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Effects of Temperature and Solvent on the Rheo-optical Behavior of Hydroxypropylcellulose Solutions

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ABSTRACT: The effects of solvent and temperature on the rheo-optical behavior of hydroxypropylcellulose (HPC) solutions in water and acetic acid have been studied using flow birefringence, quiescent circular birefringence, and intrinsic viscosity. Measurements of steady state and transient flow birefringence suggest that the flexibility of the HPC molecule in water increases with increasing temperature, while it remains relatively constant in acetic acid. The relatively small temperature-induced changes of HPC are contrasted with the flow birefringence behavior of PBLG (poly(γ-benzyl L-glutamate)) in the mixed-solvent system, dichloroacetic acid−1,2 dichloroethane, in which it undergoes a coil−helix transition. Results indicate that the effects of conformational changes on the dynamical behavior of HPC can be described in terms of a wormlike chain whose rigidity depends on the solvent as well as temperature and polymer molecular weight. A discussion of the possible roles of thermodynamic and structural effects on the molecular rigidity leads to the conclusion that structural effects are more likely.

Introduction

Hydroxypropylcellulose (HPC) is an important model, mesomorphic polymer due to its ready availability and solubility in a wide range of solvents. The HPC molecule is known to adopt a helical conformation in the crystalline state.[1−3] On the other hand, its conformations in solution and liquid-crystalline phases are not as well understood. Properties related to the conformation and rigidity of a macromolecule range from the rheology of the solution[4] and the liquid-crystalline state[5,6] to the drawability of solvent-cast films[7] and the tensile strength of coated paper products.[8] Moreover, the effects of changes in temperature on the lyotropic phase behavior of HPC solutions have been observed[9−11] and are most likely related to changes induced in the chain conformation and rigidity.[12]

The combination of temperature and solvent can be a useful tool for probing the effects of the rigidity on the associated dynamic behavior of semiflexible molecules. The present study offers an illustration of such behavior for isotropic solutions of HPC in acetic acid and water. Since the critical concentration for the appearance of the liquid-crystalline phase varies widely between these two solvents,[6,13] the additional influence of temperature-induced changes in rigidity can be conveniently studied. In this work, measurements of the quiescent optical activity, in combination with the transient and steady-state rheo-optical behavior, are used to gain quantitative insights on the role that relatively small changes in molecular flexibility can have on the dynamic behavior. Comparisons are also made to the flow behavior of PBLG (poly(γ-benzyl L-glutamate)) as it undergoes a temperature-induced, helix−coil transition in the solvent system DCA−EDC (dichloroacetic acid and 1,2-dichloroethane). These illustrate the quantitative differences in behavior that occur with a system that undergoes large conformational changes from the random-coil to the rigid-rod state.

Experiments

Materials. HPC samples, obtained from Hercules Inc., were labeled Klucel L and M. Nominal weight-average molecular weights given in the product literature are 100,000 for L and 500 000 for M. The weight-average molecular weight and polydispersity index of sample L have been reported to be 106 000 and 2.67, respectively,[14] in one study. Another more recent study reports a polydispersity index of 2.0[15] for the same sample. Poly(γ-benzyl L-glutamate) was purchased from Sigma Chemical Co. (Lot No. 123H5523), with a reported weight-average molecular weight of 333 000 and polydispersity index of 1.1. Reagent-grade glacial acetic acid and 1,2-dichloroethane (EDC), obtained from Fisher Scientific, and dichloroacetic acid (DCA), obtained from Sigma, were used as obtained. Deionized, distilled water was used to make up the water solutions.

Stock solutions of HPC were made up a few days prior to experiments by first drying the polymer for 20 h in a vacuum oven at 50 °C immediately before dissolution, followed by slow stirring with a magnetic stirrer for 24 h. Concentrated solutions were stored in the dark and rotated on a daily basis to ensure homogeneity. All solutions were filtered using a 5 μm syringe filter prior to dilution for a given experiment. PBLG solutions were made up by dissolving the polymer in a fresh solvent mixture of 76% DCA and 24% EDC, by volume. Solutions were stirred for 8−12 h for complete dissolution and then stored at 10 °C.

Optical Techniques. The variable-pathlength-cell and modulated polarimetry system used for measuring the quiescent optical rotatory power are described in detail elsewhere.[16,17] Temperature control was obtained using a Neslab RTE 111 circulating system, and the temperature at the center of the solution was monitored to within 0.1 °C, using an Omega digital thermometer. Measurements of quiescent rotatory power as a function of temperature and concentration were made using the B2 optical configuration, discussed in previous papers.[17,18] Cell path length varied from 6 to 8 cm, depending on the solution concentration and rotatory power. A couette flow cell (stationary outer cylinder, rotating inner cylinder) was used to measure linear birefringence as a function of concentration and temperature over a range of shear rates from 0.001 to 600 s^{-1}. Details of the design and assembly of the flow cell can be found elsewhere.[19] Two different gap sizes and dc motors were used to cover the shear rate range. The first motor operated from 0.001 to 1 s^{-1} with the smaller rotor (R_I = 3.67 cm, gap size 1 mm), and the second operated from 1 to 600 s^{-1} with the larger rotor (R_I = 3.70 cm, gap size 0.7 mm). All measurements were performed in the flow-shear plane; i.e., the beam propagated vertically (down the vorticity direction) through the gap. Further details on the optical configurations used to measure flow birefringence, flow dichroism, and turbidity can be found in several papers and associated thesis studies.[16−20] In the experiments reported here,

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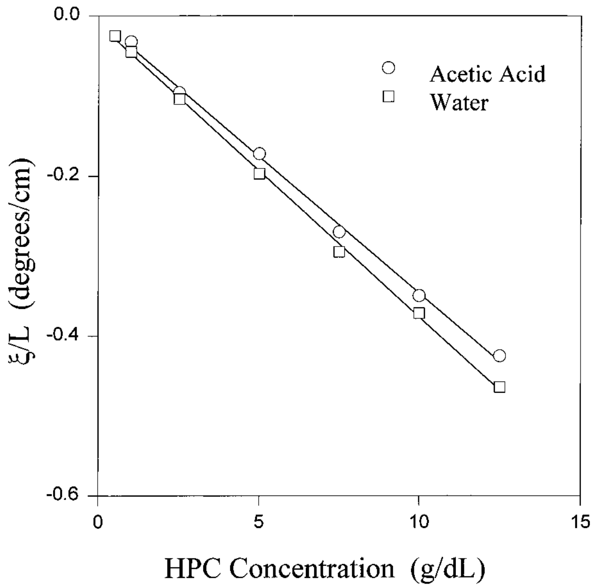

Figure 1. Optical rotatory power (deg/cm) of quiescent HPC-L solutions at 25 °C versus polymer concentration (g/dL).

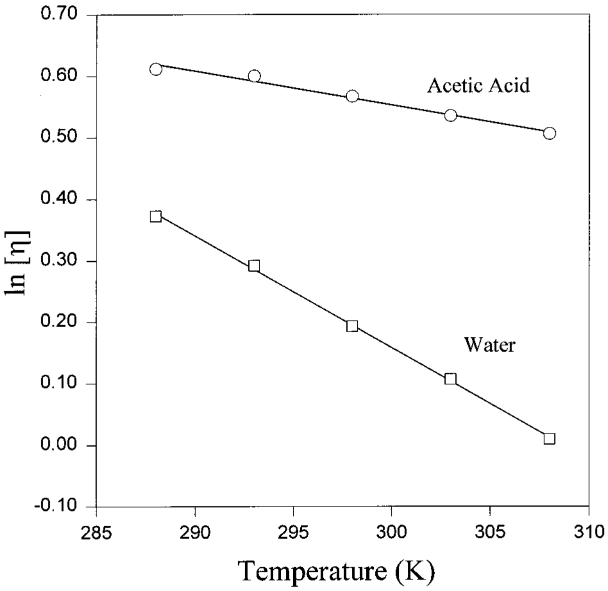

Figure 2. Intrinsic viscosity (dL/g) versus temperature (K) for HPC-L in acetic acid and in water.

scattering dichroism of the aqueous solutions was negligible (less than 10^{-10}) in the range of shear rates investigated. Moreover, transmitted beam intensity remained constant, indicating the absence of flow-induced turbidity.[21]

Rheological Measurements. Intrinsic viscosity measurements of the HPC solutions were made as a function of temperature using a Cannon–Fenske capillary viscometer, ASTM size 50, Fisher Scientific. The viscometer was housed in an insulated glass jacket, and temperature was controlled (±0.02 °C) by circulating water using the Neslab RTE 111 circulating system. The temperature of the polymer solutions was monitored using an Omega digital thermometer to ensure thermal equilibration. Flow times were measured under gravity, and approximately 5 min was allowed to elapse between successive runs. Each experiment was repeated until at least three readings agreed to within 0.1% of their mean. Relative viscosities for five concentrations were evaluated from the flow times and extrapolated to intrinsic viscosities using standard procedures.[22] Rodlike polymers are known to exhibit shear rate dependent viscosities.[23,24] According to Yang's calculations,[23] the critical shear rates for the onset of non-Newtonian behavior for HPC-L in water and acetic acid would range from 2000 to 3500 s^{-1}. These critical shear rates were evaluated using fully extended (rigid-rod) dimensions of HPC-L. It is important to point out that the critical shear rates would be even higher[23] if the macromolecule has some flexibility, which is true for HPC-L. Since the maximum values of the shear rate at the wall in our experiments ranged from 1000 s^{-1} at 15 °C to 1385 s^{-1} at 35 °C, our intrinsic viscosities are Newtonian values. Our measured values at 25 °C also agree well with those reported in the literature for the same system.[3,25] Since the critical shear rates for the onset of non-Newtonian behavior are much lower for the higher molecular weight (HPC-M) sample, discussions of the effects of rigidity on the rheological and optical measurements will be based on the data obtained with the HPC-L sample. Measurements on the HPC-M sample were used simply to confirm the expected molecular weight dependence of the rheo-optical response.

Results

Quiescent Measurements. Circular birefringence (expressed as retardation normalized with path length) of HPC-L solutions as a function of concentration in acetic acid and water at 25 °C is shown in Figure 1. The slightly lower magnitude in acetic acid is consistent with the observations of Werbowyj and Gray.[26] Since the rotatory power depends primarily on the chiral nature of the sugar residues in the chain, in addition to any ordered helical regions which may exist along the molecular backbone, conclusions about the molecular rigidity based solely on the magnitude of the optical rotation are not possible. On the other hand, the constancy of the specific rotation of both solutions over the concentration range studied indicates that the effects of intermolecular interactions on the conformational state of the macromolecule are negligible in the isotropic state.[17] Constancy of the specific rotation in the concentration range 0.5–15 g/dL was also observed in the temperature range from 15 to 35 °C, and similar behavior was found with the higher molecular weight HPC.

Intrinsic viscosities of HPC-L in acetic acid and water are plotted in Figure 2 as a function of temperature. The magnitude of the intrinsic viscosity at any given temperature is much higher in acetic acid solutions; however, the relative change with temperature in the range 15–35 °C is much higher in aqueous solutions. Such changes in intrinsic viscosity with temperature can be attributed to changes in molecular dimensions. The viscosities of both acetic acid[18] and aqueous solutions remained virtually constant with increasing shear rate.

Figure 3 shows optical rotation as a function of temperature for 5 g/dL solutions of HPC in both acetic acid and water. The magnitude of the optical rotation of the aqueous solution decreases strongly with increasing temperature in the range from 15 to 35 °C, while it remains virtually constant for the acetic acid solution in the same range, followed by a decrease with increasing temperature up to 70 °C. The aqueous solutions showed phase separation above 40 °C (LCST behavior), accompanied by large increases in solution turbidity, preventing optical measurements. On the other hand, the acetic acid solutions remained stable to temperatures higher than 70 °C. We believe the behavior of the aqueous solutions shown in Figure 3 can be attributed to a change in the conformational contributions to the net optical activity with increasing temperature. As will be discussed in the next section, the transient and steady-state flow birefringence behavior of these solutions provides a basis for a more quantitative interpretation of these changes. Comparisons of the rheo-optical

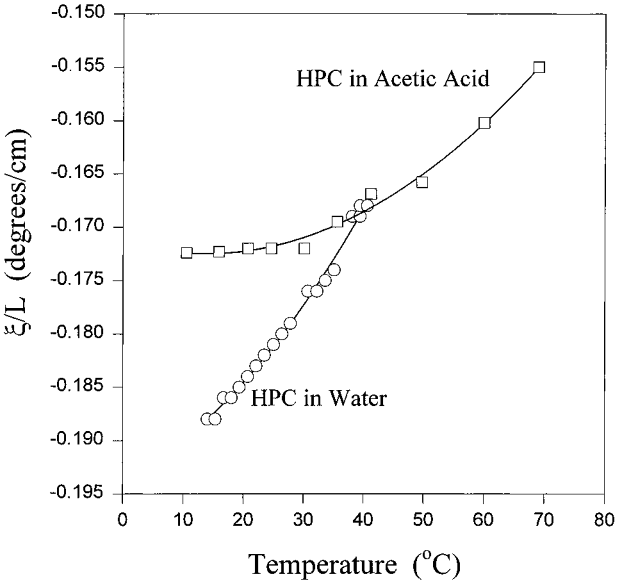

Figure 3. Optical rotatory power (deg/cm) of quiescent HPC-L solutions, in acetic acid and water, versus temperature (°C).

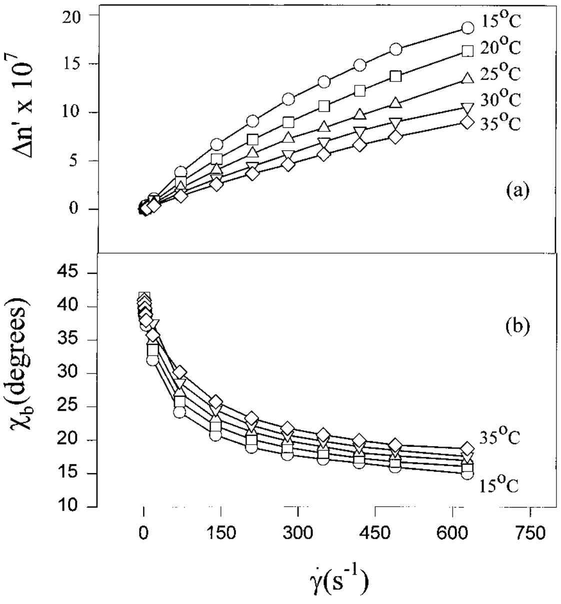

Figure 4. Linear birefringence (a) and orientation angle (b), for various temperatures, plotted as a function of shear rate (s^{-1}) for a 0.5 g/dL aqueous solution of HPC-M.

behavior of the two solutions will be limited to the 15−35 °C temperature range where the macromolecule exists in a stable solution state.

Flow Measurements. Steady-state birefringence and orientation angle are shown in Figure 4 as a function of shear rate and temperature for the 0.5 g/dL (semidilute) HPC-M solution in water. The monotonic increase in birefringence and decrease in orientation angle, with increasing shear rate, indicate molecular alignment at high shear rates. The concave downward curvature of the birefringence−shear rate curves suggests that the molecular dynamics are those of rigid or semirigid rods in solution.[27] For a given shear rate, the birefringence decreases with increasing temperature and the orientation angle increases. The birefringence of HPC-L showed a similar monotonic increase with shear rate though the orientation angle stayed close to 45 °C, as would be expected of a lower molecular weight sample.[28] One would have to go to much higher shear rates in order to see a similar decrease in orientation angle. Since the behavior of HPC-L is closer to that of a rigid rod and since we are looking at the effect of solvent and temperature on rigidity, we will henceforth focus on the dynamics of the lower molecular weight (HPC-L) samples. While the temperature dependence at fixed concentration suggests trends that may be related to changes in the molecular dimensions, the molecular orientation will also be affected by changes in the solution properties that affect the rotational diffusivity D_r. In the absence of other effects, normalization of the shear rate with respect to the latter quantity should lead to a scaling of the data. For rigid-rod molecules, the temperature dependence of D_r will be given as[29,30]

$$D_r \sim T/\eta_s \tag{1}$$

where η_s is the temperature-dependent solvent viscosity. The temperature dependence of the rotational diffusivity should follow eq 1, irrespective of the molecular weight (or size); thus, the scaling should hold despite the polydispersity of our HPC samples. On the other hand, if the molecular rigidity also changes with temperature, then the rotary dynamics should be describable in terms of the wormlike chain model, in which case the temperature dependence of D_r would be given by[31]

$$D_r \sim T/\eta_s[\eta] \tag{2}$$

where $[\eta]$ is the temperature-dependent intrinsic viscosity of the polymer molecule. Accordingly, parts a−c of Figure 5 show birefringence data for the 0.5 g/dL ($c \sim c^*$) aqueous solution of HPC-L plotted against $\dot{\gamma}$, $\dot{\gamma}(\eta_s/T)$, and $\dot{\gamma}(\eta_s[\eta]/T)$, respectively. As seen in Figure 5b, for a given value of the abscissa, the birefringence still exhibits a decrease with increasing temperature, suggesting changes in molecular dimensions. As shown in Figure 5c, using our intrinsic viscosity data (Figure 2) to reduce the shear rate in accordance with the wormlike chain behavior leads to a scaling of the birefringence. On the other hand, as shown in Figure 6b, data for the 0.5 g/dL solution of HPC-L in acetic acid scale with the expected behavior of a rodlike system whose rigidity does not vary with temperature over the given temperature range (15−35 °C). The scaling suggests that the molecular behavior of HPC-L is closer to that of a rigid rod in an acetic acid solution than in an aqueous solution, which is also what one would expect based on the respective critical concentrations for lyotropic transition of HPC in these solvents.

Transient birefringence can give a sensitive measure of the molecular rigidity, particularly through the appearance of startup overshoots and the long-time relaxation behavior.[32,33] Figure 7 shows the retardation, δ ($=2\pi L\Delta n'/\lambda$), of the linear birefringence as a function of time for various temperatures at a fixed shear rate of 2.37 s^{-1}, for a 7.5 g/dL solution of HPC-L in water. As seen, the overshoot increases with temperature and the time required for the birefringence signal to relax to its quiescent value decreases with temperature. This is consistent with the interpretation that molecular rigidity decreases with increasing temperature. Moreover, we have carried out Brownian dynamics calculations, based on a discrete version of the helical wormlike chain model, which show that dilute solutions will exhibit overshoots and long relaxation times in the transient birefringence as the chain rigidity (i.e., per-

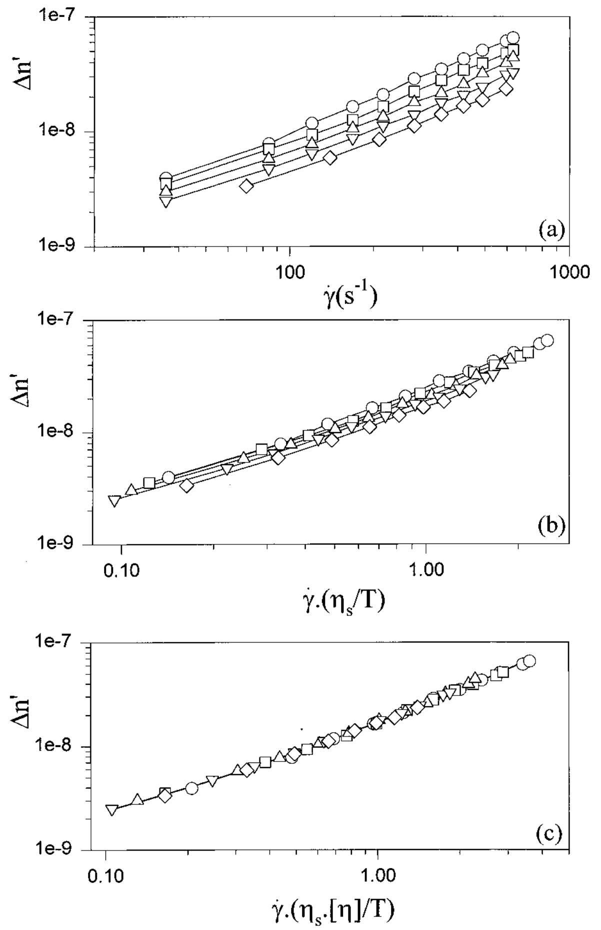

Figure 5. Linear birefringence of a 0.5 g/dL aqueous solution of HPC-L, for various temperatures, plotted as a function of (a) shear rate (s^{-1}), (b) shear rate scaled according to eq 1, and (c) shear rate scaled according to eq 2.

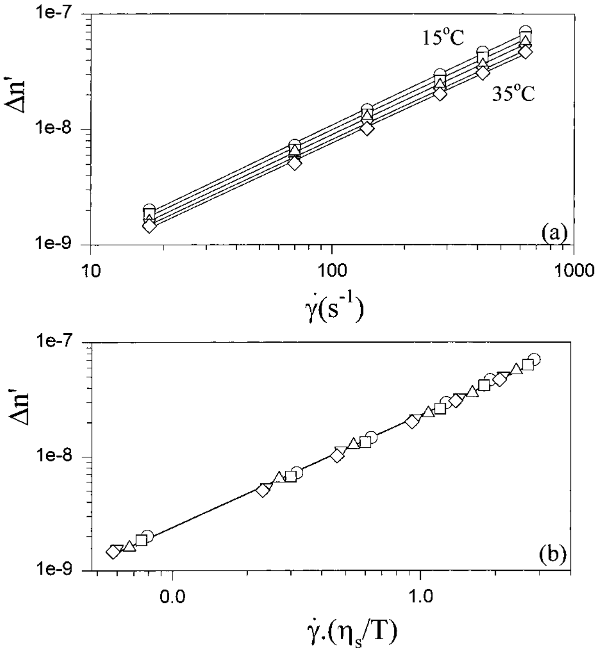

Figure 6. Linear birefringence of a 0.5 g/dL solution of HPC-L in acetic acid, for various temperatures, plotted as a function of (a) shear rate (s^{-1}) and (b) shear rate scaled by eq 1.

sistence length) is decreased.[34] We also find that start-up overshoots at the same shear rate and concentration for the acetic acid solution are negligible, consistent with results presented in our earlier study.[18]

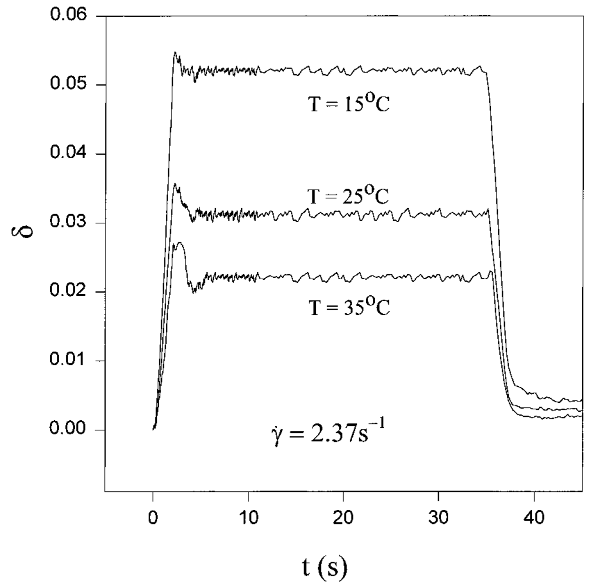

Figure 7. Retardation of linear birefringence of a 7.5 g/dL aqueous solution of HPC-L, for various temperatures, versus time at a fixed shear rate of 2.37 s^{-1}.

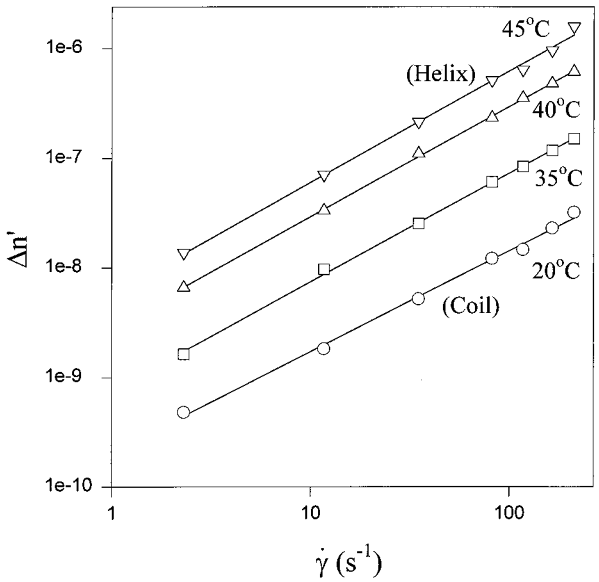

Figure 8. Linear birefringence of a 2 g/dL solution of PBLG in DCA–EDC (76–24 by volume), for various temperatures, versus shear rate (s^{-1}). The PBLG molecule is a rigid rod (α-helix) at 45 °C and a flexible coil at 20 °C.

As indicated by the above experiments, the dimensions of the HPC macromolecule appear to increase with temperature. The question arises, how large is the molecule at 35 °C compared to 15 °C and how does its dynamic behavior compare to that of a macromolecule, such as PBLG, which undergoes an inverse helix–coil conformational transition in DCA–EDC (76–24 by volume), when the temperature is raised?[35] The latter transition is readily monitored using optical rotation as a function of temperature, and the resultant S-shaped curve can be modeled as a first-order transition (Zimm–Braag model[35]) for the percent helicity as a function of temperature. Figure 8 shows the steady-state flow birefringence of PBLG as it undergoes the helix–coil transition. The remarkable difference between the helix–coil transition, and the conformational changes in HPC is evident by comparing Figures 8 and 5b. Birefringence of the PBLG increases by almost 2 orders of magnitude as the molecule goes from a flexible coil to a helical rigid rod. Note also that the viscosity of the solvent acts against orientation in this case, as the more rigid molecular conformation occurs at higher temperatures. By contrast, in the same shear rate range, the HPC-L birefringence changes by much less than an order of magnitude (Figure 5b). These results indicate that the dynamical behavior of the HPC molecule lies somewhere between the extremes of a rigid rod and a flexible coil. Furthermore, the changes in molecular dimensions in HPC-L are very small when the temperature is raised from 15 to 35 °C. Rather, the scaling arguments presented in Figure 5 suggest that the molecular behavior is better represented by a wormlike chain whose rigidity depends on temperature.

Discussion

The rheo-optical measurements presented in this work clearly suggest that the HPC molecule behaves very differently with temperature in the two solvent systems, water and acetic acid, and that these differences may be attributed to changes in the molecular flexibility. Our results, together with a number of studies of rigid and semiflexible systems in shear[32,33] and extensional flows,[36−39] suggest that the rheo-optical response of a system can provide a sensitive measure of changes in its molecular flexibility related to the molecular conformation. In the case of HPC, there has been a considerable amount of discussion in the literature concerning the effects of temperature on the solution conformation. For example, the relatively high rigidity of the macromolecule has been interpreted by a number of authors to be due to the presence of intramolecular hydrogen bonds[2,3,6] in spite of there being little direct experimental evidence for their presence. Likewise, the lack of correlation of the critical concentration for the lyotropic transition in HPC solutions[40] with polymer−solvent interaction parameters has led to the suggestion (ref 41 and references therein) that LC formation depends more on the conformation or stiffness of the macromolecule in a given solvent than on thermodynamic effects, per se. Though the specific mechanisms are unclear, solvents which enhance helicity of the chain or intramolecular hydrogen bonding would be expected to increase stiffness, and hence lower the critical concentration.[41]

Most studies of flexibility of cellulosic systems in solution have been based on intrinsic viscosity measurements and their interpretation in terms of changes in the Kuhn segment length, x_k. Several cellulose derivatives display negative values for d ln$[\eta]$/dT in a variety of solvent systems.[25,42] From Figure 2 we obtain a d ln$[\eta]$/dT value of -1.82×10^{-2} K^{-1} for aqueous HPC-L solutions and a value of -5.55×10^{-3} K^{-1} for the acetic acid solutions. Using the approach of Flory et al.,[42] this corresponds to a d lnx_k/dT of -1.22×10^{-2} K^{-1} for the aqueous solutions. As pointed out by Guido,[25] an independent estimate of d lnx_k/dT can also be obtained from the phase diagram for HPC, leading, in his case, to a value of -1.5×10^{-2} K^{-1}, which compares favorably with ours. The slightly higher magnitude obtained from the phase diagram analysis may be attributable to anisotropic soft interactions.[25]

The effect of changes in flexibility on the temperature dependence of the intrinsic viscosity may also be related to the wormlike chain model used to scale our birefringence data (Figure 5) . Yamakawa and Fujii[43] derived the following expression for the intrinsic viscosity of the wormlike chain:

$$[\eta] = \phi(N')^{3/2}/\lambda^{-3}M_w \tag{3}$$

where $N' = M_w/M_L\lambda$ is the reduced contour length, with M_L being the shift factor, ϕ is a function of N' and the reduced cylinder diameter d' $(=d/\lambda)$, and $\lambda = 2q$, where q is the persistence length. In order to develop a better understanding of the mesogenic nature of cellulosic chains, Aden et al.[44] proposed the inclusion of the temperature coefficient (d ln q/dT) in the theory for thermotropic phase behavior and were successful in explaining the temperature effects. Inclusion of a similar dependence in eq 3 would lead to a self-consistent interpretation of our results. Moreover, as noted earlier, our Brownian dyanmics calculations show that the temperature dependence of the steady-state and transient rheo-optical behavior can be modeled in terms of a discrete wormlike chain whose rigidity decreases with increasing temperature.[34]

With regard to possible thermodynamic factors, the water solubility of HPC is considered anomalous, based on the large difference between the solubility parameters[45] of the polymer and the solvent. On the other hand, HPC provides numerous sites for hydrogen bonding, thereby facilitating the formation of a highly organized structure consisting of a layer of water molecules around the polymer backbone and the propylene glycol side chains,[46,47] As temperature is raised, the enhanced water structure breaks down and attractive forces between polymer chains increase, causing phase separation. It is conceivable that the decrease in intrinsic viscosity with increasing temperature is due to changes in solvent quality affecting the molecular dimensions of HPC. In the absence of intramolecular hydrogen bonds, it is conceivable that the macromolecule would behave like an extended coil that contracts toward its θ dimensions as the temperature is raised toward its LCST, 40 °C. However, recent experimental observations based on ellipticity data,[46,48] suggest that the onset of cholesteric order occurs at temperatures slightly below those at which an aqueous isotropic HPC solution undergoes phase separation. Furthermore these mesophases were detected at very low concentrations (∼0.4% v/v). It is unlikely that HPC molecules close to their θ dimension would form an ordered phase. These observations therefore suggest that the macromolecular dimensions are dominated by structural features of HPC, rather than polymer−solvent thermodynamic interactions.

Conclusions

The results and discussion in this paper clearly indicate that changes in temperature and solvent type affect the rheo-optical response of the HPC solutions and that these affects are most likely related to structural features in the chain backbone that affect the rigidity of the molecule. Since changes in molecular rigidity affect the rotational diffusivity, it is also possible to monitor such changes by measuring flow birefringence as a function of temperature. The magnitudes of flow birefringence and intrinsic viscosity of the HPC molecule are higher in acetic acid than in water, indicating that the molecule has a more rigid structure in the former. The effects of structural changes on the dynamical behavior can be described in terms of a wormlike chain whose rigidity depends on the solvent as well as temperature.

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References and Notes

(1) Zugenmaier, P. *J. Appl. Polym. Sci., Polym. Symp.* **1983**, *37*, 223.
(2) Samuels, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1197.
(3) Wirick, M. G.; Waldman, M. H. *J. Appl. Polym. Sci.* **1970**, *14*, 579.
(4) Perex-Trejo, L.; Mendez-Sanchez, A. F.; Perez-Gonzalez, J.; de Vargas, L. *Rheol. Acta* **1996**, *35*, 194.
(5) Hongladarom, K.; Secakusuma, V.; Burghardt, W. R. *J. Rheol.* **1994**, *38*, 1505.
(6) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1980**, *13*, 69.
(7) Yanagida, N.; Takematsu, S.; Matsuo, M. *Polym. J. (Tokyo)* **1994**, *26*, 1.
(8) Chokyun, R.; Timonen, M. *U.S. Patent* 5,354,424, 1995.
(9) Guido, S.; Grizzuti, N. *Rheol. Acta*, **1995**, *34*, 137.
(10) Tsutusi, T.; Tanaka, R. *Polym. J.*, **1980**, *12*, 473.
(11) Suto, S.; Gotoh, H.; Nishibori, W.; Karasawa, M. *J. Appl. Polym. Sci.* **1989**, *37*, 1147.
(12) Gray, D. G. *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **1983**, *37*, 179.
(13) Bheda, J.; Fellers, J. F.; White, J. L. *Colloid Polym. Sci.*, **1980**, *258*, 1335.
(14) Mays, J. W. *Macromolecules*, **1988**, *21*, 3179.
(15) Nisson, S.; Sundelof, L.; Porsch, B. *Carbohydr. Polym.* **1995**, *28*, 265.
(16) Immaneni, A. M.S. Dissertation, University of Illinois, Urbana, IL, 1995.
(17) Edwards, B. J.; McHugh, A. J.; Immaneni, A. *J. Rheol.*, **1995**, *39*, 527.
(18) Edwards, B. J.; McHugh, A. J. *J. Rheol.* **1993**, *37*, 743.
(19) Immaneni, A. Ph.D. Dissertation, University of Illinois, Urbana, IL, in progress.
(20) Kishbaugh, A. J. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1992.
(21) McHugh, A. J.; Immaneni, A.; Edwards, B. J. In *Flow-Induced Structure in Polymers*; Nakatani, A. I., Dadmun, M. D., Eds.; ACS Symposium Series 597; American Chemical Society: Washington DC, 1995; p 75.
(22) Collins, E. A.; Bares, J.; Billmeyer, F. W., Jr. *Experiments in Polymer Science*; John Wiley & Sons: New York, 1973.
(23) Yang, J. T. *J. Am. Chem. Soc.* **1958**, *80*, 1783.
(24) Chakrabarty, S.; Miller, W. G. *Biopolymers* **1984**, *23*, 719.
(25) Guido, S. *Macromolecules* **1995**, *28*, 4530.
(26) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1984**, *17*, 1512.
(27) Tsvetkov, V. N.; Andreeva, L. N. *Adv. Polym. Sci.* **1981**, *39*, 95.
(28) Shtennikova, I. N.; Kolbina, G. F.; Shibaev, V. P.; Ekaeva, I. V. *Eur. Polym. J.*, **1990**, *26*, 787.
(29) Munk, P. *Introduction to Macromolecular Science*; Wiley-Interscience: New York, **1989**; Chapter 3.
(30) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, U.K., 1986; Chapter 8.
(31) Yoshizami, T.; Yamakawa, H. *J. Chem. Phys.*, **1980**, *72*, 57.
(32) Chow, A. W.; Fuller, G. G.; Wallace, D. G.; Madri, J. A. *Macromolecules* **1985**, *18*, 805.
(33) Chow, A. W.; Fuller, G. G.; Wallace, D. G.; Madri, J. A. *Macromolecules* **1985**, *18*, 793.
(34) Andrews, N. C.; McHugh, A. J.; Schieber, J. D. *J. Rheol.* **1997**, submitted.
(35) Scheraga, H. A.; Mattice, W. L. *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1987; Vol. 7, p 685.
(36) Hayakawa, I.; Hayashi, D.; Sasaki, N.; Hikichi, K. *J. Appl. Polym. Sci.* **1996**, *61*, 1731.
(37) Sasaki, N.; Atkins, E. D. T.; Fulton, W. S. *J. Appl. Polym. Sci.* **1991**, *42*, 2975.
(38) Odell, J. A.; Taylor, M. A. *Biopolymers* **1994**, *34*, 1483.
(39) Atkins, E. D. T.; Taylor, M. A. *Biopolymers* **1992**, *32*, 911.
(40) Aspler, J. S.; Gray, D. G.; *Polymer*, **1982**, *23*, 43.
(41) Gray, D. G. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1983**, *37*, 179.
(42) Flory, P. J.; Spurr, O. K., Jr.; Carpenter, D. K. *Polym. Sci.* **1958**, *27*, 231.
(43) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(44) Aden, M. A.; Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A. *Macromolecules* **1984**, *17*, 2010.
(45) Roberts, G. A. F.; Thomas, I. M. *Polymer* **1978**, *19*, 459.
(46) Fortin, S.; Charlet, G. *Macromolecules* **1989**, *22*, 2286.
(47) Winnik, F. M. *Macromolecules* **1987**, *20*, 2745.
(48) Larez-V, C.; Crescenzi, V.; Ciferri, A. *Macromolecules* **1995**, *28*, 5280.

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