monomer consumption.

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Hydrodynamic Chromatography as a Probe of Polymer Dynamics during Flow through Porous Media

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ABSTRACT: Hydrodynamic chromatography (HDC) of both flexible and stiff macromolecules provides measurements of molecular size that depend strongly on column flow rate.[1,2] This flow rate dependence is explained in terms of deformation and orientation of simple molecular models in steady uniaxial elongation, an idealized flow with many, but not all, of the properties required to describe the real flow of polymer solutions in complex porous media. The polymer/flow description discussed here follows from earlier theories for the anomalous "excess" pressure drop/flow rate behavior of low-concentration polymer solutions in porous media.

Introduction

Polymer solutions exhibit pronounced non-Newtonian flow behavior in porous media containing small converging and diverging flow channels. With flexible polymers these effects have been attributed to flow-induced molecular stretching in the Lagrangian unsteady elongational flows found in convering flow passages. Direct measurement of polymer deformation in small pores is exceedingly difficult; molecular stretching is normally inferred indirectly from pressure drop/flow rate data. Hydrodynamic chromatography offers a second probe of molecular shape in these complicated flows. The technique follows changes in molecular conformation via flow rate dependent elution volumes of molecules which are able to undergo extension and orientation by hydrodynamic stress.

Flow-induced stretching of a flexible polymer occurs when the chain is subjected to hydrodynamic forces greater in magnitude than the forces of chain relaxation arising from Brownian motion. Flows imposing hydrodynamic stresses sufficiently large for molecular deformation are terms "strong", while flows in which the polymer retains its equilibrium conformation are "weak".[3] The strength of a flow can often be correlated with its Deborah number, De. The Deborah number is defined as a ratio of the hydrodynamic forces to the Brownian forces or, equivalently, as the ratio of the relaxation time of the polymer

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to the convective time scale of the flow. Significant molecular stretching in steady flows occurs only at high Deborah numbers.

Large, difficult-to-measure strain rates possessing the characteristics of both shear and elongation (uniaxial, biaxial, planar, etc.) are common in porous media flows. Adding to this complexity, the elongation and shear rates vary with position. The definition of an effective De in a porous media flow must therefore be made cautiously, with a full appreciation of the true spatial variation of molecular stretching. We will focus on the uniaxial elongational character of porous media flows since this component generally produces, at equivalent strain rates, larger changes in conformation than other strain components possibly present in the flow;[4] simplification to a single flow type also makes the resulting analysis more tractable. Polymer flow in even simple porous media is further confounded by the Lagrangian unsteadiness of the stress; a flowing polymer experiences widely varying forces as it is convected through expansions and contractions in the pore structure. For significant perturbations from equilibrium molecular shape to occur, a flow must impose a high De for a time longer than the relaxation time of the polymer. This requirement is marginally satisfied in porous media flows[5] and is difficult to maintain even in specially designed laboratory flow devices.[6]

Despite these theoretical difficulties in describing polymer transport in porous media, the experimental results are clear—large molecular deformations occur when some appropriately defined De is larger than unity. These deformations are principally manifested in extremely large pressure drops measured for low concentration polymer solutions pumped through porous materials. Even at 50 ppm, some water-soluble polymers will increase the pressure drop nearly 2 orders-of-magnitude above that measured with pure solvent.[7] Such effects are likely to have commercial significance in processes such as oil recovery and filtration.

Since pressure drop measurements are only an indirect probe of molecular conformation, alternate hypotheses for the anomalous behavior of polymer solutions in porous media are possible. HDC can provide important additional evidence for the molecular stretching hypothesis. In an HDC experiment, a short pulse of dilute polymer solution is injected into a column packed with 10–40-μm spheres. The column provides a pore network with flow passages somewhat larger than the dimensions of individual molecular (pore size ~5 μm, polymer radius ~0.05–0.5 μm). Under the influence of Brownian motion, each molecule will sample all accessible regions of pore space during transport through the column. The accessible region, however, depends on molecular size. Due to steric repulsion, the polymer is not able to sample a region close to packing surfaces. The inaccessible regions occur where the fluid velocity is low and the velocity gradient is high. Since the thickness of the depleted layer depends on molecular size, a separation is developed; larger polymers travel more rapidly through the bed than smaller ones as a consequence of a thicker excluded layer near packing surfaces.

Although much of this discussion is focused on behavior of flexible polymer species, hydrodynamic chromatography can be employed to study polymer/flow interactions of rigid polymers as well. The dynamics of rigid nonspherical polymers in porous media flows haver rarely been examined in previous studies, since large excess pressure drops are not found for solutions of these materials. Rigid rodlike polymers, however, are able to orient in strong flows. Although not causing the dramatic rheological effects seen with flexible polymers, the orientation of rodlike polymers during flow in the small passages of the HDC column can also be detected as flow-dependent elution behavior.

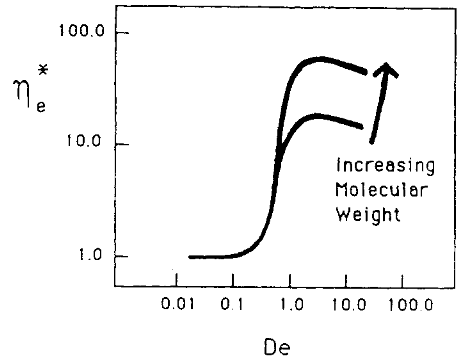

Figure 1. Sketch of excess pressure drop (expressed as the effective elongational viscosity, eq 1) as a function of Deborah number. The onset of molecular deformation is observed at De near 0.5.

Background

Flow of Flexible Polymers in Porous Media. The excess pressure drop phenomenon of polymer solutions during flow in porous media has been widely reported over the last 10 years.[7-12] The pressure drop produced by flow of a polymer solution in a packed bed of spheres has been written by Haas et al.[7,8] in terms of an effective reduced viscosity, η^*_e.

$$\eta^*_e = \frac{\Lambda_p(\eta_p/\eta_s) - \Lambda_s}{\Lambda_s[\eta_p/\eta_s - 1]} \tag{1}$$

The shear viscosities of the solvent and polymer solution are denoted by η_s and η_p, respectively. Similarly, Λ_s and Λ_p are the resistance coefficients of the two fluids in the porous packing. The resistance coefficients are defined from the friction factor, f, and the Reynolds number, Re, of the flow.

$$\Lambda = f\mathrm{Re} \tag{2}$$

where

$$f = \frac{\Delta p d_p n^3}{\rho \bar{v}^2 \Delta L(1-n)} \tag{3}$$

$$\mathrm{Re} = \frac{\bar{v} d_p \rho}{\eta_s(1-n)} \tag{4}$$

Here, the superficial viscosity is $\bar{v}$, the average packing bead diameter is d_p, n is the porosity, and ρ is the fluid density. The pressure drop per unit length is denoted $\Delta p/\Delta L$.

Figure 1 shows the typical functional form of the excess pressure drop as a function of De. The Deborah number has been defined as the product of a time constant associated with polymer relaxation, τ

$$\tau = [\eta]\eta_s M/RT \tag{5}$$

and an approximate value of the "effective" elongation rate in the bed, $\dot{\epsilon}$[7,8]

$$\dot{\epsilon} = k(\bar{v}/d_p) = k(1-n)\eta_p \mathrm{Re}/\rho d_p^2 \tag{6}$$

The intrinsic viscosity and molecular weight of the polymer are denoted $[\eta]$ and M, respectively, while R is the gas constant and T is the temperature. The constant k, which depends on pore structure, lies in the range 2–20 for packed beds of spheres, with $k = 6$ being a useful nominal value.

The time constant calculated by eq 5 is generally associated with the free-draining Hookean dumbbell model for flexible polymers; this formula may not be accurate, except to within a constant, for real flexible polymer chains. The time constant for rotation of rodlike molecules, as derived from the rigid dumbbell model, is also expressible in the form of eq 5.

Figure 1 shows a sharp transition at a Deborah number of 0.5. The critical De is normally adjusted to this theoretical value (predicted by the Hookean dumbbell theory) by adjusting the value of k; a single value of k, however, should fully characterize a single porous medium, independent of the properties of the polymer solution. The large increase in the dimensionless pressure drop at a De of 0.5 has been associated with the dramatic rise in the elongational viscosity that occurs when a solution of random-coil polymers is transformed into a solution of highly extended fiberlike chains.[13] The resulting solution of extended chains may no longer be dilute; Haas et al.,[8] however, report concentration-independent values of η^*_e. Rheological behavior as shown in Figure 1 has been the strongest evidence of coil–stretch transitions during porous media flow. A molecular understanding of polymer stretching in dilute solution can be formulated by using the kinetic theory models discussed in the next section. These models allow interpretation of excess pressure drop data in terms of polymer deformation under stress. They also will provide a basis for the interpretation of HDC data.

Models for Flexible Polymers. The simplest molecular model which displays large stretching upon imposition of a critical hydrodynamic stress is the linear elastic or Hookean dumbbell. The model consists of two centers of hydrodynamic resistance connected by a frictionless linear spring. The origin of the spring force is the conformational entropy of the chain; the entropy is reduced as the polymer stretches, and the net effect is a retractive force which is modeled as a linear spring. To solve for the dumbbell's end-to-end distance, a force balance on the connector vector which links the two beads is substituted into a conservation equation for the configurational distribution function of the chain (for details, see ref 14).

Calculations show that the root-mean-square end-to-end distance in steady flow depends strongly on the type of flow considered. In a shear flow, a moderate increase in connector length is observed as the strain rate is increased. In uniaxial elongational flow, however, a sudden jump in length is predicted at a critical De defined by a product of the relaxation time of eq 5 and the elongation rate. This simply theory predicts that the end-to-end distance grows to infinity above the critical De. This qualitatively explains the rheological transition seen in Figure 1, although the stretching is bounded in a real system so some modifications to the model are clearly indicated.

Although eq 5 was derived for the simple free-draining dumbbell model, more complete molecular models which include hydrodynamic interactions between beads predict similar expressions for the relaxation time

$$\tau = C\frac{[\eta]\eta_s M}{RT} \qquad (7)$$

where C is a constant of order 1. At equilibrium, the behavior of the random-coil molecule can often be well approximated (at least for uncharged polymers) by using the non-free-draining assumption, and the constant C is about 0.4.

Once large deformation occurs, the simple Hookean dumbbell model cannot correctly predict the magnitude of molecular stretching along the principal axis of stress. A number of papers discuss modifications to dumbbell properties which allow realistic calculation of rheological properties in high De flows.[4,15,16] The improvements have been developed on the assumption that flexible chains can be more accurately described by a dumbbell with a configuration-dependent friction coefficient (which smoothly ties the non-free-draining theory at low extensions to free-draining conditions at high extensions) and finite extensibility. The more complete models provide a reasonable correlation of pressure drop data for both the low and high De ranges. Even with these more sophisticated models, however, the unsteadiness and nonhomogeneous character of porous media flows have not yet been successfully incorporated into a comprehensive analysis. Two papers have discussed the Lagrangian unsteadiness of the stress acting on the polymer; in both cases the excess pressure drop phenomenon is apparently not predicted.[5,17] These analyses are more complete than those based on steady elongational flow, but the resulting predictions appear less accurate.

Another improvement to the simple dumbbell model is the Rouse model, which can be regarded as N beads connected by $N - 1$ linear springs[14] with hydrodynamic interactions neglected. The dumbbell model is a special case of the Rouse model for which $N = 2$. When N is greater than 2 the Rouse predictions for steady uniaxial elongational flow are similar to those obtained with the dumbbell; at De = 0.5, the end-to-end distance of the model goes to infinity. The full Rouse model, however, has more modes of relaxation available than the dumbbell, so transitions from relaxed to stretched states are more gradual. The major advantage of the Rouse model for analysis of HDC is the model's finite cross section perpendicular to the axis of molecular extension; the cross section of a dumbbell is poorly defined. (In a dumbbell model the cross section perpendicular to the mean direction of stretching arises solely from rotational Brownian motion.) The Zimm model adds equilibrium-averaged hydrodynamic interactions to the Rouse model; the stretching of the polymer chain is not fundamentally modified, although a more accurate expression for the relaxation time is obtained. The constant C in eq 7 predicted by the Zimm model is 0.42 with dominant hydrodynamic interactions.[18,19]

Models for Rodlike Polymers. Many polymers, particularly those of biological origin, are rigid and rodlike in solution. Such polymers are not easily deformed until the stress is large enough to cause breakage of backbone bonds. If the polymer is rodlike, however, flow stresses can cause a large degree of orientation before breakage occurs. To model orientation of rigid rodlike polymers in flow, a simple rigid dumbbell model will be employed.[14] The rigid dumbbell model consists of two centers of hydrodynamic resistance linked by a frictionless rigid connector. At low flow strengths Brownian forces are dominant, and the two ends of the dumbbell outline a spherical envelope about the center of the rod. As flow strength is increased, the hydrodynamic forces act on the rod ends, causing the dumbbell to become oriented along the principal axis of stress if the flow is irrotational. Vorticity in the flow will cause the molecule to tumble; the molecule will still have some orientation in a time-averaged sense.

The orientation of the rigid dumbbell is calculated in a fashion similar to the calculations for the flexible dumbbell. A balance of forces on the two beads is first formulated by using expressions for the hydrodynamic and Brownian forces. This balance is then substituted into a conservation equation for the orientational distribution function. The required averages are calculated from integrations over the complete distribution. The calculation

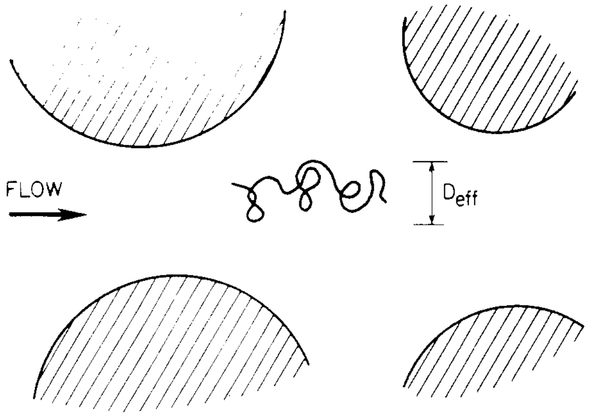

Figure 2. Schematic of a deformed polymer coil being transported through a complicated pore space in a packed bed of spheres. The molecular dimension measured by HDC reflects the ability of a polymer to approach packing surfaces. The effective diameter is thus a characteristic length transverse to the direction of flow.

of the orientational distribution functions for rodlike molecules in various flows is fully described in Bird et al.[14] The rotational time constant of the rigid dumbbell is given by eq 7 with $C = 1.0$; the rotational time constant associated with a slender rod is very nearly the same.

Experiment

Hydrodynamic Chromatography. A hydrodynamic chromatography system is nearly identical with that employed for aqueous size exclusion chromatography. In the HDC apparatus, however, nonporous spheres replace the usual porous packing support. At low ionic strength, the separation, although strongly affected by electrostatic interactions between the polymer and the packing, depends explicitly only on polymer size ("universal calibration"[20]). The position of the eluted polymer peak in this case is a function of a dimension of the molecule transverse to the axis of the pore (see Figure 2). This transverse dimension is derived, on an absolute basis, from a calibration curve for the column obtained through experiments with well-characterized latex spheres. The polymer diameter, D_{eff}, is defined by the diameter of the latex particles that elutes at the same position as the polymer.

The hydrodynamic chromatography apparatus used in this study has been described in detail in a separate publication.[1] The aqueous solvent for the polymer samples contains 2 g/L Triton X-100 (a nonionic surfactant produce by Rohm and Haas) and 0.002 M NaN_3. The support material, an ion exchange resin, Dowex50W [X16] (Dow Chemical), has been specially fractionated to an average particle size of 11 μm and packed in a 1.0-cm diameter chromatography column 24.8 cm long. Detection of the eluted polymer at the parts per million level is accomlished by fluorescent tagging of the polymer with a low substitution of fluorescein labels. This procedure is described elsewhere.[1] The flow rate through the system is variable over four orders of magnitude with a Waters M-45 pump and microflow module. Under the operating conditions chosen, universal calibration allows the separation to be interpreted solely as fractionation according to molecular size.

Model Polymers. A very high molecular weight, partially hydrolyzed polyacrylamide (SF210, American Cyanamid) is employed to probe the effects of hydrodynamic stress on conformation for a polymer with a flexible backbone. The supplier states that the average molecular weight of SF210 is 12–15 million, and titration in this laboratory of the acid groups reveals a carboxyl substitution of 9.5%. The physical properties of the polymer are similar to those of the nonionic polyacrylamides used by other investigators to obtain flow rate/pressure drop data of the type in Figure 1.[7]

The ionic strength of the solvent is sufficiently high to ensure random-coil statistics at equilibrium; at the same time, the ionic strength is low enough to ensure universal calibration. Ionic groups in this water-soluble polymer will make the coil–stretch transition more gradual on a plot of excess pressure drop versus De than with the analogous nonionic polymer; a transition at a Deborah number near 0.5 is still expected.[9] The polymer's intrinsic viscosity in the low ionic strength solvent, after fluorescent tagging, is 250 dL/g in the low shear rate plateau (measurements at less than 1.0 s^{-1} at 25.0 °C on a Contraves Low Shear 30 viscometer).

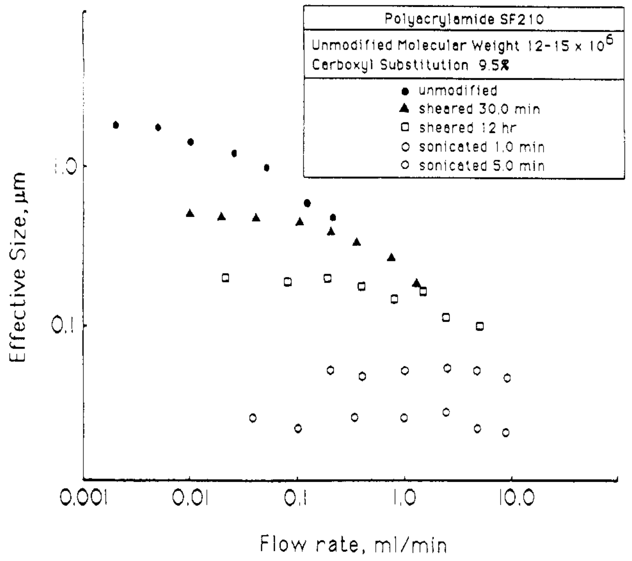

Figure 3. Effective size of five polyacrylamide samples as the flow rate in the column is varied. The top curve corresponds to the commercial polymer SF210 and the other four curves to polymers produced by degradation of the commercial polymer as indicated in the box. In each case at low flow rates the effective size reaches an equilibrium plateau. For the top three curves, the onset of molecular deformation at higher flow rates is observed.

Tobacco mosaic virus (TMV) is employed as a model rodlike polymer, although the virus is actually an aggregate of large molecules and therefore more properly regarded as a colloidal particle. The sample studied here has a particle length of 0.69 μm and a large polydispersity. The partical diameter is 0.015 μm, so the aspect ratio is approximately 45. In rheological testing, experimental results for TMV come closer to the predictions of the rigid rod model than for any other polymer.[21]

The third polymer studied in some detail is xanthan (Kelco), a naturally occurring polysaccharide with a stiff backbone. Rheological properties of the polymer suggest a slightly flexible rodlike conformation in solution. The molecular basis of the rodlike structure is unclear; some authors believe the molecule to be a double-stranded helix, while others are convinced that the molecule is single stranded.[22-25] Reported molecular weights are in the range of $(2–4) \times 10^6$, and the polydispersity in molecular weight is less than 2.0.[26] Although stiff, the xanthan molecule is not nearly as rigid as TMV nor as flexible as the hydrolyzed polyacrylamide.

Results

Flexible Polymers. Figure 3 displays the effective size, D_{eff}, of the partially hydrolyzed polyacrylamide as a function of flow rate. The different curves in Figure 3 correspond to polymer samples of different molecular size. The top curve is obtained with the commercial polymer as supplied; each of the lower curves are measured with samples prepared by intentionally degrading the commercial material before analysis. Both shearing in a high-speed mixing device and sonication were employed to produce different degraded samples. It is immediately seen that D_{eff} is not constant with flow rate, implying that polymer deformation or degradation may occur during analysis. That the decrease in size with flow rate does not reflect degradation has been established by additional sample reinjection experiments; when samples are eluted a second time, the peak position, and thus the effective size of the polymer, is unchanged. (Details of the degradation and of the reinjection experiments are presented in ref 1).

Recent papers have discussed the mechanism of degradation of polymers in flow, and a general conclusion is that polymer deformation precedes breakage of backbone bonds.[27,28] Figure 3 indicates that as the molecules are stretched longitudinally by the flow, the transverse dimension measured by HDC decreases. This is consistent with the picture sketched in Figure 2 for the mechanism of HDC separation of polymers. Degradation has been observed in some of the samples at flow rates above those plotted in Figure 3.

The zero-shear-rate intrinsic viscosities of the five solutions were measured at 25.0 °C on a Contraves low-shear viscometer in the solvent used in the HDC experiment. In descending order of molecular size, as indicated in Figure 3, the intrinsic viscosities are 250, 63, 44, 38, and 7 dL/g. The correlation between measured molecular size and intrinsic viscosity is expected. None of the degraded samples showed any indication of a bimodal molecular weight distribution in chromatography experiments.

To analyze the deformation of polymer chains in small pores by the molecular models discussed earlier, it is first necessary to estimate the molecular relaxation time. This quantity cannot be directly obtained from eq 7 since the molecular weight of the polymer samples used in this study are not known accurately. If the equilibrium condition of the macromolecule is described by non-free-draining statistics, however, the relaxation time can be obtained by combination of eq 7 and the Flory–Fox relationship[29]

$$[\eta] = 6^{3/2}\Phi\frac{\langle S^2\rangle^{3/2}}{M} \tag{8}$$

where $\langle S^2\rangle^{1/2}$ is the equilibrium root-mean-square radius of gyration and Φ is the Fox–Flory parameter ($\simeq 2.5 \times 10^{23}$ mol^{-1}). Equations 7 and 8 lead (using $C = 0.42$) to the formula

$$\tau = \frac{6.12\Phi\eta\langle S^2\rangle^{3/2}}{RT} \tag{9}$$

Since the root-mean-square radius of gyration is proportional to the molecular weight for a Gaussian chain, τ is predicted to depend on molecular weight to the power 1.5 in a Θ solvent. More complete theories, which include both excluded-volume and hydrodynamic interactions, predict an exponent of about 1.8 in good solvents.[30] Experiments in elongational flows at stagnation points, however, provide data consistent with the 1.5 exponent even in good solvents if the polymer is not expanded by polyelectrolyte effects.[31] From the same type of experiment one infers that the proper exponent for expanded polyelectrolytes is 2.0, the value predicted in the absence of hydrodynamic interactions by the Rouse model.[32] Given these complications, the simplest form that circumvents many of these uncertainties (i.e., eq 9) will be used to estimate relaxation times for flexible chains. We have been unable to measure accurately the molecular weight of any of our samples; this difficulty is not unusual for these polymer types.

Since the mean-square radius of gyration has not been directly measured, an estimate of molecular size must also be made in order to calculate τ. At very low flow rates, the molecular size measured by HDC is proportional to the equilibrium diameter of the chain. It will be assumed that this diameter is approximately twice the root-mean-square radius of gyration of the polymer at equilibrium

$$\langle S^2\rangle^{1/2} \simeq D_{\text{eff}}/2 \tag{10}$$

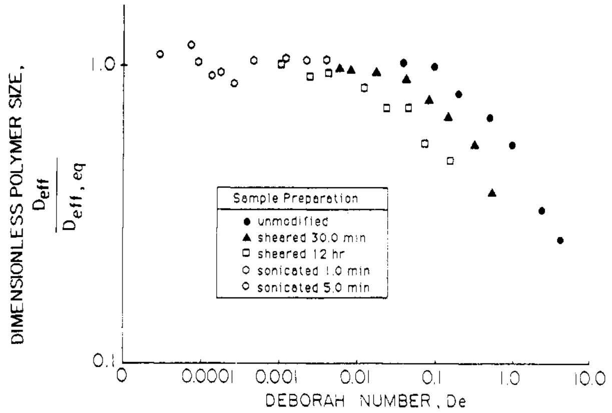

Figure 4. Data of Figure 4 replotted with the dimensionless polymer size as a function of Deborah number. For Deborah numbers much less than unity, a relaxed molecular conformation is inferred. As the Deborah number increases, molecular stretching decreases the effective polymer size. Data for the five polyacrylamide samples all fall, within experimental error, on a single master curve.

Table I
Properties of Partially Hydrolyzed Polyacrylamide Samples

sample	intrinsic viscosity, dL/g	D_{eff} (equilib), μm	τ,[a] s
unmodified SF210	250	1.75	0.414
sheared 30 min	63	0.48	8.54×10^{-3}
sheared 12 h	44	0.20	6.12×10^{-4}
sonicated 1 min	38	0.052	1.08×10^{-5}
sonicated 5 min	7	0.024	1.07×10^{-7}

[a] From eq 9.

This is likely to be a very crude approximation but will be sufficient for the present purpose of predicting how relaxation times scale with the molecular size. Equation 10 will be accurate to within an unknown constant of order 1. Values for the polymer relaxation time, calculated from eq 9 and 10, are tabulated in Table I. At first glance, some of these values seem somewhat large, even for polymers with average molecular weights well above 10×10^6. For polyelectrolyte solutions at low ionic strength, however, the polymer coil may be greatly expanded, leading to unexpectedly large relaxation times. A similar effect for polystyrene sulfonates has been observed by Miles et al.[32]

The Deborah number can now be written as a product of the quantities defined in eq 6 and 9.

$$\text{De} = k\left[\frac{\bar{v}}{d_{\text{p}}}\right]\frac{6.12\Phi\eta_{\text{s}}D_{\text{eff}}{}^{3}}{8RT} \tag{11}$$

With a nominal value of k from the literature ($k = 6$)[7,8] and the relaxed molecular size from the data set, the data in Figure 3 can be replotted as a function of De. The result is presented in Figure 4, where the effective polymer size for each sample has been made dimensionless with respect to the equilibrium size.

According to the analysis presented here, all data in Figure 4 should lie nearly on a single master curve displaying a transition near De = 0.5. Despite the crudeness of the model and the scatter in the data, the experimental results are in reasonable agreement to those predicted. Much of the scatter can be attributed to the error arising from difficulty in estimating the equilibrium value of D_{eff}, which is subsequently raised to the third power in calculating the Deborah number. An error in this calculation will shift a curve horizontally with respect to the other curves. The equilibrium size measurements are difficult

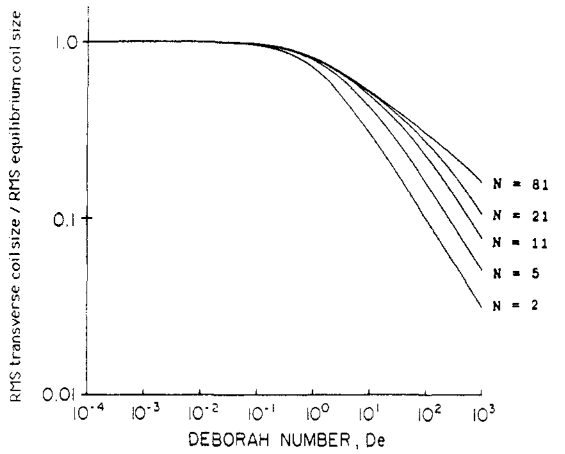

Figure 5. Root-mean-square diameter of a Rouse chain as a function of Deborah number. The diameter is defined in the direction transverse to the principal axis of stress by using a cross section through the center of mass of the chain. The flow is pure uniaxial elongation. The value of N indicates the number of beads in the model. The Deborah number has been defined by use of the longest Rouse relaxation time.

since the required run times are very long (over 24 h) for a chromatography experiment.

There is clearly a transition from the equilibrium polymer diameter to a flow-dependent diameter in the De range between 0.1 and 1.0. Given the scatter of data and the approximations made in calculating the relaxation time and the extension rate, the value obtained is consistent with the theoretical value 0.5, confirming the coil–stretch hypothesis as the basis for the flow rate dependence of molecular size observed in HDC of flexible polymers. The results are clearly not accurate enough to distinguish between the various modified dumbbell models for polymer stretching in strong flows. It must also be emphasized that HDC is sensitive to the molecular cross section, while the dumbbell models were developed to predict the maximum distorted dimension of the chain. These models are thus not suitable for quantitative analysis of HDC data.

In a separate publication,[33] a model for the deformation of flexible Rouse chains in flow is described. The molecular cross section computed with this model in steady uniaxial elongational flow compares reasonably well to the data presented in Figure 4. A quantitative comparison, however, would be difficult, given the scatter of data in the figure. The Rouse model has unexpected application to HDC since dynamics in the cross-sectional plane in the Rouse model are uncoupled from those along the axis of extension. Problems of finite chain extensibility can therefore be ignored and calculations can be carried out to De beyond 0.5. It must be remembered, however, that the flow in an HDC column is nonhomogeneous and, as viewed by the translating polymer coils, unsteady. Neither of these effects have been incorporated here—the flow considered has always been steady uniaxial elongation. This simplification has been used by many previous investigators with good success.[7-9] Given the possible impact of all assumptions, comparisons to data must be conducted cautiously. Figure 5 shows the root-mean-square cross-sectional dimension of Rouse chains in steady uniaxial elongational flow as a function of De.[33] The similarity to the experimental data in Figure 4 is obvious. These Rouse model calculations have been extended to homogeneous flows other than uniaxial elongation.[33]

Rigid Polymers. The two stiff polymers (or particles) studied in this work are TMV and xanthan. The molecular sizes of the two speices as a function of flow rate are presented in Figures 6 and 7. Although TMV is known to be a rigid rod, the conformation of xanthan is not entirely established; the data for this polymer will be compared to the predictions of the theory for rodlike species.

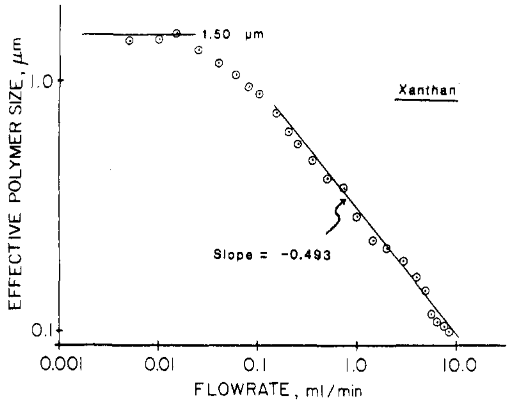

Figure 6. Effective size of xanthan as the flow rate is varied. This data can be interpreted in terms of the rigid dumbbell model, with the flow-dependent portion of the curve reflecting orientation in the flow field. The slope of the curve in this regime is very close to the theoretical value of −0.5 for rigid rods in steady uniaxial elongation.

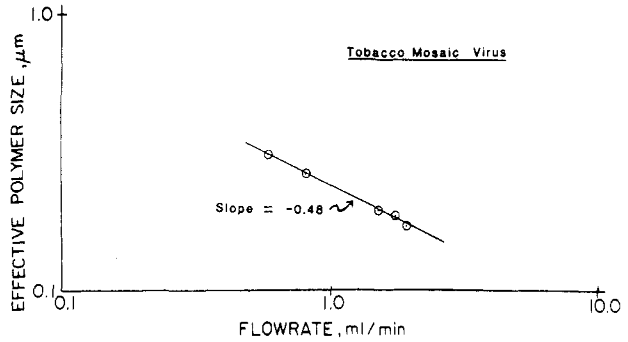

Figure 7. Effective size of TMV as the flow rate is varied. Since the TMV particle is rigid, the flow dependence must arise from orientation in the flow field. The rigid dumbbell theory predicts a slope of −0.5, very close to that observed.

Recognizing the strong influence of the elongational part of the flow field on orientation, the simple model to be discussed here considers only the motion of a rodlike polymer in steady uniaxial elongational flow. A more sophisticated model for the equilibrium (no flow) HDC behavior of rodlike polymers has been presented by LeCourtier and Chauveteau.[2] The rotational relaxation time τ for stiff rodlike polymers is obtained from eq 5. A dimensionless strain rate will be defined from τ and the elongation rate calculated from eq 6.

The effective size of the dumbbell during flow through a pore will be roughly related to a projection of the orientational distribution function onto a plane perpendicular to the direction of flow. The maximum value of this projection will qualitatively describe the transverse extent of the oriented dumbbell. Details of this simple calculation have been published previously.[34] The model leads to a theoretical prediction for D_{eff}

$$\begin{aligned} D_{\text{eff}} &= L, \qquad \tau\dot{\epsilon} < 1/9 \\ &= L[9\tau\dot{\epsilon}]^{-1/2}, \qquad \tau\dot{\epsilon} > 1/9 \end{aligned} \tag{12}$$

where L is the length of the dumbbell. The significant results are a low strain rate plateau and a strain rate dependent size at higher strain rates; this is similar to the predictions for flexible macromolecules. HDC is thus not a good technique for elucidating the flexibility of macromolecules with unknown physical structure.

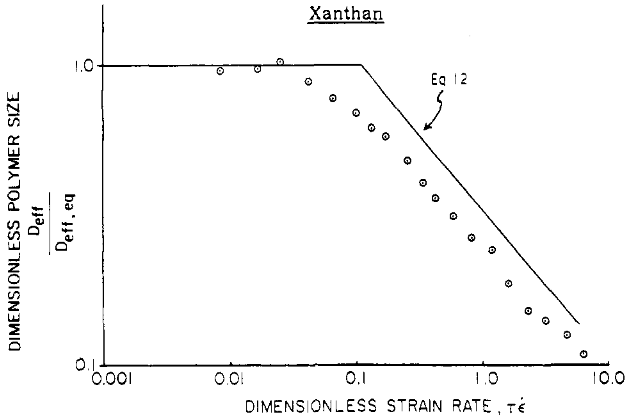

Figure 8. Dimensionless molecular size of xanthan plotted against the dimensionless elongational strain rate. The solid curve indicates the predictions of the rigid dumbbell model in steady uniaxial elongation. The polymer relaxation time, τ, has been fit with the measured intrinsic viscosity (168 dL/g) and a literature value of the average molecular weight (2×10^6).[24]

The two test polymers, xanthan and TMV, follow the behavior predicted by the rigid dumbbell model closely. Most significantly, the flow-rate dependence of D_{eff} at high strain rates is nearly as predicted. In this regime, D_{eff} is proportional to the flow rate to the −0.5 power. This exponent supports the use of uniaxial elongation as the basis for understanding flow of polymers in the porous HDC columns.

From the measured intrinsic viscosity of xanthan (168 dL/g) and the nominal molecular weight (2×10^6), eq 5 can be used to calculate the retention time of the xanthan molecule, $\tau = 0.014$ s. This value, in conjunction with eq 6, makes it possible to plot the dimensionless effective size of xanthan as a function of the dimensionless strain rate $\tau\dot{\epsilon}$. The result is presented in Figure 8 alongside the theoretical predictions of eq 12. Despite the gross approximations, the agreement between theory and experiment is remarkable.

Although there is considerably less data for TMV, due to the limited supply of material, the agreement with the predictions is also good. The results with xanthan and TMV are strong evidence that the basic orientation phenomenon discussed here is indeed responsible for flow-dependent HDC behavior. Conversely, the HDC results indicate that kinetic theory calculations for rigid solutes can be extended successfully to porous media flows.

Conclusions

The deformation and orientation of macromolecules during hydrodynamical chromatography can be understood semiquantitatively by using simple kinetic theory models. Deformation of flexible linear polymers has been correlated with the same dimensionless parameter that has correlated excess pressure drop data, the Deborah number. Similarly, orientation effects for rodlike polymers can be expressed as a function of the dimensionless strain rate $\lambda\dot{\epsilon}$. Under conditions for which *either* deformation of orientation of molecules occurs, interpretation of HDC separations in terms of equilibrium molecular size will be ambiguous.

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