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Relaxations in poly(tetramethylene terephthaloyl-bis-4-oxybenzoate): effect of substitution in the mesogenic unit and in the flexible spacer

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The relaxation behaviour of a thermotropic polymer liquid crystal, poly(tetramethylene terephthaloyl-bis-4-oxybenzoate), and its derivatives with substitution in the mesogen and/or in the spacer, have been analysed by dynamic mechanical analysis and differential scanning calorimetry (d.s.c.). By comparing the relaxation spectra of the four polymers some conclusions can be drawn. They all show a β relaxation at low temperature and an α relaxation above room temperature. The β relaxation has been associated with local motions of the mesogenic unit. The substitution of chlorine in the mesogen increases the temperature of this relaxation by 60°C, but it is not affected by substitution in the spacer. The α relaxation has been associated with the glass transition of the amorphous phase. It increases by approximately 15°C with the introduction of lateral methyls in 1,4 position in the spacer, independently of substitution in the mesogen. The presence of crystalline order, besides the nematic mesophase, broadens this relaxation. © 1997 Elsevier Science Ltd.

(Keywords: thermotropic polyesters; liquid crystal polymers; relaxations)

INTRODUCTION

Thermotropic polyesters are main-chain liquid crystal polymers which have been widely studied in order to establish the relationship between structure and properties[1-3]. One of the most important series is that in which the mesogenic unit is 4,4′-terephthaloyl dioxydibenzoic acid and polymers with linear methylene spacers have been synthesized and studied by several authors[4-11]. The introduction of substituents in the mesogen and in the spacer produces a very important effect on the thermotropic behaviour of these polyesters and on the nature of the mesophases formed. Recently, the effect of symmetric or asymmetric lateral substitution in the flexible spacer has been studied in our group[12,13]. In all cases, the presence of side groups produced a less efficient packing of the chains, leading to a reduction of transition temperatures and the loss of three-dimensional ordering. These facts are of fundamental importance in the technological applications of these materials in order to blend them with high application thermoplastic polymer matrices. Therefore, not only changes in the spacers have been reported, but also substitution in the mesogenic units has been considered to obtain lower processing temperatures and mesophases with high stability. Thus, substituents with different polarity have been incorporated onto the aromatic units[9,14]. In this sense, we have studied the thermal transitions of poly(tetramethylene terephthaloyl bis-4-oxybenzoate) (P4TOB), and its derivatives, shown in *Figure 1*, with substituents in the mesogen and/or in the spacer, in order to correlate the structure with the properties of these polymers[13,15-17].

On the other hand, the relaxation behaviour of main chain liquid crystal polymers is very complex and a detailed analysis has been carried out in only a few cases[18-25]. In most of these studies it is very difficult to correlate the maxima observed by dynamic or dielectric measurements with the type of motion and which parts of the structure are involved in them.

In this paper, we report the low and intermediate temperature behaviour of the polymers shown in *Figure 1*. Dynamic-mechanical analysis has been used to determine the transitions and relaxations presented in the temperature range from −150 to 150°C. This analysis will allow the comparison with d.s.c. measurements in order to establish the corresponding relaxation modes and its relationship with the structure of these polyesters. The four polymers form a nematic mesophase and their phase diagram have been previously studied[13,15-17]. The presence of polar groups in the mesogen and lateral branches in the spacer will affect their relaxation behaviour as well as they have affected the transitions above room temperature.

EXPERIMENTAL

The synthesis and characterization of the four polymers studied has been described elsewhere[13,15-17].

The thermal transitions were measured using a Mettler TA-4000/DSC30 d.s.c., coupled to a PC with TA-72

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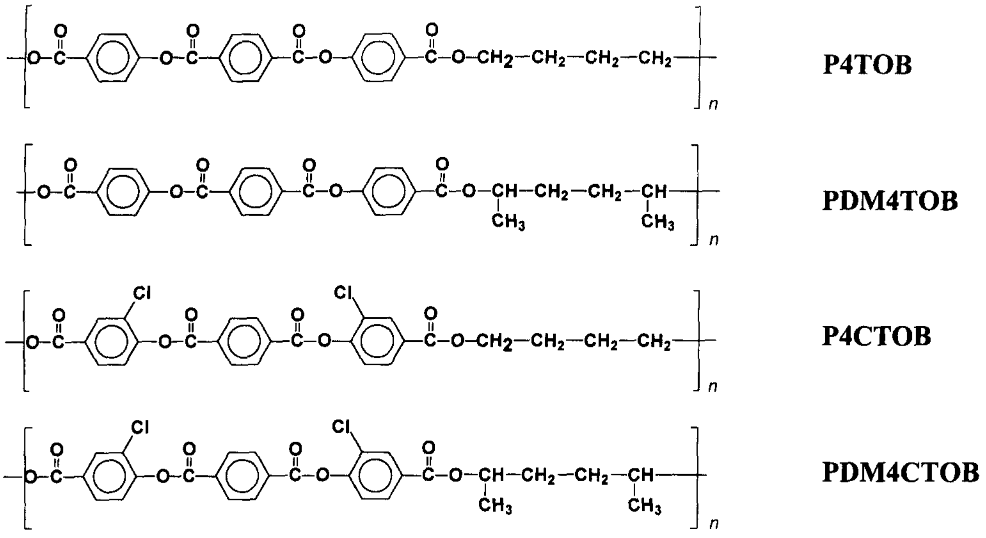

Figure 1 Schematic drawing of the four polymers studied and the nomenclature used

thermal analysis software. The heating and cooling rates were 5°C min^{-1}, and the glass transition temperatures were taken at the midpoints of the change in ΔC_p in the experimental thermograms.

Dynamic mechanical measurements were performed on a TA Dynamic-Mechanical Thermal Analyser (d.m.a.) working on the flexural-bending mode at frequencies of 0.1, 0.5 and 1 Hz. The experiments were carried out in the temperature range from −150°C to 150°C, using a heating rate of 5°C min^{-1}. The samples were prepared as films with dimension 10 × 5 × 0.5 mm by compression moulding from the nematic mesophase and cooled down to room temperature.

RESULTS AND DISCUSSION

In order to consider the influence of the structure on the thermal behaviour, the main transitions obtained by d.s.c. for the four polyesters and its thermodynamical parameters are summarized in *Table 1*.

Poly(tetramethylene terephthaloyl bis-4-oxybenzoate), P4TOB, has two crystalline forms depending on thermal treatment and a nematic mesophase[15]. The substitution of lateral methylenes at the 1,4 position in the spacer, PDM4TOB, results in a considerable lowering of the transition temperatures. The crystal–liquid crystal transition is lowered 100°C and a similar depression is observed for the mesophase–isotropic transition. The mesophase formed is also nematic but the formation of three-dimensional order is hindered and can only be obtained by long annealing processes[13]. The substitution of chlorine in the mesogen, P4CTOB, reduces only slightly the transition temperatures with respect to the unsubstituted polymer. P4CTOB presents three-dimensional order, in spite of the substitution, and two different crystalline forms have also been observed[16]. Finally, the combination of substitution in the spacer and in the mesogen, PDM4CTOB, produces the most important lowering in the transition temperatures (*Table 1*), and inhibits the formation of three-dimensional order[17].

The four samples were studied by dynamic mechanical analysis and displayed two relaxations, referred to as α and β, respectively, in order of descending temperature (*Figures 2–5*). This is a general result and appears in all cases independently that the structures correspond to linear and nonlinear spacers and to chlorinated or not chlorinated mesogenic moieties.

Table 1 Thermal transitions and thermodynamical parameters of polymers studied

Sample	T_{c-lc} (°C)	T_{lc-i} (°C)	ΔT (°C)	ΔH_{c-lc} (J mol^{-1})	ΔH_{lc-i} (J mol^{-1})
P4TOB[15]	285	350	65	11.1	–
PDM4TOB[13]	185	250	65	4.25	2.44
P4CTOB[16]	274	319	45	21.2	4.23
PDM4CTOB[17]	133	176	43	3.9	2.56

T_{c-lc}: temperature of crystal–liquid crystal transition
T_{lc-i}: temperature of liquid crystal–isotropic transition
$\Delta T = T_{lc-i} - T_{c-lc}$

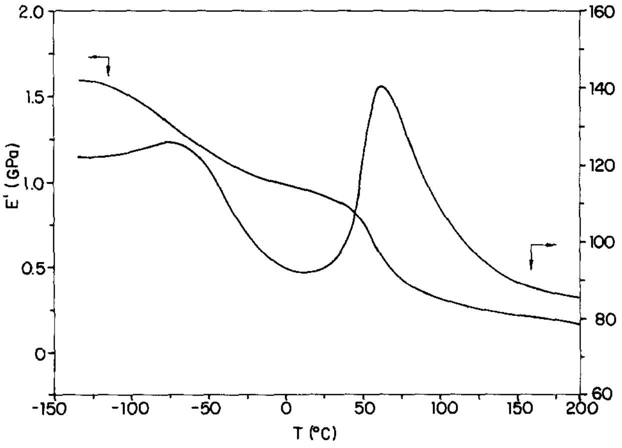

Figure 2 D.m.a. curves of a P4TOB film heated to 300°C and cooled to room temperature measured at 0.1 Hz

In *Table 2*, these results are summarized for both relaxations, stating the temperatures at which the maxima occur at indicated frequencies. These values correspond to the temperature of the loss moduli maxima. The activation energy for each relaxation has been obtained from the frequency shift of the corresponding maxima. The activation energy for the β relaxation has been calculated by Arrhenius, and for the α by the Vogel approximation[26], taking for the best fit a value of $T_0 = 50\,K$. It is important to point out that the very high values found for the activation energy for the α transition correspond to a very small range of frequencies and, therefore, to a few degrees in the maxima. In this case, the corresponding errors are high, and the energies can be regarded only as comparative and approximate ones due to the limited experimental range of frequencies.

Moreover, from *Table 2* it can be noticed that the α transition temperature for the samples P4TOB and P4CTOB and for the samples PDM4TOB and PDM4CTOB are practically identical. In other words, it seems that $T\alpha$ is very little affected by the chlorine substitution in the mesogenic unit. However, when $T\alpha$ is considered for a structure with symmetrical and nonsymmetrical spacers, there is an important increase of $T\alpha$ for the last cases, since it should correspond to a structure with more steric hindrance.

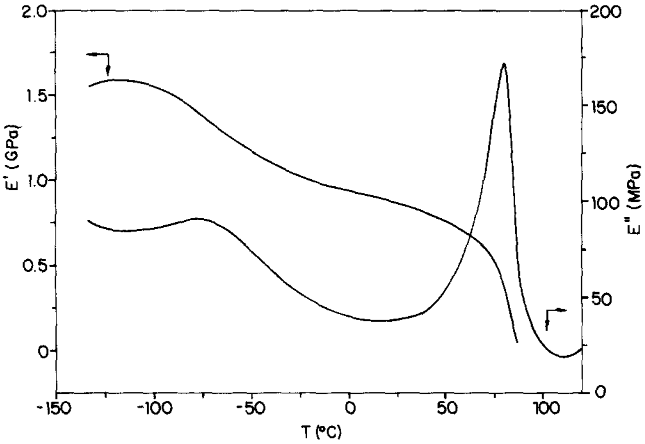

Figure 3 D.m.a. curves of a PDM4TOB film heated to 200°C and cooled to room temperature measured at 0.1 Hz

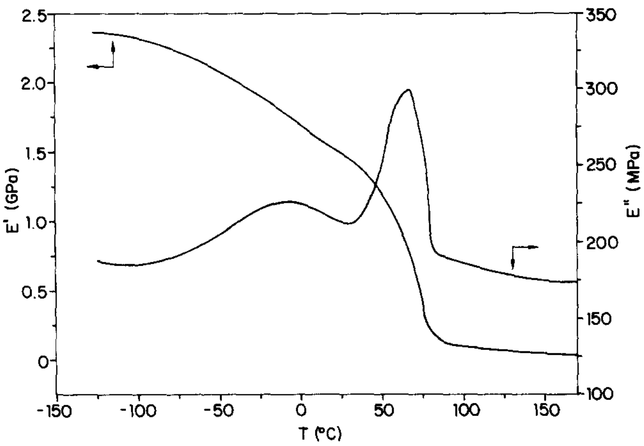

Figure 4 D.m.a. curves of a P4CTOB film heated to 290°C and cooled to room temperature measured at 0.1 Hz

In order to consider the origin of the dynamical relaxations, it is useful to compare these data with the calorimetric ones. The glass transition temperatures of the samples PDM4TOB and PDM4CTOB are 73°C and 79°C and of the samples P4TOB and P4CTOB 63°C and 67°C, respectively. It is very important to note that in these two former polymers the T_g is hardly observed by d.s.c. due to their high crystallinity (40–50%). These values are lower than the reported values for $T\alpha$, which is a general finding in polymers[27] and has been attributed to different ranges of frequency for the two experimental techniques.

With this analysis, the α relaxation can be related, in principle, with the glass transition temperature of this system. It is around 15°C lower for the structure with the linear spacer, independently of the chlorinated and non-chlorinated mesogenic unit.

Below T_g, relaxations involve motions of small sequences and several peaks have been observed in thermotropic polyesters and copolymers[18,19,28–33]. To rationalize the discussion of our results, we should first consider the general results on relaxations of liquid crystalline main chain polyesters, some precursor polymers related with the structure of this liquid crystal as poly(butylene terephthalate)[34–38] and finally, the previous analysis of polyesters based on 4,4′-terephthaloyl dioxydibenzoic acid and alkylene diols[3,24,25].

The relaxation phenomena in main chain liquid crystal

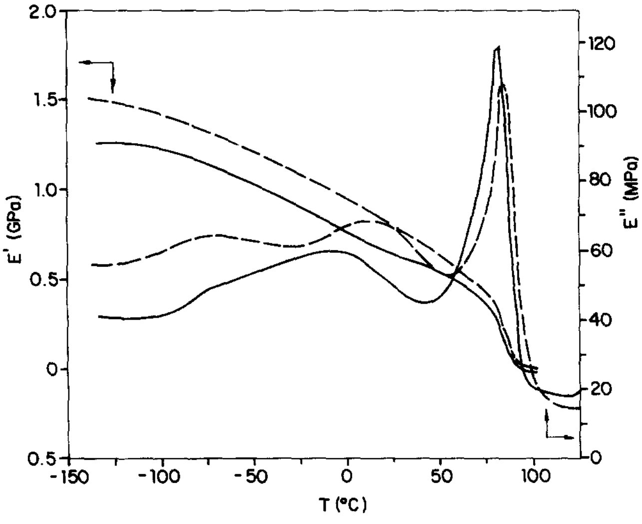

Figure 5 D.m.a. curves of a PDM4CTOB film heated to 150°C and cooled to room temperature measured at 0.1 Hz (——) and 1.0 Hz (– – –)

Table 2 Summary of data for α and β relaxation processes

Sample	P4TOB	PDM4TOB			P4CTOB	PDM4TCOB		
Freq. (Hz)	0.1	0.1	0.5	1.0	0.1	0.1	0.5	1.0
T_β (°C)	−71	−75	−62	−62	−6	−8	6	14
T_α (°C)	63	80	80	82	67	82	86	85
$E_a\ \beta^*$ (kJ mol^{-1})	–		49.4		–		48.3	
$E_a\ \alpha$ (kJ mol^{-1})	–		612.23		–		398.53	

β^*: the T_β and E_a of β corresponds to β_1 in P4CTOB and PDM4CTOB (see text) polyesters have been divided into two fundamental cases: (a) rigid polyesters; (b) semirigid polyesters. In the first case, three relaxation processes are apparent in polymers based on naphthyl and phenyl esters: an α relaxation at 110°C associated with the glass transition; a β process at 50°C associated with rotation of the naphthalene groups; and a γ process at −40°C associated with rotation of the phenyl groups[19,28,29]. Semirigid polyesters[30,31] showed only two relaxation processes: a glass transition related with the α relaxation and a sub-glass process at about −40°C. In both cases, the β and γ processes seem to exhibit an Arrhenius temperature dependence with relatively low activation energies (50–70 $\mathrm{kJ\,mol^{-1}}$). Copolymers of PET and PHB have been analysed recently, and the β relaxation has been assigned to local motions of the ester groups attached to both sides of the aromatic rings[18,21,32,33].

On the other hand, early dynamic-mechanical measurements on poly(butylene terephthalate)[34,35], PBT, reveal two relaxations. The α relaxation (at 50°C, 1 Hz) has been attributed to large scale conformational rearrangement of the chain in the amorphous region, and, therefore, can be considered the glass transition. The β relaxation (at −90°C) involves local conformational motions in the chain, and it has been related to restricted motions of the carbonyl group and of the glycol residue. These motions have been considered to occur in the amorphous region. Dielectric relaxation techniques have also been used to study molecular motion in PBT[36–38] and similar results than those described above have been obtained.

Some pioneering work has been reported on the dynamic-mechanical behaviour of supercooled mesophase in polyesters based on 4,4′-terephthaloyl dioxydibenzoic acid and alkylene diols[3,24,25]. Some of these polyesters show the usual behaviour expected for semirigid macromolecules with a β loss peak, typically characterized by a broad distribution of relaxation times. For high alkylene diols, a well pronounced γ peak centered at −125°C was always present. Because of the crystalline features of these polyesters, the dynamic-mechanical behaviour presents important differences depending on the thermal history, i.e. quenched samples from the liquid crystal state or melt crystallized samples. During quenching, the liquid crystalline phase is prevented from crystallizing and remains as a supercooled mesophase. When it is transformed into a more ordered phase, the transformation seems to be independent of the chemical structure of the flexible spacers. In other words, it seems that the rigid core of the repeating units is involved in the transformation.

A systematic study based on dielectric measurement has been performed very recently on several thermotropic polyesters[20,39], in order to correlate the spectra observed with the intramolecular motion, i.e. the mobility of individual groups contained in the mesogen or spacer.

With all the above considerations let us analyse again our data for the β relaxation. As it has been proposed from dielectric relaxation processes[20], the COO groups in the mesogenic centres and at the boundary with the spacer have different environments along the chain and, hence, conditions of the internal motions should be different. Below, T_g, the lowest temperature process is related to the mobility of the external ring because they adjoin the flexible linear spacer. At higher temperatures, the process is related with the possible reorientation of the COO groups in the central part of the mesogen. These groups are limited in their motion because they are located between two aromatic rings. In the polymers studied in this work, the chains with linear and non-linear spacers show the same β relaxation temperatures (see *Table 2*) and, therefore, for unmodified mesogenic units the β relaxation seems not to depend on the spacer. However, for the chlorinated moieties, there is a significant change. The β temperature is located at around −6°C. In other words, it is about 60°C higher than in the case of non-chlorinated mesogenic units and depends strongly on the chlorination but not on the spacer type. Moreover, the β relaxation for the polymers with chlorine in the mesogen shows a shoulder at low temperature around −70°C. This shoulder is more evident as the frequency increases and at 1 Hz for PDM4CTOB two peaks at −70°C (β_2) and 13°C (β_1) are clearly observed (*Figure 5*). The temperature of β_2 changes slightly with frequency, but β_1 increases considerably, and the activation energy in *Table 2* is calculated for β_1 in the case of PDM4CTOB. Considering the dielectric results in several polyesters[20] mentioned above, we may associate the β_2 relaxation to the motion of the external rings, and β_1 to the motion of the central one, perturbed by the proximity of the chlorine atoms. In order to clarify this last point, an in depth study of the nature of the motions involved in the β relaxation will be carried out by solid state n.m.r.

As was previously stated, the four polymers have a nematic mesophase. Therefore, the differences observed in the temperature of the maxima are not affected by changes in the nature of the mesomorphic phase. However, P4TOB and P4CTOB also have crystalline order. The presence of three-dimensional order seems not to affect the β relaxation, but there are differences in α. This is a general fact in semicrystalline systems in which T_g, related with the amorphous phase or with the interfaces, is strongly dependent on crystallinity levels[26]. If we compared P4TOB with PDM4TOB, or P4CTOB with PDM4CTOB (*Figures 2–5*), the α relaxation is a very sharp peak for the polymers with lateral substituents in the spacer, and becomes broader for the ones with linear spacers.

In summary, we have studied the effect of substitution in the mesogen and in the spacer on the relaxation behaviour of poly(tetramethylene terephthaloyl-bis-4-oxybenzoate). The β relaxation observed by d.m.a. is determined by groups localized in the mesogen and is very much affected by the introduction of polar groups in it and not by the spacer. The α relaxation is associated with the glass transition temperature of the amorphous phase and increases with the asymmetric substitution of methyls in the 1,4 position in the flexible spacer. The presence of crystalline order, besides a nematic order, broadens the α transition in the two polymers with linear spacer.

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