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# AN EXPERIMENTAL INVESTIGATION OF THE TEMPERATURE INFLUENCE ON THE VISCOUS MODULUS AND GELATION TRANSITION OF A POLYMERIC SOLUTION

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**Abstract.** *The viscoelastic modulus and the gelation transition of an aqueous polymer suspension (Polaxamer 407) is investigated experimentally. The dependence of the viscometric modulus on time, shear rate, temperature, macromolecule volume fraction and additive concentration is examined. The experimental investigations are carried out with eight samples of Polaxamer. Four of these samples are tested with the aqueous polymeric suspension in the absence of additives for different macromolecule volume fractions. The other four samples are produced from the first one by adding Clobetazol and a surfactant called Sodium Dodecyl Sulphate (SDS). All samples are sheared in a high performance rheometer of parallel disk with an automatic control of gap. The first tests are carried out under condition of steady shear over five experimental realizations. We obtain results of the Polaxamer viscosity as a function of time and we also investigate the shear rate dependence viscosity of the polymer solution for two different temperatures, 6 °C and 36 °C. While a shear thinning behavior of the polaxamer is verified for the temperature of 36 °C, a non shear rate dependence viscosity is observed at 6 °C for all samples. The second tests deals with non-isothermal experimental trials under a regime of small amplitude oscillatory shear, in a temperature range from 3.5 to 50 °C. The viscoelastic modulus of storage and loss of energy are determined as a function of the temperature. In addition, the gelation transition of the polymer solution is characterized as a sudden change in the viscoelastic modulus. We show a plot of the gelation temperature as a function of the polymer volume fractions. This interesting finding is directly associated with microstructure induced transition as the temperature increases. We also present a typical result for the shear elastic modulus of the polymer as a function of the polymer volume fraction for 6 °C. This shows that the micelles like chain formation at a given temperature leads to a solid characteristic of the polymer that can be interpreted as a yield stress.*

**Keywords:** *Rheometry, complex fluid, gelation, polymer suspension, thermosensitivity, yield stress.*

## 1. INTRODUCTION

The rheology of a viscoelastic liquid in simple and oscillatory shear with focus on the temperature dependence of the viscosity is the main context of this work. These materials represent an important class of non-Newtonian fluids characterized by solid and liquid-like behaviors. (Bird *et al.*, 1977).

Viscoelastic fluids have been extensively studied nowadays not only motivated by pure phenomenological interests, but also by its numerous applications in several industrial branches. In the oil industry, mud with drag reduction polymer additives are used to increase the efficiency of well drilling processes (Cunha and Andreotti, 2007). Besides that, the knowledge of viscometric properties are really important for the food and pharmaceutical industries due to the fact that usually food and gel-like drug carriers are viscoelastic (Dumortier *et al.*, 2006).

Since viscosity is strongly dependent on the temperature mainly for very viscous fluids (e.g. polymer solution) we have also explored this influence here. Some pharmacological gels, like the aqueous polymer suspension of Poloxamer 407, presents an anomalous behavior characterized by the growth of its viscosity as a result of an increase in the temperature. This anomalous rheological response is seen as a direct consequence of a process of successive microstructural transitions called gelation (Dumortier *et al.*, 2006). In this processes, the microstructure of the suspension are turned from separated linear chains to a tridimensional linked-chains structure called micelles (Dumortier *et al.*, 2006).

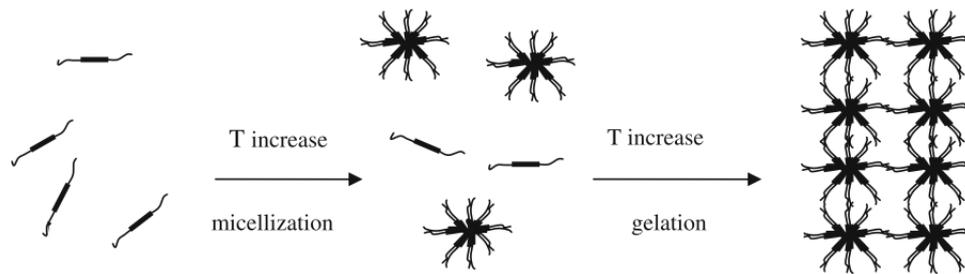


Figure 1: Microstructural transitions during the process of gelation (Dumortier *et al.*, 2006).

## 2. EXPERIMENTAL PROCEDURE

Two experimental procedures are used in order to test the suspension samples in a high performance parallel disk rheometer (see figure 2a). The first experimental procedure was carried out with an isothermal sample undergoing a steady simple shear. In contrast, the second part of the experiments were carried out varying the sample temperature under condition of small amplitude oscillatory shear (i.e. linear viscoelastic regime).

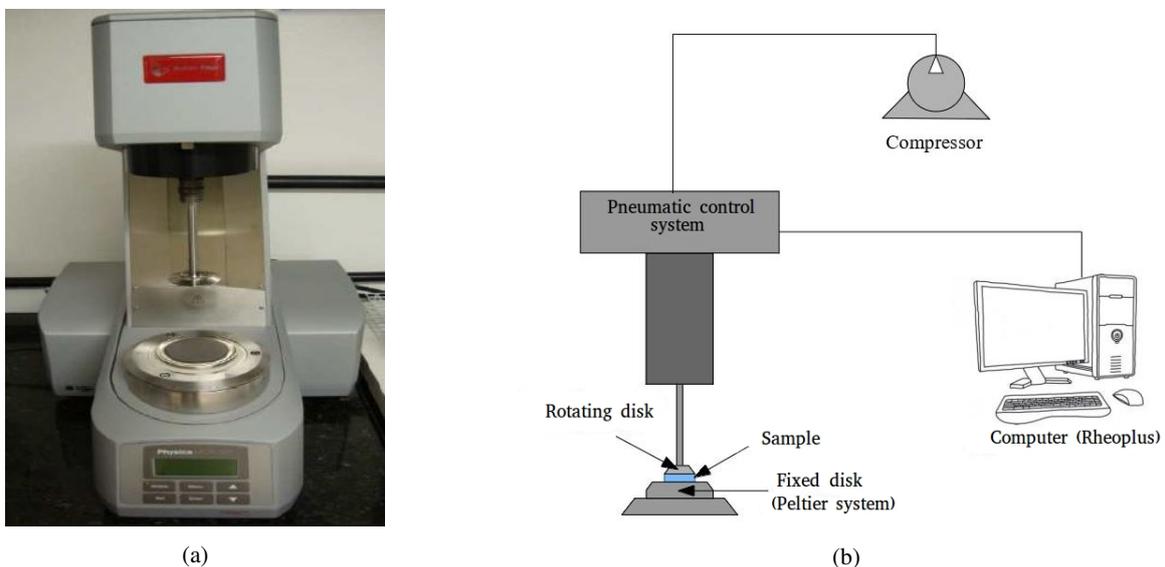


Figure 2: (a) Paralle disk rheometer Anton Paar, model Physica MCR 301 with an automatic control of fluid-gap and temperature (Peltier). (b) Schematics of the rheometer's measuring system.

The isothermal simple shear experiment starts by setting the temperature of the experimental realization, followed by the accommodation of a determined volume of the suspension sample in the gap between the two plates (see figure 2b), and then subjecting it to a constant shear rate motion.

The non-isothermal small amplitude oscillatory shear experiments were carried out by selecting a constant strain. The strain must be sufficiently small in order to ensure a linear viscoelastic regime in the experiments. For all the samples, the strain used is 0.1 and the angular frequency is  $35 \text{ rad/s}$  (approximately  $5.6 \text{ s}^{-1}$ ), what keeps the non-dimensional shear rate about 0.6. At the same time a linear temperature ramp is used and the viscoelastic modules are determined by the Rheometer software Rheoplus. Actually the viscoelastic modulus are obtained from the Fourier coefficients of the shear stress. In this stage, the gelation temperature is evaluated as well.

## 3. RESULTS AND DISCUSSIONS

In general, the experimental data from the non-isothermal oscillatory shear tests have shown a growth of the viscoelastic modulus as temperature increases (see figure 3). This behavior is observed for all samples of liquid examined. In particular, two sample temperatures in the plot of viscous modulus versus temperature are important to characterize the structure transition and, consequently, the abrupt increase of the viscous modulus. The micelization temperature corresponds to the point in the plot in which an increase of the viscoelastic modulus as the temperature increases can be observed (i.e.  $d\eta'/dT$  is greater than a small tolerance). On the other hand, the gelification temperature occurs at the point of the plot in which both viscoelastic modulus assume the same value.

Figure 3 also shows from a qualitatively point of view the possible liquid microstructures for different temperature

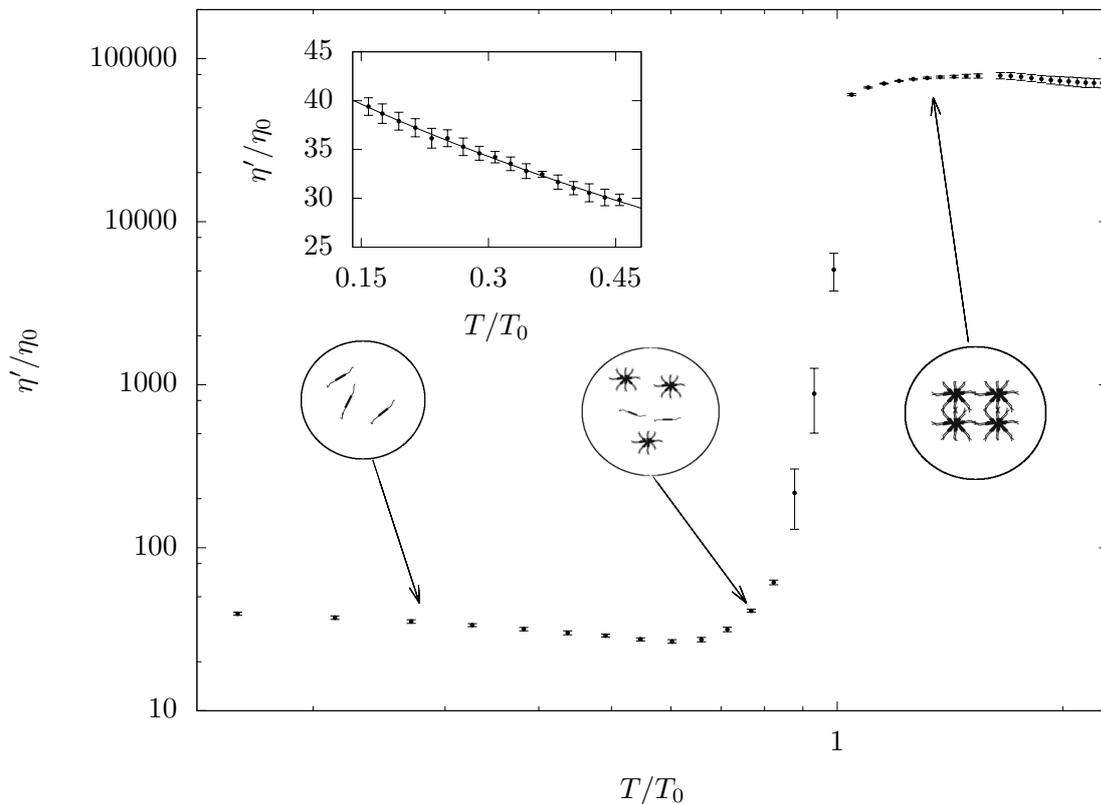


Figure 3: Relative viscous modulus as a function of the adimensionalised temperature in a viscoelastic regime with error bars ( $\eta_0 = 1.002 \times 10^{-3} Pa.s$  and  $T_0 = 25^\circ C$ ). The different structures of micells inserted in the figure represent a qualitative interpretation of the link between the rheology and microstructure of the polymer as temperature increases. This rapid  $\eta'$  jump is close connected with the structure transition as  $T \approx T_{gel}$ . In the insert is shown the behavior of the relative viscous modulus as a function of the adimensionalised temperature for a range of temperatures lower than  $T_{sol}$  with errorbars. the insert in this plot shows a fitted experimental data by the Arrhenius model (Barnes *et al.*, 1989).

range. These structure transitions are closely associated with the behavior of the viscous modulus  $\eta'$  at low frequency. The points all in this plots were measured by our experiments.

From the lowest temperature tested until the temperature of micelization, the viscosity modulus of all samples has decreased as a function of temperature. This is a typical behavior of Newtonian fluids and, as a result the experimental data has shown a strong agreement with Arrhenius' law.

The additives (Clobetazol and SDS) accelerate the polymerization process. This important property is indicates in the plots shown in figures (3b) and (3a). In the presence of these additives, the micelization and gelation transition initiate in lower temperature as compared with the behavior of the polymer sample in absence of the additives at the same polymer volume fraction. The additives seems to increase the rate of structure like chains (i.e.micelles) formation as the temperature increase.

A typical result for the shear elastic modulus of the polymer as a function of the polymer volume fraction at  $6^\circ C$  is presented in the figure (4a). This indicates that a certain amount of stress need to be applied to the solution for it to flow, even at low frequency and temperature. Besides that, it shows that the micelles-like chain formation at a given temperature leads to a solid characteristic of the polymer that can be interpreted as a yields stress.

Figure (4b) shows the behavior observed for the viscosity modulus as a function of the polymer volumetric fraction. The data is obtained in a regime of low frequency and small strain. As a consequence, regarding the principle of equivalence between steady and oscillatory shear (i.e.Cox-Merz rule (Morrison, 2001)), the viscosity modulus as a function of low frequency can be interpreted as the fluid viscosity as a function of the shear rate. In particular  $\eta_0$  is the dynamic viscosity of the fluid.

Figures 4a and 4b show the elastic modulus and the viscous modulus as a function of macromolecule volume fraction, respectively. A non-linear variation of the viscosity in relation to that parameter was verified. This behavior is sucessfully described by a power-law expression, namely  $\eta'/\eta_0 = A\phi^B$ .

As a result of the experimental procedures in isothermal simple shear flow regime, it was possible to characterize two different behaviour of the polimeric solution: at temperatures lower than the gelation one, the polymer relative viscosity

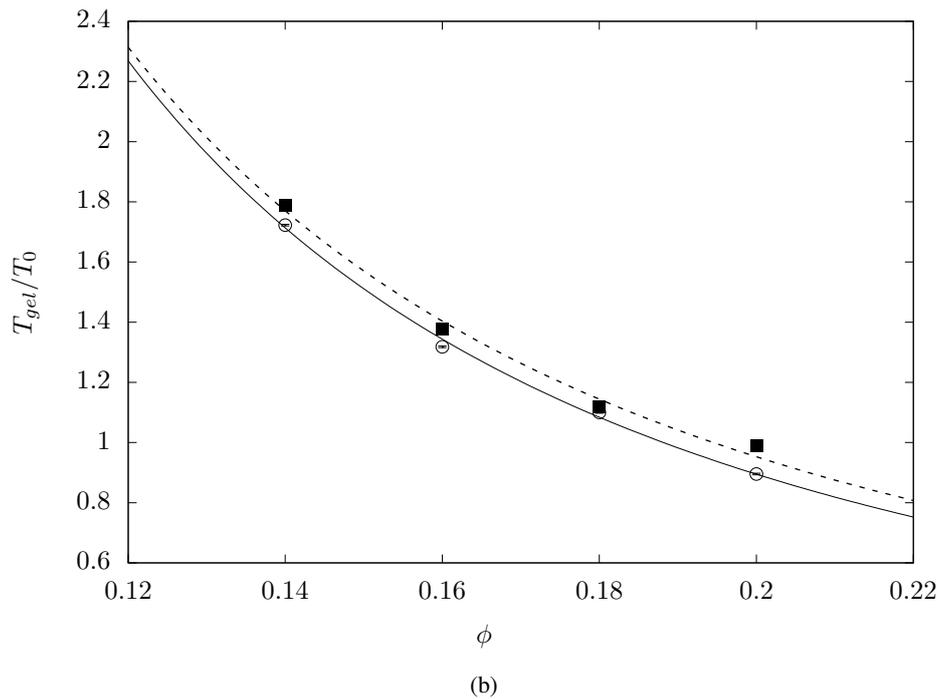
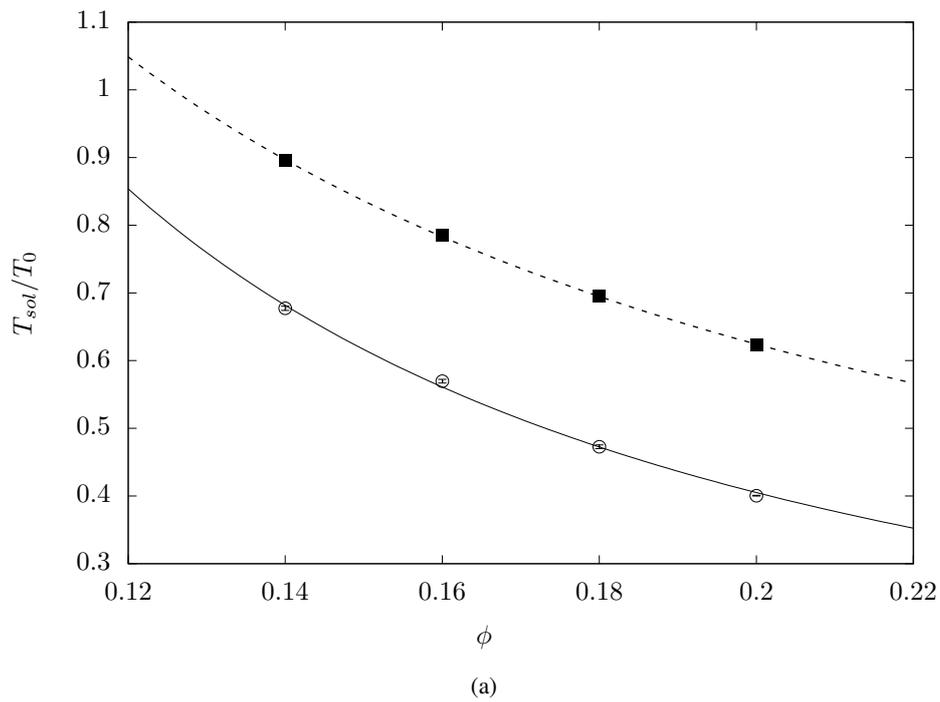


Figure 3: (a) Non-dimensional temperature of micellization as a function of the polymer volume fraction. Data points adjusted to curves of the kind  $T/T_0 = A\phi^B$ . The following parameters were obtained: (—)  $A = 0.04, B = -1.46$  and (---)  $A = 0.12, B = -1.02$  and (b) Non-dimensional temperature of gelation as a function of the polymer volume fraction. ■ - Isolated samples and ○ - samples with additives. The error bars are also shown in the plot. ( $T_0 = 25^\circ C$ )

was found to be constant as a function of the shear rate (see figure 5a), on the other hand, at temperatures above the gelation, the samples presented a shear-thinning behaviour (see figure 5b), that was effectively adjusted to a power law model (Tanner, 2000). The non-linear behavior of the relative viscosity results from the complex interactions among the polymer chains that causes a significant change in the rheology of the polymer solution. The behaviour of the relative viscosity as a function of the polymer volume fraction was effectively described by an adaptation of the Krieger-Dougherty relation (Luckham and Ukeje, 1999).

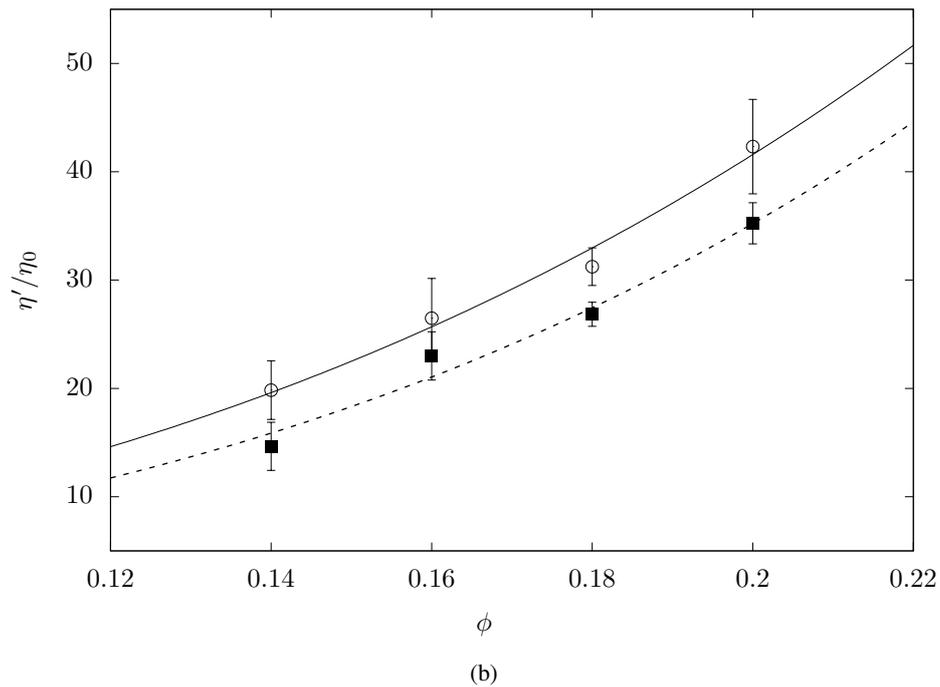
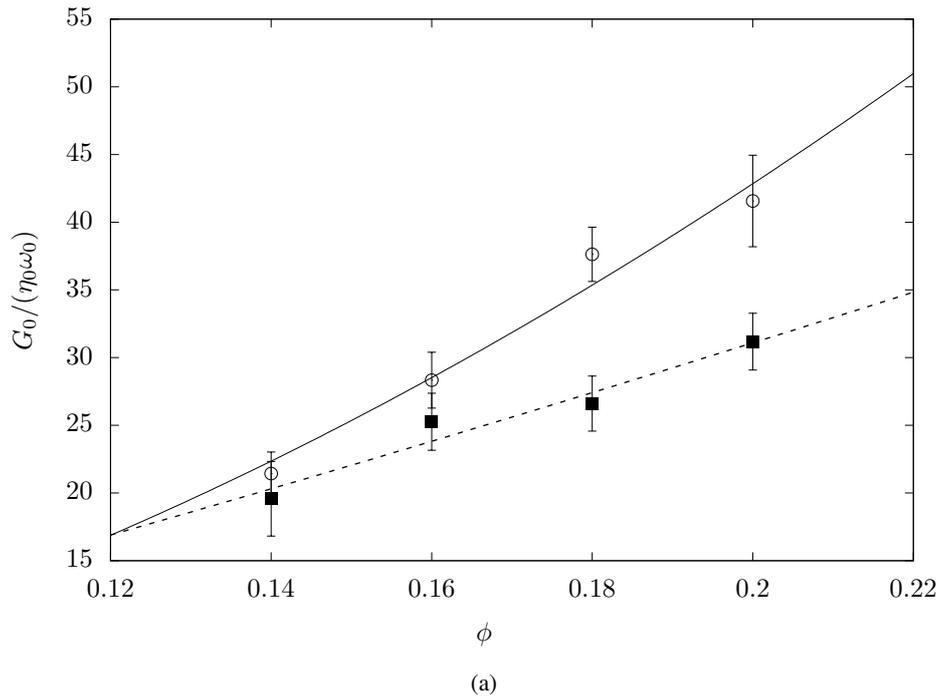


Figure 4: (a) Non-dimensional shear elastic modulus at  $6^\circ C$  as a function of the polymer volumetric fraction ( $\eta_0 = 1.002 \times 10^{-3} Pa.s$  and  $\omega_0 = 5.6 s^{-1}$ ). Data points adjusted to curves of the kind  $G_0 = a\phi^b$ . The following parameters were obtained: (—)  $a = 806.9$ ,  $b = 1.8$  and (---)  $a = 212.3$  and  $b = 1.2$ . (b) Non-dimensional viscosity modulus at  $6^\circ C$  as a function of the polymer volumetric fraction. Data points adjusted to curves of the kind  $\eta'/\eta_0 = (1 - k\phi)^{-\beta}$ , which are an adaptation of the Krieger-Dougherty expression (Luckham and Ukeje, 1999). The following parameters were obtained: (—)  $k = -6.39$ ,  $\beta = 4.32$  and (---)  $k = -10.31$  and  $\beta = 3.33$ .  $\circ$  - Aqueous polymeric suspensions with additives and  $\blacksquare$  - Aqueous polymeric suspension in the absence of additives. The error bars are also shown in the plot

#### 4. CONCLUSIONS

The polymeric solutions investigated here have presented a shear-thinning behavior at temperatures above the micelation temperature. In contrast, the suspensions behaved as a Newtonian fluid at temperatures lower than  $T_{sol}$ , characterized by the invariance of polymer relative viscosity as a function as a function of the shear rate. Besides that, in this range

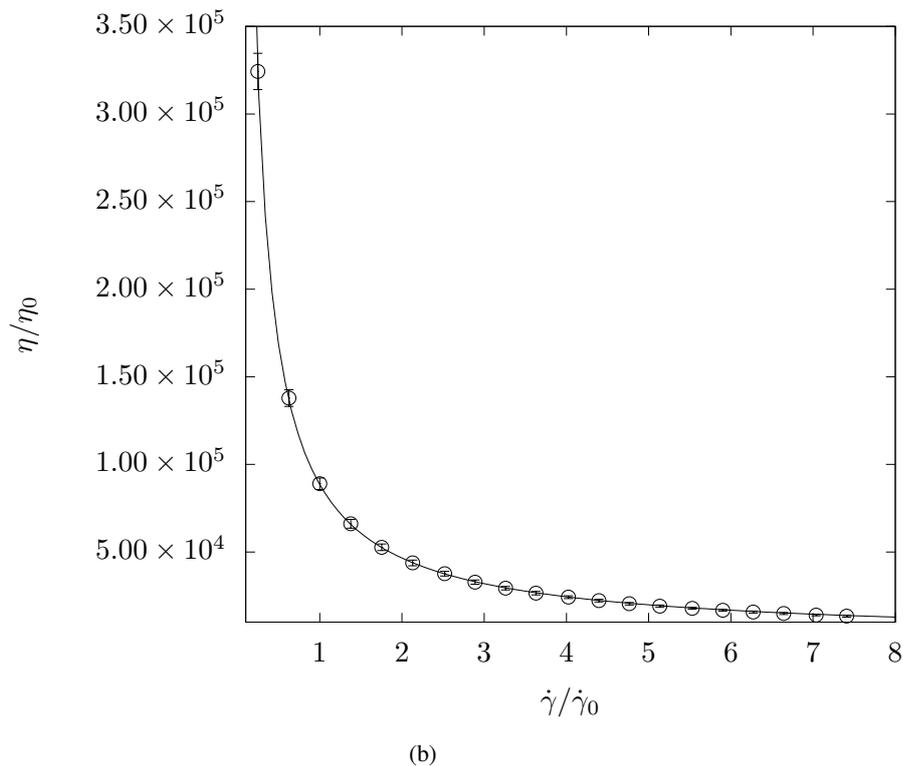
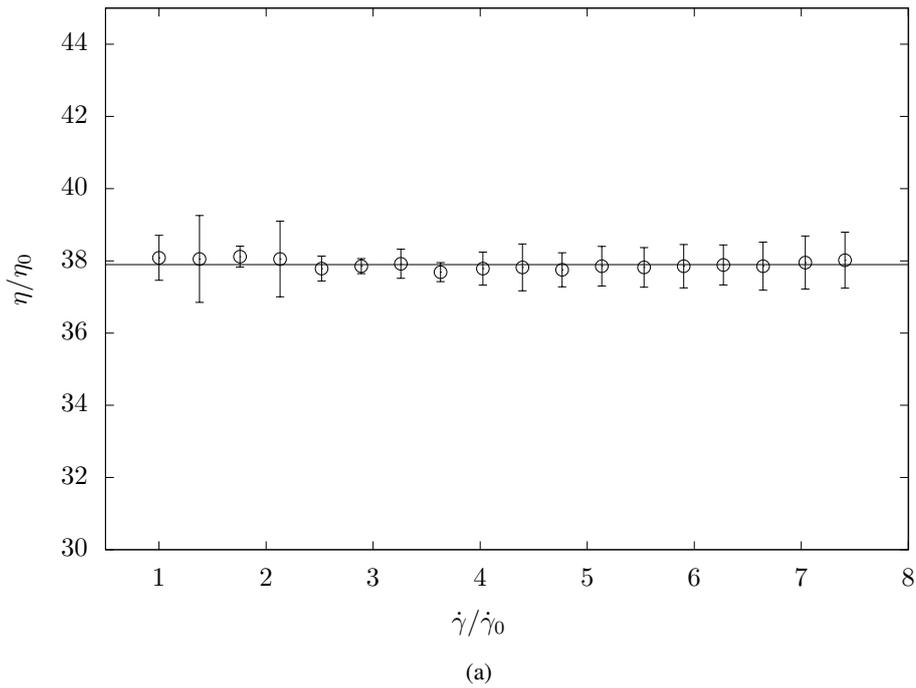


Figure 5: Polymer relative viscosity as a function of the shear rate for a macromolecule (or polymer) volume fraction  $\phi = 0.18$  of an isolated sample. ( $\eta_0 = 1.002 \times 10^{-3} Pa.s$  and  $\dot{\gamma}_0 = 4.05 s^{-1}$ ) (a)  $6^\circ C$  and (b)  $36^\circ C$ . The error bars are also shown in the plot.

of lower temperatures, the dependence of the fluid viscosity was successfully described by Arrhenius' equation (Barnes *et al.*, 1989).

At temperatures above  $T_{sol}$  the samples all have presented an anomalous behavior, characterized by a fast growth of the viscoelastic moduli associated with microstructural transitions, involving interactions and the formation of link-like-chains between the liquid macromolecules. The storage modulus was observed to be higher than the loss modulus for all

tested samples at temperatures above the temperature of micellization, indicating a predominant solid-like behavior of the polymer solution.

The addition of Clobetazol and SDS to the samples has produced a decrease of the micellization and gelification temperatures. The presence of such additives promotes a stabilization of the fluid structure avoid break-up of the link-like-chains as the temperature increases above the gelation temperature. A saturation of the viscoelastic modulus for temperatures above the temperature of gelation has been observed. Besides that, a non-linear behavior was observed for the relation between the storage modulus and the effective viscosity as a function of the volumetric fraction of polymer in the samples.

## 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

- Barnes, H.A., Hutton, J.F. and Walters, K., 1989. *An introduction to rheology*, Vol. 3. Elsevier.
- Bird, R.B., Armstrong, R.C., Hassager, O. and Charles, F.C., 1977. *Dynamics of polymeric liquids*, Vol. 1. Wiley New York.
- Cunha, F.R. and Andreotti, M., 2007. "A study of the effect of polymer solution in promoting friction reduction in turbulent channel flow". *Journal of fluids engineering*, Vol. 129, pp. 491–505.
- Dumortier, G., Grossiord, J.L., Agnely, F. and Chaumeil, J.C., 2006. "A review of poloxamer 407 pharmaceutical and pharmacological characteristics". *Pharmaceutical Research*, Vol. 23, pp. 2709–2728.
- Luckham, P.F. and Ukeje, M.A., 1999. "Effect of particle size distribution on the rheology of dispersed systems". *Journal of colloid and interface science*, Vol. 220, pp. 347–353.
- Morrison, F.A., 2001. *Understanding rheology*. Oxford University Press, USA.
- Tanner, R.A., 2000. *Engineering rheology*. OUP Oxford.

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