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Molecular Weight Distribution of Polymers from Rheological Measurements in Dilute Solution

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A method for obtaining the molecular weight distribution of linear polymers from rheological measurements in dilute solution is obtained through the use of the normal-coordinate theory of viscoelasticity as modified by Zimm to include hydrodynamic interactions.

Equations for the frequency-dependence of viscoelastic properties in dilute solutions are shown to the form $\Phi(\omega) = \sum p \lambda_{p}^{-\gamma}(\omega \lambda_{p}^{-\gamma})$, where $\Phi(\omega)$ is a measurable, frequency-dependent viscoelastic property. The summation extends over the set of characteristic values $\lambda_{p}$ which accounts for the relaxation of various normal modes of motion of the molecule as perturbed by hydrodynamic interaction with the solvent; and $f(\omega \lambda_{p}^{-\gamma})$ is directly related to the molecular weight distribution through an integral equation

$$\lambda_{p}^{-\gamma} f(\omega \lambda_{p}^{-\gamma}) = \int_{0}^{\infty} K(M, \omega) W(M) dM,$$

where $W(M)$ is the weight fraction of molecules in range $dM$ at $M$ and $K(M, \omega)$ is a kernel dependent upon the quantity measured. Inversion of the above summation has been accomplished for the particular case of characteristic values which obey the inequality, $\sum p \lambda_{p}^{-\gamma} < \lambda_{-}^{-\gamma}$, so that $f(\omega \lambda_{p}^{-\gamma})$ may be obtained directly from the experimentally measured $\Phi(\omega)$. $W(M)$ is then obtained from $f(\omega \lambda_{p}^{-\gamma})$ through a solution of the integral equation.

INTRODUCTION

RECENTLY the author and his fellow workers have been devising methods for the experimental determination of the normal-coordinate theory of viscosity for utilizing the theory to determine molecular weights of polymers. The approach here reported is different from that of the normal-coordinate theory of viscoelasticity and can be advocated until the effect of polydispersity is sufficiently well understood. In fact it may be shown that the predictions of the normal-coordinate theory are extremely sensitive to even slight departures from monodispersity.

In the past, very few measurements of the viscoelastic properties of dilute solutions of linear polymers have been made because of the great experimental difficulties involved in such measurements. However, Birnboim and Ferry have recently designed an apparatus which appears to be very successful in overcoming the difficulties involved in such measurements. How­ever, Birnboim and Ferry

$\Phi(\omega) = \sum p \lambda_{p}^{-\gamma}(\omega \lambda_{p}^{-\gamma})$,

where $\Phi(\omega)$ is a measurable, frequency-dependent viscoelastic property. The summation extends over the set of characteristic values $\lambda_{p}$ which accounts for the relaxation of various normal modes of motion of the molecule as perturbed by hydrodynamic interaction with the solvent; and $f(\omega \lambda_{p}^{-\gamma})$ is directly related to the molecular weight distribution through an integral equation

$$\lambda_{p}^{-\gamma} f(\omega \lambda_{p}^{-\gamma}) = \int_{0}^{\infty} K(M, \omega) W(M) dM,$$

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COMPLEX VISCOSITY OF WHOLE POLYMERS

The $p$th relaxation time of a polymer molecule containing $j$ monomers in a dilute solution of a whole polymer is given by

$$\tau_{pj} = \rho b^{2}/6kT \lambda_{p},$$

where $b^{2}$ is the mean-square end-to-end length of a submolecule, $\rho$ is the friction factor, $\lambda_{p}$ is the $p$th characteristic value of a polymer molecule containing $j$ monomers. For dilute polymer solutions, Zimm has obtained the following equation for the characteristic values:

$$\lambda_{p} = 4N_{j}^{3/2} \lambda_{p} \rho / \eta_{p}^{3} (12\pi)^{3/2} \lambda_{p}$$

where $N_{j}$ is the number of submolecules in the $j$th polymer molecule, $\rho$ is the friction factor, $\lambda_{p}$ is the $p$th characteristic value as calculated by Zimm, Roe, and Epstein, and $\eta_{p}$ is the viscosity of the solvent.

The complex viscosity of a polymer in dilute solution is given by the equation:

$$\eta^*(\omega) - \eta_s = \sum_{j=1}^{\infty} \left( W_j/M_j \right) c R T \sum_{p=1}^{\infty} \tau_{pj} \left[ 1 + i \omega \tau_{pj} \right]^{-1},$$

where $$W_i$$ is the weight fraction of the $$j$$th polymer molecule, $$\eta^*(\omega)$$ is the complex viscosity, $$c$$ is the polymer concentration, and $$i = (-1)^{1/2}$$. Combining Eqs. (1)–(3) with the fact

$$\sum_{j=1}^{\infty} \lambda_j^{-1} = 0.586,$$

we have the following result for the viscosity of a whole polymer at zero frequency,

$$\eta^*(0) - \eta_s = \frac{[\eta(0)]}{c n_s} = N_a (12 \pi \eta)^{3/5} \sum_{j=1}^{\infty} \frac{W_j N_j^4}{24 M_j},$$

where $$L$$ is the root-mean-square end-to-end length of the whole polymer chain defined by $$L_j = N_j b$$, and $$N_a$$ is Avogadro’s number. Equation (5) is a statement for whole polymers of Zimm’s result for polymer fractions. If in Eq. (4) we assume that the number of submolecules $$N_i$$ is proportional to the molecular weight, i.e., $$N_i = K_i M_i$$, we have

$$\eta^*(0) - \eta_s = N_a (12 \pi \eta)^{3/5} \sum_{j=1}^{\infty} \frac{W_j N_j^4}{24 M_j}.$$
For an equation of the form of Eq. (12) we require that \( \Phi(\omega) \) and \( f(\omega) \) be finite and single-valued for all values of \( \omega \). Consequently, the right-hand side of Eq. (12) must converge for all values of \( \omega \). The function \( f(\omega) \) will have a maximum value, which in our case is \( f(0) \). Consequently at \( \omega = 0 \) we have

\[
\Phi(0) = f(0) \sum_{p=1}^{N} \lambda_p^{-n}.
\]

From this we have the condition that

\[
\sum_{p=1}^{N} \lambda_p^{-n} = \Lambda,
\]

where \( \Lambda \) is finite and must remain finite even as \( N \) goes to infinity. In order to obtain an inverse of Eq. (12) we begin subtraction of

\[
\sum_{j=2}^{N} (\lambda_j^{-n} \lambda_1^n) \Phi(\lambda_j^{-m} \lambda_1^m \omega)
\]

from both sides of Eq. (12) with the result

\[
\Phi(\omega) - \sum_{j=2}^{N} (\lambda_j^{-n} \lambda_1^n) \Phi(\lambda_j^{-m} \lambda_1^m \omega) = \lambda_1^{-n} f(\lambda_1^{-m} \omega)
\]

Thus we see that the term \( \lambda_1^{-n} \Phi(\lambda_1^{-m} \lambda_1^m \omega) \) is a part of the remainder. Adding an additional term gives

\[
\Phi(\omega) - \sum_{j=2}^{N} \lambda_j^{-n} \Phi(\lambda_j^{-m} \lambda_1^m \omega)
\]

where \( \lambda_1^{-n} \Phi(\lambda_1^{-m} \lambda_1^m \omega) \) is a product of the reciprocal of \( \alpha \) characteristic values.

The criteria convergence of the inversion may be shown as follows: The function \( f(\omega) \) has its largest value at some value of \( \omega \), which for our specific case is \( \omega = 0 \). If the remainder converges to zero at this value of \( \omega \), it must converge for all other values of \( \omega \). The difference in absolute values between two successive remainders of the \((\alpha+1)\)th and \(\alpha\)th terms, respectively, is

\[
\sum_{j=2}^{N} \sum_{k=2}^{N} \sum_{p=2}^{N} \lambda_p^{(\alpha+1)n} \lambda_1^{-n} \lambda_j^{-n} \cdots \lambda_i^{-n} \lambda_1^{(\alpha+1)n} \omega
\]

\[
\{\alpha+1 \text{ sums in all}\}
\]

\[
- \sum_{j=2}^{N} \sum_{k=2}^{N} \sum_{p=2}^{N} \lambda_1^{(\alpha-1)n} \lambda_1^{-n} \lambda_j^{-n} \cdots \lambda_i^{-n} f(0)
\]

\[
\{\alpha \text{ sums in all}\}
\]

\[
= \left[ \sum_{j=2}^{N} \lambda_j^{-n} \lambda_1^n \right] \lambda_1^{-n} f(0) \left[ \sum_{j=2}^{N} \lambda_j^{-n} \lambda_1^n - 1 \right].
\]

Consequently if

\[
\lim_{\alpha \to \infty} \sum_{j=2}^{N} \lambda_j^{-n} \lambda_1^n = 0
\]

the series will converge. This will be true if

\[
\sum_{j=2}^{N} \lambda_j^{-n} / \lambda_1^{-n} < 1
\]

or

\[
\sum_{j=2}^{N} \lambda_j^{-n} < 2 \lambda_1^{-n}.
\] (15)

For the characteristic values of Rouse, \( \lambda_p = \rho \) and

\[
\sum_{p=1}^{\infty} \lambda_p^{-1} = 0.586
\]

and \( \lambda_1^{-1} = 0.25 \) so that \( \sum_{p=1}^{\infty} \lambda_p^{-1} > 2 \lambda_1^{-1} \) and this inversion formula will not converge. However,

\[
\sum_{p=1}^{\infty} \lambda_p^{-2} = 0.0703 < 2 \lambda_1^{-2} = 0.124,
\]

so that an equation of the form

\[
\Phi'(\omega) = \sum_{p=1}^{N} \lambda_p^{-1}(d/d\omega) f(\lambda_p^{-1} \omega) = \sum_{p=1}^{N} \lambda_p^{-2} f'(\lambda_p^{-1} \omega)
\]

could be inverted, provided \( \Phi'(\omega) \) and \( f'(\omega) \) are everywhere finite. The derivative of Eq. (12) is

\[
\eta''(\omega) = cB^2 RT \sum_p \lambda_p^{-2} I^*(\omega \lambda_p^{-1}),
\] (17)

where

\[
I^*(\omega \lambda_p^{-1}) = -i \int_{\omega}^{\infty} M^2 W(M) dM (1 + i \omega \lambda_p^{-2} BM)^{-2}
\]

Equation (17) has the disadvantage that the integral equation (18) is relatively difficult to solve, even for \( p = 1 \).
An alternative way of meeting this problem is to use the imaginary part of the complex viscosity (or the real part of the complex modulus) divided by the frequency as follows:

$$\xi(\omega) = cB^2RT \sum \lambda_\beta^{-2}I_2(\omega \lambda_\beta^{-1})$$  \hspace{1cm} (19)

where

$$I_2(\omega \lambda_\beta^{-1}) = \int_0^\infty M^2W(M) \frac{dM}{1 + \omega^2B^2\lambda_\beta^{-2}M^2}$$  \hspace{1cm} (20)

Before solving for $I_2(\omega \lambda_\beta^{-1})$ in terms of $\xi(\omega)$ we observe that Eq. (14) may be simplified as shown in the appendix to obtain a sum of $N$ terms rather than an infinite number. Such a sum is still rather tedious to write out so, for the present, we will deal with Eq. (14) symbolically. Consequently, if

$$\Phi(\omega) = \sum_{\beta=1}^{N} \phi(\lambda_\beta^{-m_\omega}) = \mathcal{S}_N\{ f(\omega) \}$$

and if

$$\sum_{\beta=1}^{N} \lambda_\beta^{-n} < 2\lambda_1^{-n},$$

the inverse $\mathcal{S}_N^{-1}\{ \xi(\omega) \}$ and we may write

$$\Phi(\omega) = \sum_{\beta=1}^{N} \phi(\lambda_\beta^{-m_\omega}) = \mathcal{S}_N\{ f(\omega) \}.$$  \hspace{1cm} (21)

The exact evaluation of the shortest form for $\mathcal{S}_N^{-1}\{ \xi(\omega) \}$ will be described in the Appendix. However, if $\Phi(\omega)$ is known for all values of $\omega$, then $f(\lambda_1^{-m_\omega})$ may be obtained from this equation.

### SOLUTION OF THE INTEGRAL EQUATION

If, in Eqs. (12), and (21) we set $m=1, n=2,$

$$\Phi(\omega) = \xi(\omega), \quad \lambda_\beta^{-n}f(\lambda_\beta^{-m_\omega}) = \lambda_\beta^{-2cB^2RTI_2(\omega \lambda_\beta^{-1})},$$

we have the following integral equation:

$$cB^2RT\lambda_1^{-2} \int_0^\infty M^2W(M) \frac{dM}{1 + \omega^2B^2\lambda_1^{-2}M^2} = \mathcal{S}_N\{ \xi(\omega) \},$$

making the substitution, $z = \lambda_1^{2}B^{-2}M^{-3},$ and $y = \omega^2,$ we have

$$\int_0^\infty G(z) \frac{dz}{y+z} = \mathcal{S}_N\{ \xi(\omega) \} = \text{St}[G(z)],$$  \hspace{1cm} (22)

where St is the Stieltjes transform operator and $G(z) = (cRT/3z) W(B^{-2}\lambda_1^{2}B^{-2}z^{-1/2}).$ Using the inverse Stieltjes operator $\text{St}^{-1}$ we may write the weight distribution function

$$W(M) = \frac{3\lambda_1^{2}B^{-2}M^{-3}}{cRT} \text{St}^{-1}\{ \xi(\omega) \},$$  \hspace{1cm} (23)

where $M = (\lambda_1/\omega B)^{2/3}$. Using the inverse Stieltjes operator of Hirshmann and Widder\(^{15}\) we obtain

$$W(M) = \frac{3\lambda_1^{2}B^{-2}M^{-3}}{cRT} \lim_{\nu \to \infty} (-1)^{\nu} \frac{d^\nu}{d(\omega^2)^\nu} \left[ \frac{\omega^2}{\omega^2} \right] \mathcal{S}_N\{ \xi(\omega) \}.$$

For very broad molecular weight distribution $\nu=1$ or $\nu=2$ will generally suffice. For distribution containing sharp curves or corners, this is not a practical method, and numerical methods for the inverse of this integral equation must be found. The type of numerical method selected will depend to some extent upon the type of data under study. An excellent discussion of numerical solutions of integral equations is given by Kopal.\(^{16}\) One of the simplest numerical methods is the conversion of Eq. (22) into a series of nonhomogeneous simultaneous equations using a quadrature formula to express the integral as a sum. Such a procedure gives the molecular weight distribution from matrix inversion of the simultaneous equations.

Sums of the form of Eq. (21) as well as matrix inversions are easily performed by use of modern high-speed computers.

### APPENDIX

The infinite sum

$$\mathcal{S}_N\{ \xi(\omega) \},$$

may be written

$$\Phi(\omega) = \sum_{\beta=1}^{N} \phi(\lambda_\beta^{-m_\omega}) = \mathcal{S}_N\{ f(\omega) \} = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{(-\lambda_1^{-n})^i}{i!} \frac{(-\lambda_1^{-n})^j}{j!} \frac{(-\lambda_1^{-n})^k}{k!} \lambda_\beta^{-ns} \phi(\lambda_\beta^{-m_\omega}),$$

where each term contains an increasing number of sums of products, and there are an infinite number of terms. This sum may be simplified considerably. The index number of a term is defined as the number of sums (or products) it contains. We will call an internal term a particular product in some given term.

Let us consider a particular term, say, for example, the fourth term. This term has an index number of 4 and may be written

$$(-\lambda_1^{-n})^4 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \lambda_\beta^{-ns} \phi(\lambda_\beta^{-m_\omega}) \times \mathcal{S}_N\{ \xi(\omega) \}. $$

When all of the subscripts are different there will be $4!$ internal terms of exactly the same quantity. Thus all of the internal terms with unlike indices of index number


4 may be groupd together to give

\[ 4!(-\lambda^n_i)\sum_{i>j>k}^{N-1} \sum_{i>j}^{N-2} \sum_{i>j}^{N-3} \lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_i^{-n} \times \Phi(\lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_i^{-n} \omega) \]

Similarly there will be only one of each internal term of index 4 with identical indices,

\[ (-\lambda^n_i)\sum_{i=1}^{N-1} \lambda_i^{-n} \Phi(\lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_i^{-n} \omega) \]

In general there will be an internal term for each partition of the index number, in this case 4. The partitioning of 4 may be illustrated as follows:

\[
\begin{align*}
1/1/1/1 & \text{ all different} \\
1 & \text{ 1/1/1 two alike; two different} \\
1 & \text{ 1/1/1 two alike; two alike} \\
1 & \text{ 1/1 three alike; one different} \\
1 & \text{ 1 1 1 four alike.}
\end{align*}
\]

The collection of internal terms illustrated above are for the first and last of these partitions. The collection together of all of the internal terms of index 4 in which two indices are alike and two are different gives

\[
\frac{4!}{2!}(-\lambda^n_i)\sum_{i>j>k}^{N-1} \sum_{i>j}^{N-2} \sum_{i>j}^{N-3} \lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_i^{-n} \times \Phi(\lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_i^{-n} \omega) \quad \text{(28)}
\]

For the \(\alpha\)th term, there will be a collection of internal terms for each of the partitions of \(\alpha\). If these collections of internal terms are added together, they equal the original sum, but, all of the terms in the new sum are now completely different from each other. This results in an enormous reduction in work necessary to compute \(\Phi(\omega)\).

The new terms may be written as follows:

\[
\Phi(\omega) = \Phi(\omega) + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-\lambda^n_i) \lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_l^{-n} \lambda_m^{-n} \lambda_n^{-n} \times \Phi(\lambda_i^{-n} \lambda_j^{-n} \lambda_k^{-n} \lambda_l^{-n} \lambda_m^{-n} \lambda_n^{-n} \omega) \quad \text{(29)}
\]

Thus the very complicated sum of Eq. (25) containing an infinite number of terms may be replaced with a sum which contains only \(N\) terms; in this case \(N=3\).

In our previous publication, Menefee and the author\(^1\) gave a recursion formula for use in the inversions of finite sums where the characteristic values were integers. It appears, however, that for finite sums, the approach outlined here might be preferable even when the characteristic values are integers.