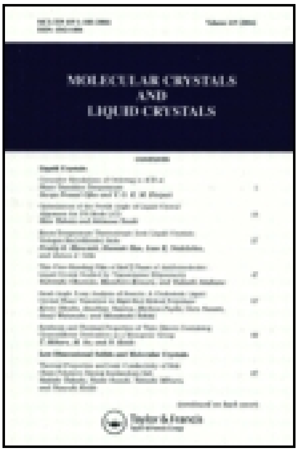

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Rheological Properties of Acetoxypropylcellulose in the Thermotropic Chiral Nematic Phase

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RHEOLOGICAL PROPERTIES OF ACETOXYPROPYLCELLULOSE IN THE THERMOTROPIC CHIRAL NEMATIC PHASE

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Abstract Experimental data for the rheological behavior of two thermotropic liquid crystalline (LC) samples of acetoxypropylcellulose (APC) with different molecular weights, at 120°C, and in shear rates between 0.01 and 10 s^{-1}, are presented and analyzed in the framework of the continuum theory for LC polymers recently proposed by Martins[1]. The viscosity $\eta(\dot{\gamma})$ shows a strong shear thinning in the range of shear rates $\dot{\gamma}$ studied, with an hesitation at shear rates of about 0.1-0.2 s^{-1}, depending on the molecular weight, and the first normal stress difference $N_1(\dot{\gamma})$ shows only positive values, increasing with shear rate $\dot{\gamma}$, with an hesitation at shear rates of an order of magnitude higher, i.e. about 1-2 s^{-1}, also depending on the molecular weight. The hesitation points of the flow functions are displaced towards lower values of the shear rate, with increasing molecular weight. For small and intermediate $\dot{\gamma}$ the shear viscosity of the higher molecular weight sample is greater than the corresponding viscosity for the lower molecular weight sample, but this pattern is reversed at higher $\dot{\gamma}$, the crossover point being at $\dot{\gamma} \approx 1.5\ s^{-1}$. The molecular weight dependence of the first normal stress difference follows a similar pattern. All these observations can be interpreted by Martins' theory. The expressions for $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ derived from this theory fit very well to the experimental data, therefore allowing for some fundamental viscoelastic parameters to be estimated.

INTRODUCTION

Liquid crystalline polymers (LCP's) have been the subject of increasing interest because of their exceptional mechanical properties. Rheological studies of these polymers are of major technological importance and have attracted the attention of many researchers in recent years. Despite this interest, a clear understanding of the rheological behavior of LCP's is still missing. Experiments gave results that are, in some cases, controversial. Some researchers have found a viscosity curve $\eta(\dot{\gamma})$ composed of three different regions[2-5], as proposed by Onogi and Asada[6], for lyotropics, others have found one single shear thinning region[7-9]. For the first normal-stress difference $N_1(\dot{\gamma})$ some researchers have found a region of negative[2,3,10,11-14] N_1, others have found only positive[5,7,15] values of N_1. The theoretical explanations so far proposed for such phenomena, namely a molecular approach of Marrucci and Maffettone[16] based on Doi's theory[17] and latter developed by Larson and co-workers[18], and a continuum approach by Fahroudi and Rey[19], give only qualitative agreement with experiments.

In this work we present experimental data for the rheological behavior of two thermotropic liquid crystalline samples of acetoxypropylcellulose (APC) with different molecular weights, at 120°C, and in shear rates between 0.01 and 10 s^{-1}. To interpret the experimental data, we use a continuum theory recently proposed by Martins[1] which modifies the Leslie-Ericksen theory for low molecular weight nematic liquid crystals in order to account for the viscoelasticity of liquid crystalline polymers.

EXPERIMENTAL

For the experiments described here, two batches of APC were prepared through the reaction of hydroxypropylcellulose (HPC) of two different molecular weights (Klucel E, nominal molecular weight of 60000 g/mol and Klucel L, nominal molecular weight of 100000 g/mol) with acethylchloride (Merck), following a (slightly modified) well known method[20].

The structures of the end products were confirmed by infrared spectroscopy (IR) (using a Buck Scientific 500 spect.) and by nuclear magnetic resonance (NMR) (Bruker CXP, operating at 300 MHz). Their weight-average molecular weights were 94000 and 129000 g/mol, as determined from measurements of the viscosity limiting number (Schöt Geräte AVS 400 visc.) at 25 °C and Mark Houwink constants extracted from[21]. Hereafter the two batches will be called APC 94000 and APC 129000 respectively. The mean molar substitution MS and mean degree of substitution DS, as determined by proton NMR[22], were, respectively, 3.67 and 1.65 for APC 94000, and 3.49 and 1.71 for APC 129000. The samples were chiral nematic (cholesteric) at rest, with isotropization temperatures of 170 °C for both molecular weights, as determined by differential scanning calorimetry (DSC) (Setaram DSC92), with a heating rate of 2 °C/min.

The samples used in the rheological measurements were premolded in the form of discs with appropriate diameter and thickness, at 100 °C, after being dried under vacuum ($<$ 1 mm Hg) at 60 °C for several hours, and kept in a desiccator until use.

The rheological measurements were carried out on the Rheometrics Mechanical Spectrometer RMS-800, using a cone and plate geometry (cone angles of 0.04 and 0.1 rad, and plate diameters of 50 mm and 25 mm, with APC 94000 and APC 129000, respectively) in the steady-shear/step shear-rate mode, at shear rates ranging from ca 0.01 to 10 s^{-1}, under nitrogen atmosphere. The zero values of the normal force and torque were set, for each testing temperature, before introducing the sample. Thereafter, the sample was compressed between the cone and plate, the excess material removed, and a pre-shearing of 1 s^{-1} during 180 s was applied. The normal force was allowed to decrease back to its true zero value before the test took place. Thirty minutes time was typically allowed for thermal equilibration.

Different measurements carried out with two polymer samples showed good reproducibility. The material has shown to be very stable, allowing experiments for several hours.

THEORY

For nematic polymers in steady simple shear flow with constant shear rate $\dot{\gamma}$, with the director lying in the shear plane, Martins[1] derived the following expressions for the viscosity, $\eta(\dot{\gamma})$, the first normal-stress difference, $N_1(\dot{\gamma})$, and the second normal-stress difference, $N_2(\dot{\gamma})$, as functions of the shear rate:

$$\eta(\dot\gamma) = \eta_0 \exp(-\tau_0 \dot\gamma) + [a_0 (\tau \dot\gamma)^2 + b_0\tau\dot\gamma + c_0]\cdot[1+(1-\epsilon^2)\tau^2\dot\gamma^2]^{-1} \qquad (1)$$

$$N_1(\dot\gamma) = \sigma_{11} - \sigma_{22} = N_{10} + \dot\gamma\, [a_1(\tau\dot\gamma)^2 + b_1\tau\dot\gamma + c_1]\cdot[1+(1-\epsilon^2)\tau^2\dot\gamma^2]^{-1} \qquad (2a)$$

$$= N_{10} + \dot\gamma\, [a_1\tau^2(\dot\gamma - r_2)\, (\dot\gamma - r_3)]\cdot[1+(1-\epsilon^2)\tau^2\dot\gamma^2]^{-1} \qquad (2b)$$

$$N_2(\dot\gamma) = \sigma_{22} - \sigma_{33} = N_{20} - \tfrac{1}{2}\,(1-\epsilon)\, [N_1(\dot\gamma) - N_{10}] + \beta\dot\gamma \qquad (3)$$

where a_i, b_i, c_i ($i = 0,1$) and β are known functions[1] of the "Leslie's viscosity coefficients"[23] α_i, N_{10} and N_{20} represent Ericksen stresses that may exist at $\dot\gamma = 0$, τ is the relaxation time of the polymer memory function, τ_0 is related to texture relaxation modes and ϵ ($-1 \le \epsilon \le 1$) is a measure of the non-affine character of the motion.

RESULTS AND DISCUSSION

The observed shear rate dependencies of $\eta(\dot\gamma)$ and $N_1(\dot\gamma)$, for the two samples described above, are displayed in Figures 1 and 2, along with the theoretical curves as computer fitted to the experimental data with the MINUIT routine[24]. In both cases, the experimental data shown corresponds to the first running with a virgin sample.

Note also that the polymer analyzed here is cholesteric at rest and equations (1)-(3) have been derived for nematics, which is not an impediment since the cholesteric helix is known to unwound by the shear forces, giving rise to a nematic structure, at shear rates below the lowest values considered in our experiments.

Table I displays the parameters obtained from the fitting of expressions (1) and (2a) to the experimental data for both samples of APC, at 120 °C. We can see that, for a given molecular weight, the parameters τ and ϵ obtained from independent fits of $\eta(\dot\gamma)$ and $N_1(\dot\gamma)$ are in rather good agreement. The value of τ increases with increasing molecular weight, as expected, and ϵ is nearly molecular weight independent.

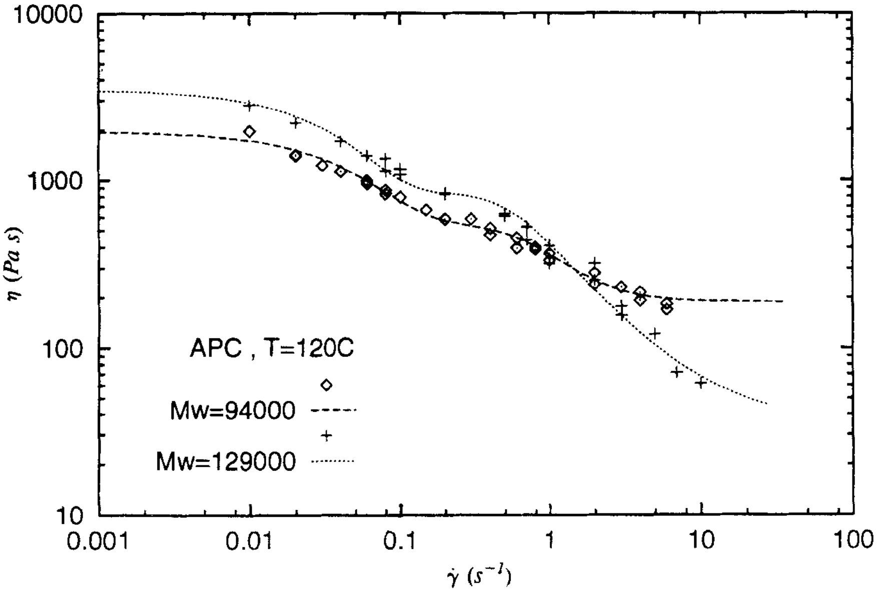

Figure 1 Shear viscosity vs shear rate for APC 94000 and APC 129000, at 120°C. Symbols: experimental data; dotted lines: theory[1].

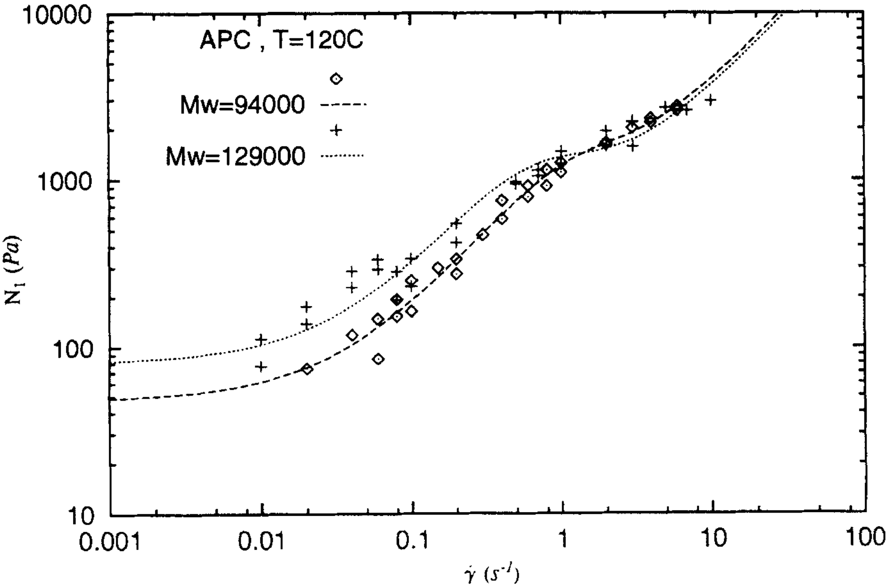

Figure 2 First normal stress difference for APC 94000 and APC 129000, at 120°C. Symbols: experimental data; dotted lines: theory[1].

The characteristic time τ_0 is an order of magnitude greater than τ, which means that the texture relaxation process is much slower than the viscoelastic process.

TABLE I Most important fitting parameters of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ for two samples of APC with different molecular weights, at 120 °C (SI units).

Fitting parameter		APC 94000	APC 129000
$\eta(\dot{\gamma})$	τ	1.8	3.5
	τ_0	20.0	25.0
	ϵ	0.8	0.8
	η_0+c_0	1969.0	2848.0
$N_1(\dot{\gamma})$	τ	1.9	3.3
	ϵ	0.9	0.9

The relaxation time τ is undoubtly the most important parameter in the theory since expressions (1) to (3) show that the basic quantity characterizing the shear flow behavior of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ is the dimensionless number $\tau\dot{\gamma}$, which we may identify with the Weissenberg (or Deborah) number. The values of τ extracted from the fits are fairly confident in spite of the rather monotonous character of the curves, which renders more difficult to fix with equal confidence some other parameters in expressions (1) and (2a).

Figure 1 shows, for each molecular weight, that the shear viscosity decreases with increasing shear rate over roughly the whole range of $\dot{\gamma}$ values probed experimentally. A deviation from this trend is, however, observed at shear rates about 0.1-0.2 s^{-1}, depending on the molecular weight, the curves $\eta(\dot{\gamma})$ tending to get constant in a narrow region above these points. This is similar to the typical behavior of anisotropic hydroxypropylcellulose solutions. This "hesitation" region is followed by a level off of $\eta(\dot{\gamma})$, which is controlled by the parameter τ. The sharp decrease of $\eta(\dot{\gamma})$ observed just below the hesitation region is controlled by the parameter τ_0. The shear viscosity is higher for the higher molecular weight, at small and intermediate shear rates, and becomes smaller at higher $\dot{\gamma}$, with a crossover at $\dot{\gamma} \approx 1.5\ s^{-1}$. This crossover may be explained as the effect of the simultaneous increase of the "zero-shear" viscosity ($\eta_o + c_o$) and the relaxation time τ with the polymer molecular weight, as predicted by expression (1).

Figure 2 shows that $N_1(\dot{\gamma})$ is an increasing function of $\dot{\gamma}$ over the whole range of shear rates probed, and also shows an hesitation slightly above the point $\dot{\gamma} = 1/\tau$ (about the crossover point for the viscosities). The function $N_1(\dot{\gamma})$ increases with molecular weight at small and intermediate shear rates and decreases with molecular weight at high shear rates. In fact the experimental data available in the region of high $\dot{\gamma}$ is not sufficient to unambiguously support this last statement; it is, however, suggested by the fitting curves extrapolating from the data and is indeed observed in the case of lyotropic systems[13,14].

The hesitation points of both flow functions are displaced towards lower values of the shear rate as the polymer molecular weight increases, in agreement with their dependence on τ and the expected increase of this parameter with the polymer molecular weight.

In contrast to the behavior of $N_1(\dot{\gamma})$ for PBLG and other lyotropic systems[2,11,13,14], a double sign inversion of this function is not observed for our (thermotropic) system. This can be understood from expression (2a). The numerator of the second term in the r.h.s. of this expression is a cubic polynomial with one real root at $\dot{\gamma} = 0$ and two other roots (r_2 and r_3 in expression (2b)) which may be either real (therefore giving rise to a double sign inversion of $N_1(\dot{\gamma})$) or complex conjugate, depending on the value of the discriminant $\Delta = b_1^2 - 3a_1c_1$. In the present case we have $\Delta < 0$ and therefore $N_1(\dot{\gamma})$ is an always increasing function of $\dot{\gamma}$ (for $a_1 > 0$ in order that $N_1 > 0$ for $\dot{\gamma} \rightarrow \infty$). The hesitation of $N_1(\dot{\gamma})$ around the value $\dot{\gamma} \approx 1.4\ s^{-1}$ is due to the influence of the denominator $[1 + (1-\epsilon^2)\tau^2\dot{\gamma}^2]$ of the second term in the r.h.s. of expression (2), which significantly departs from one above that value of the shear rate.

CONCLUSION

In conclusion, we observed that the shear rate and molecular weight dependencies of the viscosity $\eta(\dot{\gamma})$ and first normal stress difference $N_1(\dot{\gamma})$ in the thermotropic liquid crystalline phase of acetoxypropylcellulose show several new interesting features. $\eta(\dot{\gamma})$ shows an "hesitation" in the shear thinning region (previously reported for different materials by several authors) and $N_1(\dot{\gamma})$ shows another one in the high shear rate region. A crossover of the viscosity (and $N_1(\dot{\gamma})$) curves for two APC samples with different molecular weights is also observed for the first time, which means that, for a given polymer, the shear thinning effect is more pronounced for the higher molecular weight samples. These peculiarities, together with the general behavior of the flow functions, are well accounted for by the continuum theory for nematic liquid crystalline polymers recently proposed by Martins[1]. This theory has been shown[13,14] to accurately model, as well, the more striking behavior of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ in lyotropic systems .

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