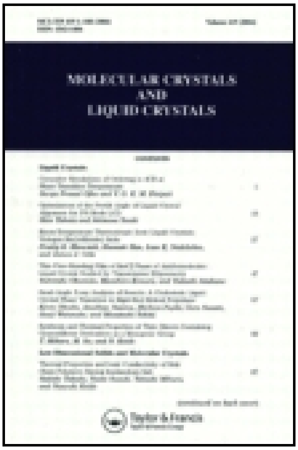

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Temperature Dependence of the Rheological Properties of Acetoxypropylcellulose in the Thermotropic Chiral Nematic Phase

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The rheological behaviour of two different molecular weights of a thermotropic liquid crystalline cellulose derivative, acetoxypropylcellulose (APC), at T=120°C, has already been reported [1]. In this work we present the temperature dependence of the rheological properties of two molecular weights of APC.

The shear viscosity, η, and first normal stress difference, N_1, were measured at temperatures T=120, 130 and 140°C, for $\overline{M}_W = 94000$ g/mole, and T=120 and 140°C for $\overline{M}_W = 129000$ g/mole, and for shear rates, $\dot{\gamma}$, between 0.01 and 10 s^{-1}.

The shear viscosity $\eta(\dot{\gamma})$ decreases with increasing T, for both samples, showing a strong shear thinning behaviour at all temperatures and over the whole range of $\dot{\gamma}$ studied, except for shear rates between about 0.2 and 1 s^{-1} (depending on $\overline{M}_W$ and T), where a quasi-Newtonian plateau is observed. The first normal stress difference $N_1(\dot{\gamma})$ also decreases with increasing T at a given $\dot{\gamma}$. It increases with shear rate over the whole $\dot{\gamma}$ range studied, and shows an inflection at $\dot{\gamma}$ values slightly above $\dot{\gamma} = 1/\tau$, where τ is the relaxation time of the polymer memory function.

The temperature dependence of the shear viscosity was fitted to an Arrhenius law, giving an apparent activation energy (E_a) in the order of 8–15 kcal/mole, depending on molecular weight and shear rate. The activation energy was found to increase with molecular weight (at a given $\dot{\gamma}$). The variation of E_a with $\dot{\gamma}$,, for $\overline{M}_W = 94000$ g/mole, shows a minimum at $\dot{\gamma} \approx 2\ s^{-1}$.

Using a continuum theory for nematic polymers, proposed by Martins [2], some fundamental parameters were obtained from the fit of the theory to the experimental data. Using these parameters it was possible to construct a "master curve" for the viscosity, $\eta(\dot{\gamma})$, in good agreement with the experimental data.

Keywords: liquid crystalline polymers; rheology; shear viscosity; first normal stress difference

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INTRODUCTION

The rheological behaviour of liquid crystalline polymers (LCP's) is attracting an increasing interest due to its physical peculiarities and because of the technological importance of some materials based on them, namely the high strength, high modulus fibres obtained from the extrusion of lyotropic systems, and the high performance matrices obtained from thermotropic melts.

A large amount of work has been done in this field during the past fifteen years, specially in what concerns the dependence of shear viscosity and first normal stress difference on shear rate, for both thermotropic [3–16] and lyotropic systems [13,17–30], and the influence of the defect structure, or texture, in the rheology of such systems (the most famous case of which is the appearance of a characteristic texture – band texture – in relaxation processes), also for thermotropic [31–36] and lyotropic systems [37–45].

Another matter of concern has been the theoretical explanation of the rheological experimental data. Marrucci and Maffettone [46] proposed an explanation, based in the molecular theory of Doi [47], for the existence of negative N_1 values, theory that was later on developed by Larson [48]. A continuum theory proposed by Farhoudi and Rey [49] has achieved qualitative agreement with experimental data. A different continuum theory, proposed by Martins [2], extends the Leslie-Ericksen theory initially for low molecular weight nematic liquid crystals so as to account for the viscoelasticity of liquid crystalline polymers. Some attempts have also been made to explain the observed textural phenomenon of sheared liquid crystalline polymers [31,35,36,50–53].

The dependence of the rheological properties of liquid crystalline polymers with temperature is of great importance for the processing of these materials and has been under study especially in case of lyotropic systems of poly(benzyl L-glutamate) (PBLG) [20,29] and hydroxypropyl cellulose (HPC) [28,30,54]. Gonzalez et al [5] has also studied this dependence for a thermotropic polyesteramide.

In this work we present the experimental data, and theoretical modelling using Martins' theory [2], for the flow functions $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ as a function of temperature, for two molecular weights of acetoxypropylcellulose (APC). These data will be used to determine the activation energy of the $\eta(T)$ function. From the values of the relaxation time, τ, obtained by the fitting of the theory to the data, we also determined the dependence of this parameter with temperature. Finally, using a shear rate-temperature superposition technique along with Martins' theory [2], we were also able to build a "master curve", and to determine some of the fundamental parameters of the theory.

EXPERIMENTAL

The synthesis and characterisation of our polymers have been described elsewhere [1]. Their relevant physical properties are given in Table I, where the APC polymer is labelled after its average molecular weight.

TABLE I Physical Properties of Acetoxypropylcellulose⁽¹⁾

Polvmer	$\overline{M}_W$(g/mol)	$\overline{MS}$	$\overline{DS}$	*T_i (°C)*
APC 94000	94000	3.67	1.65	170
APC 129000	129000	3.49	1.71	170

(1) from [1]: $\overline{M}_W$ – weight average molecular weight; $\overline{MS}$ – average molar substitution; $\overline{DS}$ – average degree of substitution; T_i – isotropization temperature.

The rheological measurements were performed with a Rheometrics Mechanical Spectrometer – RMS 800, with a cone and plate geometry, during steady shear, at shear rates ranging from 0.01 to 10 s^{-1}, using the step-shear rate mode (increasing of shear rate by logarithmic steps) and under nitrogen atmosphere. Details of the geometry used and experimental procedure have already been described in reference [1]. However it is important to point out that the normal force was allowed to decrease back to its true zero value, after loading, before the tests took place, in order to avoid unreliable measurements of N_1.

Contrary to what happens to thermotropic HPC [26,30], thermotropic APC is very stable, allowing experiments to be conducted for a few hours. Several measurements of $N_1$and η, during steady state, were carried out for each value of $\dot\gamma$ with the two samples, showing a good reproducibility. In the analysis below, only the first measurement, on a virgin sample, is considered.

RESULTS AND DISCUSSION

Rheological properties

The observed shear rate dependencies of $\eta(\dot\gamma)$ and $N_1(\dot\gamma)$ for APC 94000 at 120, 130 and 140 °C, and for APC 129000, at 120 and 140 °C, are displayed in figures 1 to 4, along with the theoretical curves given by the following equations:

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

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

as computer fitted to the experimental data with the MINUIT routine [55].

The equations (1) and (2) above have been derived by Martins [2] for nematic polymers in steady simple shear flow at constant shear rate, with the director lying in the shear plane. In these equations a_i, b_i, c_i ($i = 0,1$) are known functions [2] of the Leslie's viscosity coefficients α_i [56], N_{10} represents 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 $\varepsilon(-1 \leq \varepsilon \leq 1)$ is a measure of the non-affine character of the motion.

Note that although the polymer analysed here is cholesteric at rest and equations (1)-(2) have been derived for nematics in simple shear flow, the cholesteric helix is known to unwound by comparatively small shear forces, giving rise to a nematic structure [57].

Figures 1 and 2 show a decrease of the shear viscosity with increasing temperature for each molecular weight and at each experimentally probed shear rate. The viscosity decreases with increasing shear rate over the whole range of $\dot{\gamma}$, except for shear rates between about 0.2 and 1 s^{-1} (depending on the molecular weight and temperature) where a quasi-Newtonian plateau is observed. This plateau is similar to the one found for liquid crystalline solutions of hydroxypropylcellulose [18], which corresponds to the region II in the Onogi-Asada terminology [58]. The sharp decrease of $\eta(\dot{\gamma})$ observed just below the quasi-Newtonian plateau is controlled by the parameter τ_0, while the new decrease after this plateau is controlled by the parameter τ. These features are supported by equation (1) above.

Figures 3 and 4 show that the first normal stress difference decreases with increasing temperature and that $N_1(\dot{\gamma})$ is an increasing function of $\dot{\gamma}$ over the whole range of shear rates probed. $N_1(\dot{\gamma})$ shows an inflection for values of $\dot{\gamma}$ slightly above $1 s^{-1}$. Actually the experimental data could lead us to believe that a level off of N_1 at the high shear rate end or even an onset of a decreasing of N_1 for higher shear rates was occurring, however the inflection found by fitting the experimental data to the theory is supported by the experimental data on other systems [26,27,30]. Fried et al [27] found for the system HPC/acetic acid, a change from the usual double sign inversion on the curve $N_1(\dot{\gamma})$ to a curve with only positive values of N_1, with an inversion at relatively low shear rates, by the increasing of the concentration from 45 wt % to a 63 wt %. Baek et al [26] found the same phenomenon for the system HPC/m-cresol, at T=25 °C, increasing the concentration from 45 wt % to 50 wt %, even though negative values of N_1 reappear for the 50 wt % solution, with an increase of 10°C in the temperature. At a slightly higher concentration of 55.5 wt % they reported that the temperature must exceed 50 °C before a narrow window of negative N_1 values appears. The same phenomena was found by Huang et al [30] for a 55 wt % HPC/m-cresol

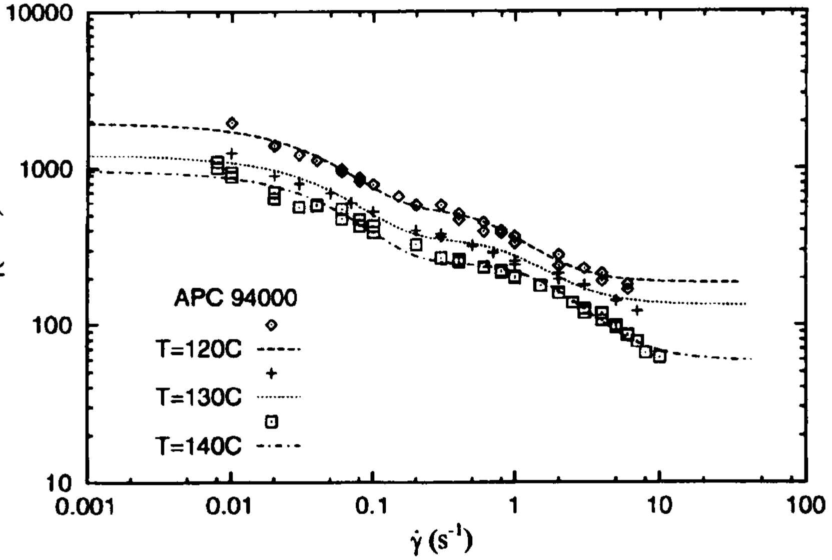

FIGURE 1 Shear viscosity vs shear rate for APC 94000 as a function of temperature. Symbols: experimental data; dotted lines: theory (Martins, 1994)

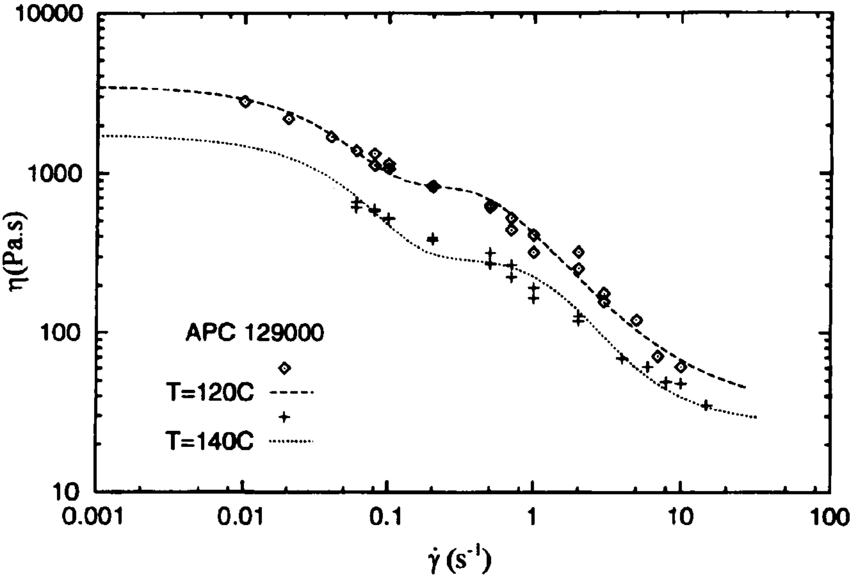

FIGURE 2 Shear viscosity vs shear rate for APC 129000 as a function of temperature. Symbols: experimental data; dotted lines: theory (Martins, 1994)

solution for which an increase in temperature from 25 °C to 37 °C was needed for the reappearance of negative N_1 values.

Thermotropic state could be thought, in that sense, as the upper limit in a continuing increase in concentration, thus presenting the same type of curve as the highly concentrated solutions. Actually, Baek et al [26] measured $N_1(\dot{\gamma})$ for the thermotropic HPC, at 160 °C, but it is not clear if some inflection occurs due to the large dispersion of points in the middle shear rate range.

The non-existence of negative N_1 values could be an indication that thermotopic APC does not tumble, probably due to the semi-flexible nature of the polymers chains, as hypothesised by Baek et al [26]. However Huang et al [30] has recently shown that the existence of a relative minimum, even if this minimum has a positive value, can be an indication of tumbling, which means that actually APC may also present a tumbling regime. The question that remains to answer is whether the inflexion presented by APC can be though as a relative minimum and for answering this question more reliable data must be obtained for higher shear rates.

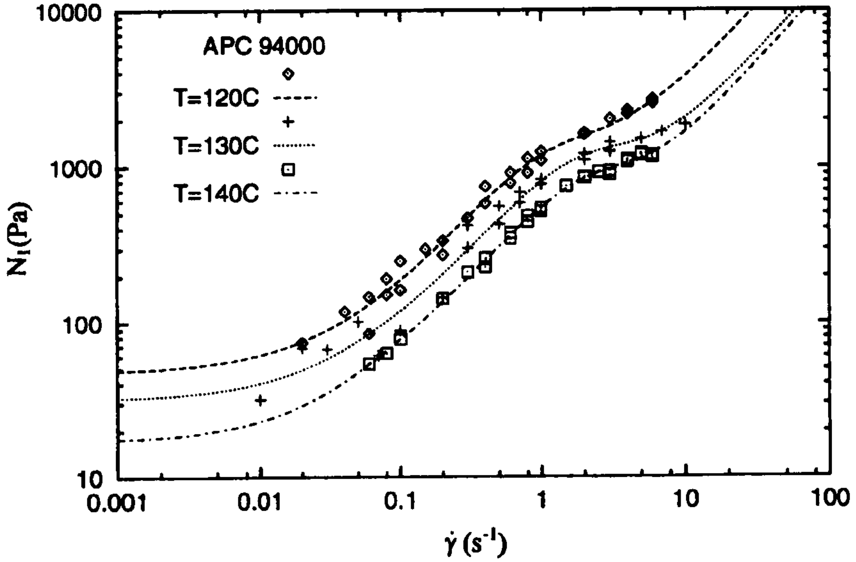

FIGURE 3 First normal stress difference vs shear rate for APC 94000 as a function of temperature. Symbols: experimental data; dotted lines: theory (Martins, 1994)

Tables II and III display the most important parameters obtained from the fitting of expressions (1) and (2) to the experimental data, for APC 94000 and APC 129000 respectively.

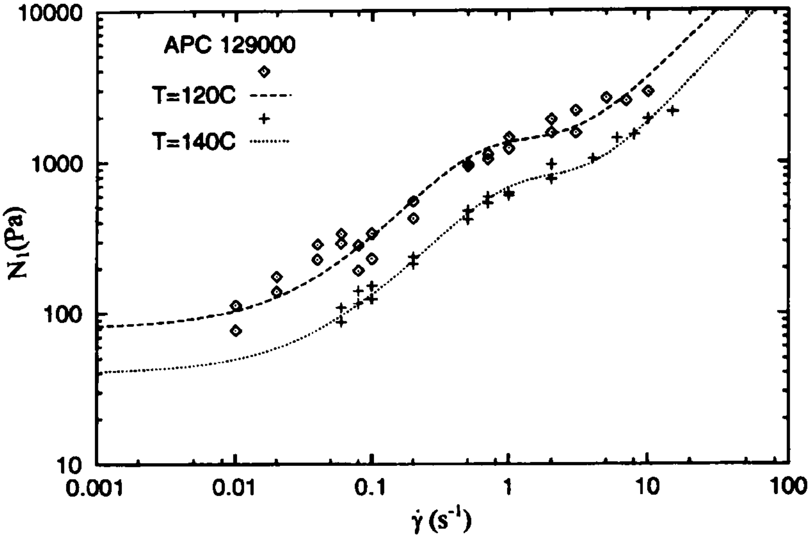

FIGURE 4 First normal stress difference vs shear rate for APC 129000 as a function of temperature. Symbols: experimental data; dotted lines: theory (Martins, 1994)

TABLE II Most important fitting parameters of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ for APC 94000 at three different temperatures

Fitting parameter		*T = 120°C*	*T = 130°C*	*T = 140°C*
	τ (s)	1.8	1.3	0.8
$\eta(\dot{\gamma})$	τ_0(s)	20.0	17.5	16.6
	ε	0.8	0.8	0.8
	η_0+c_0 (Pa.s)	1968.7	1222.3	969.2
$N_1(\dot{\gamma})$	τ (s)	1.9	1.0	1.0
	ε	0.9	0.9	0.9

TABLE III Most important fitting parameters of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ for APC 129000 at two different temperatures

Fitting parameter		*T=120°C*	*T= 140°C*
$\eta(\dot{\gamma})$	τ (s)	3.5	1.7
	τ_0(s)	25.0	21.0
	ε	0.8	0.9
	η_0+c_0 (Pa.s)	2848.0	1764.7
$N_1(\dot{\gamma})$	τ (s)	3.3	1.3
	ε	0.9	0.8

In reference [1] we have already presented some considerations concerning the fitting of the experimental data to the theory and the magnitudes of the parameters obtained, that hold for the new results presented here.

For $\overline{M}_W = 94000$ g/mole, from which we had three temperatures, we have tested an Arrhenius type law for the dependence of the viscosity with temperature, that showed to be adequate for the temperature range considered. Table IV present the apparent activation energy, E_a, found for this molecular weight at different shear rates. Assuming the same type of dependence for the higher molecular weight, we were also able to determine the activation energy for $\overline{M}_W = 129000$ g/mole, at different shear rates, which are also presented in table IV.

The results presented in table IV show that the apparent activation energy, for a giving $\dot{\gamma}$ increases with molecular weight. The variation of E_a with $\dot{\gamma}$ for APC 94000 shows a minimum at $\dot{\gamma} \approx 2\ s^{-1}$ (the same phenomena is probably observed for APC 129000 but we can not support such statement with only one point). This change in behaviour suggests a change in the mechanism that governs the dynamics of the system. Baek et al [26] found the evidence of a different mechanism for the high and the low concentrations of HPC/m-cresol which they attribute to a different degree of shear thinning. That could also be responsible for the change we have observed for the dependence of the activation energy with shear rate. Note that the shear rate at which the type of dependence of E_a with $\dot{\gamma}$ changes is slightly above the shear rate that corresponds to the beginning of the region III in the Onogi-Asada terminology [57].

TABLE IV Activation energies for APC 94000 and 129000, for different shear rates

$\dot{\gamma}$ (s^{-1})	*E (kJ/ mol)*	
	APC 94000	*APC 129000*
0.01	53.6	
0.02	51.1	
0.03	53.6	
0.06		54.4
0.1	45.2	53.2
0.2	40.6	52.7
0.3	54.0	
0.5		51.9
1.0	38.1	49.4
2.0	33.9	58.6
3.0	43.5	
5.0	52.7	
7.0	61.9	

The same type of dependence of viscosity on temperature has been found by Moldenaers and Mewis [19], on lower concentrations of nematic solutions of PBLG. In particular they found an activation energy of 46 kJ/mole for a 12 wt % PBLG/m-cresol solution. For higher concentrations of the same system, Walker et al [29] found values of the activation energy of 49.9 and 50.3 kJ/mole, for concentrations of 34 and 37 wt %, respectively. However increasing the concentration up to 40 wt % E_a increases approximately 3 times. The lyotropic solutions of HPC present also a dependence of the shear viscosity on temperature of an Arrhenius type but, contrary to what happens to the low concentrations of PBLG/m-cresol solutions, for which E_a is approximately the same as the pure solvent, the HPC/m-cresol and HPC/water solutions present, for all studied concentrations, a value of E_a that is about 33 kJ/mole higher than the activation energy of the pure solvent [28,30]. The explanation seems to lie on the flexibility of the molecules. Solutions of more rodlike polymers should present (at least for low concentrations) an activation energy very close to the one presented by the pure solvent, while for solutions of semi-flexible polymers E_a becomes much higher.

For thermotropic APC we could expect higher activation energies than the ones calculated. However since the experimental temperatures are only 30–50 degrees below the clearing temperature the values presented seem to be acceptable even though higher values could be expected for measurements at lower temperatures. Also, measurements at constant shear stress rather than at constant shear rate should lead to higher values of E_a, according to Walker and Wagner [28]. Future measurements must then be performed in order to clarify this point.

The values of τ shown in table II show that this parameter varies linearly with T, with a slope of –0.05 for APC 94000. For APC 129000 and assuming also linearity, the slope found was –0.09.

Master curves

The prediction of the behaviour of $\eta(\dot{\gamma})$ for different temperatures has lead, for traditional polymers, to build a master curve by using a shear rate-temperature superposition technique. In this method, the amount of shifting of one curve at a temperature T, to superimpose the master curve (chosen at a reference temperature) along the $\dot{\gamma}$ range, can be measured by the shift factor a_T which is given by $a_T = \dot{\gamma}(\text{reference})/\dot{\gamma}(T) = \eta\ (T)/\eta\ (\text{reference})$. It is usual, in this case, to plot, in *log* scale, the reduced viscosity η/η_0 vs. $\dot{\gamma}\ \eta_0$, where η_0 denotes for the zero shear viscosity.

This procedure is convenient for conventional polymers since η_0 is proportional to the mean relaxation time and the ratio of the zero shear viscosity at two different temperatures must equal the ratio of the relaxation times at the same temperatures. This may not be true for the liquid crystalline polymers due to the dependence of the zero shear viscosity on the order parameter, S, which is a function of temperature. In such a case the usual time-temperature shifting may not be valid. Nevertheless, far away from the clearing temperature where changes to the order parameter are not so important, the same procedure may be applied, and has in fact been applied in case of PBLG/m-cresol [20,29] and HPC/water [28] lyotropic systems, as well as in case of a thermotropic polyesteramide [5].

In this work, however, we used a different procedure. Since we have two relaxation times, τ and τ_0, and between $\tau_0\dot{\gamma} = 1$ and $\tau\dot{\gamma} = 1$ the $\eta(\dot{\gamma})$ curve shows an "hesitation" in the beginning of the shear-thinning region that follows the "Newtonian plateau", we used a different scaling factor to obtain the reduced viscosity master curve. The "building" of our "master curve" has been obtained by plotting, in *log* scale the reduced viscosity η / (η_0+c_0) vs. the reduced shear rate $\dot{\gamma}/\dot{\gamma}_0$, where (η_0+c_0) is the zero shear viscosity and $\dot{\gamma}_0 = 1/\tau_0$, as obtained by fitting the theory to the data. Figures 5 and 6 present the "master curve" obtained for both molecular weights.

The fact that we use η / (η_0+c_0), given by the fit of the theory to the data, as the reduced viscosity has an added advantage, since it is difficult to assign unambiguously a value to η_0 for many LCP's.

A "second fit" of $\eta(\dot{\gamma})$, with $\tau_0=1$, to the total set of the reduced experimental data gives the characteristic relaxation time for both molecular weights i.e. $\tau=5\text{x}10^{-2}$ s for APC 94000 and $\tau=1.8\text{x}10^{-1}$ s, for APC 129000.

CONCLUSIONS

The shear viscosity $\eta(\dot{\gamma})$ and the first normal stress difference $N_1(\dot{\gamma})$ both decrease with increasing temperature, as observed for isotropic polymers. For a constant shear rate, and for the temperature range considered here, the dependence of the shear viscosity on temperature obeys a power law of the Arrhenius type, with apparent activation energies in the order of 33.5–58.6 kcal/mole, depending on molecular weight and shear rate. These are usual values for E_a for the semiflexible isotropic polymers and close to the values obtained for the PBLG/m-cresol, HPC/m-cresol and HPC/water lyotropic solutions, even though higher values of the activation energy are expected for lower temperatures and using constant shear stress rather than constant shear rate measurements, The activation energy increases with molecular weight and its variation with $\dot{\gamma}$ for APC 94000 shows a minimum at $\dot{\gamma} \approx 2\ \text{s}^{-1}$. The relaxation time decreases linearly with increasing T, as predicted. Using a scaling factor different from the one

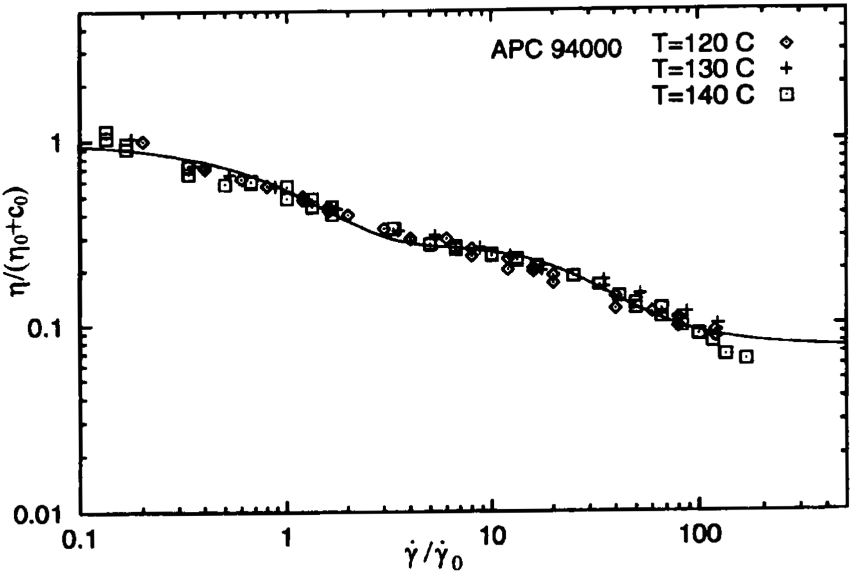

FIGURE 5 Reduced viscosity master curve for APC 94000. Symbols: experimental data; line: theory (Martins, 1994)

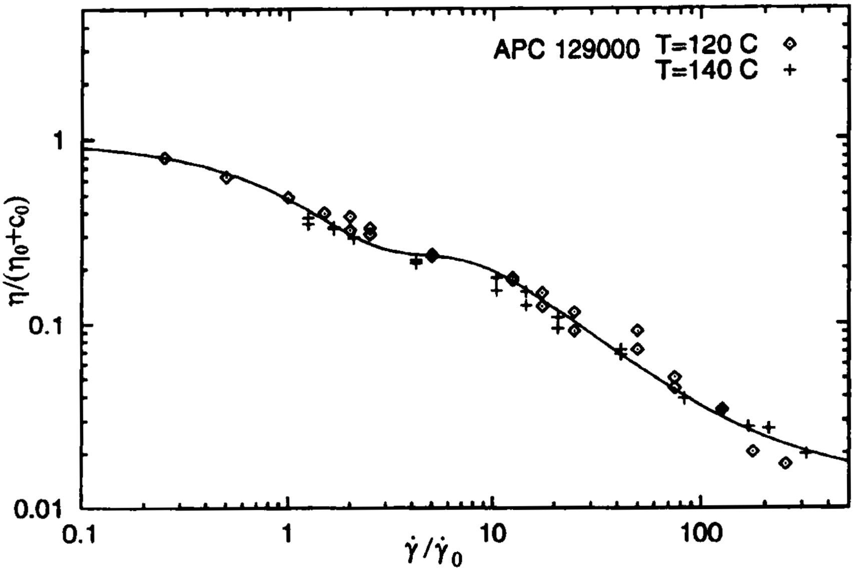

FIGURE 6 Reduced viscosity master curve for APC 129000. Symbols: experimental data; line: theory (Martins, 1994)

used for isotropic polymers, it has been possible to build a “master curve” and to determine the characteristic relaxation time for each molecular weight.

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