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Dilute-Solution Dynamic Viscoelastic Properties of Schizophyllan Polysaccharide[†]

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ABSTRACT: The frequency dependences of the storage and loss shear moduli, G' and G'', of dilute solutions of the three-stranded helical rodlike polysaccharide schizophyllan were measured at 25.0 °C by the Birnboim–Schrag multiple-lumped resonator. The frequency range was 100–8000 Hz and the concentration range usually 0.6–3 g/L. The solvents were water, glycerol–water mixtures, dimethyl sulfoxide (Me$_2$SO), and Me$_2$SO–water mixtures. The hybrid model previously used to interpret viscoelastic properties of solutions of semiflexible rodlike macromolecules and the Yamakawa–Yoshizaki and Hagerman–Zimm theories for relating the intrinsic viscosity $[\eta]$ and rotational relaxation time τ_0, respectively, to the persistence length q were modified to take into account a moderate degree of molecular weight heterogeneity with assumption of a Schulz–Flory distribution. Data in water and glycerol–water (in which the only function of glycerol was to increase the effective frequency range by changing solvent viscosity) could be fitted by the hybrid model with a persistence length (based on number-average molecular length) of 116 nm, as compared with 140 nm calculated from $[\eta]$. In Me$_2$SO, the viscoelastic data could be fitted to the Zimm theory for flexible coils as expected from evidence of Fujita and collaborators that the helix is dissociated into single strands with random coil configuration. In a water–Me$_2$SO mixture with water weight fraction $w_H = 0.155$, the viscoelastic properties and intrinsic viscosity could be interpreted as indicating either a slight softening of the helix in a solvent composition with water content just above the critical composition for helix dissociation or else a mixture of coils and semiflexible rods, the latter having the same partial flexibility as in pure water. In a mixture with $w_H = 0.150$, the viscoelastic properties appeared more consistent with a very soft undissociated helix.

Introduction

Schizophyllan is an extracellular polysaccharide secreted by the bacterium *Schizophyllan commune*. It consists of linear chains of β-1, 3-D-glucose residues with one β-1,6-D-glucose side chain for every three backbone chain residues.[1,2] Extensive studies of light scattering and intrinsic viscosity by Fujita and collaborators[3-5] have shown that in aqueous solution the molecule contains three linear chains wound in a rodlike triple helix. The natural product can be sonicated and fractionated to obtain samples of different molecular weights. When dissolved in dimethyl sulfoxide (Me$_2$SO), the helix dissociates and the individual chains assume random coil configurations.[3-5] In Me$_2$SO–water mixtures, with increasing Me$_2$SO concentration, the dissociation occurs almost discontinuously at a water weight fraction w_H of about 0.13.

Measurements of the frequency dependence of viscoelastic properties in dilute solution, extrapolated to infinite dilution, can distinguish clearly between completely rigid

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[†] This paper is dedicated to Dr. Pierre Thirion on the occasion of his retirement.

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Table I
Solvent Densities and Viscosities at 25.0 °C

solvent	ρ, g/cm^3	η_s, cP
water	0.997	0.89
50% glycerol	1.123	4.93
75% glycerol	1.192	26.8
H_2O-Me_2SO, w_H = 0.155	1.100	2.96
H_2O-Me_2SO, w_H = 0.150	1.099	2.83
Me_2SO	1.096	1.96

and semiflexible rodlike macromolecules, and for the latter it can provide an estimate of the persistence length and the molecular stiffness.[6-9]

In the present paper, such measurements on schizophyllan are described. Data in water are supplemented by data in glycerol–water mixtures to extend the effective frequency range by varying the solvent viscosity; the molecular configuration is found not to be affected by admixture of glycerol. Measurements have also been made in water–Me_2SO mixtures near the transition concentration and in pure Me_2SO. Interpretation by the semiempirical hybrid theory used previously[6-9] is complicated by the presence of molecular weight distribution in schizophyllan. The equations relating the calculation of persistence length q from viscoelastic data, as well as from intrinsic viscosity by the theory of Yamakawa and Yoshizaki[10] and from the rotational relaxation time by the theory of Hagerman and Zimm,[11] have been modified to take into account a moderate degree of molecular weight heterogeneity. For this purpose, a distribution of the Schulz–Flory form has been somewhat arbitrarily assumed.

Experimental Section

Materials. A sample of schizophyllan was kindly donated by Dr. T. Yanaki of Taito Co., Tokyo, Japan. Its viscosity-average molecular weight was given as 3.6×10^5 and its zero-shear intrinsic viscosity as 353 mL/g at 25 °C. It had been sonicated and fractionated by precipitation from water–ethanol mixtures. Samples fractionated similarly by Dr. Yanaki had M_w/M_n ratios from 1.7 to 2, whereas M_z/M_w ratios determined by Dr. T. Norisuye, Osaka University, on similar samples (personal communication) were 1.2–1.4; a ratio of 1.3 corresponds to M_w/M_n = 1.45 if a Schulz–Flory distribution is assumed.[12] In our calculations we have taken two alternative M_w/M_n ratios of 1.4 and 1.7 and approximated M_w by the viscosity-average value.

Intrinsic viscosity measurements in water and water–glycerol mixtures were made at 25.0 °C with a Cannon-Ubbelohde four-bulb shear dilution viscometer, Type 755-249. The values extrapolated to zero wall shear rate were 350 mL/g in water, 358 in 50% glycerol by weight, and 352 in 75% glycerol by weight. These agreed very well with the value communicated by Dr. Yanaki and indicated that the molecular configuration is independent of glycerol concentration over this range.

Solvents. The glycerol and dimethyl sulfoxide (Me_2SO) were obtained from Aldrich; the latter was redistilled before use. Densities (ρ) and viscosities (η_s) of the solvents are listed in Table I.

Viscoelastic Measurements. The storage and loss shear moduli, G' and G'', were measured by use of the Birnboim–Schrag multiple-lumped resonator apparatus.[13] Recent improvements in construction, experimental operation, and data reduction have been described elsewhere.[9,14,15] The procedures for cleaning and filling of the apparatus and the sequences of dilutions and solvent runs were similar to those described previously.[8] All measurements were made at 25.0 °C. Two resonators were used, providing a frequency range from about 100 to 8000 Hz. The concentration range was from about 0.6 to 0.6 to 3 mg/mL except in Me_2SO, where it was from about 3 to 8 mg/mL.

Results

Table II
Intrinsic Viscosities and Parameters from Viscoelastic Measurements[a]

solvent	$[\eta]$, mL/g	τ_{0x}/τ_{1x}	τ_{0x}, μs	τ_{1x}, μs	q,[b] nm	q,[c] nm
water, glycerol–water	350	10	11	1.1	116	140
water–Me_2SO, w_H = 0.155	320	7	9	1.3	81	105
water–Me_2SO, w_H = 0.150	144			5.6[d]		20
Me_2SO	83			1.1[d]		10

[a] Relaxation times reduced to water at 25.0 °C. [b] From τ_{0x}/τ_{1x}. [c] From $[\eta]/[\eta]_R$. [d] Longest relaxation time of Zimm theory.

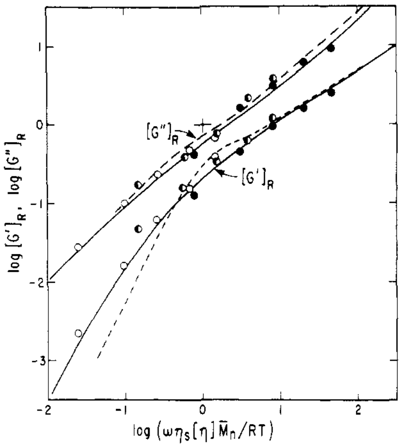

Figure 1. Reduced intrinsic moduli, $[G']_R$ and $[G'']_R$, plotted logarithmically against reduced frequency for solutions in water and water–glycerol mixtures. Open circles, water; half-black circles, 50% glycerol; black circles, 75% glycerol. Dashed curves, calculated from hybrid theory for uniform molecular weight; solid curves, calculated with molecular weight distribution as described in text (eq A1 and A2).

The intrinsic viscosities were measured in all solvents, and the values are listed in Table II. (The values in water and glycerol–water mixtures agreed within experimental error as stated above, but that in water is taken since it is probably the most accurate.) The sharp drop with decreasing water content in water–Me_2SO mixtures agrees with the results of Norisuye, Yanaki, and Fujita,[3] although their transition appeared at a slightly higher value of w_H. Our value of 83 mL/g in pure Me_2SO may be compared with an interpolated value of 72 from their data.

For extrapolation of the viscoelastic measurements to infinite dilution, the following plots (not shown) were made as in previous studies:[7-9] $(G'M_n/cRT)^{1/2}$ and $(G'' - \omega\eta_s)M_n/cRT$ were plotted against c for about eight different concentrations. Here M_n is number-average molecular weight, c concentration in g/mL, ω radian frequency (2π times frequency in Hz), η_s solvent viscosity, R the gas constant, and T the absolute temperature. The respective intercepts are defined as the dimensionless quantities $[G']_R^{1/2}$ and $[G'']_R$. The molecular weight used must be number average because $[G']_R$ and $[G'']_R$ represent the contributions to the moduli per mole of solute. On the basis of the studies of Fujita and collaborators,[3-5] M_w may be taken as 360 000 in all solvents except pure Me_2SO where it is 120 000, corresponding to single chains. Then M_n depends on the choice of M_w/M_n, which in the plots shown is taken as 1.4, so that M_n = 260 000 and 86 000 respectively.

In Figure 1, $[G']_R$ and $[G'']_R$ in water and glycerol–water mixtures are plotted logarithmically against the usual reduced frequency $\omega\eta_s[\eta]M_n/RT$. (The use of M_n here is somewhat arbitrary but is chosen for consistency.) The data in the different solvents fall together on single curves, providing additional evidence that the molecular configuration is not altered by the presence of glycerol, and the results cover about 3.5 logarithmic decades of frequency.

A similar plot for the water–Me_2SO solvent with w_H = 0.155 is shown in Figure 2. The plots for w_H = 0.150 and pure Me_2SO are combined in Figure 3, since the frequency dependences are

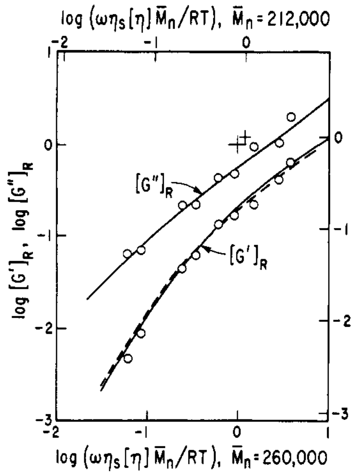

Figure 2. Reduced intrinsic moduli plotted logarithmically against reduced frequency for solution in water–Me$_2$SO with w_H = 0.155. Coordinates left and bottom, reduced with M_n = 260 000 to compare with solid curves for hybrid theory for semiflexible rods with $\tau_{0\bar{x}}/\tau_{1\bar{x}} = 7$; coordinates right and top, reduced with M_n = 212 000 to compare with dashed curves for mixture of coils and semiflexible rods with $\tau_{0\bar{x}}/\tau_{1\bar{x}} = 10$.

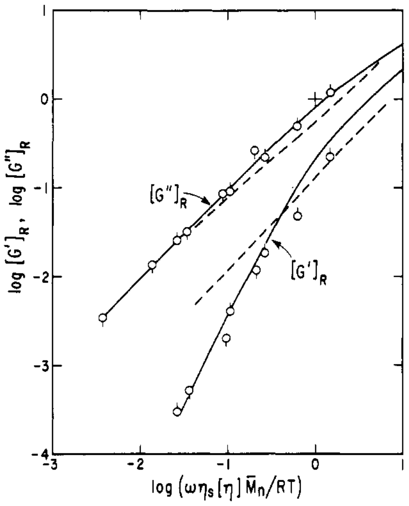

Figure 3. Reduced intrinsic moduli plotted logarithmically against reduced frequency for solution in water–Me$_2$SO with w_H = 0.150 (pip up) and in pure Me$_2$SO (pip down). The reduced frequency is calculated taking M_n = 260 000 at w_H = 0.150 and M_n = 86 000 in pure Me$_2$SO. Curves calculated from Zimm theory with molecular weight distribution (eq A5 and A6).

very similar in the range covered, though distinctly different from those in Figure 2. (If these two plots in Figure 3 were made against absolute frequency, they would be widely separated because of the different values of M_n and $[\eta]$ that appear in the reduced frequency.)

Discussion

In order to compare the observed frequency dependences of viscoelastic properties with predictions of the hybrid model to deduce values of the persistence length q and also to apply the Hagerman–Zimm and Yamakawa–Yoshizaki theories to estimate q from the rotational relaxation time or the intrinsic viscosity, it is necessary to take into account molecular weight distribution. The calculations are rather uncertain because they are based on the assumption of a Schulz–Flory distribution and values of M_w/M_n that are not confirmed. However, qualitative conclusions concerning the effect of solvent composition should not be affected.

The hybrid model provides the following relations for the intrinsic storage and loss shear moduli of semiflexible rods of uniform molecular weight:[6-9]

$$[G']_R = m_1\omega^2\tau_0^2(1 + \omega^2\tau_0^2)^{-1} + Z'(\omega\tau_1) \qquad (1)$$

$$[G'']_R = \omega\tau_0[m_1(1 + \omega^2\tau_0^2)^{-1} + m_2] + Z''(\omega\tau_1) \qquad (2)$$

$$\tau_0 = m[\eta]\eta_s M/RT \qquad (3)$$

where τ_0 is the rotational relaxation time; τ_1 is the longest of a spectrum of relaxation times following the spacing of the Zimm theory for flexible coils,[17] which is here attributed to a fundamental bending mode;[17] m_1 and m_2 are numerical factors, m_1 usually being 0.6 (same as for a rigid rod) and m_2 being between 0.1 and 0.2; and Z' and Z'' are the reduced moduli specified by the Zimm theory,[16] in which the shorter relaxation times are attributed to other bending modes. In eq 3, $m = (m_1 + m_2 + 2.37\,\tau_1/\tau_0)^{-1}$. The conventional reduced frequency used in Figures 1–3 is $\omega\tau_0/m$.

For a Schulz–Flory distribution of molecular weights, these are replaced by some rather lengthy summations shown in the Appendix, in which the parameters are k, the index of polydispersity ($k^{-1} = M_w/M_n - 1$), $\tau_{0\bar{x}}$, and $\tau_{1\bar{x}}$, the latter being the values of τ_0 and τ_1 appropriate for the species with the same molecular weight as the number average. The assumptions on which the calculations are based are given in the Appendix, but the actual derivations are recorded elsewhere.[18] The reduced moduli are then plotted logarithmically as before against $\omega\eta_s[\eta]M_n/RT = \omega\tau_{0\bar{x}}/m$; in this case m is a more complicated function of m_1, m_2, k, and $\tau_{1\bar{x}}/\tau_{0\bar{x}}$ (eq A3 of the Appendix).

The solid curves in Figures 1 and 2 are shown from eq A1 and A2 of the Appendix, with M_w/M_n = 1.4 (k = 2.5), m_1 = 0.6, m_2 = 0.2, and the values of $\tau_{0\bar{x}}/\tau_{1\bar{x}}$ listed in Table II. In Figure 1, dashed curves are also shown for uniform molecular weight distribution, eq 1 and 2, with the same values of m_1, m_2, and τ_0/τ_1. The fit of data in Figure 1 with the calculation including molecular weight distribution is quite good; the calculation with uniform molecular weight shows the greatest deviation for $[G']_R$ at low frequencies, as expected. The parameter $\tau_{0\bar{x}}$ (or τ_0/τ_1) is determined primarily by the spacing on the abscissa scale between the two approximately linear segments of the $[G'']_R$ curve. An alternative fit (not shown) was made to calculated curves for M_w/M_n = 1.7 with the same values of m_1, m_2, and $\tau_{0\bar{x}}/\tau_{\bar{x}}$. The agreement with the data was equally good, in fact indistinguishable. The fit in Figure 2 for M_w/M_n = 1.4 is also good but less convincing because of the narrower range of reduced frequency.

The data in Figure 3 do not fit the hybrid model but correspond to the ordinary Zimm theory with dominant hydrodynamic interaction (h^* = 0.25) when modified for molecular weight distribution with M_w/M_n = 1.4 (eq A5 and A6 of the Appendix). The data do not extend to high enough reduced frequencies for a complete fit to the Zimm theory, but at low frequencies $[G']_R$ clearly corresponds to coils rather than semiflexible rods. It should be emphasized that molecular weight distribution affects the Zimm theory for flexible coils quite differently from the Zimm function as used for flexing rods in the hybrid model; in the former case, τ_{1x} for species with degree of polymerization x is proportional to $x^{3/2}$, in the latter to x^4.

The values of $\tau_{0\bar{x}}$ and $\tau_{1\bar{x}}$ obtained by curve fitting are included in Table II. They are reduced to the viscosity of water at 25.0 °C, assuming proportionality to viscosity. Values of $\tau_{1\bar{x}}$, the longest Zimm relaxation time for the species with the same molecular weight as the number average, are also given for the data of Figure 3.

From the ratio $\tau_{0\bar{x}}/\tau_{1\bar{x}}$, the persistence length q can be calculated from the relation (eq A4 of the Appendix)

$$\tau_{0\bar{x}}/\tau_{1\bar{x}} \simeq 10q/\bar{L}_n$$

where $\bar{L}_n$ is the number-average molecular contour length. From the mass per unit contour length deduced by Fujita and collaborators,[4] $\bar{L}_w$ = 166 nm; the value of $\bar{L}_n$ depends on the choice of M_w/M_n, 1.4 and 1.7 giving 120 nm and 97 nm, respectively. The values of q from $\tau_{0\bar{x}}/\tau_{1\bar{x}}$ in Table II are based on $M_w/M_n = 1.4$; the alternative would decrease them by a factor of 0.82.

The persistence length can also be calculated from the intrinsic viscosity by the Yamakawa–Yoshizaki theory[10] modified for molecular weight distribution (see Appendix), in which the ratio of $[\eta]$ to $[\eta]_R$, the intrinsic viscosity of a completely rigid rod with the same contour length, is expressed as a function of $\bar{L}_n/q$. The values of q from $[\eta]/[\eta]_R$ in the table are again based on $M_w/M_n = 1.4$; the alternative would decrease them by a factor of about 0.94. In principle, q can also be calculated from $\tau_{0\bar{x}}$ by modifying the theory of Hagerman and Zimm[11] to take into account molecular weight distribution. However, these values are not cited because $\tau_{0\bar{x}}$ is derived from data at low frequencies where the sensitivity to the choice of M_w/M_n is greatest.

The persistence length in pure water, 128 ± 12 nm, agrees fairly well with the deduction by Fujita and collaborators[4] from light scattering; their value of 180 ± 30 nm on a weight-average basis would correspond to 130 on a number-average basis. (The difference depends on whether $\bar{L}_n$ or $\bar{L}_w$ is chosen in connection with the ratio q/L.)

In water–Me$_2$SO with $w_H = 0.155$, the somewhat lower values of $[\eta]$ and $\tau_{0\bar{x}}/\tau_{\bar{x}}$ correspond to a decrease in q as shown in the table. This can be interpreted as a softening in the triple helix at a solvent water content slightly higher than the transition composition at which dissociation occurs. However, there is an alternative interpretation: a mixture of semiflexible rods with the properties observed in water ($\tau_{0\bar{x}}/\tau_{1\bar{x}} = 10$) and coils with the properties observed in pure Me$_2$SO. In the studies of Fujita and collaborators,[5] the average radius of gyration and weight-average molecular weight in the transition region of solvent composition can be interpreted on this basis. From $[\eta]$, such a mixture would have the proportions w_R:w_c = 0.88:0.12. The viscoelastic properties have been calculated for this mixture (with M_n = 212 000, the number average over both species) and are plotted as dashed curves in Figure 2. The fit with the data (reduced by the appropriate M_n) appears to be equally good.

The fits to the Zimm theory for flexible coils in Figure 3 are restricted to low frequencies where the data are most sensitive to molecular weight distribution. The behavior in pure Me$_2$SO is just what would be expected for the complete dissociation of the helix that has been demonstrated by Fujita and collaborators.[3-5] The behavior in the solvent with $w_H = 0.150$, where the fit is made to the Zimm theory with the molecular weight of 260 000, would correspond to an intact helix with high flexibility. In this case, the data cannot be fitted by a mixture of rod and coil species; from $[\eta]$, the proportions would be w_R:w_c = 0.23:0.77, and the reduced moduli, shown by dashed curves in Figure 3, diverge substantially at low frequencies. Data over a wider frequency range are needed to interpret the viscoelastic properties in the transition region of solvent composition.

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Appendix

In calculating the reduced storage and loss shear moduli for the hybrid model with a Schulz–Flory distribution of molecular weights, it is assumed that all molecules have the same cross-section area so that contour length L is proportional to molecular weight and that the contributions of species to G' and G'' at infinite dilution are additive on a molar basis,[18] also that the breadth of the relaxation time distribution is independent of molecular weight. The results are given by the following equations:

$$[G']_R = \sum_{x=1}^{x_{\max}} \frac{m_1 m^2 \omega_R^2 (x/\bar{x}_n)^6}{1 + m^2\omega_R^2(x/\bar{x}_n)^6} \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} + \sum_{x=1}^{x_{\max}} \sum_{p=1}^{N} \frac{m^2\omega_R^2 r^2 (x/\bar{x}_n)^8 (\tau_p/\tau_1)^2}{1 + m^2\omega_R^2 r^2 (x/\bar{x}_n)^8 (\tau_p/\tau_1)^2} \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} \quad \text{(A1)}$$

$$[G'']_R = \sum_{x=1}^{x_{\max}} m\omega_R (x/\bar{x}_n)^3 \{m_1[1 + m^2\omega_R^2(x/\bar{x}_n)^6]^{-1} + m_2\} \times \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} + \sum_{x=1}^{x_{\max}} \sum_{p=1}^{N} \frac{m\omega_R r (x/\bar{x}_n)^4 (\tau_p/\tau_1)}{1 + m^2\omega_R^2 r(\tau_p/\tau_1)^2 (x/\bar{x}_n)^8} \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} \quad \text{(A2)}$$

Here x is a degree of polymerization based on an arbitrary monomer unit, $x_{\max}$ is chosen large enough to make the sums converge, N (the total number of modes attributed to bending) is chosen sufficiently large to make the sums converge in the frequency range of interest, $k^{-1} = M_w/M_n - 1$, $\beta = k/x_n$, $\omega_R = \omega\tau_{0\bar{x}}/m$, $r = \tau_{1\bar{x}}/\tau_{0\bar{x}}$, m_1 and m_2 are the numerical coefficients of the hybrid model, τ_p/τ_1 are the relaxation time ratios of the Zimm theory,[16] x_n is the number-average value of x, Γ is the gamma function, and m is given as follows:

$$m^{-1} = (m_1 + m_2)(k+2)(k+1)/k^2 + 2.37(\tau_{1\bar{x}}/\tau_{0\bar{x}})(k+3)(k+2)(k+1)/k^3 \quad \text{(A3)}$$

where $\tau_{1\bar{x}}$ and $\tau_{\bar{x}}$ are the relaxation times of the hybrid model corresponding to the species with the same molecular weight (or contour length) as the number average.

Modification[16] of the equations of Ookubo et al.[17] and Broersma[11,19] for τ_1 and τ_0 respectively in terms of L_n, q, and d (where d is the rod diameter) to take into account molecular weight distribution provides, after considerable simplification, the relation

$$\tau_{0\bar{x}}/\tau_{1\bar{x}} \simeq 10q/\bar{L}_n \quad \text{(A4)}$$

where $\bar{L}_n$ is the number-average contour length.

The reduced storage and loss moduli for the Zimm theory for flexible coils with dominant hydrodynamic interaction are given by the following equations:

$$[G']_R = \sum_{x=1}^{x_{\max}} \sum_{p=1}^{N} \frac{m^2\omega_R^2 (x/\bar{x}_n)^3 (\tau_p/\tau_1)^2}{1 + m^2\omega_R^2 (x/\bar{x}_n)^3 (\tau_p/\tau_1)^2} \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} \quad \text{(A5)}$$

$$[G'']_R = \sum_{x=1}^{x_{\max}} \sum_{p=1}^{N} \frac{m\omega_R (x/\bar{x}_n)^{3/2} (\tau_p/\tau_1)}{1 + m^2\omega_R^2 (x/\bar{x}_n)^3 (\tau_p/\tau_1)^2} \times \frac{\beta^{k+1}x^{k-1}\bar{x}_n e^{-\beta x}}{\Gamma(k+1)} \quad \text{(A6)}$$

where the symbols are the same as before except that $\tau_{1\bar{x}}$ is the longest relaxation time of the Zimm theory, corresponding to the species with the same molecular weight as the number average, N is the number of modes in the Zimm theory for flexible coils, $\omega_R = \omega\tau_{1\bar{x}}/m$, and m^{-1} =

$2.37\Gamma(k + 3/2)/k^{1/2}\Gamma(k + 1)$.

Modification of the theory of Yamakawa and Yoshizaki[10] for the intrinsic viscosity $[\eta]_R$ of a completely rigid rod macromolecule for a Schulz–Flory distribution of molecular weights provides an equation of the form[18]

$$[\eta]_R = [(k + 2)(k + 1)/k^2](\pi N_A \bar{L}_n^3/24M_n)g(k,d,\bar{L}_n)$$

where g is a very complicated relation which is cited elsewhere.[18] The ratio $[\eta]/[\eta]_R$, where $[\eta]$ is the intrinsic viscosity of semiflexible rods with the same contour length, can be expressed by an equation related to that given by those authors[10] which is a function of $\bar{L}_n/q$ and k.

It is possible also to modify the theory of Hagerman and Zimm[11] for the effect of partial flexibility on the rotational relaxation time τ_0 to take into account molecular weight distribution as described elsewhere.[18]

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Dynamic Rheology and Molecular Weight Distribution of Insoluble Polymers: Tetrafluoroethylene–Hexafluoropropylene Copolymers

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ABSTRACT: Dynamic melt viscoelasticity for four insoluble copolymers of tetrafluoroethylene and hexafluoropropylene of the same comonomer content but different molecular weights is measured and analyzed to obtain their molecular weight distribution curves by deconvolution of the dynamic modulus spectrum in the terminal and plateau zones. The results are also used to study the polymerization kinetics, polydispersity effects on steady-state compliance, and the relationship between zero-shear viscosity and molecular weight. It is found that the free radical dispersion polymerization proceeds essentially by binary coupling of growing chains. The steady-state compliance J_e° is related to the polydispersity ratio by $J_e = \{6/(5G_N^\circ)\}(M_z/M_w)^{3.7}$ for $M > M_c'$, where M_c' is the critical entanglement molecular weight for steady-state compliance, G_N° is the plateau modulus, and M_z and M_w are z-average and weight-average molecular weights. The zero-shear viscosity η_0 for $M > M_c$ is found to be given by $\eta_0 = \eta_0(M_c)(M/M_c)^3 \exp\{2.26(1 - (M_c/M)^{0.5}\}$, where $\eta_0(M_c)$ is the zero-shear viscosity at the critical entanglement molecular weight M_c for zero-shear viscosity. This relation is obtained by a modification of Doi–Edwards reptation theory for tube length fluctuation and indicates that the n in the power law $\eta_0 = \eta_0(M_c)(M/M_c)^n$ is not a constant but rather varies from 4.1 at $M = M_c$ and asymptotically decreases to 3 at $M \rightarrow \infty$. In the range $1 < M/M_c < 100$ typical for conventional polymers, the relation predicts $n = 3.5$ as the best least-squares fit, in agreement with the well-known empirical results.

Introduction

Recently, we developed a method for obtaining the molecular weight distribution of polymers by deconvolution of linear melt viscoelasticity in the terminal and plateau zones.[1,2] The method is applicable to insoluble as well as soluble polymers and was verified with a series of narrow- and broad-distribution polystyrenes.[1,2]

In this work, we apply the method to a series of tetrafluoroethylene–hexafluoropropylene copolymers (FEP), which are insoluble in any suitable solvents and whose molecular weight distributions cannot be determined by traditional methods such as light scattering, osmometry, and gel permeation chromatography. The results obtained are also used to analyze polymerization kinetics, the effect of polydispersity on steady-state compliance, and the relation between zero-shear viscosity and molecular weight.

Dynamic Theory and Methodology

The dynamic modulus spectrum of a polymer melt in the terminal and plateau zones contains a complete spectrum of molecular relaxation times, which can be deconvoluted to obtain the molecular weight distribution curve. The linear viscoelastic storage modulus for a polydisperse polymer is given by[1]

$$G'(\tau) = \int_{-\infty}^{\infty} D(\tau) \frac{8}{\pi^2} G_N^\circ \sum_{\text{odd } p} \frac{(1/p^2)(\omega\tau/p^2)^2}{1 + (\omega\tau/p^2)^2} \, d \log \tau \qquad (1)$$

where $G'(\omega)$ is the dynamic storage modulus at angular

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