

## CALORIMETRIC STUDY OF DIEPOXIDE CHAIN-EXTENDED POLY(ETHYLENE TEREPHTHALATE)

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### Abstract

A series of chain-extended PET samples were obtained by the use of different amounts of a diepoxide as chain extender, which was prepared for this purpose. These samples exhibited different intrinsic viscosities and degrees of branching or cross-linking. The effects of this differentiation on the thermal properties were studied by differential scanning calorimetry. The thermal parameters studied were the glass transition temperature ( $T_g$ ), the cold-crystallization temperature ( $T_{cc}$ ), the melting temperature ( $T_m$ ), the enthalpy ( $\Delta H_m$ ) and the degree of crystallinity. The data revealed that, the higher the quantity of chain extender or the chain extension time, the higher  $T_g$  and  $T_{cc}$ , but the lower  $T_m$  and  $\Delta H_m$ , i.e. the more amorphous the chain-extended samples, as also shown by density measurements.

**Keywords:** branching, chain extension, cross-linking, diepoxides or bis-epoxides, DSC, PET, poly(ethylene terephthalate)

### Introduction

Poly(ethylene terephthalate) (PET) has become a very important commercial plastic with satisfactory thermal stability. This plastic is one of the major synthetic fibers (Dacron, Terylene, etc.), but is also used in the manufacture of soft-drink bottles, photographic films, audio and video recording tapes, films for food packaging, and even thermostable electrical insulating material for capacitors.

A relatively high molecular weight and a low carboxyl content provide the polymer with improved mechanical and chemical properties, such as toughness and hydrolytic stability. However, these are rarely achieved to the optimum extent, since further heating during the preparation of the polyester by the melt polycondensation process (at 280–290°C) causes undesirable degradation reac-

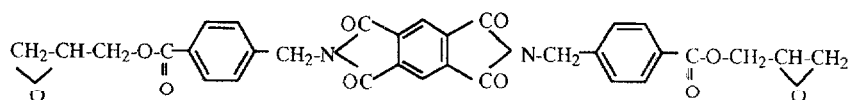
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tions with a significant increase in carboxyl end-groups. In this case, the use of chain extenders seems very attractive. When bifunctional compounds are reacted with low molecular weight polyesters coming, for example, from recycling operations, they form bridges between two oligoester chains, increasing the molecular weight significantly. This coupling of macromolecules can take place during the last stage of production of the polymer or even in the extruder.

Compounds that can be used as chain extenders are bifunctional, easily preparable, thermally stable, non-volatile at the temperature of polymer melting, and capable of fast reaction with polymer chain ends in a nearly irreversibly manner to yield non-volatile products; it is desirable for such reactions to be of addition or ring-opening type. One of the main types of chain extenders proposed are the bis-epoxides or diepoxides [1].

Chain extension of the polyesters with diepoxides leads to the formation of secondary hydroxyl groups, which are capable of creating branching or cross-linking, depending on the reaction conditions [1–4].

In previous work [2, 3], in an effort to produce effective chain extenders for polyesters, we obtained one series of PET samples chain-extended by the diepoxide:



These samples were differentiated from each other primarily because of the duration of their stay in the reactor with diepoxide (5, 10, 15, 20, 30 or 60 min), but three different amounts of chain extender (half, theoretical or double) were also used.

Accordingly, we could study the effects of molecular weight and branching or cross-linking on the thermal properties of PET by using differential scanning calorimetry (DSC). Supplementary density measurements were made for a better evaluation of the degree of crystallinity.

## Experimental

### *Sample preparation by chain-extension reaction*

To a 250 mL three-necked, round-bottomed flask equipped with a mechanical stainless-steel stirrer and an argon inlet and outlet tube, 30 g of well-dried PET chips was added. Under a flow of argon and stirring (60 rpm), the chain extender I was added and the flask was placed in a salt ( $\text{NaNO}_2/\text{KNO}_3$ , 40:60, w/w) bath heated at  $280 \pm 1^\circ\text{C}$ . After complete melting of the chips, the stirring speed was increased to 200 rpm and samples of approximately 5 g were taken from the flask during temporary increase of the argon flow rate. The sample, taken out

with a spoon-shaped spatula, was cooled in a desiccator at room temperature. Sampling was performed 5, 10, 15, 20, 30 and 60 min after complete melting.

### Measurements

All thermal parameters were determined on a Perkin-Elmer DSC-2 instrument. The temperature scale of the calorimeter was calibrated with indium ( $T_m=156.60^\circ\text{C}$ ,  $\Delta H_m=28.46\text{ J g}^{-1}$ ) and lead ( $T_m=327.47^\circ\text{C}$ ,  $\Delta H_m=23.03\text{ J g}^{-1}$ ) for the scanning rate under investigation and for the heat flow. The purge gas was nitrogen ( $1.5\text{ L h}^{-1}$ ), the sample mass was about 8 mg, the scanning rate was  $10^\circ\text{C min}^{-1}$  for both heating and cooling and the sensitivity range was  $5\text{ mcal s}^{-1}$ . The DSC peak areas were determined five times with a planimeter (Allbrit).

Density measurements were made in a Quantachrome multipycnometer at room temperature. This instrument determines the true density of a solid or powdered polymer by measuring the pressure difference when a known quantity of helium under pressure is allowed to flow from a precisely known reference volume into a sample cell containing the solid or powdered material. Each reported density value is the average of at least two measurements on different samples with the same thermal history.

The degree of crystallinity was determined as

$$X = \Delta H_m / \Delta H_f$$

where  $\Delta H_m$  is the measured heat of fusion of the semicrystalline PET sample and  $\Delta H_f$  is the heat of fusion of fully crystalline PET, which was estimated as  $166\text{ J g}^{-1}$  [5]. The degree of crystallinity was also determined as

$$X = (d - d_a) / (d_c - d_a)$$

where  $d$  is the actual measured density of the sample in  $\text{g cm}^{-3}$ , and  $d_a$  and  $d_c$  are the densities of the perfectly amorphous and crystalline phases, which have been reported to be  $1.338$  and  $1.490\text{ g cm}^{-3}$ , respectively.

## Results and discussion

In previous work [3], the synthesized diepoxide I was reacted with a PET sample ( $[\eta]=0.60\text{ dL g}^{-1}$ ) for different reaction times (5, 10, 15, 20, 30 or 60 min). Through the use of three different amounts (half, theoretical and double) of the chain extender, four sets (including the blank) of differentiated PET samples were obtained. The theoretical amount was taken as the quantity of chain extender needed for 1 mol of chain extender to react with 2 mol of polyester, assuming that only the carboxyl end-groups react in this process [3].

While the heating of a thoroughly predried PET melt is accompanied by a decrease in intrinsic viscosity, an opposite effect was observed in the presence of

the diepoxide. In general, the higher the reaction time or the amount of chain extender, the higher the intrinsic viscosity, but when double the theoretical amount was added, a decrease in viscosity was observed after a reaction time of 30 min (Table 1).

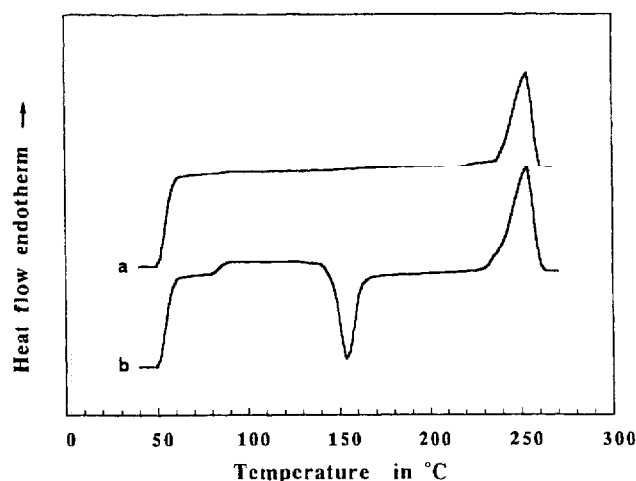
**Table 1** Intrinsic viscosity of the chain-extended PET samples

Time <sup>a</sup> / min	[ $\eta$ ]/dL g <sup>-1</sup>			
	Control (blank)	Half amount	Theoretical amount	Double amount
0	0.60	0.60	0.60	0.60
5	0.55	0.71	0.73	0.76
10	0.54	0.77	0.79	0.86
15	0.54	0.82	0.85	0.95
20	0.54	0.87	0.94	1.07
30	0.55	0.96	0.95	1.16
60	0.58	1.08	0.96	0.94

<sup>a</sup>Duration of chain extension

This is most probably due to the concurrent formation of branching through the reaction of pendant hydroxyl groups of the macromolecules with the excess of diepoxide. On the other hand, insoluble matter [3] was detected for the most chain-extended samples (after 60 min of chain extension and a double amount of chain extender) by means of viscometry; this was attributed to cross-linking.

The variation in the carboxyl or hydroxyl content with the reaction time for the samples studied was reported earlier [3].



**Fig. 1** Typical DSC TG of a semicrystalline (trace *a*) and an amorphous (trace *b*) PET sample

Figure 1 depicts a TG of a PET sample as received from the reaction vessel (trace *a*). In this trace, only an endotherm can be seen (melting) without a glass transition and cold crystallization. Thus, the as-received samples are crystalline. After melting, the sample is quenched at  $-70^{\circ}\text{C}$  and a second heating trace is obtained (trace *b*). This trace is typical of an amorphous or semicrystalline PET sample.

### Glass transition temperatures

All samples after quenching display a glass transition at around  $81.5^{\circ}\text{C}$  (blank, or control) or higher for the chain-extended samples (Fig. 2).

Wiesener [7] stated that the glass transition temperature depends on the molecular weight, but Rao and Dweltz [8] found that this parameter is much less affected by the weight-average molecular weight, which ranged from 29,000 to 46,800.

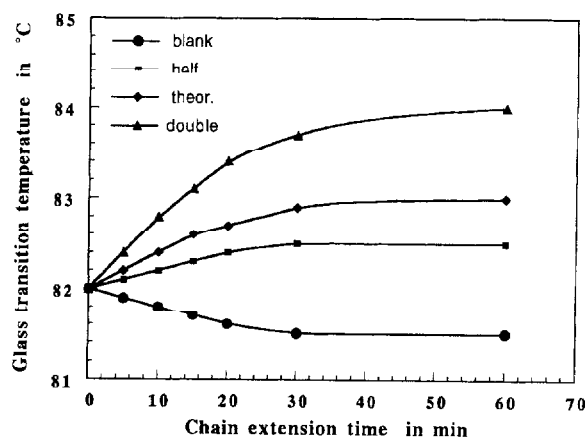


Fig. 2 Variation in  $T_g$  of PET samples with the duration of the chain extension reaction and the quantity of the chain extender

The higher  $T_g$ s in this work are most probably due more to the branching and mainly to the cross-linking than to the higher molecular weight.

### Cold-crystallization temperatures

From the  $T_{cc}$  maxima of heating traces of fully amorphous samples (second heating after quenching), it can be seen that the cold-crystallization temperature changes. In general, the crystallization during dynamic heating begins at around  $120^{\circ}\text{C}$  and finishes at around  $160^{\circ}\text{C}$ , with a maximum at  $\approx 145^{\circ}\text{C}$  (Fig. 3)

For the control samples, the cold crystallization peak temperature decreases with reaction time; this means that heat treatment without the chain extender reduces the molecular weight of the macromolecules and consequently facilitates

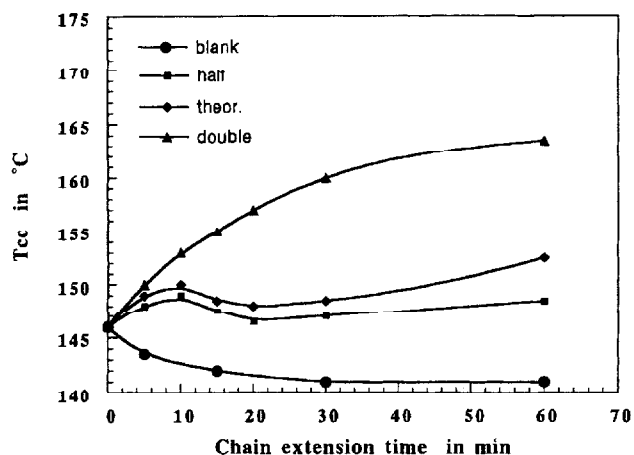


Fig. 3 Effects of the duration of chain extension and the quantity of the chain extender on the cold-crystallization temperatures of PET samples

crystallization during heating. For the chain-extended samples (half and theoretical amount of chain extender), a small trend of 3–5°C to higher  $T_{cc}$ s was observed, while for the most chain-extended sample (double amount)  $T_{cc}$  increased more strongly (15–20°C). This means that these samples require higher temperatures for cold crystallization because of the presence of partially cross-linked macromolecules or even because of the increased entanglement of the macromolecules [8]. For the same reason, the melts of these samples crystallize at temperatures 40–50°C lower (170–180°C) when they are cooled. This is in contrast with the control samples, which crystallize at around 220°C at a cooling rate of 2.5°C min<sup>-1</sup>.

### Melting temperatures

Figure 4 reveals that the  $T_m$  of the PET blank sample is 255°C. This  $T_m$  remains stable after heat treatment without the chain extender, even after 60 min (blank). For the chain-extended samples, the melting point undergoes a gradual decrease and assumes a lower value after 60 min in each series (Fig. 4).

This effect is in good agreement with the results of Rao *et al.* [8], who concluded that the low-molecular-weight polymers possess higher crystallinity and higher crystallite perfection than those of high-molecular-weight polymers.

A close dependence of the melting points on the degree of crystallinity is demonstrated when the same samples are run after quenching; in this case, all melting points are 3–5°C lower, and it is also known that the equilibrium melting point of the hypothetical fully crystallized PET sample is much higher: 280°C [10, 11], 282±2°C [5], 285°C [12] or 290°C [13].

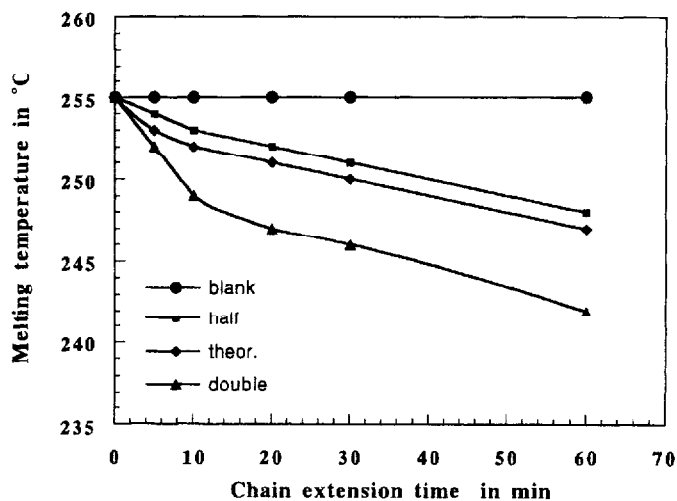


Fig. 4 Effects of the chain extension time and the quantity of the chain extender on the melting temperatures of PET samples

### Heats of fusion

The heats of fusion were calculated from the DSC curves of semicrystalline PET samples (Fig. 1). The heats of fusion of the control samples were 44–45 J g<sup>-1</sup>. This means that all the control samples have the same degree of crystallinity. In contrast, the chain-extended samples afforded lower heats ( $\approx 40$  J g<sup>-1</sup>) and those for the most chain-extended (cross-linked) samples were even lower ( $\approx 33$  J g<sup>-1</sup>).

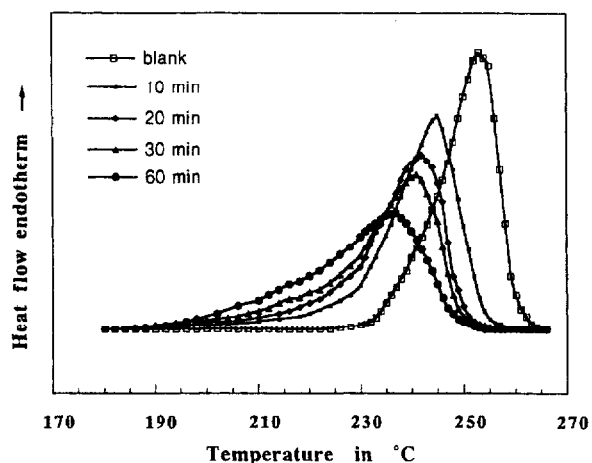


Fig. 5 Superimposed melting endotherms of chain-extended PET samples with a double quantity of the chain extender

It is interesting to examine the melting endotherms of four chain-extended samples, including the control one with the double quantity of chain extender (Fig. 5).

These endotherms allow the important observation that both the onset and peak temperature of melting shift to lower values with increasing molecular weight [8, 14], branching [9] or cross-linking.

### Degree of crystallinity

The effect of chain extension on the crystallinity was studied on the as-received semicrystalline samples.

Figure 6 illustrates the variation in the degree of crystallinity with the quantity of chain extender used and the reaction time. This crystallinity was determined via the heat of fusion found previously, or via density measurements. For this determination, the heat of fusion of fully crystalline PET was taken as  $166 \text{ J g}^{-1}$  [5]. Table 2 lists some of the density values reported so far in the literature for fully amorphous and crystalline PET.

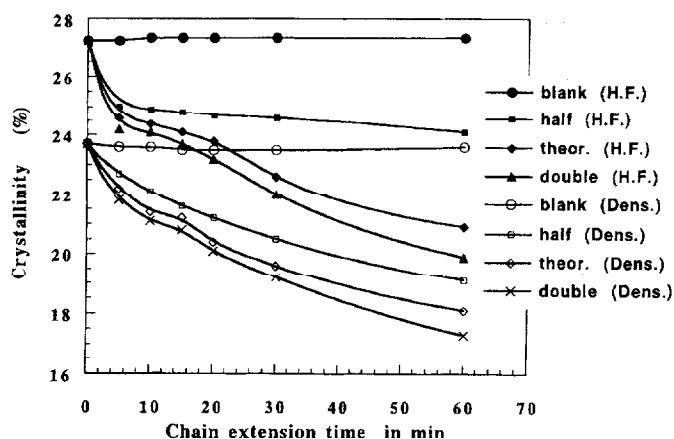


Fig. 6 Effects of the duration of chain extension and the quantity of the chain extender on the crystallinity determined via heat of fusion (H. F.) or density (Dens.) measurements

Table 2 Densities of fully amorphous ( $d_a$ ) and perfectly crystalline ( $d_c$ ) poly(ethylene terephthalate)

$d_a$	$d_c$	Literature sources
g cm <sup>3</sup>		
1.335	1.455	[15]
1.338	1.490	[6]
—	1.495	[16]
—	1.501	[17]
—	1.515	[10]



From these data, we selected the values found by Gehrke and Zachmann [6], because the crystallinity estimated in this work is closer to that determined from the thermal data.

In all cases, the crystallinity determined via the heat of fusion is higher than that found via the density, although the highest value ( $166 \text{ J g}^{-1}$ ) found in the literature [6, 10, 15–17] was used.

As a result, it may be stated that after the chain-extension reaction the extent of crystallization is reduced significantly. The latter observation is consistent with the main effect of chain-extension, i.e. increased molecular weight, branching or cross-linking decreases the ability for crystallization.

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