Viscoelastic measurements on main-chain thermotropics

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Rheological properties, determined by torsion experiments, of three main-chain thermotropics are investigated. Stable, time-independent measurements are obtained in two of these polymers, and the corresponding dynamic viscoelastic and first normal difference results are analysed. In the nematic state both storage and loss moduli scale as $G', G'' \propto \omega^{1/2}$, and no shear modulus associated with an entanglement network is detected. Recoverable compliances J_e^0, which are determined from steady-state N_1 values, are several orders of magnitude higher than those of isotropic polymers. For one of the polymers, the characteristic molecular weight between entanglements, M_c, is determined from Newtonian viscosities of isotropic solutions. Although the molecular weight of our sample is above M_c, viscoelastic measurements at temperatures corresponding to the nematic state show no vestige of the entanglement network.

(Keywords: liquid-crystalline polymers; nematic state; dynamic viscoelasticity)

INTRODUCTION

Many kinds of thermotropic liquid-crystalline polymers have been developed since Jackson and Kuhfuss[1] published the synthesis of the copolyester of *p*-hydroxybenzoic acid (PHBA) and poly(ethylene terephthalate) (PET) and their melt anisotropy. The structures used to promote melt anisotropy at reasonable temperatures have been described in the excellent review of Calundann and Jaffe[2]. The copolyesters and poly(ester–amide)s produced by Hoechst Celanese, ICI, Eastman Kodak, etc., are defined as 'main-chain thermotropics' because the mesogenic units are in the main chain. The rheology of this type of anisotropic polymer is a subject of current interest, notwithstanding mostly unexplored. From an academic point of view, these materials are interesting because they display curious behaviours, which are a mixture of their polymeric and nematic characters. On the other hand, these polymers are technologically interesting owing to their ease of processing. There is a noticeable lack of experimental data and viscoelastic parameters that characterize the terminal response region, like the plateau modulus, G_N^0, and the characteristic molecular weight, M_c, which have not been determined for these polymer species. Apart from difficulties in characterizing molecular parameters, this is also due to the fact that the viscoelastic functions of these materials are very sensitive to thermal and mechanical history[3–5], and time-independent measurements are only obtained under certain conditions.

In the present work we investigate dynamic viscoelasticity, as well as normal stress differences, of two copolyesters and one copoly(ester–amide) in the nematic state.

EXPERIMENTAL

Materials

Three polymers were used in this study. One of them, known commercially as X7G®, was supplied by Eastman Kodak, and has a composition of 60 mol% *p*-hydroxybenzoic acid (PHBA) and 40 mol% poly(ethylene terephthalate) (PET). An inherent viscosity (*IV*) of 0.71 dl g^{-1} was reported by the supplier. It has been measured at 25°C in 60/40 (by volume) phenol/tetrachloroethane at a concentration of 0.50 g/100 ml. Jackson and Kuhfuss[1] reported values of molecular weight of 14 800 and 20 600 for two samples of 60/40 PHBA/PET with *IV* of 0.57 and 0.70 dl g^{-1} respectively; $IV = 0.71$ dl g^{-1} corresponds to an approximate molecular weight of 21 000. The other two liquid-crystalline polymers are Vectra A950 and Vectra B950, supplied by Hoechst Celanese. Vectra A950 is a copolyester, which consists of 73 mol% *p*-hydroxybenzoic acid and 27 mol% 6-hydroxy-2-naphthoic acid; whereas Vectra B950 is a copoly(ester–amide) with a composition of 60 mol% 6-hydroxy-2-naphthoic acid, 20 mol% terephthalic acid and 20 mol% *p*-aminophenol.

Sample preparation

Two kinds of discs were prepared for viscoelastic measurements.

Disc samples of the three liquid-crystalline polymers were prepared in a Mini Max moulder CS-183MMX. This moulder has a capacity of 4 cm^3 and the material is injected manually into the mould. The geometry of the discs obtained was: diameter = 20 mm and thickness = 2 mm. X7G samples were injected at 250°C and Vectra samples were injected at 290°C. All polymers were dried before moulding at 120°C for a period of 16 h. Then 25 mm diameter discs were cut from plates 1 mm thick

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obtained by compression moulding of X7G at 250°C and Vectra A950 at 290°C.

Solutions of X7G in *m*-cresol (Merck-Schuchar) were prepared by gentle warming and stirring. In order to avoid water absorption, the polymer was dried at 120°C for 16 h and the solvent was kept dry using a molecular sieve.

Viscoelastic measurements

Viscoelastic measurements were carried out in a Carri-Med CSL100 rheometer supplied with a high-temperature system. This system has a heating coil, which operates by induction heating of the moving and fixed plates up to 400°C. The geometry was parallel plates with a diameter of 2 cm and the gap elected in each measurement was the disc's thickness. The measurements were performed in oscillatory shear mode over a range of frequency (10^{-2}–10 Hz). At each temperature, the displacement was selected from a torque sweep in the linear viscoelastic region (where G' and η' are independent of the applied torque). The torque range was 10^{-5}–4×10^{-3} N m. In the measurements performed with solutions of X7G in *m*-cresol, the geometry used was cone and plate. In this case the sample was heated with a Peltier system placed in the plate. The cone used has a diameter of 4 cm and an angle of 1°58′00″. The measurements were accomplished in the steady flow mode and each measurement took 20 min.

Measurements of normal stresses were performed in the Technical Center of Rheometrics GmbH Europa (Frankfurt) on a Rheometrics RMS800 in the cone–plate mode. The angle was 0.1 rad and the radius 12.5 mm. Rate sweeps at steady state were carried out at several shear rates on X7G and Vectra A950. After loading the sample, measurements were made when complete relaxation of the stresses was reached (when the N_1 gauge returns to zero value). This technique avoids having a difference between the software zero and the actual zero of the transducer before loading the sample and gives rise to reproducible measurements.

Microscopy

Nematic state of X7G was observed by polarized light microscopy, conducted using a Reichert polarizing optical microscope equipped with a Mettler FP82 hot stage. A small piece of X7G was heated to 300°C, flattened and cooled to room temperature. The sample remains at room temperature at least 24 h and then a scan is made with a heating rate of 10°C min^{-1} up to 250°C and 1°C min^{-1} at higher temperatures. In *Figure 1a* we can observe a threaded texture, typical of nematic phase, at 260°C; this texture died away as the temperature increases (see *Figure 1b*).

RESULTS AND DISCUSSION

Time sweep experiments

This type of measurement, shown in *Figures 2* and *3*, was carried out to determine the temperatures at which rheological steady state can be attained. Our experimental results can be interpreted within the framework of the studies undertaken by Lin and Winter[3–5] about the effect of the formation of high-melting crystals on the rheology of Vectra A950 and Rodrun® LCP300 (Unitika Ltd), a random copolyester containing the same mole percentages of PET and PHBA as Eastman Kodak's X7G.

In the case of Vectra B950 (*Figure 2*) the storage modulus increases constantly with time, showing no steady state even at temperatures up to 340°C, well above its nominal melting temperature (292°C). This polymer seems to be very sensitive to the formation of high-melting crystals, which impedes the possibility of performing reliable dynamic viscoelastic measurements, although time-independent viscosities have been determined by capillary rheometer measurements[6]. The possibility of polymerization during torsion-mode measurements can also be envisaged[7]. Much more encouraging conditions have been found for Eastman Kodak's X7G (also in *Figure 2*), for which steady-state measurements are obtained at 240°C and above. The data of ref. 8, included in *Figure 2*, refer to 60/40 PHBA/PET copolyester (supplied also by Eastman Kodak) at 275°C, and the fact that our results at 280°C differ significantly can be attributed to differences in molecular weight or to the previous treatment to prepare the samples. The dynamic mechanical properties of a 60/40 PHBA/PET copolyester developed by Unitika Ltd (Rodrun) have been studied by Huang *et al.*[5], who show that in the time scales of our work the storage modulus grows continuously at 245, 250 and 255°C, a result that differs substantially from that reported in *Figure 2* for Eastman Kodak's copolyesters. Concerning this difference we have to point out that a new production process developed by Unitika Ltd would have improved its properties by aligning the monomer sequence distribution randomly[9].

In *Figure 3* our Vectra A950 data are compared with those of Lin and Winter[4] (actually obtained for Vectra A900). We observe that stable measurements are obtained at a temperature of 295°C, and that at 290°C our samples present a considerably lower growth than those of Lin and Winter.

Measurements in frequency sweep mode

Figure 4 presents the storage modulus, as a function of frequency, at various temperatures for X7G copolyester; the behaviour of G' and G'' is compared at 240 and 290°C in *Figure 5*. At 240°C, storage modulus G' prevails over loss modulus, whereas at 290°C viscous-dominant behaviour is envisaged, although the predictions of the linear viscoelastic model ($G' \propto \omega^2$ and $G'' \propto \omega$) are far from being fulfilled. Instead, both moduli at 290°C scale at low frequencies as G', $G'' \propto \omega^{1/2}$. The fact that X7G is non-random with respect to the chain structure rather than completely random, as was suspected initially by Tennessee Eastman's researchers, gives rise to an inhomogeneous material, which possesses the peculiar rheological behaviour observed in *Figures 4* and *5*. Dynamic mechanical analyses have been carried out by Sun *et al.*[10] to understand the phase transition of a 60/40 PHBA/PET copolyester. From the plots of G' and G'' (taken at 10 rad s^{-1}) as a function of temperature, these authors have characterized four temperature regions. Our data (except those obtained at 240°C) correspond to what they define as region III, a range of temperatures which implies that both liquid-crystal formation in the PHBA-rich domain and the melting of PET are completed. However, in our case we do not find the positive thermal coefficient of G', shown in Figure 5 of ref. 10, between 270 and 310°C. We also remark that the breakdown of time–temperature superposition is obvious.

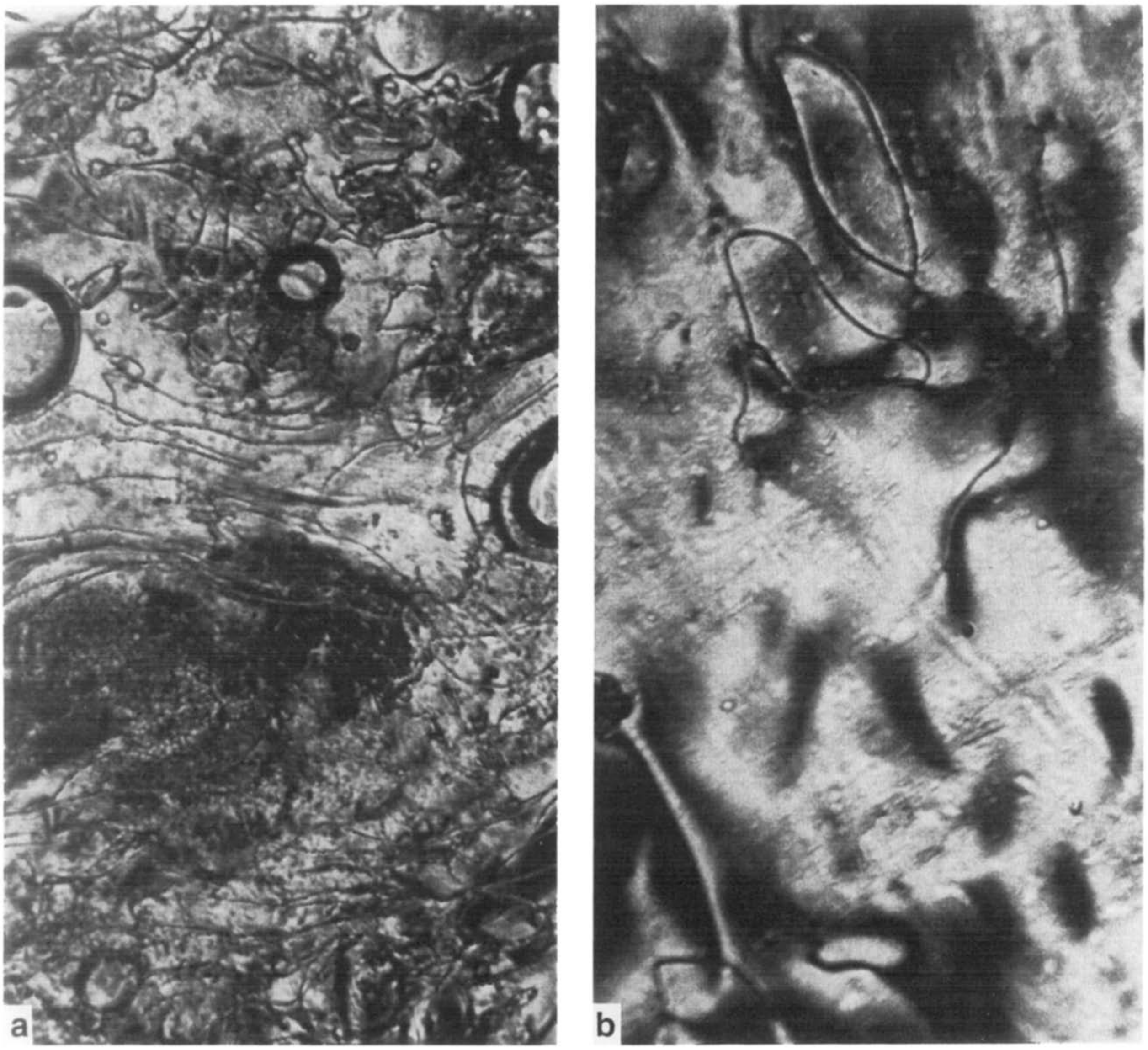

Figure 1 Photographs taken with a polarizing microscope of nematic phase of X7G at (a) 260°C and (b) 330°C

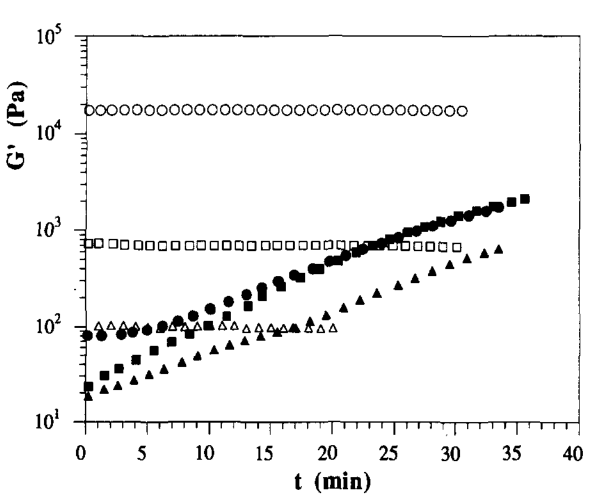

Figure 2 Storage modulus *versus* time for X7G (open symbols) and Vectra B950 (full symbols). Our data of X7G at 240°C (○), 280°C (□) and from literature data[8] at 275°C (△). Data of Vectra B950 at 320°C (●), 330°C (■) and 340°C (▲)

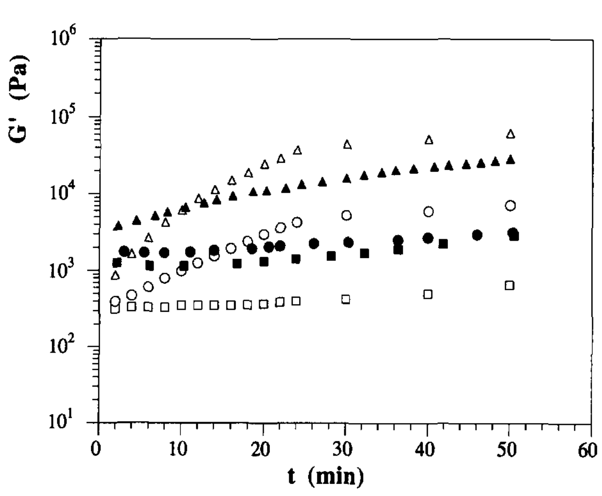

Figure 3 Storage modulus *versus* time for Vectra A950 at various temperatures: (▲) 285°C, (●) 290°C and (■) 295°C. Open symbols correspond to data of ref. 4 at the same temperatures

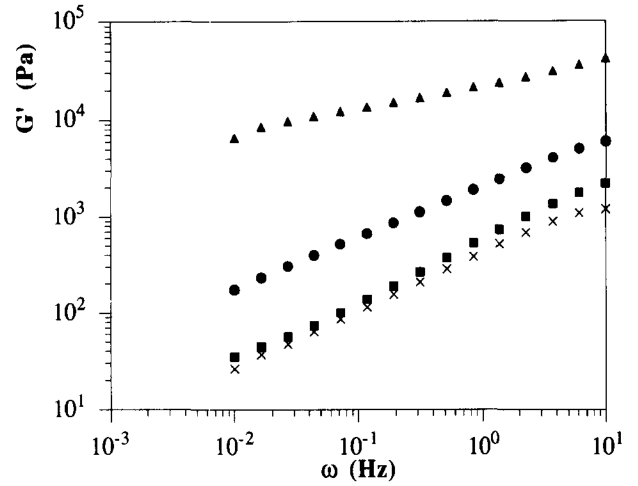

Figure 4 storage modulus as a function of frequency for X7G at various temperatures: (▲) 240°C, (●) 260°C, (■) 280°C and (×) 290°C

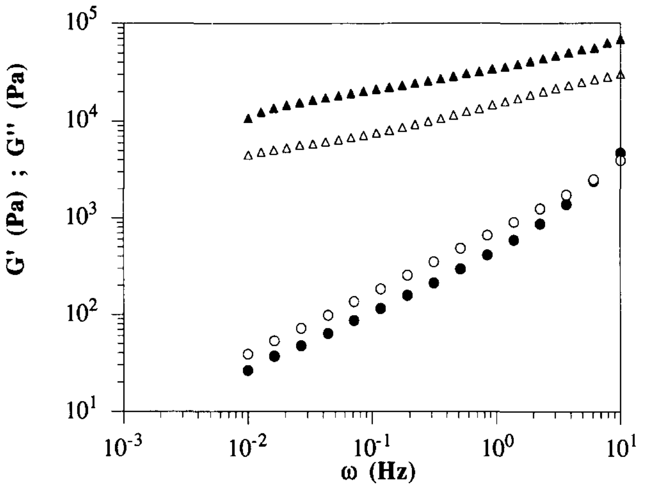

Figure 5 Storage and loss moduli for X7G at 240°C (▲, △) and at 290°C (●, ○)

Actually X7G copolyester displays the same behaviour (characterized by a 0.5 power dependence on the frequency of both G' and G''), i.e. that heterogeneous block copolymer melts like 1,4-polybutadiene–1,2-polybutadiene diblock copolymers[11] and polystyrene–polyisoprene–polystyrene triblock copolymers[12]. Han and Kim[12] proposed a rheological criterion, based on the analysis of log G' *versus* log G'' plots, for determining the transition of block copolymers; homogeneous melts, like low-density polyethylene in the range 160–230°C, exhibit no temperature dependence when this type of plot is performed. Though, in the case of X7G, *Figure 6* shows a temperature dependence of the plots that becomes more significant at high frequencies, this indicates that the heterogeneity of the thermotropic copolyester manifests in the region where the plateau modulus, associated with entanglements, should appear.

The behaviour of Vectra A950 at 290°C (*Figure 7*) is marked by a viscous-dominant feature and a 0.5 power dependence of both moduli (G', $G'' \propto \omega^{1/2}$ like in the case of X7G), although at low frequencies G' prevails over G'' and tends to level off. The latter is typical of charged or slightly crosslinked polymers[13] which display a plastic behaviour.

Our data of X7G and Vectra A950 (*Figures 4, 5* and *7*) show no sign of the existence of a shear modulus associated with an entanglement network, G_N^0, which is typical of polymers with molecular weight above the so-called critical molecular weight. To our knowledge, only in one case has the entanglement modulus been detected for thermotropic copolyesters; very high values of G_N^0 (10^6–10^7 Pa) are envisaged in the work of Ober *et al.*[14] for two random copolyesters based on bromoterephthalic acid, methylhydroquinone and hexanediol. In order to establish if the molecular weights of our polymers are too low to allow the chain to entangle, we have determined the characteristic molecular weight between entanglements, $M_c = 2M_e$, from Newtonian viscosity measurements of X7G/*m*-cresol solutions (*Figure 8*). The experimental data show a variation at 12 wt% of X7G, corresponding to a critical volume fraction $\varphi_2^* = 0.09$. Using the equation:

$$\varphi_2^* = M_c/M \tag{1}$$

We obtain a value of $M_c = 1900$ for an estimated molecular weight of $M \approx 21\,000$ (see 'Experimental' section). Based on data of many polymer species, Graessley and Edwards[15] have proposed the following equation for M_c:

$$M_c = \frac{(\rho N_A)^{(1-a)} m_0^a}{K l_0^{3(a-1)} C_\infty^{2a-3}} \tag{2}$$

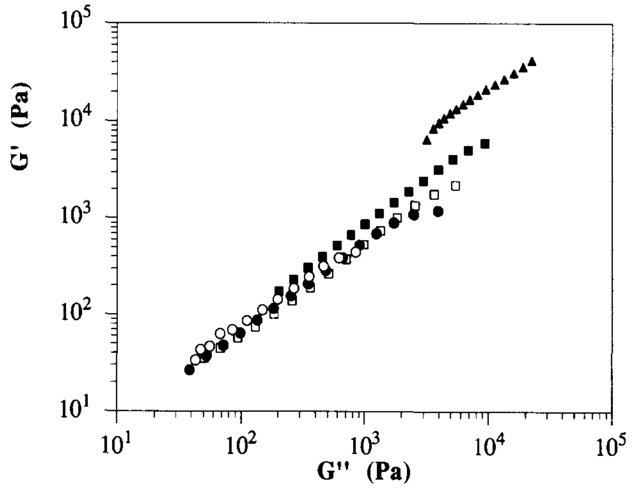

Figure 6 Storage modulus *versus* loss modulus for X7G at various temperatures: (▲) 240°C, (■) 260°C, (□) 280°C and (○) 320°C

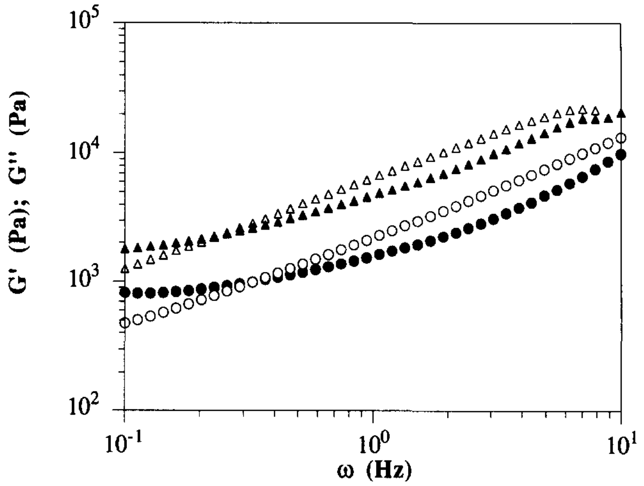

Figure 7 Storage and loss moduli for Vectra A950 at 290°C (▲, △) and at 300°C (●, ○)

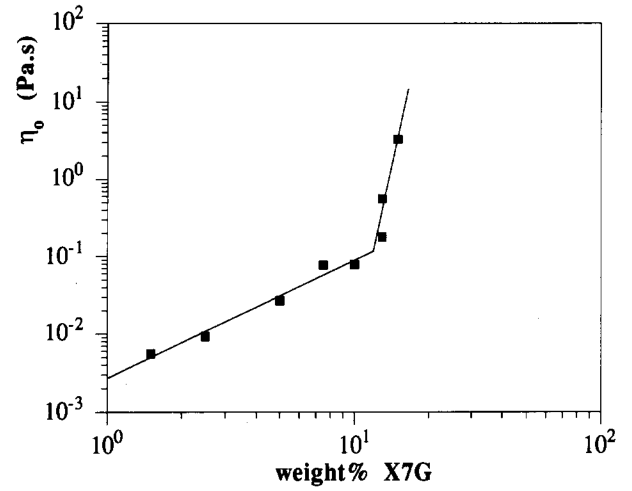

Figure 8 Newtonian viscosity of X7G/*m*-cresol solutions as a function of weight percentage X7G

Table 1 Parameters of equation (2)

l_0^a	2.97 Å
m_0	48.86 g mol^{-1}
C_∞^b	4.56
ρ^c	1.35 g cm^{-3}

[a] Average calculated from the main-chain bond lengths
[b] $C_\infty = [(K/\phi)^{2/3} m_0]/\langle l^2 \rangle$ where K is obtained from *IV* data of ref. 1
[c] At 25°C

where l_0 is the average length of the main-chain bonds, m_0 is the average molecular weight for main-chain bonds, C_∞ is the characteristic ratio ($C_\infty = \langle R^2 \rangle_0 / n l_0^2$), ρ is the density and a and K are constants. The parameter values of equation (2) for X7G thermotropic copolyester are presented in *Table 1*: using $a = 2.3$ and our experimental $M_c = 1900$ value, we obtain $K = 6.6 \times 10^{-3}$. Although this value is slightly higher than the values presented by Graessley and Edwards[15] for 12 polymers, which vary from 2.1×10^{-3} for poly(vinyl acetate) to 5.8×10^{-3} for poly(ethylene oxide), we consider that the relation between entanglements and the chain contour length per unit volume, established in equation (2), is also observed in the case of X7G. Both experimental and theoretical results lead us to assert that the molecular weight of these copolyesters is well above the critical molecular weight for entanglements. Now we can use the widely accepted relationship between the plateau modulus, G_N^0, and the molecular weight between entanglements, $M_e = M_c/2$:

$$G_N^0 = \rho RT / M_e \qquad (3)$$

where $\rho = 1.17\,\mathrm{g\,cm^{-3}}$ at 280°C[16] and $M_e = 950$, to give a value of $G_N^0 = 6 \times 10^6$ Pa, which is at the top of values for 70 polymers reported previously[17]. To elucidate if this value can be attained experimentally, we would need to achieve measurements at extremely high frequencies (10^5–10^6 Hz) since the time–temperature superposition method does not hold in this copolyester. This apparently incongruous behaviour may be a consequence of the peculiarity of the liquid-crystalline thermotropic state. In fact, in the temperature range of our dynamic viscoelastic measurements, X7G displays a nematic phase (see *Figure 1*), whereas the estimation of φ_2^* and M_c (used in equation (3)) was undertaken with clear, isotropic polymer solutions. This leads us to suggest that the entanglement network effect on the viscoelastic behaviour is particular in the anisotropic state.

In the following section, we present data of the recoverable compliance, J_e^0, which are related to entanglement modulus, G_N^0.

First normal stress difference

Steady-state values of the viscosity and the first normal stress difference at several shear rates have been obtained for both X7G and Vectra A950 liquid-crystalline copolyesters. The results of the normal stress measurements for Vectra A950 and X7G are shown in *Figure 9* together with data of Vectra A950 from the literature[7].

Although negative values of the first normal stress difference have been reported in the literature[18–20], including the case of Vectra A950 at 290°C[20], in our set of steady-state measurements we have not obtained negative values of N_1. Our data agree reasonably well with those of Cocchini *et al.*[7] and we remark that above a certain shear rate N_1 becomes proportional to $\dot{\gamma}_{21}$, as predicted by the rheological equation formulated by Volkov and Kulichikhin[21].

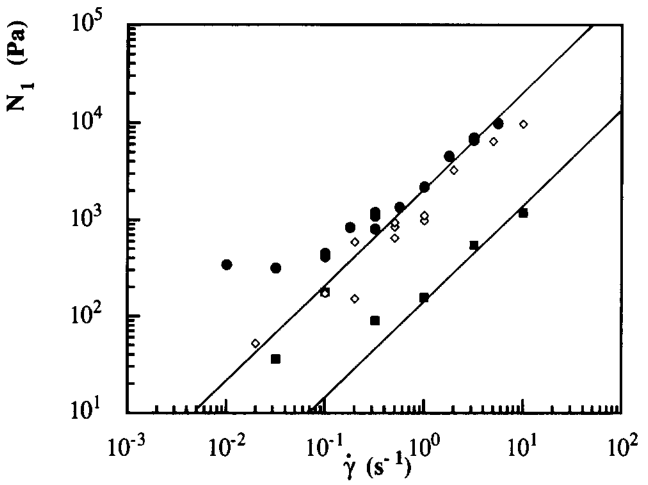

Figure 9 First normal stress difference as a function of shear rate for Vectra A950 at 300°C (●) and X7G at 245°C (■). Also shown are data of Vectra A950 at 310°C (◇) from Cocchini *et al.*[7]. Data at high shear rates are fitted to a line of slope = 1

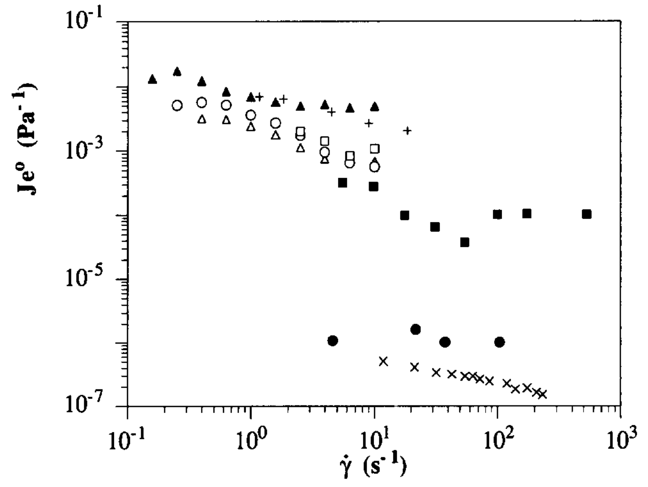

Figure 10 Recoverable compliance as a function of shear rate for various polymers: experimental data of X7G at 280°C (▲) and of Vectra A950 at 290°C (△), 300°C (○) and 320°C (□). Data from literature: HDPE[22] (×), PHB50[23] (+), 60PHB/40PET[24] at 285°C (■) and PET[24] at 285°C (●)

The recoverable compliance values J_e^0 for Vectra A950 and X7G, which are obtained from the well known equation:

$$J_e^0 = N_1/(2\sigma_{21}^2) \tag{4}$$

are presented in *Figure 10*, where we also include literature data[22–24] of anisotropic and isotropic polymers. The J_e^0 values of the polymers in the anisotropic state are several orders of magnitude higher than those which correspond to two typical flexible polymers, like PET[24] and high-density polyethylene[22]. Above $10^0\,s^{-1}$ the X7G data level off giving a value of $J_e^0 = 5 \times 10^{-3}\,Pa^{-1}$, whereas for Vectra A950 a value of $J_e^0 = 10^{-3}\,Pa^{-1}$ can be estimated. These high values are consistent with the low values of G' presented in *Figures 4, 5* and *7*. In fact the relation $G_N^0 \propto 1/J_e^0$ has been well established in the literature[25,26], and from experimental data[15,27] we obtain the average value:

$$J_e^0 G_N^0 = 4 \tag{5}$$

with a minimum of 2.4 for polybutadiene and a maximum of 5.5 for *cis*-1,4-polyisoprene. Using this equation the corresponding values of G_N^0 are 800 Pa for X7G and 4000 Pa for Vectra A950. Notwithstanding these values are in the range of the data of G' show in *Figures 5* and *7*, no entanglement network is detected in these figures, since the viscous behaviour ($G'' > G'$) prevails in the spectrum.

Within this framework it is interesting to note the difference between, on the one hand, main-chain thermotropic polymers containing long flexible spacers and, on the other hand, fully aromatic copolymers (such as Vectra A950) and PHBA/PET copolyesters, which contain short spacers. As we point out above, frequency sweep measurements[14] confirmed the formation of entanglements in copolyesters based on poly(methylphenylene bromoterephthalate-*co*-hexamethylene bromoterephthalate) with flexible spacers consisting of six methylene groups (see Figure 1 of ref. 14), whereas the lack of an entanglement plateau seems to be one of the features of fully aromatic and PHBA/PET (e.g. X7G) liquid-crystalline polymers.

For X7G, a characteristic molecular weight between entanglements $M_c = 1900$ is determined from Newtonian viscosities of isotropic solutions; this leads to a value of $G_N^0 = 6 \times 10^6$ Pa for the entanglement modulus. This modulus was not detected by dynamic viscoelastic measurements in frequency sweep mode.

CONCLUSIONS

Stable rheological measurements are obtained for X7G and Vectra A950 at temperatures above 240 and 290°C respectively. In the case of Vectra B950 the viscoelastic moduli increase continuously with time in all the range of temperatures considered in this work.

Both copolyesters exhibit a viscous-dominant behaviour (except at 240°C in the case of X7G) and a 0.5 power dependence on the frequency of both G' and G''.

For both copolyesters, the recoverable compliance values, J_e^0, which are determined from values of N_1, are several orders of magnitude higher than those of isotropic polymers.

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