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Studies of the γ→α Transition in Syndiotactic Polystyrene

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SUMMARY: In this work we compare calorimetric and X-ray diffraction experiments realized on annealed sPS in helical γ forms resulting by different treatements: from clathrate δ form and from interaction of amorphous sample with acetone.The experimantal results show that the γ form obtained by acetone converts into the more ordered final α″ form modification; while the γ form, obtained by thermal treatments of δ form, transforms into the poorly ordered final α′ form.

Introduction

Syndiotactic polystyrene (sPS) shows a very complex polymorphism, dependent on the crystallization conditions. Thermal crystallization, both from the melt and from the glassy state, is characterized by chains in zig-zag planar conformation (α and β forms) [1)], whereas helical conformations are obtained by crystallization in the presence of solvents (δ and γ forms).[2)] It has been shown that the sorption of suitable solvents can induce crystallization in amorphous sPS samples and also can transform the α form toward clathrate structures, which include solvent molecules [3)]. At variance, other solvents, as acetone, can directly induce the crystallization of the γ form, without solvent molecules [2)].

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Experimental

Syndiotactic polystyrene ($Mw=6.6\times10^5$ determined by GPC) was kindly supplied by Istituto Guido Donegani of Montedison. Amorphous films were obtained by moulding the powders at 300°C in a film shape 0.1 mm thick and rapidly quenching in an ice-water bath at 0°C. The crystalline δ form (Sample A) was obtained by immersing the amorphous film in dichloromethane for 24 hours, and then drying for 24 hours at room temperature under vacuum. The crystalline γ form (Sample B) was obtained with the same procedure in acetone. Sample A and sample B were annealed at 160°C for 1 hour, 24 and 48 hours, 7 and 16 days. Experimental investigations were realized using a Thermal analyzer Mettler TA-4000 for calorimetric data and a Phylips PW –1710 Power diffractometer for X-ray investigations.

Results and discussion

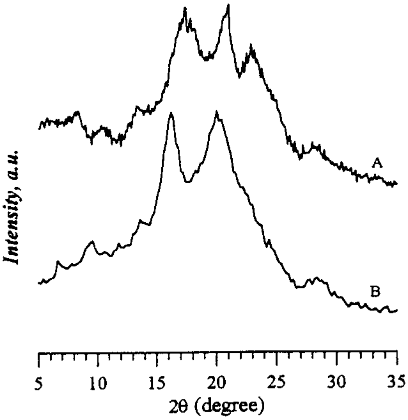

Fig. 1 X-ray diffraction patterns of samples A and B

In fig. 1 the X-ray diffraction patterns of the starting samples A and B are reported. Sample A shows the crystalline diffractogram of the δ form 4), with the peaks appearing at 8.3, 10.6, 13.1, 17.1, 21.1 and 23.7 degree of 2θ. The peaks appearing in the pattern of sample B at 9.2, 16.0, 19.9 and 28.3 degree of 2θ are representative of γ form.

In fig. 2a the DSC curves of the clathrate δ form (sample A) and the same annealed at 160°C for 1, 7 and 16 days are shown. In the curve of the original sample A many transitions are evident. The first, indicated as (a), occurring at 110°C, is due to the transformation of the δ into the γ form; it appears as an endotherm followed by an exotherm 5). A very small new endotherm appears at 180°C (b), soon followed by an exotherm at 200°C (c). These transitions allow the transformation of the γ structure into the α structure, with the chains in zig-zag planar conformation. The main endotherm, occurring at 270°C (d) is due to the melting of the α form of sPS. In the thermograms of sample A annealed at 160°C, we do not observe the first (a) transition. In fact, the transition from the δ to the γ form has already occurred. At variance there is a progressive increase of the (b) endotherm and a corresponding decrease of the (c) exotherm; a similar trend is observed for sample B, as indicated in fig. 2b.

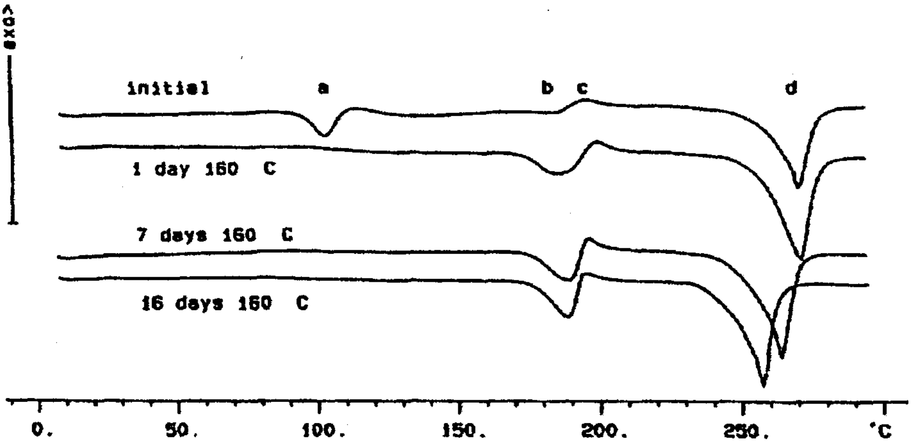

Fig. 2a DSC curves of sPS sample A

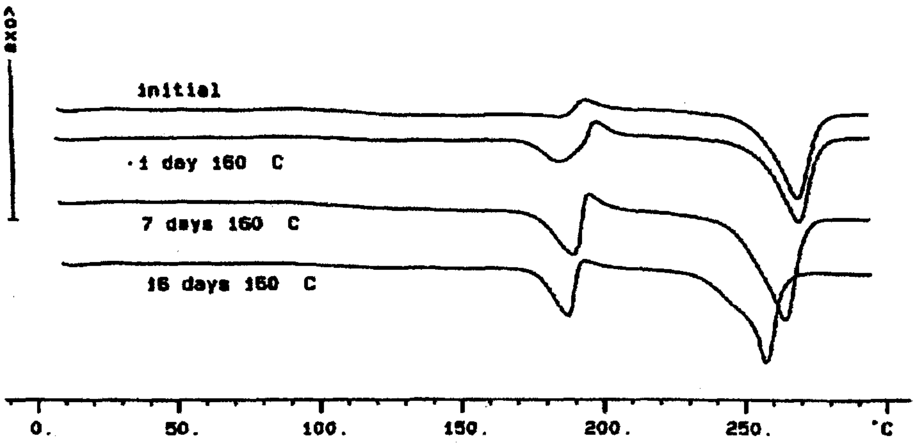

Fig. 2b DSC curves of sPS sample B

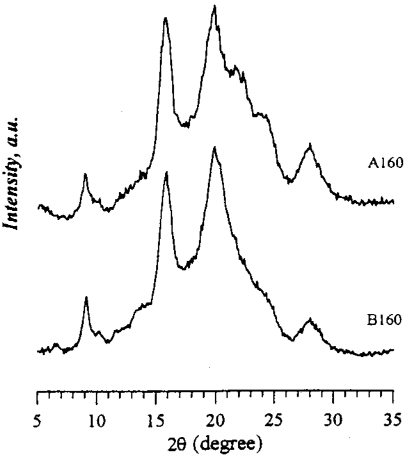

Fig. 3 X-ray diffraction patterns of samples A160 and B160

Fig. 3 shows the diffraction spectra for samples A and B annealed 16 days at 160 °C (indicated with A160 and B160 respectively).For sample A160 the observed reflections are those indicative of the γ form. As already reported, annealing treatments above 120 °C induced the transition from δ to γ form.The X-ray diffractogram of sample B160 indicates that the structure obtained is a γ form characterized by sharper reflections and a higher degree of crystal perfection with respect to the previous.

In fig. 4 the enthalpy of the (b) endotherm is reported as a function of the annealing time, for sample A and sample B. We observe that the enthalpy increases up to 7 days of annealing and then it remains constant. It is also worth noting that the values for the two samples are very similar.

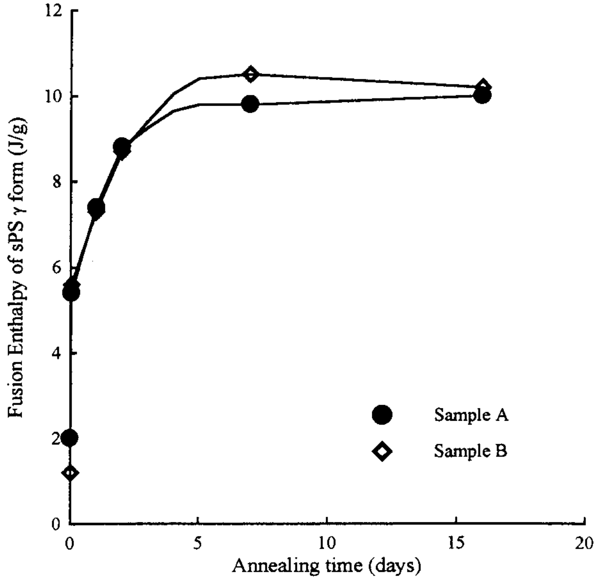

Fig. 4 Enthalpic values of (b) endotherm vs annealing time for samples A and B

In fig. 5 the cristallization enthalpy of (c) exotherm as a function of annealing time for samples A and B is reported. It is worth nothing that the deacrease of crystallization enthalpy is very rapid in the first hours and more gradual after 2 days, with a total decrease about 77% after 16 days.

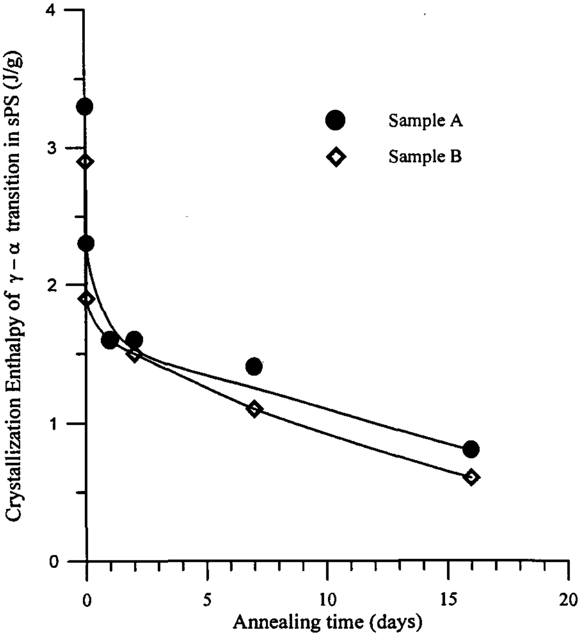

Fig. 5 Crystallization Enthalpy values of (c) exotherm vs annealing time for samples A and B

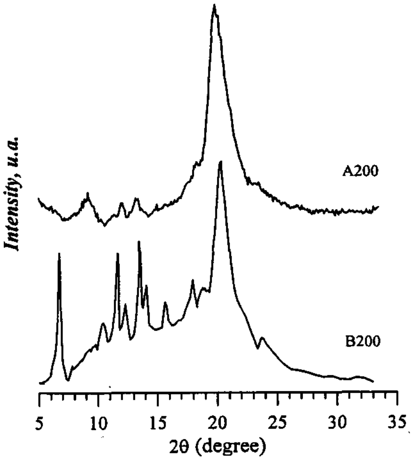

Fig. 6 X-ray diffraction patterns of samples A200 and B200

In fig.6 the x-ray diffraction patterns of samples A160 and B160 annealed 2 minutes at 200 °C (denoted with A200 and B200 respectively) are reported. This thermal treatment transforms the γ form into the crystalline α form.The structure obtained for sample A200 is very different from that shown for sample B200. The pattern of sample A200 corresponds to that reported in literature 6,7) for samples crystallized in the disordered α' form. The pattern of sample B200 corresponds to that of the limiting ordered modification α″(typical reflections at 6.7, 10.3, 11.7, 12.36, 13.6, 14.1, 15.6, 18.0,20.4 and 23.8 degree of 2θ). [8-10]

Conclusions

The analyzed transition from the helical γ form to the planar zig-zag α form occurs through an endotherm soon followed by an exotherm. Annealing the γ form we observe a contemporaneous increase of the enthalpy of the endotherm and a decrease of the enthalpy of the exotherm.

The results of X-ray diffraction experiments show that the structure of the final α form is correlated to the structural organization of the γ form. In fact the γ form obtained by acetone converts into the most ordered α″ form modification; while the crystalline γ form, obtained by annealing treatments on δ form, transforms to the poorly ordered α′ modification. Further investigations, in progress in our laboratories [11], with infrared spectroscopy (FTIR) on these different helical forms, show higher conformational order for sample A160.

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