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Polymer 47 (2006) 7078–7084

polymer

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Molecular dynamics of poly(butylene *tert*-butyl isophthalate) and its copolymers with poly(butylene terephthalate) as revealed by broadband dielectric spectroscopy

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Received 7 June 2006; received in revised form 20 July 2006; accepted 22 July 2006
Available online 17 August 2006

Abstract

The dynamic behaviour of a set of copolyesters made of 1,4-butanediol, terephthalic acid and 5-*tert*-butyl isophthalic acid, as well as the two parent homopolymers was studied. Although the insertion of the *tert*-butyl isophthalate units in the main chain of poly(butylene terephthalate) modified the glass transition, the β relaxation did not change dramatically. By using broadband dielectric spectroscopy we have obtained a detailed picture of the dynamic behaviour of these systems. In all cases, a strong correlation between the α relaxation and the β relaxation above T_g was observed in accordance with recent proposals based on the coupling model.

Keywords: Dielectric spectroscopy; Alpha relaxation; Beta relaxation

1. Introduction

When studying the dynamic origin of the observed processes in the relaxation map of a polymer system or a glass forming system in general, traditionally, the attention has been focussed on the α relaxation, i.e., the one that occurs at temperature above the glass transition temperature, T_g, and that it is attributed to the segmental motions of the chains [1,2]. However, the complete relaxation map of a glass forming system usually consists of more than one relaxation [3]. It is only recently that the origin of β relaxation has drawn the attention of researchers [4,5], specially considering the viewpoints provided by those theories and models that attempt to describe the phenomenon of the glass transition, such as the mode-coupling [6] and the coupling model [7].

In polymers, the β relaxation has been attributed to localized motions of pendant groups. When studying the β relaxation in a narrow frequency range, generally the temperature dependence of the corresponding relaxation time, τ_β, can be described by an Arrhenius behaviour [8]. However, the possibility of measuring in a wide dynamic range, offered by modern relaxation techniques like dielectric spectroscopy, has contributed extensively to a more precise description of the β or secondary relaxation. In particular, now it is known that in the region of merging between the α and β, the secondary relaxation exhibits a quite complex behaviour. In particular, its relaxation time τ_β deviates from the Arrhenius behaviour found below the T_g [4,9]. This feature may indicate that in some cases, the β relaxation can be considered to be a Johari–Goldstein (JG) relaxation [10–12] defined as that in which the relaxation affects the entire molecule. According to the coupling model [10–14], there are some primary

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doi:10.1016/j.polymer.2006.07.044

species that relax at a rate τ_0 (primitive relaxation time). The relaxation function of the primary species can be described by a simple exponential decay as described in Eq. (1):

$$F_\alpha(t) = \exp\left(-\frac{t}{\tau_0}\right) \quad t < t_c \tag{1}$$

However, after a given time t_c, there is a coupling between the motion of the different primary species, and the relaxation function is no longer a single exponential decay, but a stretched exponential or Kolrausch–Williams–Watts (KWW) function:

$$F_\alpha(t) = \exp\left(-\left(\frac{t}{\tau_\alpha}\right)^{1-n}\right) \quad t > t_c \tag{2}$$

Therefore, at $t = t_c$, there is a direct relation between the relaxation time of the primary species and the one of the α relaxation of the form [13]:

$$\tau_0 = (t_c)^n (\tau_\alpha)^{1-n} \tag{3}$$

The crossover time t_c from independent to cooperative relaxation has been estimated to be 2×10^{-12} s from neutron scattering experiments [15]. Remarkably, a relationship between primary and secondary relaxation times of the type $\tau_0(T) \approx \tau_\beta(T)$ has been observed in a great variety of low molecular weight materials and polymers including aromatic polyesters [9,13]. The physical properties of side-chain polymers can be very different as compared to those displayed by unsubstituted main-chain polymers. In one hand, by copolymerizing a side-chain monomer with its main-chain counterpart, dramatic changes in the glass transition temperatures are expected. On the other hand, the local dynamics, giving rise to the secondary relaxation, is not expected to change dramatically. Therefore, the validity of the above relationships for the relaxation behaviour of such copolymers may help to understand the interrelationship between primary and secondary relaxations in polymers. With these ideas in mind, in this work we have studied by broadband dielectric spectroscopy the relaxation behaviour of a series of polyesters based on poly(butylene terephthalate) (PBT), specifically the copolyesters made of 1,4-butanediol and mixtures of terephthalic acid and isophthalic acid bearing a *tert*-butyl group attached to the 5 position of the benzene ring. The study includes also the two parent homopolymers poly(butylene terephthalate) and poly(butylene 5-*tert*-butyl-isophthalate). The *tert*-butyl group is a bulky substituent that restricts the molecular mobility altering significantly the free-volume depending properties of the polymer. The aim of this work is to show how the insertion of the *tert*-butyl substituted isophthalate units (^{t}BI) modifies the relaxation behaviour of PBT, in particular the α and β relaxations of this polyester.

2. Experimental section

2.1. Sample description

A scheme of the investigated copolymers studied in this work is presented in Fig. 1. The copolymers and homopolymers were synthesized by polycondensation of 1,4-butanediol with mixtures of dimethyl-terephthalate and 5-*tert*-butyl isophthalic acid as reported elsewhere [16]. The nomenclature used to label the samples in this work and some of their characteristics relevant to this study are shown in Table 1. The powdered samples coming from the synthesis were dried under vacuum at 90 °C for several hours. After drying, samples for the first frequency range measurements ($10^{-1} < F$ (Hz) $< 10^7$) were melt-pressed between two gold-coated electrodes with 2-cm diameter and quenched subsequently in ice water. In order to control the thickness, 70 μm thick kapton spacers were located between the electrodes. For the second frequency range ($10^6 < F$ (Hz) $< 10^9$) measurements disk-shape films 0.5 cm of diameter and about 0.01 cm in thickness were cut out from a melt-pressed sheet. With exception of PBT all the samples were obtained as amorphous specimens.

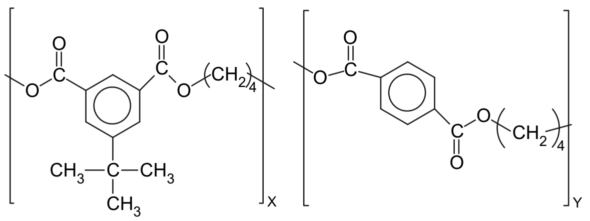

Fig. 1. Chemical formula of the studied copolymers.

2.2. Experimental techniques

Dielectric loss measurements $\varepsilon'' = \mathrm{Im}(\varepsilon^*)$, where ε^* is the complex dielectric permittivity, were performed over a broad frequency window $10^{-1} < F$ (Hz) $< 10^9$ in a temperature range of $-150 < T$ (°C) < 150. To cover the above frequency interval, two different experimental set-ups were used. In the 10^{-1}–10^6 Hz range, a Novocontrol system integrating an ALPHA dielectric interface was employed. In the range 10^6–10^9 Hz, dielectric measurements were obtained by means of an HP 4291 coaxial line reflectometer. In this case, the dielectric loss was calculated by measuring the reflection coefficient at a particular reference plane [3,17]. The measurement of ε^* at 10^6 Hz obtained with the reflectometer was used for calibration. These two instruments were integrated in a Novocontrol broadband dielectric spectrometer.

Table 1
Characteristic of the studied samples

Label[a]	Sample[b]	M_n[c]	Polydispersity[d]	T_g (°C)[e]	T_m (°C)[f]
BT100	PBT	19 900	2.3	32	223
BT70	$\mathrm{PBT}_{70}{}^t\mathrm{BI}_{30}$	24 000	2.5	42	156
BT50	$\mathrm{PBT}_{50}{}^t\mathrm{BI}_{50}$	22 500	1.9	48	–
BT00	$\mathrm{PB}^t\mathrm{BI}$	19 500	1.9	59	120

[a] Labelling used in this work for the studied samples.

[b] Original acronyms of samples as described in Ref. [16] (sub indexes in the copolymers refer to the molar fraction of BT and ^{t}BI units).

[c] Number-average molecular weight.

[d] Polydispersity measured by GPC.

[e] Glass transition temperature (T_g).

[f] Melting temperature (T_m) determined by differential scanning calorimetry.

Temperature control was obtained by a nitrogen jet (QUATRO from Novocontrol) with a temperature error, during every single sweep in frequency, of 0.1 K.

3. Results

Fig. 2 shows the values of ε'' obtained for the sample BT00 as a function of temperature and frequency. These dielectric spectra exhibit two main relaxations, β and α in the order of increasing temperature, as revealed by the presence of two maxima, the higher temperature one (α relaxation) being the most prominent. These two relaxations are present in the dielectric spectra of the whole series. Fig. 3 shows ε'' values in the temperature range where the β relaxation is prominent. As observed in this figure, the β relaxation is very similar for all the samples of the studied series. The shape of the relaxation curves has been analyzed within the Havriliak Negami semi-empirical formalism [3]. The Havriliak Negami (HN) equation gives for ε'', the following dependence with frequency:

$$\varepsilon'' = \left(\frac{\sigma}{\varepsilon_0\omega}\right)^s + \mathrm{Im}\left(\sum_{k=\beta,\alpha}\frac{\Delta\varepsilon_k}{\left[1+(\mathrm{i}\omega\tau_{\mathrm{HN}k})^{b_k}\right]^{c_k}}\right) \tag{4}$$

where ω is the angular frequency ($\omega = 2\pi F$), τ is the central relaxation time, $\Delta\varepsilon$ is the dielectric strength and b and c are shape parameters related to the symmetric and asymmetric broadening of the relaxation curve. The low temperature relaxation observed in P(B^{t}BI-*co*-BT) systems (β relaxation) may be well described by a symmetric version of the HN, where the c parameter takes the value of 1. Continuous lines in Fig. 3 correspond to the best fits of the experimental data to the HN equation, with $c = 1$. The mean relaxation time τ_β as a function of the reciprocal temperature is presented in Fig. 4. At low temperatures, it exhibits a linear dependence indicating an Arrhenius behaviour of the β relaxation:

$$\tau_\beta = \tau_\infty \exp\left(\frac{E_a}{RT}\right) \tag{5}$$

where τ_∞ is the pre-exponential factor, E_a is the activation energy and R is the gas constant.

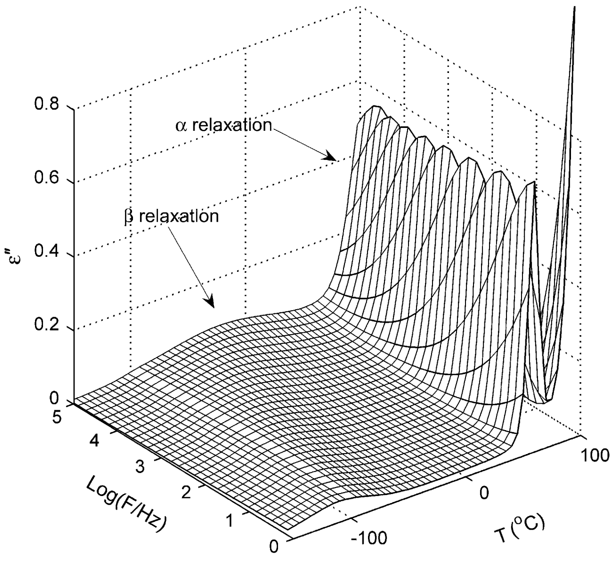

Fig. 2. Dielectric loss values (ε'') as a function of frequency and temperature for the sample PB^{t}BI.

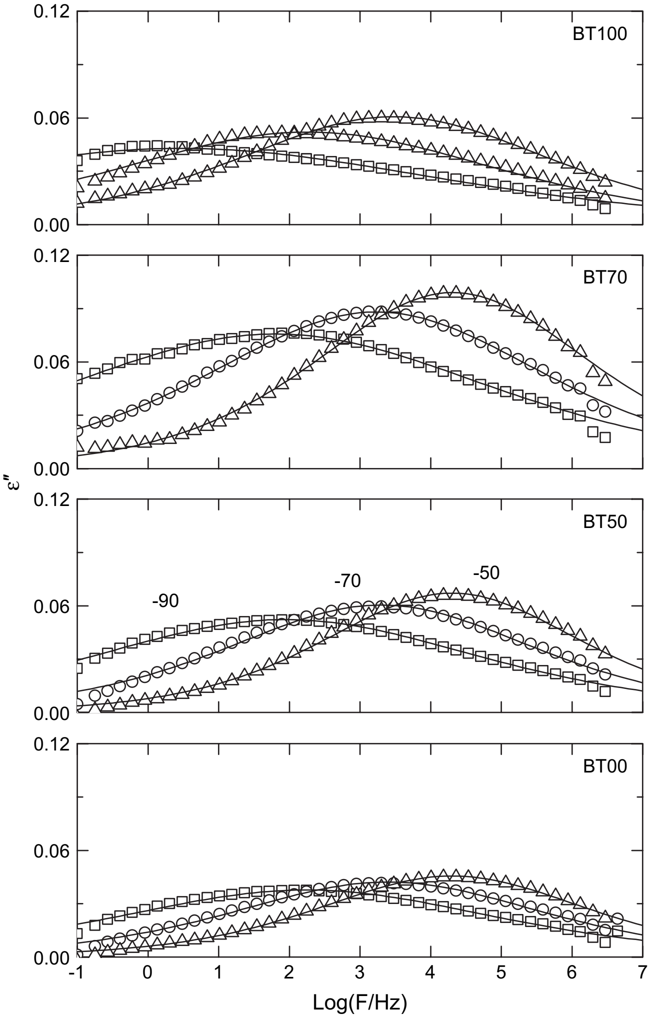

Fig. 3. Dielectric loss values (ε'') as a function of frequency of copolyesters and homopolyesters for different temperatures in the frequency range where the β process is the most prominent.

The activation energies of the β relaxation for all the polymer in the studied series are presented in Table 2. The E_a for the two homopolymers is different, being higher in the case of PBT. For the copolymers E_a increases with the content in BT units. At higher temperatures (in the region where the contribution from the α process starts to become important) there is slight perturbation of the Arrhenius behaviour.

The α relaxation exhibits a clear dependence with the amount of ^{t}BI units present in the copolymer. The values of ε'' in the temperature region of the α relaxation as a function of frequency are plotted in Fig. 5. At higher frequencies it is possible to observe also the contribution from the β relaxation. In Fig. 5 it is observed that the α relaxation appears at different

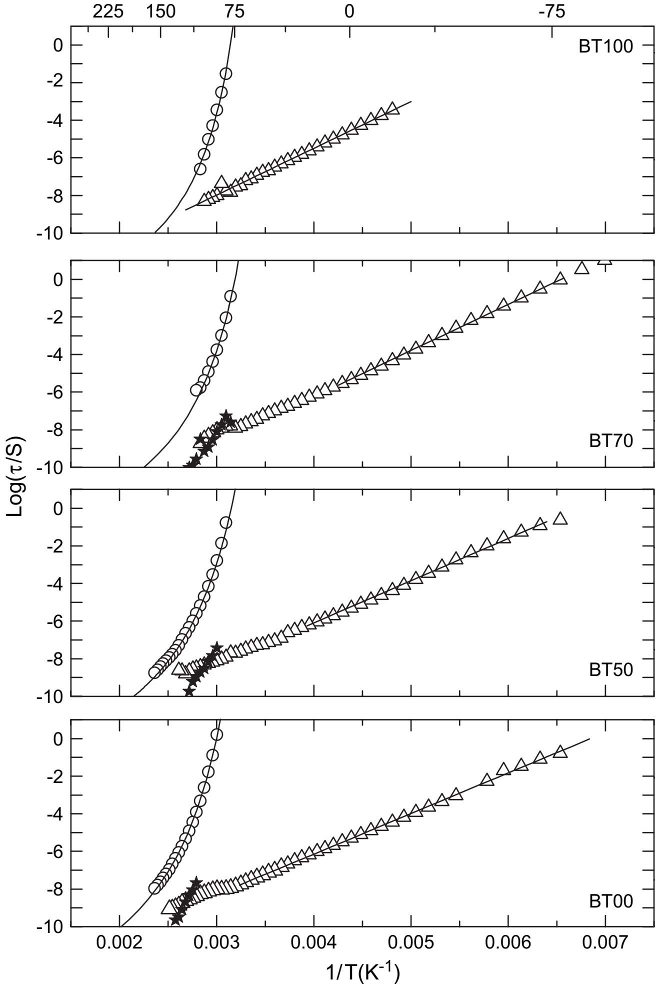

Fig. 4. Relaxation map of the studied series of polymers. Circles correspond to the mean relaxation time of the α process whereas triangles correspond to the β relaxation. Continuous lines represent the best fit of the points to the VFT equation (α relaxation) and to the Arrhenius equation (low temperature side of the β process). Filled stars represent τ_0 values obtained according to the coupling model.

temperatures depending on the content in the copolyester in ^{t}BI units. Continuous lines in Fig. 5 represent the best fit of the experimental points to the HN equation (Eq. (4)) whereas dotted lines indicate the contribution from both, the α and the β relaxations. The average relaxation time of the α relaxation has been estimated by means of:

$$\tau_\alpha = \tau_{\mathrm{HN}}\left[\sin\frac{b\pi}{2+2c}\right]^{-1/b}\left[\sin\frac{bc\pi}{2+2c}\right]^{1/b} \tag{6}$$

Table 2
Activation energy (E_a) and pre-exponential factor for the β relaxation (τ_∞^β)

Sample	E_a (kJ/mol)	τ_∞^β (s)	T_0 (K)	τ_∞^α (s)	D	m
BT00	41.2	1.70×10^{-15}	268	1×10^{-14}	7.9	91.1
BT50	42.6	1.02×10^{-15}	258	1×10^{-14}	7.4	95.3
BT70	46.5	1.20×10^{-16}	261	1×10^{-14}	6.5	106.9
BT100	48.3	3.72×10^{-16}	276	1×10^{-14}	4.9	136.4

T_0, Vogel temperature; τ_∞^α, pre-exponential factor and D and m, fragility parameters.

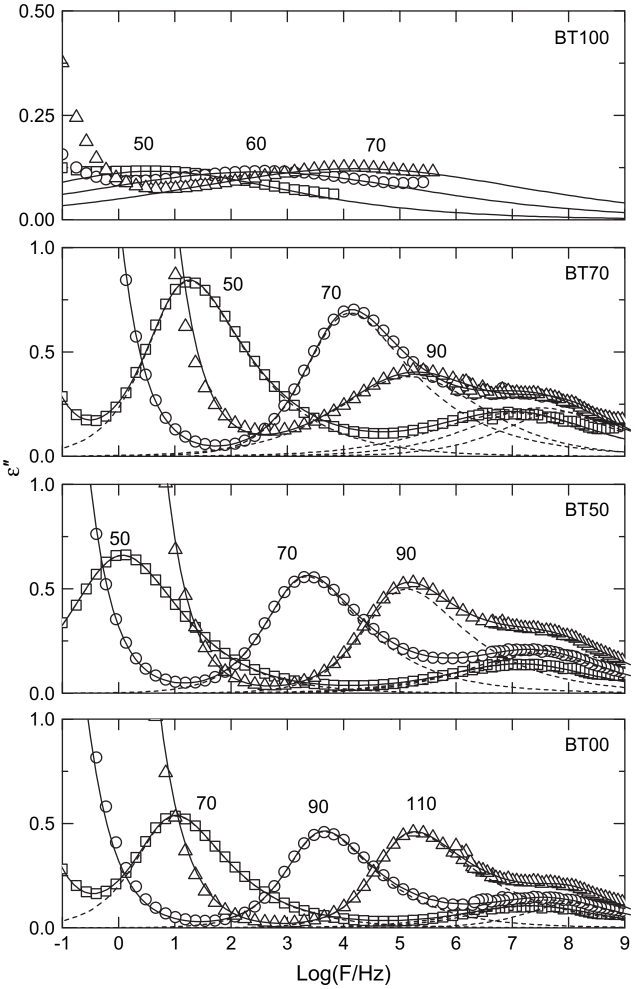

Fig. 5. ε'' as a function of frequency of copolyesters and homopolyesters for different temperatures in the range where the α process is the most relevant contribution.

The mean relaxation time of the α relaxation exhibits a different behaviour with the reciprocal temperature than the one of τ_β. In this case, the values of τ_α are described by the phenomenological Vogel–Fulcher–Tamman equation (Eq. (7)):

$$\tau_\alpha = \tau_\infty \exp\left(\frac{DT_0}{T-T_0}\right) \tag{7}$$

where τ_∞ is the pre-exponential factor, D is a parameter related to the fragility and T_0 is the Vogel temperature [20]. It is noteworthy that the fits have been performed considering $\tau_\infty = 10^{-14}$ s [20]. The parameters that provide the best fit of the average relaxation time to the VFT equation are given in Table 2. The VFT dependence exhibited by the relaxation time of the α process implies the presence of some curvature in the Arrhenius plot (log(τ) vs $1/T$), as can be observed in Fig. 4. Continuous lines in this figure show the best fits of the experimental data to the VFT equation. In the case of sample BT70, τ_α values deviate from the expected VFT behaviour at high temperatures (low $1/T$ values) due to the fact that, during the dielectric measurements, the sample crystallizes. It is known that crystallization produces a slowing down of the

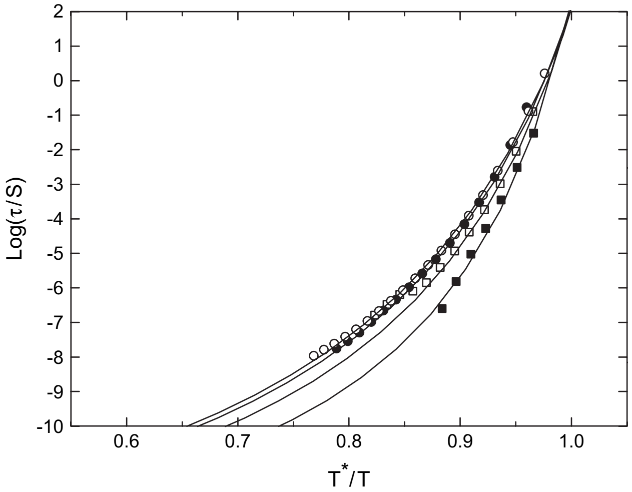

Fig. 6. Angell plot: τ_α vs T^*/T for the different copolymers. T^* is the calculated temperature at which $\tau_\alpha = 100$ s. Symbols are as in Fig. 4. Continuous lines represent the best fit to the data according to the VFT equation. (■) BT100, (□) BT70, (●) BT50 and (○) BT00.

α relaxation, and therefore, higher relaxation times [18,19]. Extracting accurate τ_α values in the case of BT100 is particularly difficult since it is a semicrystalline sample, and therefore the α relaxation in this case is very broad, and it presents a very high conductivity contribution (very high values of ε'' at low frequencies). In order to emphasize the different dependencies of τ_α vs $1/T$ with the ^{t}BI units content, we have replotted in Fig. 6 the τ_α data of Fig. 4 as an Angell plot [20] (τ_α vs T^*/T) where T^* is a reference temperature calculated from the VFT equation, as the absolute temperature at which $\tau_\alpha = 100$ s. As can be observed, the divergence of τ_α values as one approaches the glass transition temperature ($T^*/T \approx 1$) is steeper for the samples with lower concentration of ^{t}BI units. The shape of the α relaxation has been also analyzed in terms of the HN equation (Eq. (4)). The dielectric strength (Δε) of both relaxations is presented as a function of the temperature (Fig. 7a and b). For the sake of clarity, the temperature has been normalized by the respective T_g of each polymer.

4. Discussion

The main objective of this work is to establish the disrupting effect of the presence of isophthalic units enhanced by the presence of a *tert*-butyl group in the dynamics of PBT copolymers. The more important facts in these regards that are found in this investigation are the following. The β relaxation exhibits an Arrhenius behaviour below T_g. At high temperatures (close to the glass transition temperature, T_g) the behaviour is slightly changed. In general, a change of behaviour of τ_β around T_g has been observed previously in low molecular weight glass formers [21], and just recently, in another series of aromatic copolyesters with isophthalate moieties [9]. The disruption of the linear tendency of $\log(\tau_\beta)$ vs $1/T$ observed below and above T_g is accompanied by an increase of $\Delta\varepsilon_\beta$ as the temperature approaches T_g. These two features reveal the influence of the onset of the α relaxation on the β process. In glass forming systems, there are different origins for the observed β relaxation. In some polymeric systems, the observed dielectric β relaxation can be associated to the local motion of pendant or lateral groups [8,22]. Recently, Boyd and Bravard [23] have proposed that the dielectric β relaxation in PET and its copolymers with PEN has its origin in the coupling of the motion of different parts of the monomeric unit. In the present case, as mentioned in Section 3, the β relaxation is symmetric ($c_\beta = 1$). This fact differs from the observation of an asymmetric relaxation found in poly(ethylene terephthalate-*co*-isophthalate) copolymers studied before [9] and from the multicomponent β relaxation observed by Boyd and Bravard [23]. In the system studied here, the presence of the *tert*-butyl group seems to affect the shape of the β process. Dielectric spectroscopy analysis of poly(isophthalamide)s had shown before the sensitivity of secondary relaxations to the presence of the *tert*-butyl group [24]. Based on those results, we may speculate here that the presence of the *tert*-butyl group

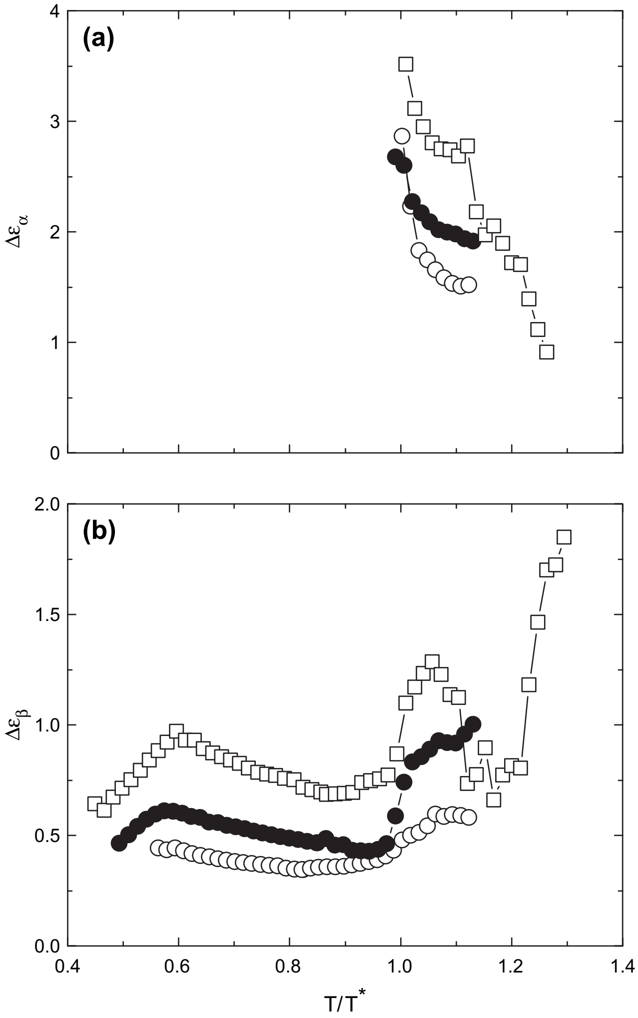

Fig. 7. Δε and shape parameters for the two relaxation processes observed in all the studied samples as a function of the normalized temperature. (a) $\Delta\varepsilon_\alpha$ and (b) $\Delta\varepsilon_\beta$. Symbols are same as in Fig. 6.

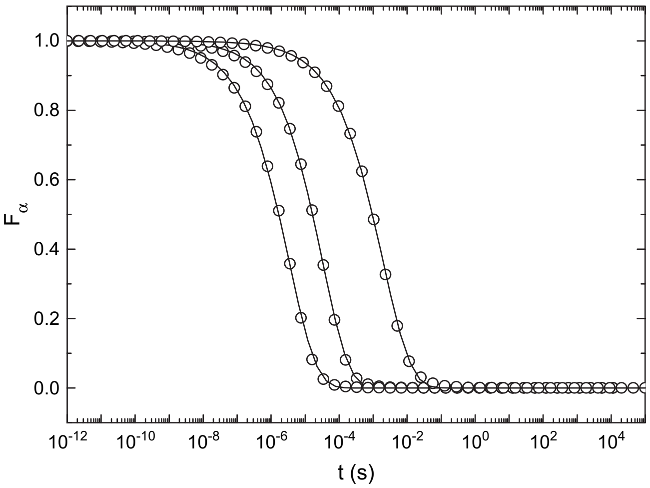

Fig. 8. Examples of KWW functions obtained for sample PB^{t}BI at three different temperatures ($T = 75$ °C, 85 °C and 95 °C). The circles represent the time-domain transformed dielectric loss corresponding to the α relaxation (see text). Continuous lines show the best fit to the KWW equation. A coupling parameter $n = 0.49$ is obtained.

modified the activation energy of the motions involving the aromatic unit, and therefore, the part of the β relaxation associated to those motions has been shifted out of the measured spectra. If the β relaxation fulfils a set of characteristics, it can be classified as a Johari–Goldstein (JG) relaxation [10]. Among these characteristics are the change of slope of the τ_β around T_g (see Fig. 4) and the increase of $\Delta\varepsilon_\beta$ around T_g (see Fig. 7). As mentioned in Section 1, recently, it has been proposed by Ngai and coworkers that in particular cases, there is a direct relation between the β relaxation above T_g and the α process. This happens when the β process can be considered as a true JG relaxation. In the framework of the coupling model (CM), the JG relaxation is considered to be the primitive of the α relaxation. Within the CM, estimation for the relaxation time of the primitive relaxation (τ_0) can be obtained through Eq. (3). The values for the coupling parameter n exponent were calculated after inverse Laplace transformation of the HN functions describing the α relaxation and subsequent fitting to the KWW curve (Eq. (2)) of the time-domain data [25]. An example of the transformed dielectric loss values and the corresponding fit to the KWW equation is shown in Fig. 8. From our data, we have obtained τ_0 and it has been plotted in Fig. 4 superimposed to the obtained values for τ_β for all the studied samples but except for the homopolymer BT100. In this particular case, the sample is semicrystalline. As it is known, the presence of crystallinity strongly affects the shape and position of the α relaxation [18,26]. Therefore, in the particular case of BT100, any estimation of τ_0 based on the shape and position of the α relaxation can lead to misleading results. As observed in Fig. 4, there is an agreement between τ_0 and τ_β above T_g (calculated from the dielectric data as the temperature at which the relaxation time is 100 s), although they exhibit different activation energies. The agreement between τ_0 and τ_β supports the idea of a β process in this series of polymers being a true JG relaxation and strongly related to the α relaxation. This should indicate a certain level of intrasegmental cooperativity of the β relaxation which could be attributed to the interconnection of the different molecular components involved in it. Similar results have been previously reported for a series of random copolymers of poly(ethylene terephthalate) (PET) and poly(ethylene isophthalate) (PEI) where the aromatic counterpart of the chain has a similar nature as in the present case [9]. Therefore, in spite of the strong dependence of the glass transition temperature on the presence of *tert*-butyl groups in the poly(ethylene terephthalate-*co*-isophthalate) copolymers (Table 1), the validity of Eq. (3) probing the relationship between β and α relaxations seems to be fulfilled.

5. Conclusions

Broadband dielectric spectroscopy provided an excellent tool to analyze the dynamic behaviour of poly(butylene terephthalate) copolymers containing 5-*tert*-butyl isophthalate units including the homopolymer entirely made of these units in a wide frequency and temperature ranges. This powerful technique coupled with the possibility of varying the chemical structure of aromatic copolyesters provides a tandem to understand the origin of the relaxational behaviour of these polymers. By analyzing the temperature dependence of the α and β relaxations, it is observed that, as temperature is increased, there is a strong correspondence between the relaxation time of the primitive relaxation and the relaxation times of the β process. This allows us to propose that the observed β relaxation has a certain JG character, implying a picture where the motion that gives rise to the β process possesses a certain degree of cooperativity extended all along the repeat unit (the so-called intrasegmental cooperativity).

Acknowledgements

The authors thank Prof. K.L. Ngai for helpful discussions. This research has been financed with grants MAT2005-01768 and MAT2002-04600-CO2 from MCYT, Spain. A. N. thanks the Ramon y Cajal program of the Spanish MCYT.

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