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Citation: J. Chem. Phys. 91, 7193 (1989); doi: 10.1063/1.457286
View online: http://dx.doi.org/10.1063/1.457286
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v91/i11
Published by the American Institute of Physics.
Light scattering power of randomly cut random coils with application to the
determination of depolymerization rates

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(Received 8 May 1989; accepted 27 July 1989)

The scattering of light by a dilute monodisperse population of random-coil molecules is
approximately described by the well-known function

\[ P(\theta) = \left( \frac{2}{u^2} \right) (e^{-u} + u - 1), \]

where \( u = R_g^2 q^2, \) \( R_g \) is the radius of gyration of the random coils, and \( q = (4\pi n\lambda) \sin(\theta/2) \) is the
magnitude of the scattering vector. We show that if the molecules in this population undergo
random scission, then \( P(\theta) \) is still given by the above formula where, however, \( u \) is now equal
to \( R_g^2 q^2 + r, \) where \( r \) is the average number of scissions per molecule in the originally
monodisperse population and \( R_g \) is the original radius of gyration. It is suggested that this
could be useful for determining depolymerization rate constants, and for investigating whether
various forms of scission are actually random. Results from initial experiments which apply
the theory to the acid hydrolysis of hyaluronic acid are presented. The rate constants found are
in reasonable agreement with values in the literature.

I. INTRODUCTION

The purpose of this paper is to discuss the change in
intensity and angular distribution of the light scattered by an
initially monodisperse population of noninteracting ran-
dom-coil-like molecules as they are subjected to random
scission, with an eye toward applying the results to experi-
mental studies of scission of long chain molecules in dilute
solution. The resulting formula is simple and rather interesting.
In the slightly more than 40 years since Zimm, Stein,
and Doyl2 and Debye3 calculated the light scattering power
of random-coil molecules, much work has been done on light
scattering from polymers. Although one would think that
every possible modification and application, or at least all
of scission is truly random, and, if it is, in finding the rate at
which it proceeds.

Before proceeding with the calculation or discussing its
possible relevance, we review the assumptions made in deriving
this form for \( P(\theta). \) Consider a dilute solution of a large
number of polymer molecules. Each molecule is a linear
polymer made of a large number, \( n, \) of identical units, \( n \)
being the same for each polymer. The molecules are con-
sidered to be Gaussian random coils. This assumption is jus-
tified in a theta solvent at the theta temperature.4,5 Each unit
is assumed to be optically isotropic. The concentration \( c \)
of these molecules is high enough that they are the major
contributor to the scattering of light by the solution, yet low
enough to prevent multiple scattering. Since the interior of
an isolated Gaussian random coil would be mostly solvent, it
is plausible that any individual molecule changes the index
of refraction of the solvent within itself by so little that the
phase of the incident light across it does not change signifi-
cantly, and also that multiple scattering within a molecule
can be neglected. This is the "Rayleigh–Gans" (or what
Kerker6 calls the "Rayleigh–Debye") approximation. The amplitude of light scattered by a single such molecule is the
sum of the amplitudes of light scattered from its individual
units.

Let the scattered light from one such unit be \( I_1(\theta), \)
where \( \theta \) is the scattering angle, with \( \theta = 0 \) being forward
scattering. The angular dependence of \( I_1(\theta) \) depends on the
polarization of the incident beam. The scatterers are as-
sumed to be isotropic. Then if the incident beam is polarized
perpendicular to the scattering plane, so is the scattered
light, and \( I_1 \) is independent of theta. If the incident beam is
polarized parallel to the scattering plane, then so is the
scattered light, and \( I_1 \) varies as \( \cos^2(\theta). \) If the incident beam is
unpolarized then \( I_1 \) varies as \( [1 + \cos^2(\theta)]. \) Let the scat-
tered light intensity of the whole molecule be \( I(\theta). \) Then

\[ I(\theta) = n^2 I_1(\theta) P(\theta). \]  \hspace{1cm} (1)

The factor \( P(\theta) \) contains the interference effects between the
light scattered from the different units. If the units of the
molecule are numbered from one to \( n, \) according to their
position on the molecule,

\[ P(\theta) = \frac{1}{n^2} \left| \sum_{j=1}^{n} e^{iq(r_j)} \right|^2, \]  \hspace{1cm} (2)

where \( r_j \) is the location of the center of unit \( j, \) and \( q \) is the
scattering vector: \( q = k_f - k_r, \) where \( k_f \) and \( k_r \) are the
wave vectors of the incident and scattered light, respectively.
The magnitude of \( q \) is \( q = (4\pi \lambda) \sin(\theta/2) \) where \( \lambda \) is the wave-
length of light in the solvent.

The usual formula for a dilute solution of monodisperse
random coils is\(^{1-3}\)

\[ P(\theta) = D(q^2 R_g^2), \]  \hspace{1cm} (3)

where

\[ D(u) = (2/u^2)(e^{-u} + 1 - u). \]  \hspace{1cm} (4)

A graph of \( D(u) \) is given in Fig. 1.

The present work considers what happens when the


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coils are subjected to random scission. Let the average number of scissions per chain be \( r \). Then, using arguments analogous to those used to derive the above expression, we shall find

\[
I(\theta) = n^2 I_1(\theta) P(r, \theta),
\]
where \( R_\infty^2 \) is the radius of gyration of the original coils.

Two derivations are given below. The first is modeled on the Zimm, Stein, and Doty derivation as modified to include scission. We then give an alternate derivation of our result. In it we assume that the light scattering by a random coil is given by \( D(q) = \sum_{n} \sum_{j=1}^{n} e^{i q R_{\infty}^2} \), the number distribution function resulting from random scission of an initially monodisperse population of random coils, and, assuming that \( R_g \) is proportional to the square root of chain length, show that \( P(r, \theta) = D(r + q^2 R_\infty^2) \). The rationale for this second derivation is that molecules which cannot actually be Gaussian random coils are sometimes observed to scatter light similarly random coils, in which case the result still holds.

II. THEORY

A. First derivation

Simple manipulations of the above sum for \( P(\theta) \) gives, for a single orientation of the molecule,

\[
P(\theta) = \frac{1}{n^2} \left[ n + \sum_{j=1}^{n} \sum_{j=1}^{n} e^{i q R_{\infty}^2} \right],
\]
where \( r_{jk} = r_{kj} \), and the term \( n \) is the result of the sum with \( j = k \). It gives a contribution of \( 1/n \) to the final result for \( P(\theta) \). Since the final result is of order \( 1 \), and since we are going to let \( n \) be large, it can be discarded.

We now wish to discuss the averaging of \( P(\theta) \) over all molecular configurations. Dropping the \( 1/n \) term, the configurational average of \( P(\theta), \langle P(\theta) \rangle \), is given by

\[
\langle P(\theta) \rangle = \frac{1}{n^2} \sum_{j=1}^{n} \sum_{k=1}^{n} \langle e^{i q R_{\infty}^2} \rangle.
\]

If \( W_{jk}(r_{jk}) \) is the normalized probability density of \( r_{jk} \),

\[
\langle e^{i q R_{\infty}^2} \rangle = \int W_{jk}(r_{jk}) e^{i q R_{\infty}^2} d^3 r_{jk}.
\]

For a Gaussian random coil, one assumes that

\[
W_{jk}(r_{jk}) = \left[ \frac{3}{2 \pi b^2} \right]^{3/2} \exp \left[ -\frac{3 r^2}{2 b^2} \right],
\]
where \( b \) is the step size, or root-mean-square distance between adjacent monomers in the coil. Substituting Eq. (10) into Eq. (9) and integrating yields

\[
\langle e^{i q R_{\infty}^2} \rangle = e^{-\left[ q^2 b^2 |j-k|/\alpha \right]}.
\]

Thus, for a random coil the average contribution of any pair of units to \( P(\theta) \) falls off exponentially with the number of links between them.

Now we modify this to describe a randomly cut random coil. This is done by multiplying the average phase for any pair of units by the probability that no cuts have occurred between the two units after an average of \( r \) cuts have been made on the initial chain of \( n-1 \) total links, and then performing the double sum in Eq. (8). Thus we are assuming that when a strand is severed, the two pieces diffuse away from each other so that, for any pair of units on different pieces of the strand, the phase \( q R_{\infty}^2 \) modulo \( 2\pi \) is equally likely to have any value, and the average contribution to \( P(\theta) \) will be zero.

By random scission is meant that every link in a solution of polymers has an equal probability, \( p \), of being cut each time a new cut occurs. The average number of links cut per original chain is \( r = (n-1)p \). Let \( P(r, |j-k|) \) be the probability that after \( r \) cuts on a random coil no links between segment \( j \) and segment \( k \) have been cut. Then elementary arguments show that

\[
P(r, |j-k|) = \left[ \frac{1 - n^{-1}}{n-1} \right]^{r-|j-k|} e^{-r/n} \quad \text{as } n \to \infty,
\]
where we made the approximation \( 1/(n-1) \approx 1/n \).

The contribution from two units after \( r \) cuts is now given by

\[
\langle e^{i q R_{\infty}^2} \rangle = e^{-\left[ q^2 b^2 |j-k|/\alpha \right]} e^{-|j-k|/n}.
\]

The above expression shows how the simple additivity of \( \langle q^2 R_\infty^2 \rangle \) and \( r \) in the argument of Eq. (6) arises. The completely random nature of both the "walk" producing the initial random coil and of the subsequent scissions leads to exponential decays of both the average phase and the probability of surviving scission as a function of number of links between monomers.

Since the expected value of \( e^{i q R_{\infty}^2} \) depends on \( j \) and \( k \) only through \( |j-k| \) we can convert the double sum over \( j \) and \( k \) in Eq. (8) into a single sum over \( |j-k| \):

\[
P(r, \theta) = \frac{2}{n^2} \sum_{|j-k|} [n - |j-k|] \langle e^{i q R_{\infty}^2} \rangle.
\]

Letting \( t = |j-k|/n \) become a continuous variable of...
integration in the limit of large \( n \), whose limits run from 0 to 1, allows conversion of the above sum into the integral

\[
P(r,\theta) = \int_0^\infty (1 - t) e^{-1/2t} dt.
\]

(13)

Here, \( nb^2/6 = R_g^2 \). This integral yields the result given in Eqs. (4) and (6).

B. Second derivation

In this alternate derivation the polymer molecules are assumed to scatter light like random coils whether or not they actually are random coils. That is, it is assumed that the number density resulting from random scission of an initial molecule then gives the light scattering power and to clarify the practical difficulties involved in making this assumption.

\[
\frac{d}{dx} \left( \frac{P(r,\theta)}{2} \right) = \frac{d}{dx} \left( \frac{N}{2} \right) \delta(x - 1) + \frac{d}{dx} \left( \frac{N}{2} \right) \frac{2x}{\sqrt{\pi}} e^{-x^2/4}.
\]

(15)

The \( e^{-1/2} \delta(x - 1) \) represents the fraction of the original chains that remain. Graphs of \( f(r,x) \) (without the delta function) are given in Fig. 2 for various values of \( r \). In the integral for \( P(r,\theta) \), one uses \( l = \lambda l_\theta \) and \( u = x(R_g/q)^2 \), where \( R_g \) is the original radius of gyration. The result is, as advertised, that \( P(r,\theta) = D \left( r + (R_g/q)^2 \right) \).

Using \( f(r,x) \) the number average molecular weight, \( \bar{M}_n \), and the weight average molecular weight, \( \bar{M}_w \), are readily obtained

\[
\bar{M}_n = M_0 / (1 + r),
\]

(16)

\[
\bar{M}_w = M_0 (2/r^2) (e^{-r} - 1 + r).
\]

(17)

As \( r \) becomes large, the ratio of \( \bar{M}_w \) to \( \bar{M}_n \), a commonly used indicator of polydispersity, increases monotonically from a value of 1 at \( r = 0 \) to a limiting value of 2 at \( r = \infty \), because, for large \( r \), \( f(r,x) \) approaches the well-known exponential distribution, for which the number average, weight average, and \( z \) average are in the ratio 1:2:3.

III. EXPERIMENTAL EXAMPLE

In order to make the calculations above more concrete and to clarify the practical difficulties involved in making use of the present work a brief experimental section is included.

The polymer used was hyaluronate, an animal polysaccharide, obtained from Sigma (No. 5388), prepared as described in Ref. 8. Briefly, it was dissolved in 0.3 molar NaCl, run through a DEAE-Sephadex column to remove nucleic acids and sulfated glycosaminoglycans, dialyzed repeated times against deionized water, and freeze-dried and redissolved in distilled H\(_2\)O at 1 mg/ml to get back to a known concentration. It was then sonicated for several hours in a low power ultrasonic cleaner (Branson 1200) and filtered through a 0.45 \( \mu \) nylon filter. We believe that this treatment breaks up tangles of hyaluronate molecules and leaves it as isolated random coils. Before use the hyaluronate was centrifuged to remove dust that was not caught by the filter.

The scission process used was hydrolysis in HCl. Cleland\(^7\) reports that the rate of this process is proportional to hydrogen ion concentration with an activation energy of 30.5 kcal/mol. In our notation, his results can be written as

\[
r = 2.3 \times 10^{-9} (M_0 c t) \left[ e^{(30.5 \text{ kcal/K}_t)/e} - (30.5 \text{ kcal/K}_t/e) \right],
\]

(18)

where \( r \) is the number of scissions, \( M_0 \) the molecular weight in daltons, \( c \) the concentration in moles of hydrogen ions, \( T \) the temperature in degrees K, and \( t \) the elapsed time in minutes. The equation should only apply for \( r < n \). Cleland\(^8\) does not give uncertainties in the above parameters.

To ensure a reasonably large number scissions would occur over an observation period of several hours, equal volumes of 1 mg/ml hyaluronate and concentrated hydrochloric acid were combined. The hydrochloric acid had been centrifuged to remove dust. The estimated concentration of the resulting hydrochloric acid solution, allowing for the dependence of density on concentration, was between 5.96 and 6.22 molar. Equation (18) was used despite the fact that extrapolating to such high hydrochloric acid concentrations may be questionable. The temperature used was about 29.9°C.
The observations were made using a static and dynamic light scattering system which has previously been described in more detail. The light was of 4880 Å wavelength from a Coherent Innova Model 90-5 laser.

First, an angular scan was performed immediately after adding 5 ml of HCl to 5 ml of 1 mg/ml hyaluronate, yielding an estimate of the radius of gyration of the hyaluronate in the hydrochloric acid of $R_g = 550 \pm 50$ Å. The accuracy is not very high because the scan was performed quickly so as to minimize the number of scissions occurring during it, and no extrapolation to zero concentration was attempted. It was also affected by dust which escaped the centrifuging process.

Next, the intensity of the scattered light was monitored as a function of time at a scattering angle of 110°. Nine hundred equally spaced samples were collected; each sample consisted of the number of photons counted by a phototube in 10 s. Because of some dead time between points (the computer was doing cumulant analysis of dynamic light scattering between points) the elapsed time for the 900 data points was 267.5 min.

Finally, the light scattering intensity of the acidified hyaluronate solution was measured after five days, by which time most of the light scattering was done by pure solvent and some “dust.” (This was apparent by visual observation.) To compare with the time dependent measurements the intensity was recorded as a ratio to toluene scattering. The ratio of hyaluronate to toluene scattering had been measured before and after the time dependent run.

The intensities from the first measurement were fitted to the equation

$$I(N) = A \left( (2/u^2)(e^{-u} - 1 + u) \right) + B,$$

$$u = u_0 + RN,$$

where $A$, $B$, $R$, and $u_0$ are parameters in a nonlinear least-squares fit. Here $u_0 = (R_g g)^2$, $N$ is channel number, $R$ is the number of scissions per channel (about 17.8 s), $A$ is the estimated initial scattering intensity of the hyaluronate solution at zero angle without background scattering, and $B$ is the background level of scattering after the depolymerization is complete.

The fitting program used the Marquardt algorithm and was taken from Bevington’s book. It had previously been found that the fitting program performed very poorly when all four parameters were allowed to vary. Accordingly, the value of the background $B$ was set to its experimentally measured value and a three parameter fit was performed. Even this fit was unsatisfactory, as the convergence was slow and there were multiple local best fits. The measured value of $R_g$, was then used in fixing $u_0$, allowing a two parameter fit for $A$ and $R$ to be performed.

This two parameter fit converged rapidly to a unique result regardless of the initial values of $A$ and $R$. The intensity vs channel number results of the first measurement are plotted in Fig. 3(a). The peaks lying above the trend of the data are due to dust particles which wandered into the laser beam. The scatter in the data points is, we believe, due to counting statistics of the detector, concentration fluctuation of the base line, and dust particles which wandered into the laser beam. The scatter in the data points is, we believe, due to counting statistics of the detector, concentration fluctuations of an inherently polydisperse population, and dust. Because the scatter in the data points is about equal at all scattering intensities, all data points were weighted equally in the least-squares fit. The most egregious of the peaks due to dust particles were truncated before performing the fit. To do this an initial fit was performed with the dust peaks included. Then all points lying more than three standard deviations away from the fitting curve had their weights set to zero. This set of weights was used in all subsequent fits.

Figure 3(b) shows the results of a two parameter fit to this pruned data using a value for $B$ of 185 000 and 550 Å for $R_g$, yielding $u_0 = q^2 R_g$, of 2.58. The end result, considering the uncertainties in $R_g$ and $B$ is that the total number of scissions occurring during the 267.5 min of the run was $4.11 \pm 1.1\%$. From the formula, using $M_e = 645 000$ from the absolute scattering of an angular scan with no extrapolation to zero concentration, and approximately confirmed from a separate Zimm plot in water, we get a predicted number of scissions of $5.64 \pm 20\%$. This agreement is quite reasonable since we are extrapolating Cleland’s result to very high hydrogen ion concentrations and have assumed the starting material to be monodisperse. This latter assumption is based on an average polydispersity index of 0.19 (defined as the ratio of the second cumulant to the first cumulant squared in the power series expansion of the logarithm of the electric field autocorrelation function), which, from experience, represents a somewhat polydisperse sample. The scatter in the data points also contributed to the uncertainty.

Part of the reason for the existence of multiple fits even with the base line $B$ specified can be seen by inspecting Eq. (19) in the limit of large $u$:

$$I(N) \approx 2A / (u_0 + RN) + B.$$  (21)

Thus in the limit of large $u$, there are only three independent parameters and $I - B$ is not changed at all if $A$, $u_0$, and $R$ are multiplied by a constant factor.

In experiments where $u_0$ is large, or where the reciprocal of the base line subtracted intensity, $1/[I(N) - B]$, is lin-
ear over the entire observation period, it is insufficient to measure intensity vs time at a fixed angle: $R_{go}$ must be found independently, as in the current example, in order to determine the rate constant. Despite this disadvantage, a large starting value of $u_0$, or linear $1/[I(N) - B]$, has the pleasant feature of allowing a simple linear fit to the data.

Figure 4(a) shows a plot of the reciprocal of Eq. (4), $D^{-1}(u)$. The dashed lines show that the function is linear in the limiting cases of small $u$ and large $u$. The slopes are 1/3 (the familiar Zimm plot limit) and 1/2, and the $y$-intercepts 1 and 1/2, for the low $u$ and high $u$ limits, respectively. Intermediate ranges of $u$ may give approximately straight lines such as the data in Fig. 3(c), for example, and hence still be amenable to simple linear analysis. The rate constant for average cuts per molecule per channel $R$ can be estimated by

$$ R = \frac{D^{-1}(u_0) \int f(N_{tot}) - f(1)}{s(u) \int f(1)(N_{tot} - 1)}, \quad (22) $$

where $f(N) \equiv 1/[I(N) - B]$, $N_{tot}$ is the total number of data points, and $s(u)$ is the first derivative of $D^{-1}(u)$, and is plotted for convenience in Fig. 4(b).

For plots of $f(N)$ showing nonlinearity a second iteration may be performed to obtain a more accurate value of $R$, which will be called $R_2$. After first determining $R$ by Eq. (22) the improved value can be obtained by

$$ R_2 = \frac{D^{-1}(u_0) \int f(N_{tot}) - f(1)}{s[u_0 + R(N_{tot} - 1)/2] \int f(1)(N_{tot} - 1)}. \quad (23) $$

Using the midpoint for the improved rate constant $R_2$ is just a rule of thumb and should be employed with caution. Depending on the actual curvature of $f(N)$ it may be better to find the average slope by an appropriate averaging technique.

The linear fit to Fig. 3(c) yields a value for $r = RN_{tot}$ of 4.40 using values of $D^{-1}(u_0)$ and $s(u_0)$ in Eq. (22) of 2.010 and 0.4362, respectively, for $u_0 = 2.58$. This value is about 7% above the nonlinear least-squares value of 4.11. Applying the correction of Eq. (23) gives a value of $r = 4.06$, which is about 1% below the nonlinear least-squares value.

In principle, using a small angle to obtain a small $u_0$ would allow fixed angle intensity measurements to yield both $R_{go}$ and the rate constant. In practice, however, it is suspected that a small $u_0$ will be inaccurately fit if many cuts occur. Thus, a large $u_0$ may be preferable in these experiments, since it offers the use of a high observation angle, significantly reducing data scatter from dust, and also simplifies data analysis. The penalty, of course, is the need to find $R_{go}$ by an initial angular scan.

A second experiment carried out on hyaluronate of measured $R_{go} = 425 \pm 25\%$ at an observation angle of 90° ($u_0 = 1.14$) and a temperature of about 34.2°C yielded 7.7 to 12.9 total cuts over a 308 min run. For $M = 750,000$, determined by a separate Zimm plot, the value according to Cleland's results is 15.1.

Since one measures $P(\theta,t)$ in time dependent light scattering experiments, and the above theory gives $P(\theta,r)$, one needs a model to determine $r(t)$. A general rate equation for chemical depolymerization is

$$ \frac{d[B]}{dt} = -k[B][D], \quad (24) $$

where $[B]$ is the concentration of polymer bonds remaining, $[D]$ is the concentration of the depolymerizing agent, and $k$ is the second order rate constant. Given the original assumption that all bonds have the same probability of being severed, this equation yields no dependence of scission rate on the number of bonds in a polymer. (This assumption may fail for depolymerization reactions limited by the polymer diffusion.) $[B]$ is related to $r$ by $[B]_r(n - r)$, where $[B]_r$ is the original concentration of polymer bonds and $n$ is the original number of bonds per molecule. Thus

$$ \frac{dr}{dt} = k[D](n - r). \quad (25) $$

If $[D]$ is nearly constant and $r \ll n$ the assumption of constant rate of change of $r$ holds and the rate constant $k$ can be determined knowing $[D]$ and $n$. If $[D]$ is not constant then a model must be made for $[D]$ as a function of time or $[B]$.

For the acid hydrolysis of hyaluronate the encounter rate between hyaluronate and HCl should be limited by the HCl diffusion rate, so that the scission rate is expected to be independent of the hyaluronate polymers' chain lengths. The initial number of bonds per hyaluronate $n$ is about 3209, taking the average monomer weight of the monosaccharide in the disaccharide repeat unit to be 201, and the initial hyaluronate molecular weight to be 645 000. Since $r = 4.11$ in the first example, the criterion $n \gg r$ is fulfilled, so that from Eq. (25):

$$ k = \frac{dr}{dt} \frac{1}{n[HCl]}. \quad (26) $$

This yields a second order rate constant of $1.31 \times 10^{-8}$ (s mol) for hyaluronate at 29.9°C.

For the second experiment at 34.2°C, using $r = 10.3$ over 308 min, an initial number of bonds of 3712 and 6.09 M MCI yields $k = 2.46 \times 10^{-8}$ (s mol). Using Cleland’s activation energy of 30.5 kcal/mol gives a theoretical value of 0.49 for the ratio of rate constants at 29.9 and 34.2°C. The
ratio of the rate constants determined by the light scattering results presented in this section is 0.53, in reasonably good agreement with the theoretical value.

IV. DISCUSSION

We discuss the extent to which the assumptions made in the calculation, and especially the assumption of random scission, limit its applicability to static light scattering, and, finally, consider its significance for the related techniques of turbidimetry, low angle laser light scattering, and small angle x-ray scattering.

A major limitation on the practical usefulness of this technique is the need to prepare an approximately monodisperse starting sample. This could require repeated fractionation and be very tedious. As discussed in more detail below, it has sometimes been found that high power sonication breaks polymers down only to a certain minimum size, and yields low polydispersity. Perhaps this could sometimes help in preparing an approximately monodisperse starting solution.

The results presented above should be most useful for large molecules which scatter enough light enough to dominate the contributions from the solvent or from minor amounts of dust. It is anticipated that such studies would be done mostly with \( n < 10 \). In that case the approximations that \( n \) is large, and \( n \gg r \), should be good. However, it would also be necessary to use molecules that do behave much like random coils. This should be true if one can find a theta solvent for the polymer and operate at the theta temperature, and if the persistence length times the maximum \( r \) used is much less than the contour length of the original population. Under theta conditions the second virial coefficient, which has been ignored in this treatment, would be zero.\(^5\)

In a “good solvent” the molecule should eventually depolymerize from a random coil as \( n \) increases and the radius of gyration should then increase significantly faster than the 0.5 power of \( n \), as the 0.6 power\(^6\) or perhaps as the 0.588 power (from renormalization group calculations).\(^11\) However, this may not occur until the coil becomes extremely long. It is worth repeating that long polymers in “good” solvents often do scatter light much like random coils. If there is a nonzero excluded volume effect, one would expect there to be a significant second virial coefficient,\(^5\) making it necessary to extrapolate all results to zero concentration. If the polymer molecules tend to entangle and remain entangled for some time, even that must be done cautiously.

It should be possible to treat the second virial coefficient for light scattering approximately along the lines of Sec. 27d of Yamakawa.\(^5\)

We would like to say something about which forms of scission or degradation would be expected to be random. For a less superficial view one may consult Refs. 12 and 13. A model for many forms of scission, especially those due to chemical attack, considers them to be a mixture of random scission and “unzipping.”\(^12,13\) The nature of the polymerization/depolymerization reaction determines the rate of “unzipping” and an “unzipping distance,” i.e., the distance along the polymer the depolymerization proceeds before being terminated. Then the ratio of the original polymer contour length divided by the maximum value of \( r \) used to the unzipping distance is an important parameter. If this ratio is high, then, from the point of view of light scattering, the process closely resembles random scission. If there is no unzipping, then one might expect the process to be very near to random scission, with \( r \) nearly proportional to time if the attacking chemical was not depleted.

We also mention an extreme case of nonrandom scission in which there is only attack from the end(s) of a polymer. An example is attack by an exoenzyme on a biopolymer. The point is that here one gets a different function of angle and the amount of attack than that discussed above. Let \( l_0 \) be the distance by which the molecules have been shortened. Since \( n \) is large, and since the shortening is assumed to occur at the same average rate for all molecules, the distribution of \( l_0 \) should be very narrow. As a first approximation we therefore say that \( l_0 \) is the same for all molecules. Then the molecules new contour length is \( l_0 = l_n \), and, still assuming that they scatter like random coils, and ignoring the scattering from dissociated monomers, which should be negligible, we get

\[
P(l_n, \theta) = D(u) = \frac{2}{u^2} (e^{-u} - 1 + u),
\]

where

\[
u = q^2 R_g^2 \left( 1 - l_n/\ell_0 \right)
\]

which is qualitatively different from the form \( u = q^2 R_g^2 \) which we found above. For example, if one does an angular scan, one finds that \( P(\theta) \approx D(q^2 \times \text{constant}) \). which is not true for random scission. Thus, the two forms of scission can in principle be experimentally distinguished.

In mechanical degradation it is often found that the polymer is broken down only to a certain minimum size.\(^12,13\) Degradation by means of ultrasound is one of the more studied forms of mechanical degradation. As already mentioned above, some success has been enjoyed by the rather crude model\(^12\) that scission by ultrasound is random for chains above a certain critical length, which depends on the intensity of the ultrasound, and no scission at all occurs for shorter chains.

Finally, Mazur\(^14\) considers two mathematical models for enzymatic degradation of polysaccharides; the “multiple attack” model and the “preferred attack” model. Random scission is a special case of both models, and both models, except at the smallest product sizes, are predicted to produce results similar to random scission. Thus, random scission is an important special case of all the models mentioned above.

In these experiments the assumption made at the outset of the derivations lead to the prediction of relatively simple behavior. If it does not occur then at least one of these assumptions is incorrect. For example if one is looking at scission of a biopolymer by an enzyme, and the enzyme is deactivated by the product, the rate of scission will decline below that predicted. Or, if one were sonicating long molecules, and polymers of less than a certain size tended not to break during sonication while longer molecules broke almost randomly, the process should resemble random scission at first but...
the intensity as a function of time should level off at a final value higher than predicted. If one failed to find such a deviation one could say that, within the usual limitations of static light scattering, the assumption of random scission was justified.

It should be pointed out that light scattering methods have been used to investigate a considerable variety of causes of scission or degradation of polymers, including enzymatic attack, photolysis, and mechanical degradation by forcing a polymer through a GPC column. Most commonly this has been done by measuring $M_w$, by either static light scattering or low angle laser light scattering. The current discussion is offered as a supplement rather than a replacement to such methods.

In summary, two interesting results can be gained from time dependent static light scattering measurements of depolymerization. First, it can be determined, in principle, for example by an angular scan, if the depolymerization reaction being studied is really of the random scission type. If it is, then the rate or rate constant for the scission can be found, as in the experimental example above. Perhaps, relaxing the assumption of a constant rate of scission, more than the initial rate of the reaction could be determined. For example, with a nonconstant rate model for $r$, it may be possible to determine if there is end-point inhibition of an enzyme.

The turbidity $\tau$ of a solution is the inverse of the distance an incident plane wave must travel through the solution before its strength is decreased to $1/e$ of its original strength. Assuming no absorption it can be found by integrating the total light scattering by the solution over $4\pi$ steradians. If single scattering by polymer molecules is dominant, the integral is

$$\tau = \frac{2\pi n^2_0 M}{N_e \lambda^4} \left[ \frac{dn}{dc} \right]_0^\infty \int_0^\infty P(r, \theta) [1 + \cos^2(\theta)] d\theta$$

(29)

regardless of the polarization of the incident beam. Here, $N_e$ is Avogadros' number, $M$ is the molecular weight, $n_0$ is the index of refraction in solvent, and $(dn/dc)_0$ is the rate of change of index of refraction with solute concentration at zero solute concentration. The integral for $\tau$ can be readily expressed in terms of the exponential integral: the result is messy and not particularly illuminating and so will not be reproduced here. In turbidimetry one can of course follow scission as a function of time, but cannot say anything about the angular dependence of the scattering. Furthermore, the turbidity of many polymer solutions is quite low and so not amenable to accurate measurements.

In low angle laser light scattering, one observes the light scattering at a very small angle to the incident beam so that the scattering vector $q$ is very small. If dust has been removed, one can then measure the weight-average molecular weight, which for random scission of a long polymer is given by Eq. (17).

By contrast, for small angle x-ray scattering, one can measure the scattering at larger values of $q$ than for static light scattering. The present calculation probably has only limited applicability to small-angle x-ray scattering, because it assumes the interunid distances to be larger than the persistence length of the polymer, while for many polymers small-angle x-ray scattering can measure the persistence length directly. Thus the present calculation applies to small-angle x-ray scattering only at sufficiently low scattering angles.

V. CONCLUSIONS

Random scission is an important special case of many forms of polymer degradation. If an initially monodisperse population of randomly coiled molecules is subjected to random scission its light scattering power is a function of $(qR_{sc})$ plus the average number of scissions per molecule. The authors know of no other polymer mass distribution other than the random coil for which random scission preserves the functional form of the form factor $P(\theta)$.

The experimental example contained in this work illustrates a simple light scattering methodology for determining the depolymerization rate constant of hyaluronate under acid hydrolysis. Performing the time dependent scattering measurements at large $\omega_0$, both reduces data scatter from dust and allows for a simple linear data fitting analysis, providing that $R_{sc}$ is independently measured.

The authors hope that the results presented here will be useful for the study of polymer degradation in dilute or semidilute by means of time dependent total intensity light scattering. They may also have some applicability to low angle laser light scattering and turbidimetry, and to small-angle x-ray scattering at sufficiently low values of $q$.

ACKNOWLEDGMENTS

Support for this work from the National Science Foundation under Grant No. DMB-8803760 and from the Louisiana Board of Regents is gratefully acknowledged.