Crystallization of syndiotactic polystyrene under pressure

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Effects of annealing under pressure on the polymorphic behaviour of crystalline syndiotactic polystyrene (sPS) have been investigated using X-ray diffraction and d.s.c. thermal methods. sPS exhibited the normal α crystalline form when annealed at atmospheric pressure, but transforms to the β form when annealed at higher pressures. A planar zigzag chain conformation was retained after the pressure-induced α to β transition and the molecular chains packed more densely in the lateral direction.

(Keywords: syndiotactic polystyrene; crystallization; annealing)

Introduction

Recent structural studies by Guerra *et al.*[1] have revealed several polymorphic forms for syndiotactic polystyrene (sPS). Currently, four major crystalline forms, α, β, γ and δ, have been identified. Among these, the α and β crystalline forms, which both possess planar zigzag conformations, are of particular interest, since the extended chain conformation imparts an inherently stiff backbone to the polymer leading to the improved mechanical properties. Vittoria *et al.*[2] have observed the β form of sPS to have better solvent resistance than the α form, raising a question about what processing conditions control the transformation of α to β such that improved physical properties of sPS could be achieved.

Systematic melt crystallization studies of sPS by Guerra *et al.*[1] demonstrated that either α or β forms could be produced depending on the thermal history of the sample. Factors such as cooling rate, melt residence time and maximum melt temperature all influence the polymorphic behaviour of sPS. In addition to thermal history, external pressure is another important factor for inducing changes of crystalline polymeric structures. The present paper examines the influence of applied pressure on sPS crystallization and provides interpretations of the experimental results.

Experimental

The sPS used in this study was supplied by Dow Chemical Company. The particular lot had a number average molecular weight of 212 000 and a weight average molecular weight of 470 000. The specimens prepared were annealed in a rectangular plaque matched mould, using a microprocessor controlled heated compression press (MCHCP) (Tetrahedron Associates). Annealing temperatures of the samples were monitored using a thermocouple probe inserted in the mould and connected to the MCHCP temperature control system. The maximum temperature used for the annealing experiments was 260°C. The applied external pressure levels used in the experiments were: atmospheric (or zero external pressure), 118 and 628 kPa. A Philips X-ray diffractometer with CuKα radiation was used to record the diffraction patterns. Thermal analyses were carried out using a Dupont 912 DSC purged with nitrogen. D.s.c. scans were made from ~25 to 350°C using ~15 mg of each specimen and a heating rate of 10°C min^{-1}.

Results and discussion

Crystallization of polymers under pressure has attracted particular interest since this provides a means of preparing different crystal structures and morphologies[3]. Such altered molecular conformations may exhibit remarkable changes in the polymer's solvent resistance and mechanical performance. To investigate the effects of pressure on the sPS crystalline structure, specimens were prepared in a matched mould by heating the polymer from room temperature to 260°C, while applying external pressure (0, 118 or 628 kPa) and holding at these conditions for ~3 min, then cooling the mould down while still under external pressure.

Figure 1a shows the X-ray diffractometer scan for a sample annealed at 260°C at atmospheric pressure. Measured *d*-spacings and relative intensities for the Bragg reflections are listed in *Table 1*. All of them agree well with the results known for the α form of sPS[4] with hexagonal unit cell dimensions: $a = 26.3$ and $c = 5.1$ Å. A diffractometer scan for a specimen annealed at 260°C under 118 kPa external pressure is displayed in *Figure 1b*, and deviates from that generated by the α form of sPS although the overall degree of crystallinity remains about the same. The occurrence of Bragg diffraction at 14.2 Å adjacent to the 13.2 Å peak (from the α form) is a clear indication of the presence of the β form. The emergence of the β form is also demonstrated from a strong Bragg reflection occurring in the vicinity of 7.4 Å. This reflection appears to be a composite peak of two intense reflections, one at $d = 7.55$ Å contributed by the α form and the other at $d = 7.18$ Å contributed by the β form. *Figure 1c* shows the diffraction scan for a specimen annealed under 628 kPa external pressure. The characteristic diffraction peak for the α form at $d = 13.2$ Å has completely disappeared. Measured *d*-spacings and relative intensities (*Table 1*) from the diffraction scan in *Figure 1c* compare well with those of the β form obtained by other investigators[1], and all these observed reflections are able to be indexed by a monoclinic unit cell proposed

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by Chatani *et al.*[5] with the dimensions: $a = 19.8, b = 12.9$ and $c = 5.1$ Å and $\gamma = 95°$. Calculated crystalline densities for the two forms, $\rho_\alpha = 1.03$ and $\rho_\beta = 1.07\ g\ cm^{-3}$, suggest the β form is slightly denser than the α form, although actual density measurements are still needed for confirmation. Since all X-ray diffractometer traces identify a Bragg reflection (*hkl*: 002) at about $d = 2.5$ Å, which is strong evidence for a planar zigzag chain conformation, we believe that applied compressive force has little influence on unit cell dimension in the *c* direction and only modifies the lateral packing of molecular chains.

Figure 2 displays d.s.c. traces of the α and β crystalline forms, which exhibit slight differences in thermal behaviour. Besides one major melting peak at ~270°C, the d.s.c. trace of the β form shows an additional small endothermic peak. The possibility of a polymorphic β to α transition can be ruled out by the convincing X-ray data of the β form of sPS at a temperature close to the melting point[1]. Bassett *et al.*[6] have shown that the amount of available volume constraints applied during the crystallization will influence lamellar thickness, and thus the melting behaviour of the crystalline structure. For the β form of sPS, the imposed volume constraints on a crystallizing sample will reduce the lamellar thickness. The smaller endotherm indicates melting of small thin lamellae. This is followed by a rapid recrystallization to large lamellae due to the relatively high supercoolings involved[7]. The double endotherm phenomenon is not observed in the d.s.c. traces for the α form of sPS, which occurs upon crystallization at atmospheric pressure. In this case, no similar volume constraints are placed.

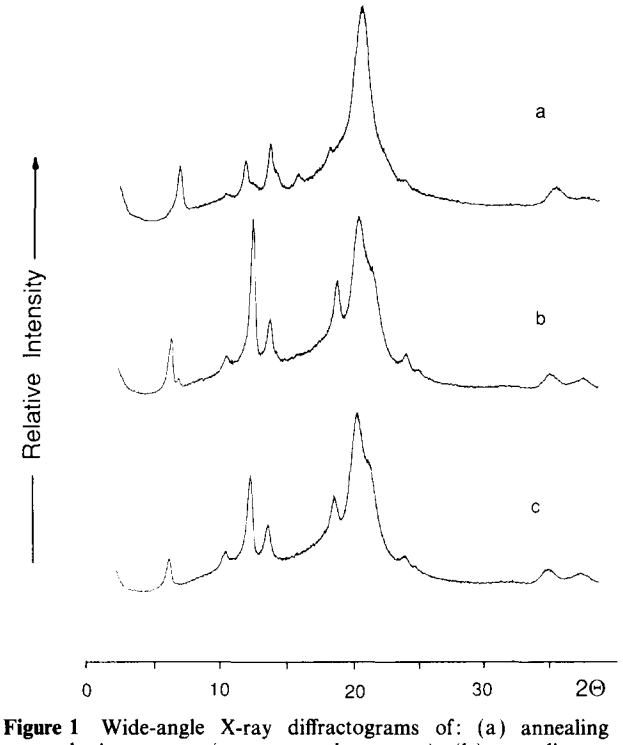

Figure 1 Wide-angle X-ray diffractograms of: (a) annealing at atmospheric pressure (zero external pressure); (b) annealing at an external pressure of 118 kPa; (c) annealing at an external pressure of 628 kPa

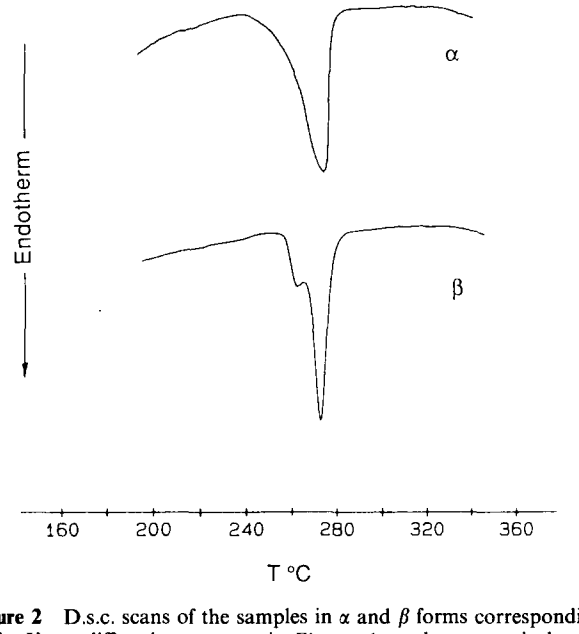

Figure 2 D.s.c. scans of the samples in α and β forms corresponding to the X-ray diffraction patterns in *Figures 1a* and *c*, respectively

Table 1 Observed *d*-spacings and relative intensities from X-ray diffractometer scans for the α and β forms of sPS

α form		β form	
d (Å)	Intensity[a]	*d* (Å)	Intensity[a]
13.20	s	14.20	s
8.61	w	8.43	m
7.55	s	7.18	s
6.52	s	6.47	s
5.68	w	4.73	m
4.98	m	4.36	vs
4.35	vs	3.70	w
3.74	w	2.56	m
2.54	m	2.39	m
2.39	w		

[a]Very strong, vs; strong, s; medium, m; weak, w

In conclusion, pressure-annealing of sPS causes the transformation of the α crystalline form to the more densely packed β crystalline form as confirmed by the X-ray diffraction data. Volume constraints imposed by pressure-annealing result in the formation of thin lamellar crystallites of the β form as indicated by the small endotherm found in the d.s.c. thermograms. Only small levels of external pressure are needed to cause the α to β transition.

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