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Transient and stationary flow behaviour of side chain liquid-crystalline polymers: Evidence of a shear-induced isotropic-to-nematic phase transition

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Abstract. – This letter describes the non-linear rheology of the isotropic phase of a thermotropic side chain liquid-crystal polymer (SCLCP), from which we infer a flow-induced isotropic-to-nematic (IN) phase transition above a critical shear stress and construct non-equilibrium phase diagrams. In contrast to the well-studied wormlike-micellar solutions and predictions for simple liquid-crystalline systems, the critical stress does not vanish as the equilibrium transition temperature is approached from the above. We postulate that this is due to: i) the coupling between mesogens and the polymer backbone, whose equilibrium oblate nematic backbone conformation contrasts with the prolate non-equilibrium conformation; and ii) the peculiar topological constraints in SCLCP melts, which have been previously postulated as leading to long-lived clusters.

Introduction. – Shear flow dramatically influences the microstructural order in complex fluids, and can sometimes induce phase transitions. Examples include the shear-induced isotropic-to-nematic (IN) phase transition in liquid-crystalline systems [1, 2] and in colloidal suspensions [3]. The possibility of inducing an isotropic-to-nematic (IN) transition by shear flow is appealing, and has been reported experimentally in semiflexible wormlike micelles [2]. Although this system is well studied, polymeric-like entanglements, the annealed length distribution, and solvent greatly complicate the physics. Mather *et al.* [4] have recently studied a linear thermotropic polymer and shown that it can undergo a flow-induced IN transition. A similar transition was then discovered in side chain liquid-crystalline polymers (SCLCPs) [5], based on birefringence measurements. In one SCLCP system, Small-Angle Neutron Scattering (SANS) demonstrated that, while the mesogenic side group is perpendicular to the polymeric backbone in the equilibrium nematic phase, flow induces *parallel* alignment, with backbone and mesogen distribution functions prolate and oriented generally in the flow direction [5]. The aim of this paper is to continue this work with a study of the non-linear rheology of this system.

The constitutive behaviour of a typical flow-induced shear-thinning phase transition is shown in fig. 1. For imposed strain rates in the unstable region, in which the stress decreases

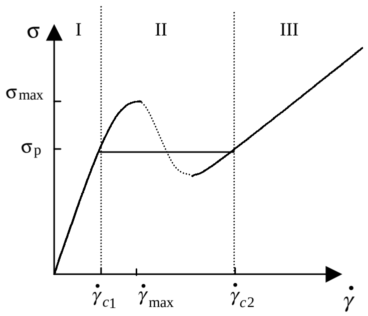


Fig. 1

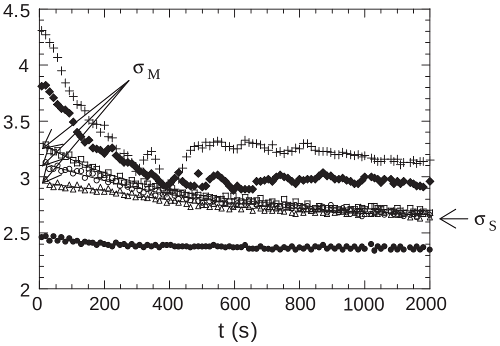


Fig. 2

Fig. 1 – Schematic representation of a non-monotonic constitutive relation between the shear stress and the shear rate.

Fig. 2 – Shear stress as a function of time at $T = 115\,°\mathrm{C}$ for shear rates $\dot{\gamma}$ of (●) $1.6\,\mathrm{s}^{-1}$, (△) $2\,\mathrm{s}^{-1}$, (○) $2.1\,\mathrm{s}^{-1}$, (□) $2.2\,\mathrm{s}^{-1}$, (◆) $2.6\,\mathrm{s}^{-1}$, (+) $3\,\mathrm{s}^{-1}$. Small oscillations (2% of the stress) in phase with the shear cell rotation (probably due to slightly non-uniform gap around the cone) are superposed on the stress signal.

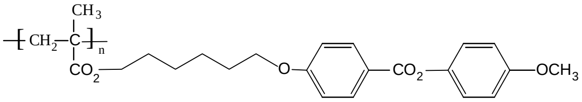
with increasing strain rate, the system "phase-separates" into homogeneous bands of material flowing at strain rates $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$, to maintain the average imposed strain rate. Such a system will display a stress plateau upon applying an increasing average strain rate and the selected stress is predicted to depend on the nature of the interface between the coexisting phases [6,7]. This phenomenon has been well studied in wormlike micelles [2,8–11], in which there appear to be at least two sources of the constitutive instability. Concentrated systems are often near a nematic transition, which is known to yield a non-monotonic flow curve of this form [2,7], while more dilute systems exhibit a non-monotonic flow curve due to the effect of flow on the reptation-reaction dynamics of wormlike micelles [12].

In thermotropic liquid-crystalline systems a flow-induced IN transition is primarily due to orientational fluctuations. For rigid-rod systems the lifetime τ_n of the fluctuations is of order $\tau_n \approx 10^{-6}$ s, necessitating extremely high strain rates to induce a transition. In SCLCPs the orientation fluctuations are of order $\tau_n \approx 10^{-3}$ s [13]. However, the mesogen is coupled to the polymer backbone, and the terminal times τ_d for stress relaxation of these systems is of order $\tau_d \approx 1$ s [14,15]. Moreover, SCLCP rheology is very different from flexible polymers and poorly understood. The average number of monomers between two neighbouring entanglements in a chain for SCLCPs is about ten times greater than for the entangled polystyrene [15]. The zero shear viscosity and terminal time scale with the molecular weight as $M^{1.3}$ and $M^{2.6}$, respectively, instead of the Rouse values M^1 and M^2 [15]. The terminal time separates a viscous regime from a wide range (decades) of frequencies in which the storage and loss moduli are similar in magnitude and scale as the same power of frequency $G', G'' \sim \omega^{0.6}$, rather than the Rouse behavior $\omega^{0.5}$ [14–16]. The simultaneous scaling of the viscoelastic moduli is also characteristic of a system near its gel point [17], and has been observed in branched flexible polymers [18]. These results on SCLCPs are relevant of non-trivial long-lived topological constraints. Furthermore, linear rheology on successively thinner samples has revealed an elastic response for gaps ($\leq 100\,\mu$m), consistent with long-lived clusters of order in size of tens of μm [17]. Finally, light scattering experiments on melts of side-on fixed liquid-crystalline polymers show a strong angular dependence explained by the existence of large globular structures [19].

TABLE I – *Parameters for stress decay, fitted to* $\sigma(t) = \sigma_\mathrm{S} + \Delta\sigma \cdot \exp[-(t/\tau_\mathrm{ng})^\delta]$, *for* $T = 115\,°\mathrm{C}$.

	$\Delta\sigma$ (Pa)	τ_ng (s)	δ
$\dot\gamma = 2.2\,\mathrm{s}^{-1}$	657	362	0.94
$\dot\gamma = 2.1\,\mathrm{s}^{-1}$	493	452	1.07
$\dot\gamma = 2\,\mathrm{s}^{-1}$	293	504	1.4

Experimental. – The following SCLCP was synthesised at the Laboratoire Léon Brillouin, with the succession of mesophases T_g - 40 °C - $\mathrm{S_{A1}}$ - 72 °C - N - 108 °C - I:



In the nematic phase, the polymer backbone is characterised by an oblate conformation [5]. The molecular weight and polydispersity index, respectively, are $M_\mathrm{w} = 350000$ g/mol and $M_\mathrm{w}/M_\mathrm{n} = 2.7$. Measurements were performed with a Rheometrics Dynamic Analyser (RDA II) using a cone and plate cell (diameter: 12 mm, angle: 0.17 rad) in controlled shear rate mode.

Transient measurements. – Transient measurements were performed first in the isotropic phase; at $t = 0$, a controlled strain rate was applied and the stress response monitored until steady state was reached. The time delay applied between two successive measurements guaranteed no shear history effect.

Figure 2 presents the data for $T = 115\,°\mathrm{C}$; data for $T = 117\,°\mathrm{C}$ were similar. We identify three regimes that correspond roughly to the regimes I, II, and III in fig. 1. In regimes I and III (respectively, $\dot\gamma = 1.6\ \mathrm{s}^{-1}$ and $\dot\gamma = 2.6, 3.0\ \mathrm{s}^{-1}$), the stress overshoots and then quickly attains a stationary value that varies with strain rate, characteristic of a homogeneous liquid. For shear rates $\dot\gamma = 2.0,\ 2.1,\ 2.2\ \mathrm{s}^{-1}$, in regime II, the stress curves converge with time to the same stress value $\sigma_\mathrm{S} \cong 2660\,\mathrm{Pa}$, indicating the existence of a stress plateau. For these shear rates, the stress first increases to a maximum value (σ_M) and then slowly decreases to a stationary value (σ_S) within about 1000 s. This time seems to decrease weakly with increasing temperature or with increasing shear rate. Finally, the shear stress σ_M increases with the applied shear rate (fig. 2). These three distinct regimes reproduce the scheme of fig. 1, and are consistent with a flow-induced IN transition.

The transient response in region II is similar to that seen in wormlike micelles [9], which display an overshoot, followed by a slow sigmoidal decay to the plateau value [10]. This stress decay, in analogy with crystallisation processes, has been modelled by $\sigma(t) = \sigma_\mathrm{S} + \Delta\sigma \cdot \exp[-(t/\tau_\mathrm{ng})^\delta]$, where the time τ_ng might be interpreted as the characteristic time for nucleation and one-dimensional growth of the flow-induced phase [10]. Close to $\dot\gamma_\mathrm{c1}$, values of about $\delta \approx 2$–3 were originally measured for wormlike micelles [9]. More recently, Berret and Porte found a sigmoidal decay ($\delta \approx 2$) for shear rates close to $\dot\gamma_\mathrm{c1}$, and an exponential decay ($\delta \approx 1$) for higher shear rates [11]. Hence, for applied strain rates less than $\dot\gamma_\mathrm{max}$ the system might be termed metastable, and the band formation requires nucleation and slow growth; while for larger strain rates the system responds immediately, like an equilibrium system after an unstable quench. We stress that such analogies with equilibrium systems are only formal and perhaps accidental, and do not imply the applicability of equilibrium ideas. We have fitted the slow decay, and found an exponent $\delta \approx 1.4$ for the smallest shear rate and $\delta \approx 1.0$

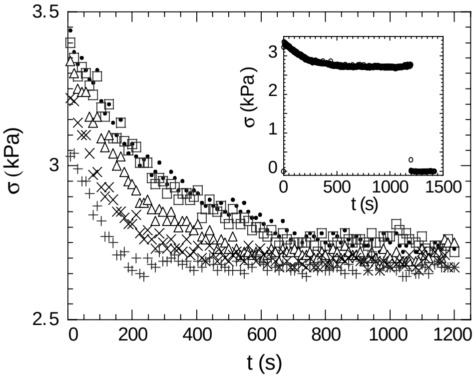


Fig. 3

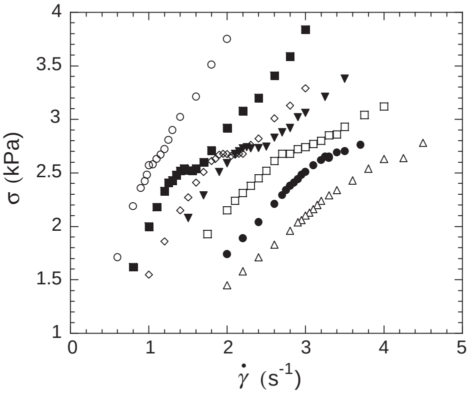


Fig. 4

Fig. 3 – Shear stress as a function of time at $T = 115\,°\mathrm{C}$, for $\dot\gamma = 2.2\,\mathrm{s}^{-1}$, starting (●) at rest, and after delays of (+) 0.5 min, (×) 1 min, (△) 2 min, and (□) 5 min. In the inset, the effect of flow cessation on the stress is shown. At $t = 1250\,\mathrm{s}$ the shear rate $\dot\gamma = 2.2\,\mathrm{s}^{-1}$ is stopped, the macroscopic shear stress then relaxes in less than 5 s.

Fig. 4 – Shear stress *vs.* shear rate with $t_\mathrm{w} = 1000\,\mathrm{s}$ and $t_\mathrm{R} = 100\,\mathrm{s}$ at (○) 109 °C, (■) 112 °C, (◇) 115 °C, (▼) 117 °C, (□) 120 °C, (●) 122 °C, (△) 125 °C.

for larger shear rates, and $\tau_\mathrm{ng} \approx 300$–$500\,\mathrm{s}$ (table I).

Although it took less than 5 seconds for the stress to relax after stopping the flow (insert of fig. 3), immediately repeating the same time-dependent stress measurement does not lead to identical results. Figure 3 shows measurements recorded after different time intervals (at $\dot\gamma = 2.2\,\mathrm{s}^{-1}$ and $T = 115\,°\mathrm{C}$). The upper curve corresponds to the initial state, with no shear history. For waiting times longer than 2 minutes, the behaviour is identical to the initial curve, while for shorter waiting times the overshoot stress value decreases and the stress relaxes more quickly to its stationary value. Hence, stress measurements do not detect all the relaxation processes in the melt, and there are other slower degrees of freedom with a time $\tau_\mathrm{slow} \cong 120\,\mathrm{s}$; this time could be related to the proposed clusters in SCLCP melts [15, 17, 19].

Steady-state rheology. – To measure the steady-state behavior, each strain rate was applied for a time $t_\mathrm{w} = 1000\,\mathrm{s}$, after which the measured stress value was averaged over a time $t_\mathrm{r} = 100\,\mathrm{s}$. These measurements are independent of transient ones since the shear rate is systematically incremented without relaxing between two successive values. Figure 4 shows the resulting steady-state flow curves at different temperatures above T_IN, in which the regimes I, II, and III can be identified. As can be seen, with increasing temperature the critical strain rate $\dot\gamma_\mathrm{c1}$ increases, while the width of the stress plateau first increases and then decreases until a critical temperature at which the plateau disappears: this is consistent with a predicted non-equilibrium critical point [1c)]. These plateaus are particularly narrow compared to wormlike micellar solutions, where they were observed over 1 or 2 decades in strain rate. This implies a slight difference in viscosities between the nascent and shear-induced phases. This is most probably due to the strong contribution of the highly viscous polymeric backbone to the stress, while the contribution to the stress of the mesogen orientation is expected to be relatively weak. The phase diagram in the temperature-strain rate plane deduced from the flow curves is shown in fig. 5. This phase diagram is similar to those obtained for wormlike micelles (in which concentration is analogous to the inverse temperature in the SCLCP system) and to predictions for simple liquid crystals involving only orientational degrees of freedom [1]. A

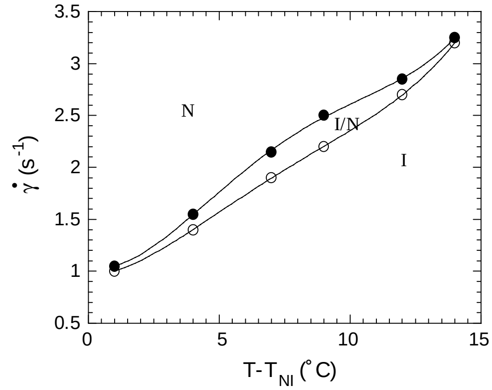


Fig. 5

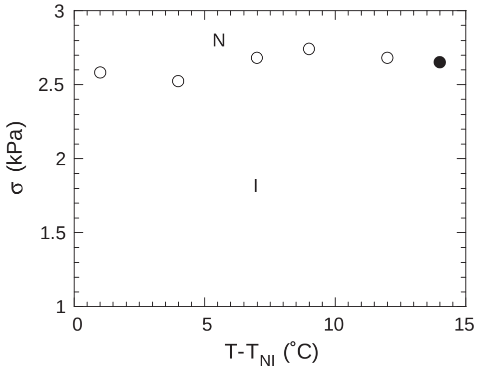


Fig. 6

Fig. 5 – Non-equilibrium phase diagram: shear rate as a function of temperature: at the onset of the plateau ($\dot{\gamma}_{\mathrm{c}1}, \circ$) and at the end of the plateau ($\dot{\gamma}_{\mathrm{c}2}, \bullet$).

Fig. 6 – Non-equilibrium phase diagram: plateau shear stress σ_{p} as a function of temperature.

second representation of the phase diagram, in the stress-temperature plane, can be extracted from the steady-state plateau stress σ_{p}. Figure 6 shows that σ_{p} is roughly constant as a function of temperature. This behaviour differs clearly from wormlike micelles, in which the stress plateau decreases with increasing concentration [8], and is not predicted by theories of simple liquid crystals [1].

Discussion. – There are several points to note. The inverse of the critical strain rate is of order 0.3–1.0 s, which is much longer than the orientation fluctuation lifetime but of the order of the terminal time, $\tau_d \approx 1\,\mathrm{s}$ [14]. This implies that the appearance of the shear-induced nematic phase is related to the mesogen–main-chain coupling or to the slow cluster dynamic. In simple liquid crystals, as in SCLCPs, pretransitional orientation fluctuations increase near the equilibrium transition temperature T_{IN}, and the stress required to induce the transition is expected to vanish at T_{IN} [1]. However, fig. 6 implies that, in this SCLCP system, a *finite* stress is necessary to induce a transition for temperatures arbitrarily close to T_{IN}. A natural candidate for this behaviour involves the coupling between the mesogen and polymer backbone degrees of freedom; indeed, the fact that the inverse of the critical shear rate correlates well with the terminal time leads us to consider the polymer chain. In the equilibrium nematic phase the polymer main chain is, on average, oblate and oriented perpendicular to the mesogen orientation, implying a barrier between parallel and perpendicular orientations. However, in the shear-induced nematic phase the backbone is prolate and oriented parallel to the mesogens [5]. Consider applying shear only slightly above T_{IN}. In the absence of the polymeric backbone the mesogens would align with the flow, at a stress that vanishes as T_{IN} is approached. But to switch from the perpendicular orientation at rest to the observed parallel orientation in the flow-induced nematic phase requires an additional stress to overcome the barrier between orientations. This is consistent with the non-vanishing of the plateau stress as the temperature approaches T_{IN}, and in fact implies a transition as a function of increasing strain rate from oblate to prolate polymer conformations, for temperatures slightly *below* T_{IN}. Although there are no calculations for such a transition in shear flow, Rey has predicted a series of related orientation transitions from a phenomenological model for SCLCPs in extensional flow [20].

We have presented the first rheological study of the non-linear properties of SCLCPs near the IN phase transition. Steady-state measurements demonstrate the existence of a stress plateau indicative of a first-order transition, and a non-equilibrium critical point. The transient measurements yield three primary characteristic times: $\tau_{\mathrm{ng}} \approx 300$–$500\,\mathrm{s}$, governing conversion to the induced nematic phase under steady imposed strain rate, possibly via nucleation and one-dimensional growth; a fast stress relaxation time of order 5 seconds upon cessation of shear flow (in the shear-induced regime); and a further slow relaxation time $\tau_{\mathrm{slow}} \approx 120\,\mathrm{s}$ upon cessation of shear flow, due to relaxation of degrees of freedom that do not couple to the macroscopic stress. A unique aspect of the flow-induced IN transition in this SCLCP system is the non-vanishing of the transition stress as the equilibrium IN transition temperature is approached: we suggest that this is related to both the antagonistic tendencies of simultaneous parallel ordering backbone and mesogen degrees of freedom and the existence of topological constraints in the melt.

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