

Self-Assembly of Well-Defined PS-*b*-PDMS Copolymers in Bulk and in Selective Solvent

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As an extension of our previous work regarding the controlled synthesis of siloxane homopolymers, the synthesis of poly(styrene)-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS) copolymers through sequential anionic polymerization, and their self-assembly behavior in bulk (thin films) and in solution (nanoparticles) is herein reported. The results obtained in bulk showed the formation of original island-type nanostructures with periodic separation and uniform height for thin films prepared by spin coating on silicon substrates followed by thermo- or solvent annealing, as evidenced by atomic force microscopy (AFM). In selective solvent (dimethylformamide), micellar core (PDMS)-shell (PS) nanoparticles originated upon direct dissolution, and the corresponding structure was determined in details by combining static and dynamic light scattering (SDLS) measurements.

Introduction

Block copolymer systems exhibit well-known ability to self-assemble into a wide variety of morphologies either in bulk (lamellas, gyroids, cylinders, spheres, etc.) or in solution (spherical micelles, vesicles, cylinders, etc.). They constitute, therefore, a collection of elementary building blocks for the precise construction of advanced materials via bottom-up, atom- and energy-efficient approaches (Lazzari et al., 2006). The shape and size of self-organized morphologies can be suitably controlled through a number of factors, such as the relative block lengths, the chemical nature of the blocks, and the type of solvent for the solution preparation (Hamley, 2005). In this direction, considerable efforts have been made in the quest for manipulation methods enabling the preparation of surfaces with tunable physical and chemical properties via block copolymer approach. The results in this field have lead to a common sense that the development of clever film preparation strategies is the mainstream for obtaining novel nanomaterials with heterogeneous surfaces and controlled orientation at long-range

order. For instance, block copolymer self-assembled thin films can be obtained by spin-coating from either molecularly dissolved chains (unimers in a thermodynamically good solvent) or pre-organized systems (micelles, vesicles, cylinders, etc., in selective media) (Riess, 2003; Bates and Fredrickson, 1990).

The poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS) block copolymer, in particular, exhibits very interesting thin film properties for soft nanolithography, which is the key to obtain electronic, optoelectronic, and magnetic devices for specific industrial applications. The high value of the Flory-Huggins interaction parameter (χ) contributes decisively for the usually high degree of ordering observed in PS-*b*-PDMS films provided the building blocks at the origin (individual chains) are well-defined. Besides, this copolymer system has an appreciably etch-resistant block due to the high density of Si in the backbone PDMS segment, thus facilitating pattern transfer into underlying materials (Jung and Ross, 2007). In this work we report the synthesis of highly defined PS-*b*-PDMS copolymers through sequential anionic polymerization, and their self-assembly behavior in bulk (thin films) and in solution (nanoparticles). In bulk, island-type structures with periodic separation and uniform height have been successfully and reproducibly obtained under specific experimental conditions as evidenced by atomic force microscopy (AFM). In solution, monodisperse micellar core-shell nanoparticles were observed in dimethylformamide, and corresponding structure was determined in details by static and dynamic light scattering (SDLS).

Experimental

All copolymers were synthesized by standard anionic polymerization procedures. The initiator employed, *sec*-butyl lithium (*sec*-Bu⁻Li⁺), was prepared *in vacuo* from *sec*-butyl chloride (Fluka) and lithium metal (Fluka). The monomers styrene (S, Fluka) and hexamethylcyclotrisiloxane (D₃, Sigma-Aldrich) were purified according to conventional routines described elsewhere (Hadjichristidis et al., 2000). Tetrahydrofuran (THF) was used as promoter of D₃ polymerization whereas cyclohexane and degassed methanol were used as the solvent and terminating agent.

Synthesis of model PS-*b*-PDMS copolymers

All manipulations were performed under a high-vacuum glass line in glass reactors equipped with break-seals for the addition of the reagents and constrictions for removal of products (Uhrig and Mays, 2005; Morton and Fetters, 1975). A scheme of the polymerization apparatus used for the synthesis is shown in Figure 1. A description of the synthetic pathway employed is briefly described as follows. The apparatus was connected to the vacuum line, checked for pinholes, flame-dried and pumped for 20-30 min in order to remove the volatile species. Then, 5 mL of 2 mol/L *n*-BuLi⁺ solution in hexane (Aldrich) were injected through the purge constriction (PC) into the purge section flask. The whole apparatus was pumped for additional 30 min, and an appropriate amount of pure cyclohexane (40-50 mL) was then distilled and degassed over 45 minutes. The apparatus was removed from the vacuum line by heat-sealing the constriction (VLC), and was washed with the diluted *n*-BuLi⁺ solution inside by gentle manual agitation. After washing, the purge section was removed by heat-sealing the middle constriction (MC) leaving the clean reactor with an appropriate amount of pure

distilled solvent. The break-seal of the S monomer was first broken and the content was poured into the reactor flask, followed by addition of the *sec*-Bu⁻Li⁺ ampoule. The polymerization was left to proceed until all the S monomer was consumed (usually, 24 h). An ampoule of living PS was then collected for characterization. Subsequently, the break-seal of the ampoule containing the D₃ monomer was broken, and the reaction was left to proceed for ~ 20 h at room temperature. Then, the break-seal of THF ampoule was broken to promote D₃ polymerization. This polymerization was carried out in two steps: first at room temperature, and propagation in a mixture of cyclohexane/THF (1/1 v/v) up to 50 % conversion; and then at -20 °C until completion. The addition of 1-3 mL of well-degassed methanol terminated the reaction. The *block* copolymer thus obtained was precipitated in stabilized methanol, dried under vacuum and chemically characterized.

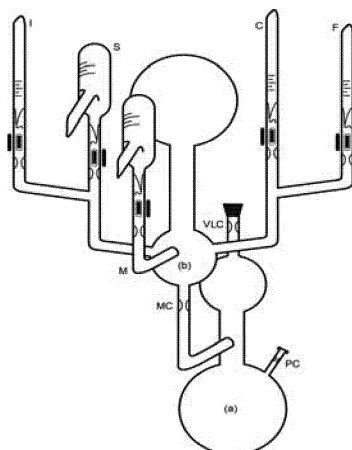


Figure 1. Polymerization apparatus for the synthesis of PS-*b*-PDMS copolymers. References: I: *sec*-Bu⁻Li⁺ ampoule. S: THF ampoule. M: S monomer ampoule. C: D₃ monomer ampoule. F: methanol ampoule. (a): Purge section. (b): Reactor. VLC: vacuum line constriction. PC: purge constriction. MC: middle constriction.

Molecular characterization of PS-*b*-PDMS copolymers

Size Exclusion Chromatography (SEC). SEC experiments were performed on a Waters model 410 differential refractometer (equipped with 4 columns with a porosity range of 10²-10⁶ Å). The solvent employed was toluene at 25 °C with a flow rate of 1 mL/min. The injection volume was 200 µL, and polystyrene standards were used for calibration.

Nuclear Magnetic Resonance (¹H NMR). The ¹H-NMR spectra of PS-*b*-PDMS copolymers were recorded on a Bruker 300 MHz instrument using deuterated chloroform as solvent. The chemical composition of the PS-*b*-PDMS copolymer was obtained by the ratio of the integrated areas of the aromatic to methylic ¹H signals.

Self-Assembly of PS-*b*-PDMS copolymers

Thin films. Thin copolymer films were prepared by the spin-coating (3000 rpm, 1 min) of 1 wt% PS-*b*-PDMS solutions in different solvents (cyclohexane, toluene, and THF) onto 10 mm x 10 mm Si wafers with native oxide layer previously subjected to standard cleaning procedures. Subsequently, selected copolymer thin films were thermo- and/or solvent-annealed, as indicated below. The atomic force microscopy (AFM)

measurements have been performed using a multimode AFM Nanoscope IIIa (Digital Instruments) in the tapping mode using BSTap300-50 tips (Nanoscience Instruments). Through this method both topography (surface profile) and phase scans (surface domains arrangements) of explored surfaces can be accessed. The collected data were processed using the WSxM[®] software from Nanotec Electronica.

Nanoparticles in solution. Solutions were prepared by directly dissolving the dry polymer in pure solvents (cyclohexane or DMF), and the resulting solutions were gently stirred at room temperature overnight. Afterward, samples were left at 50 °C for about 12 h to achieve equilibrium structures. The light scattering measurements were performed at room temperature (20 ± 1 °C) using an ALV CGE photogoniometer equipped with a Uniphase 22 mW He-Ne laser ($\lambda = 632.8$ nm) as the light source, an ALV 6010 correlator, and a pair of avalanche photodiodes operated in pseudo cross-correlation mode.

Results and Discussion

The synthesis of PS-*b*-PDMS copolymer involves a sequential monomer addition procedure. First, the polymerization of S monomer with *sec*-BuLi⁺ as initiator was carried out for 24 h to ensure the complete conversion of S to PS⁻Li⁺. Then, the polymerization of D₃ monomer was carried out by a two-step methodology, where the controlled and complete polymerization of D₃ was achieved (Bellas et al, 2000). The macromolecular characteristics of the block copolymers samples obtained by SEC and ¹H NMR are summarized in Table 1. In all cases, the polymer chains were found to have a remarkably uniform distribution in terms of size ($M_w/M_n = 1.01$), in agreement with conventional living anionic polymerization protocols. These are, therefore, very attractive model systems for self-assembling studies as long as the well-known dispersity effects of the building blocks are minimized.

Among the samples listed in Table 1, we first elected to investigate in details the self-assembly properties of PS-*b*-PDMS **B** copolymer, for which self-organization into cylindrical morphology with PDMS domains dispersed in a PS-based matrix is anticipated based on the volume fraction of the forming-blocks (Bates and Fredrickson, 1990). Upon spin-casting copolymer solutions on Si wafers without any further treatment, the thin films were typically colorless and exhibited smooth surfaces in both topography and phase scans (results not shown). Such an observation suggests that microphase separation most probably led to structures with in-plane orientation and homogeneous surfaces.

Table 1. Chemical characterization of model PS-*b*-PDMS copolymers

Sample	M_n (g/mol) ^a	M_w/M_n ^a	x_{PDMS} ^b	w_{PDMS} ^b
PS- <i>b</i> -PDMS A	18,200	1.01	0.032	0.023
PS- <i>b</i> -PDMS B	15,500	1.01	0.275	0.212
PS- <i>b</i> -PDMS C	13,200	1.01	0.430	0.350

^a Number average molar mass (M_n) and molar mass dispersity (M_w/M_n) determined by SEC.

^b Mol (x_{PDMS}) and weight (w_{PDMS}) fraction of PDMS block determined by ¹H NMR.

Even though the PS-*b*-PDMS systems show high χ -values that favor self-organization (Jung and Ross, 2007), the formation of non-organized films cannot be excluded. Original topography arrangements were, however, immediately seen in thin films prepared from THF solutions, and then subjected to thermo-annealing at 150 °C for 12 h (Figure 2a-c) or solvent-annealing in *n*-heptane for 12 h (Figure 2d-e).

The island-type structures (Figure 2b) have a typical base diameter of ~ 700 nm and a height above the surface of ~ 20 nm (Figure 2c), independently of experimental conditions (i.e.: thermo- or solvent-annealed samples). Whilst the characteristic height could, in principle, be directly correlated with the size of fully stretched blocks (~ 36 nm for PS and 14 nm for PDMS), their width is comparably too large, thus implying that such protrusions probably have a rather complex inner structure. Moreover, in all measurements the phase scan images revealed that the surface film composition is homogenous (one surface phase is observed in Figure 2e). Such a behavior might suggest an arrangement probably of PDMS cylinders oriented perpendicular to the surface, with PDMS segments also extending to the air-film interface since PDMS has a much lower surface energy than PS (Wu et al., 2007). Indeed, the presence of PDMS at the surface is favored by *n*-heptane annealing provided that this is a selective solvent for PDMS. The existence of structural order in the bulk of films and the distribution of elements at the uppermost surface are currently under investigation by grazing-incidence small angle x-ray scattering (GISAXS) and x-ray photoelectron spectroscopy (XPS) experiments, respectively.

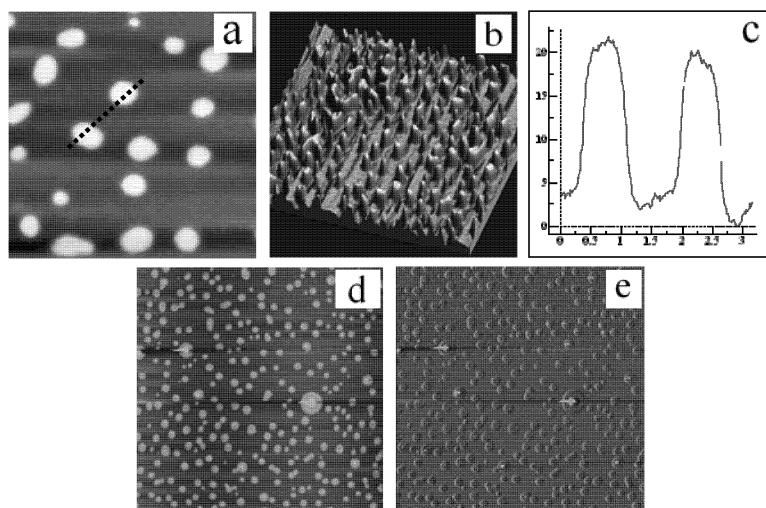


Figure 2. AFM images of PS-*b*-PDMS **B** thin films (a) spin-coating from THF and thermo-annealed at 150 °C for 12 h (topography, 7 μm x 7 μm , Z scale 11 nm); (b) 3D image of the same sample (20 μm x 20 μm); (c) profile graph of scan indicated in (a) where the dark dashed line indicates the cut path (the x and y scales are given in μm and nm, respectively); (d) spin-coated from toluene and vapor-annealed in *n*-heptane (topography, 50 μm x 50 μm , Z scale 50 nm); (e) phase scan of (d) (Z scale 10 nm).

When the same block copolymer was dissolved in a selective solvent for PS and precipitant for PDMS (in the current case, DMF), a single relaxation process was observed in DLS measurements, which was associated with the diffusive motion of particles with mean hydrodynamic radius (R_H) of 16 nm. Such particles consist of a PDMS compact core and a PS solvated shell. Using the Zimm formalism in SLS and considering that DMF is isorefractive with PDMS, the M_w of the micelles was found to be 4.49×10^5 g/mol. The aggregation number (N_{agg}) determined by the ratio $M_{w(micelle)}/M_{w(unimers)}$ is therefore ~ 30 chains/micelle. The relative small N_{agg} is probably related to the small fraction of core-forming block in the copolymer composition.

Conclusions

A series of poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS) copolymers with uniform molar mass distributions was successfully synthesized by conventional anionic polymerization. Nanostructure surface films could be successfully obtained by spin-coating copolymers from thermodynamically good solvents, followed by thermo- and/or solvent-annealing. In particular, we have evidenced the formation of protrusions on the surface (island-type objects) with well-defined dimensions. Combined with selective etching technologies, the morphology of such films is of interest for developments in the soft nanolithography field. Further investigations focusing on long-range orientation and ordering are however required for practical applications.

Acknowledgements

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