

# Thermomechanical Analysis of Chain-Extended PET and PBT

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## SYNOPSIS

Two series of samples, one of PET and another of PBT, were received after chain extension at different reaction times with two new chain extenders (diimidodiepoxides). These samples showed different intrinsic viscosity and degree of branching or crosslinking. The effect of this differentiation on thermal properties was studied by thermomechanical analysis (TMA). The parameters studied were the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and the linear expansion coefficient ( $\alpha$ ). It is remarkable that, in the case of PET amorphous or semicrystalline samples, two peaks appeared next to the  $T_g$  in the TMA thermogram. The first peak appeared at a temperature very close and lower to the  $T_g$ , and the other peak, at higher temperature into the "cold crystallization region." The presence of two such peaks was not detected in the DSC thermogram of PET samples either in the TMS or DSC thermograms of PBT. The  $T_g$  values were found to agree to within  $\pm 1^\circ\text{C}$  of those obtained from DSC; on the contrary, the  $T_m$  values varied significantly from those received from DSC. The linear expansion coefficient of samples was found to increase with the degree of chain extension. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have become very important commercial plastics with satisfactory thermal stability. PET is known as one of the major synthetic fibers, but it is used also in the manufacturing of soft-drink bottles, photographic films, recording audio and video tapes, films for food packaging, or even as electrical insulating material for capacitors. PBT, on the other hand, with its lower glass transition temperature, inevitably gives rise to a lower dimensional stability under heat, but this disadvantage can be substantially restored by glass fiber reinforcement. So, PBT, because of its better rheological properties, is selected for the manufacture of various engineering components (bearings, rollers, screws, buttons, handles, etc.) and even for electronic equipment housing.

In any case, a relatively high molecular weight and a low carboxyl content gives to both polymers improved mechanical and chemical properties, such

as toughness and hydrolytic stability. But this is rarely achieved, since further heating during the preparation of the polyester by the melt polycondensation process causes an undesirable degradation reaction with a significant increase in carboxyl end groups. The solid-state polycondensation overcomes this problem, but it is slow and requires special equipment for large-scale operation. For this reason, the use of the so-called chain extenders seems to be very attractive. The chain extenders cited in the literature, generally for polymers, are bifunctional compounds which react very easily with some end groups of macromolecules, e.g.,  $-\text{COOH}$ ,  $-\text{OH}$ , and  $-\text{NH}_2$ . When these bifunctional compounds are reacted directly with low molecular weight polycondensated polymers coming, e.g., from recycling operations, they form bridges between two polymer chains, increasing the molecular weight significantly. This coupling of macromolecules can take place during the last stage of the production of the polymer or even in the extruder. As chain extenders can be used as compounds which are bifunctional, easily preparable, thermally stable, nonvolatile in the melt temperature of the polymer, and capable for fast reaction with polymer chain ends in a nearly irre-

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versibly manner with no volatile products, it is desirable for such reactions to be of addition or ring-opening type. Two of the main chain extenders of this type which have been proposed are bisepoxides and diepoxides.

On chain extension of the polyesters with diepoxides, secondary hydroxyl groups are produced, which are capable of creating branching or crosslinking depending on the reaction conditions.<sup>1-3</sup> In our previous work,<sup>2,3</sup> in an effort to produce new effective chain extenders for polyesters, we received one series of PET and another of PBT samples chain-extended by diepoxides. These samples were differentiated from each other, because they stayed in the reactor with the diepoxide for different periods of time (10, 20, 30, or 60 min). So, we could study the effect of molecular weight and branching or crosslinking on the thermal properties such as  $T_g$ ,  $T_m$ , or the linear expansion coefficient  $\alpha$ . As is known from the literature,<sup>4-6</sup> these parameters can be assessed successfully by thermomechanical analysis. The above samples were analyzed on a thermomechanical system (TMS-2, Perkin-Elmer), and the results are discussed in the present article.

## EXPERIMENTAL

### Chain-extending Reaction

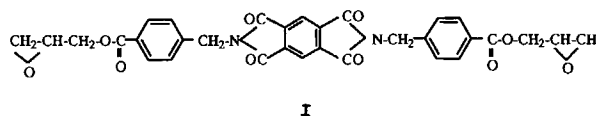
To a 250 mL three-necked, round-bottom flask equipped with a mechanical stainless-steel stirrer, argon inlet, and outlet tube, 30 g of well-dried polyester chips were added. Under a flow of argon and stirring (60 rpm), a chain extender was added and the flask was placed in a salt ( $\text{NaNO}_2/\text{KNO}_3$  40 : 60 w/w) bath heated at  $280 \pm 1^\circ\text{C}$  in the case of PET and at  $250 \pm 1^\circ\text{C}$  in the case of PBT. After the complete melting of the chips, the speed of stirring increased to 200 rpm and samples of approximately 5 g were taken from the flask by increasing instantaneously the argon flow rate. The sampling time was 10, 20, 30, and 60 min after the complete melting. The used quantity of diepoxide was double the theoretical one demanded. The theoretical amount of the chain extender to be added in the polyester was calculated from eq. (1):

$$w\% = \frac{MW \times CC_0}{2 \times 10^4} \quad (1)$$

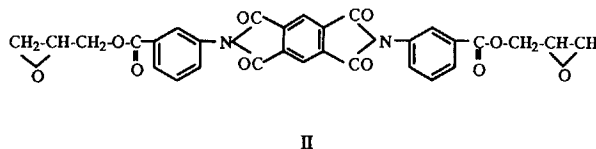
where  $MW$  is the molecular weight of the chain extender, and  $CC_0$ , the carboxyl content of the initial polymer. As the theoretical amount, we mean the

quantity of the chain extender which is needed so that a mol of chain extender reacts with 2 mol of polyester, assuming that only the carboxyl groups will be the reactive groups of this process. The characterization of samples were reported in previous articles.<sup>1,2</sup> The intrinsic viscosity and the insoluble residue (due to crosslinking) of each sample are given in Table I.

The PET samples were taken from the chain extension of virgin PET with diepoxide I:



and the PBT samples from the chain extension of virgin PBT with diepoxide II:



Both diepoxides were synthesized in our lab and they are not commercially available. They worked successfully and analogously, i.e., they increased the initial molecular weight of PET, and of PBT, about three times. For this reason, no mention is made in the Results and Discussion section of this parameter. The  $MW$  of all samples was measured by viscometry and determination of the hydroxyl and carboxyl group content (end-group analysis).

### Measurements

The determination of the glass transition and melting temperature was done directly on the TMS-2 (Perkin-Elmer) using the penetration probe in the following way: The samples were prepared having parallel sides (film) by melt-pressing in a hydraulic heated press (Paul-Otto Weber, Type PW 30) at a temperature of  $265 \pm 5^\circ\text{C}$  for PET and  $240 \pm 5^\circ\text{C}$  for PBT under a pressure of 6 kN on a ram of 110 mm. The final sample was punched out of the prepared film and its height was measured using a micrometer. The samples prepared had the following characteristics:

Diameter: 6 mm.  
Height:  $0.5 \pm 0.05$  mm (For penetration measurements).

**Table I** Intrinsic Viscosity and Insoluble Residue of the Chain-extended PET and PBT Samples

| Time <sup>a</sup><br>(Min) | PET               |                 |                              | PBT               |                 |                              |
|----------------------------|-------------------|-----------------|------------------------------|-------------------|-----------------|------------------------------|
|                            | [ $\eta$ ] (dL/g) |                 | Insoluble Residue<br>(w/w %) | [ $\eta$ ] (dL/g) |                 | Insoluble Residue<br>(w/w %) |
|                            | Blank             | CE <sup>b</sup> |                              | Blank             | CE <sup>c</sup> |                              |
| 0                          | 0.60              | 0.60            | —                            | 0.84              | 0.84            | —                            |
| 10                         | 0.54              | 0.85            | 2.9                          | 0.83              | 1.16            | —                            |
| 20                         | 0.54              | 0.98            | 5.1                          | 0.81              | 1.48            | —                            |
| 30                         | 0.55              | 1.19            | 6.8                          | 0.80              | 1.84            | 3.2                          |
| 60                         | 0.58              | 0.94            | 25.3                         | 0.79              | 1.53            | 23.8                         |

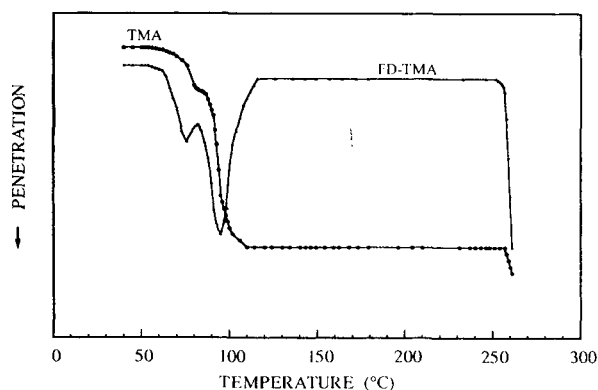
<sup>a</sup> Time of chain extension.

<sup>b</sup> Chain-extended PET samples with diepoxide I.

<sup>c</sup> Chain-extended PBT samples with diepoxide II.

Height:  $1.5 \pm 0.05$  mm (For expansion measurements).

The penetration probe made contact with the sample's upper surface, whose temperature was exactly controlled by a linearized resistance thermometer in a low mass furnace. As the sample softened ( $T_g$ ), the position of the probe changed, and this position was accurately monitored by a linear variable differential transformer (LVDT). The penetration probe<sup>6</sup> with the flat tip whose surface is  $0.621 \text{ mm}^2$  was used and a weight of 6.21 or 31.05 g was added to the loading platform, corresponding to a pressure on the sample of 10 or 50 g/mm<sup>2</sup>. All runs were done under a helium atmosphere at a heating rate 5°C/min. This heating rate is relatively low in comparison with that used in DSC runs, but the manufacturer suggests this rate, because the analyzed samples could sometimes be very thick, up to 12–13 mm in height. However, in our case, thin films were used.



**Figure 1** Thermal response of initial amorphous PET sample. TMA: Thermomechanical analysis curve (loading 50 g/mm<sup>2</sup>). FD-TMA: First derivative of the TMA curve.

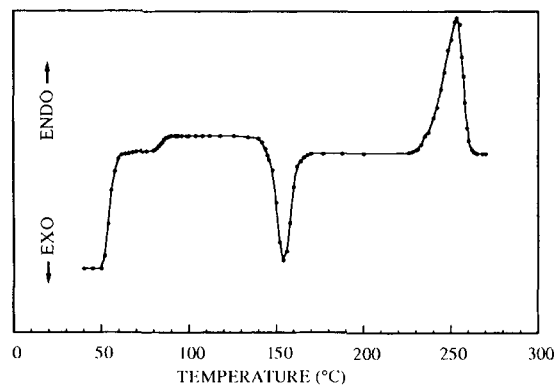
### Linear Expansion Coefficient

Another basic probe supplied with the Model TMS-2 is the expansion probe.<sup>6</sup> This probe was rested on the sample with a weight of only 1.8 g and pushed up as the sample expanded. The expansion coefficient is generally designated with the Greek letter  $\alpha$  and is defined as

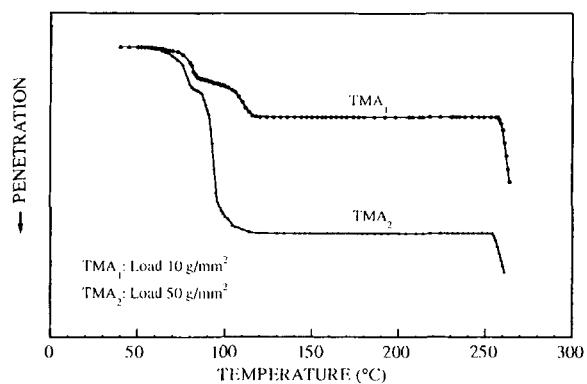
$$\alpha = \Delta L / L_0 \Delta T$$

where  $\Delta L$  = change in length,  $\Delta T$  = change in temperature, and  $L_0$  = original length (generally the length at room temperature).

For the most precise work, the instrument was calibrated by measuring the expansion coefficient of an aluminum standard provided by Perkin-Elmer. The measurements were done between 0 and 200°C for all samples. The PET amorphous samples before the measurement were crystallized by annealing at 200°C for 30 min, because a penetration in the "cold crystallization region" interfered with the measure-



**Figure 2** Thermal response of initial amorphous PET sample. DSC: Differential scanning calorimetry curve.

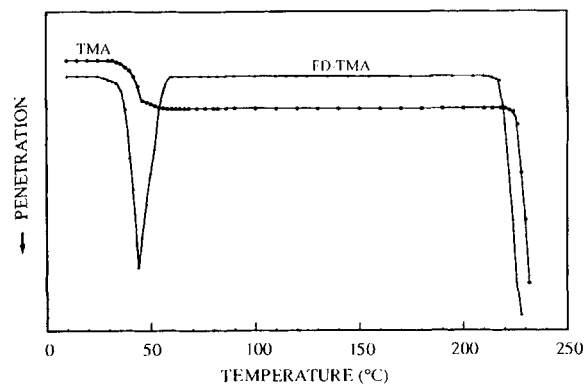


**Figure 3** TMA curves of an amorphous PET sample. Penetration effect of loading.

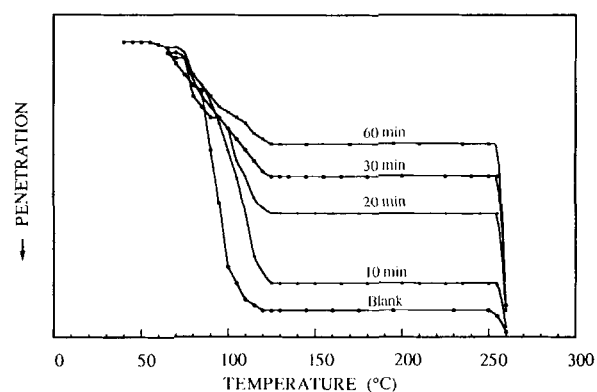
ment. On the contrary, the PBT samples with the probe in place were heated briefly through the  $T_g$  region and cooled to relieve stress from the punch.

## RESULTS AND DISCUSSION

The results of thermomechanical analysis of PET and of PBT chain-extended samples are given and discussed. The aforementioned samples had the characteristics listed in Table I. As one can see from the table, in the blank experiment for both PET and PBT, i.e., in the case where the melted sample is heated under stirring for 10, 20, 30, or 60 min in the absence of the chain extender, the intrinsic viscosity decreases, because of the thermal decomposition that takes place.<sup>2</sup> On the contrary, in the presence of the chain extender, the intrinsic viscosity gradually increases with reaction time up to 30 min; longer chain extension leads to a decrease of viscosity due to branching.



**Figure 4** TMA and FD-TMA curves of a PBT sample with the penetration probe.

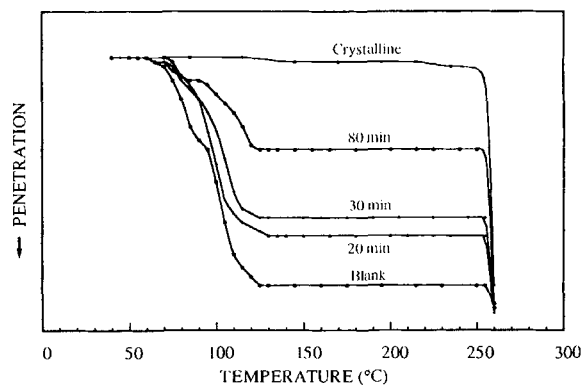


**Figure 5** TMA curves of the chain-extended PET samples at various reaction times (loading  $50 \text{ g/mm}^2$ ).

## Glass Transition Temperature

The above PET and PBT diversified samples were subjected to thermomechanical analysis for their characterization. A typical thermogram obtained (curve TMA) with its first derivative (curve FD-TMA) of the amorphous PET sample is shown in Figure 1.

It is remarkable that the penetration curve shows two steps near the  $T_g$  region. These steps are better shown by the first derivative curve as two distinct peaks (peak 1 at  $79^\circ\text{C}$  and peak 2 at  $95^\circ\text{C}$ ). The temperature corresponding to peak 1 coincides with  $T_g$  as it is obtained by DSC, while peak 2 represents a penetration in the cold-crystallization region. These results are in good agreement with those found by other investigators<sup>7</sup> who relied on dielectric measurements. Two relaxation regions were identified by using the dielectric analyzer in that work: the relaxation region from the pure amorphous phase of the PET sample and the relaxation region from the spherulitic phase. This explanation is very



**Figure 6** TMA curves of the initial PET sample annealed at various times and temperatures.

**Table II Glass Transitions Temperatures of PET and PBT Chain-extended Samples Determined by the TMA Penetration Technique and DSC**

| Time <sup>a</sup><br>(min) | PET          |              |              | PBT          |              |              |
|----------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                            | $T_g^b$ (°C) | $T_g^c$ (°C) | $T_g^d$ (°C) | $T_g^b$ (°C) | $T_g^c$ (°C) | $T_g^d$ (°C) |
| 0                          | 79           | 81           | 80           | 44           | 45           | 43           |
| 10                         | 81           | 82           | 82           | 45           | 46           | 45           |
| 20                         | 82           | 82           | 83           | 46           | 45           | 46           |
| 30                         | 83           | 83           | 83           | 48           | 49           | 47           |
| 60                         | 83           | 84           | 83           | 51           | 52           | 49           |

<sup>a</sup> Time of chain extension.

<sup>b</sup> Determined by TMA: penetration probe loaded with 31.05 g (50 g/mm<sup>2</sup>).

<sup>c</sup> Determined by TMA: penetration probe loaded with 6.21 g (10 g/mm<sup>2</sup>).

<sup>d</sup> Determined by DSC.

reasonable, but, unfortunately, it is not explained how this second penetration step is much greater than the first one. This peculiar behavior is not discernible in the DSC thermogram of the same initial amorphous PET sample (Fig. 2). In this thermogram, three events can be recognized: the glass transition temperature at 80°C, the cold-crystallization temperature at 150°C, and the melting temperature at 255°C.

It is worthwhile noting that the penetration observed in the second step considerably depends on the applied load on the sample. In Figure 3 are shown the curves recorded with two different loads, 10 and 50 g/mm<sup>2</sup>. So, in order to have comparable results, in all subsequent penetration trials a load of 50 g/mm<sup>2</sup> was used.

PBT is crystallized much faster than is PET; even after quenching, it presents a 30% degree of crystallinity.<sup>8</sup> For this reason, the TMA thermogram is simpler than that of PET (Fig. 4). The glass transition temperature occurs in one step and is shown

more distinctly by the first derivative curve. The penetration in the region of the  $T_g$  is smaller than that of PET, because PBT samples are received less amorphous than is PET under the same conditions of quenching.

When the PBT samples are heated above the  $T_g$ , no other penetration is observed up to the melting temperature. This indicates that the crystallites consist of the greater part of the polymer mass and form the coherent matrix, while the amorphous phase is dispersed in the voids.

It is well known that, generally, the introduction of crosslinks reduces the molecular packing and crystallization, leading to a more or less amorphous material with a lower modulus and hardness. The PET and PBT of this work have a significant content of crosslinks after chain extension, especially those that reacted with the chain extender for 1 h. In Figure 5, one can observe the gradually decreasing penetration in the chain-extended PET samples with increasing crosslinking.

**Table III Melting Temperatures of PET and PBT Chain-extended Samples Determined by the TMA Penetration Technique and DSC**

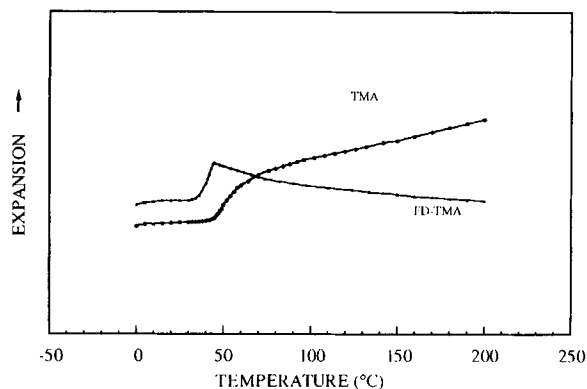
| Time <sup>a</sup><br>(Min) | PET          |              |              | PBT          |              |              |
|----------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                            | $T_m^b$ (°C) | $T_m^c$ (°C) | $T_m^d$ (°C) | $T_m^b$ (°C) | $T_m^c$ (°C) | $T_m^d$ (°C) |
| 0                          | 260          | 260          | 254          | 227          | 228          | 224          |
| 10                         | 254          | 255          | 249          | 224          | 227          | 222          |
| 20                         | 253          | 254          | 243          | 223          | 226          | 222          |
| 30                         | 253          | 253          | 242          | 222          | 223          | 221          |
| 60                         | 247          | 252          | 237          | 222          | 224          | 217          |

<sup>a</sup> Time of chain extension.

<sup>b</sup> Determined by TMA: penetration probe loaded with 31.05 g (50 g/mm<sup>2</sup>).

<sup>c</sup> Determined by TMA: penetration probe loaded with 6.21 g (10 g/mm<sup>2</sup>).

<sup>d</sup> Determined by DSC.



**Figure 7** TMA and FD-TMA curves of the initial PBT sample suitable for the determination of the linear expansion coefficient  $\alpha$ .

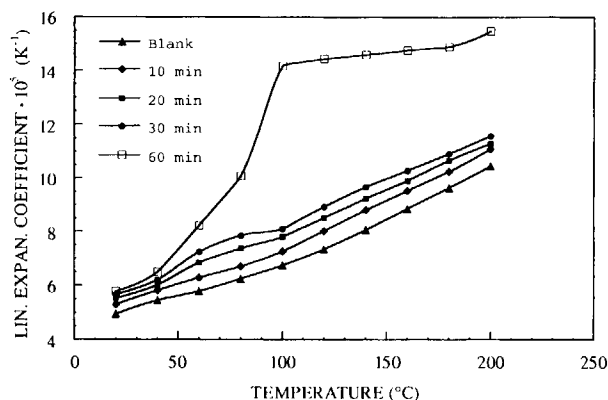
An analogous phenomenon was observed when the initial amorphous PET sample (blank) was crystallized at different times (20, 30, or 80 min) at 130°C or at another higher temperature 220°C for 30 min, in order to obtain a series of samples with different degrees of crystallinity (Fig. 6). The higher the crystallinity, the lower the penetration; it is obvious that no penetration was detected in the less amorphous sample (crystalline).

In Table II are presented the  $T_g$  values of chain-extended PET and PBT samples, obtained by TMA and DSC measurements. For both polyesters, the  $T_g$  values obtained by TMA are very close with those obtained by DSC. It is interesting to note the gradual increasing of  $T_g$  values of PBT with the chain-extension time. An analogous effect is not observed in the  $T_g$  values of PET.

### Melting Temperature

On the contrary to  $T_g$ , the  $T_m$  values determined by TMA do not coincide with those obtained by DSC. As shown in Table III, the latter are higher most probably because of the different heating rate used in the TMA and DSC. The heating rate for DSC runs is usually 20°C/min and this rate was also used in this work, while the heating rate for TMA was 5°C/min, as explained in the Experimental part. So, during the TMA run, the samples remained longer under heat before the melting temperature. During this time (four times more), the crystallization of the sample could be increased, leading to a higher  $T_m$ .

It should be also noted that the  $T_m$  values of more chain-extended samples are lower. This is quite reasonable, because these samples having a significant extent of crosslinking cannot be crystallized as eas-



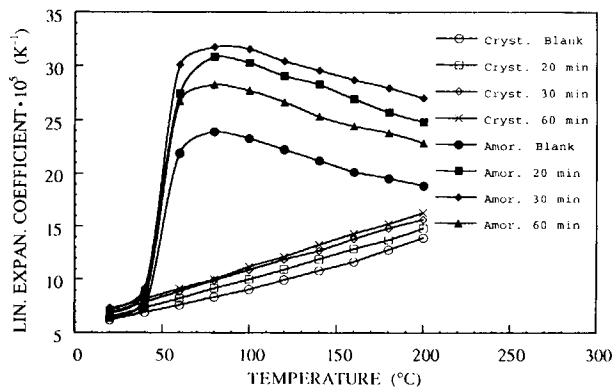
**Figure 8** Effect of the chain extension of PET samples on the linear expansion coefficient.

ily. So, they have lower melting temperatures. As reported, the  $T_m$  of fully crystalline PET is 290°C,<sup>9</sup> and of PBT, 250 ± 4°C.<sup>10</sup>

### Linear Expansion Coefficient (LEC)

As reported in the Experimental part, it is impossible to assess the LEC of amorphous PET samples between 0 and 200°C, because of the cold crystallization that takes place in this region (140–150°C). To overcome this problem, all samples were annealed at 200°C for 30 min. The cold crystallization of PBT takes place after 200°C, just before its melting point (223°C); so, there is not problem for this polymer.

Figure 7, depicting the linear expansion behavior of the PBT blank sample, shows a normal expansion up to the glass transition temperature. At  $T_g$ , an abrupt increase takes place, and after that, the increase of LEC with temperature becomes again normal.



**Figure 9** Effect of the chain extension and crystallinity of PBT samples on the linear expansion coefficient.

Figure 8 shows the variation of LEC with temperature of the chain-extended PET samples. The increase of the LEC for the first four samples, i.e., for the blank and those received after chain extension for 10, 20, or 30 min, is normal without very much difference. On the contrary, the sample received after 60 min showed a very different behavior. The increase of the LEC was greater in the region 80–100°C and after that remained about constant. This behavior must be attributed to the great extent of crosslinking that took place during chain extension and, consequently, to the smaller degree of crystallinity.<sup>11</sup> To prove that amorphous samples show a greater LEC than do crystalline ones, four amorphous and their corresponding crystalline PBT samples were subjected to thermal expansion measurements (Fig. 9).

The amorphous samples showed a much greater LEC than did the crystalline ones. It is remarkable that the linear expansion coefficient curves of the amorphous samples have a great slope in the region of 30–60°C (high increasing rate of the LEC). This slope tends to zero around 75°C and then becomes negative (100–200°C). This can be explained by the crystallization of the samples that occurred during the measurement heating that was accompanied by shrinkage. It is interesting to note that the sample received after 60 min of chain extension, being the most amorphous, did not show the highest values of the LEC, as in the case of PET. Its curve was placed between that of the blank sample and that of the one received after 20 min of chain extension.

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