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PAPER

Amine-functionalized nanoporous thin films from a poly(ethylene oxide)-*block*-polystyrene diblock copolymer bearing a photocleavable *o*-nitrobenzyl carbamate junction†

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The synthesis of a poly(ethylene oxide)-*block*-polystyrene (PEO-*b*-PS) diblock copolymer bearing an *o*-nitrobenzyl carbamate junction is reported *via* a one-pot atom transfer radical polymerization (ATRP)–copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC). The accordingly obtained block copolymer was self-assembled into thin films showing, after solvent annealing, ordered PEO cylinders oriented normal to the film surface and embedded in a PS matrix. In the next step, the easy photocleavage of the *o*-nitrobenzyl carbamate junction and the subsequent removal of the PEO nanophase were demonstrated. This led to amine-functionalized nanoporous PS thin films as evidenced by the successful coupling of a fluorescent dye bearing a carboxylic acid group. The possibility to obtain fluorescent nanopores was then further exploited to pattern the films using a photolithographic mask.

Introduction

Due to their ability to self-assemble at the nanoscale into well-ordered periodic structures, block copolymers play a major role in the field of nanotechnology.[1] This self-assembly behaviour can be described by a phase diagram indicating regions of miscibility or immiscibility between the constituent blocks. In the immiscibility region, different morphologies, *e.g.* spheres, cylinders, and lamellae, can be obtained depending on the block length ratio.[1] The cylindrical morphology is of particular interest since it can be transformed into an array of nanopores after elimination of the minor component. The accordingly obtained materials exhibit the pore size and pore topology of their parent structure and can be used in many applications including templating, separation, catalysis, and sensoring.[2] The most widely used methods for the removal of the minor component are ozonolysis,[3] chemical etching[4–6] and UV degradation.[7–10] However, these methods require the use of harsh conditions such as strong acids, strong bases or elevated temperatures. Moreover, they are limited to a few polymers that can be degraded under conditions that do not damage or even destroy the entire material.

Recently, alternative strategies based on the use of cleavable junctions between the different blocks of the precursor block copolymers have been developed. Such approaches allow the selective cleavage of the block junction under relatively mild conditions without altering the rest of the material and are applicable to a wider variety of block copolymers. In this respect, different junctions have been considered so far such as those sensitive to chemical stimuli[11–13] (*e.g.* metal–ligand complexes, tritylether linkages, and disulfide bonds) or to light[14] (photolabile groups).

Photolabile groups are indeed appealing protective tools in organic synthesis and in life sciences because their removal process can typically take place under neutral conditions without using any additional chemical reagents. Among the available photolabile groups, *o*-nitrobenzyl (ONB) derivatives have gained wide acceptance and are commonly used as protecting groups for carboxylic acids, amines and alcohols in the form of *o*-nitrobenzyl esters, carbamates and carbonates, respectively.[15,16]

However, the use of ONB derivatives as junctions to cleave block copolymers in order to obtain nanoporous materials is relatively recent. Only a few recent examples based on ONB ester groups have been reported up to now. Kang and Moon[14] were the first to prepare photocleavable block copolymers based on an ONB derivative. In their approach, a PEO-*b*-PS block copolymer was synthesized by the atom transfer radical polymerization (ATRP) of styrene initiated by a PEO macroinitiator bearing an ONB ester group located just beside the initiating site of the macroinitiator. The self-assembly of the obtained PEO-*b*-PS diblock copolymer led to thin films presenting a PS matrix with well-ordered PEO cylinders, which were removed after UV irradiation resulting in the cleavage of the ONB block junction, by selective extraction in a methanol/water mixture. Recently, our group developed a versatile strategy to synthesize

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a wide range of diblock copolymers where the two blocks are held together by an ONB ester junction using a one-pot simultaneous ATRP and copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC-click reaction).[17] This approach has been adapted to a RAFT-click reaction by Theato and coworkers[18] to prepare ONB ester-based photocleavable PEO-*b*-PS block copolymers used as precursors for the preparation of nanoporous thin films.

Beyond the preparation of nanoporous materials, it can be interesting to functionalize pores in order to perform selective chemistry (attachment of specific molecules such as catalysts, dyes and biomolecules) on the pore walls as well as to tune the surface properties of the pores in terms of hydrophobicity, charge density, *etc.* As a consequence, the corresponding functionalized membranes could be used in different fields of applications such as nano-purification, nano-catalysis and nano-sensing. However, this concept of pore functionalization in nanoporous films is poorly reported. The main previous works in this field reported by Hillmyer and coworkers[19,20] concern the preparation of nanoporous polymer monoliths from ABC triblock copolymer precursors that assemble into a cylindrical morphology, where the A block constitutes the matrix, C is the removable minor component, and B provides the functionality on the surface of the pores. Following this strategy and using polystyrene-*block*-poly(dimethylacrylamide)-*block*-polylactide and polystyrene-*block*-polyisoprene-*block*-polylactide as block copolymer precursors, they prepared nanoporous polystyrene films decorated with carboxylic acid functions and alkene groups in the pores, respectively.

Another interesting approach is the use of an ONB junction between blocks of polymers, since ONB derivatives can provide functionalized pores after removal of the minor phase. In the case of ONB ester groups for example, we have recently highlighted the presence of carboxylic acid groups on the surface of the pores from PEO-*b*-PS block copolymers by coupling with a fluorescent dye.[21]

In this work, we have successfully synthesized a new type of photocleavable PEO-*b*-PS block copolymers bearing an ONB carbamate block junction. Since the photoisomerization of an ONB carbamate derivative leads to an *o*-nitrosobenzaldehyde and the release of the corresponding amine, we here show the possibility to prepare PS nanoporous thin films with nanopores uniformly covered with primary amine groups. The presence of these amine functions inside the pores is demonstrated by reacting them with a fluorescent dye bearing a carboxylic acid group. Finally, patterned fluorescent nanoporous thin films are prepared using a photolithographic mask (Fig. 1).

Results and discussion

The synthesis of the photocleavable PEO-*b*-PS block copolymer investigated in the present study was conducted using a previously reported strategy[17] which consists of the simultaneous ATRP of styrene and CuAAC-click reaction of the ATRP initiator bearing the photocleavable junction to the PEO block. This strategy directly results in a PEO-*b*-PS block copolymer bearing a photocleavable junction between the PS and the PEO block. Since both reactions are catalyzed by the same copper(I) catalyst a one-pot reaction becomes possible.

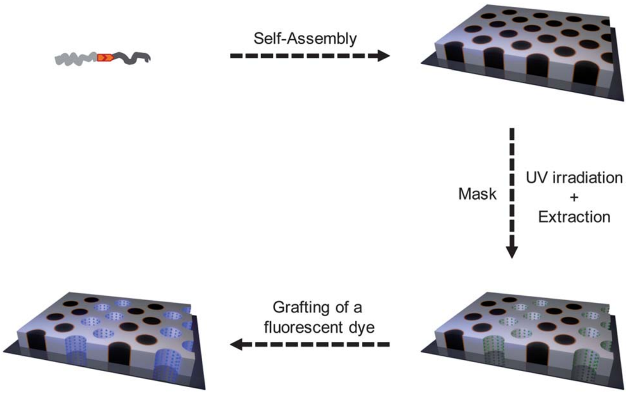


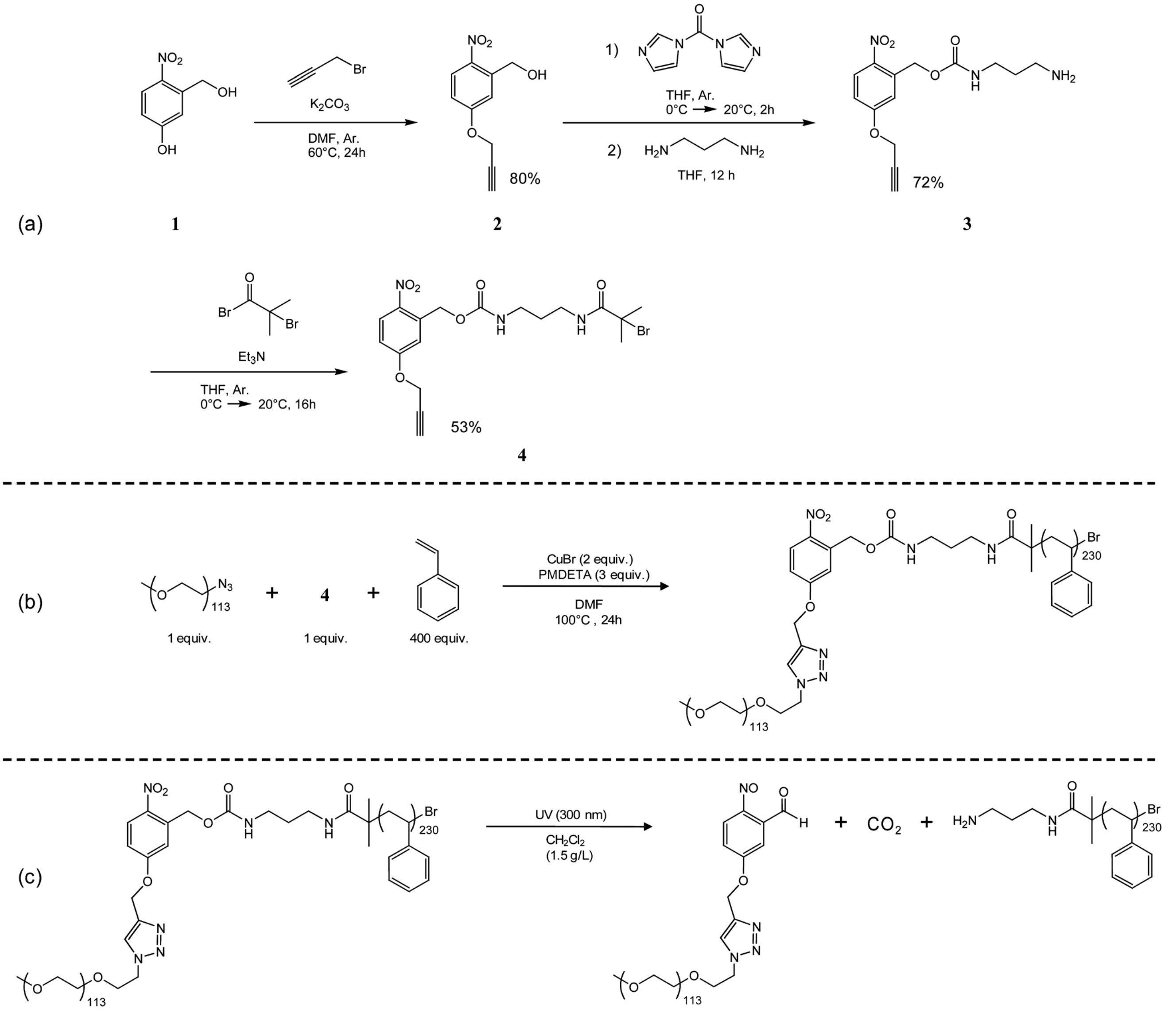
Fig. 1 General strategy for the preparation of patterned fluorescent nanoporous thin films.

The *o*-nitrobenzyl carbamate-based ATRP initiator was synthesized in three steps from a commercially available diol (Scheme 1a). In the first step, the diol **1** is reacted with propargyl bromide in a K_2CO_3/DMF mixture to selectively etherify the phenol. The second step is the preparation of the carbamate following a convenient procedure described by D'Addona and Bochet.[22] This procedure involves the reaction of the alcohol **2** with 1,1′-carbonyldiimidazole to give an imidazolide with the release of one equivalent of imidazole. This imidazolide intermediate is easily trapped by a diamine to yield the carbamate **3** without requiring an additional base. In the last step, the photocleavable initiator **4** is obtained by coupling **3** with bromoisobutyrate bromide.

As shown in Scheme 1b, the initiator **4** was then used for the ATRP of styrene and the concomitant CuAAC with an azide terminated PEO, which was obtained from a commercially available mono-hydroxyl PEO. The one-pot reaction was performed in DMF at 100 °C, with CuBr and PMDETA as a catalytic system. Those reactions were successful and the resulting block copolymer was characterized by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC) as summarized in Table 1.

The styrene conversion obtained after 24 hours of polymerization was 57.5% while the efficiency of the click coupling was estimated to be 73% (see ESI, Fig. S1†), which implies the presence of non-coupled blocks. After removal of the residual non-coupled homopolymers by extraction with selective solvents for each block (diethyl ether for PS and a mixture of methanol/water for PEO), the accordingly obtained PEO_{113}-*hv*-PS_{230} (the numbers in subscript indicate the average degree of polymerization of the corresponding block) diblock copolymer displays a narrow polydispersity index with a clear shift towards higher molecular weight as evidenced by SEC (Fig. 3b).

The next step is the self-assembly of this copolymer in order to generate a cylindrical morphology with the cylinders oriented normal to the film surface. As abundantly reported in the literature,[23–25] a better control of both the orientation and the lateral ordering of the nanoscopic domains during the self-assembly of block copolymers requires the use of external fields, such as electric fields, shear, temperature gradients, chemically patterned substrates, controlled interfacial interactions or solvent evaporation. Among those methods, solvent annealing has attracted



Scheme 1 (a) Synthesis of the *o*-nitrobenzyl carbamate-based initiator, (b) ATRP and CuAAC-click one-pot reaction and (c) photoisomerisation of the *o*-nitrobenzyl carbamate junction.

increasing interest since it is a simple and versatile process to produce highly ordered thin films. For example, Russell and coworkers[26,27] have shown for thin films prepared from PS-*b*-PEO diblock copolymers that highly ordered arrays of nanoscopic cylindrical domains oriented normal to the surface of the film and spanning the entire film thickness can be obtained by solvent annealing.

Inspired by these studies and previous works reported by our group,[11,28] thin films were prepared by spin-coating solutions of the PEO_{113}-*hν*-PS_{230} diblock copolymer in benzene (a good solvent for both PEO and PS blocks) onto silicon substrates and annealed in benzene/water vapours at room temperature for four hours. Using these conditions, ordered cylinders oriented normal to the film surface were obtained as evidenced by atomic force microscopy (AFM) in Fig. 2. In this AFM picture PS constitutes the matrix while PEO, the minor component, forms the cylindrical domains with an average centre-to-centre distance between the cylinders of 32.3 nm and an average cylinder diameter of 21.5 nm.

Table 1 Synthesis of the PEO_{113}-*hν*-PS_{230} block copolymer using ATRP and CuAAC-click one-pot reaction. The starting PEO_{113}-N_3 block is characterized by M_n = 5000 g mol^{-1} and PDI = 1.05

Copolymer[a]	Styrene conversion[b] (%)	$M_{n,RMN}$/g mol^{-1}	$M_{n,SEC}$/g mol^{-1}	PDI[c]
PEO_{113}-*hν*-PS_{230}	57.5	28 900	45 900	1.30

[a] *Reaction conditions*: initiator **4**/PEO_{113}-N_3/CuBr/PMDETA = 1 : 1 : 2 : 3 at a temperature of 100 °C for 24 hours. [b] Determined by ^{1}H NMR. [c] PDI: polydispersity index.

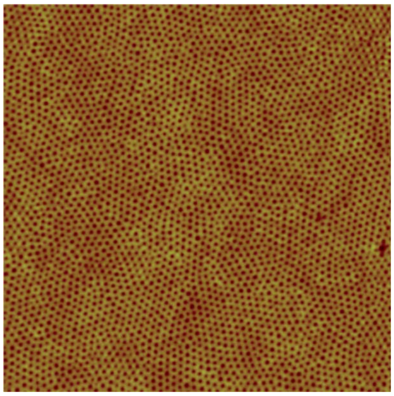


Fig. 2 AFM height image (2 × 2 μm) of a film of PEO$_{113}$-*hv*-PS$_{230}$ spin-coated from a benzene solution (10 g L^{-1}) and annealed in benzene–water vapours for 4 hours.

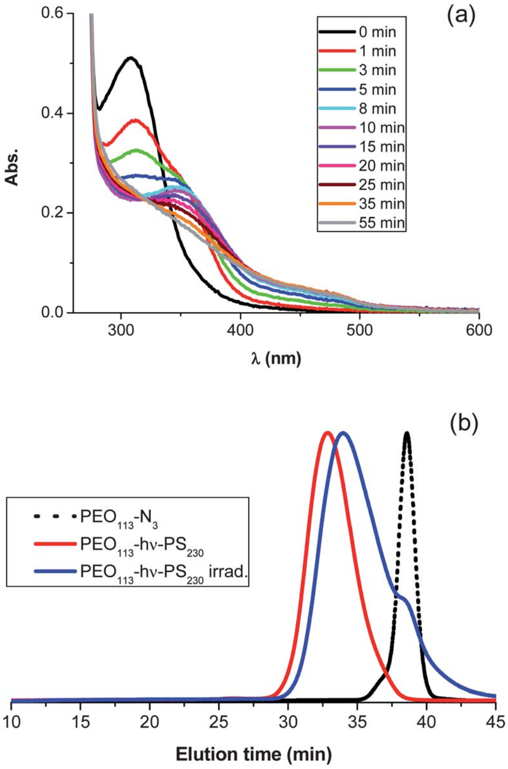


Fig. 3 Cleavage of the PEO$_{113}$-*hv*-PS$_{230}$ block copolymer in CH$_2$Cl$_2$ (without semicarbazide hydrochloride). (a) Evolution of the UV-visible absorption spectra as a function of irradiation time and (b) SEC traces of the azide-functionalized PEO block and the PEO$_{113}$-*hv*-PS$_{230}$ block copolymer before and after UV irradiation at 300 nm for 55 minutes.

As mentioned previously, the mechanism of photo-isomerisation[15] of an *o*-nitrobenzyl carbamate derivative is well known and leads to the corresponding *o*-nitrosobenzaldehyde with the release of a free primary amine group and CO$_2$ (Scheme 1c). However, a possible side-reaction which consists in the formation of an imine, resulting from the reaction of the released amine with the aldehyde photoproduct, can decrease the yield in the obtained free amine groups. This can be avoided by adding a carbonyl scavenger, such as semicarbazide hydrochloride, to the reaction mixture.[29]

The photocleavage of the PEO$_{113}$-*hv*-PS$_{230}$ diblock copolymer was initially investigated by exposing solutions of this copolymer in CH$_2$Cl$_2$ to UV irradiation ($\lambda_{max} = 300$ nm, $I = 38.5$ mW cm^{-2}) without semicarbazide hydrochloride. The evolution of the UV-visible absorption spectrum with the irradiation time is shown in Fig. 3a. The intensity of the band located at 310 nm and associated with the nitro-aromatic moiety decreases with irradiation time, while additional bands appear between 350 and 500 nm due to the formation of the nitroso compound. Furthermore, SEC analysis of the irradiated product (after 55 minutes) shows the disappearance of the peak associated with the copolymer while two new peaks appear on the chromatogram (Fig. 3b), corresponding to the freed PS and PEO blocks. These results clearly demonstrate the efficiency of the cleavage under UV light irradiation, allowing thereby the further preparation of nanoporous structures.

The preparation of nanoporous films from solvent annealed PEO$_{113}$-*hv*-PS$_{230}$ thin films was performed by exposing them, in the solid state, to UV light at 300 nm for 60 min in order to cleave the *o*-nitrobenzyl carbamate junction, followed by the extraction of the PEO nanophases with a mixture of methanol/water (9/1, v/v). The removal of the PEO cylinders and the subsequent formation of nanopores were investigated by transmission electron microscopy (TEM). Fig. 4a and b show the TEM images of stained films (staining in RuO$_4$ vapours for 45 min) before and after PEO extraction, respectively. A homogeneous staining of the TEM specimen is observed before removal of the PEO cylinders (Fig. 4a) while bright circles corresponding to the nanopores are visible after PEO extraction as demonstrated in Fig. 4b. Scanning electron microscopy (SEM) was also performed on the cross-section of a thin film, after extraction of the PEO nanophases (Fig. 4c). This SEM image clearly evidences the formation of a nanoporous thin film.

In order to demonstrate the presence of amine functions inside the pores, we then used Coumarin 343, a fluorescent dye bearing a carboxylic acid group. The reaction between the carboxylic acid groups of the dye and the amines on the pore walls was

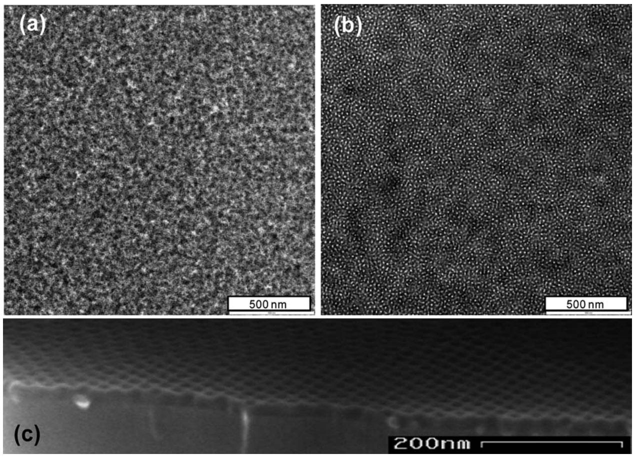


Fig. 4 Microscopy images of PEO$_{113}$-*hv*-PS$_{230}$ thin films after annealing in benzene–water vapours. (a) TEM image of the annealed film stained with RuO$_4$, (b) TEM image of the annealed film stained with RuO$_4$, after extraction of the PEO nanophases and (c) SEM image of the cross-section of a nanoporous thin film (after PEO extraction).

performed by a classical approach[30–32] using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) and hydroxybenzotriazole (HOBt) as peptide coupling reagents.

Fig. 5 shows the fluorescence emission spectra ($\lambda_{ex} = 410$ nm) of the nanoporous film before and after coupling with Coumarin 343. As a reference, we used this dye without peptide coupling reagents. A typical coupling procedure is described as follows. Nanoporous thin films were immersed for 17 hours at room temperature in a methanol solution containing Coumarin 343 and the appropriate peptide coupling reagents (EDAC/HOBt). Then, the films were abundantly washed and rinsed in pure methanol for 18 hours in order to remove unreacted dyes. As shown in Fig. 5, there is almost no difference in the fluorescence signal between the untreated nanoporous films and those soaked in a solution of Coumarin 343 without peptide coupling reagents. However, an intense and characteristic spectrum appears after treatment with Coumarin 343 in the presence of EDAC and HOBt that clearly proves the success of the coupling between the amine groups located on the pore walls and the carboxylic acid groups of the fluorescent dye.

Furthermore, in order to evaluate the impact of the side-reaction leading to the formation of an imine just after photocleavage of the *o*-nitrobenzyl carbamate junction, the yield of the released amine groups was estimated on thin films prepared from the PEO_{113}-*hν*-PS_{230} copolymer exposed to UV light with and without addition of semicarbazide hydrochloride as an *o*-nitrosobenzaldehyde scavenger. The accordingly obtained nanoporous films were then treated with Coumarin 343 (in the presence of EDAC and HOBt) and characterized by fluorescence spectroscopy. The results do not show any significant differences in fluorescence between films irradiated in the solid phase and those irradiated in methanol with or without semicarbazide hydrochloride (see ESI, Fig. S2†). This means that the side-reaction leading to the formation of an imine is minimized, probably due to a steric effect of polymer chains and/or the lack of mobility.

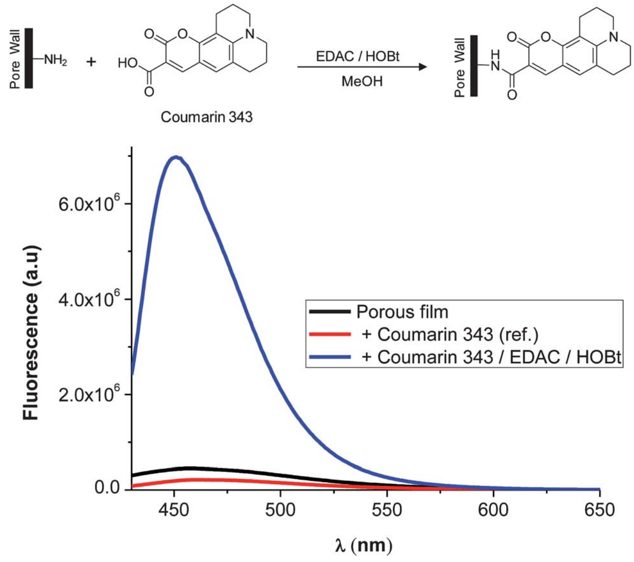


Fig. 5 Grafting of a functionalized fluorescent dye on the pore walls. Fluorescence spectra of: starting nanoporous thin film (black curve), nanoporous thin film soaked in a Coumarin 343 solution without coupling reagents (red curve) and nanoporous thin film soaked in a Coumarin 343 solution with EDAC and HOBt coupling reagents (blue curve).

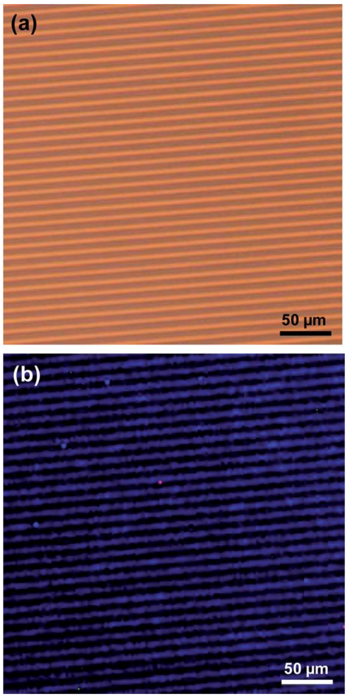


Fig. 6 (a) Optical microscopy image of the photolithographic mask and (b) fluorescence microscopy image of the corresponding pattern transferred to a thin film from the PEO_{113}-*hν*-PS_{230} block copolymer.

Finally, the possibility to graft a fluorescent dye on the pore walls was utilized to pattern thin films from the PEO_{113}-*hν*-PS_{230} diblock copolymer. To this end, the nanostructured films were exposed to UV irradiation ($\lambda_{max} = 365$ nm) for an hour through a photolithographic mask before being washed in a methanol/water solution to remove the cleaved PEO nanophases and then treated with Coumarin 343. The aim here was to elaborate fluorescent nanoporous thin films with non-porous domains corresponding to the pattern of the photolithographic mask.

Fig. 6a and b show, respectively, the optical microscopy image of the photolithographic mask and the fluorescent microscopy image of a PEO_{113}-*hν*-PS_{230} thin film after successive patterning and functionalization with Coumarin 343. As shown by Fig. 6b, one can observe a successful replica of the pattern with blue regions corresponding to parts of the film functionalized with Coumarin 343 since this colour is characteristic of the maximum emission wavelength of Coumarin 343 ($430 < \lambda_{em} < 450$ nm).

Conclusion

We have shown for the first time the possibility to prepare amine-functionalized nanoporous thin films from a PEO-*b*-PS diblock copolymer bearing an *o*-nitrobenzyl carbamate junction. The synthesis of this photocleavable block copolymer was performed using a combined ATRP–click chemistry approach. The accordingly obtained block copolymer was self-assembled into thin films that were further annealed in benzene/water vapours affording a cylindrical morphology oriented normal to the film surface. After UV exposure and removal of the PEO nanophases, nanoporous PS thin films were obtained with nanopores covered by primary amine groups. As a potential application, these functionalized nanoporous films could be used as membranes for selective separation at the nanoscale. Indeed, primary amine groups on the pore walls are interesting anchoring sites for further chemical reactions including peptide coupling or imine formation with biomolecules.

Finally, the amine functionality inside the nanopores has then allowed the grafting of a fluorescent dye. The possibility to functionalize a predetermined area of the film has been demonstrated by irradiating the film through a photolithographic mask. Only the exposed areas have been functionalized with a fluorescent dye demonstrating the success of the patterning.

Experimental part

Materials and instrumentation

Poly(ethylene oxide) monomethylether (PEO_{113}-OH, $M_n = 5000$ g mol^{-1}, PDI = 1.05) was purchased from Polymer Source Inc. and was dried by azeotropic cycles with toluene prior to use. Styrene (Aldrich, 99%) was passed through an activated basic alumina column before use. 5-Hydroxy-2-nitrobenzyl alcohol (Aldrich, 97%) was dried *in vacuo*. Potassium carbonate (K_2CO_3, 99%) was dried for 24 hours in a vacuum oven at 100 °C. Triethylamine (Et_3N) was dried over KOH. *N*,*N*-Dimethylformamide (DMF) was distilled on CaH_2. Tetrahydrofuran (THF) was distilled on sodium/benzophenone. Propargyl bromide (Aldrich, 8 wt% in toluene), CuBr (Aldrich, 99.999%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), tosyl chloride (TsCl, Fluka, 99%), ethyl 2-bromoisobutyrate (Acros, 98%) and all other chemicals were used as received. Flash chromatography was performed on a silica gel (0.040–0.063 μm grade).

^1H and ^{13}C NMR spectra were recorded on a 300 MHz or 500 MHz Bruker Avance II spectrometer. Molecular weights and polydispersity indices of the polymer were measured on a Waters SEC system equipped with a Waters 510 pump and a 410 differential refractometer (40 °C; eluent: DMF; flow rate of 0.5 mL min^{-1}). The calibration was performed using polystyrene standards. Atomic force microscopy (AFM) was performed on a Digital Instruments Nanoscope V scanning force microscope in tapping mode using NCL cantilevers (Si, 48 N m^{-1}, 330 kHz, Nanosensors). Irradiation intensities have been measured with a radiometer RM12 from Dr Gröbel UV-electronik GmbH equipped with UVA (315–400 nm) and UVB (280–315 nm) sensors. UV-vis spectra were recorded on a Varian spectrometer (Cary, 50 Conc). Transmission electron microscopy (TEM) was performed on a LEO 922 microscope, operating at 200 kV accelerating voltage in bright field mode. Samples for TEM experiments were prepared by spin-coating the polymer solution onto a silicon substrate with a large silicon oxide top layer (400 nm). The samples were then floated on a HF solution (5 wt%). After about 90 seconds, they were transferred onto pure water and they were detached from their support, floating on water. Parts of the films were then picked up on TEM grids (pure copper, mesh: 300). The grids were then dried in a vacuum for 15 hours. The staining step was performed by exposing the samples to RuO_4 vapours for 45 minutes. Scanning electron microscopy (SEM) was performed on a Zeiss LEO 982 microscope operating at an acceleration voltage of 10 kV. Cross-sectional analyses were performed at a tilt angle of 15°. Fluorescence spectroscopy measurements were performed on a SPEX-Fluorolog spectro-fluorometer (Horiba-Jobin Yvon) in a front face (FF) mode with an excitation wavelength (λ_{ex}) of 410 nm. Fluorescence Microscopy (FM) was performed on an Olympus AX70 microscope operated in the reflection mode. The fluorophore was excited (λ_{ex} = 290–400 nm) with a UV lamp (Hamamatsu LC5) equipped with a 150 W xenon lamp (L8253). A band pass filter (LOT-Oriel, 360 nm, FWHM = 40 nm) was placed in the excitation path. The fluorescence images were captured through a long working distance objective (×50, NA 0.45) using an Olympus Color View III camera (2576 × 1932 pixels resolution). Ellipsometry was performed using an SE 800 PV spectroscopic ellipsometer (Sentech). The photolithography was performed using a contact aligner (K&W) equipped with an Hg lamp.

Synthesis of 5-propargylether-2-nitrobenzyl alcohol (2)

This synthesis was previously described.[17]

Synthesis of 5-propargylether-2-nitrobenzyl carbamate (3)

1,1-Carbonyldiimidazole (120 mg, 0.74 mmol) was dissolved in anhydrous THF (2 mL) and the solution was cooled to 0 °C. Under argon, 5-propargylether-2-nitrobenzyl alcohol (**2**, 152.5 mg, 0.74 mmol) was added dropwise as a solution in THF (2 mL). The mixture was stirred at room temperature for 3 hours. This mixture was slowly added *via* a cannula to a solution of 1,3-diaminopropane (138.5 μL, 1.66 mmol) in THF (4 mL) previously cooled to 0 °C. The obtained solution was then slowly brought to room temperature and stirred overnight. THF was removed under reduced pressure and the residue was dissolved in ethyl acetate. The mixture was washed four times with 10% HCl, and twice with brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to give the carbamate **3** as a yellow crystalline solid (164 mg, 72%).

^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.20 (d, 1H, $^3J = 9.1$ Hz, H_{Ar}), 7.15 (s, 1H, H_{Ar}), 6.98 (d, 1H, $^3J = 9.1$ Hz, H_{Ar}), 5.65 (s, 1H, $-NH-$), 5.54 (s, 2H, $-CH_2-OCO-$), 4.79 (d, 2H, $^4J = 2.3$ Hz, $C{\equiv}C-CH_2-$), 3.34 (q, 2H, $^3J = 6.2$ Hz, $^3J = 12.4$ Hz, $-NH-CH_2-$), 2.83 (t, 2H, $^3J = 6.4$ Hz, $-CH_2-NH_2$), 2.60 (t, 1H, $^4J = 2.3$ Hz, $-C{\equiv}CH$), 1.67 (m, 2H, $-CH_2-$), 1.44 (s, 2H, $-NH_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 161.7 ($C_{Ar}-O-$), 157.4 (C=O), 141.6 ($C_{Ar}-NO_2$), 137.8 ($C_{Ar}-CH_2-$), 126.0 ($H-C_{Ar}$), 115.8 ($H-C_{Ar}$), 114.7 ($H-C_{Ar}$), 79.2 ($H-C{\equiv}C-$), 78.5 ($H-C{\equiv}C-$), 64.2 ($-CH_2-OCO-$), 59.3 ($C{\equiv}C-CH_2-$), 39.4 ($-NH-CH_2-$), 38.0 ($-NH-CH_2-$), 31.3 ($-CH_2-$).

Synthesis of 5-propargyl-2-nitrobenzyl carbamate bromoisobutyrate (4)

Under argon, a solution of bromoisobutyrate bromide (53.6 μL, 0.43 mmol) in 1 mL of THF was added dropwise to a stirred solution of 5-propargylether-2-nitrobenzyl carbamate **3** (120.9 mg, 0.39 mmol) and triethylamine (60.3 μL, 0.43 mmol) in THF

(1.5 mL) at 0 °C. The mixture was gradually brought to room temperature and stirred overnight. THF was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with water. The organic phases were combined, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified on flash chromatography (eluent: chloroform/acetone, 93/7, v/v) affording a yellow viscous product (95 mg, 53%).

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.21 (d, 1H, $^{3}J = 9.1$ Hz, H_{Ar}), 7.17 (s, 1H, H_{Ar}), 7.09 (s, 1H, –N*H*–), 6.99 (d, 1H, $^{3}J = 9.1$ Hz, H_{Ar}), 5.56 (s, 2H, –C*H*$_2$–OCO–), 4.79 (d, 2H, $^{4}J = 2.4$ Hz, –C≡C–C*H*$_2$–), 3.37 (q, 2H, $^{3}J = 6.3$ Hz, $^{3}J = 12.5$ Hz, –NH–C*H*$_2$–), 3.27 (q, 2H, $^{3}J = 6.3$ Hz, $^{3}J = 12.5$ Hz, –NH–C*H*$_2$–), 2.62 (t, 1H, $^{4}J = 2.4$ Hz, –C≡C*H*), 1.96 (s, 6H, C*H*$_3$), 1.71 (m, 2H, –C*H*$_2$–).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 173.1 (C=O), 162.0 (C_{Ar}–O), 156.5 (C=O), 141.0 (C_{Ar}–NO_2), 137.1 (*C*$_{Ar}$–CH_2), 128.1 (H–C_{Ar}), 114.8 (H–C_{Ar}), 113.6 (H–C_{Ar}), 77.3 (H–C≡*C*–), 77.1 (H–*C*≡C–), 63.8 (*C*H_2–OCO–), 62.6 (C–Br), 56.6 (C≡C–*C*H_2), 37.9 (–NH–*C*H_2), 37.1 (–NH–*C*H_2), 32.8 (–CH_3), 30.2 (–CH_2–).

Synthesis of PEO_{113}-N_3

This synthesis was previously described.[17]

Synthesis of PEO_{113}-*hν*-PS_{230}

Under argon, a Schlenk tube with CuBr (17.3 mg, 0.12 mmol, 2 equiv.) was filled with a solution containing styrene (2512 mg, 24.12 mmol, 400 equiv.), PMDETA (41.8 mg, 0.24 mmol, 3 equiv.), PEO_{113}-N_3 (303 mg, 0.06 mmol, 1 equiv.), and DMF (925 μL) previously degassed by three freeze–pump–thaw cycles. The mixture was stirred for 5 minutes and was then frozen. Under argon, 215 μL (0.06 mmol, 1 equiv.) of a solution of the photocleavable initiator **4** in DMF ($C = 100$ g L^{-1}) was added. The mixture was degassed by three freeze–pump–thaw cycles, filled with argon, and stirred in an oil bath at 100 °C for 24 hours (styrene conversion = 57.5%). The mixture was diluted with CH_2Cl_2 and washed with aqueous EDTA (0.04 mol L^{-1}) to remove the copper catalyst. The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was precipitated twice in hexane, filtered and dried *in vacuo* at 35 °C for 24 hours. Residual homo-PEO and homo-PS were removed by extraction with selective solvents (diethyl ether for PS and a mixture of methanol/water, 90/10, v/v for PEO).

M_n (SEC) = 45 900 g mol^{-1}; PDI (SEC) = 1.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 8.17 (m, 1H, H_{Ar} in the *ortho* position of –NO_2; junction), 7.89 (s, 1H, =CH triazole; junction), 7.47 (s, 1H, N*H*–CO; junction), 7.30–6.24 (m, 1152H, H_{Ar}; PS + junction), 5.53 (s, 2H, –C*H*$_2$–OCO–; junction), 5.31–5.28 (m, 3H, C*H*$_2$–O, ether; junction + C*H*–Br, end chain), 3.64 (s, 452H, C*H*$_2$; PEO), 3.38 (s, 3H, C*H*$_3$–O, PEO), 2.4–1.2 (m, 690H, $H_{backbone}$; PS).

Nanoporous thin films preparation

Silicon substrates were cleaned by a piranha solution and abundantly rinsed with ultra-pure water. Solutions of the copolymer in benzene (10 g L^{-1}) were spin coated onto these substrates at 2000 rpm for 40 s. The obtained films were annealed in benzene/water vapours for 4 hours before being evaluated by ellipsometry (film thickness of 69 nm for a polymer concentration of 10 g L^{-1}). To cleave the PEO phase, the block copolymer films were placed under three UV lamps (Rayonet photochemical reactor) emitting at a wavelength (λ_{max}) of 300 nm with an intensity of 38.5 mW cm^{-2}. After 1 hour of exposure, the films were immersed in a methanol/water (9/1, v/v) solution for 18 hours.

Grafting of Coumarin 343

The nanoporous thin films were soaked in 5 mL of a solution containing Coumarin 343 (14 mg L^{-1}), HOBt (10 mg L^{-1}) and EDAC (10 mg L^{-1}) in methanol. After 17 hours, the films were abundantly rinsed and immersed overnight in pure methanol.

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References

1 I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692–1712.
2 M. Hillmyer, *Adv. Polym. Sci.*, 2005, **190**, 137–181.
3 P. Mansky, C. K. Harrison, P. M. Chaikin, R. A. Register and N. Yao, *Appl. Phys. Lett.*, 1996, **68**, 2586.
4 J. M. Leiston-Belanger, T. P. Russell, E. Drockenmuller and C. J. Hawker, *Macromolecules*, 2005, **38**, 7676–7683.
5 M. Glassner, J. P. Blinco and C. Barner-Kowollik, *Polym. Chem.*, 2011, **2**, 83–87.
6 K. Satoh, J. E. Poelma, L. M. Campos, B. Stahl and C. J. Hawker, *Polym. Chem.*, 2012, DOI: 10.1039/c1py00484k.
7 C. Tang, K. Sivanandan, B. C. Stahl, G. H. Fredrickson, E. J. Kramer and C. J. Hawker, *ACS Nano*, 2010, **4**, 285–291.
8 T. Thurn-Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Bal, M. Tuominen, C. J. Hawker and T. P. Russell, *Adv. Mater.*, 2000, **12**, 787–791.
9 T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell, *Science*, 2000, **290**, 2126–2129.
10 J. Bang, S. H. Kim, E. Drockenmuller, M. J. Misner, T. P. Russell and C. J. Hawker, *J. Am. Chem. Soc.*, 2006, **128**, 7622–7629.
11 C. A. Fustin, B. G. G. Lohmeijer, A. S. Duwez, A. M. Jonas, U. S. Schubert and J. F. Gohy, *Adv. Mater.*, 2005, **17**, 1162–1165.
12 M. Zhang, L. Yang, S. Yurt, M. J. Misner, J. T. Chen, E. B. Coughlin, D. Venkataraman and T. P. Russell, *Adv. Mater.*, 2007, **19**, 1571–1576.
13 J.-H. Ryu, S. Park, B. Kim, A. Klaikherd, T. P. Russell and S. Thayumanavan, *J. Am. Chem. Soc.*, 2009, **131**, 9870–9871.
14 M. Kang and B. Moon, *Macromolecules*, 2009, **42**, 455–458.
15 J. F. Cameron and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1991, **113**, 4303–4313.
16 A. Patchornik, B. Amit and R. B. Woodward, *J. Am. Chem. Soc.*, 1970, **92**, 6333–6335.
17 J.-M. Schumers, J.-F. Gohy and C.-A. Fustin, *Polym. Chem.*, 2010, **1**, 161–163.
18 H. Zhao, W. Gu, E. Sterner, T. P. Russell, E. B. Coughlin and P. Theato, *Macromolecules*, 2011, **44**, 6433–6440.
19 J. Rzayev and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2005, **127**, 13373–13379.
20 T. S. Bailey, J. Rzayev and M. A. Hillmyer, *Macromolecules*, 2006, **39**, 8772–8781.
21 J.-M. Schumers, A. Vlad, I. Huynen, J.-F. Gohy and C.-A. Fustin, *Macromol. Rapid Commun.*, 2012, **33**, 199–205.
22 D. D'Addona and C. G. Bochet, *Tetrahedron Lett.*, 2001, **42**, 5227–5229.

23 S. H. Kim, M. J. Misner, L. Yang, O. Gang, B. M. Ocko and T. P. Russell, *Macromolecules*, 2006, **39**, 8473–8479.

24 C. Park, Y. Yoon and E. L. Thomas, *Polymer*, 2003, **44**, 6725–6760.

25 M. Li and C. K. Ober, *Mater. Today*, 2006, **9**, 30.

26 S. H. Kim, M. J. Misner, T. Xu, M. Kimura and T. P. Russell, *Adv. Mater.*, 2004, **16**, 226–231.

27 Z. Q. Lin, D. H. Kim, X. D. Wu, L. Boosahda, D. Stone, L. LaRose and T. P. Russell, *Adv. Mater.*, 2002, **14**, 1373–1376.

28 C.-A. Fustin, P. Guillet, M. J. Misner, T. P. Russell, U. S. Schubert and J.-F. Gohy, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 4719–4724.

29 C. G. Bochet, *J. Chem. Soc., Perkin Trans. 1*, 2002, 125–142.

30 S.-Y. Han and Y.-A. Kim, *Tetrahedron*, 2004, **60**, 2447–2467.

31 J. M. Humphrey and A. R. Chamberlin, *Chem. Rev.*, 1997, **97**, 2243–2266.

32 A. Fernando, *Curr. Opin. Chem. Biol.*, 2004, **8**, 211–221.