Directing the Self-Assembly of Mesostructured Hybrid Materials: Effect of Polymer Concentration and Solvent Type

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Herein we explore the possibility to control the fabrication of non-equilibrium nano-patterns of spin-coated organic-inorganic hybrid materials based on diblock copolymers and metal nanoparticles in thin films. It is demonstrated that the type of solvent and the initial solution concentration, among other factors, can serve as tools to direct the morphology of spin-coated thin films. The driving forces leading to the pattern formation are reviewed with respect to these parameters — type of solvents and polymer concentration. As a result well-defined surface patterns of functional hybrid materials are obtained. Moreover, the same tools used to direct the pattern formation can be applied to gain control over the particle size and size distribution.

Introduction

Well-defined surface patterns are required in numerous applications ranging from simple coatings to biotechnology, sensors, optics, and electronics. In principle there are two main approaches to fabricate these patterns — top-down and bottom-up. The top-down approach relies on structuring larger entities using a complex sequence of process steps including lithography, etching, and deposition techniques. This concept has been well proven to enable the fabrication of surface patterns with complex geometries and a high degree of perfection. However, the onward request for smaller dimensions to meet the requirements of future applications may not be accomplished by means of conventional techniques. Thus, the bottom-up approach is highly beneficial to create nanostructures with dimensions in the range of 1–100 nm by assembling basic building blocks into complex architectures.
Self-assembly is a bottom-up approach that generates regular structures by minimizing the free energy balance of a system.[2] The advantage of self-assembly lies in its simplicity as a fast and cost-effective way to fabricate well-defined nanostructures. A system that has been reviewed extensively during the past decade is A-B diblock copolymers, its ability to self-assemble stems from the microphase separation, which is a result of the chemical incompatibility of its building blocks (A and B). Depending on the relative block length of the blocks (A and B) mainly five different morphologies can be obtained in the bulk material.[3] A much larger diversity of morphologies was discovered for ABA and ABC triblock copolymers.[4] When the polymer is confined to a thin film, the number of possible morphologies increases due to the interaction with the underlying substrate.[5] However, targeting a certain thin film morphology remains rather demanding. Recently, great efforts have been made for example to control the orientation of cylinders in a block copolymer thin film perpendicular to the film’s surface, an orientation that does not represent the most stable configuration.[6] Such a high degree of control is essential, since the fabrication of nearly defect-free films with a preferential orientation (anisotropy) of the microphase separated domains is required in numerous applications such as coatings, optics, and electronics among many others.

Herein we focus on controlling the fabrication of non-equilibrium nanostructures; a possibility that until now received little attention. Such non-equilibrium patterns in thin films are obtained during solvent evaporation when a copolymer solution is spin-coated onto a solid substrate. The advantage over simple microphase separated thin films is that a much larger diversity of morphologies is accessible.

An attempt to explore the formation of nano-patterns in spin-coated copolymer films was presented by Zhao et al.[7] They found that both the solvent and the nature of the substrate significantly affect the microstructure in thin film. Mechanisms to control the morphology were also explored by Müller-Buschbaum et al.[8] who studied the interplay between (micro-)phase-separation and dewetting of a thin (co-)polymer film. Despite some recent efforts attempting to evaluate the role of individual factors, there are only few studies covering a wider range of parameters. Hence, controlling the microstructure of self-assembled thin films is still a challenging aim, especially for non-equilibrium morphologies. Additionally, the particularly interesting case of using hybrid materials to generate functional nanostructures has received little attention. Self-assembled block copolymer thin films are interesting from a scientific point of view but possess only limited functionality. As one of the first, Brinker et al.[9] developed a simple concept to self-assemble functional materials into nanoscale hierarchical architectures by means of sol-gel chemistry. This approach, known as evaporation-induced self-assembly (EISA) is usually applied to fabricate mesostructured thin films of silica/surfactant hybrid materials. The self-assembly process is dependent on a large number of parameters such as chemical composition and the concentration of both the surfactant and the inorganic precursor, the wetting behavior of the sol on the substrate, as well as the humidity.[10] Control the formation of mesostructures in thin films using the EISA approach becomes increasingly difficult as the film thickness decreases.[11] However, a number of reports demonstrate the successful preparation of mesoporous structures in ultra-thin films.[12,13]

The present work explores the possibility to fabricate and control well-defined nanostructures in ultra-thin films of functional hybrid materials based on amphiphilic diblock copolymers and metallic nanoparticles. Additionally the block copolymer not only stabilizes the nanoparticles but allows to control the self-assembly. A brief overview over some of the mechanism driving the self-assembly in thin films is given with respect to the control parameters. It is demonstrated that the morphology of self-assembled thin films can be directed by a narrow selection of tools including the nature of the solvent and the initial polymer concentration. Simultaneously, these parameters are used to control the particle size and size distribution resulting in a flexible approach to design functional nano-patterns.

Recently it was established that microphase separated block copolymers can be used to template the preparation of inorganic materials.[13] This approach already provides a flexible way to generate well-defined and periodic nanostructures of inorganic materials. However, multiple step processes are required that increase both the complexity and time consumption of this technology, while the number of possible morphologies is still limited. We present, herein, a simpler approach which is to generate inorganic nanoparticles in situ and simultaneously direct their spatial arrangement through the self-assembly of the diblock copolymer. Wiesner and coworkers[14] applied this concept to generate inorganic nano-objects in a block copolymer matrix by means of sol-gel synthesis. An early way to generate inorganic nanostructures in thin film was presented by Müller and coworkers,[15] who used metal loaded block copolymer micelles to create hexagonally ordered arrays of metallic nanoparticles. The micelle geometry provides an excellent nano-reactor to synthesize and stabilize inorganic nanoparticles with controlled size and size distribution. Recently a number of research groups presented fairly similar routes to generate metallic nanostructures by depositing metallic elements from copolymeric micelles.[16] For example, our recent work demonstrated the fabrication of nanoporous thin films by controlled deposition of metal loaded micelles.[17]
The scope of this article is to control the fabrication of nanostructured hybrid materials in thin film. The nanopatterns are generated by spin-coating solutions of the hybrid material onto solid substrates. It is demonstrated that the type of solvent and the polymer concentration can serve as tools to direct the pattern formation. The same parameters are used to control the particle size and size distribution. Simultaneously, mechanisms are explored that can be used to guide the self-assembly into specific surface patterns.

**Experimental Part**

**Block Copolymer Solutions**

Polystyrene-block-poly(4-vinyl pyridine) (PS-b-P4VP) \( \left[ M_n(PS) = 34,000 \, \text{g} \cdot \text{mol}^{-1}; M_n(\text{P4VP}) = 2,900 \, \text{g} \cdot \text{mol}^{-1} \right] \) was purchased from Polymer Source Inc. and used as received. The polydispersity index was \( \frac{M_w}{M_n} = 1.05 \). Solutions of the block copolymer were prepared at various concentrations between 0.01 and 0.100 mg/mL using different solvents and solvent mixtures. The solvents were purchased from Fisher Scientific and used without further purification. Metallic nanoparticles were generated in situ via complexation and reduction of an inorganic precursor within the copolymer scaffold.

**Dynamic Light Scattering**

Dynamic light scattering (M802 DLS, Viscotek) was performed to determine the radius of gyration and the hydrodynamic radius of the copolymer-hybrid material in solution.

**Thin Film Preparation**

Oxidized silicon wafers (111) were used as a substrate; they were treated in a piranha solution \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O} = 2:1:1 \) at 80 °C for 20 min to remove organic contaminations from the surface. A second cleaning step in RCA-1 solution \( \text{H}_2\text{O}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O} = 1:1:1 \) was performed at 60 °C for another 20 min. After rinsing in distilled water the substrates were blown with dry air. The block-copolymer solutions were spin-coated on the substrates at 3 000 rpm. The film thickness was measured using atomic force microscopy (AFM) by partially removing the film with a razor blade (SI-1).

**Atomic Force Microscopy**

The morphological characterization was performed by Tapping Mode™ AFM in air at ambient conditions using a Dimension IVa Nanoscope (Digital Instruments). We used standard silicon cantilevers with a resonance frequency of about 330 kHz, a spring constant of 45 N m⁻¹, and a tip radius of less than 10 nm (Pointprobe SPM Cantilevers, Nanoworld). The operating frequency was chosen to be far on the repulsive side of the resonance frequency to increase scanning performance and stability.

**Transmission Electron Microscopy (TEM and HR-TEM)**

Thin films were produced by spin-coating the polymer solution on carbon coated copper grids (400 mesh/AGAR Scientific) attached to a solid substrate support. The copper grid was then peeled off from the substrate and analyzed in a Tecnai Biotwin (FEI Ltd.) transmission electron microscope at 100 k eV⁻¹. The instrument was operated at low beam intensities to prevent electron damage of the polymer samples. HR-TEM measurements were performed using a JEOL JEM-2110F operated at 200 kV; the instrument was equipped with an Orius SC1000 digital camera.

**X-Ray Diffraction**

Powder diffraction (XRD) measurements were performed on a Bruker D8 Advance. The instrument was operated with CuKα (1.54056 Å) and a Vario monochromator.

**Sub-Microbeam Grazing Incidence Small Angle X-Ray Scattering**

The sub-microbeam grazing incidence small angle X-ray scattering (sub-μ GISAXS) experiments were performed at the ID13 beamline (ESRF, Grenoble). A wavelength of \( \lambda = 0.0997 \) nm was chosen. To emphasize on small lateral structures the detector (MARCCD, 2048 × 2048 pixels array) was placed at 0.84 m from the sample. A fixed beamstop was used to shield the high intensity of the direct beam and therefore to protect the detector. With a movable and semi-transparent beamstop the specular peak was shielded. Thus the non-specular as well as the specular intensity was recorded a function of the exit angle \( \alpha_t \) and the out-of-plane angle \( \phi \). A fixed incident angle of \( \alpha_i = 0.63^\circ \) was selected to allow for a good angular separation between the Yoneda peak and the specular peak. Successively increasing counting times were used in combination with a lateral shifting of the sample with respect to the X-ray beam to test for radiation damage and to ensure absence of radiation damage in the measurements. Due to the used sub-micrometer beamsize it was possible to avoid over illumination of small samples.

**X-Ray Photoelectron Spectroscopy**

The samples were analyzed in a Kratos AXIS ULTRA instrument with a monochromated Al Kα X-ray source (1.4866 eV) operated at 15 mA emission current and 10 kV anode potential. For nonconducting samples a charge neutralizer filament above the sample surface gives a flux of low energy electrons providing uniform charge neutralization. The ULTRA was used in FAT (fixed analyzer transmission) mode, with pass energy of 80 eV for wide scans. High resolution scans with pass energy of 20 eV were collected at an electron emission angle of 90° with respect to the sample plane. The sampling depth at this take-off angle was estimated to be approximately 10 nm.
Results and Discussion

The morphology of self-assembled block copolymer thin films depends on a large number of factors such as the chemical nature of the copolymer, its volume fraction, the character of the solvent and the substrate material among many others. Controlling these factors provides a powerful tool to direct the self-assembly process with the ultimate goal of targeting specific surface patterns. In the present article we study the effects of the type of solvent and the polymer concentration structure formation in spin-coated thin films. These are two important factors that can be used to direct the morphology of self-assembled functional hybrid materials in thin film. The influence of substrate, molecular weight of the copolymer, and its volume fraction cannot be neglected. Therefore, these factors were kept constant throughout the experiments presented here; we used only one diblock copolymer (PS327-b-P4VP28) on Si/SiO₂ substrates. A detailed study of the influence of the molecular weight of the block copolymer, its volume fraction, and the substrate material will appear in future publications.

Preparation of Organic-Inorganic Hybrid Nanostructures

Functional hybrid materials are prepared as shown in Figure 1. Due to the interesting properties of Au-nanoparticles, tetrachloro-auric acid (HAuCl₄) was used as a gold precursor.[19] However, the same concept can be applied to generate a variety of metallic and semi-conducting nanoparticles.[20] Starting from the neat PS-b-P4VP diblock copolymer in step I, a new hybrid material is designed successively. Initially, the block copolymer is dissolved in a selective or non-selective solvent. In step II an inorganic precursor (HAuCl₄) is coordinated to the block copolymer in stoichiometric amounts with respect to the number of pyridine units. The inorganic precursor protonates the P4VP units and due to strong acid-base interaction the chloro-aurate counterion forms a complex with the pyridine groups.[21] Metallic Au-nanoparticles are formed upon reduction of the precursor (Au³⁺) to metallic gold (Au⁰) due to the addition of reducing agent (LiBH₄) to the copolymer solution (Step III). The nanoparticles are generated in situ within the block copolymer matrix, which act as nano-reactors and allow controlling the particle size and size distribution. Additionally, the nanoparticles are located solely in the P4VP block. Thus, self-assembly of the PS-b-P4VP block copolymer provides means to direct the spatial arrangement of the nanoparticles. Spin-coating this solution on solid substrates results in the formation of compact films of spherical aggregates of the hybrid material. We found that the morphology of self-assembled thin films can be controlled much easier, if the precursor loaded material PS-b-P[4VP(HAuCl₄)] (Step II) is used to deposit the films prior to the reduction step. Subsequently, different methods such as wet-chemical processes,[22] UV irradiation,[23] or O₂-plasma etching[24] can be applied to generate Au-nanoparticles.

The size and size distribution of metallic nanoparticles was determined by transmission electron microscopy (TEM) measurements. Figure 2a shows a typical TEM micrograph; the Au-nanoparticles appear as dark spots due to their higher electron density. The inset is a HR-TEM micrograph of an individual Au-nanoparticle; the presence of fringes suggests that these particles are single crystals. Further, the existence of crystalline gold nanoparticles was confirmed by XRD. A typical diffraction pattern is shown in Figure 2b; the peak positions corresponding to the fcc structure of the gold lattice (space group Fm3m) are observed.

Oxygen plasma is used to selectively etch the polymer matrix, leaving behind metallic Au-nanoparticles. Since the particles are generated within the P4VP block of the copolymer, their spatial distribution represents the self-assembled morphology of the copolymeric matrix. Quantitative analysis of the chemical composition is performed using X-ray photoelectron spectroscopy (XPS). Figure 2c shows the XPS spectra of the copolymer thin films containing Au-nanoparticles after O₂-plasma treatment. Compared to the non-etched samples, the carbon signal decreases significantly, indicating complete removal of the organic matrix. In contrast to that a strong gold (Au4f) signal is observed before and after the etching process, signifying the existence of Au nanoparticles.

Effect of Solvent on the Pattern Formation

The type of solvent used to spin-coat thin films of the hybrid material PS-b-P[4VP(HAuCl₄)] onto a solid substrate has been found to influence the polymer structure formation significantly. The reason is that different solubilities of the
two blocks of the block copolymer can lead to the formation of aggregates such as spherical micelles. The quality of a solvent for a given polymer depends on the solubility parameters of both blocks in that solvent. The polymer-solvent interaction can be expressed in terms of Hildebrandt solubility parameters.\[25\]

\[
x = x_p + \frac{V_S}{RT} (\delta_{T,S} - \delta_{T,P})^2
\]  

(1)

Where \(x_p\) is the entropic contribution, \(V_S\) is the molar volume of the solvent, \(R\) is the gas constant, and \(T\) is the absolute temperature. The total or Hildebrandt solubility parameter (\(\delta_T\)) of the solvent (S) and the polymer (P) are given by

\[
\delta_T = \left( \delta_{d}^2 + \delta_{p}^2 + \delta_{h}^2 \right)^{1/2}
\]

(2)

where the factors \(\delta_d\), \(\delta_p\), and \(\delta_h\) denote the dispersion-, the polar-, and the hydrogen bonding component or Hansen solubility parameters.

Based on its solubility parameters, at a given temperature, a solvent can be either selective or non-selective for the PS-b-P4VP diblock copolymer (Table 1). In a common- or non-selective solvent \([(\delta_{T,S} - \delta_{T,P})^2 \approx (\delta_{T,S} - \delta_{T,P4VP})^2]\) both blocks of the diblock copolymer are soluble. Thus the copolymer chains remain practically free. In contrast to that, a selective solvent dissolves only one of the blocks (\(x < 0.5\)), while the other one is not soluble (\(x > 0.5\))\[27\] e.g., \([(\delta_{T,S} - \delta_{T,P})^2 \ll (\delta_{T,S} - \delta_{T,P4VP})^2]\). As a result micelles are formed above the critical micelle concentration (cmc). The copolymer self-assembles in such a way that the interface between the less-soluble block and the solvent is minimized. Different micelle morphologies can be observed, depending on the stretching of core-forming chains and the interfacial tension between the core and the shell. Besides simple spherical micelles for example, cylindrical aggregates and vesicles were found\[28\].

When a polymer film is spin-coated from a solution based on different types of solvents, regular surface patterns may evolve. A variety of morphologies can be obtained as shown in Figure 3. These results clearly demonstrate that using different types of solvents dramatically affects the thin film morphology. The films are obtained by spin-coating the same hybrid system of PS-b-P[4VP(HAuCl4)] onto a native oxidized silicon wafer using both selective- and non-selective solvents.

Dissolving PS-b-P[4VP(HAuCl4)] in selective solvents for the PS block, such as toluene (Figure 3a) and chlorobenzene (Figure 3b), spherical micelles are formed prior to the deposition process. Subsequently, solvent evaporation drives the self-assembly into hexagonally ordered patterns (Figure 3a), which results from interactions among the shell (PS block) of the micelles and the substrate. As demonstrated in the TEM micrograph (inset in Figure 3a), the nanoparticles are located in the core of the micelles. Hence,
their spatial distribution represents the hexagonal order of the micellar films.

In contrast, in non-selective solvents such as chloroform (Figure 3c), tetrahydrofuran (THF) (Figure 3d), and N,N-dimethylformamide (DMF) (Figure 3e) the copolymer does not form aggregates at the initial solution concentration. Therefore, the film morphology is purely a result of the solvent evaporation. Moreover, in non-selective solvents both blocks of the diblock copolymer contribute to the structure formation. The number of interactions increases because the copolymer chains are practically free in solution, permitting interactions among both blocks of the copolymer, the inorganic component, the solvent, and the substrate. Hence a larger diversity of morphologies is accessible if the hybrid material is spin-coated from non-selective solvents, where no aggregates are formed. In this case, the inorganic nanoparticles are randomly distributed within the P4VP phase (inset Figure 3c). Competing effects such as the microphase separation of the PS-\textit{b}-P4VP copolymer, preferential wetting on the substrate, and thin film instabilities due to solvent evaporation can induce order in the spatial arrangement of nanoparticles. The film spin-coated from DMF (Figure 3e) shows a compact worm-like structure. The solvent (DMF) is a good solvent for both blocks of the copolymer and additionally wets the Si/SiO2 substrate well. Hence, during spin-coating the solvent (DMF) mediates the wetting of both blocks of the copolymer. As the solvent evaporates completely the wetting behavior is dominated by the

### Table 1. Properties of solvents and polymers\[7,26\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\delta_r) MPa(^{1/2})</th>
<th>(\delta_d) MPa(^{1/2})</th>
<th>(\delta_p) MPa(^{1/2})</th>
<th>(\delta_h) MPa(^{1/2})</th>
<th>Solvent character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
<td>Selective (PS)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19.0</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
<td>Non-selective</td>
</tr>
<tr>
<td>THF</td>
<td>19.4</td>
<td>16.8</td>
<td>5.7</td>
<td>8.0</td>
<td>Non-selective</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>19.6</td>
<td>19.0</td>
<td>6.3</td>
<td>3.3</td>
<td>Selective (PS)</td>
</tr>
<tr>
<td>DMF</td>
<td>24.8</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>Non-selective</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26.5</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>Selective (P4VP)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>19.0</td>
<td>18.1</td>
<td>1.0</td>
<td>4.1</td>
<td>–</td>
</tr>
<tr>
<td>Poly(vinyl pyridine)</td>
<td>21.8</td>
<td>19.0</td>
<td>8.8</td>
<td>5.9</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 3. AFM images demonstrating the influence of the solvent on the morphology of self-assembled block copolymer hybrid thin films PS-\textit{b}-P[4VP(HAuCl4)]. The insets show the corresponding FFT image, in (a) and (c) the insets also display TEM micrographs of the structures. The films were spin-coated from solutions in (a) toluene, (b) chlorobenzene, (c) chloroform, (d) THF, and (e) DMF. In (f) the corresponding values of the most prominent in-plane length are shown. The corresponding film thicknesses are (a) 5.1 nm, (b) 5.4 nm, (c) 8.7 nm, (d) 9.3 nm, and (e) 4.6 nm.
interactions of both blocks of the copolymer with the substrate. While the non-polar PS block dewets, the polar P[4VP(HAuCl4)] block preferentially wets the Si/SiO2 substrate. However, due to the low mobility of polymer chains in the last stage of solvent evaporation, the formation of dewetting polymer droplets is suppressed and the film is trapped in a non-equilibrium state. Hence, dewetting polymer droplets are rarely observed after spin-coating of block copolymer solutions.

A characteristic length scale can be observed in the patterns shown in Figure 3; this is a result of the surface undulations caused by the different solvent evaporation rates from both blocks of the copolymer and its microphase. Each morphology can be described by a characteristic value e.g., the most prominent in-plane length (A), which is accessible by radial averaging over the corresponding FFT image (insets Figure 3a–e) and sub-µ GISAXS measurements (example shown in Figure 7). As shown in Figure 3f, the values of A vary between 30 nm for chlorobenzene and 400 nm for chloroform. These characteristic length scales are dependent on the evaporation rate of the solvent, the different solubility of both blocks of the copolymer, and the wettability of the polymer solution on the substrate. Therefore, the type of solvent also provides a means to control the lateral dimensions of self-assembled thin films and allows tuning the morphology.

In order to utilize these tools, the driving forces leading to the formation of nanostructured surface patterns have to be understood. Describing the evolution of nanostructures in thin liquid films under solvent evaporation is complicated due to the complex hydrodynamic behavior, the inherent unstable nature of the process, as well as heat- and mass transfer within the film. Besides the EISA approach, various mechanisms have been proposed to describe the generation of regular patterns in evaporating films; these include dewetting and surface tension driven effects such as the Marangoni instability. These phenomena are, among other factors, dependent on the surface tension and the film thickness, which are a function of solvent and polymer concentration. For instance, the self-assembly of diblock copolymer in an evaporating thin film is driven by a concentration gradient, which is the result of continuous solvent evaporation from the film surface. This evaporation process is characterized by the formation of a copolymer-rich surface layer, while the copolymer concentration near the substrate surface represents the initial solution concentration. During the drying process, the film composition is time-dependent and varies over the thickness of the film. Hence concentration gradients are formed within the film; the thickness of the fluid layer, and the evaporation rate of the solvents are the most important factors that determine the steepness of the concentration gradient and therefore significantly effects the pattern formation. A reasonable approximation is that evaporation is a constant throughout spinning, as long as the rotation rate is held constant, which results in the equation obtained by Meyerhofer:

$$\frac{\partial h}{\partial t} = -2kh^3 - e$$

Where h is the film thickness, t the time, and e the evaporation rate of the solvent, which is described by the scaling constant C_e and accounts for the vapor pressure and diffusion through the boundary layer over the substrate. The factor K constitutes the fluid density (ρ), viscosity (η), and the angular velocity (ω) during spin-coating. This approach is strictly valid only when K is constant. However, for spin coating of sol-gel or other complex solutions this may not hold true during all stages of spinning. Both viscosity and density are expected to increase as evaporation progresses. The exact estimation of the polymer concentration due to the absence of a more elaborate theoretical approach is difficult.

Integration over the Meyerhofer equation (3) is a strong approximation to estimate the polymer concentration and film thickness during the spin-coating process as a function of time, because it assumes K to be constant which is strictly valid only for single solvent systems. Thus the result of this integration shown in Figure 4 has to be understood as a pictorial way to illustrate the time-dependent evolution of the concentration. Due to solvent evaporation from the top of the film, its thickness is decreasing, while both the polymer concentration and viscosity of the liquid film are increasing over several orders of magnitude. When the copolymer concentration reaches c > cmc, aggregates begin to form. Depending on the actual solvent composition regular assemblies of copolymer chains are formed. This mechanism is similar to the organization of surfactant molecules in the EISA approach. Due to rapid solvent evaporation, the high molecular weight, and high concentration of copolymer in the liquid film, the system quickly reaches the overlap concentration (c*) and may be characterized as a highly viscous solution (c > c*) with a low mobility of polymer chains. Therefore, the time scale for rearrangements of copolymer chains increases dramatically and the micelle formation may be delayed or even totally prevented in the late stages of spinning. As the remaining solvent evaporates the film morphology is trapped in a non-equilibrium state.

In order to target specific morphologies the type of solvent has to be chosen not only from the point of its solvation power for a specific copolymer but also with respect to its evaporation rate, viscosity, and surface tension. For example, very volatile solvents, such as THF and chloroform, create a strong concentration gradient upon evaporation. Hence, the nano-patterns obtained are far from the thermodynamic equilibrium. In contrast, less
volatile solvents, which evaporate slower, allow relaxation of the copolymer chains to reach structures closer to the equilibrium state. Depending on the solvent evaporation rate, the film morphology is trapped in a kinetic equilibrium state without reaching thermodynamic equilibrium conditions. The latter can be achieved by post-deposition treatments such as thermal- or solvent annealing over long periods.\(^{[32]}\)

Regarding the special case of organic-inorganic hybrid materials, we have found that the character of the solvent not only affects the morphology in thin film but also the particle formation. For example, the particle size and size distribution significantly depend on the chosen solvent. The TEM micrographs presented in Figure 5 demonstrate that the type of solvent significantly affects the size and size distribution of Au-nanoparticles obtained from PS-\(b\)-P[4VP(Au)] from a DMF solution. As the solvent evaporates, the polymer concentration increases; when the cmc is reached, aggregates are formed. As the concentration reaches the overlap concentration (\(c^\ast\)), the aggregates (micelles) interact leading to the formation of a nanoscopically ordered highly viscous solution. When the solvent evaporated completely, this structure is trapped in a glassy copolymer film. The final stage may be extended over a long period of time, especially for low-volatile solvents such as DMF. The inset shows a zoom into the concentration regime close to the point of complete solvent evaporation.

Figure 4. Pictorial representation of the development of the film thickness and the polymer concentration during the spin-coating process of PS-\(b\)-P[4VP(Au)] from a DMF solution. As the solvent evaporates, the polymer concentration increases; when the cmc is reached, aggregates are formed. As the concentration reaches the overlap concentration (\(c^\ast\)), the aggregates (micelles) interact leading to the formation of a nanoscopically ordered highly viscous solution. When the solvent evaporated completely, this structure is trapped in a glassy copolymer film. The final stage may be extended over a long period of time, especially for low-volatile solvents such as DMF. The inset shows a zoom into the concentration regime close to the point of complete solvent evaporation.

such as chloroform (Figure 5c) and THF (Figure 5d) a much wider particle size distribution is obtained with a maximum at around 4.5 nm. Significantly smaller particles (2 nm) are formed in DMF (Figure 5e); however, the particle size distribution is wider than in the case of selective solvent, where micelles are formed. The reason for smaller particles in DMF lies in the stretching of the P[4VP(HAuCl4)] block due to the swelling with solvent. Additionally the solvent (DMF) may also contribute to the stabilization of gold ions through the interaction with the lone electron pairs. A comparison of the particle sizes and size distributions is presented in Figure 5f. If no reduction agent is added, the gold precursor (\(\text{Au}^{3+}\)) is reduced due to the exposure to electron beam during the TEM measurements. In this case, the particle growth is limited due to the low mobility of Au clusters in the glassy polymer matrix. In contrast, if the reduction agent (LiBH\(_4\)) is added to the solution prior to film deposition, the gold precursor (\(\text{Au}^{3+}\)) is reduced simultaneously to \(\text{Au}^0\) followed by particle growth; thus the average metal particle diameter increases with increase in the time of the chemical treatment. As a result large particles and relatively broad size distributions are obtained in common solvents such as THF, DMF, and chloroform while the confined environment of the micelles in selective solvents (toluene, chlorobenzene) limits both the particle size and size distribution.

Based on these observations it is assumed that the particle size is correlated to the aggregation number of copolymeric aggregates and the radius of gyration (\(R_g\)) of the particle-host P4VP block. Therefore, factors such as relative block chain length and solvent quality are of significant importance to control the particle size. Table 2 gives a comparison between the hydrodynamic radius of the PS\(_{227}\)-\(b\)-P4VP\(_{28}\) copolymer measured by DLS and the particle size (\(D_p\)) obtained upon metallization and reduction. However, a direct relationship had not been derived due to the contribution of the PS block to \(R_h\) as well as micellization in case of selective solvents.

It can be difficult to find a solvent for the hybrid material, which also fulfils the requirements to generate the desired morphology in self-assembled thin films. An alternative way to tune the solution properties is based on mixing two or more different solvents in order to solubilize the copolymer, control the generation of aggregates in solution, and finally direct the pattern formation upon solvent evaporation. The aggregation behavior in such solvent mixtures can also be described in terms of solubility parameters, which are estimated by:

\[
\delta_d = \sum \phi_i \delta_{d,i}; \quad \delta_p = \sum \phi_i \delta_{p,i} \quad \text{and} \quad \delta_h = \sum \phi_i \delta_{h,i}
\]

(4)

Where \(\delta_{d,p}\), \(\delta_{p,b}\) and \(\delta_{h,i}\) are the Hansen solubility parameters of the \(i\)th solvent in the mixture and \(\phi_i\) is its
volume fraction. Based on that, a non-selective solvent can be designed by adjusting the volume ratio of different solvents in a blend to yield solubility parameters between those of the blocks of the diblock copolymer. Considering the case of hybrid materials, the effect of the inorganic precursor or the nanoparticles on the solubility has to be taken into account. For example due to the polar character of the gold precursor, micelles may form in solutions of the PS-\(b\)-P[4VP(HAuCl4)] hybrid material even in a non-selective solvent for the neat copolymer.[33] These effects can be compensated by re-adjusting the volume ratio of solvents in the mixture. Moreover, the composition of the solvent blend provides a powerful tool that can be used to direct the structure formation in thin films. An example is presented in Figure 6; well-defined nanostructures are obtained by spin-coating the copolymer hybrid material PS-\(b\)-P[4VP(HAuCl4)] from mixtures of DMF and toluene. The sub-\(\mu\) GISAXS experiments confirm the quite well-developed lateral order in these films. As an example, Figure 7 shows a typical sub-\(\mu\) GISAXS pattern together with a horizontal slice of the 2D intensity called out-of-plane scan. The existence of a strong first order Bragg peak is a fingerprint of the lateral order.

The morphology can be tuned simply by changing the volume fraction of the solvent mixture. Spherical micelles are obtained in pure toluene (6a), which is a selective solvent for the PS block of the diblock copolymer. Above DMF contents of 16% DLS showed no micellization because the solvent mixture dissolves both blocks of the copolymer. Thus a non-selective solvent for hybrid material is designed by blending a selective solvent for the PS block (toluene) with a non-selective solvent (DMF). Spin-coating of PS_{327}-b-P[4VP(HAuCl4)]_{28} from DMF-toluene mixtures onto native oxidized silicon wafers leads to the formation of nano-patterns, morphologies of which differ from the

Table 2. Hydrodynamic radius and particle size of PS_{327}-b-P[4VP(Au)]_{28}.

<table>
<thead>
<tr>
<th>PS-b-P[4VP(Au)] in solvent</th>
<th>(R_h)</th>
<th>(D_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene(^a)</td>
<td>18.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Chlorobenzene(^a)</td>
<td>6.5</td>
<td>3.6</td>
</tr>
<tr>
<td>THF</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Chloroform</td>
<td>5.1</td>
<td>4.5</td>
</tr>
<tr>
<td>DMF</td>
<td>4.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^a\)Due to c > cmc reverse micelles are formed.
structure obtained from non-mixed pure solvents. An example is shown in Figure 6b; the worm-like structure was obtained by spin-coating PS327-b-P[4VP(HAuCl4)]28 from mixtures of DMF and toluene having a ratio of 1:1 (Figure 7 shows the corresponding sub-μ GISAXS data). A more detailed series of morphologies at intermediate DMF contents is shown in the supporting information (SI-1). At high DMF/toluene ratios, the patterns are comparable to the structure obtained from DMF. Therefore the characteristic length scale of the nano-patterns can be adjusted in a wide range by changing the solvent composition of the polymer solution (Figure 6d).

Describing the pattern formation in thin films of hybrid materials spin-coated from solvent mixtures is intricate compared to using a single solvent. Again, a concentration gradient over the film thickness drives the self-assembly of the copolymer hybrid material but the process becomes more complex when solvent mixtures are involved. Figure 8a demonstrates the evolution of the film composition during solvent evaporation of block copolymer dissolved in a binary solvent blend of DMF and toluene. Due to its higher vapor pressure, toluene evaporates faster than DMF. Hence the composition of the liquid film changes during the deposition process depending on the evaporation rate of both the solvents. As most of the toluene evaporated, the remaining solvent (DMF) dominates the structure formation provided that the mobility of polymer chains is sufficiently high. Hence adjusting the composition of the DMF-toluene blend allows tuning the surface patterns. In Figure 8b the evolution of the film composition is shown in a schematic phase diagram for spin-coating PS327-b-P[4VP(HAuCl4)]28 from DMF-toluene mixtures. The starting point A marks the initial composition of the block copolymer solution. Depending on these initial conditions (A) the composition evolves along different trajectories in the phase diagram (Figure 8b). As the concentration of copolymer increases, the cmc (B) is reached, leading to the formation of micellar aggregates. However, with increase in copolymer concentration, also the viscosity of the liquid film increases, thus reducing the mobility of polymer chains and preventing
reorganization of copolymer chains. At this stage interactions among the residual solvent, both blocks of the hybrid material, and the substrate surface gains significant importance. Instabilities in the liquid film due to thermally exited perturbations and non-uniform solvent evaporation may lead to local breakup of the film, a consequence of which regular surface patterns are formed having a wavelength which is dependent on the film thickness and the surface tension of the film. In the case of PS-\(b\)-P[4VP(HAuCl4)] spin-coated from DMF-toluene mixtures (Figure 6b) onto native oxidized silicon, the PS block dewets the hydrophilic Si/SiO2 surface, while both the P4VP block and the residual solvent (DMF) wet the substrate. Since both polymer blocks are well-soluble in DMF, swelling of the PS block with solvent mediates the wetting of the PS block with the hydrophilic substrate. As solvent evaporation is completed (C), the film morphology is trapped in this non-equilibrium state; further modification requires a high mobility of polymer chains, e.g., thermal annealing above \(T_g\) or swelling with solvent vapor. It is important to note, that the hybrid material PS\(_{327}\)-\(b\)-P[4VP(HAuCl4)]\(_{28}\) in a binary solvent blend displays a rich phase behavior. The simple model given in Figure 8b does not yield a sufficient description of the phase diagram. Yet even this simple model signifies that depending on the initial composition (A), the material undergoes various phase transitions (B) until the final composition (C) is reached, where some solvent remains entrapped in the film. The morphology of spin-coated thin films reflects the entire deposition process, summarizing the phase transitions occurring during solvent evaporation. Therefore, the initial solution composition is an important factor that can be adjusted to control morphology of spin-coated thin films.

Effect of Polymer Concentration

The morphology of the hybrid material in thin film also depends on the initial block copolymer concentration. There are two main factors relating the polymer concentration with the pattern formation in spin-coated thin films. These factors are the film thickness obtained after the deposition process and the viscosity of the copolymer solution during solvent evaporation. Both parameters change over several orders of magnitude. The film thickness increases with the initial concentration simply because more material is applied onto the substrate. Additionally, as indicated by equation (3), the solution viscosity significantly affects the thinning of a film during spin-coating. Therefore, besides controlling the solvent quality and evaporation rate, also the initial polymer concentration can also be adjusted in order to control the morphology of the hybrid material in thin films.

The effect of the polymer concentration on the morphology in thin films of PS-\(b\)-P[4VP(HAuCl4)] is demonstrated in Figure 9a–d. The films were deposited on Si/SiO2 substrates from toluene solutions of varying initial solution concentrations between 0.05 and 10 mg·mL\(^{-1}\). At very low polymer concentrations such as 0.05 mg·mL\(^{-1}\) (Figure 9a) a disordered, micellar morphology is formed. These micelles are randomly distributed within the film. However, drying mediated phenomena and dewetting of both the corona forming chains (PS block) and the solvent (toluene) can lead to the formation of regular surface patterns such as rings shown in Figure 9a. As the initial polymer concentration
increases the film coverage is increased and hexagonally ordered regions of compact micellar layers are formed (Figure 9b). Yet the film is not continuous, consequently networks of densely packed micelles are formed (inset Figure 9b). At concentrations of 1.0 mg·mL⁻¹ a continuous monolayer of hexagonally ordered micelles are obtained (Figure 9c). Well-defined, hexagonally ordered domains are formed over short length scales (≈1 μm). However, defects can be cured through fine tuning of the film thickness followed by thermal- or solvent annealing, leading to perfectly ordered thin films. As expected thick multilayer films having a hexagonal close-packing of spherical micelles are formed at high initial solution concentrations (Figure 9d). The film surface appears smooth and almost featureless; however as indicated by the inset in Figure 9d the top-most layer consists of densely packed spherical micelles.

The development of micellar films with increase in solution concentrations is shown schematically in Figure 10; three different regions can be defined with respect to the initial solution concentration. At low polymer concentrations, well-separated micelle bumps are formed (region A); both the solvent (toluene) and the PS shell of the micelles dewet the hydrophilic Si/SiO₂ substrate. Micellar monolayer can be fabricated, when a certain concentration threshold is reached (region B). Entanglements among the shell forming PS chains of the micelles lead to relatively smooth films. Therefore, the micellar bump height \(h_M\) is reduced significantly. Additionally, the average spacing between the micellar bumps decreases due to the formation of domains with hexagonal-closest packing of spherical micelles. At much higher concentration, compact multilayers are formed; both the micellar spacing and the micelle bump height remain constant (region C).

The characteristic distance \(A\) and micelle bump height as a function of the initial solution concentration are shown in Figure 10b and c; the regions A, B, and C are highlighted in both plots. The transition between the A and C marks the threshold (≈0.15 wt.% = 1.3 mg·mL⁻¹) for the formation of a monolayer (region B) of closely packed spherical micelles of PS-b-[4VP(HAuCl₄)]. Below this threshold discontinuous films are formed; there is a strong correlation between the initial solution concentration and the micellar bump height as well as the average spacing between surface micelles. In the opposite case, high concentrations result in the formation of multilayer. Hence, adjusting the initial solution concentration of the hybrid material provides means to control both the dimensions and the morphology in micellar thin films.

The structure formation is different in the case of non-selective solvents, where the hybrid material does not form...
aggregates. As demonstrated for mixtures of DMF and toluene, a non-selective solvent can be designed by blending two different solvents. The concentration dependence of the morphology of thin films deposited from these solvent mixtures is shown in Figure 11. At low concentrations (0.05 mg·mL⁻¹) a disordered morphology is obtained (Figure 11a); dewetting droplets of PS-b-P[4VP(HAuCl₄)] are randomly distributed over the substrate. In contrast to that, nano-patterns with a characteristic spacing of \( \lambda = 41 \) nm and hexagonal short-range order (Figure 11b) can be generated at higher polymer concentrations (0.1 mg·mL⁻¹). Since the surface energy of PS is lower than those of P4VP, the PS block enriches at the polymer-air interface, while the precursor loaded P4VP block P[4VP(HAuCl₄)] preferentially wets the hydrophilic Si/SiO₂ substrate. Hence the surface patterns consist of a core of P[4VP(HAuCl₄)] and a dewetting shell of PS.

As the solution concentration increases, ribbon-like morphologies are formed having a spacing of 48 nm (Figure 11c and d). Eventually, these ribbons merge to form a continuous worm-like morphology with \( \lambda = 50 \) nm (Figure 11e). The corresponding FFT image (inset) shows a sharp ring indicating a regular but isotropic structure. As expected a continuous and mainly featureless thin film (Figure 11f) is generated when a certain concentration threshold (≈1 mg·mL⁻¹) is reached. Moreover, at higher polymer concentrations (Figure 11g and h) aggregates of the hybrid material are formed during the deposition process; the resulting morphology represents network-structures of spherical and rod-like micelles.

It is well known, that the film thickness plays an important role in microphase separated block copolymer films. For example, for a symmetrical diblock copolymer having a lamellar morphology with domain orientations parallel to the substrate, the total film thickness (\( h \)) has to obey the relation \( h = (n + 1/2)L_0 \) to form a continuous film; where \( n \) is a positive integer and \( L_0 \) is the bulk lamellar period of the copolymer.[36] If the film thickness does not match this natural film thickness of the copolymer, islands or holes are formed to compensate for the excess or deficiency material. Spin-coated thin films are usually trapped in non-equilibrium morphologies rather than an ordered microphase separated structure; therefore this quantization of the film thickness does not hold true. However, the formation of non-equilibrium patterns in spin-coated thin films also depends on the film thickness. For instance the pattern formation at low film thicknesses (<100 nm) is dominated by molecular interactions between the fluid (copolymer and solvent) layer and the substrate.[37] In thick films however, thermo-capillary effects play an important role. For example the characteristic wavelength (\( \ell \)) of liquid film instabilities such as spinodal

![Figure 11. AFM height images demonstrating the development of the surface morphology of PS-b-P[4VP(HAuCl₄)] films, spin-coated from a DMF-toluene solution on native oxidized silicon. The initial solution concentration was (a) 0.05, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.7, (f) 1.0, (g) 3.0, (h) 5.0 mg·mL⁻¹, leading to an average heights of the surface features of 7.3, 8.6, 7.9, 7.6, 6.5, 6.2, 12.4 and 16.1 nm respectively. The corresponding FFT images are shown in the insets.](image-url)
dewetting\textsuperscript{38} and thermo-capillary effects\textsuperscript{39} is a function of the film thickness, the viscosity, and the surface tension of the film; which are strongly related to the polymer concentration.

The high evaporation rate during the spin-coating process relates to a steep concentration gradient; resulting in high Marangoni numbers\textsuperscript{69,70} which in return lead to relative short wavelengths of the corresponding surface patterns. Unfortunately, there is no easy way of assessing the Ma of polymer blend solutions during spin-coating directly. In theory, the Ma instability leads to regular pattern formation can be neglected. Therefore, the morphology of ultra-thin spin-coated thin films of PS-b-P[4VP(HAuCl\textsubscript{4})] cannot be described by the Ma effect only; additionally (spinodal-) dewetting of both polymer blocks (PS and P4VP) as well as polymer-solvent and solvent-substrate interactions have to be taken into account. However, the Ma effect will gain significant importance in thicker films deposited and spin-coated at higher polymer concentrations. Altogether, controlling the morphology of block copolymer hybrid materials in thin film is an important issue. The morphology of thin films of hybrid materials based on a diblock copolymer and inorganic nanoparticles is largely unpredictable. Yet, herein we demonstrated that both the type of solvent and the initial polymer concentration can serve as tools to control the morphology of spin-coated thin films.

**Conclusion**

In this article we presented a way to control the formation of non-equilibrium nano-patterns in spin-coated thin films of functional hybrid materials. The hybrid material based on the diblock copolymer (PS-b-P4VP) and metallic nanoparticles was designed through metallization of the pyridine units’ in situ using a wet chemical process. Subsequently, solutions were spin-coated on a solid substrate to obtain nanostructured thin films. It was found that the type of solvents and the polymer concentration can be used as parameters to direct the morphology of spin-coated thin films. In particular, control over the morphology of hybrid materials, particle size and size distribution is achieved. We demonstrated that the type of solvent not only affects the pattern formation but also the particle size and size distribution. Moreover, the initial concentration can also serve as a tool to direct the pattern formation due to its effect on thermo-capillary forces. As a result not only the morphology and the particle size can be controlled but also the characteristic length scale and the height of the surface patterns may be adjusted. Other structural determinant factors such as the molecular weight, the volume fraction of the copolymer, and the influence of annealing are currently under investigation.

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