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Vapour induced ordering phenomena in syndiotactic polystyrene amorphous films

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Summary

Films of amorphous syndiotactic polystyrene were exposed to dichloromethane vapour at varying activity, up to a=1. Infrared analysis and wide angle X-ray scattering were used to follow the development of ordered structures, induced by the vapour. It has been found that characteristic bands in the infrared spectrum appear after activity a=0.45, whereas X-rays show that the sample is still amorphous. The appearance of the crystalline reflections occurs at higher activities and a continuous improvement up to a=1 in the X-ray pattern is observed.

Keywords : Syndiotactic polystyrene, FTIR, Wide-angle X-ray Scattering, ordering phenomena.

Introduction.

Highly syndiotactic polystyrene (sPS) crystallizes from the melt into two different forms, both having the chains in zig-zag planar conformation (1-3). On the other hand, crystallization can be induced by sorption of different liquids in amorphous sPS, and crystalline forms having the chains in a helical conformation are obtained (4). The presence of chains in this conformation is well manifested in the infrared spectrum, where specific conformational bands are present(5-6). Solvent induced crystallization (SINC) has been so far studied in the liquids at activity a=1, and the possibility of formation of ordered yet not truly crystalline structures, preceding the crystallization phenomenon, has already been suggested (7).
In this paper we present a study of SINC in the vapour activity range of dichloromethane. In this range it is possible to follow the process in a more gradual way, reaching activity a=1 step by step, and following for each step the development of the ordered structure, by infrared and X-rays analysis.

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Experimental

Highly syndiotactic polystyrene (sPS) was kindly supplied by Donegani spa (Novara - Italy). Amorphous films were obtained by molding at 300° C, in a film shape 0.01 cm thick and rapidly quenching either at -70° C in a dry-ice acetone bath (sample QR), or at 0° C in an ice-water bath (sample QO).

Different strips of the amorphous film were exposed to the vapours of dichloromethane at different activities. The activity $a=p/p_o$ was varied by changing the pressure, p, to which the sample was exposed; p_o is the saturation pressure at the experimental temperature, that is 25° C.

Each sample, after attainment of the equilibrium concentration of vapour, was dried under vacuum many days. Afterwards, the infrared spectrum and the X-ray diffractogram were detected.

Wide angle X-ray diffraction patterns (WAXD) were obtained by using a Seifert Debyeflex 1001 diffractometer and photographic recording in a cylindrical camera with 114.6 mm radius; Cu$K\alpha$ Ni filtered radiation was used. From the photographic patterns the intensity curves were obtained by means of an Optronic P-1000 densitometer.

Infrared spectra were detected by using a Nicolet 5DXB FTIR spectrophotometer, collecting for each sample 30 scans, with a resolution of 4 cm^{-1}.

Results

The WAXD analysis shows that samples QR and QO are completely amorphous.

In Fig. 1 the infrared spectra of the amorphous sample QO (a), and the same immersed in liquid dichloromethane at 25° C and dried (b) are shown. The bands, characteristic of the helical structure (marked with an arrow) appear at 499, 575, 935, 1170, 1277 cm^{-1}.

The growth of the helical structure in the vapour activity range was followed measuring a structure dependent parameter H, which represents the ratio between the absorbance of a helical band and the absorbance of an internal reference band.

The chosen helical bands were those observed at 575 cm^{-1}, and 935 cm^{-1}, whose absorbances were normalized by the bands respectively at 840 cm^{-1}, and 906 cm^{-1}, used as internal reference bands. In particular we determined

$$H_1 = \text{Absorbance } 575 \text{ cm}^{-1} / \text{Absorbance } 840 \text{ cm}^{-1}$$
$$H_2 = \text{Absorbance } 935 \text{ cm}^{-1} / \text{Absorbance } 906 \text{ cm}^{-1}$$

In Fig. 2 the H_1 and H_2 parameters are reported as a function of the vapour activity to which the sample had been exposed.

We can observe a constant value of H_1 and H_2 parameters up to activity a=0.4; afterwards H_1 increases to a maximum value, after which a slight decrease and a constant value up to activity a=1 is observed. H_2 increases sharply between 0.45 and 0.6 and then more slowly up to activity a=1, where the maximum of this parameter is observed.

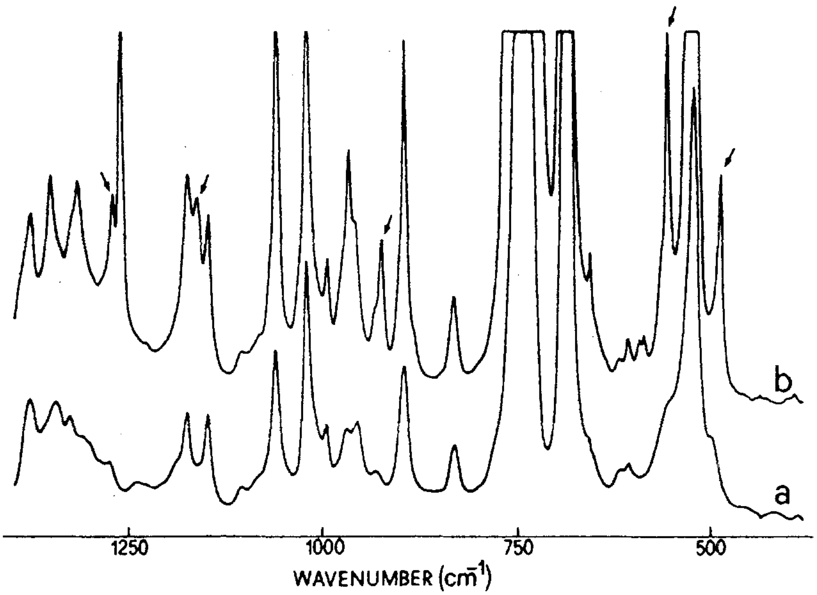

Fig.1 Infrared spectra of sample QO(a), and QO after immersion in liquid dichloromethane(b).

This result is the same for either of the two amorphous samples. It is therefore possible to deduce that the conformational transition occurs at activity of dichloromethane vapour a=0.45 , and that there is a continuous growth of the helical structure up to activity a=1.

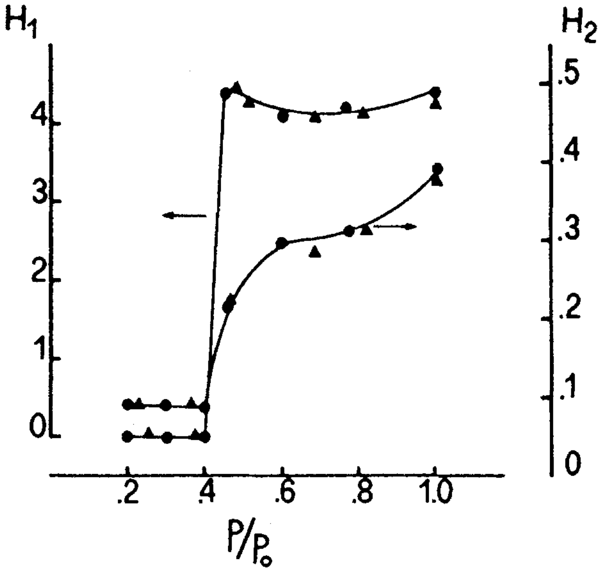

Fig.2 H_1 and H_2 versus the vapour activity.
Sample QR (●)
Sample QO (▲).

In Fig. 3 we show the X-ray diffractograms of sample QO exposed to dichloromethane vapour at activity a=0.5 (a); 0.7 (b); and a=1 (c), and in Table 1 we report the diffraction angles (2ϑ) detected on sample QR after exposure to different activities of vapour.

Both the samples QO and QR, exposed to activity a=1 and dried, show the crystalline form first reported by Immirzi et al.(8), in which the chains are in a helical conformation. This form was named δ form (9). Sample QR exposed at activity 0.45 is still amorphous, in spite of the presence in the infrared spectrum of the helical bands; the appearance of the diffraction peaks of the δ form is a gradual phenomenom, increasing on increasing the vapour activity.

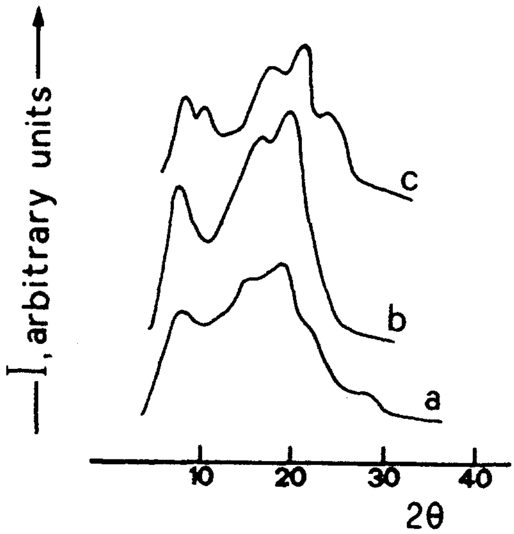

Fig.3 WAXD of sample QO exposed to the vapour at activity a=0.5 (a); a=0.7 (b); a=1 (c).

Table 1

X-ray diffraction angles (2ϑ) for sample QR exposed to different activities of dichloromethane vapour.

activity	2ϑ				
0.45	9.5		20		
0.60	9.2	17.2	22.8	26	
0.76	9.2	17.2	22.8	26	
1.0	8.3	11.0	17.0	21.5	23

Infrared analysis and wide angle X-ray scattering suggest that the vapour induces a conformational ordering, without development of crystalline order, at activity a=0.45. At this

activity, in fact , the 575 cm^{-1} band is completely developed, whereas the 935 cm^{-1} begins increasing , and only at activity a=1 reaches its maximum value.
Also the diffractograms show a continuous improvement towards the diffractogram of the δ form, which is obtained only in the liquid dichloromethane.

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