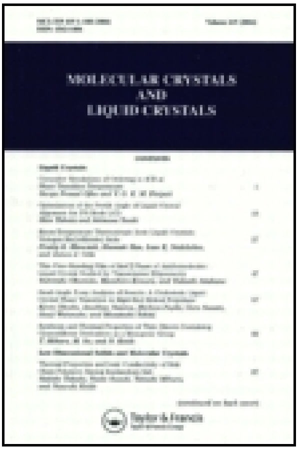

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Transient Rheological Behaviour of A Lyotropic Polymeric Liquid Crystal

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TRANSIENT RHEOLOGICAL BEHAVIOUR OF A LYOTROPIC POLYMERIC LIQUID CRYSTAL

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Abstract The stress transients resulting from stepwise changes in shear rate have been investigated for a liquid crystalline solution of PBLG in m-cresol. In step-up experiments these transients display a complex profile which includes multiple maxima, even in the Newtonian region. To a first approximation the curves scale with strain. A stepwise decrease in shear rate also causes a stress pattern with multiple maxima. The initial decay is related to the stress relaxation upon cessation of flow. Many of these features are not described by the existing theories. They are explained in terms of supermolecular structures such as domains.

INTRODUCTION

Although there already exists a substantial literature on the rheology of polymeric liquid crystals (PLCs), as reviewed by e.g. Wissbrun[1], no adequate rheological models have, as yet, been developed for this class of materials. The Leslie-Ericksen theory[2], which proved useful for low molecular weight LCs, is only valid for polymers in a limited range of conditions. The molecular theory of Doi[3] shows some interesting features but has only been tested to a limited extent[4]. Recent experimental evidence[5,6] suggests considerable shortcomings. This might be due to the fact that the Doi theory does not take into account the presence of domain structures[7]. Recently, ways have been suggested to incorporate the domain effects in rheological models[8,9].

The amount of experimental data, that are suitable for model testing and development, is very limited. Transient data are essential in verifying the viscoelastic behavior and are hardly available in the literature[5,10]. Therefore systematic experiments of this nature were performed on a lyotropic model system. The objective of this work is to identify some of the characteristics of polymeric liquid crystals which should be described by rheological constitutive equations.

EXPERIMENTAL

As a model system a 12% by weight solution of poly(-γ-benzyl-L-glutamate) (PBLG) in m-cresol has been used. PBLG solutions have been investigated in detail in the past[10-12]. This synthetic polypeptide develops a helix structure which is responsible for the formation of a liquid crystal. The basic rheological behaviour of the particular sample under consideration, molecular weight approximately 250000, is also known[5,6,10]. Its most prominent feature is the occurrence of a negative normal stress in an intermediate shear rate region (fig. 1), which is well documented in the literature[5,11,12].

Suitable transient experiments for model evaluation should be technically feasible and theoretically tractable. These requirements are met by stepwise changes in shear rate between an initial ($\dot{\gamma}_i$) and a final ($\dot{\gamma}_f$) value. The initial shear rate is zero in a start-up experiment. On the other hand the final shear rate is zero in a stress relaxation experiment. The final value can be smaller (step-up experiment) or larger (step-down experiment) than the initial one. All tests have been performed on a Rheometrics

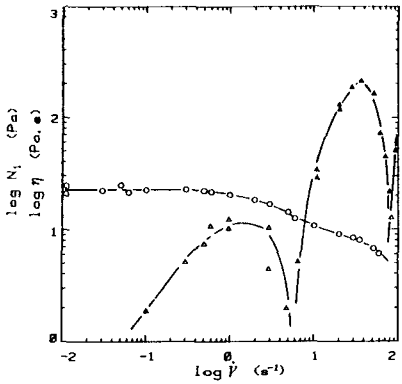

Figure 1. Steady shear flow results at 293 K (o : viscosity; △ : positive N_1; ▲ : negative N_1)

RMS 705F, using cone-and-plate geometry. The latter guarantees a constant shear history throughout the sample. It can be shown[13] that relaxation times which are sufficiently larger than $1x10^{-2}$ s^{-1} are physically meaningful in the present case.

START-UP EXPERIMENTS

Start-up experiments are frequently used to measure the viscoelastic properties of isotropic polymer fluids, both in the Newtonian and in the non-Newtonian region. A few isolated data are also available for PLCs[4,14]. Figure 2 displays some results for the PBLG solution. The shape of the stress transient is more complex than usually seen for isotropic fluids but agrees qualitatively with available results on PLCs.

Multiple maxima can be expected theoretically in systems which contain anisotropic inclusions whenever convective flow effects dominate rotational Brownian motion[15]. In the present case the complex transients are obtained in the Newtonian region (fig. 1). Furthermore the transients depend strongly on the time the material has been at rest before the start-up, even after more than 10 hours. Obviously the material has a different structure at rest than under shear in the Newtonian region. This has been detected earlier by means of oscillatory measurements[5], although the present changes seem to occur over an even larger time range. This conclusion also fits in with visual observations in polarized light[16] and with birefringence measurements[17].

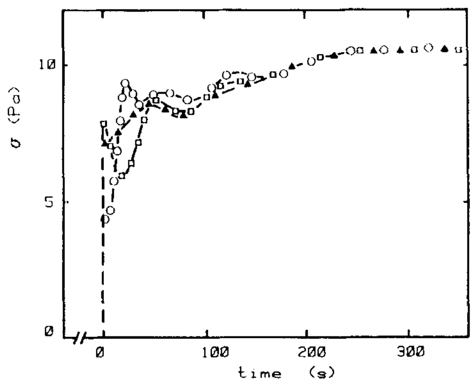

Figure 2. Stress growth curves after various periods of rest ($\dot{\gamma}$ = 0.5 s^{-1}; rest periods in hours: □: 11; ▲: 14; ○: 16)

The previous observations have normally been related to changes in domain structure[16]. There is also a transition in this sample from a nematic structure during flow to a cholesteric one after the flow stops[11]. From a theoretical point of view, the Doi theory can predict transients but the rest period creates an initial condition which is not defined in that theory. For these various reasons start-up experiments do not seem suitable at this stage.

They do provide a sensitive probe to structural changes, which however cannot be exploited yet.

STEP-UP EXPERIMENTS

The structural changes which interfere with the interpretation of the start-up experiments can be overcome in part in step-up experiments. Therefore systematic measurements of this nature were performed, keeping the shear rates in the Newtonian region. From earlier work, involving oscillatory measurements after cessation of flow[5], it is known that the structure changes even in the Newtonian region. Hence it is necessary to verify how this affects transient behaviour.

Even in step-up experiments the stress transients depend on the shearing time (fig. 3). The time required to obtain a transient, that is independent of the previous shearing time, is longer than the time necessary to obtain

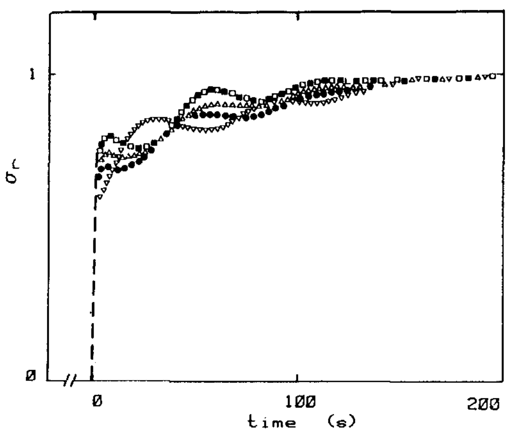

Figure 3. Effect of shearing time at the initial shear rate on the stress transient ($\dot{\gamma}_i$ = 0.05 s^{-1}; $\dot{\gamma}_f$ = 0.5 s^{-1}; shearing time in minutes: ▽ : 10; ● : 20; △ : 30; □ : 120; ■ : 180)

a constant shear stress or normal stress. Hence a structural change seems to take place to which the stresses are not sensitive. The required time also changes inversely proportional to the applied shear rate, making the measurements quite time-consuming at low shear rates. A comparison of the transients after 120 and 180 minutes in fig. 3 clearly shows that reproducible transients can be obtained if a suitable shearing time is accepted.

Transients are particularly susceptible to instrumental artefacts, especially to gap size effects[18]. Figure 4 shows repeat measurements for two different cone angles. This figure clearly proves the absence of gap size effects and also illustrates the degree of reproducibility that can be achieved if the necessary precautions are taken.

The stress transients during a step-up in shear rate closely resemble those obtained during a start-up experiment. The multiple maxima in the Newtonian region still persist when there is a previous shearing. The transients were further investigated by using the final shear rate $\dot{\gamma}_f$ as a parameter. In runs with the same initial shear rate the structure must be identical at the onset of the transient, which simplifies the comparison between experiments. The data are conveniently presented in a plot of reduced stress σ_r versus strain, where the stress is reduced by scaling with respect to the step size:

$$\sigma_r = (\sigma_t - \sigma_0)/(\sigma_\infty - \sigma_0)$$

The results are shown in fig. 5. Obviously the maxima occur at nearly constant values of strain for the different shear rates, not at constant times. Again this suggests a strong convective flow mechanism in the Newtonian region. The first maxima seem to occur at strains of 3, 28 and 60.

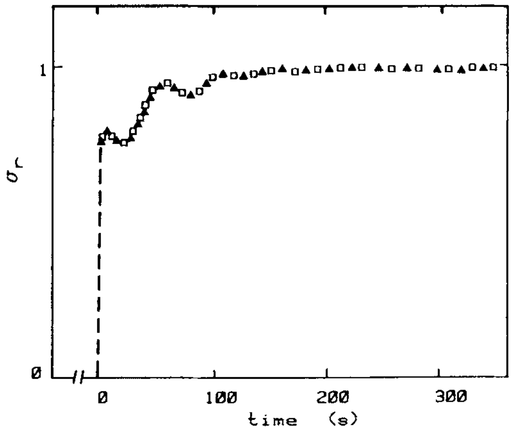

Figure 4. Effect of test geometry on step-up transients ($\dot{\gamma}_i$ = 0.05 s^{-1}; $\dot{\gamma}_f$ = 0.5 s^{-1}; □ : α = 0.02 rad; ▲ : α = 0.04 rad)

A value of order unity seems logical for the first peak if rotational phenomena are involved. From fig. 3 it can be seen that this strain is smaller for short shearing times. The amplitude of the damped oscillation that follows the initial peak, scales roughly with the stress jump, as can be seen from the superposition of the curves in fig. 5. At very low shear rates the amplitude seems to decrease faster than the stress jump (curve at 0.2 s^{-1}). This might suggest that the stress is primarily controlled by strain but that there is an additional, time-controlled damping.

As a next step step-up experiments were performed in which the initial shear rate was systematically varied. The results are shown in fig. 6. It was stated above that the structure is expected to depend on shear rate, even in the Newtonian region. Hence the transients of fig. 6 could differ from those in fig. 5. Indeed, more pronounced changes can be seen in fig. 6. Both the amplitude and the strain values at the stress extrema decrease with increa-

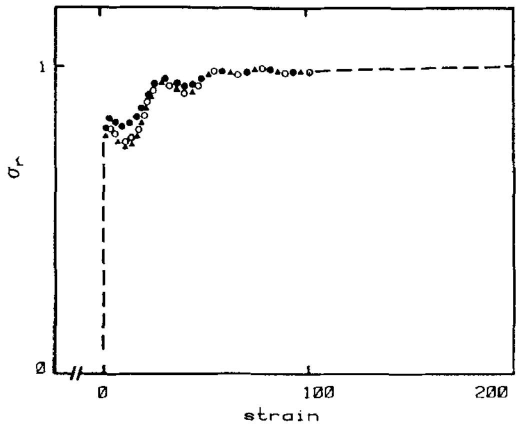

Figure 5. Effect of the final, Newtonian shear rate on the stress transients in step-up experiments ($\dot{\gamma}_i$ = 0.05 s^{-1}; $\dot{\gamma}_f$: ●: 0.2 s^{-1}; ○: 0.5 s^{-1}; ▲: 1 s^{-1})

sing initial stress. There is some similarity with the secondary effect of step size in fig. 5. However, a common explanation must be disregarded. Firstly, the effect of step size on the first stress peak is much more pronounced

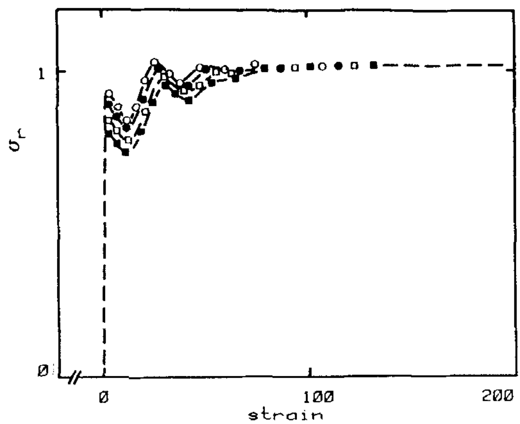

Figure 6. Effect of initial, Newtonian shear rate on the transients in step-up experiments ($\dot{\gamma}_f$ = 1 s^{-1}; $\dot{\gamma}_i$:■: 0.05 s^{-1}; □: 0.1 s^{-1}; ●: 0.3 s^{-1};○ : 0.5 s^{-1})

when the initial shear rate is changed. On the other hand, the subsequent drop in stress towards the first minimum is not affected by this shear rate. If the global transient were represented by an average rising curve on which an oscillation is superposed, the initial shear rate would mainly affect the steepness of this average rising curve.

STEP-DOWN EXPERIMENTS

Stress transients can also be studied under a stepwise decrease in shear rate. With the final shear rate equal to zero this reduces to stress relaxation upon cessation of flow. In fig. 7 such an experiment is compared with a step-down experiment starting from the same initial shear rate. The result for stress relaxation is qualitatively comparable with that for isotropic fluids. On the other hand, the step-down experiments display multiple maxima similar to the step-up transients. The extrema even occur at similar values of the strain in both experiments. If this results

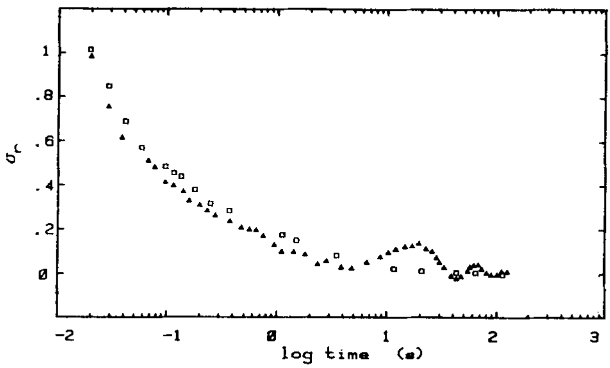

Figure 7. Effect of the final Newtonian shear rate on the stress transients in step-down experiments ($\dot{\gamma}_i$ = 1 s^{-1}; $\dot{\gamma}_f$: ▲: 0.5 s^{-1}; □: 0 s^{-1}, i.e. stress relaxation)

proves generally valid it provides a useful test for rheological constitutive equations of PLCs. The initial drop in stress is identical for the two experiments of fig. 7 and consequently does not depend on the final shear rate. Again this provides a test for model assessment.

REFERENCES

1. K. F. Wissbrun, J. Rheol., 25, 619(1981)
2. F. M. Leslie, in Advances in Liquid Crystals, edited by G. H. Brown (Academic Press, 1979), Vol. 4, pp. 1-81
3. M. Doi, J. Polym. Sci. Polym. Phys. Ed., 19, 229(1981)
4. A.B. Metzner and G.M. Prilutski, J. Rheol., 30, 661 (1986)
5. P. Moldenaers and J. Mewis, J. Rheol., 30, 567(1986)
6. J. Mewis and P. Moldenaers, Chem. Eng. Commun., in press, (1987)
7. S. Onogi and T. Asada, in Rheology, edited by G. Astarita, G. Marrucci and L. Nicolais (Plenum, New York, 1980), Vol. 1, pp. 127-146
8. K. F. Wissbrun, Faraday Disc. Chem. Soc., 79, paper 13 (1985)
9. G. Marrucci, in Advances in Rheology, edited by B. Mena, A. Garcia-Rejon and C. Rangel-Nafaile (Universidad Nacional Autonoma de Mexico, Mexico, 1984), Vol. 1, pp. 441-448
10. P. Moldenaers and J. Mewis, in Proc. World Congress III of Chem. Eng., (Tokyo, 1986), Vol. IV, pp. 546-549
11. G. Kiss and R.S. Porter, J. Polym. Sci.: Polym. Symp., 65, 193(1978)
12. G. Kiss and R.S. Porter, J. Polym. Sci.: Polym. Phys. Ed., 18, 361(1980)
13. P. Moldenaers, Ph. D. thesis, Univ. of Leuven (1987)
14. D.G. Baird, A. Gotsis and G. Viola, Polymer Preprints, 24(2), 292(1983)
15. E.J. Hinch and L.G. Leal, J. Fluid Mech., 51, 753(1973)
16. G. Kiss and R.S. Porter, Mol. Cryst. Liq. Cryst., 60, 267(1980)
17. T. Asada, S. Onogi and H. Yanase, Polym. Eng. Sci., 24, 355(1984)
18. J. Meissner, J. Appl. Polym. Sci., 16, 2877(1972)