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Rheological features of thermotropic and isotropic poly(ester imide)s

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Rheological properties of two poly(ester imide)s with a similar chemical structure are studied in this paper. Both polymers contain the same mesogenic unit and flexible spacer: the only difference is the orientation of the connecting ester groups. The liquid crystalline nature of one of the poly(ester imide)s in the range 170–235°C gives rise to typical peculiar rheological features of nematic polymer such as two shear-thinning regions in the viscosity curves, $\partial\eta/\partial T>0$ when isotropization takes place and orientation during the injection process.

(Keywords: liquid crystallinity; rheology; poly(ester imide)s)

INTRODUCTION

The rheology of main chain thermotropics is a subject of current interest, because these materials combine the features of low molecular weight liquid crystals and ordinary polymers. Peculiar viscoelastic results, like for instance negative first normal stress differences, have been reported in the literature[1,2] and the interpretation of these results is a matter of controversy. From a theoretical point of view, the assumption that thermotropics behave as nematics subjected to director tumbling allows some authors[3] to explain the transient and steady state flow behaviour of liquid crystalline polymers (LCPs).

In this paper we present and discuss rheological results of two poly(ester imide)s (PEIs), liquid crystalline and isotropic, respectively, involving oscillatory and flow measurements in a wide temperature range. Polymers 1F and 2E are aliphatic-aromatic PEIs of the same molecular formula (see repeat units in *Figure 1*). Both contain the mesogen unit *N*-phenylphthalimide and a spacer consisting of a methylenic chain of eight CH_2 groups. The only difference is the orientation of the connecting ester groups. Because of the opposite orientation of the ester groups, the thermotropic behaviour of PEIs 1F and 2E is completely different: while PEI 1F is an enantiotropic material that shows a reversible and reproducible thermotropic mesophase between 170°C and 235°C, PEI 2E behaves as an ordinary semicrystalline polyester that does not show any mobile LC mesophase. Thus, it is interesting to study the rheology of such systems that are analogous in their chemical structure and yet so different in their thermotropic behaviour, and to outline a consistent relationship between the primary structure, particularly the orientation of the –COO– groups, and thermal and rheological properties.

EXPERIMENTAL

Materials

The polymers employed in this study are two PEIs with chemical structure as shown in *Figure 1*.

The method of preparing these two PEIs is described in the literature[4,5]. PEI 1F was prepared from *N*-(4-hydroxyphenyl)-4-hydroxyphthalimide diacetate and decanodioic acid by transesterification (acidolysis) in the melt in the presence of a catalytic amount of MgO. The polymer was obtained in 94% yield and showed an inherent viscosity (chloroform/trifluoroacetic acid, 1/1) of 0.68 dl g^{-1}. PEI 2E was prepared in 90% yield from *N*-(carboxyphenyl)-4-carboxyphthalimide and 1,8-octanodiol by an ester interchange polycondensation reaction in the melt, in the presence of titanium isopropoxide. The polymer showed an inherent viscosity of 0.81 dl g^{-1} (chloroform/trifluoroacetic acid, 1/1, 0, 5%, 25°C).

Sample preparation

Before moulding both polymers were dried at 120°C for 16 h. Rectangular samples for d.m.t.a. measurements were cut from plates 1 mm thick obtained by compression moulding of both polymers at 250°C. Disc samples for viscoelastic measurements were prepared in a Mini-Max moulder CS-183MMX and the material at 250°C was injected manually into the mould. The discs obtained had diameters of 20 mm and were 2 mm thick.

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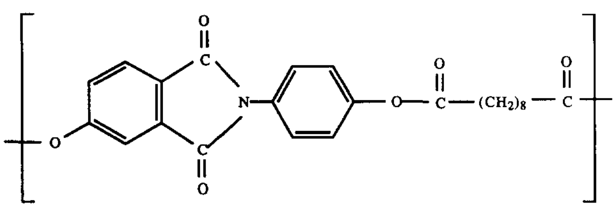
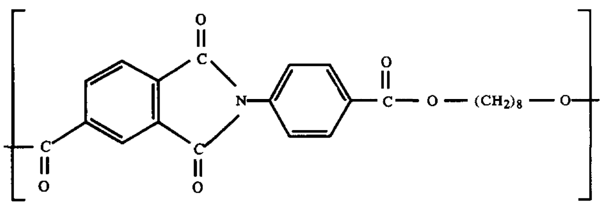


Poly(ester imide) 1F



Poly(ester imide) 2E

Figure 1 The chemical structures of the poly(ester imide)s

Measurements

D.s.c. measurements were performed with a Perkin–Elmer DSC-7 apparatus, under nitrogen, using heating and cooling rates of 20°C min^{-1}. The melting and isotropization temperatures, T_m and T_i, were taken at the maxima of the corresponding endotherms.

Dynamic viscoelastic properties were measured in a Polymer Laboratories DMTA apparatus. Temperature scans at frequencies of 0.3, 1, 3, 10 and 30 Hz were carried out in bending mode at a heating rate of 4°C min^{-1}.

Viscoelastic measurements were carried out in a Carri-Med CSL-100 rheometer supplied with a high temperature system, a heating coil which operates by induction heating of moving and fixed plates up to 400°C. The parallel plates had a diameter of 2 cm and the gap selected in each measurement was the thickness of the disc. The measurements were performed in oscillatory and shear flow mode and each measurement took 30 and 20 min, respectively. In oscillatory mode at each temperature the displacement was selected from a torque sweep in the linear viscoelastic region (where the shear storage modulus, G', and dynamic viscosity, η', are independent of the applied torque). The repetition of measurements showed very good reproducibility.

RESULTS AND DISCUSSION

Characterization of polymers

The pair of PEIs selected for this study were synthesized by a general method described previously. Since they were newly prepared, to be used as model polymers for the rheological measurements involved in this work, the materials were characterized by general methods, particularly by the determination of their thermal properties. Characterization data are given in *Table 1*. The LC mesophase of PEI 1F was confirmed by d.s.c. and polarizing microscopy. The d.s.c. curves obtained for PEI 1F are given in *Figure 2*.

Two reproducible endotherms corresponding to the transformations solid→nematic and nematic→isotropic could be observed on the first and the second heating at ~200 and 250°C for PEI 1F, while the two exotherms associated with the opposite transformation (shifted to lower temperatures) could be observed on the cooling curve (*Figure 2*). However, for PEI 2E only the melting endotherms of solid to isotropic melt were observed, confirming its non-enantiotropic behaviour.

Dynamic mechanical measurements

Temperature scans of storage modulus, E', and loss factor, $\tan\delta$, for both PEIs are shown in *Figures 3* and *4*. Data concerning α and β relaxations are summarized in *Table 2* which also includes the activation energies at the glass transition temperature (T_g) obtained from a simple model of relaxation time[6] and assuming an Arrhenius-like relation between relaxation time and temperature:

$$v = B\exp\left(-\frac{\Delta H}{RT_g}\right) \tag{1}$$

where B is a constant, ΔH is the activation energy and R is the gas constant.

The spectra of both PEI 1F and PEI 2E are very similar and the T_gs, determined by d.s.c., are close to the α relaxation temperatures. The low intensity α peaks observed in *Figures 3* and *4* and reported in *Table 2* are due to the semicrystalline nature of both polymers. Following previous studies on β-loss processes in LCPs containing 2,6-naphthyl groups[7], we attribute the β relaxation found in both PEIs to the rotation motion of the imide rings about the main axis, i.e. to the rotation

Table 1 Properties of poly(ester imide)s

			D.s.c.		Polarizing microscopy	
Polymer	I.v. (dl g^{-1})	T_g (°C)	T_m (°C)	T_i (°C)	T_m (°C)	T_i (°C)
1F	0.68	80	190	245	185	236
2E	0.81	82	202	–	190	–

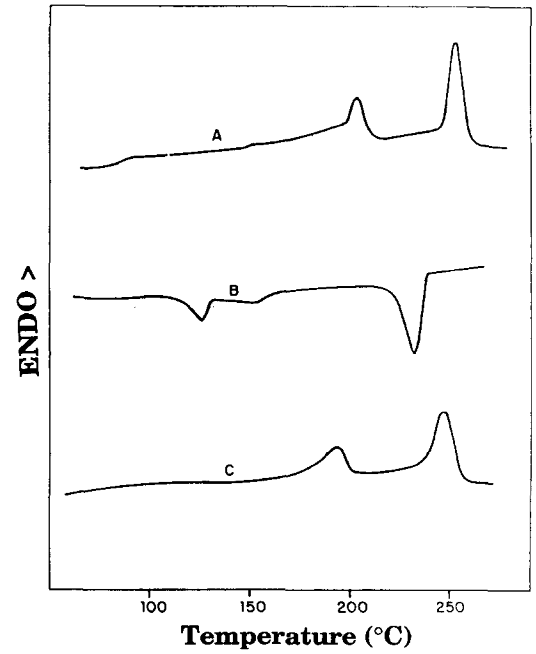


Figure 2 D.s.c. scans of PEI 1F: (A) first and (C) second heating curves, respectively; (B) cooling curve

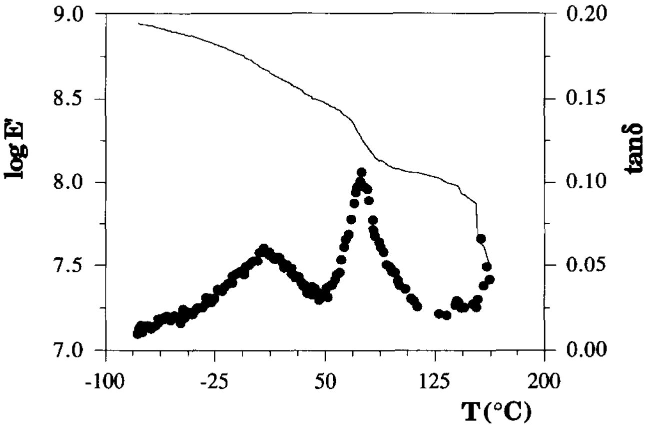


Figure 3 Temperature scan of storage modulus and loss factor for PEI 1F carried out at $\nu=1$ Hz: (——) $\log E'$ (Pa); (●) $\tan\delta$

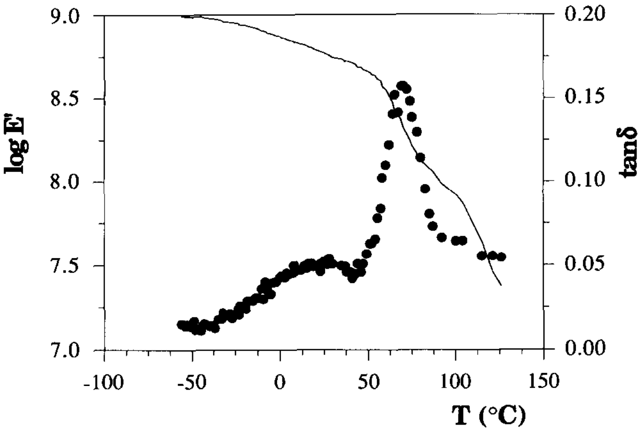


Figure 4 Temperature scan of storage modulus and loss factor for PEI 2E carried out at $\nu=1$ Hz: (——) $\log E'$ (Pa); (●) $\tan\delta$

Table 2 Thermal properties of poly(ester imide)s

Polymer	T_α (°C)	T_β (°C)	$(\tan\delta)_{\max}$	ΔH (kcal mol^{-1})
1F	74.5	9.5	0.11	112
2E	69	20	0.16	114

α and β transitions were measured at $\nu=1$ Hz

around the aromatic carbon–oxygen bend in polymer 1F, and around aliphatic carbon–oxygen in polymer 2E. The higher β-relaxation temperature found for PEI 2E can be explained assuming that rotation can only take place about the oxygen–aromatic links on each side.

Oscillatory flow

Effect of temperature. In *Figure 5* plots of the complex viscosity, η^*, *versus* temperature are shown for both PEIs. In the case of PEI 1F the progressive isotropization of the nematic state gives rise to a positive viscosity–temperature coefficient ($d\eta^*/dT>0$) in the range 235–250°C: with increasing temperature the growing amount of isotropic melt leads to an increase in viscosity. Optical microscopy measurements give $T_i=236$°C which correlates well with the rheological results presented in *Figure 5*. PEI 2E gives rise to much higher viscosities than PEI 1F due to its isotropic nature rather than to its higher molecular weight (see below). Cooling PEI 1F from the isotropic state produces higher viscosities than those obtained during heating, so we can consider that during the cooling process at 2°C min^{-1} the nematic state is not completely formed. This behaviour is in contrast to that found in LC polyurethanes[8], which after heating to the isotropic state gave viscosities four orders of magnitude lower during the cooling process. It appears from these conflicting results that in the case of the LC polyurethanes a considerable degree of three-dimensional crystallinity coexists with the LC phase up to the clearing temperature; on cooling, the viscosity is lower since the melt behaves like a low molecular weight polymer free of the three-dimensional network. However for PEI 1F a sheer nematic phase remains up to the beginning of isotropization and the rheological hysteresis (*Figure 5*) is due to the long time required for the nematic texture to regenerate during cooling.

Effect of frequency. The complex viscosity, η^*, at 210 and 270°C, of both PEIs as a function of frequency are presented in *Figure 6*. The viscosity of PEI 1F at 210°C does not show a plateau zone but grows following a scale law of $\eta^* \propto 1/\dot{\gamma}$ at low frequencies. This result is typical of viscoplastic systems and has also been observed in nematic copolyesters[9]. However, at 270°C, well above T_i, η^* levels off to a frequency independent viscosity, $\eta_0=50$ Pa s. This value is four times lower than that of PEI 2E and this result is explained by the differences in the molecular weights of both polymers. The intrinsic viscosities of PEI 1F and PEI 2E are 0.68 and 0.81 dl g^{-1},

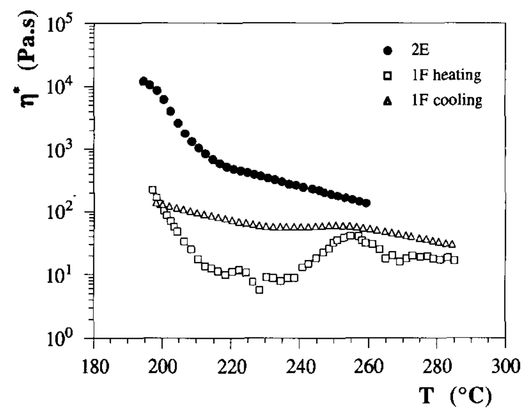


Figure 5 Complex viscosity at $\nu=1$ Hz *versus* temperature for PEI 1F and PEI 2E

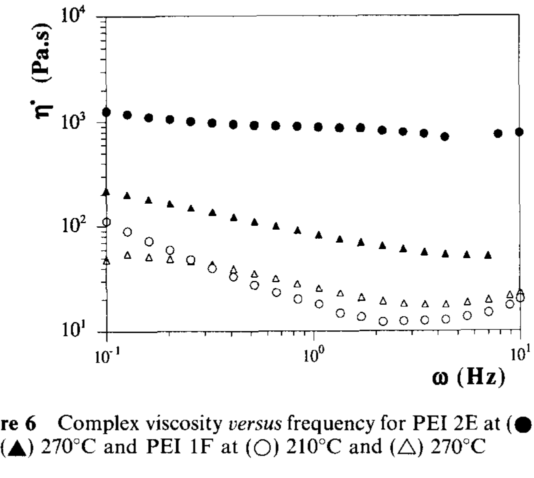


Figure 6 Complex viscosity *versus* frequency for PEI 2E at (●) 210°C and (▲) 270°C and PEI 1F at (○) 210°C and (△) 270°C

respectively. Thus, applying the well known $[\eta] \propto M^{\alpha}$ $(0.5 \leqslant \alpha \leqslant 1)$ and $\eta_0 \propto M^{3.5}$ equations leads us to the differences observed in *Figure 6*. When PEI 1F flows in the nematic state, e.g. at 210°C, its complex viscosity is more than one decade lower than that of PEI 2E confirming the low viscosities envisaged for this type of LC mesophase. The nematic phase gives way to a fibrillar morphology in the solid state, observable by SEM, which is due to the orientation produced during the injection of the material into the mould used to prepare the samples for rheological measurements. The morphology is rather similar to that observed, under similar mechanical history, in the Hoechst Celanese's thermotropic Vectra® A950 and differs from that of the non-liquid crystalline PEI 2E.

Steady-state flow

The steady-state shear viscosity, $\eta(\dot{\gamma})$, of both PEIs at 210 and 230°C are presented in *Figure 7*. Comparing with data of *Figure 6* we observe that the Cox–Merz rule[10]:

$$\eta(\dot{\gamma}) = [\eta^*(\omega)]_{\omega=\dot{\gamma}} \tag{2}$$

does not hold for PEI. This empirical rule, which has proven useful for polymers like polystyrene and polyethylene, fails for main chain thermotropic copolymers[11–13]. In the case of the LC PEI 1F sample the typical three flow regions defined by Onogi and Asada[14] for nematic LCPs can be envisaged: at low shear rates the viscosity decreases with increasing shear rate (region I); there then follows a region where the viscosity is almost constant (region II); finally the material becomes shear thinning again (region III). Region I has been explained by the polydomain structure formed in LCPs due to the fact that there are many defects or a complex distortion pattern. It is assumed that throughout region I and part of region II, the polydomain structure is preserved in spite of the flow and that at higher shear rates the flow orients the director, as the polydomains coalesce into a monodomain. Within this framework our viscosity data are fitted to Marrucci's model[15] for regions I and II:

$$\eta = \frac{\eta_0}{1 - x} \tag{3}$$

$$x = \frac{A}{A_0} \quad \text{and} \quad (1 - x)\left(\frac{1}{x^2} - 1\right) = \frac{A_0^2 \eta_0 \dot{\gamma}_{21}}{K} \tag{4}$$

where A is the radius of the domain at a certain shear rate $\dot{\gamma}$, A_0 is the radius of the quiescent domain and K is an elastic constant. A_0 is estimated using the equation:

$$\dot{\gamma}_{\mathrm{tr}} = \frac{K}{A_0^2 \eta_0} \tag{5}$$

Theoretical considerations led Wissbrun[16] to calculate $K = 10^{-10}$ N for polymeric liquid crystals and recently[17] a value of 3×10^{-9} N has been calculated for Vectra® B950. In our case, we take $K = 10^{-10}$ N and η_0 and $\dot{\gamma}_{\mathrm{tr}}$ are obtained adjusting experimental data to equation (4) by an iterative program. The model parameters are presented in *Table 3*.

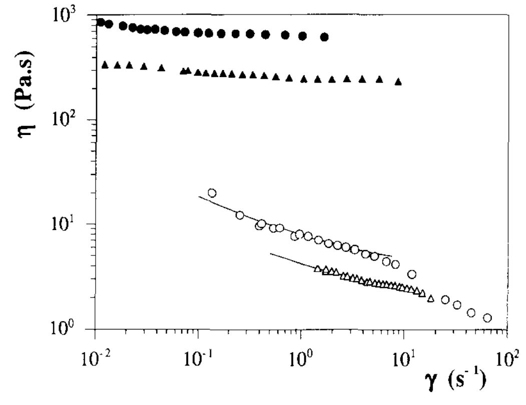


Figure 7 Viscosity, η, as a function of shear rate, $\dot{\gamma}$, for PEI 2E at (●) 210°C and (▲) 230°C and PEI 1F at (○) 210°C and (△) 230°C. The lines correspond to Marrucci's model

Table 3 Marrucci's model parameters for PEI 1F

Temperature (°C)	η_0 (Pa s)	$\dot{\gamma}_{\mathrm{tr}}$ (s^{-1})	A_0 (μm)
210	3.50	1.0	5.3
230	1.75	1.2	6.9

CONCLUSIONS

The results have shown the great influence of –COO– group orientation on the rheological properties of PEIs of identical composition and confirm that spacers linked by ether groups are much more effective than those linked by carbonyl groups to produce LC thermotropic materials.

The rheological results discussed in this work demonstrate the thermotropic nature of PEI 1F which compared to the isotropic PEI 2E shows the following features: viscosity increases with temperature in the range 235–260°C, due to isotropization of the sample; the viscosity of PEI 1F in the nematic state is considerably lower than that which corresponds to the scaling law $\eta_0 \propto M^{3.5}$; the viscosity curves display the three regions typical of LCPs; an orientation, observable by SEM only in the case of PEI 1F, was produced during the injection process in a mould.

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