



# Solvent- and solvothermal-induced phase transitions and crystallisations in syndiotactic polystyrene and multiblock copolymer syndiotactic polystyrene-co-cis-1,4-polybutadiene

Antonio Buonerba<sup>\*</sup>, Paola Rizzo, Carmine Capacchione, Alfonso Grassi

Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università degli Studi di Salerno, via Giovanni Paolo II, 84084 Fisciano (SA), Italy

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## ABSTRACT

*The complex polymorphism of nanoporous syndiotactic polystyrene never stops to amaze.* Simple and rapid solvent- and solvothermal-induced crystallisation of syndiotactic polystyrene (sPS) and syndiotactic polystyrene polymer segments in the multiblock copolymer syndiotactic polystyrene-co-cis-1,4-polybutadiene (sPSB) into the desired crystalline form have been disclosed and herein reported. Stirring polymer powders of sPS in the chloroform/water solvent mixture allows crystallisation of the amorphous phase and the conversion of the co-crystalline  $\delta$  forms into the highly crystalline  $\delta$  form; variable combinations of water with other common non-polar solvents, or of chloroform with methanol failed in this transformation. The  $\gamma$  form has been obtained by solvothermal treatment of the  $\delta$  form by simple refluxing in acetonitrile. Stirring the  $\gamma$  form in chloroform/water mixture affords its rapid conversion into the  $\varepsilon$  form with elevated crystallinity. Finally, applying the chloroform/water treatment to the  $\beta$  form yields the  $\delta$  form with high crystallinity. The complex polymorphism of the sPS was also found in sPSB copolymer, even with short styrene segments. The thermal behaviour, in terms of melting enthalpy and temperature, was investigated at the variance of styrene content.

## 1. Introduction

Among the polymers of interest in industry, syndiotactic polystyrene (sPS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are, to date, the only ones to exhibit nanoporous-crystalline (NC) phases [1–4]. In particular, the NC phases of sPS show voids or channels [5–9] that are able to include low molecular mass molecules in the crystalline lattice to produce co-crystalline (CC) phases [10–19] (see Fig. 1). sPS is characterised by excellent physical and chemical properties such as high glass transition ( $T_g = 105$  °C) and melting temperature ( $T_m = 270$  °C), excellent resistance to the attack of strong oxidants, Brønsted-Lowry and Lewis acids or bases, good electrical insulating properties, good dimensional stability and low moisture absorption [1,20,21]. Remarkable is the crystallisation rate, which is higher than isotactic polystyrene and comparable to polyethylene [21,22]. The complex polymorphism comprises five crystalline phases denoted as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\varepsilon$  [1,3,23–25]. Commonly, sPS crystallises in the  $\delta$  form in the course of the solution polymerisation process carried out in toluene. The  $\alpha$  and  $\beta$  forms [26–29] show the polymer chains in a *trans*-planar (*zig-zag*) conformation, while in the  $\gamma$ ,  $\delta$ , and  $\varepsilon$  forms [5,6], the polymer chains adopt a

helical conformation. Thermal and solvent treatments affect the crystalline phase of sPS [23]. The  $\alpha$  and  $\beta$  forms are obtained from the molten state by rapid or slow cooling, respectively [26,30]. The  $\beta$  form is also obtained by heating the  $\delta$  form at temperatures higher than 150 °C [31]. The  $\gamma$  form can be obtained by heating the  $\delta$  form at a temperature exceeding 110 °C or by crystallisation of the amorphous sPS induced by bulky solvents (such as 1-chlorodecane) [32], *i.e.* molecules too big to be enclosed as guest into CC phases [32,33]. The exposition of the  $\gamma$  form to chloroform vapour or dipping the polymer powder in the same solvent yield crystallisation in the  $\varepsilon$  form [34]. The crystalline structures of these crystalline forms, except for  $\gamma$ , have been elucidated by WAXD analysis of powders or films. The  $\alpha$  and  $\beta$  forms are characterised by compact packing of the polymer chains in *zig-zag* planar conformation. The packing of the polymer helices in the  $\delta$  form yields the formation of nanometric isolated cavities (diameter of about 120 Å, see Fig. 1), whereas the same conformation of the polymer chains in the  $\varepsilon$  form produces channels [35]. Various organic molecules can be hosted in the voids and channels of the  $\delta$  and  $\varepsilon$  forms to create co-crystalline phases [14–17,36].

sPS and multiblock copolymer syndiotactic polystyrene-co-cis-1,4-

<sup>\*</sup> Corresponding author.

E-mail address: [abuonerba@unisa.it](mailto:abuonerba@unisa.it) (A. Buonerba).

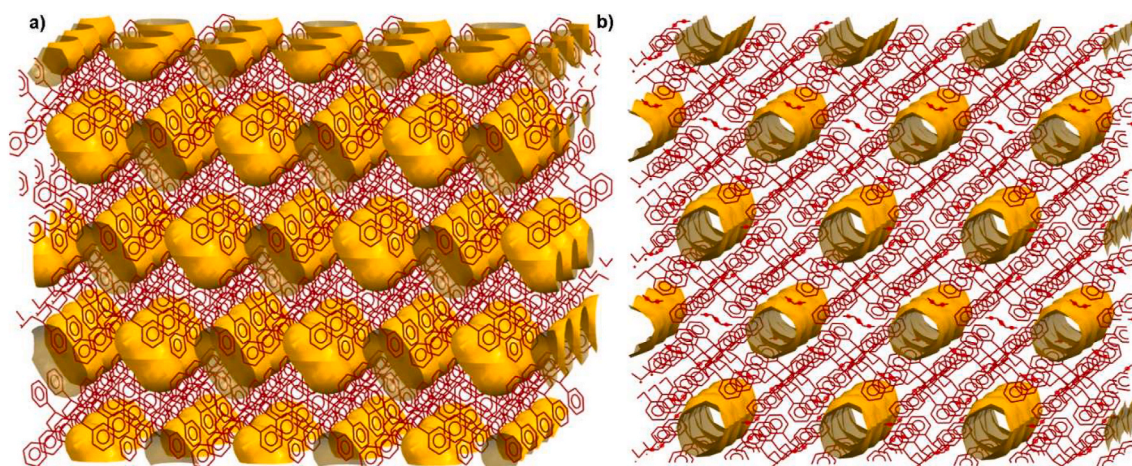
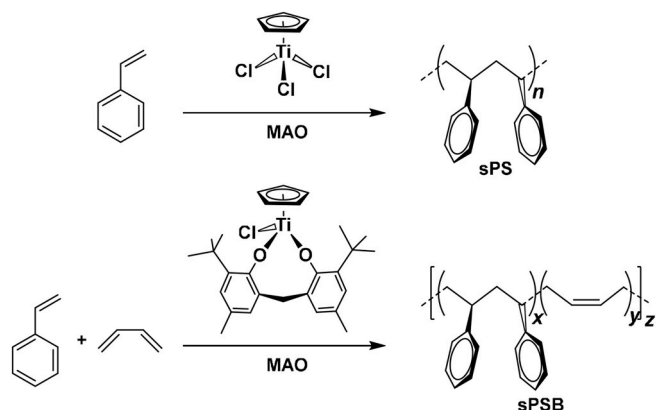


Fig. 1. NC forms of sPS highlighting isolated voids and nanochannels, respectively, in  $\delta$  (a) and  $\epsilon$  (b) forms.



Scheme 1. Synthesis of syndiotactic polystyrene (sPS) and multiblock copolymers syndiotactic polystyrene-co-1,4-cis-polybutadiene (sPSB).

*cis*-polybutadiene (sPSB) have been applied as support of gold nanoparticles (AuNPs) to produce interesting examples of confined catalysis. Actually, the peculiar properties of the polymer matrix, in terms of permeability to solvents and small reactants, allowed new reactivity patterns in organic synthesis [37–44]. AuNPs embedded in sPSB polymer matrix in the  $\epsilon$  nanoporous form (AuNPs-sPSB) were successfully applied in the aerobic oxidation of various aromatic, allylic and alkyl alcohols [37,38,40,42,45]. The elective aerobic oxidation of benzyl alcohol to benzaldehyde was achieved with a complete conversion of the reagent in 6 h with selectivity of 97% [37]. The head-to-head comparison of geraniol and 1-butanol yielded different results under the same experimental conditions: for the former, conversion and selectivity were respectively 29% and >99%, whereas 1-butanol was not reactive at all. These findings were explained considering the different accessibility of the alcohol to the gold catalyst throughout the polymer support [39,46,47]. This hypothesis was further confirmed in the study of the cascade aerobic oxidative esterification of cinnamyl alcohol with alkyl alcohols. Cinnamyl alcohol is rapidly oxidised to cinnamaldehyde following first-order kinetics; the hemiacetal resulting from the nucleophilic attack of the alkyl alcohol to cinnamaldehyde is further oxidised to alkyl cinnamate following zero-order kinetics [38]. The permeability of the alkyl alcohol is controlled precisely by the nanoporous polymer support in  $\epsilon$  form. Another excellent example is the reduction of nitroarenes with  $\text{NaBH}_4$  catalysed by polymorphic AuNPs-sPSB [39]. The polymer

support in the  $\beta$  and  $\gamma$  crystalline forms, scarcely permeable to small molecules, led to the partial reduction of nitrobenzene to azoxybenzene and diazobenzene. In contrast, the polymer support in the nanoporous  $\delta$  and  $\epsilon$  crystalline forms, highly permeable to nitrobenzene, efficiently catalysed its complete reduction to aniline [39].

Interesting selectivity patterns were also observed using nanoporous PPO as support of AuNPs. The advantage of using this polymer support comes from the commercial availability, its high thermal stability ( $T_g = 211^\circ\text{C}$ ,  $T_m = 268^\circ\text{C}$ ), for which it is mainly employed in electronics, structural parts, household and automotive items [43]. Heating of commercial semi-crystalline PPO powders at  $170^\circ\text{C}$  or  $220^\circ\text{C}$  for 5 h, as well as the solvent treatment with decalin, toluene or chloroform, produce amorphous PPO. Crystalline PPO is obtained through treatment with e.g. 1,2-dichloroethane or tetralin [4]. The AuNPs-PPO catalyst was successfully applied in alcohol oxidation in water as solvent [43].

Considering the intriguing reactivity patterns obtained with the gold catalysts at the variance of crystallinity of the polymer support, reaction solvent and temperature, we aimed to investigate the polymorphic behaviour of sPS and sPSB and herein reported [48–56]. The complex polymorphism of the sPS was also found in sPSB copolymers, even with short styrene segments. The thermal behaviour of these copolymers, in terms of melting enthalpy and temperature, was investigated at the variance of styrene content.

## 2. Experimental section

### 2.1. General considerations and materials

The manipulation of air- and moisture-sensitive compounds was performed under a nitrogen atmosphere using standard Schlenk techniques and an MBraun glovebox. Toluene (99.5%, Carlo Erba) was used as received or dried over calcium chloride, refluxed over sodium for 48 h and distilled under nitrogen atmosphere before use in moisture- and oxygen-sensitive reactions. Acetonitrile (99.9%, Romil), chloroform (99.5%, Sigma-Aldrich), tetrahydrofuran (99.9%, Romil), methanol (99.8%, Sigma-Aldrich), 1-chlorodecane (98%, Aldrich), potassium bromide (FTIR grade, Sigma-Aldrich) and 1,1,2,2-tetrachloroethane- $d_2$  (TCE- $d_2$ ; Sigma-Aldrich) were used as received. Syndiotactic polystyrene (sPS) and multiblock copolymers syndiotactic polystyrene-co-1,4-cis-polybutadiene (sPSB) [48–56] were synthesised according to literature procedures (Scheme 1) [53]. Polymer composition [51], syndiotacticity [51] and average styrene block length [48] were determined by NMR spectroscopy, according to previous reported procedures [48,51]. The syndiotacticity for the polymers used in this study was higher than 95%. The in Polybutadiene (PB) segments showed mainly *cis*-1,4

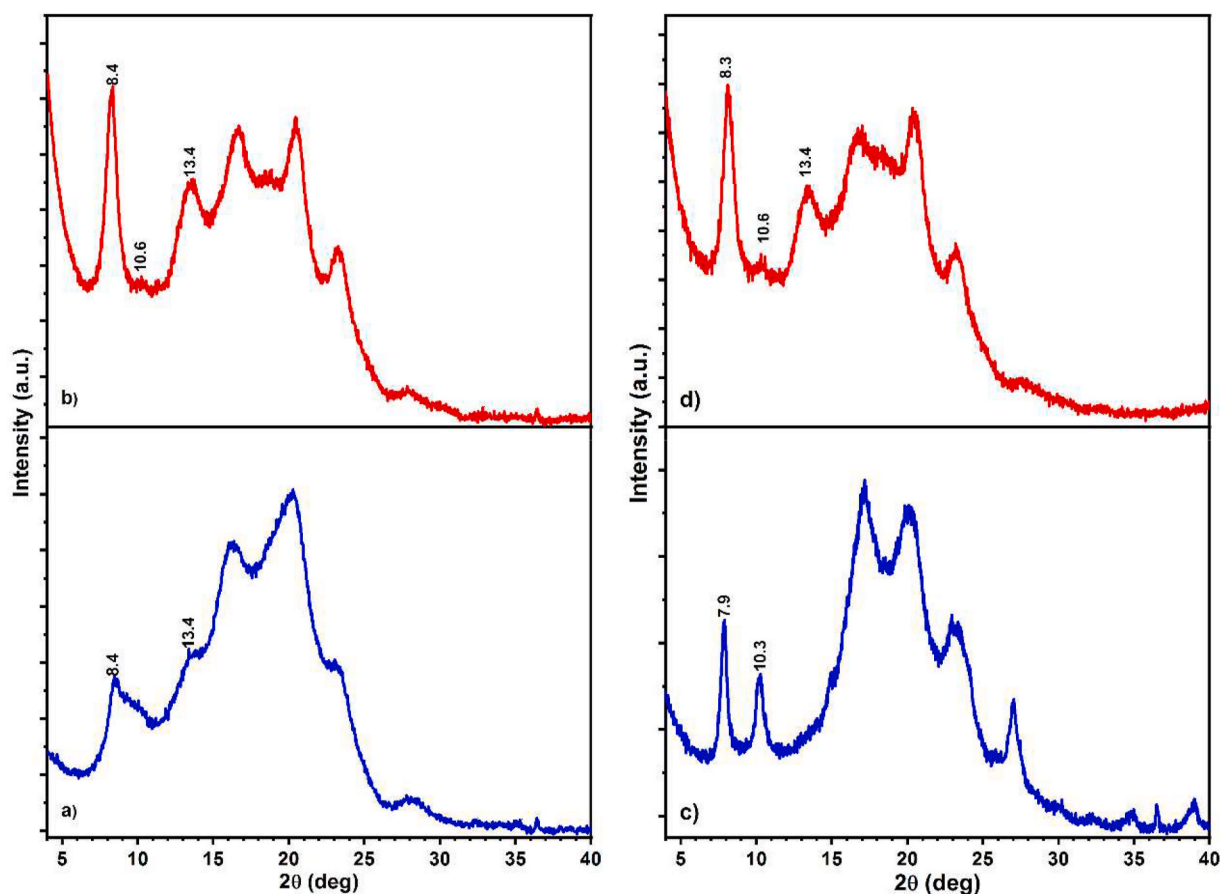


Fig. 2. X ray diffraction patterns of sPS (on the left) and sPS<sub>88B</sub> (on the right) powders: a) sample 1—CC  $\delta_{\text{tol}}$ ; b) sample 1—NC  $\delta$ ; c) sample 2—CC  $\delta_{\text{tol}}$ ; d) sample 2—NC  $\delta$ .

Table 1

Thermal, solvent and solvothermal treatments of sPS and sPS<sub>88B</sub>.

Entry	Polymer <sup>a</sup>	Sample N.—starting crystalline form	1st treatment	Sample N.—intermediate crystalline form	2nd treatment	Sample N.—final crystalline form
1	sPS	1—CC $\delta_{\text{tol}}$	CH <sub>3</sub> CN, rt	1—NC $\delta$	CHCl <sub>3</sub> /H <sub>2</sub> O	1—NC $\delta$
2	sPS <sub>88B</sub>	2—CC $\delta_{\text{tol}}$	—	—	CHCl <sub>3</sub> /H <sub>2</sub> O	2—NC $\delta$
3	sPS	1—CC $\delta_{\text{tol}}$	1) 280 °C, 2h; 2) -196 °C	3—am	CHCl <sub>3</sub> /H <sub>2</sub> O	3—NC $\delta$
4	sPS <sub>88B</sub>	2—CC $\delta_{\text{tol}}$	1) 280 °C, 2h; 2) -196 °C	4—am	CHCl <sub>3</sub> /H <sub>2</sub> O	4—NC $\delta$
5	sPS	1—NC $\delta$	THF/H <sub>2</sub> O	5—CC $\delta_{\text{THF}}$	—	—
6	sPS	1—NC $\delta$	Tol/H <sub>2</sub> O	6—CC $\delta_{\text{tol}}$	—	—
7	sPS	1—NC $\delta$	Cl-decane/H <sub>2</sub> O	7— $\gamma$	—	—
8	sPS	1—NC $\delta$	CHCl <sub>3</sub> /CH <sub>3</sub> OH	8—CC $\delta$	—	—
9	sPS	1—NC $\delta$	135 °C, 2h	9— $\gamma$	CHCl <sub>3</sub> /H <sub>2</sub> O	9— $\epsilon\delta$
10	sPS	1—NC $\delta$	CH <sub>3</sub> CN, reflux	10— $\gamma$	CHCl <sub>3</sub> /H <sub>2</sub> O	10— $\epsilon\delta$
11	sPS <sub>88B</sub>	2—CC $\delta_{\text{tol}}$	CH <sub>3</sub> CN, reflux	11— $\gamma$	CHCl <sub>3</sub> /H <sub>2</sub> O	11— $\epsilon\delta$
12	sPS	1—NC $\delta$	1) 135 °C, 2h; 2) 280 °C, 2h; 3) slow cooling	12— $\beta$	CHCl <sub>3</sub> /H <sub>2</sub> O	12— $\delta$
13	sPS <sub>88B</sub>	2—CC $\delta_{\text{tol}}$	1) 135 °C, 2h; 2) 280 °C, 2h; 3) slow cooling	13— $\beta$	CHCl <sub>3</sub> /H <sub>2</sub> O	13— $\delta$

<sup>a</sup> Subscript number indicates the styrene molar per cent content.

regiochemistry (85–87 mol%) and 1,2-vinyl units (12–15 mol%). Average molecular weights were in the range of 40–50 kDa, and dispersity indexes ( $M_w/M_n$ ) were in the range of 1.6–2.2, according to gel permeation chromatography (GPC) analyses.

## 2.2. Measurements and Characterisations

NMR spectra were recorded on AVANCE Bruker spectrometers: the chemical shifts are referred to tetramethylsilane as an external reference, using the residual protio signal of 1,1,2,2-tetrachloroethano-*d*<sub>2</sub> (TCE-*d*<sub>2</sub>). Wide angle x-ray diffraction (WAXD) patterns were obtained, in

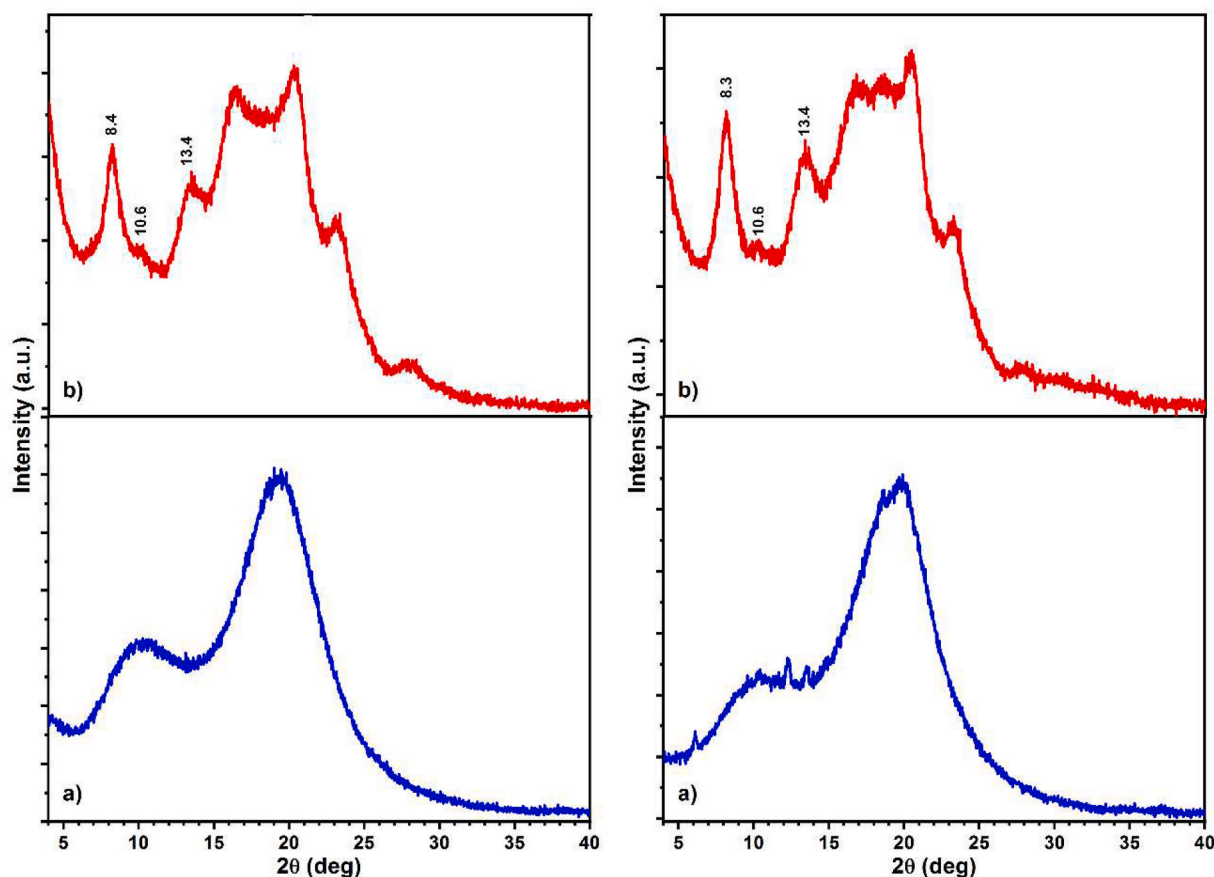


Fig. 3. X ray diffraction patterns of amorphous sPS (on the left) and sPS<sub>88B</sub> (on the right) powders: a) sample 3—am; b) sample 3—NC δ; c) sample 4—am; d) sample 4—NC δ.

reflection, with an automatic Bruker D8 powder diffractometer using nickel-filtered Cu K $\alpha$  radiation. Fourier transform infrared (FTIR) spectra (64 scans, resolution of 2 cm $^{-1}$ ) were recorded as KBr disks on a Bruker Vertex 70 spectrometer equipped with deuterated triglycine sulphate detector and a Ge/KBr beam splitter. Diffuse infrared reflectance Fourier transform (DRIFT) measurements were performed by mounting a dedicated module on the FTIR spectrometer: the polymer gels were poured on paper sheet, in order to remove the water, loaded on the sample holder and rapidly analysed. Differential scanning calorimetry (DSC) analysis was carried out on a TA Instrument DSC 2920 calorimeter (heating rate of 10 °C/min). The thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 (heating rate of 10 °C/min). GPC analyses were performed with GPCV 2000 chromatograph from Waters Instruments equipped a set of four columns (PSS-USA), a viscosimeter detector and a refractive index detector. The calibration was performed with PS standards with molecular weight in the range of 10 $^6$  to 10 $^2$  Da. The analyses were carried out using 1,2-dichlorobenzene as solvent carrier at 135 °C with a flow rate of 1.0 mL min $^{-1}$ .

## 2.3. Protocols for phase transformations

### 2.3.1. Emptying of the clathrated forms

300 mL of acetonitrile and 1.00 g of sPS were introduced in a 500 mL round bottom flask equipped with a stir bar and stirred for 24h. The suspension was filtered, the polymer was washed with fresh acetonitrile, recovered and dried in vacuo.

### 2.3.2. Phase modification by treatments with solvent mixtures

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 7.5 mL of chloroform and 7.5 mL of water and under stirring were introduced 0.50 g of sPS. The suspension was kept under vigorous stirring (1200 rpm) for 120 h, poured in 200 mL of methanol, filtered, washed with fresh methanol and the recovered polymer was dried in vacuo. For the different solvent mixture treatments explored was maintained the ratio: 0.50 g of polymer/7.5 mL of non-polar solvent/7.5 mL of polar solvent.

### 2.3.3. Phase modification by thermal treatments

sPS samples in  $\gamma$  form were obtained by treatment directly at 135 °C for 2 h, under a protective N $_2$  atmosphere. Polymers in  $\beta$  form were obtained from the melt by treatment directly at 280 °C of the sample previously converted in  $\gamma$  form, for 2 h under N $_2$  atmosphere, followed by slow cooling performed on the hot plate turned off and allowed to cool at room temperature. Amorphous polymers were obtained by direct treatment at 280 °C for 2 h under a protective N $_2$  atmosphere followed by quenching in liquid N $_2$ .

### 2.3.4. Phase modification by solvothermal treatments

The conversion of sPS or sPSB powders in  $\gamma$  form by reflux in acetonitrile (depicted for the sample 10— $\gamma$ ) is below reported. 1.00 g of sPS and 30 mL of acetonitrile were introduced in a 500 mL round bottom flask equipped with a magnetic stir bar, a condenser and an oil bath, heated to the reflux of the solvent and kept for 15 min. The suspension was allowed to cool to room temperature, filtered, and the polymer was recovered by filtration and dried in vacuo.

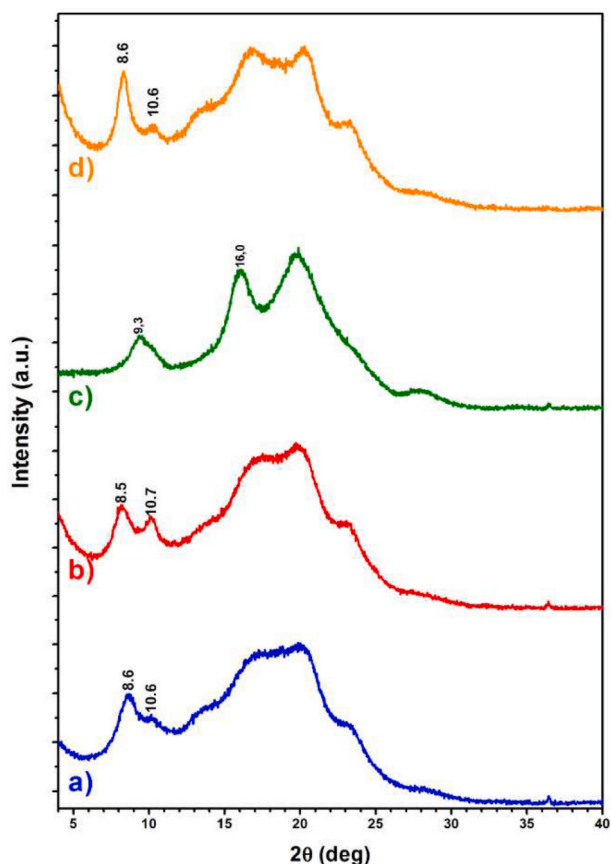


Fig. 4. WAXD patterns of sPS powders: a) sample 5—CC  $\delta_{\text{THF}}$ ; b) sample 6—CC  $\delta_{\text{tol}}$ ; c) sample 7— $\gamma$ ; d) sample 8—CC  $\delta$ .

### 3. Results and discussion

The pristine sPS and sPSB samples used in this study were obtained by solution polymerisation processes in toluene (Scheme 1) that produces crystalline polystyrenic domains in the co-crystalline phase with toluene (sample 1—CC  $\delta_{\text{tol}}$ ); the corresponding x-ray diffraction patterns (WAXD) are reported in Fig. 2a and c, respectively. The treatment of CC  $\delta_{\text{tol}}$  samples with a chloroform/water solvent mixture and the precipitation of the polymer in methanol followed by drying ( $\text{CHCl}_3/\text{H}_2\text{O}$  v/v = 1/1; see the experimental section for details) afforded the formation of the NC  $\delta$  phase, highly crystalline, as clearly evidenced by the strong intensities of the x-ray reflection peaks located at  $2\theta = 8.4^\circ$  and  $2\theta \sim 13.4^\circ$  associated to (010) and (101) crystallographic planes of NC  $\delta$  phase [25] (entries 1 and 2 of Table 1; see the diffractograms b and d in Fig. 2).

The observed enhancement of the polymer crystallinity suggests the conversion of the amorphous phase in the  $\delta$  form. To confirm this possibility, sPS and sPSB were amorphized by rapid quenching from the molten state (sample 3—am and 4—am, entries 3–4 of Table 1, diffractogram a and c in Fig. 3), stirred in chloroform/water, washed in methanol followed by drying: the formation of the NC  $\delta$  phase was observed (sample 3— $\delta$  and 4— $\delta$ , entries 3–4 of Table 1, diffractogram b and d in Fig. 3).

The relative crystallinity of the pristine sample 1—CC  $\delta_{\text{tol}}$ , determined from the WAXD data [57,58], was of 30%, and after treatment with  $\text{CHCl}_3/\text{H}_2\text{O}$ , for the corresponding sample 3—NC  $\delta$ , the crystallinity reached the relative value of 43%. Starting from the amorphous sPS (sample 3—am), after treatment with  $\text{CHCl}_3/\text{H}_2\text{O}$ , the crystallinity was of 35%.

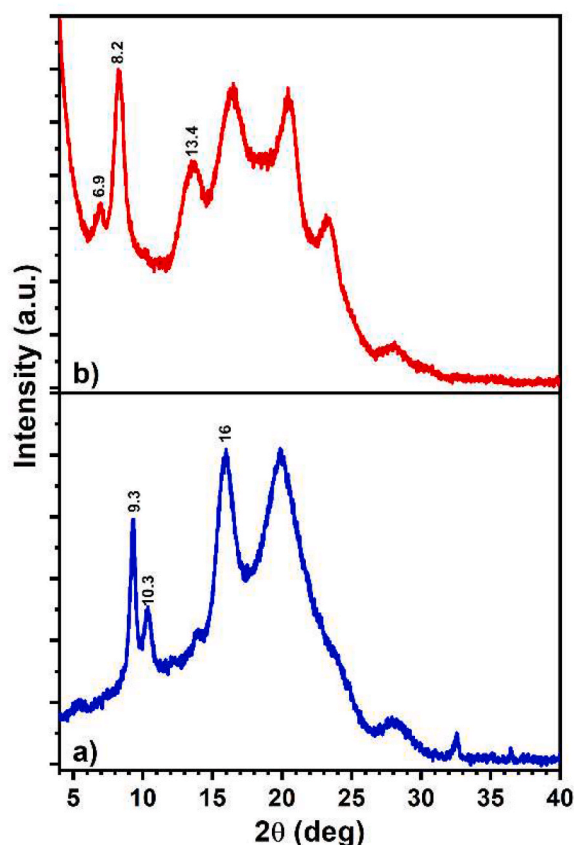


Fig. 5. Treatment of sPS  $\gamma$  form (thermally obtained at  $135^\circ\text{C}$ ; diffractogram a; sample 9— $\gamma$ ) by stirring in  $\text{CHCl}_3/\text{H}_2\text{O}$  solvent mixture (diffractogram b; sample 9— $\epsilon\delta$ ).

The mixture of chloroform and water was the unique able to address the formation of the highly crystalline NC  $\delta$  form. Replacement of chloroform with other hydrophobic solvents, guest molecules for the sPS, such as tetrahydrofuran (THF) and toluene, leads to the formation of the CC  $\delta$  phases (sample 5—CC  $\delta_{\text{THF}}$  and 6—CC  $\delta_{\text{tol}}$ , entries 5 and 6 of Table 1; Fig. 4 a and b). Different was the result of the replacement of chloroform with a bulky non-guest molecule, such as 1-chloro-decane [32]: the  $\gamma$  form showing the typical diffraction peaks located at  $2\theta = 9.3^\circ$  and  $2\theta = 16^\circ$  was obtained by the treatment with 1-chlorodecane/water solvent mixture (sample 7— $\gamma$ ; entry 7 of Table 1; Fig. 4c). On the other hand, replacing water with another polar solvent, such as methanol, did not produce further improvement in crystallinity, leading to the formation of the CC  $\delta$  phase (sample 8—NC  $\delta$ , entry 8 of Table 1; Fig. 4d).

The  $\gamma$  form can be converted into the  $\epsilon$  phase by treatment with chloroform vapours [59]. Powder of sPS in  $\gamma$  form, obtained by treatment of 1—NC  $\delta$  at  $135^\circ\text{C}$  for 2 h (sample 9— $\gamma$ , entry 9 of Table 1, Fig. 5a), even if finely grounded, were converted into a mixture of  $\gamma$  and  $\epsilon$  forms by exposition to chloroform vapour for 14 days, accounting for the difficult formation of the  $\epsilon$  form from bulk polymer powders. On the contrary, the treatment of 9— $\gamma$  with the solvent mixture of chloroform and water converted the total amount of  $\gamma$  phase into  $\epsilon$  phase already in only 1 h (see peaks at  $2\theta = 6.9^\circ$  and  $8.2^\circ$  associated to the diffraction of (110) and (020) crystallographic planes typical of  $\epsilon$  phase [6]) with a high crystallinity degree too; the presence of  $\delta$  phase was also identified by the strong intensity of the peak at  $2\theta = 13.4^\circ$  typical of  $\delta$  phase (sample 9— $\epsilon\delta$ ; entry 9 of Table 1; Fig. 5b). The presence of the  $\delta$  phase can be ascribed to the crystallisation of the amorphous phase, as above

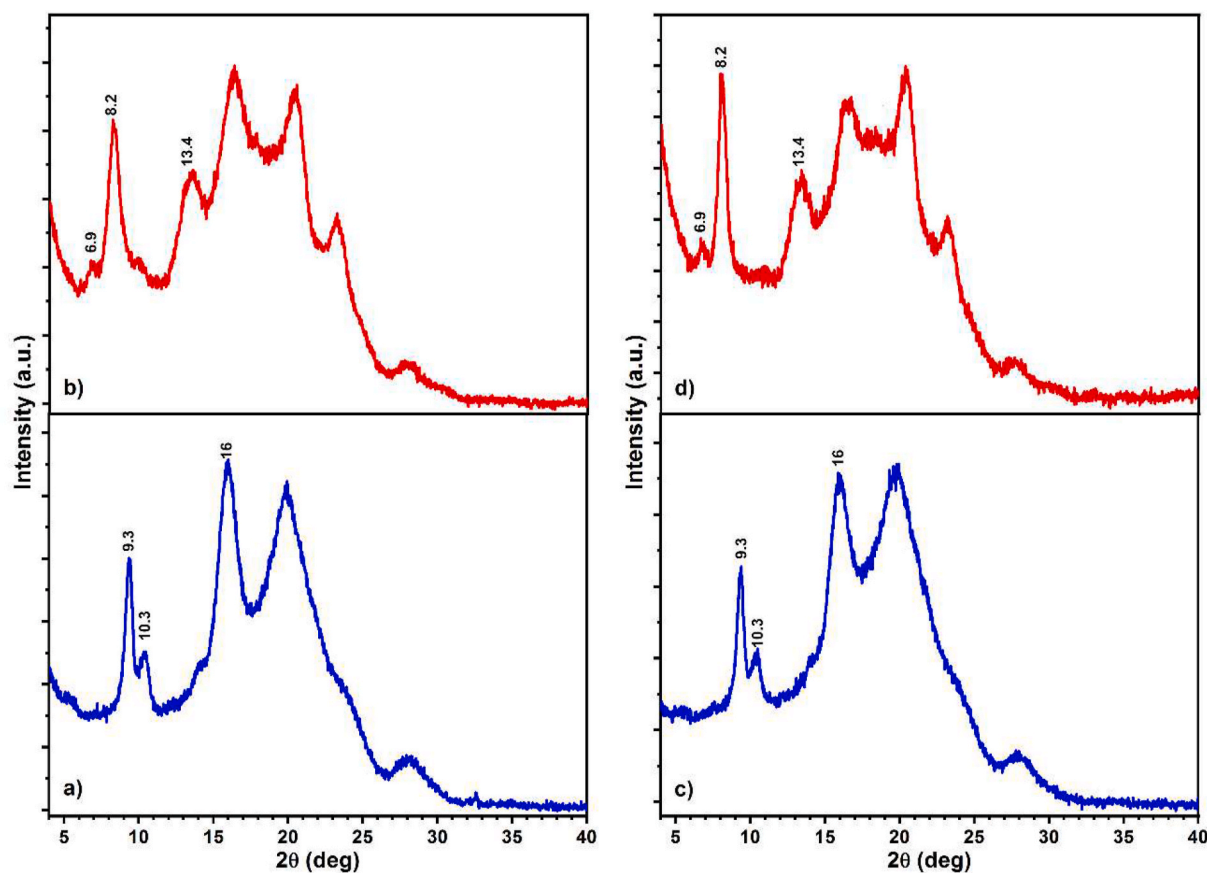


Fig. 6. Solvothermally obtained  $\gamma$  form (by reflux in  $\text{CH}_3\text{CN}$ ) of sPS (on the left) and sPS<sub>88B</sub> (on the right) and subsequent conversion in  $\epsilon+\delta$  mixture ( $\text{CHCl}_3/\text{H}_2\text{O}$  treatment).  $p$ -WAXD patterns of: a) sample 10- $\gamma$ ; b) sample 10- $\epsilon\delta$ ; c) sample 11- $\gamma$ ; d) sample 11- $\epsilon\delta$ .

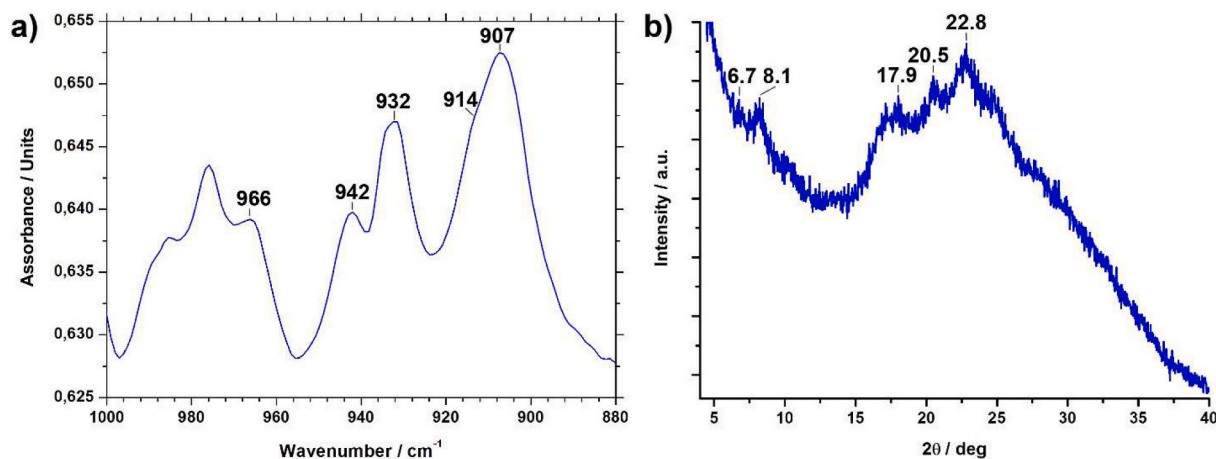


Fig. 7. DRIFT (a) and WAXD (b) analyses of the suspension in  $\text{CHCl}_3/\text{H}_2\text{O}$  of sPS, initially in  $\gamma$  form (sample 10- $\gamma$ ), converted in CC phases.

demonstrated (see entries 3–4 of Table 1).

Interestingly, the  $\gamma$  form can also be obtained via a solvothermal treatment. Refluxing sPS or sPSB in acetonitrile for only 15 min affords the quantitative formation of the  $\gamma$  form (samples 10- $\gamma$  and 11- $\gamma$ ; entries 11 and 12 of Table 1; see Figs. 8a and 9a), which can be transformed into the  $\epsilon$  form by treatment with chloroform and water solvent mixture (samples 10- $\epsilon\delta$  and 11- $\epsilon\delta$ ; entry 10 and 11 of Table 1; see

Fig. 6 b and d); intense diffraction peaks at  $2\theta = 8.2^\circ$  and  $13.4^\circ$  reveal the presence of  $\delta$  phase also in these samples (Fig. 6 b and d). Refluxing sPS (sample 1-NC) samples in bulky non-guest solvent molecules, such as 1-chlorodecane, 1-bromo-octane, ethyl nonanoate, 1-dodecene, 3,5-di-tertbutyltoluene, or 1-chloro-tetradecane, also induce the formation of the  $\gamma$  form.

To evaluate if the illustrated phase modifications occur during the

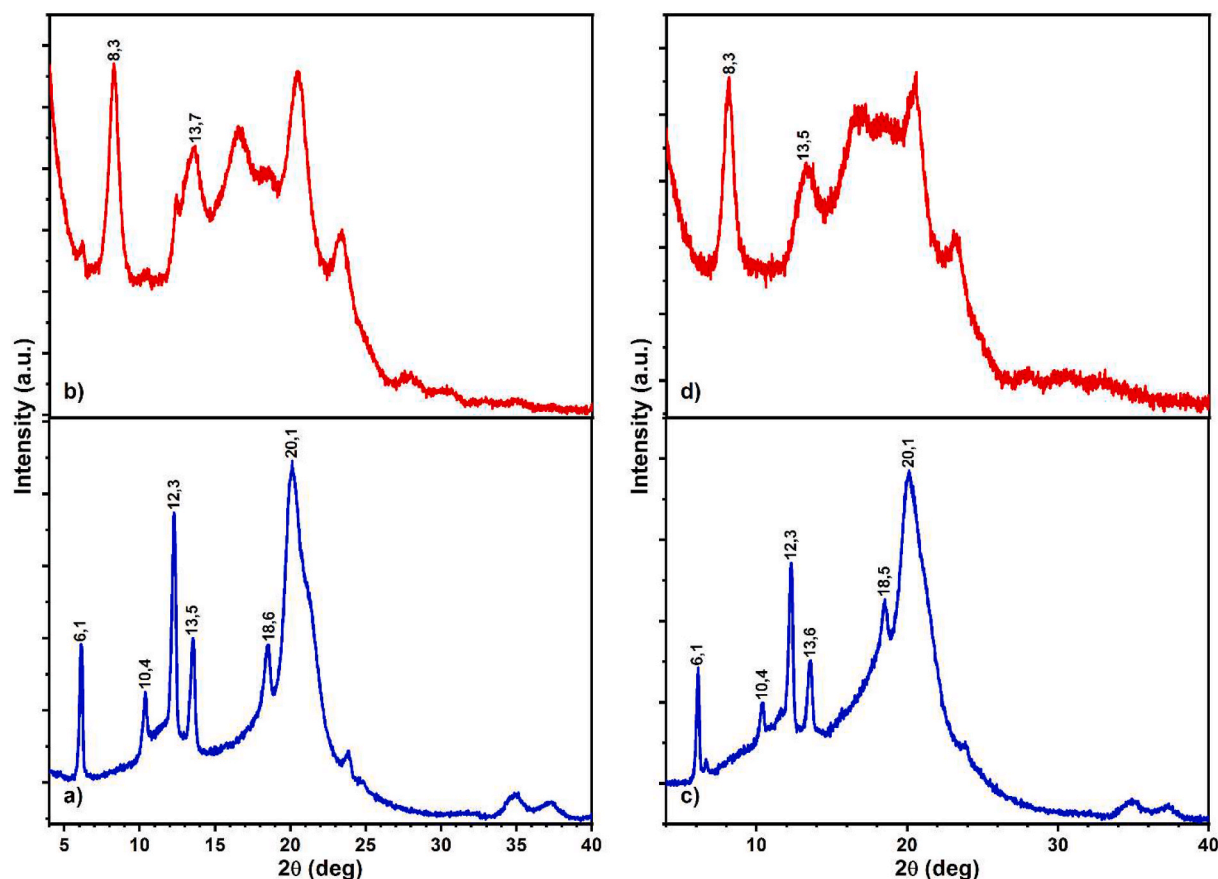


Fig. 8. Conversion of  $\beta$  form of sPS (on the left) and sPS<sub>88B</sub> (on the right) into  $\delta$ . WAXD patterns of: a) sample 12- $\beta$ ; b) sample 12- $\delta$ ; c) sample 13- $\beta$ ; d) sample 13- $\delta$ .

solvent treatment, during the precipitation in methanol or even at the stage of the solvent evaporation, the sPS suspension was analysed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and WAXD. sPS in  $\gamma$  form (sample 10- $\gamma$ ) was stirred in chloroform and water for 24 h, deposited onto a paper sheet to remove the excess of water, transferred to the DRIFT sample holder and rapidly analysed, identifying the formation of the  $\epsilon$  phase in this stage of the treatment. Fig. 7a reports the DRIFT spectrum of the polymer gel attributed to the  $\epsilon$  phase (diagnostic bands at  $907\text{ cm}^{-1}$  with shoulder at  $914\text{ cm}^{-1}$ ). The attribution was also confirmed by WAXD analysis of the same gel deposited on a glass slide (WAXD pattern in Fig. 7b labelled with diagnostic reflections). This information confirms the formation of the co-crystalline phases during the treatment with chloroform/water mixture.

Typically, the compact and scarcely permeable  $\beta$  form cannot be converted into other crystalline forms of sPS. Samples of sPS and sPSB were transformed into the  $\beta$  form by slow cooling of the melt polymers and treated with chloroform and water (entry 12 and 13, Table 1); unexpectedly, the conversion of this phase into NC phase was assessed (sample 12- $\delta$  and 13- $\delta$ , Table 1; Fig. 8).

The sPSB multiblock copolymer, remarkably, present the same polymorphism of sPS (see Fig. 9).

Samples of the sPSB copolymers with styrene composition higher than 40 mol%, *i.e.* with an average styrene block length higher than nine units, are semi-crystalline [48,52]. Crystallinity in the sPSB samples was determined at variance of styrene concentration using the melting enthalpy in the DSC profiles (Fig. 10). As styrene concentration increases in the polymer samples at values higher than 40 mol%, the melting temperature gradually increases from  $230\text{ }^{\circ}\text{C}$  to  $260\text{ }^{\circ}\text{C}$  along with melt

enthalpy values as a result of longer syndiotactic polystyrene homosequences and ticker crystalline domains.

#### 4. Conclusion

Solvent annealing is proven as a valid alternative to thermal treatments for addressing crystal structure and the crystallinity degree in sPS and sPSB samples. The treatment of polymer powders of sPS in the NC and CC  $\delta$  forms with a mixture of chloroform and water led to a remarkable increase of the polymer crystallinity, likely because of crystallisation of the amorphous phase; this proposal was also confirmed by crystallisation of fully amorphous polymers. Alternative solvent mixtures were explored, replacing chloroform with suitable guest solvents for sPS (e.g. toluene, THF) or not guest solvent (1-chlorodecane), but they do not promote further enhancement of crystallisation of sPS. The treatment of the  $\gamma$  form with the chloroform/water mixture produces the formation of the NC  $\epsilon$  form with enhanced crystallinity.

A method for obtaining  $\gamma$  phase samples has been described. When polymer powders in the  $\delta$  form were stirred in boiling acetonitrile, the quantitative conversion in the  $\gamma$  form was observed. Likely, this solvent, at its boiling temperature, causes the lowering of the glass transition ( $T_g$ ) of the sPS, allowing the transition of the  $\delta$  into the  $\gamma$  form at a lower temperature (normally occurring at  $135\text{ }^{\circ}\text{C}$ ).

The crystalline sPSB multiblock copolymers with styrene composition higher than 40 mol% showed the same complex polymorphism of sPS. The crystallinity and the melting temperature depend on the styrene content.

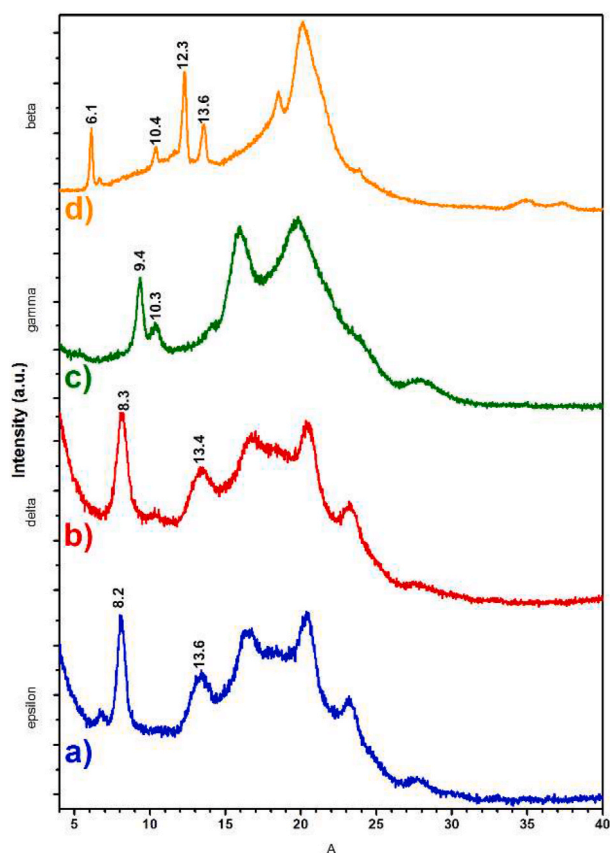


Fig. 9. Polymorphism of sPSB: WAXD patterns of sPS<sub>88</sub>B with  $\epsilon$  (a),  $\delta$  (b);  $\gamma$  (c) and  $\beta$  forms.

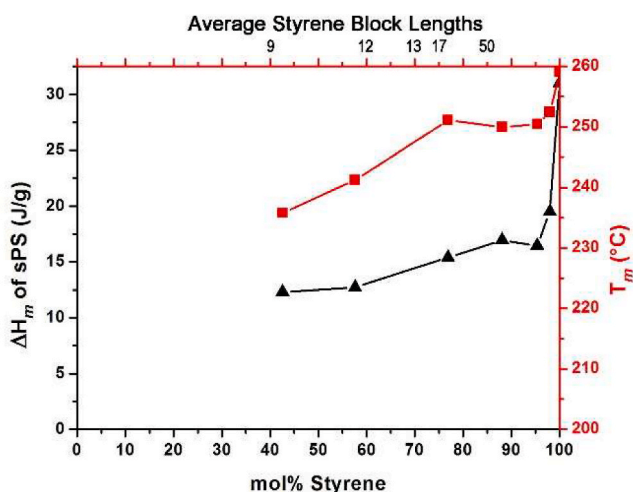


Fig. 10. Variation of melting enthalpy ( $\Delta H_m$ ,  $\blacktriangle$ ) and temperature ( $T_m$ ,  $\blacksquare$ ) of crystalline sPS domains in sPSB copolymers at variance of the styrene molar content and the relative length of polystyrene segments.

#### CRedit authorship contribution statement

**Antonio Buonerba:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Paola Rizzo:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Carmin Capacchione:** Writing – review & editing, Validation, Investigation, Funding acquisition, Formal analysis. **Alfonso**

**Grassi:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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