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Vapor induced crystallization of syndiotactic random copolymers of styrene with *p*-*n*-butylstyrene

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Summary

The vapor induced modification of bulk samples of syndiotactic random copolymers of styrene and p-n-butylstyrene is studied by wide-angle X-ray scattering and light microscopy. Two samples with p-n-butylstyrene contents of 4 and 11 mol% are compared. It is shown that treatment with $CHCl_3$ leads to the formation of a clathrate modification similar to that of neat syndiotactic polystyrene. The change of the surface topography of the copolymers as a result of $CHCl_3$ vapor exposition is studied by tapping-mode / height-mode atomic force microscopy.

Introduction

Syndiotactic polystyrene (s-PS) has a complex polymorphism. Three different crystal structures (α,β,γ) and one clathrate structure (δ) have been described (1-3). The α- and β-modification contain planar zig-zag chains with an identity period c = 0.51 nm, the crystalline γ-form and the clathrate modification (δ) contain (2/1)2 helices with an identity period of c = 0.78 nm (3). The clathrate form δ of neat s-PS includes up to 14 wt% solvent (3,4). At elevated temperatures (approximately at 120°C, depending on the solvent) the clathrate modifications (δ) shows a transition to the solvent free γ-modification (3). The morphology of the δ- and γ-form of s-PS was studied by De Candia et al. using a scanning electron microscope (5).

Syndiotactic copolymers of styrene with relatively small p-n-butylstyrene (BuS) contents up to 7 mol% are crystallizable from the melt. It is shown that under these crystallization conditions the α-modification is favored relative to the β-modification. Copolymers up to a BuS content of 27 mol% are crystallizable in the presence of solvents. Under these conditions the δ-modification is formed (6). Copolymers with higher contents of BuS are not crystallizable under any conditions.

This contribution deals with the influence of $CHCl_3$ vapor on the crystallization behavior of two syndiotactic random copolymers of styrene and p-n-butylstyrene (s-P(S-co-BuS)) having BuS contents of 4 and 11 mol%. The copolymer with low BuS content is able to crystallize from the melt whereas the copolymer with higher BuS content can only form the clathrate modification in the presence of solvents. This is studied by wide angle X-ray scattering (WAXS) and polarized light microscopy. Changes of the sample topography upon $CHCl_3$ exposure are studied by tapping-mode / height-mode atomic force microscopy (AFM).

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Experimental

Synthesis: The samples were polymerized using the metallocene catalyst system $CpTiCl_3$ (Cp = cyclopentadienyl) / MAO. All details are given in ref. 6.

Tab.1 Polymer data

Sample	BuS-content [mol%]*	M_n [g/mol]**	M_w/M_n**
s-P(S-co-BuS)-4	4	81000	2.2
s-P(S-co-BuS)-11	11	124000	1.6

* calculated from ^1H- and ^{13}C-NMR spectra

** determined by size exclusion chromatography using polystyrene standards

Light Microscopy: The light microscopic investigations are carried out with an Olympus-Vanox AH2 microscope. The samples used were prepared by melting the powder of the as-prepared and dried polymer between two cover glasses. The layer thickness between the glasses was about 30 to 50 µm. These samples were treated with saturated $CHCl_3$-vapor at room temperature for different times.

Atomic Force Microscopy: The AFM experiments were carried out with a 'Nanoscope III' scanning probe microscope (Digital Instruments) at ambient conditions in the tapping-mode / height-mode.

WAXS measurements: The measurements were carried out with a Siemens D500 apparatus. For WAXS measurements the CuKα radiation of a wavelength of $\lambda = 0.154$ nm was used.

Results and discussion

Fig. 1 shows WAXS traces of s-P(S-co-BuS)-4 and s-P(S-co-BuS)-11 that are crystallized by exposing amorphous films to $CHCl_3$ vapor at room temperature (bottom traces). Both samples crystallize then in the δ-modification. At elevated temperatures (in the range of about 120°C) the clathrate modifications (δ) of the copolymer with 4 mol% BuS shows a transition to the solvent free γ-modification as known for s-PS (3). There does not exist any transition of this kind for s-P(S-co-BuS)-11. Upon heating the δ-modification melts in the temperature range between 110 and 120°C indicated by the appearance of two halos in the WAXS traces at high temperatures characteristic for molten polystyrene (6)

Fig. 2a shows a polarized light micrograph of s-P(S-co-BuS)-11 treated for 25 min with $CHCl_3$ vapor at room temperature. The inset depicts the sample geometry. Prior to the $CHCl_3$ vapor treatment the sample was completely amorphous. For that reason the bulk material appears dark between crossed polarizers. Only the interphase to the $CHCl_3$ vapor phase appears bright. The interphase of a similarly prepared atactic amorphous polystyrene remains dark. Therefore, the brightness can be related to crystalline material formed during the vapor exposure. The thickness of the crystalline layer, d, depends on the exposure time. Fig. 2b shows the thickness of the crystalline layer as a function of the exposure time. In the time interval studied, the growth of the crystalline layer is constant. The growth rate is about 15µm/min.

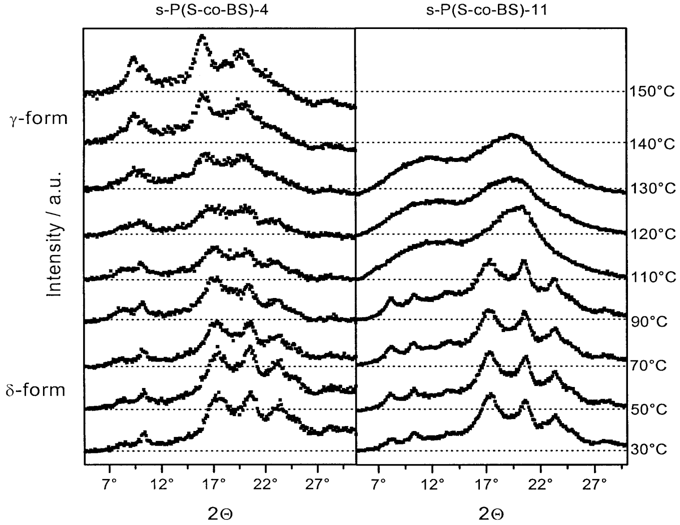


Fig.1: WAXS traces of quenched s-P(S-co-BuS)-4 and s-P(S-co-BuS)-11 samples after solvent induced crystallization in $CHCl_3$ vapor at room temperature and after slowly heating to different annealing temperatures.

Fig. 3 shows AFM tapping-mode / height-mode micrographs of s-P(S-co-BuS)-4 after vapor induced crystallization of samples with different degrees of crystallinity. After $CHCl_3$ vapor treatment of a completely amorphous sample that was quenched in acetone at -100°C a granular morphology is visible (Fig. 3a). Granular crystalline structures are also found e.g. for linear low density polyethylene and they are assumed to be formed by fringed micelles (7). These morphologies were not observable prior to solvent vapor exposure of the samples. Fig. 3b depicts an AFM micrograph of a sample that was originally quenched under less vigorous conditions. A small degree of crystallinity can be detected by WAXS measurements. After $CHCl_3$ vapor treatment a similar granular morphology is visible, but some additional, elongated morphologies appear. These elongated entities are obviously formed during the quenching process. A sample of s-P(S-co-BuS)-4 slowly cooled to room temperature and space filling crystallized is depicted in Fig. 3c. Exposure to $CHCl_3$ vapor has only a small influence on the surface topography. Some small swollen areas are visible. The majority of the surface appears extremely flat and unchanged. It can be assumed the regularly distributed swollen areas are formed in regions with a lower crystallinity, probably between the spherulites of s-P(S-co-BuS)-4. Note that for all AFM micrographs of samples exposed to $CHCl_3$ vapor the roughness is in the nm range. Figure 3d shows an AFM micrograph of a totally amorphous sample that was quenched in acetone at -100°C and treated with liquid $CHCl_3$ for 1 hour at room temperature. In contrast to the vapor treated samples the surface of this sample is very rough. A crater-like morphology is very characteristic and leads to a roughness in the µm range.

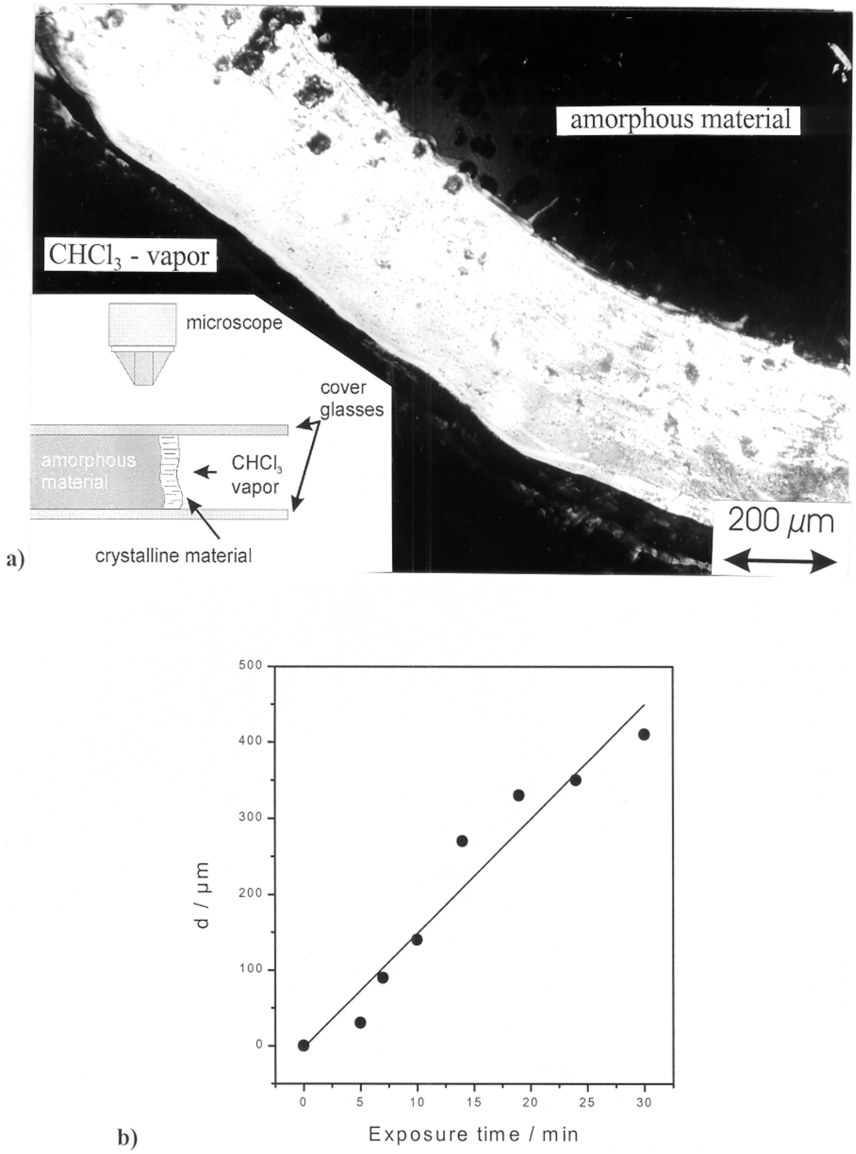
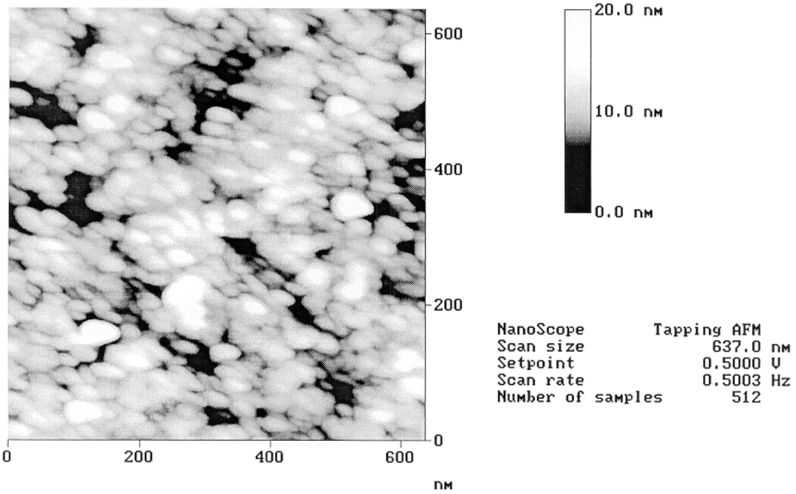


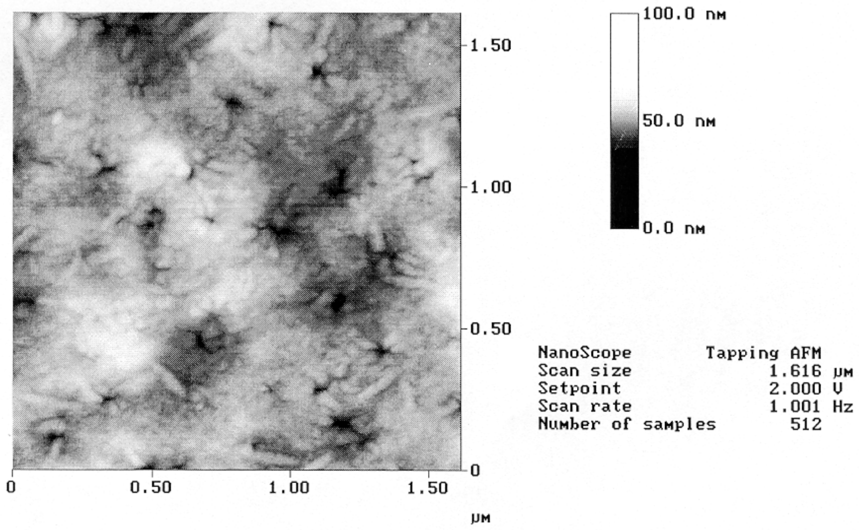
Fig. 2 a) Polarized light micrograph of the vapor induced crystalline layer in s-P(S-co-BuS)-11 (t = 25min). The inset shows the sample geometry. b) Thickness of the crystalline layer, d, in s-P(S-co-BuS)-11 versus the exposure time in $CHCl_3$-vapor at room temperature.

3a)



NanoScope Tapping AFM
Scan size 637.0 nm
Setpoint 0.5000 V
Scan rate 0.5003 Hz
Number of samples 512

3b)



NanoScope Tapping AFM
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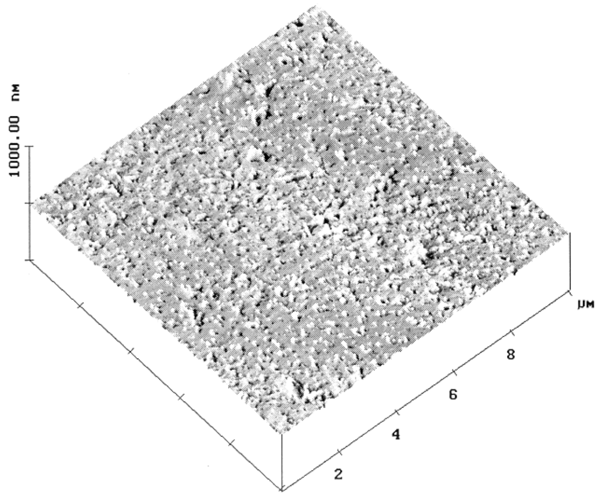
Setpoint 2.000 V
Scan rate 1.001 Hz
Number of samples 512

3c)



3d)

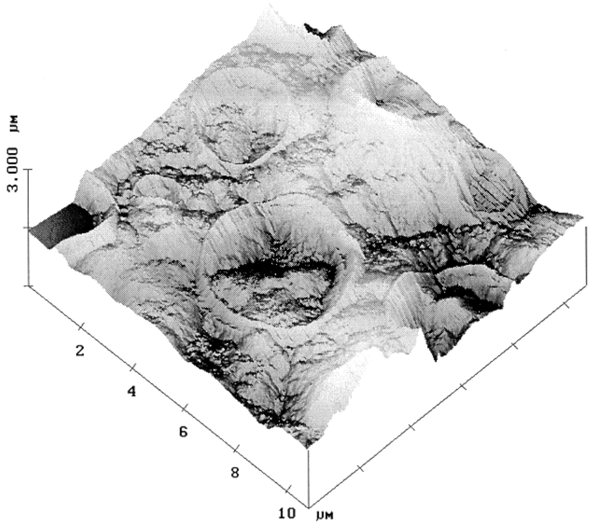


Fig 3: AFM micrographs of s-P(S-co-BuS)-4 after solvent induced crystallization in $CHCl_3$ vapor. a) Granular morphology after treating a totally amorphous sample with $CHCl_3$ vapor. b) Granular morphology and elongated crystalline entities after $CHCl_3$ vapor treatment of a sample with a small degree of crystallinity. c) Surface of a space filling crystallized sample treated with $CHCl_3$ vapor d) Surface of a totally amorphous sample treated with liquid $CHCl_3$ for 1h.

Conclusion

It is demonstrated by WAXS measurements and polarized light microscopy that s-P(S-co-BuS) samples are able to form clathrate structures similar to s-PS. In contrast to s-PS homopolymer s-P(S-co-BuS)-11 is not crystalline after removing the solvent by heating above 120°C. Therefore, it might be used as a reversible absorber material e.g. for chlorinated solvents. AFM micrographs show that the surface of the copolymers can be modified by vapor treatment. Copolymers with a higher BuS content, which are not crystallizable from the melt can be covered with a crystalline layer of well-defined thickness.

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