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(17) The saddle point on the potential energy surface corresponds to the configuration $\mathbf{r}^* = (\mathbf{r}_1^* \ldots \mathbf{r}_N^*)$ in which all the bond lengths, bond angles, and nontransforming torsional angles are at potential minima and the single transforming rotational angle is at the top of the barrier between the trans and gauche states. In the vicinity of $\mathbf{r}^*$ the potential $V(\mathbf{r})$, defined relative to the conformation in which all the bond lengths, bond angles, and torsional angles are at potential minima, may be expanded about $\mathbf{r}^*$ to give

$$V(\mathbf{r}) = E^* + \tfrac{1}{2}\sum_{i,j=1}^{3N} W_{ij}(x_i - x_i^*)(x_j - x_j^*)$$

Note that since all the bond lengths, bond angles, and torsional angles associated with $\mathbf{r}^*$ are at potential extrema, the gradient of $V(\mathbf{r})$ evaluated at $\mathbf{r}^*$ must vanish. The potential matrix $\boldsymbol{W}$ has a single negative eigenvalue λ, whose eigenvector ρ^* points in the direction of the path of steepest descents. $\boldsymbol{W}$ is diagonalized numerically to give both λ and ρ^*.
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Degradation of Chain Molecules. 1. Exact Solution of the Kinetic Equations†

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ABSTRACT: A general solution of the rate equations representing the degradation of chain molecules is given. The treatment can be applied to any set of equations and to any initial distribution. Model calculations are performed for random scission, for Gaussian probability of scission, and for scission exclusively at the midpoint of the chain. The starting molecular weight distribution is of the Schulz type, differing in the nonuniformity. The results clearly demonstrate that, by fitting the model parameters to experimental distributions, the full kinetic information concerning the degradation process is obtained.

Since the days of Staudinger,[1] it has been known that polymer chains can break due to high shear mechanical action. The cleavage of bonds by chemical attack, e.g., by hydrolysis, is also a well-investigated phenomenon.[2,3] A third possibility of degradation is by radiation-induced chain scission.[4,5]

The first theoretical treatments of these phenomena were given by Kuhn[6] and by Montroll and Simha,[7] who elaborated a statistical method to solve the problem of random scission. In this model it is assumed that the accessibility to cleavage is independent of the position of the bond in the chain. Furthermore, the starting material is taken to be uniform. Starting from Saito's integrodifferential equation,[8] Kotliar[9] and Inokuti and Dole[10] have derived expressions for the average molecular weights resulting from random scission. The starting molecular weight distribution is of the Schulz–Zimm type.[11] The problem of calculation of the entire molecular weight distribution (MWD) of the degraded polymers instead of different molecular weight averages only was studied by Kotliar[12] by means of a Monte Carlo approach. In order to solve this problem analytically, Jellinek and White elaborated a kinetic scheme,[13] which was refined by Mostafa[14] applying matrix algebra. Glynn, van der Hoff, and Reilly developed a numerical scheme to fit different theoretical breakage models, including nonrandom processes to experimental molecular weight distributions.[15] A set of equations describing the degradation process was given by Basedow, Ebert, and Ederer[3] and solved exactly for the case of random scission.

Over the past few years gel permeation chromatography has become a convenient and reliable method and it is now possible to measure not only the different molecular weight averages (M_n, M_w, M_z) but also the MWD of the degraded samples with sufficient accuracy in short time. Obviously knowledge of the change in the MWD throughout the degradation gives more insight into the mechanisms involved than that of the molecular weight averages as functions of time.

The general aim of a kinetic study is to obtain the individual rate constants k_i for the degradation of a species with degree of polymerization i and the individual rate constants $k_{i,j}$ for the scission of a chain of length i into two fragments with j and $i - j$ subunits, respectively. Clearly k_i is given by the sum over all $k_{i,j}$ of a molecule with i subunits

$$k_i = \sum_{j=1}^{i-1} k_{i,j} \tag{1}$$

There is one simple case where k_i can be obtained directly from the MWD, namely, if the molecules are essentially broken in the middle of the chain. Assuming this model, the reaction rates for the highest molecular weights present in the original sample can directly be determined by their disappearance in the degraded samples.

In all cases studied in this way so far,[16,17] the order of the reaction (dependence of the rate on the concentration of the i-mers) is 1. The disadvantage of this method lies in the fact that only a small part of the MWD can be treated in such a way. The obtainable insight into the mechanism of the degradation is therefore rather limited and the results may become quite uncertain. Consequently, one should apply a method which utilizes all information contained in the MWD and not only that of its

† Dedicated to Professor Dr. G. V. Schulz in honor of his 75th birthday.
‡ Part of the thesis of M. Ballauff.

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high molecular part. In the present paper it is demonstrated that an analytical solution can be obtained for the kinetic model given by Basedow, Ebert, and Ederer[3] for each case of interest. It must be stressed that the solution is achieved completely avoiding numerical steps. In a following paper the methods described here will be applied to shear degradation experiments.

Procedure

We start with eq 17 of ref 3

$$dn_i/dt = -(\sum_{j=1}^{i-1} k_{i,j})n_i + (k_{i+1,1} + k_{i+1,i})n_{i+1} + \ldots + (k_{r,i} + k_{r,r-i})n_r \quad (2)$$

where dn_i/dt is the reaction rate of the species i (containing i monomer units), $k_{i,j}$ is the individual rate constant described above, n_i is the number of molecules of species i, and r is the highest degree of polymerization under consideration. Defining the vectors

$$d\vec{n}/dt = \begin{vmatrix} dn_1/dt \\ \cdot \\ dn_i/dt \\ \cdot \\ dn_r/dt \end{vmatrix} \quad (3)$$

$$\vec{n} = \begin{vmatrix} n_1 \\ \cdot \\ n_i \\ \cdot \\ n_r \end{vmatrix} \quad (4)$$

we rewrite eq 2 as

$$d\vec{n}/dt = \mathbf{A}\vec{n} \quad (5)$$

with $\mathbf{A}$ the matrix of kinetic coefficients

$$\mathbf{A} = \begin{vmatrix} 0 & k_{2,1} + k_{2,1} & k_{3,1} + k_{3,2} & \cdots & k_{r,1} + k_{r,r-1} \\ 0 & -k_{2,1} & k_{3,2} + k_{3,1} & \cdots & k_{r,2} + k_{r,r-2} \\ & & -\sum_{j=1}^{2} k_{3,j} & \cdots & k_{r,3} + k_{r,r-3} \\ & & & & \cdot \\ & & & & -\sum_{j=1}^{r-1} k_{r,j} \end{vmatrix} \quad (6)$$

(see eq 19 in ref 3). Note that $\mathbf{A}$ has a triangular form due to the fact that there is no recombination of fragments to larger molecules. The solution of eq 5 can be achieved by solving the eigenvalue problem of matrix $\mathbf{A}$. For this purpose we introduce a new vector $\vec{z}$ by linear transformation of $\vec{n}$

$$\vec{n}(t) = \mathbf{C}\vec{z} \quad (7)$$

with

$$z_i'(t) = \lambda_i z_i(t) \quad (8)$$

for all components of $\vec{z}$. Therefore it follows that

$$z_i(t) = \alpha_i \exp(\lambda_i t) \quad (8a)$$

Combining eq 6–8 yields

$$\mathbf{AC} = \mathbf{C}\tilde{\lambda} \quad (9)$$

with $\tilde{\lambda}$ the diagonal matrix of eigenvalues. There is a simple physical meaning of eq 7–9: The eigenvalues λ_i are the pure degradation rate constants of molecules with i subunits. Insertion of eq 8a into eq 7 gives the net effect of the simultaneously occurring production and scission of different species. Since $\mathbf{A}$ is triangular, the eigenvalues λ_i are directly given by the diagonal elements, in agreement with the above considerations

$$\lambda_i = -\sum_{j=1}^{i-1} k_{i,j} \quad (10)$$

For calculating the matrix of eigenvectors $\mathbf{C}$ we write

$$\begin{vmatrix} & & \\ A & & \end{vmatrix} \begin{vmatrix} C_{1,j} \\ \cdot \\ C_{i,j} \\ \cdot \\ C_{r,j} \end{vmatrix} = \lambda_j \begin{vmatrix} C_{1,j} \\ \cdot \\ C_{i,j} \\ \cdot \\ C_{r,j} \end{vmatrix} \quad (11)$$

There are two cases to be discussed.

1. **Case I. No Degeneration.** For this case, for all $i \neq j$

$$\lambda_i \neq \lambda_j \quad (12)$$

holds true.

Starting with $i = j$, we rewrite eq 11 as

$$A_{r,r}C_{r,r} = \lambda_r C_{r,r} \quad (13)$$

when j is set equal to r. $C_{r,r}$ can be chosen to be 1 (see later) and the calculation can be continued with $i = r - 1$

$$A_{r-1,r-1}C_{r-1,r} + A_{r-1,r}C_{r,r} = A_{r,r}C_{r-1,r} \quad (14)$$

which yields $C_{r-1,r}$. The general form of eq 14 is

$$\sum_{k=1}^{r} A_{i,k}C_{k,j} = A_{j,j}C_{i,j} \qquad i = r, r-1, \ldots \quad (15)$$

since $A_{j,j} = \lambda_j$ (eq 10). For $i > j$ it is possible to show that $C_{i,j} = 0$ by starting with $i = r$ and $j \neq r$

$$A_{r,r}C_{r,j} = A_{j,j}C_{r,j}$$

and

$$A_{r-1,r-1}C_{r-1,j} + A_{r-1,r}C_{r,j} = A_{j,j}C_{r-1,j} \quad (16)$$

Since $A_{r,r} \neq A_{j,j}$ (see eq 10 and 12), all $C_{i,j}$ are zero up to $i = j$. Subsequently the same formalism as described in eq 15 is used again to calculate the other coefficients $C_{i,j}$. Thus we have obtained the whole matrix $\mathbf{C}$ without any approximation. We further proved that it is a triangular matrix like $\mathbf{A}$, which is a fact of great importance for introducing the initial distribution.

2. **Case II. Degeneration.** A set of physically meaningful coefficients $k_{i,j}$ normally leads to nondegenerate eigenvalues λ_i. Nevertheless, it is useful to discuss the calculation if there are some $k_{i,j}$ for which

$$\lambda_k = \lambda_j$$

meaning

$$A_{k,k} = A_{j,j} \quad (17)$$

We start with $r \geq k > j$. By means of eq 14–16 it is possible to show that all $C_{i,j}$ vanish for $i > k$. Setting $C_{k,j}$ equal to zero, one can prove by the same equations that the coefficients $C_{i,j}$ for $k > i > j$ must vanish too. For i smaller than j, the calculation already described is used again (see eq 13–15). If $C_{k,j} \neq 0$, we could obtain the $C_{i,j}$ by applying eq 15. But there is a simple reason for choosing $C_{k,j} = 0$ so that all $C_{i,j}$, $i > j$, vanish, namely, the following:

The number of molecules $n_i(t)$ of a certain species is given by a linear combination of pure decay terms $z_i(t)$ (cf. eq 7). Since in our model bigger molecules cannot be produced by smaller ones, $n_i(t)$ must not depend on $z_j(t)$ if j is smaller than i. Therefore all $C_{i,j}$ must be equal to zero for this case without loss of generality.

If $j > k$, another algorithm has to be used. Beginning with $i = j$ we obtain

$$A_{k,k}C_{j,j} = A_{j,j}C_{j,j}$$
$$A_{j-1,j-1}C_{j-1,j} + A_{j-1,j}C_{j,j} = A_{j,j}C_{j-1,j} \quad (18)$$

and so on until $i = k$ is reached

$$A_{k,k}C_{k,j} + A_{k,k+1}C_{k+1,j} + \ldots + A_{k,j}C_{j,j} = A_{j,j}C_{k,j} \quad (18a)$$

Choosing $C_{k,j} = 1$ in eq 18a, one obtains from eq 18 a system of $j - k$ independent equations for the $j - k$ nonzero coefficients $C_{i,j}$. For $i < k$ the other $C_{i,j}$ can be calculated as described. Therefore it turns out that also in the case of degeneration the problem is soluble without approximation. Furthermore, we have shown that **C** again is triangular and that all $C_{i,j}$ are obtainable by a simple calculation scheme. It should be borne in mind that none of the diagonal elements $C_{i,i}$ is zero. Otherwise **C** would become singular.

We now incorporate the initial distribution by setting $t = 0$ in eq 7

$$\vec{n}_0 = \mathbf{C}\vec{\alpha} \quad (19)$$

with $\vec{n}_0$ the vector of the initial number distribution $(x_{0,i})$ multiplied by the total number of moles present in the system

$$\vec{n} = \sum_{i=1}^{r} n_{0,i} \begin{vmatrix} x_{0,1} \\ \cdot \\ x_{0,i} \\ \cdot \\ x_{0,r} \end{vmatrix} \qquad \vec{\alpha} = \begin{vmatrix} \alpha_1 \\ \cdot \\ \alpha_i \\ \cdot \\ \alpha_r \end{vmatrix} \quad (20)$$

$\vec{\alpha}$ is the vector of coefficients α_i. Again we determine all α_i by stepwise application of a simple scheme. With $\det \mathbf{C} \neq 0$ and $C_{i,j} = 0$ for $i > j$ we obtain

$$n_{0,r} = C_{r,r}\alpha_r \Rightarrow \alpha_r$$
$$n_{0,r-1} = C_{r-1,r-1}\alpha_{r-1} + C_{r,r}\alpha_r \Rightarrow \alpha_{r-1} \quad (21)$$

and so on. Therefore our concept can be applied to any initial distribution. All steps of the above calculation can be easily handled by means of a computer. Since there is no time-consuming numerical step involved in the calculation, the number of equations in (2) can be varied over a wide range. Nevertheless, restrictions imposed by computer memory capacity do not permit one to take all possible rupture sites along the chain into account. The polymer molecule is therefore divided into a certain number of subunits. It has to be checked in each case that the results of the calculation do not depend on the length of the subunits (see later).

We now discuss some special models suitable for describing polymer chain scission under various experimental conditions.

Results and Discussion

1. Random Scission. All rupture sites or bonds have the same probability of breaking; therefore

$$k_{i,j} = k \quad (22)$$

There are many treatments of this case in the literature (see introduction) leading to more or less complicated expressions. The calculation scheme as described above gives a very simple solution of the problem. As already stated by Basedow, Ebert, and Ederer,[3] the matrix **A** in eq 6 is given by

$$\mathbf{A} = k \begin{vmatrix} 0 & 2 & 2 & 2 & 2 & 2 & \cdots & 2 \\ 0 & -1 & 2 & 2 & 2 & 2 & \cdots & 2 \\ 0 & 0 & -2 & 2 & \cdots & \cdots & \cdots & 2 \\ & & & -3 & 2 & \cdots & \cdots & 2 \\ & & & & & & \cdot & \cdot \\ & & & & & & & -(r-1) \end{vmatrix} \quad (23)$$

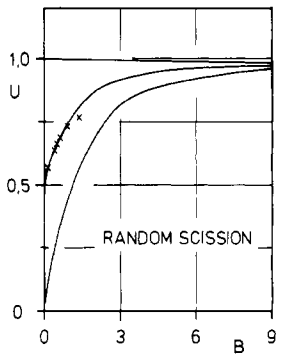

Figure 1. Random scission of polymers of different nonuniformity $U = P_w/P_n - 1$. The starting molecular weight distributions of the polymolecular samples is of the Schulz type. The initial P_n amounts to 500 in all cases. B is the average number of broken bonds per molecule (cf. eq 25). The solid lines were calculated taking into account that the polymer can break at each monomer link. The crosses show how the results are changed in the case of a starting U of 0.5 when one assumes that the scission can take place every 20th monomer unit only.

(see eq 20 of ref 3). The matrix **C** of eigenvectors also has a very simple form

$$\mathbf{C} = \begin{vmatrix} 1 & -2 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 \cdots & 0 \\ & & & 1 & -2 & 0 \cdots & 0 \\ & & & & & \cdot & \cdot \\ & & & & & & 1 \end{vmatrix} \quad (24)$$

This band structure of **C** can be used to elaborate a scheme for calculating P_n, P_w, U, and the entire MWD as a function of time (see Appendix). The calculations were performed on a Honeywell-Bull 66/80 computer. Figure 1 shows the results for molecularly uniform starting material and for the case of initial Schulz distributions differing in the nonuniformity U. For the sake of comparison, the data are plotted vs. B, the number of broken bonds per molecule, where B is given by[3]

$$B = (P_{n,0} - P_{n,t})/P_{n,t} \quad (25)$$

Since the calculation scheme is very easy to handle, all bonds of the polymer chain under consideration can be treated as rupture sites. Thus there is the possibility of controlling the results of the calculations where the cleavage is assumed to occur at certain bonds only. As is demonstrated (Figure 1) for random scission and a starting MWD (Schulz) of $U = 0.5$, this simplifying assumption produces negligible effect if B is less than 1.0.

In this example the chains have been divided into subunits of 20 monomers. The discrepancy of the results of calculations with 1 and 20 monomers in such a subunit is due to the fact that the weight fraction of oligomers with DP (degree of polymerization) less than 20 is no longer negligible.

At high values of starting nonuniformity U ($U > 1$) it has to be checked that neglecting the high molecular part of the distribution does not affect the higher moments.[18]

When the starting material is molecularly uniform, the calculation can be compared with the results of Montroll and Simha.[7] The agreement is excellent. The data plotted in Figure 1 clearly demonstrate that U tends to unity for different starting nonuniformities, in accord with the early results of Kuhn[6] and Montroll and Simha.[7] As B becomes larger, a small decrease of U becomes noticeable, caused by an increasing amount of material which is converted to the monomer. After very long degradation times U

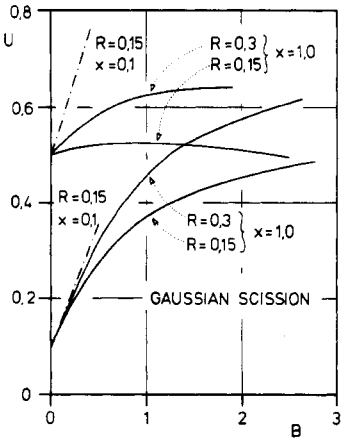

Figure 2. Gaussian scission of polymers of different nonuniformity $U = P_w/P_n - 1$. The starting molecular weight distribution is of the Schulz type. The initial P_n amounts to 500. B is the average number of broken bonds per molecule (cf. eq 25). The different lines were calculated for the parameters R and x (eq 29) indicated in the graph. R is the normalized standard deviation of the scission probability with respect to the position of the bond in the chain (central cleavage being approached as R vanishes); x measures the chain length dependence of the rate of degradation. For $U(B = 0) = 0.1$ every 10th bond and for $U(B = 0) = 0.5$ every 20th bond is accessible to scission.

should approach zero because of survival of the monomer only. The results of random scission are in qualitative agreement with experiments of Schnabel and Sotobayashi.[4] Starting with a narrow initial distribution, these authors have observed a broadening during irradiation with γ rays.

2. Gaussian Scission. The probability of a chain scission is assumed to be Gaussian about the midpoint of the chain, as proposed by Glynn et al.[15] The standard deviation is set proportional to the chain length

$$\sigma_i = R(\mathrm{DP}_i) \tag{26}$$

The diagonal elements of **A** are normalized with respect to the number of bonds present in chain

$$\sum_{j=1}^{i-1} k_{i,j} = \lambda_i = -k(\mathrm{DP} - 1)^x \tag{27}$$

or if the molecules are divided in i subunits

$$\sum_{j=1}^{i-1} k_{i,j} = \lambda_i = -k(i - 1)^x \tag{28}$$

Thus the constants $k_{i,j}$ are given by

$$k_{i,j} = (\mathrm{DP}_i - 1)^x \frac{1}{\sigma_i(2\pi)^{1/2}} \exp[-(j - i/2)^2/2\sigma_i^2] \tag{29}$$

For $R > 10$ and $x = 1$ the model approaches the case of random scission; if $R < 0.05$ the molecules are split practically at the midpoint only. Calculations were performed with Schulz distributions of $U = 0.1$ and 0.5, respectively. The length of the subunit is chosen to be 20 monomer units; the calculation is stopped when the weight fraction of oligomers with DP < 20 is no longer negligible. The results as plotted in Figure 2, again as function of B, clearly show the dependence of U on the model parameters R and x, especially for the broader initial MWD. In order to determine these model parameters by fitting U to the experimental data, a starting material with a not too narrow distribution should therefore be used. Figure 3 shows some typical examples of distributions calculated for different degrees of degradation.

The exponent x gives the dependence of the degradation rate on the degree of polymerization DP_i. According to

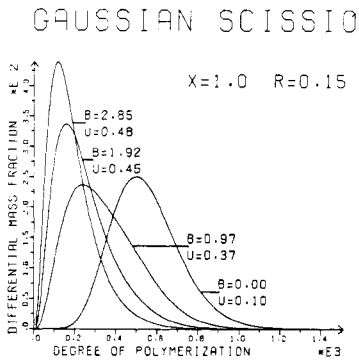

Figure 3. Molecular weight distributions for different degrees of degradation, measured by B, the average number of broken bonds. The initial P_n amounts to 500. The initial distribution is of the Schulz type. The scission probability varies in a Gaussian manner along the chain; R measures the standard deviation and x the influence of the chain length (cf. eq 29). The cleavage can occur at every 10th bond. The U values indicated in the graph give the nonuniformity $U = P_w/P_n - 1$.

ref 3 such an exponent can be obtained from experimental data by means of the relation

$$-\mathrm{d} \ln P_n/\mathrm{d}t = kP_n^a \tag{30}$$

Therefore a plot of $1/P_n^a$ vs. the degradation time t should yield straight lines. Our exponent x is not identical with the exponent a, since $P_{n,t}$ is given by

$$P_n = \sum_{i=1}^{r}(\mathrm{DP}_i)n_i(t)/\sum_{i=1}^{r} n_i(t) = \frac{\sum_{i=1}^{r}\mathrm{DP}_i\sum_{j\geq i}^{r} C_{i,j}\alpha_j \exp(\lambda_j t)}{\sum_{i=1}^{r}\sum_{j\geq i}^{r} C_{i,j}\alpha_j \exp(\lambda_j t)} \tag{31}$$

The numerator of eq 31 is the total number of monomer units in the system, which does not change during degradation. Therefore

$$\mathrm{d} \ln P_n/\mathrm{d}t = \frac{\sum_{i=1}^{r}\mathrm{DP}_i\sum_{j\geq i}^{r}\lambda_j C_{i,j}\alpha_j \exp(\lambda_j t)}{\sum_{i=1}^{r}\sum_{j\geq i}^{r} C_{i,j}\alpha_j \exp(\lambda_j t)} \tag{32}$$

$$\mathrm{d} \ln P_n/\mathrm{d}t = \frac{-k\sum_{i=1}^{r}\mathrm{DP}_i\sum_{j\geq i}^{r}(\mathrm{DP}_j - 1)^x C_{i,j}\alpha_j \exp(\lambda_j t)}{\sum_{i=1}^{r} n_i(t)} \neq -kP_n^x \tag{33}$$

Thus it is not possible to obtain the exponent x from P_n values measured for different degradation times but only by fitting the parameters R and x to the experimental distribution curve.

3. Central Scission. The molecules are only split at the midpoint of the chain. Therefore the constants in eq 6 are given by

i odd

$$k_{i,j} = 1 \quad \text{if} \quad j = (i - 1)/2$$

$$k_{i,j} = 0 \quad \text{if} \quad j \neq (i - 1)/2 \tag{34a}$$

i even

$$k_{i,j} = 0.5 \quad \text{if} \quad j = (i - 1)/2 \pm 0.5$$

$$k_{i,j} = 0 \quad \text{if} \quad j \neq (i - 1)/2 \pm 0.5 \tag{34b}$$

Again the sum of all constants $k_{i,j}$ belonging to the species

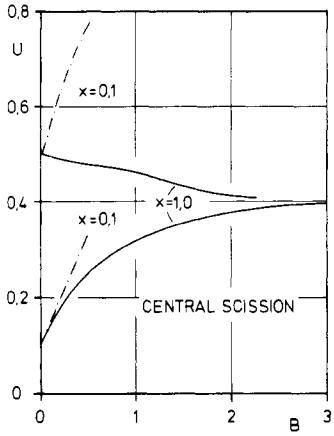

Figure 4. Central scission of polymers of different nonuniformity $U = P_w/P_n - 1$. The starting molecular weight distribution is of the Schulz type. The initial P_n amounts to 500. B is the average number of broken bonds per molecule (cf. eq 25). The different lines were calculated for the indicated x values, which measure the influence of the chain length on the degradation rate (eq 35). For $U(B = 0) = 0.1$ every 10th bond and for $U(B = 0) = 0.5$ every 20th bond is accessible to scission.

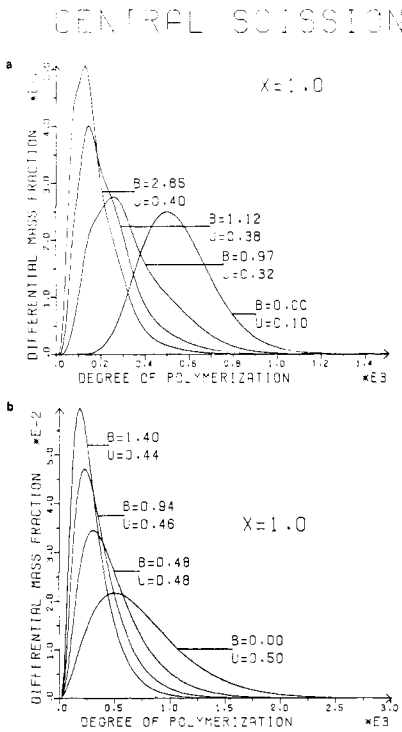

Figure 5. Molecular weight distributions calculated for different degrees of degradation, measured by B, the average number of broken bonds per molecule. The initial distributions are of the Schulz type; the initial P_n amounts to 500. The chains can break at their midpoint only (eq 34); x measures the influence of the chain length (eq 35). The U values indicated in the graphs give the nonuniformity $U = P_w/P_n - 1$. For $U(B = 0) = 0.1$ (Figure 5a) every 10th bond and for $U(B = 0) = 0.5$ (Figure 5b) every 20th bond is accessible to scission.

i is normalized with respect to the number of bonds $(i - 1)$ or $DP_i - 1$

$$\sum_{i=1}^{r} k_{i,j} = \lambda_i = -k(i-1)^x \quad \text{or} \quad -k(DP_i - 1)^x \qquad (35)$$

Calculations of U as function of B are performed again with two Schulz distributions with $U = 0$, 1 and $U = 0.5$ (Figure 4). Figure 5 shows the change of the distributions during degradation. Note that in the case of the starting value of $U = 0.5$, the distribution does not become bimodal even for $B = 1.4$.

Conclusion

It has been shown that each model of interest can be solved by the above procedure. The individual rate constants $k_{i,j}$ are available by fitting the model parameters to experimental distributions. Thus it is possible to get the full kinetic information about the chain scission process. Knowledge of the dependence of the $k_{i,j}$ values on the different experimental conditions, like shear rate, molecular weight, etc., should give more insight into the molecular background of the degradation process. At present an analysis of the shear degradation of polystyrene in poor solvents[19] by the methods described above is under way.

Appendix (Cf. Ref 3)

$n_i(t)$ is given by

$$n_i(t) = \sum_{j \geq i}^{r} C_{i,j}\alpha_j \exp(\lambda_j t) \qquad \text{(see eq 7)}$$

In the case of random scission

$$\lambda_j = -k(DP_i - 1) \qquad \text{(see eq 23)}$$

and

$$\begin{aligned} C_{i,j} &= 1 \quad \text{for} \quad i = j \\ &= -2 \quad \text{for} \quad j = i + 1 \\ &= 1 \quad \text{for} \quad j = i + 2 \\ &= 0 \quad \text{for} \quad j = i + 2 \text{ and } i > j \end{aligned} \qquad \text{(see eq 24)}$$

Therefore starting with $i = r$

$$\alpha_r = n_{r,0}$$

$$\alpha_{r-1} = n_{r-1,0} + 2\alpha_r \qquad \text{(see eq 21)}$$

$$\alpha_i = n_{i,0} + 2\alpha_{i+1} - \alpha_{i+2}$$

Combining the above equations yields a simple scheme for evaluation of the distribution and the average molecular weight as a function of time.

References and Notes

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