Effect on TSDC Relaxation Spectra of Substitutions in the Mesogenic Unit and in the Flexible Spacer of Poly(tetramethylene terephtaloyl-bis-4-oxybenzoate)

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ABSTRACT: A family of four thermotropic polyesters starting with the poly(tetramethylene terephthaloyl bis-4-oxybenzoate), substituting either asymmetrically in the tetramethylene spacer or incorporating polar substituents onto the aromatic units of the mesogen, is studied by the Thermally Stimulated Depolarization Currents (TSDC) technique. The results are compared to the Dynamic-Mechanical Analysis at frequencies ranging from 0.1 to 1 Hz from 123 to 423 K. The unsubstituted polymer has a complex low-temperature TSDC spectrum corresponding to local reorientation modes due to the motion of the COO groups with different locations along the main chain. By comparing the effect of the Cl and CH_3 substituents on the relative intensity and on the mean energies of the distribution of relaxation times determined by the DSA procedure, the lowest temperature mode is attributed to the COO peripheral groups and the modes located at higher temperatures, to the internal COO groups, which may be accompanied by adjacent segments. The mechanic and dielectric α-transitions are also very sensitive to the substituents, the addition of CH_3 in the 1,4 flexible spacer shifting the glass transition temperature above room temperature. The existence of the three-dimensional order that is present in the materials with a linear spacer significantly broadens the α-relaxation. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 3038–3049, 1999

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INTRODUCTION

The introduction of substituents in the mesogen and in the flexible spacer of main chain liquid–crystal polymers is a very well-known method of lowering the transition temperatures of these materials.[1–5] Depending on polarity and size of the substituents, not only the thermotropic behavior but also the nature of the mesophases formed may be affected. The correlation between these structural aspects and the liquid–crystal character of these polymers is of extraordinary importance for their technological applications due to the enhancement in processability and, very recently, the possibility of blending them with high-performance thermoplastic polymer matrices.[6]

In this sense, we have been studying the relationship between different structural parameters and properties on one of the most important families of thermotropic polyesters in which the mesogenic unit is 4,4′-terephthaloyl dioxydibenzoic acid. The series, with linear methylene spacers, have been synthesized and studied by several authors.[5,7–11] We have studied the effect of symmetric or asymmetric lateral substitution in the
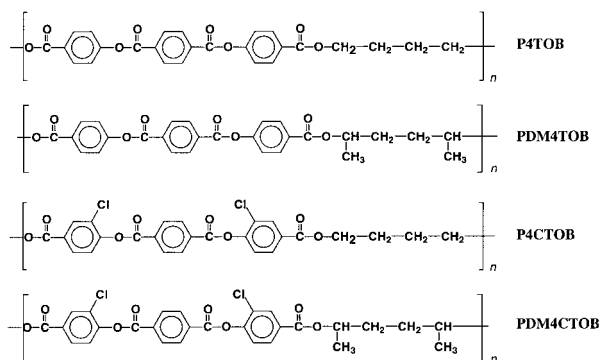
Figure 1. Schematic drawing of the four polymers studied and nomenclature used in this work.

spacer,[12–15] as well as the incorporation of polar substituents onto the aromatic units,[14–16] in some members of this family. The presence of side groups in the spacer causes a less efficient packing of the chains, resulting in a reduction of the transition temperatures, the loss of three-dimensional ordering, and in some cases a change in the type of mesophase. In the case of the mesogenic substitutions studied here, the lowering effect is less efficient and the crystal order is preserved despite the atoms introduced.

On the other hand, the relaxational behavior of main chain liquid–crystal polymers is very complex due to the coexistence of different anisotropic phases and the amount of motions that may take place corresponding to segments of very different flexibility. The understanding of the molecular mobility in these materials is of great interest because it plays a very important role in the formation of the mesomorphic structures. Dynamic-mechanical and dielectric experiments have been performed on rigid and semirigid thermotropic polyesters by several authors.[17–24] The main difficulty observed in most of these studies is to correlate the maxima detected in the dielectric or mechanical measurements with the type of motion and which segments of the structure, contained in the mesogen or the spacer, are involved in them. Only very few studies have been carried out on these materials by Thermally Stimulated Depolarization Current techniques, TSDC.[25–28]

In this work, we report the dielectric relaxation spectra observed by TSDC from 80 to 380 K on the series of polymers whose structures are shown in Figure 1. The advantage of using TSDC is the high resolution of the method and its capability for resolving overlapping peaks and extracting the relaxation time distribution[29] for the different

polar species, which disorientation originates the TSDC peaks. These results will be compared with previous thermal,[10,13–15] structural,[10,13–16] and dynamic-mechanical[23] studies on the same polymer liquid–crystals to assign the motion of the different molecular segments to the various relaxation modes observed. The fine structure of the low-temperature modes will be especially studied, as this zone of the relaxation spectra has been neglected in some of the dielectric and mechanical studies on this type of materials due to the low intensity and lack of resolution of the signals recorded. The inclusion of asymmetric lateral substituents either in the spacer and/or in the mesogenic unit will affect the relaxation spectra in the whole temperature range studied here. The existence of these polar molecular entities will serve as probes for their localized motion at low temperature and for the cooperative motions of the chain, which are the dielectric manifestation of the segmental motions that occur at the glass transition temperature associated to the amorphous zones of the material. The type of mesophase is nematic in all cases, but three-dimensional order is only observed for the materials with linear spacers. These structural aspects will also be correlated with the relaxation modes found in these materials.

EXPERIMENTAL

The four polymers shown in Figure 1 were synthesized in three stages using the method described by Bilibin et al.,[8,9,30] and the details can be found in previous works.[10,13–15] The intermediate products and the final polymers were characterized using elemental analysis, ^{1}H-NMR, ^{13}C-NMR, and vibrational spectroscopy, which assured the structure and the purity of the materials. The inherent viscosity of the four polymers was measured in p-chlorophenol at 45°C, and found to range between $0.29 - 0.39 \ dL \cdot g^{-1}$.

The determination of the transitions and the identification of the different phases were carried out by DSC, X-ray diffraction, and optical microscopy, whose specific technical details can be found elsewhere.[10,13–15]

Dynamic-mechanical studies were performed on the four polymers on a TA Dynamic Mechanical Thermal Analyzer, working in the flexural bending mode. The experiments were carried out in a temperature range from 123 to 423 K at

frequencies varying from 0.1 to 1 Hz using a heating rate of 5 K/min.

Films for the TSDC experiments are compression molded at temperatures where the samples are in the isotropic state and slowly cooled to room temperature. Disks, of approximately 16 mm in diameter and 0.3 mm thick are cut and placed in the measuring cell designed in our laboratory and described elsewhere.[31] Sapphire disks 20 mm in diameter and 0.25 mm thick are intercalated between the polymer film and the metallic electrodes. The applied voltage is 1000 V, unless otherwise specified. The temperature range explored here goes from 80 to 380 K, and the heating rate, b_h, was always 4.2 K/min. Complex spectra are recorded after polarizing at temperatures higher than the maximum of the peak under study. A clean peak is obtained by polarizing at $T_p = T_M$, and by partially discharging the contribution of the lower temperature modes. In this way the peak intensity is optimized, and the presence of intense relaxations that occur at higher temperatures is minimized. If precise information on the enthalpy and entropy parameters of each relaxation process is sought, the whole experimental profile is fitted, and it is found that the simple Debye model is not adequate, as the experimental curves are always too broad compared to the predictions of a single-valued relaxation time process. The Direct Signal Analysis (DSA),[31] or the Simulated Annealing Direct Signal Analysis (SADSA),[32] are fitting procedures recently introduced and discussed in great details elsewhere. The basic idea is to decompose the complex profile in N elementary curves (labeled energy bin), whose characteristic reorientation energies are equally spaced in a chosen energy interval. The expression for the depolarization current density, $J_D(T)$, is now given by:

$$J_D(T_j) = \sum_{i=1}^{N} \frac{P_{0i}}{\tau_i(T_j)} \exp\left[-\frac{1}{b} \int_{T_0}^{T_j} \frac{dT'}{\tau_i(T')} \right],$$

$$(j = 1, m), \quad (N \le m)$$

The curve-fitting procedure will find the best combination of the N components contribution to the total polarization, P_{0i}, and of the preexponential factors, τ_{0i}, corresponding to each energy bin. These parameters will fully characterize the Relaxation Times Distribution, RTD, describing each mode, provided that the temperature dependence of the relaxation times is assumed. For the

sub-T_g modes in polymers, the Arrhenius law, $\tau(T) = \tau_{0i} \exp(E_{0i}/kT)$ is found to be satisfactory in the description of localized reorientations, which do not involve main chain motions. At $T \geq T_g$ the Vogel–Tammann–Fulcher expression, VTF, or its equivalent the Williams–Landel–Ferry dependence is to be used, as many previous experimental works have shown; this expression has received a theoretical justification by using either the free volume concept or statistical mechanics. A VTF energy and preexponential factor can be introduced if the VTF relaxation time is written as: $\tau(T) = \tau'_{0i} \exp(E'_{0i}/k(T - T_0))$, where T_0 is the VTF temperature where all the chain motions are frozen in the sample. The DSA and the SADSA codes will perform the whole profile fitting by using either a nonlinear least-squares Marquardt–Levenberg algorithm, or the simulated annealing Monte Carlo procedure, which is more reliable as the parameters space is explored randomly and the absolute minimum of the function to minimize is more securely reached.

The idea of the DSA is similar to the Thermal Sampling, TS, that is performed experimentally. Both are different approaches to decompose the complex peak in elementary relaxations. TS activates polarization windows in a narrow temperature interval, and the recorded peaks are analyzed as Debye modes. The comparison and complementarity of the two approaches will be published elsewhere.

RESULTS AND DISCUSSION

As these materials had been previously studied with a variety of experimental techniques, a summary of the results reached referring to the packing and conformation of the molecular chains, leading to the different phases observed as a function of temperature, together with the temperatures and relaxation parameters involved in the transitions between these phases, is given below.

Poly(tetramethylene terephthaloyl bis-4-oxybenzoate) (P4TOB), which has no substituents either in the flexible spacer or in the mesogenic unit, is our reference polymer. It presents two crystalline forms, depending on the thermal treatment of the sample.[10] Form I exists when the sample is precipitated from solution, and shows an irreversible solid–solid transformation upon heating prior to the crystal–nematic mesophase transition. Form II is obtained when the sample is
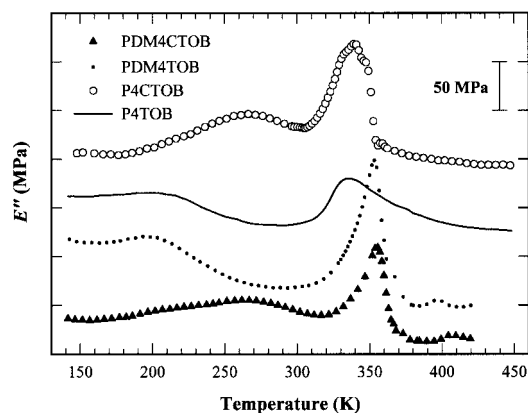
Figure 2. DMA curves at 0.1 Hz for the four polymers described in Figure 1.

slowly cooled or quenched from the mesophase. The P4TOB TSDC samples are prepared under thermal conditions that lead to Form II, which has a nearly planar conformation in the flexible spacer and differences in the orientation of phenyl rings compared to Form I. The estimated crystallinity by wide-angle X-ray diffraction is 46%. This polymer shows a crystal–nematic transition at 558 K, and a nematic–isotropic transition at 623 K as measured by DSC.[10] The glass transition is hardly observed by this technique due to the crystallinity, but T_g was found to be equal to 336 K as measured by the position of the DMA peak assigned to this transition (see Fig. 2). The DMA P4TOB trace shows a wide low-temperature re-

laxation centered around 202 K, which indicates a multicomponent origin. All these results are summarized in the first row of Table I.

When two chlorine atoms are substituted in the external rings of the mesogenic unit of P4TOB, the resulting polymer labeled P4CTOB (Fig. 1), has also a crystalline phase with two modifications, depending upon thermal treatment.[15] Form I appears when the sample is crystallized from solution and coexists with a second form if the sample is cooled from the mesophase. Thermal treatment governs the relative amount of each modification, and the samples used for the TSDC work has a majority of Form II crystals. In this polymer the structural differences between Form I and II seem to be located in the mesogenic unit and not in the linear spacer.[15] A value of 40% crystallinity is estimated by WAXS[15] for the TSDC sample. The presence of the asymmetric chlorine atoms slightly affects the temperatures of the phase transitions reported in Table I. The most important effect is observed in the 31 K shift to lower temperature of the nematic–isotropic transition. It is to be noted that the glass transition temperature measured by DMA only increases 4 K compared to P4TOB. However, the low-temperature band is considerably shifted to higher temperatures, and maintains the same multicomponent character also observed in P4TOB (Fig. 2).

When P4TOB is substituted in the flexible spacer with asymmetric methylene in the 1,4

**Table I.** Thermal, Mechanical, and Dielectric Transitions of the Polymer Liquid–Crystals Studied

Material	T_{decomp} (K)	T_{β}^{*} (K)	T_g (K)	T_{c-n} (K)	T_{n-i} (K)	T_{ρ} (K)	X_c (%)
P4TOB	623	202[a] 145[b] 236[b]	337[a] 304[b]	558[c]	623[c]	354[b]	40 to 50%
PDM4TOB	573	197[a] 165[b] 230[b]	353.4[a] 348[b]	458[c]	523[c]	363[b]	Amorphous
P4CTOB	623	267[a] 140[b] 225[b]	340[a] 321[b]	547[c]	593[c]	368[b]	40%
PDM4CTOB	> 523	265[a] 115[b] 228[b]	355.5[a] 350[b]	406[c]	449[c]	368[b]	Amorphous

[a] DMA, $f = 0.1$ Hz.
[b] TSDC $f_{eq} \approx 1$ mHz.
[c] DSC and optical microscopy.
[d] TSDC reported temperatures correspond to the two more prominent components of the β peak.
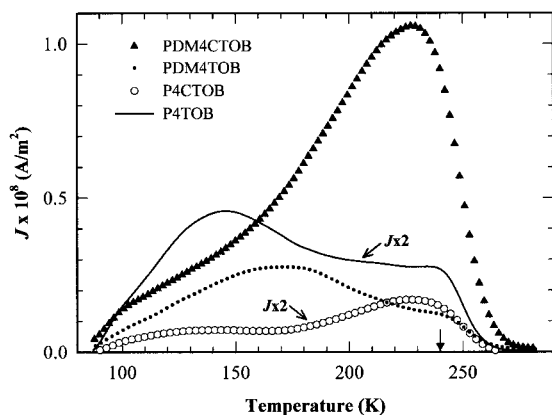
Figure 3. TSDC low-temperature spectra for the four polymers described in Figure 1, normalized to the same sample size and polarizing field ($E_p = 1$ V/μm).

positions, the polymer labeled PDM4TOB does not present three-dimensional order unless long annealing processes are carried out,[13] which is not the case for the samples used in this study. This substitution results in a drastic variation of the transition temperatures, as shown in Table I. It is observed a 100 K lowering of the nematic–isotropic transition and the crystalline–nematic transition (when three-dimensional order is present). The T_g is increased at 353 K, which indicates the loss of chain mobility due to the CH_3 substituents, but the DMA band at low temperature is essentially centered at the same position as P4TOB, as shown in Figure 2.

Finally, when P4TOB is substituted in the flexible spacer with asymmetric methylenes and in the mesogenic unit with chlorines, all the transition temperatures listed in Table I are affected, and this polymer, PDM4CTOB, does not present crystalline order unless extensive thermal treatments are performed[14] as it is the case for PDM4TOB. The DMA experiments show that the T_g is mostly affected by the addition of CH_3 groups, as can be observed in Figure 2, while the position of the low-temperature peak is determined by the presence of chlorine in the mesogen. This polymer has the lowest isotropization temperature and the highest T_g of this series. The character of the mesophase is nematic as in the other three polymers.

In Figure 3, the low-temperature region of the TSDC spectra for the four liquid–crystal polymers are plotted. The polarization temperature ($T_p = 240$ K) and field strength are the same for all the samples that have been quenched from $T > T_g$ to erase any aging effect. Dimensional nor-

malization was carried out to be able to compare the intensities. It is to be noted that the intensity of the traces corresponding to P4TOB and P4CTOB have been multiplied by 2 to allow the observation of the complicated structure of these low-temperature bands. The four polymers show a multicomponent spectra that covers the same temperature region, and the large differences in intensity clearly observed in Figure 3 are related to changes in the relative abundance of the reorientable dipolar species that originate the different components of this complex peak. Three components can be clearly distinguished in these broad bands. The unsubstituted polymer, P4TOB, has a predominant β_1-mode at 145 K, which is the lowest value of the series studied here. Another maximum (β_3) is observed at 236 K, and in between a third mode (β_2) must exist to explain the observed plateau. The polymer with chlorine atoms in the mesogen, P4CTOB, has the less intense TSDC spectrum, which is to be expected, as the crystallinity is quite high as well as in P4TOB, and the relaxations observed here originated in the amorphous regions of the material. Moreover, the highest intensity is at higher temperature, i.e., at 228 K. Obviously, the presence of the chlorine atoms has strongly affected the number of polarizable entities (orientable dipoles) reversing their relative concentration. The polymers that have substituents in the linear spacer, i.e., PDM4TOB and PDM4CTOB, give more intense bands with a better defined structure formed by the overlap of at least three modes. In these two materials, as was previously stated, no crystalline order is detected. The most intense spectrum is given by PDM4CTOB, with a huge increase for the β_3-peak and the intermediate β_2-peak.

From Figures 4–7 the results of the DSA procedure applied to the low-temperature bands for the samples quenched from T_g, are presented. It is readily seen that the quality of the fitting is excellent, with the sum of least squares residual values ranging from 10^{-9} to 10^{-12}. All these fittings were performed by using the Arrhenius temperature-dependent relaxation times, which are appropriate for localized reorientation modes. The energy histograms that represent the contribution to the total polarization of each energy bin, quantitatively manifest the distribution of energies that result from the overlapping of the various relaxation modes. From these figures the reorientation energies, preexponential factor, and width of the distributions for each mode can be
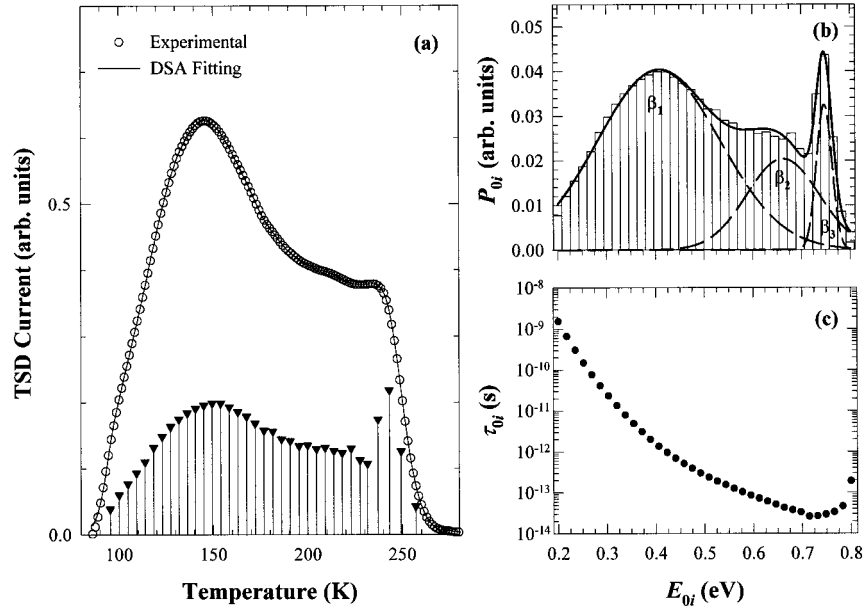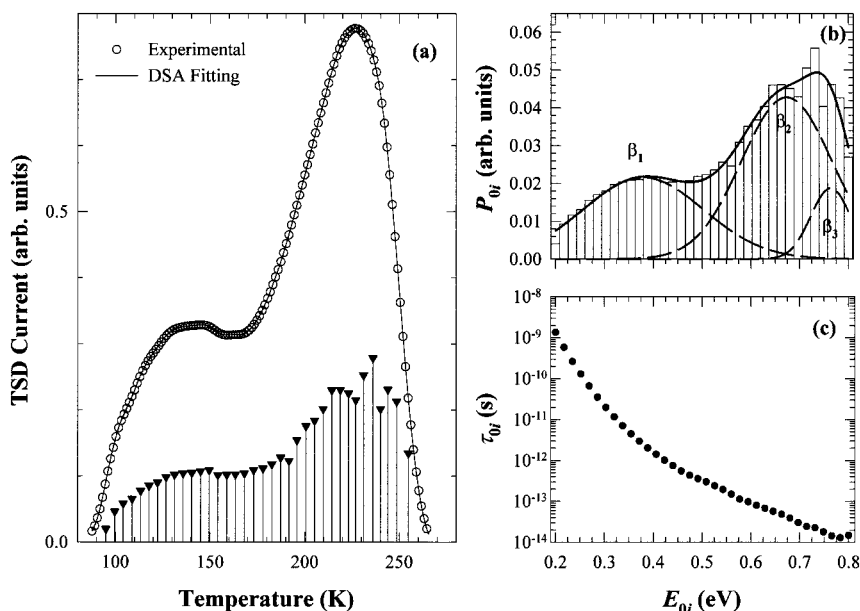
Figure 4. Results of the DSA for the β-band of P4TOB with Arrhenius relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value.

determined. The energy bins that contribute to the polarization of the sample range from 0.2 to 0.8 eV as observed in Figures 4–7, part (b). The

continuous lines in the energy histograms, are tentative separation of these histograms in three Gaussian contributions. When P4TOB is com-
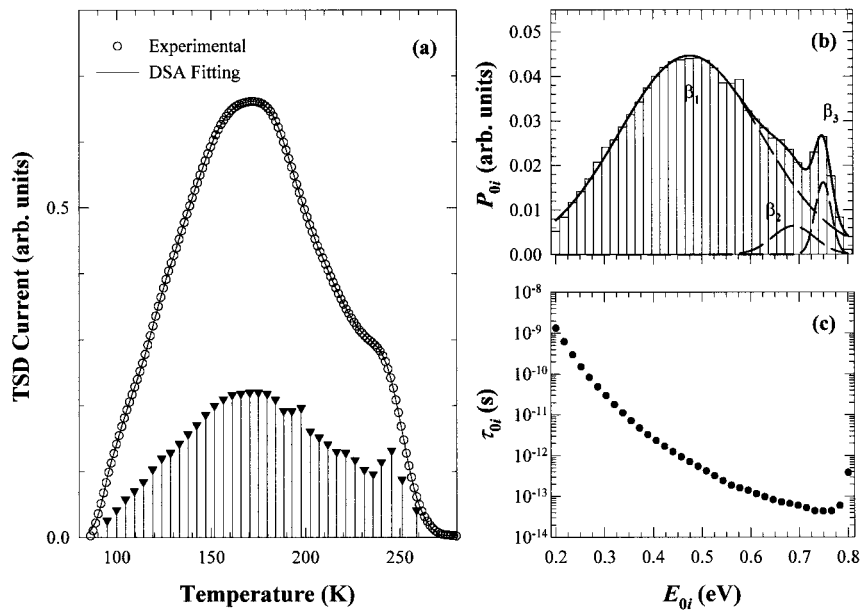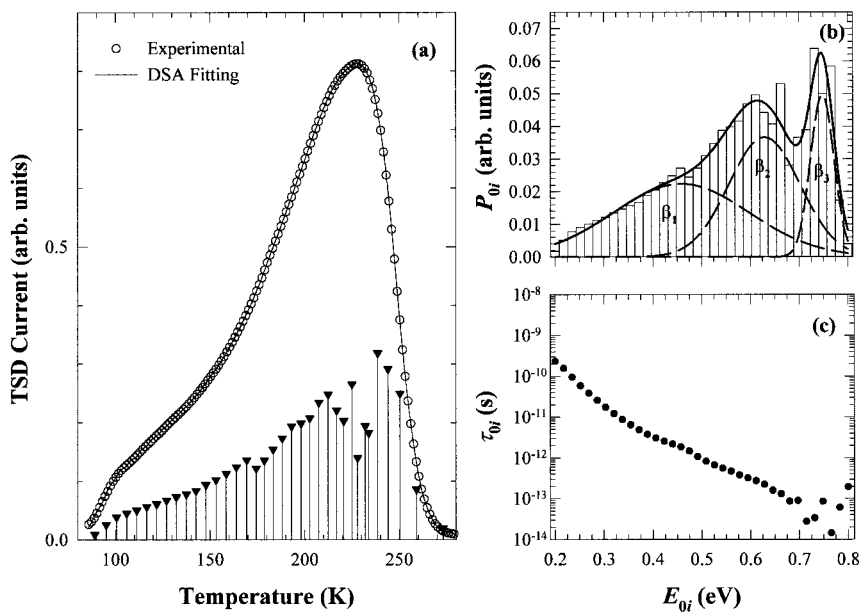

Figure 5. Results of the DSA for the β-band of PDM4TOB with Arrhenius relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value.

Figure 6. Results of the DSA for the β-band of P4CTOB with Arrhenius relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value.

pared to P4CTOB, it can be seen that the chlorine addition favors the most energetic β_2 and β_3 components, already present in the original unsubstituted polymer; this is also true for the chlorinated polymer with the branched alkyl spacer. Here again, the presence of the three relaxations is

Figure 7. Results of the DSA for the β-band of PDM4CTOB with Arrhenius relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value.

Table II. Mean Relaxation Parameters for the Low Temperature Spectrum of Polymers Studied

Sample	P4TOB	PDM4TOB	P4CTOB	PDM4CTOB
β_1-mode				
Mean energy (eV)	0.41	0.48	0.38	0.46
Proportion (%)	71	92	37	44
β_2-mode				
Mean energy (eV)	0.66	0.69	0.67	0.63
Proportion (%)	21	4	54	39
β_3-mode				
Mean energy (eV)	0.74	0.75	0.76	0.75
Proportion (%)	8	4	9	17

clearly seen. The effect of the CH_3 groups is to shift the mean energy of the β_1 and β_2 modes from 0.41 to 0.48 eV and from 0.66 to 0.69 eV, respectively, and to enhance the relative intensity of the β_1-mode as seen in Table II. The mean energy of the β_3-mode seems the less affected by the substitutions in the chain. Part (c) of these figures, which represent the variation of the preexponential of the Arrhenius relaxation times, show in every case reasonable values and similar variations over less than five decades. A compensation law, i.e., a linear relation among the prefactor and the reorientation energies, can be roughly drawn for each zone that covers each of the β-modes, thus indicating a certain degree of cooperativity necessary for the reorientation processes of each molecular entity responsible for the observed relaxation modes. The β_2-relaxation is strongly enhanced by the addition of the methyl groups, PDM4TOB, but when the mesogen is also substituted, PDM4CTOB, the effect of the chlorine is still the leading feature of the spectrum.

Let us now compare these TSDC detailed results with the previous DMA measurements on the same materials. The equivalent frequency for a TSDC experiment is in the range of mHz compared to the 0.1-Hz DMA frequency; consequently, the resolution of the TSDC bands is much better than that of the dynamic measurements. Moreover, the possibility of varying the polarization conditions to eliminate the contribution of the higher temperature peaks that are orders of magnitude more intense than the β-peaks, allows an exhaustive analysis of these processes and a better assignment to the molecular motions that causes the relaxation modes. However, a qualitative comparison among the β-relaxations observed by both techniques show an excellent agreement, the DMAs always being

located at higher temperatures than the TSDC peaks due to the higher working frequency. In Figure 2 it can be observed that the DMA profile for the β-relaxation always agrees with the highest peak in the clearly multicomponent TSDC band. The DMA trace corresponding to PDM4CTOB, which is the only one that shows some structure, agrees completely with the corresponding more complex TSDC curve.

After all the above considerations let us tentatively assign specific molecular motion to each of the identified β-modes. It is clear that the COO groups, which have a dipolar character, are immersed in different energy landscapes due to their location along the main chain. The motion of a carbonyl group attached to the flexible spacer must occur at temperatures below those corresponding to the reorientation of this same group located between two aromatic rings. Borisova[21] has shown in thermotropic linear polyesters with a similar mesogenic unit as P4TOB, that the low temperature relaxations observed by dielectric spectroscopy is made by two components attributed to the localized motions of the COO group. The lowest temperature one being attributed to a low-amplitude oscillational motion of the peripheral ester groups, and the following one to the carbonyl groups in the central part of the mesogenic fragment, located between two aromatic nuclei.

We have previously performed the same kind of TSDC experiments in thermotropic polyesters, which have the same mesogen than P4TOB attached to three or four oxyethylenic units that form the flexible spacer.[26,27] Even if these two latter polymers have more flexible chains, the low temperature TSDC spectrum is very similar to the one plotted in Figure 3 for P4TOB. In both cases three relaxations are clearly present, the

intensity of the intermediate one being more relevant in the polymers with the oxyethylene spacer. Also, the very weak variation of the prefactor with the energy bin (Fig. 7 in ref. 26) seems to indicate an absence of cooperative motions in these two polymers. In Figures 4–7 the decrease of τ_0 as the energy bin increases may result from the existence of some cooperativity degree involved in the motion of these polar groups due to the significant reduction in the number of atoms involved in the flexible spacer for the series of four polymers studied in this work.

Considering all these previous works, a tentative assignment can be done in the four materials under study. In P4TOB the most intense peak, β_1, is originated by the reorientation of the peripheral COO groups, while the other two modes are related to the motion of the internal COO, which may be accompanied or not in their reorientation by adjacent segments. This interpretation agrees with the observed variation in the spectra when chlorine is added. The relative increase of the β_2 and β_3 mode compared with β_1 in P4CTOB and PDM4CTOB, indicates that a larger number of dipoles has the possibility to orient in the field due to the presence of the chlorine in these two polymers. Moreover, the changes observed by the addition of CH_3 in the linear spacer, i.e., a shift of β_1 to a slightly higher temperature, and consequently higher reorientation energies, in PDM4TOB, reflects the impedance of the lateral methyls on the peripheral COO groups, which reduce their mobility. In PDM4CTOB, the chlorine effect is the most relevant, but a shoulder in the same position as in PDM4TOB is now present.

As the temperature is increased, the intense α-transition appears, which is the dielectric manifestation of the glass transition occurring in the amorphous regions of the polymers. In the two polymers where three-dimensional order is absent, the TSDC T_g varies from 349 to 350 K (see Fig. 8 and Table I), which are 4 to 5 K lower than the DMA T_g values. P4TOB has the lowest T_g of the series, 304 K by TSDC and 336 K by DMA at 0.1 Hz. The addition of chlorine in P4CTOB shifts the TSDC α-relaxation +17 K when compared with the unsubstituted polymer, P4TOB. However, the T_g value obtained by DMA is shifted by only +4 K. Also, these two dielectric α-relaxations are the least intense and the widest of the whole series. These characteristic features are also present in the DMA transitions, as seen in Figure 2. The low intensity of these curves is easily un-
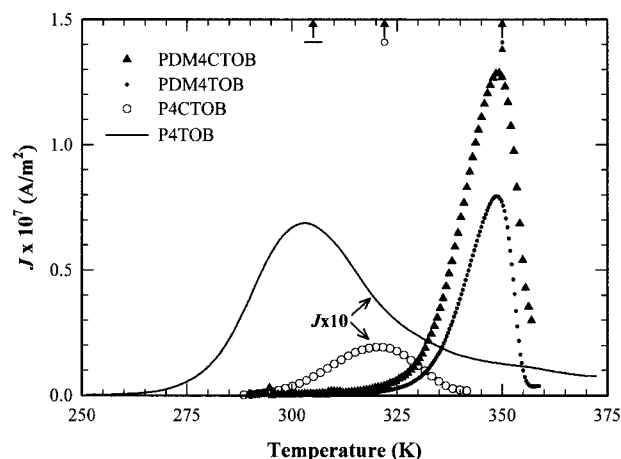

Figure 8. α-Transitions for the four polymers described in Figure 1, normalized to the same sample size and polarizing field ($E_p = 1$ V/μm).

derstood due to the high crystallinity of these materials, whereas the long tail on the high-temperature side shows the existence of a wider distribution of relaxation times, which may be attributed to the multiphase character of these materials. This is clearly seen on Figure 9(b), where the distribution of relaxation times calculated by the SADSA procedure, using Vogel–Tammann–Fulcher dependences, is shown in the case of P4CTOB. The difference between the TSDC result and the previous DMA ones is that Cl addition leaves the α-curve position unchanged in the mechanical case, whereas the TSDC shows a translation to slightly higher temperatures. This seems to indicate that the threshold for the cooperative molecular motions that are detected by each technique differs by a small amount.

The noncrystalline samples show, as expected, narrower distributions of relaxation times [see Fig. 10(b)] for PDM4CTOB, and intensities more than 10 times greater than those of the samples with three-dimensional order. The presence of asymmetric methyls in these two polymers significantly reduces the chain mobility and causes a considerable shift to higher temperatures as observed by both techniques. Also, the mean energy of the distribution has considerably shifted to higher values.

The complete TSDC spectra of these materials includes a very intense peak located at temperatures above T_g; in Figure 11 the TSDC spectra shown are polarized at temperatures always higher that the peak maxima, as indicated in the figure. This high-intensity peak overlaps the rest
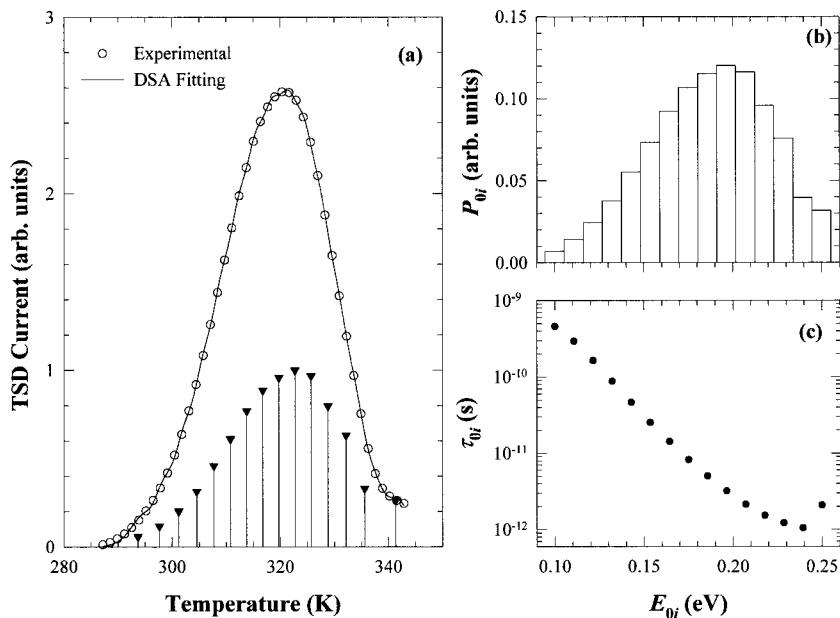
Figure 9. Results of the DSA for the α-mode of P4CTOB with VTF relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value; $T_0 = 247$ K.

of the spectrum, and it is labeled as the ρ-transition (T_ρ), which, in polymers, is attributed to the charge accumulation by trapping at the bound-aries between the various phases that coexist in these complicated materials. It is observed that, again, the two samples with CH_3 in the spacer are
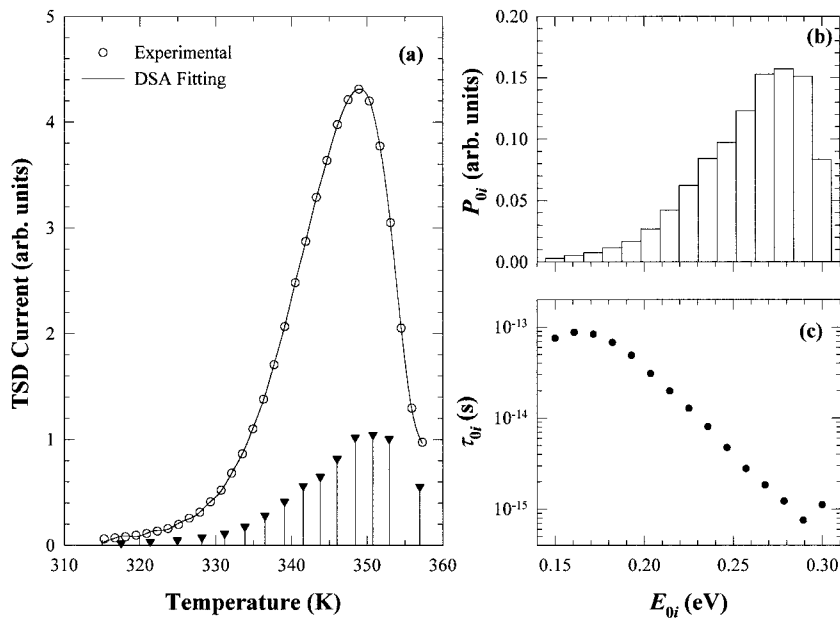
Figure 10. Results of the DSA for the α-mode of PDM4CTOB with VTF relaxation times: (a) experimental and fitted profiles, ▼ indicates the position in temperature and relative contribution of the elementary processes; (b) energy histogram; (c) variation of τ_{0i} with the energy bin value; $T_0 = 265.3$ K.
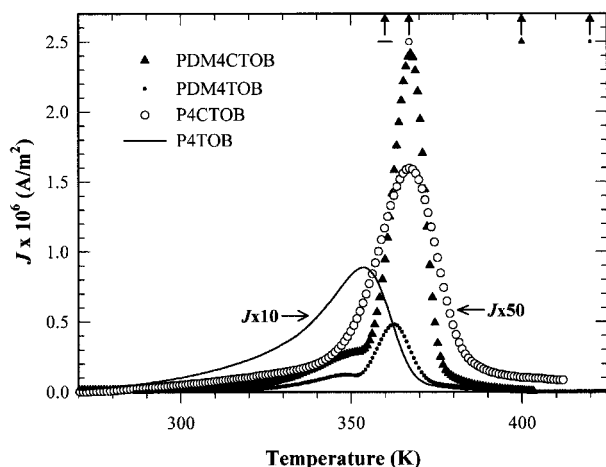
Figure 11. Complex high-temperature TSDC spectra for the four polymers listed in Figure 1, normalized to the same sample size and polarizing field (E_p = 1 V/μm).

more intense than those with linear ones. The T_ρ values range from 354 to 368 K, as seen in Table I. These values are far too low to be related to the crystal–nematic transitions (T_{c-n} in Table I) or the nematic–isotropic transition (T_{n-i} in Table I) measured in the same materials by DSC. Also, in the TSDC case the ρ-modes are closely located in temperature whereas the crystal–liquid crystal transitions span a 152 K interval.

The high intensity of the ρ-peak on a different family of thermotropic polyesters with longer methylene spacers but naphthoic groups in the center of the mesogen, has been explained by Liu and Lee,[25] with large interface amounts. They relate the ρ-transition in the anisotropic glasses with the space charge in the interface between the oriented regions and in the isotropic glasses to the microscale multiphase, which came from the conformation of the polymer chains. In our case, the polymers with methyls, quenched from the nematic state, consist of several oriented domains, each of them with a different director. The boundaries of these domains provides the necessary sites for the trapping process of the mobile charges that relax at T_ρ. When P4TOB and P4CTOB are quenched from the polarization temperatures, which vary from 198 to 180 K below their crystal–nematic transition, the samples consist of crystals and isotropic glass. Even though the interfacial regions are abundant and the mobile charges may be trapped at the crystal–amorphous regions interfaces, the constrains imposed by the crystalline lamellae make the relaxation

process of the trapped charges less effective, which is reflected in the low intensity of the TSDC ρ-peaks.

CONCLUSIONS

The effect of substitution in the mesogen and in the spacer on the low and high temperature TSDC spectra has been studied in detail in Poly-(tetramethylene terephthaloyl bis-4-oxybenzo-ate). The β-relaxation at low temperatures is a multicomponent band with at least three reorientation modes involving the local motions of the polar groups. The variations in position and intensity observed in the four samples with different substitutions allows one to attribute these relaxations to the COO groups in different environments. The peripheral COO groups are the most mobile in the absence of substitutions, and are at the origin of the lowest temperature mode that is the most intense in P4TOB. The other two, β_2 and β_3, relaxations are attributed to the motions of the internal COO, which may be accompanied or not in their reorientation by adjacent segments. At higher temperatures, the dielectric manifestation of the glass transition, the α-mode, is also very sensitive to the existence and placement of substituents, always shifting to higher temperature in their presence. The most significant effect being observed on the mobility when the CH_3 groups are present in the 1,4 flexible spacer. Also, the presence of crystalline order additionally to the nematic order broadens the dielectric and mechanical manifestation of the glass transition mode in the two polymers with a linear spacer.

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