$$R_m^2 \propto N^{6/(d+2)}, \quad 1 \le d \le 4$$

$$R_m^2 \propto N, \quad 4 \le d \quad \text{expanded state} \tag{18}$$

which gives the correct results for all d greater than or equal to 1. For the collapsed state we use $\alpha^{-d}N^{(-d+2)/2} = A$ as a trial solution

$$R_m^2 \propto N^{2/d} \quad \text{collapsed state} \tag{19}$$

which again is the correct result for all d.

Modification of our treatment places us in contact with existing work. Were we to use the radius of gyration S rather than R as our measure of polymer size and were we to take better account of the energetics, then the result would be very much like the Sanchez development.[8]

Our treatment should prove useful when attempting to solve a larger polymer problem in which excluded volume is only one factor. Common sense then suggests that the "simplest possible treatment" for the excluded volume problem would be most easily incorporated into the solution of the larger problem.

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Communications to the Editor

Concentration-Dependent Relaxation Times of Linear Polymers in Dilute Solutions

The relaxation of a distorted polymer chain in dilute solutions to its equilibrium configuration has been of considerable experimental and theoretical investigation over the past several decades.[1] Extensive studies[1-5] of the oscillatory flow birefringence and linear viscoelastic properties of polymer solutions have provided much insight into this relaxation process. Experimental work has shown that the intermolecular interactions (both hydrodynamic and excluded volume) occurring in dilute solutions affect the relaxation times of the various "Rouse–Zimm modes" significantly. The measurements of the flow birefringence and the viscoelastic properties of linear chains by Schrag and co-workers[2-5] show that the longest relaxation time is affected the most by the presence of other chains. Recently, the initial concentration dependence of the relaxation time (τ_p) of the pth mode of the bead–spring model has been derived by Muthukumar and Freed[6] to be

$$\tau_p/\tau_p^0 = 1 + cAp^{-\kappa} + \ldots \tag{1}$$

where τ_p^0 is the value of τ_p at infinite dilution, c is the polymer concentration, A is a constant in units of inverse concentration and κ is a positive constant. Both A and κ depend on the strength of the excluded volume interaction. κ is 0.5 in Θ solvents and 0.65–0.80 in good solvents. The experimental data of Schrag and co-workers[3-5] and Dill[7] on a variety of polymers show that the mode dependence of τ_p given by eq 1 is an adequate description at low concentrations of $c[\eta] < 1$, where $[\eta]$ is the intrinsic viscosity. The oscillatory flow birefringence data on the linear 390 000 MW PS and the 400 000 MW PMS for $1 \le c[\eta] \lesssim 5$ show that $\tau_p(c[\eta])$ can be empirically fitted[3,4] by

$$\tau_p = \tau_p^0 \exp(Acp^{-\kappa}) \tag{2}$$

For $c[\eta] \gtrsim 5$, the experimental data deviate from eq 2. Here we present a simple derivation to obtain the nonlinear dependence of τ_p on c.

By considering the interplay of the equilibrium screening length (due to the excluded volume effect) and the dynamic screening length (arising from the hydrodynamic interaction), Muthukumar and Edwards[8-10] have recently derived the following coupled equations for the shear viscosity (η) of the polymer solution as a function of polymer monomer density ρ and the chain contour length L (see eq 20–22 of ref 8)

$$(\eta - \eta_0)/\eta_0 = \lim_{k\to 0} k^{-2}\xi_H^{-2}(k) \tag{3}$$

$$\xi_H^{-2}(k) = \frac{\rho l}{\pi\eta_0}\int_{2\pi/L}^{\infty} dq \, \frac{(k^2 l_1/3)J(q)}{\left(\frac{k^2 l_1}{6}\right)^2 + q^2} \tag{4}$$

$$J^{-1}(q) = \frac{1}{3\pi^2\eta_0}\int_0^{\infty} dj \, \frac{j^2}{j^2 + \xi_H^{-2}(j)} \, \frac{j^2 l_1/3}{\left(\frac{j^2 l_1}{6}\right)^2 + q^2} \tag{5}$$

Here, η_0 is the shear viscosity of the solvent and l is the Kuhn step length. The variables k and j are wavevectors which are Fourier conjugate variables to the spatial position. The q variable is a wavenumber conjugate to the arc length position of a monomer along the chain configuration. This mode variable q is related to the pth "Rouse–Zimm mode" through $q = 2\pi p/L$. These equations are the generalization of the original equations of Freed and Edwards[11] for Θ solutions to non-Θ conditions. l_1 is the renormalized Kuhn step length due to the excluded volume effect and is dependent on both q and the static screening length, ξ_s, through (see eq 4.9 and 6.1 of ref 9)

$$l_1^3\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{12w\xi_s}{\pi} \, \frac{1 + \xi_s\left(\frac{3q}{l_1}\right)^{1/2}\left(\frac{6q\xi_s^2}{l_1} - 1\right)}{1 + \frac{36q^2\xi_s^4}{l_1^2}} \tag{6}$$

where

$$\xi_s^{-2} = \frac{6w\rho/l_1}{1 + \frac{27}{8\pi}\frac{w\xi_s}{l_1^2}} \tag{7}$$

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with wl^2 the effective binary cluster integral for a pair of segments. The inverse hydrodynamic screening length $\xi_H^{-1}(k)$ is, in general, wavevector dependent. From eq 4 it is obvious that for large length scales such as the size of the system, $k \to 0$, $\xi_H^{-2} = 0$, showing that there is no hydrodynamic screening and thus ensuring the fluid flow symmetry for the whole polymer solution. However, as argued in ref 8 and demonstrated in ref 10, for length scales shorter than the typical size of a chain, $k > (Ll_1)^{-1/2}$, $\xi_H^{-2}(k)$ is independent of k and the hydrodynamic interaction is screened for such a length scale. This is indeed responsible for the crossover from Zimm behavior to Rouse behavior as the polymer concentration is increased rather than the interchain entanglements (even in dilute solutions) as suggested by other authors.[12] Whether there is screening or not for a given ρ and length scale, η can be readily calculated form eq 3–5, and both the Zimm and the Rouse limits emerge in the appropriate limits.[8] It is clear from eq 3 and 4 that $l_1J(q)/q^2$ is the relaxation time (τ_q) of the qth mode ($q = 2\pi p/L$). In determining τ_q, $\xi_H^{-2}(j)$ of eq 5 should be eliminated self-consistently between eq 4 and 5. Thus the transition from Zimm behavior to Rouse behavior can be readily obtained from eq 3–7, which contain even the polymer density correlations under the semidilute conditions. Although this will be presented elsewhere, we provide below a simple rederivation of eq 1 and extend it to still higher concentrations.

First we calculate $(\eta - \eta_0)/\eta_0$ by an iterative procedure. Since $\xi_H^{-2}(k)$ is linearly proportional to ρ for dilute solutions (from eq 4), $J^{-1}(q)$ is found to this order of ρ by ignoring $\xi_H^{-2}(j)$ in eq 5. This gives

$$J^{-1}(q) = 1/\pi\eta_0(3l_1q)^{1/2} \tag{8}$$

Substitution of this result into eq 4 and combining with eq 3 for small k give the familiar Kirkwood–Riseman result. However, for k not very small, we get

$$\xi_H^{-2}(k) = 2^{1/2}k\rho l\int_0^\infty dx\,\frac{l_1(x)x^{1/2}}{1+x^2} \simeq \pi k\rho l l_1(L) \tag{9}$$

where for the sake of analytical simplicity we have argued that only the longest modes affect the renormalized step length l_1. The use of eq 9 for $\xi_H^{-2}(j)$ in eq 5 and further substitution of the resulting $J(q)$ in eq 4 yield

$$\frac{\eta - \eta_0}{\eta_0} = \frac{\rho l}{3^{1/2}}\int_{2\pi/L}^\infty dq\,\frac{l_1^{3/2}(q)}{q^{3/2}}\left[1 + \frac{\pi\rho l l_1^{3/2}(q)}{(12q)^{1/2}} + \dots\right] \tag{10}$$

so that

$$\frac{\tau_p}{\tau_p^0} = 1 + \frac{\pi\rho l l_1^{3/2}(q)}{(12q)^{1/2}} + \dots \tag{11}$$

For dilute solutions (where $\xi_s \to \infty$) we obtain the q dependence of $l_1(q)$ from eq 6 as

$$l_1^{5/2}\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{w}{\pi}\left(\frac{12}{q}\right)^{1/2} \tag{12}$$

This gives the mode dependence of l_1 for the extreme situations as

$$l_1(q) = \left(12^{1/2}\frac{w}{\pi}\right)^{2/5}q^{-1/5} \qquad \text{good solutions} \tag{13a}$$

$$l_1(q) = l \qquad \Theta \text{ solutions} \tag{13b}$$

Substitution of eq 13 into eq 11 reduces to

$$\tau_p/\tau_p^0 = 1 + cAp^{-\kappa} + \dots \tag{1}$$

with κ $^4/_5$ for good solutions and $^1/_2$ for Θ solutions. The interpolation between these two limits is provided by the identification

$$cAp^{-\kappa} = \pi\rho l l_1^{3/2}(q)(12q)^{-1/2} \tag{14}$$

and eq 12 for any given strength of the excluded volume effect. This derivation provides for the first time the concentration dependence of τ_p for any arbitrary value of w, in addition to being much simpler than the original derivation of ref 6.

Now we proceed to extend eq 1 to even higher concentrations. As mentioned above, the only length regime where the hydrodynamic interaction is screened is where the characteristic length is smaller than or about the size of the chain. For distances of this length scale, chain properties which are functions of k can alternatively be described[13] by functions of q. Representing this in terms of some unknowm ξ_H, we do the integral of eq 5 to get

$$J^{-1}(q) = \frac{1}{\pi\eta_0(3l_1q)^{1/2}}\,\frac{1 - Q^{-1} + 2^{1/2}Q^{-3/2}}{1 + Q^{-2}} \tag{15}$$

where

$$Q^{-1} = l_1\xi_H^{-2}/6q; \qquad q = 2\pi p/L$$

Substitution of eq 15 into eq 4 yields τ_p as

$$\tau_p/\tau_p^0 = (1 + Q^{-2})/(1 - Q^{-1} + 2^{1/2}Q^{-3/2}) \tag{16}$$

$$= 1 + 1/Q + \mathcal{O}(Q^{-3/2}) \tag{17}$$

Since ξ_H^{-2} should be linearly proportional to ρ for dilute solutions, comparison of eq 1 and 17 gives

$$Q^{-1} = cAp^{-\kappa} \tag{18}$$

Therefore the dependence of τ_p on polymer concentration and the mode label p is given by eq 16, for low concentrations, as

$$\tau_p/\tau_p^0 = 1 + cAp^{-\kappa} - 2^{1/2}(cAp^{-\kappa})^{3/2} + 2(cAp^{-\kappa})^2 + \mathcal{O}(c^{5/2}) \tag{19}$$

Furthermore, the dependence of τ_p on the strength of the excluded volume interaction for a marginal solvent is obtained by combining eq 19 and 14.

The prediction of eq 19 has been compared with the extensive experimental measurements of oscillatory flow birefringence for the linear 390 000 MW PS and the 400 000 MW PMS by Schrag and co-workers.[5] Equation 19 provides accurate predictions for the concentration dependence of τ_1 even up to $c[\eta] \gtrsim 5$. In addition, both the relaxation time breadth and the spacings (sometimes up to $c[\eta] \simeq 11$) are predicted well by eq 19. A detailed comparison between the experimental data and eq 1, 2, and 19 is reported in ref 5, and eq 19 is found to be the most satisfactory.

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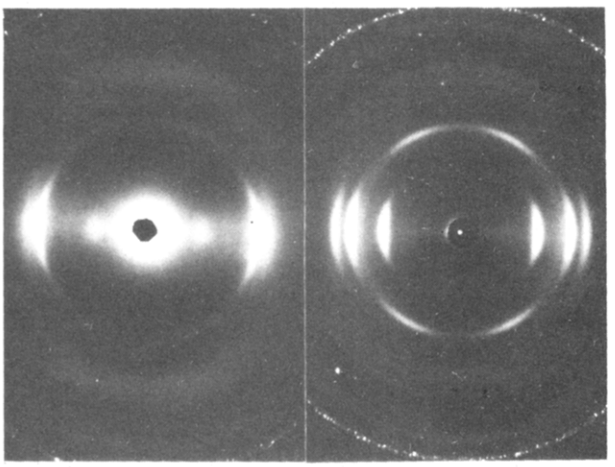

a b

Figure 1. X-ray diffraction patterns of the oriented chitosan A films: (a) before annealing at 75% relative humidity; (b) after annealing in water at 200 °C, under vacuum.

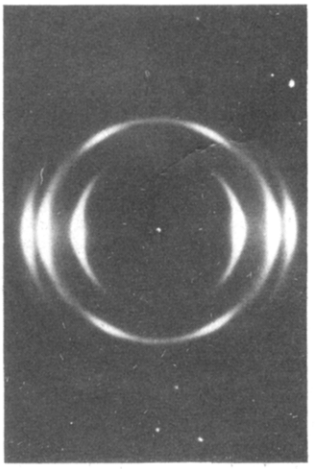

Figure 2. Fiber pattern of the oriented chitosan B film after annealing in water at 200 °C, under vacuum.

A New Polymorph of Chitosan

Chitosan, the N-deacetylation product of chitin, is a promising biomass for industrial purposes and is under intensive investigation for this application.[1] However, only a few studies on the molecular conformation of chitosan have been reported. The first X-ray fiber diagram was published by Clark and Smith in 1937.[2] They obtained an X-ray diffraction pattern from a chitosan fiber prepared by deacetylating the naturally oriented chitin fiber of lobster tendon: we call this sample "tendon chitosan". Each reflection spot of the pattern was well separated but somewhat diffuse because of the low crystallinity of the chitosan. The unit cell was determined to be orthorhombic with a = 8.9, b = 17.0, and c (fiber axis) = 10.25 Å. Darmon and Rudall[3] suggested that the lattice showed the same symmetry as the unit cell of α-chitin.

Recently, two other polymorphs have been obtained by Samuels[4] from chitosan films prepared from formic acid solutions. The unit cells of these polymorphs were orthorhombic with a = 7.76, b = 10.91, and c (fiber axis) = 10.30 Å and a = 4.4, b = 10.0, and c = 10.3 Å, respectively.

The possibility of fruitful X-ray diffraction analysis is solely dependent on the sample crystallinity. Recently, annealing in a solvent, usually water, at high temperature was found to be effective in improving the crystallinity of several polysaccharides: (1→3)-β-D-glucan,[5] (1→3)-α-D-glucan[6] and its acetyl derivative,[7] Lichenan,[8] Konjac glucomannan and its acetate,[9] and (1→3)-α-D-mannan.[10] We report a new chitosan polymorph induced by annealing and publish the clearest fiber pattern of any obtained hitherto. On the basis of this pattern, we propose a chitosan conformation.

A chitosan powder (sample A) was prepared from the chitin of crab shell, *Chionecetes opilio* O. Fabricus, by sodium hydroxide deacetylation.[11] The degree of deacetylation was measured by elemental analysis to be 99.5%, and the reduced viscosity, $\eta_{sp}C^{-1}$, in 0.2 M acetic acid was 5.5 L g^{-1} at a chitosan concentration of 5 mg L^{-1} at 30 °C. Another chitosan powder (sample B) having no acetyl group and $\eta_{sp}C^{-1}$ of 4.0 L g^{-1} at 5 mg L^{-1} was also prepared from the same crab shell chitin by repeating the deacetylation procedure. Each chitosan powder was prepared as a 0.2 M acetic acid solution (c 0.3 g L^{-1}), deposited onto a poly(ethylene terephthalate) film, and allowed to evaporate. The film thus prepared was immersed in 1 M aqueous NaOH for 30 min to make an acetate-free chitosan film. After washing with water, a strip of the film was stretched to three times its original length in water at 95 °C. The film prepared from sample A was well oriented but of low crystallinity (Figure 1a). The same film annealed in water at 190 °C or more in a closed bomb, with the film length kept constant, was of higher crystallinity (Figure 1b). The X-ray diffraction patterns were recorded by using a flat-film camera with a Rigaku Geigerflex X-ray diffractometer employing Ni-filtered Cu Kα radiation generated at 40 kV and 15 mA.

The stretched chitosan film before annealing (Figure 1a) showed a pattern similar to that from the tendon chitosan reported by Clark and Smith[2] except for the presence of a very weak equatorial reflection having a d spacing of 5.90 Å, which corresponded to the (120) reflection of the annealed chitosan. The fiber pattern was observed when the film was exposed to X-rays at 75% relative humidity. However, when irradiated under vacuum, the film showed a very diffuse diffraction pattern. That this change was brought about by changing the relative humidity indicates that the unit cell has water molecules, as suggested by Averbach.[12]

On the other hand, the fiber pattern of the annealed chitosan A film (Figure 1b) did not show any variation even when the relative humidity was changed from 0 to 100%: the same fiber pattern was obtained under vacuum even when the annealed film was dried under vacuum at 110 °C for 7 h. From the sharpness of each reflection, it is clear

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