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(Article begins on next page)

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# Control of morphology orientation in thin films of PS-*b*-PEO diblock copolymers and PS-*b*-PEO/resorcinol molecular complexes

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## **Abstract**

One of the main limits in the use of block copolymers for nanotechnological applications lies in the poor control over the alignment of the nanoscopic domains. The self-assembling behavior of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) has been modified by stoichiometric complexation of the ethylene oxide units with resorcinol and a simple procedure to prepare nanostructured films with normally oriented cylinders is reported. By direct spin-coating of a series of complexated PS-*b*-PEO samples with different molecular weight and composition, films with the same morphology and orientation (i.e. normally oriented packed cylinders) have been obtained, also when different nanostructures and alignments were expected on the basis of the volume fraction composition and self-assembling behavior of pure copolymers. Tuning of the cylinder diameters in the range from 20 to 50 nm was possible by varying the length of the PEO block. The effects of resorcinol complexation have been studied by differential scanning calorimetry and X ray diffraction and the morphologies of PS-*b*-PEO and PS-*b*-PEO/resorcinol films have been monitored by atomic force microscopy and electron microscopies. DSC and XRD analyses demonstrate that resorcinol significantly influences the crystallization behavior of the PEO block. The varied interfacial and surface energies of the PEO domains and the overall reduction of the crystalline phase in PS-*b*-PEO/resorcinol films appear to be strictly related to the morphological changes occurring by complexation.

## **Keywords**

Block copolymers; orientation; self-assembly; supramolecular interactions.

## **1. Introduction**

In the last decade block copolymers have received an ever increasing attention in the nanoscience and nanotechnology research [1-4]. The main reasons that have made block copolymers promising and

efficient candidates for the preparation of a wide range of periodic structures in the nanoscopic length scale are: a) the dimension of the domains, which is in the range of tens of nanometers; b) the self-assembling capability of block copolymers, that is related to the thermodynamic incompatibility of the blocks and that drives them to segregate in different domains, e.g. lamellar, gyroid, hexagonal and body-centered cubic for diblock copolymers; and c) the convenient size and shape tunability of these nanodomains, provided by simply changing their molecular weights and compositions, the chain architecture and the chemical interactions existing between the blocks [5].

In many advanced applications (functional membranes and coatings, optoelectronic devices, etc.) polymers are used in the form of thin films. It is under this form that block copolymer systems are exploited with the aim of obtaining controlled morphological patterns well extended in surface and with the desired orientation. It is well known that structural behavior of thin layers compared with bulk materials is often much more complicated. Due to the prevalence of surface and interface forces, thin films of block copolymers may undergo both surface relaxations and reconstruction, thus showing unexpected structural shapes [6,7]. In general, structural order over large extension can be created in self-organizing materials through several molecular interactions including hydrophilic and hydrophobic effects, hydrogen bonding, columbic interactions and van der Waals forces [8-11]. Different techniques have been used to increase the level of order in block copolymer films [12], such as application of electric fields [13,14], chemically patterned substrates [15,16], shear forces [17,18], controlled interfacial interactions [19] and temperature gradient [20]. Also thermal and solvent annealing have a great influence on the morphology of thin films formed by deep casting or spin coating [21-24]. Both the rate of solvent evaporation and solvent annealing have been invoked for interpreting strong effects of ordering and orientation on the nanostructured morphologies of block copolymers [25]. In particular, solvent annealing may improve the ordering in copolymer thin films, removing the defects of domain organization and achieving a long range lateral order [26-28]. The effects of solvent vapor treatments

appear to be time-dependent, showing high initial rates in the ordering behavior or differences in the nanostructures with treatment times [7,29].

A supramolecular approach to block copolymer self-assembly, based on attractive hydrogen bonding interactions between different block copolymers [30] or between one of the blocks and small molecules bearing hydroxyl and/or carboxylic groups [31], has been also proposed. This approach appears to provide a simple and powerful technique for fine tuning of the block copolymer morphologies, and has been successfully applied in bulk and in thin films.

Interesting results have been obtained by complexation of polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) copolymers with different small molecules like, for example, 1,5-dihydroxynaphthalene [32], 3-*n*-pentadecylphenol [33,34] and 2-(4'-hydroxybenzeneazo)benzoic acid [35]. In all such cases the small molecules contain hydroxyl groups which selectively interact with the pyridine nitrogen of PS-*b*-P4VP via hydrogen bonding, driving the block copolymer complex to the formation of ordered nanostructured films with specific domain orientations depending on the applied experimental conditions of solvent annealing.

Most of the studies on the supramolecular approach to nanoscale structures have been so far performed with PS-*b*-P4VP copolymers, however the same strategy may be positively adopted with other block copolymers as long as one of the blocks may interact specifically with some probe molecules. In particular polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers appear to be a natural choice as they are already known to form thin films with nanostructured patterns whose extent and orientation is affected by solvent treatments [19,28].

In this work we present the most significant results of a basic and comprehensive study carried out on self-assembled PS-*b*-PEO thin films with the final aim to propose a methodology of wider applicability for the fabrication of well-oriented block copolymer morphologies. We have investigated in some detail the self-assembling behavior of three different PS-*b*-PEO samples, taking into account the consequence

of introducing supramolecular interactions in the block copolymer films. We showed for the first time that by spin coating PS-*b*-PEO solutions containing resorcinol is possible to obtain directly nanostructured films with relatively well ordered PEO/resorcinol packed cylinders oriented perpendicularly to the substrate, independently on the block copolymer molecular weight. This behavior is likely to depend on the changes introduced in the crystalline block: complexated PEO has a different crystallographic structure than pure PEO, interfacial and surface energies of PEO domains must be affected by complexation with resorcinol and the overall amount of crystalline phase in the complexated block copolymer films decreases with respect to the amorphous one.

## **2. Experimental**

### *2.1. Materials*

PS<sub>563</sub>-*b*-PEO<sub>705</sub> ( $M_n = 58600$ -*b*- $31000$ ), PS<sub>308</sub>-*b*-PEO<sub>250</sub> ( $M_n = 32000$ -*b*- $11000$ ) and PS<sub>183</sub>-*b*-PEO<sub>145</sub> ( $M_n = 19000$ -*b*- $6400$ ) were purchased from Polymer Source Inc. (Dorval, Canada) and used without further purification in this study. The volume fraction of the PEO block ( $\Phi_{PEO}$ ) is:  $\Phi_{PEO} = 0.36$  for PS<sub>563</sub>-*b*-PEO<sub>705</sub> and  $\Phi_{PEO} = 0.24$  for both PS<sub>308</sub>-*b*-PEO<sub>250</sub> and PS<sub>183</sub>-*b*-PEO<sub>145</sub>. Resorcinol and benzene were both purchased from Sigma-Aldrich.

### *2.2. Films preparation*

PS-*b*-PEO benzene solutions were prepared at a concentration of 5 wt%. PS-*b*-PEO and resorcinol mixtures with a molar ratio resorcinol:ethylene oxide (R:EO) of 1:2 were also dissolved in benzene. A few drops of each solution were spin-coated onto mica substrates, using a 8'' Desk-top Precision Spin Coating System, model P-6708D vs. 2.0. All the films were prepared following the same spin coating program in order to reproduce the film thickness and therefore avoid variations in the film nanostructure. After spin coating the films were dried in a hood at ambient temperature for at least 12

hours in order to have a complete evaporation of the solvent. Post-evaporation solvent vapor treatments were performed under a saturated benzene atmosphere in a hermetic Pyrex flask preheated at 60°C.

### *2.3. Characterization*

Atomic Force Microscopy (AFM) was used to obtain information on the block copolymer film morphologies. Analysis were performed in air at room temperature with a Park Systems instrument, model XE-100, operating in tapping mode. A silicon microcantilever with the reflective side coated with aluminium (force constant 20 N/m and resonance frequency of 265 kHz) and conical silicon tips (radius of curvature less than 10 nm, tip height 15~20 µm, full tip cone angle less than 30°) were used for the scanning. Scan rates were set between 1 and 2 Hz. Topographic (height-mode) and viscoelastic (phase-mode) data were recorded simultaneously.

Transmission electron microscope (TEM) studies were performed on a Philips CM-12, working at an accelerating voltage of 100 kV or on a Zeiss Libra 120. In order to prepare cross sectional specimens, films were embedded in a low viscosity modified Spurr epoxy resin, which was cured at 60 °C. After trimming to shape by a Leica EM TRIM, ultrathin sections (less than 100 nm) were cut at room temperature using a Leica Ultracut UCT microtome equipped with a diamond knife. At the end, ultrathin sections were collected in a trough filled with water and lifted onto Formvar coated copper grids. In order to prevent the diffusion of the epoxy resin into the polymer film, a thin layer of carbon was evaporated over the film surface. Top-view specimens were prepared by separating the thin films from the mica substrate, spun-coated as reported above, by floating it on water, due to the strong affinity of water for mica. Film fragments were then collected using Formvar coated copper grids. Scanning electron microscope (SEM) were performed with a Zeiss UltraPlus field emission SEM equipped with a Inlens detector.

Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the hydrogen bond interactions between block copolymers and resorcinol. Samples were prepared by solvent casting from



benzene onto silica wafers and transmission infrared spectra were collected with a Thermo-Nicolet FTIR Nexus instrument with a DTGS detector. The measurements were carried out in the spectral range of 4000-400  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and 32 scans.

Thermal analysis were carried out with a Q200 (TA Instruments) Differential Scanning Calorimeter equipped with a refrigerated cooling system in the temperature range from -100 to 150°C, with a scanning rate of 20°C/min and under nitrogen atmosphere. Sealed aluminium pans containing ~5 mg of samples were used.

X-ray diffraction (XRD) measurements of polymer films were carried out with a conventional rotating anode source (Siemens D5005). The drive axis was  $2\theta$  for a scan range of 10–35° with a step of 0.02°. High intensity Cu  $K\alpha$  X-rays, obtained after passing through both a  $k\beta$  filter and counter monochromator, were employed for the diffraction experiments.

### **3. Results and discussion**

Spun-cast thin films of PS-*b*-PEO copolymers with different composition in terms of block length and volume fraction have been prepared following the procedure described in the experimental section.

PS-*b*-PEO melts and solutions are systems in a hard confinement regime, that is PEO is expected to crystallize confined in microdomains since crystallization occurs at temperatures below the glass transition of the PS matrix. According to their volume fraction composition, the block copolymer samples considered in this study predominantly self-segregate in cylindrical morphologies or in mixed cylinders and lamellae when the PEO composition is closed to the domain transition composition. The film surfaces shown in Figures 1a-c exhibit non-equilibrium morphologies obtained by spin-coating PS-*b*-PEO solutions on mica sheets. Figures 1d-f show the improved and regular morphologies obtained by solvent annealing spun-cast films. On the basis of theoretical considerations PEO microdomains should be oriented parallel to the surface due to preferential interactions of the PEO

blocks with either air or the mica substrate. On the contrary some of the resulting morphologies are normally oriented. As already mentioned in the introduction, a number of factors can interfere in the ordering and orientation of nanodomains during the drying of the swollen film, and the dynamics of solvent evaporation and post-evaporation treatments appear to be among the most important ones. Being a non-selective solvent for both PS and PEO, benzene is able to effectively dissolve either blocks and to reduce preferential interactions not only in polymer solutions but also after casting, when the solvent still swells the film, thus allowing thermodynamically unfavorable morphologies. The AFM phase images of Figures 1a-c demonstrate that by spin coating block copolymer solutions nanophase separation occurs, but the morphology obtained is far from the equilibrium one.

Kinetic factors can direct nanophase separation as well. Solvent evaporation is a highly directional process and if it is sufficiently fast nanodomains may arrange in a vertical morphology, even if the in-plane one is more thermodynamically stable. On the other hand, low evaporation rate will produce a lower perpendicular orientation but higher lateral order because the chains have enough time to approach their thermodynamically stable equilibrium. Moreover, the solvent evaporation rate and the formation of a solvent evaporation gradient in the film depend on the solvent mobility, which is related to the domain size and shape, and to the copolymer chemical composition, molecular weight and, as it will be discussed further in this paper, to crystallinity.

For the samples with  $\Phi_{\text{PEO}} = 0.24$ , molecular weight, or some other molecular weight depending parameter, is clearly the key parameter that determines the final orientation: under the same, fast drying conditions, the PS<sub>308</sub>-*b*-PEO<sub>250</sub> sample has PEO cylinders aligned in the plane of the film (Figure 1b), while the lower molecular weight PS<sub>183</sub>-*b*-PEO<sub>145</sub> arranges preferentially in a vertical cylinder morphology (Figure 1c). In both cases the degree of lateral order is low and spinning speeds faster than 1000 rpm, i.e. the speed applied in the last step of preparation of the reported films, did not seem to significantly affect the orientation of the resulting morphologies.

A great improvement in the lateral ordering of nanodomains was achieved by placing the films under a benzene atmosphere for 24h at 60°C (Figure 1d,e,f). Post-evaporation solvent annealing induces a transition from the disordered to the ordered state which results in the highly regular morphologies shown in Figures 1d,e and f. These findings confirm the reported studies by Russell et al. [28,36-38] on the possibility to obtain normally oriented cylindrical arrays from a PS-*b*-PEO copolymer with very similar composition (around 25000 g/mol and  $\Phi_{\text{PEO}}$  of ca. 0.24) of the lowest molecular weight sample chosen for this study. Figure 1 demonstrates that this possibility can be extended to PS-*b*-PEO copolymers with longer chains and different molar composition thus obtaining highly oriented vertical lamellae and in-plane parallel cylinders.

Another important parameter affecting microdomain segregation in block copolymer films is the length of the annealing treatment. During solvent annealing of PS-*b*-PEO films under benzene vapor, which is a good solvent for both blocks, a number of morphological transitions have been observed. For example, after one hour of solvent annealing the unaligned PEO cylinders (Figure 1b) obtained by spin coating PS<sub>308</sub>-*b*-PEO<sub>250</sub>, acquire a periodic vertical orientation. Continued annealing to 15 hours causes another transition approaching the equilibrium morphology, that consists of long and extended cylinders oriented parallel to the substrate (Figure 1d). This structure is maintained also at longer annealing time, but after 48 hours the morphology appears altered due to the high mobility given by the solvent vapor to the block copolymer chains and to dewetting phenomena.

These observations demonstrate that both thermodynamic and kinetic effects can be exploited to guide self-assembling, but at the same time the number of factors affecting nanophase segregation is such that at the present level of knowledge it is very difficult to gain a full control over ordering and orientation on block copolymer films. As for the majority of nanotechnological applications the desired morphology is that of hexagonal-packed cylinders perpendicularly oriented, the design of a simple and straightforward method to prepare nanostructured films with this morphology is of great interest.

In this respect a supramolecular approach based on the addition of a small molecule that preferentially interacts with one of the block is very promising. Russell et al. showed that salt complexation of block copolymer films dramatically affects the orientation of cylindrical nanodomains producing normally orientated cylinder arrays with enhanced lateral order [39]. Here, we demonstrate that also the capability of resorcinol to complex EO units by hydrogen bonding can strongly affect the copolymer film morphology especially because of the modification either of surface and interface interactions and of the crystallization behavior of the PEO block. It is known that, compared with other molecules bearing hydroxyl groups, the hydrogen bond between resorcinol and PEO is relatively strong. The binary phase diagram for PEO/resorcinol blends exhibits two eutectic phase transitions at 40 and 80 °C, corresponding at resorcinol molar compositions of approximately 10 and 50%. In between the liquidus curve shows a maximum at 33 molar % resorcinol, pointing to the formation of a stoichiometric complex. In particular, the 2:1 molar ratio PEO/resorcinol complex may crystallize in two allotropic modifications,  $\alpha$  and  $\beta$ . The  $\alpha$  form consists in an orthorhombic unit cell containing eight EO monomer units and four resorcinol molecules and melts at approximately 90°C [40]. As for the scope of this work the  $\beta$  form can be ignored because it is rather unstable and rapidly transforms into the more stable  $\alpha$  form, as demonstrated by the presence of a single endotherm peak at approximately 90°C in DSC analyses (the melting signal of the  $\beta$  form is expected around 70°C).

By spin-coating the various copolymer/resorcinol solutions considered in this study, independently from the molecular weight and the composition of the PS-*b*-PEO copolymers, the PEO/resorcinol phase self-segregate in cylindrical domains with relatively good lateral order and perpendicular orientation, as clearly highlighted by TEM. Top-view and cross-sectional TEM images of unstained films from a PS-*b*-PEO/resorcinol solution (PS<sub>563</sub>-*b*-PEO<sub>705</sub>, molar ratio resorcinol:ethylene oxide 1:2) are shown in Figures 2a and b. In bright field images the PS matrix appears darker than the PEO domains possibly due to a greater electronic contrast, whereas the partial dishomogeneity of cylinder diameter in the top

view, apparently in contrast with the more homogeneous pattern visible in the AFM and SEM images (Figures 3a and b), is ascribed to a partial swelling (i.e. water solubilization) during the procedure of specimen preparation. In particular, the most direct evidence of the presence of well-oriented nanodomains came from cross section, where cylinders are seen to span perpendicularly across the entire film.

The topography of the film surface (Figure 3a) exhibits a regular assembly of nanosized depressions, approximately 7 nm deep, probably arising from shrinkage of the PEO/resorcinol domains during crystallization. The color contrast in AFM phase images proves that PEO/resorcinol cylinders are softer than the surrounding PS matrix. The result is a nanostructured polymer thin film with a medium surface roughness of few nanometers. Moreover, the AFM phase images in Figure 4 show the capability, through the simple procedure of film preparation here described, of tuning the cylinder diameters by varying the length of the PEO block. The films investigated had cylindrical nanophases with average cylinder diameters ranging from 18 nm for the copolymer with the shorter PEO block ( $M_n=6400$  g/mol), to 26 nm for the medium one ( $M_n=11000$  g/mol) and 45 nm for the longer PEO block ( $M_n=31000$  g/mol). High dimensional homogeneity was observed within each film.

Together these results indicate that complexation significantly modify the self-assembling behavior of PS-*b*-PEO copolymers. Assuming volumetric additivity of PEO and resorcinol, and ignoring any other effect directing the microdomain segregation, a lamellar structure should result from each of the three copolymer complexes. On the contrary the observed morphology is always normally oriented cylinders and this proves that the nanophase segregation process is governed by additional factors than the thermodynamic of self-assembling. To fully disclose the nature and number of forces that determine the final observed morphology further studies will be required, but it appears reasonable that the reduced difference between the glass transition temperature of PS (around 100°C) and the melting point of the PEO/resorcinol complex (90°C, also see the discussion of the DSC analyses reported below), with

respect to the PEO one (between 50 and 60°C), must have an effect on the crystallization forces acting almost at the same as the film formation. In these conditions the strong hydrogen bonds acting in the crystalline PEO phase, and in the amorphous one as well, allow to overcome the interfacial interactions governing the orientation of nanodomains in PS-*b*-PEO films.

The formation of hydrogen bonding between resorcinol and ethylene oxide units of PS-*b*-PEO copolymers has been demonstrated by infrared spectroscopy and differential scanning calorimetry. Figure 5 shows the infrared spectra of PS<sub>563</sub>-*b*-PEO<sub>705</sub> (a), resorcinol (b) and of the PS-*b*-PEO/resorcinol complex (c). According to Spěvák et al., that studied the formation of hydrogen bonding between PEO and different small molecules bearing polarized hydrogen atoms, the presence of a maximum in the hydroxyl absorption range at 3315 cm<sup>-1</sup> is specific of the hydrogen bonding interaction between resorcinol and the oxygen atoms of the PEO block [41]. Another evidence is in the spectral range from 1200 to 1000 cm<sup>-1</sup>, where some characteristic absorption peaks assigned to the C-O stretching of the ethylene oxide units (1114 and 1148 cm<sup>-1</sup>) and of resorcinol (1151 and 1167 cm<sup>-1</sup>) are slightly and regularly shifted indicating that in the presence of EO/resorcinol complexes the molecular environment is modified and characterized by a complex infrared absorption with maxima at 1087, 1110, 1147 and 1163 cm<sup>-1</sup>.

The formation of a complex between the PEO block and resorcinol is also proved by the shifting of the melting signal in the DSC curves [42]. Crystalline phases are strongly stabilized by hydrogen bonding and the strength of the hydrogen bond is reflected by the change in the melting transition. The PEO/resorcinol complex (curve c in Figure 6), that is entirely in the  $\alpha$  form, melts at a temperature approximately 30°C higher than the corresponding pure block copolymer (curve b in Figure 6). In curve c the absence of the melting signal of resorcinol confirms the complexation with EO. Moreover, the changes observed in the DSC curves of PS-*b*-PEO films and PS-*b*-PEO/resorcinol ones perfectly match with those expected for PEO and PEO/resorcinol complexes. This also confirms that the phase diagram

of the PEO/resorcinol system is negligibly affected by polystyrene. The glass transition temperature of the PS block, and as a consequence its chains mobility, does not appear to be influenced by resorcinol, which is totally embedded in the PEO domains, either in the 2:1 EO/resorcinol complex crystalline phase and in the amorphous PEO phase.

In addition to the weakened energy of the various interfaces the presence of resorcinol also influences the amount of crystalline phase in the copolymer films. An overview of the calorimetric data obtained from all the copolymer systems considered in this study is given in Table 1. From these values it is possible to make some interesting considerations on the development of the crystallization degree of the PEO block by effect of resorcinol. In the PS-*b*-PEO copolymers the heat of fusion decreases with decreasing the chain length. In particular, the DSC curve of the lowest molecular weight copolymer does not show a definite endothermic melting signal preventing the calculation of the heat of fusion. The films prepared after complexation of the block copolymer with resorcinol in stoichiometric proportion do not contain crystalline resorcinol phases and show a general reduction of the copolymer crystallization degree, especially for the higher molecular weight PEO block.

The same trend of the crystalline phase was also confirmed by X-ray diffraction analysis. The X-ray diffraction pattern of the PS-*b*-PEO/resorcinol complexes (Figure 7a,b and c, lower curves) differ from both pure copolymers (Figure 7a,b and c, upper curves) and resorcinol (Figure 8d) and this demonstrates that the complex has a different crystallographic structure, with smaller crystalline size. The structure is reasonably the same found for the 2:1 PEO/resorcinol system, even if SAXS should be performed to confirm this hypothesis [40]. In the complexated block copolymers of lower molecular weight the diffraction peaks of the PEO/resorcinol complex become proportionally less intense and the diffraction curve is dominated by the contribution of the amorphous phase, e.g. the introduction of the high crystalline resorcinol into PS<sub>563</sub>-*b*-PEO<sub>705</sub> and PS<sub>183</sub>-*b*-PEO<sub>145</sub> copolymers entailed a reduction of total crystallinity down to 9.2 % (from 13 %) and 2.5 % (from 9.7 %), respectively.

The observations done on the changes occurring to the crystalline block and to the degree of crystallization, combined with the morphologies of the PS-*b*-PEO copolymers studied, demonstrate that these two aspects are related to each other. Going back to Figure 1, the only copolymer that was able to arrange in perpendicular cylinders was the low molecular weight one, which is also the less crystalline sample. At the beginning of this discussion we explained the perpendicular orientation of Figure 1c in terms of a solvent evaporation directional effect able to orientate mobile low molecular weight polymer chains. It may be expected that under the same experimental conditions of solvent evaporation, chain mobility increases with decreasing the chain length. It is also well known that the presence of crystalline domains reduces the overall mobility of polymer chains. Thus, the formation of PS-*b*-PEO/resorcinol complexes, reducing the crystallinity of the polymer film and enhancing the mobility of polymer chains during film formation, must be a significant factor ‘forcing’ the complexed copolymers to self-segregate by spin coating giving perpendicular oriented PEO/resorcinol cylinders.

#### **4. Conclusions**

Self-assembling PS-*b*-PEO copolymers have been investigated for their capability of forming nanostructured thin films. Two different strategies have been followed to optimize and control order and alignment of the domains, namely solvent evaporation and selective supramolecular interaction of one of the blocks with an additional component.

Solvent annealing of block copolymer films has proved to increase lateral order resulting in well aligned nanodomains over large surface extension, but it is through the supramolecular approach that it was possible to achieve a unique control on the self-assembling, obtaining the desired morphology and orientation of the domains directly by spin coating block copolymer solutions. Well-oriented cylinders perpendicular to the film substrate, with diameters from around 20 to 45 nm, were obtained by resorcinol complexation of block copolymers with total molecular weight from 25400 (PS<sub>183</sub>-*b*-PEO<sub>145</sub>,



$\Phi_{\text{PEO}}=0.24$ ) to 89600 g/mol ( $\text{PS}_{563}\text{-}b\text{-PEO}_{705}$ ,  $\Phi_{\text{PEO}}=0.36$ ), respectively, thus emphasizing the simplicity and the general applicability of this procedure. Long range order is not always as good as in other works but no additional treatments to increase the domain periodicity were applied and the capability of producing films with the desired nanostructure and orientation is in itself an interesting result. In this study resorcinol molecules were used to hydrogen-bind the semicrystalline PEO blocks thus giving a PEO/resorcinol complex that is also able to crystallize, but at a minor extent than the original PEO block. The changed interfacial interactions due to the presence of resorcinol and the reduction in the crystalline phase appear to be related with the tendency of PS-*b*-PEO polymers and of their resorcinol complexes to self-assemble in perpendicular oriented PEO cylinders, also when different morphologies and alignments were expected. For example the  $\text{PS}_{563}\text{-}b\text{-PEO}_{705}$  ( $\Phi_{\text{PEO}}=0.36$ ) sample, when annealed under benzene vapour, arranges in well ordered vertical lamellae and in principle its stoichiometric resorcinol complex should also have a lamellar morphology (being  $\Phi_{\text{PEO/Res}}$  equal to 0.51). By spin-coating  $\text{PS}_{308}\text{-}b\text{-PEO}_{250}$  in benzene solution in-plane PEO cylinders are obtained, while following the same film deposition procedure the PEO/resorcinol domains arrange according to a perpendicular orientation.  $\text{PS}_{183}\text{-}b\text{-PEO}_{145}$  is the only sample that gives the same type of alignment both in the presence of resorcinol and in its absence.

The very regular superstructures obtained, with controlled features on the nanometer scale, make them of great interest for a number of nanotechnological applications and especially as templates for the production of nanoporous membranes and for the ordering of metallic nanoparticles and oxides.

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## Figure captions

Figure 1. AFM phase images of PS-*b*-PEO spin-coated films: (a,d) PS<sub>563</sub>-*b*-PEO<sub>705</sub>, (b,e) PS<sub>308</sub>-*b*-PEO<sub>250</sub> and (c,f) PS<sub>183</sub>-*b*-PEO<sub>145</sub>; (a,b,c) before and (d,e,f) after solvent annealing.

Figure 2. TEM micrographs of spin-coated thin films from a PS<sub>563</sub>-*b*-PEO<sub>705</sub>/resorcinol solution (molar ratio resorcinol:ethylene oxide 1:2): dark field (a) top-view and bright field cross-section image (b) of unstained samples.

Figure 3. AFM 3D topography and height profile (a), and FESEM image (b) of spin-coated thin films from a PS<sub>563</sub>-*b*-PEO<sub>705</sub>/resorcinol solution (molar ratio resorcinol:ethylene oxide 1:2). PEO cylinders appear as depressions in the PS matrix surface.

Figure 4. AFM phase images of spin-coated films of PS-*b*-PEO/resorcinol samples: (a) PS<sub>183</sub>-*b*-PEO<sub>145</sub>, (b) PS<sub>308</sub>-*b*-PEO<sub>250</sub> and (c) PS<sub>563</sub>-*b*-PEO<sub>705</sub>. Molar ratio resorcinol:ethylene oxide 1:2.

Figure 5. FTIR spectra of (a) PS<sub>563</sub>-*b*-PEO<sub>705</sub>, (b) resorcinol and (c) of PS<sub>563</sub>-*b*-PEO<sub>705</sub>/resorcinol complex (Molar ratio resorcinol:ethylene oxide 1:2). The absorption at 3315 cm<sup>-1</sup> is specific for the hydrogen bonding interaction between resorcinol and the oxygen atoms of PEO.

Figure 6. DSC traces of resorcinol (a), PS<sub>563</sub>-*b*-PEO<sub>705</sub> (b) and PS<sub>563</sub>-*b*-PEO<sub>705</sub>/resorcinol stoichiometric complex (c).

Figure 7. X-ray diffraction curves of: PS<sub>563</sub>-*b*-PEO<sub>705</sub> (a), PS<sub>308</sub>-*b*-PEO<sub>250</sub> (b), PS<sub>183</sub>-*b*-PEO<sub>145</sub> (c), and the corresponding resorcinol complexes with molar ratio resorcinol:ethylene oxide 1:2 (lower curves), compared with that of pure resorcinol (d).

## Tables

Table 1. Melting temperatures ( $T_m$ ) and heat of fusions of PS-*b*-PEO samples and PS-*b*-PEO and resorcinol in stoichiometric proportion. Values are averages calculated from triplicates. Melting temperature and heat of fusion of resorcinol were 115.7°C and 207.6 J/g respectively.

	$T_m$ (°C)		Heat of fusion (J/g)		
	pure copolymer	with resorcinol	pure copolymer	with resorcinol (experimental)	with resorcinol (theoretical <sup>a</sup> )
PS <sub>563</sub> - <i>b</i> -PEO <sub>705</sub> ( $M_n$ = 58600- <i>b</i> -31000)	63.8	92.6	51.2	40.4	98.5
PS <sub>308</sub> - <i>b</i> -PEO <sub>250</sub> ( $M_n$ = 32000- <i>b</i> -11000)	57.7	87.5	19.9	16.9	65.5
PS <sub>183</sub> - <i>b</i> -PEO <sub>145</sub> ( $M_n$ = 19000- <i>b</i> -6400)	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>b</sup>	-

<sup>(a)</sup> calculated following the mixing rule

<sup>(b)</sup> not determined



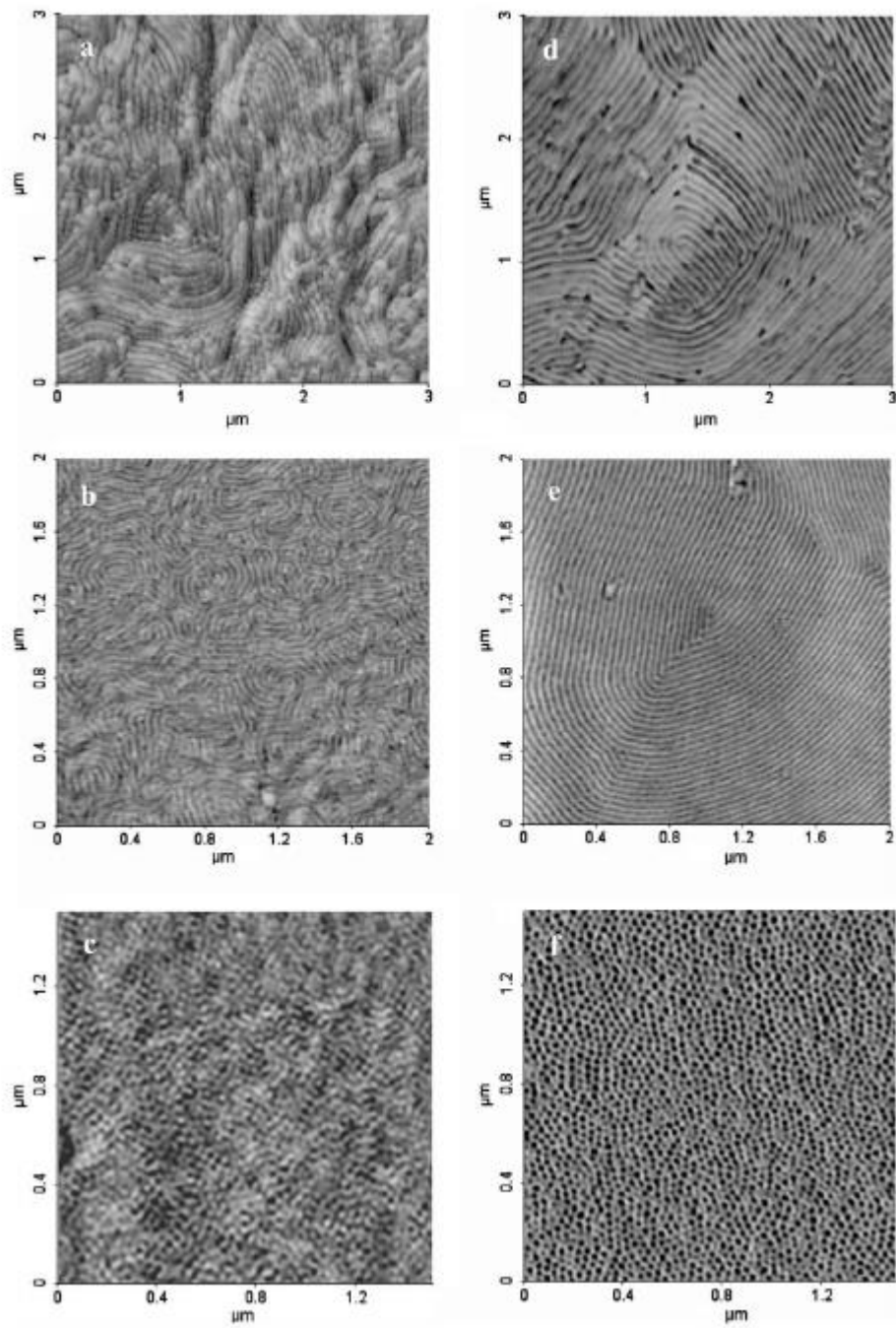
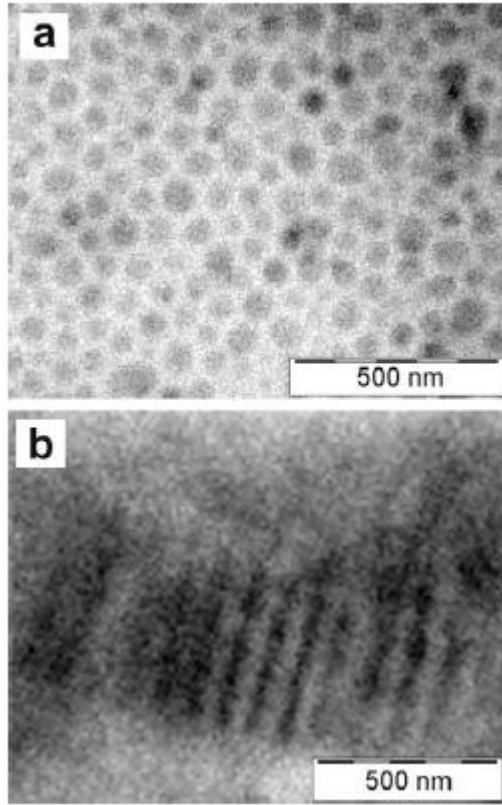
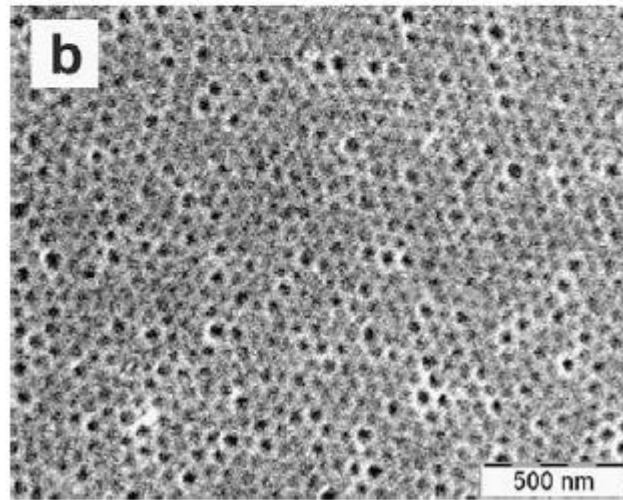
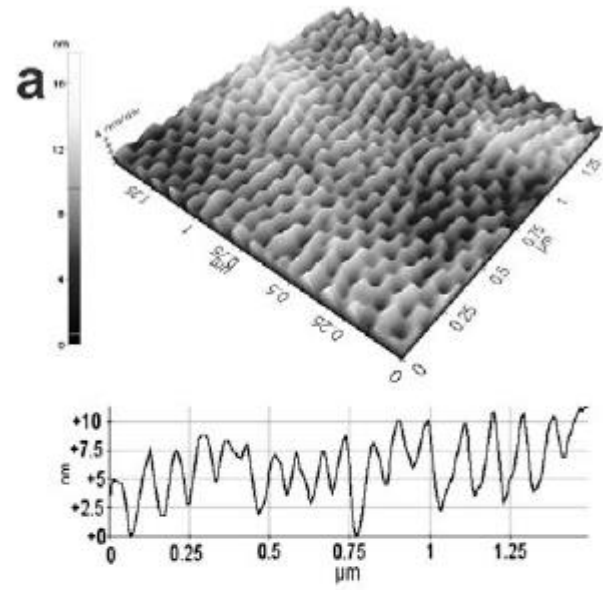


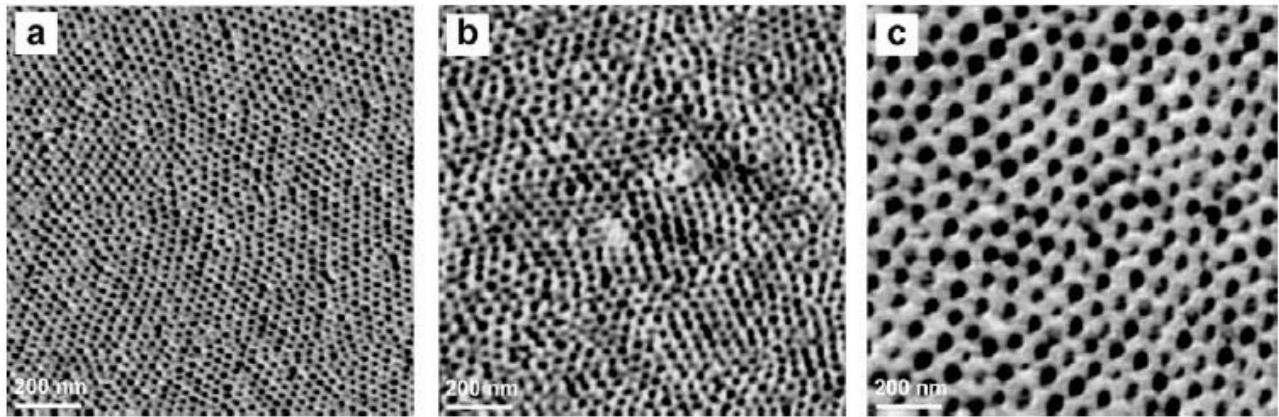
Figure 1



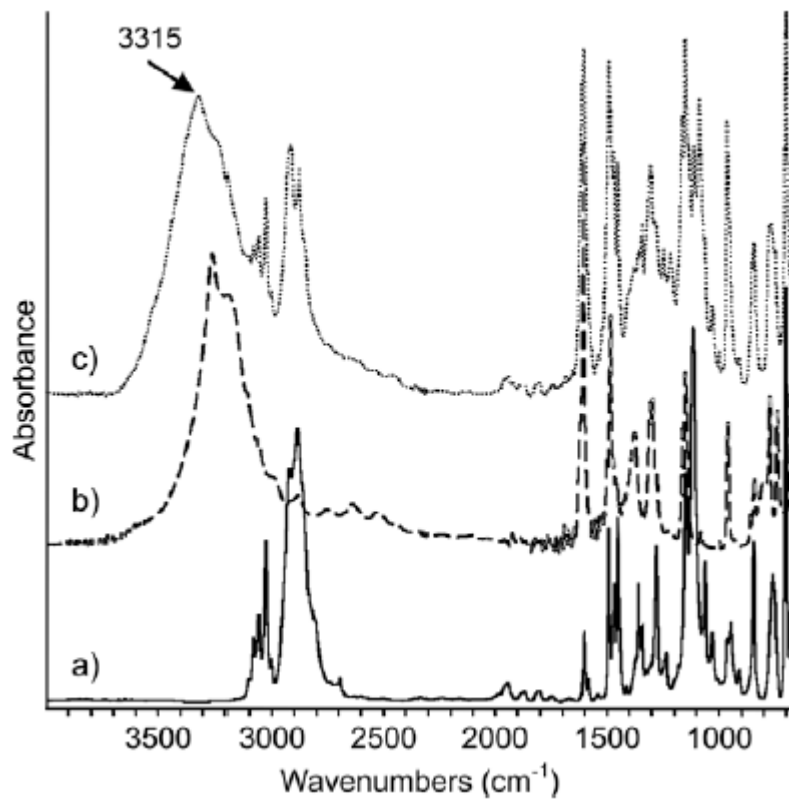
**Figure 2**



**Figure 3**



**Figure 4**



**Figure 5**

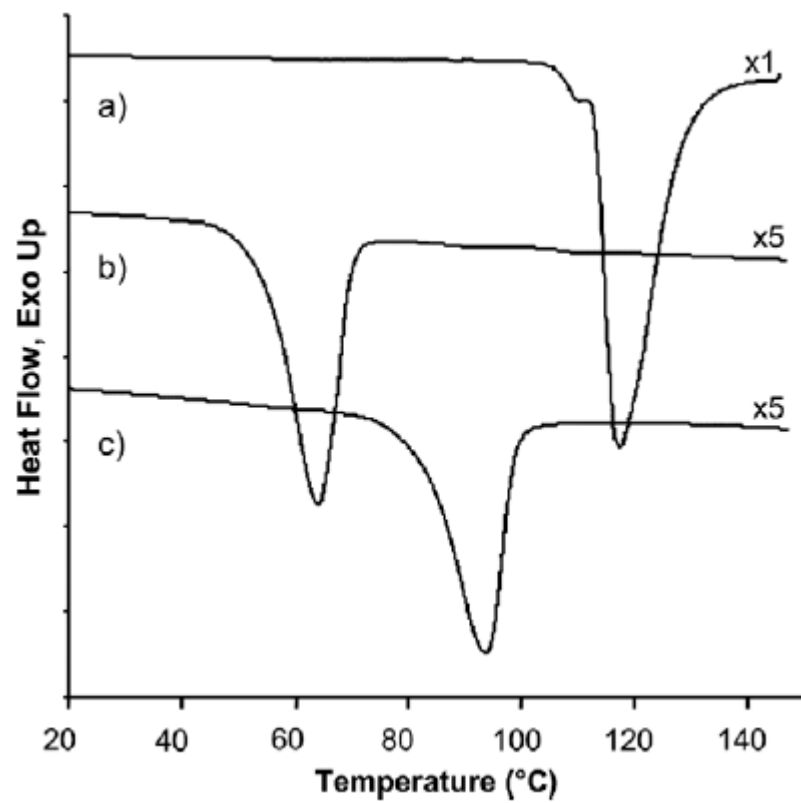


Figure 6

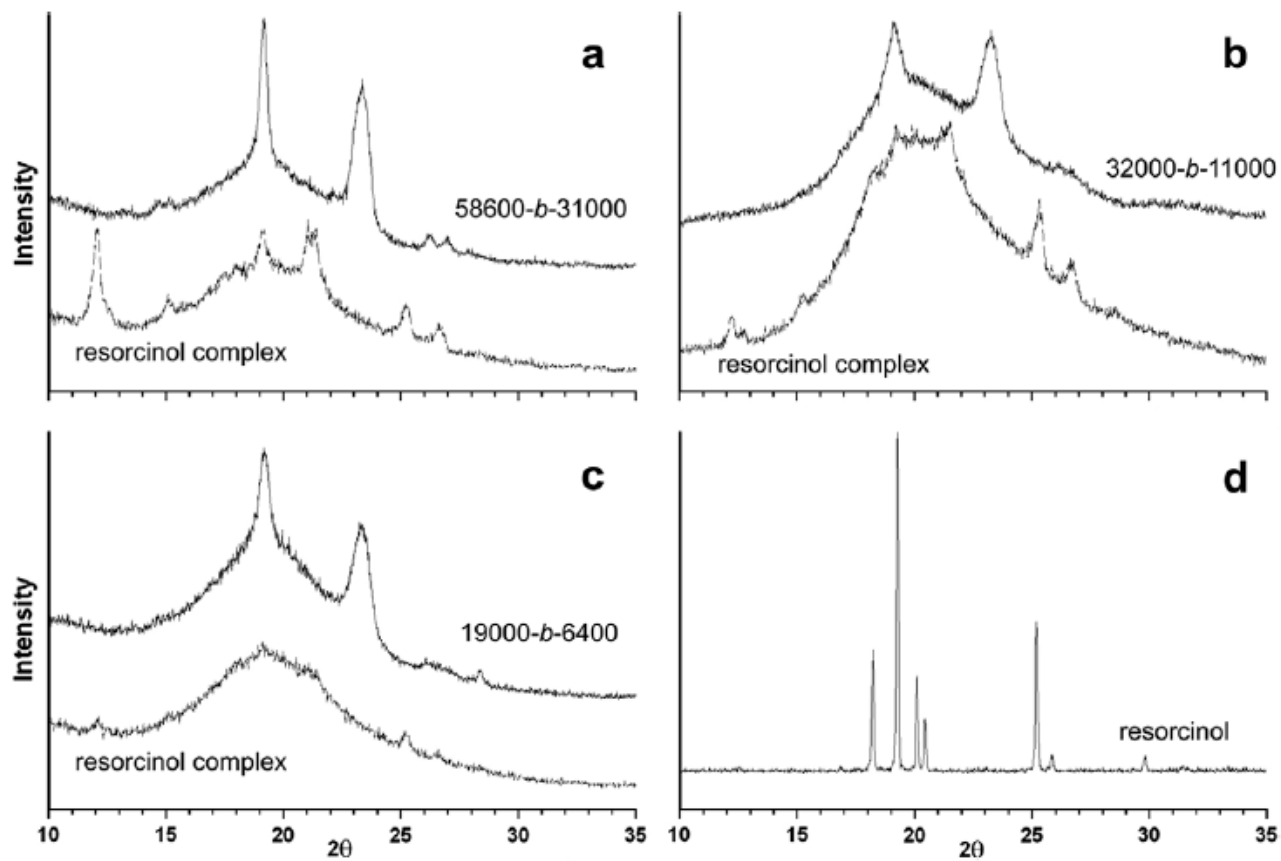


Figure 7