

Dynamic mechanical relaxations of liquid crystalline copolyesters derived from bibenzoic acid

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Viscoelastic relaxations have been studied in thermotropic copolyesters synthesized by transesterification of diethyl *p,p'*-bibenzoate and different ratios of triethylene glycol (TEG) and 1,8-octanediol. A liquid crystal glass is obtained in these copolymers by fast quenching from the isotropic melt, as revealed by d.s.c. and X-ray measurements. Three relaxations, α , β and γ in order of decreasing temperature, appear in all the samples. The α relaxation is identified as the glass transition of the mesophase, and the results are compared with those obtained from d.s.c. measurements. The glass transition temperature of the mesophase of these copolymers shows a relationship with the composition similar to that for amorphous copolymers. The shape, intensity and temperature location of the α relaxation are very much dependent on the composition. More intense and sharper α peaks, shifted to lower temperatures, are obtained when the TEG content increases. The β relaxation, associated with the carboxyl group, is also affected by the structure of the flexible oxyalkylene spacer. Finally, the γ relaxation shifts to slightly lower temperatures when the TEG content increases. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Thermotropic polyesters have received considerable attention in recent years, owing to increasing industrial and academic interest. Several studies have been performed on polymers derived from bibenzoic acid and different oxyalkylene glycols^{1–8}, showing that smectic mesophases are obtained in these polyesters and that the presence of oxygen atoms in the spacer reduces significantly the ability to develop three-dimensional structures^{4–8} and increases considerably the range of stability of the mesophase.

Several studies^{6–11} have reported on the thermal properties, liquid crystalline behaviour and conformational aspects of poly(triethylene glycol *p,p'*-bibenzoate) (PTEB) and poly(octamethylene *p,p'*-bibenzoate) (P8MB). The results showed that the presence of oxyethylene units in the spacer of PTEB slows down the crystallization rate from the mesophase, which is a very rapid process in the analogous polyester with an all-methylene spacer, P8MB. Thus, the mesophase of PTEB experiences a very slow transformation to the crystalline state. Moreover, this mesophase exhibits a second order transition into a liquid crystalline glass. At temperatures below this transition, the mesophase is stable. For simplicity, the temperature of that transition will be referred to as T_g , although it has to be considered that a

liquid crystalline glass is involved and not an amorphous glass.

Other effects of the presence of ether groups in the spacer are the change from a monotropic behaviour in P8MB to an enantiotropic one in PTEB, as well as the reduction in the glass transition temperature^{9–11}. This rather interesting behaviour led us to perform a detailed study of the properties of copolymers of these two polyesters, by using calorimetric and dynamic mechanical techniques. One of the main reasons for studying the dynamic mechanical properties is that it is often possible to relate the peaks in the plots of loss modulus or loss tangent as a function of temperature or frequency to particular types of molecular motion in the polymer.

The aim of this work is to investigate the effect of the composition on the viscoelastic behaviour and on the T_g of the mesophase for a series of copolymers prepared from diethyl bibenzoate and different ratios of octamethylene and triethylene glycol, testing the applicability to liquid crystalline glasses of the empirical relations used for amorphous glasses.

EXPERIMENTAL

Several samples of poly[(triethylene glycol *p,p'*-bibenzoate)-*co*-(octamethylene *p,p'*-bibenzoate)] were synthesized by melt transesterification of diethyl *p,p'*-bibenzoate and varying proportions of triethylene glycol (TEG) and 1,8-octanediol (OMG), using isopropyl titanate as

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Table 1 Molar compositions, intrinsic viscosities and molecular weights for the different samples

	P8MB	C27	C44	C63	C76	C84	PTEB
f_{TEG}	0	0.27	0.44	0.63	0.76	0.84	1
$[\eta]$ (dl g ⁻¹)	1.3	1.0	0.9	0.7	0.8	0.7	0.4
$10^{-4} M_p$	—	6.7	4.8	6.0	8.0	—	1.5

catalyst. Due to the transesterification process, the copolymers must be statistical. The copolyesters were purified by dissolution in chloroform and precipitation in methanol. The composition was determined from the ¹³C n.m.r. spectra in deuterated chloroform (the spectra of the two homopolymers have been reported previously⁶). The corresponding molar compositions in TEG, f_{TEG} , are shown in Table 1. The values of the intrinsic viscosity, measured at 25°C in tetrachloroethane, are also presented in Table 1. The P8MB homopolymer sample is the same as that previously reported^{6,10}, while a new sample of PTEB has been synthesized for this work.

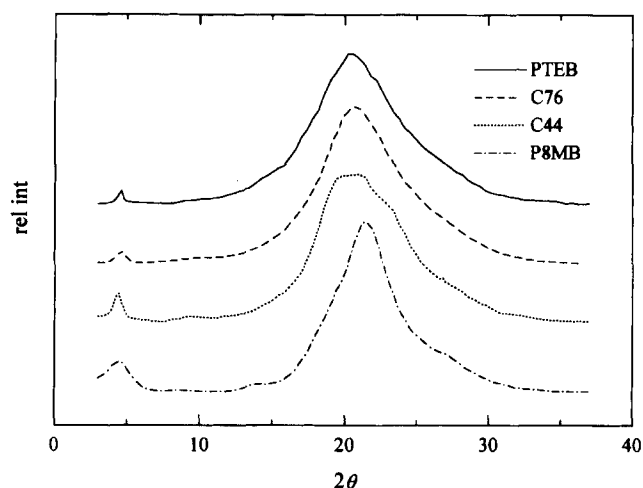
The molecular weights of the samples were determined by size exclusion chromatography in a Waters 150C equipment, using chloroform as eluent. The universal calibration plot was obtained from the data of several samples of monodisperse polystyrene (with molecular weights ranging from 1800 to 2 300 000). The molecular weights of the different polybenzoate samples, represented by the peak maximum, M_p , are shown in Table 1 (P8MB homopolymer is not soluble in chloroform). They were calculated from the elution volume of the peak and the intrinsic viscosity of the whole sample.

Initial copolymer films were prepared in a Collin press. The liquid crystal glass of the different samples was obtained by quenching from the isotropic melt. For that purpose, the film samples were melted at a temperature 20°C higher than the isotropization point in a Mettler FP82HT hot stage connected to a Mettler FP80HT temperature controller, and then transferred to the quenching agent. The homopolymer P8MB and the copolymers C27 and C44, owing to their fast mesophase-crystal transformation, were quenched into liquid nitrogen, while the remaining samples, with higher TEG content, were quenched to ambient conditions. All the samples were analysed after quenching.

X-ray diffraction patterns were obtained at room temperature with a Geiger counter X-ray diffractometer from Philips, employing nickel-filtered CuK α radiation.

A Perkin-Elmer DSC7 calorimeter, connected to a CCA7 cooling system, was used for detecting the transition temperatures. A heating rate of 20°C min⁻¹ was employed for the study of the glass transition. The glass transition temperature was taken as the temperature at which the increment of the specific heat capacity, ΔC_p , is half of the total value at the transition.

Dynamic mechanical measurements were carried out 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 100°C or less, depending on the glass transition temperature of the samples. The experiments were carried out in a dry nitrogen atmosphere at a heating rate of 2°C min⁻¹. The specimens used were

**Figure 1** X-ray diffractograms, recorded at room temperature, of the indicated polybenzoate samples freshly quenched from the melt

rectangular strips 2.2 mm wide with length and thickness around 13–16 mm and 0.2–0.5 mm, respectively. All relaxation intensities based on loss tangent values have been evaluated relative to the minimum value recorded for each experimental curve. The apparent activation energies were tentatively calculated according to an Arrhenius-type equation, from the maximum values of the loss tangent at the three mentioned frequencies.

RESULTS AND DISCUSSION

Phase behaviour and thermal properties

The X-ray diffractograms of the quenched copolybenzoate samples show the typical features of a smectic phase, i.e. a low-angle sharp diffraction (around $2\theta = 5^\circ$) arising from the smectic planes repeat, and a broad peak due to the disordered lateral arrangement of the smectic layers. A small degree of crystallinity may be present in the samples with lower TEG content (P8MB, C27 and C44), even after quenching in liquid nitrogen. Thus, the X-ray profiles for samples P8MB and C44 (Figure 1) show a broad peak not so smooth as that for samples C76 and PTEB, which may be indicative of the presence of a small degree of crystallinity (this possible crystallinity cannot be ascertained from d.s.c., since no endotherm corresponding to the melting of crystallites in the initial samples was identified). The X-ray diffractogram of the quenched P8MB sample has been previously reported¹⁰ and compared to that of a well crystallized sample. The influence of crystallinity on the viscoelastic relaxations in the case of P8MB will be commented on below.

The d.s.c. heating curves corresponding to the two quenched homopolymer samples are shown in Figure 2. It can be observed that PTEB presents a very clear glass transition at 13°C. The curve of P8MB shows the glass transition at 42°C, with a significantly smaller increment of specific heat and an endotherm at the top of the transition corresponding to the physical ageing of the sample¹⁰, which is also observed in PTEB. The enthalpy relaxation corresponding to the ageing is much higher for P8MB owing to the fact that this sample ages appreciably at room temperature, while PTEB does not, because its glass transition is lower than room

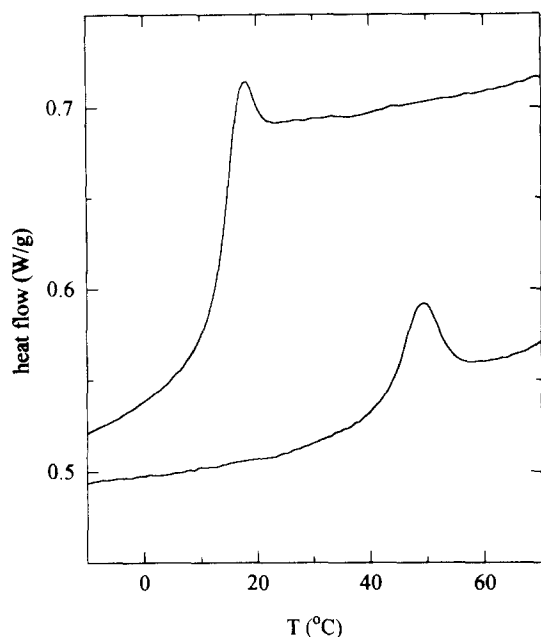


Figure 2 D.s.c. heating curves of quenched P8MB (lower) and PTEB (upper). Scanning rate $20^{\circ}\text{C min}^{-1}$

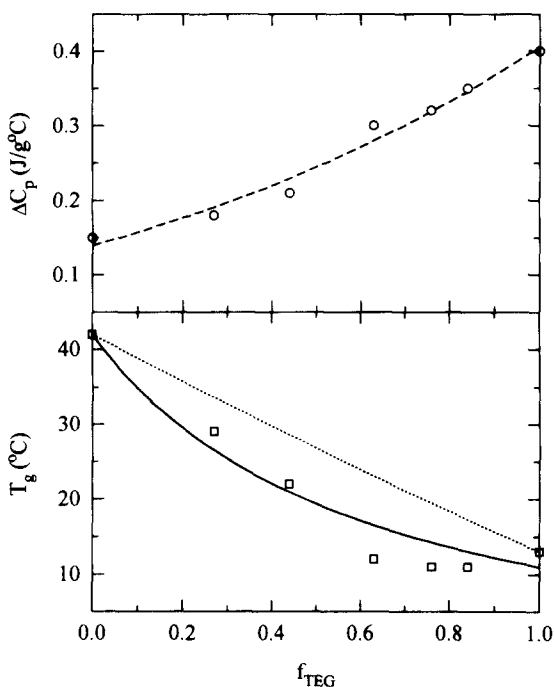


Figure 3 Variation of ΔC_p (upper) and experimental and calculated glass transition temperatures (lower) as a function of the molar composition in triethylene glycol, f_{TEG} . Dotted line: Fox equation. Continuous line: Gordon equation (see text)

temperature. The small peak at the top of the glass transition of PTEB arises from the short time necessary for equilibration at the initial temperature of the experiment (-30°C). It has been shown that a similar polybenzoate experiences appreciable ageing at the time scale of minutes at temperatures 10 – 20°C below the glass transition of the mesophase^{12,13}.

The values of the glass transition temperature for the different samples are shown in the lower part of *Figure 3* as a function of the copolymer composition. Taking

into account that the experimental uncertainty is $\pm 2^{\circ}\text{C}$, a rather smooth, but not linear, decrease of T_g with the fraction of TEG in the copolymer is observed. A possible influence of molecular weight in these results cannot be disregarded, since the molecular weight for sample PTEB is considerably lower than those for the other samples (*Table 1*). However, the value of T_g for a PTEB sample with a presumably much higher molecular weight ($[\eta] = 1.04 \text{ dl g}^{-1}$) was found¹¹ to be 14°C , i.e. only 1°C higher than that obtained in this work, and this difference is inside the experimental uncertainty. Therefore, we conclude that the mentioned decrease of T_g in the present samples is mainly due to an increase in the flexibility of the chain.

The decrease of T_g is higher than that obtained by considering a simple rule of mixtures of the two homopolymers:

$$T_g = c_1 T_{g1} + c_2 T_{g2} \quad (1)$$

where c_1 and c_2 are the compositions and T_g , T_{g1} and T_{g2} are the glass transition temperatures of the copolymer and the two homopolymers, respectively. Other semi-empirical relationships between T_g and the composition of copolymers^{14–17} have been proposed, which can be grouped into the general equation:

$$T_g = \frac{k c_1 T_{g1} + c_2 T_{g2}}{k c_1 + c_2} \quad (2)$$

where the parameter k takes the value $\Delta\alpha_1/\Delta\alpha_2$, $\Delta C_{p1}/\Delta C_{p2}$ or T_{g2}/T_{g1} (equations of Kelley and Bueche¹⁵, Gordon *et al.*¹⁶ or Fox¹⁷, respectively), $\Delta\alpha$ being the difference between the thermal expansion coefficients of the liquid and the glass. The values of $\Delta\alpha$ are not known, but the other variables can be determined from the d.s.c. curves. Thus, the increments in heat capacity at the glass transition are shown in the upper part of *Figure 3*. Even though the uncertainty of these values is rather high, $\pm 0.05 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$, a significant increase of ΔC_p with the TEG content is observed.

From the specific heat data of the homopolymers, the equations of Fox and Gordon *et al.* have been plotted in the lower part of *Figure 3*, compared with the experimental d.s.c. results. It can be observed that the depression of T_g in the copolymers is much higher than that predicted by the Fox equation. However, a good agreement is found with the Gordon equation and the continuous curve in *Figure 3* corresponds to equation (2) with the following parameters: $k = \Delta C_{p1}/\Delta C_{p2} = 2.7$, $T_{g1} = 284 \text{ K}$ (i.e. 11°C) and $T_{g2} = 315 \text{ K}$ (42°C).

In conclusion, the glass transition temperature of the mesophase of these copolymers seems to follow a relationship with the composition similar to the case of amorphous glasses.

Dynamic mechanical relaxations

Typical dynamic mechanical thermal analysis (d.m.t.a.) scans of these polyesters, including storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) as a function of temperature, are given in *Figure 4*. Three relaxations, α , β and γ in order of decreasing temperature, were found, in a similar manner to other polybenzoates with flexible spacers^{8–11,18}. The three relaxations will be considered separately in the following.

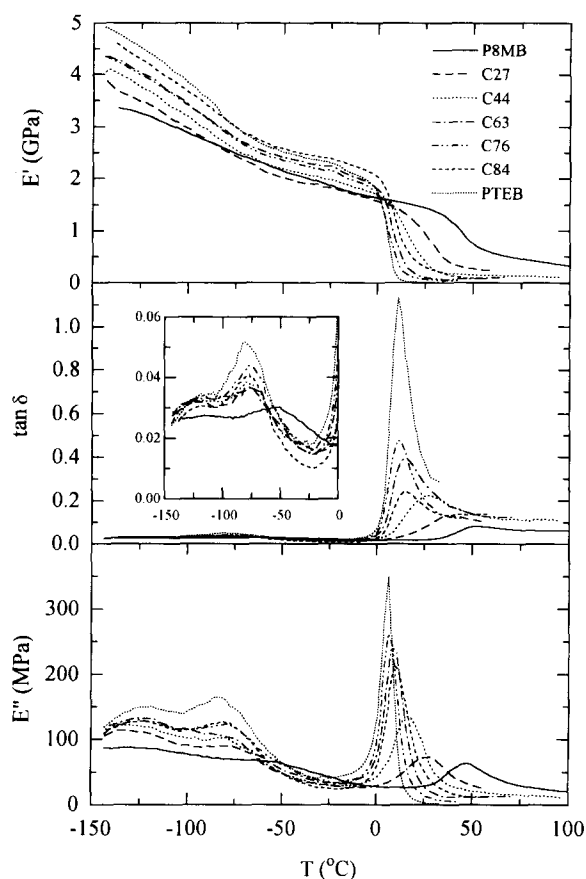


Figure 4 Temperature dependence of the storage modulus (upper), loss tangent (middle) and loss modulus (lower) of the quenched copolybibenzoates, at 3 Hz

α -Relaxation. The intense peaks in E'' and $\tan \delta$ curves corresponding to the α relaxation are accompanied by a pronounced decrease of E' at about the same temperature (Figure 4). Moreover, the α relaxation of the copolybibenzoates displays a high value of the apparent activation energy (around 400 kJ mol^{-1}). These concurrent features lead one to consider this relaxation as the glass transition of the liquid crystalline polymers studied in this work, associated with the initiation of micro-Brownian motions of the molecular chain from the frozen state.

The variation of the temperature location of this relaxation as a function of the composition is shown in the upper part of Figure 5. The values determined from the $\tan \delta$ and E'' plots are both compared with the d.s.c. measurements. It can be observed, first, that the location of the α peak shows a gradual decrease from P8MB to PTEB, in accordance with the expected increase in flexibility of the chains caused by the introduction of oxyethylene units in the spacer. Moreover, the d.s.c. value of P8MB is lower than that for d.m.t.a. ($\tan \delta$ basis), as is observed for conventional polymers. However, the difference between the two T_g values becomes smaller as the TEG content increases, and for PTEB the T_g determined by d.s.c. is slightly higher than the corresponding value from $\tan \delta$. On the other hand, the values obtained from the E'' plots always remain below the d.s.c. determinations, except for P8MB.

The reduction in T_g is accompanied by a marked increase (1500%) of the intensity for the α relaxation, measured on a $\tan \delta$ basis, as seen in the middle part of

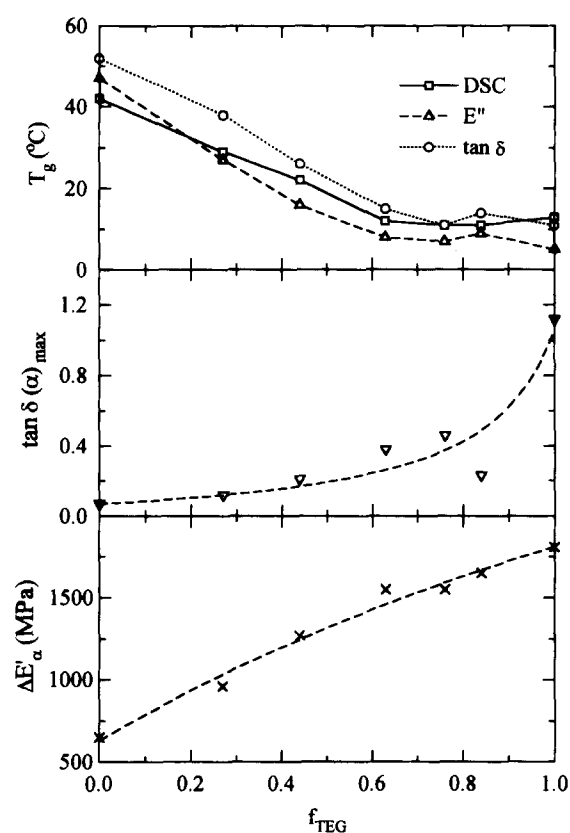


Figure 5 Variation with the composition of the glass transition temperature determined with different techniques (upper), maximum loss tangent of the α peak (middle), and fall of the storage modulus at the glass transition (lower)

Figure 5. Although a parallel sharpening of the α peak is also obtained as the TEG content increases (Figure 4), the total area under this peak also experiences a very important increase on passing from P8MB to PTEB (it is about 10 times higher for PTEB, on the $\tan \delta$ plots). Therefore, the intensity of the α relaxation seems to be dependent on the proportion of oxygen atoms in the spacer, confirming the previous results on polybibenzoates with oxyethylene spacers¹¹. In that work, the $\tan \delta$ maximum for the α peak was found to be as high as 1.8 for the polymer with four oxyethylene units in the spacer. The influence of the structure of the spacer on the shape and location of the α relaxation of polybibenzoates is readily deduced from the results discussed here. Moreover, the fall of the storage modulus, $\Delta E'$, at the glass transition is also dependent on the TEG content, as shown in the lower part of Figure 5. This parameter was found to be also dependent on the number of oxyethylene units in the spacer of polybibenzoates¹¹.

As mentioned above, the presence of a small degree of crystallinity on samples P8MB, C27 and C44 cannot be disregarded, with a possible effect on the shape, intensity and location of the α peak. This effect of crystallinity has previously been analysed for P8MB, by comparing the behaviour of a quenched sample with that of a slowly crystallized one¹⁰ (with a crystallinity of about 50%). It was found that the temperature location is practically unaffected, and only a very slight change of the intensity of the α peak was found, although the peak broadens with crystallinity. However, the magnitude of this broadening is considerably smaller than that observed

Table 2 Temperature location ($\tan \delta$ basis, 3 Hz) and activation energies^a of the β and γ relaxations for the different samples

Sample	T_β (°C)	ΔH_β (kJ mol ⁻¹)	T_γ (°C)	ΔH_γ (kJ mol ⁻¹)
P8MB	-55	138	-116	41
C27	-76	124	-120	36
C44	-76	90	-124	33
C63	-77	86	-123	35
C76	-78	104	-123	36
C84	-79	84	-122	49
PTEB	-78	94	-122	42

^a Estimated errors: ± 25 and ± 10 kJ mol⁻¹ for ΔH_β and ΔH_γ , respectively

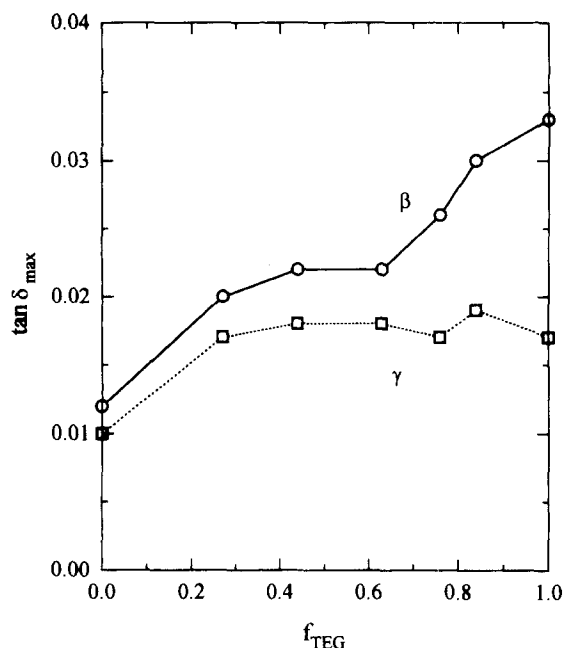
on passing from PTEB to P8MB. Moreover, a smooth variation with the TEG content is found for $\Delta E'$ and $\tan \delta$ for all the samples (Figure 5). We believe, therefore, that the TEG content is the most important factor determining the character of the α relaxation.

β Relaxation. The β relaxation in polyesters has been studied extensively by d.m.t.a. and dielectric measurements. It takes place in both cases in the temperature interval between -70 and -50°C . This relaxation in polyesters is believed to be a complex mechanism arising from movements of several groups^{8-11,18-20}.

Figure 4 shows that the β relaxation increases in intensity with the content in TEG. The maximum peak of the β relaxation for P8MB appears at approximately -55°C , although the curve is broad, indicative of a complex relaxation. In the case of the copolyesters the intensity increases and the peak is sharper, but the location of the maximum does not change appreciably with composition (Table 2).

The apparent activation energy of P8MB is higher than for the other copolyesters (Table 2) and there is a small decrease in the value when increasing the proportion of TEG, although the values from C44 to PTEB are within the experimental error. On the other hand, the activation energy corresponding to the β relaxation of PTEB is similar to that found for a different sample in a previous work¹¹, and slightly higher than the values corresponding to other thermotropic polybibenzoates with different oxyethylene spacers. However, in the case of poly(ethylene terephthalate)²⁰, the activation energy had a value around 80 kJ mol^{-1} . These different results are probably related to the conformational changes which take place due to the introduction of more flexible spacers that facilitate the movement of the carboxyl group around the biphenyl mesogenic moiety.

γ Relaxation. This subglass relaxation takes place at the lowest temperature, overlaps with the β relaxation (Figure 4), and coincides in location and activation energy with the γ relaxation of polyethylene²¹⁻²³, and also of polyethers²⁴ and polyesters¹⁹ with three or more methylene units. The polyesters studied in the present work show a diffuse γ relaxation over a temperature range from -130 to -110°C (Figure 4). PTEB and the copolyesters show the maximum at a temperature which is practically constant, slightly lower than that for P8MB. The γ relaxation is usually associated with crankshaft movements of methylene chains containing at least three consecutive methylene units. Previous work⁸⁻¹¹ reported that the ether group can cooperate with this

**Figure 6** Maximum values of the loss tangent for the β and γ relaxations as a function of the TEG content in the copolybibenzoates

restricted motion of the main chain when one of the methylene units is substituted by an oxygen atom. The present experimental results confirm this fact. Moreover, the activation energy is relatively low ($\sim 40 \text{ kJ mol}^{-1}$), a usual value for this relaxation, since this local motion of the chain requires a relatively small volume when the intervening bonds move as a crankshaft.

The results for the γ relaxation, compared with those of the β one, give a deeper insight into the influence of the spacer structure on the viscoelastic properties. The substitution of methylene groups by ether groups produces a significant increase of the intensity of the β relaxation, whereas the intensity increase of the γ relaxation is relatively small (Figure 6). These results hold for all pairs of polybibenzoates with the same number of groups (methylene and/or ether) in the spacer^{8,9,18}.

In summary, the influence of the spacer on the temperature location, intensity and broadness of the α relaxation is clearly observed in these liquid crystalline copolybibenzoates. Moreover, the $\tan \delta$ maximum of the β and γ relaxations shows a tendency to increase when the TEG content increases, although the increase in the γ relaxation is considerably smaller than that for the β peak. Given that the $\tan \delta$ value is a damping term, we expect that liquid crystal polybibenzoates containing oxygen atoms in the main chain would be suitable as reinforcement materials in applications requiring a large dissipation of energy at temperatures near the glass transition.

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