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# Original route to polylactide-polystyrene diblock copolymers containing a sulfonyl group at the junction between both blocks as precursors to functional nanoporous materials

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#### ABSTRACT

Novel functionalized nanoporous polymeric materials could be derived from poly(D,L-lactide)-*block*polystyrene (PLA-*b*-PS) diblock copolymers with a sulfonyl group at the junction between both blocks were synthesized by a combination of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) using a synthetic difunctional initiator through a three-step sequential methodology. Different  $\omega$ -bromo PLA polymers with various molar masses ranging from 3640 to 11,440 g mol<sup>-1</sup> were first produced by coupling  $\omega$ -hydroxy PLA precursors to a chlorosulfonyl-functionalized ATRP initiator previously prepared, thus leading to the formation of suitable macroinitiators for the subsequent ATRP polymerization of styrene. Consequently, PLA-*b*-PS diblock copolymers were obtained with a finely tuned PLA volume fraction ( $f_{PLA}$ ) in order to develop a microphased-separation morphology. The resulting copolymers as well as the intermediate compounds were carefully analyzed by size exclusion chromatography and <sup>1</sup>H NMR. Upon shear flow induced by a channel die processing, oriented copolymers were generally afforded as characterized by small-angle-X-ray scattering (SAXS). Such copolymers were finally submitted to mild alkaline conditions so as to hydrolyze the sacrificial PLA block, and the presence of the sulfonic acid functionality on the pore walls of the resulting nanoporous materials was evidenced by means of a post-modification reaction consisting in the corresponding sulfonamide formation.

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## 1. Introduction

Over the last decade, porous polymeric materials displaying finely tuned and regular pore sizes have been extensively investigated due to their diverse applications in many research fields, e.g. supports for catalysis or gas storage, separation, and filtration [1,2], as well as biosensors or biomedical devices [3,4]. In this rapidly expanding field, researchers have particularly focused their investigation on the control of pore size and pore size distribution [5]. Another important feature of these porous materials that has to be taken carefully into account relies on the proper selection and positioning of chemical functions that line the pore walls, regarding the potential applications further considered. Indeed, the functional group should be appropriately placed without the need to require to tedious post-polymerization functionalization strategies.

For many years, block copolymers have represented fascinating macromolecular architectures in different research areas. In particular, block copolymers are versatile hybrid macromolecules that have been used as nanostructured precursors for the generation of a wide variety of nanoporous materials [6]. Indeed, the incompatibility of distinct macromolecular segments in diblock copolymers leads to their nanoscopic self-organization, and as a consequence to their potential utilization as structure directing agents [7]. For instance, it has been shown that self-organized block copolymers can lead to the formation of well-defined nanostructures in which the morphology and domain sizes are tunable on the nanoscopic length scale. In this regard, a classical example was given by Hillmyer's group [6] that showed that AB diblock copolymers comprising two-thirds of A monomer and one-third of B monomer, and that displays high enough overall molar mass, form long cylinders of B with nanometer-scale (5-50 nm) diameters that organize on a hexagonal lattice within a continuous A matrix. Unfortunately, the effects of polydispersity on the orderdisorder transition have potential implications on the morphology of block copolymers. Especially, domain spacing increases as the polydispersity index (PDI) increases, and the PDI increase in one block of an asymmetric diblock copolymer results in transitions to morphologies with increased mean interfacial curvature toward that block [8,9].



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The preparation of (co)polymers from multifunctional initiators is also an area of intense research as it enables the generation of telechelic (co)polymers that can undergo further post-polymerization modifications [10–12]. Recently, one of our groups [13,14] successfully demonstrated that the positioning of a particular functional group between the two distinct blocks of semi-degradable diblock copolymers can lead to the formation of novel functionalized nanoporous materials. By employing an asymetric difunctional initiator suitable for two distinct polymerization mechanisms, i.e. atom transfer radical polymerization (ATRP) of styrene and ring-opening polymerization (ROP) of lactide, polystyrene-block-poly(D,L-lactide (PS-b-PLA) copolymers were obtained. The orientation of the resulting copolymers, followed by the hydrolysis of the PLA sacrificial block, could afford highly ordered arrays of nanochannels with varying pore diameters and a carboxvlic acid functionality lining the nanochannel walls.

In continuation of our recent efforts on the direct and straightforward generation of functionalized nanoporous polymers, we report on an original three-step methodology to synthesize PLA-*b*-PS copolymers possessing a sulfonyl group at the junction point between both blocks. Their macroscopic orientation and the subsequent hydrolysis of the sacrificial PLA block leads to the formation of porous polymeric materials decorated with a sulfonic acid functionality in the inner part of the nanochannels. The presence of this particular functionality was proved *via* a post-modification reaction during which sulfonic acid groups were transformed into sulfonamide functions upon reaction with a small aliphatic amine.

#### 2. Experimental section

## 2.1. Materials

All polymerizations were performed using standard Schlenk techniques under argon atmosphere.  $\omega$ -hydroxy PLA precursors



**Fig. 1.** Synthetic strategy adopted for the preparation of PLA-*b*-PS diblock copolymers containing a sulfonyl group at the junction between both blocks.

(2) were synthesized by ring-opening polymerization (ROP) of D,L-lactide initiated by the butanol/tin(II) octanoate system according to a literature procedure [15].

D,L-lactide, 4-isopropylbenzenesulfonyl chloride (97%), bromine (Br<sub>2</sub>,  $\geq$  99.5%) pentamethyldiethylenetriamine (PMDETA, 99%), tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>, ~95%) and 2-methoxyethylamine (99%) were purchased from Aldrich and used as received. CuBr (99%, Aldrich) was stirred in glacial acetic acid, washed with MeOH, and dried under vacuum at room temperature. Styrene ( $\geq$  99%, Aldrich) was stirred over KOH, and distilled over CaH<sub>2</sub> under vacuum just before use. Triethylamine (99%, Aldrich) was stirred in the presence of KOH at 70 °C during 12 h and distilled under argon. Anisole (99%, SDS, France) was dried over sodium/ benzophenone overnight at 90 °C and distilled under argon. Anhydrous toluene, CCl<sub>4</sub> and methanol with the highest purity grade were purchased from SDS and used as received.

# 2.2. Synthesis of the chlorosulfonyl-functionalized ATRP initiator (1)

A solution of bromine  $(2.9 \text{ g}, 1.82 \times 10^{-2} \text{ mol})$  in 16 mL of carbon tetrachloride was dropwise added to a refluxing solution of 4-isopropylbenzene sulfonyl chloride  $(3.98 \text{ g}, 1.82 \times 10^{-2} \text{ mol})$  dissolved in 16 mL of carbon tetrachloride [16]. The reaction mixture was finally refluxed for 10 min and the solvent was evaporated under reduced pressure. The product was then washed with water and dried overnight under reduced pressure to give the desired brominated product **1** as a white solid (yield = 96%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K) δ (ppm): 2.22 (s, 6H, CH<sub>3</sub>), 7.86 (d, 2H, CH<sub>aromatic</sub>, *J* = 8.8 Hz), 8.01 (d, 2H, CH<sub>aromatic</sub>, *J* = 8.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298 K) δ (ppm) 35.3 (2C, C–(CH<sub>3</sub>)<sub>2</sub>), 60.8 (1C, C–Br), 127.3, 127.5, 143.4 (1C, C–SO<sub>2</sub>Cl), 154.5 (5C, C<sub>arom</sub>); FTIR v (cm<sup>-1</sup>): 577 (C–Br), 1174 and 1370 (SO<sub>2</sub>); elementary analysis: exp C (36.09%), H (3.01%), Cl (11.96%), S (10.32%), O (10.48%), Br (28.14%), theor (36.3%), H (3.4%), Cl (11.9%), S (10.7%), O (10.8%), Br (26.9%).

#### Table 1

Molecular characteristics of  $\omega$ -hydroxy PLA (2) precursors synthesized by ROP of LA initiated by butanol.

Precursor PLA <sub>n</sub> <sup>a</sup>	$M_n^b$ (theoretical) (g mol <sup>-1</sup> )	$M_n^c$ (SEC-RI) (g mol <sup>-1</sup> )	PDI <sup>c</sup>	$\frac{M_n^{d}}{(g \text{ mol}^{-1})}$	Yield <sup>e</sup> (%)
PLA <sub>46</sub> ( <b>2a</b> )	3030	4600	1.23	3380	80
PLA <sub>96</sub> ( <b>2b</b> )	6840	8800	1.40	6980	94
PLA <sub>154</sub> ( <b>2c</b> )	8060	10,000	1.40	11,200	74

<sup>a</sup> *n*: number-average degree of polymerization of PLA as determined by <sup>1</sup>H NMR.

<sup>b</sup>  $M_{n,\text{theor}} = \text{conversion} \times (2[\text{LA}]_0/[\text{initiator}]_0) \times 72 + M_n \text{ (end groups)}.$ 

<sup>c</sup> Obtained from SEC equipped with RI detection (PS standards) eluting with THF as the mobile phase.

<sup>d</sup> Actual molar mass as calculated by <sup>1</sup>H NMR from PLA.

<sup>e</sup> Conversion as determined by gravimetry for ROP of lactide initiated by butanol.

Table 2				
Characteristics	of ω-bromo	PLA-based	macroinitiators	(3).

Macroinitiator	PLA <sub>n</sub> <sup>a</sup>	$M_n^{b}$	Yield	Functionalization yield
PLA <sub>n</sub> -Br ( <b>3</b> )		(g mol <sup>-1</sup> )	(%)	( <sup>1</sup> H NMR) (%)
PLA <sub>46</sub> -Br ( <b>3a</b> )	PLA <sub>46</sub>	3640	68	54
PLA <sub>96</sub> -Br ( <b>3b</b> )	PLA <sub>96</sub>	7240	60	89
$PLA_{154}$ -Br ( <b>3c</b> )	PLA <sub>154</sub>	11,440	78	66

<sup>a</sup> n: number-average degree of polymerization of PLA as determined by <sup>1</sup>H NMR.
 <sup>b</sup> Molar mass of PLA as determined by <sup>1</sup>H NMR.

#### 2.3. Synthesis of $\omega$ -bromo PLA macroinitiators (3)

The sulfonyl chloride group of the initiator **1** was reacted with the hydroxyl terminus of the previously synthesized PLA polymers (**2**) to provide  $\omega$ -bromo PLA macroinitiators (**3**). A typical synthesis is described next. The PLA<sub>96</sub> sample (**2b**) (5 g, 7.16 × 10<sup>-4</sup> mol) was freeze-dried from toluene overnight under vacuum prior to the reaction. The chlorosulfonyl-functionalized initiator **1** (0.61 g,  $2 \times 10^{-3}$  mol) dissolved in 5 mL of distilled dichloromethane was added, dropwise and under argon, to the PLA dissolved in 20 mL of dichloromethane in the presence of triethylamine (0.199 g,  $1.4 \times 10^{-3}$  mol) [17]. The reaction mixture was stirred for 48 h at room temperature, and then 4 h at 40 °C. The product was washed twice with water to remove the salts and the hydrolyzed proportion of the initiator. The organic layer was concentrated, and the resulting macroinitiator was precipitated in diethyl ether to remove the excess of the unreacted initiator **1**. The obtained macroinitiator **3b** was dried under vacuum (yield = 60%). The functionalization yield was evaluated by <sup>1</sup>H NMR to be equal to 89%.

## 2.4. Synthesis of PS-b-PLA diblock copolymers

PS-*b*-PLA diblock copolymers with a sulfonyl group at the junction between both blocks were prepared by atom transfer radical polymerization (ATRP) of styrene initiated by ternary systems constituted of PLA macroinitiators, CuBr, and PMDETA, at 110 °C for 18 h in anisole. In a typical experiment, the macroinitiator **3a** (1.74 g,  $2.4 \times 10^{-4}$  mol) and CuBr (0.03 g,  $2 \times 10^{-4}$  mol) were introduced into an oven-dried Schlenk tube. Styrene (3.23 g,



Fig. 2. <sup>1</sup>H NMR spectrum of PLA<sub>96</sub> precursor (2b).



Fig. 3. <sup>1</sup>H NMR of PLA<sub>96</sub>-Br macroinitiator (3b).

 $3.1 \times 10^{-2}$  mol) and PMDETA (51 µL,  $2.4 \times 10^{-4}$  mol) were added under argon. The reagents were diluted with 5 mL of anisole, and the flask was submitted to three freeze-pump-thaw cycles. The polymerization was triggered by immersion of the flask in an oil bath at 110 °C. After 80 h, the obtained diblock copolymer **4a** was precipitated in methanol to remove the PLA fraction non-functionalized with a bromide moiety.

### 2.5. Homopolymerization of styrene from initiator 1

The initiator **1** (20 mg,  $6.72 \times 10^{-5}$  mol) and CuBr (9.6 mg,  $6.72 \times 10^{-5}$  mol) were introduced into an oven-dried flask. Styrene (2.09 g,  $2 \times 10^{-2}$  mol) and PMDETA (16.8 µL,  $8 \times 10^{-5}$  mol) were added under argon atmosphere. The reagents were diluted with 5 mL of anisole before submitting the polymerization feed to three freeze-pump-thaw cycles. The polymerization was finally triggered by immersion of the flask into an oil bath at 110 °C. Three samples were withdrawn during the polymerization course at t = 14, 24 and 86 h in order to determine  $M_n$  and PDI values of the as-obtained PS homopolymers.

#### 2.6. Orientation of PS-b-PLA diblock copolymers

A home-made channel die (3 mm wide and 60 mm long) was used to align the nanodomains in the block copolymers. 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 upon constant load (compression ratio of ~10) and quenched under load to room temperature over a period of 1 h. The samples were post-annealed overnight at 160 °C before removing them from the channel die with a sample thickness between 0.5 and 1.0 mm.

#### 2.7. Hydrolysis of PLA block in PS-b-PLA diblock copolymers

In order to selectively degrade the sacrificial PLA block, the different PS-*b*-PLA samples were immersed in a mixture containing methanol and a  $0.5 \text{ mol L}^{-1}$  NaOH aqueous solution (MeOH/

 $H_2O = 40/60 \text{ vol.\%}$ ) at 65 °C for 5–7 days. The obtained porous samples were washed abundantly with water and methanol, then vacuum-dried at room temperature.

#### 2.8. End-group functionalization

In a first step, 4.48 µL of thionyl chloride dissolved in 1 mL of dichloromethane was dropwise added to 82 mg  $(2.06 \times 10^{-6} \text{ mol})$  of the mesoporous PS sample  $(M_n \sim 4000 \text{ g mol}^{-1})$  dissolved in 4 mL of dichloromethane in the presence of 12.5 µL of triethylamine  $(9.27 \times 10^{-5} \text{ mol})$  under argon at 0 °C. The reaction mixture was stirred for 48 h at room temperature and was used without any further purification. In the second step, 1.85 mg  $(2.45 \times 10^{-5} \text{ mol})$  of 2-methoxyethylamine in 1 mL dichloromethane was dropwise added into the previous mixture in the presence of 4.3 µL  $(3.09 \times 10^{-5} \text{ mol})$  of triethylamine at 0 °C. After stirring the reaction mixture overnight, the polymer was precipitated several times in methanol, then dried under vacuum. <sup>1</sup>H NMR analysis was used to determine the ratio of sulfonic acid groups that were converted into the corresponding sulfonamide functions (functionalization yield close to 100%).

### 2.9. Instrumentation

Size exclusion chromatography (SEC) was performed on a system equipped with a Spectra Physics P100 pump, two PL gel 5  $\mu$ m mixed-C columns (Polymer Laboratories), and a Shodex RI 71 refractive index detector. The mobile phase was tetrahydrofuran at a flow rate of 1 mL min<sup>-1</sup>. Calibration curves were obtained with polystyrene standards obtained from Polymer Laboratories.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker Avance II spectrometer operating at a resonance frequency of 400 and 100 MHz respectively. For <sup>1</sup>H NMR analysis, the sample concentration was ~10 mg mL<sup>-1</sup>, while it was ~30 mg mL<sup>-1</sup>, for <sup>13</sup>C NMR experiments. CDCl<sub>3</sub> was used as solvent and internal standard (7.26 ppm in <sup>1</sup>H NMR; 77.2 ppm in <sup>13</sup>C NMR).



Fig. 4. <sup>1</sup>H NMR of PLA<sub>96</sub>-*b*-PS<sub>91</sub> diblock copolymer (4b) before hydrolysis.



Fig. 5. SEC traces of PLA<sub>96</sub>-Br macroinitiator (**3b**, solid line) and corresponding PLA<sub>96</sub>-*b*-PS<sub>91</sub> copolymer (**4b**, dotted line).

FTIR spectra were recorded on a Bruker Tensor 27 DTGS spectrometer in attenuated total reflection (ATR) mode between 4000 and 450 cm<sup>-1</sup> by averaging 32 consecutive scans with a resolution of 4 cm<sup>-1</sup>.

The small-angle X-ray scattering (SAXS) experiments were performed on a laboratory setup described in details elsewhere [18]. It consists of a rotating Cu anode generator (Rigaku), graded layer Ni/ C mirror optics (Osmic), vacuum tubes (inserted between the sample and the detector), and a CCD camera (Princeton) with typical exposure times ranging from 1 to 10 min. This setup allowed us to probe the  $0.1-2.0 \text{ nm}^{-1} q$ -range, where  $q = (4\pi/\lambda)\sin\theta$  is the scattering vector modulus,  $\lambda = 0.1541 \text{ nm}$  is the X-ray wavelength, and  $2\theta$  is the scattering angle. The two-dimensional (2-D) patterns were analyzed with the *Image* software (Orsay, France).

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 cryofractured and coated with a 3 nm layer of palladium/platinum alloy in a Cressington 208 HR sputter-coater.

## 3. Results and discussion

#### 3.1. Synthesis and characterization of functional diblock copolymers

PS-*b*-PLA diblock copolymers with a sulfonyl group at the junction between the two constituent blocks were generated through a three-step sequential method (Fig. 1). Such a methodology required the utilization of an asymmetric difunctional initiator that enables the creation of both blocks from different orthogonal functionalities of the initiator. For this purpose, we specifically prepared an aromatic initiator molecule (1) containing a potential sulfonic acid functionality within its structure and two different functional end groups, i.e. a chlorosulfonyl moiety and a tertiary bromide (step 1). Such an initiator was thus able to react with a  $\omega$ -hydroxy PLA (2), previously prepared, by condensation between the terminal hydroxyl group from PLA and the chlorosulfonyl group of the initiator **1** (step 2), while ATRP of styrene was promoted *via* the homolytic cleavage of the carbon-bromine bond of the as-obtained PLA macroinitiator **3** (step 3).

The PLA precursors (**2a**, **2b**, **2c**) were produced by ROP of D,Llactide initiated by butanol, and they were obtained with low to moderate molar masses ( $M_{n(SEC)}$  ranging from 4600–10,000 g mol<sup>-1</sup>). It is noteworthy that the PDI values of the PLA polymers increased with increasing their molar masses (Table 1). This clearly indicated that the degree of control over the ROP of D,L-lactide

Table 3	3
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Molecular featu	es of PLA-b-PS	copolymers (4	I)
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Copolymer PLA <sub>n</sub> -b-PS <sub>m</sub> <sup>a</sup> ( <b>4</b> )	M <sup>, b</sup> (theoretical) (g mol <sup>-1</sup> ]	$M_n^c$ (SEC-RI) (g mol <sup>-1</sup> )	PDI <sup>c</sup>	$M_n^{d}$ ( <sup>1</sup> H NMR) (g mol <sup>-1</sup> )	Yield <sup>e</sup> (%)	$f_{PLA}{}^{\mathrm{f}}$
$PLA_{46}-b-PS_{46}$	8220	13,100	1.44	8430	88	0.37
PLA <sub>96</sub> -b-PS <sub>91</sub> ( <b>4b</b> )	17,100	23,300	1.62	16,700	95	0.38
PLA <sub>154</sub> - <i>b</i> -PS <sub>240</sub> ( <b>4c</b> )	30,500	87,000	1.58	36,400	92	0.27

 $^{\rm a}$  n,m: number-average degrees of polymerization of PLA and PS blocks as determined by  $^{\rm 1}{\rm H}$  NMR.

<sup>b</sup>  $M_{n,\text{theor}} = [\text{conversion} \times ([S]_0/[\text{macroinitiator}]_0) \times 104] + M_n (\text{PLA-Br}).$ 

<sup>c</sup> Obtained from SEC equipped with RI detection (PS standards) eluting with THF as the mobile phase.

<sup>d</sup> Actual molar mass as calculated by <sup>1</sup>H NMR from macroinitiator (PLA block) and PS block.

<sup>e</sup> Conversion as determined by gravimetry for ATRP of styrene initiated by the different macroinitiators.

<sup>f</sup> Volume fraction of PLA as calculated by <sup>1</sup>H NMR, assuming that the densities of PS and PLA are 1.02 and 1.25, respectively.

 Table 4

 Molecular features of polystyrene samples obtained by ATRP of styrene using functional initiator 1.

Polymer PS <sub>m</sub> <sup>a</sup>	Time <sup>b</sup> (h)	<i>M</i> <sup>°</sup> <sub>n</sub> (theoretical) (g mol <sup>-1</sup> )	$M_n^d$ (SEC-RI) (g mol <sup>-1</sup> )	PDI <sup>d</sup>	Yield <sup>e</sup> (%)	
$PS_{83}(5a)$	14	8960	27,700	1.87	29	
$PS_{124}(5b)$	24	13,280	36,800	1.75	43	
$PS_{294}(5c)$	86	30,900	40,000	1.74	100	

<sup>a</sup> *m*: theoretical number-average degree of polymerization of PS sample.

<sup>b</sup> Duration of the reaction of polymerization.

<sup>c</sup>  $M_{n,\text{theor}} = \text{conversion} \times ([S]_0/[\text{macroinitiator}]_0) \times 104.$ 

<sup>d</sup> Obtained from SEC equipped with RI detection (PS standards) eluting with THF as the mobile phase.

<sup>e</sup> Conversion as determined by gravimetry for ATRP of styrene initiated by the initiator **1**.

decreased when the initial ratio of monomer-to-initiator concentrations increased. The as-obtained PLA precursors were characterized by <sup>1</sup>H NMR. The spectra displayed the typical chemical displacements of PLA characterized by broad resonance bands at 5.10–5.30 and 1.40–1.60 ppm corresponding respectively to the – CH– and –CH<sub>3</sub> moieties of the repeating lactide units (Fig. 2). Other characteristic peaks at 0.94 and 4.36 ppm arising from the aliphatic protons of the initiator, i.e. butanol, were observed.

The presence of the  $\omega$ -hydroxyl end group, which has a crucial role regarding the anchoring to the initiator **1**, was evidenced by the presence of a characteristic peak at 2.71 ppm. It was reacted with the chlorosulfonyl group of the difunctional initiator **1** *via* a condensation reaction to yield the corresponding brominated PLA-based macroinitiator (**3**). For this purpose, the reaction was set up for 48 h in different experimental conditions so as to maximize the conversion yield. The non-reacted free initiator **1** was eliminated by precipitation of the macroinitiator **3** in diethyl ether. Yet, a part of  $\omega$ -hydroxy PLA **2** was also present along with the macroinitiatior product, and could not be removed before the following ATRP step.

The functionalization rate was calculated from the <sup>1</sup>H NMR spectra of the macroinitiators (Fig. 3, as an example) by using the ratio between the signal intensities associated with the doublet of the initiator moiety at 7.87 and 7.94 ppm and the characteristic broad bands due to the –CH– group of the repeating lactide units at 5.1–5.2 ppm. The main features of the  $\omega$ -bromo PLA macroinitiators (**3**) are gathered in Table 2.

The ATRP process of styrene triggered by these macroinitiators was carried out in typical experimental conditions using CuBr/ PMDETA as the catalytic system. The effective formation of the PLA-*b*-PS diblock copolymers (**4**) was verified by a combination of <sup>1</sup>H NMR spectroscopy and SEC. First, the <sup>1</sup>H NMR spectra of PLA-*b*-PS copolymers were consistent with the expected structures, especially with the appearance of broad peaks at ~6–7 and 1.41–1.84 ppm that corresponded respectively to the aromatic and aliphatic protons of PS (Fig. 4, as an example). Furthermore, Fig. 5 displays the typical SEC traces obtained for a PLA macroinitiator and the corresponding PLA-*b*-PS copolymer. All SEC chromatograms of copolymers exhibited monomodal distributions and a shift of the peaks toward lower retention times, thus confirming the formation of diblock copolymers.

It is noteworthy that the diblock copolymers were formed with a PLA volume fraction  $(f_{PLA})$  ranging from 0.27–0.41 in

order to develop a morphology of hexagonally close-packed cylinders of PLA cylinders surrounded by a PS matrix (Table 3). In a previous contribution [19], Hillmyer's group has thoroughly investigated the equilibrium phase diagram of PS-b-PLA with low PDI values. However, our synthesized samples displayed rather broad molar mass distributions. This might be ascribed not only to the relatively high polydispersity indices of PLA precursors (1.2-1.4), but also to a difficult control over styrene ATRP from the brominated PLA macroinitiators. The styrene homopolymerization using the initiator **1** was monitored as a model study to investigate whether the ATRP process was proceeding in a controlled manner under the selected experimental conditions (Table 4). High PDI values as well as experimental molar masses higher than the theoretical ones clearly indicated a rather low degree of control, probably due a slow dynamics of exchange between active and dormant species.



Fig. 6. Schematic representation of a home-made channel die used to align the nanodomains in the diblock copolymers.



**Fig. 7.** 2-D SAXS patterns of PLA-*b*-PS copolymers oriented by channel die processing (pattern recorded parallel to the flow direction) and corresponding radial profiles of scattering intensity relative to (a) PLA<sub>46</sub>-*b*-PS<sub>46</sub> (**4a**), (b) PLA<sub>96</sub>-*b*-PS<sub>91</sub> (**4b**), and (c) PLA<sub>154</sub>-*b*-PS<sub>240</sub> (**4c**) copolymers.



Fig. 8. <sup>1</sup>H NMR spectra of (a) PLA<sub>96</sub>-*b*-PS<sub>91</sub> (4b) after hydrolysis of the PLA block, (b) 2-methoxyethylamine, and (c) resulting PS matrix upon reaction of the SO<sub>3</sub>H chain-end groups with 2-methoxyethylamine.



Fig. 9. Cross-sectional SEM micrographs of the porous polymeric material obtained from PLA<sub>96</sub>-*b*-PS<sub>91</sub> (4b) after channel die processing and hydrolysis of the PLA sacrificial block.

#### 3.2. Macroscopic orientation of diblock copolymers

The macroscopic orientation of copolymer nanodomains in bulk materials was realized through a channel die processing [20]. During this procedure, diblock copolymers 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 as shown in Fig. 6.

Fig. 7 displays the 2-D SAXS patterns (for the first-order scattering  $q^*$  peak) and the corresponding radial profiles of scattering intensity for the investigated PLA-*b*-PS copolymers. For the PLA<sub>46</sub>-*b*-PS<sub>46</sub> sample, we observed an intense and anisotropic halo, and a domain spacing of 19 nm could be determined from the radial profile, while two scattering spots were detected for the PLA<sub>96</sub>-*b*-PS<sub>91</sub> specimen and a domain spacing equal to 37 nm was estimated. Even though these patterns indicated the occurrence of some degree of orientation in the channel die-processed copolymers, they did not permit to identify the cylindrical morphology expected for these structures. Yet, the PLA<sub>96</sub>-*b*-PS<sub>91</sub> pattern corresponded to a column-like structure with oriented domains along the flow direction. Obviously enough, for the diblock copolymer with the highest molar mass, the isotropic halo observed in the 2-D pattern attested the absence of any orientation on a large scale.

The rather high PDI values associated with the PLA-*b*-PS diblock copolymers might account for this material inhomogeneity as several recent reports have 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 [8,9,21–23].

#### 3.3. Generation of functionalized nanoporous polymeric materials

Under mild alkaline conditions, functionalized nanoporous polymeric materials were obtained by selective and quantitative hydrolysis of the minor sacrificial block (PLA) in channel-die processed PS-*b*-PLA block copolymers. The completion of this hydrolytic process was checked by <sup>1</sup>H NMR through the total disappearance of the characteristic broad bands associated with PLA at 5.20 ppm (signal assigned to –CH– motif of lactide repeating units in Fig. 8).

Scanning electron micrographs of the resulting materials revealed nonoscale porous structures, as observed in Fig 9. It is worth mentioning that the higher the molar mass of the PLA block, the larger the pore diameters (data not shown). In addition, the presence but more importantly the accessibility of the sulfonic acid functionality displayed at the surface of the porous polymeric materials was highlighted by a post-modification reaction. Experimentally, sulfonic acid groups (SO<sub>3</sub>H) were activated in a first step with thionyl chloride to provide the corresponding chlorosulfonyl (SO<sub>2</sub>Cl) groups which were reacted in a second step with 2-methoxyethylamine, thus leading to the formation of sulfonamide functions: end group functionalization efficiency close to 100% was determined by <sup>1</sup>H NMR (Fig. 8). This chemical reaction demonstrated that the chemical functionalities of the nanoporous materials are accessible and modifiable, and are not sterically hindered within the PS matrix. The presence of such tailored functionalities at the pore interface is very important regarding the potential applications of these nanoporous frameworks as catalytic supports or scaffolds for nanomaterials synthesis for instance.

#### 4. Conclusions

We have reported on an original route to novel functionalized nanoporous materials through the use of nanostructured PLA-*b*-PS diblock copolymers with a sulfonyl group at the interface between the two distinct blocks. Such copolymers can be successfully synthesized by a three-step sequential approach starting from a purposely designed asymmetric difunctional initiator. The postmodification of the sulfonic acid functionality that line the pore walls can be achieved with a model amine compound, which reveals the availability of the chemical functions at the interface with the substances that can be drawn into the voids. Our research efforts are currently devoted to the full exploitation of the sulfonic acid-functionalized nanoporous materials for diverse applications but also to the tuning of the chemical functionality positioned at the junction between both blocks of copolymer precursors.

These polymer-based nanoporous materials have expected potential applications especially in the field of chemistry in confined media where they could find a crucial importance as catalytic supports or scaffolds for nanomaterial synthesis, as well in the area of advanced separation techniques as selective membranes.

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