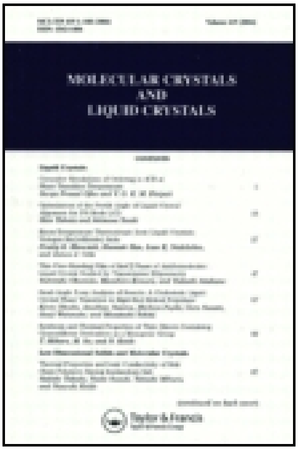

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The Influence of Polymer Molecular Weight on the First Normal-Stress Difference and Shear-Viscosity of LC Solutions of Hydroxypropylcellulose

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The first normal-stress difference $N_1(\dot{\gamma})$ and the shear viscosity $\eta(\dot{\gamma})$ have been measured for liquid crystalline solutions of HPC in acetic acid (AA) as functions of the shear rate $\dot{\gamma}$ and the molecular mass of HPC. The measurements were done over four decades in $\dot{\gamma}$, for two samples of HPC with M_w =60,000 and 100,000 (Klucel E and L, respectively) and solution concentration c = 37% (c > c*). $N_1(\dot{\gamma})$ is observed to change from positive to negative and again to positive, as the shear rate $\dot{\gamma}$ increases. The $\dot{\gamma}$ values at which N_1 changes sign depend on M_w. The viscosity $\eta(\dot{\gamma})$ shows a small Newtonian plateau at low shear rates and a strong shear-thinning at higher values of $\dot{\gamma}$, including an "hesitation" similar to one previously observed in LC solutions of PBLG [2]. All these observations are rationalized within the framework of the constitutive equations for liquid crystalline polymers recently proposed by one of us [1]. Expressions for $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ derived from this theory fit very well (quantitatively) to the experimental data and some fundamental viscoelastic parameters of the system are thereby obtained for the first time.

INTRODUCTION

Hidroxypropylcellulose (HPC) is a biocompatible polymer with important industrial applications. It is soluble in water and many organic solvents and forms liquid crystalline (LC) phases above a certain concentration c* depending on the solvent and the temperature. A clear understanding of the rheology of such LC phases is therefore required in practical circumstances but has been limited so far by the lack of a reliable theoretical framework. In this communication we apply the constitutive equations for nematic LC polymers recently proposed by one of

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us [1] to interpret the rheological behavior of the lyotropic LC phases of this material.

Several lyotropic systems obtained from HPC have been chosen so far for rheological studies, namely HPC/H_2O [3–10], HPC/dimethylacetamide (DMAc) [9,11,12], HPC/dimethylsulfoxid (DMSO) [9], HPC/dichloroacetic acid (DCA) [13], HPC/acetic acid (AA) [14,15,20] and HPC/m-cresol [16–18]. Some rheological phenomena observed in these systems are very peculiar and characteristic of LC behavior, e.g., the double sine inversion [19] observed in the first normal stress difference, $N_1(\dot{\gamma})$, and the "hesitation" [2] shown by the viscosity function, $\eta(\dot{\gamma})$, in the shear thinning region. These phenomena are still not completely understood and characterized. The complexity of the rheological behavior observed in LC polymer systems is even higher when the influence of such factors as the polymer concentration and the polymer molecular weight are considered.

In this work we describe the influence of the polymer molecular weight on the rheological properties of the lyotropic system HPC in acetic acid (AA), which forms anisotropic solutions above the critical concentration c^*=30% of HPC. In previous papers we reported on the effects of concentration [20] and aging [21] on the rheological behavior of this system. Other studies about the influence of polymer molecular weight on the rheology of LC polymers have been reported by Gleeson et al. [22] for the lyotropic system PBLG in m-cresol and more recently by Sigillo and Grizzuti [10] for the lyotropic system HPC/H_2O. Significant similarities in the rheological behaviors of the various systems show up when comparing the published data with the results obtained in this work. The experimental behavior observed for the first normal-stress difference, $N_1(\dot{\gamma})$, and shear-viscosity, $\eta(\dot{\gamma})$, is analyzed below in terms of the continuum theory for nematic LC polymers recently proposed by Martins [1], which allows for a quantitative interpretation to the observed behaviors.

THEORY

Novel constitutive equations for nematic LC polymers were proposed recently by Martins [1]. For a steady, simple shear flow of a nematic LC polymer system, at constant shear rate $\dot{\gamma}$, with the velocity in the X direction, the velocity gradient in the Y direction, and with the director (**n**) lying in the XY plane, explicit expressions were derived in [1] for the main flow functions, namely, the shear viscosity:

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

the first normal-stress difference:

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

$$= N_{10} + \dot{\gamma}\,[a_1\tau^2\,(\dot{\gamma} - r_1)\,(\dot{\gamma} - s_1)].[1 + (1-\varepsilon^2)\tau^2\dot{\gamma}^2]^{-1} \quad (2b)$$

and the second normal-stress difference:

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

where σ_{33} =0 for the flow considered, and N_{10} and N_{20} represent Ericksen stresses that may exist at $\dot{\gamma}$ =0. The coefficients a_i, b_i and c_i (i=0, 1) and β in the above equations are known functions of the "Leslie's viscosity coefficients" α_i [23], the relaxation time τ characterizes the polymer memory function, the parameter ε measures the non-affine character of the motion ($-1 \leq \varepsilon \leq 1$), and τ_0 is related to the texture relaxation modes [1]. The most significant parameter in this theory is the dimensionless product $\dot{\gamma}\tau$, which we can interpret as the Deborah number.

EXPERIMENTAL

As already mentioned, the lyotropic system chosen for the present study was a solution of hydroxypropylcellulose (HPC), a semi-flexible mesomorphic polymer, in acetic acid (AA) (for short, this system will be referred to below as HPC/AA). Samples with a single concentration c = 37% were prepared from two different batches of HPC manufactured by Hercules Inc. and labeled Klucel E and L, with nominal average molar masses $M_w = 6\times10^4$ and $M_w = 10^5$ g/mol, respectively. Solution concentrations (c) are expressed as weight ratios: (polymer weight/solution weight) × 100. All solutions, kept in vessels sealed with a solvent tight film (parafilm), were matured for at least 24 hours. The experiments were performed at room temperature.

An Instron 3250 cone and plate rheometer was employed to analyze the steady state shearing flow behavior of the samples. The torque and the accompanying normal force thrust were measured, in function of the shear rate $\dot{\gamma}$, to determine respectively the shear stress σ_{12} and thus the shear viscosity η, and the first normal stress difference N_1. The rheological device was equipped with cone and plate of radius 2 cm. The cone angle was 0.042 rad and it was verified that this angle was low enough to ensure that the conditions for a pure shear flow were fulfilled.

To ensure that the conditions for steady state measurements were also fulfilled, various experimental runs with different rheological histories were performed, namely regular and aleatory increasing and decreasing steps of shear rate, with and without passage at zero shear rate between the measurements, and each time with new loadings of the cone and plate gap from the same mother solution. Despite shear rate dependent transient responses, the stationary values of shear stresses which are reported here, at a given shear rate, lie within the inherent experimental dispersion.

At low shear rates, typically when $\dot{\gamma} < 1\ \mathrm{s}^{-1}$, the torque and the normal force generated by the application of the shear were low, and the precision of the measurements was limited by the inherent precision of the apparatus: the minimum detectable torque and force were respectively 2.5×10^{-2} Nm and 10^{-2} N. In a rather large range of shear rates the precision was better than a few percent, provided that special care was taken to ascertain the establishment of the steady state regime.

At high shear rates the solution tends to be thrown off the gap. Fortunately, in our experiments the time required to attain the stationary regime was relatively short, and the solution stayed inside the gap during the measuring time. Nevertheless, the cell was refilled for nearly each new value of the shear rate. We remark here that the beginning of the region of negative normal stress difference can be "felt" by the experimenter. Indeed, just before entering this regime, the solution tends to be ejected from the cell, while in the negative zone it seems to be dragged inside the gap between cone and plate. We must also note that for solutions of high molecular weight polymers ($M_w \geq 3\times10^5$) at high concentrations, a tendency to slippage has been observed, probably related to the viscoelastic gel character of the solutions. The effects of the viscous heating of the solutions and the mechanical breaking of some macromolecules induced by the strong frictional forces may be neglected in the $\dot{\gamma}$ -range of our experiments.

RESULTS AND DISCUSSION

The experimental data obtained for the HPC/AA system with two different polymer molecular weights are shown in Figs. 1 and 2, and were analyzed in the theoretical framework proposed by Martins [1]. Expressions (1) and (2) for the shear viscosity $\eta(\dot{\gamma})$ and first normal-stress difference $N_1(\dot{\gamma})$, were computer fitted to these data by using the MINUIT routine [24]; $N_2(\dot{\gamma})$ was not measured in these experiments. Values for the most significant viscoelastic parameters obtained directly from the fits are given in Table I.

A double sign inversion of $N_1(\dot{\gamma})$ and an "hesitation" [2] of $\eta(\dot{\gamma})$ in the shear-thinning region can be observed for both samples, and the influence of the polymer molecular weight on these peculiar phenomena is very clear.

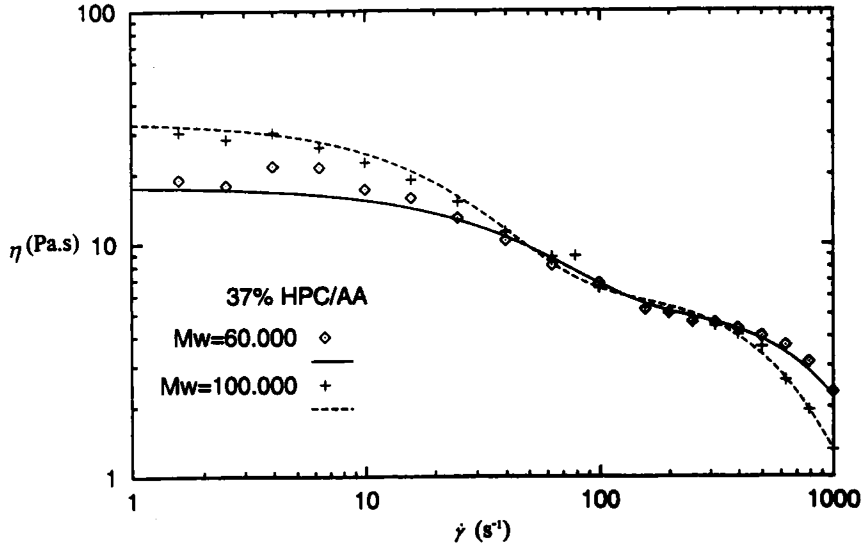

FIGURE 1 Shear viscosity vs shear rate, for the LC system (37% HPC/AA) obtained from two polymer samples with different molecular weights. Lines: theory [1]; points: experimental data

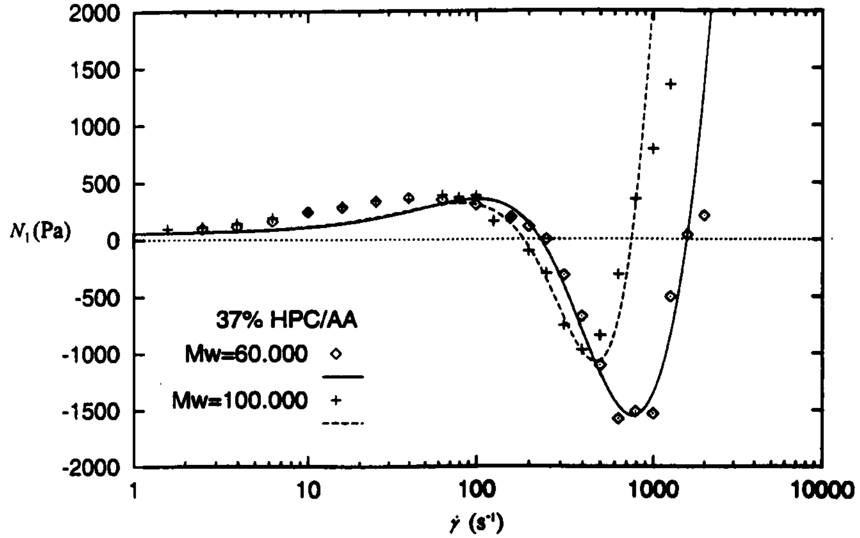

FIGURE 2 First normal-stress difference vs shear rate, for the LC system (37% HPC/AA) obtained from two polymer samples with different molecular weights. Lines: theory [1], points: experimental data

TABLE I Viscoelastic parameters obtained from the fit of theory [1] to the experimental data

Fitting Parameter	*37% HPC/AA* M_w *= 60.000 g/mol*	*37% HPC/AA* M_w *= 100.000 g/mol*
τ (s)	3.5×10^{-3}	6.7×10^{-3}
τ_0 (s)	2.1×10^{-2}	4.2×10^{-2}
$\eta_0 + c_0$ (Pa.s)	17.8	33.9

From Fig. 1 it can be seen that at low shear rates the viscosity increases with the polymer molecular weight, but at the highest measured shear rates the reverse occurs. The curves $\eta(\dot\gamma)$ for the two samples cross over at intermediate shear rates, when the Deborah number $\tau\dot\gamma \approx 1$. This cross over is due to the fact that both τ and τ_0 increase with M_w but give different contributions in different regions of the $\eta(\dot\gamma)$ curve, as it can be seen from eq. (1).

The $\eta(\dot\gamma)$ curves in Fig. 1 do not show the so called "Region I" of Onogi and Asada [5]. The same behavior was found by Baek et al. [16] and by Gleeson et al. [22] for PBLG/m-cresol. It should be noted, however, that the lowest accessible value of the shear rate in our measurements was $\dot\gamma$ =0.1 s^{-1} and the Region I described in [5, 10] for the system HPC/H_2O appears below this value (and the solvent is different). The data of Baek et al. [16] extends to shear rates as low as $\dot\gamma$ =0.01 s^{-1}. These authors have suggested that the Region I of $\eta(\dot\gamma)$ might not be related to the liquid crystalline nature of the system, because it does not appear for all LC solutions but only for those having a high volume fraction of polymer.

Fig. 2 shows that an increase of the polymer molecular weight induces a shift of the negative region of $N_1(\dot\gamma)$ to lower values of $\dot\gamma$ (The opposite effect is observed for an increase of the polymer concentration [4]). This shift can be explained from expression (2) by noting that the abscissa $(\dot\gamma)$ of the mid-point between the non-zero roots of $N_1(\dot\gamma)$ is proportional to $1/\tau$. For our samples the mid-points are located at $\dot\gamma$ =470 and 900 s^{-1} and the ratio of these values is in good agreement with the inverse ratio $6\times10^4/10^5$ of the corresponding polymer molecular weights. Similar effect of the polymer molecular weight on $N_1(\dot\gamma)$ was observed in PBLG/m-cresol by Gleeson et al. [22], and in HPC/H_2O by Sigillo and Grizzuti [10]. This effect seems to be rather general.

A final remark is in order. The theory [1] involves two relaxation times, τ and τ_0 (see equations (1–3) above). The first one (τ) is of molecular origin and manifests itself in the region where $N_1(\dot\gamma)$ changes sign: $\dot\gamma \approx 1/\tau$ is roughly the abscissa of the inflection point of the cubic curve $N_1(\dot\gamma)$ and situates also the region where an "hesitation" [2] is observed in the upper shear thinning region of $\eta(\dot\gamma)$. The second one (τ_0) is related to the mesoscopic polydomain structure (texture) of the polymer and has its major influence on the rheology at low shear rates, mainly on the apparent viscosity $\eta(\dot{\gamma})$. Table I shows that for the LC system under study these times differ by an order of magnitude. The texture relaxation appears to be much slower than the molecular relaxation, as expected. The same qualitative features were found by Sigillo and Grizzuti [10] with the system HPC/H_2O (different solvent). These authors used two superposed Carreau-type power-law models to extract values of the relaxation times from the shear rate dependence of the viscosity.

CONCLUSIONS

Analytical expressions for the flow functions of nematic liquid crystalline polymers recently derived by Martins [1] were used to interpret the behavior of the shear viscosity $\eta(\dot{\gamma})$ and the first normal-stress difference $N_1(\dot{\gamma})$ measured for liquid crystalline solutions of hydroxypropylcellulose (HPC) in acetic acid (AA) as functions of the shear rate $\dot{\gamma}$ and the molecular mass of HPC. All main features of the experimental data could be rationalized within the framework of the theory [1]. The expressions for $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ derived from this theory fitted very well (quantitatively) to the data and a few fundamental viscoelastic parameters of the system under study were thereby obtained for the first time.

Acknowledgements

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