

Rheology and flow-induced liquid crystal phase transitions in thermotropic polyethers

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This work investigates the interdependence of the phase behaviour, viscosity, temperature, molecular weight and shear rates of thermotropic liquid crystalline polyethers. The viscosity of the isotropic and nematic phases are quantitatively compared; a positive variation in viscosity with respect to temperature is found, with the isotropic viscosity being about an order of magnitude higher than the liquid crystalline viscosity. The dependence of viscosity upon molecular weight of well defined fractions is investigated in both the liquid-crystal and isotropic phases. In the liquid crystalline state the viscosity scales with $M^{3.5-5}$. Variations in the viscosity due to temperature changes affect the isotropic phase more than the liquid crystal phase. No evidence for a negative first normal stress difference is seen. Finally, it is shown how the phase diagram of the material can be altered by shearing the material in the isotropic phase. This is evident by the onset of a shear thinning region at temperatures slightly above T_i , which can be attributed to the formation of shear induced liquid crystallinity.

1. Introduction

The rheology of liquid crystalline polymers is characterized by a number of unusual phenomena: high shear thinning behaviour, low extrudate swell and often negative normal forces have been reported [1]. These rheological properties provide distinct advantages for processing in comparison to random coil isotropic melts; and processing in the liquid crystalline state can result in high molecular alignment and high modulus and mechanical anisotropy in the solid artefact, even at low shear rates. These properties are thought to originate in the ease of alignment of liquid-crystalline domains, providing an easy shear direction in the fluid.

For lyotropic systems this behaviour is quite well documented and understood. Generally, the viscosity of a thermotropic liquid crystal polymer is assumed to be higher in the isotropic state than in the liquid crystalline state. Thus, the viscosity of a polymer liquid crystal decreases with decreasing temperature. The majority of rheological data on thermotropic liquid crystals has been published on random aromatic copolyesters [2, 3], although some reports deal with copolyesters containing flexible methylene spacers [4, 5]. The positive variation of viscosity with respect to temperature was not found for these materials, although in some instances the isotropic state could not be attained prior to sample degradation or transesterification.

The explanations of the rheological behaviour of liquid crystals have concentrated predominantly on

the effect of shear on the domain texture (and hence director) of the liquid crystal. A rheo-optical study of Onogi and Asada [6] led them to propose a mechanism to account for the shear viscosity of polymer liquid crystals. A plot of the logarithm of the viscosity versus the logarithm of the shear rate shows three distinct regions. Region I encompasses low shear rates, where the material is shear thinning and flow occurs by the relative motion of the liquid crystal domains without a net orientation of the directors. In region II the viscosity is nearly constant and the increased shear rate breaks down some of the domains which then act as a solvent for the remaining domains. Lastly, in region III, the material is again shear thinning and the texture becomes a continuous monodomain structure oriented in the shear direction.

A molecular theory due to Doi [7] applies a Maier-Saupe type potential to the isotropic model to successfully describe many aspects of liquid crystal behaviour. The theory accounts for the discontinuity in viscosity between the isotropic and liquid crystalline phases; it cannot, however, address the problems of strong flows or polydomain textures encountered in real processing conditions. The Doi theory has been modified, however, to account for a polydomain structure of a sample under high shear rates by averaging the response of many individual domains [8, 9]. These modified theories have met some success in explaining the behaviour of lyotropic systems. They specifically predict that the effect of flow would be to move the phase transition boundary between isotropic and

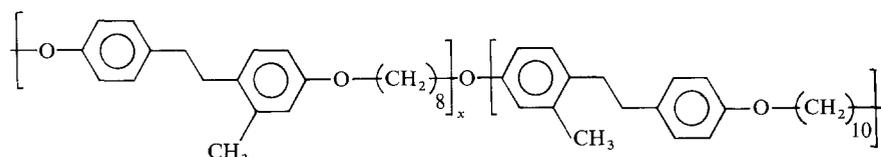
liquid crystal states, the flow orientation favouring the ordered liquid crystal state. In lyotropics this would produce a liquid crystal transition at lower concentrations under flow; in the thermotropic case it would produce a liquid crystal phase at a higher temperature.

The verification of these theories in thermotropic systems has been difficult because of the degradation and transesterification of the aromatic liquid crystals at high temperatures. Liquid crystal polyethers with flexible spacers in the backbone do not undergo transesterification reactions and have transition temperatures well below their degradation temperatures. These materials are, therefore, excellent candidates for rheological studies of polymer liquid crystals. This paper will focus on several aspects of polymer liquid crystal rheology which have not yet been reported in the literature. In particular, the interdependence of the phase behaviour, viscosity, temperature, molecular weight and shear rates are presented.

2. Experimental procedure

2.1. Material

The polymers used in this study had the structure



MBPE 8/10 (1-(4-hydroxyphenyl)-2-(methyl-4-hydroxyphenyl)ethane)

The polymer was a 50:50 mixture of flexible sequences consisting of eight and ten methylene units. There was a random placement of head-to-tail linkages of the mesogen and the flexible spacers.

The polymers were previously studied by simultaneous synchrotron X-ray analysis and differential scanning calorimetry [10]. The polymer was found to be an enantiotropic liquid crystal that exhibited a stable nematic phase at temperatures between 96 and 112 °C.

2.2. Fractionation

The material used in the determination of the phase behaviour performed earlier had a number average molecular weight M_n of 39 000 and a weight average molecular weight M_w of 74 000 (polydispersity = 1.90). In order to determine better the effects of molecular weight on the phase transitions and the rheological behaviour, the original material was fractionated into narrower molecular weight fractions. The fractionations were conducted according to the successive fractionation procedure [11] at 38 °C with toluene as the solvent and methanol the non-solvent. The collected fractions were dried overnight in a vacuum oven at 75 °C. The molecular weights were determined relative to polystyrene standards in chloroform at 40 °C. The molecular weights of each fraction are listed in Table I, and the corresponding gas permeation chromatography (GPC) traces are shown in Fig. 1 (fraction No. 3 was omitted since it was not used in the experiments because of its low yield).

It is evident that the molecular weight distributions of the fractions have been reduced relative to the original material, but some overlap of the traces occurs for each fraction. Nevertheless, the fractionation must be considered a success because a high and a low molecular weight tail have been removed in each successive fractionation. A comparison of molecular weights of samples before and after the rheological measurements indicated that no appreciable change in molecular weight occurred during the experiments.

2.3. Differential scanning calorimetry

The effect of the molecular weight on the phase transitions was investigated by differential scanning calorimetry (DSC). As an example of the phase behaviour of the MBPE-8/10 fractions, Fig. 2 illustrates the cooling and subsequent reheating curves of fraction No. 2 (recorded at 10 °C min⁻¹). The MBPE 8/10 polymers underwent two transitions on cooling from the isotropic melt; the first was the isotropic to nematic transition (T_i) occurring at 112 °C, and the second was the crystallization of the nematic phase at a lower temper-

TABLE I Molecular weights of fractions obtained

Fraction	M_D	M_w	M_w/M_n	Yield (mg)
Original	39.0	74.0	1.90	750.0
F1	80.7	127.0	1.57	98.7
F2	55.3	79.8	1.44	167.0
F4	32.4	45.4	1.40	89.8

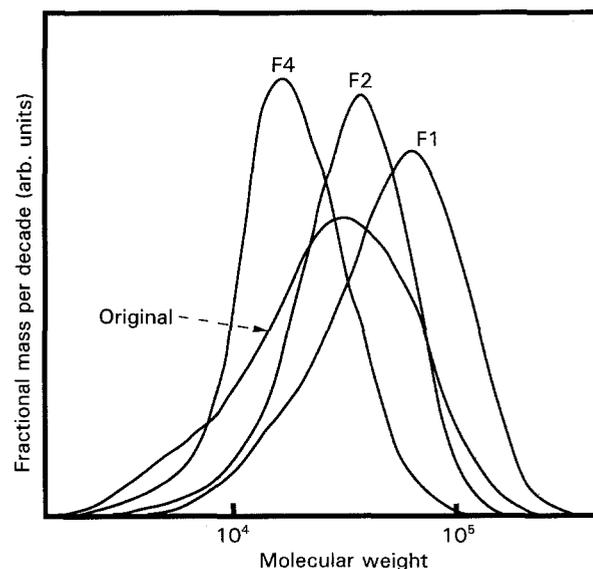


Figure 1 GPC traces of the original and subsequent fractions (F1, F2, F4).

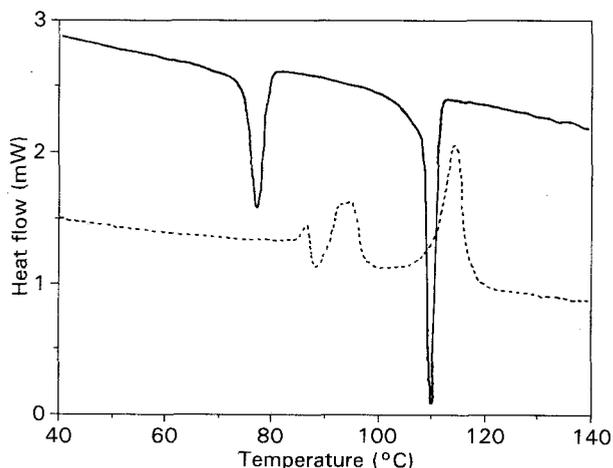


Figure 2 DSC trace of fraction No. 2 recorded on heating (dotted line) and cooling (solid line) at $10^{\circ}\text{C min}^{-1}$.

ature. The crystal melting endotherm was shifted to slightly higher temperatures on reheating, while the onset of the liquid crystal to isotropic transitions occurred at the same location. All molecular weight fractions exhibited identical phase behaviour; apparently the molecular weight was above a limiting value and had no effect upon the transition behaviour.

2.4. Rheology

The rheological determinations were conducted on a Rheometrics RMS-800 rheometer using the cone and plate fixture. The cone had a radius of 12.5 mm and an angle of 0.014 rad. A constant cone and plate separation of $10\ \mu\text{m}$ was used in all experiments. All experiments were allowed to reach thermal equilibrium prior to measurement and were conducted in a nitrogen atmosphere to limit sample degradation. Start-up experiments were conducted to determine the strain required to reach a steady state viscosity, and all viscosities were determined in the plateau region. As an example, Fig. 3 shows the stress as a function of time for fraction No. 1 on start-up and cessation of shear. In all samples the viscosity initially overshoots, going through a pronounced peak. The strain at which this peak occurred was around 100–200% and was invariant with molecular weight and strain rate. A steady state value for the viscosity was only attained after approximately 30–180 s depending upon molecular weight. A corresponding delay time was used before measurement for the frequency sweep experiments. The viscosities were recorded as the material was constantly and continuously sheared only in the clockwise direction (no reversal of direction was used).

The torque values recorded at the lowest strain rates were near the limitations of the rheometer. To determine the point at which the data became meaningful the baseline torque (the torque recorded with no sample) was subtracted from the recorded values. The experimental data reported were those which were larger than the lower limit of the rheometer. The torque was then converted to viscosity data using the appropriate equations. The shallow angle of the cone and the small cone and plate separation made the

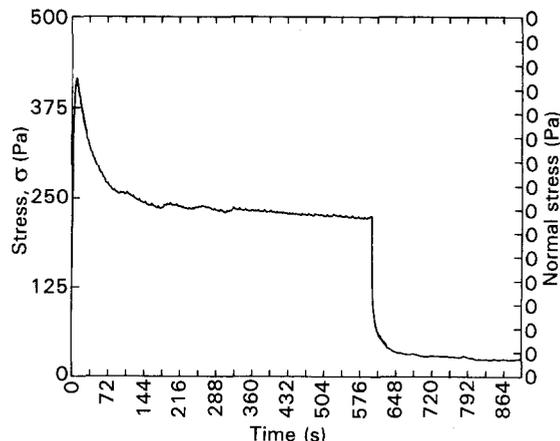


Figure 3 Stress as a function of time at the start-up and cessation of shear for fraction No. 1 (shear rate = $0.1\ \text{s}^{-1}$) at 103°C .

normal force measurements sensitive to small fluctuations in temperature. The thermal expansion and contraction due to the heater switching on and off created a background noise which made normal force measurements even more difficult. Even so, no evidence was seen of negative normal stresses. The oscillatory shear experiments were conducted with the cone and plate geometry with a strain of 1%. The rheometer was calibrated according to standard procedures prior to the measurements. Visual observation of the sample confirmed the occurrence of the phase transitions.

The previous shear history of the nematic phases was removed by heating the sample into the isotropic phase (this treatment was shown to remove shear history in reference [5]). This was repeated for each measurement. The time required for thermal equilibrium also provided for the total relaxation of the material prior to measurement.

3. Results

The start-up stresses shown in Fig. 3 were typical across all samples and strain rates. The stress overshoots by around 60% before settling back to a steady state value. As mentioned above, the time required for the achievement of the steady state stress was a function of molecular weight; high molecular weights require longer times. The settling times were 180, 45 and 30 s for fraction Nos 1, 2 and 4, respectively, when using a strain rate of $1\ \text{s}^{-1}$. These values were not strongly dependent upon strain rate. These settling times are significantly longer than those recorded on a liquid crystal polyester which contained 10 methylene spacer units [5]. The peak of the overshoot, however, occurred at essentially the same time for all samples, it varied with strain rate in such a way that it occurred at a constant value of total fluid strain of about 100–200%.

Fig. 4 illustrates the steady state viscosity as a function of shear rate for fraction No. 2 at five temperatures: the two lowest temperatures (103 and 108°C) were within the nematic phase, the two highest temperatures (118 and 140°C) represent the behaviour of

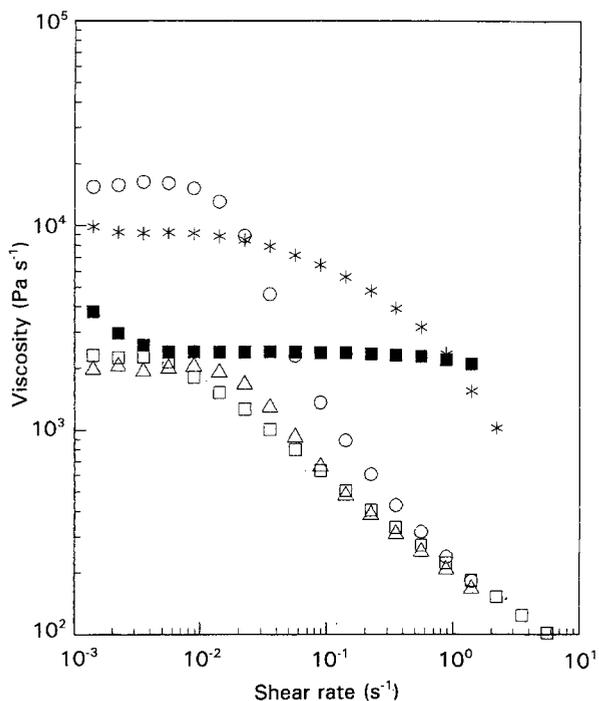


Figure 4 Viscosity as a function of shear rate and temperature for fraction No. 2. (\square) 103 °C, (\triangle) 108 °C, (\circ) 113 °C, ($*$) 118 °C, (\blacksquare) 140 °C, $M_w = 55$ K; baseline torque subtracted.

the isotropic phase, and the remaining temperature (113 °C) is slightly above the liquid crystal to isotropic transition temperature. The viscosity of the nematic liquid crystal did not vary significantly with temperature, as evident by the nearly superimposed curves for 103 and 108 °C. For both temperatures there was a plateau region at low shear rates, followed by a shear thinning region at higher shear rates. The viscosity of the isotropic phase was around one order of magnitude higher than the viscosity of the nematic phase (113 compared to 108 °C). The viscosity of the isotropic phase, however, decreased with increasing temperature (as shown by a comparison of 118 and 140 °C) in a manner typical of flexible polymers, such that the low shear rate viscosities at 103 and 140 °C were approximately equal.

The behaviour of the isotropic phase at temperatures only slightly above T_i was dramatic. At low shear rates there was an initial plateau in the viscosity, but as the shear rate increased the viscosity quickly decreased as the material became shear thinning. The shear rate required for the onset of shear thinning decreased as the temperature decreased. The transition occurred at 0.1 s^{-1} at 118 °C, but fell to 0.01 s^{-1} at 113 °C. The viscosity at 113 °C decreased and became similar to the viscosity of the liquid crystal phase at the highest shear rates. The viscosity at 118 °C also decreased with increasing shear rate, but it never equalled the liquid crystal viscosity with the strain rates used. There is no evidence of a shear thinning region in the behaviour observed at 140 °C.

Fig. 5 shows the viscosities of fraction No. 4 at the same shear rates and temperatures as shown for fraction No. 2. Generally, the behaviour was similar to fraction No. 2. The plateau and shear thinning regions of the nematic liquid crystal state appeared, and again

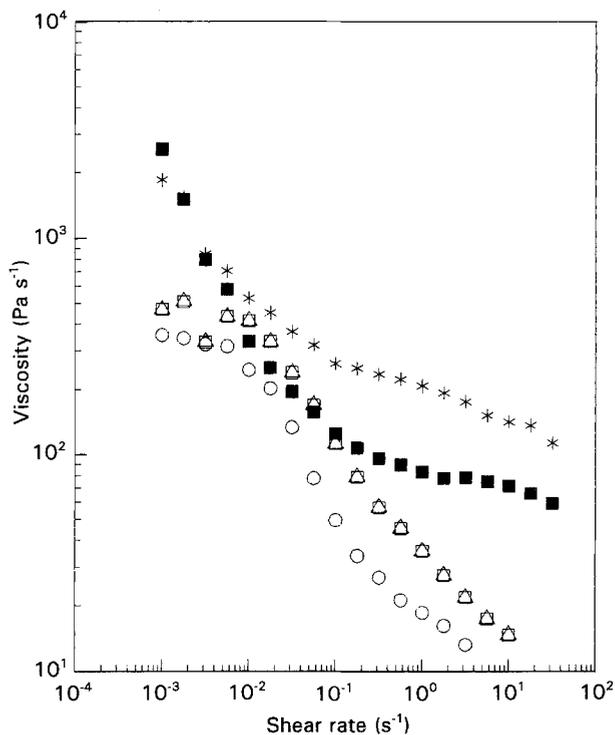


Figure 5 Viscosity as a function of shear rate and temperature for fraction No. 4. (\square) 103 °C, (\triangle) 108 °C, (\circ) 113 °C, ($*$) 118 °C, (\blacksquare) 140 °C, $M_w = 32$ K; baseline torque subtracted.

there was little change in the viscosity with temperature between 103 and 108 °C. The isotropic phase exhibited two shear thinning regions. The first being a steep decrease in viscosity at low shear rates and the second a more gradual decrease at higher shear rates. In the first region the viscosities at 140 and 118 °C were approximately equal, but as the shear rates increased the viscosity at 140 °C was reduced relative to the viscosity at 118 °C. Over most shear rates at these temperatures, again it was clear that the isotropic phase had a larger viscosity than the nematic phase. The largest difference in the behaviour between fraction No. 2 and fraction No. 4 concerns the viscosity recorded at 113 °C, just above the temperature at which the material becomes isotropic. The viscosity behaviour at 113 °C for fraction No. 4 was very similar to that seen for the nematic phase at 103 and 108 °C, throughout the strain rate range, the viscosity being about 30% lower than that recorded at 103 and 108 °C. This is in contrast to fraction No. 2 where the viscosity of the isotropic phase at 113 °C only approached that of the nematic phase beyond a shear rate of 1 s^{-1} .

The variation of the viscosity with molecular weight is displayed in the following two diagrams. In Fig. 6 the viscosity of the nematic phase at 103 °C as a function of shear rate is shown for the three molecular weight samples. Fraction Nos 2 and 4 exhibited the plateau and shear thinning region as previously mentioned, but the plateau region was absent for fraction No. 1. The most dramatic observation in Fig. 5 is the change in the viscosity with molecular weight. The viscosity increased by approximately two orders of magnitude with a 2.5 times increase in the molecular weight (fraction No. 4 to fraction No. 1, respectively).

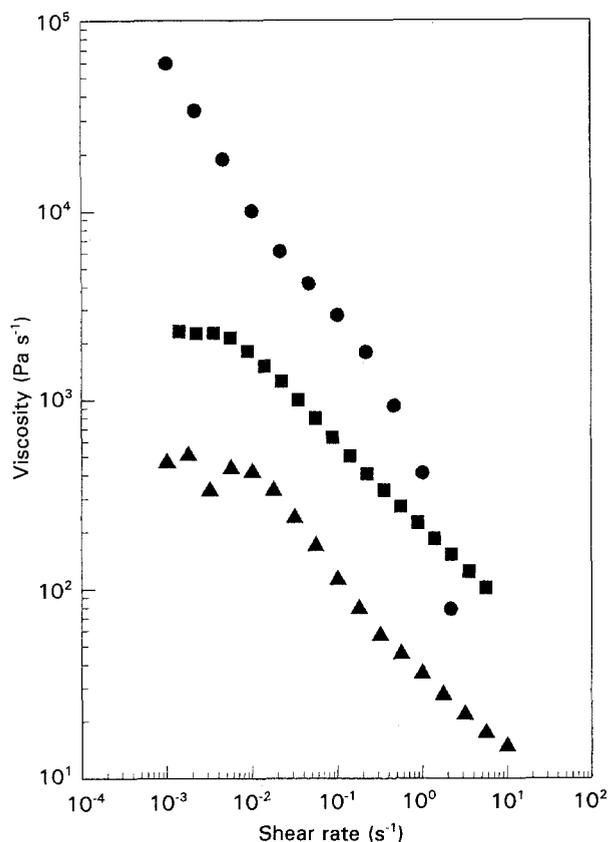


Figure 6 A comparison of the steady state shear viscosities of the three molecular weight fractions in the nematic state at 103°C. (●) fraction No. 1, $M_n = 80.7$ K; (■) fraction No. 2, $M_n = 55.3$ K; (▲) fraction No. 4, $M_n = 32.4$ K.

Comparing the low strain rate plateau viscosities of fraction Nos 2 and 4, would suggest a dependence of viscosity upon molecular weight to about the power of 3.5. Inclusion of the lowest shear rate results for fraction No. 1 (as a lower bound, since it has not reached a plateau) suggests an even higher dependence of viscosity upon molecular weight, around M^5 . The data at the highest shear rates for the fraction No. 1 are suspect because the sample began to flow out from between the cone and plate either because of centrifugal or elastic forces.

A more complete illustration of the effect of molecular weight on the viscosity of the isotropic phases is illustrated in Fig. 7. This is a replotting of the data already presented for fraction Nos 2 and 4. It is evident that the viscosity, regardless of the phase, is roughly an order of magnitude higher for fraction No. 2 at a given temperature. Qualitatively, the change in the viscosity with molecular weight was as great in the isotropic phase as the nematic phase.

On cessation of steady shear the stress takes a considerable time to decay away. Fig. 3 shows an illustrative example for fraction No. 1 at 103°C. This relaxation can be well described by a double exponential where the characteristic relaxation times depend upon molecular weight. At 103°C the fast and slow relaxation times for fraction No. 1 are 2s and 100s, while for fraction No. 4 they are considerably longer, at 5s and 1000s. In each case the slower time scale corresponds with the onset of banding in the optical texture and with the time scale for the relaxa-

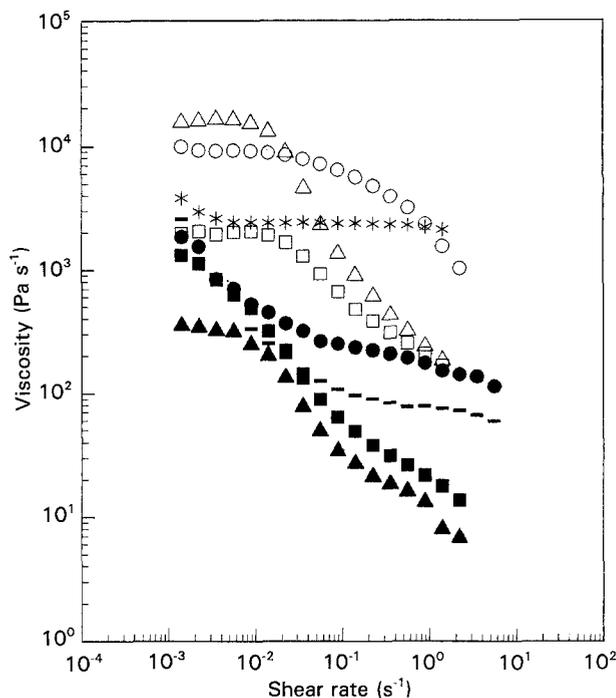


Figure 7 A comparison of the viscosities of fraction No. 2 and fraction No. 4 as a function of shear rate at four temperatures. Fraction No. 2: (□) 108°C, (△) 113°C, (○) 118°C, (*) 140°C. Fraction No. 4: (■) 108°C, (▲) 113°C, (●) 118°C, (-) 140°C.

tion of $\langle P_2 \rangle$ as assessed by X-ray diffraction [12]. Stress relaxation in the isotropic state occurs much more rapidly and is complete on a time scale of a few seconds; comparison with X-rays shows that the orientational order completely relaxes on this time-scale [12].

The final figure Fig. 8 compares the oscillatory shear behaviour of fraction No. 4 in the isotropic and nematic phases. The results were similar for each case; with increasing shear rates the storage modulus G' and the loss modulus G'' increased (resulting in an increase in $\tan \delta$) and the complex viscosity decreased. An amplitude of strain of 1% was used for these results.

4. Discussion

The low transition temperatures of the MBPE 8/10 polyether made it possible to investigate the rheological behaviour of both the anisotropic liquid crystal phase and the isotropic phase without sample degradation. The nematic liquid crystal phase was found to have a quite different flow behaviour to the isotropic phase; most notably the viscosity of the liquid crystal phase was much lower than the isotropic phase even though its temperature was lower. The positive dependence of the viscosity upon temperature has been explained by the ordered alignment of the molecules in the liquid crystal phase, which allows for easier movement relative to the random isotropic melt. This behaviour has been confirmed in a number of reports [4, 5] and has even been used to determine the phase diagram of a commercial main chain polyesteramide [13]. The viscosities of both the liquid crystal and isotropic phases decreased as the temperature increased, as expected for polymer melts. The effect of

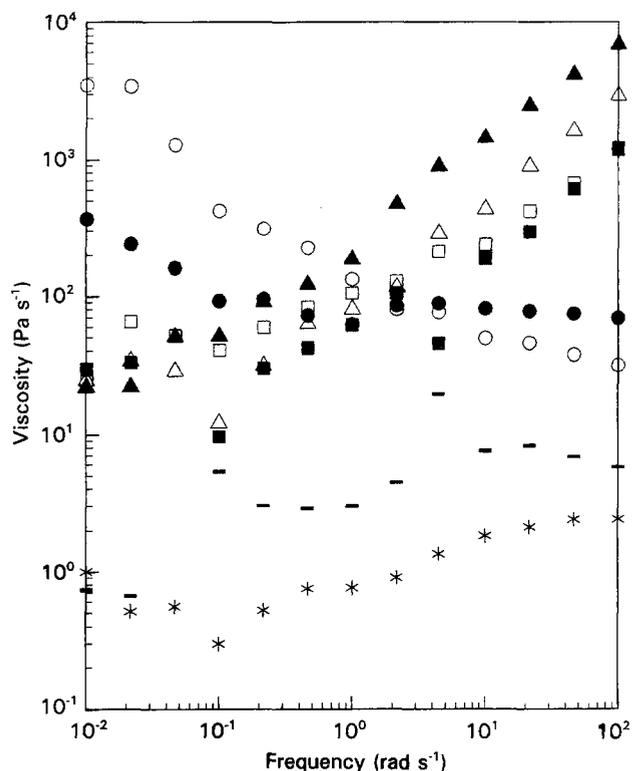


Figure 8 The oscillatory shear behaviour of fraction No. 4 at 140 °C (isotropic state) and at 105 °C (nematic state). $M_w = 32$ K. At 140 °C: (□) G' (Pa), (△) G'' (Pa), (○) η (Pa s^{-1}), (*) $\tan \delta$. At 105 °C: (■) G' (Pa), (▲) G'' (Pa), (●) η (Pa s^{-1}), (-) $\tan \delta$.

temperature was more pronounced on the isotropic phase: a change of five degrees from 113 °C to 118 °C resulted in a ten-fold drop in the viscosity for fraction No. 2 (see Fig. 4), while the same temperature change within the nematic state (103 and 108 °C) produced only negligible changes. The viscosity values used for 113 and 118 °C were those at the lower shear rates, before the onset of shear thinning which was due to a phenomenon discussed below.

The isotropic phase (at temperatures $\gg T_i$) exhibited near Newtonian behaviour, while the liquid crystalline phase exhibited two different flow regions. From Fig. 4 one can see that there is a plateau in the viscosity at low shear rates followed by a shear thinning region at higher shear rates. The Newtonian plateau and shear thinning behaviour has been observed in lyotropic systems, most notably PBLG [14] and PBZT [15]. This behaviour is typified by a region II to III transition as predicted by the theory of Onogi and Asada. Thus, if this were the case then the polymer would have been converted from a polydomain material into a monodomain structure, with a regular ordering of the directors about the shear direction. The ordering of the MBPE 8/10 polymer under shear has been determined through synchrotron X-ray experiments [12]. The orientation is found to be quite high corresponding to a $\langle P_2 \rangle$ value of 0.85. The plateau regions are absent in fraction No. 1; but because of the shift in the plateau to lower shear rates upon going from fraction No. 4 to fraction No. 2 one could expect the plateau to occur at shear rates lower than those used. If this were indeed region II, then the larger molecular weight would be expected to undergo

deformation of domains at lower shear rates because of the greater entanglement density and longer relaxation times of the higher molecular weight.

One might ask why one did not observe a region I (polydomain) shear thinning behaviour at the lowest shear rates. The shear rates used may not have been low enough, or perhaps the yield stress that occurs during start-up (see Fig. 3) corresponds to region I [5]. The yield stress and the higher viscosities at the lower shear rates indicate that some stress is needed to induce alignment and, therefore, facilitate flow. The initial stress could break down some of the domains but still leave a polydomain structure intact, which concurrently breaks down in the region II to III transition at higher shear rates. This would be in good agreement with the rheo-optic results of Onogi and Asada [6] and with results on PBLG [16] and thermotropic systems [17].

The start-up instabilities can also be accounted for by a numerical extension to Doi's molecular theory due to Larson [9], this does not require the break-up of domains. This theory predicts a transition in the motion of the mesogens from continuous tumbling, through a damped oscillation around the flow direction, to a steady state high orientation as shear rate is increased. At high shear rates start-up transients, very similar to those observed are predicted to occur at fixed low strains independent of the precise strain rate.

The sharp drop in the viscosity with increasing shear rates of the isotropic melt, at temperatures only just above T_i , to values similar to those of the liquid crystal phase, indicates that shear induces a liquid crystal like state from the isotropic phase. The alteration of a phase diagram by shear has been previously observed, where flow has been found to decrease the concentration required to form a lyotropic liquid crystal [13], and also it was both predicted [18] and found experimentally to extend the nematic region to higher temperatures [19]. The reasons for the extension or alteration of the phase diagram by shear is that, in addition to the thermodynamic order present in the liquid crystal or the isotropic melt, there is also a contribution from mechanical forces. A decrease in viscosity could result from either a local ordering of the polymers due to volume restrictions (the normal thermodynamic consideration) or from shear induced orientation of the molecules. The shear forces affect the Brownian motion of the molecules and leads to an increase in the stiffness of the molecules. The effect is more pronounced in semi-rigid polymers where flow fields increase the persistence length [13, 20]. Thus, in a system whose mesogen is based upon conformation isomerism, the effect could be expected to be quite large.

One is now in a position to discuss why the shear thinning behaviour is not observed at temperatures far from T_i and why the behaviour is dependent upon the polymer molecular weight. The key lies in the response time of the material to the shear flows in comparison to the relaxation rates of the molecular species. The relaxation time will decrease with both increasing temperature and decreasing molecular weight. Therefore, in order to observe the shear thinning behaviour

one would have to use increasingly higher shear rates as the temperatures were increased or the molecular weight decreased. This is observed in Fig. 4 for fraction No. 2, which shows that the shear rate at which the shear thinning region begins shifts from 0.01 s^{-1} to 0.1 s^{-1} for 113 and 118 °C, respectively, and that no shear thinning regions are observed at 140 °C. Since the relaxation times are a strong function of the molecular weight (maybe the sixth power [7]) the effects of molecular weight should also be significant. This is apparent in the comparison between the behaviour of fraction Nos 2 and 4; the isotropic phase of fraction No. 4 does not exhibit shear thinning at any temperature or shear rate.

Relaxation is essentially complete in a few seconds above the temperature at which the material becomes isotropic. This presumably reflects the strong entropic driving force towards disorder in the isotropic state. This is entirely consistent with the observed molecular disorientation from X-ray synchrotron diffraction experiments [12].

The molecular weight also affects the magnitude of the viscosity, as illustrated in Figs 7 and 8. The viscosity of both the liquid crystal and isotropic phases increased as the molecular weight increased. In the MBPE 8/10 system, the viscosity of the liquid crystalline phase was found to scale to the power of $M^{3.5}$ to M^5 . The molecular weight dependence of viscosity in the isotropic phase is not as clear since only two data points are available, but the results show that fraction No. 2 is around ten times the viscosity of fraction No. 4 over most of the shear rate range and at both 118 and 140 °C. This corresponds to an approximately viscosity scaling dependence of M^4 , this is broadly in line with the expectation for the scaling of viscosity for an isotropic entangled melt $M^{3.4}$ and with the predictions of reptation theory [21].

The lack of great differences observed in the oscillatory behaviour could be either a temperature effect or it could be due to the low strain of 1% used in the experiment. This strain is much lower than that required to overcome the start-up effects (100–200%) and so may not be large enough to create structural changes within the material. It has been shown that the strain amplitude does not affect the liquid crystal state oscillatory properties, but it did affect the isotropic melt results; however those authors used much larger strains than that used here [22]. Further investigations at a variety of strains and temperatures would be required before making definite conclusions about the MBPE 8/10 system.

5. Conclusions

This work has increased the knowledge of the rheological properties of thermotropic liquid crystals in several ways. First, the viscosity of the isotropic and nematic phases has been quantitatively compared; the material had a positive variation in viscosity with respect to temperature, with the isotropic viscosity being about an order of magnitude higher than the

liquid crystalline viscosity. Second, the dependence of viscosity upon molecular weight has been investigated in both the liquid-crystal and isotropic phases. The variations in the viscosity due to temperature changes affected the viscosity of the isotropic phase more than the liquid crystal phase. No evidence for a negative first normal stress difference was seen. Finally, it was shown how the phase diagram of the material can be altered by shearing the material in the isotropic phase. This is evident by the onset of a shear thinning region at temperatures slightly above T_i which was attributed to the formation of shear induced liquid crystallinity.

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