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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 ω-bromo PLA polymers with various molar masses ranging from 3640 to 11,440 g mol^{-1} were first produced by coupling ω-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 ^{1}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.

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 order–disorder 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 carboxylic 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. ω-hydroxy PLA precursors (**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].

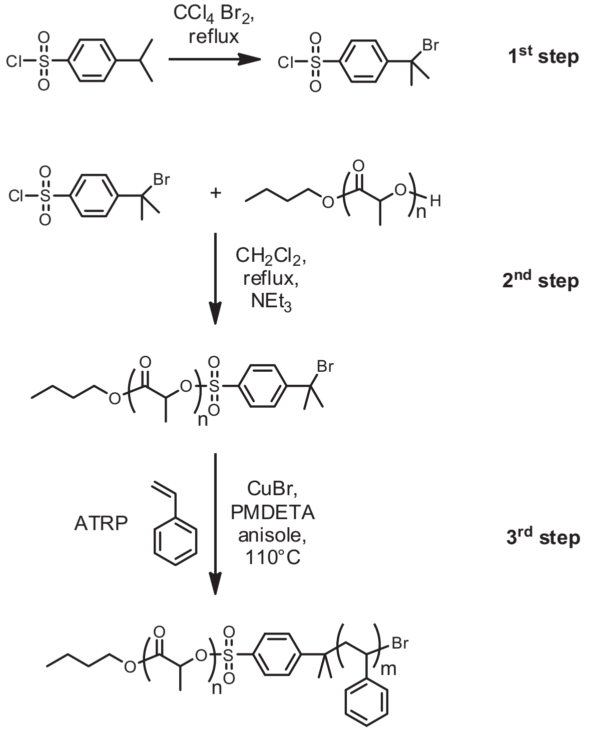

Fig. 1. Synthetic strategy adopted for the preparation of PLA-*b*-PS diblock copolymers containing a sulfonyl group at the junction between both blocks.

D,L-lactide, 4-isopropylbenzenesulfonyl chloride (97%), bromine (Br_2, ⩾99.5%) pentamethyldiethylenetriamine (PMDETA, 99%), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, ~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 (⩾99%, Aldrich) was stirred over KOH, and distilled over CaH_2 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 vacuum. Dichloromethane was dried over CaH_2 and distilled under argon. Anhydrous toluene, CCl_4 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 g, 1.82×10^{-2} mol) in 16 mL of carbon tetrachloride was dropwise added to a refluxing solution of 4-isopropylbenzene sulfonyl chloride (3.98 g, 1.82×10^{-2} 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%).

^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ (ppm): 2.22 (s, 6H, CH_3), 7.86 (d, 2H, $CH_{aromatic}$, $J = 8.8$ Hz), 8.01 (d, 2H, $CH_{aromatic}$, $J = 8.8$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ (ppm) 35.3 (2C, C–$(CH_3)_2$), 60.8 (1C, C–Br), 127.3, 127.5, 143.4 (1C, C–SO_2Cl), 154.5 (5C, C_{arom}); FTIR ν (cm^{-1}): 577 (C–Br), 1174 and 1370 (SO_2); 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 ω-hydroxy PLA (**2**) precursors synthesized by ROP of LA initiated by butanol.

Precursor PLA_n[a]	M_n[b] (theoretical) ($g\ mol^{-1}$)	M_n[c] (SEC-RI) ($g\ mol^{-1}$)	PDI[c]	M_n[d] (^1H NMR) ($g\ mol^{-1}$)	Yield[e] (%)
PLA_{46} (**2a**)	3030	4600	1.23	3380	80
PLA_{96} (**2b**)	6840	8800	1.40	6980	94
PLA_{154} (**2c**)	8060	10,000	1.40	11,200	74

[a] *n*: number-average degree of polymerization of PLA as determined by ^1H NMR.
[b] $M_{n,theor}$ = conversion × (2[LA]$_0$/[initiator]$_0$) × 72 + M_n (end groups).
[c] Obtained from SEC equipped with RI detection (PS standards) eluting with THF as the mobile phase.
[d] Actual molar mass as calculated by ^1H NMR from PLA.
[e] Conversion as determined by gravimetry for ROP of lactide initiated by butanol.

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

Macroinitiator PLA_n-Br (**3**)	PLA_n[a]	M_n[b] ($g\ mol^{-1}$)	Yield (%)	Functionalization yield (^1H NMR) (%)
PLA_{46}-Br (**3a**)	PLA_{46}	3640	68	54
PLA_{96}-Br (**3b**)	PLA_{96}	7240	60	89
PLA_{154}-Br (**3c**)	PLA_{154}	11,440	78	66

[a] *n*: number-average degree of polymerization of PLA as determined by ^1H NMR.
[b] Molar mass of PLA as determined by ^1H NMR.