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Nanoporous Thin Films from Self-Assembled Metallo-Supramolecular Block Copolymers**

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Block copolymers have attracted increasing interest due to their ability to self-assemble into well-ordered periodic structures. The size of these structures is determined by the molecular weight of the polymer blocks and thus lies in the nanometer range. Different morphologies, e.g., spheres, cylinders, and lamellae, can be obtained depending on the block length ratio and interaction parameter.^[1] The cylindrical morphology is of particular interest since it can be transformed into an array of nanopores after elimination of the minor component.^[2,3] These porous materials can in turn be used as templates for functional nanostructures, such as high-density nanorod arrays for information-storage applications.^[4,5] To exploit the full potential of these block copolymers, the cylindrical microdomain orientation has to be controlled. An orientation normal to the substrate is particularly desirable. The main reported methods to achieve this target require the use of external fields such as electric fields,^[6,7] controlled interfacial interactions,^[8,9] and solvent evaporation.^[10,11]

In contrast to the intensively studied self-assembly of conventional block copolymers, i.e., composed of two or more distinct macromolecules linked together through covalent bonds, very few studies so far have reported on “metallo-supramolecular” block copolymers;^[12–17] most of these reports dealt with block copolymer self-assembly in a selective solvent (micelle formation).^[12–14] In these compounds, the different polymer blocks are linked together by metal–ligand complexes.^[18,19] These copolymers offer several advantages over their covalent counterparts. The reversibility of the supramolecular bond potentially allows for improved control over the material properties, e.g., the construction of “smart” materials. Moreover, the presence of a metal complex in the copoly-

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mer structure introduces additional electrochemical and photochemical properties. These novel copolymers therefore represent highly promising candidates for the formation of functional nanostructured materials. A few other examples of block copolymers bearing a reversible linkage at the junction have been reported. They include the use of electrostatic interactions to link the blocks,^[20] and the incorporation of a photocleavable group at the junction.^[21]

In this paper, we report on a new approach to obtain nanoporous thin films using metallo-supramolecular block copolymers. The first step involves the self-assembly of a polystyrene-[Ru]-poly(ethylene oxide) diblock copolymer, (PS-[Ru]-PEO), where -[Ru]- represents a ruthenium(II)-terpyridine bis-complex (Scheme 1), directly yielding cylindrical microdomains oriented normal to the substrate. The second step consists of opening the ruthenium(II)-terpyridine bis-complex via redox chemistry and extracting the PEO block to create the nanopores. This approach thus offers a high degree of control over the removal of the minor block by precisely cleaving the two blocks right at their junction. All methods reported up to now for the creation of nanopores rely on the degradation of the minor block by ozonolysis of polydienes,^[22] UV etching of poly(methyl methacrylate),^[2] hydrolysis of polyesters,^[23] or HF etching,^[24] thus providing less control over the chemistry of the process.

Figure 1a shows the atomic force microscopy (AFM) phase image of a 74 nm thick, spin-coated, PS₃₇₅-[Ru]-PEO₂₂₅ metallo-supramolecular block copolymer film. An array of nanoscopic cylindrical domains, oriented normal to the substrate, is seen at the surface of the film where the cylinders are formed by the minor component (PEO), the matrix being formed by the major component (PS). The average center-to-center distance of the cylindrical domains is 63 nm, with an average cylinder diameter of 33 nm. As reported by Russell and co-workers for covalent PS-*b*-PEO,^[10] cylinders oriented normal to the substrate are obtained directly after spin-coating due to a solvent-evaporation front propagating through the film from its surface to the interface with the substrate.

Before removing the PEO, the copolymer films were briefly exposed to deep-UV radiation to stabilize them by slightly crosslinking the PS matrix. The samples were then immersed for 1 h in an aqueous 10⁻² M Ce(SO₄)₂ solution brought to pH 1 with sulfuric acid, immersed for 30 min in water, and finally dried with a flux of nitrogen. Due to the water solubility

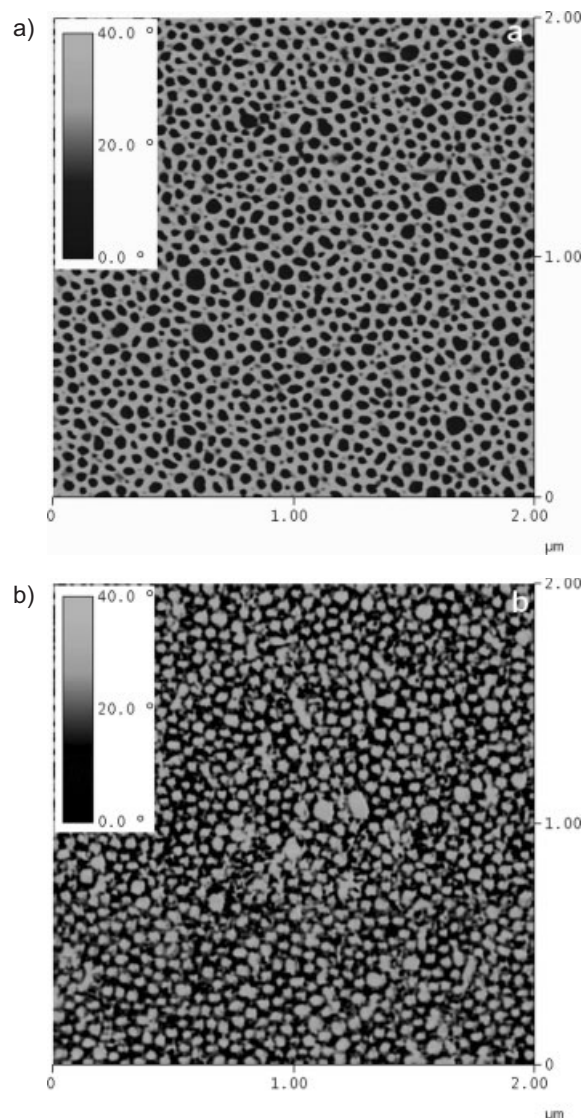
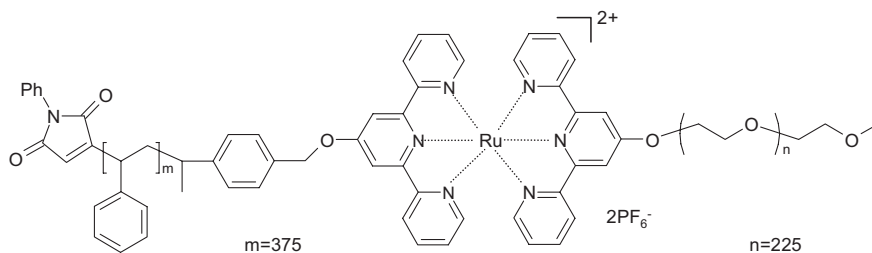


Figure 1. AFM phase images of a) PS₃₇₅-[Ru]-PEO₂₂₅ film (74 nm in thickness) obtained by spin-coating on silicon, showing the PEO cylindrical microdomains oriented normal to the film surface, and b) of the same film after creation of the pores by treatment with Ce(SO₄)₂ solution. The phase scale is shown in the inset.

of PEO, the solution can swell the polymer in the cylinders, and the cerium(IV) sulfate can access the ruthenium(II)-terpyr-



Scheme 1. Schematic representation of the chemical structure of the PS₃₇₅-[Ru]-PEO₂₂₅ metallo-supramolecular block copolymer used in this study. The numbers in the subscripts represent the average degree of polymerization of each block.

idine bis-complexes located at the interface with the PS matrix. Ce^{IV} can then oxidize Ru^{II} into Ru^{III} . Ce^{IV} has a reduction potential of 1.43 V vs. saturated calomel electrode (SCE),^[25] which is sufficient for the oxidation of the Ru^{II} -terpyridine bis-complex to Ru^{III} (the oxidation potential of the bis-complex is 1.19 V vs. SCE). Since Ru^{III} ions are known to form mono-complexes with terpyridine ligands,^[26] the aforementioned redox reaction results in the breaking of the Ru^{II} -terpyridine bis-complex and in the formation of $\text{PS}[\text{Ru}^{\text{III}}]$, $\text{PS}-$, $\text{PEO}[\text{Ru}^{\text{III}}]$, and $\text{PEO}-$ species (where “-” denotes the free terpyridine ligand, and “ $[\text{Ru}^{\text{III}}]$ ” denotes the ruthenium-terpyridine monocomplex). Because this reaction was carried out in an aqueous medium, the water-soluble $\text{PEO}[\text{Ru}^{\text{III}}]$ and $\text{PEO}-$ blocks were extracted into the water phase while the insoluble, partly crosslinked $\text{PS}[\text{Ru}^{\text{III}}]$ and $\text{PS}-$ nanoporous matrix remained on the substrate. Shown in Figure 1b is the AFM phase image of a copolymer film after treatment with the $\text{Ce}(\text{SO}_4)_2$ solution. The inversion of the phase contrast compared to Figure 1a is clearly seen, evidencing the removal of the PEO blocks.

To provide further evidence for the removal of the PEO blocks and the creation of the pores, X-ray photoelectron spectroscopy (XPS) and X-ray reflectometry (XRR) experiments have been performed on this sample. Figure 2 shows the C_{1s} XPS spectra recorded on a $\text{PS}_{375}\text{-[Ru]}-\text{PEO}_{225}$ copolymer film and on the same film treated with the $\text{Ce}(\text{SO}_4)_2$ solution. For the initial copolymer film (solid line in Fig. 2), the

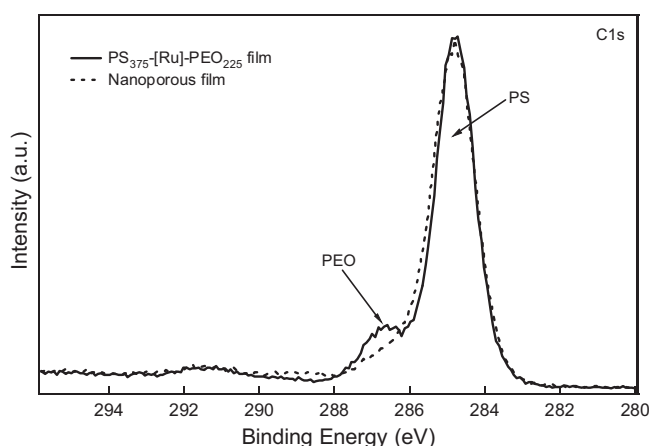


Figure 2. C_{1s} XPS spectra of a metallo-supramolecular copolymer film before (solid line) and after (dashed line) creation of the pores by treatment with a $\text{Ce}(\text{SO}_4)_2$ solution.

components associated with the two polymer blocks are clearly detected, and their intensity ratio exactly matches the copolymer stoichiometry. After treatment, the XPS spectrum (dashed line in Fig. 2) is identical to a pure PS film cross-linked by UV (data not shown), evidencing that only the PS component remains. Moreover, the easily detectable F_{1s} signal of the PF_6^- counterions associated with the initial Ru^{II} -terpyr-

idine bis-complexes completely disappears (data not shown). These observations clearly indicate that the majority of the PEO has been effectively removed from the film and that only the PS matrix remains.

XRR measurements enable the quantification of the film porosity. The critical angle (θ_c) is related to the electron density of the studied film by the equation

$$\theta_c = \lambda(\rho_e r_e / \pi)^{0.5} \quad (1)$$

where λ is the wavelength of the X-rays, ρ_e is the electron density of the film, and r_e is the classical radius of the electron.^[27] The ratio of the electron densities of the sample before and after treatment with the $\text{Ce}(\text{SO}_4)_2$ solution provides a good estimate for the volume fraction of polymer in the treated film, since the electron densities of PS and PEO are very close (0.34 electrons \AA^{-3} and 0.37 electrons \AA^{-3} , respectively). The complement, which is the porosity, corresponds to the volume fraction of removed PEO. The electron densities have been obtained by two methods: directly from the critical angle values (Fig. 3), and from the electron-density profiles of the samples, derived from the reflectogram fits. The first method yields a porosity of 19 %, while the second one gives a value of 22 %. These results show that the PEO has been effectively removed, since the porosity is very close to the PEO volume fraction of 20 %.

In conclusion, we have demonstrated that nanoporous thin films can be obtained using self-assembled metallo-supramolecular block copolymers. In a first step, cylindrical microdomains oriented normal to the substrate are easily obtained by spin-coating without need for further treatment. In a second step, the metal-ligand complexes located at the junction between the two blocks are opened by redox chemistry, which releases the minor block, creating the nanopores. This simple procedure, exploiting the reversibility of a supramolecular linker, provides a higher degree of control over the chemistry of

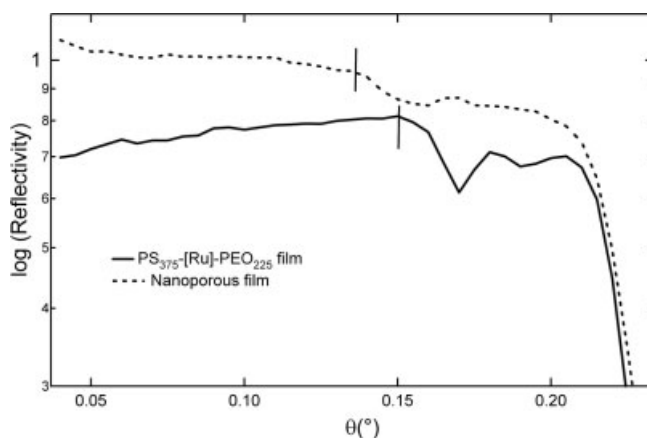


Figure 3. X-ray reflectograms in the critical angle region of a metallo-supramolecular copolymer film before (solid line) and after (dashed line) creation of the pores by treatment with a $\text{Ce}(\text{SO}_4)_2$ solution.

the process as compared to classical approaches using covalent block copolymers. Moreover, this opens the way to functional nanostructures by the possibility of forming new bis-complexes between the terpyridines expected to be present on the pore walls and terpyridine attached to molecules of interest such as dyes, conducting oligomers, nanoparticles, catalysts, polymerization initiators, etc. Such functional nanostructures could find applications as selective membranes, sensors, and templates for polymerization or fabrication of nanorods and nanocylinders.

Experimental

The polystyrene (PS) and poly(ethylene oxide) (PEO) metallo-supramolecular copolymer PS₃₇₅-[Ru]-PEO₂₂₅ was prepared according to procedures described elsewhere [12,28]. The starting PEO₂₂₅ and PS₃₇₅ have been synthesized by living anionic polymerization and nitroxide-mediated controlled radical polymerization using a terpyridine-modified initiator, respectively, and both have a polydispersity index lower than 1.2. The PEO hydroxyl end group was reacted with 4'-chloro-2,2':6',2''-terpyridine to yield the terpyridine-terminated polymer. The two blocks were further used in a two-step synthesis process with ruthenium ions.

Silicon substrates were cleaned using piranha solution and carefully rinsed with ultrapure water. Solutions of the copolymer in benzene were then spin-coated onto these substrates. The spinning speed and/or the solution concentration were used to control the film thickness.

Atomic force microscopy (AFM) images were obtained using a Digital Instruments Nanoscope IV scanning force microscope in tapping mode. X-ray photoelectron spectroscopy (XPS) was performed on a SSIX probe (SSX 100/206) spectrometer from Fisons. Spectra were recorded at a take-off angle of 35° (angle between the plane of the sample surface and the entrance lens of the analyzer) with a pass energy of 150 eV. X-ray reflectometry (XRR) was performed with a two-circle D5000 Siemens goniometer, mounted on a Siemens copper rotating anode (X-rays of 1.5418 Å wavelength). The vertical divergence of the beam was 0.0084°. A special automated alignment procedure allowed us to position the sample within a few micrometers of the goniometer center, which is required for an accurate determination of the critical angle. XRR data were scaled to unit incident intensity and corrected for spill-over.

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