Polystyrene-*block*-Polylactide Obtained by the Combination of Atom Transfer Radical Polymerization and Ring-Opening Polymerization with a Commercial Dual Initiator

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ABSTRACT: A polystyrene (PS)-*b*-polylactide (PLA) block copolymer was prepared from the combination of atom transfer radical polymerization and ring-opening polymerization with commercially available 2,2,2-tribromoethanol as a dual initiator in a sequential two-step procedure. Hydroxyl-terminated polystyrene (PS-OH)s with various molecular weights were first prepared with polydispersity indices lower than 1.3; these provided valuable macroinitiators for the polymerization of D,L-lactide. A block copolymer with a composition allowing the formation of hexagonally packed PLA cylinders in a PS matrix was then obtained. The PS-*b*-PLA thin films revealed, after vapor solvent annealing, a hexagonally packed organization of the PLA cylinders, which was oriented perpendicularly to the surface of the film. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2944–2951, 2011

Key words: atom transfer radical polymerization (ATRP); block copolymers; nanotechnology; ring-opening polymerization; thin films

INTRODUCTION

Beyond their traditional applications areas in emulsions, polymer blends, and thermoplastic elastomers, the potential of self-assembled block copolymers for nanotechnologies is now well recognized.[1–3] In solid states, thermodynamic incompatibility between the blocks that compose these hybrid macromolecules (at least two in the simplest category of AB diblock) forces the system to self-organize via micro-phase separation, leading to materials that are structured on the nanometer scale.[4] The morphology and typical domain sizes at equilibrium are then governed by the composition (nature and relative ratio of A and B) and the degree of polymerization (N) of the block copolymer.[5,6] In most cases, the principal spacing of these ordered structures ranged from a few nanometers to 100 nm; this enables the use of these systems for nanotechnological applications.

One of the now well-established approaches for this is to convert these nanostructured materials into a porous system by the removal of the minor component (the A or B block).[7,8] This is particularly useful in systems where a full accessibility of the minor component exists (in hexagonally packed cylinders or a bicontinuous gyroïde morphology); this creates the exact porous replica of the parent system with an open porosity. These nanoporous systems can then be used for various applications, such as nanolithographic masks,[9,10] separation membranes,[11] or templates for nanoparticle growth.[12–15] Among the various kinds of sacrificial blocks that have been successfully used to generate porous materials,[16–19] polylactide (PLA) has emerged as a promising candidate because PLA etching only requires mild chemical treatment[20–22] (with a diluted aqueous base solution) and because PLA can be obtained from renewable sources. This renders the process more environmentally friendly compared to other candidates [e.g., hydriodic acid (HI) for poly(ethylene oxide) etching]. In this domain, polystyrene (PS)-*b*-PLA is a block copolymer that constitutes an interesting target for practical applications and leads to porous PS materials with valuable thermal and mechanical properties (which can even be improved by

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hydrogenation to form polycyclohexylethylene[23]). The properties and characteristics of this block copolymer are now well documented,[24] and several works have demonstrated the ability of PS-*b*-PLA to be oriented in the bulk[25,26] or in the form of thins films.[27–29] This large body of interest makes PS-*b*-PLA very close to industrial use for nanotechnological applications.

Because of this, any new insight concerning the preparation of such a block copolymer is worthy of interest. The preparation of a block copolymer such as PS-*b*-PLA and its analogs requires the combination of two mechanistically distinct polymerizations. Although the polyester segment is generally obtained by ring-opening polymerization (ROP), the second block is formed by living/controlled polymerization, involving either ionic or free-radical mechanisms. Although the living anionic polymerization of a styrenic monomer followed by the ROP of the cyclic ester monomer provides an elegant and straightforward route of synthesis,[30] many efforts in the literature have been focused on the use of living/controlled free-radical polymerization instead of anionic polymerization, combined with ROP either with sequential sequences or in a simultaneous one-step strategy.[31–39] Atom transfer radical polymerization (ATRP) is indeed known to be easier to carry out (it does not require stringent experimental conditions, e.g., high purities in the solvent and reactants) and is much more tolerant to functional groups existing on the monomer.[40–44] In this article, we report a direct and robust strategy for generating PLA-based copolymers in view of practical applications. For this purpose, a combination of ATRP and ROP with a commercial dual initiator (easily affordable tribromoethanol) was employed to synthesize PS-*b*-PLA with a composition allowing the formation of hexagonally packed PLA cylinders in a PS matrix.

EXPERIMENTAL

Materials

Styrene (Acros, Aldrich, Merck, 99%) was vacuum-distilled. CuBr (Acros, 98%) was purified by stirring in glacial acetic acid, washed with ethanol, and dried *in vacuo*. 3,6-Dimethyl-1,4-dioxane-2,5-dione (D,L-lactide, Acros, 99%) was recrystallized from ethyl acetate. Tin(II) bis(2-ethylhexanoate) was purchased from Aldrich (95%) and was dissolved in dry toluene (0.5*M*). CuBr$_2$ (Acros, >99%), 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA; Acros, 97%), 2,2,2-tribromoethanol (Acros, 99%), and dichlorodimethylsilane (Acros, >99%) were used as received. Neutral aluminum oxide (Acros, 20–200 μm) and silica (Merck, 40–63 μm) were used for the purification of Hydroxyl-terminated polystyrene (PS-OH) and PS-*b*-PLA, respectively.

Characterization

The molecular weights of the polymers were determined with a size exclusion chromatography (SEC) apparatus composed of a PL-GPC50 unit with an integrated refractive-index detector (Varian, Les Ulis, France), equipped with two columns 300 mm in length (mixed-C PLgel 5 μm from Polymer Laboratories), and calibrated with PS standards, with tetrahydrofuran (THF) as the mobile phase at 35°C with a flow rate of 1 mL/min. ^{1}H-NMR spectra of the polymers were obtained with a Bruker 400-MHz instrument with CDCl$_3$ as the solvent. Atomic force microscopy (AFM) characterizations were performed with a Nanoscope III from Digital Instrument Corp. in tapping mode.

Synthesis of hydroxyl-terminated PS by ATRP

In a typical experiment (PS-OH.2, entry 2 in Table III, shown later), a 50-mL, round-bottom flask was charged with styrene (10.4 g, 100 mmol), CuBr (0.050 g, 0.352 mmol), CuBr$_2$ (0.004 g, 0.018 mmol), and HMTETA (0.080 g, 0.349 mmol). After the mixture was stirred for 15 min and the Cu(I) complex was formed (when the mixture turned green), the mixture was degassed with dry nitrogen for 30 min, and 2,2,2-tribromoethanol (0.1 g, 0.353 mmol) was added. The flask was placed and stirred in an oil bath at 100°C. After 4 h (conversion = 60%, as calculated from ^{1}H-NMR), the flask was removed from the oil bath, and the reaction mixture was diluted with toluene and passed through a neutral alumina column to remove the catalyst. The obtained polymer (PS-OH.2) was precipitated into cold methanol and dried *in vacuo* at 50°C for 24 h. PS-OH was characterized by SEC [number-average molecular weight (M_n) = 24,300 g/mol, polydispersity index (PDI) = 1.3] and ^{1}H-NMR.

Synthesis of PS-*b*-PLA by ROP

A 50-mL, round-bottom flask and syringes were treated with a 90/10 solution of methylene chloride/dichlorodimethylsilane and dried at 70°C for 14 h. In a glovebox, to the silanized flask were added 1 g of PS-OH (24,300 g/mol, 0.04 mmol) and 7 mL of dry toluene, and the mixture was stirred for 5 min. Then, a 0.5*M* solution of Tin(II) bis(2-ethylhexanoate) in toluene (40 μL, 0.02 mmol) was slowly added to the flask with a syringe. D,L-Lactide (1 g, 6.94 mmol) was then added to the flask. The reaction flask was sealed and removed from the glovebox, immersed into an 80°C oil bath, and stirred for 15 h. After the reaction was quenched with 1*N* HCl (1 mL), the block copolymer was precipitated in cold methanol, collected by vacuum filtration, and then dried
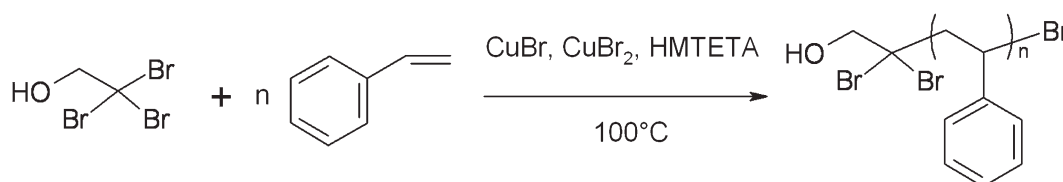
Figure 1   Synthesis of PS-OH by ATRP.

in vacuo at 80°C for about 24 h. The crude copolymer was dissolved in CHCl₃, passed through a short SiO₂ column, and then, the solvent was removed. The resulting polymer was characterized by SEC (PDI = 1.55, M_n = 30,600 g/mol) and ¹H-NMR spectroscopy.

Preparation of the thin films

The Si substrates (1 cm²) were first cleaned by soni-cation in dichloromethane, methanol, and distilled water for 10 min each, followed by (1) immersion in an HF:HCl:H₂O 1 : 1 : 5 solution for 5 min to remove the native oxide layer and (2) immersion in an NH₄OH:H₂O₂:H₂O 1 : 1 : 5 solution for 10 min to generate a hydroxide-functionalized hydrophilic sur-face. The PS-*b*-PLA thin films, with a thickness of approximately 100 nm (as measured by AFM on a scratch), were prepared by the spin-coating of a chlorobenzene solution of PS-*b*-PLA (20 mg/mL) on the Si substrates at 300 rpm for 15 s and 2000 rpm for 40 s.

Exposure to solvent vapors

Some films were exposed either to chlorobenzene or THF vapors to improve the organization/orientation of the PLA domains. For that purpose, the thin films onto their Si substrates were placed in a closed glass vessels (1.5-L desiccator) at 20°C above (5 cm) a res-ervoir of solvent (15 mL). After 4 h of exposition, the substrates were promptly removed from the vessel and allowed to dry at room temperature.

RESULTS AND DISCUSSION

Block polymer synthesis

As demonstrated in the seminal study of Jerome et al.,[31] tribromoethanol can be employed as a dual initiator for living free-radical and ROP and was used with this aim for the synthesis PS-*b*-poly(ε-cap-rolactone) and poly(methyl methacrylate)-*b*-poly (ε-caprolactone). Compared to other popular dual initiators, such as hydroxyl α-haloester (e.g., α-halo-propionates or α-haloisobutyrate),[45,46] tribromoetha-nol does not require additional synthesis preparation steps. In this study, 2,2,2-tribromoethanol was first used to prepare PS-OH by ATRP of styrene at

100°C, which was catalyzed by a CuBr/HMTETA system with 5% added CuBr₂ relative to CuBr. Like other polyhalogenated initiators of ATRP, tribromoe-thanol behaves like a monofunctional initiator,[31,47–49] according to the reaction in Figure 1.

The obtained polymer displayed the typical ¹H-NMR spectrum of PS, with peaks at 6.2–7.2 ppm, corresponding to the five aromatic protons of PS, and other peaks at 0.7–2.4 ppm, corresponding to the aliphatic protons of PS (Fig. 2). The preservation of the functional —OH end groups, which is of prime importance for the initiation of the polymer-ization of the second block, was examined on a low-molecular-weight PS-OH sample (M_n = 11,000 g/mol, PDI = 1.10). Besides signals at 6.2–7.2 and 0.7–2.4 ascribed to PS, a series of signals was observed between 4.2 and 4.8 ppm and assigned to the pro-tons of chain ends e[31] and b'.[50,51] The existence of such peaks in the ¹H-NMR spectrum of PS was con-sistent with the presence of —Br and —OH end func-tionality. The ratio of the peak integration of the sig-nals at 4.2–4.8 ppm (three protons, chain ends) and 6.2–7.2 ppm (aromatic protons in the chains) gave a molecular weight of 10,800 g/mol, which was very close to the SEC value. The preservation of the chain ends was also confirmed, as we discuss later, by growth of the second block of PLA by ROP from the PS-OH macroinitiator.
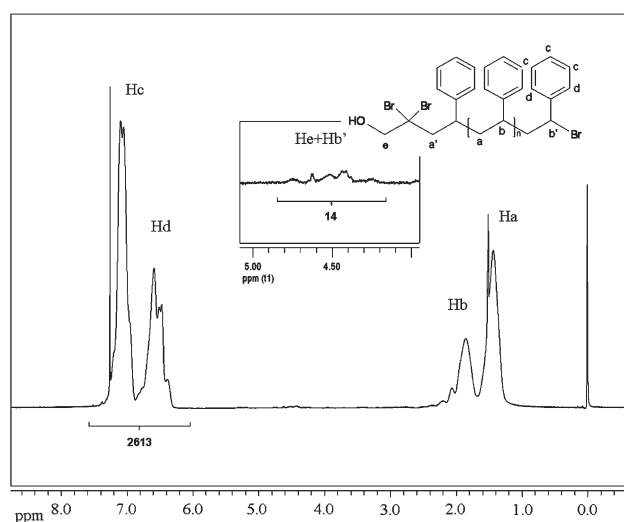

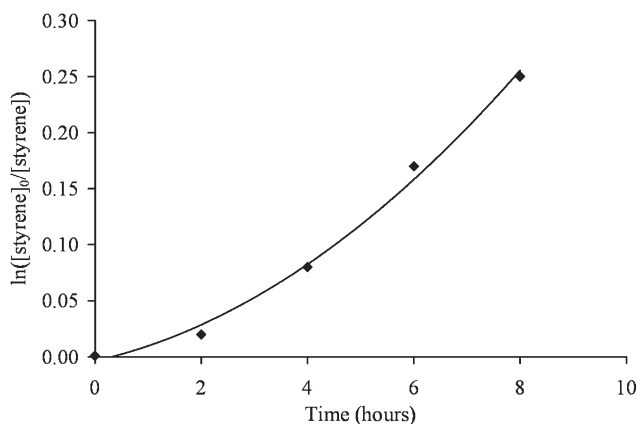**Figure 2**   ¹H-NMR spectrum (400 MHz, CDCl₃) of PS (M_n = 11,000 g/mol, PDI = 1.1).

Figure 3 Plot of ln([Styrene]$_0$/[Styrene]) versus time for the bulk ATRP of styrene with tribromoethanol/CuBr/HMTETA/CuBr$_2$ (initial molar composition = 1/1/1/0.05) and [Styrene]$_0$/[Tribromoethanol]$_0$ = 1000.

The kinetics of this polymerization are displayed in Figure 3 with a plot of ln([Styrene]$_0$/[Styrene]) versus time for a ratio of [Styrene]$_0$/[Tribromoethanol]$_0$ = 1000. One could observe an acceleration of the polymerization, which indicated that the radical concentration continuously increased during the polymerization. This reflected a slow initiation of the polymer chains (relative to propagation) from tribromoethanol. As shown in Table I, it could be observed that the experimental molecular weight ($M_{n,exp}$) values were higher than the theoretical molecular weights ($M_{n,th}$'s); this indicated that the initiation efficiency ($f = M_{n,th}/M_{n,exp}$) was lower than unity. The efficiency was in the range 0.5–0.7 (which was similar to values reported elsewhere for this initiator[52]) and increased with the reaction time. The PDI decreased with the conversion, and it could be seen that despite the slow initiation, the polymerization of styrene under the conditions used in this kinetic study eventually provided PS of low PDI (1.20 < PDI < 1.35). A slow initiation, relative to propagation, is sometimes observed for low-activated initiators (high R—X bond energy of the initiator related to the P—X bond of the dormant chains, with X

TABLE I
Synthesis of PS by ATRP with [Styrene]$_0$/
[Tribromoethanol]$_0$ = 1000 at Different Reaction Times

Time (h)	$M_{n,exp}$ (g/mol; SEC)	PDI	Conversion (%)[a]	$M_{n,th}$ (g/mol)[b]	f[c]
4	15,000	1.35	8	8,600	0.57
6	28,000	1.22	16	16,900	0.60
8	34,000	1.20	22	23,100	0.68

[a] Determined by ^{1}H-NMR spectroscopy of the crude reaction medium.
[b] $M_{n,th}$ = [Styrene]$_0$ × 104 × Conversion/[Tribromoethanol]$_0$ + 282.
[c] f = efficiency = $M_{n,th}/M_{n,exp}$.

TABLE II
Synthesis of PS by ATRP with [Styrene]$_0$/
[Tribromoethanol]$_0$ = 170 at Different Reaction Times

Time (h)	$M_{n,exp}$ (g/mol; SEC)	PDI	Conversion (%)[a]	$M_{n,th}$ (g/mol)[b]	f[c]
3	11,000	1.10	25	4,700	0.40
4	18,000	1.08	37	6,800	0.40
5	23,000	1.14	62	11,200	0.50
6	26,500	1.17	100	18,000	0.70

[a] Determined by ^{1}H-NMR of the crude reaction medium.
[b] $M_{n,th}$ = [Styrene]$_0$ × 104 × Conversion/[Tribromoethanol]$_0$ + 282.
[c] f = efficiency = $M_{n,th}/M_{n,exp}$.

being the halogen atom involved in the ATRP process) and/or for highly propagating monomers (high propagation rate constant). This is typically the case for the block polymerization of methyl methacrylate starting from a poly(butyl acrylate)–Br macroinitiator in the presence of a CuBr catalyst. Improvements are possible by using poly(butyl acrylate)-Br and CuCl catalysts (instead of CuBr) and this is known as the halogen exchange process.[53] Although it was not required in this study to further optimize the conditions of polymerization, a possible improvement could be obtained with halogen exchange conditions. Thus, the use of CuCl instead of CuBr should have fastened the initiation by tribromoethanol relative to propagation.

A similar kind of behavior can be observed in Table II for a ratio of [Styrene]$_0$/[Tribromoethanol]$_0$ = 170. In these later conditions, a faster polymerization occurred because of the higher initiator concentration. It could be noticed that the initiation of tribromoethanol remained not quantitative, even for 100% monomer conversion.

With this procedure, PSs of various molecular weights were synthesized with different ratios of [Styrene]$_0$/[Tribromoethanol]$_0$ (Table III). In the studied conditions, PSs with molecular weights between 23,000 and 66,000 g/mol were successfully prepared with PDIs lower than 1.3; this provided valuable macroinitiators for the synthesis of well-defined PS-*b*-PLA.

One of the hydroxyl-terminated PSs previously obtained by ATRP of styrene from tribromoethanol (PS-OH.2, 24,300 g/mol, PDI = 1.3) was selected to perform the controlled polymerization of D,L-lactide. For this purpose, the selected PS-OH was converted into a macroinitiator by reaction with Sn(Oct)$_2$ and then allowed to react with lactide in toluene at 80°C (Fig. 4). This temperature was chosen to ensure a reasonable reaction time (15 h) with a minimal level of side reactions.[54]

The formation of the diblock copolymer PS-*b*-PLA was verified by a combination of SEC and ^{1}H-NMR

TABLE III
Characteristics of the PS-OH Macroinitiator

Reference	$[Styrene]_0/$ $[Tribromoethanol]_0$	Targeted M_n (g/mol)[a]	Conversion (%)[b]	$M_{n,th}$ (g/mol)[c]	$M_{n,exp}$ (g/mol; SEC)	PDI	f[d]
PS-OH.1	173	18,300	62	11,300	23,000	1.1	0.49
PS-OH.2	288	30,200	60	18,100	24,300	1.3	0.75
PS-OH.3	540	56,400	68	38,400	44,300	1.3	0.87
PS-OH.4	1000	104,300	48	50,100	66,000	1.3	0.76

[a] $M_{n,targeted} = [Styrene]_0/[Tribromoethanol]_0 \times 104 + 282$.
[b] Determined by ^{1}H-NMR of the crude reaction medium.
[c] $M_{n,th} = [Styrene]_0 \times 104 \times Conversion/[Tribromoethanol]_0 + 282$.
[d] $f = Efficiency = M_{n,th}/M_{n,exp}$.

spectroscopy. Figure 5 shows the SEC curves of the macroinitiator (PS-OH.2) and the polymer prepared therefrom. It was clearly seen that the product of reaction shifted to higher molecular weights; this indicated that the hydroxyl function in PS-OH effectively initiated the polymerization of the D,L-lactide. ^{1}H-NMR spectroscopy confirmed the grafting of a PLA segment with the appearance of new peaks at 5.16 and 1.58 ppm, which corresponded to the protons of PLA. After purification of the PS-b-PLA on an SiO$_2$ column (mainly to remove the homopolymer contaminants), the composition of the block copolymer was calculated from the ratio of the integrated intensity of the peaks at 5.16 ppm (PLA, one proton) and 7 ppm (PS, five protons). For the obtained block copolymer, the PLA molar fraction extracted from the NMR shown in Figure 6 was 0.33; this corresponded to a PLA molecular weight of 8100 g/mol, which gave an overall molecular weight of the diblock of 32,400 g/mol, in good agreement with the SEC results (30,600 g/mol, PDI = 1.55). It is worth mentioning that tribromoethanol, which has so far been restricted to the polymerization of ε-caprolactone,[31] was herein used for the first time to prepare a PLA-based block copolymer in a very straightforward procedure.

Morphological study of the PS-b-PLA thin films

One important aim of this study was to prove that block copolymers obtained according to this procedure were able to form valuable thin-film precursors for nanolithography. To reach this goal, thin films of PS-b-PLA were first obtained by the spin coating of a solution of the block copolymer (in chlorobenzene) onto a silica substrate and then annealed in solvent vapor.

An AFM image of a representative as-spun PS-b-PLA thin film is shown in Figure 7(a). Because PLA was the minor phase, this image was in good agreement with a microphase separation, leading to segregated domains of PLA dispersed in a continuous matrix of PS. This was confirmed by a mild hydrolysis of the films, which led to a more pronounced depression in place of the dispersed domain (PLA). The surface contrast observed in Figure 7 could have been the result of a difference in height (PS and PLA had different surface energies, which could have led to different curvatures at the surface), but it might have also resulted from a difference of oscillation amplitude damping between PS and PLA[55] and/or a difference of adhesion.[56,57] This morphology was consistent with a nonequilibrium state resulting from the evaporation of the solvent during the preparation of the film. Domains of PLA showed poor long-range order, and the hexagonally packed cylinders self-assembled morphology was not evident from this image.

We recently explored the impact of solvent exposure on the behavior of PS-b-PLA thin films as a function of the solvent nature and exposure times.[28] We demonstrated that well-ordered perpendicularly oriented cylindrical domains of PLA could be successfully obtained by the exposure of thin PS-b-PLA films at room temperature in solvent vapor, such as THF or chlorobenzene, for moderate exposure times (4 h). Domain reorganization was obtained during solvent vapor exposure by plasticization of the block copolymer. In this previous study, PS-b-PLA was obtained by a combination of anionic and ROP
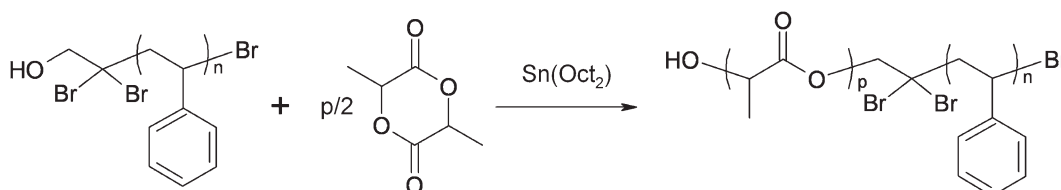

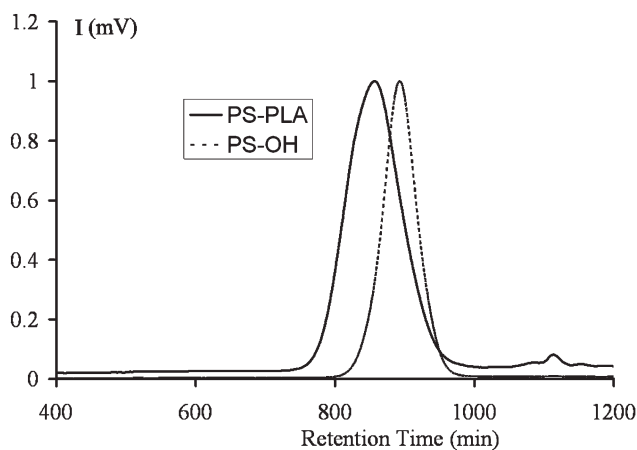Figure 4 Synthesis of PS-b-PLA block copolymers from PS-OH by ROP of D,L-lactide.

Figure 5 Overlay of the size exclusion chromatograms for (- - -) a PS-OH homopolymer (M_n = 24,300 g/mol, PDI = 1.3) and (—) a PS-*b*-PLA diblock copolymer (M_n = 30,600 g/mol, PDI = 1.55) I = intensity of the refractive-index detector.

polymerization, and M_n of the studied PS-*b*-PLA was 90,000 g/mol with a PLA volume fraction of 0.34. Figure 7(b,c) shows the morphology of PS-*b*-PLA thin films obtained by the ATRP/ROP combination after solvent annealing in chlorobenzene and THF vapors, respectively. The PLA volume fraction of the diblock, with densities[24] of PLA of 1.18 and PS of 1.02, was found to be 0.22. According to the morphology diagram of the PS-*b*-PLA reported by Hillmyer et al.,[24] the copolymers synthesized in this study should have exhibited hexagonally packed cylinder self-assembled morphologies. This was evident from these images, although the two-dimensional long-range order was not maintained over the totality of the image scale (confirmed by the Fourier transform in inlet, which exhibited broad diffraction spots). This differed from our previous study,[28] where similar solvent annealing led to well-ordered structures, with long-range order over the totality of
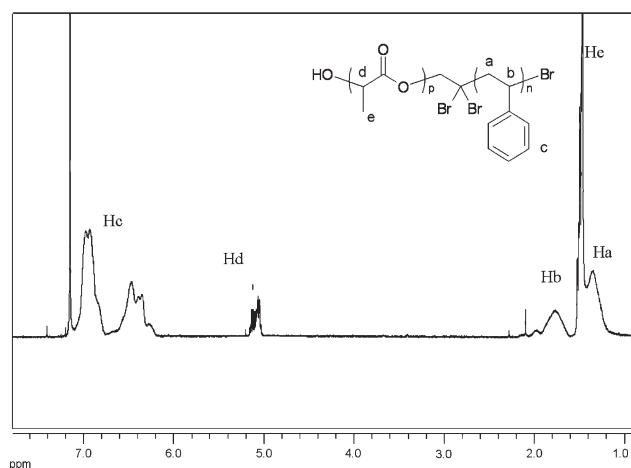

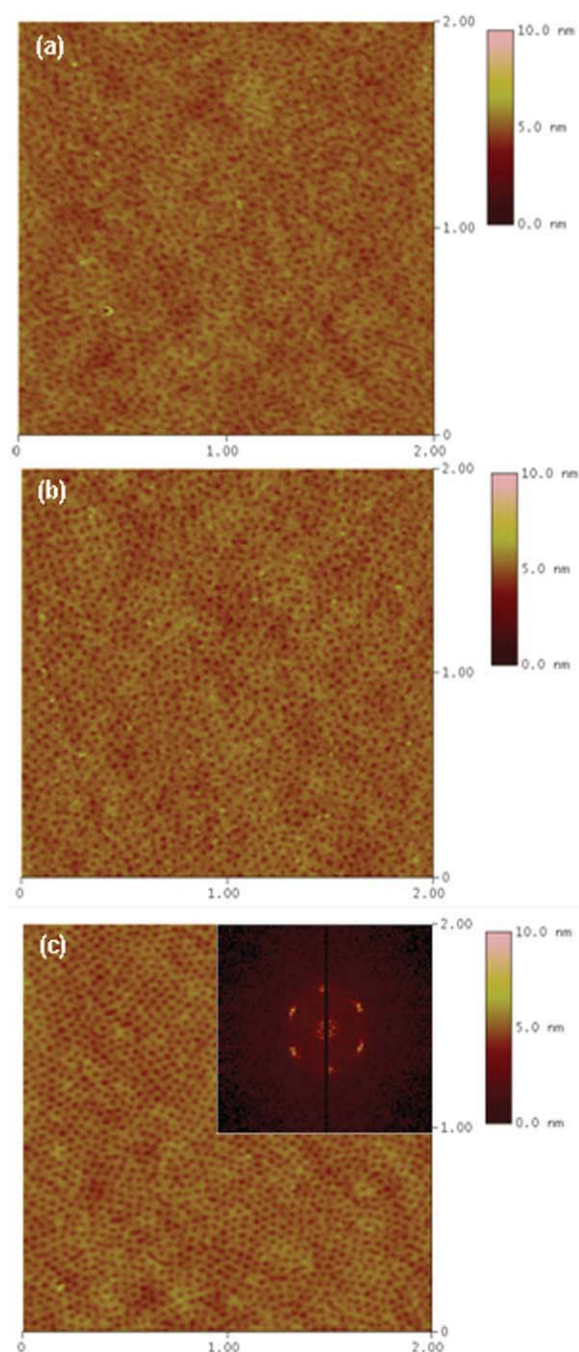**Figure 7** AFM image of the surface of a thin film of the PS-*b*-PLA block copolymer (M_n = 32,400, f_{PLA} = 0.22) on the Si substrate: (a) as spun, (b) after annealing with chlorobenzene vapors for 4 h, and (c) after annealing with THF vapors for 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of PS-*b*-PLA ($M_{n,NMR}$ = 32,400 g/mol, PDI = 1.55).

the image scale probed by AFM (2 × 2 μm^2). The differences between the block copolymer studied here and the block copolymer studied in this previous work were (1) the molecular weights of the copolymers (32,400 and 90,000 g/mol, respectively) and (2) the volume fractions of PLA (0.22 and 0.34, respectively). The change in molecular weight had a

direct effect on the value of χN (where χ is the Flory–Huggins parameter). With an assumed value of χ of 0.22 at 25°C,[24] the corresponding values of χN at 25°C were found to be 61 (32,400 g/mol) and 165 (90,000 g/mol). It could be seen that the block copolymer studied in this article belonged to the intermediate segregation regime, whereas the block copolymer studied previously was in the strong segregation regime and corresponded to a higher incompatibility between the blocks. Also, it could be seen from Hillmyer's work that PLA volume fraction (f_{PLA}) = 0.22 corresponded to the extreme limit of the cylindrical phase. These two effects (lower χN and lower f_{PLA}) could account for the lower degree of order obtained with the block copolymer studied in this work, as probed by AFM. However, and apart from this absence of long-range order, it was worth noting that the rather broad molecular weight distribution of the block copolymer (PDI = 1.55) did not prevent from self-organization, as already shown in other work.[58]

From the AFM image [Fig. 7(c)], we estimated a cylinder center-to-center distance of 43 nm and a diameter of cylinders of 25 nm. These values could be compared to the values predicted by the strong segregation theory. Indeed, and despite that large values of χN are theoretically required for this approach, strong segregation theory has been shown to be acceptable in most of the intermediate segregation regime.[59] In this theory, the equilibrium domain size (R) takes the form

$$ R = a \left(\frac{\beta}{2(\alpha^A + \alpha^B)} \right)^{1/3} \chi^{1/6} N^{2/3} $$

where α^A, α^B, and β are coefficients that can be expressed for the cylindrical phase with the conventional unit-cell approximation (the Wigner–Seitz cells are replaced by circular unit cells of radius R).[59] From the radius R, the diameter of the cylinders (D) can be obtained with the volume fraction of PLA, whereas principal domain spacing (d^*; and then the center-to-center distance) is extracted by equalization of the volume of approximate (circular) and actual Wigner–Seitz cells. This gives[59]

$$ D = 2f^{1/2}R $$

and

$$ d^* = (3\pi^4/4)^{1/6}R $$

With a value of $N = 61$, obtained from an M_n of 32,400 g/mol, these expressions gave a diameter of the PLA cylinders of 10 nm and a center-to-center

distance of 26 nm; these were significantly lower than the experimental ones. This could have been related to the high PDI of the block polymer obtained in this study. PDIs as high as 1.55 indicated that macromolecules with higher Ns were present in the system, shifting the characteristic distances of the systems toward higher values. This could be seen when we calculated the standard deviation (σ) from the values of M_n and weight-average molecular weight (M_w; $\sigma = M_n \sqrt{M_w/M_n - 1}$), where a value as high as $\sigma = 22,700$ g/mol was obtained.

CONCLUSIONS

Diblock copolymers of PS and PLA were prepared by a combination of ATRP and ROP with a commercial 2,2,2-tribromoethanol dual initiator. We demonstrated that these block copolymers could be used to prepare nanostructured thin films by spin coating on an Si substrate. Vapor solvent exposure was shown to efficiently tune the organization and orientation of the domains to obtain perpendicularly oriented cylinders of PLA in a continuous matrix of PS. This sequential ATRP/ROP from tribromoethanol provided a convenient and effective route toward mesoporous thin films useful for nanotechnology.

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