material dissolved is considerable, M and M_w will differ from N and N_w, respectively. In that case, if M and M_u are used in the formulas commonly employed instead of N and N_w, considerable errors are to be expected.

The values of p, M, and M_w may be determined by experiment. Our purpose is to show that if any two of these three parameters are known, the following may be calculated: (a) the third of these three parameters; (b) the extent of degradation α, and hence the average DP's N and N_w; (c) the degree of polymerization n of the longest molecules still in solution; (d) the number-average DP, m, and the weight-average DP, m_w, of the dissolved material. These magnitudes are defined by the formulas

$$m = \left(\sum_{k=1}^{n} kn_k \right) \Big/ \sum_{k=1}^{n} n_k$$

and

$$m_w = \left(\sum_{k=1}^{n} k^2 n_k \right) \Big/ \sum_{k=1}^{n} kn_k \tag{7}$$

(e) the number fraction of the undissolved chains A and the number fraction of the dissolved chains a, defined as

$$A = \left(\sum_{k=n+1}^{\infty} n_k \right) \Big/ \sum_{k=1}^{\infty} n_k$$

and

$$a = 1 - A = \left(\sum_{k=1}^{n} n_k \right) \Big/ \sum_{k=1}^{n} n_k \tag{8}$$

It is easily seen that the parameters determined above are connected by following relations:

$$M = pN/A \tag{9}$$

$$m = qN/a \tag{10}$$

$$pM_w + qm_w = N_w \tag{11}$$

In the considerations which follow, we shall use the following well known elementary identities, which are valid for any real value of x and any positive integer n:

$$(1 - x)\sum_{k=1}^{\infty} x^{k-1} = 1 - x^n \tag{12}$$

$$(1 - x)^2\sum_{k=1}^{n} kx^{k-1} = 1 - (n + 1)x^n + nx^{n+1} \tag{13}$$

$$(1 - x)^3\sum_{k=1}^{n} k^2x^{k-1} = 1 + x - (n + 1)^2x^n + (2n^2 + 2n - 1)x^{n+1} - n^2x^{n+2} \tag{14}$$

$$(1 - x)^4\sum_{k=1}^{n} k^3x^{k-1} = 1 + 4x + x^2 - (n + 1)^3x^n + (3n^2 + 6n^2 - 4)x^{n+1} - (3n^3 + 3n^2 - 3n + 1)x^{n+2} + n^3x^{n+3} \tag{15}$$

Kuhn's Model

According to Kuhn's model, the following equalities are valid:[1,3]

$$n_k \Big/ \sum_{k=1}^{\infty} n_k = \alpha(1 - \alpha)^{k-1} \tag{16}$$

$$kn_k \Big/ \sum_{k=1}^{\infty} kn_k = k\alpha^2(1 - \alpha)^{k-1} \tag{17}$$

It is also known[4] that

$$N = 1/\alpha \tag{18}$$

$$N_w = (2 - \alpha)/\alpha = 2N - 1 \tag{19}$$

We shall immediately see that p, q, M, M_w, n, m_w, A, and a may be expressed as functions of α and n only. According to eqs. (2) and (17),

$$q = \alpha^2\sum_{k=1}^{n} k(1 - \alpha)^{k-1} \tag{20}$$

Using the identity (13) and substituting $x = 1 - \alpha$ we obtain

$$q = 1 - (1 - \alpha)^n(1 + n\alpha) \tag{21}$$

hence

$$p = (1 - \alpha)^n(1 + n\alpha) \tag{22}$$

In view of eqs. (8) and (16), we get

$$a = \alpha\sum_{k=1}^{\infty} (1 - \alpha)^{k-1} \tag{23}$$

Hence, in view of the identity (12)

$$a = 1 - (1 - \alpha)^n \tag{24}$$

and therefore

$$A = (1 - \alpha)^n \tag{25}$$

In view of the relations (9) and (10), the parameters M and m may be expressed by using eqs. (18) and (21)–(25). In particular, we obtain

$$M = 1/\alpha + n \tag{26}$$

In view of eq. (2) the parameter m_w defined as in eq. (7), may be written as

$$m_w = (1/q) \left(\sum_{k=1}^{n} k^2 n_k \right) \Big/ \sum_{k=1}^{\infty} k n_k \tag{27}$$

From eq. (17) we get

$$m_w = (\alpha^2/q) \sum_{k=1}^{\infty} k^2 (1 - \alpha)^{k-1} \tag{28}$$

Hence, using the identity (14) and equality (21) we obtain

$$m_w = \frac{2 - \alpha - (1 - \alpha)^n [(1 + \alpha n)^2 + 1 - \alpha]}{\alpha [1 - (1 - \alpha)^n (1 + \alpha n)]} \tag{29}$$

and therefore, from eqs. (11), (19), (21) and (22) we get

$$M_w = \frac{(1 + \alpha n)^2 + 1 - \alpha}{\alpha (1 + \alpha n)} \tag{30}$$

If any two of the three parameters p, M, and M_w are known, two suitable equations from eqs. (22), (26), and (30) may be chosen, which, on being simultaneously solved, will yield the values of α and n. The latter values will permit us to find the remaining parameters.

We may distinguish between three cases, depending on which two parameters have been experimentally determined.

Case I. Let us first consider the mathematically simplest case, when the values of M and M_w are known. By eliminating n from eqs. (26) and (30), we obtain the following equation for α

$$\alpha^2 (M_w M - M^2) + \alpha - 1 = 0 \tag{31}$$

Hence, since $M_w > M$ we get

$$\alpha = (\sqrt{1 + 4M(M_w - M)} - 1)/2M(M_w - M) \tag{32}$$

and, in view of eq. (26), we get

$$n = M - 1/\alpha \tag{33}$$

It follows from the definition of M and N that $M > N$. Hence, in view of eq. (18),

$$\alpha > 1/M \tag{34}$$

Since M and M_w are large numbers, we may obtain from eq. (32) an approximate expression for α:

$$\alpha \doteq 1/\sqrt{M(M_w - M)} \tag{35}$$

The value of p may now be calculated from eq. (22) by using eqs. (32) and (33). Since p is easy to determine experimentally, the agreement between the experimental and calculated value of p may be used to check the validity of the fundamental assumptions.

Case II. Let us now consider the second case, when the values of p and M are determined experimentally. Let us take eqs. (22) and (26). By eliminating n we obtain for α the equation

$$p = \alpha M(1 - \alpha)^{M - 1/\alpha} \tag{36}$$

By applying suitable approximations, the value of α may be calculated with any desired accuracy, and n may then be calculated by using eq. (33).

However, eq. (36) is quite complex, since α cannot be explicitly expressed. We shall now show that in view of the fact that the value of α is in practice always a small number, eq. (36) may be replaced by another equation, which is only approximate but which is much simpler. It is known that

$$\lim_{\alpha \to 0} \quad (1 - \alpha)^{1/\alpha} = e^{-1} \tag{37}$$

where e is the base of natural logarithms. Equation (36) may be written in the form

$$p = \alpha M[(1 - \alpha)^{1/\alpha}]^{M\alpha - 1} \tag{38}$$

Using eq. (37), if α is sufficiently small, we obtain the approximate equation

$$p = \bar{\alpha} M \exp\{1 - \bar{\alpha} M\} \tag{39}$$

Let us denote $\bar{\alpha} M = t$. Equation (39) may then be written as

$$p = t \exp\{1 - t\} \tag{40}$$

This equation for an unknown t is much simpler than eq. (36) for an unknown α. From the known value of p we may calculate t, and therefore α by

$$\alpha \doteq \bar{\alpha} = t/M \tag{41}$$

Owing to the fact that eq. (40) contains p as the single parameter, a table such as Table I may be constructed, giving the values of t as function of p.

Example 1. Let $p = 0.75$, $M = 100$; eq. (36) now becomes

$$0.75 = 100\alpha(1 - \alpha)^{100 - 1/\alpha} \tag{42}$$

A rather elaborate calculation gives the solution $\alpha = 0.01942$. As against that, we obtain from Table I that $t = 1.961$ for $p = 0.075$. Hence we obtain the approximate solution $\bar{\alpha} = 0.01961$. We shall prove in what follows that $\bar{\alpha}$ is always greater than α. The relative error

$$\delta = (\bar{\alpha} - \alpha)/\alpha = \Delta\alpha/\alpha \tag{43}$$

TABLE I

p	t
1.000	1.000
0.999	1.045
0.998	1.065
0.997	1.080
0.996	1.092
0.995	1.103
0.990	1.149
0.980	1.215
0.970	1.268
0.960	1.314
0.950	1.355
0.940	1.394
0.930	1.431
0.920	1.466
0.910	1.499
0.900	1.532
0.890	1.563
0.880	1.594
0.870	1.624
0.860	1.654
0.850	1.683
0.840	1.712
0.830	1.741
0.820	1.769
0.810	1.797
0.800	1.824
0.790	1.852
0.780	1.879
0.770	1.907
0.760	1.934
0.750	1.961
0.700	2.097
0.650	2.235

caused by using eq. (39) instead of the exact eq. [eq. (36)] is $\delta = 0.00019/0.01942 < 1\%$. A rigorous proof is given in the Appendix that this relative error is bounded from above by $\bar{\alpha}/2$ and does not exceed 1%, when the experimental values of the parameters p and M satisfy the inequalities $p \geq 0.75$, $M \geq 100$.

Case III. Let us now consider the last case, when p and M_w are the values found experimentally. We use eqs. (22) and (30). Equation (30) may be written as

$$\alpha^2 n^2 + \alpha n(2 - \alpha M_w) + (2 - \alpha - \alpha M_w) = 0 \tag{44}$$

it is obvious that $M_w > N_w$; hence, in view of eq. (19),

$$M_w > (2 - \alpha)/\alpha$$

We therefore obtain from eq. (44)

$$n = (\alpha M_w - 2 + \sqrt{\alpha^2 M^2{}_w - 4 + 4\alpha})/2\alpha \tag{45}$$

If this expression is substituted in eq. (22), an equation is obtained with α as the sole unknown, which is, however, too complex to be directly used. We shall show that the method previously employed is also applicable to the present case.

In view of eq. (26), eq. (30) may be written as

$$M_w = [(M\alpha)^2 + 1 - \alpha]/\alpha(M\alpha) \tag{46}$$

But, as has been seen, the product $(M\alpha)$ is determined with a good approximation solely by the value of p. This means that the equality (41) is valid to a good approximation. Therefore, the following equation is also valid to a good approximation

$$M_w \doteq (t^2 + 1 - \alpha)/(\alpha t) \tag{47}$$

hence

$$\alpha \doteq (t^2 + 1)/(tM_w + 1) \tag{48}$$

If the value of α is known, n may be calculated by

$$n \doteq (t - 1)\alpha \tag{49}$$

This formula follows from eqs. (33) and (41).

Example 2. Let $p = 0.87$, $M_w = 110$. We obtain from Table I that $t = 1.624$ for $p = 0.87$. Hence, by eq. (48), we obtain the approximate solution $\alpha = 0.0202$ and, by eq. (49), $n = 30.9$. The remaining parameters can now be calculated from the equations developed above.

We shall prove in the Appendix that in the present case, too, the relative error in the value of α, caused by using the approximate equation, eq. (48), does not exceed 1% when the values of p and M_w satisfy the inequalities $p \geq 0.75$, $M_w \geq 100$.

The Model of Montroll and Simha

For the Montroll and Simha model the following equalities are valid:[2,3]

$$\frac{n_k}{\sum_{k=1}^{N_0} n_k} = \begin{cases} \dfrac{\alpha(1-\alpha)^{k-1}}{1+\alpha(N_0-1)}\,[2+\alpha(N_0-1)-\alpha k] & \text{if } 1 \le k \le N_0 - 1 \\ \dfrac{(1-\alpha)^{N_0-1}}{1+\alpha(N_0-1)} & \text{if } k = N_0 \end{cases} \tag{50}$$

$$\frac{k n_k}{\sum_{k=1}^{N_0} k n_k} = \begin{cases} \dfrac{k}{N_0}\,\alpha(1-\alpha)^{k-1}[1+\alpha(N_0-1)-\alpha k] & \text{if } 1 \le k \le N_0 - 1 \\ (1-\alpha)^{N_0-1} & \text{if } k = N_0 \end{cases} \tag{51}$$

where N_0 denotes the initial chain length, which is considered to be known (e.g., in cellulose).

It is known that[2,5]

$$N = N_0/[1+\alpha(N_0-1)] \tag{52}$$

$$N_w = \frac{\alpha^2 N_0 + 2(1-\alpha)[(1-\alpha)^{N_0} + \alpha N_0 - 1]}{\alpha^2 N_0} \tag{53}$$

Using the formulas (50) and (51) and the identities (12)–(15), all the parameters defined in the introduction may be expressed in terms of α and n only, as has been done for Kuhn's model. According to eqs. (2) and (51)

$$q = \frac{\alpha}{N_0}\,[2+\alpha(N_0-1)] \sum_{k=1}^{n} k(1-\alpha)^{k-1} - \frac{\alpha^2}{N_0} \sum_{k=1}^{n} k^2(1-\alpha)^{k-1} \tag{54}$$

and hence, by using eqs. (13) and (14),

$$q = 1 - (1-\alpha)^n[1+\alpha n - \alpha n(n+1)/N_0] \tag{55}$$

also

$$p = (1-\alpha)^n[1+\alpha n - \alpha n(n+1)/N_0] \tag{56}$$

According to eqs. (8) and (50)

$$a = \frac{\alpha[2+\alpha(N_0-1)]}{1+\alpha(N_0-1)} \sum_{k=1}^{n} (1-\alpha)^{k-1} - \frac{\alpha^2}{1+\alpha(N_0-1)} \sum_{k=1}^{n} k(1-\alpha)^{k-1} \tag{57}$$

and hence, by using eqs. (12) and (13),

$$a = 1 - (1-\alpha)^n[1 - \alpha n/(\alpha N_0 + 1 - \alpha)] \tag{58}$$

also

$$A = (1-\alpha)^n[1 - \alpha n/(\alpha N_0 + 1 - \alpha)] \tag{59}$$

Let α be the root of the exact eq. (36). According to the above inequality

$$M\alpha \exp \{-M\alpha + 1\} = p + \Delta p \tag{65}$$

where $\Delta p > 0$ and

$$1 < 1 + \Delta p/p < [1/(1 - \alpha)]^{M\alpha - 1} \tag{66}$$

The function $f(t) = t \exp \{1 - t\}$ is a monotonic decreasing function in the interval $(1, \infty)$, since its derivative is negative for $t > 1$. It follows that if $\bar{\alpha}$ is the root of the approximate eq. (39), $\bar{\alpha}$ is always greater than α. Let us denote $\bar{\alpha} = \alpha + \Delta\alpha$; then $\Delta\alpha > 0$ and

$$p = M(\alpha + \Delta\alpha) \exp \{1 - M\alpha - M\Delta\alpha\} \tag{67}$$

In view of eq. (65) we obtain

$$\frac{\exp \{M\Delta\alpha\}}{1 + \Delta\alpha/\alpha} = 1 + \Delta p/p \tag{68}$$

Hence, in view of inequality eq. (66) and of the inequality

$$\exp \{M\Delta\alpha\} > 1 + M\Delta\alpha \tag{69}$$

we obtain

$$\delta(M\alpha - E) < E - 1 \tag{70}$$

where δ is the relative error [eq. (43)] and E denotes the expression

$$E = [1/(1 - \alpha)]^{M\alpha - 1} = [1 + \alpha/(1 - \alpha)]^{M\alpha - 1} \tag{71}$$

Let us now estimate the value of E. To do this we have to lay down certain limitations as to the intervals within which p and M may vary. Let us first assume that

$$0.75 \leq p < 1 \tag{72}$$

This range is sufficiently wide for most practical purposes. It has been proved that $\bar{\alpha} > \alpha$ and hence also $\alpha M < \bar{\alpha} M = t$. But, as may be seen from Table I,

$$1 < t \leq 1.961 < 2 \tag{73}$$

in the entire interval (72). Therefore, in view of the inequality (34), if p satisfies (72), then

$$1 < M\alpha < 2 \tag{74}$$

whatever the value of M. Let us now assume that

$$M > 4 \tag{75}$$

then

$$0 < \alpha < 0.5$$

and

$$0 < \alpha/(1 - \alpha) < 1 \tag{76}$$

It is therefore legitimate to develop the expression (71) in a power series of $\alpha/(1 - \alpha)$:

$$E - 1 = \left[\frac{(M\alpha - 1)}{1}\right]\left(\frac{\alpha}{1 - \alpha}\right) + \left[\frac{(M\alpha - 1)(M\alpha - 2)}{1 \cdot 2}\right]\left(\frac{\alpha}{1 - \alpha}\right)^2 + \left[\frac{(M\alpha - 1)(M\alpha - 2)(M\alpha - 3)}{1 \cdot 2 \cdot 3}\right]\left(\frac{\alpha}{1 - \alpha}\right)^3 + \ldots \tag{77}$$

By the inequality (74) the following inequality is valid for any positive integer n:

$$\left|(M\alpha - n)/n\right| < 1 \tag{78}$$

Because of (74) and (76), it follows that this series is an alternating series, the general term of which monotonically tends to zero. It follows that $(E - 1)$ is smaller than the sum of the three terms written above. These considerations bring us to the following estimate:

$$E < 1 + [\alpha(M\alpha - 1)]/[2(1 - \alpha)] \tag{79}$$

Hence, in view of inequality (76), *a fortiori* $E < M\alpha$. We may now deduce from the expression (70) that $\delta < (E - 1)/(M\alpha - E)$ and hence, by relation (79)

$$\delta < \alpha/(2 - 3\alpha) \tag{80}$$

since $\bar{\alpha} > \alpha$, also $\delta < \bar{\alpha}/(2 - 3\bar{\alpha})$. Since $2 \gg 3\bar{\alpha}$, we may deduce that the value of the relative error δ is bounded from above by $\bar{\alpha}/2$. This is true if the limitations (72) and (75) are accepted. But, in view of eqs. (41) and (73), $\bar{\alpha}/2 = t/(2M) < 1/M$. It follows that for any p and M which satisfy the conditions $0.75 \leq p < 1$, $M \geq 100$, the value of δ will not exceed 1%.

It follows from the numerical example that this estimate cannot be further improved to any significant extent.

Let us now consider the case where α is determined from the experimental values of p and M_w.

Denote

$$\tilde{\alpha} = (t^2 + 1)/(tM_w + 1) \tag{81}$$

Let α be the root of the accurate equations. Then, in view of eq. (46),

$$\alpha = [(M\alpha)^2 + 1]/[(M\alpha)M_w + 1] \tag{82}$$

Hence, since $M\alpha < t$, $\tilde{\alpha} > \alpha$. Let

$$\delta_w = (\tilde{\alpha} - \alpha)/\alpha \tag{83}$$

It may be deduced from eqs. (81) and (82) that

$$\delta_w = \delta \frac{(M\alpha)^2}{(M\alpha)^2 + 1}\left\{1 - \frac{M_w - t}{tM_w + 1}\right\} \tag{84}$$

where δ is determined by eq. (43).

However, if the condition (72) is satisfied, the relation (74) is valid and hence $(M\alpha)^2/[(M\alpha)^2 + 1] < 0.8$ and, in view of eq. (84), $\delta_w < 0.8\delta$.

Because of relation (80) and since $\tilde{\alpha} > \alpha$,

$$\delta_w < (0.8\tilde{\alpha})/(2 - 3\tilde{\alpha}) \tag{85}$$

If, in addition to (72), we also require $M_w \geq 100$, then it follows from eq. (81) that $\tilde{\alpha} < 0.0246$ and $\tilde{\alpha}/(2 - 3\tilde{\alpha}) < 0.0125$. From relation (85) we may deduce that for any p and M_w which satisfy the conditions $0.75 \leq p < 1$, $M_w \geq 100$, the relative error δ_w does not exceed 1%.

It may be pointed out in conclusion that the error introduced in the calculated values of the other parameters through the use of $\bar{\alpha}$ and/or $\tilde{\alpha}$ will also be negligible, except for the value of m_w: it may be seen from eq. (11) that a small error in the value of α may cause a considerable error in the value of m_w, if q is very small.

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References

1. Kuhn, W., *Ber.*, **63,** 1503 (1930).
2. Montroll, E. W., and R. Simha, *J. Chem. Phys.*, **8,** 721 (1940).
3. Mejzler, D., J. Schmorak, and M. Lewin, *J. Polymer Sci.*, **46,** 289 (1960).
4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 325.
5. Grassie, N., *Chemistry of High Polymer Degradation Processes*, Butterworths, London, 1956, p. 128.
6. Pólya, G., und G. Szegö, *Aufgaben und Lehrsätze aus der Analysis*, Part I, Springer, Berlin, 1925, p. 31.

Résumé

Certains processus de dégradation statistique de chaînes polymériques en suspension sont accompagnés par une dissolution de la partie du polymère possédant la chaîne la plus courte. Alors on préfère ne plus faire de déterminations de poids moléculaires sur le total du matériel dégradé, mais seulement sur la partie restée indissoute. On a trouvé que, si on connaît deux des valeurs expérimentales suivantes: (1) la fraction en poids du matériel dégradé *non-dissous* (2) poids moléculaire moyen en poids du matériel dégradé *non-dissous*, (3) poids moléculaire en nombre du matériel dégradé *non-dissous*, on peut dès lors calculer: (1) la troisème valeur expérimentale, (2) le degré de dégradation du matériel dégradé global, et par la suite les valeurs réelles des poids moléculaires moyens en nombre et en poids du matériel total, (3) la longueur maximum de la chaîne du matériel dégradé en solution, (4) le poids moléculaire moyen en nombre et en poids de la partie dissoute du matériel dégradé, (5) les fractions respectives en nombres des chaînes dissoutes et non-dissoutes, dans le matériel dégradé. On a fait des calculs sur les deux modèles conventionels de dégradation statistique, c.à.d. celui de Kuhn et celui de Montroll-Simha. Pour le premier modèle on a trouvé des formules approximatives qui donnent des résultats avec que précision suffisante.

Zusammenfassung

Bei gewissen statistischen Abbauprozessen an Kettenpolymeren in Suspension geht ein Teil des abgebauten Materials, nämlich jener mit der geringsten Kettenlänge, in Lösung. Die Molekulargewichtsbestimmungen werden dann gewöhnlich nicht am gesamten abgebauten Material, sondern nur an dessen ungelösten Anteil ausgeführt. Es wird gezeigt, dass bei Kenntnis von zweinen der folgenden drei experimentell bestimmbaren Grössen, nämlich: (1) Gewichtsbruch des ungelösten abgebauten Materials, (2) Zahlenmittel des Polymerisationsgrades (DP) des ungelösten abgebauten Materials und (3) Gewichtsmittel des Polymerisationsgrades (DP) des ungelösten abgebauten Materials, folgende Grössen berechnet werden können: (1) Die dritte experimentell bestimmbare Grösse; (2) das Ausmass des Abbaues des gesamten abgebauten Materials und somit die wahren Werte des Zahlen- und des Gewichtsmittels von DP des gesamten Materials; (3) die maximale Kettenlänge des gelösten abgebauten Materials; (4) Zahlen- und Gewichtsmittel von DP des gelösten Anteils des abgebauten Materials; (5) Die Molenbrüche der gelösten bzw. ungelösten Ketten im abgebauten Material.—Die Berechnungen werden für die beiden üblichen Modelle des statistischen Abbaues, nämlich das von Kuhn und das von Montroll-Simha, ausgeführt. Für das erstere werden auch einfache Näherungsformeln angegeben, die Resultate von befriedigender Genauigkeit liefern.

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