Relaxation processes in thermotropic polydibenzoates with oxyethylene spacers in the main chain*

Rosario Benavente, José M. Pereña†, Ernesto Pérez and Antonio Bello
Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3,
28006 Madrid, Spain
(Received 7 May 1992; revised 13 August 1992)

A dynamic mechanical analysis has been performed on three thermotropic polydibenzoates, designated PDEB, PTEB and PTTB, synthesized from *p,p'*-dibenzoic acid and di-, tri- or tetraethylene glycol, respectively. The isotropization temperature decreases greatly as the length of the spacer increases, and the mesophase of PTTB is not detected at all. Three dynamic mechanical relaxations are found for each polymer in the temperature range from −150 to 100°C. The α relaxation corresponds to the glass transition of the polydibenzoates, the β relaxation is typical of polyesters and the γ relaxation has its origins in the crankshaft motions of the oxyethylene units in the spacer, i.e. the oxygen atom can cooperate in this movement when substituting for a methylenic unit.

(Keywords: dynamic mechanical relaxations; thermotropic polydibenzoates; main-chain liquid-crystalline polymers; oxyethylene spacers)

INTRODUCTION

Several studies have been performed on polyesters derived from dibenzoic acid and different alkylene glycols, showing the ability of the diphenyl group to produce mesophase structures[1–4], although the liquid-crystalline phase of these polymers usually undergoes a rapid transformation into a three-dimensional crystal. The introduction of oxygen atoms in the spacer of polydibenzoates has been employed in order to prevent or to slow down this transformation[5,6]. Thus, a comparative study of the thermotropic and conformational properties of poly(triethylene glycol *p,p'*-dibenzoate) and its analogous polyester with an all-methylene spacer has been reported[6]. Moreover, some aspects of the thermotropic behaviour and solubility of three polydibenzoates with oxyethylene spacers in the main chain have recently been reported[7]. These polymers, prepared from *p,p'*-dibenzoic acid and di-, tri- and tetraethylene glycol, are designated PDEB, PTEB and PTTB, respectively, and their structural units are depicted in *Figure 1*. The number of oxyethylene units in the spacer clearly affects the phase behaviour of these polydibenzoates, and it is of major importance for the thermal stability of the mesophase. The isotropization temperature decreases greatly as the length of the spacer increases[7], changing from 192°C for PDEB to only 114°C for PTEB. In the case of PTTB, the mesophase is not obtained at all, and this polymer was found to be amorphous at room temperature (at least on a timescale of several days). A decrease in the glass transition temperature T_g with the length of the spacer was also found[7].

The aim of this work is, first, to study the origin of the different relaxations and the changes in their localization as a function of the number of oxyethylene units in the spacer of polydibenzoates. Second, the influence of the nature of the phase (amorphous or liquid crystalline) on the location and intensity of these relaxations will also be examined. The fact that these polydibenzoates present glass transition temperatures close to ambient conditions is an important factor to be considered for possible annealing or ageing effects.

EXPERIMENTAL

The polymers used in this investigation are the same as those used in a previous paper[7], obtained by melt transesterification of the diethyl ester of *p,p'*-dibenzoic acid and the corresponding glycol, using isopropyl titanate as catalyst. They were purified by dissolution in chloroform and precipitation in methanol. The values of the intrinsic viscosities, measured at 25°C in chloroform,

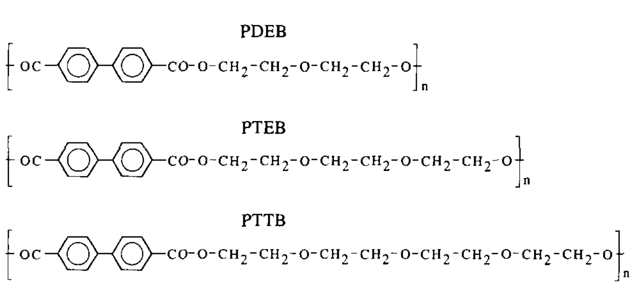

Figure 1 Repeat units of PDEB, PTEB and PTTB

---

* Dedicated to Professor Ricardo Granados on the occasion of his 75th birthday

† To whom correspondence should be addressed

0032-3861/93/112344-04

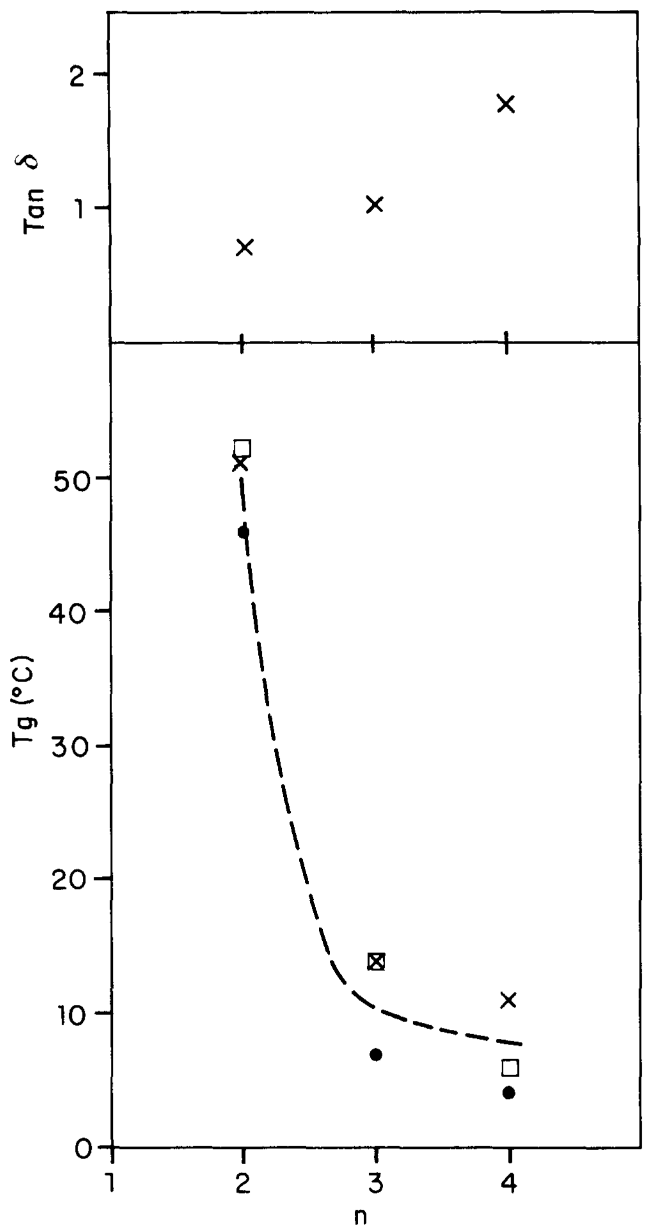

Figure 2 Variation of the glass transition temperature T_g and of the maximum tan δ of polydibenzoates with the number of oxyethylene units in the spacer: (●) and (×) d.m.t.a. results at 3 Hz, E'' and tan δ basis, respectively; (□) d.s.c. results, heating rate 10°C min^{-1}

are 1.02, 1.04 and 0.87 dl g^{-1} for PDEB, PTEB and PTTB, respectively.

Considering the important ageing effects found for PDEB at room temperature (see below) and their influence on the shape of the glass transition, the onset of this transition will be considered for comparative purposes, and freshly quenched samples (except otherwise indicated) will be used throughout this work. Therefore, we have re-examined the T_g values of the three polyesters. A Perkin–Elmer DSC7 calorimeter connected to a cooling system has been employed for those determinations. The heating rate was 10°C min^{-1}.

Viscoelastic properties were measured with a Polymer Laboratories Mk II Dynamic Mechanical Thermal Analyzer working in the tensile mode. The specimens for the measurements were moulded in a Collin press fitted with smooth-polished plates and hot-pressed at 1 MPa and at temperatures 20°C above those of isotropization for 5 min. The cooling process, under the same pressure, was carried out by quenching the molten polymer with water.

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 150°C, at a heating rate of 2°C min^{-1}. The specimens used were rectangular strips 2.2 mm wide, with length and thickness around 7–12 mm and 0.3–0.5 mm, respectively. The tan δ results were constant for the different sample sizes. The maximum values of the loss modulus and the loss tangent are considered to measure the intensity of the relaxations. The apparent activation enthalpy values were calculated according to an Arrhenius-type equation, considering an accuracy of 0.5°C in the temperature assignment from the maximum.

RESULTS AND DISCUSSION

The onset values of the glass transition determined by d.s.c. corresponding to the three polydibenzoates are represented in *Figure 2* as a function of the number of oxyethylene units in the spacer. It has to be considered that this transition corresponds to an amorphous glass in the case of PTTB, while it arises from a liquid-crystal glass for PTEB and PDEB. It would be very interesting to be able to obtain both the amorphous and the liquid-crystal glasses for the three polymers, in order to analyse the two glass transitions. Unfortunately, we were unable to quench the isotropic state of PDEB and PTEB (as usual for mesophase-forming polymers[8]), and even with very severe quenching conditions the X-ray diagrams of these two polymers present the characteristic reflections corresponding to the smectic layers. Moreover, the annealing of PTTB at different temperatures (and for reasonable times) always leads to amorphous polymers.

With these considerations, the fact that the decrease in the T_g value on passing from PTEB to PTTB is much smaller than from PDEB to PTEB (see *Figure 2*) might indicate that the transition corresponding to the amorphous glass occurs at a temperature equal to or higher than that for the liquid-crystal glass.

Regarding the dynamic mechanical analysis, the polymers studied show three viscoelastic relaxations, which are labelled α, β and γ in order of decreasing temperature. They will be studied separately in the following, and the main results are listed in *Table 1*.

α Relaxation

The α relaxation of the polydibenzoates is very intense (see upper part of *Figure 2*). The consideration of this relaxation as associated with long-range motions taking place in the glass transition zone of the polyesters agrees with the baseline change in the d.s.c. traces and the high

Table 1 Loss modulus results (maximum temperature and E'' values at each maximum, 3 Hz) and activation energies for the three relaxations of polydibenzoates

	T(°C)			E'' (MPa)			ΔH(kJ mol^{-1})		
Polymer	α	β	γ	α	β	γ	α	β	γ
PDEB	46.5	−58.5	[a]	276	64	[a]	380	75	–
PTEB	7.0	−77.5	[a]	398	186	[a]	320	85	–
PTTB	3.5	−81	−126.5	185	110	112	330	70	27

[a] Weak shoulder

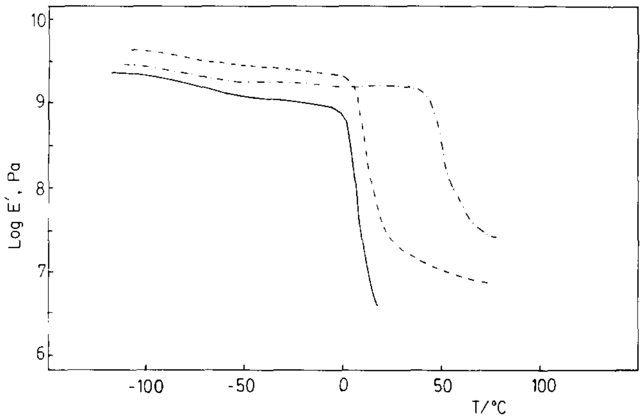

Figure 3 Dependence of the storage modulus on temperature for freshly quenched polydibenzoate samples: (–·–·–) PDEB; (– – –) PTEB; (——) PTTB

activation energy values obtained from the dynamic mechanical results (see *Table 1*).

The modulus drop between the glass and rubbery states ranges from two to three decades and it increases as the length of the spacer increases (*Figure 3*). This remarkable reduction of modulus is due to the initiation of micro-Brownian motion of the molecular chains from the frozen state with increasing temperature. Thus, the storage modulus decreases rapidly, and the loss modulus and tan δ exhibit maxima at the glass transition temperature T_g, depending on the chemical structure and flexibility of the molecular chain. The variation of T_g with the length of the spacer can be seen in *Figure 2*, showing that the glass–rubber absorption shifts towards lower temperatures for longer spacers. Moreover, the magnitude of the α peak, considering the tan δ values, increases with the length of the spacer.

The three polymers studied display remarkable ageing effects, with a strong increase of modulus and changes in the location and intensity of the glass transition. This phenomenon is exemplified in *Figure 4*, where the changes of dynamic moduli in a PDEB sample aged for 14 months are very apparent. A more complete study of the ageing process in these polymers is under way.

β Relaxation

The second relaxation in the members of this polyester series takes place in the temperature interval around −70°C and its temperature location decreases as the length of the spacer increases. The β relaxation of polyesters has been considered a complex mechanism arising by movements of phenyl[9], carboxyl[10] and methylene[11] groups, and it has been found by us previously in poly(trimethylene terephthalate)[12], poly(heptamethylene *p,p'*-dibenzoate)[13] and poly(ditrimethylene glycol *p,p'*-dibenzoate)[13].

We have also found this relaxation in an amorphous copolyester of poly(ethylene terephthalate) and poly(1,4-cyclohexylenedimethylene terephthalate) (3:1 by weight) plasticized with tricresyl phosphate[14]. In this case, the location (∼ −70°C at 3 Hz) and activation energy (∼60 kJ mol^{-1}) of the β relaxation remain constant, irrespective of the diluent concentration. However, the intensity of the β relaxation (measured through the maximum values of either tan δ or loss modulus) decreases linearly when the amount of plasticizer increases.

Diaz-Calleja *et al.* have studied the viscoelastic relaxations of several aromatic polyesters, including poly(triethylene glycol terephthalate)[15], poly(diethylene glycol isophthalate)[15], poly(propylene glycol terephthalate)[16] and poly(dipropylene glycol terephthalate)[16]. All these polyesters display a wide subglass relaxation, extending from about −60 to −140°C and composed of two overlapping peaks. This relaxation is not affected by isomerism of the phthaloyl residues[15] and its splitting is more apparent when the length of the glycol residue increases. Therefore, the two overlapped peaks, named β_1 and β_2 by those authors, are very clear for poly(dipropylene glycol terephthalate)[16] and only partially resolved in the case of poly(diethylene glycol terephthalate)[17].

In our results, all the polydibenzoates display two overlapped peaks below 0°C, although the resolution of the peaks for poly(tetraethylene glycol *p,p'*-dibenzoate) is better than in the case of poly(diethylene glycol *p,p'*-dibenzoate). This fact has allowed us to calculate also the activation energy of the lower peak for PTTB, as will be commented upon below. The resolution of the β peaks is better observed in the loss modulus plots (see *Figure 4*) because the tan δ maximum is very broad and tan δ values are low (0.04, 0.05 and 0.07 for PDEB, PTEB and PTTB, respectively).

The present results seem to confirm the complex character of the β relaxation and the possibility of different steric hindrances of the reorganizational motions of the carboxyl and phenylene groups depending on the spacer length, because the activation energy of this relaxation increases slightly with the length of the spacer (and is smaller in the case of the amorphous polymer). Moreover, its temperature location decreases as the length of the spacer increases.

γ Relaxation

The relaxation at the lowest temperature takes place below −100°C. The two polymers with shorter spacers (PDEB and PTEB) show weak relaxations overlapped with the β ones, owing to the low tan δ values (0.03 and 0.04, respectively). Notwithstanding this, the γ relaxation is clearly distinguished when using loss modulus plots, even in the case of PDEB, which shows the weakest one (see *Figure 4*). For PTTB, tan δ values in the γ relaxation interval are of the order of 0.05 and the activation energy can be calculated straightforwardly (*Table 1*).

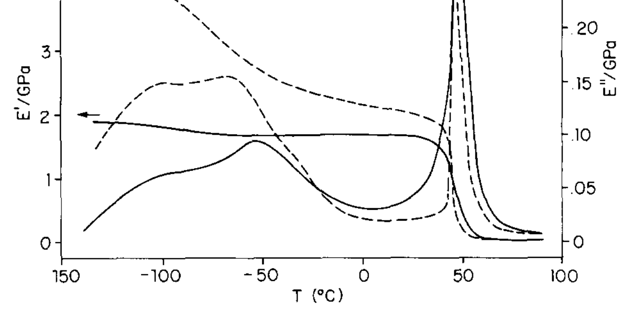

Figure 4 Variation of the storage, E', and loss, E'', parts of the complex elasticity modulus, at 10 Hz, for two PDEB specimens: (——) freshly quenched; (– – –) aged for 14 months

Other cycloaliphatic polyesters containing diethylene glycol units[18] also show a relaxation at low temperature (−110°C at 0.1 Hz, which should appear at −85°C for 3 Hz considering an activation energy of 35 kJ mol^{-1}). However, this low-temperature relaxation does not show appreciable shifting when the frequency changes, and disappears in the stretched networks[18]. Therefore, the low-temperature relaxation of those cycloaliphatic polyesters does not seem to correspond to the typical γ relaxation produced by methylenic motions.

It is usually considered that the γ relaxation arises from crankshaft movements of polymethylenic sequences, but the clear maximum of $\tan\delta$ and loss modulus for the three polymers studied leads to the conclusion that the motion responsible for this relaxation also takes place when one of the methylenic units is substituted by an oxygen atom. (A similar results has recently been found for the aromatic polyester poly(diethylene glycol terephthalate)[17]. The consideration of this relaxation as a γ relaxation is further confirmed by its activation energy, which amounts to ~30 kJ mol^{-1}, i.e. the common value of the activation energy of the γ relaxation.

In conclusion, the results reported in the present work confirm that the oxygen atom can cooperate in the crankshaft movement, responsible for the γ relaxation, when substituting for a methylenic unit in the polyethylene link.

ACKNOWLEDGEMENT

The financial support of the Comisión Interministerial de Ciencia y Tecnología (Projects Nos. MAT91-0380 and IN89-0066) is gratefully acknowledged.

REFERENCES

1 Meurisse, P., Noel, C., Monnerie, L. and Fayole, B. *Br. Polym. J.* 1981, **13**, 55
2 Krigbaum, W. R. and Watanabe, J. *Polymer* 1983, **24**, 1299
3 Watanabe, J. and Hayashi, M. *Macromolecules* 1988, **21**, 278
4 Pérez, E., Bello, A., Marugán, M. M. and Pereña, J. M. *Polym. Commun.* 1990, **31**, 386
5 Bello, A., Pérez, E., Marugán, M. M. and Pereña, J. M. *Macromolecules* 1990, **23**, 905
6 Pérez, E., Riande, E., Bello, A., Benavente, R. and Pereña, J. M. *Macromolecules* 1992, **25**, 605
7 Pérez, E., Benavente, R., Marugán, M. M., Bello, A. and Pereña, J. M. *Polym. Bull.* 1991, **25**, 413
8 Wunderlich, B. and Grebowicz, J. *Adv. Polym. Sci.* 1984, **60–61**, 1
9 Chung, C. and Sauer, J. A. *J. Polym. Sci. (A2)* 1971, **9**, 1097
10 Illers, K. H. and Breuer, H. *J. Colloid Sci.* 1963, **18**, 1
11 Farrow, G., McIntosh, J. and Ward, I. M. *Makromol. Chem.* 1960, **38**, 147
12 González, C. C., Pereña, J. M. and Bello, A. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 1397
13 Pereña, J. M., Marugán, M. M., Bello, A. and Pérez, E. *J. Non-Cryst. Solids* 1991, **131–133**, 893
14 Benavente, R., Pereña, J. M., Pérez, E., Bello, A. and Lorenzo, V., in 'Trends in Non-Crystalline Solids' (Eds A. Conde, C. F. Conde and M. Millán), World Scientific, Singapore, 1992, p. 317
15 Diaz-Calleja, R., Riande, E. and Guzmán, J. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 337
16 Diaz-Calleja, R., Riande, E. and Guzmán, J. *Macromolecules* 1989, **22**, 3654
17 Diaz-Calleja, R., private communication, unpublished
18 Diaz-Calleja, R., Riande, E. and Guzmán, J. *J. Polym. Sci., Polym. Phys. Edn.* 1991, **29**, 93