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Shear-induced alignment and relaxation of orientation in smectic side-chain liquid-crystalline polymers

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Infrared rheometry showed that the mesogenic groups of two smectic side-chain liquid-crystalline polymers were aligned by shear until a steady-state value was achieved after approximately 10 s. The shear experiments were carried out at temperatures 10–50°C below the isotropisation temperature. The alignment of the mesogenic groups was always perpendicular to the shear flow direction. The degree of orientation increased with increasing shear rate and the highest reported value for the Hermans orientation function was -0.35 (-0.5 corresponds to perfect perpendicular orientation; it was assumed that the mesogen-group-orientation was unixaial). The turbidity of the sheared smectic samples indicates the presence of small domains in spite of their high level of orientation. A gradual loss of mesogen group orientation occurred after cessation of shear, and full recovery of the original isotropic state was in no case achieved within 60 000 s. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

Side-chain liquid-crystalline (LC) polymers may in the near future find applications in non-linear optics, e.g. for data storage, optical logic, and sensor protection. There is generally a requirement of a high degree of macroscopic orientation for the materials used in these applications.

Side-chain LC polymers have been effectively aligned in electric, magnetic or surface fields [1–10]. Mesomorphic monomers have been aligned prior to polymerisation to give specimens with a very high degree of orientation [11–15]. These methods are applicable only to relatively thin films and, in the case of electric or magnetic alignment, very high field strengths are required.

Early papers of Ide and Ophir [16] and Viola *et al.* [17] reported that extensional flow was more efficient than shear flow for orienting nematic main-chain LC polymers. The early studies on the rheology of side-chain LC polymers stated that the rheological response was controlled by the flexible backbone and that shear flow was ineffective in inducing orientation [18–20]. This conclusion was based on the observation that the isotropic-to-nematic phase transition was accompanied by an increase in shear viscosity [18–20]. However, more recent papers by Kannan *et al.* [21] and Rubin *et al.* [22] reported shear-induced alignment of nematic side-chain polymers contrary to the early reports. Oscillatory shearing resulted in a decrease in dynamic modulus at the isotropic–nematic transition, and samples sheared in the nematic state exhibited an increase in both birefringence and transparency [21,22]. A lower modulus was also observed in smectic side-chain polymers subjected to long-term high-amplitude oscillatory shearing, although these samples never became transparent [21,22].

This paper presents *in situ* infrared spectroscopy data on shear-induced orientation and relaxation of orientation of two smectic side-chain LC polymers subjected to steady shear at different shear rates. The infrared rheometer technique permitted assessment of the Hermans orientation

function in real time during shearing and after the cessation of shear.

Experimental

Two polymers, both showing smectic A mesomorphism have been studied. The synthesis and the smectic structure of the studied polymers are described elsewhere [23]. The homopolymer (denoted poly(A)) was a polyvinylether with an 11-carbon methylene spacer and a biphenyl mesogen with a terminal cyano group (A). The copolymer (poly(A/B)) was a 50/50 copolymer between A and isobutyl vinyl ether (B). The number average molar masses of poly(A) and poly(A/B) were 9600 g mol^{-1} ($\overline{M}_w/\overline{M}_n = 2.4$) and 11 400 g mol^{-1} ($\overline{M}_w/\overline{M}_n = 1.4$), respectively. The chemical structure together with the thermal transitions obtained by differential scanning calorimetry, hot-stage polarised microscopy and X-ray scattering of the studied polymers are shown in *Figure 1*.

The rheo-optical apparatus consisted of a flow cell of the rotating parallel plate type. This apparatus permits simultaneous measurement of the infrared dichroic ratio, shear stress and normal stress difference ($N_1 - N_2$) at shear rates between 0.05 and 1000 s^{-1}. A detailed portrait of the rheometer design and optical system, together with a description of the control and data acquisition system, is given elsewhere [24]. Briefly, the light source is a ceramic element (Oriel) operating in the infrared wavelength range between 750 nm and 30 μm. The infrared beam is directed through a polariser and a rotating chopper wheel before it impinges on the sample, which is held between two parallel infrared-transparent zinc selenide plates. The transmitted beam continues via gold-plated mirrors and a zinc selenide lens, which focuses the beam, into a monochromator. A MCT-detector collects the beam and the signal from the MCT-detector is fed, first through a pre-amplifier and then through a lock-in amplifier, which is locked onto the frequency of the chopper wheel. The signal is finally recorded and further analysed by a PC system.

Polymer powder (20 mg) was placed on the centre of the

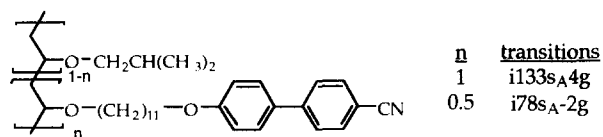* To whom correspondence should be addressed

Figure 1 Chemical structure and phase transitions of the studied copoly(vinylether)s

lower window, and the upper window was then positioned and slowly fastened tight, controlled by a micropositioner. The sample was heated to the isotropic state to ensure that the sample was macroscopically isotropic and then cooled to the shearing temperature. A PID regulator permitted temperature control within 0.5°C. The separation between the plates was set to 30–40 μm. The gap size is limited in order to allow sufficient light to pass through the partly opaque smectic sample. Owing to the parallelism between the plates (with an accuracy of 1 μm) provided for by an xy-translation stage, a uniform pressure was applied to the melt while it was being compressed. The samples were spread evenly in this way. The samples were then allowed to rest until the normal force reached a zero value. Before each shearing experiment, a check was made to ensure that the LC melt looked homogeneous and optically clear, without trapped air bubbles. By aligning the polariser parallel and perpendicular to a fixed reference direction, chosen in the direction of flow, it was also established that no initial chain orientation was present in the samples prior to the start of the shearing. Before another shearing experiment was carried out, the previous history was erased by heating the sample above the isotropisation temperature.

The Hermans orientation function (f) was obtained from the dichroism of the resolved nitrile band located at 2220 cm^{-1} [25]. The dipole moment of this vibration is parallel with the long axis of the outer phenylene group and approximately parallel to the entire mesogenic group. The orientation function was obtained according to Gedde [26]:

$$f = \frac{R-1}{R+2} \qquad (1)$$

where R is the dichroic ratio given by A_0/A_{90}. It should be noted this formula assumes that the orientation of the mesogens is uniaxial. Absorption peaks were constructed from three monochromator settings: the peak value and the wavenumber locations to obtain the baseline.

Results and discussion

Figure 2 shows the nitrile absorbance peak obtained by a stepwise change in the monochromator setting. Comparison with the spectrum of the same sample obtained from a Perkin–Elmer 1760 infrared spectrometer showed perfect agreement. A reasonable baseline can thus be constructed based on the absorbance values at 2180 and 2250 cm^{-1}. The nitrile absorbance band peaks at 2220 cm^{-1}, and this was selected as the wavenumber value for the analysis of the infrared dichroism. The baseline was in all cases obtained from the absorbance values recorded at 2180 and 2250 cm^{-1}.

Both poly(A) and poly(A/B) immediately exhibited infrared dichroism on shearing. The dichroism increased from zero to a constant, steady-state value within a 5–20 s time period. The majority of samples reached steady-state in dichroism within 5–10 s. There was only a slight variation in the time to establish a steady-state dichroism with shear

rate and temperature. Compared with the behaviour at the higher shear temperatures, shearing at the lower temperature levels of the polymers, for poly(A) at 80°C and for poly(A/B) at 55°C, required a slightly longer time to reach the steady-state values in infrared dichroism. The time to reach steady-state in the normal force was 10–40 s.

Figure 3 shows the steady-state values of the Hermans orientation function (f) for the mesogens of poly(A) and poly(A/B) on shearing. The director was chosen along the flow direction (circumferential direction). There was a pronounced decrease in f from 0 to $-$ 0.2 to $-$ 0.35 with increasing shear rate (*Figure 3*). The mesogens thus strived towards a perpendicular alignment with respect to the shear flow direction. Note that $f = -0.5$ corresponds to perfect perpendicular orientation of the mesogens. At the highest shear temperatures, both poly(A) and poly(A/B) showed a gradual decrease in the Hermans orientation function with increasing shear rate. Both polymers showed an increase in degree of orientation (thus a decrease in f) with decreasing temperature (*Figure 3*). One of the data points shown falls outside this general trend: poly(A/B) sheared at 10 s^{-1} and 55°C.

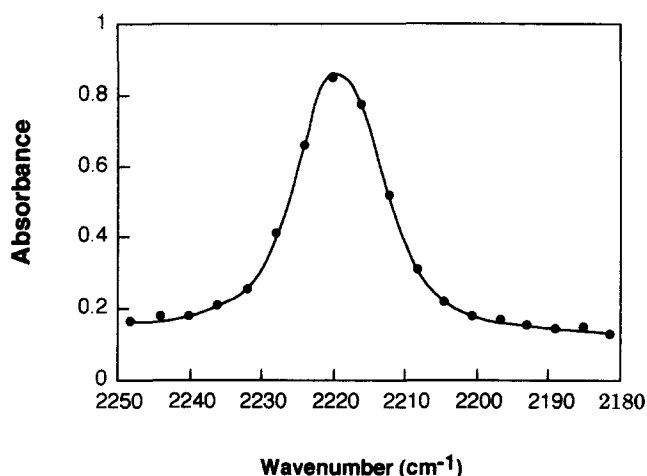The use of equation (1) to calculate f from the dichroic

Figure 2 Infrared spectrum of poly(A) showing the nitrile absorption band. The spectrum was obtained by a stepwise change of the monochromator setting
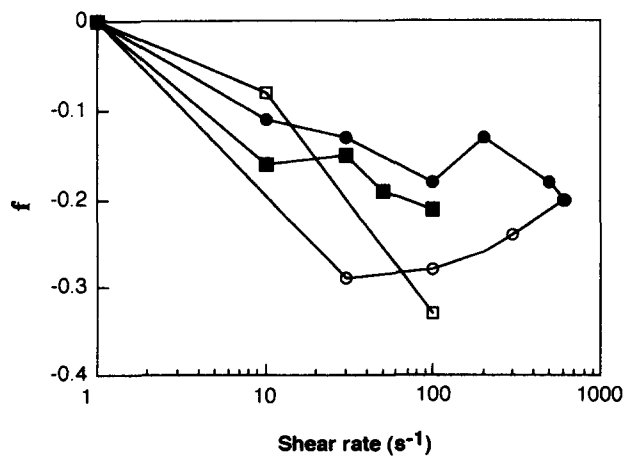

Figure 3 Steady state orientation values as a function of shear rate at different temperatures for poly(A): 120°C (●), 80°C (○); and poly(A/B): 70°C (■), 55°C (□)

ratio (*R*) assumes that the orientation of mesogens is uniaxial. This is not experimentally confirmed in this study. The study showed that there was a higher proportion of mesogens pointing in a direction perpendicular to the flow than parallel to the flow in the shear plane. The proportion of mesogens in the third direction, the velocity gradient direction ('thickness direction'), cannot be assessed by the used technique. It seems however unlikely that the stiff mesogens would align with a maximum of shear acting on them which rather should make them rotate and adapt the planar orientation.

Optical transparency was never obtained during shearing according to visual observation, which is different from the observations made by Kannan et al. [21] and Rubin et al. [22] on sheared nematic side-chain polymers, but similar to what was observed for smectics. They concluded that the shearing of the nematics led to an increase in domain size practically eliminating domains a few micrometres in size. The turbidity of our sheared smectic samples indicated that small domains were still present in the sheared samples despite the fact that the samples showed a considerable global orientation of the mesogens.

Figure 4 shows that the alignment of the mesogens of poly(A) is gradually lost after the cessation of shear. Full recovery was not achieved within a time period of 60 000 s and extrapolation to longer times indicated that it was unlikely to occur within 10^6 s. Poly(A/B) exhibited basically the same behaviour. There is considerable scatter in the recovery data and it is not meaningful to fit any particular model equation to the experimental data. The normalised relaxation time data for the samples sheared at a shear rate below 100 s^{-1} fell essentially on a single curve whereas the sample that was sheared at 500 s^{-1} showed a much slower relaxation. In fact, it seems that full recovery of a globally isotropic structure is not attainable. Kannan et al. [21] observed, after cessation of shear of a nematic side-chain polymer, a gradual increase in turbidity (i.e. a decrease in alignment), a process which took 1000 s to several 10 000 seconds depending on the conditions. This behaviour is clearly different from the behaviour of magnetic-field-aligned low molar mass liquid crystals, which preserve their high alignment after removal from the field [27].
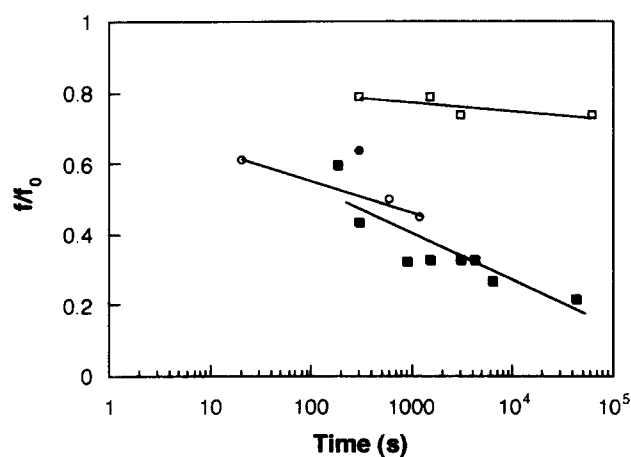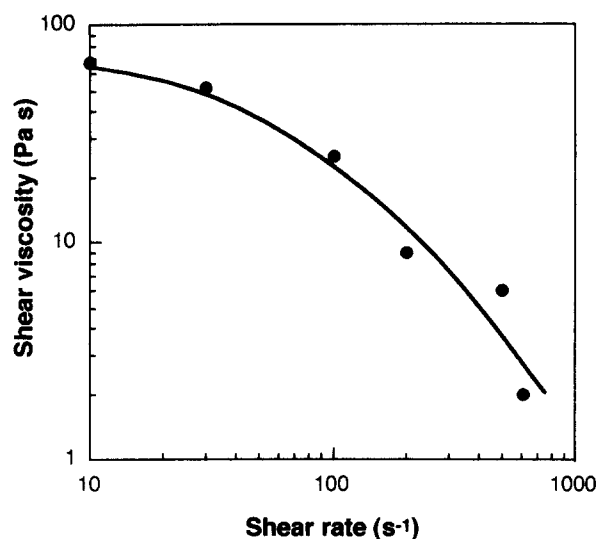

Figure 5 Steady-state shear viscosity at 125°C as a function of shear rate for poly(A)

All systems exhibited shear thinning (pseudoplasticity); the shear viscosity decreased by two orders of magnitude with an increase in shear rate from 10 to 1000 s^{-1} (*Figure 5*).

Conclusion

Smectic LC polymers of the side-chain type were aligned in a shear field. The mesogen groups were aligned perpendicular to the major flow direction. The highest observed value of the Hermans orientation function was about -0.35 (-0.5 corresponds to perfect perpendicular orientation). All polymers exhibited a slow and gradual relaxation of orientation after the cessation of shear, but full recovery to a fully isotropic state was not attained within 60 000 s. The studied polymers exhibited pseudoplasticity.

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Figure 4 Normalized Hermans orientation function ($f_{norm} = f(t)/f^0$; where $f(t)$ is the degree of orientation after time t after the cessation of shear, and f^0 is the steady-state value during shear) for poly(A) as a funtion of the time after the cessation of shear: (●) 10 s^{-1}, (○) 30 s^{-1}, (■) 100 s^{-1}, (□) 500 s^{-1}

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