

# **THERMAL BEHAVIOUR OF DRAWN SEMI-CRYSTALLINE POLY(ETHYLENE TEREPHTHALATE) FILMS**

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## **Abstract**

Behaviours of drawn semi-crystalline poly(ethylene terephthalate) films are investigated by DSC, X-ray diffraction and birefringence measurements. The comparison of the different results confirms the coexistence of two structures into the amorphous part of the material: a completely disordered amorphous phase and a mesomorphic amorphous one. Moreover, for the strongest draw ratio, the calorimetric results show that the drawing effect on the strain induced crystalline structure proceeds by a better orientation of this structure rather than by nucleation and growth of new oriented crystallites.

**Keywords:** DSC, PET films, strain induced structure

## **Introduction**

Among semi-crystalline polymers, the poly(ethylene terephthalate) (PET) is a material of interest because its semi-crystalline structure could be obtained either by thermal treatment (isotropic structure) or by drawing (anisotropic structure). It is well known that thermal treatment on amorphous PET can lead to the appearance of entities known as spherulites which consist of numerous crystal lamellae radiating from a central nucleus. On the other hand in amorphous PET uniaxially drawn at temperature below  $T_g$ , a 'shish kebab' structure appears consisting in extended chain crystal core surrounded by folded chain lamellae [1]. When amorphous PET is uniaxially drawn at temperature above the glass transition temperature and below the isotropic crystallization temperature, a fibrillar morphology is obtained [1, 2] and the number of gauche isomer bonds in the non crystalline regions, associated with disordered chains, decreases with draw ratio [3, 4]. The morphology of oriented semi-crystalline PET is too complicated to allow definitive conclusions regarding this critical aspect of the structure. However various works [4-9] suppose the existence of two

amorphous phases in drawn PET fibers and films: a completely disordered phase and a mesomorphic phase with a nematic order (phase characterized by the trans conformation of all the polymeric units).

The aim of this paper is to study the existence of these amorphous phases in homogeneous hot drawn PET by a calorimetric method.

## Experimental

For this study, chill rolled PET films from Eastmann Kodak (7352) of 0.63 mm thickness are used. The films have a number-average molecular weight of 46 000 and a number-average molecular number of 23 000. They are almost isotropic (the birefringence is less than  $10^{-3}$ ) and amorphous (the absence of initial crystallinity is confirmed by density and wide angle X-ray scattering measurements). After an isothermal annealing (15 min) at  $100^{\circ}\text{C}$ , initial rectangular samples are drawn at a strain rate of  $0.14\text{ s}^{-1}$  by means of an Instron tensile machine equipped with a heating chamber. The draw ratio  $\lambda$  is the ratio of the extended length on the original length determined from displacement of ink marks, it varies from 1 to 7. The drawing temperature, included between the glass transition temperature and the crystallization temperature (cf. Fig. 2,  $\lambda = 1$ ), allows homogeneous drawn and no thermal crystallized samples to be obtained. Then, the material is cold air quenched down to room temperature in order to freeze in its structural state. Finally the different samples are punched into the drawn film.

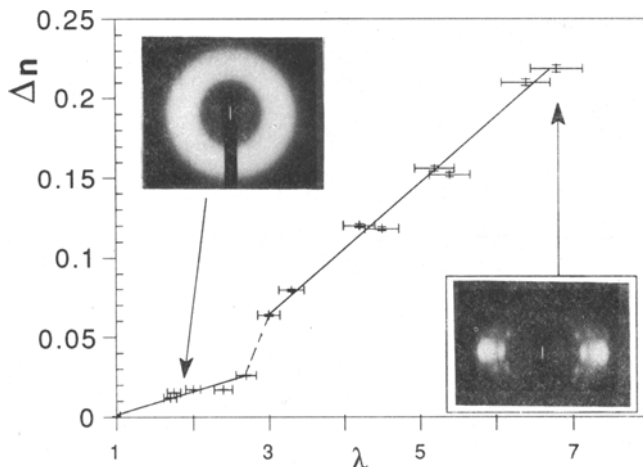
Birefringence and X-ray diffraction measurements are performed at the room temperature on these drawn samples. The birefringence ( $\Delta n$ ) is measured using the spectrophotometric method, and X-ray diffraction measurements (Debye Scherrer) is carried out in a classical wide angle scattering (WAXS) set up using a  $\text{CuK}\alpha_1$  radiation (0.154 nm). Enthalpic analysis are performed at  $10\text{ deg}\cdot\text{min}^{-1}$  between room temperature and melt temperature (Perkin Elmer DSC7).

## Results and discussion

### *a) Birefringence and X-ray analysis*

The discontinuity and the change on the slope observed on the  $\Delta n$  variations for  $\lambda = \lambda_c = 2.8$  show that a strain-induced crystallization occurs [1, 2] (Fig. 1); indeed for  $\lambda < \lambda_c$  the values of  $\Delta n$  are characteristic of a weakly oriented and amorphous polymer while for  $\lambda > \lambda_c$  the increase in  $\Delta n$  indicates a gradual increase of the anisotropy of the samples. In the same way, for  $\lambda < \lambda_c$  X-ray diffraction patterns are characteristic of an amorphous state of the material while

for  $\lambda > \lambda_c$  they show: i) the existence of an anisotropic crystalline structure and ii) the enlargement of the orientation of this structure in the drawing direction; the preferential orientation of the crystal  $c$ -axis is in the draw direction [8].



**Fig. 1** Variations of the birefringence vs. draw ratio. X-ray diffraction patterns show: i) amorphous state (upper left corner), ii) strain induced crystallized state (lower right corner)

### b) Differential scanning calorimetry analysis

The thermal behaviour of the drawn samples depends greatly on the draw ratio (Fig. 2). During the heating, the DSC curves show for  $\lambda < \lambda_c$  i) the shift of the thermal crystallization peak to the glass transition region ii) the decrease of the crystallization enthalpy. The drawing have clearly modify the thermic crystallization of these amorphous samples. For  $\lambda > 5$  i) the thermal crystallization disappears, ii) the glass transition temperature shifts towards the higher temperatures and iii) the glass transition region widens. These behaviours are detailed on Figs 3 to 5.

### c) Discussion

The melting temperature increases weakly with  $\lambda$  (Fig. 3) and for the highest values of  $\lambda$ , the narrowing of the shape of the melting peak indicates that the width of the crystallite size distribution decreases. The variations of the enthalpy of fusion show that the crystallinity of the samples increases with  $\lambda$ . For  $\lambda < \lambda_c$ , only the spherulitic phase melts but the global crystallinity rate of these annealed samples increase greatly with  $\lambda$ . While for  $\lambda > \lambda_c$  the stretching adds a strain-induced crystallization to the thermal one. In this region, compare to the

strong relative variations of  $\Delta n$  (80%) the variations of  $\Delta H_f$  (10%) indicates that the drawing acts on crystallization by orientation of the strain-induced crystallized phase rather than by nucleation and growth of new crystallites (this is confirmed by X-ray patterns and by the vanishing of the thermal crystallization peak in DSC measurements).

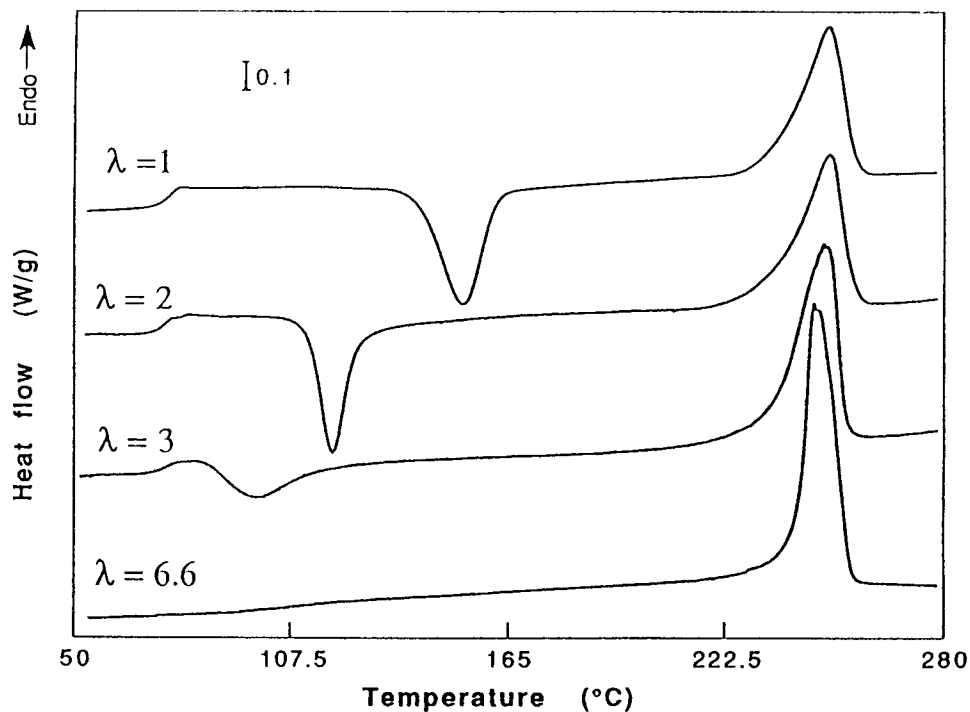


Fig. 2 DSC curves of various drawn PET samples. The diagrams are normalized to 1 g of matter and the scan rate is equal to  $10 \text{ deg}\cdot\text{min}^{-1}$ . The draw ratios are indicated on the figure

The variations of the enthalpy of crystallization (Fig. 4) show that the amount of PET which could crystallize in a spherulitic way decreases. On the other hand, the onset temperature of crystallization peak decreases. That means that the amorphous oriented phase enhances the thermal crystallization of non oriented amorphous fraction; a possible mechanism [3] could be describe as follow: at first the mesomorphic phase crystallizes and, secondly, a part of the heat given out by this exothermal effect is used in the spherulitic thermal crystallization. Simultaneously, the increase of the oriented amount leads the crystallization of the non oriented amorphous phase to vanish. The slight increase

of the  $T_c$  values for  $\lambda_c > 3$  could be explained by the overlapping of the  $T_c$  and  $T_g$  regions.

Several experimental parameters give indications of the behaviour of the amorphous part of the material: i) the onset temperature  $T_g$  (linked to the stiffness of the amorphous phase) ii) the width  $\Delta T_g$  ( $\Delta T_g = T_{gh} - T_{gl}$ , characteristic of the heterogeneity of the a-phase) of the glass transition iii) the variation

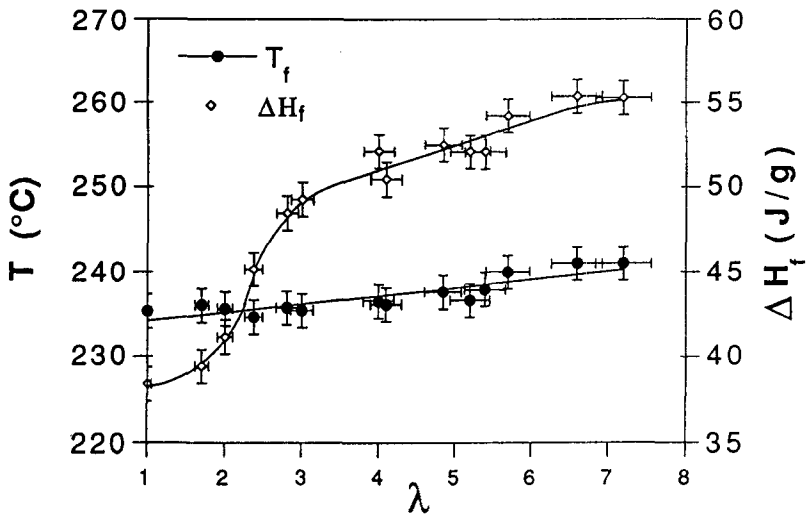


Fig. 3 Variations of the onset of the melting peak and its apparent enthalpy vs.  $\lambda$

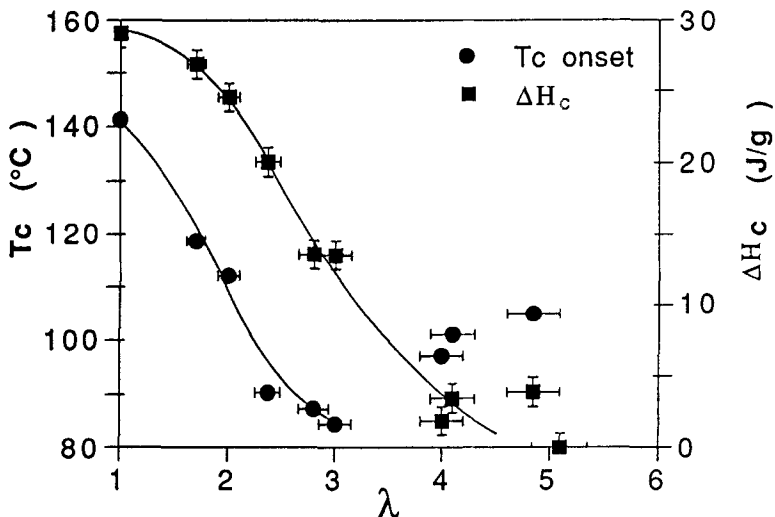


Fig. 4 Variations of the onset of the thermal crystallization peak and its apparent enthalpy vs.  $\lambda$

$\Delta C_p$  of the specific heat (during the heating the material undergoes the glass transition and  $C_p$  increases from  $C_p(T_{gl})$  to  $C_p(T_{gh})$ ).

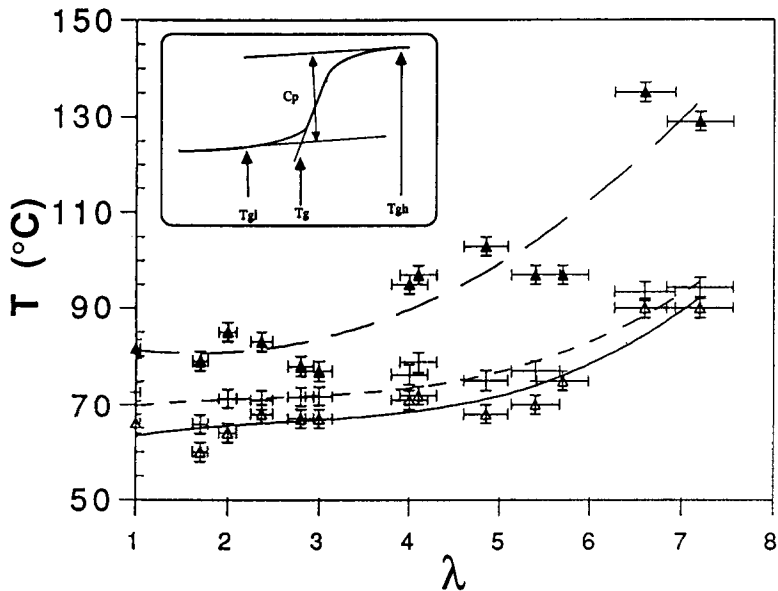


Fig. 5 Variations of the glass transition temperatures  $T_{gl}$ ,  $T_g$ ,  $T_{gh}$  defined on the figure vs.  $\lambda$   
 ( $\Delta$ ):  $T_{gl}$ ; (+):  $T_g$ ; ( $\blacktriangle$ ):  $T_{gh}$

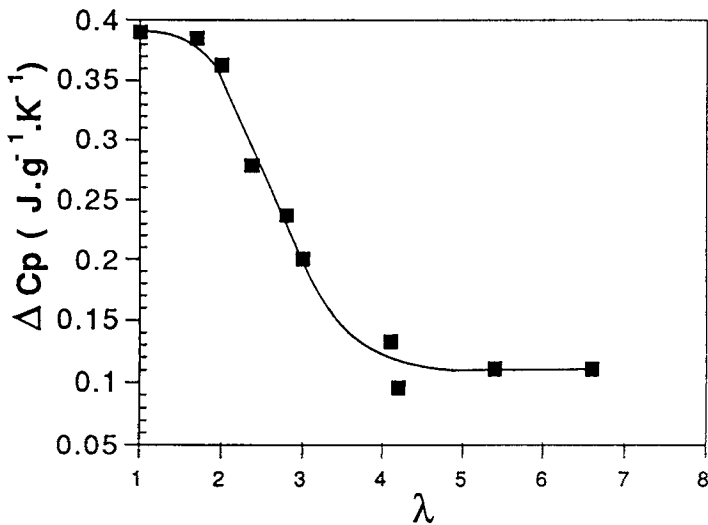


Fig. 6 Variations of  $\Delta C_p$  (increase of  $C_p$  between  $T_{gl}$  and  $T_{gh}$ ) vs.  $\lambda$

Indeed, the increase in  $T_g$  and  $\Delta T_g$  over the critical ratio  $\lambda_c$  shows the emergence of mesomorphic regions into the amorphous phase (Fig. 5). The appearance of these strongly oriented and ordered regions leads to an augmentation of the heterogeneity of the amorphous phase as well as its stiffness.  $\Delta C_p$  decreases from  $0.39 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  to  $0.11 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  when the draw ratio increases from  $\lambda = 1$  (0% of strain-induced crystallization) to  $\lambda = 6.6$  (39% of strain-induced crystallization) (Fig. 6). This variation of  $\Delta C_p$  ( $0.28 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ ) is nearly twice the difference ( $0.15 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ ) observed between an amorphous isotropic PET and a semi-crystalline one (39% of thermal crystallization). Therefore, this additional decrease in the  $\Delta C_p$  variations could be attributed to the appearance of the mesomorphic phase.

Finally, thermal analysis measurements support the three phases model in drawn PET films.

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**Zusammenfassung** — Mittels DSC, Röntgendiffraktion und Messung der Doppelbrechung wurde das Verhalten von gezogenen semikristallinen Poly(ethylenterephthalat)-Filmen untersucht. Ein Vergleich der verschiedenen Ergebnisse bestätigt die Koexistenz zweier Strukturen im amorphen Teil der Substanz: einer vollständig ungeordneten amorphen Phase und einer mesomorphen Phase. Weiterhin zeigen die kalorimetrischen Ergebnisse für das größte Zugverhältnis, daß der Zugeffekt auf die dehnungsinduzierte Kristallstruktur durch eine bessere Ausrichtung dieser Struktur gekennzeichnet ist, als dies durch Keimbildung und das Wachstum neu ausgerichteter Kristallite der Fall ist.