

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Velocity profiles in simple shear flow of liquid-crystalline polymers

I. Sardi^a; N. Grizzuti^a; J. B. Riti^b; E. Thoelen^b; L. Vanrusselt^b; P. Navard^b

^a Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, Napoli, Italy ^b Centre de Mise en Forme des Matériaux, URA CNRS 1374, Ecole Nationale Supérieure des Mines de Paris, France

To cite this Article Sardi, I. , Grizzuti, N. , Riti, J. B. , Thoelen, E. , Vanrusselt, L. and Navard, P.(1992) 'Velocity profiles in simple shear flow of liquid-crystalline polymers', *Liquid Crystals*, 12: 4, 593 – 601

To link to this Article: DOI: 10.1080/02678299208029095

URL: <http://dx.doi.org/10.1080/02678299208029095>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Velocity profiles in simple shear flow of liquid-crystalline polymers

by I. SARDI, N. GRIZZUTI

Dipartimento di Ingegneria Chimica,
Università di Napoli Federico II, 80125 Napoli, Italy

J. B. RITI, E. THOELLEN, L. VANRUSSELT and P. NAVARD*

Centre de Mise en Forme des Matériaux, URA CNRS 1374,
Ecole Nationale Supérieure des Mines de Paris, BP 207,
06904, Sophia Antipolis, France

(Received 25 November 1991; accepted 1 March 1992)

The velocity profiles of isotropic and anisotropic solutions of hydroxypropylcellulose in water have been measured by a tracer method. The velocity profile is the usual linear one for steady state experiments and also for transient experiments if a short waiting time (less than 3 hours) is left between loading and the experiment. For long waiting times (more than 12 hours), the profile is S-shaped. This could be due to the establishment of a cholesteric superstructure.

1. Introduction

The velocity profile in simple shear flow is always linear for newtonian or viscoelastic fluids. Recent measurements of displacement and velocity profiles of liquid-crystalline polymers in one or two dimensional geometries [1-3] have shown an intriguing behaviour. While the isotropic solutions showed the usual linear profile, the anisotropic solution of the same polymer had a different behaviour which departs from the classical one. The mechanical and physical reasons of this behaviour were unknown. In order to gain more information on this peculiar and challenging phenomenon, the two laboratories involved in the previously reported papers, namely the University of Naples (UON) in Italy and the CEMEF in France, decided to conduct a joint, more detailed study with similar procedures. In particular, transient experiments were performed at CEMEF. Two different experimental set-ups were used: (i) a rotational instrument in Sophia Antipolis for transient and steady state measurements and (ii) a translating parallel plate-and-plate device at the University of Naples for only transient experiments.

This paper is divided into two parts. First, a description of the equipment and the methods of measurement are given. Velocity profiles obtained for both isotropic and anisotropic solutions of hydroxypropylcellulose in water are presented in the second part.

2. Materials and methods

Aqueous solutions of hydroxypropylcellulose (HPC), $M_w = 100,000$, of 30 and 50 per cent (UON) or 30 and 55 per cent (CEMEF) weight concentration have been

* Author for correspondence.

prepared. The preparation procedure was the same in the two laboratories and was as follows: (i) HPC was dried overnight under vacuum at 80°C. (ii) Distilled water, tracer particles and HPC were mixed at room temperature; the tracer particles were polystyrene spheres of 6–12 μm diameter or glass spheres of 20–30 μm diameter. (iii) Solutions were then centrifuged at 5000 rpm for 5 hours in order to remove air bubbles. The 30 per cent solution is fully isotropic and was used as a reference system with respect to the two more concentrated anisotropic solutions. Although the two phases show different rheological behaviour, the concentration of the isotropic sample was chosen in order to match approximately the viscosity of the anisotropic solutions in the range of shear rate explored [4].

Despite the fact that the equipment at UON and CEMEF are substantially different they are based on the same experimental principles. The material is confined between two transparent high quality fused silica walls, one of which can be moved; this produces a simple shear flow. No special treatment was applied to the glass walls. Micron size tracer particles were dispersed in the polymer sample; their motion during the flow and consequently their velocity can be monitored with a microscope.

The device used at UON consists of two optical glass plates which can be made parallel to within 20 μm over a distance of 10 cm. The gap can be set to any value greater than a few tens of micron. One of the plates can be displaced parallel to its major length (10 cm), with a velocity in the range of 0.01–16 mm s^{-1} . A simple shear flow is then imposed to the sample between the plates. Further details on the apparatus can be found in [5]. It must be noted that both the shear rate and the sample thickness were uniform throughout. The motion of tracer particles (glass spheres of 20 to 30 μm) was tracked by means of a video camera attached to a microscope. The microscope focus can be adjusted micrometrically with 5 μm steps. Only the motion of one particle was followed for the entire duration of the shear flow; in this way, velocity versus time plots for a single particle were obtained. The velocity profile was then derived as a cross-plot of tracer velocities at different depths for a fixed time. Since the plate motion is translational, only a limited deformation of 40 units can be applied. Therefore, this system only permits a study of transient velocity profiles.

The device used at CEMEF is composed of two transparent glass discs fixed to an Instron 3250 rotational rheometer [6]. Both cone-and-plate or plate-and-plate configurations can be used. The rotational motion of the upper cone or plate induces a one dimensional shear flow with unlimited deformations. Therefore, steady state velocity profile measurements can be performed. The visualization of the flow and consequently, the velocity profile measurement was obtained by monitoring the motion of the polystyrene particles by means of a microscope. Two simultaneous measurements were made: (i) the flight time of a tracer between two fixed marks in the field of view of the microscope; (ii) the depth of this tracer between the plates by focusing it with the microscope and by measuring the vertical microscope position with a micrometer (the accuracy is $\pm 5 \mu\text{m}$). Repeated measurements on different tracers at different depths allow the determination of the velocity profile through the gap.

Transient experiments can also be performed with the CEMEF device by using the following procedure: after a tracer has been focused under the microscope and its depth has been measured, the moving plate is rotated backwards by a known amount of angular displacement which determines the value of the deformation before measuring the velocity. The system was kept at rest for a given time T_w in order for the solution to achieve an equilibrium state. Then, the shear flow was started forwards. When the tracer transits under the microscope field of view, its velocity was measured. By

repeating this experiment for different values of the first counter-flow shear deformation, the velocity versus the previous deformation of the polymer can be obtained.

3. Results and discussion

3.1. Steady state experiments

These experiments were performed at CEMEF with the rotating device and the two different geometries were used, cone-and-plate or parallel plates. Measurements were taken after at least 100 shear units after start-up. Velocity values were measured at a distance of 10 mm from the plate centre, in order to avoid boundary effects. The kinematic conditions run as follows: for the cone-and-plate configuration, the gap at the measurement region was about $350\ \mu\text{m}$ and the shear rate $0.3\ \text{s}^{-1}$. For the parallel-plate configuration, the gap was $1000\ \mu\text{m}$ and the shear rate $0.1\ \text{s}^{-1}$. Identical results were obtained for the cone-and-plate or parallel-plate geometries: both isotropic and anisotropic solutions display the usual linear velocity profile. Figure 1 shows the reduced velocity V/V_c profiles (where V_c is the cone velocity) along the depth D . Moreover, neither stagnant layer nor slip were observed, even very close to the walls. All the observed tracers moved at constant speed and no detectable velocity component out of the shear plane was observed.

3.2. Transient experiments

Start-up experiments were performed by both CEMEF and UON using the methods described previously. Moreover, the influence of the waiting time T_w was checked. Different kinematic behaviours were found with T_w ranging from 0 to 24 h.

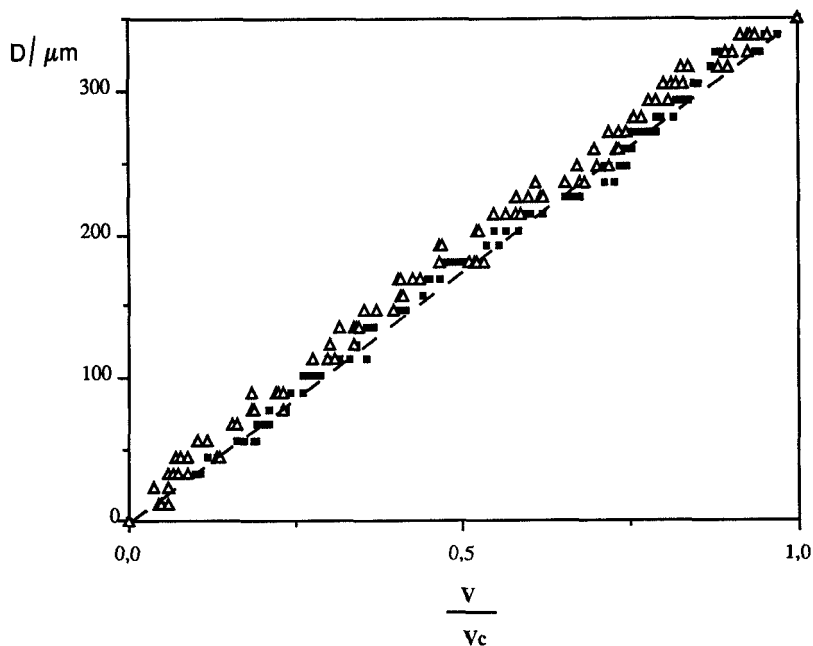


Figure 1. Steady state velocity profiles for HPC isotropic (■) and anisotropic (△) solutions. Cone-and-plate geometry, shear rate of $0.3\ \text{s}^{-1}$ (CEMEF). ---, Theoretical linear velocity profile; V_c , cone velocity.

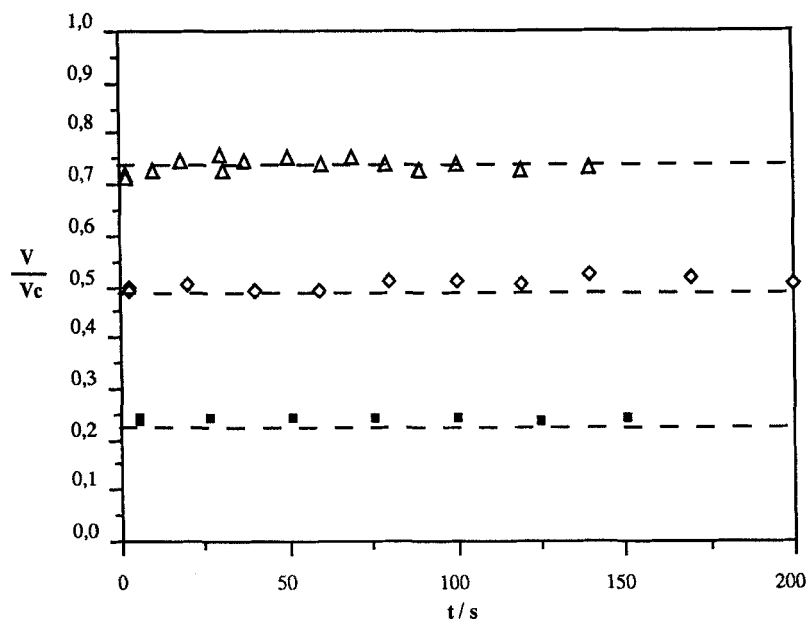


Figure 2. Reduced tracer velocity as a function of time during the start-up shear flow. HPC anisotropic solution 55 wt %. Parallel-plate geometry, gap thickness: 1000 μm , shear rate: 0.1 s^{-1} . Tracer depth from the bottom plate: \blacksquare , 217 μm ; \diamond , 500 μm ; \triangle , 730 μm (CEMEF); ---, theoretical linear velocity profile.

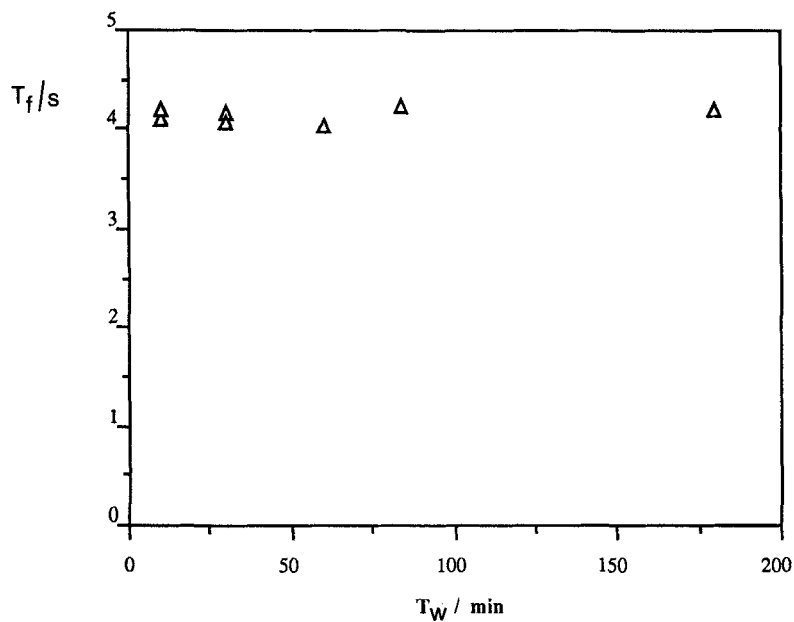


Figure 3. Flight time T_f of the tracers as a function of the waiting time before the start-up. HPC anisotropic solution 55 wt%. Parallel-plate geometry, gap thickness: 1000 μm , shear rate: 0.1 s^{-1} (CEMEF).

3.2.1. Transient experiments at short waiting time ($T_w < 3$ h)

As seen in figure 2, the velocity profile is linear at very short times after start-up, this is for both the isotropic and anisotropic solutions. The kinematic conditions were as follows: parallel plates, gap of 1 mm and shear rates of 0.1 s^{-1} (UON and CEMEF). Figure 3 shows that there is no influence of the waiting time on the flight time T_f with $T_w < 3$ h.

3.2.2. Transient experiments at long waiting time ($T_w > 12$ h)

Although up to three hours of waiting time gives linear transient and steady-state velocity profiles, the situation changes if a longer waiting time is imposed. Very pronounced and reproducible under and overshoots show up during the transient if $T_w > 12$ h. When $3 < T_w < 12$ h, under and overshoots were less pronounced and their values were not reproducible. Figure 4 shows typical velocity versus time plots (gap = $1000 \mu\text{m}$, plate velocity = 0.1 mm s^{-1}) which correspond to depths below and above the layer mid-plane. In the lower half of the layer (see figure 4), the velocity is characterized by an initial, relatively large overshoot. The velocity then evolves towards its steady state value which corresponds to the linear velocity profile already observed with the isotropic solution. At depths above the mid-plane layer, a symmetric behaviour was observed. In this case, the velocity displays a relatively large undershoot, before evolving towards the steady state.

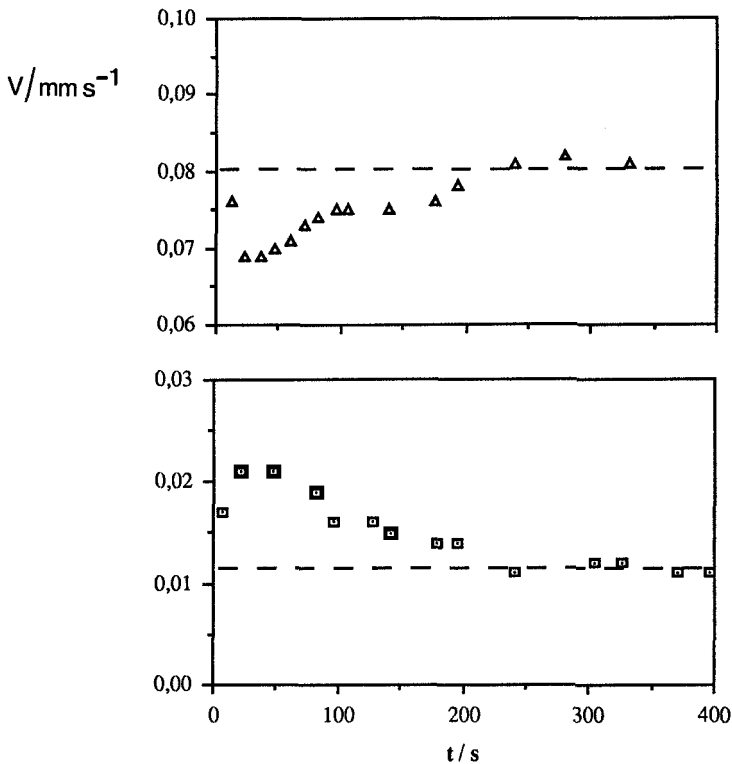


Figure 4. Tracer velocity V as a function of the time during the start-up of the shear flow. HPC anisotropic solution 50 wt%. Gap thickness: $1000 \mu\text{m}$, shear rate: 0.105 s^{-1} . Tracer depth from the bottom plate: \square , $110 \mu\text{m}$; \triangle , $759 \mu\text{m}$ (UON); ---, theoretical linear velocity profile.

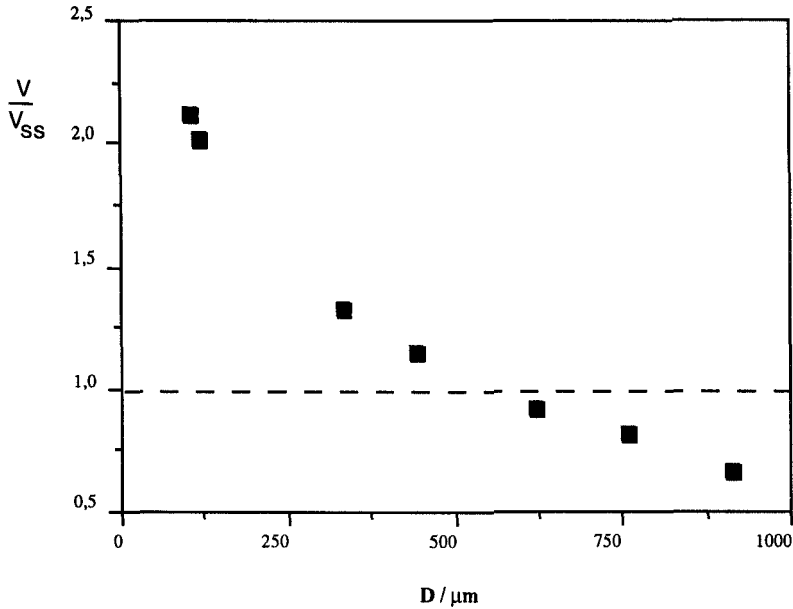


Figure 5. Relative tracer overshoot (lower half of the layer) or undershoot (upper half of the layer) velocity V/V_{ss} as a function of the depth D . HPC anisotropic solution 50 wt% (UON).

All of the undershoots or overshoots take place at approximately the same time after the shear start-up, independent of the position in the layer. This time is about 50 s which, for the shear rate of 0.1 s^{-1} , corresponds to a deformation of five shear units. On the other hand, the amplitude of the velocity extrema is a function of the measured depth. This is shown in figure 5, where the ratio of the velocity extrema (the velocity at the overshoot for the points of the lower half layer or the velocity at the undershoot for the points of the upper half layer) and the corresponding steady state velocity V_{ss} , is plotted as a function of the depth. It can be observed, that this velocity extrema ratio decreases as the depth coordinate approaches the mid-plane position.

The velocity versus time plots can be translated into velocity profiles by cross-plotting the velocity values along the sample thickness at a fixed time. Due to the presence of the velocity extrema, it can be easily predicted that the velocity profile during the transient will not be linear, whereas it will recover the usual linear shape at long shear times. This is confirmed by the results in figure 6, where the velocity profile is plotted at two different times from the start-up: 50 s and 400 s (in fact the data denoted by 400 s represent an average over velocity measurements taken between 400 s and 500 s from the start-up). It is clear that, during the transient, the velocity profile is S-shaped, i.e., the deformation is larger at the walls than in the middle of the gap. At long times, the typical linear profile is recovered. These results are in agreement with the data of Guido *et al.* [1], who measured the total deformation of HPC solutions under shear with the same experimental apparatus. In this work, deformation profiles were obtained by measuring the total displacement of glass spheres dispersed in the material. It was found that for liquid-crystalline solutions the integral deformation profiles deviate considerably from linearity, whereas a linear profile was confirmed for isotropic liquids.

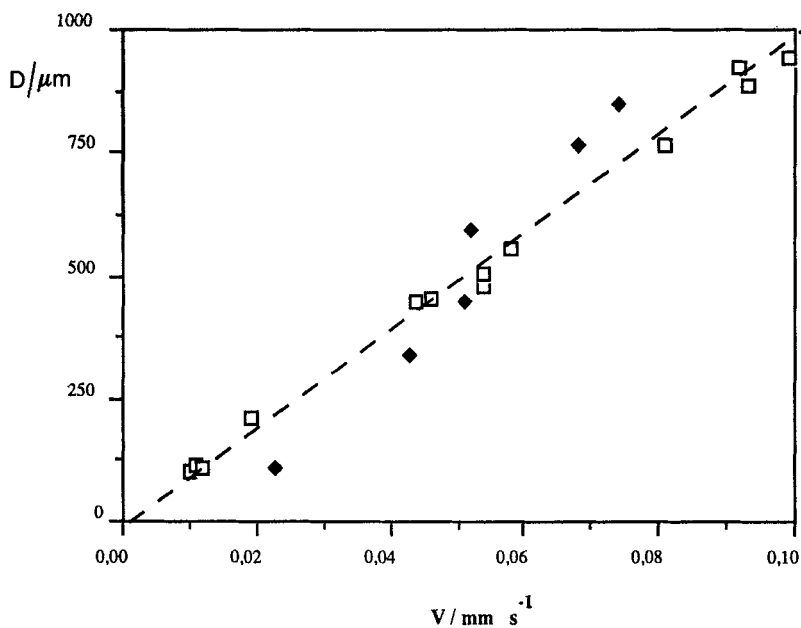


Figure 6. Instantaneous velocity profiles after 50 s (◆) or 400 s (□) from the start-up of a shear flow. HPC anisotropic solution 50 wt%. Shear rate of 0.1 s^{-1} , gap thickness of $1000 \mu\text{m}$ (UON). ---, Theoretical linear velocity profile.

3.3. Discussion

Discrepancies and agreements are found between the previously published results and those reported here. It now seems clear that in steady state shear, there is no out of shear plane component of the velocity and that the tracers move at a constant speed as reported in [2]. In addition, the velocity profile is the usual linear profile. The faint S-shape found in [2] was probably an artifact. We can thus conclude that in steady state, there is a classical behaviour and that all of the various phenomena that may occur in these anisotropic solutions, such as director tumbling, defect motions or wall interactions do not perturb the macroscopic velocity field.

Transient experiments show a very interesting behaviour. When the fluid is sheared with a short rest time (less than 3 hours) before the shear experiment, the profile is linear. Conversely, long waiting times (12 hours and more) give over and undershoots at small deformations which in turn give an S-shaped velocity profile as reported in [1, 3]. This means that the deformation is mainly localized near the walls. This is similar to the so-called plug flow sometimes encountered in capillaries when there is slip at the walls. If there is a resistance to flow by the fluid close to the mid-plane, this should show up by measuring the stress during start-up. This is indeed the case, as can be seen in figure 7 where an overshoot is present only at long waiting times corresponding to the necessary conditions to have the S-shaped velocity profile. The origin of this phenomenon is probably linked to the reformation of a supermolecular structure. Several structures can be observed with HPC in water. First, the solution is cholesteric at rest. Under flow, this cholesteric order is unwound to give a nematic-like state. This is the case when the sample is loaded. Then, depending on the temperature and the concentration, the cholesteric structure begins to reform. Gilli *et al.* [7] have observed a

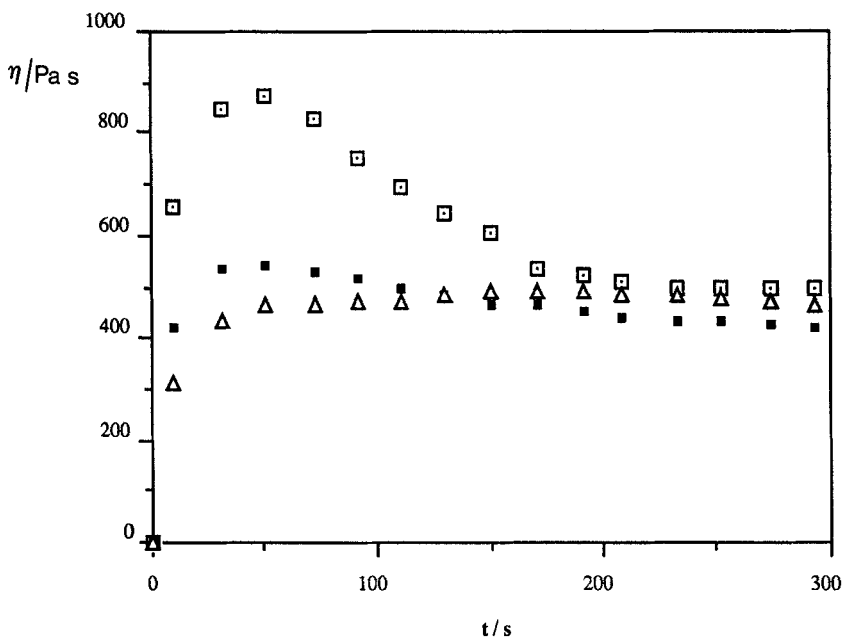


Figure 7. Viscosity η as a function of time during the start-up of a shear flow for different waiting times T_w : \triangle , 10 min; \blacksquare , 2 h; \square , 12 h. HPC anisotropic solution 50 wt%. Shear rate of 0.1 s^{-1} (UON).

variation of the refractive index of HPC solutions, due to the modification of the structure, after shearing. The typical time range for this rewinding is from 3 to 27 hours. Secondly, this cholesteric structure forms a complex texture with time, called the polygonal texture [8]. In [8] Navard and Meeten wrote that such a texture is formed in a few days. We have repeated this experiment and found that this structure begins to appear after 8 to 10 hours, and is fully formed after 36 hours. All of these experiments show that there is the formation of supermolecular structures in a time range corresponding to the waiting time which gives the S-shaped velocity profile. Other evidence is given by Grizzuti *et al.* [9]. They have measured the relative peak stress after the start-up of cone-and-plate rheological experiments as a function of the resting time before the start-up. Thus, they show the influence of the initial structure on the flow. In this case, the measured parameter (the relative peak stress) reaches a steady state value between 3 and 24 hours which also corresponds to the waiting time necessary for us to obtain under or overshoots in the velocity measurements. We believe that it is the formation of such a molecular superstructure which is responsible for the solid-like behaviour during the transient. It needs a certain amount of deformation to destroy it, during which the velocity profile is not linear.

4. Conclusion

The complementary methods used at the UON and at the CEMEF have allowed us to obtain an overview of all of the phenomena that occur from the start-up to the final deformation including the measurement of the influence of the waiting time between loading the sample and starting the flow. This paper gives now a clear picture of the velocity profile of anisotropic hydroxypropylcellulose solutions. Long waiting times

produce a non-linear transient velocity profile, maybe due to the establishment of a cholesteric superstructure. On the other hand, transient flows after short waiting times and steady-state flows give the classical linear velocity profile.

Financial support from the European Economic Community under the contract BREU-0125-C(A) is gratefully acknowledged. Hydroxylpropylcellulose samples were kindly provided by AQUALON, an Hercules Incorporated Company, Wilmington, Delaware, U.S.A. E. Thoelen and L. Vanrusselt thank the EEC for providing them with an Erasmus grant.

References

- [1] GUIDO, S., GRIZZUTI, N., and MARRUCCI, G., 1990, *Liq. Crystals*, **7**, 279.
- [2] PEUVREL, E., and NAVARD, P., 1990, *Macromolecules*, **23**, 4874.
- [3] GRIZZUTI, N., GUIDO, S., NASTRI, V., and MARRUCCI, G., 1991, *Rheol. Acta*, **7**, 71.
- [4] NAVARD, P., 1986, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 435.
- [5] MARRUCCI, G., GRIZZUTI, N., and BUONAURO, A., 1988, *Molec. Crystals liq. Crystals*, **153**, 263.
- [6] ERNST, B., and NAVARD, P., 1989, *Macromolecules*, **22**, 1419.
- [7] GILLI, J. M., LAIVINS, G., and SIXOU, P., 1986, *Liq. Crystals*, **1**, 491.
- [8] MEETEN, G. H., and NAVARD, P., 1988, *J. Polym. Sci. Polym. Phys. Ed*, **26**, 413.
- [9] GRIZZUTI, N., CAVELLA, S., and CICARELLI, P., 1990, *J. Rheol.*, **34**, 1293.