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Molecular Weight Distribution of Water-Soluble Polymers: A New Absolute Method

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ABSTRACT: A new absolute MWD method for polymers, based on band sedimentation and low-angle laser light scattering (LALLS), has been demonstrated. It is especially useful for water-soluble polymers. Unlike size-exclusion chromatography/LALLS, polymers with $M > 10^7$ are readily analyzed, no shear degradation should occur, and adsorption is minimal. Excellent light-scattering data are obtained, even with water, because band sedimentation not only separates the sample according to M but also clarifies the solution. The resolution of the method was demonstrated with clean separations of mixtures of two narrow-MWD poly(sodium styrenesulfonates), PNaSS, with $M_w = 100\,000$ and $400\,000$. Another PNaSS sample with nominal $M_w = 1.2 \times 10^6$ was found to have three distinct peaks with $M = 1.3$, 1.8, and 2.8×10^6. The power of the method for $M > 10^7$ was further demonstrated by analysis of a broad-MWD poly(sodium 2-(acrylamido)-2-methylpropanesulfonate) sample, PNaAMPS ($M_w = 43 \times 10^6$), and with a monodisperse viral DNA(T5) having $M = 68 \times 10^6$. The T5 polymer exhibited a very sharp peak with $M_w = 66 \times 10^6$ and $M_n = 65 \times 10^6$.

Introduction

Size-exclusion chromatography (SEC) has become the most commonly used method for measuring the molecular weight distribution (MWD) of polymers. Since SEC fractionates according to size rather than mass, suitable calibrations and standards are needed.[1] Recently, low-angle laser light scattering (LALLS) has been coupled with SEC to create an absolute MWD method.[2-4] This technique requires no external standards. Nevertheless, any SEC method (with or without LALLS detection) has polymer molecular weight and polarity limitations.[5-9]

For example, very large molecules ($M_w > 5\text{–}10 \times 10^6$) are subject to shear degradation in the SEC column or related hardware.[6,7] In addition, water-soluble polymers often exhibit undesirable non size exclusion effects such as ion exchange, ion exclusion, and adsorption. Case by case studies of columns, solvents, and additives are required to render water-soluble polymers tractable for SEC[9-15] or SEC/LALLS.[4,16,17]

This paper describes a new absolute MWD technique based on a combination of band sedimentation and LALLS. Band sedimentation alone has been applied previously to biological particles with M as large as 10^8.[18,19] Like SEC, band sedimentation by itself is not an absolute method; it fractionates according to mass M and inversely with friction factor f. Its potential as a separation technique for polydisperse synthetic macromolecules has been largely eclipsed by SEC. Two methods have been used previously to obtain an absolute M from sedimented bands. Sedimentation and diffusion coefficients, measured by inelastic light scattering on the centrifuge tube, have been shown to give accurate M's for two biological particles having $M = 1.7 \times 10^6$ and 3.8×10^6.[20] Band sedimentation and intrinsic viscosity have been used to obtain the MWD of two commercial polydisperse water-soluble polymers, xanthan[21] and polyacrylamide.[22] A third combination, band sedimentation with LALLS, is presented here. It offers absolute MWD's well beyond the SEC range, without shear degradation or adsorption. Moreover, because centrifugation also clarifies the sample, excellent light-scattering data are obtained, even with aqueous samples. We call this combination of sedimentation and light scattering S/LALLS.

Principle

Band sedimentation is a technique for separating particles according to their sedimentation velocity.[18,19] A thin band of polymer solution is first layered onto the top of a centrifuge tube otherwise filled with solvent. The tube is then accelerated to an angular frequency of 400–667 Hz (24000–40000 rpm). Under the resultant centrifugal field, the polymer molecules move from the meniscus toward the bottom of the tube. Their radial velocity dr/dt is equal to $s\omega^2 r$, where s is the sedimentation coefficient, r is the distance from the rotor center, and ω is the rotor angular velocity. Separation occurs because s depends on M according to the Svedberg equation,[23,24]

$$s = M(1 - v_2\rho)/N_A f \qquad (1)$$

where v_2 is the partial specific volume of the polymer, ρ is the solvent density, N_A is Avogadro's number, and f is the friction factor. For coils, $s = HM^a$, where H is a constant and $a = 0.4\text{–}0.5$. When the fastest molecules have almost reached the bottom of the tube, the rotor is decelerated, and the tube is analyzed to determine the polymer concentration and M at different heights.

Figure 1 shows the analysis scheme; it consists of a density gradient analyzer, a concentration detector, the LALLS detector, and a computer. The gradient analyzer, a syringe pump, slowly injects a dense chase solution through a needle into the bottom of the tube. The chase solution displaces the tube contents out of the top of the tube in a pistonlike manner to minimize mixing.[25]

The tube contents then flow to the concentration detector. A variety of techniques could be used to determine polymer concentration c_p at each point in the tube; we used UV absorbance at 214 nm because of its sensitivity and convenience with the polymers of interest to us. After flowing through the UV detector, the solution moves on to the flow-through cell of the LALLS photometer (Figure 1).

The intensity of scattered light measured by the LALLS detector is given by the relation[2,4,26]

$$i_s = I_0 K c_p M/(1 + A_2 c_p M) \qquad (2)$$

where I_0 is the incident beam intensity; the constant K includes determinable instrumental, solvent (n), and solute (dn/dc) parameters that do not depend on M. The simplicity of eq 2 is a consequence of the small scattering angles (2–6°) in the photometer which make it unnecessary to measure i_s at several angles in order to obtain M. For

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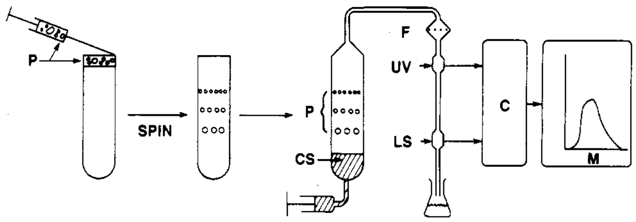

Figure 1. Schematic description of the S/LALLS experiment. At the left, a thin layer of polymer solution P is applied with a syringe to the top of a centrifuge tube. The tube is then spun; this separates heavy molecules (large circles) from lighter ones (small circles). The tube is analyzed by injection of a dense chase solution CS into the bottom of the tube; this displaces the sample through filter F, the UV detector, and the LALLS detector LS. The computer C takes data from the UV and LALLS detectors and computes the molecular weight distribution.

precise work, especially for high molecular weights, the virial coefficient A_2 for the polymer–solvent system must be considered unless the solution is very dilute.

The electrical signals from the concentration and LALLS detectors are fed to a small digital computer. The computer calculates and plots the MWD curve in various forms.

Materials and Methods

Density Gradients. Sample tubes were prepared in plastic tubes for a Beckman SW40 rotor, which has six buckets. This allows simultaneous centrifugation of duplicate samples, different polymer concentrations, or different samples in a single run of the ultracentrifuge. An Isco Model 570 gradient maker was used to partially fill the tubes with a linear density gradient prepared from mixtures of solutions A and B: A = 0.70 M Na_2SO_4 + 50 mM NaH_2PO_4/Na_2HPO_4 buffer, pH 7.0, ρ = 1.087 g/cm^3; B = 0.35 M Na_2SO_4 + 50 mM NaH_2PO_4/Na_2HPO_4 buffer, pH 7.0, ρ = 1.046 g/cm^3. Solutions A and B were filtered through 0.2-μm Millipore filters prior to use.

The function of the density gradient is to stabilize the tube against convection. It must be steep enough to ensure band stability,[19] but if it is too steep, corrections must be applied for the gradient in n, dn/dc, and A_2. The salt Na_2SO_4 was chosen because it is transparent at 214 nm, gives low-viscosity solutions, and is nonaggressive toward the stainless steel encountered in a parallel HPLC study.

The polymer sample, typically containing 50–500 μg/mL of polymer dissolved in 0.18 M Na_2SO_4 + 25 mM PO_4 buffer, pH 7, was layered slowly onto the top of the gradient by a motorized syringe pump; the applied volume was 0.2–0.5 mL. Finally, the syringe pump was used to apply a 0.8-mL "blanket buffer" containing 0.09 M Na_2SO_4, 12.5 mM NaH_2PO_4/Na_2HPO_4, pH 7. The blanket separated the sample from the meniscus, which tended to collect dust and thus gave poor light-scattering data.

Polymer Samples. Poly(sodium styrenesulfonates) were purchased from Pressure Chemical Co., as follows: (1) M_w (Na salt) = 100 000, M_w/M_n = 1.10; (2) M_w = 400 000, M_w/M_n = 1.1; (3) M_w = 780 000, M_w/M_n = 1.1; (4) M_w = 1 200 000, M_w/M_n = 1.1.

Poly(sodium 2-(acrylamido)-2-methylpropanesulfonate), PNaAMPS, was a nonstandard, high molecular weight sample from Lubrizol Co. Two DNA's, from bacteriophages λ and T5, were purchased from Sigma Chemical Co. Their molecular weights were 31 × 10^6 and 68 × 10^6, respectively.

All polymer samples were dissolved in distilled water without purification. Before layering onto the centrifuge tube, a concentrated buffer was added to each sample to make its solvent 0.18 M Na_2SO_4 + 25 mM PO_4, pH 7.

Centrifugation and Tube Analysis. The tubes were spun for 3–18 h at 23 °C in a Beckman L8-70 ultracentrifuge at 25 000–40 000 rpm (70000–190000g). After centrifugation, a density-gradient analyzer (Isco Model 185) was used to displace the tube contents upward at a rate of 0.75 mL/min through a Nuclepore or Millipore filter with 0.4–1.0-μm pore diameter; the tube contents then traversed an Isco UV analyzer operating at 214 nm and finally passed through the LALLS detector (Chromatix KMX-6). The UV optical path length was 0.2 or 1.0 cm; the LALLS path length was 1.5 cm. Figure 1 shows the analysis scheme diagrammatically.

The data from the UV analyzer and LALLS photometer were plotted directly on a two-pen recorder and simultaneously stored digitally by an HP 9836 computer. Two-hundred LALLS readings were collected, despiked, and averaged by the computer in 6 s; 20 UV readings were then collected in 1 s and averaged, and the process was repeated with a 10-s period. About 80 such cycles occurred during the analysis of a single tube. After UV and LALLS data were recorded for a tube, the LALLS beam intensity I_0 was recorded. On the KMX-6 instrument, this is done by sending an accurately attenuated laser beam directly to the detector at 0 angle.[26] The entire data set was then stored for analysis at a later time.

Data Analysis. The polymer concentration c_p was determined from the measured absorbance A at 214 nm and the optical path length L by using the relation $c_p = kA/L$. To determine k, a sample of the polymer was first purified by dialysis. After A was determined for this solution, the value of c_p was determined by lyophilizing a measured volume of the solution and determining the mass of polymer by thermogravimetric analysis. The value of k for PNaSS was 28 μg/(mL·OD); for PNaAMPS, 400 μg/(mL·OD). For DNA, k = 53 μg/(mL·OD) was estimated from published UV spectra.

The optical constant K in eq 2 required values of the refractive index increment dn/dc. A literature value of dn/dc was used for DNA (0.166 mL/g).[27] For PNaSS and PNaAMPS the values 0.17 and 0.20 mL/g were measured with a Chromatix KMX-16 instrument. In the sedimentation experiment itself, the solvent is slightly different at the top and bottom of the tube because of the density gradient. No correction was applied for this. The refractive index of water was used as n in all instances; n for 0.70 M Na_2SO_4 is only 1% greater than for water.

The light-scattering data were converted into absolute values of the Rayleigh scattering factor R by using the relation, $R = i_s/I_0V$ where V is the scattering volume of the LALLS cell. The value of V is provided by the manufacturer of the LALLS instrument. The calibration was checked by measuring the molecular weight of NBS standard polystyrene.

The molecular weights, weight fractions, and sedimentation coefficients were then computed at each of about 80 points from the top to the bottom of the tube, and M_n, M_w, and M_z were evaluated. The spacing between these points was not uniform on the molecular weight scale; instead, it was uniform in volume displaced from the tube. To convert the data into an absolute, method-independent scale, we computed $c_p/(\mathrm{d} \log M)$ for each fraction and plotted this against log M. The quantity (d log M) expresses the range in log M assignable to a particular sample cut. Because d log M is a small difference between large numbers, small errors in M grossly distort the calculation of $c_p/(\mathrm{d} \log \mathrm{M})$. To eliminate this problem, we used the measured values of s to smooth the calculated M values, as follows. First, an equation of the form $s = HM^a$ was fitted to the experimental data by using the robust "least-first-power" algorithm of Barrodale and Roberts[28,29] to obtain the slope a. The value of H was determined by requiring that M_w for the smoothed data set M' be identical with that obtained from the original data set M. The smoothed values M' were then computed from the relation $M' = (s/H)^{(1/a)}$. All these computations were done rapidly and automatically by the computer. The functional form $s = HM^a$ has extensive experimental support over broad ranges of M for diverse polymer systems: polyisobutylene,[30] poly(methyl methacrylate),[31] and DNA.[32]

Results

Figure 2 shows raw data for both UV absorption and light-scattering intensity after centrifugation of a mixture of two narrow MWD PNaSS samples with nominal M_w = 100 000 and 400 000. Several features of these curves are noteworthy. First, the resolution of the method was excellent; the two samples were separated almost to the base line. Second, the light-scattering signal was almost devoid of spikes except at the very top of the tube, although the solvent was water. Water is notorious as a difficult solvent

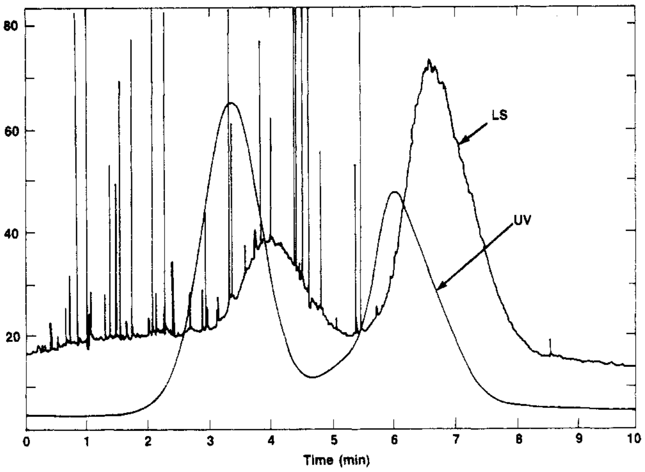

Figure 2. Raw UV and LALLS data obtained by the S/LALLS method. UV designates the UV data; LS designates light-scattering intensity. The sharp spikes in the light-scattering trace were caused by dust particles traversing the scattering volume. The sample was a mixture of two narrow-MWD poly(sodium styrenesulfonates) with M_w = 100 000 and 400 000, both at starting-zone concentrations of 500 μg/mL, respectively. Sample volume 0.5 mL. Sedimentation was for 17 h, 31 000 rpm, 23 °C. LALLS scattering angle 6–7°, UV cell path 0.2 cm. Abscissa full scale (0–100) corresponds to 2 OD in absorbance and a Rayleigh factor of 1.75×10^{-5} cm^{-1} in light scattering.

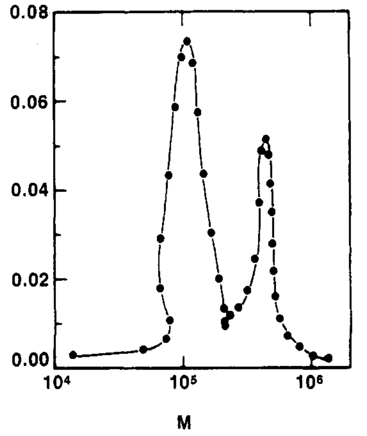

Figure 3. Plot of relative polymer concentration against log (molecular weight) for the data of Figure 2, which were obtained for a mixture of two narrow-MWD PNaSS samples with M_w = 100 000 and 400 000. Each point represents a separate calculation of M. No smoothing has been applied except to eliminate spikes in the raw light-scattering data.

for light-scattering analysis.[33,34]

Figure 3 shows the same data as Figure 2, but processed to obtain M. Each point involved a separate calculation of M from the UV and LALLS data at a particular position in the tube corresponding to a 0.15-mL increment. No smoothing was applied to the data. The unphysical inward curvature of the curve at the base of the low-M peak probably arose from systematic partial mixing or dead space which could occur between the UV flow cell and the LALLS flow cell in our apparatus. The first peak had M_w = 122 000; the second had M_w = 447 000. Both values are about 20% higher than the supplier's value of M. The most likely source of this discrepancy is the value used for dn/dc. A direct evaluation of $\sum M_iN_i/\sum N_i$ and $\sum M_ic_i/\sum c_i$ for each band gave M_w/M_n = 1.11 for the smaller polymer species and M_w/M_n = 1.07 for the larger species. The manufacturer claims M_w/M_n = 1.1 in both cases.

The strengths of the sedimentation method increase as M increases. In Figure 4 is shown the MWD of PNaSS with nominal $M = 1.2 \times 10^6$. This was also claimed to be a narrow MWD material. We found the value of M_w to be 1.3×10^6, which was quite close to the manufacturer's value. However, in contrast to the polymers from the same manufacturer with M = 100 000 and 400 000 (Figure 3), the MWD of this sample clearly showed three bands. The three components had peaks at 1.3, 1.8, and 2.8×10^6. This sample also showed a pronounced low-M tail. The polydispersity index M_w/M_n was 1.8. The PNaSS polymer with M = 780 000 also showed much greater breadth than expected from the supplier's description.

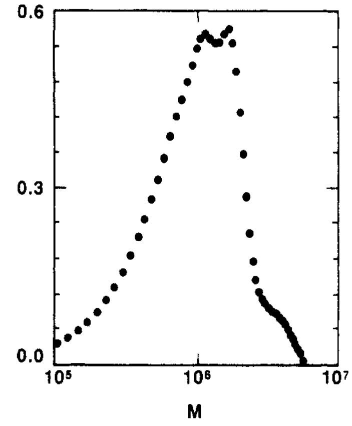

Figure 4. Molecular weight distribution of PNaSS, nominal $M_w = 1.2 \times 10^6$, as determined by S/LALLS. Sample size 0.5 mL, sample concentration 310 μg/mL, scattering angle 6–7°, UV path length 0.2 cm. The units of c on the abscissa are gram per unit (log M), normalized to give unit area.

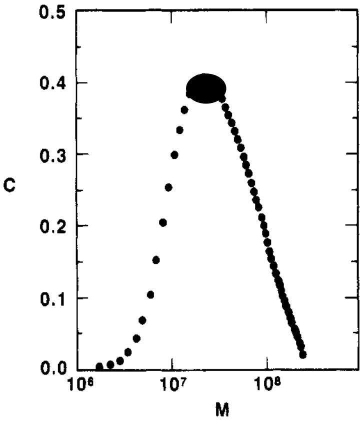

Figure 5. MWD of PNaAMPS obtained by S/LALLS. Sedimentation time, 2.8 h; centrifuge speed 29 000 rpm. Sample concentration 300 μg/mL; UV path 1.0 cm. The units of c on the abscissa are gram per unit (log M) normalized to unit area.

Two polymer classes with M beyond the SEC range were studied to demonstrate the utility of the method. Figure 5 shows smoothed MWD data for a high-M PNaAMPS sample specially synthesized by Lubrizol Co. The observed distribution was broad and yielded $M_w = 43 \times 10^6$. The weight-average value of the sedimentation coefficient was 36 S. Both M_w and s were surprisingly high for a synthetic polymer, but comparable results were obtained by static LALLS measurement.

Monodisperse viral DNA's should be excellent standards, since their molecular weights are known with accuracy. T5 DNA and λ-DNA, with $M = 68 \times 10^6$ and 31×10^6, were studied by the S/LALLS method. Figure 6 shows the sharp peak exhibited by T5 DNA. The uncorrected weight average of s given by this peak was 46 S, in good agreement with the literature value 49 S.[35] The values of M_n and M_w for this peak were 65×10^6 and 66×10^6, also in good accord with the literature value. For

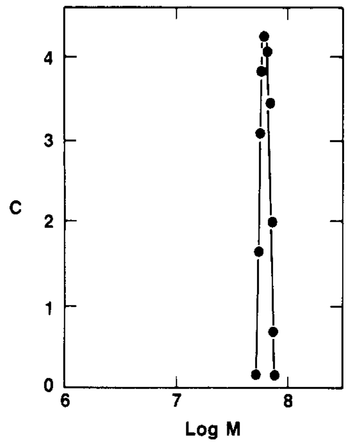

Figure 6. MWD of T5 DNA obtained by S/LALLS. Sedimentation time 1.75 h; centrifuge speed 35 000 rpm. Sample concentration 45×10^{-6} g/mL; sample volume 0.2 mL. UV path length 1.0 cm. The units of c on the abscissa are gram per unit (log M) normalized to unit area.

λ-DNA we obtained $s_w = 32$ S and $M_w = 32 \times 10^6$.

Discussion

The data presented show that band sedimentation is a useful method for characterizing the MWD of high molecular weight polymers. It is particularly suitable for aqueous solutions. It has several distinct advantages over SEC and SEC/LALLS: (1) the upper M limit is much higher; (2) the samples are automatically clarified prior to LALLS detection; (3) adsorption problems are minimal; and (4) the technique is gentle compared to SEC, so degradation can be avoided unless M becomes very large. Other separation techniques such as hydrodynamic chromatography[36,37] have been explored as alternatives to SEC, but their success has been limited.

The upper M limit is determined by three factors. First, the polymer concentration must be reduced as M increases so as to keep the solution dilute. This reduces the relative accuracy of the c_p determination, because the UV absorbance of the polymer becomes indistinguishable from the base line. Second, even light-scattering measurements at 2–6° scattering angle will require extrapolation to 0 angle if the radius of gyration of the polymer is large enough. Third, as M increases, shear degradation may occur during preparation and analysis of each tube, especially at the filter F (Figure 1).

One might ask why a filter is still needed even though the sample has been centrifuged. One explanation is that the sample gets recontaminated during the interval between centrifugation and analysis when it is open to the air; water is notorious for this. Alternatively, centrifugation may not remove *all* the particulate matter; the samples were not precleaned in any way.

A major strength of S/LALLS is its utilization of proven commercial apparatus. No new apparatus needs to be constructed. The system functions quite well even with fairly impure samples containing gel particles; these travel to the bottom of the tube and never reach the detector. Because of the density gradient, remixing of dust or gel is suppressed, so that sample tubes remain "clean" for hours after centrifugation.

It was anticipated that the density gradient might lead to anomalous light-scattering signals because of schlieren effects. In practice these were not observed, although the setup had other limitations. The most important of these was the presence of excess holdup volume in the filter, UV detector, LALLS cell, and connecting tubing. This is probably the source of the systematic distortions of the processed data (Figure 3). Mathematical correction techniques have been developed to meet similar dispersion problems in SEC,[38,39] but in our opinion, a hardware approach deserves exploration first. Indeed, improved data have recently been obtained by shortening all interconnecting tubing. A second problem was limited UV absorbance at 214 nm by some polymer species. Shorter wavelengths or fluorescent tagging[21,22] are possible solutions to this problem. If the sedimentation was run a too high a concentration, the molecules interfered with each other's free movement, leading to anomalous band shapes and concentration-dependent results.

The preparative ultracentrifuge used here lacked two desirable features of the analytical centrifuge. The first was sector-shaped cells, which prevent molecules from striking the tube walls. The second was the ability to analyze the sample while it was spinning. Both of these factors are less important for polydisperse polymers than for biological polymers with a single value of M. The major advantage of the present method, absolute MWD data, cannot be obtained by band sedimentation in the analytical centrifuge.

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Registry No. PNaAMPS (homopolymer), 35641-59-9; poly(sodium styrenesulfonate) (homopolymer), 62744-35-8.

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Correlations between Chain Parameters and the Plateau Modulus of Polymers

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ABSTRACT: Plateau modulus, $G_N°$, values of over 50 polymers were correlated with long-distance chain parameters such as M_c, N_c, and L_c and with short-distance chain parameters such as the chain diameter, d, and the Kuhn segment length, A. For the flexible and semiflexible polymers, it was found that essentially no correlation exists between $G_N°$ and any of the long-distance chain parameters. The correlation of $G_N°$ and short-distance chain parameters was marginal with A and reasonably good with A/d for well-behaved flexible and semiflexible polymers: $G_N° \propto A/d$. It was further observed that when $G_N°$ is multiplied by A^3/kT to render the product dimensionless, the correlation of this variable with $(A/d)^2$ is dominated by the magnitude of A^3 and does not reflect the relationship between $G_N°$ and $(A/d)^2$. Plots of the relationship between A and d clearly divide the polymers into four groups: flexible, semiflexible, semirigid, and rigid. The difference in behavior between the more flexible polymers and the more rigid ones appears to be related to the ratio of L_c, the chain contour length between entanglements, to A. In the case of the flexible polymers $L_c \gg A$ and for the rigid polymers $L_c \ll A$.

Introduction

The presence of entanglements or interchain contact points seems to be a prerequisite for a polymeric system to exhibit a plateau modulus, $G_N°$. It is widely accepted[1] that an inverse relationship exists between the plateau modulus and the molecular weight between entanglements, M_e, of a polymer in its elastoviscous state

$$G_N° = c\rho RT/M_e \qquad (1)$$

Here ρ is the polymer density under test conditions, R is the gas constant, T is the temperature, and c is a numerical factor solely or largely consisting of the polymer concentration. In the case of linear polymers in the undiluted state, $c = 1.0$. The same relationship holds for cross-linked elastomers, where M_e is the molecular weight between cross-link junctions[2]

$$G_N° = \rho RT/M_e \qquad (2)$$

Since the density of most organic polymers is in the neighborhood of 1, a reasonable estimate of M_e for the pure polymer may be obtained from the measured $G_N°$ by

$$G_N° \simeq RT/M_e \qquad (3)$$

When the viscosity of fractions of a pure polymer, measured in the molten fluid state, is plotted in log-log scale against the molecular weight, M, of the fractions, a break in the curve is observed at the point where the molecular weight dependence of the viscosity changes over a relatively narrow range from dependence on $M^{1.0}$ to a dependence on $M^{3.4}$. The molecular weight at which the break in the curve occurs is termed the characteristic molecular weight for entanglement, M_c. M_c is observed also in solutions. Here, a high molecular weight polymer is used, with $M \gg M_c$. Comparison of the results obtained in solution and in the melt indicates that[3]

$$(cM)_c = M_c \qquad (4)$$

where c is the concentration. When the M_c and M_e values of the same polymers are compared, it is found[4,5] that the ratio M_c/M_e is about 2. Therefore, an approximate value of $G_N°$ can be calculated from the known M_c or M_c estimated from $G_N°$

$$G_N° \cong 2c\rho RT/M_c \qquad (5)$$

and for the neat polymer in a weaker approximation

$$G_N° \simeq 2RT/M_c \qquad (6)$$

Because the $G_N°$ and M_c values are obtained from two independent measurements, we believe that attempted correlations between the two variables are valid. Similarly, correlations between $G_N°$ and N_c or L_c are valid, N_c being the number of chain backbone atoms or bonds corresponding to M_c and L_c the chain contour length defined by M_c. On the other hand, attempted correlations between pairs of $G_N°$ and M_e values are invalid since both variables of each pair were obtained from the same measurement or the same kind of measurement. By the same token, correlations of $G_N°$ with N_e or $G_N°$ with L_e are also invalid.

The purpose of this work is to determine if correlations between $G_N°$ and M_c, N_c, or L_c are statistically valid and whether there exist better correlations relating $G_N°$ to other chain parameters.

Data Acquisition and Treatment

All plateau modulus values were obtained from the literature. Most were from bulk polymers, but a few were extrapolated from the plateau modulus of polymeric solutions. In several instances the value of $G_N°$ was esti-

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