Influence of annealing on the thermal and viscoelastic behaviour of poly(triethylene glycol *p,p*′-dibenzoate)

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The effect of thermal history on the phase behaviour and viscoelastic relaxations of poly(triethylene glycol *p,p*′-dibenzoate) (PTEB) was studied. The mesophase of PTEB can be converted into a three-dimensional crystal by annealing at appropriate temperatures and for appropriate times. Three PTEB samples were analysed, one of them freshly quenched from the melt and the other two annealed under different conditions (room temperature and 85°C). The phase structure was investigated by differential scanning calorimetry and X-ray diffraction, both at wide and low angles (using synchrotron radiation in the latter case). This structure affects slightly the β and γ relaxations, whereas the glass (α) transition is more intense and narrow and appears at a lower temperature for the sample freshly quenched from the melt, which exhibits only the liquid crystalline phase.

(Keywords: phase behaviour; dynamic mechanical relaxations; thermotropic polydibenzoates)

INTRODUCTION

Dynamic mechanical analysis provides information about the molecular processes taking place in polymers and many studies of this kind have been devoted to amorphous and semicrystalline polymers. However, similar investigations on polymers exhibiting liquid crystalline phases are scarce.

Several studies have been performed on polyesters derived from dibenzoic acid and different alkylene glycols that show the ability of the diphenyl group to produce mesophase structures[1–5], although the liquid crystalline phase of these polymers usually undergoes a rapid transformation into a three-dimensional crystal. The introduction of oxygen atoms into the polydibenzoate spacers has been employed to prevent or slow down this transformation. Thus, a comparative study of the thermotropic and conformational properties of poly(triethylene glycol *p,p*′-dibenzoate) (PTEB) and its analogue polyester with an all-methylene spacer, poly(octamethylene glycol *p,p*′-dibenzoate) (P8MB), has been reported[6]. The smectic mesophase of PTEB is stable for a few days at any temperature below its isotropization point, although the transformation into a three-dimensional crystal can be attained by annealing at the appropriate temperature.

Taking advantage of this phase behaviour, the aim of this paper is to analyse the effect of thermal history on the viscoelastic behaviour of PTEB and the implications of the different phases for the dynamic mechanical relaxations of this polymer.

EXPERIMENTAL

The polymer used in this investigation was the same as that used in earlier work[6,7]. It was obtained by transesterification of the diethyl ester of *p,p*′-dibenzoic acid with triethylene glycol using isopropyl titanate as the catalyst. It was purified by precipitation from a chloroform solution using methanol. The intrinsic viscosity measured at 25°C in chloroform was 1.04 dl g^{-1}.

Three samples were prepared from a film moulded in a Collin press at 150°C for 5 min and then cooled at constant pressure by quenching the polymer between two water-cooled plates. One of the samples, PTEB-Q, was analysed immediately after quenching. The second sample was left at room temperature (which can be as high as 40°C during the summer) for 13 months (sample PTEB-RT) and the third sample was annealed in a thermostatic bath at 85°C for 12 days and then left at room temperature for more than one year (sample PTEB-85).

The thermal transitions were determined by differential scanning calorimetery (d.s.c.) with a Perkin–Elmer DSC7

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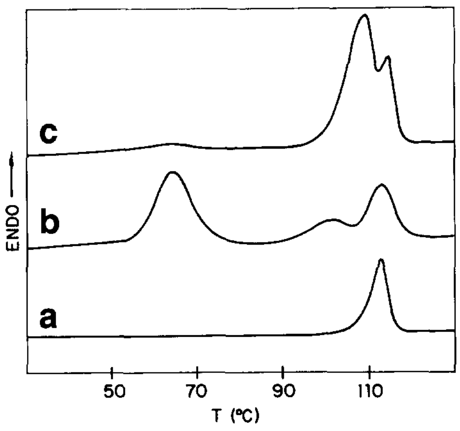

Figure 1 D.s.c. melting curves of the three PTEB samples: (a) PTEB-Q; (b) PTEB-RT; (c) PTEB-85

calorimeter connected to a cooling system. The heating rate was 20°C min^{-1}. X-ray diffraction patterns of samples at wide angles (WAXD) were obtained by using a Geiger counter X-ray diffractometer made by Philips that used nickel-filtered CuKα radiation.

The samples were also analysed by small-angle X-ray scattering (SAXS) using synchrotron radiation in the Daresbury Laboratory (UK). The sample–detector distance was 1.6 m and rat-tail collagen (L= 67.0 nm) was used for calibration. The spacings covered by the experimental set-up ranged from about 1.4 to 35 nm.

Viscoelastic properties were measured with a Polymer Laboratories MK II dynamic mechanical thermal analyser working in the tensile mode. The complex modulus and the loss tangent of each sample were determined at 3, 10 and 30 Hz over a temperature range from −140 to 90°C at a heating rate of 2°C min^{-1}. The apparent activation energy values were calculated according to an Arrhenius-type equation, employing an accuracy of 0.5°C in the temperature assignments of the tan δ maxima.

RESULTS AND DISCUSSION

Phase behaviour

The effect of thermal history on the different PTEB samples is clearly reflected in the melting patterns. Thus, *Figure 1* shows that the freshly quenched sample presents only a sharp endotherm at 114°C, corresponding to the isotropization of the smectic (S_c) mesophase[6,7]. In contrast, the annealed samples present several endotherms, and the main peak is located at a temperature about 20–30°C higher than the annealing peak. These two samples also exhibit the isotropization endotherm, similar to the freshly quenched sample, which corresponds to regular thermotropic behaviour, in contrast to the monotropic transition of the crystal to the isotropic phases found in P8MB[6].

To gain a deeper insight into the phase structure, the different samples were analysed by WAXD. It has been shown[6] that the freshly quenched sample presents only two sharp diffractions and a diffuse outer halo. The sharp diffractions correspond to the spacing of the smectic layers (1.85 nm) and its second order, while the outer halo, at 0.43 nm, is attributed to the laterally disordered arrangement within the layers. On the other hand, *Figure 2* shows the X-ray diffractograms of the annealed specimens. Several sharp diffractions, characteristic of three-dimensional order, are observed for these annealed samples. Therefore, it is concluded that the main endotherms in the melting of the annealed samples are caused by transformation of the crystals, formed during the annealing process, into a mesophase structure.

A third endotherm of smaller intensity occurs (see *Figure 1*) in the melting curves of the annealed samples, at about 100°C for PTEB-RT and at about 65°C for PTEB-85. From the comparison of these two samples, it is concluded that the peak at 65°C for PTEB-85 corresponds to some crystals formed when the sample was left at room temperature, i.e. the annealing time at 85°C was not enough to complete the transformation of the liquid crystalline phase into the three-dimensional crystal. The nature of the peak at 100°C for PTEB-RT is not so obvious. It could be caused by: (i) a mesophase–mesophase transformation, i.e. the main peak at 65°C may have produced a mesophase different from the S_c mesophase found in the freshly quenched sample; (ii) the transition of a second crystalline form into the S_c mesophase; or (iii) the transformation of the same crystal structure as that appearing at 65°C through recrystallization and perfection, as has been reported in the melting of other polyesters[8–11]. A closer look at the diffractograms in *Figure 2* reveals that there are some differences between the two annealed samples as the relative intensities of the different diffractions are not the same. The differences may be caused by different crystal structures (or a highly ordered mesophase) in the original samples which cannot be directly correlated with the various endotherms found in the dynamic scanning calorimetry (d.s.c.) experiments. Variable temperature X-ray experiments, as well as the annealing of PTEB at other temperatures, are being pursued in order to elucidate these problems.

D.s.c. endotherms can also arise from the enthalpy relaxation (physical ageing) of amorphous polymers at temperatures below the glass transition. This process may be present in the PTEB sample annealed at room temperature, but, considering the results found[12] for poly(diethylene glycol p,p'-dibenzoate) (a polymer similar to PTEB but with only two ethylene oxide units in the spacer), possible endotherms from enthalpy relaxation should appear at temperatures a few degrees (less than 10) higher than T_g.

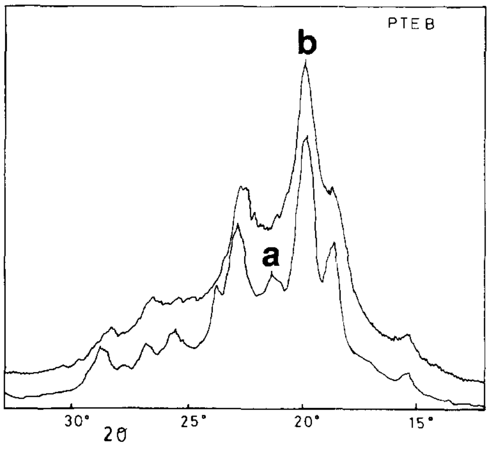

Figure 2 Wide-angle X-ray diffraction patterns for (a) PTEB-85 and (b) PTEB-RT

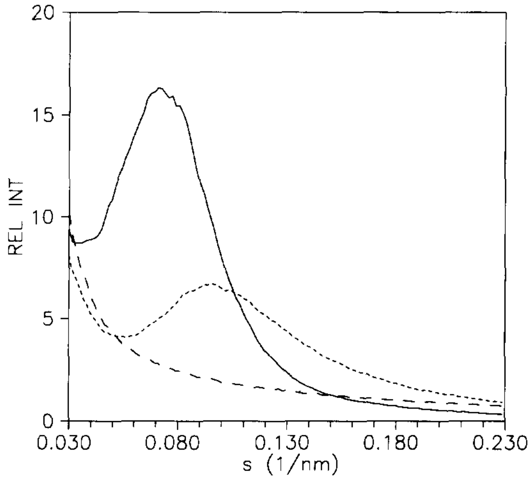

Figure 3 Small-angle synchrotron curves as a function of the scattering vector *s* for the three PTEB samples: (——) PTEB-Q; (- - -) PTEB-RT; (——) PTEB-85

Table 1 Long spacings (*L*), degrees of crystallinity (f_c) and crystal thicknesses (l_c) of the PTEB samples with different thermal histories

Sample	Thermal history	*L* (nm)	f_c	l_c (nm)
PTEB-Q	Freshly quenched	–	0	–
PTEB-RT	Room temperature (13 months)	10.5	0.40	4.2
PTEB-85	85°C (12 days)	13.8	0.46	6.3

The SAXS analysis of the samples was performed at room temperature using synchrotron radiation. The SAXS profiles for the three samples are shown in *Figure 3*. It can be seen that the sample presenting only the liquid crystalline phase does not exhibit any defined long spacing (up to the experimental limit* of 35 nm). In contrast, the annealed samples lead to the typical distributions of long spacings found for semicrystalline polymers. The maxima of these distributions appear at 13.8 and 10.5 nm for the samples annealed at 85°C and at room temperature over a long time, respectively. Therefore, the results show a very apparent increase of the most probable long spacing with increasing annealing temperature. Considering a two-phase model for a sample of known crystallinity, the calculation of the crystal thickness is straightforward. The crystal fractions f_c were determined from the X-ray diffractograms in *Figure 2* by subtracting the broad halo. The corresponding values are shown in *Table 1*, as are the calculated crystal thicknesses l_c. The increase in the most probable crystal thickness with annealing temperature is very significant. Moreover, it can be seen that the distribution of long spacings for PTEB-RT extends to very low values, probably because of the wide range of temperatures in the ambient conditions (typically from 15 to 40°C).

Viscoelastic relaxations

Each of the three PTEB samples displays three relaxations, α, β and γ in order of decreasing temperature. The α relaxation, associated with the glass transition, is much more intense than the β and γ relaxations. The influence of thermal history on the location and intensity of the α peak can be observed in *Figures 4* and *5*, and the results are summarized in *Table 2*. It can be seen that the intensity of this relaxation (measured on both E'' and tan δ basis) decreases considerably on passing from the liquid crystalline sample (PTEB-Q) to the annealed samples, owing to the appearance of the crystalline phase (*Figure 5*). Moreover, the annealing increases the temperature of the α peak, as well as the broadness of the relaxation (*Figure 5*). These results suggest that the liquid crystalline phase produces an α relaxation similar to that of amorphous polymers, despite the existence of the two-dimensional order characteristic of smectic mesophases, and the α relaxation changes following the same trend as that in semicrystalline polymers. In addition to this, an Arrhenius analysis shows for the apparent activation energy of this relaxation a high value, of the order of 400 kJ mol^{-1}, as can be expected for a glass transition in the range of frequencies studied.

The glass transition temperature of the sample maintained at room temperature for a long time (PTEB-RT) is somewhat higher than that of the PTEB-85 sample, contrary to expectations when considering that

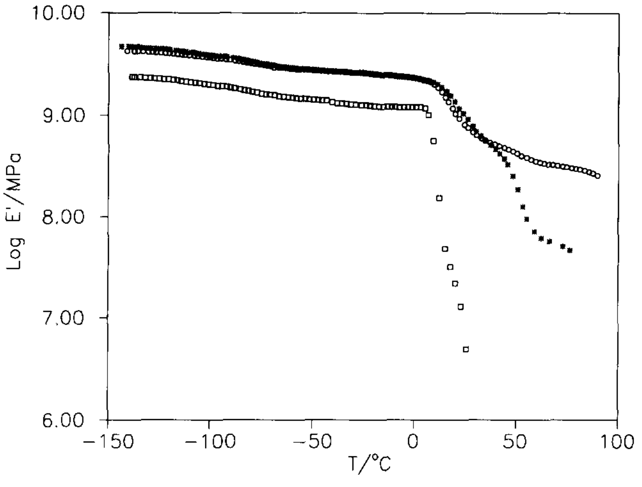

Figure 4 Effect of thermal history on the temperature dependence of the storage modulus (3 Hz) for (□) PTEB-Q, (○) PTEB-85 and (*) PTEB-RT

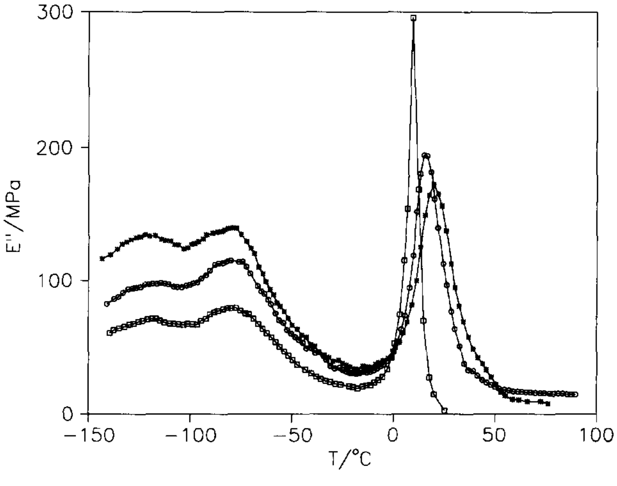

Figure 5 Temperature dependence of the loss modulus (3 Hz) for (□) PTEB-Q, (○) PTEB-85 and (*) PTEB-RT

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[*] In a different SAXS experiment using a longer sample–detector distance (with an upper limit of 65 nm), no long spacing was detected in the PTEB-Q sample

Table 2 Relaxation temperatures ($\tan \delta$ basis, 3 Hz) and activation energies for the three relaxations of the PTEB samples. The numbers in parentheses refer to the relative values of $\tan \delta$

Sample	T_α (°C)	$(\tan \delta)_\alpha$	ΔH (kJ mol^{-1})	T_β (°C)	$(\tan \delta)_\beta$	ΔH (kJ mol^{-1})	T_γ (°C)	$(\tan \delta)_\gamma$	ΔH (kJ mol^{-1})
PTEB-Q	15	1.2 (84)	>400	−75	0.047 (3.3)	65	−110	0.032 (2.3)	40
PTEB-RT	26	0.151 (12)	340	−77	0.042 (3.2)	80	−114	0.031 (2.4)	–
PTEB-85	19	0.155 (13)	>400	−76	0.036 (3.0)	95	−112	0.025 (2.1)	48

PTEB-85 presents higher values of crystallinity and crystal thickness. The reason may be the very broad distribution of spacings found for sample PTEB-RT (see *Figure 3*) that probably leads to a very high number of crystallites (of small thicknesses), therefore restricting the possibility of movement in the amorphous region and giving rise to a slightly higher value of T_g. This explanation is supported by the fact that the α relaxation of PTEB-RT is broader than that of PTEB-85 (see *Figure 5*). On the other hand, the possibility of different crystal forms between these two samples cannot be disregarded, although a higher degree of crystal perfection is expected for sample PTEB-85, with low T_α.

Unfortunately, the glass transitions of the two annealed samples are not well defined in the d.s.c. curves, as is usual in many semicrystalline polymers. Only the freshly quenched sample exhibits a clear T_g centred[13] at 14°C, which compares very well with the T_α value shown in *Table 2*.

Regarding the storage modulus, there are some meaningful differences between the annealed samples and the freshly quenched sample. Thus, *Figure 4* shows a considerably higher value of this modulus for the two annealed samples, owing to the presence of three-dimensional order. Moreover, the profound decrease of the storage modulus found for the quenched sample in the vicinity of the glass transition is less marked in the two semicrystalline specimens, and that decrease appears to be very sensitive to thermal history.

The β relaxation of polyesters is considered to have a complex mechanism involving movements of phenyl, carbonyl and methylene groups[14,15]. The present results seem to indicate that the phase structure and thermal history do not have an important effect on the intensity of this relaxation. Thus, *Figures 4* and *5* and *Table 2* show that the temperature location of the β relaxation is approximately the same for the freshly quenched sample (exhibiting a liquid crystalline phase), the sample annealed at 85°C and the sample annealed at room temperature for a long time. Referring to the intensity of the β relaxation, the results show a slight increase of the $\tan \delta$ maximum as the degree of crystallinity decreases. This increase can be observed either by considering the maximum values of $\tan \delta$ at the temperature of the β relaxation or by considering the relative values of $\tan \delta$ (figures in parentheses in *Table 2*). The relative values were obtained by dividing each maximum value by the corresponding minimum $\tan \delta$ in order to avoid the possible influence of geometrical form factors of the samples on the measurements. Moreover, this relaxation is very broad in all the samples and overlaps the γ relaxation. The activation energy of the β peak is about 85 kJ mol^{-1} for each of the three samples, of the same order of magnitude as that of other polyesters[14,16].

Finally, the γ relaxation is associated with crankshaft movements of polymethylenic sequences of at least three units in length. This relaxation is found in the three samples of PTEB with no remarkable influence of thermal history (*Table 2*). Thus, both the maximum value of $\tan \delta$ at the γ relaxation temperature and the temperature location of this relaxation change very slightly with the annealing conditions. The maxima of the γ relaxations, considering the loss modulus dependence with temperature (*Figure 5*), are more pronounced than those of the $\tan \delta$ values. As can be seen in *Figure 5*, the loss modulus values for PTEB-RT are much higher than those for PTEB-85, owing to the fact that both the $\tan \delta$ and storage modulus values for PTEB-RT are higher than the corresponding values for PTEB-85. It is difficult to calculate the activation energy from $\tan \delta$ maxima because of their broadness. However, it can be easily obtained from the more marked loss modulus maxima, giving a value of 39 kJ mol^{-1} for each of the three samples. The temperature and activation energy for this relaxation are similar to those reported for other polymers[17,18], and a similar result was found for the γ relaxation of a liquid crystalline polyester of the same series, namely poly(diethylene glycol *p,p'*-dibenzoate)[13], thereby confirming that the oxygen atoms in the methylenic chains also contribute to the γ relaxation.

In conclusion, the different thermal histories imposed on PTEB have a minor effect on the β and γ relaxations, while the α transition is greatly dependent on the annealing of the samples, being considerably more intense and narrower for the specimen freshly quenched from the melt, which exhibits only a liquid crystalline order. Moreover, the increase of the storage modulus produced by crystallization is very apparent in the dynamic mechanical results. Finally, the presence of a clear loss maximum in PTEB, at the temperature of the typical γ relaxation of polymethylenic moieties, further confirms our earlier results[13] on the possibility of crankshaft motions around −120°C when one methylenic unit in the polymethylenic sequence is substituted by an oxygen atom.

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