Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Application of Continuous Kinetics to Polymer Degradation

Dieter Browarzik[a]; Anne Koch[a]
[a] Institute of Physical Chemistry Martin-Luther University, Halle-Wittenberg, Merseburg, Germany

To cite this Article Browarzik, Dieter and Koch, Anne(1996) 'Application of Continuous Kinetics to Polymer Degradation', Journal of Macromolecular Science, Part A, 33: 11, 1633 — 1641
To link to this Article: DOI: 10.1080/10601329608010928
URL: http://dx.doi.org/10.1080/10601329608010928

J.M.S.—PURE APPL. CHEM., A33(11), pp. 1633–1641 (1996)

APPLICATION OF CONTINUOUS KINETICS TO POLYMER DEGRADATION

DIETER BROWARZIK* and ANNE KOCH

Institute of Physical Chemistry
Martin-Luther University Halle-Wittenberg
06217 Merseburg, Germany

ABSTRACT

Degradation of polydisperse polymers is studied in the framework of continuous kinetics which is directly based on continuous distribution functions which depend on the molecular weight and the time. A first-order formalism is presumed. A Schulz–Flory distribution (with time-dependent parameters) is assumed to be valid during the entire time of degradation. Thus, an essential simplification of the solution procedure of the continuous rate equation is achieved. As a proof of accuracy, the approximation solution and the exact solution are compared for the case of "random scission." Furthermore, the developed method is shown to be suitable for describing the experimental data of dextran degradation caused by acid hydrolysis, by ultrasonic irradiation, and by enzymatic attack. The model parameters fitted to the experimental data allow the evaluation of the scission probability as a function of the molecular weight and of the location of the bond to be broken within the molecule.

INTRODUCTION

Polydisperse polymers are composed of a large number of similar species, differing mainly in their molecular weights M. Therefore, the experimental characterization of polymers does not lead to the amounts of individual species but only to a continuous distribution function $w(M)$. This function is defined by the statement that $w(M)dM$ gives the amount of substance of all species with molecular weights between the values M and $M + dM$.

In analogy to continuous thermodynamics of polymers [1–4] also, the kinetic treatment of chemical reactions of polymers (such as polymer degradation) should be based on continuous distribution functions. In this treatment, called continuous kinetics, a continuous rate equation describes the evolution of the distribution function (which additionally depends on the time t).

Presuming all reactions involved to be first order and all occurring species to be of the same type, the continuous rate equation for the time-dependent distribution function $w(M,t)$ reads

$$\frac{\partial w(M,t)}{\partial t} = \int_M^\infty \kappa(M',M)\ w(M',t)\ dM' - \frac{1}{2}\, w(M,t) \int_0^M \kappa(M,M'')\ dM'' \tag{1}$$

The rate function $\kappa(M',M)$ is the continuous generalization of the rate constants in usual kinetics. It describes the breakage of a molecule with molecular weight M' into two molecules with molecular weights M and $M' - M$. The first term on the right-hand side of Eq. (1) describes the formation of molecules with molecular weight M by degradation of larger molecules. The second term describes the destruction of such molecules by splitting into smaller molecules.

Equation (1) was written in 1958 by Saito [5], and as a limiting case of the coagulation–fragmentation equation (for a zero coagulation rate) was studied in 1945 by Blatz and Tobolski [6]. A detailed derivation of Eq. (1) from usual kinetics was given by Kehlen, Rätzsch, and Bergmann [7].

There are a variety of mechanisms of polymer degradation, such as shear action, chemical attack, and nuclear, ultraviolet, and ultrasonic irradiation. Prediction of the evolution of molecular weight distribution during such a process is of great interest. The first work about polymer degradation dates back to Kuhn [8] in 1930 and to Montroll and Simha [9] in 1940. These works were based on the case of "random scission", assuming all bonds to be split with equal probability. In our notation that means $\kappa(M',M) =$ constant.

More recently, in the works by Basedow, Ebert, and Ederer [10] and by Ballauf and Wolf [11], efforts were made considering the scission probability as a function of the length of the polymer chain and of the location of the bond to be split within the chain. However, explicit solutions were not found, and numerical solution by computer was very expensive. Experimental studies on polymer degradation by Keller and Odell [12] and by Ballauf and Wolf [13] showed that in some cases the bonds in the middle of the chains break preferentially to those at the ends. The opposite case was found by Basedow, Ebert, and Ederer [10] in the degradation of dextran. Therefore, the function $\kappa(M',M)$ will depend on the type of the polymer and on the type of degradation.

In recent years an essential advantage in solving Eq. (1) has been reached by Ziff and McGrady [14–16]. For some special functions of $\kappa(M',M)$ they found explicit solutions of the continuous rate equation. However, for functions of $\kappa(M',M)$ as they occur in practice, the exact solution of Eq. (1) is usually unknown.

Recently, Williams [17] described a procedure to find general solutions of Eq. (1). At present, this very complicated method has not been demonstrated for a realistic case of $\kappa(M',M)$.

Therefore, a less complicated approach to solve Eq. (1) for realistic functions of $\kappa(M',M)$ is needed. An approximation is developed here for this purpose.

APPROXIMATION SOLUTION OF CONTINUOUS RATE EQUATION

For a wide class of functions $\kappa(M',M)$, an approximation solution of continuous rate Eq. (1) is possible by assuming that the type of distribution function is always the same. In this paper the method is demonstrated by using a Schulz–Flory distribution:

$$w(M,t) = n \frac{k^k}{\overline{M}_n \Gamma(k)} (M/\overline{M}_n)^{k-1} \exp(-kM/\overline{M}_n) \tag{2}$$

In Eq. (2) the quantities n, $\overline{M}_n$, and k are functions of time t. Here, n is the total amount of substance, $\overline{M}_n$ is the number-average molecular weight, and k is given by

$$k(t) = 1/U(t); \qquad U(t) = \overline{M}_w(t)/[\overline{M}_n(t) - 1] \tag{3}$$

where U is the nonuniformity describing the breadth of the distribution and $\overline{M}_w$ is the weight-average molecular weight.

Introducing a general definition of moments of $w(M,t)$ by

$$\overline{M}^{(r)}(t) = \int_0^\infty M^r \, w(M,t) \, dM; \qquad r \geq 0 \tag{4}$$

the quantities $n(t)$, $\overline{M}_n(t)$, and $\overline{M}_w(t)$ may be expressed by

$$n(t) = \overline{M}^{(0)}(t); \qquad \overline{M}_n(t) = \frac{\overline{M}^{(1)}(t)}{\overline{M}^{(0)}(t)}; \qquad \overline{M}_w(t) = \frac{\overline{M}^{(2)}(t)}{\overline{M}^{(1)}(t)} \tag{5}$$

According to Eq. (2), the time dependence of the distribution function is reduced to the time dependence of the total amount of substance n and of the parameters $\overline{M}_n$ and k.

Although the method may be applied to numerous complicated expressions of $\kappa(M',M)$, here it is restricted to

$$\kappa(M',M) = \alpha(M')^{\varepsilon}\left[1 - \beta\frac{M}{M'}\left(1 - \frac{M}{M'}\right)\right]; \qquad \beta \leq 4 \tag{6}$$

This three parameter relation seems to be very simple, but the corresponding exact solution of Eq. (1) is unknown. Despite its simplicity, Eq. (6) describes the scission probability in its dependence on the molecular weight of the polymer molecule and on the location of the bond to be broken within the molecule. If $\varepsilon > 0$ ($\varepsilon < 0$), a larger molecule is degraded more (less) rapidly than a smaller one. If $\beta < 0$, the bonds near the middle of a molecule break preferentially to those near the ends. If $\beta > 0$, the opposite case occurs.

Using Eqs. (1), (4), and (6), the relation

$$\frac{d\overline{M}^{(r)}}{dt} = \alpha\overline{M}^{(\varepsilon+r+1)}\left[\frac{1}{r+1} - \frac{1}{2} - \beta\left(\frac{1}{r+2} - \frac{1}{r+3} - \frac{1}{12}\right)\right] \tag{7}$$

can be verified.

Setting $r = 1$, because of the conservation of mass during the reaction, $d\overline{M}^{(1)}/dt = 0$ or $n(t)\overline{M}_n(t)$ = constant is obtained. If Eq. (7) is additionally applied to $r = 0$ and $r = 2$ with the aid of Eqs. (3) and (5), the temporal changes of the number-average molecular weight $\overline{M}_n$ and of the nonuniformity U obey the relations

$$\frac{d\overline{M}_n}{dt} = -\frac{\alpha}{2}(1 - \beta/6)\,\overline{M}_n\overline{M}^{(\varepsilon+1)}/n \tag{8}$$

$$\frac{dU}{dt} = -\frac{\alpha}{6}(1 - \beta/5)\,\frac{\overline{M}^{(\varepsilon+3)}}{n} + \frac{\alpha}{2}(1 - \beta/6)(U + 1)\,\frac{\overline{M}^{(\varepsilon+1)}}{n} \tag{9}$$

Assuming the Schulz–Flory distribution given by Eq. (2), by using Eq. (4) the rth moment ($r \geq 0$) reads

$$\overline{M}^{(r)} = n(\overline{M}_n)^r k^{1-r}\,\frac{\Gamma(k + r)}{\Gamma(k + 1)} \tag{10}$$

Introduction of Eq. (10) into Eqs. (8) and (9) leads to

$$\frac{d\overline{M}_n}{dt} = -\frac{\alpha}{2}(1 - \beta/6)(\overline{M}_n)^{\varepsilon+2}U^{\varepsilon}\,\frac{\Gamma(\varepsilon + 1 + 1/U)}{\Gamma(1 + 1/U)} \tag{11}$$

$$\frac{dU}{dt} = \frac{\alpha}{3}(1 - 3\beta/20)(\overline{M}_n)^{\varepsilon+1}U^{\varepsilon}\,\frac{\Gamma(\varepsilon + 1 + 1/U)}{\Gamma(1 + 1/U)}(1 + pU + qU^2) \tag{12}$$

where

$$p = \frac{\beta/20 - \varepsilon(1 - \beta/5)}{1 - 3\beta/20}; \qquad q = -\frac{1}{2}\,\frac{(1 - \beta/5)(\varepsilon + 1)(\varepsilon + 2)}{1 - 3\beta/20} \tag{13}$$

Combining Eqs. (11) and (12), the following relation, which allows the calculation of $\overline{M}_n$ if U is known, is obtained:

$$\overline{M}_n(t) = \overline{M}_n(0)\left\{\frac{1 - \lambda_2 U(t)}{1 - \lambda_1 U(t)}\,\frac{1 - \lambda_1 U(0)}{1 - \lambda_2 U(0)}\right\}^{\delta} \tag{14}$$

where λ_1 and λ_2 are solutions of a quadratic equation given by

$$\lambda_1 = -p/2 - \sqrt{p^2/4 - q}; \qquad \lambda_2 = -p/2 + \sqrt{p^2/4 - q} \tag{15a}$$

and δ is defined as

$$\delta = \frac{3}{4}\,\frac{1 - \beta/6)}{1 - 3\beta/20} \bigg/ \sqrt{p^2/4 - q} \tag{15b}$$

The combination of Eqs. (12) and (14) results in a differential equation which permits the separation of the variables U and t. Thus, the solution reduces to a numerical integration. If $U(t)$ is known, direct calculation of $\overline{M}_n(t)$ based on Eq. (14) is possible. Because of the presumed validity of the Schulz–Flory distribution, the molar distribution function $w(M,t)/n(t)$ may also be determined. Considering the requirement $n(t)\overline{M}_n(t)$ = constant, one can also easily calculate the function $n(t)$.

Finally, note that $\overline{M}_n(t)$ and $U(t)$ change continuously with t where $\overline{M}_n(t)$ decreases with t. $U(t)$ decreases with t if $U(0) > \lambda_2$ and $U(t)$ increases with t if $U(0)$

$< \lambda_2$. In the case where $U(0) = \lambda_2$, the function $U(t)$ is a constant with respect to time t. Generally, $U(t)$ approaches the long time limit $U_\infty = \lambda_2$; a maximum does not occur.

PROOF OF APPROXIMATION

To determine the accuracy of the previously introduced assumptions, a comparison between the approximated and the exact distribution functions is necessary. For this reason, the case of "random scission" corresponding to $\kappa(M',M) = \alpha$ was studied. The well known [7] exact solution of the continuous rate equation reads

$$w(M,t) = \exp\left(-\frac{\alpha}{2}tM\right)\left\{w(M,0) + \alpha t \int_M^\infty w(M',0)\,dM' + (\alpha t/2)^2 \int_M^\infty (M' - M)\,w(M',0)\,dM'\right\} \tag{16}$$

In the framework of the introduced approximation, $\kappa(M',M) = \alpha$ is obtained by setting $\varepsilon = 0$ and $\beta = 0$.

Applying Eq. (1) or Eq. (16) to an arbitrarily chosen distribution function $w(M,0)$, it is easy to show that the $\overline{M}_n$ is governed by the simple equation

$$1/\overline{M}_n(t) = 1/\overline{M}_n(0) + \frac{\alpha}{2}t \tag{17}$$

Using Eq. (11) with $\varepsilon = 0$ and $\beta = 0$, the approximation also results in Eq. (17).

Furthermore, if $w(M,0)$ is a Schulz-Flory distribution with $k(0) = U(0) = 1$, one can verify with the aid of Eq. (1) that $w(M,t)$ remains a Schulz-Flory distribution with $k(t) = U(t) = 1$ for the entire time range. $\overline{M}_n(t)$ is given by Eq. (17). Introducing $\varepsilon = 0$ and $\beta = 0$ in Eqs. (12) and (13) (which means $p = 0, q = -1$), the approximation developed is verified to be exact if $U(0) = 1$.

To give a more significant proof of the approximation, the approximated and the exact distribution functions $W(\tilde{M},\tau)$ are compared with respect to $\kappa(M',M) = \alpha$ for a special case [$w(M,0)$ is a Schulz-Flory distribution with $k(0) = 0.2$ or with $U(0) = 5$]. Here, $W(\tilde{M},\tau)$ is the weight distribution function

$$W(\tilde{M},\tau) = \overline{M}_n(0)\; w(M,t)M \Big/ \int_0^\infty w(M',t)M'\,dM' \tag{18}$$

depending on the reduced molecular weight $\tilde{M}$ and the reduced time τ, where these dimensionless quantities are given by

$$\tilde{M} = M/\overline{M}_n(0); \qquad \tau = \frac{\alpha}{2}t\overline{M}_n(0) \tag{19}$$

In Fig. 1 the curves corresponding to the exact solution are based on Eq. (16) by solving the integrals numerically. The approximated curves are based on Eq. (2) where $\overline{M}_n(t)$ and $k(t)$ are calculated with the aid of Eqs. (3), (11), (12), and (13) by applying $\varepsilon = 0$ and $\beta = 0$. In this case, analytical solutions are obtained. $\overline{M}_n(t)$ fulfills Eq. (17) and $k(t)$ obeys the relation

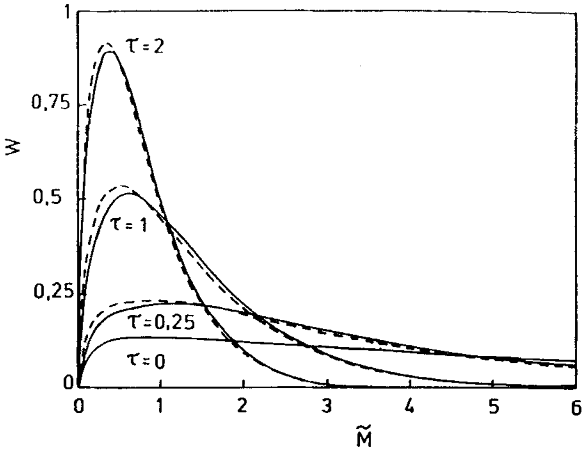

FIG. 1. Weight distribution function $W(\tilde{M}, \tau)$ of some values of reduced time τ corresponding to an initial Schulz-Flory distribution with $k(0) = 0.2$ or $U(0) = 5$:(——) exact solution, (- - -) approximated solution.

$$k(t) = \frac{k(0) + 1 - [k(0) - 1]\left[1 + \frac{\alpha}{2} t \overline{M}_n(0)\right]^{-4/3}}{k(0) + 1 + [k(0) - 1]\left[1 + \frac{\alpha}{2} t \overline{M}_n(0)\right]^{-4/3}} \tag{20}$$

Although the initial distribution is very broad, Fig. 1 shows only small differences between the exact and the approximate solutions. During the reaction these differences first increase but later they decrease considerably, corresponding to a decrease of U. After a long time, $U(t)$ approaches the limit $U_\infty = 1$, i.e., the approximate solution and the exact solution coincide.

On the whole, the developed approximation shows sufficient accuracy to justify further application.

APPLICATION TO DEXTRAN DEGRADATION

The approach introduced by this paper may be applied to the degradation of polymers whose splitting products are of the same type as the polymer before degradation. Therefore, experimental data of dextran degradation ought to be suitable for proving the accuracy of the developed approximation method. Fortunately, some experimental data for different types of dextran degradation are available. Degradation by acid hydrolysis was studied by Basedow, Ebert, and Ederer [10], degradation by ultrasonic irradiation was investigated by Basedow and Ebert [18], and degradation by enzymatic attack was measured by Basedow [19].

The acid hydrolysis [10] was carried out at 80°C in 0.12 N sulfuric acid. The initial concentration of dextran [$\overline{M}_n(0) = 117{,}000$ g/mol; $U(0) = 0.29$] was 1%. The molecular weight distributions were measured by GPC in a time range of 450 minutes.

The degradation by ultrasonic irradiation [18] was carried out at 82°C in water and in 0.60 M phosphoric acid. Ultrasonic energy was applied by a generator operating at a frequency of 20 kHz and an intensity of 10 W/cm^2. The initial concentration of dextran [$\overline{M}_n(0)$ = 72,600 g/mol; $U(0) = 0.14$] was 0.5 mg/mL. The molecular weight averages were determined by GPC in a time range of 60 minutes.

The degradation by enzymatic attack [19] was carried out at 25°C in acetate buffer of pH 5.2 using an endo-dextranase (0.05 units/mL). The initial concentration of dextran [$\overline{M}_n(0)$ = 76,900 g/mol; $U(0) = 0.14$] was 1%. The molecular weight averages were measured by GPC in a time range of 100 minutes.

Usually, the number-average $\overline{M}_n$, the weight-average $\overline{M}_w$ and the z-average $\overline{M}_z$ of the molecular weight for various times were measured. Instead of $\overline{M}_w$ and $\overline{M}_z$, the nonuniformity U and the "combined polydispersity ratio" CPR $= (\overline{M}_w)^2/(\overline{M}_n\overline{M}_z)$ are often given (in some cases, only one of them). Presuming a Schulz-Flory distribution, CPR may be expressed by U according to CPR $= (1 + U)^2/(1 + 2U)$.

With the aid of Eqs. (12)-(15), the parameters α, β, and ε were fitted to the experimental data of $\overline{M}_n(t)$ and $U(t)$, or of $\overline{M}_n(t)$ and CPR(t) if $U(t)$ was not available. In this way, the parameter fit to experimental data of degradation by acid hydrolysis [10] results in

$$\alpha = 3.219 \times 10^{-6}(\text{mol/g})^{0.5477}\text{s}^{-1}; \qquad \beta = 2.903; \qquad \varepsilon = -0.4523$$

In the case of the experimental data of degradation by ultrasonic irradiation [18], the parameters take the values

$$\alpha = 2.983 \times 10^{-9}(\text{mol/g})^{1.3566}\text{s}^{-1}; \qquad \beta = 4.000; \qquad \varepsilon = 0.3566$$

and the experimental results of degradation by enzymatic attack [19] provide

$$\alpha = 5.746 \times 10^{-8}(\text{mol/g})^{1.1039}\text{s}^{-1}; \qquad \beta = 4.000; \qquad \varepsilon = 0.1039$$

In the latter two cases, β-values larger than 4 would improve the description of experimental data. However, according to Eq. (6), $\beta \leq 4$ has to be fulfilled for $\kappa(M',M) \geq 0$ to be possible for all values of M and M'.

Considering the ε-values, smaller molecules are preferentially broken in degradation by acid hydrolysis. On the other hand, larger molecules are more easily degraded than smaller ones in degradation by ultrasonic irradiation. In degradation by enzymatic attack, there is no significant dependence on the molecular weight. According to the positive β-values, the bonds near the ends of a dextran molecule break easier than those near the middle. Considering the occurrence of the limit $\beta = 4$, in two cases Eq. (6) does not seem to be flexible enough to describe the dependence on M/M'. Perhaps exponential terms with respect to M/M' would be more suitable.

For all three types of dextran degradation, the calculated number-averages $\overline{M}_n(t)$ and the calculated nonuniformities $U(t)$ (based on the given values of α, β, and ε) were compared with the corresponding experimental values. The results are presented in Fig. 2 (for $\overline{M}_n$) and in Fig. 3 (for U). Because the time t_E of the end of the degradation experiment was different in the cases considered, the ratio t/t_E is plotted on the abscissa instead of the time t. In the case of degradation by ultrasonic irradiation, only experimental CPR values are available. For the sake of uniform

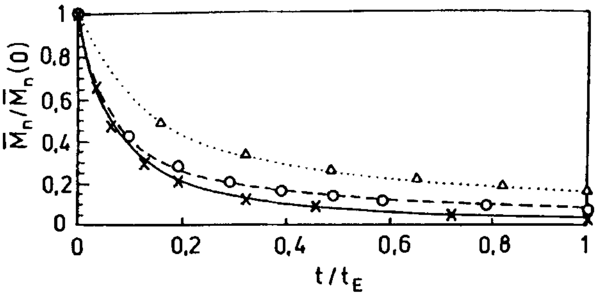

FIG. 2. Comparison of the calculated (lines) and the experimental (points) time-dependence of the number average $\overline{M}_n$ of the molecular weight in degradation by acid hydrolysis (——), by ultrasonic irradation (· · ·), and by enzymatic attack (- - -).

presentation, these values were converted into U values, presuming a Schulz–Flory distribution.

Figure 2 shows a very accurate description of the experimental number averages by the introduced of our approximation method for all three types of degradation. On the whole, the description of the experimental values of nonuniformity U is also satisfactory (Fig. 3).

However, in the cases of degradation by ultrasonic irradiation and by enzymatic attack, the agreement of calculated and experimental values of U is not quite perfect. The reason is that in both cases the experimental $U(t)$ curve shows a maximum, but based on Eq. (6) in $U(t)$, a maximum cannot occur. In degradation by ultrasonic irradiation (t_E = 60 minutes), this maximum is reached after a shorter time than in degradation by enzymatic attack (t_E = 100 minutes). Because of this shorter time, there is a relatively large slope dU/dt, the description of which is not easy to determine by using Eq. (6). Therefore, the degradation of dextran by ultrasonic irradiation is less perfectly modeled than degradation by enzymatic attack. Finding expressions for $\kappa(M',M)$ which are more flexible than Eq. (6) and, with

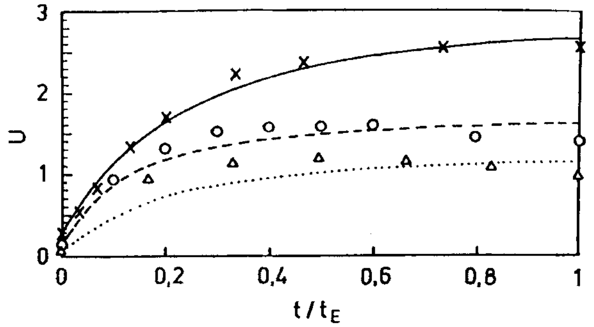

FIG. 3. Comparison of the calculated (lines) and the experimental (points) time-dependence of the nonuniformity U in degradation by acid hydrolysis (——), by ultrasonic irradation (· · ·), and by enzymatic attack (- - -).

respect to $U(t)$, allowing for the occurrence of a maximum, is a challenge for the future.

CONCLUSIONS

1. Assuming a Schulz–Flory distribution with time-dependent parameters, an essential simplification in solving the continuous rate equation is achieved.

2. The developed approximation permits a good description of the exact solution in the case of "random scission," and of the experimental data of dextran degradation by acid hydrolysis, by ultrasonic irradiation, and by enzymatic attack.

3. The fitted model parameters show that the bonds near the ends of a dextran molecule break easier than those near the middle. However, there are essential differences between the three types of dextran degradation when the dependence of the splitting probability on the molecular weight is considered.

4. Unfortunately, calculation of the time-dependence of nonuniformity U by the developed method does not allow a maximum to occur. Therefore, more flexible expressions for the rate function $\kappa(M',M)$ are needed.

REFERENCES

[1] M. T. Rätzsch and H. Kehlen, *J. Macromol. Sci.—Chem., A22*, 323 (1985).
[2] M. T. Rätzsch, D. Browarzik, and H. Kehlen, *Ibid., A26*, 903 (1989).
[3] M. T. Rätzsch and H. Kehlen, *Prog. Polym. Sci., 14*, 1 (1989).
[4] D. Browarzik, H. Kehlen, and M. T. Rätzsch, *J. Macromol. Sci.—Chem., A27*, 549 (1990).
[5] O. Saito, *J. Phys. Soc. Jpn., 13*, 198 (1958).
[6] P. J. Blatz and A. V. Tobolski, *J. Phys. Chem., 49*, 77 (1945).
[7] H. Kehlen, M. T. Rätzsch, and J. Bergmann, *Chem. Eng. Sci., 43*, 609 (1988).
[8] W. Kuhn, *Ber. Chem. Dtsch. Ges., 63*, 1503 (1930).
[9] E. W. Montroll and R. Simha, *J. Chem. Phys., 8*, 721 (1940).
[10] A. M. Basedow, K. H. Ebert, and H. J. Ederer, *Macromolecules, 11*, 774 (1978).
[11] M. Ballauf and B. A. Wolf, *Ibid., 14*, 654 (1981).
[12] A. Keller and J. A. Odell, *Colloid Polym. Sci., 263*, 181 (1985).
[13] M. Ballauf and B. A. Wolf, *Macromolecules, 17*, 209 (1984).
[14] R. M. Ziff and E. D. McGrady, *J. Phys. A, 187*, 3027 (1985).
[15] R. M. Ziff and E. D. McGrady, *Macromolecules, 19*, 2513 (1986).
[16] R. M. Ziff, *J. Phys. A, 24*, 2821 (1991).
[17] M. M. R. Williams, *Aerosol Sci. Technol., 12*, 583 (1990).
[18] A. M. Basedow and K. H. Ebert, *Polym. Bull., 1*, 299 (1979).
[19] A. M. Basedow, *Ibid., 2*, 337 (1980).

Received October 23, 1995
Revision received January 17, 1996