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Synthesis of Triazole-Functionalized Diblock Copolymers as Templates for Porous Materials

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Abstract

A versatile approach toward porous polystyrene-based frameworks functionalized with triazolyl moieties is reported. These porous materials were prepared from poly(D,L-lactic acid)-*block*-poly(styrene-*stat*-4-azidomethylstyrene) (PLA-*b*-P(S-*stat*-4-AMS)) diblock copolymer precursors. Upon macroscopic orientation and subsequent alkaline hydrolysis of the PLA block, such triazolyl-containing porous polystyrenes were produced. Experimentally, a PLA macroinitiator was synthesized by ring-opening polymerization (ROP) of D,L-lactide using a heterobifunctional initiator. The prepared macroinitiator containing a terminal tertiary α -bromo ester group allowed for further ATRP statistical copolymerization of styrene and 4-azidomethylstyrene, affording the second block, *i.e.* the P(S-*stat*-4-AMS) block. The styrene to 4-azidomethylstyrene molar ratio was tuned to obtain various compositions of the hydrophobic block. PLA macroinitiators and corresponding PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers were fully characterized by size exclusion chromatography (SEC), ¹H and ¹³C NMR, Fourier Transform Infrared (FT-IR) spectroscopy, and differential scanning calorimetry (DSC). Functionalization of PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers with *p*-tolylacetylene or 2-methyl-3-butyn-2-ol was carried out *via* copper-catalyzed azide-alkyne cycloaddition (CuAAC), yielding triazole ring in high yields (>90%). Finally, the porous structure of such functional polystyrene frameworks was examined by SEM.

Keywords: diblock copolymers; CuAAC “click” reaction; triazole; porous materials

1. Introduction

Over the last decade, functionalized porous materials have gained increasing interest from the research community in different areas, such as microelectronics, [1] energy storage, [2] photonics, [3] separation, [4-5] environmental remediation, [6] and biotechnology, [7] among others. The real breakthrough in these applications deals not only with their peculiar morphology but also with the specific properties they may offer, such as interaction between the porous material and the target molecules through a fast mass transfer, high specific surface area, and when hierarchically structured, they develop the capability of mimicking natural structures. [8-9] Actually, the porous materials by themselves cannot improve any useful property in the above-mentioned applications and require, in most cases, the introduction of chemical groups inserted in the backbone that can interact with metal ions, especially in the preparation of metal-organic frameworks (MOFs) [10] or mesoporous metal-based materials (MMBMs). [11]

To date, porous polymeric materials can be prepared through several self-assembling procedures according to a bottom-up strategy; this technique notably relies on functional block copolymers, constituted of an inert block and a labile (sacrificial) one, [12-13] which undergo self-assembly followed by the elimination of the labile block. Polystyrene-*block*-poly(D,L-lactic acid) (PS-*b*-PLA) semi-degradable diblock copolymers have been widely used in the two last decades for the preparation of such nanoporous polymers. The porosity has been created either by selective degradation of the PLA block or alternatively by a smarter strategy implying the selective cleavage of a chemical junction present between alien blocks. [14-27] The latter has notably allowed for the facile release of chemical functionalities of interest that can be further implemented for pore surface functionalization. When porous metal-based materials are demanded, the addition of metal ions are common; however, the only expected interactions between the copolymer backbone and the metal ion are through Van der Waals forces. In this regard, few publications emphasize improving the strength of these interactions by functionalizing a stable block copolymer with chemical groups of interest that can reach stronger interactions with the metal ions by coordinate covalent bonds. [28-31]

The use of amphiphilic block copolymers followed by an induced or cooperative self-assembly has noteworthy advantages; the extent of the interactions between antagonist blocks could be predicted, based on the chemical nature of each block and their intrinsic physicochemical properties

such as molar mass, molar mass distribution, block composition and solubility. [32] Amphiphilic block copolymers with tunable molar masses, narrow molar mass distributions, and high end-functionality can be obtained by controlled radical polymerization (CRP) techniques. Particularly, reactive/functional end-groups can promote post-polymerization reactions to obtain functionalized macromolecules. [15, 24, 28] Atom Transfer Radical Polymerization (ATRP) is one of the most employed CRP processes due to its viability to polymerize a wide spectrum of functional monomers in a controlled manner, particularly for post-polymerization reactions, such as block extension or end group functionalization. Besides, adding one or more blocks with dissimilar chemistry is possible towards the preparation of biphasic systems when ATRP is combined with other polymerization techniques. These chemical features inherent to each block enable their phase segregation, promoting self-assembly of the domains at a nano/mesoscale, resulting in a hierarchically ordered structure.

Herein, we report on the synthesis of functionalized poly(D,L-lactide)-*block*-poly(styrene-*statistical*-4-azidomethylstyrene) (PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers and their further functionalization to afford the corresponding diblock copolymers exhibiting various quantities of triazolyl moieties which could be used in the preparation of porous functional polymeric materials. The as-obtained amphiphilic block copolymer is constituted of a stable block containing a tuned quantity of triazolyl groups embedded in the polymer chain and of a degradable PLA block that is notably sensitive to alkaline conditions. In the functionalized polystyrene block, the triazolyl groups are incorporated through the concomitant polymerization of styrene and 4-azidomethylstyrene (4-AMS), used as co-monomer, followed by the copper-catalyzed azide-alkyne cycloaddition (CuAAC) of two different acetylenic compounds. Further, some features of the porous morphology arising from such triazolyl functionalized diblock copolymers are given.

2. Experimental Section

2.1. Materials

The solvents were dried, as already reported in the literature. [33] Copper (I) bromide and copper (I) chloride (Aldrich, 99%) were purified by stirring in glacial acetic acid, then with several successive washings with methanol, and finally with anhydrous diethyl ether before drying overnight under vacuum. Dimethylaminopyridine (DMAP, >99%), 2-bromoisobutryl bromide (>98%), *N,N,N',N'',N'''*-

pentamethyldiethylenetriamine (PMDETA, 99%), 4-chloromethyl styrene (97%), triethylamine (TEA, 99.5%), ethylene glycol (99.8%, anhydrous), and sodium azide (NaN_3 , $\geq 99.5\%$) were obtained from Aldrich and used as received. Styrene (Aldrich, 99%) was washed with NaOH and distilled from LiAlH_4 under vacuum prior to use. D,L-Lactide (Aldrich, 99%) was lyophilized from toluene overnight prior to use. Other reagents and solvents were used without any further purification procedures unless otherwise stated.

2.2. Synthesis of 2-hydroxyethyl 2-bromoisobutyrate (HEBI) (1)

The synthesis of HEBI is adapted from an already reported procedure. [34] It is as follows: Ethylene glycol (5.54 g, 89.4 mmol) and TEA (6.78 g, 67.0 mmol) were placed into a 250 mL round-bottom flask and diluted with 50 mL of dichloromethane. 2-bromoisobutyryl bromide (5.14 g, 89.0 mmol) was added dropwise into the mixture in a time-lapse of 2 h at 0 °C. Upon completion of the addition, the reaction mixture was warmed to room temperature, and a catalytic amount of DMAP was added to the reaction. Finally, the reaction mixture was refluxed for 3 additional h. The obtained product was purified *via* vacuum distillation, isolating a colorless viscous liquid (10.19 g, 45 % yield). ^1H NMR (CDCl_3 at 25 °C, 500 MHz): δ (ppm): 4.2 (t, 2H, $J = 4.30$ Hz, $\text{C}(=\text{O})\text{O}-\text{CH}_2$); 3.8 (t, 2H, $J = 4.5$ Hz, CH_2-OH); 1.9 (s, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3 at 25 °C, 125 MHz): 171.3 ($\text{C}=\text{O}$), 64.1 ($-\text{CH}_2-$), 60.7 ($-\text{OCH}_3$), 51.4 ($\text{C}-\text{Br}$), 33.6 ($-\text{CH}_3$). FT-IR (film in KBr): ν_{OH} 3300 cm^{-1} , $\nu_{\text{C}=\text{O}}$ 1740 cm^{-1} . GC-MS (E.I.): m/z : [M^+]: 210 (30), 212 (30)

2.3. Synthesis of 4-azidomethylstyrene (4-AMS) (3)

4-chloromethylstyrene (10.0 g, 65 mmol) and sodium azide (8.45 g, 130 mmol) were mixed with 70 mL acetone in a 100 mL round-bottom flask. The mixture was refluxed for about 90 h. The organic phase was diluted with CHCl_3 , washed with H_2O , dried over MgSO_4 , and vacuum-dried to afford the desired product as an orange viscous liquid (10.21 g, 98% yield). ^1H NMR (CDCl_3 at 25 °C, 500 MHz): δ (ppm): 7.38 (d, 2H, H_A , $J_{\text{H}_A-\text{H}_B} = 8.09$ Hz); 7.23 (d, 2H, H_B , $J_{\text{H}_B-\text{H}_A} = 8.23$ Hz); 6.68 (dd, 1H, H_3 , $J_{\text{H}_3-\text{H}_1} = 10.97$ Hz, $J_{\text{H}_3-\text{H}_2} = 17.63$ Hz); 5.73 (dd, 1H, H_2 , $J_{\text{H}_2-\text{H}_1} = 0.84$ Hz, $J_{\text{H}_2-\text{H}_3} = 17.57$ Hz); 5.24 (dd, 1H, H_1 , $J_{\text{H}_1-\text{H}_2} = 0.64$ Hz, $J_{\text{H}_1-\text{H}_3} = 10.75$ Hz); 4.26 (s, 2H, $-\text{CH}_2-\text{N}_3$). ^{13}C NMR (CDCl_3 at 25 °C, 125 MHz): δ (ppm): 137.7 (Aromatic Carbon), 136.2 ($-\text{CH}=\text{CH}_2$), 134.8 (Aromatic Carbon), 128.4 (Aromatic Carbon), 126.6 (Aromatic Carbon), 114.4 ($-\text{CH}=\text{CH}_2$), 54.6 ($-\text{CH}_2-\text{N}_3$). FT-IR (film in KBr): $\nu_{\text{C}=\text{C}-\text{H}}$ 3000 cm^{-1} , ν_{N_3} 2097.60 cm^{-1} . GC-MS (E.I.): m/z : [M^+]: 159 (30), 116.9 (100).

2.4. General procedure for the synthesis of poly(D,L-lactic acid) PLA macroinitiator (**2**)

2-hydroxyethyl-2-bromo-2-methyl propanoate (HEBI, 0.39 g, 1.87 mmol) and tin (II) 2-ethylhexanoate (1.53 g, 3.75 mmol) were mixed with 40 mL dry toluene in a 100 mL Schlenk tube. The solution was degassed with 3 freeze-pump-thaw cycles. Inside a glove box, 1,4-dioxane-2,5-dione (D, L-lactide) (5.0 g, 69.3 mmol) was added into a 30 mL quartz tube containing one-third of the solution previously prepared. This process was repeated twice in two more tubes. Each tube was placed independently in a microwave reactor at 110 °C for 5 h and 30 min. The device was programmed to reach such a temperature after 5 min from room temperature. At the end of the reaction, toluene was evaporated, the residue was dissolved in dichloromethane and precipitated in a mixture 1/1 hexane/diethyl ether: 1/1 (v/v). The obtained solid (4.65 g, 93% yield) was dried under vacuum for at least 12h in each case and was further analyzed by ^1H NMR, ^{13}C NMR and SEC.

2.5. General procedure for the synthesis of poly(D,L-lactic acid)-block-poly(styrene-stat-4-azidomethylstyrene) copolymer (**4**)

Herein is described the general procedure to prepare a P(S-stat-4-AMS) block containing 5 mol. % 4-azidomethylstyrene in the hydrophobic segment of the block copolymer. In a 100 mL Schlenk tube, copper (I) chloride (0.055 g, 0.55 mmol) and PMDETA (0.14 g, 0.83 mmol) were mixed to form the catalytic complex using toluene as solvent (5 mL). After 15 min, the PLA macroinitiator (**2**) (4.61 g) dissolved in 15 mL toluene was added to the reaction flask. Then, 4-azidomethylstyrene (0.54 g, 3.4 mmol) diluted in styrene (6.26 g, 60.2 mmol) and 15 mL toluene were successively added to the reaction mixture. Upon homogenization of the reaction mixture, it was submitted to three freeze-pump-thaw cycles, placed into an oil bath at 90 °C so as to trigger the polymerization and stirred at this temperature for 8 h. At the end of the reaction, the solution was concentrated under vacuum, dissolved in CHCl_3 , and passed through a pad of silica to remove the copper catalyst. The polymer solution was concentrated and precipitated into a large volume of methanol. This operation was repeated 2-3 times to remove totally unreacted monomer. After the pure polymer was vacuum-dried, it was analyzed by ^1H NMR, ^{13}C NMR, and SEC.

2.6. General procedure for the diblock copolymer triazole functionalization (5)

In a 50 mL round-bottom flask, copper (I) bromide (0.011 g, 0.077 mmol), PMDETA (0.013 g, 0.077 mmol) and toluene (10 mL) were mixed. In a second 50 mL round-bottom flask, the synthesized copolymer (1.0 g, 0.077 mmol) and 4-ethynyltoluene (0.05 g, 5.5 mmol) were mixed and dissolved in 5 mL toluene, the resulting solution was transferred *via* a cannula into the reaction flask containing the catalyst under inert atmosphere. The reaction mixture was stirred for 24 h at room temperature (~25 °C). Afterward, the reaction mixture was passed through a pad of silica to remove the copper catalyst, and the functionalized polymer was precipitated in a large volume of methanol. The functionalized polymer, obtained as a powder (0.64 g, 65% yield), was vacuum-dried and analyzed by ¹H NMR, ¹³C NMR, and FT-IR.

2.7. Mechanical orientation of diblock copolymer matrices

A stainless-steel channel die was used to help the phase separation to occur and thus obtain oriented nanodomains in the different copolymers. Further characteristics of this device can be found in a previous report. [15] Briefly, a small amount of previously pressed copolymer film was placed in the channel die between two stripes of Teflon. The channel die was heated at 120 °C in a hydraulic press and subjected to constant pressure load for 1 h. Afterward, the channel die was annealed in a vacuum oven at 160 °C overnight.

2.8. Solvent vapor annealing orientation of diblock copolymers

A few drops of diblock copolymer solution (concentration of 20 mg.mL⁻¹ in dichloromethane) were deposited onto a small silicon wafer surface (approximately 1 cm²) and spin-coated at 400 rpm for 15 sec and 2000 rpm for 40 sec. The obtained thin films were vacuum-dried prior to the annealing. The supported thin films were later placed inside a closed glass chamber and exposed to solvent vapors of tetrahydrofuran for different periods of time. Samples were vacuum-dried prior to SEM observations.

2.9. Selective hydrolysis of PLA block in oriented block copolymer thin films

The oriented PLA block was removed using a 3M NaOH aqueous solution. Experimentally, the specimen sample was immersed in the alkaline solution at 60 °C and gently shaken on an orbital shaking plate. The hydrolysis reaction times were very different depending on the morphology of the samples: overnight for the thin films prepared on silicon wafer surfaces and almost one month for the parallelograms obtained by mechanical orientation through channel die processing. Once hydrolysis was completed, the samples were rinsed successively with water and ethanol before vacuum-drying overnight and further observation by SEM.

2.10. Instrumentation

The ^1H and ^{13}C NMR studies were realized on a Bruker Avance III spectrometer (500 MHz and 125 MHz, respectively) in CDCl_3 with TMS as an internal standard. FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer using the attenuated total reflection (ATR) and KBr sample holder, between 4000 and 450 cm^{-1} , with an average of 32 consecutive scans and a resolution of 4 cm^{-1} . Size Exclusion Chromatography (SEC) analyses were 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 along with a Wyatt Technologies eight-angle laser light scattering (LLS) detector. The eluent was THF at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$. Calibration curves for the RI detector were obtained with polystyrene standards from Polymer Labs (PS standards in the range of 1350–1,997,000 Da). Scanning Electron Microscopy (SEM) was performed on a MERLIN microscope from Zeiss equipped with InLens and SE2 detectors using a low accelerating tension (2–3 kV) with a diaphragm aperture of 30 μm . Field Emission SEM was performed on a JEOL JSM 7401F coupled with an energy dispersive X-ray (EDX) detector. The samples were first coated with a 4-nm thin layer of palladium/platinum alloy in a Cressington 208 HR sputter-coater. Thermal analyses were realized on a calorimeter model 9105 from TA Instruments.

3. Results and Discussion

3.1. Synthetic pathway

Inserting chemical functions of interest at the pore surface of polymer-based membranes is often a challenging task and is mainly driven by the synthetic strategy implemented to prepare the precursor block copolymers. Azide moieties seem to be chemical functionalities of choice to introduce chemical grafts on the pending chains of a (co)polymer through further post-polymerization modification *via* the well-known copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, a so-called “click” reaction. Such a versatile chemical reaction has hitherto been widely applied in polymer chemistry for easy and straightforward functionalization of various natural or synthetic macromolecules, either on pending chains or on termini of the backbone, as reported by different reviews. [35-37] The CuAAC reaction indeed allows for the formation of triazolyl groups, well-known as metal cations scavengers, as they allow for the formation of coordination bonds with diverse oxidized metallic species. To that extent, a certain number of examples dealing with 4-azidomethylstyrene-based homo- or copolymer materials has been reported in the recent literature to design such azido-functionalized macromolecular structures/materials. [38-48] These macromolecular materials can be engaged in CuAAC reaction with various alkynes to produce the corresponding triazolyl-containing (co)polymers. Such materials can present some interesting coordination properties with metallic ions. Such homo- or copolymers in which are embedded 4-AMS can be obtained from the (co)polymerization of 4-chloromethylstyrene (4-CMS) and further azidation of the corresponding (co)polymers. [38-42, 45-47] Another alternative relies on the direct (co)polymerization of 4-AMS. [43-44, 48] This functional monomer can be homo- or copolymerized in the presence of other monomer, *e.g.* (2,3,4,5,6-pentafluoro)styrene. The proposed synthetic route (**Figure 1**) followed in this work entails the preparation of a poly(D,L-lactic acid) (PLA) macroinitiator (**2**) from a heterobifunctional initiator (**1**) containing both a terminal tertiary α -bromoester and a primary alcohol function. The latter should allow for the controlled ring-opening polymerization of D,L-Lactide. In contrast, the α -bromoester moiety should allow for the polymerization of the second block, namely a poly(styrene-*stat*-4-azidomethylstyrene) (P(S-*stat*-4-AMS)) (**4**), *via* Atom Transfer Radical Polymerization (ATRP) methodology from PLA macroinitiator (**2**). Finally, the post-polymerization functionalization of the as-prepared isolated diblock copolymers was assessed by CuAAC reaction, [49] to afford the

corresponding triazolyl containing macromolecular materials (**5a**) or (**5b**), depending on the alkyne grafted.

3.2. Synthesis of initiator (**1**) (HEBI) and PLA macroinitiator (**2**)

Heterobifunctional initiator 2-hydroxyethyl-2-bromoisobutyrate (**1**) (HEBI) was selected as the starting initiator to prepare the functional diblock copolymers through two successive polymerization reactions. Indeed, this molecule contains a terminal tertiary α -bromoester, commonly used as ATRP initiator in styrene polymerization, [50] and another hydroxyl terminus that can promote the ring-opening polymerization (ROP) of D,L-lactide in the presence of a metal-based catalyst, *i.e.* SnOct₂. According to the reported method, HEBI was synthesized and characterized by spectroscopic techniques to ensure its chemical structure. [34] Afterward, SnOct₂-catalyzed synthesis of poly(D,L-lactic acid) (PLA) from HEBI initiator and D,L-lactide monomer was achieved at 110 °C in a microwave reactor for 5.5 h under moisture-free conditions. The experimental molar masses calculated by ¹H NMR were close to those theoretically expected, *i.e.* 8.0 and 15.0 kg.mol⁻¹, as shown in **Table 1**, thus demonstrating the good control of the ROP process. The PLA macroinitiator was purified by precipitation in a mixture hexane/diethyl ether, and the molar mass given by size exclusion chromatography (SEC) equipped with an eight-angle laser light scattering (LLS) detector. The molar mass distribution ($\mathcal{D}$) was also given by SEC, while the functionalization degree was determined by ¹H NMR (**Figure 2**). The ¹H NMR spectrum of the vacuum dried product (**2**), shown in **Figure 2**, clearly demonstrated that the ROP of D,L-lactide from HEBI was successful. Characteristic PLA signals were observed, notably those with chemical shifts $\delta \sim 5.2$ and 1.6 ppm for methine and methyl groups, respectively, together with those from the HEBI initiator, notably the 4 methylene protons at $\delta \sim 4.5$ ppm. Additionally, a singlet at $\delta \sim 1.95$ ppm was assigned to the six protons of the two equivalent methyl groups from the initiator in α -position of the bromine. The ultimate lactide unit inserted in the PLA block during ROP, was identified in the ¹H NMR spectrum with protons at $\delta = 5.05$ ppm and at $\delta = 1.68$ ppm, again assigned to the methine and methyl end group, respectively.

3.3. Synthesis of 4-azidomethylstyrene (4-AMS) (**3**)

4-azidomethylstyrene (4-AMS) (**3**) was obtained by nucleophilic substitution of chlorine from 4-chloromethylstyrene by sodium azide in acetone, as already reported elsewhere. [51] Viscous orange liquid was obtained after evaporation of the acetone and isolated with nearly quantitative yield (98%). FT-IR spectroscopy (**Figure S1** in Supplemental Information) confirmed the presence of the targeted compound with the appearance of a stretching absorption band $\nu_{\text{C-N}_3} = 2090 \text{ cm}^{-1}$, characteristic of the azide group covalently attached to the benzylic carbon. In addition, ^1H NMR spectrum of the pure product (**Figure S2** in Supplemental Information) exhibited the shift of the singlet resonance peak of methylene protons in α -position of the chlorine from $\delta = 4.61 \text{ ppm}$ to a new singlet resonance peak at $\delta = 4.26 \text{ ppm}$ in agreement with the chemical shift of the methylene protons that are now in α -position of the azide moiety, a less electron withdrawing group than the halogen. ^{13}C NMR also corroborated these findings; a displacement of the chemical shift of the benzylic carbon was observed from 46.1 to 54.6 ppm, (**Figure S3** in Supplemental Information), thus demonstrating the success of the nucleophilic substitution reaction. Mass spectrometry analysis (**Figure S4** in Supplemental Information) indicated the presence of a molecular ion mass $[M]^{++} = 116.9 \text{ m/z}$ which confirmed the chemical structure of 4-azidomethylstyrene. This latter was stored in a glove box at -30°C , due to its high reactivity.

3.4. Preliminary studies on styrene/4-azidomethylstyrene copolymerization from PLA macroinitiator

The preparation of diblock statistical copolymers from the PLA macroinitiator (**2**), styrene and 4-AMS was investigated. The synthesis of P(S-*stat*-4-AMS) (**4**) was assessed through a typical ATRP methodology. Hence, the copolymerization reaction of the 34 mol. % 4-AMS with styrene was performed in toluene using PMDETA/Cu (I) catalytic complex. The polymerization feed was kept at 100°C for 20 h. After purification of the polymer by successive precipitations in methanol and vacuum-drying, the product was isolated as a light-yellow powder with 92% conversion, as calculated by gravimetric analysis. Upon dissolution of the PLA-*b*-P(S-*stat*-4-AMS) (**4**) diblock copolymer with chloroform, the copper-based catalyst was removed by passing the solution through a pad of silica. Nonetheless, larger solvent amounts were required to dissolve the product, despite this, a gel-like product was unexpectedly observed. 500 MHz ^1H -NMR analysis of the gel through a high-resolution magic angle spinning (HR-MAS) probe exhibits a resonance peak at 9.2 ppm which was assigned to an aldehyde proton. It was assumed that this type of products could arise from the redox reaction of the azide group with the PMDETA-copper (I) complex, involving some N_2 release

and leading to the formation of an imine group that can be further hydrolyzed to the corresponding aldehyde moiety. [52] Hence, we stated that the copper (I) complex could promote the reduction of the azide group and an aldehyde molecule could be produced, as depicted in **Figure S5** (Supplemental Information). We thus hypothesized that 4-AMS generates free radicals by releasing N_2 gas, [53] the nitrene radicals may be capable of initiating the polymerization by itself and therefore, promoting the crosslinking with other growing chains in a non-controlled fashion. Consequently, gel formation may be promoted by an excess of radical species in the reaction medium: chain growing radicals and *in situ* formation nitrene radicals. It is likely that some of these nitrene radicals were accessible to react with the catalytic copper complex (Cu-L-X) and further yield aldehyde groups. To prove the extent of interactions between azide groups and other reagents employed in the ATRP polymerization, a kinetic study was performed. For such experiments, a 4-AMS/styrene molar ratio comprised between 5/95 to 34/66 and time lapses between 1 and 24 h were considered, while the temperature was kept constant at 90 °C (see **Table S1** in Supplemental Information). Monomer conversion and gel content were routinely calculated and monitored, respectively. It was found out that higher amounts of 4-AMS were incorporated in the polystyrene chain when the initial 4-AMS/styrene molar fraction was lower than 0.15 and when the reaction time did not exceed 10 h. Under these specific experimental conditions, no gel formation was observed.

3.5. Preparation of PLA-*b*-PS and PLA-*b*-P(S-*stat*-4-AMS) copolymers (4)

Once the PLA macroinitiator was obtained, the tertiary α -bromo ester group capping one terminus of the polymer chain was used as a classic ATRP initiator. The PLA volume fraction (f_{PLA}) targeted for such PS-*b*-PLA diblock copolymers was close to 0.35 since a hexagonally packed morphology is generally promoted after phase segregation in this case. However, it is also important to consider the 4-AMS/styrene molar ratio which is no longer higher than 0.15 in the stable polymer block. Considering these variable parameters, two sets of PLA macroinitiators were employed for the concomitant ATRP polymerization of styrene and 4-AMS monomers: PLA₁₂₆ ($M_{n\ SEC} = 9.3\text{ kg.mol}^{-1}$) and PLA₁₆₇ ($M_{n\ SEC} = 12.3\text{ kg.mol}^{-1}$). For each macroinitiator, styrene degrees of polymerization of 140 and 185 were envisioned to obtain suitable PLA volume fractions, respectively. Moreover, three different 4-AMS/styrene molar ratios, *i.e.* 0, 0.05 and 0.10, were investigated for each PLA macroinitiator considered. The copolymerization reaction was carried out by dissolving the PLA

macroinitiator in toluene in the presence of 4-AMS and styrene as the comonomers and PMDETA/Cu(I)Cl as catalyst under stirring at 90 °C for 10 h under inert atmosphere. The purification of the resulting copolymer was completed by removing the Cu(I)Cl/PMDETA catalytic complex by passing the polymerization mixture on a silica column and successive precipitations in a large volume of methanol. The diblock copolymers were characterized by spectroscopic techniques, such as ATR FT-IR and ^1H NMR but also thermal analysis and SEC. The molecular features of the obtained diblock copolymers are gathered in **Table 2**. Copolymerization of styrene and 4-AMS *via* ATRP proceeded with high conversions in the 90-100% range, regardless of the PLA size or initial comonomers/PLA macroinitiator ratio. Additionally, M_n SEC values close to the theoretical ones and $\bar{D}$ in the 1.2-1.5 range indicate that chain growth occurs in a controlled fashion. The ^1H NMR spectrum of the PLA₁₂₆-*b*-P(S₃₂₉-*stat*-4-AMS₁₃) diblock copolymer in CDCl₃ is shown in **Figure 3**. As expected, signals of the aromatic protons characteristic of the styrene and 4-AMS repeating units can be observed at $\delta = 7.4$ -6.3 ppm. Particularly, signals at $\delta = 7.40$ and 7.26 ppm were assigned to the 4 aromatic protons of the 4-AMS repeating unit. The poly(D,L-lactic acid) repeating unit was identified by the presence of resonance peaks at 5.20 (-CH-) and 1.58 ppm (-CH₃) together with a broad signal at $\delta = 4.24$ ppm, assigned to the benzylic protons in α -position of the azide function. The integration of these protons was used to quantify the 4-AMS composition in the P(S-*stat*-4-AMS) polymer block. Finally, the methylene hydrogens bonded to the oxygen atoms belonging to the initiator, display broad signals in the 3.95-4.11 ppm region. In these sets of experiments, the synthesis of PS-*b*-PLA copolymers with no 4-AMS inserted in the chain was also considered. These materials were used as a reference, and characterization of such polymers was also achieved *via* ^1H NMR. ATR FT-IR analysis of the PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers (**4**) (**Figure S6** in Supplemental Information) showed characteristic absorption bands for the stretching of the carbonyl group at $\nu_{\text{C=O}} = 1750\text{ cm}^{-1}$, and the bending absorption band at $\delta_{\text{C-H aromatic}} = 750$ and 700 cm^{-1} for the aromatic protons of styrene. Finally, the stretching band of the C-N₃ group at $\nu_{\text{C-N}_3} = 2094\text{ cm}^{-1}$ was also observed in the copolymers inserting 4-AMS. The DSC analysis of these diblock copolymers indicated the presence of two glass transition temperatures (T_g), namely $T_{g1} = 54.5\text{ °C}$ and $T_{g2} = 105\text{ °C}$ assigned to PLA and PS blocks, respectively (see **Table S2** in Supplemental Information). Interestingly, a slight shift of each block T_g values was observed as compared to the theoretical T_g values of their respective homopolymers ($T_{g\text{ PLA}} = 50\text{ °C}$, $T_{g\text{ PS}} = 100\text{ °C}$). It is more likely that azido groups randomly distributed along the PS block may promote Van der Waals interactions with the lactide repeating units due to its intrinsic lability and may alter in consequence the block

conformation. The molar mass distribution curve of the PLA₁₂₆ ($M_{n\text{ SEC}} = 9.3 \text{ kg.mol}^{-1}$) macroinitiator was compared with those of corresponding PLA₁₂₆-*b*-P(S_m-*stat*-4-AMS_n) copolymers. **Figure 4** notably shows that SEC monomodal traces of such block copolymers, *e.g.* PLA₁₂₆-*b*-P(S₁₁₁-*stat*-4-AMS₁₀) and PLA₁₂₆-*b*-P(S₉₇-*stat*-4-AMS₄), are shifted towards higher molar masses when compared to the corresponding PLA₁₂₆ macroinitiator (**2**), as expected from the polymerization of styrene and 4-AMS from the latter. Analogous results (**Figure S7** in the supporting information) were obtained for the PLA₁₆₇ ($M_{n\text{ SEC}} = 12.3 \text{ kg.mol}^{-1}$) macroinitiator when compared to its corresponding PLA₁₆₇-*b*-P(S_m-*stat*-4-AMS_n) copolymers after copolymerization of styrene and 4-AMS.

3.5. Functionalization of diblock copolymers

The azido groups present along the PS backbone enable the functionalization of the copolymer to afford triazole derivatives (**5a**) or (**5b**) *via* CuAAC between PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers and *p*-tolylacetylene or 2-methyl-3-butyn-2-ol, respectively, as depicted in **Figure 1**. The presence of triazole moieties in the porous polystyrene matrix will enhance its capacity to interact with metallic cations. It is worth mentioning that a different behavior in phase segregation of the triazolyl-functionalized copolymers is expected when compared to non-functionalized counterparts. This phenomenon relies on the presence of 4-AMS repeating units randomly inserted in the polystyrene block, leading to an increment of the polarity in the hydrophobic block. After functionalization, triazole functionalized polymers were obtained after precipitation in methanol and vacuum drying. ¹H NMR spectra of the CuAAC-mediated functionalized PLA-*b*-P(S-*stat*-4-AMS) diblock copolymers (see **Figure 5**, for instance) showed the presence of new resonance signals when compared to their copolymer precursors. Indeed, a new broad singlet appeared at $\delta = 7.6 \text{ ppm}$, ascribed to the aromatic triazolyl proton. Additionally, a clear shift of the signal ascribed to the benzylic protons, previously in α -position of the azide groups on the PLA-*b*-P(S-*stat*-4-AMS), observed from $\delta = 4.2$ to 3.5 ppm , demonstrated the success of the CuAAC-mediated functionalization of the azido-functionalized diblock copolymer with *p*-tolylacetylene. The functionalization yield was determined by ¹H NMR and calculated by comparing the integration of the triazole ring proton at $\delta = 7.82 \text{ ppm}$ with that of the benzylic methylene protons of the polystyrene block at $\delta = 1.92 \text{ ppm}$. **Table 3** summarizes the so calculated CuAAC-mediated functionalization yields for the obtained copolymers. Furthermore, ATR FT-IR (**Figure S6** in Supplemental Information) analysis of the functionalized copolymers did not show the presence of

any characteristic asymmetric stretching band of the $-N_3$ group at 2090 cm^{-1} upon CuAAC “click” reaction, thus demonstrating the success of the functionalization strategy. Additionally, absorption bands for the stretching band of the carbonyl group at 1750 cm^{-1} , and the bending of C-H aromatic bonds at 750 and 700 cm^{-1} were observed, demonstrating the presence of lactide and styrene in the copolymer and thus no degradation during the CuAAC reaction.

3.6. Macroscopic orientation of functional copolymers and pore generation

The prepared diblock copolymers (**5a-b**) have specific features to assist microphase segregation and further promote a hierarchical array to obtain nanostructured materials. As previously stated, the volume fraction of each block is one of the most important variables, and it has been previously reported that for PS-*b*-PLA copolymers, an asymmetric phase is preferable. To develop PLA cylinders within a PS matrix, values of PLA volume fraction (f_{PLA}) must be equal to approximately 0.35. [34] For all synthesized block copolymers, f_{PLA} was calculated according to the molar mass given by ^1H NMR spectroscopy. These block dimensions should enhance phase segregation towards a hexagonally close packed morphology, after the alignment of PLA domains in the PS matrix. We implemented two different orientation techniques to promote mesoscopic order in the copolymer matrix. The first technique relied on the mechanical orientation of the sample in solid state, thus obtaining a parallelepiped due to shear stress applied to a pre-oriented film of the copolymer in a confined space (*i.e.*, channel die). Theoretically, the stress applied to the copolymer forced the chains to rearrange into a higher ordered conformation, shifting the system towards its most stable structure. After PLA hydrolysis, a nanoporous morphology of the resulting material could be observed, as depicted in **Figure S8** (Supplemental Information), for the SEM image of a porous P(S_{329} -*stat*-4-AMS $_{13}$) sample. Pore sizes of around 100 nm were detected. The second technique employed consisted in the orientation of the copolymer phases promoted by the swelling effect undergone in the presence of solvent vapors. SEM images showed the formed cavities in the functional polystyrene surface, after PLA alkaline hydrolysis (**Figure 6** and **Figure 7**). Overall, pore formation was clearly observed; however, the magnitude of pore sizes was higher than that obtained with the channel die technique. Indeed, pore sizes in the range of 100 nm to $1\mu\text{m}$ were detected. Such broad pore size distributions might be attributed to ill-controlled solvent vapor annealing conditions for the copolymer precursors.

4. Conclusions

We have developed a new synthetic route to obtain functional diblock copolymers by utilizing a heterobifunctional ROP-ATRP initiator, *i.e.* 2-hydroxyethyl-2-bromoisobutyrate (HEBI). A poly(D,L-lactic acid) macroinitiator was synthesized possessing a tertiary carbon-bromine end-group. Further copolymerization of 4-azidomethylstyrene (4-AMS) and styrene from PLA-Br macroinitiator was successfully carried out to generate the second azido-functionalized polystyrene block (P(S-*stat*-4-AMS)). Better copolymerization results were obtained with a 90/10: styrene/4-azidomethylstyrene molar ratio. Subsequent CuAAC reaction of the azide pending groups on the polymer backbone with two acetylenes was carried out, affording the resulting triazolyl functionalized copolymers with high functionalization yield. The 4-(azidomethyl) group present in the polystyrene block slightly shifted the PLA and PS glass transition temperatures toward lower values compared with the reference PLA-*b*-PS block copolymers.

Upon macroscopic orientation and subsequent alkaline hydrolysis of the PLA block, triazolyl-containing porous polystyrenes were formed with varying pore sizes depending on the orientation technique used for the copolymer precursors. This straightforward approach paves the way to the versatile generation of functional porous polystyrene frameworks with tunable functionality *via* “click” chemistry.

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1
 2 **Figure 1** Synthetic route applied for the preparation of PLA-*b*-P(S-*stat*-4-AMS) azido functionalized
 3 diblock copolymers.

1

2 **Figure 2.** ^1H NMR spectrum of PLA macroinitiator (**2**) in CDCl_3 .

3

1

2 **Figure 3.** ^1H NMR spectrum of $\text{PLA}_{126}\text{-}b\text{-P}(\text{S}_{111}\text{-stat-4-AMS}_{10})$ (4) in CDCl_3 .

Figure 4. Size exclusion chromatographic traces of synthesized PLA₁₂₆ macroinitiator and corresponding PLA₁₂₆-b-P(S_m-stat-4-AMS_p) block copolymers.

Figure 5. ^1H NMR spectrum of $\text{PLA}_{126}\text{-}b\text{-P}(\text{S}_{111}\text{-stat-4-AMS}_{10})$ in CDCl_3 after functionalization with *p*-tolylacetylene.

1

2

3

Figure 6. SEM micrograph of porous P(S_{111} -stat-4-AMS₁₀) thin film sample.

1

2 **Figure 7.** SEM micrograph of porous $\text{P}(\text{S}_{152}\text{-stat-4-AMS}_{10})$ thin film sample.

Table 1. Molecular features of synthesized poly(D,L-lactic acid) macroinitiators.

PLA_n^a	Conv.^b(%)	<i>M_n</i>^{theor^c} (kg.mol⁻¹)	<i>M_n</i>^{NMR^d} (kg.mol⁻¹)	<i>M_n</i>^{SEC^e} (kg.mol⁻¹)	<i>Đ</i>^e	<i>F</i>^f (%)
PLA₁₂₆	91	7.2	8.2	9,300	1.54	97
PLA₁₆₇	93	14.0	14.8	12,300	1.50	96

^a *n* : number-average polymerization degree of PLA as determined by ¹H NMR.^b Conversion as determined by gravimetry.^c *M_n*^{theor} = conversion × DP_n × M₀ (Lactide).^d *M_n*^{NMR}: number-average molar mass as evaluated by ¹H NMR.^e Values from SEC/LLS measurements with PS standards.^f End-group functionality as determined by ¹H NMR.**Table 2.** Molecular features of synthesized PLA_n-*b*-P(S_m-stat-4-AMS_p) diblock copolymers.

PLA_n-<i>b</i>-P(S_m-stat-4-AMS_p)^a	Conv.^b (%)	<i>M_n</i>^{theor^c} (kg.mol⁻¹)	<i>M_n</i>^{SEC^d} (kg.mol⁻¹)	<i>Đ</i>^d	<i>X_{St}</i>^e	<i>f</i>_{PLA}^f
PLA₁₂₆-<i>b</i>-P(S₁₁₀-stat-4-AMS₀)	98	19.8	20.2	1.12	1.00	0.18
PLA₁₂₆-<i>b</i>-P(S₉₇-stat-4-AMS₄)	92	20.2	19.9	1.51	0.96	0.40
PLA₁₂₆-<i>b</i>-P(S₁₁₁-stat-4-AMS₁₀)	92	20.5	22.3	1.35	0.91	0.36
PLA₁₆₇-<i>b</i>-P(S₁₉₅-stat-4-AMS₀)	90	37.1	32.8	1.21	1.00	0.33
PLA₁₆₇-<i>b</i>-P(S₁₅₂-stat-4-AMS₁₀)	88	37.7	28.3	1.38	0.93	0.38
PLA₁₆₇-<i>b</i>-P(S₁₇₅-stat-4-AMS₃₈)	93	38.3	36.5	1.59	0.82	0.30

^a *n*, *m*, *p* : number-average polymerization degree of PLA and of P(S-*stat*-4-AMS) blocks as determined by ¹H NMR.^b Conversion as determined by gravimetry.^c *M_n*^{theor} = conversion × DP_n × M₀ (styrene) + *M_n*^{PLA}^d Values from SEC/LLS measurements with PS standards.^e Styrene molar fraction in the P(S-*stat*-4-AMS) random block.^f PLA volume fraction as determined by ¹H NMR, assuming that densities of PS and PLA are 1.02 and 1.25 g/mL, respectively.

1

2 **Table 3.** Functionalization yields observed for the CuAAC “click” modification of various PLA-*b*-P(S-
 3 *stat*-4-AMS) diblock copolymers with alkyne-appended compounds.

PLA _n - <i>b</i> -P(S _m - <i>stat</i> -4-AMS _p)	Alkyne grafted	Functionalization yield ^a (%)
PLA ₁₂₆ - <i>b</i> -P(S ₉₇ - <i>stat</i> -4-AMS ₄)	2-methyl-3-butyn-2-ol	85
PLA ₁₂₆ - <i>b</i> -P(S ₁₁₁ - <i>stat</i> -4-AMS ₁₀)	2-methyl-3-butyn-2-ol	98
PLA ₁₆₇ - <i>b</i> -P(S ₁₅₂ - <i>stat</i> -4-AMS ₁₀)	2-methyl-3-butyn-2-ol	--
PLA ₁₆₇ - <i>b</i> -P(S ₁₇₅ - <i>stat</i> -4-AMS ₃₈)	2-methyl-3-butyn-2-ol	91
PLA ₁₂₆ - <i>b</i> -P(S ₉₇ - <i>stat</i> -4-AMS ₄)	<i>p</i> -tolylacetylene	--
PLA ₁₂₆ - <i>b</i> -P(S ₁₁₁ - <i>stat</i> -4-AMS ₁₀)	<i>p</i> -tolylacetylene	97
PLA ₁₆₇ - <i>b</i> -P(S ₁₅₂ - <i>stat</i> -4-AMS ₁₀)	<i>p</i> -tolylacetylene	97
PLA ₁₆₇ - <i>b</i> -P(S ₁₇₅ - <i>stat</i> -4-AMS ₃₈)	<i>p</i> -tolylacetylene	87
^a Functionalization yield as calculated by ¹ H NMR.		

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