Novel Functional Mesoporous Materials Obtained from Nanostructured Diblock Copolymers

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Summary: Novel carboxy (COOH)-functionalized mesoporous polystyrene membranes were prepared from polystyrene-*block*-poly(D,L-lactide) (PS-*b*-PLA) diblock copolymers through the selective degradation of the PLA block. The combination of atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) techniques enabled the synthesis of nanostructured diblock copolymers possessing carboxylic acid functionality at the junction between both blocks. Such copolymers were subjected to shear flow through the use of a channel die to align their nanodomains. Under mild alkaline conditions, the quantitative hydrolysis of the polyester nanodomains afforded mesoporous materials with COOH-coated pore walls. The PS-*b*-PLA precursors as well as the resulting porous systems were carefully analyzed by size exclusion chromatography (SEC), ^{1}H NMR, scanning electron microscopy (SEM), and two-dimensional small-angle X-ray scattering (2-D SAXS). Moreover, the specific surface area and pore size distribution were determined by nitrogen sorption porosimetry.

Keywords: atom transfer radical polymerization (ATRP); diblock copolymers; mesoporous polymers; orientation; ring-opening polymerization (ROP)

Introduction

Over the last decade, the generation of organic porous materials with controlled pore sizes and narrow pore size distributions as well as desired functionalities has been the subject of increasing attention in materials science.[1] Such well-defined porous frameworks possessing additionally good mechanical and chemical stabilities are of great interest, mainly due to the large variety of applications in which they are involved, *e.g.* monoliths, filters, supports for catalysis, sensors, etc.[2] Much progress has recently been achieved toward engineering porous polymers with controlled morphology.[3] Miscellaneous approaches are now applied by selectively removing single domains acting as porogen templates from macromolecular architectures, *e.g.* molecular imprinting,[4] removal of self-assembled molecules from supramolecular architectures,[5] selective thermal or photochemical destruction of a thermoplastic polymer homogeneously blended within a thermostable matrix,[6] as well as selective removal of one partner from (semi-) Interpenetrating Polymer Networks (IPNs).[7] Furthermore, block copolymers develop well-defined equilibrium domain morphologies (*i.e.* lamellar, hexagonally packed cylindrical, bicontinuous gyroid, and spherical, in linear diblock copolymers), and thus constitute arguably ideal nanostructured precursors for the formation of ordered

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mesoporous polymers.[8] In this context, the selective removal of the sacrificial minority block from self-organized block copolymers constituted of at least two components of contrasted degradability has proven to be a very prolific route to a wide array of nanoporous materials with a defined porosity.[9]

In the present paper, we report on an original strategy for generating mesoporous polystyrene membranes with a simultaneous control over the porosity and functionality through the synthesis of polystyrene-*block*-poly(D,L-lactide) (PS-*b*-PLA) diblock copolymers with a carboxyl group at the junction between both blocks, followed by their macroscopic orientation, and the subsequent selective hydrolysis of the PLA block.

Experimental Part

Materials

All polymerizations were performed with standard Schlenk techniques under argon atmosphere. (2-Hydroxy)ethyl 2-bromopropionate (HEBP) was synthesized according to a literature method.[10] Toluene (SDS, France) was dried over sodium and stored over freshly activated 4 Å molecular sieves until needed. CuBr (99%, Aldrich) was stirred in glacial acetic acid, washed with acetone, and dried under vacuum at room temperature. Styrene (Aldrich) was stirred over KOH and distilled over CaH_2 under vacuum just before use. D,L-lactide, anisole, 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99%), tin (II) 2-ethylhexanoate ($Sn(Oct)_2$, $\sim$ 95%), 1-hydroxybenzotriazole (HOBt), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI), and 2-methoxyethylamine were purchased from Aldrich and used as received. Triethylamine (99%, Aldrich) was stored over freshly activated 4 Å molecular sieves until needed. DMF and methanol were purchased from SDS and used as received.

Synthesis of PS-*b*-PLA Copolymers

PS-*b*-PLA block copolymers with a COOH group at the junction between both blocks were prepared by a simultaneous one-step procedure using HEBP as a dual initiator (see Figure 1). In a typical experiment, 10 g (69.5 mmol) of D,L-lactide and 0.168 g (1.168 mmol) of CuBr were introduced into a dry and carefully purged with argon Schlenk flask. The components were freeze-dried from toluene and dried overnight under vacuum. 13.5 mL (117.7 mmol) of styrene, 20 mL of anisole, 0.21 mL (1.0 mmol) of PMDETA, and 0.18 mL (0.76 mmol) of $Sn(Oct)_2$ were added *via* oven-dried syringes. The flask was degassed under vacuum and back-filled with argon three times. 0.163 g (0.83 mmol) of HEBP was introduced and the flask was immersed in an oil bath at 110 °C. After 24 h, the reaction medium was diluted with CH_2Cl_2 and precipitated into methanol. The obtained polymer was dried under vacuum. Alternatively, a sequential two-step procedure was implemented (see Figure 1): PS-OH was first synthesized by atom transfer radical polymerization (ATRP) from HEBP (CuBr/PMDETA; 110 °C; 18 h; anisole), and the PS-*b*-PLA copolymer was then produced by ring-opening polymerization (ROP) of D,L-lactide from the obtained PS macroinitiator ($Sn(Oct)_2$; 110 °C; 72–120 h; anisole).

Alignment of Diblock Copolymers

A home-made channel die (3 mm wide and 60 mm long) was employed to orient the nanodomains in the block copolymer precursors. Previously pressed pieces of PS-*b*-PLA were placed in the center of the channel die which was then heated to 120 °C in a laboratory press. The samples were subjected to compression with a constant load (compression ratio $\sim$ 10) and quenched under load to room temperature over a period of 1 h. The samples were post-annealed at 160 °C overnight before removing them from he channel die with a sample thickness between 0.5 and 1 mm.

Hydrolysis of PLA Block in Diblock Copolymers

In order to selectively degrade the PLA block, PS-*b*-PLA samples were immersed in

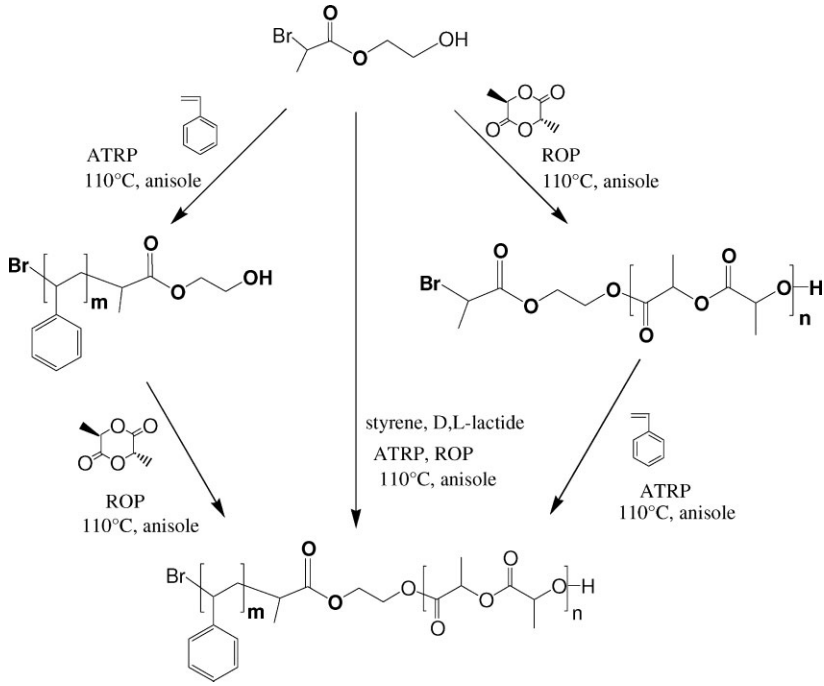

Figure 1.
Alternative routes to PS-*b*-PLA diblock copolymers with a carboxyl group at the junction between both blocks from HEBP as a dual initiator.

a mixture containing methanol and a $0.5\,mol \cdot L^{-1}$ NaOH aqueous solution ($MeOH/H_2O = 40/60$ vol %) at 65 °C for 5 to 7 days. The porous samples derived therefrom were washed abundantly with water and methanol, and then vacuum-dried at room temperature.

End-Group Functionalization

50 mg ($4.55 \cdot 10^{-6}$ mol) of mesoporous PS material ($M_n \sim 11{,}000\,g \cdot mol^{-1}$) were dissolved in 0.2 mL of DMF. 2.2 mg ($2.93 \cdot 10^{-5}$ mol) of 2-methoxyethylamine was added (molar ratio amine/PS ~ 6/1). The reaction was performed in the presence of 1-hydroxybenzotriazole (HOBt)/*N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI) as catalytic coupling reagents and triethylamine. After 48 h, the polymer was precipitated into methanol three times to ensure that all the excess amine was removed, and then dried under vacuum before ^1H NMR analysis.

Analytical Techniques

Size Exclusion Chromatography (SEC) was performed on a system equipped with a Spectra Physics P100 pump, two PL gel 5 μm mixed-C columns (Polymer Laboratories), and a Shodex RI 71 refractive index detector. The eluent was tetrahydrofuran at a flow rate of $1\,mL \cdot min^{-1}$. Calibration curves were obtained with polystyrene standards.

^1H NMR spectra were recorded at room temperature on a Bruker Avance II spectrometer operating at a resonance frequency of 400 MHz. The sample concentration was $10\,mg \cdot mL^{-1}$, and $CDCl_3$ was used as solvent and internal standard (7.27 ppm).

The small-angle X-ray scattering (SAXS) experiments were performed on a laboratory setup that was described in detail elsewhere.[11] It consists of a rotating Cu anode generator (Rigaku), graded layer Ni/C mirror optics (Osmic), vacuum tubes

(inserted between the sample and the detection), and a CCD camera (Princeton) with typical exposure times ranging from 1–10 min. This setup allowed us to probe the 0.1–2 nm^{-1} q-range, where $q = (4\pi/\lambda)\sin\theta$ is the scattering vector modulus, $\lambda = 0.1541$ nm is the X-ray wavelength, and 2θ is the scattering angle. The two-dimensional (2-D) patterns were analyzed with the *Image* software (LPS, Orsay).

Scanning Electron Microscopy (SEM) was performed on a LEO 1530 microscope equipped with InLens and Secondary Electron detectors using low accelerating voltage (3 kV). Prior to analyses, the samples were exposed to RuO_4 vapors or were coated with a 3 nm layer of palladium/platinum alloy in a Cressington 208 HR sputter-coater.

The nitrogen sorption measurements were carried out at 77 K with a Micromeritics ASAP 2010 analyzer. The specific surface area values of porous polymers were quantified using the BET method in the relative pressure (P/P^0) range from 0.05 to 0.3, while the pore volume values and pore size distribution profiles were determined by the BJH method using the adsorption portion of the isotherms.

Results and Discussion

PS-*b*-PLA diblock copolymers with a carboxyl group at the junction between the two constituent blocks were synthesized by a tandem method combining two distinct polymerization mechanisms: ROP and ATRP (Figure 1). Such a methodology required the utilization of a so-called asymmetrical dual initiator for the creation of both blocks. For this purpose, we specifically prepared (2-hydroxy)ethyl 2-bromopropionate (HEBP), as this molecule contains both a potential carboxylic acid functionality within its structure and two different functional end groups. HEBP was thus able to trigger the aforementioned polymerization processes at 110 °C: ROP of D,L-lactide was initiated by the OH function, while ATRP of styrene was promoted *via* the tertiary bromine. Interestingly, PS-*b*-PLA block copolymers could be generated through a sequential two-step procedure or by a simultaneous one-step strategy (Figure 1). The main molecular characteristics of the samples considered in this investigation are listed in Table 1.

It is noteworthy that the diblock copolymers were formed with low to moderate molar masses and a volume fraction of PLA ranging from 0.24 to 0.36 in order to develop a morphology of hexagonally packed PLA cylinders in a PS matrix. In a previous contribution,[9g] Hillmyer's group has thoroughly investigated the morphology diagram of PS-*b*-PLA with low polydispersity indices. However, our samples displayed rather broad molar mass distributions particularly that synthesized in one-pot (sample 1, Table 1). This might be ascribed to possible interferences of the two polymerization mechanisms involved: indeed, the catalyst used for the ROP of lactide, *i.e.* $Sn(Oct)_2$, could also interact in the ATRP mechanism. Recently, Matyjaszewski has shown that $Sn(Oct)_2$ can act as reducing agent for Cu^{II} species, thus coining a new ATRP procedure, namely "Activator Regenerated by Electron Transfer for ATRP" (ARGET ATRP).[12] The sequential method, starting by the synthesis of hydroxy-functionalized PS from HEPB, and followed by the polymerization of D,L-lactide from one such

Table 1.
Molecular characteristics of PS-*b*-PLA diblock copolymers.

Copolymer sample	M_n PS [a] [kg/mol]	M_n PLA [b] [kg/mol]	PDI [c]	f_{PLA} [d]
PS-*b*-PLA (Sim.) 1	10.9	7.2	1.53	0.35
PS-*b*-PLA (Seq.) 2	27.6	10.8	1.30	0.24
PS-*b*-PLA (Seq.) 3	27.6	18.8	1.40	0.36

[a] calculated from SEC or ^{1}H NMR (in the case of sample 1).
[b] calculated from ^{1}H NMR of block copolymer and SEC of macroinitiator for samples 2 and 3 or ^{1}H NMR only in the case of sample 1.
[c] polydispersity index (M_w/M_n) of copolymer sample obtained from SEC.
[d] volume fraction of PLA calculated from ^{1}H NMR assuming that the densities of PS and PLA are 1.02 and 1.25 at room temperature, respectively.

macroinitiator, afforded diblock copolymers exhibiting lower polydispersity indices (samples 2 and 3, Table 1), as expected.

In order to investigate the morphology of the copolymer precursors, the samples were dissolved in chlorobenzene (good solvent for both blocks) and spin-coated onto a SiO_2 substrate to form a thin layer. The samples were further annealed overnight at 160 °C, *i.e.* a temperature well above the T_g of PS, to avoid nonequilibrium effects. Figure 2a shows a representative SEM picture of a spin-coated PS-*b*-PLA sample that was stained with ruthenium tetroxide to enhance the chemical contrast (RuO_4 vapors selectively react with PS domains). PLA cylinders (visible as dark dots) oriented perpendicularly to the substrate in the PS matrix could be clearly observed. In the particular case reported here, the average diameters of PLA nanodomains were determined to be in the range of 10–14 nm.

The macroscopic orientation of nanodomains in bulk materials was realized through a channel die processing, as reported elsewhere.[13] During this processing, block copolymer samples were subjected to shear flow that induced a stress in the materials. This shear stress could then be relieved by a rearrangement of copolymers in such a way that the nanodomains might orient along the shear direction. The quality of the achieved orientation was evaluated by SAXS: the 2-D patterns were azimuthally integrated to a 1-D plot of scattering intensity *versus* azimuthal angle ϕ by summing the intensity of a band Δq, equal to the full-width-at-half-maximum of the first-order scattering peak (q^*). Figure 2b displays a typical two-spot 2D-SAXS pattern and the corresponding normalized orientation distribution function $P(\phi)$ for a copolymer sample after channel die alignment. The narrow shape of the peaks suggested a high degree of orientation in the samples.

Advantage of the well-known hydrolytic degradability of PLA was taken to engineer functionalized mesoporous membranes with narrow pore size distributions through the selective hydrolysis of the PLA minority block in aligned diblock copolymers, under alkaline conditions. This degradation was conducted at 65 °C, namely an intermediate temperature between the T_g of PLA (*i.e.* around 50 °C) and that of PS (*i.e.* around 100 °C) to avoid the collapse of the residual porous structures, while allowing for an efficient degradation of PLA. The resulting materials revealed nanoscale porous morphologies by SEM: mesopores with an average diameter of 7–9 nm could be observed in the typical example shown in Figure 3. Taking into account the 3 nm thickness of the coating used in SEM analyses, such pore sizes were in reasonable agreement with the PLA domain sizes determined for the copolymer precursor. It should be stressed that ordered mesoporous polymer frameworks with a hexagonal array of hollow cylinders could be observed locally at least over several hundreds of nanometers. However, in the

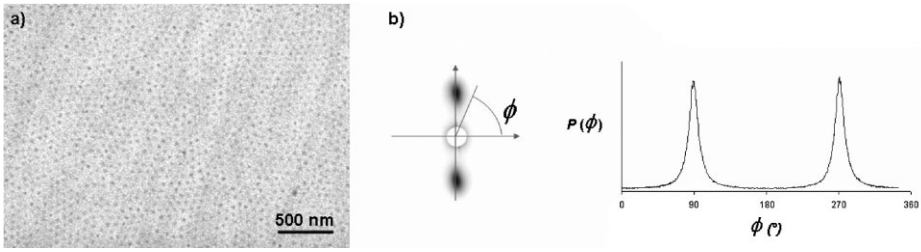

Figure 2.
(a) SEM picture of a PS-*b*-PLA copolymer (sample 1, Table 1) spin-coated onto a SiO_2 substrate and stained by RuO_4. (b) 2-D SAXS pattern of this sample after channel die processing and corresponding normalized orientation distribution function $P(\phi)$ *vs.* azimuthal angle ϕ for the first-order scattering peak.

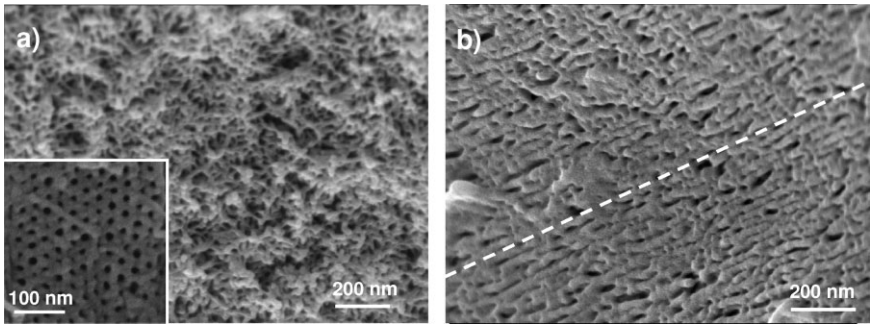

Figure 3.
SEM micrographs of cryofractured porous material derived from a PS-*b*-PLA precursor (sample 1, Table 1) aligned by channel die processing: (a) perpendicular and (b) parallel view to the shear direction (marked by dashed lines). In Figure 3a, the inset shows hexagonally packed hollow cylinders that are locally observed.

case of the material derived from the copolymer synthesized in one-pot, next to the region with cylinders, we could also observe alternating lamellae (not shown). The relatively high polydispersity index of the block copolymer investigated might account for the coexistence of both well-ordered regions. Several recent reports have indeed discussed how broad molar mass distributions in diblock copolymers influence interfacial curvature and domain spacing, and eventually have a significant impact on their overall phase behavior.[14]

The completion of the hydrolysis process was verified by ^{1}H NMR through the total disappearance of the characteristic bands associated with PLA (in particular C<u>H</u> of repeating units at 5.1–5.2 ppm). Furthermore, the presence of carboxylic acid functions as chain-end groups was evidenced through a post-modification reaction. The COOH groups from porous PS

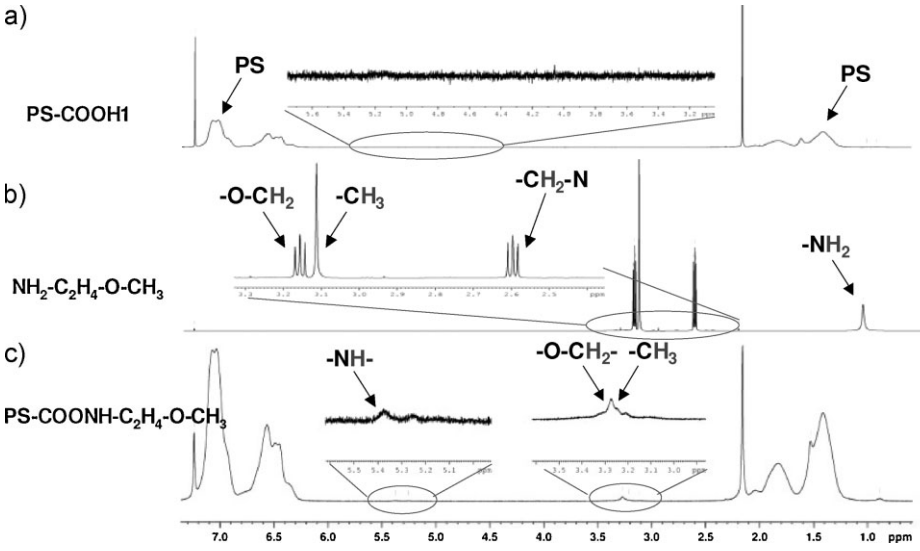

Figure 4.
^{1}H NMR spectra of (a) PS-COOH material derived from a PS-*b*-PLA precursor (sample 1, Table 1), (b) 2-methoxyethylamine, and (c) resulting PS matrix upon reaction of 2-methoxyethylamine with COOH groups from PS polymer.

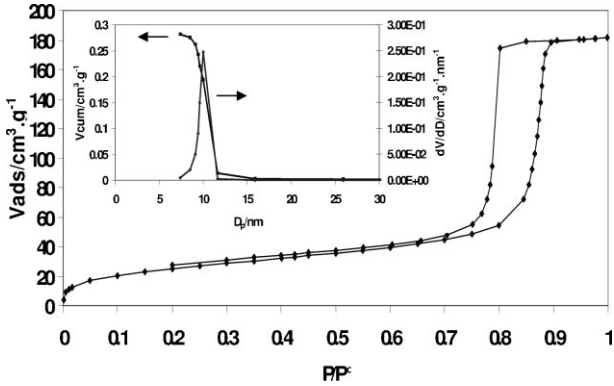

Figure 5.
N_2 adsorption-desorption isotherms for mesoporous material derived from a PS-*b*-PLA precursor (sample 1, Table 1), and corresponding pore size distribution (inset).

polymers were reacted with 2-methoxyethylamine, thus leading to the formation of amide functions: an end-group functionalization ratio close to 100% was calculated by ^{1}H NMR (Figure 4). This experiment strongly suggested that the carboxylic acid functionality lies on the pore walls of mesoporous frameworks.

Lastly, the nitrogen sorption by the porous PS membranes exhibited a Type IV isotherm which was identified by an H1-type hysteresis loop between the adsorption and desorption branches (Figure 5 as a typical example). This feature represent the signature of nanoporous materials with a defined porosity. Values of specific surface areas as high as $102\,m^2\,g^{-1}$ were determined (sample 1, Table 1). The isotherm of adsorption *versus* relative pressure was transformed to give a narrow pore size distribution centered around a diameter of 10 nm, in the particular case reported here. Such a result was in a good agreement with those obtained from SEM and SAXS analyses. The BJH method also allowed for the determination of a pore volume close to $0.3\,cm^3 \cdot g^{-1}$, which was consistent with the PLA volume fraction of 0.35 in the copolymer precursor.

Conclusion

The use of nanostructured PS-*b*-PLA diblock copolymers with a carboxyl group at the interface between both alien blocks provides a straightforward and effective route to mesoporous membranes with controlled porosity and carboxylic acid-coated pore walls. A better control over the morphology of the aligned copolymer precursors, as well as the further investigation of the diblock copolymers with higher molar masses are currently in progress in order to fine-tune the porosity in terms of pore size and shape.

The potential applications of such functional nanoporous materials are mainly expected in the areas of heterogeneous catalysis, advanced filtration techniques, selective transport, and chemistry in confined media.

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