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Development and relaxation of orientation in sheared concentrated lyotropic solutions of hydroxypropylcellulose in *m*-cresol

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Abstract

Shear-induced orientation and the relaxation of orientation after the cessation of shear in 45 and 50 wt% solutions of cholesteric hydroxypropylcellulose (HPC) in *m*-cresol have been studied in situ by infrared spectroscopy and polarised microscopy. The shearing experiments were conducted at 30–80 °C at shear rates of 1–300 s^{-1}, which covered the director tumbling, wagging and a small part of the steady-state shear rate regimes. The steady-state order parameter was proportional to the shear rate and the proportionality constant increased with increasing HPC concentration and decreasing temperature. The concentrated solutions studied showed steady-state alignment even in the tumbling regime. Three different shear-rate regions with different behaviours of the solutions after the cessation of shear were found in these concentrated HPC solutions. At low shear rates (1–5 s^{-1}, referring to the 50% HPC solution) the polymer remained isotropic during shear but became gradually more oriented a few minutes after the cessation of shear, an observation that was substantiated by polarized microscopy. The order parameter reached a final plateau value and stayed constant at this level for long periods of time (~24 h). At intermediate shear rates (from 5 to 50 s^{-1} for the 50% HPC solution), a detectable order parameter was recorded at steady shear and, after the cessation of shear, the structure returned to an almost isotropic state within a few minutes, after which the orientation gradually started to increase to approach a plateau value after about 150 min. At even higher shear rates (~100 s^{-1} for to the 50% HPC solution), the initial steady shear order parameter relaxed to an almost isotropic state and remained constant at this level for time periods extending up to 24 h.

Keywords: Lyotropics; Shearing; Orientation

1. Introduction

When liquid crystalline polymers are processed into fibres, films, or injection-moulded components, the properties of the final product are strongly dependent on the molecular orientations induced by the process flow. For example, certain liquid crystalline polymers have a commercial potential as high-barrier packaging materials, provided that biaxially oriented films can be produced by extrusion [1]. Larson and Mead [2] showed that simple shear flow by itself is sufficient to remove all the defects initially present in a liquid crystalline solution (lyotrope) of polybenzylglutamate (PBG) in *m*-cresol, yielding a sample with a permanent high degree of orientation. To achieve this in the case of PBG/*m*-cresol, the shear rate must exceed a critical value related to the suppression of 'director tumbling' at a molecular level [2–4]. Similar success in obtaining a high value for the macroscopic order parameter after shear flow has not been achieved to date with any other lyotropic liquid crystalline polymer. Director tumbling means that the shear forces favour continuous rotation of the director, and that the director executes a periodic tumbling orbit within the deformation plane. Both experimental data obtained by measurements of birefringence on PBG solutions and theory suggest that tumbling lyotropics show flow-induced orientation [5].

Fig. 1 shows a generalised scheme over the different shear-rate regimes for a dilute to semi-dilute lyotrope, based on the Doi molecular theory for rodlike polymers [3–8]. At low shear rates, when the first normal stress difference (N_1) is positive, the director will rotate or tumble with the flow and produce a striped texture, so-called roll cells [2]. At intermediate shear rates, when the flow is only slightly slower than the reciprocal of the longest molecular relaxation time, there is a competition between tumbling and steady alignment of the director along the flow and the director oscillates about a steady value [2]. This phenomenon, which is a characteristic of polymer lyotropes, is referred to as wagging. In this regime, N_1 is negative (Fig. 1).

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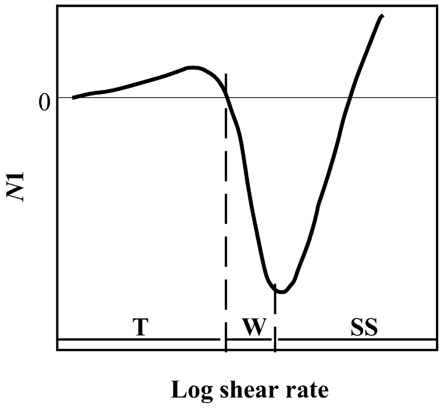

Fig. 1. Schematic presentation of different shear rate regimes, T = 'tumbling'; W = 'wagging' and SS = 'steady-state flow alignment', in lyotropes showing the first normal stress difference (N_1) as a function of the logarithm of the shear rate.

The observation of negative normal forces in lyotropic polymers was first reported by Kiss and Porter [9] and they have later published an excellent review paper on this topic [10]. At further higher shear rates, the dynamics changes to steady state and flow alignment of the director (Fig. 1). The transitions between the different regimes occurs according to Larson and Mead [2] at the following Deborah numbers ($De = \tau\dot{\gamma}$, where τ is the longest molecular relaxation time and $\dot{\gamma}$ is the shear rate): tumbling at $De \leq 1$; wagging at $De \sim 2$ and steady-state alignment at $De \geq 5$.

The idealized behaviour sketched in Fig. 1 has largely been confirmed for lyotropic solutions of PBG in *m*-cresol, but there are significant differences in the orientation response to shear flow among various other liquid crystalline polymers. Despite considerable study [5,11–19], the reasons for these differences remain poorly understood. For example, the macroscopic value of the order parameter during shear flow for the PBG/*m*-cresol system exhibits a non-zero plateau at low shear rates, according to birefringence, X-ray, and neutron scattering measurements at the lowest accessible shear rates [5,12,13]. Occurrence of a low-shear-rate plateau in orientation is consistent with a modified form of the Doi theory [20]. However, if *m*-cresol is replaced by benzyl alcohol, the macroscopic value of the order parameter is essentially zero at low shear rates [11]. Burghardt et al. [13] suggested that this lack of appreciable orientation at low shear rates is associated with so-called 'Region I' shear-thinning and the 'piled domain texture' postulated by Onogi and Asada [21]. Another widely studied model lyotropic polymer is hydroxypropylcellulose (HPC) [12–15,18,19,22–28], which is believed to be much more flexible than PBG [25]. For dilute liquid crystalline solutions of HPC in both water [13–15] and *m*-cresol [12,13], the macroscopic value of the order parameter during flow is close to zero at low shear rates. However, when this polymer is melted to form a liquid crystalline phase without solvent (i.e. a 'thermotrope'), X-ray scattering measurements show that the macroscopic order parameter has a non-zero low shear rate plateau reminiscent of PBG/*m*-cresol [19,28]. At high shear rates, lyotropic solutions of PBG in *m*-cresol exhibit an abrupt increase in molecular orientation that is clearly connected to the sign change of N_1 that occurs at approximately the same value of the shear rate [5]. This transition in orientation is thought to reflect the predicted suppression of director tumbling at high shear rates, as shown in Fig. 1. Dilute liquid crystalline solutions of HPC in both water [24] and *m*-cresol [25] also have N_1 values that changes sign twice as a function of shear rate, which strongly implies that these systems also obey the generalised scheme for tumbling lyotropes sketched in Fig. 1. The degree of molecular orientation for HPC in water or *m*-cresol shows a transition at high shear rates, but the increase in orientation at this transition is less abrupt than that observed for PBG in *m*-cresol [12,13]. Negative N_1 values have not been observed at any shear rate for liquid crystalline phases of HPC without solvent, and director tumbling has not been established to occur.

The behaviour of the macroscopic order parameter after shear flow is also complex. A lyotropic solution containing 13.5 wt% PBG in *m*-cresol sheared at a shear rate below the critical value, showed an increase in the macroscopic order parameter with time after flow cessation [13,29]. However, a solution with 19 wt% PBG showed a time dependence of the order parameter after flow with a relative minimum [13]. For shear rates above the critical value, the increase in order parameter after flow cessation is slight, presumably because the PBG molecules are almost fully aligned during the flow. For lyotropic solutions of HPC in both water and *m*-cresol [12,26] the macroscopic order parameter is reported to decay towards zero after cessation of flow, although a relative maximum was observed in some cases.

This paper reports data obtained by infrared spectroscopy and polarised light microscopy of sheared liquid crystalline solutions containing 45 and 50 wt% HPC in *m*-cresol at 30–80 °C. The study was undertaken to bridge the gap between lyotropes and thermotropes. The critical HPC concentration for liquid crystal formation in *m*-cresol is unusually low, e.g. 23 wt% at 25 °C [23,27] compared to the value in water, the solvent used in most previous flow orientation and microscopy studies of HPC. Thus the HPC concentrations discussed here are well above the critical value for liquid crystal formation, and also well above the concentration (≈35 wt%) at which the rheological behaviour begins to depart from the predictions of the Doi theory [25,27]. The rheological properties of HPC/*m*-cresol have recently been investigated throughout the entire phase diagram, and qualitative changes in the rheology were observed as the solvent-free thermotropic state was approached [25,27]. Previous results for the orientation response of lyotropic HPC/*m*-cresol are limited to a single polymer concentration of 27 wt% at room temperature [12,13]. These results were obtained by another research group using birefringence and X-ray scattering measurements at room temperature with a polymer of similar molar mass [12,13]. This group found a very low degree of orientation even at the lowest shear rates, $\dot{\gamma} < 0.02\ \mathrm{s}^{-1}$. Shear thinning and an increase in the order parameter occurred at higher shear rates, above $\dot{\gamma} \sim 0.1\ \mathrm{s}^{-1}$. A further increase in the order parameter occurred at the transition from tumbling to wagging. Since the literature survey suggests that solvent and polymer concentration can have profound effects on shear flow orientation, it is perhaps not surprising that the results presented here are qualitatively different from those reported earlier at the lower polymer concentration. The work presented here also differs from most previous studies in that the chain orientation has been measured at very long times, longer than $10^4\ \mathrm{s}^{-1}$, following cessation of shear flow. Neutron scattering studies suggest that lyotropic PBG may not reach its final orientation state until the time t after flow satisfies the expression $\dot{\gamma}t > 10^4$, where $\dot{\gamma}$ is the previously applied shear rate [16].

2. Experimental

Two solutions (45 and 50 wt%) of HPC in *m*-cresol were studied. The HPC, Klucel E-Lot 10766, was received from Hercules/Aqualon Corp., Wilmington, USA and was used after drying under vacuum. The molar mass of the studied HPC according to intrinsic viscosity measurements was $\bar{M}_\mathrm{W} = 106{,}000\ \mathrm{g\ mol}^{-1}$ [27]. The solutions were prepared by thorough mixing of the dry HPC and *m*-cresol followed by self-diffusion for 6 weeks while encapsulated to eliminate loss of solvent. The same polymer sample was used to study the rheological behaviour of HPC/*m*-cresol throughout much of the phase diagram [25,27]. Table 1, which has been extracted from this earlier work, contains the transition shear rates obtained by measuring N_1 and noting its sign changes.

Shear-induced orientation and relaxation of orientation after the cessation of shear were studied in a rotational parallel-plate rheometer. The apparatus permitted simultaneous measurement of the infrared dichroism, the shear stress and the normal force. The raw data were continuously collected with a response time of 0.07 s. Both transient and steady-state measurements were made at 30, 60, and 80 °C and shear rates between 1 and $300\ \mathrm{s}^{-1}$. A detailed description of the rheometer design and of the optical system, together with a description of the control and data acquisition system, is given elsewhere [30]. Briefly, the light source was a ceramic element (Oriel) operating in the infrared wavelength range between 750 nm and 30 μm. The infrared beam was directed through a polariser and a rotating chopper wheel before it impinged the sample, which was held between two parallel infrared-transparent zinc selenide plates. The transmitted beam continued via gold-plated mirrors and a zinc selenide lens, which focused the beam into a monochromator. An MCT-detector collected the beam and the signal from the MCT-detector was fed first through a pre-amplifier and then through a lock-in amplifier, which was locked onto the frequency of the chopper wheel. The signal was finally recorded and further analysed by a PC system.

The solution of HPC in *m*-cresol was placed at the centre of the lower window, and the upper window was then positioned and slowly fastened tight, controlled by a micropositioner. A PID-regulator permitted temperature control to within 0.5 °C. The separation of the plates was set to 50 ± 1 μm, which resulted in the build-up of pressure and the samples were squeezed out. The samples were allowed to rest until the normal force reached a zero value before the onset of shear. After establishment of steady-state torque and transmitted IR light, the shear was stopped and the relaxation of orientation was studied as a function of time. The chain orientation was assessed by measurement of the dichroic ratio ($R = A_{\|}/A_{\perp}$, where $A_{\|}$ is the absorbance of the radiation polarised parallel to the shear direction and $A_{\perp}$ is the absorbance of radiation polarised perpendicular to the shear direction at $1324\ \mathrm{cm}^{-1}$).

The 50 wt% HPC solution was also sheared between two parallel quartz plates in a hot stage (temperature control within ± 1 °C using a Eurotherm PID regulator; temperature calibration was achieved by melting a series of highly pure organic substances) in a polarised light microscope (Leitz Ortholux). The sample was sheared at constant shear rate ($1–300\ \mathrm{s}^{-1}$) after which the shearing was stopped and the structure was examined over a period of time.

Table 1
Transition shear rates estimated from N_1 measurements on lyotropic HPC solutions in *m*-cresol (from Refs. [25,27])

HPC (wt%)	Temperature (°C)	$\dot{\gamma}_\mathrm{T/W}$ (s^{-1})[a]	$\dot{\gamma}_\mathrm{W/SS}$ (s^{-1})[b]
45	25	50	100
45	37	~125	~400
45	50	600–700	1000–1100
45	60	~1200	–[c]
45	71	~1500	–[c]
45	80	2200	3600
50	25	20	30
50	37	80	~100
50	50	300	~500

[a] Shear rate at which N_1 changes sign from positive to negative.

[b] Shear rate at which N_1 vs. shear rate exhibits negative relative minimum.

[c] No data are available.

3. Results and discussion

3.1. Chain orientation from infrared spectroscopy data and general features

The assessment of the chain orientation was complicated by the presence of absorption peaks originating from *m*-cresol. This excluded the majority of the dichroic HPC absorption bands from quantitative treatment due to overlap; only the 1324 cm^{-1} could be used without difficult curve resolution. The 1324 cm^{-1} band is associated with the coupled bending vibration of the OH and CH groups in the ring and it is approximately parallel to the chain axis [31]. The order parameter (s) with the shear direction as the director was obtained from the dichroic ratio (R) according to (see Ref. [32] for further explanation)

$$s = \frac{(R-1)}{(R+2)}\frac{(2\cot^2\psi + 2)}{(2\cot^2\psi - 1)} \approx \frac{R-1}{R+2} \quad (\psi \approx 0) \qquad (1)$$

where ψ is the angle between the transition moment vector and the chain axis; $\psi = 0$ for the vibration associated with 1324 cm^{-1} band. Eq. (1) is only valid in the case of uniaxial orientation [32].

Fig. 2(a) shows the infrared spectrum of an isotropic 45 wt% HPC solution. Fig. 2(b) and (c) shows the parallel and perpendicularly polarised IR absorbance spectra for uniaxially stretched solution-cast HPC film. The stretching evidently induced molecular alignment, as judged by the pronounced dichroism of the 1324 cm^{-1} band. The spectra displayed in Fig. 2(a) and (b) were obtained by a Perkin–Elmer 1760 infrared spectrometer. Fig. 2(c) shows the spectra for the oriented film as obtained by stepwise changes of the monochromator setting in the IR-rheometer. The dichroic ratio obtained in the IR-rheometer was within 10% of the value obtained by the Perkin–Elmer instrument (Fig. 2(b) and (c)).

Since the method utilised is a single-wavelength technique, the shearing measurements were performed while recording the transmitted intensity at the absorption peak (1324 cm^{-1}) as well as at 1300 and 1400 cm^{-1} to obtain the baseline. It was assumed that m-cresol is unaffected by shear and that changes in absorption are caused only by orientation of the HPC molecules.

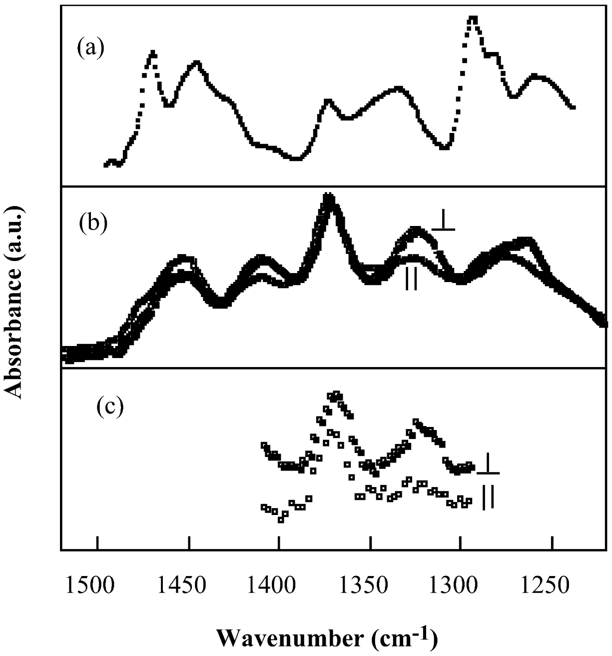

Fig. 2. (a) Infrared spectrum of the 45 wt% HPC-m-cresol solution. (b) IR spectra of oriented HPC film with polarised IR (recorded by a Perkin–Elmer 1760 spectrometer), parallel and perpendicular to the orientation direction. (c) IR spectra of oriented HPC (the same specimen as shown in (b); polarised parallel and perpendicular to the shear direction) obtained by a stepwise change of the monochromator setting in the IR-rheometer.

A typical experiment involved starting the shearing and keeping the shear at constant rate until a constant order parameter value was attained. This is referred to as the steady state order parameter (s_{ss}). The shearing time required to establish steady-state orientation was typically 10 s. The data for s_{ss} are presented and discussed in Section 3.2. The instrument used (parallel plate rheometer) is capable of taking rheological data but these were not seriously considered because the shear-rate range included in a single experiment was from zero to a value that was twice the value at the recording window. Therefore, only order parameter data were taken and they were compared with the rheological data of Huang et al. [27]. The shear was switched-off and the change in the order parameter was recorded as a function of time (up to 10,000 s). The data for the relaxation of orientation are presented in Section 3.3.

3.2. Steady-state orientation

Fig. 3(a) and (b) show the steady-state order parameter during shear flow as a function of the shear rate at the location of the IR window. The steady-state order parameter was strictly proportional to the shear rate and the proportionality constant increased with increasing HPC concentration and decreasing temperature (Fig. 3(a) and (b)). It is interesting to note that at the lower temperatures the systems undergo transitions from tumbling to wagging and from wagging to flow alignment according to the rheological data of Table 1. Nonetheless, there was thus a steady (linear) increase in the steady-state order parameter in these different rheological regimes. According to Table 1, the tumbling regime for the 45 wt% HPC solution is at shear rates $<90\ \mathrm{s}^{-1}$ at 30 °C, at shear rates below about 1000 s^{-1} at 60 °C, and the transition from tumbling to wagging is at even higher shear rates at 80 °C. This locates at least six data points for the 45 wt% HPC solution with steady-state order parameter values significantly greater than zero within the tumbling regime. For the 50 wt% HPC solution, the corresponding number of data points is 4. The concentrated solutions studied showed steady-state alignment even in the tumbling regime, presumably because a balance is reached between tumbling forces and Franck elastic stresses [20]. This is also in accordance with earlier experimental data on PBG solutions and theory [5]. There is no evidence of a low-shear-rate plateau in orientation, in contrast with the results for thermotropic HPC [19,28], but in agreement with results for HPC/m-cresol at a lower concentration [12]. However, it should be pointed out that director tumbling has not been established for thermotropic HPC.

The slope coefficients obtained by linear regression of $s_{\mathrm{ss}} = f(\dot{\gamma})$ data were as follows: 45 wt% HPC solution:

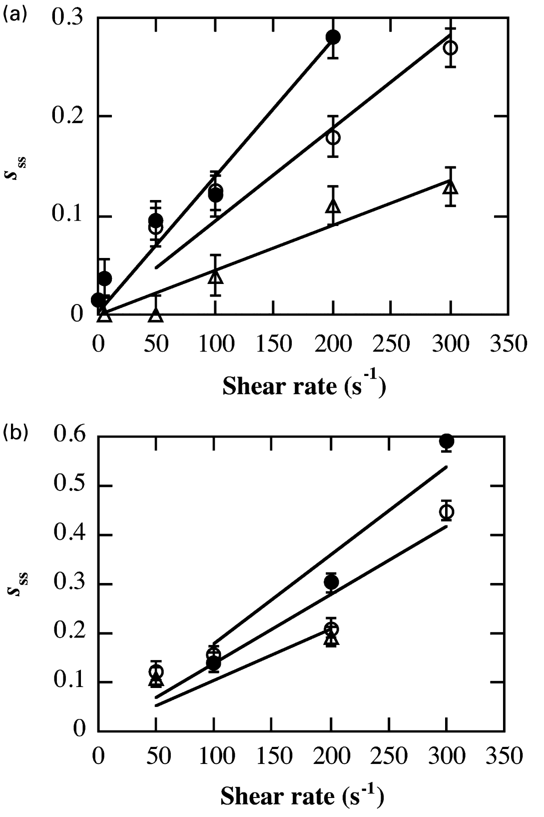

Fig. 3. (a) The order parameter at steady shear (s_{ss}) as a function of the local shear rate value at the IR window for the 45 wt% HPC solution at 30 °C (●), 60 °C (○) and 80 °C (△). Continuous lines show the linear regression (intercept constrained to 0) of the experimental data. (b) The order parameter at steady shear (s_{ss}) as a function of the local shear rate value at the IR window for the 50 wt% HPC solution at 30 °C (●), 60 °C (○) and 80 °C (△). Continuous lines show the linear regression (intercept constrained to 0) of the experimental data.

0.00139 s (30 °C); 0.00094 s (60 °C); 0.00046 s (80 °C); 50 wt% HPC solution: 0.00180 s (30 °C); 0.00140 s (60 °C); 0.00103 s (80 °C). The coefficient of determination (r^2) was approximately 0.95. It should be noted that the intercept was in all cases constrained to zero. The goodness of fit was, however, only moderately improved by allowing both the slope coefficient and the intercept to vary.

3.3. Relaxation of orientation after cessation of shear

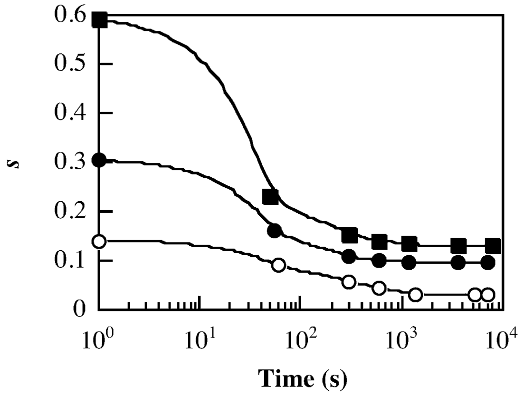

Fig. 4. The order parameter (s) as a function of time after the cessation of shear for the 50 wt% HPC solution sheared at 30 °C at local shear rate value of 100 s^{-1} (○), 200 s^{-1} (●) and 300 s^{-1} (□).

The relaxation of orientation following on the cessation of shear exhibited a complicated pattern depending on the actual values of the initial shear rate and temperature. Figs. 4–7 show the relaxation of the 50 wt% HPC solution. According to the estimated transition shear rates given in Table 1, all of the curves in Fig. 4 correspond to pre-shearing at shear rates high enough to suppress director tumbling. On the other hand, all of the curves shown in Figs. 5 and 6 correspond to pre-shearing in the tumbling regime, and yet the curves corresponding to the lowest pre-shear rate (50 s^{-1}) are qualitatively different. Solutions exposed to a high initial shear rate showed almost complete relaxation within a few hundred seconds (Figs. 4 and 5; the solution sheared at 50 s^{-1} showed a different behaviour). The solutions sheared at 30 °C showed a final plateau value of the order parameter greater than zero, whereas the solutions sheared at 60 °C relaxed to a globally isotropic state (Figs. 4 and 5).

The 50 wt% HPC solution sheared at 50 s^{-1} and 60 °C relaxed to an isotropic state ($s = 0$) within 200 s and then, very unexpectedly, it showed a clear increase in the order parameter. A similar behaviour was observed in the 50 wt% HPC solution sheared at 50 s^{-1} and 80 °C (Fig. 6). At even lower initial shear rates, 1 and 5 s^{-1}, a different behaviour was observed (Fig. 7). These solutions showed very low or essentially no orientation during shear and they remained unoriented during the first 100 s after flow cessation, after which their orientation increased. The solutions sheared at a lower rate (1 s^{-1}) had a shorter onset time for the increase in orientation. The solutions sheared at the higher rate (5 s^{-1}) exhibited higher rates of increase in orientation at the later stages (Fig. 7). All the 50 wt% HPC solution samples finally showed a levelling-off at $s \approx 0.15$, which was very similar to the final plateau value reached for the solutions sheared at 50 s^{-1} (Figs. 5 and 6). Another striking feature is the

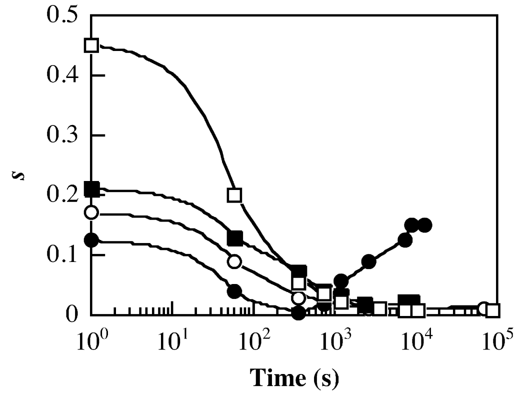

Fig. 5. The order parameter (s) as a function of time after the cessation of shear for the 50 wt% HPC solution sheared at 60 °C at local shear rate value of 50 s^{-1} (●), 100 s^{-1} (○), 200 s^{-1} (■) and 300 s^{-1} (□).

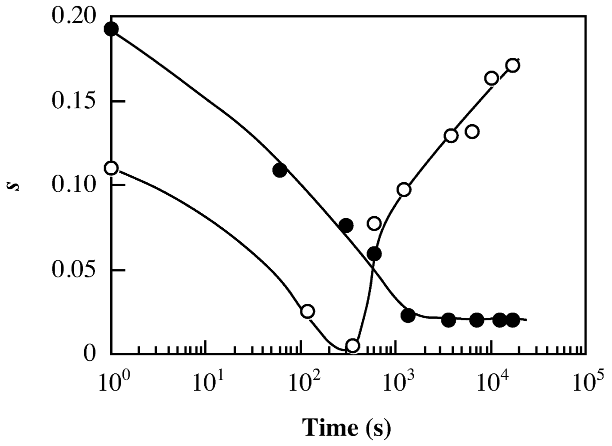

Fig. 6. The order parameter (s) as a function of time after the cessation of shear for the 50 wt% HPC solution sheared at 80 °C at local shear rate value of 50 s^{-1} (○), 200 s^{-1} (●).

temperature-independence of the behaviour (Figs. 5–7), in contrast to the strong temperature dependence of the transition shear rates based on N_1 (Table 1). The onset time for the increase in order parameter displayed shear-rate dependence (and insensitivity to the temperature): after shear at 1 s^{-1} it occurred after 20–50 s, whereas after shear at 50 s^{-1} it occurred after 200–300 s (Figs. 5–7).

The relaxation behaviour of the 45 wt% HPC solution was basically the same as that of the 50 wt% HPC solution but the relaxation regimes are shifted towards lower shear rates (Figs. 8 and 9). The 45 wt% HPC solutions sheared at 50 and 100 s^{-1} showed only relaxation to the globally isotropic state (Fig. 8). Shearing at 1 and 5 s^{-1} led to very low order parameter values (0.01 and 0.04), which after cessation relaxed to the isotropic state and showed a very small increase in orientation after ~1000 s.

The sheared 50 wt% HPC solution was also studied in situ in the polarized microscope. The orientation of the sheared solutions was very obvious from their white colour (the polariser/analyser pair was at 45° angle to the shear direction). When the shear was stopped a banded texture developed within 10–30 s. The regular bands were mostly perpendicular to the original shear direction. The banded texture appeared after shearing at the studied shear rates, 1–300 s^{-1}. After shear at 1–5 s^{-1}, bands at angles of 40–50° and 80–90° to the shear direction were formed. During the first minutes after the cessation of shear, the bands were sharp. The banded structure was gradually lost after another 2–3 min and a more uniform structure with fewer bands developed. This structure also became brighter with time, indicating an increase in orientation. It is thus concluded that the data obtained by polarized microscopy is in qualitative accordance with the data obtained by infrared dichroism measurements.

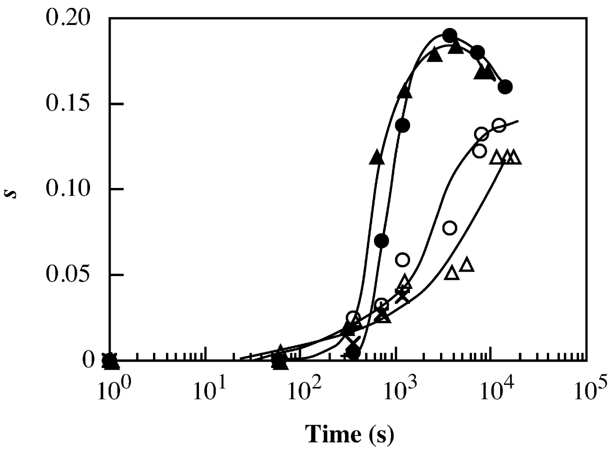

Fig. 7. The order parameter (s) as a function of time after cessation of shear for the 50 wt% HPC solution at local shear rate 1 s^{-1} and 30 °C (○), 5 s^{-1} and 30 °C (●), 1 s^{-1} and 60 °C (△), 5 s^{-1} and 60 °C (▲), 1 s^{-1} and 80 °C (×) and 5 s^{-1} at 80 °C (+).

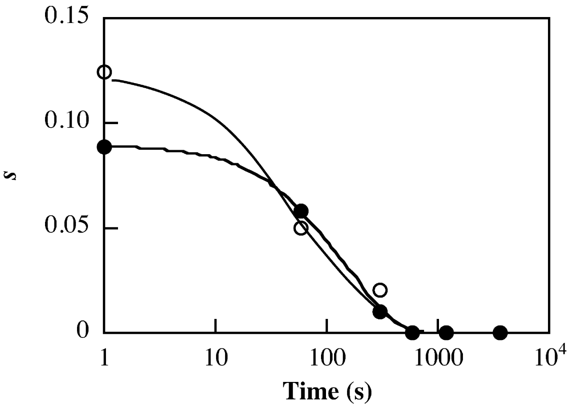

Fig. 8. The order parameter (s) as a function of time after the cessation of shear for the 45 wt% HPC solution sheared at 60 °C at local shear rate value of 50 s^{-1} (●) and 100 s^{-1} (○).

The increase in orientation after flow cessation is in accordance with previously reported data for lyotropic PBG in m-cresol [13,29], but in qualitative disagreement with all previous orientation relaxation studies of liquid crystalline HPC solutions [12,13,26]. The reasons for this discrepancy are uncertain. As pointed out in the Introduction, the HPC/m-cresol solutions studied here are higher in concentration than have been studied previously. Furthermore, thinner

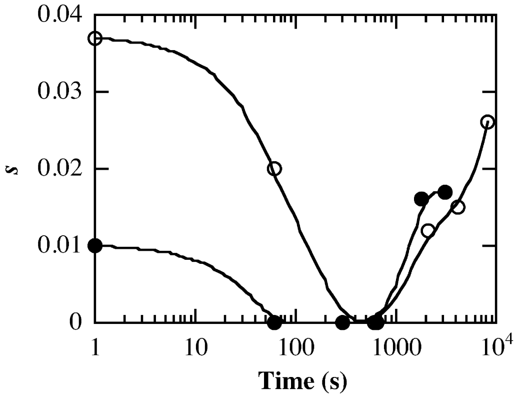

Fig. 9. The order parameter (s) as a function of time after the cessation of shear for the 45 wt% HPC solution sheared at 30 °C at local shear rate 1 s^{-1} (●) and 5 s^{-1} (○).

samples have been investigated, and the orientation relaxation has been measured at considerably longer times than in previous studies. Based on polarized microscopy observations on sheared lyotropic solutions of HPC/water, Hongladarom and Burghardt [26] speculated that by shearing below a critical value of the shear rate, one can obtain a higher degree of molecular organization after flow, due to the persistence of the HPC cholesteric structure during flow at low shear rates. The relaxation results presented here are consistent with this speculation, especially since we have shown that the relaxation regimes are not related to the transition shear rates for N_1. Hongladarom and Burghardt [26,33] also speculated that persistence of the cholesteric structure is responsible for Region I shear-thinning at low shear rates, and Region I shear-thinning should also be present at the HPC/*m*-cresol polymer concentrations studied here [12].

It is interesting to compare the unexpected finding (increase in order parameter after the cessation of shear) with a similar phenomenon found in a thermotrope (Vectra) which on annealing at constant length showed an increase in the degree of orientation [34]. The analogy is even stronger. The Vectra samples were oriented beforehand in a shear field. The Vectra samples showed, however, no initial drop in orientation. It was argued by Wiberg and Gedde [34] that the increase in orientation was due to annihilation of disclination pairs. The concentrated HPC lyotropes studied here were also held at constant length during the experiment after the cessation of shear, but no attempt is made to speculate further on the cause of the unusual phenomenon.

4. Conclusions

Concentrated (45 and 50 wt%) solutions of HPC in *m*-cresol do not exhibit a low-shear-rate plateau in orientation, in agreement with previous studies of lyotropic HPC solutions but in disagreement with thermotropic HPC studies. The steady-state order parameter was proportional to the shear rate, even within the director-tumbling-shear rate regime, and the proportionality constant increased with increasing HPC concentration and decreasing temperature. The final orientation state of a liquid crystalline HPC/*m*-cresol solution depends on the shear rate at which it is pre-sheared. This in itself is not surprising, since the final value of the elastic storage modulus is known to depend on the pre-shear rate for lyotropic HPC/water solutions [13]. However, HPC molecular orientation increases after steady flow at low shear rates, which has not been reported previously for any HPC solution. The development of orientation in these concentrated HPC solutions showed three different types of behaviour after the cessation of shear. At very low shear rates with no detectable orientation at steady shear, the order parameter gradually started to increase a few minutes after the cessation of shear and a plateau value was reached within a few hours. At intermediate shear rates, with a detectable degree of orientation at steady shear, an isotropic state was reached within a few minutes, after which the order parameter started to increase, reaching a plateau value after ~150 min. At even higher shear rates, with comparatively high orientation at steady shear, the order parameter decreased to an almost isotropic value within a few minutes after the cessation of shear and remained so for at least 24 h.

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