

## **ON THE SUB- $T_g$ ANNEALING OF UNIAXIALLY ORIENTED AND UNORIENTED ATACTIC POLYSTYRENE**

*C. Carfagna, L. Nicodemo\* and L. Nicolais\**

DIPARTIMENTO DI CHIMICA, UNIVERSITÀ DI NAPOLI, NAPOLI, ITALY

\*DIPARTIMENTO DI INGEGNERIA DEI MATERIALI E DELLA PRODUZIONE,  
UNIVERSITÀ DI NAPOLI, NAPOLI, ITALY

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DSC analysis was performed on uniaxially oriented and unoriented atactic polystyrene samples prior to and after annealing at 80 °C. With increasing annealing times, an endothermic peak appeared, whose area increased with the duration of the annealing period. No difference was found between the endotherm areas for the oriented and the unoriented polymer.

The DSC curve of the unannealed oriented polystyrene exhibited a relaxation exotherm. DSC and relaxation studies indicated that this relaxation exotherm was independent of the main chain orientation; it may rather be due to sample densification.

Differential scanning calorimetry is a tool increasingly used to detect the state of a glassy polymer. Due to the relative ease of performance of thermal analysis, many papers have been devoted to correlating the physical properties of polymers with their thermal behaviour [1-5]. On the other hand, few authors have pointed out the misunderstandings arising from a superficial use of the calorimetric technique in the characterization of polymeric materials [6-8].

It is well known that sub- $T_g$  annealing changes the physical state of glassy polymers; it reduces the excess volume and enthalpy relative to the extrapolated equilibrium liquid state [1, 2, 5].

In this paper we report preliminary results on the influence of the orientation of atactic polystyrene on the DSC curves, to establish whether the orientation induced in the glassy polymer by hot drawing can be detected with the usual DSC measurements.

### **Experimental**

The oriented polystyrene samples were obtained by extruding under hot drawing an SNL 400 atactic polystyrene ( $M_w = 290,000$ ), kindly supplied by Montedison.

The extruded films had a thickness of 0.14 mm. The extent of orientation was evaluated by exposing a disk 4.0 mm in diameter, cut from the sheet, to a temperature of 180° for 30 min under a nitrogen atmosphere. The temperature and duration of the annealing were fixed on the basis of data in ref. [9]. Due to the shrinkage in the drawing direction, the disks deformed to ellipses. After the thermal treatment the ratio between the original diameter and the length of the minor axis was nearly 5, showing that the film is strongly oriented. The use of disks 4.0 mm in diameter was necessary since specimens with larger dimensions showed irregular shrinkage, due to the inhomogeneous orientation and thickness caused by oscillation in the feed flow rate of the extruder.

The unoriented samples were annealed at 80° for increasing times. DSC curves were obtained at the end of each annealing period with a Mettler TA 3000 differential scanning calorimeter at a heating rate of 10 deg/min. For the instrument calibration an indium Fluka 99.999% sample was used. The same procedure was followed for the oriented samples, cut directly from the drawn sheet.

## Results

Figure 1 shows the portion of interest of some DSC curves of the unoriented samples after different annealing periods at 80°. The shape of the DSC trace for the unannealed, unoriented sample is typical of a quenched amorphous polymer, showing the characteristic glass transition zone, from which an apparent  $T_g$  of 98° can be established as the temperature of onset of the DSC baseline shift. (If  $T_g$  is defined as the temperature of 50% devitrification, its value is 102°.)

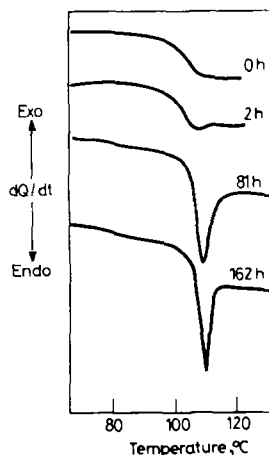


Fig. 1 DSC curves for unoriented polystyrene prior to and after annealing at 80° for the times shown

With increasing annealing times an endothermic peak appears, whose area increases as the annealing period becomes longer. The area of this endotherm is a measure of the extent of enthalpy relaxation on annealing [1, 2].

Figure 2 shows the DSC curves for oriented samples after different annealing periods at 80°. Leaving out for the moment the curve relating to the unannealed sample (0 h), the shape of the curves is identical to that for the unoriented samples.

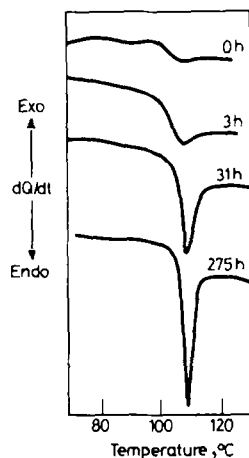


Fig. 2 DSC curves for uniaxially oriented polystyrene prior to and after annealing at 80° for the times shown

In Fig. 3 the area of the endothermic peak is reported vs. the annealing time, for both oriented and unoriented samples. The difference between the two sets of data is negligible and of the order of the experimental errors.

Figure 4 depicts the temperature at the beginning of the endothermic peak; the highest difference between the two sets of data is 1.5%.

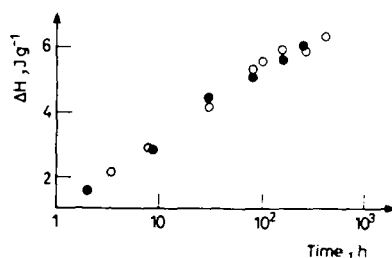


Fig. 3 Development of the endotherm area with the annealing time at 80° for uniaxially oriented and unoriented polystyrene. ○ oriented; ● unoriented

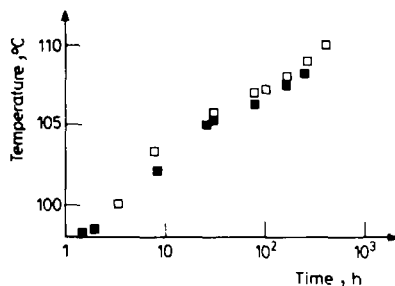


Fig. 5 Effect of annealing time on the temperature at the end of the endothermic peak. □ oriented; ■ unoriented

In Fig. 5 the temperature at the end of the endothermic peak is given. In this case too the difference between the two sets of data is negligible.

The temperatures reported in Figs 4 and 5 are only apparently related to the glass transition temperature of the annealed polymer. In fact, due to the well-known tendency of the annealed material to superheat, the calculation of  $T_g$  from the  $C_p$  discontinuity, as observed from the DSC traces in Figs 1 and 2, yields a value which is higher than that for the quenched material, the opposite of the true situation. In this case  $T_g$  must be extracted from an enthalpy vs. temperature plot [6-8, 10].

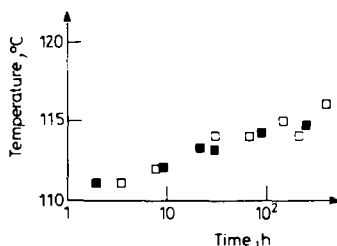


Fig. 5 Effect of annealing time on the temperature at the end of the endothermic peak. ■ oriented; □ unoriented

## Discussion

It must be mentioned that the orientation is not lost during this sub- $T_g$  treatment, or at least a loss is not detectable by a simple measurement of the specimen dimensions. In fact, the disks annealed at  $80^\circ$  for various times do retain their shapes, and once exposed at  $180^\circ$  show approximately the same shrinkage ratio of 5 as the unannealed samples.

Therefore, it can be said that orientation does not change the DSC traces relative

to those of sub- $T_g$  annealed samples, and consequently orientation is not detectable in this way.

The difference between the DSC traces of oriented and unoriented polymers is only detectable at 0 h, or with very short periods of annealing at 80°. From an analysis of Figs 1 and 2, it can be seen that in the DSC trace of the unannealed, oriented sample, the glass transition region is enlarged in the lower limit by the presence of an endothermic peak, followed by an exotherm. This apparently unusual behaviour does not seem related to the orientation of the main chain of polystyrene, which causes the shrinkage of the film, once exposed to higher temperatures. In fact, the same behaviour appears in the DSC experiment described in the paper by Weitz and Wunderlich [5], relative to a polystyrene sample obtained by cooling the melt under elevated hydrostatic pressure. In this case, the sample being isotropically compressed, it can not be possible that a preferential orientation is induced in the main chain. The authors related the shape of the DSC traces to a densification of the sample. They observed a progressive shift of the lower limit of the glass transition region towards lower temperatures with increasing hydrostatic pressures. The lowering of the glass transition region parallels the increase in density. Weitz and Wunderlich regarded the pressure-densified polystyrene as a highly stressed system rather than a normal glass. In our case too, densification occurs due to the drawing. In fact, the density of the uniaxially drawn polystyrene is higher than that of the unoriented polymer, the difference being of the order of 1%. A previous study on different polymers showed that the chain orientation obtained by drawing the sample can induce a densification of the order of 3% for a draw ratio of 5 [11].

A study on drawn polystyrene samples showed that both specific heat capacity and birefringence were decreased after thermal treatment at temperatures well below the glass transition of the polymer, but in any case before any significant shrinkage could occur [3]. The authors explained this phenomenon on the basis of the motion of the phenyl groups and the local oscillation modes of the main chain. The decrease in the birefringence was related to the decrease in the optical anisotropy of the benzene ring aligned perpendicularly to the chain axis. This local orientation rapidly disappears due to sub- $T_g$  annealing, without affecting the overall orientation of the main chain. This can be confirmed by the substantial equivalence of the DSC traces for the oriented and unoriented samples after various annealing periods at 80°; while the different shapes of the DSC curves at 0 h for oriented and unoriented samples could be explained on the basis of the orientation of the phenyl groups.

This interpretation implies that in the densified polystyrene of Weitz and Wunderlich orientation of the phenyl groups occurs, but this can hardly be imagined for an isotropically pressurized melt.

In conclusion, it can be said that the orientation of the main chain of polystyrene, caused by drawing, can not be detected by DSC; at the present time, it seems at least not supported by experimental evidence that the difference between the DSC curves of oriented and unoriented polymer at 0 h (or for short periods of annealing at 80°) is related in a direct or indirect way (orientation of the phenyl groups) to the orientation of the main chain. In fact, if it is supposed, as a hypothesis, that the phenyl groups are oriented in the isotropically densified polystyrene, the shape of the DSC traces at 0 h would not prove that the main chain is oriented, since no orientation can be assumed in the experiment of Weitz and Wunderlich.

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**Zusammenfassung** — Uniaxial orientierte und unorientierte ataktische Polystyrenproben wurden vor und nach dem Tempern bei 80° mittels DSC untersucht. Mit länger werdender Temperungszeit erscheint in endothermer Peak, dessen Fläche mit der Dauer der Temperungsperiode ansteigt. Die Flächen der endothermen Peaks von orientierten und unorientierten Polymeren unterscheiden sich nicht. Die DSC-Kurve von ungetempertem orientiertem Polystyren zeigt einen exothermen Relaxationseffekt. DSC und Relaxationsuntersuchungen ergaben, daß dieser exotherme Relaxationseffekt unabhängig von der Orientierung der Hauptkette ist und eher einer Probeverdichtung zuzuschreiben ist.

**Резюме** — Проведен ДСК анализ одноосно ориентированных и неориентированных атактических образцов полистирола до и после их отжига при температуре  $80^{\circ}$ . При увеличении времени отжига появляется эндотермический пик, площадь которого увеличивается с увеличением периода отжига. Не наблюдалось различий между площадью эндотермического пика ориентированного и неориентированного образцов полимера. На кривой ДСК ориентированного полистирола, не подвергнутого отжигу, наблюдается релаксационная экзотерма. ДСК и релаксационные исследования показали, что релаксационная экзотерма не зависит от ориентации главной цепи полимера, а обусловлена скорее уплотнением образца.