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# Effects of Cold Drawing and Annealing on the ADSC Response and Microhardness of Amorphous and Crystalline Poly(ethylene naphthalate)\*

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The tensile loading – induced necking in notched specimens of amorphous poly(ethylene naphthalate) (PEN) was studied by conventional (DSC) and alternating differential scanning calorimetry (ADSC) and microhardness measurements. It was shown that in this PEN, similarly to amorphous copolyesters, necking occurred *via* cold drawing and not *via* true plastic deformation. The variation of the microhardness along the height and width of the necked region of the specimen reflects the specific orientation of the material during tensile loading. It was observed that the tensile loading provokes a drastic (jump-like) orientation of the macromolecules in draw direction, which even increases in the vicinity of the tip of the necked zone.

**Keywords:** Poly(ethylene naphthalate) (PEN); Cold crystallization; Cold drawing; Necking; Alternating differential scanning calorimetry (ADSC); Microhardness

## 1. INTRODUCTION

In the last few years the tensile loading induced necking in notched specimens of amorphous copolyesters was intensively studied [1–6].

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Characteristic feature of these studies was that the necked area of the specimens was produced by cold drawing and not by plastic deformation. The onset of cold drawing was substantiated by shape recovery of the necked region when heated above the glass transition temperature,  $T_g$  [2, 4, 6]. Recently [5] this statement was proved also by means of modulated differential scanning calorimetry (MDSC). It was shown that necking occurred by cold drawing since the enthalpy of cold crystallization and that of the subsequent melting agreed fairly well with each other. Further, it was found that the cold crystallization capability of the amorphous copolyesters studied depends also on the local deformation and deformation rate [5]. Note that the studied copolyesters contained apart from ethyleneglycol and terephthalic acid various amount of cyclohexyldimethylene glycol.

It was interesting to extend the study of this effect to other amorphous polymers. For the present study poly(ethylene naphthalate) (PEN) was chosen as one of the most interesting advanced thermoplastic polyesters with promising technical applications. In addition, the aim of this work was the detailed study of the local deformation along the height and width of the necked region of specimens used to determine the post-yield fracture mechanical response [6].

## 2. EXPERIMENTAL

### 2.1. Material

Amorphous PEN sheet was supplied by the Eastman Chemical Company, Kingsport, TN, USA. Its inherent viscosity (IV) was 0.963 dl/g, determined at 25°C using a solution containing 0.5 g of polymer per 100 ml of a 60/40 pentafluorophenol/trichlorobenzene mixture.

### 2.2. Specimens

Deeply double-edge notched (DDEN-T) specimens were prepared from the 0.5 mm thick PEN sheets and subjected to tensile loading. Loading of the DDEN-T specimens occurred at room temperature

using a crosshead speed of 1 mm/min. The broken half of such a DDEN-T specimen is displayed in Figure 1 (top). The necked region developed during loading is indicated by arrow. Note that this necked area is the subject of this study. Determination of the plane stress fracture mechanical parameters, for which the DDEN-T specimens were used, is not reported here. The interested reader is addressed to Ref. [7] in this respect.

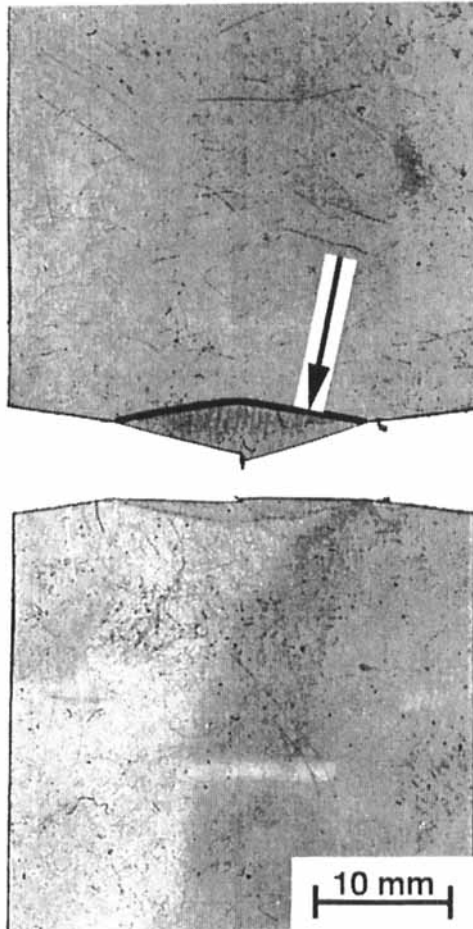


FIGURE 1 DDEN-T specimen after fracture: Necked region developed during tensile loading (top); Restored shape after annealing (bottom).

## 2.3. Testing

### 2.3.1. DSC and ADSC

The thermal response was studied on samples taken from the top of the necked region of the DDEN-T specimens and from the bulk (unstressed) material, respectively. DSC traces were registered by a Mettler Toledo device DSC 821 between room temperature and 300°C at heating rate of 10°C/min.

Alternating DSC (ADSC) is a new extension to conventional DSC which provides information about the reversing and non-reversing characteristics of thermal events. For ADSC the same DSC device was used with a sinusoidal modulation overlaid on the standard temperature ramp. A “heat only” mode with a heating rate of 1°C/min, modulation amplitude of 0.159°C/min and a period of 60 s was chosen. The Fourier transformation of the modulated heat flow was performed by the related software package STAR<sup>®</sup> V6.0 of Mettler Toledo.

### 2.3.2. Microhardness

For microhardness measurements a Shimadzu ultramicrohardness tester DUH-202 was used with continuous load-displacement monitoring when the indenter is driven into and out from the surface of the sample. The measurements were performed at room temperature with a Vickers indenter – a square-based diamond pyramid. A load range of 150 mN, a loading and unloading speed of 6.4 mN/s and a holding time of 6 s after completing the indentation were set. Two values were obtained from each measurement – (i) the universal (or dynamic) microhardness HU and (ii) the Vickers microhardness HV.

The universal microhardness HU [MPa] was calculated on the basis of the indenter penetration depth  $h$  (mm) under the applied test force  $P$  [N] using the formula:

$$HU = P/26.43 h^2[\text{MPa}] \quad (1)$$

Accordingly, HU represents the strength characteristics of the material, including both plastic and elastic deformation of the test piece.

After removal of the test load the Vickers microhardness HV [MPa], which is an indicator only of the irreversible plastic deformation of the material, was derived from the residual projected area of the indentation, according to the equation:

$$HV = 1.854 P/d^2 [\text{MPa}] \quad (2)$$

where  $P$  [N] is the maximal load applied and  $d$  [mm] is the length of the impression diagonal.

For oriented materials an anisotropic shape of the indentation appears [8, 9], due to the greater instant elastic recovery in the draw direction after removal of the test load. The indentation anisotropy  $\Delta HV$  in % was calculated using the expression:

$$\Delta HV = 1 - (d_{\parallel}/d_{\perp})^2 \quad (3)$$

where  $d_{\parallel}$  and  $d_{\perp}$  are the impression diagonals parallel and perpendicular to the draw axis respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Orientation

##### 3.1.1. DSC and ADSC

Figure 2 shows the DSC traces taken from the necked region and bulk of a DDEN-T specimen, respectively. The enthalpy of the exothermic cold crystallization agrees well with that of the subsequent melting in both cases. This hints at the amorphous structure of the studied PEN. As seen, the cold crystallization peak appears at about 36°C earlier in the necked region and the corresponding enthalpy is about three times greater than in the bulk region. This fact is explained by the orientation of the polymer macromolecules as result of the tensile loading. The latter facilitates the crystallization during heating.

The ADSC traces of the bulk and necked region, (Figs. 3 and 4 respectively), give more information about the crystallization behaviour. Similar to the case of amorphous copolyesters [5], one may conclude that in PEN the cold crystallization is fully non-reversible.

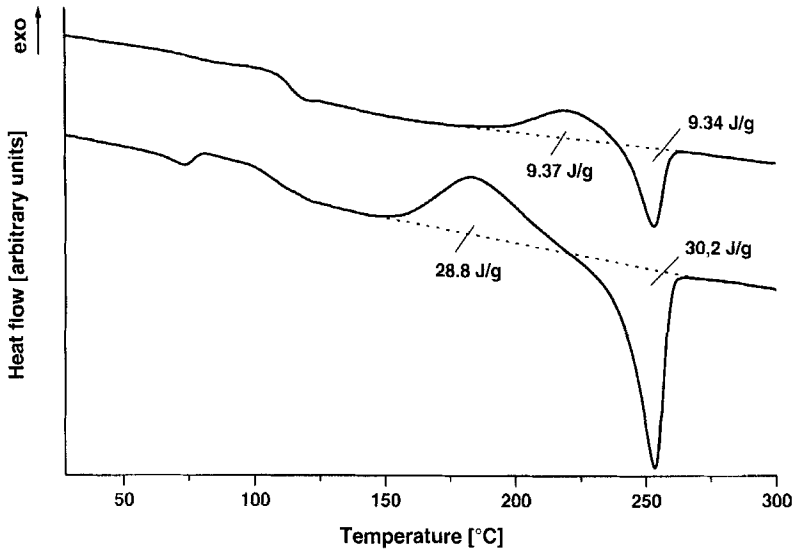


FIGURE 2 DSC traces of the necked region (lower) and bulk (upper) of the DDEN-T specimen.

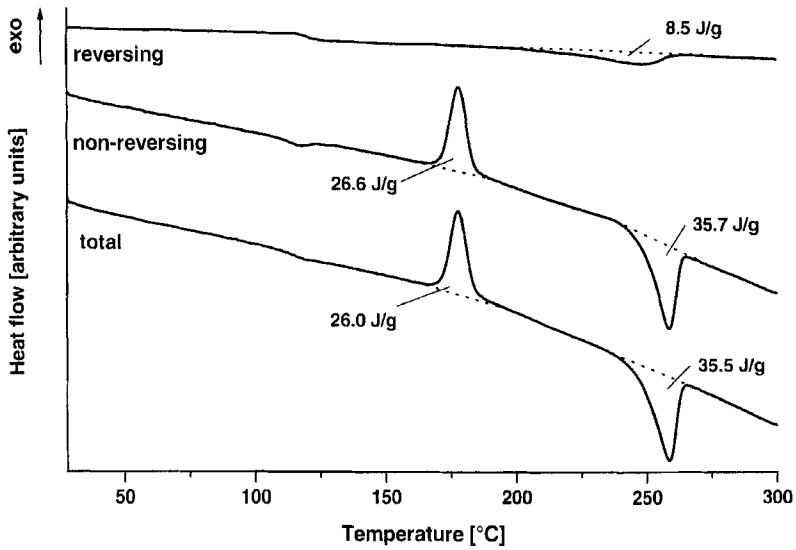


FIGURE 3 ADSC traces of the bulk PEN.

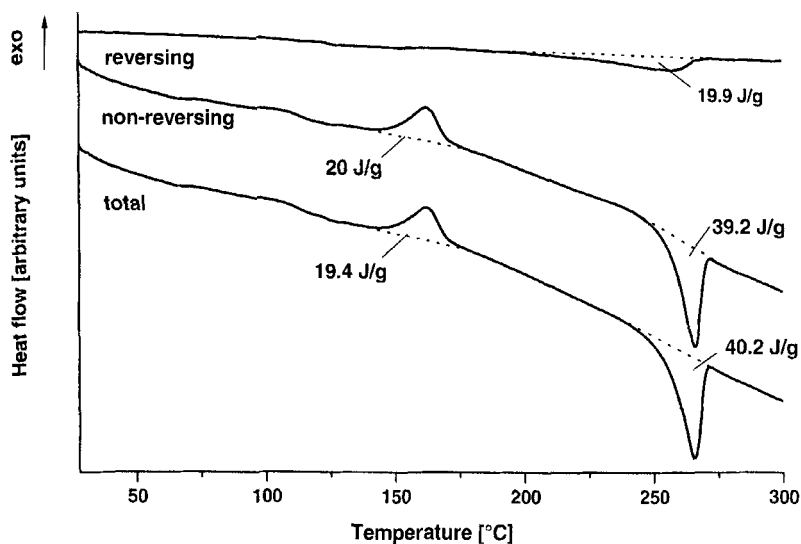


FIGURE 4 ADSC traces of the necked region of amorphous PEN.

The melting, on the other hand, contains both reversible and non-reversible parts. Note that the enthalpy of the cold crystallization (non-reversible) agrees fairly well with that of the melting (non-reversible) if the reversible melting contribution is deduced from it. This claim holds for both the necked and bulk samples (*cf.* Figs. 3 and 4). The specific enthalpy of reversible melting is strongly increased by the orientation. Wide angle X-ray scattering measurements evidenced that no cold crystallization took place in the necked region owing to mechanical loading. Therefore the appearance of the reversible melting cannot be ascribed to the presence of initial (*i.e.*, mechanical loading – induced) microcrystallinity. Thus, the onset of reversible melting likely demonstrates a crystalline perfection process. Needless to say that the latter is strongly favored by the mechanical loading – induced orientation. Unfortunately, the authors are not aware of the mechanism of this crystalline perfection.

### 3.1.2. Microhardness

In order to study the local deformation, microhardness measurements were performed (i) with step of 0.5 mm along the height AB in the



middle of the necked region and (ii) with step of 1 mm in  $x$  direction along a line CD perpendicular to the height, as schematically shown in Figure 5.

The height  $h$  of the necked zone was approximately 3.5 mm. Figure 6 depicts the variation of the universal hardness  $HU$ , calculated

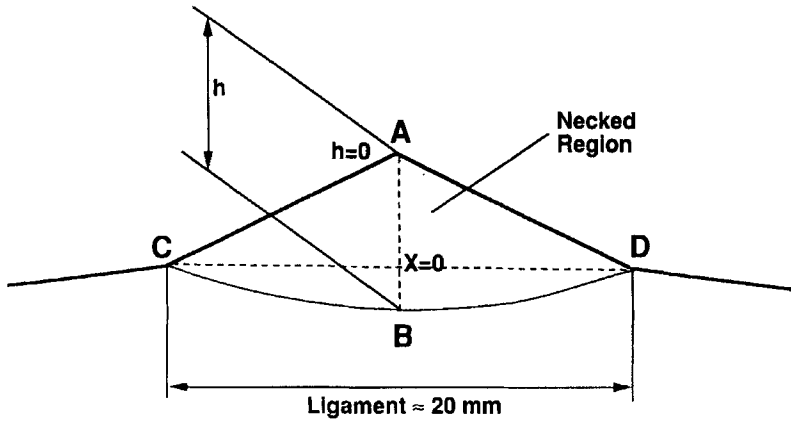


FIGURE 5 Schematic of the microhardness mapping within the necked region.

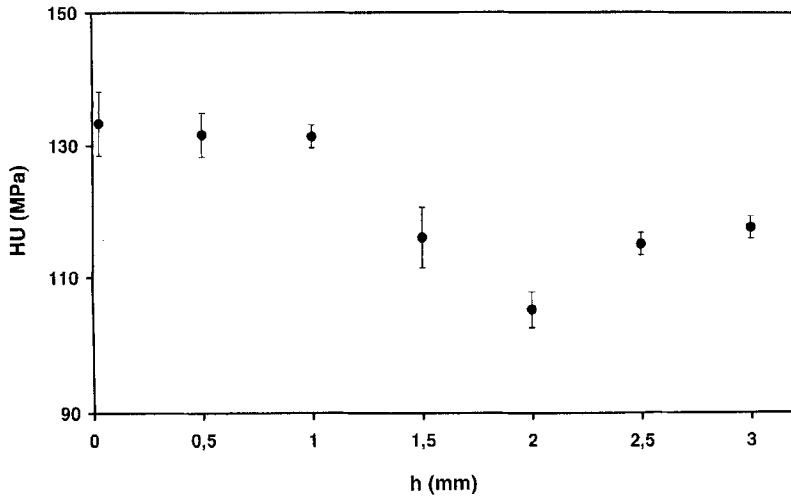


FIGURE 6 Variation of the universal hardness  $HU$  along the height  $h$  of the necked zone (line AB).

according to formula (1), over the height  $h$  from the top point A ( $h=0$  in Fig. 5) toward the bulk.

The universal hardness  $HU$  presents an interesting variation: near the centre of the necked zone  $HU$  decreases up to 12 MPa (*i.e.*, about 10%) respective to the value in its bottom part (point B). Towards the tip (point A) this drop is recovered and an increase of  $HU$  with other 10 MPa is observed.

This  $HU$  decrease is better expressed in Figure 7, where the variation of  $HU$  in "x" direction is presented. The hardness decreases nearly continuously from the right and left ends of the sample towards the centre ( $x=0$ ). A symmetry in the  $HU$  values around the y-axis (the height of the sample) is also observed.

The above results lead to the conclusion that in the middle of the necked zone a "softer" region (with larger compliance) was built. This fact is probably due to the peculiarities in the material orientation during the fracture of the DDEN-T specimen. As stated in a previous study [7] the tensile stress causes a stretching of the initial entanglement network in the amorphous sample and aligns the macromolecules in the loading direction. Obviously the stretching generates an orientation anisotropy in the DDEN-T specimen during

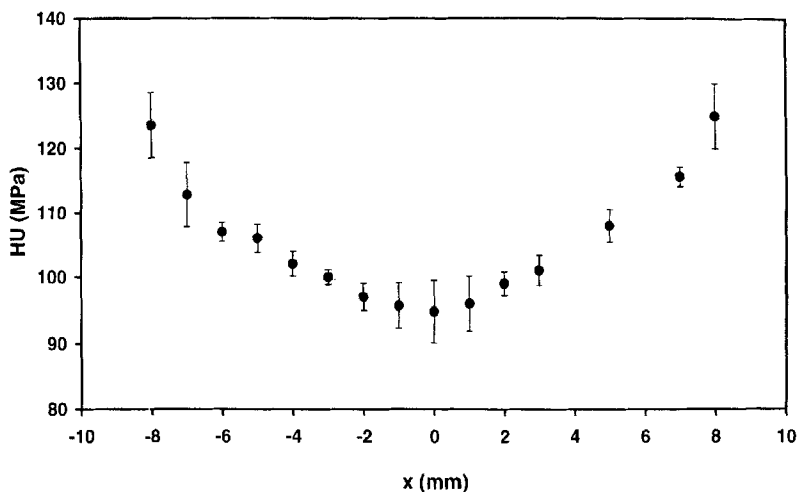


FIGURE 7 Variation of the universal hardness  $HU$  along the width  $x$  of the necked zone (line CD).

loading. The network stretching in the CA and DA directions is considerably higher than along the BA line (*cf.* Fig. 5). Thus, the apparent network mesh is tighter at the edges of the necked area than in its mid plane (*i.e.*, BA line). This affects the resistance to the penetration of the indenter during the microhardness measurement and consequently the  $HU$  values, too.

Near the tip and along the edges of the necked area the orientation and the apparent density of the stretched network increase, which is reflected by an increase of  $HU$  in this region (Figs. 6 and 7). This statement is supported also by the results presented in Figure 8. As mentioned above, in oriented materials an anisotropic shape of the microhardness indentation appears. This anisotropy, calculated according to Eq. (3), can be related to the degree of orientation of the macromolecules. According to Figure 8 the anisotropy does not show a gradual increase, but a jump from 0 (unstressed bulk material) to a nearly constant value of about 16% in the necked zone. This observation indicates that during the tensile loading a severe stretching of the amorphous network of the DDEN-T specimens took place. In the region next to the tip the anisotropy increases up to 21% as a result of the greater orientation there. In "x" – direction (along the line CD – see Fig. 5) no substantial variations in the Vickers hardness anisotropy were detected.

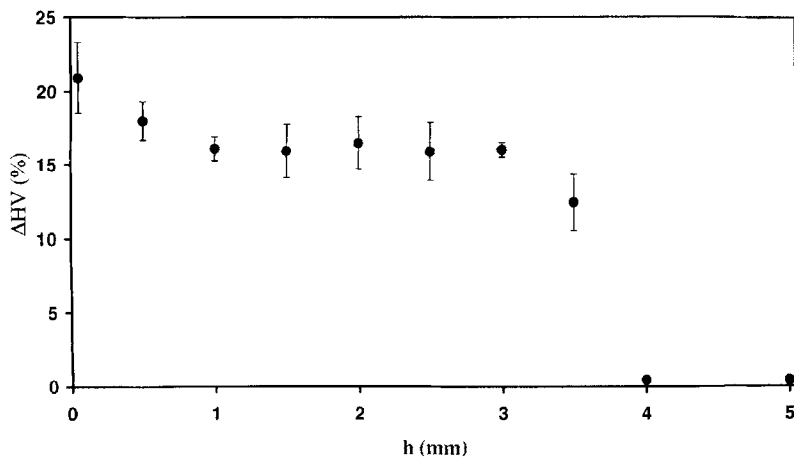


FIGURE 8 Anisotropy of the Vickers hardness  $\Delta HV$  along the height  $h$  of the necked zone (line AB).

### 3.2. Effect of Annealing

It was shown earlier that after keeping the broken DDEN-T specimens for a few minutes just above the glass transition temperature of PEN, the plastic zone disappeared and the original shape of the DDEN-T specimen half was restored (as shown in Fig. 1 on the bottom picture) [7]. This fact supported the statement that the deformation of the glassy PEN had occurred *via* cold drawing and not by true plastic deformation. The presence of a stretched entanglement network guarantees the shape recovery observed.

It was interesting to check this statement also by microhardness measurements. In fact, mapping of the recovered zone in “x” and “y” directions with a step of 0.5 mm yields constant values for  $HU = 150 \pm 4$  MPa and  $HV = 181 \pm 3$  MPa, which are in best agreement with those measured in the bulk. Consequently, a recovery of the microhardness is observed. This would not be possible if the initial entanglement network structure was disrupted (except the fracture zone) and not merely stretched during the tensile loading. As a conclusion, the microhardness results are also in favour of the above-presented explanation *via* cold drawing.

The amorphous PEN sample was crystallized by annealing at 180°C for 30 minutes. The DSC traces of the crystalline sample (Fig. 9) show the usually observed dual melting behaviour induced by annealing of glassy PEN [10,11]. The position of the mean melting peak at 256°C in Figure 9 almost coincides with that of the melting peak after cold crystallization (see Fig. 2). The degree of crystallinity  $w_c = 36.7\%$  was estimated using for the ideal (*i.e.*, 100% crystalline PEN) melting enthalpy  $\Delta H_m^0$  the value of 103.3 J/g [12].

The hardness characteristics of the crystalline sample are:  $HU = 191 \pm 3$  MPa and  $HV = 234 \pm 4$  MPa. It has been shown [13] that the Vickers hardness  $HV$  of semicrystalline polymers follows an additivity rule:

$$HV = H_c w_c + H_a (1 - w_c), \quad (4)$$

where  $H_c$  and  $H_a$  are the Vickers hardness of the fully crystalline and fully amorphous polymer respectively, and  $w_c$  is the degree of crystallinity. Using for  $H_a$  the value of 181 MPa, measured on the PEN

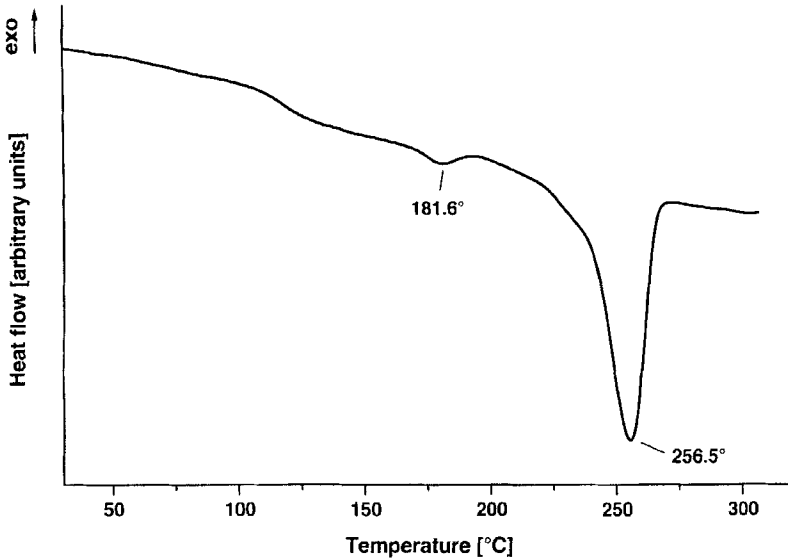


FIGURE 9 DSC trace of a crystallized DDEN-T specimen of PEN (crystallization at 180°C for 30 min).

bulk sample, we derived for the Vickers hardness of the fully crystalline PEN the value  $H_c = 325$  MPa. This value is somewhat lower than 341 MPa, reported in [14] for fully crystalline PEN. On the other hand, the measured Vickers hardness (234 MPa) is somewhat higher as that one reported for PEN samples crystallized from glass by annealing at similar conditions [15]. These small differences can be explained as arising from the differences in the intrinsic viscosities (*i.e.*, mean molecular mass) of the studied samples, which affect the crystallization [7] and the probably different perfection of the PEN crystals built during the annealing in each case. As was recently shown [16] that the microhardness is very sensitive to the perfection of the crystalline structure of the polymers.

#### 4. CONCLUSIONS

Based on this study devoted to the mechanical loading – induced anisotropy and related crystallization behavior of an amorphous

PEN of high mean molecular mass, the following conclusions may be drawn:

- (1) The DSC and ADSC study performed on the bulk and necked zones of the DDEN-T specimens of glassy PEN confirmed that its necking occurred *via* cold drawing and not *via* plastic deformation.
- (2) The microhardness technique allowed us to map the local deformation in the necked zone of the DDEN-T specimen, (travelling along its height and width, respectively).
- (3) It was observed by microhardness testing that the tensile loading provokes a drastic (jump-like) orientation of the macromolecules in the necked zone formed.

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