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Rheology of a Semi-Rigid Thermotropic Liquid Crystalline Polymer

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Summary: In this work the rheological behaviour of different M_w samples of a thermotropic liquid crystalline polymer (TLCP), the random copolymer HBA/HNA 73/27 produced by Ticona, has been investigated. The linear viscoelastic behavior has been discussed. The G' (shear storage modulus) and G'' (shear loss modulus) have been monitored as a function of frequency and of different annealing times. Rheological data obtained in steady state conditions have been used to define the viscosity flow curves for the different M_W samples. In all the cases a three regions flow curve has been detected, with the plateau zone being M_w dependent.

Keywords: rheology; TLCP; viscoelasticity

Introduction

In last 30 years, the new class of liquid crystalline polymers (LCPs) has been developed and has received a great deal of attention from both industry and academia. The state of their solutions (*lyotropic LCPs*) or melts (*thermotropic LCPs*) is between the boundaries of solid crystals and isotropic liquids. The importance of these materials stays in the good balance between the good processing and mechanical properties (*strength* and *stiffness*) of the final products. Most of the industrial applications concern the thermotropic LCPs (TLCPs), whereas the lyotropic LCPs have been mainly used as model materials to validate the theoretical predictions[1].

Main-chain liquid crystal polymers (TLCPs) can be either wholly aromatic or can contain flexible spacers in the backbone (semi-flexible TLCPs). The semi-flexible TLCPs, however, remain of academic interest due to their quite poor mechanical and thermal properties and high solubility in common solvents. On the other hand, the wholly aromatic TLCPs show outstanding physical properties and excellent chemical resistance finding many industrial applications[2]. Usually they are random copolymers synthesized from different aromatic units that can be melt-processable with the conventional plastics processing techniques[3]. Many experimental works have shown that both lyotropic and thermotropic LCPs are characterized by unusual rheological behaviours such as the

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existence of a three regions steady state viscosity flow curve[4-5], damped oscillations of the shear and normal stress in transient experiments[6-9]. Recently, the attention of the literature has been focused on the microstructure development of TLCPs under shear flow and the related interconnections with the rheological behaviour[10-12].

In this work the rheological properties of the HBA/HNA 73/27 copolyester has been studied. The shear storage (G') and loss (G") moduli are monitored as a function of frequency and of different annealing times. Moreover, the steady state viscosity data are presented and compared with the complex viscosity data obtained in the small amplitude oscillatory tests.

Materials and methods

Rheological measurements have been performed on the thermotropic random copolyester based on 1,4 hydroxybenzoic acid (HBA) (73%) and 2,6 hydroxynaphtoic acid (HNA) (27%). The sample with M_w=30000 is marketed as Vectra A950 and commercialized by Ticona. Two other samples with weight average molecular weight (M_w) of 48000 and 51000, produced for research purpose and kindly supplied by Ticona, have also been investigated. The melting temperature for these samples is about 280°C.

The rheological tests in dynamic conditions have been performed with a Rheometrics RDSII equipped with a parallel plate configuration (gap=1mm, R=12.5mm). The steady state tests for the evaluation of the steady state viscosity data have been obtained by means of the RMS800 (Rheometrics), with a cone and plate geometry (angle=0.1rad, R=12.5mm). The RMS800 was equipped with a force rebalanced stress transducer for torque and normal force, with full scale ranges of 2000 g*cm and 2000 g, respectively. Finally, for the viscosity data at high shear rates a Rheoscope 1000 (Ceast) has been used. End corrections and Rabinowitch corrections were not applied and the results obtained with the L/D=40 die have been used (D=1mm).

The test temperature in all the experiments is 310°C. This temperature, as demonstrated by Cocchini et al.[8] and afterwards by other researchers groups[9,13], seems the best one to avoid re-crystallization phenomena[14] and also to reduce post-polymerisation processes. The polymer, in pellets form, was dried prior to testing under vacuum at 120°C for 12h, then loaded in the rotational rheometer and tested under a continuous nitrogen purge. In the range of shear rates investigated at 310°C no edge fracture was observed.

Results and Discussions

The linear viscoelastic limit for the different M_w samples of the TLCP HBA/HNA 73/27 has been investigated at the constant frequency of 1, 10, 30, and 100 rad/s. In Figure 1 the complex modulus (G*) is shown as a function of the strain amplitude for the sample with M_w=48000, in the frequency range 1-100rad/s. The onset for nonlinearity (γ_c) significantly decreases as the applied frequency (ω) increases, differently from conventional flexible polymers where γ_c is generally independent of frequency. Similar results have also been obtained for the other samples with molecular weight of 30000 and 51000[15,16]. A decrease of γ_c with increasing the applied ω has been first mentioned for the Vectra A950 (M_w=30000) by Guskey and Winter[17].

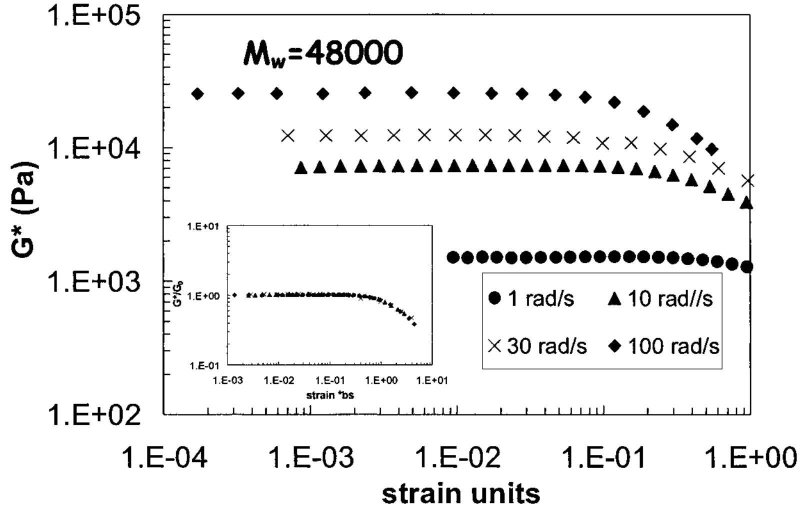

Figure 1. G* (complex modulus) as a function of strain at different frequencies (ω), M_w=48000, T=310°C. Inset: master curve.

In order to better analyze the nonlinear onset dependence on the frequency, the G*(γ) profiles of Figure 1 have been normalised to their linear viscoelastic value G^*_0 and the curves at different ω values have been horizontally shifted by a factor named bs relative to the one at ω=1 rad/s (the reference curve). By this procedure, indeed, all the curves at different ω collapse upon each other and the corresponding master curve is reported in the inset of Figure 1. Similar master curves have also been obtained for the other M_w samples[15,16]. The shift factors increase as ω increases, thus reflecting the reduction in the limit strain amplitude (γ_c). In Table 1 the shift factors are reported at the different investigated frequencies. The bs found is almost proportional to $\omega^{0.5}$, independently of M_w over the investigated range (30000÷51000).

Table 1. Shift factors (bs) at different frequencies (ω) for the different M_w samples.

ω (rad/s)	**bs** **M_w=30000**	**bs** **M_w=48000**	**bs** **M_w=51000**
1	1	1	1
5			2.1
10	2.6	3	3.7
30	3.3	4.1	4.6
50			6
100	8	8.1	8

Once defined the linear viscoelastic range the frequency response of the thermotropic random copolyester HBA/HNA 73/27 has been analyzed.

In Figure 2a, the G'(ω) and G''(ω) for the M_w=30000 are reported for an experiment started immediately after the loading of the material in the rheometer. The storage modulus of M_w=30000 displays a clear upward concavity over the frequency range investigated. This behaviour seems characteristics of thermotropic melts[18-19]. Moreover, G' tends to level off to a plateau value indicating a solid-like elasticity in the material. This result conforms to the previous findings on Vectra A950[9,18-19]. In the literature the levelling off of the storage modulus is generally associated to disclination lines related to the polydomain structure of the sample which gives the material the enhanced elasticity. The same *frequency sweep* test on the Vectra A950 sample has been performed after different annealing times (time between the end of the loading phase and the beginning of the test), with the aim to verify weather time effects on the moduli exist. The results are reported in the Figures 2 (b-d). For short annealing times (480s (Figure 2b) and 600s (Figure 2c)), the moduli do not significantly differ from the situation without annealing (Figure 2a). In the low frequency range the elastic response is prevailing over the viscous one and a clear plateau in G' is still present. More significant effects on the viscoelastic parameters are recorded after an annealing time of 1400s. In this case G'' is higher than G', in the low ω range, i. e. a prevailing elastic response is no longer observed. This event can be justified in terms of the structural changes subsequent to the squeezing flow occurring in the loading phase[9,20].

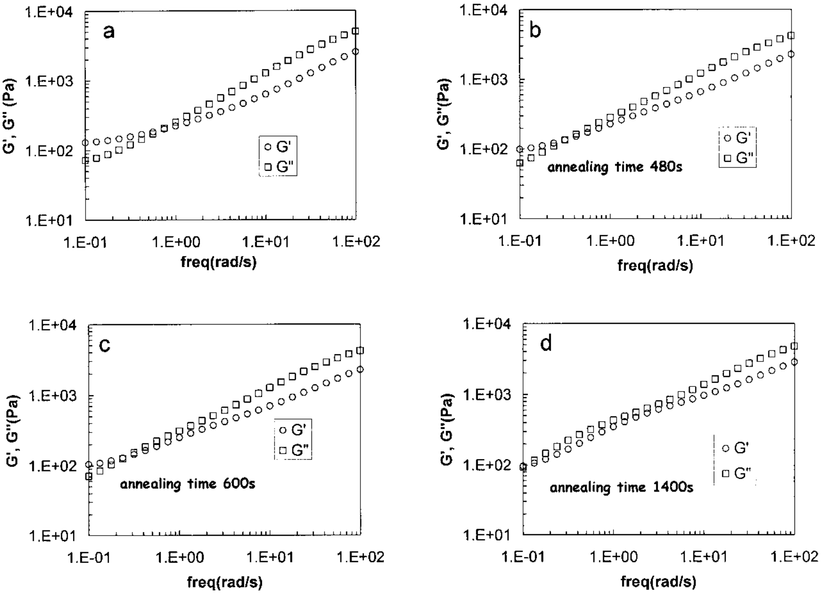

Figure 2. Storage modulus (G') and loss modulus (G") as a function of frequency for the M_w=30000 sample. T=310°C. a) without annealing time, b) annealing time= 480s, c) annealing time=600, d) annealing time=1400s.

The steady state behaviour of these samples has been analysed as a function of the molecular weight. In Figure 3 the flow curves η versus shear rate for the samples M_w=48000 and M_w=51000 are reported. We have verified that the steady state viscosity data do not depend on the annealing time. Indeed, the shear flow can drive the samples to similar configurations independent of their initial state[8,15]. The results are compared with those obtained by Cocchini et al.[8] for the Vectra A950 (M_w=30000). Both the higher molecular weights (M_w=51000 and M_w=48000) as well as the Vectra A950 (M_w=30000) show a flow curve characterised by 3 regions. The viscosity data relative to the high shear rates have been obtained by using the capillary rheometer. We observe, according to the results obtained by Sigillo and Grizzuti[5], that the viscosity flow curve (with the relative 3 regions) shifts toward lower shear rates as the M_w increases and the plateau region becomes less evident. Indeed for the Vectra A950 (M_w=30000) the Newtonian plateau is in the shear rate range ~$0.5s^{-1}$–$2s^{-1}$, instead for M_w=51000 it is in the range ~$0.1s^{-1}$–$0.8s^{-1}$.

The existence of a 3 regions viscosity flow curve has been detected not only for the semi-rigid TLCP Vectra A950 [8-9,21-22], but also for the semi-flexible DHMS 7-9 thermotropic LCP[23] and for some lyotropic LCPs[4-5,24-25].

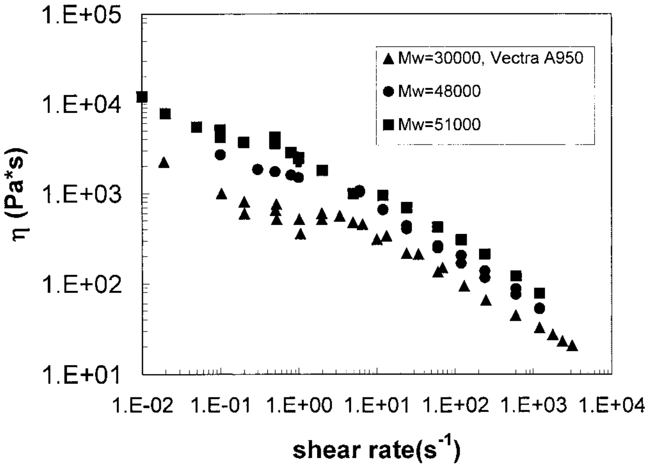

Figure 3. Steady state viscosity (η) vs. shear rate, M_w=30000[8], M_w=48000, M_w=51000, T=310°C.

A structural reason for this unusual rheological behaviour has been proposed by Onogi and Asada[4]. At low shear rates the system is characterised by many domains which are randomly oriented. Indeed, in this situation (region I) when the flow is applied this structure starts to orient. As the shear rate increases the structure starts to modify (region II), and a refinement process occurs. Indeed, there is a reduction of the characteristic dimension of the domains in order to guarantee a balance between hydrodynamic and elastic forces (Frank elasticity). Finally, as the shear rate further increases a higher degree of order is realised in the system, indeed it moves toward a monodomain situation. Zhou et al.[23] proposed a different 3 regions-orientation mechanism for the semi-flexible DHMS-7,9 TLCP. Indeed, in their paper the WAXD measurements show a nearly constant orientation, as the shear rate increases from region I to III, contrary to a progressive increase in the orientation recorded for the lyotropic LCP HPC in water. Zhou et al.[23], therefore, conclude that for the DHMS-7,9 TLCP only a flow aligning molecular dynamic is present in the overall shear rate range. This result, however, is limited to TLCPs characterized by chain flexibility.

In the Figures 4, 5, 6 the flow curves (η versus shear rate) together with the complex viscosity profiles (η* versus ω) obtained without annealing, for the TLCPs samples with M_w=30000, M_w=48000, M_w=51000 respectively are reported. The Cox-Merz law fails for the sample M_w=30000, in fact the complex viscosity profile shows an upward concavity that clearly cannot superpose with the opposite trend of the steady state viscosity data. In the case of annealing time of 1400s (Fig. 2d) the complex viscosity profile is modified and the upward concavity becomes less evident. Nevertheless the Cox and Merz rule fails for this sample. Increasing M_w (M_w=48000 and M_w=51000) a better comparison between the complex and the steady state viscosity curve is recorded. In this case, indeed, the complex viscosity data show a downward concavity, more similar to the behaviour of flexible polymers.

Finally, the η_0 viscosity, the pseudo Newtonian plateau, of the semi-rigid HBA/HNA 73/27 TLCP depends on the molecular weight according to the relationship: $\eta_0 \propto M_w^{3.2}$. The ~3.2 power is not far from the 3.4 power, typical of flexible polymers and quite well compares with the value of 4 indicated by Romo-Uribe and Windle[26] for a series of HBA/HNA 75/25 samples having molecular weights (4600÷30000) lower than those analysed here (30000÷51000). Instead Kim and Han[27] found that η_0 depends on the 6th power of the molecular weight for the semi-flexible TLCP PSHQ10.

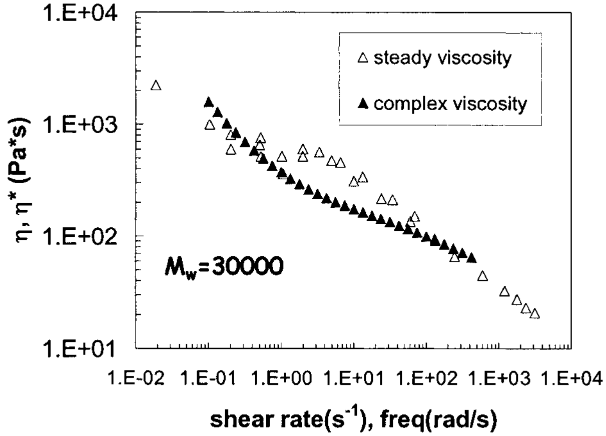

Figure 4. Steady state viscosity (η) vs. shear rate[8] and complex viscosity (η*) vs. ω. M_w=30000, T=310°C.

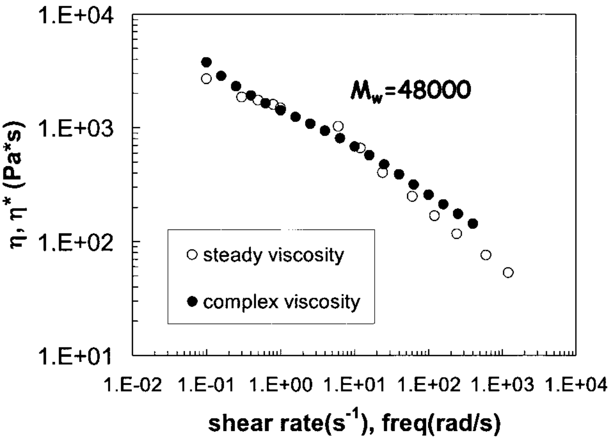

Figure 5. Steady state viscosity (η) vs. shear rate and complex viscosity (η*) vs. ω. M_w=48000, T=310°C.

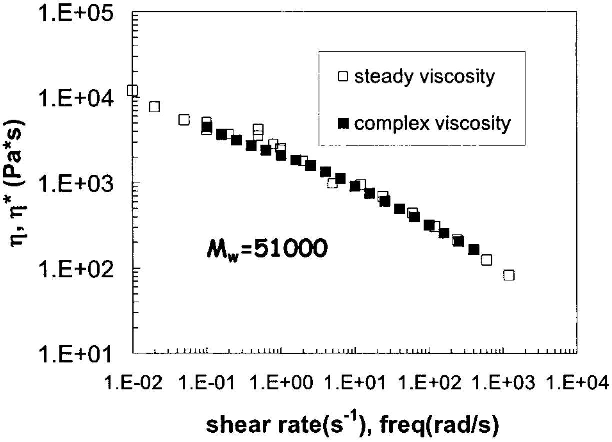

Figure 6. Steady state viscosity (η) vs. shear rate and complex viscosity (η*) vs. ω. M_w=51000, T=310°C.

Conclusions

The rheological behaviour of the semi-rigid TLCP HBA/HNA 73/27 has been investigated. The linear viscoelastic G' and G'' moduli have been monitored as a function of different annealing times. Significant changes have been detected after long annealing times (1400s) as a consequence of the structural changes subsequent to the squeezing flow occurring in the loading phase. Rheological data obtained in steady state conditions have been used to define the viscosity flow curves for the different M_W samples. In all the cases a three regions flow curve has been detected, with the plateau zone being M_w dependent.

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[1] M. Doi, J. of Polym. Sci. Polym. Phys. Ed., **1981**, 19, 229-243.
[2] L. C., Sawyer, H. C. Linstid, and M. Romer, Plastics Eng., **1998**, 54, 37-41.
[3] G.W. Calundann, M. Jaffe, in Proc. of the Robert A. Welch Foundation Conferences on Chemical Research, XXVI, Synthetic Polymers, Houston, Texas, Nov 15-17, **1982**, 247-291.
[4] S. Onogi and T. Asada, Proceedings of the 8th international Congress on Rheology, edited by G. Astarita, G. Marrucci and L. Nicolais, **1980**, vol.1, pp.127-147.
[5] I. Sigillo, N. Grizzuti, J. of Rheol., **1994**, 38, 589-599.
[6] H. L. Doppert, S. J. Picken, Mol. Cryst. Liq. Cryst., **1987**, 153, 109-116.
[7] J. Mewis, P. Moldenaers, Mol. Cryst. Liq. Cryst., **1987**, 153, 291-300.
[8] F. Cocchini, M. R. Nobile, D. Acierno, J. Rheol., **1991**, 35, 1171-1189.
[9] H. C. Langelaan, A. D. Gotsis, J. Rheol., **1996**, 40, 107-129.
[10] L. Gervat, M. R. Mackley, T. M. Nicholson, A. H. Windle, Philos. Trans. R. Soc. London Ser., A, **1995**, 350, 1-27.
[11] A. Romo-Uribe, A. H. Windle, Proc. R. Soc. London, **1999**, 455, 1175-1201.
[12] A. Romo-Uribe, Proc. R. Soc. London, **2001**, 457, 207-229.
[13] A. Romo-Uribe, T. J. Lemmon, A. H. Windle, J. of Rheol., **1997**, 41, 1117-1145.
[14] Y. G. Lin, H. H. Winter, Macromolecules, **1988**, 21, 2439-2443.
[15] E. Somma, PhD thesis, University of Salerno, edited by CUES **2003**.
[16] E. Somma, M. R. Nobile, J. of Rheol., **2004**, 48, 1407-1423.
[17] S. M. Guskey and H. H. Winter, J. Rheol., **1991**, 35, 1191-1207.
[18] K. F. Wissbrun, G. Kiss, F. N. Cogswell, Chem. Engin. Comm., **1987**, 53, 149-173.
[19] D. S. Kalika, L. Nuel, M. M. Denn, J. Rheol., **1989**, 33 , 1059-1070.
[20] A. D. Rey, J. of Rheol. **1996**, 40, 1233-1237.
[21] L. Nuel, M. M. Denn, Rheologica Acta, **1991**, 30, 165-170.
[22] D. W. Giles, M. M. Denn, J. Rheol., **1994**, 38, 617-637.
[23] W. J. Zhou, J. A. Kornfield, V. M. Ugaz, W. R. Burghardt, D. R. Link, and N. A. Clark, Macromolecules, **1999**, 32, 5581-5593.
[24] B. Ernst, P. Navard, Macromolecules, **1989**, 22, 1419-1422.
[25] L. Walker, N. Wagner, J. of Rheol., **1994**, 38, 1525-1547.
[26] A. Romo-Uribe, A. H. Windle, Macromolecules, **1995**, 28, 7085-7087.
[27] S. S Kim., C. D. Han Macromolecules, **1993**, 26, 6633-6642.