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Effect of crystallinity on the dynamic mechanical relaxations of poly(butylene isophthalate)

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Summary

The viscoelastic spectrum of poly(butylene isophthalate) annealed at 90 °C for different times has been examined by dynamic mechanical spectroscopy.

Crystallinity affects both the main α absorption associated with the glass to rubber transition and the sub-ambient secondary β relaxation region. The latter results from two overlapping processes, β_1 and β_2, that have been evidentiated by a resolution procedure. Values of 52 and 76 kJ/mol have been obtained for the activation energies of the low (β_1) and high (β_2) temperature component respectively. It is suggested that these values are not affected by the methylene chain length and by the isomerism of the phthaloyl residue.

Introduction

The relaxation behaviour of various poly(n-methylene terephthalates) has been the subject of several investigations (1-10), poly(ethylene terephthalate) (PET) being the most widely studied member of the homologous series. The viscoelastic spectrum is characterized by the presence of α and β relaxation regions, located above and below room temperature respectively.

The temperature of the primary α relaxation, associated with the glass transition, has been found to decrease with increasing methylene sequence length, i.e. chain flexibility (1, 6-8), and to be affected by the level and nature of crystallinity (1, 2, 6-8, 10).

In the glassy state, both dielectric and dynamic mechanical measurements have revealed the presence of a rather complex secondary β absorption which has been suggested to result from at least two overlapping processes (1-9) associated with localized motions of carbonyl and glycol groups in the gauche and trans conformations.

Little work has been published concerning the viscoelastic properties of polyesters derived from isophthalic acid and linear glycols (8,9) aimed at investigating the effect of symmetrical and non-symmetrical substitution in the benzene ring. In the present paper, attention is focused on the relaxation behaviour of poly(n-butyl isophthalate). Results are presented with regard to the influence of changes in crystallinity, induced by thermal treatments at 90°C.

Experimental

Poly(butylene isophthalate) (PBI) was prepared from dimethyl isophthalate and 1,4-butandiol using $Ti(OBu)_4$ as catalyst. Polymerization was performed in a 1.8 liter stainless steel reactor according to the

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*To whom offprint requests should be sent standard two stage polycondensation procedure (11). In the first stage, at atmospheric pressure, the temperature was progressively raised from 140 to 200° C and maintained at this value until about 90% of the theoretical methanol was distilled off. In the second stage the pressure was reduced to about 0.5 mbar keeping the temperature at a value in the range 200-230 °C. The number average molecular weight was measured by end group titration and a sample of M_n= 24500 was selected for investigation.

Suitable specimens for dynamic mechanical measurements were obtained by injection moulding in a Mini Max Molder (Custom Scientific Instruments), supplied with a rectangular mould (30 x 8 x 1.6 mm). Immediately after moulding, samples were quenched in liquid nitrogen, annealed at 90 °C for different times and then stored in a desiccator under vacuum.

Calorimetric measurements were carried out by means of a Thermal Analyser 9900 (Du Pont) at a heating rate of 20°C/min. Three high purity standards were used for cell calibration: benzene, lauric acid and indium.

A Dynamic Mechanical Thermal Analyser (DMTA, Polymer Laboratories) in the dual cantilever mode was used to investigate the dynamic mechanical properties in the temperature range -160/+50°C usually at a frequency of 3 Hz and a heating rate of 3°C/min unless otherwise specified.

Results and discussion

Calorimetric curves of poly(butylene isophthalate) annealed at 90°C for different times are shown in Fig.1 and the corresponding data are collected in Table 1.

The quenched sample exhibits a sharp increment of heat capacity in the glass to rubber transition region at Tg= 21°C and a quite small melting peak at 139°C. With increasing annealing time the endotherm area increases and a small additional peak is observed 35-40°C lower than the main melting temperature given in Table 1. Correspondingly, the glass transition region widens, shifts slightly to higher temperature and the specific heat increment at Tg decreases from 0.41 for the almost totally amorphous PBI to 0.19 J/g°C for the more crystalline sample.

The degree of crystallinity reported in Table 1 was calculated from the total area of melting using the value of ΔH= 192 J/g (12) for the heat of fusion of 100% crystalline PBI. The 23% crystallinity percentage was the maximum value attainable at 90°C; no further increase was observed for annealing time higher than 24 hr.

Table 1 . Calorimetric data of Poly(butylene isophthalate) annealed at 90°C.

Annealing time (hr)	$Tg^{a)}$ (°C)	$\Delta c_p^{\ b)}$ (J/g°C)	$Tm^{c)}$ (°C)	ΔHm (J/g)	$Wc\%^{d)}$
0	21	0.41	139	3.9	2
0.5	23	0.38	140	5.3	3
1	24	0.27	142	35.5	19
2	25	0.24	143	40.3	21
24	25	0.19	142	44.9	23

a) Glass transition temperature from baseline deviation
b) Specific heat increment at Tg
c) Peak temperature of the main melting endotherm
d) Crystallinity percentage

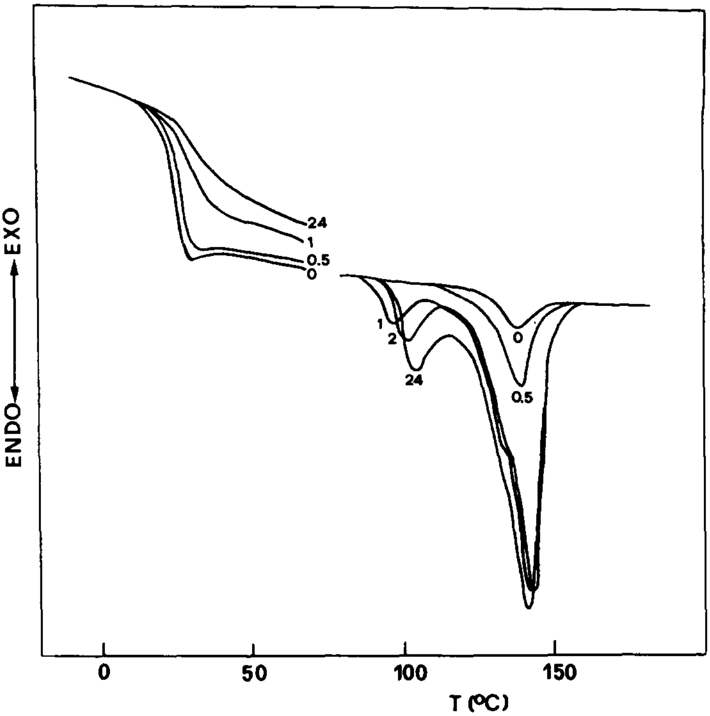

Fig.1 Calorimetric curves of Poly(butylene isophthalate) annealed at 90°C for different times (hr). The glass transition region is enlarged for the sake of clarity.

The dynamic mechanical spectrum of quenched PBI is compared in Fig.2 with the spectrum of the 23% crystalline sample. Crystallinity strongly influences both the secondary β relaxation at low temperature and the primary α dispersion associated with the glass transition.

As regards the main relaxation α, which is related to the micro-brownian motions of the chains in the amorphous regions, the quenched sample exhibits a very narrow and intense peak in the loss tangent $\tan\delta$ at a temperature T_α= 31 °C and a steep decrease of the dynamic storage modulus E', as usually found for highly amorphous polymers. The process appears to be influenced by the amount of crystallinity, both in position and shape: as the degree of crystallinity is raised, the α loss peak decreases in magnitude, broadens and moves to higher temperature, reaching a value of T_α= 43 °C at Wc= 23%. Also the steepness and intensity of the modulus drop in the α transition region show a great reduction with increasing crystallinity, reflecting the typical behaviour of partially crystalline polymers (3).

The α relaxation peak has been examined at different frequencies in order to evaluate the influence of crystallinity on the frequency dependence of the maximum loss temperature. Since the α process is associated with the glass transition, the plots of $\ln\nu$ vs 1/T should in principle follow the WLF relation (13). However, within the limited frequency range explored (1-30 Hz), the curves obey the Arrhenius equation as illustrated in Fig.3. Although the points for the more crystalline sample lie at higher temperatures at a given frequency than those obtained

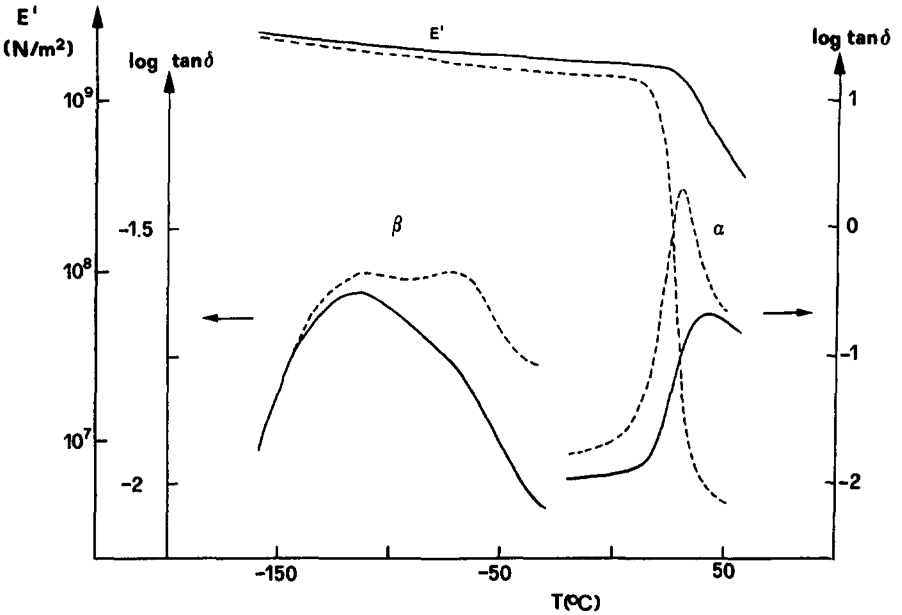

Fig.2 Dynamic mechanical spectrum of quenched (- -) and 23% crystalline (——) Poly(butylene isophthalate).

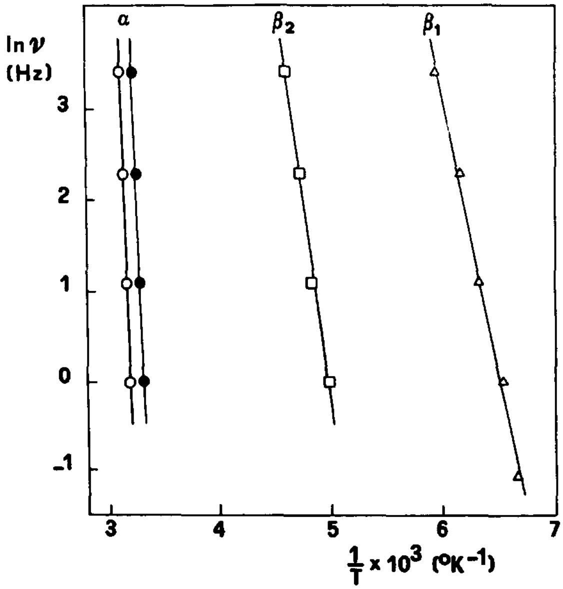

Fig.3 Ln frequency against 1/Tmax for the dynamic mechanical relaxations of Poly(butylene isophthalate) : (●) amorphous ; (○) 23% crystalline.

for the amorphous polymer, the activation energy of the process does not appear to be sensitive to crystallinity, being 316 and 319 kJ/mol for the quenched and annealed sample respectively. Activation energies of this magnitude are commonly found for the α relaxation process of polymers (3) and compare well with the value reported in the literature (8,10) for poly(butylene terephthalate) (PBT).

Referring to the viscoelastic behaviour of PBI in the glassy state, Fig.2 shows a quite complex sub-ambient relaxation region which extends over a wide temperature range. When quenched from the melt, the polymer exhibits two distinct overlapping loss processes; on the contrary, the β absorption of the annealed sample appears as an asymmetric peak, the loss curve being steeper on the low-temperature side. Similar behaviour has been previously reported both for PBI (9) and poly(hexamethylene terephthalate) (7).

The effect of crystallinity on the β relaxation is seen in more detail in the upper part of Fig.4, where the loss curve of PBI annealed at 90°C for different times is plotted on a linear scale. On crystallization,

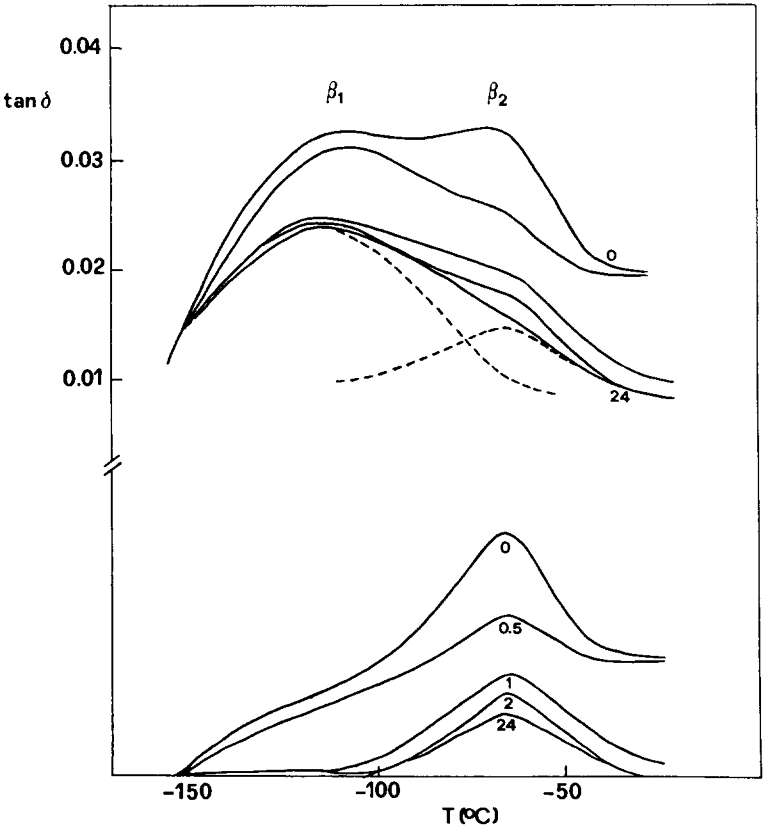

Fig.4 Tan δ vs temperature in the β relaxation region of Poly(butylene isophthalate) annealed at 90°C for different times (hr). Top: experimental curves. Bottom: subtracted curves (see text).

the shape of the β peak changes significantly: the low temperature component (β_1) of the absorption is only partially reduced by the initial increase of crystallinity while the high temperature component (β_2) is progressively depressed, appearing as a shoulder in the 23% crystalline sample. This behaviour suggests that the loss process responsible of the β_2 peak is due to local motions of amorphous, crystallizable chain segments. As already mentioned in the introduction, the β process of poly(methylene-based terephthalates) has been suggested to arise from motions of carbonyl groups associated with gauche and trans conformations of the glycol segments. On the basis of this attribution, since PBI crystallizes in a planar all trans conformation (14), the high temperature relaxation, which is depressed by crystallization, can be associated with the trans isomers and the lower temperature β_1 relaxation with the gauche isomers of the polymer chain.

In order to evidentiate the dependence of the β_2 process on crystallinity, the β absorption of the more crystalline sample was resolved into two components (dotted lines in Fig.4) by assuming a symmetrical shape of the β_1 process (peak temperature $T_{\beta 1}$= -115°C at 3 Hz). The β_1 peak so obtained was subtracted from the experimental loss curves and the results are plotted in the lower part of Fig.4. This procedure brings into evidence that, although the height of the β_2 maximum is strongly decreased with increasing crystallinity, the peak position remains unchanged ($T_{\beta 2}$= -67°C at 3 Hz).

The same procedure was applied to dynamic mechanical spectra obtained at different frequencies, in order to find the frequency-temperature locations of each of the two absorption maxima, shown in Fig.3. The apparent activation energies evaluated from the Arrhenius plots yield values of 52 and 76 kJ/mol for β_1 and β_2 process respectively.

Literature data concerning ethylene glycol-based poly(terephthalates) usually refer to the β relaxation as a single process in the evaluation of ΔH_β and cover a range from 52 to 71 kJ/mol, as shown in Table 2. Only in the case of poly(hexamethylene terephthalate) (P6T), the β peak has been resolved into β_1 and β_2 contributions and activation energies of 52 and 78 kJ/mol for the low and high temperature process respectively have been reported (7). These values are in excellent agreement with the results obtained in the present paper for PBI, suggesting that the molecular

Table 2 . Temperature locations (°C) and activation energies (kJ/mol) of the sub-ambient relaxation processes of poly(methylene tere and isophthalates)

	T_β a)	ΔH_β	$T_{\beta 1}$ a)	$\Delta H_{\beta 1}$	$T_{\beta 2}$ a)	$\Delta H_{\beta 2}$	ref
PET	-65	71	-105	-	-70	-	2
	-	52	-	-	-	-	2
	-64	67	-117	-	-67	-	5
	-62	71	-	-	-	-	6
PBT	-68	55	-	-	-	-	10
P6T	-	-	-126	52	-75	78	7
PBI	-	-	-115	52	-67	76	this work

a) measurement frequency: ref 2 and 5: 1Hz; ref 6: 3.5Hz; ref 7: 11 Hz; ref 10: 110 Hz.

mechanisms responsible for the two relaxations are not affected by the substitution of the para-phenylene with the meta-phenylene linkage. It has to be recalled that the ΔH_β values reported in the third column of Table 2 have been derived from different experimental methods and different samples and that the Arrhenius plots have been constructed using the peak temperature of the complex β maximum, i.e. neglecting the fact that the β peak arises from more than one motional process.

It may be observed that lower figures (52-55 kJ/mol) are obtained from dielectric than from mechanical measurements (67-71 kJ/mol). Taking into account that the two experimental methods span a different range of frequencies, it can be suggested that the ΔH_β values reported in Table 2 do not belong to molecular motions of the same groups. As a consequence, it may be inferred that dielectric measurements are more sensitive to motional processes of segments in the gauche conformations (β_1 component) while dynamic mechanical results reflect motions pertaining to the trans isomers (β_2 component).

In this hypothesis, constant values of 52 and 76 kJ/mol would be a good estimate of the activation energies of the β_1 and β_2 processes, irrespective of the length of methylene sequences and of the symmetrical or non symmetrical substitution of the phenyl ring. These variables would influence the relative contributions of the two processes, but not the energetic requirements of the molecular motions involved.

Conclusions

Crystallinity induced by annealing treatments at 90°C influences the dynamic mechanical α and β relaxations of PBI in a different way. While the temperature location of the α process is increased by crystallinity, the low and high temperature components of the β peak are not affected. The intensity of both α and β relaxations decreases with increasing annealing time.

Activation energies of 52 and 76 kJ/mol characterize the two processes responsible of the complex β absorption region, resulting from motions of carbonyl groups associated with the gauche and trans conformations of the polymer chain. The results suggest that in poly(methylene tere and isophthalates) the energetic requirements (ΔH) for the two different molecular motions are not particularly affected by the number of methylene groups and by the isomerism of the phthaloyl residue.

Acknowledgment

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