

Rheological properties of some thermotropic liquid crystalline polymers

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Abstract

Rheometry testing and the DSC measurement of five thermotropic liquid crystalline polymers (TLCP) have been carried out. The dynamic viscosities of the five TLCPs show a typical shear-thinning behaviour obeying the power-law with the power indices from 0.2 to 0.3. When these TLCPs are heated above the melting temperatures determined by the DSC measurements, the dynamic viscosities first rapidly decrease by 2~3 orders of magnitude then level off, finally increase gradually with the further increasing of temperature. The steady shearing exhibited the same behaviour as the dynamic shearing, but serious edge fracture of material slippage out of the plates occurred. The abnormal temperature dependence of the viscosities can be explained by the nematic-isotropic transition. By using the concept of activation energy, we propose a simple model which can fit the shear-thinning behaviour quite well and predict qualitatively correct temperature effects.

Keywords: thermotropic liquid crystalline polymers, viscosity, temperature effects

1. Introduction

The rheology of thermotropic liquid crystalline polymers (TLCP) is a topic of practical importance because of their unique properties; these include low coefficients of thermal expansion, low viscosity in melting states, high modulus, low permeability to gases and chemical resistance. Rheological studies can provide effective means of improving the processes of TLCPs or blends of TLCPs with conventional isotropic polymers. There have been numerous studies on the rheological behaviour of TLCPs in the last two decades (Chan *et al.*, 2001; Gao *et al.*, 1996; Graziano and Mackley, 1983; McLeod and Baird, 1999; Wilson and Baird, 1992). The main features observed may be summarized as follows: 1) in the liquid crystalline phase TLCPs possess much lower viscosities than their isotropic counterparts; 2) TLCPs may show multiple melting behaviour in the DSC measurement, and in the range of high temperature a transition from nematic phase to isotropic phase may occur, making the viscosity increase as the temperature increases (Hsieh *et al.*, 1999); 3) TLCPs usually exhibit little or no die swell and sometimes a negative normal stress difference; 4) some TLCPs have a three-zone dependence of viscosity, i.e., a shear thinning zone at very low shear rate, a plateau region of nearly constant viscosity and another shear thinning zone at high shear rate (Walker and Wagner, 1994). In reality the rheology of TLCPs varies

significantly, and a comprehensive theory or molecular model that can explain or predict the observed complex behaviour has not yet been established.

In this study we have accomplished dynamic and steady shearing tests, as well as DSC measurements, of some TLCP materials. In order to understand the observed temperature effects on the viscosities we propose a semi-empirical model by using the concept of activation energy and examine its performance in predicting the viscosities of these materials.

2. Experimental

Five aromatic nematic TLCP samples were provided by MOLDFLOW Pty. in the form of pellets. These materials are named by the production serial number as follows: 1712 (Sumikasuper E6807LHF), 1741 (Titan LG441), 1746 (Vectra T840), 1768 (VENO LCP 2030G), 1769 (VENO LCP 6040GM).

The samples were first dried in a vacuum oven according to recommended drying time and temperature listed in the data sheet prior to any use. For differential scanning calorimetry (DSC) the dried pellet was used immediately on removal from the vacuum oven. The measurements were performed on a TA Instruments DSC 2920 Modulated. The test samples ranged in weight from 10 to 15 mg, as determined using a [®]Sartorius digital high precision scale. In testing, the samples were heated from room temperature to 400°C, at which it was held for 2 min to establish thermal equilibrium. It was then cooled to 40°C and reheated to 400

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°C. All the heating and cooling were carried out at a rate of 10°C/min under a protective nitrogen atmosphere.

For the rheometry study, the dried pellets were compressed into discs with a thickness of 2 mm and a diameter of 25 mm. The dynamic oscillatory shear and steady shear tests were carried out on a Bohlin VOR rheometry using a parallel plate fixture with a 25 mm diameter. Prior to any test the zero-gap between the parallel plates was calibrated at the required temperature. In the measurements, the sample was placed between preheated fixtures and 10 min were allowed to reach thermal equilibrium, then the gap was set to 1 mm. The fixtures and sample were enclosed in a high temperature chamber purged with dry nitrogen at about 5 atm pressure. For temperature changes, the control

system needs about 5 min to reach a target equilibrium temperature with an error of 1°-2°. For dynamic oscillatory shearing the linear viscoelastic region of 1% strain was first obtained by strain sweep tests and no preshear was applied. The measurement consisted of up- and down frequency sweeps between 0.1 Hz and 10 Hz at a constant temperature, and the average values of the dynamic modulus G' , G'' , dynamic viscosity η^* were obtained from the up- and down sweeps. In steady shearing, the range of shear rate was set from 0.11/s to 11.0/s and we confronted with serious edge fracture or slippage of the materials out of the plates. Edge fracture is an instability phenomenon in cone-plate and parallel plate flows of viscoelastic liquids and suspensions, it is believed to be caused by the second nor-

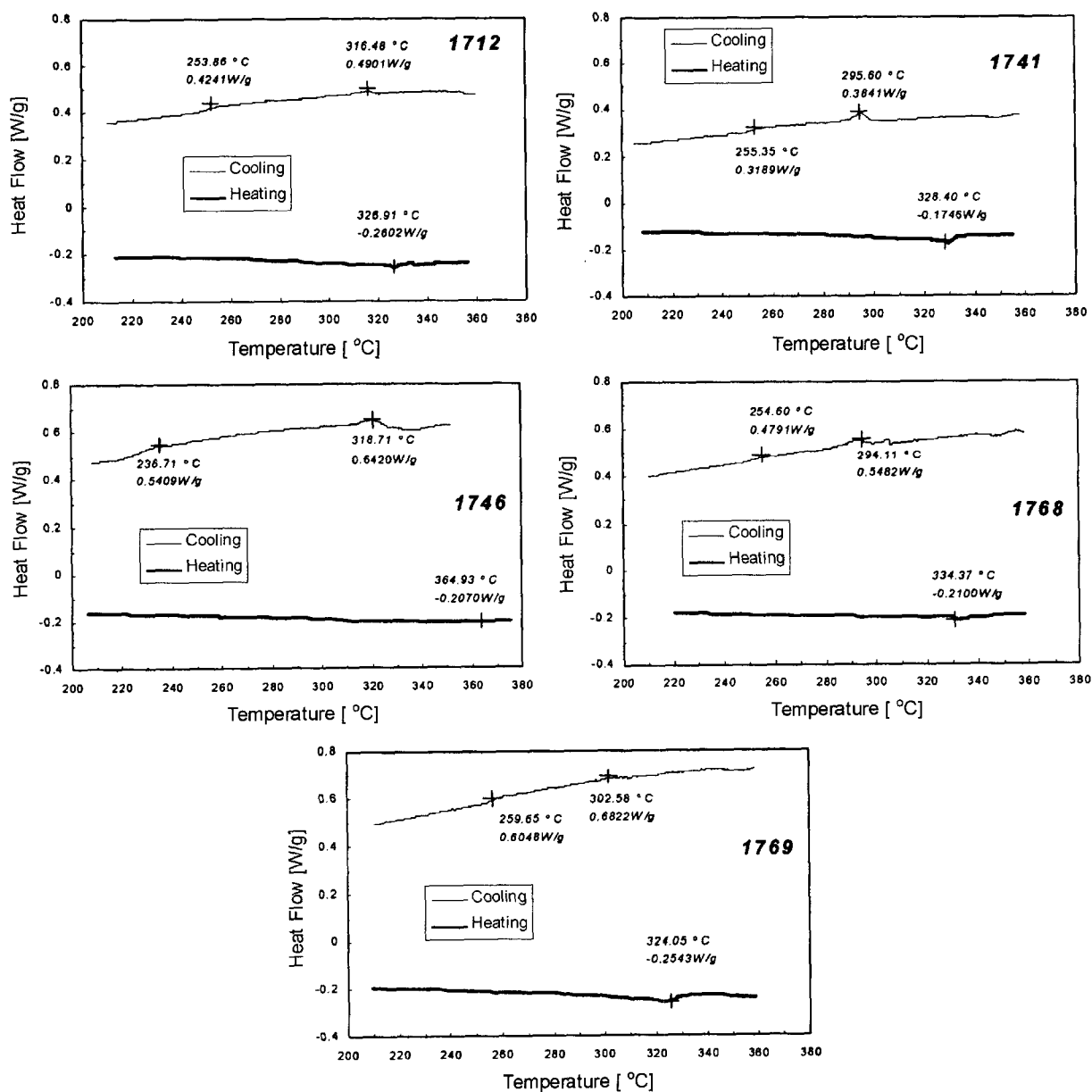


Fig. 1. DSC thermographs for the material 1712,1741,1746,1768,1769; the heating and cooling rate is 10°C/min.

mal stress difference in steady shearing flows (Keentok and Xue, 1999). At the present stage little is known about the second normal stress difference of TLCPs and we found it very difficult to eliminate the edge fracture even by further reducing the shear rate. Thus the data of steady shear viscosity are not quantitatively reliable and in this study we will concentrate on analysing the results of dynamic viscosity.

3. Results of DSC measurement

The DSC thermograms for the materials 1712, 1741, 1746, 1768 and 1769 are shown in Fig. 1 and reveal several transitions. The qualitative behaviours of all the five materials are similar: The heating curve exhibits only a weak endothermal peak which we judge to be associated with the crystalline-to-nematic melt transition and the corresponding material can be easily processed above this temperature. The cooling curve exhibits two exothermal peaks, one of them we judge to be the delayed melting temperature while another may be the glass transition temperature. From these thermograms we can conclude the melting temperature of the materials 1712, 1741, 1768 and 1769 is

approximately 330°C while that of the material 1746 is about 360°C. Our later dynamic and steady shearing measurements confirmed these observations.

4. Results of rheological measurement.

Fig. 2 to 6 present the magnitude of the measured dynamic viscosity $|\eta^*|$ for the materials 1712, 1741, 1746, 1768, 1769, respectively. The viscosity-frequency curves exhibit typical shear thinning of the power law and the curves are parallel for various temperatures implying that for one material a unique power-law index can be found to represent the dynamic viscosity at different temperatures. Similar behaviours were observed in steady shearing tests but with stronger shear-thinning behaviours, partly due to the material slippage out of the plates. In the range of our experiments no constant-viscosity plateau was found even with frequencies (shear rates) much lower than that depicted in the figures. One can observe three stages in the viscosity-temperature behaviours: at the first stage, with the temperature increasing from the melting temperatures determined by the DSC measurements, the dynamic vis-

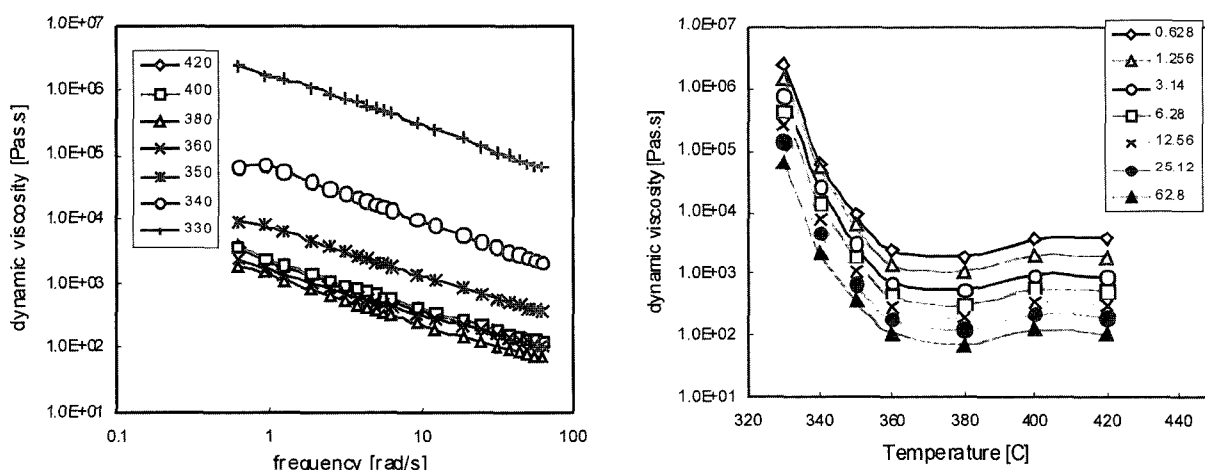


Fig. 2. Measurements for the material 1712; dynamic viscosity versus the frequency and the temperature.

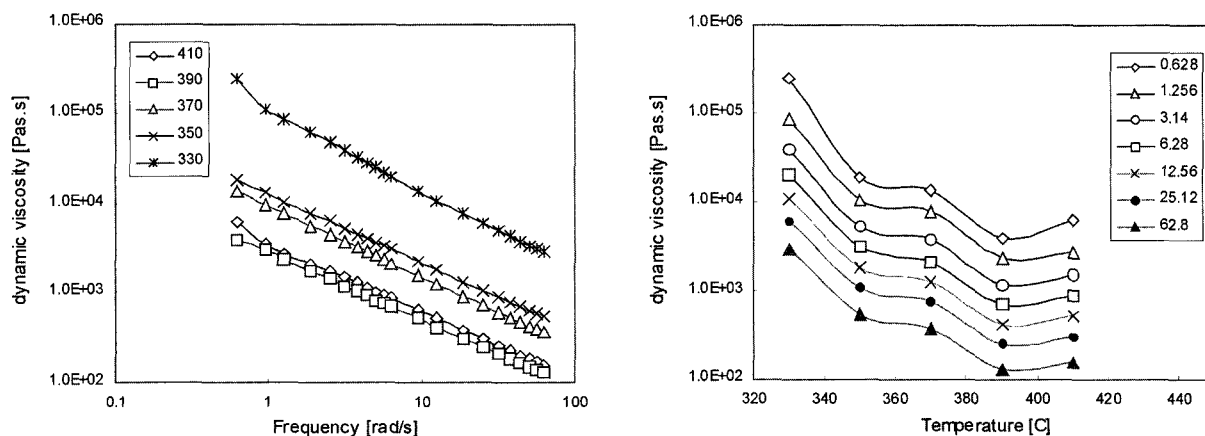


Fig. 3. Measurements for the material 1741; dynamic viscosity versus the frequency and the temperature.

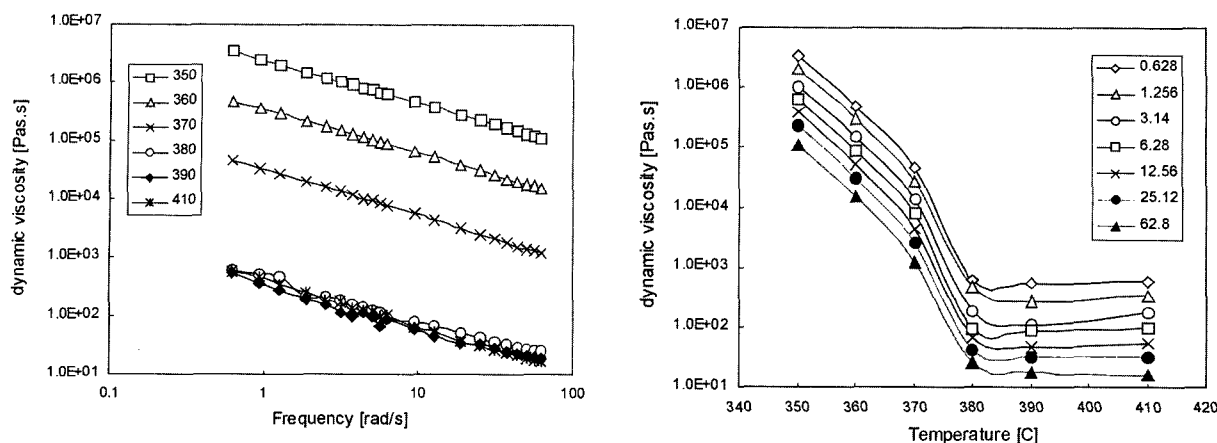


Fig. 4. Measurements for the material 1746; dynamic viscosity versus the frequency and the temperature.

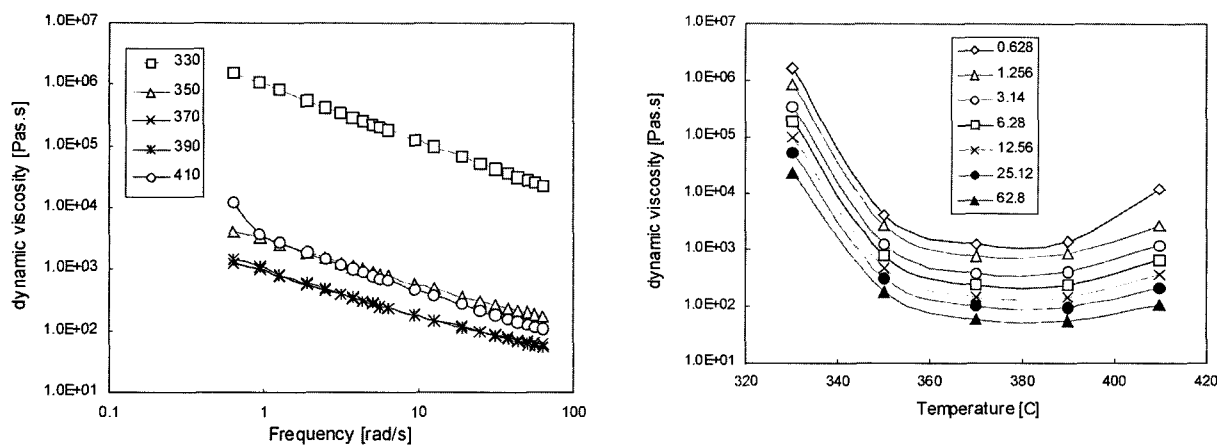


Fig. 5. Measurements for the material 1768; dynamic viscosity versus the frequency and the temperature.

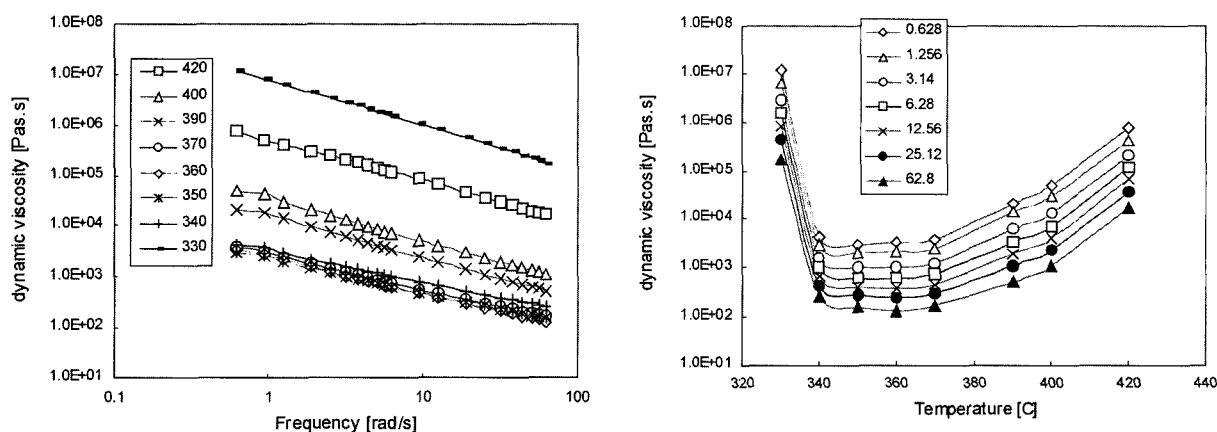


Fig. 6. Measurements for the material 1769; dynamic viscosity versus the frequency and the temperature.

cosities decrease rapidly by 2~3 orders of magnitude; at the second stage, the dynamic viscosities level off; and at the third stage the viscosities gradually increase with the further increasing temperatures. The dramatic decreasing of viscosity with increasing temperature is a typical behaviour of TLCPs, it can be well understood by the solid-nematic phase transition where the stiff rod-like molecules are

aligned preferentially along the shear direction and the liquid is positionally disordered but orientationally ordered. The gradual increases of viscosities at higher temperatures can be attributed to the biphasic nature of these TLCPs, that is, due to thermal activation, part of the rod-like molecules become a more viscous isotropic phase and the increase of temperature gives rise to increasing portion of

isotropic phase at the expense of anisotropic phase (Guo *et al.*, 1996; Hsieh *et al.*, 1999). The level of the nematic-isotropic transition is marginal for the material 1746 but is remarkable for the material 1769. Hsieh *et al.* (1999) observed a similar temperature effect of the nematic-isotropic phase transition in their experiments on two aromatic nematic TLCPs. However, temperature effect on the lyotropic liquid crystalline polymers may be different from that of thermotropic liquid crystalline polymers, for example, Mewis and Moldenaers (1987) found that the steady and dynamic viscosity of their lyotropic samples monotonically decrease with temperature increasing and can be reduced to master curves by using the limiting values of zero shear rate or zero frequency as the shift factors. Here

it is obvious that the time-temperature superposition rule for polymer melts can not be applied to these TLCP materials.

5. Modeling the dynamic viscosity

The flow of liquids can be conceptually modeled as an activated process of driven molecular motion. The activation energy controlling the rate of molecular motion can often be related to the molecular structure of the fluid (Bird *et al.*, 1960). The classical formulation for the temperature dependence of viscosity can be expressed as

$$\ln(\eta) = A_0 + \frac{\Delta G}{RT} \quad (1)$$

Table 1. Parameters of the equation (2) obtained by using the least-square method to fit the experimental data

Material No.	1712	1741	1746	1768	1769
K	68.35	49.54	1.681	68.45	88.76
N	-0.7369	-0.7927	-0.7477	-0.7735	-0.7611
$\Delta G_0/R$	101.23	204.34	138.14	90.71	105.33
T_0 (°C)	320	300	340	320	320
T_c (°C)	380	390	380	380	370

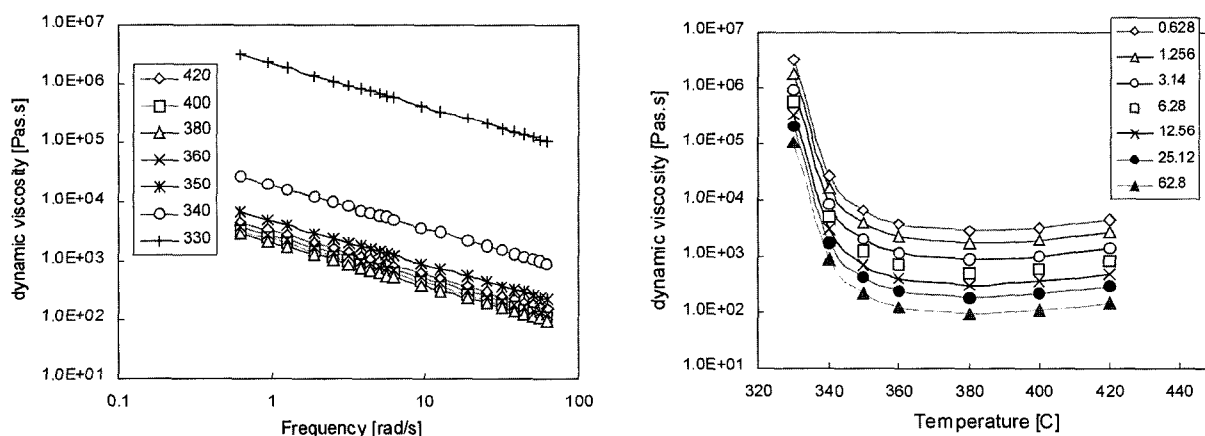


Fig. 7. Predictions for the material 1712; dynamic viscosity versus the frequency and the temperature.

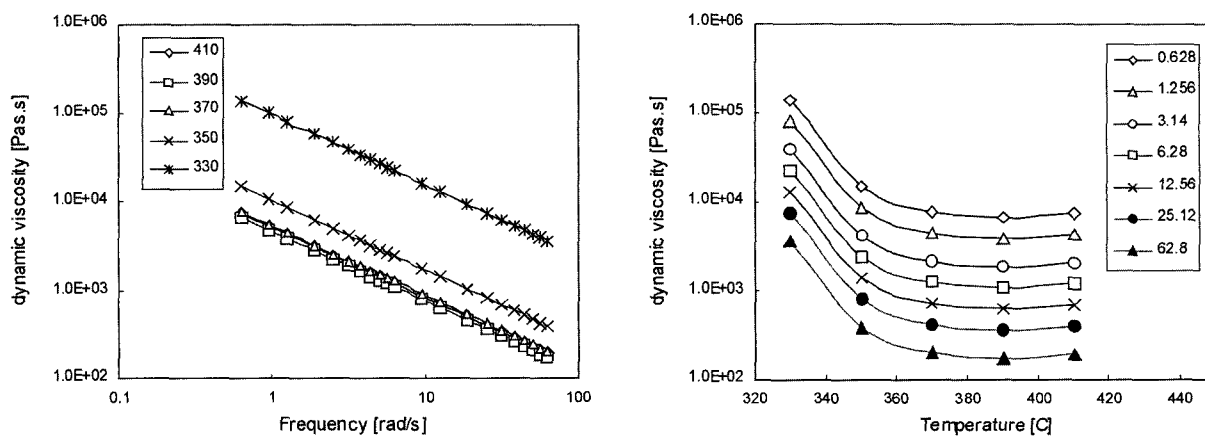


Fig. 8. Predictions for the material 1741; dynamic viscosity versus the frequency and the temperature.

where ΔG is the activation energy, R the gas constant and T the absolute temperature. For our TLCP materials the viscosities have a strong shear thinning character obeying the power law, thus A_0 should be a function of the frequency or shear rate. The equation (1) predicts monotonic decreasing viscosity with temperature increasing for common liquids whose activation energies are approximately

constant. In order to take into account the abnormal temperature dependence of our TLCP materials, we assume that there is a critical temperature, T_c , above which the nematic-isotropic phase transition makes significant contribution to the activation energy such that the viscosity starts to increase with the temperature. By allowing the activation energy to be a function of temperature, we pro-

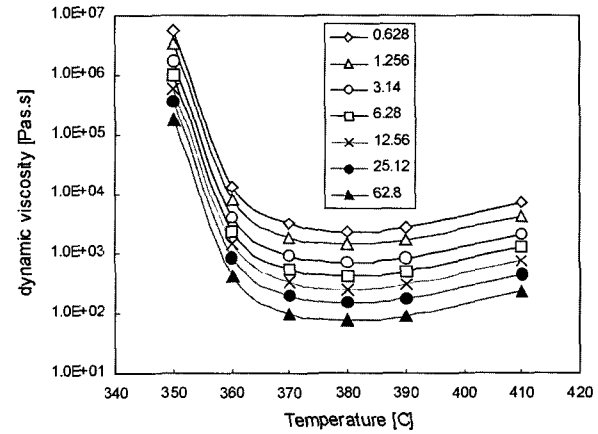
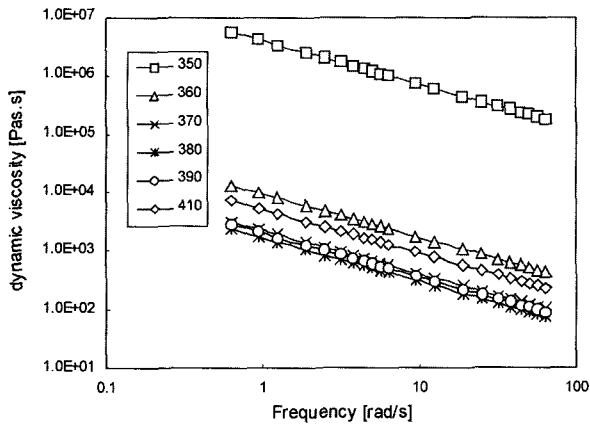


Fig. 9. Predictions for the material 1746; dynamic viscosity versus the frequency and the temperature.

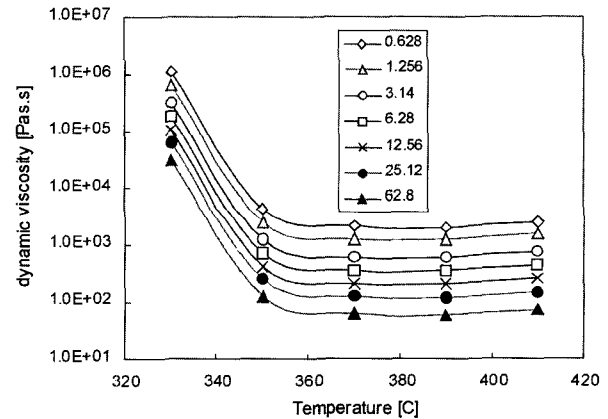
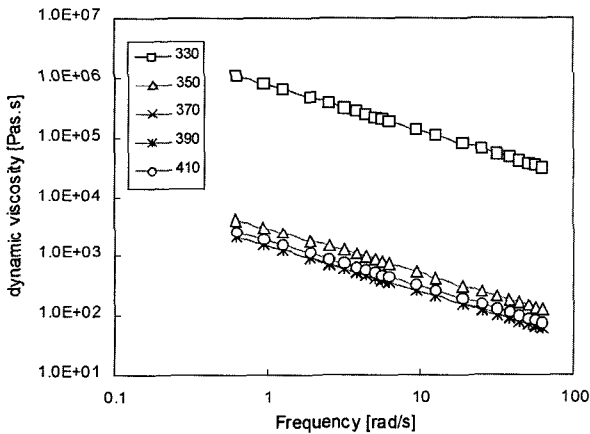


Fig. 10. Predictions for the material 1768; dynamic viscosity versus the frequency and the temperature.

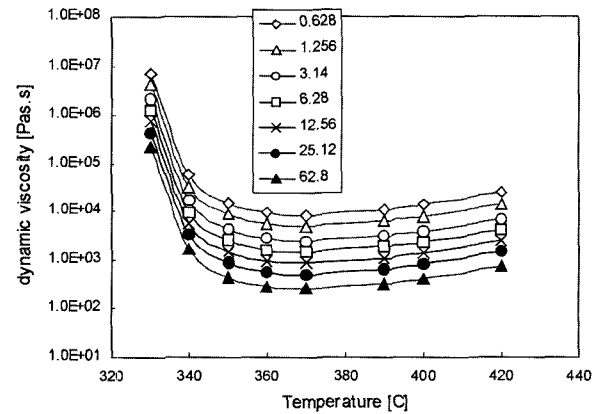
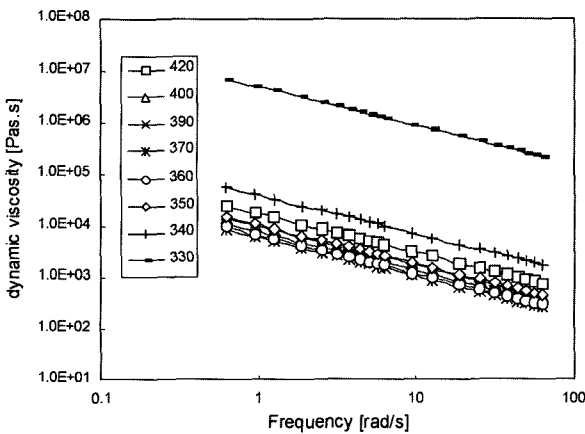


Fig. 11. Predictions for the material 1769; dynamic viscosity versus the frequency and the temperature.

pose the following modification of the equation (1),

$$|\eta^*| = K\omega^n \exp\left[\frac{\Delta G_0}{R(T-T_0)}\left(1 + \frac{(T-T_0)^2}{(T_c-T_0)^2}\right)\right] \quad (2)$$

where K , ΔG_0 are constants, ω the angular frequency, n is the power index. At the temperature T_0 the viscosity becomes infinite. It seems reasonable that T_0 is taken as lower than but near the melting temperatures determined by the DSC measurements. If T_0 is chosen to be the absolute zero temperature, the matrix produced in the two-dimensional data fitting would be near singular. The formulation (2) satisfies the condition of minimum viscosity at the critical temperature, *i.e.*,

$$\frac{\partial |\eta^*|}{\partial T} = 0 \quad \text{at } T=T_c \quad (3)$$

By inspecting the experimental curves we can a priori choose the values of T_c and T_0 . Then the parameters left to be determined are K , n and G_0 . The set of independent data is two-dimensional, it consists of the experimental frequencies and temperatures. We employed the least square method to fit the measured dynamic viscosities, frequencies and temperatures according to the function (2), the corresponding values of the parameters obtained for the five TLCPs are listed in Table 1. Fig. 7 to 11 graph the predicted dynamic viscosities of the five TLCPs, respectively, by using the equation (2). Comparing with the experimental results, Fig. 2 to 6, one can observe that this model predicts the shear-thinning behaviors quite well. As to the variation with temperature, this model gives rise to the correct orders of magnitude and the trend of rapid decreases followed by gradual increases of the dynamic viscosities with the increase of temperature.

6. Conclusion and discussion

The dynamic viscosities of the five TLCPs show a typical shear-thinning behavior obeying the power-law with the power indices from 0.2 to 0.3. As to the temperature effects, the dynamic viscosities first rapidly decrease by 2~3 orders of magnitude as these TLCPs are heated above the melting temperatures determined by the DSC measurements, then the viscosities level off and increase gradually with the further increasing of temperature. The abnormal temperature dependence of the dynamic viscosities can be explained by the nematic-isotropic transition, in which the rod-like molecules lose part of their orientation ordering and become partially isotropic. Based on the concept of activation energy, which should be linked with the molecular configuration, we propose a simple model which can fit the shear-thinning behaviours quite well and predict qualitatively correct temperature effects.

Table 2. Suggested values of the ratio between the steady-shear viscosity and the dynamic-shear viscosity

Material No.	1712	1741	1746	1768	1769
Y	0.022	0.031	0.037	0.0066	0.0004

As we mentioned in section 2, in steady shearing tests we confronted with serious edge fracture or material slippage out of the plates. Thus the steady-shear viscosities measured are not quantitatively reliable. The problem of slippage needs to be addressed and overcome in future investigations. However, qualitatively, the steady-shear viscosities of the five TLCPs show the same shear-thinning behaviors and the same temperature effects as the dynamic-shear viscosities. Based upon the experimental data obtained, we recommend a modification factor, Y , that should be multiplied to the dynamic-shear viscosities to obtain the approximate steady-shear viscosities, provided that the angular frequency ω in the equation (2) be replaced with the shear rate, $\dot{\gamma}$. Table 2 lists the suggested values of Y for the five TLCPs, they are crude estimates of the ratios for possible industrial applications.

References

- Bird, R.B., W.E. Stewart and E.N. Lightfoot, 1960, *Transport Phenomena*, John Wiley & Sons, Inc.
- Chan, C.K., C. Whitehouse, P. Gao and C.K. Chai, 2001, Flow induced chain alignment and disentanglement as the viscosity reduction mechanism within TLCP/HDPE blends, *Polymer*, **42**, 7847-7856.
- Gao, P., X.H. Lu and C.K. Chai, 1996, Rheology of low nematic transition temperature thermotropic liquid crystalline copolyester HBA/HQ/SA, *Polym. Eng. Sci.*, **36**, 2771-2780.
- Graziano, D.J. and M.R. Mackley, 1983, Stress relaxation after oscillatory shear in a thermotropic liquid crystalline polymer, *J. Non-Newt. Fluid Mech.*, **13**, 243-257.
- Hsieh, T.T., C. Tiu, G.P. Simon and R.Y. Wu, 1999, Rheology and miscibility of thermotropic liquid crystalline polymer blends, *J. Non-Newt. Fluid Mech.*, **86**, 15-35.
- Keentok, M. and S.C. Xue, 1999, Edge fracture in cone-plate and parallel plate flows, *Rheol. Acta*, **38**, 321-348.
- McLeod, M.A. and D.G. Baird, 1999, The crystallization behavior of blends of thermotropic liquid crystalline polymers, *Polymer*, **40**, 3743-3752.
- Mewis, J. and P. Moldenaers, 1987, Effect of temperature on the rheology of polymeric liquid crystals, *Chem. Eng. Comm.*, **53**, 33-47.
- Walker, L. and N. Wagner, 1994, Rheology of region I flow in a lyotropic liquid-crystal polymer: the effects of defect texture, *J. Rheol.*, **38**, 1525-1547.
- Wilson, T. S. and D.G. Baird, 1992, Transient elongational flow behavior of thermotropic liquid crystalline polymers, *J. Non-Newt. Fluid Mech.*, **44**, 85-112.