

Martine Mortier  
Paula Moldenaers  
Jan Mewis

## Transient rheological behaviour of poly-para-phenylenetherephthalamide (PpPTA) in sulphuric acid

Received: 14 August 1995  
Accepted: 31 October 1995

**Abstract** Nearly all the available information on the transient flow behaviour of liquid crystalline polymers has been obtained on model systems, especially on solutions of polybenzylglutamate (PBG) and hydroxypropylcellulose (HPC). The assessment of rheological models has been based almost entirely on these model systems. It is not clear how much of the available theoretical and experimental knowledge can be applied to systems of industrial relevance, which have quite different molecular structures. Here, an industrial lyotropic system, poly(p-phenylene-therephthalamide) (PpPTA) in sulphuric acid (TWARON from AKZO), is investigated. Various techniques to study transient behaviour are used, these include measurements of transient shear and normal stresses after sudden changes in shear rate, dynamic

moduli and stress relaxation after cessation of flow and elastic recoil. At all shear rates studied the PpPTA solution is shear thinning, and the first normal stress difference remains positive. For the stress transients a strain scaling applies reasonably well as it did in model systems. The moduli increase with time upon cessation of flow, indicating that the molecules become less oriented in the previous flow direction. This particular behaviour is similar to that of HPC. Transients also resemble more closely those of HPC rather than those of PBG. This latter difference might be attributed to the higher flexibility of HPC and PpPTA chains as compared with PBG molecules.

**Key words** Rheology – poly-para-phenylenetherephthalamide – liquid crystals – transients

M. Mortier · P. Moldenaers  
Prof. J. Mewis (✉)  
Department of Chemical Engineering  
Katholieke Universiteit Leuven  
De Croylaan 46  
3001 Heverlee, Belgium

### Introduction

Liquid crystalline polymers (LCPs) constitute a class of materials that exhibit anisotropic properties due to the orientational ordering of the rigid molecules. These properties make LCPs very suitable for producing ultra-strong fibres and self reinforced moulded parts. The anisotropic characteristics affect the flow behaviour during processing as well as the final properties of the material. Because processing is a fast process, transient phenomena are important. Rheological transients are known to be sensitive

to changes in the microstructure during flow and have been reported to be very complex for anisotropic polymeric materials. Systematic transient rheological data have already been gathered on liquid crystalline model systems such as solutions of polybenzylglutamates (PBG) or hydroxypropylcellulose (HPC). This work has recently been reviewed by Moldenaers (1995). Similar transient measurements are lacking for industrial systems, although some data have been reported on thermotropics (Viola and Baird, 1986; Kalika et al., 1990; Guskey and Winter, 1991; Cocchini et al., 1991; Kim and Han, 1993; Han and Kim, 1994 a, b). Obtaining reliable transient data

on thermotropics is hampered by interference from recrystallization and chemical changes such as hydrolysis and transesterification. This is especially problematical in LCPs because they display time-dependent effects that are much slower than those encountered in regular isotropic polymers.

In the present investigation the transient behaviour of an industrial lyotropic system, poly-para-phenylenetherephthalamide (PpPTA) in sulphuric acid, is studied. Fragmentary data on PpPTA solutions were reported by Viola and Baird (1986), Doppert and Picken (1987), Xu and Qian (1990) and Picken et al. (1991). In this work we will discuss the major aspects of the transient rheological response in a more systematic manner. This includes both transients during flow as well as upon cessation of flow. Moreover, both shear and normal stress transients are studied, the latter are usually lacking in the literature. Most published data on PpPTA solutions have been recorded on solutions with relatively low concentrations, i.e. only up to 15%, well below the industrially relevant concentrations. In addition, the solutions were often prepared by redissolving PpPTA fibres. In the present work we will use fresh PpPTA samples at an industrially relevant concentration of 20%.

By comparing the results on PpPTA with published data on PBG and HPC, we are able to assess the effect of the molecular flexibility on the rheology. PpPTA is known to have a relatively flexible backbone structure with a persistence length of 29 nm (Ying and Chu, 1984). PBG on the other hand has a persistence length of 90 nm in *m*-cresol and approaches the "ideal" liquid crystal (Parthasarathy et al., 1988), whereas HPC in water has a persistence length of only 10 nm (Shtennikova et al., 1990; Brelford and Krigbaum, 1991).

The monodomain theory developed by Doi (1981) is not able to describe, in its original version, the various rheological transients observed in model systems. It is only valid at high shear rates, where the material becomes fully aligned. Recently, agreement between experimental and theoretical stress transients in the high shear, flow-aligning regime has been reported by Maffettone et al. (1994), using both a two-dimensional solution of the Doi theory (Marrucci and Maffettone, 1989), and a three-dimensional constitutive equation (Maffettone, 1992). For both approaches it was, however, necessary to include the viscous contribution to the stress. At lower shear rates problems arise with the closure approximation (Marrucci and Maffettone, 1989; Larson, 1990) and the formation of defects and domains has to be taken into account (Marrucci and Maffettone, 1990b; Larson and Doi, 1991). No fundamental treatment of this complex problem is available yet.

## Materials and methods

Measurements are performed on two batches of poly(*p*-phenylenetherephthalamide) (PpPTA) (TWARON from AKZO) in 99.8% sulphuric acid. The polymer has a molecular weight of 32000 Dalton. The concentrations of the solutions are 19.7% and 19.4% PpPTA by weight. They are solid at ambient temperature and are available as pellets. It is essential to keep the samples in well-sealed bottles in a dry atmosphere during storage to avoid contamination with water. This can easily happen due to the hygroscopic nature of the material. Measurements are performed at 83 °C, at which temperature the solutions are liquid crystalline. The degradation of the polymer becomes problematic at temperatures above 130 °C, which is well below the clearing temperature (Picken, 1989). Temperature is controlled by means of an oven around the sample holder. The cell is preheated with hot air. Once the sample is loaded in the rheometer it becomes necessary to heat with dry nitrogen to avoid degradation of the sample by hydration. After 5 min the sample reaches the measurement temperature. Using this procedure it was possible to perform measurements for 1 h without any serious degradation.

The measurements are performed on a Rheometrics Stress Rheometer 8600 (RSR 8600) and on a Rheometrics Mechanical Spectrometer 800 (RMS 800). The former is a stress-controlled device whereas the latter is strain controlled. The RMS 800 is equipped with a 2000 gcm torque and 2000 g normal-force transducer. A cone and plate geometry ( $r = 12.5$  mm,  $\alpha = 0.1$  rad) has been used on this instrument. The large cone angle has two advantages. First of all, it is possible to measure normal stress transients more accurately with large cone angles than with small ones because the effect of misalignment becomes smaller. In addition, the characteristic response time of the instrument is inversely proportional to the third power of this angle (Tanner, 1975). The RMS 800 has a force-rebalanced system, making it possible to avoid interference from squeezing flow during the normal stress transients. Tests on a polyisobutene solution with a viscosity similar to that of the PpPTA showed that normal stresses could be measured at 0.1 to 0.2 s after a sudden change in shear rate. The shear stress transients are reliable after even shorter times. Large cone angles have the disadvantage of inducing shear fracture, thus limiting the highest attainable shear rate. In addition to the two rotational rheometers, an Instron capillary rheometer is used to obtain viscosity data at high shear rates.

The kinematics studied here include steady state shear flow, flow reversal, sudden increase in shear rate, intermittent shear flow and stress relaxation. The evolution of the moduli upon cessation of flow has also been investigated, as this type of experiment is known to be of special interest when studying liquid crystals (Moldenaers and Mewis, 1986; Grizzuti et al., 1993; Hongladarom et al., 1994).

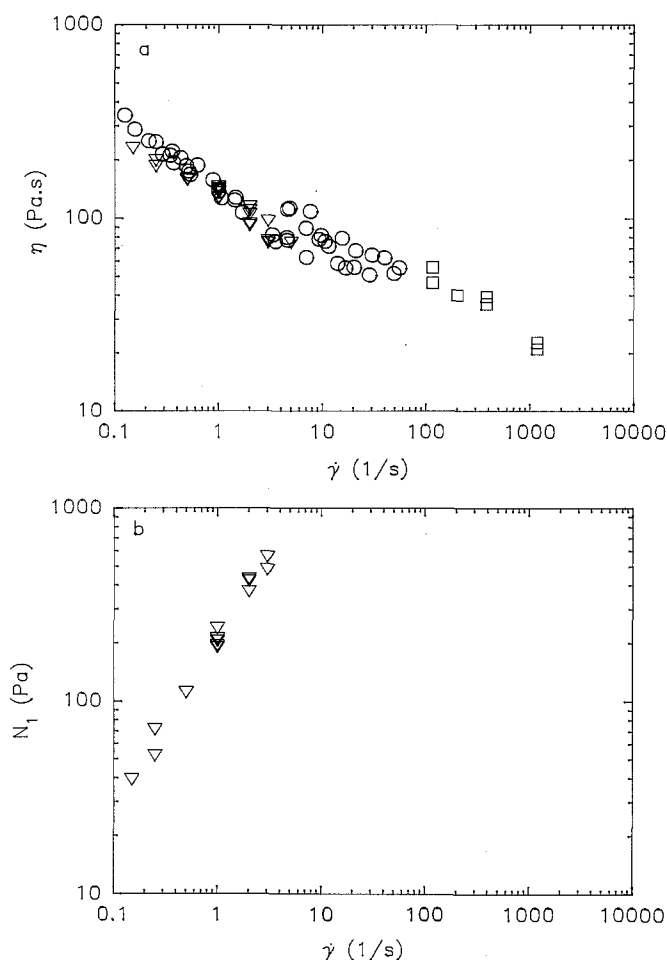
Steady state and recoil experiments are performed on the RSR 8600 (parallel platens,  $r = 12.5$  mm). In all cases the samples are conditioned by shearing until steady state is reached before the flow is suddenly changed and transients measured. For the recoil experiments the 19.7% PpPTA sample is used, while the other data are obtained on the 19.4% sample.

### Steady state shear behaviour

Figure 1 a and b shows the steady state values for both the viscosity  $\eta$  and the first normal stress difference,  $N_1$ , measured with the 19.4% sample. In Fig. 1 a the viscosity data obtained with the 19.7% sample are also included. When using parallel platens the data have been corrected for the shear rate distribution. It is clear from Fig. 1 a that the slight difference in concentration has no major effect on the viscosity data. The material shows shear-thinning

behaviour over the whole range of shear rates investigated here. At low shear rates a slope of  $-0.5$  is obtained on a double logarithmic plot of viscosity versus shear rate. This value has been observed in many LCPs (Wissbrun, 1981; Walker and Wagner, 1994) and is not unexpected from a theoretical point of view (Marrucci and Greco, 1993). At intermediate shear rates the viscosity curve levels off (slope  $-0.2$ ), whereas for high shear rates the slope increases again towards  $-0.4$ . The three regimes might be associated with regions I, II and III in the typical three-region flow curve of Onogi and Asada (1980). The present data agree quite well with those obtained by Doppert and Picken (1987), who used a very similar solution. Xu and Qian (1990) investigated other concentrations and worked at room temperature, hence a comparison with their data is not possible.

The first normal stress values (Fig. 1 b) are all positive and there is no indication of a change in the slope over the limited shear rate range where measurements were possible. It can, of course, not be excluded that negative  $N_1$  values exist at higher shear rates. However, the presence of a region with negative  $N_1$  values is not required by theory, it is actually known to disappear when the concentration of PBG or HPC solutions is increased (Baek et al., 1993, 1994). In the literature only positive values have been reported for  $N_1$  of nematic PpPTA samples (Baird, 1980; Xu and Qian, 1990). The slope of  $N_1$  versus shear rate in a logarithmic plot is 0.9, a value close to unity and in agreement with results reported on other LCPs (Kiss and Porter, 1978; Moldenaers and Mewis, 1986; Ernst and Navard, 1989).

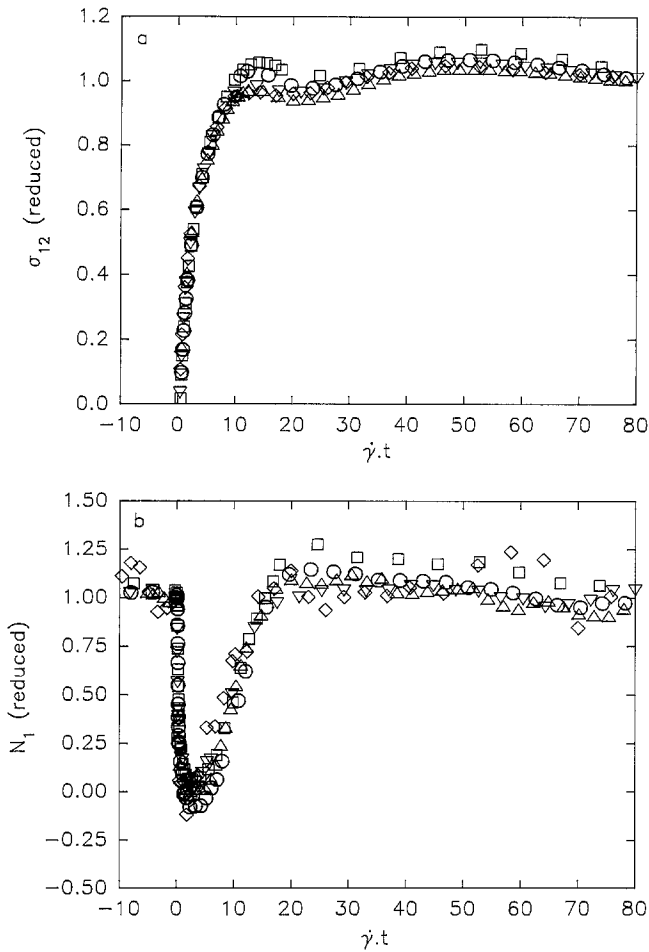


**Fig. 1** Steady state shear data for the PpPTA solution at 356 K (a: viscosity, b: first normal stress difference) (( $\circ$ ) 19.7% (RSR 8600), ( $\nabla$ ) 19.4% (RMS800), ( $\square$ ) 19.7% (Instron))

### Transients during flow

#### Flow reversal

Figure 2 a and b displays the shear and normal stress transients, after reversing the direction of the flow at time zero, for a series of shear rates ranging from 0.25 to  $3 \text{ s}^{-1}$ . The stresses have been divided by their steady state values and are represented as a function of strain. Both the shear and normal stress transients show a strongly damped oscillatory pattern. The curves for the five shear rates superimpose rather well in this representation. For the shear stress transients a maximum, a minimum and finally a broad second maximum can be detected. The initial maximum occurs at about 13 strain units. The normal stresses pass through a minimum at around three strain units before reaching steady state conditions. The minimum in the normal stress transients is slightly negative although no negative steady state normal stresses are measured. Such a negative minimum has also been reported for materials such as a nematic poly-p-phenylenebenzobisthiazole (PBZT) solution, in which case the



**Fig. 2** Reduced stresses after flow reversal for the PpPTA solution at 356 K (a: shear stress, b: first normal stress difference) ( $\dot{\gamma}$ : ( $\diamond$ )  $0.25 \text{ s}^{-1}$ ; ( $\triangle$ )  $0.50 \text{ s}^{-1}$ ; ( $\nabla$ )  $1.00 \text{ s}^{-1}$ ; ( $\circ$ )  $2.00 \text{ s}^{-1}$ ; ( $\square$ )  $3.00 \text{ s}^{-1}$ )

steady state normal stresses were also always positive (Chow et al., 1992).

In the Newtonian part of the tumbling regime the following scaling relation should hold for the transient stresses:

$$\sigma_{red} = \frac{\sigma - \sigma_{in}}{\sigma_{fin} - \sigma_{in}} = f\left(\dot{\gamma}_{fin} \cdot t, \frac{\dot{\gamma}_{fin}}{\dot{\gamma}_{in}}\right) \quad (1)$$

for a stepwise change in shear rate from an initial ( $\dot{\gamma}_{in}$ ) to a final value ( $\dot{\gamma}_{fin}$ ) (Marrucci and Greco, 1993). The scaling of Eq. (1) is valid for a large class of materials without an internal time scale as was shown by Doi and Ohta (1991). In the case of a flow reversal experiment the relation becomes:

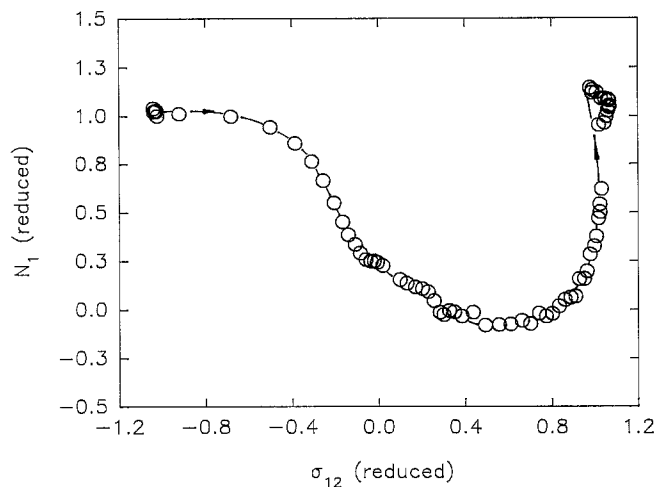
$$\sigma_{red} = f(\dot{\gamma}_{in} \cdot t) \quad (2)$$

It can be concluded from Fig. 2 that the present data obey this scaling quite well. The fact that the curves do not superimpose perfectly is not surprising because the shear rate range under investigation ( $0.25 - 3 \text{ s}^{-1}$ ) does not coincide with a real Newtonian region (see Fig. 1 a) as required for this scaling.

The flow reversal transients for PpPTA are very similar to those obtained in the tumbling regime for PBG and HPC solutions (Moldenaers et al., 1990, 1994). For PBG solutions typically 2 to 3 oscillations could be recorded whereas for HPC the curves are more damped. The response of a 50% HPC solution of  $M_w = 100000$  in water is actually very similar to the behaviour of PpPTA. One can characterize the period of the oscillation by determining the distance between the two maxima in shear stress. For PpPTA (Fig. 2a) this would give a value of 38 strain units. For a 50% HPC solution a value of approximately 36–40 strain units was obtained. For PBG solutions in m-cresol at low concentrations (e.g., 12%) the value is 24 strain units, it increases to approximately 31 strain units at 25% and 38 strain units at 37 wt-% PBG (Walker et al., 1995). The period is rather insensitive to molecular weight.

Plotting the instantaneous values of normal stress versus those of shear stress provides a representation of the coupling between the two stress components and thus a very critical test for assessing models. This kind of plot, called a stress path, was suggested for LCPs by Maffettone and Marrucci (1994). To calculate the stresses in the flow-aligning regime they used the two-dimensional approach of the Doi theory (Marrucci and Maffettone, 1989) and a three-dimensional constitutive equation (Maffettone, 1992). Maffettone et al. (1994) found that, in addition to the “elastic” stress, also the “viscous” stress (i.e. the frictional contribution) had to be included to describe even qualitatively the experimental results. The “viscous” part of the stress results in counterclockwise rotating spirals, as observed experimentally for liquid crystalline PBG solutions in the flow-aligning region. The elastic part of the stress is predicted to give a clockwise rotation for the stress path.

For PpPTA, the stress path for a flow reversal experiment at a shear rate of  $2 \text{ s}^{-1}$  is shown in Fig. 3. Reduced stresses are used, putting the beginning and end points of the stress path at  $(-1, 1)$  and  $(1, 1)$ , respectively in this figure. The main part of the curve evolves counterclockwise, the clockwise evolution of the last part is associated with the very small maximum in the normal stress and might be caused by scatter. There is a striking similarity between the stress paths calculated from the monodomain theory in the flow-aligning regime (Maffettone et al., 1994) and Fig. 3. Yet the present system is expected to be in the tumbling region. Stress paths in the tumbling region for PBG and HPC solutions have been found to rotate also in a counterclockwise fashion (Moldenaers et al., 1994). Recently Larson (to be published) used a mesoscopic



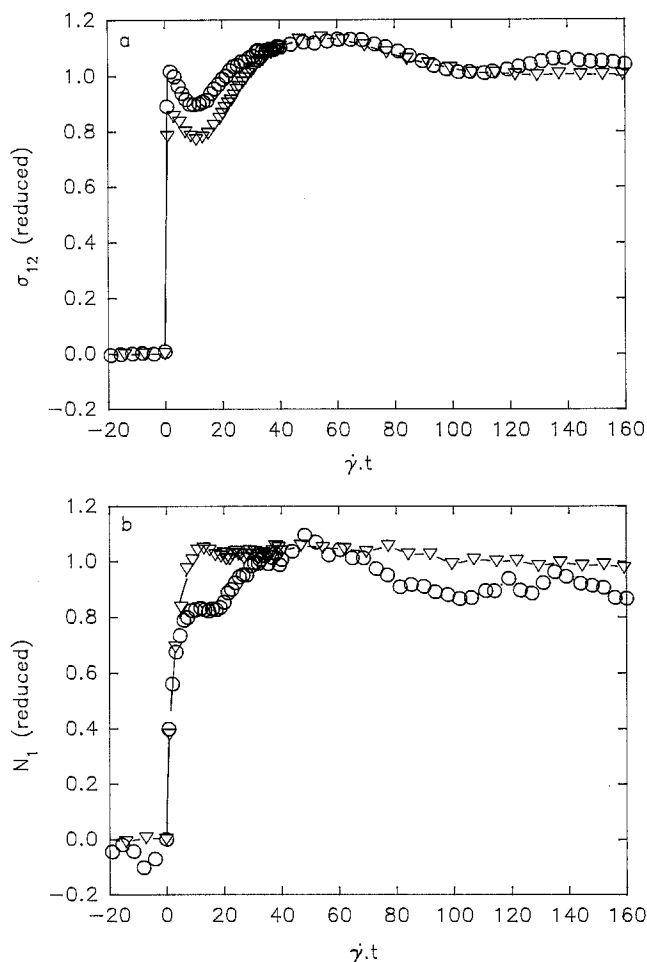
**Fig. 3** Reduced normal stress versus reduced shear stress after flow reversal for the PpPTA sample at 356 K ( $\dot{\gamma} = 2 \text{ s}^{-1}$ )

polydomain model to describe stress paths in the tumbling regime by counterclockwise spirals. This did not require substantial viscous contributions. Contrary to the results of Maffettone et al. (1994), the mesoscopic model is not able to predict such a large time lag between the extrema in shear and normal stress.

#### Stepwise changes in shear rate

In Fig. 4a and b the reduced shear and normal stress transients after a sudden increase in shear rate are presented. Data are shown for two experiments with the same ratio between the initial and final shear rate. The scaling of Eq. (1) still applies for the shear stresses as far as the extrema appear at identical strain values, but the relative heights of the extrema do not superimpose. As in the case of the flow reversal experiments, the absence of a Newtonian region is probably responsible for the lack of a complete scaling. The normal stress clearly oscillates less than the shear stress.

In Fig. 5a and b the stress transients obtained at  $\dot{\gamma} = 2.0 \text{ s}^{-1}$  for a flow reversal and a step-up experiment from  $\dot{\gamma} = 0.5 \text{ s}^{-1}$  are compared. For the shear stress the strain at the minimum stress in the step-up coincides with that of first maximum after flow reversal. At strain units above 20 the phase shift between the two curves seems to disappear. No oscillatory transients can be detected for the normal stress during step-up, whereas only a minimum is observed in flow reversal. A phase shift of  $180^\circ$  between the shear stresses in step-up and flow-reversal experiments was already reported by Moldenaers et al. (1990) for PBG. This shift can be attributed to a large re-orientation of the domains and the average director in flow-reversal experiments as compared to the smaller re-

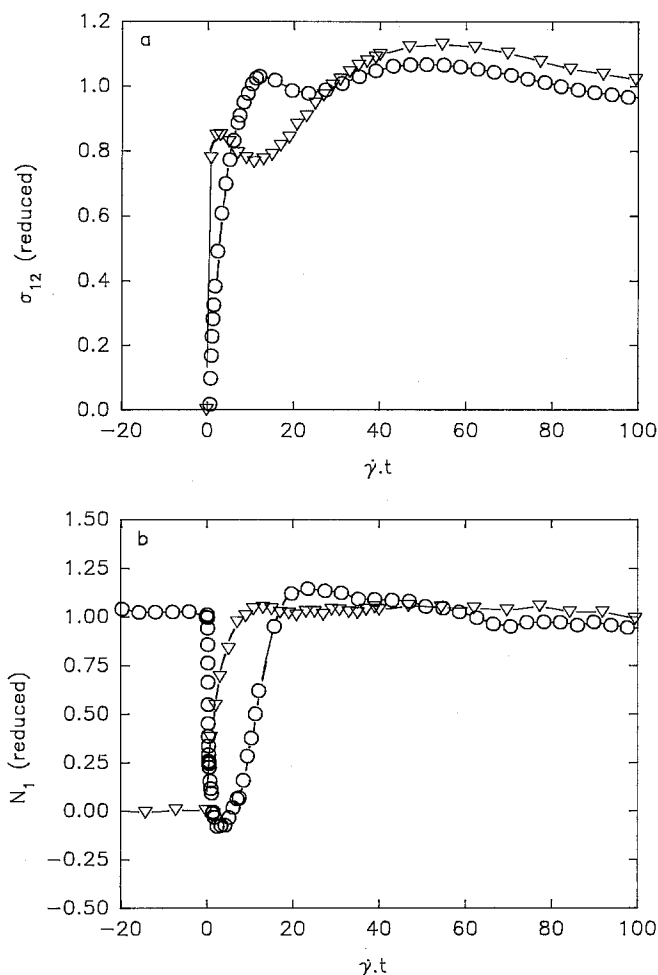


**Fig. 4** Reduced stresses (see Eq. (1)) (a: shear stress, b: first normal stress difference) after stepwise increase in shear rate with a constant shear rate ratio for the PpPTA solution at 356 K (( $\circ$ )  $\dot{\gamma}_{in} = 0.25 \text{ s}^{-1}$ ,  $\dot{\gamma}_{fin} = 1.00 \text{ s}^{-1}$ ; ( $\nabla$ )  $\dot{\gamma}_{in} = 0.50 \text{ s}^{-1}$ ,  $\dot{\gamma}_{fin} = 2.00 \text{ s}^{-1}$ )

orientation after a sudden increase in shear rate. The transients for PpPTA are much more damped than those recorded for PBG solutions. In this sense PpPTA resembles HPC behaviour (Moldenaers et al., 1994). The differences could possibly be explained on the basis of chain stiffness, stiffer molecules giving stronger oscillations. Differences in the polydomain structure, however, could also be responsible for drastic changes in the stress transients (Yang and Shine, 1992).

#### Behaviour upon cessation of flow

After the flow has been arrested the structure still evolves in polymeric liquid crystals. Various rheological experiments can be used to follow this evolution of the flow-induced structure. Here we will use the dynamic moduli,

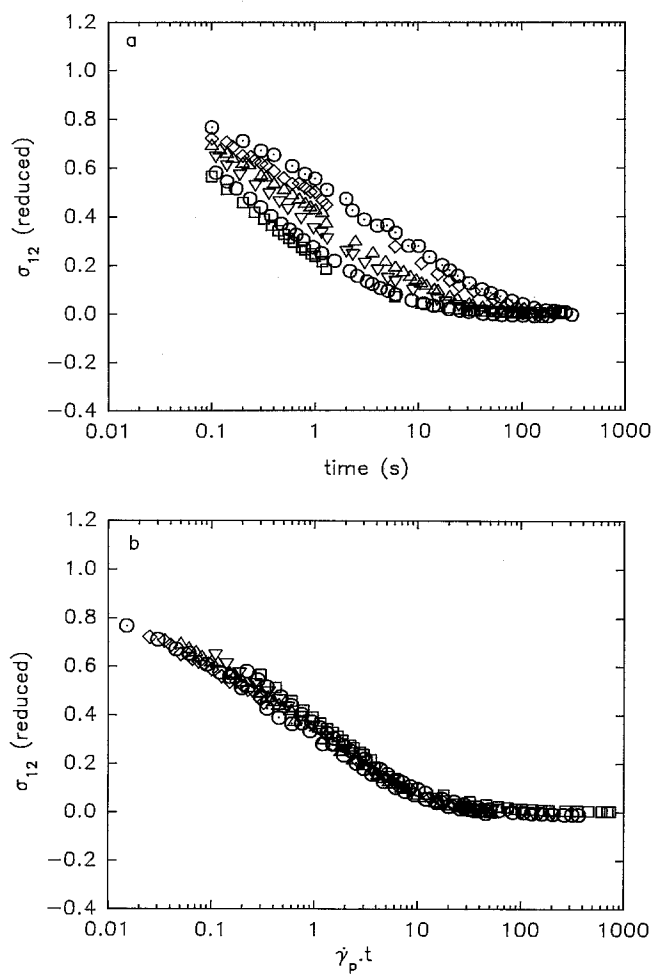


**Fig. 5** Comparison of the reduced stresses after flow reversal ( $\circ$ ) ( $\dot{\gamma} = 2.0 \text{ s}^{-1}$ ) and after stepwise increase in shear rate ( $\nabla$ ) ( $\dot{\gamma}_{in} = 0.5 \text{ s}^{-1}$ ,  $\dot{\gamma}_{fin} = 2.0 \text{ s}^{-1}$ ) for the PpPTA solution at 356 K (a: shear stress; b: first normal stress difference)

recoil and intermittent shear flow to probe the structural evolution after cessation of flow. In addition stress relaxation experiments will be performed for comparison.

#### Stress relaxation

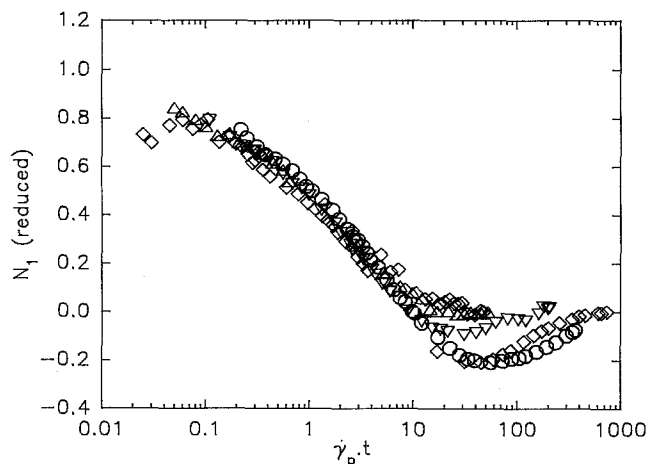
Figure 6a shows the relaxation of the shear stress upon cessation of flow for shear rates between 0.15 and  $3.00 \text{ s}^{-1}$ . In order to compare the curves, the stresses have been divided by their steady state values. The transient stress is reliable for times larger than 0.1 s after stopping the flow. The curves of the reduced shear stress, plotted as a function of time multiplied by the previous shear rate (Fig. 6b), superpose very well; as was the case for other LCPs (Moldenaers and Mewis, 1990). This scaling should hold in the Newtonian region but apparently re-



**Fig. 6** Reduced shear stress after stopping the shear flow for the PpPTA solution at 356 K (a: as a function of time, b: as a function of time multiplied by the previous shear rate) ( $\odot$ )  $0.15 \text{ s}^{-1}$ ; ( $\diamond$ )  $0.25 \text{ s}^{-1}$ ; ( $\triangle$ )  $0.50 \text{ s}^{-1}$ ; ( $\nabla$ )  $1.00 \text{ s}^{-1}$ ; ( $\circ$ )  $2.00 \text{ s}^{-1}$ ; ( $\square$ )  $3.00 \text{ s}^{-1}$ )

mains approximately valid over a wider range of conditions. Especially at the lowest shear rates it can be seen that an intermediate plateau exists in the relaxation curves. The height of this plateau reflects the portion of the stress that does not relax rapidly and hence represents the textural contribution to the stress. The level of the plateau is around 80% of the initial stress for the PpPTA solution (Fig. 6b). This value is around 90% for a 50% HPC solution in water and 30 to 40% for a 12% PBLG solution in m-cresol.

The major part of the relaxation of the first normal stress difference obeys the same scaling as the shear stress but the detailed shape of the curves is more complex (Fig. 7). At high shear rates a negative undershoot appears, which has also been reported by Threefoot (1991) for measurements on a HPC solution using a similar device. Tests performed here with the same geometry on



**Fig. 7** Reduced normal stresses after stopping the shear flow for the PpPTA solution at 356 K as a function of time multiplied by the previous shear rate (symbols as in Fig. 6)

a polyisobutene solution showed no undershoot for the normal stress relaxation with the same geometry at such long time scales. Tool inertia could cause damped oscillatory transients, including an undershoot for the normal stresses, especially for less viscous samples. This phenomenon, however, occurs at shorter times than that of the negative  $N_1$  transients in Fig. 7 and does not scale with  $\dot{\gamma} \cdot t$ .

When comparing the relaxation of the shear and normal stress in Figs. 6b and 7, it can be seen that the quasi-instantaneous drop of the stress amounts to 20% for both. In addition, they both reach a zero stress level after approximately 20 units of  $\dot{\gamma}_p \cdot t$ . At intermediate times the shear stress relaxes somewhat faster than the normal stress. The undershoots in  $N_1$  at longer times do not have a counterpart in the shear stress. There are hardly any relaxation data of the normal stress available in the literature to be compared with the present results. Only Han and Kim (1994a) mentioned very long relaxation times for the normal stress in a thermotropic material. According to the Doi theory, assuming a monodomain structure and using only the “elastic” stress, one expects only a very rapid relaxation. Hence the domain or defect structure is expected to be important in the present stress relaxation, this agrees with the  $\dot{\gamma} \cdot t$  scaling.

#### Evolution of the dynamic moduli after cessation of flow

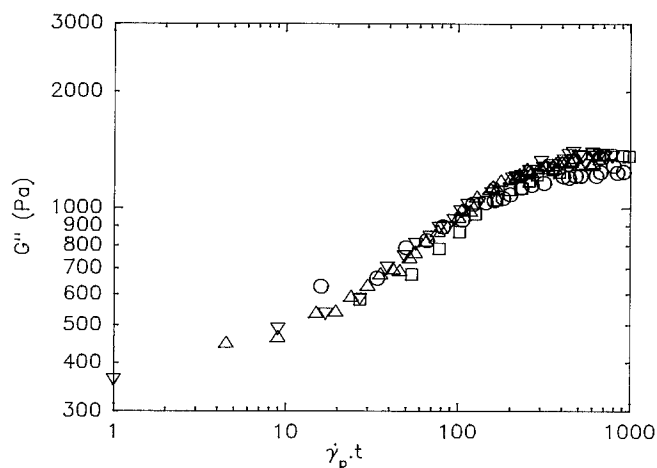
It has been demonstrated by several authors that the time necessary for the structure to evolve to its equilibrium state is much longer than the time required for the shear stress to relax (Asada et al., 1984; Hashimoto et al., 1986;

Moldenaers and Mewis, 1986). It is possible to probe the relaxation of the flow-induced structure after stopping the flow by following the subsequent evolution of the moduli. In this type of experiment the sample is first sheared until steady state conditions are reached. After the flow is stopped, small oscillatory deformations are applied to measure the storage modulus  $G'$  and the loss modulus  $G''$  as a function of time. In this manner the change in structure can be followed in a nondestructive fashion as long as the amplitude of the oscillation is small enough (Moldenaers and Mewis, 1986). For the PpPTA system under investigation an amplitude of 1%, at a frequency of 10 rad/s, is found to be sufficiently small to be in the linear response regime of the material. The evolution of the moduli is observed not to depend on the frequency, as was already reported for other lyotropic systems (Moldenaers and Mewis, 1986; Grizzuti et al., 1993).

Before considering the effect of the previous shear rate on the dynamic response of the sample, the reproducibility of such measurements was verified. The behaviour of the dynamic moduli upon cessation of flow for the PpPTA sample was measured for three samples from the same batch with a preshear rate of  $1 \text{ s}^{-1}$ . Differences up to about 15% were obtained. Due to the ageing of the material it was not possible to measure the evolution of the moduli upon cessation of flow for more than three different shear rates with a single sample. As an experimental procedure the response after a preshear rate of  $\dot{\gamma}_p = 2 \text{ s}^{-1}$  was measured for each sample and used as a reference to determine the effect of shear history. The results for the storage and loss moduli were observed to be similar but the data of  $G'$  scatter more than those of  $G''$ . Here, only data for  $G''$  are reported.

Figure 8 displays the results of the evolution of  $G''$  as measured for four different preshear rates. It is clear from this figure that multiplying time with the previous shear rate essentially superimposes the curves for different preshear rates, in agreement with the stress relaxation data. Over the shear rate range covered here, the material seems always to evolve to the same equilibrium structure, even with the shear rates being in region I. The defect structure in region I could in principle impede the evolution to equilibrium as can be seen in HPC solutions (Grizzuti et al., 1993; Walker and Wagner, 1994). In PpPTA this defect structure does not seem to interfere with structure development at rest, at least in the shear rate range under investigation.

As for HPC (Grizzuti et al., 1993) the moduli increase with time after stopping the shear flow, however the kinetics are faster for the PpPTA solution. For thermotropic systems the moduli also increase upon cessation of flow (Cocchini et al., 1991; Han and Kim, 1994a), while for lyotropic systems this is not always the case. Measurements on polybenzylglutamates indicate either a monotonic decrease (Moldenaers and Mewis, 1986) or an in-

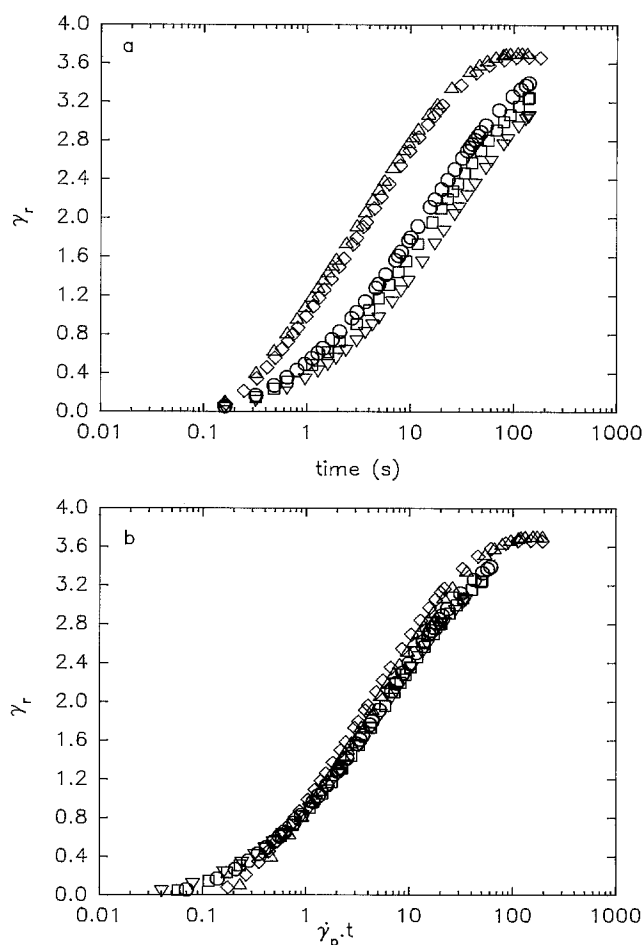


**Fig. 8** Evolution of the loss modulus  $G''$  upon cessation of flow for the PpPTA solution at 356 K as a function of time multiplied by the previous shear rate ( $\omega = 10$  rad/s,  $\gamma = 1\%$ ,  $\dot{\gamma} = (\triangle) 0.5$  s $^{-1}$ ; ( $\nabla$ ) 1.0 s $^{-1}$ ; ( $\circ$ ) 2.0 s $^{-1}$ ; ( $\square$ ) 3.0 s $^{-1}$ )

crease followed by a decrease (Moldenaers et al., 1990), depending on the concentration. A similar evolution has recently been reported for concentrated HPC solutions at low temperatures (Grizzuti, 1995). Rheo-optical measurements confirm that the decrease in moduli after cessation of flow in PBG corresponds to an evolution towards a higher orientation in the direction of the preceding flow. This is illustrated by the increase in birefringence upon cessation of flow for PBG solutions (Hongladarom and Burghardt, 1993). The increase in moduli for HPC corresponds to a decrease in birefringence, although the relation between moduli and birefringence is less pronounced than in PBGs (Hongladarom et al., 1994). The evolution of the moduli for PpPTA indicates that the flow-induced orientation is lost after stopping the flow. This is in agreement with orientation relaxation measurements, using x-ray scattering, by Picken et al. (1991). The time constant of the latter experiments is consistent with that of the moduli in Fig. 8.

### Recoil

Elastic recovery experiments were performed on the RSR 8600 using a parallel plate geometry. The samples were presheared until a steady state was reached. Subsequently, the stress was removed and the recoil was recorded as a function of time for initial stress levels between 70 and 200 Pa, corresponding to shear rates between 0.25 and 1.43 s $^{-1}$  at the rim of the platens. Figure 9a shows the recoil as recorded for five previous stress levels. When the recoverable strain is plotted versus time multiplied by the previous shear rate at the edge of the geometry, the curves superimpose again (Fig. 9b). Because of the



**Fig. 9** Recoverable strain for the PpPTA solution at 356 K (a: as a function of time, b: as a function of time multiplied by the previous steady state shear rate) ( $\sigma = (\nabla) 70$  Pa, ( $\square$ ) 90 Pa, ( $\circ$ ) 100 Pa, ( $\diamond$ ) 160 Pa, ( $\triangle$ ) 200 Pa)

specific nature of this scaling, it also holds for curves obtained with a parallel plate geometry in which the shear rate is not constant. The final value of the recoverable strain is about 3.6 and seems to be independent of the previous stress level. This value is close to the equilibrium values recorded for HPC and PBLG (Larson and Mead, 1989) and for PpPTA (Picken et al., 1991). Recoil measurements on a thermotropic copolyester provided a final value of 4.0 (Mewis, 1993). A slow, large recoil of order 4 seems to be quite general for liquid crystalline polymers, at least at relatively low shear rates where tumbling occurs.

Not surprisingly, the monodomain theory does not describe the experimental results well (Larson and Mead, 1989). A mechanism of "unwinding" is required which can be provided by a coupling between domains through Frank elasticity. Using a mesoscopic model, Larson and Doi (1991) could scale the elastic recovery properly. In such models the domain coupling is also responsible for



the damping of the oscillatory stress transients during flow.

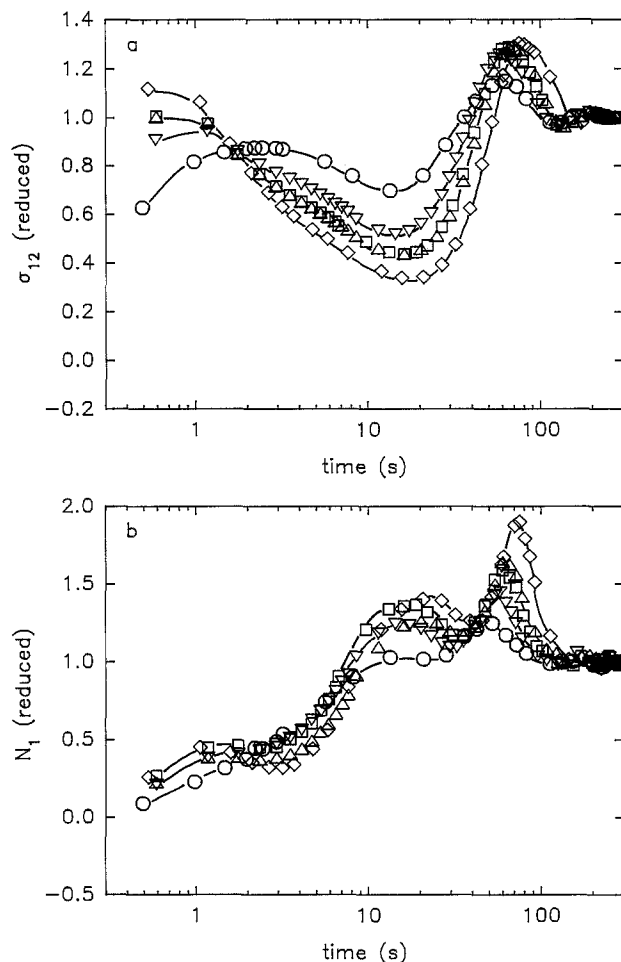
#### Intermittent flow behaviour

A start-up experiment after a given rest period can also be used to probe the evolution of the structure, even after long rest periods when stress relaxation or recoil is completed. In contrast to measuring the dynamic moduli, intermittent flow is a destructive technique which however provides some additional information. In the present experiments the sample was presheared at a shear rate of  $1 \text{ s}^{-1}$  until a steady state was reached. Subsequently, the sample was allowed to relax over different rest periods, after which the stress transients were measured during start-up at the same shear rate. The measurements were performed with a single sample, but in random order of rest period to avoid interference of the degradation of the sample with the structural changes after stopping the flow. Figures 10a and b shows the shear and normal stress transients for rest periods varying between 50 and 600 s. This covers the time period over which the dynamic moduli change after stopping the flow at the same shear rate (Fig. 8). Picken et al. (1991) also mention that a rest period of 10 min suffices to obtain transients that are independent of the rest time on a 20% PpPTA solution after shearing at  $1 \text{ s}^{-1}$ .

The shear stresses in Fig. 10a show a very sharp initial peak which increases with the rest time. The curves for both shear and normal stress show an oscillatory part, the period and amplitude of which increase with rest time. After 200 s of rest the normal stress transients develop a shoulder around 2 strain units, i.e., in the strain range where the shear stress reaches its first maximum. Eventually a shallow minimum develops after this shoulder. The similarity between the results obtained after 200 and 219 s of rest illustrates the reproducibility of the transients.

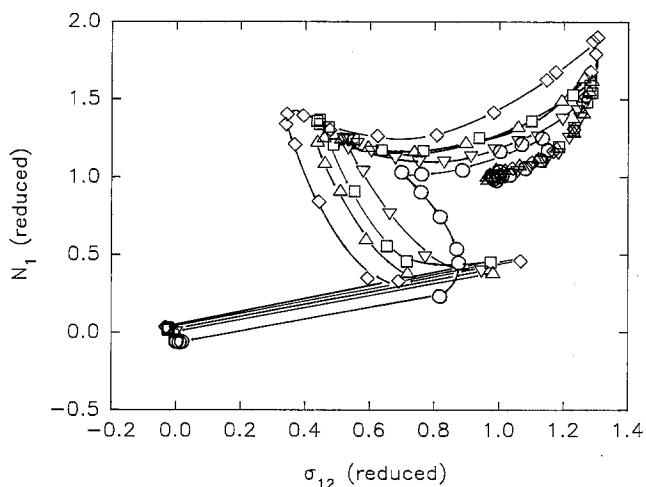
The general shape of the shear stress transients agrees with earlier results on other LCPs, the main difference being the damping of the oscillatory part. In PBG solutions more pronounced oscillations are seen (Moldenaers et al., 1991), while the damping in PpPTA is comparable to that in HPC solutions and in thermotropic materials (Viola and Baird, 1986; Cochini et al., 1991; Guskey and Winter, 1991; Han and Kim, 1994a). This seems to be consistently the case for several kinds of transients and possibly can be attributed to differences in molecular rigidity or to domain interactions.

The initial evolution of the normal stresses during start-up after rest differs strongly in the various LCPs.  $N_1$  either starts to increase immediately or it can first pass through a (negative) minimum. An instantaneous increase of  $N_1$  has been observed here for the PpPTA solution under investigation and has been reported also for



**Fig. 10** Reduced stresses (a: shear stress, b: first normal stress difference) for various rest times in intermittent flow experiments for the PpPTA solution at 356 K ( $\dot{\gamma} = 1.0 \text{ s}^{-1}$ ). ( $\circ$ ) 50 s; ( $\nabla$ ) 100 s; ( $\square$ ) 200 s; ( $\triangle$ ) 219 s; ( $\diamond$ ) 600 s

anisotropic HPC solutions (Mortier, 1995). With PBG solutions the situation is more complex as both types of initial responses have been recorded. The occurrence of an initial (negative) minimum is however the most common. The cases where an immediate increase is recorded are limited to highly concentrated PBG solutions after short rest periods. When comparing these start-up transients with the evolution of the dynamic moduli upon cessation of flow it turns out that the immediate increase in  $N_1$  is related to structures that cause the moduli to increase with time (Moldenaers et al., 1990). The initial minimum in the  $N_1$  curves is related to structures that cause the dynamic moduli to decrease with time. This decrease of the moduli is explained by an increasing orientation of the material in the shear flow direction. Strongly negative  $N_1$  transients upon inception of flow have been observed in poly(n-hexylisocyanate) which was electricaly ordered in the gradient direction (Yang and Shine,



**Fig. 11** Reduced normal stresses versus reduced shear stresses for various rest times in intermittent flow experiments for a PpPTA solution at 356 K ( $\dot{\gamma} = 1 \text{ s}^{-1}$ ) (symbols as in Fig. 10)

1993). These observations are in agreement with the predictions of either the continuum mechanics or molecular monodomain theories (Marrucci and Maffettone, 1990a; Yang and Shine, 1993). Strong orientation in either the flow or the gradient direction thus seems to lead to an initial minimum in  $N_1$ . Intermediate orientations or a distribution of the director orientations would then reduce or eliminate this phenomenon.

The stress paths for the intermittent experiments after different rest periods are shown in Fig. 11. These stress paths do not change their intrinsic shape with rest time. Compared with other transient experiments, such as flow reversal, the stress paths for start-up in intermittent shear flow depend strongly on the materials used. It is remarkable that samples of HPC or PpPTA display a simpler evolution (i.e. without intrinsic shape changes) in intermittent flow than PBG (Mortier, 1995). In the case of PBG solutions the shape of the stress paths changes dramatically with rest time. It must be concluded that the change in structure in PBG is more complex than in HPC or PpPTA. This seems to be in agreement with microscopic observations (Vermant et al., 1994) which indicate more involved changes in the band structure in PBG than in the other two materials.

## Conclusions

The steady and transient rheological behaviour of an industrial lyotropic system, PpPTA in sulphuric acid, has been investigated. Three regions can be distinguished in the viscosity curve with the viscosity not being totally constant in the central region. The steady state values of the normal stress are always positive but can only be measured at relatively small shear rates; the flow-aligning regime could not be reached. During transient experiments both the shear and first normal stress difference have been measured. Flow reversal and step-up in shear rate have been examined. The corresponding stresses scale with time multiplied by shear rate. The oscillatory transients are more damped than those in PBG and resemble those for HPC. This might be explained by the higher rigidity of the PBG molecules. Structural changes after stopping the flow have also been followed by measuring stress relaxation, intermittent flow, elastic recoil and the evolution of the moduli. The time evolutions of the moduli, relaxation and recoil all scale with the previous shear rate. The moduli increase in time, as in HPC but unlike those in PBG, indicating a gradual decrease of orientation in the flow direction. The scaling with shear rate is characteristic for LCPs in a Newtonian region with director tumbling. The large value of the equilibrium recoil ( $\pm 4$ ) points in the same direction. This investigation proves that most of the results on transient rheological and structural behaviour for model systems can also be applied to this industrial system. Some differences in structure exist between the various materials and are picked up in rheological measurements. These include the time scales for structural changes, the amount of quasi-instantaneous relaxation and the detailed shape of the stress transients. Overall, PpPTA displays a somewhat intermediate behaviour between PBG and HPC. Dynamic stress paths are very sensitive to subtle changes in structure, and although their shape can be modeled, the detailed structural descriptions that are required to fit the curves are still lacking.

**Acknowledgements** Partial financial support for this project, by the European BRITE/EURAM programme (contract BREU 0125) and by FKFO (Nationaal Fonds voor Wetenschappelijk Onderzoek), is gratefully acknowledged. The samples have been provided by AKZO-NOBEL International Research, Arnhem, The Netherlands. The authors wish to thank Dr. S. Picken for stimulating discussions.

## References

- Asada T, Onogi S, Yanase H (1984) A rheo-optical study on the reformation of structure in racemic poly( $\gamma$ -benzyl glutamate) liquid crystals. *Polym Eng Sci* 24:355–360
- Baek SG, Magda JJ, Larson RG (1993) Rheological differences among liquid-crystalline polymers. I. The first and second normal stress differences of PBG solutions. *J Rheol* 37:1201–1223
- Baek SG, Magda JJ, Cementwala S (1994) Normal stress differences in liquid crystalline hydroxypropylcellulose. *J Rheol* 38:1473–1503
- Baird DG (1980) Rheological properties of liquid crystalline solutions of poly-*p*-phenyleneterephthalamide in sulphuric acid. *J Rheol* 24:465–482
- Brelsford GL, Krigbaum WR (1991) Experimental evaluation of the persistence length for mesogenic polymers. In: Ciferri A (ed) *Liquid crystallinity in polymers*. VCH Publishers Inc. New York, p 61–94
- Chow AW, Hamlin RD, Ylitalo CM (1992) Transient shear response and flow-induced microstructure of isotropic and nematic rigid-rod poly(*p*-phenylenebenzobisthiazole) solutions. *Macromolecules* 25:7135–7144
- Cocchini F, Nobile MR, Acierno D (1991) Transient and steady rheological behavior of the thermotropic liquid crystal copolymer 72/27 HBA/NA. *J Rheol* 35:1171–1189
- Doi M (1981) Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. *J Polym Sci* 19:229–243
- Doi M, Ohta T (1991) Dynamics and rheology of complex interfaces. I. *J Chem Phys* 95:1242–1248
- Doppert HL, Picken SJ (1987) Rheological properties of aramid solutions: transient flow and rheo-optical measurements. *Mol Cryst Liq Cryst* 153:109–116
- Ernst B, Navard P (1989) Band textures in mesomorphic (hydroxypropyl)cellulose solutions. *Macromolecules* 22:1419–1422
- Grizzuti N, Moldenaers P, Mortier M, Mewis J (1993) On the time-dependency of the flow-induced dynamic moduli of a liquid crystalline hydroxypropylcellulose solution. *Rheol Acta* 32:218–226
- Grizzuti N (1995) Investigation of the phase behaviour of lyotropic hydroxypropylcellulose solutions by oscillatory shear rheology. Presented at the 67th Annual Meeting of the Society of Rheology, Sacramento
- Guskey SM, Winter HH (1991) Transient shear behavior of a thermotropic liquid crystalline polymer in the nematic state. *J Rheol* 35:1191–1207
- Han CD, Kim SS (1994a) Transient rheological behavior of a thermotropic liquid-crystalline polymer. II Intermittent shear flow and evolution of the dynamic moduli after cessation of shear flow. *J Rheol* 38:13–30
- Han CD, Kim SS (1994b) Transient rheological behavior of a thermotropic liquid-crystalline polymer. II. Step strain experiment and shear stress relaxation modulus. *J Rheol* 38:31–40
- Hashimoto T, Takebe T, Suehiro S (1986) Apparatus to measure small-angle light scattering profiles of polymers under shear flow. *Polym J* 18:123–130
- Hongladarom K, Burghardt WR (1993) Molecular alignment of polymer liquid crystals in shear flows. 2. Transient flow behavior in poly(benzyl glutamate) solutions. *Macromolecules* 26:785–794
- Hongladarom K, Secakusuma V, Burghardt WR (1994) Relation between molecular orientation and rheology in lyotropic hydroxypropylcellulose solutions. *J Rheol* 38:1505–1523
- Kalika DS, Giles DW, Denn MM (1990) Shear and time-dependent rheology of a fully nematic thermotropic liquid crystalline copolymer. *J Rheol* 34:139–154
- Kim SS, Han CD (1993) Transient rheological behavior of a thermotropic liquid-crystalline polymer. I. Start-up of shear flow. *J Rheol* 37:847–866
- Kiss G, Porter RS (1978) Rheology of concentrated solutions of poly( $\gamma$ -benzylglutamate). *J Polym Sci: Polym Symp* 65: 193–211
- Larson RG, Mead DW (1989) Time and shear-rate scaling laws for liquid crystal polymers. *J Rheol* 33:1251–1281
- Larson RG (1990) Arrested tumbling in shearing flows of liquid crystal polymers. *Macromolecules* 23:3983–3992
- Larson RG, Doi M (1991) Mesoscopic domain theory for textured liquid crystalline polymers. *J Rheol* 35:539–563
- Larson RG (to be published 1995) On the relative magnitudes of viscous, elastic and texture stresses in liquid crystalline PBG solutions
- Maffettone PL (1992) A constitutive equation for monodomains of nematic polymers. *J Non-Newtonian Fluid Mech* 45:339–354
- Maffettone PL, Marrucci G (1994) Analysis of the rheological transient response of nematic polymers at high shear rates. In: Gallegos C, Guerrero A, Munoz J, Berjano M (eds) *Proceedings of the fourth European Rheology Conference, Sevilla* p 317–319
- Maffettone PL, Marrucci G, Mortier M, Moldenaers P, Mewis J (1994) Dynamic characterization of liquid crystalline polymers under flow-aligning shear conditions. *J Chem Phys* 100:7736–7743
- Marrucci G, Maffettone PL (1989) Description of the liquid-crystalline phase of rodlike polymers at high shear rates. *Macromolecules* 22:4076–4082
- Marrucci G, Maffettone PL (1990a) Nematic phase of rodlike polymers. I. Prediction of transient behaviour at high shear rates. *J Rheol* 34:1217–1230
- Marrucci G, Maffettone PL (1990b) Nematic phase of rodlike polymers. II. Polydomain predictions in the tumbling regime. *J Rheol* 34:1231–1244
- Marrucci G, Greco F (1993) Flow behavior of liquid crystalline polymers. In: Prigogine I, Rice S (eds) *Advances in Chemical Physics* Wiley Publishers New York Vol 86:331–404
- Mewis J (1993) Flow and flow-induced structure during the processing of liquid crystalline polymers. BREU-125 Project Nr BE-3137-89 Report Sept 1993
- Moldenaers P, Mewis J (1986) Transient behaviour of liquid crystalline solutions of poly(benzylglutamate). *J Rheol* 30:567–584
- Moldenaers P, Mewis J (1990) Relaxational phenomena and anisotropy in lyotropic polymeric liquid crystals. *J Non-Newtonian Fluid Mech* 34:359–374
- Moldenaers P, Yanase H, Mewis J (1990) Effect of shear history on the rheological behavior of lyotropic liquid crystals. *ACS Symposium Series* 435:370–380
- Moldenaers P, Yanase H, Mewis J (1991) Flow-induced anisotropy and its decay in polymeric liquid crystals. *J Rheol* 35:1681–1699
- Moldenaers P, Mortier M, Mewis J (1994) Transient normal stresses in lyotropic liquid crystalline polymers. *Chem Eng Sci* 5:699–707
- Moldenaers P (1995) Time-dependent effects in lyotropic systems. In: Acierno D, Collyer AA (eds) *Rheology and processing of liquid crystal polymers*. Chapman and Hall Chapter 9
- Mortier M (1995) PhD Thesis Rheology and structure anisotropy in polymeric liquid crystals. K.U. Leuven, Belgium
- Onogi S, Asada T (1980) Rheology and rheo-optics of polymer liquid crystals. In: Astarita G, Marrucci G, Nicolais L (eds) *Rheology*. Proc VIIIth Int Congr on Rheology, Naples, Vol 1:127–147
- Parthasarathy R, Houpt DJ, Dupré DB (1988) Chain flexibility and elastic constants of solutions of a polymer liquid crystal. *Liq Cryst* 3:1073–1086

- Picken SJ (1989) Clearing temperatures of aramid solutions in sulfuric acid. *Macromolecules* 22:1766–1771
- Picken SJ, Aerts J, Doppert HL, Reuvers AJ, Northolt MG (1991) Structure and rheology of aramid solutions: transient rheological and rheo-optical measurements. *Macromolecules* 24:1366–1375
- Shtennikova IN, Kolbrina GF, Shibaev VP, Ekaeva IV (1990) Conformational properties of hydroxypropylcellulose – II. Flow birefringence and optical anisotropy of hydroxypropylcellulose macromolecules. *Eur Polym J* 26:787–790
- Tanner RI (1975) Theoretical Rheology. In: Hutton JF, Pearson A, Walters K (eds) Applied Science Publishers, London
- Threefoot SA (1991) Ph.D. Thesis Stress relaxation modes in liquid crystalline polymers. University of Delaware, USA
- Vermant J, Moldenaers P, Mewis J, Picken S (1994) Band formation upon cessation of flow in liquid-crystalline polymers. *J Rheol* 38:1571–1590
- Viola GG, Baird DG (1986) Studies on the transient shear flow behavior of liquid crystalline polymers. *J Rheol* 30:601–628
- Walker LM, Wagner NJ (1994) Rheology of region I flow in a lyotropic liquid-crystal polymer: the effects of defect texture. *J Rheol* 38:1525–1548
- Walker LM, Wagner NJ, Larson RG, Mireau PA, Moldenaers P (1995) The rheology of concentrated PBLG solutions. *J Rheol* 39:925–952
- Wissbrun KF (1981) Rheology of rod-like polymers in the liquid crystalline state. *J Rheol* 25:619–662
- Xu Y, Qian R (1990) Rheological studies on solutions of poly-p-phenylene terephthalamide in H<sub>2</sub>SO<sub>4</sub>. *Intern Polymer Processing* 4:258–263
- Yang I, Shine AD (1992) Electrorheology of a nematic poly(n-hexyl isocyanate) solution. *J Rheol* 36:1079–1104
- Yang I, Shine AD (1993) Transient shear flow of a unidomain liquid crystalline polymer. *Macromolecules* 26:1529–1536
- Ying Q, Chu B (1984) Persistence length of poly(1,4-phenyleneterephthalamide) in concentrated sulphuric acid. *Makromol Chem Rapid Commun* 5:785–791