Rheooptical Response of Rodlike, Shortened Collagen Protein to Transient Shear Flow

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ABSTRACT: This paper reports the rheooptical response of a new collagen sample using the technique of two-color flow birefringence (TCFB). This sample is prepared by a preparation procedure by which shortened and more rodlike collagen chains can be obtained. The procedure entails the use of pepsin digestion to break the collagen helix into $^1/_4$-length and $^3/_4$-length rods. Since the average contour lengths of the molecules are shorter with respect to the persistence length, these broken molecules are better approximations of rigid rods. Transmission electron microscopy has been used to confirm the more rodlike character of the shortened molecules. The TCFB measurements under both steady-state and transient flow conditions have been found to yield very good quantitative agreement with the Doi–Edwards–Marrucci–Grizzuti (DEMG) model, indicating that this model does provide a good description for the dynamics of strongly interacting rodlike polymer solutions. The effects of slight flexibility on the flow dynamics of rigid-chain-polymer solutions are also studied by comparing the transient flow results of the shortened bovine collagen to those obtained on two less rodlike collagen samples. The comparison indicates that the relaxation rates for a rigid, rodlike molecule and a slightly flexible molecule are significantly different, suggesting that the relaxation mechanism could also be different.

Introduction

Research on understanding the flow properties of rigid rodlike macromolecules in moderate concentration has made rapid advances in the past few years. One recent theoretical development, the Doi–Edwards model describing the dynamics of entangled rods in semidilute solutions,[1] predicts a strong concentration and length dependence of the rod rotational diffusivity resulting from the steric hindrance between neighboring rods. These predictions have been found to be in good qualitative agreement with dynamic and rheological measurements obtained on both synthetic and naturally occurring macromolecules assuming rodlike configurations.[2-4] Quantitative comparison between the experimental data and the model, however, is less successful. The discrepancies have been mostly attributed to either the slight flexibility of the molecules or the molecular weight polydispersity of the samples used for the experiments. However, no explanations have been offered as to how these two effects individually affect the flow dynamics.

The effects of polydispersity on the flow dynamics of rodlike polymer solutions have recently been investigated theoretically by Marrucci and Grizzuti,[5] and experimentally in our laboratory using two-color flow birefringence (TCFB) measurements obtained on type I collagen proteins.[6,7] Collagen assumes a triple-helical configuration of three polypeptide subunits, resulting in a rigid structure with contour length 300 nm and diameter 1.4 nm.[8] The molecule, however, is not perfectly rodlike, having a persistence length of about 170 nm determined from hydrodynamic measurements.[9,10] The polydispersity of the sample results from the cross-linking between individual collagen molecules which occurs before the protein is extracted from the animal tissue. The resulting solution contains collagen nomomers (molecular weight 300 000), dimers (600 000), and sometimes higher aggregates. The molecular weight distribution can be determined by transmission electron microscopy using the technique of rotary shadowing.[11]

Our previous study[7] confirmed the concentration scaling predicted by the Doi–Edwards model. Further comparison of the transient flow data with the original Doi–Edwards model showed significant qualitative disparity. The comparison was greatly improved by incorporating polydispersity into the model as proposed by Marrucci and Grizzuti (the DEMG model). We believe that some of the remaining quantitative discrepancies, such as the magnitude of the birefringence overshoot upon the inception of shear, are direct consequences of the limited flexibility possessed by the molecules.

It would be possible to directly study the effects of slight flexibility on the flow dynamics of rigid-chain polymers if a means to vary the rigidity of the molecules could be achieved. Recently, we have devised a new procedure by which more rodlike bovine collagen can be prepared by reducing the contour length of the molecule close to the persistence length. Transmission electron microscopy and TCFB measurements have been used to demonstrate the more rodlike characger of the shortened molecules. In this paper, we report this procedure for preparing shortened bovine collagen. The DEMG model will be tested quantitatively against the experimental results obtained on this collagen sample.

Experimental Section

Material Preparation and Characterization. Collagen is isolated from cowhide by a modification of the method of Drake et al.[12] The source, bovine corium, is swollen and pulverized in dilute acid, followed by solubilization with porcine pepsin at a weight ratio of pepsin to collagen of 1:100. Pepsin is a porcine proteolytic enzyme which cleaves most of the telopeptides that form cross-links between molecules, but leaves the helix intact. Such preparations have also been found to contain imperfect helices in small amount, however.[13] The imperfections have been demonstrated by two techniques. First, the method of poly-

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acrylamide gel electrophoresis under denaturing conditions[14] showed that there were shortened polypeptide chains present in the collagen. These broken chains were particularly evident as fragments of α chains with higher mobility than the α_2 chains.[7] Second, melting curves were carried out in a Jasco Model DIP-40 polarimeter equipped with a water-jacketed cell. The cell was connected to a water bath which was programmed to heat from 22 to 52 °C at 0.4 °C/min. The specific optical rotation at 498 nm ($[\alpha]_D$) was recorded during heat denaturation and typical sigmoid curves were observed.[15] Intact, native collagen had an $[\alpha]_D$ of −400, while fully denatured collagen exhibited a much lower value, $[\alpha]_D = -140$. These melting curves by polarimetry revealed helical components which had lower heat stability (melting temperature near 32 and 36 °C in 5 mM acetic acid) compared to the native helix (melting temperature, 42 °C). The results of both methods, melting curves and polyacrylamide gel electrophoresis, are consistent with the presence of either shortened or nicked helices.

The probable point of nicking or cleavage is about 225 nm from the N-terminal end of the helix, since this is the site for attack by vertebrate collagenase.[16] If cleavage is complete, this will result in a rod $^3/_4$ the length of the native helix. If only one or two of the three chains were cleaved, however, there would be a highly flexible region at that point. If the result is that the helix is completely cleaved, the shorter rods will be better approximations of rigid rods since their length is closer to the persistence length. We will demonstrate by both electron microscopy and TCFB measurements that the cleavage was indeed mostly complete and produced shortened collagen molecules.

It has been observed that imperfect helices are preferentially excluded from collagen fibrils,[13] which provides a means for their fractionation. Prior to precipitation, the imperfect helices constitute 10–15% of total collagen as measured by polarimeteric melting curves. When collagen molecules are precipitated at neutral pH, melting curves revealed that the supernatant contains up to 50% of imperfect molecules. This supernatant, supplied by Collagen Corp. of Palo Alto, CA, was filtered to remove residual dibrillar collagen and its pH was brought down to 2 by adding HCl. The acidic solution was subsequently concentrated up to about 7 mg/mL by using an Amicon (Danvers, MA) ultrafiltration cartridge with a 50 000 molecular weight cutoff. Glycerin (80 vol %) was added to the collagen solutions to increase the solution viscosity for the TCFB measurements. The concentrations of the final solutions were determined by the Biuret method[17] using a Gilford 2500 spectrophotometer at a wavelength of 550 nm.

The molecular weight distributions of the pepsin-cleaved collagen samples were determined morphologically by using the rotary shadowing techniques. Length determinations and counting methods have been described in previous papers.[7,18]

Two-Color Flow Birefringence Measurements. Flow birefringence has been used extensively to study the flow-induced conformational changes of macromolecules as the measurements provide information on the degree of optical anisotropy and hence structural anistropy. It has been recently demonstrated that flow birefringence measurements under transient shear flow are very sensitive to the flexibility of the molecules.[7,19] Compared to the mechanical devices currently used for stress measurements, the flow birefringence technique is intrinsically capable of following faster response times, and it does not disturb the system being studied. On the other hand, this optical method is generally restricted to two-dimensional flows since the measurements are averaged through the material along the propagation direction of the light beam. The TCFB technique, which is a modification of the conventional flow birefringence setup and is capable of nonlinear rheological measurements under very fast, transient flow conditions, is used to study the flow dynamics of the shortened collagen rods. The TCFB setup allows two flow birefringence experiments simultaneously by the use of the two principal spectral lines emitted from an argon ion laser. These two measurements are needed to uncouple two unknowns—the flow-induced optical anisotropy and the average orientation of the macromolecules. A detailed description of the TCFB setup can be found in previous publications.[20,7]

Experimental Results

Figure 1 is a representative transmission electron micrograph of the shortened bovine collagen. Out of seven TEM pictures containing over 500 particles, no collagen dimers or higher aggregrates were found. Analysis of these micrographs, as previously described,[7,18] indicated that our sample contains 54% monomers and 23% each of the $^1/_4$- and $^3/_4$-length broken rods. The lengths of the broken chains were determined by the most probable lengths measured for the two fragments since slight variations in the chain lengths were observed. The values for the distribution are also consistent with the proportion of imperfect helices determined from polarimetric melting curves. The monomers, as observed in Figure 1, appear to be mostly rigid with no observable nicked points along the helix. This is consistent with the hypothesis that our preparation procedure does indeed produce mostly shortened instead of nicked collagen molecules.

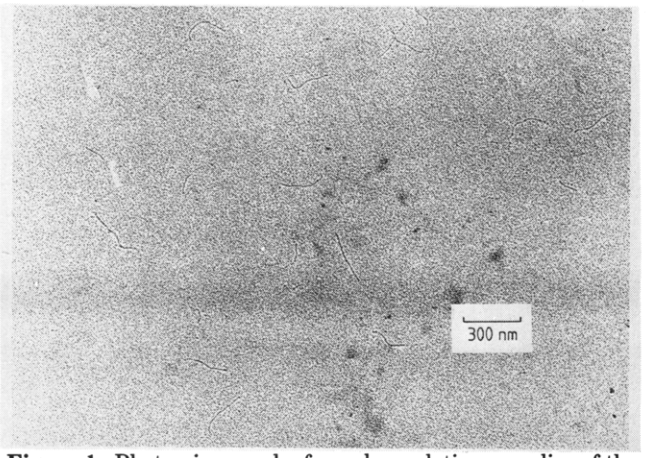

Figure 1. Photomicrograph of a carbon–platinum replica of the "shortened bovine collagen". The collagen is observed as monomeric, with approximately half of the molecules having contour lengths of 300 nm and the remaining molecules having lengths of 225 and 75 nm in an equal distribution. No dimers or higher aggregates were noted. Original magnification = 75000×.

Two solutions with concentrations 1.09 and 1.45 mg/mL in glycerin–water were prepared for the TCFB experiment. Figures 2a and 3a are the steady-state results of these two solutions using TCFB. The flow birefringence (Figure 2a), which is a measure of the degree of orientation and deformation of the macromolecules by the applied flow field, increases sharply at low shear rates as more rods are aligned. The rise in the birefringence slows down at higher shear rates as the orientation effect saturates. The average angle of orientation (Figure 3a), on the other hand, decreases with shear rate toward the direction of the flow.

Such rheooptical response for rodlike polymer solutions at moderate concentration can be predicted by the Doi–Edwards model for monodisperse systems and by the DEMG model for polydisperse systems. At concentrations below the isotropic–nematic phase transition where the rods are strongly interacting with each other, the rotational Brownian motion of the rods is impeded by the neighboring rods because of the close proximity of the rods. As a result, the rotational diffusiviity of the rods, D_r, is drastically lowered. The doi–Edwards model predicts that D_r is strongly dependent on the concentration c and the rod length L by the following relation:

$$D_r = \beta(cL^3)^{-2}D_{r0} \quad (1)$$

D_{r0} is the rotational diffusivity of a single, unimpeded rod, and β is a constant of proportionality anticipated to be of O(1).

The Doi–Edwards model also suggests that both the steady-state and the transient flow measurements on the

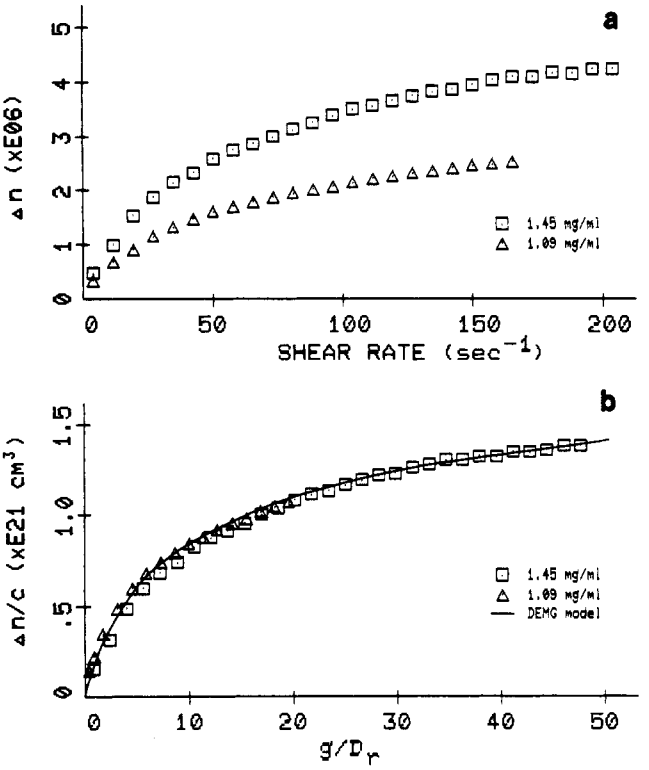

Figure 2. (a) Steady-state birefringence vs. the applied shear rate for two shortened collagen solutions. (b) Same set of data reduced by the concentration scaling suggested by the DEMG model.

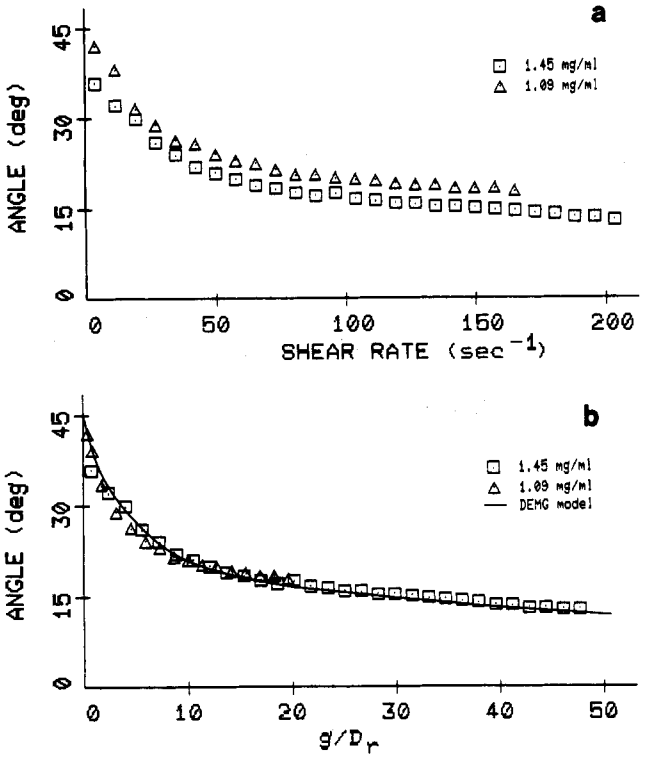

Figure 3. (a) Steady-state orientation angle vs. the applied shear rate for two shortened collagen solutions. (b) Same set of data reduced by the concentration scaling suggested by the DEMG model.

flow birefringence Δn and the orientation angle χ can be normalized by the concentration as follows:

$$\Delta n/c = Mf_1(g/D_r,D_rt) \quad (2)$$

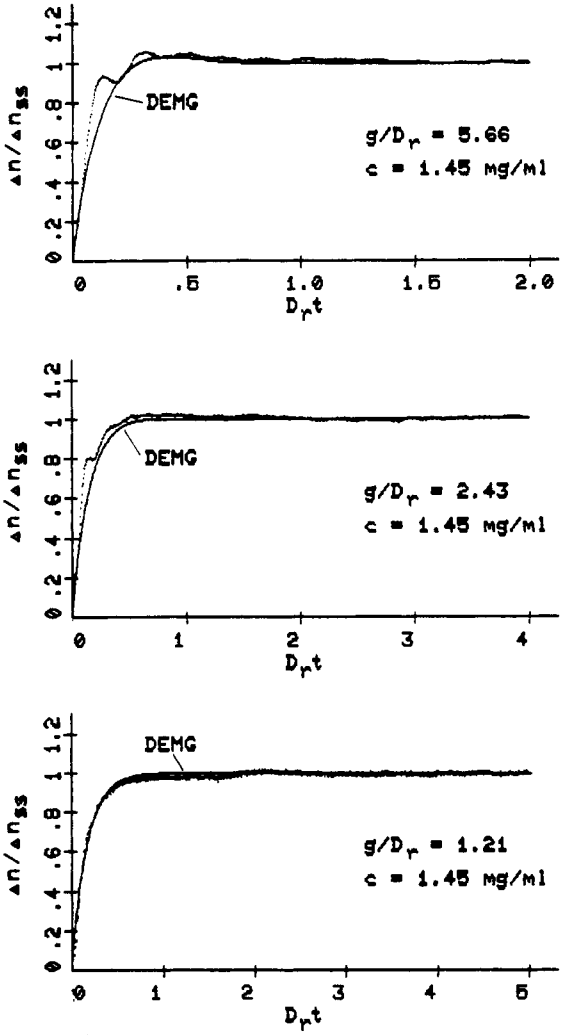

Figure 4. Birefringence normalized by the steady-state value as a function of the dimensionless time following the inception of shear flow for a shortened bovine collagen solution. The lines denoted by DEMG are the model calculations.

$$\chi = f_2(g/D_r,D_rt) \quad (3)$$

Here, g is the applied shear rate, t is the time, and M is a proportionality constant related to the intrinsic anisotropy of the polarizability of the system. f_1 and f_3 are two universal functions describing the rheooptical properties, $\Delta n/c$ and χ, for semidilute rodlike solutions. f_1 and f_2 are also functions of the molecular weight distribution when polydispersity is incorporated into the Doi–Edwards model (the DEMG model).

Figures 2b and 3b are plots of the steady-state data reduced by the concentration as described by eq 1–3. The solid lines in these graphs are the numerical solutions of the DEMG model using the method of infinite series expansion, and the model has been examined in detail elsewhere.[6] Since D_r is strongly dependent on the rod length, the value of D_r for the $^1/_4$-length rod is more than 3 orders of magnitude higher than those for the $^3/_4$-length and full-length rods. Consequently, at any given value of g/D_r, the effective shear rate experienced by the $^1/_4$-length rods is at least 3 orders of magnitude lower, and these shortest rods thereby contribute practically nothing to the flow birefriengence measurements over the shear rate range studied in this paper. So, for data comparison purposes, we have used the numerical solutions for a bimodal system instead of a trimodal system to save computation time. Comparisons with calculations involving the full trimodal

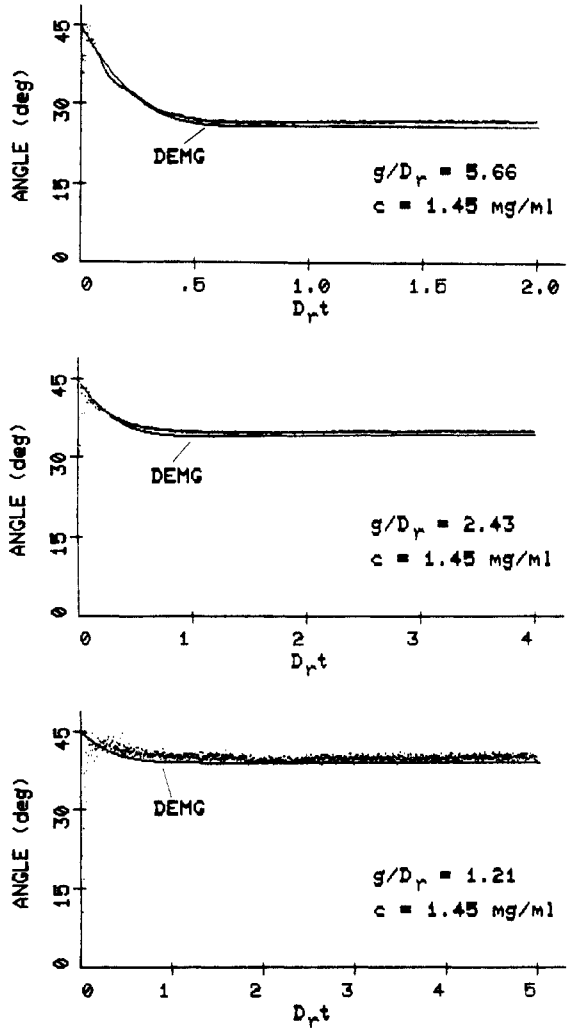

Figure 5. Orientation angle as a function of the dimensionless time following the inception of shear flow for the shortened bovine collagen solution. The lines denoted by DEMG are the model calculations.

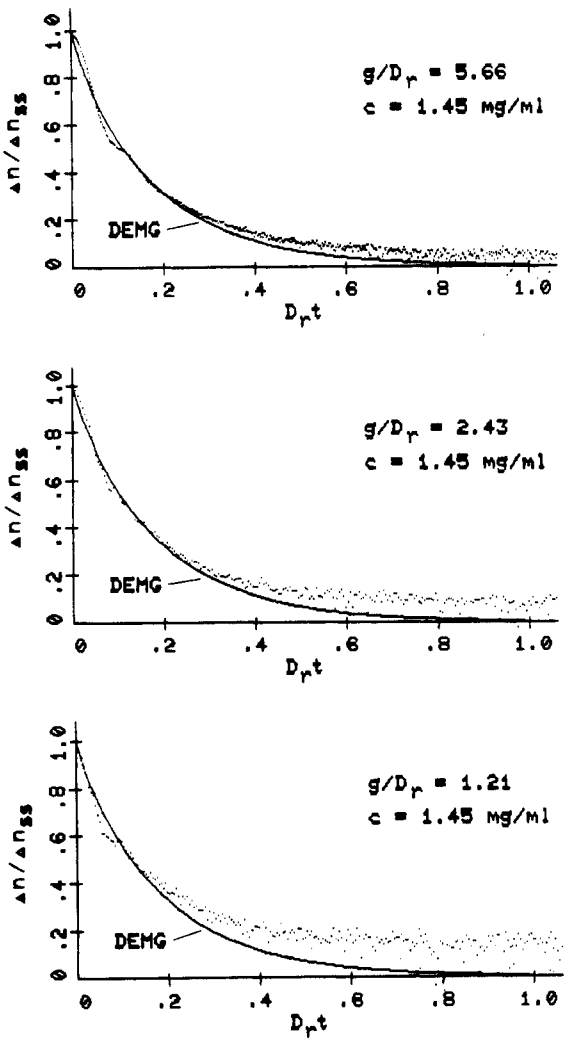

Figure 6. Birefringence normalized by the steady-state value as a function of the dimensionless time following the cessation of shear flow for the shortened bovine collagen solution. The lines denoted by DEMG are the model calculations.

distribution have justified this assumption. The parameters used for the DEMG model calculations were $c_1 = 0.30$, $c_2 = 0.70$, $L_1 = 0.8047$, and $L_2 = 1.073$. The subscripts 1 and 2 denote the $^3/_4$-length and monomeric collagen molecules. The number concentrations c_i have been normalized by the total concentration and the lengths L_i by the characteristic length $(\sum c_i L_i^2)^{1/2}$.

Two adjustable parameters, M and β (see eq 1 and 2), are needed for quantitative fitting of the steady-state data to the model. These same values of M and β are also used for fitting the transient flow data presented later. As indicated in Figures 2 and 3, the concentration scaling of the data by eq 2 and 3 indeed reduces all data onto two master curves. Furthermore, the quantitative agreement with the DEMG model is very good.

Figures 4–7 show results obtained under transient flow conditions. Figures 4 and 5 are the birefringence and the orientation angle following the inception of shear flow, and Figures 6 and 7 are plots of the birefringence and the angle following the cessation of shear flow. The birefringence has been normalized by the steady-state value Δ_{nss}. Shear rates ranging from $g/D_r = 1.21$ to 5.66 have been studied. Since our previous study on two somewhat more flexible collagen samples[7] indicated that the quantitative disparity in the comparison was grater at lower shear rates due to flexibility, we are more interested in the flow response of this more rodlike sample in the low shear rate regime.

All four figures indicate excellent quantitative comparison between the model and the data. In Figure 4, both the data and the model predictions yield a monotonic increase in the birefringence upon the inception of shear when g/D_r is near unity, and a small overshoot at higher shear rates. In our previous study, on the other hand, both collagen samples exhibited overshoots even at g/D_r near and below unity as shown in Figure 8. In this figure, the birefringence overshoot is plotted as a function of the normalized shear rate for all three collagen samples. The solid lines are the best-fit lines through the data. We attributed the larger overshoots produced by the other two collagen samples to the finite but limited flexibility of the molecules since flexibility allows another mode of deformation by stretching of the coiled configuration in addition to the alignment effect of the flow. Therefore, the monotonic increase in the flow birefringence observed here at very low shear rates is believed to be a good indication of the increased rodlike character possessed by the shortened molecules.

Measurements obtained upon the cessation of shear flow are also believed to be very sensitive to the flexibility of the molecules. Relaxation data on the previous two collagen samples produced only fair model comparisons which worsen at lower shear rates. In contrast, the results plotted in Figures 6 and 7 showing the relaxation data for the

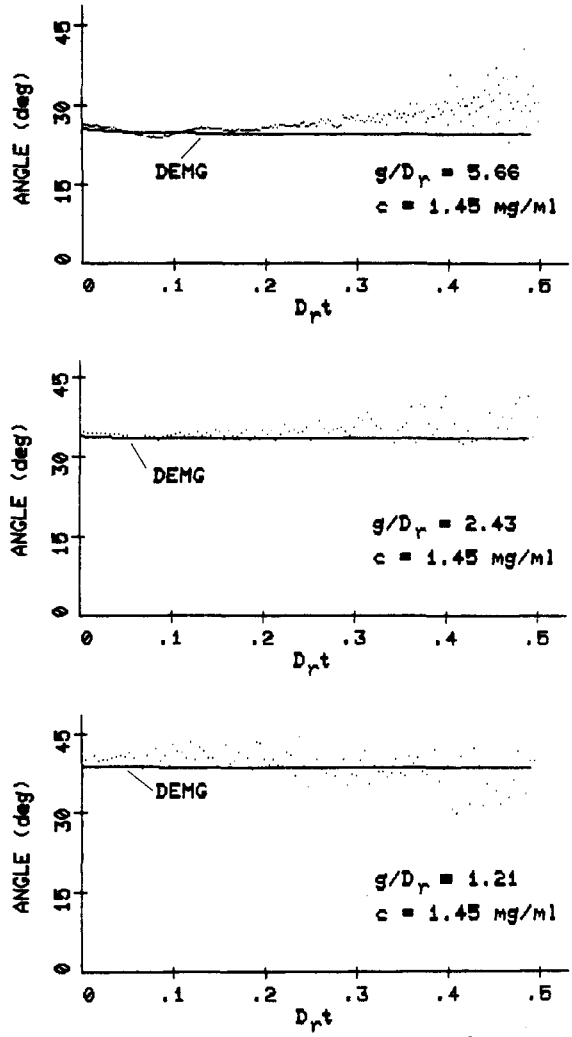

Figure 7. Orientation angle as a function of the dimensionless time following the cessation of shear flow for the shortened bovine collagen solution. The lines denoted by DEMG are the model calculations.

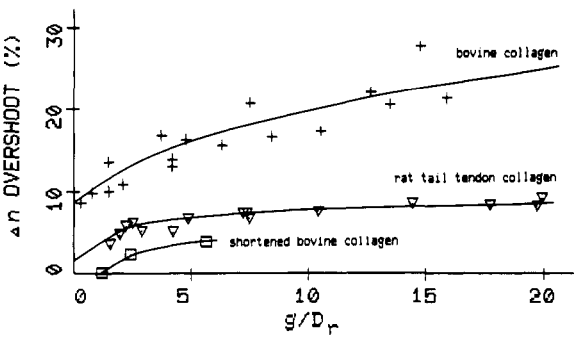

Figure 8. Percent overshoot in the birefringence upon the inception of shear flow vs. the dimensionless shear rate for three collagen samples. The solid lines are the best-fit curves correlating the data.

shortened bovine collagen yield very good agreement betwen the model and the data even at the lowest value of g/D_r.

Discussion

The excellent quantitative agreement between the DEMG model and the experimental results obtained on the shortened collagen is strong evidence that this model provides an accurate description of the flow dynamics of moderately concentrated rodlike polymer solutions. The agreement with the transient flow results is of particular significance since measurements under fast, transient flow are regarded as more stringent tests of theoretical models and constitutive equations.

The value of M, which is related to the intrinsic polarizability of collagen, is 3.6×10^{-21} cm^3 for the broken bovine collagen solutions. When normalized by the characteristic length, M is extrapolated to be 4.3×10^{-21} cm^3 for monomeric bovine collagen. This value is low compared to that obtained previously for monomeric bovine collagen, which is 6.0×10^{-21} cm^3.[7] This discrepancy could be attributed to the nonuniform composition along a collagen molecule which yields different local polarizability along the molecule. As a result, when a collagen molecule is broken into the $^1/_4$- and $^3/_4$-length segments, the normalized intrinsic polarizability of the segments would likely be different. On the other hand, the $^3/_4$-length rods are always more oriented by the flow and therefore they contribute more to the value of M than the $^1/_4$-length rods. Consequently, the normalized value for M obtained for the broken bovine collagen is expected to be different from that measured for the unbroken bovine solutions.

The value of β needed for the quantitative fitting of the model to the data is 10^4, which is much higher than the $O(1)$ quantity originally anticipated by Doi and Edwards.[1] It is nonetheless lower than the values of β of $O(10^6)$ calculated for the other two more flexible collagen samples.[7] Therefore, we believe that even a perfectly rodlike system will produce a high value of β. An explanation to account for this high value of β offered by others studying rodlike polymers[21,22] suggests that an entangled rod only needs to translate a fraction of its rod length instead of the full rod length in order to remove the steric hindrance from neighboring rods. Since D_r is a strong function of the length scale ($O(L^{-9})$ for a monodisperse system), a small reduction in the effective length scale results in a large value for β. Flexibility, on the other hand, also tends to reduce the effective length and therefore increase the value of β even more.

The transient flow measurements have been found to be a sensitive measure of the flexibility of the system. Following the inception of shear, the Doi–Edwards and DEMG models predict an overshoot in the birefringence with a magnitude always less than 13% of the steady-state value even at moderate and high shear rates.[6] Previous experimental studies on both semiflexible and flexible polymers indicated that the magnitude of the overshoot was much larger (sometimes over 200%) for more flexible systems,[19,20] suggesting that the magnitude of the overshoot in the birefringence could be used as a direct measure of the degree of flexibility.

Measurements following the cessation of shear are also greatly influenced by the limited flexibility of the macromolecules. Our previous study on the slightly more flexible collagen molecules indicated good quantitative agreement between the model and the relaxation data only at high shear rates and at short times. The more rodlike collagen prepared for this study, however, produced good comparison even at low shear rates and also at longer times. This difference could be attributed to the fact that at higher shear, the less rigid molecules are stretched out by the flow to assume a more rodlike configuration. Upon the cessation of flow, the extended molecules start to disorient by the Brownian motion and at the same time relax their configuration back to the slightly coiled conformation. Therefore, at times shorter than the flexural relaxation time and at the high shear regime, the relaxation data tend to agree better with the rigid-rod model. The disparity

observed at low shear rates and at long times suggests that the relaxation mechanism for a slightly coiled molecule could be significantly different from that for a perfectly rodlike molecule.

Conclusions

We have demonstrated by TCFB measurements and TEM that the shortened bovine collagen prepared by the procedure described in this paper is indeed characterized by a shorter average contour length. The molecules are more rodlike since the contour length is now closer to the persistence length. The TCFB measurements under both steady-state and transient flow conditions were in excellent quantitative agreement with the DEMG model, thereby confirming the validity of the model. Comparisons with the results obtained on two slightly more flexible collagen samples reported previously suggested that the relaxation mechanism for a semiflexible molecule could be completely different from that for a rodlike molecule.

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References and Notes

(1) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560, 918.
(2) Chu, S. G.; Venkatraman, S.; Berry, G. C.; Einaga, Y. *Macromolecules* **1981**, *14*, 939.
(3) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.
(4) Maguire, J. F.; McTague, J. P. *Phys. Rev. Lett.* **1980**, *45*, 1891.
(5) Marrucci, G.; Grizzuti, N. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 83.
(6) Chow, A. W.; Fuller, G. G. *Macromolecules*, first of two preceding articles in this issue.
(7) Chow, A. W.; Fuller, G. G.; Wallace, D. G.; Madri, J. A. *Macromolecules*, second of two preceding articles in this issue.
(8) Eyre, D. R. *Science (Washington, D.C.)* **1980**, *207*, 1315.
(9) Nestler, F. H. M.; Hvidt, S.; Ferry, J. D.; Veis, A. *Biopolymers* **1983**, *22*, 1747.
(10) Saito, T.; Iso, N.; Miauno, J. H.; Onda, N.; Yamato, H.; Odashima, H. *Biopolymers* **1982**, *21*, 715.
(11) Furthmayr, H.; Madri, J. A. *Collagen Relat. Res.: Clin. Exp.* **1982**, *2*, 349.
(12) Drake, M. P.; Davidson, P. F.; Bump, S.; Schmitt, F. O. *Biochemistry* **1966**, *5*, 301.
(13) McPherson, J.; Sawamura, S.; Conti, A.; Condell, R., manuscript in preparation.
(14) Laemmli, U. K. *Nature (London)* **1970**, *227*, 680.
(15) von Hippel, P. H.; Wong, K.-kY. *Biochemistry* **1963**, *2*, 1399.
(16) Gross, J.; Harper, E.; Harris, E. D., Jr.; McCroskery, P.; Highberger, J. H.; Corbett, C.; Kang, A. H. *Biochem. Biophys. Res. Commun.* **1974**, *61*, 605.
(17) Gordall, A. G.; Bardawill, C. J.; David, M. W. *J. Biol. Chem.* **1949**, *177*, 751.
(18) Madri, J. A.; Foellmer, H. G.; Furthmayr, H. *Biochemistry* **1983**, *22*, 2797.
(19) Zebrowski, B. E.; Fuller, G. G. submitted for publication in *J. Polym. Sci., Polym. Phys. Ed.*
(20) Chow, A. W.; Fuller, G. G. *J. Rheol.* **1984**, *28*, 23.
(21) Jain, S.; Cohen, C. *Macromolecules* **1981**, *14*, 759.
(22) Odell, J. A.; Atkins, E. D. T.; Keller, A. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 289.

Chain Dynamics and Molecular Weight Dependence of Carbon-13 and Hydrogen-1 Relaxation Times in Polystyrene and Polyethylene Melts

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ABSTRACT: It is shown that nuclear magnetic relaxation is a suitable tool for the investigation of global motions in polymer melts. The transverse relaxation time of the quaternary carbon of polystyrene shows the double-break molecular weight dependence predicted in a previous paper. The break at low molecular weights coincides with the rheological M_c value. The longitudinal relaxation times above 10 MHz show a molecular weight independent plateau indicating the existence of entirely local motions. The results are discussed in context with some statements concerning a recent Monte Carlo study by Kremer.

Introduction

The nuclear magnetic relaxation times T_1 and T_2 are sensitive to interactions in the close neighborhood of the observed nuclei. The technique nevertheless is not restricted to the investigation of *local* processes. Rather, T_1 at low frequencies ($\approx 10^4$ Hz) and T_2 show a molecular weight dependence[1] implying the features of that of the zero-shear viscosity. This finding was based on proton resonance data of polyethylene melts. Thus, it has been proved that *global* motions can be relevant for NMR relaxation.

Moreover, the NMR methods show additional effects hitherto unknown in rheology. Several "characteristic molecular weights" have been found. With polyethylene melts it turned out, for instance, that the molecular weight dependence of T_2 or of T_1 at low frequencies ($\approx 10^4$ Hz) is characterized by a *double-break* behavior, where the lower break virtually coincides with the critical molecular weight[1,2] M_c known from rheology. The upper break at a frequency-dependent molecular weight M_{BC} is due to a crossover to a region where coil-internal motions dominate. At high frequencies ($>10^7$ Hz) finally a transition to a molecular weight independent region has been observed.

The molecular weight dependence of the NMR relaxation times is generally weaker than that of rheological quantities. In the temperature/frequency range permitting measurements below M_{BC}, for instance, the molecular weight dependence of T_1 and T_2 is roughly half as strong

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