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Xanthan Fractionation by Surface Exclusion Chromatography

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ABSTRACT: In chromatographic columns packed with nonporous particles, entropic effects exclude macromolecule centers of mass from the vicinity of pore walls over a distance closely related to the dimensions of these molecules; this causes a size fractionation based on surface exclusion. The efficiency of such a method for characterizing samples of high-molecular-weight xanthan depends on both shear rate and polymer concentration. The relation between polymer velocity and the molecule length–pore size ratio can be predicted by using a capillary model. The molecular weight distribution of two xanthan samples ($\bar{M}_w \simeq 2 \times 10^6$ and 3×10^6) was determined with good reproducibility.

Some recent papers[1,2] have suggested that conventional chromatographic techniques such as gel permeation chromatography (GPC) fail when applied to the characterization of very large macromolecules. Such polymers are easily oriented or deformed by hydrodynamic forces occurring in columns. Hence, steric pore exclusion mechanisms are disturbed, separation efficiency is poor, and the relationship between elution volume and molecular weight is found no longer to be valid for the highest molecular weight polymers.

A new technique based on surface exclusion, commonly called hydrodynamic chromatography, has been developed for rigid-particle size determination.[3] This technique, using nonporous column packing, has been shown to be efficient for size separation of proteins[4] and latexes.[5-8]

In a polymer solution near a repulsive wall such as a nonabsorbent solid surface, macromolecule centers of mass are sterically excluded from the wall vicinity over a distance related to macromolecule size. This phenomenon, which was theoretically predicted in static conditions for both flexible[9] and rodlike[10] polymers, leads to a depletion layer at the solid interface where polymer solution viscosity is lower than in the bulk.[11] During flow, this exclusion of macromolecules from the slowest stream lines near the wall induces a mean polymer velocity higher than the solvent one, thus giving a chromatographic polymer size fractionation. In this way, Prud'homme[12] eluted large macromolecules on a nonporous chromatographic packing and showed that macromolecules move ahead of solvent and that their velocity increases with their molecular weight. Nevertheless, the efficiency of the size fractionation observed was poor due to the too high flow rates used.

Table I
Chromatographic Column Characteristics

SiC packing, μm	length, cm	diameter, cm	permeability, 10^{11} cm^2	porosity
18	65	2.7	78	0.47
8	90	2.6	29	0.48

Table II
Characteristics of Xanthan Samples and Solutions

sample	mol wt[a]	intrinsic visc, cm^3/g	equiv molecular length, μm
I	1.8×10^6	4300	0.7
II	2.8×10^6	6900	1.0

[a] Light scattering.

This paper describes the first results of a study of shear rate and polymer concentration effects on the efficiency of xanthan fractionation by hydrodynamic chromatography. At sufficiently low shear rates and polymer concentrations, efficient separation is reached and the complete molecular weight distribution can be determined.

Experimental Section

The characteristics of the chromatographic columns used are given in Table I. They were dry packed with sharp-edged SiC particles, the mean dimension of which was 8 and 18 μm according to the manufacturer. Particle size distribution is relatively narrow as revealed by Coulter counter analysis (reduced standard deviation $\bar{\sigma}_r \simeq 0{,}25$).

Two xanthan microgel-free samples, the characteristics of which are given in Table II, were studied. The solutions obtained by

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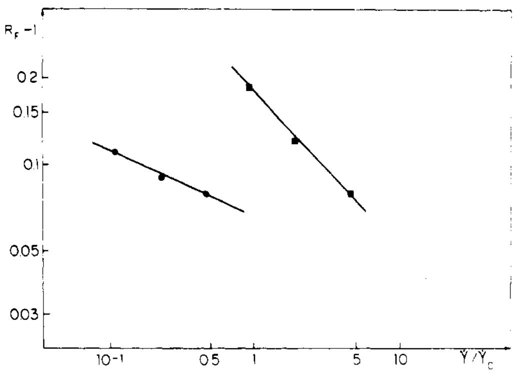

Figure 1. R_F variations as a function of $\dot{\gamma}/\dot{\gamma}_c$ for the two xanthan samples eluted on the 18-μm SiC column: (●) $\bar{M}_{w1} = 1.8 \times 10^6$; (■) $\bar{M}_{w2} = 2.8 \times 10^6$.

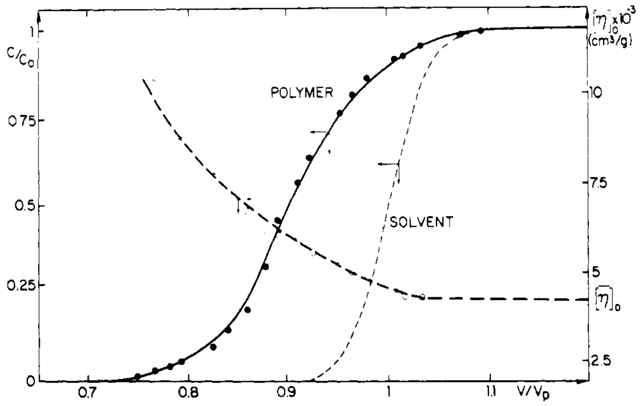

Figure 2. Polymer front at the outlet of the 18-μm SiC column ($\bar{M}_{w1} = 1.8 \times 10^6$; $C_0 = 200$ ppm; $\dot{\gamma}/\dot{\gamma}_c = 0.12$).

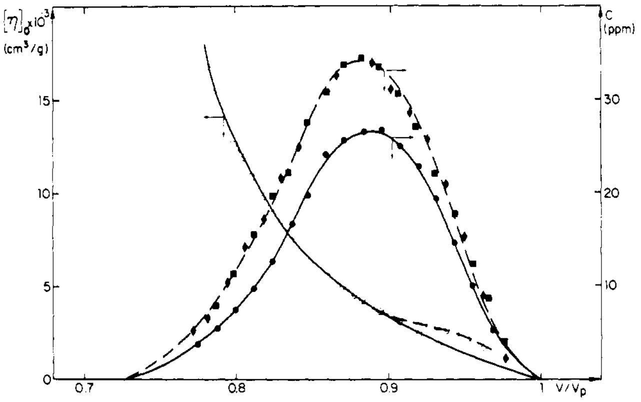

Figure 3. Xanthan solution slugs at the outlet of the 8-μm SiC column: (●, ○) $C_0 = 100$ ppm; (♦, □, ■) $C_0 = 200$ ppm. $\bar{M}_{w1}$ + 1.8×10^6; $\dot{\gamma} = 12$ s^{-1}.

diluting fermentation broths were clarified and filtered in order to remove both bacteria cells and any possibly remaining microgels according to a method previously described.[13] Low molecular impurities were eliminated by standard ultrafiltration. The salinity of the solutions (5 g/L NaCl + 400 ppm NaN_3 as a bactericide) was high enough to obtain a semirigid rodlike conformation.[14]

Polymer solution slugs were eluted at 30 °C with a constant flow rate pump. The eluent used was the polymer solvent. At the outlet of the columns, xanthan was detected by a Jobin-Yvon differential refractometer, and small samples were collected. Polymer concentrations were measured by a Dohrmann organic-carbon analyzer, and Newtonian viscosities were determined by a Contraves low-shear viscometer.

Results and Discussion

Polymer Size Fractionation. The mean velocity of polymer molecules in a chromatographic column is usually expressed by a dimensionless parameter R_F, which is the ratio of mean polymer velocity $\bar{V}_p$ to solvent velocity $\bar{V}_s$.

In porous-media flows, the maximum shear rate in pore throats can be calculated by a simple equation:

$$\dot{\gamma} = \alpha \frac{4V}{(8k/\Phi)^{1/2}} \tag{1}$$

where α, which is a parameter characteristic of pore structure, has a value close to 1.7 for porous beds packed with uniform-size particles.[11] V is the frontal velocity, k the perrmeability, and Φ the porosity.

The critical shear rate $\dot{\gamma}_c$, which characterizes the onset of shear rate dependence for xanthan solutions, was evaluated by viscosity measurements. For $C_0 = 200$ ppm, we found $\dot{\gamma}_{c1} \simeq 60$ s^{-1} and $\dot{\gamma}_{c2} \simeq 12$ s^{-1}.

Large slugs of xanthan solutions ($C_0 = 200$ ppm) were injected through the 18-μm SiC column at increasing velocities, and R_F values were determined. Figure 1 shows the variations of R_F as a function of $\dot{\gamma}/\dot{\gamma}_c$ for the two samples. R_F is always greater than 1 and decreases as shear rate increases. This phenomenon is easily explained by the exclusion distance decrease due to shear-induced molecule orientation. As expected, this effect is more sensitive for the higher molecular weight polymer. The intrinsic viscosity $[\eta]_0$ of the polymer fraction corresponding to R_F values, i.e. at concentration $C = C_0/2$, is close to 6500 cm^3/g while $\dot{\gamma}_c$ was determined with the unfractionated polymer solution ($[\eta]_0 = 4300$ cm^3/g). Thus, R_F is expected to be constant only at values of $\dot{\gamma}/\dot{\gamma}_c$ much smaller than 1.

Both polymer concentrations C and zero-shear-rate intrinsic viscosities $[\eta]_0$ are plotted in Figure 2 as a function of elution volume expressed in pore volume V/V_p. The size fractionation occurring in the column is well displayed by the intrinsic viscosity decrease from 15 000 cm^3/g to the mean value 4300 cm^3/g as the elution volume increases.

Molecular Weight Distribution. In order to obtain maximum separation efficiency during peak elution in the column, the experimental conditions were chosen as follows: (1) shear rate small enough to prevent molecular orientation by hydrodynamic forces; (2) polymer concentrations low enough to minimize viscous fingering at the trailing edge of the slug; (3) low flow rates so as to remain in a diffusion regime where hydrodynamic dispersion is minimized (low Peclet number).

The results of three experiments carried out with the lowest molecular weight sample ($\bar{M}_{w1} = 1.8 \times 10^6$) eluted on the 8-$\mu$m SiC column are given in Figure 3. The reproducibility tested by two different experiments at C_0 = 180 ppm is very good (square and diamond points in Figure 3). However, for this concentration we observe the effects of viscous fingering at the trailing edge of the slug ($0.9 < V/V_p < 1$), which gives poor separation efficiency in the low-molecular-weight range. For $C_0 = 100$ ppm, these effects are negligible.

Consequently, the molecular weight distribution was deduced from the 100 ppm experiments. For calculating $\bar{M}_w$, we used the Mark–Houwink relation $[\eta] \sim \bar{M}_w{}^a$, where a was found to be nearly equal to 1 by Holtzwarth[15] for xanthan samples having molecular weight higher than 10^6. This relatively low a value ($a \simeq 1.8$ for rigid rods), which is quite consistent with our measurements on the two samples studied (see Table II), means that these very long molecules behave like semirigid rods.

The curves giving molecular weight distributions are plotted in normal coordinates in Figure 4. Within experimental accuracy these distributions are log normal. The same polydispersity index $I_p \simeq 1.4$ is obtained for the two samples tested. This I_p value agrees quite well with

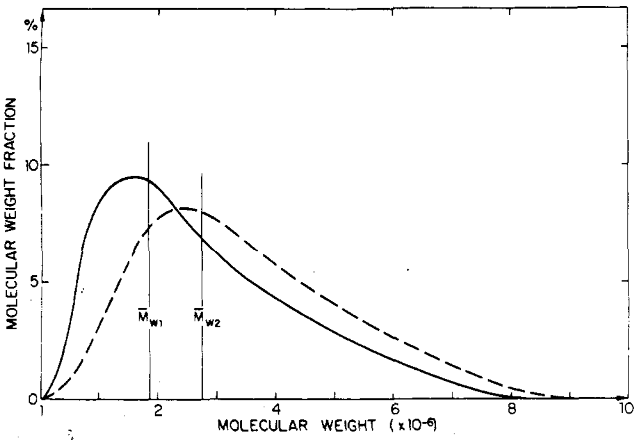

Figure 4. Molecular weight distribution of the two studied samples: (—) $\bar{M}_{w1} = 1.8 \times 10^6$; (---) $\bar{M}_{w2} = 2.8 \times 10^6$.

Wellington's[16] results ($I_p \simeq 1.35$) using a new electron microscopy method. As expected, this polydispersity index is significantly higher than values deduced from standard GPC experiments[2] ($I_p \simeq 1.25$) performed at such higher shear rates that the steric exclusion mechanism was perturbed.

Prediction for Polymer Velocity through Porous Media. If the porous medium is simulated by a bundle of straight capillaries with radius r, the velocity of a rigid rod molecule with a length L can easily be calculated by using the Poiseuille equation and taking into account the molecule exclusion from the vicinity of the pore wall.

The concentration of macromolecule centers of mass $C_{M,Z}$ as a function of the distance Z from a repulsive wall was predicted by Auvray:[10]

$$C_{M,Z} = C_B \frac{2Z}{L} \qquad \text{for } 0 < Z < L/2 \tag{2}$$

where C_B is the bulk concentration of macromolecule center of mass and L is the rod length.

Due to the eluent's high ionic strength, the large polymer dimensions, and the chemical nature of the packing, the effects of electrostatic repulsions and van der Waals forces near the wall can be neglected. If we assume that the solute's center of mass moves with the local solvent velocity, R_F can be calculated for dilute solutions as follows:

$$R_F = 2\left\{\left[\int_0^{r-L/2}\left(1-\frac{x^2}{r^2}\right)x\,dx + \int_{r-L/2}^{r}\frac{2}{L}(r-x)\left(1-\frac{x^2}{r^2}\right)x\,dx\right]\Big/ \left[\int_0^{r-L/2}x\,dx + \int_{r-L/2}^{r}\frac{2}{L}(r-x)x\,dx\right]\right\} = \left[1-\frac{1}{3}\frac{L^2}{r^2}+\frac{1}{8}\frac{L^3}{r^3}-\frac{1}{80}\frac{L^4}{r^4}\right]\Big/ \left[1-\frac{1}{2}\frac{L}{r}+\frac{1}{12}\frac{L^2}{r^2}\right] \tag{3}$$

For $L/r < 1$, this expression can be approximated by

$$R_F \simeq 1 + \frac{L}{2r} - \frac{L^2}{6r^2} - \frac{L^4}{720r^4} \tag{4}$$

The comparison of eq 4 with the one previously proposed[17] for rigid spheres having a diameter $2R$

$$R_F = 1 + \frac{2R}{r} - \frac{R^2}{r^2} \tag{5}$$

shows that surface exclusion is less important for rodlike particles than for spheres having the same size $2R$ = L.

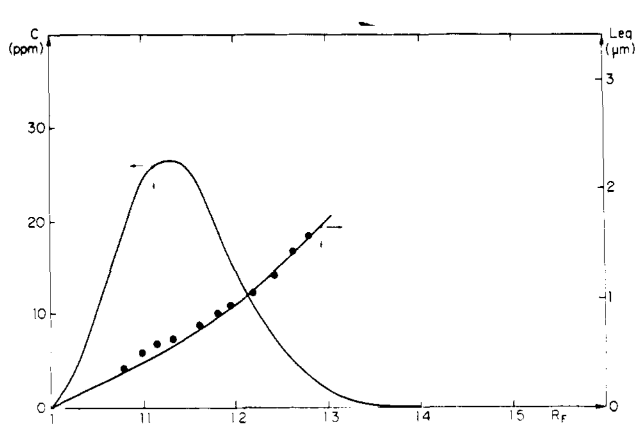

Figure 5. Experimental data (●) and theoretical curve $L_{eq} = f(R_F)$ in the case of the 8-µm SiC column.

Validity of Theoretical Model Predictions. As previously mentioned, the $[\eta]_0$–$\bar{M}_w$ relation determined by Holtzwarth shows that the xanthan molecule is not strictly rigid. A reasonable way to estimate exclusion distance from the wall is to calculate the length of the equivalent rigid rod L_{eq} having the same intrinsic viscosity.

The relations between intrinsic viscosity and macromolecular dimensions for rigid particles were predicted for ellipsoids[18] and rods.[19] For the highest values of length-to-diameter ratio p ($p > 50$), these relations between p and viscosity factor $V_0 = [\eta]_0/V_{sp}$ ($V_{sp} = 0.62$ is the specific volume for oligosaccharides) can be approximated by the same power-law function:[20]

$$V_0 = 0.141p^{1.812} \tag{6}$$

L_{eq} is then deduced from the value of diameter $d \simeq 19$ Å, a value widely accepted for the single-stranded structure of xanthan.[21] The mean values are given in Table II.

Experimental data (R_F and L_{eq}) are plotted in Figure 5 and compared with the theoretical ones deduced from eq 3 and 6. The best fit of experimental results using a least-squares method gives $r \simeq 2$ µm. This r value is consistent with the particle dimensions of the packing.

Conclusion

The application of hydrodynamic chromatography as a new technique for high-molecular-weight polymer characterization, is still in its early stage of development. Our first results show that, under suitable conditions, i.e. low polymer concentrations and low shear rate elution, hydrodynamic chromatography is an efficient method for determining the complete polymer size distribution.

The term "surface exclusion chromatography" seems more suitable than "hydrodynamic chromatography" in order to outline the physical mechanisms responsible for the separation process.

A capillary model is proposed to predict polymer velocity in porous media when the polymer size to pore diameter ratio is not negligible. The predictions of this model are in good agreement with experimental results.

However, the determination of optimum conditions for the separation of high-molecular-weight polymer by this new chromatographic method requires further studies.

Registry No. Xanthum gum, 11138-66-2.

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Self-Diffusion of Linear and 4- and 18-Armed Star Polyisoprenes in Tetrachloromethane Solution

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ABSTRACT: We have measured the diffusion of polyisoprene molecules, linear as well as 4- and 18-armed star branched, at 50 °C in dilute and semidilute CCl_4 solution over 4 orders of magnitude in molecular weight, using pulsed-gradient spin-echo NMR techniques. Flory's theory of dilute solutions (good solvent) and the Pyun–Fixman model account for the molecular weight and concentration dependences of the diffusivities for each architecture. Dilute diffusivity of the stars is significantly faster than that of linear molecules of equal molecular weight; the resulting hydrodynamic ratios h are independent of molecular weight and in good agreement with the Stockmayer–Fixman calculation. Certain predictions of scaling theory are confirmed.

I. Introduction

Regular star-branched polymer molecules permit convenient study of the influence of molecular architecture on molecular size and hydrodynamics, particularly in dilute solutions.[2] Given star molecules with f equal arms (linear molecules are described as $f = 2$), their ratio of translational friction coefficient F to that of linear molecules of equal molecular weight M in an identical solvent is defined as a hydrodynamic ratio[3]

$$h = F_0(f,M)/F_0(f = 2,M) \qquad (1)$$

The subscript 0 denotes infinite dilution. The Einstein relation $F = kT/D$ permits h to be inferred from translational diffusion coefficients D:

$$h(f,M) = D_0(f = 2,M,T)/D_0(f,M,T) \qquad (2)$$

Application of the Kirkwood–Riseman theory[4] to random-flight chain molecules of star architecture yielded,[3] for Θ solvents,

$$h(f) = f^{0.5}[2 - f + 2^{0.5}(f - 1)]^{-1} \qquad (3)$$

Experimental results for h tend to exceed this value at Θ conditions, but results for good solvents are typically somewhat lower.[5] Another ratio[3] may be derived from measurements of intrinsic viscosity $[\eta]$:

$$g' = [\eta](f,M,T)/[\eta](f = 2,M,T) \qquad (4)$$

For regular stars, a semiempirical result, also for Θ conditions, is[6,7]

$$g' = g^m, \qquad 0.5 \leq m \leq 0.6 \qquad (5)$$

where[8]

$$g = (3f - 2)/f^2$$

Because of the greater ease of making precise intrinsic viscosity measurements and the greater sensitivity of g' to f, determination of h from diffusion measurements has until recently been comparatively neglected. Given the emergence of several techniques of precise self-diffusion measurement[9-12] as well as excellent control and characterization of molecular architecture,[2] the study of the ratio h (theoretically exactly calculable) is now becoming increasingly attractive.

An understanding of g' and h in regular stars with large f is of considerable current interest. Recent work[7] (intrinsic viscosity and sedimentation rate) has shown clear evidence that the deviations of g' and h from eq 5 and 3 increase with increasing f and decreasing M, pointing to a perturbation of Gaussian chain statistics by interference among arms, in qualitative agreement with current theoretical concepts.[13] The present work was undertaken principally to add an alternate experimental viewpoint to this subject.

We have used the pulsed-gradient spin-echo (PGSE) method[12] of measuring self-diffusion (proton NMR) of polyisoprenes (f = 2, 4, and 18) in a proton-free good solvent (CCl_4)[14,15] to determine $h(f)$ and its dependence on molecular weight. In two previous investigations[15,16] we had found that $h(f)$ could probably be distinguished from unity for large f (polyisoprenes) but not[16] for $f = 3$ (polybutadienes and polystyrenes). In the process, the M dependence of D_0 had been shown[16,17] to obey the Flory theory[18,19] of dilute solutions

$$D_0 = AM^s, \qquad -0.6 \leq s \leq -0.5 \qquad (6)$$

while the concentration (c) dependence of D was in accord

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