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Mixed Molecular Brushes with PLLA and PS Side Chains Prepared by AGET ATRP and Ring-Opening Polymerization

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ABSTRACT: Brush macromolecules having poly(L-lactide) (PLLA) and poly(styrene) (PS) side chains were prepared on the backbone of partially esterified poly(2-hydroxyethyl methacrylate) (PHEMA) by using a combination of atom transfer radical polymerization (ATRP) and ring-opening polymerization. The number-average degrees of polymerization of PLLA side chains and PS side chains were determined by ^{1}H NMR spectroscopy, and the apparent molecular weights of the brush molecules were measured by gel permeation chromatography. The relationship between the crystallization of PLLA with PLLA and PS side chain lengths was investigated. Inside a brush molecule due to the unfavorable interaction between PLLA and PS two phases were formed. Brush molecules adsorbed on mica tend to make a starlike conformation; however, they change to a globular conformation after thermal treatment.

Introduction

During the past decade, synthesis of molecular brushes, also called bottle brushes or cylindrical brushes, has attracted much interest due to their specific conformation.[1] Because of the long densely grafted side chains, the main chain of a molecular brush is extended, and as a result the molecule tends to make a wormlike or cylindrical configuration in a good solvent.[2] At solid state more conformations can be found which depend on the fraction of side chains and the interaction of side chains with substrate.[3,4] In the past not only molecular brushes with all of the arms composed of one polymer were synthesized but also molecular brushes with different structures and compositions, including comb-on-comb,[5] star comb,[5−7] comb block,[8] comb−coil,[9] and gradient polymer brushes.[10] These polymers are very interesting for their specific architectures and properties. Generally speaking, molecular brushes can be synthesized through three routes, i.e., grafting through (polymerization of macromonomers), grafting onto (attachment of polymer chains to the backbone via specific interaction or reaction), and grafting from (grafting polymer chains from the backbone via in-situ polymerization). Over the past decade, many polymerization strategies have been applied in the synthesis of molecular brushes, such as free-radical polymerization,[11] anionic polymerization,[5,12] ring-opening metathesis polymerization (ROMP),[13] and living radical polymerization.[7,9,10,14] Because of its tolerance to a wide range of functional monomers and less rigorous reaction conditions, atom transfer radical polymerization (ATRP) has been the most frequently used technique in the synthesis of molecular brushes.

Recently, Matyjaszewski's group reported an improved ATRP method—activator generated by electron transfer (AGET) ATRP.[15] In a typical AGET ATRP system, an alkyl halide is used as initiator, and a transition metal complex in its oxidatively stable state (e.g., Cu(II)/ligand) is used as catalyst. The activator is generated by using an electron transfer to reduce the higher oxidation state transition metal. In their experiments tin(II) 2-ethylhexanoate was used as the reducing agent. The AGET ATRP method has all benefits of normal ATRP and remains tolerant to air during the operation. Because the reducing agent can also be used as catalyst in ring-opening polymerization, AGET ATRP and ring-opening polymerization can take place at the same time in the same reaction system. This method provides a simple way to generate two different polymer chains at the same backbone.

In a previous paper, we reported preparation and characterization of poly(DL-lactide)−poly(butyl acrylate) (PLA−PBA) comb−coil polymer brushes on the surface of silica nanoparticles by using a combination of AGET ATRP and ring-opening polymerization.[16] By using AGET ATRP and ring-opening polymerization PLA combs and PBA coils were prepared on the backbone and at the terminal sites of poly(2-hydroxyethyl methacrylate) (PHEMA) main chains, respectively. In this paper we report the synthesis of mixed PLLA and PS molecular brushes, a kind of polymer brushes with two different kinds of long arms randomly distributed on a main chain (Scheme 1). This type of polymer has many interesting properties and will find applications in the fields such as compatibilization of immiscible polymer blends and colloid science, etc.

Experimental Section

Materials. L-Lactide (LLA, 99.7%, mp 94−96 °C) purchased from Tian-yuan Biomaterials Co. was purified by recrystallization from ethyl acetate and dried in a vacuum at room temperature. 2-Hydroxyethyl methacrylate (HEMA, 99.5%) was purchased from Tian Jin Institute of Chemical Agents. It was purified by washing an aqueous solution of monomer with hexanes to remove ethylene glycol dimethacrylate, salting the monomer out of the aqueous phase by addition of NaCl, drying over $MgSO_4$, and distilling under reduced pressure.[17] 2,2′-Dipyridine (bpy, 99.7%), CuBr (99.5%), and $CuBr_2$ (99.7%) were purchased from Guo Yao Chemical Co. Before use dipyridine was recrystallized from hexane and dried in a vacuum. CuBr was purified by washing with glacial acetic acid. Before use $CuBr_2$ was dried in a vacuum oven at 100 °C. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), 11-bromo-1-undecanol (98%), 2-bromo-2-methyl propionyl bromide (98%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), and trimethylamine (99%) were purchased from Aldrich and used as received. All the solvents were distilled before use.

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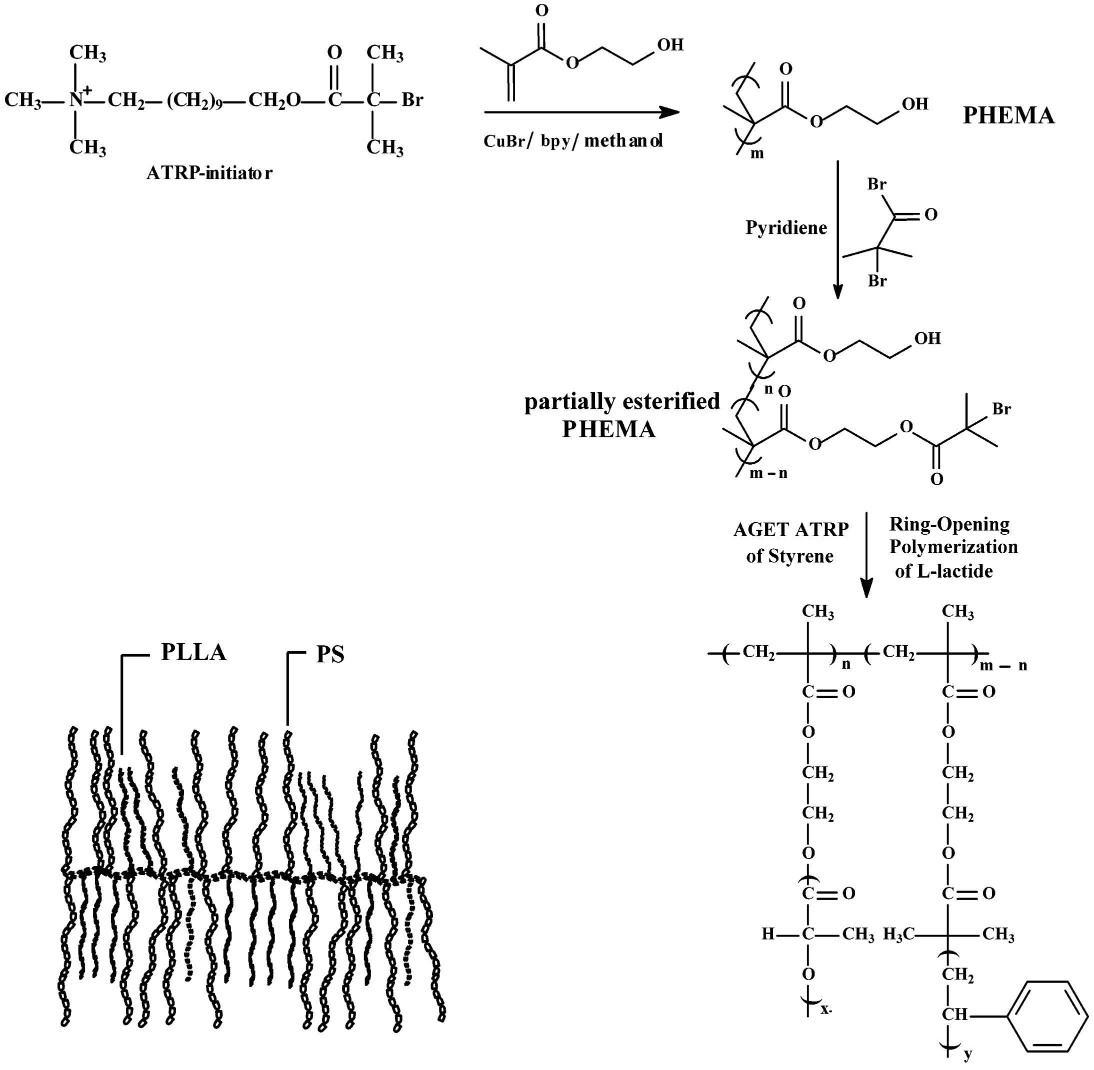
Scheme 1. Outline for the Preparation of Poly(L-lactide) (PLLA) and Poly(styrene) (PS) Mixed Molecular Brushes by Using a Combination of Ring-Opening Polymerization and Atom Transfer Radical Polymerization (ATRP)



Preparation of ATRP Initiator. ATRP initiator 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate was synthesized by using a procedure similar to the literature.[18,19] A solution of 2-bromo-2-methylpropionyl bromide (5.75 mL, 46.5 mmol) and diethyl ether (20 mL) was added dropwise, over 1 h at 0 °C, into a mixture of 11-bromo-1-undecanol (6.5 g, 25.9 mmol), pyridine (5.8 mL, 71.8 mmol), and diethyl ether (94.2 mL) and was stirred for 6 h. After filtration the reaction mixture was reduced and washed with distilled water three times. The ester was further purified with silica column chromatography (a mixture of petro ether and ethyl acetate with a volume ratio of 20:1). The yield of the product 11′-bromoundecyl-2-bromo-2-methyl propionate was about 80.5%.

11′-(*N*,*N*,*N*-Trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate was prepared by a reaction of 11′-bromoundecyl-2-bromo-2-methyl propionate (8.151 g, 20.375 mmol) with trimethylamine (16.815 g, 285 mmol) in 70 mL of ethanol at room temperature for 50 h. After removing of ethanol, the product was precipitated and washed with cold ether. Isolated yield is about 85.1%. The structure of the initiator is shown in Scheme 1. ^{1}H NMR (300 MHz, dimethyl sulfoxide (DMSO)-d_6): 1.28 (m, 14H, $(CH_2)_7$), 1.55−1.74 (m, 4H, $2CH_2$), 1.88 (s, 6H, $(CH_3)_2$), 3.03 (s, 9H, $N(CH_3)_3$), 3.21−3.32 (m, 2H, CH_2N), 4.12 (t, 2H, CH_2O).

Preparation of Partially Esterified PHEMA. PHEMA was prepared by ATRP initiated by 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate. A typical polymerization was described as follows. In a Schlenk flask 0.1 g (0.218 mmol) of ATRP initiator was dissolved in 1.2 mL (10 mmol) of HEMA. In another flask 32 mg (0.218 mmol) of CuBr and 70 mg (0.436 mmol) of bpy were dissolved in 1.2 mL of methanol. The methanol solution was transferred to HEMA monomer solution. After three freeze−pump−thaw cycles the polymerization was stirred at room temperature for 24 h. Copper ions were removed from the polymer solution with silica column chromatography.

PHEMA (0.89 g) was dissolved in 10 mL of anhydrous pyridine. At 0 °C, 0.94 g (4.1 mmol) of 2-bromo-2-methylpropionyl bromide was added dropwise into the solution. The solution was stirred at 0 °C for 3 h and at room temperature for 24 h. After filtration pyridine was removed by rotating evaporation. The partially esterified PHEMA was washed with distilled water and dried under vacuum. The degree of esterification was determined to be 46% by ^{1}H NMR.

Synthesis of Poly(L-lactide) (PLLA) and Poly(styrene) (PS) Mixed Macromolecular Brushes. A typical polymerization was described as follows. LLA (2.58 g, 17.9 mmol) and styrene (2.06 mL, 17.9 mmol) were added into a 25 mL Schlenk flask, and the mixture was bubbled with nitrogen for 15 min. Partially esterified PHEMA macroinitiator (0.1 g) with 46% degree of esterification was dissolved in 2 mL of dry *N*,*N*-dimethylformamide (DMF) and transferred via a syringe to the Schlenk flask with monomers. PMDETA (42.37 mg, 0.24 mmol) and $CuBr_2$ (54.6 mg, 0.24 mmol) were added to the flask. After 15 min stirring $Sn(Oct)_2$ (78 mg, 0.2 mmol) was added. The solution was degassed by three freeze−pump−thaw cycles. The polymerization was conducted at 110 °C for 34 h after the mixture was stirred for 1 h at room temperature. The polymerization was stopped by exposure to air. The polymer solution was diluted by $CHCl_3$, and the polymer was precipitated in cold methanol. After filtration the polymer was dried under high vacuum. In this paper mixed molecular brushes are assigned as d-PLLA$_m$-PS$_n$, where d is the degree of esterification and m and n are number-average degrees of polymerization of PLLA and PS side chains, respectively. For example, the sample prepared as we described above was designated 0.46-PLLA$_{36}$-PS$_{36}$.

To remove the remaining PLLA and PS homopolymers, the mixed macromolecular brushes were extracted with acetonitrile and hot cyclohexane, respectively. For 0.46-PLLA$_{36}$-PS$_{36}$ molecular brushes 4.86 and 2.21 wt % losses were found after being extracted with acetonitrile and cyclohexane.

Characterization. Differential scanning calorimeter (DSC) measurements were run on a Netzsch DSC 204 from −50 to 200 °C at a heating rate of 10 °C/min. Before measurements all the samples were annealed at 90 °C. ^{1}H NMR spectra were recorded on a Varian 300 spectrometer. ATRP initiator and PHEMA were measured in deuterated DMSO, and brush molecules were measured in deuterated chloroform. The conversion of styrene was detected by a gas chromatograph (GC) equipped with a flame ionization detector and a capillary column (Agilent Technologies 6890, HP-5. 0.25 mm i.d. × 30 m), using DMF as an internal standard. The apparent molecular weight and molecular weight distributions of the brush molecules were determined with a gel permeation chromatograph (GPC) equipped with a Waters 717 autosampler, Waters 1525 HPLC pump, three Waters UltraStyragel columns with 5K−600K, 500−30K, and 100−10K molecular ranges, and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. Molecular weights were calibrated using PS standards. X-ray diffraction (XRD) study was carried out on a D/max-2500 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Atomic force microscopy (AFM) images were collected on a Nanoscope IV atomic force microscope (Digital Instruments Inc.). The microscope was operated in tapping mode using Si cantilevers with a resonance frequency of 320 kHz. The voltage was between 2 and 3 V, and a tip radius was less than 10 nm. A drive amplitude of 1.2 V and a scan rate of 1.0 Hz were used.

Results and Discussion

As shown in Scheme 1, three steps are involved in the synthesis of PLLA and PS mixed molecular brushes. In the first step PHEMA was synthesized by ATRP. In the second step, partially esterified PHEMA was achieved by a reaction of PHEMA with 2-bromo-2-methylpropionyl bromide. In the last step by using a combination of ring-opening polymerization and AGET ATRP, PLLA and PS mixed polymer brushes were prepared on the backbone of PHEMA. In the polymerization system Cu(II)/ PMDETA complex was used as a catalyst for AGET ATRP of PS, and Sn(Oct)$_2$ was used as a reducing agent. Meanwhile, Sn(Oct)$_2$ was also used as a catalyst in the ring-opening polymerization of LLA. PS chains and PLLA chains grow independently from the same backbone via two different mechanisms (radical and ring-opening). The process is illustrated in Scheme 1. PHEMA was prepared by ATRP initiated by 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate. This ATRP initiator was ever used in the preparation of polymer/clay nanocomposites by the in-situ ATRP method.[18,19] The reason why this ATRP initiator was used in the preparation of mixed macromolecular brushes is that in the ^{1}H NMR measurements the ammonium end group of the initiator can be used in the calculation of the number-average degree of polymerization (DP$_n$) of PHEMA backbone and degree of esterification of PHEMA. Using ^{1}H NMR spectroscopy, the DP$_n$ values of PLLA and PS side chains on the PHEMA backbone can also be obtained. Furthermore, mixed molecular brushes with functional end groups can also be used in the study of interaction of brush molecules with negatively charged flat surface, particles, or polymers. It has to be pointed out that the PHEMA backbone was synthesized by ATRP; two terminal groups of the backbone were ammonium and bromide. Therefore, after AGET ATRP the main chain is always terminated by a PS chain (as shown in Scheme 1).

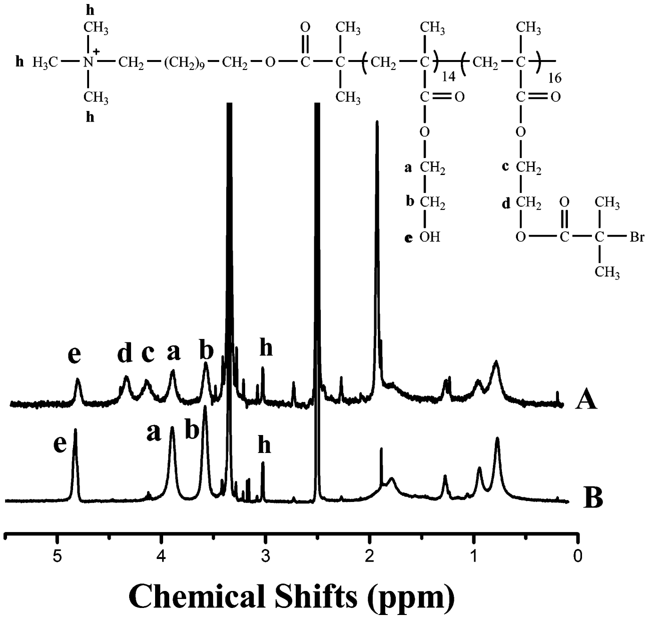


Figure 1. ^{1}H NMR spectra of (A) partially esterified poly(2-hydroxyethyl methacrylate) (PHEMA) with 46% degree of esterification and (B) original PHEMA. A magnification of peak h representing ^{1}H NMR spectrum of ammonium group at the end of polymer chains was also shown.

Figure 1 shows the ^{1}H NMR spectra of PHEMA and a partially esterified PHEMA. Chemical shifts of protons on PHEMA are described as follows: ^{1}H NMR (DMSO-d_6): $\delta =$ 4.83 (−OH), 3.89 (−CH$_2$−OCO), 3.58 (−CH$_2$−OH), 3.02 ((CH$_3$)$_3$−N−), 2.1−1.1 (−CH$_2$−C), 1.3−0.7 ppm (−CH$_3$). For partially esterified PHEMA some new peaks appeared at $\delta =$ 4.33, 4.14 ppm (−CH$_2$−OCO). The DP$_n$ of PHEMA can be obtained on the basis of integration of the peaks at $\delta = 3.02$, 3.89, and 3.58 ppm on the ^{1}H NMR spectrum of PHEMA. In this paper two PHEMA samples with DP$_n$ values of 30 and 48 were prepared. The degree of esterification of PHEMA can be calculated on the basis of integration of the peaks at $\delta = 4.33$, 4.14, 3.89, and 3.58 ppm. The degrees of polymerization and esterification of PHEMA are listed in Table 1.

PLLA and PS mixed molecular brushes were synthesized by using ring-opening polymerization and AGET ATRP. After partially esterification, the hydroxyl groups on PHEMA chains were used in the ring-opening polymerization of LLA, and the bromide groups on the backbone of PHEMA were used as initiators in AGET ATRP of styrene. In this polymerization system, the Cu(II)/PMDETA complex was used as catalyst for AGET ATRP, and Sn(Oct)$_2$ was used as a reducing agent. In the meanwhile, Sn(Oct)$_2$ was also used as a catalyst for the ring-opening polymerization of LLA.

Figure 2 shows plots of LLA and styrene monomer conversions vs polymerization time. The polymerization rate for the ring-opening polymerization of LLA is faster than AGET ATRP of styrene. In 25 h the conversion of LLA monomer reaches 90%; however, the conversion of styrene stays at about 40% at that time. Ring-opening polymerization of lactide typically follows first-order kinetics below 80% monomer conversion.[20] In the polymerization of LLA a linear kinetic plot of ln([M]$_0$/[M]) vs time can be observed below 90% conversion (Figure 2), which means that concentration of catalyst in the ring-

Table 1. Summary of PS and PLLA Mixed Molecular Brushes Prepared by a Combination of AGET ATRP and Ring-Opening Polymerization

		DP$_n$^{b}				
sample	deg of esterification	PHEMA backbone	PS side chains	PLLA side chains	$M_n \times 10^{-3\,c}$	PDI^c
0.46-PLLA$_{36}$-PS$_{36}$^{a}	0.46	30	36	36	48	1.42
0.46-PLLA$_{24}$-PS$_{76}$	0.46	30	76	24	42	1.61
0.46-PLLA$_{45}$-PS$_{19}$	0.46	30	19	45	16	1.80
0.46-PLLA$_{110}$-PS$_{15}$	0.46	30	15	110	123	1.20
0.71-PLLA$_{26}$-PS$_{29}$	0.71	48	29	26	55	1.41
0.71-PLLA$_{41}$-PS$_{30}$	0.71	48	30	41	63	1.59

[a] Mixed molecular brushes are assigned as *d*-PLLA$_m$-PS$_n$, where *d* is the degree of esterification and *m* and *n* are number-average degrees of polymerization of PLLA and PS side chains, respectively. [b] Measured by ^{1}H NMR spectroscopy. [c] Number-average molecular weight (M_n) and molecular weight dispersity (PDI) were measured on a gel permeation chromatograph (GPC) on PS standards.

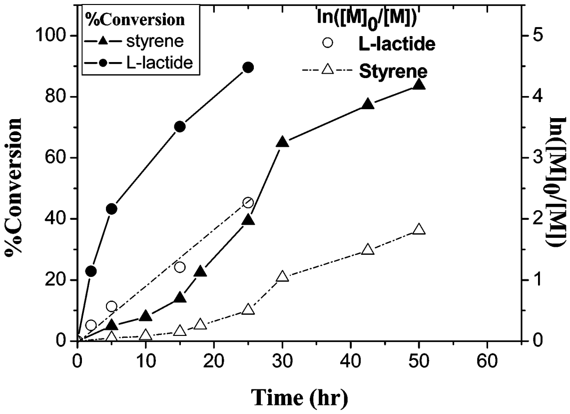


Figure 2. Percentage monomers conversion (filled symbols) and first-order kinetic plot of monomer consumption (open symbols) as a function of time for ring-opening polymerization of LLA and activator generated by electron-transfer ATRP (AGET ATRP) of styrene, with $[LLA]_0/[styrene]_0/[PMDETA]_0/[CuBr_2]_0/[Sn(Oct)_2]_0 = 90/90/1.2/1.2/1$ at 110 °C in *N*,*N*-dimethylformamide.

opening polymerization is constant. However, for the AGET ATRP of styrene the first-order kinetic plot shows curvature, indicating that the concentration of the active species is not constant during the polymerization. But it can be found that the first-order kinetic plot keeps linear when the polymerization of LLA is basically finished (after 30 h). This probably means after the ring-opening polymerization of LLA the equilibrium between the reduction of Cu(II) to Cu(I) by Sn(Oct)$_2$ and the production of Cu(II) was reached, and the concentration of the active species keeps constant.

The DP$_n$ values of PLLA and PS side chains were determined by ^{1}H NMR. Figure 3 shows the ^{1}H NMR spectrum of 0.46-PLLA$_{36}$-PS$_{36}$ mixed molecular brushes. In Figure 3 the peak at 3.8 ppm assigned to the methylene protons adjacent to the −OH group in PHEMA basically disappears, which indicates the successful ring-opening polymerization of LLA. In the spectrum the peaks at 5.14 ppm (a) and 6.3−7.2 ppm (g) represent the methine protons in PLLA and phenyl protons, respectively. Using these peaks, the molar radio of LLA to styrene is calculated to be about 2:1.78. The peak at 0.94 ppm (c ,d) is attributed to the methyl group of PHEMA. Using this peak and the peak at 5.14 ppm (a), the molar ratio of PHEMA repeating units to PLLA repeating units can be obtained. Assuming all −OH groups of partially esterified PHEMA take part in the ring-opening polymerization, the DP$_n$ values of PLLA and styrene side chains are both 36. The apparent number-average molecular weight of this brush molecule was measured by GPC. The GPC result showed that the molecular weight (M_n) of the polymer is about 48 000 with a polydispersity of 1.42. The DP$_n$ obtained by ^{1}H NMR, number-average molecular weights, and molecular weight distributions measured by GPC are summarized in Table 1.

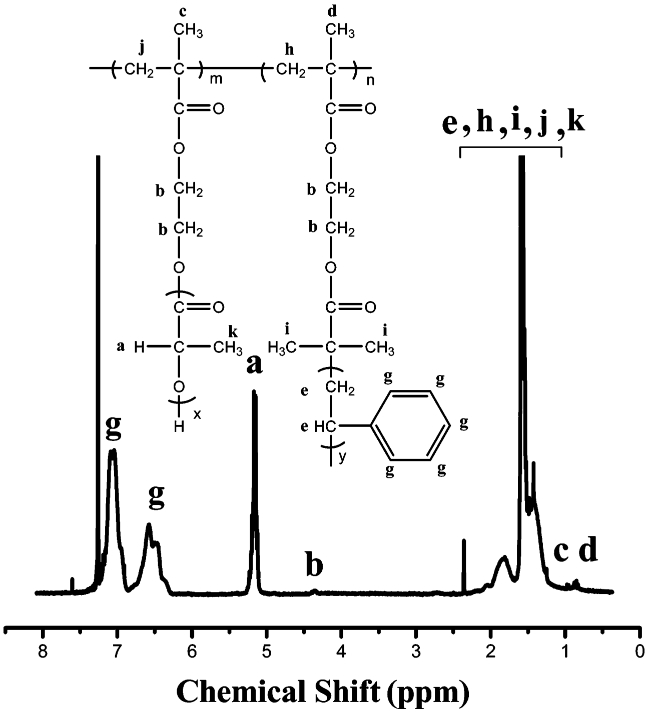


Figure 3. ^{1}H NMR spectrum of 0.46-PLLA$_{36}$-PS$_{36}$ molecular brushes.

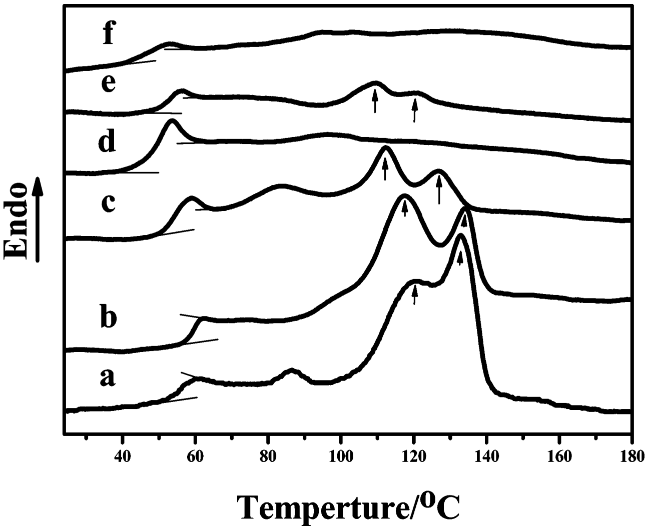


Figure 4. DSC curves of PLLA brush polymer and mixed macromolecular brushes: (a) PLLA$_{108}$ brush polymer, (b) 0.46-PLLA$_{110}$-PS$_{15}$, (c) 0.46-PLLA$_{45}$-PS$_{19}$ (d) 0.46-PLLA$_{36}$-PS$_{36}$, (e) 0.71-PLLA$_{41}$-PS$_{30}$, and (f) 0.71-PLLA$_{26}$-PS$_{29}$ mixed molecular brushes.

Figure 4 shows the differential scanning calorimetry (DSC) curves of mixed molecular brushes and one PLLA brush polymer. Before measurements all the samples were annealed at 90 °C. The glass transition temperature of PLLA side chains was determined at the midpoint of the transition. For $PLLA_{108}$ brush polymer, it exhibits a glass transition at about 56 °C. For 0.46-$PLLA_{110}$-PS_{15}, 0.46-$PLLA_{45}$-PS_{19}, and 0.46-$PLLA_{36}$-PS_{36} mixed molecular brushes, the glass transition temperatures of PLLA side chains are at 58.8, 55.5, and 50.2 °C, respectively, which means the glass transition temperature of PLLA side chains increases with chain length. The glass transition temperatures of PS side chains immerge into the wide melting peaks of PLLA, so they cannot be detected here. For $PLLA_{108}$ brush polymer, two melting peaks (indicated as arrowheads on curve a), located at 132.8 and 120.6 °C, can be observed. The small peak at about 85 °C is due to the melting of the PLLA crystalline with very thin lamella thickness. The melting temperature of PLLA in mixed molecular brushes is strongly affected by side chain lengths of PLLA and PS on the backbone. The melting temperature of PLLA decreases with increasing PS side chain length and increases with increasing PLLA side chain length. Curves b and c in Figure 4 represent DSC curves of 0.46-$PLLA_{110}$-PS_{15} and 0.46-$PLLA_{45}$-PS_{19}. For 0.46-$PLLA_{110}$-PS_{15} two melting peaks at 133 and 117.4 °C can be observed. Comparing curve b with c, it can be found that when DP_n of PS side chains is kept almost the same (one is 15 and the other is 19) and DP_n of PLLA side chains decreases from 110 to 45, the melting peaks of 0.46-$PLLA_{45}$-PS_{19} shift to 126.5 and 112 °C (curves b and c). Curve d represents DSC curve of 0.46-$PLLA_{36}$-PS_{36}. Comparing curves d and c, it can be found that when DP_n of PLLA side chains decreases slightly from 45 to 36 and DP_n of PS side chains increases from 19 to 36, the melting peak of 0.46-$PLLA_{36}$-PS_{36} disappears totally (curve d). The degrees of the crystallinity of the mixed macromolecular brushes were obtained:

$$X_c = \Delta H_m/(W_{PLLA}\Delta H_{m,0})$$

where ΔH_m is the enthalpy of fusion of the polymer, W_{PLLA} is the weight percent of PLLA in the brushes, and $\Delta H_{m,0}$ is the heat of fusion of 100% PLLA crystalline (93.1 J/g).[21] Our calculation results show that degrees of crystallinity of PLLA in $PLLA_{108}$, 0.46-$PLLA_{110}$-PS_{15}, 0.46-$PLLA_{45}$-PS_{19}, and 0.46-$PLLA_{36}$-PS_{36} are 39.2%, 27.9%, 15.3%, and 0%, respectively. Crystallization of PLLA side chains is greatly affected by PLLA and PS chain lengths.

DSC curves of 0.71-$PLLA_{41}$-PS_{30} and 0.71-$PLLA_{26}$-PS_{29} mixed molecular brushes are shown as curves e and f in Figure 4. The glass transition temperatures of PLLA side chains of the two samples are located at 53 and 48 °C, respectively. Because of longer PLLA side chain length, the glass transition temperature of 0.71-$PLLA_{41}$-PS_{30} is 5 °C higher than that of 0.71-$PLLA_{26}$-PS_{29}. For 0.71-$PLLA_{41}$-PS_{30} two melting peaks of PLLA at 120 and 109 °C can be observed (indicated as two arrowheads on curve e). However, no melting peaks can be detected for 0.71-$PLLA_{26}$-PS_{29}. Our calculation results show that degrees of crystallinity of PLLA in 0.71-$PLLA_{41}$-PS_{30} and 0.71-$PLLA_{26}$-PS_{29} are 13.54% and 0%, respectively.

WAXD can also be employed as a powerful tool in study of crystal structure of PLLA. Figure 5 shows wide-angle X-ray diffraction (WAXD) profiles of four PLLA and PS mixed molecular brushes and one PLLA brush polymer. In Figure 5, $PLLA_{108}$ and 0.46-$PLLA_{45}$-PS_{19} both exhibit strong peaks at $2\theta = 16.6°$ due to diffraction from (200) plane accompanied by two diffraction peaks at $2\theta = 18.9°$ and $2\theta = 14.7°$. The peaks at $2\theta = 18.9°$ and $2\theta = 14.7°$ are due to diffraction from (203) plane and (010) plane, respectively.[22] Because of lower degree of crystallinity 0.71-$PLLA_{41}$-PS_{30} only shows one small diffraction peak at $2\theta = 16.6°$ For 0.46-$PLLA_{36}$-PS_{36} and 0.71-$PLLA_{26}$-PS_{29}, only very broad peaks representing diffraction of amorphous phase can be found at 2θ from 12° to 25°. The WAXD results indicate that the crystalline structure of PLLA brushes in molecular brushes was strongly affected by PS brushes on the same backbone. The PS brushes limit the movement of PLLA segments to the growth front, which is unfavorable for the crystallization of PLLA. With the increase of PS side chain length, PLLA chains are more difficult to move, so the diffraction peaks rapidly decrease with increasing PS chain length. WAXD results keep consistent with the previous DSC results.

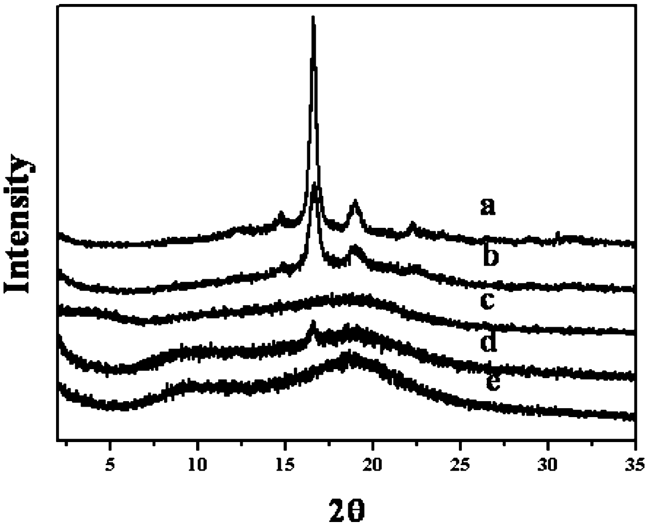


Figure 5. Wide-angle X-ray diffraction curves of (a) $PLLA_{108}$ brush polymer, (b) 0.46-$PLLA_{45}$-PS_{19}, (c) 0.46-$PLLA_{36}$-PS_{36}, (d) 0.71-$PLLA_{41}$-PS_{30}, and (e) 0.71-$PLLA_{26}$-PS_{29} mixed molecular brushes.

Figure 6 shows AFM tapping mode height images of 0.46-$PLLA_{36}$-PS_{36} and 0.71-$PLLA_{26}$-PS_{29} mixed molecular brushes dispersed on mica surface from dilute solutions. Because of their long side chains and relative short main chains, in AFM images these two polymers appear starlike rather than wormlike. From the images one can also observe that all the molecules exhibit core−shell structure. Similar structure was also found previously for macromolecular brushes with block copolymer side chains.[23] Because the nonpolar PS brushes have weak interaction and polar PLLA brushes have strong interaction with the polar mica substrate, PS chains tend to aggregate so that the interfacial energy between PS and PLLA as well as PS and air can be reduced. Meanwhile, PLLA brushes keep tightly adsorbed to the surface of mica substrate due to the favorable interaction between the substrate and the polymer chains. The structure is illustrated in Scheme 2.[24]

In previous papers conformational transitions of brush polymer molecules were studied.[3,25] For example, Sheiko et al. reported that a transition from a rodlike to a globular conformation was observed upon compression of a monolayer of poly(*n*-butyl acrylate) on a water surface.[3] Here it is very interesting to investigate the effect of temperature on the conformational transitions. Figure 7 shows an AFM tapping mode height image of 0.46-$PLLA_{36}$-PS_{36} after annealed at 110 °C, in which globular conformation with core−shell structure can be observed. A conformation change from starlike to globular structure occurs after thermal treatment. Conformational changes of a brush molecule with a flexible backbone and densely grafted side chains are dependent on the interplay of the intramolecular and surface forces.[3] At a higher temperature the globular conformation is favored entropically by coiling of the side chains at the expense of the interaction with the surface. Both PLLA and PS

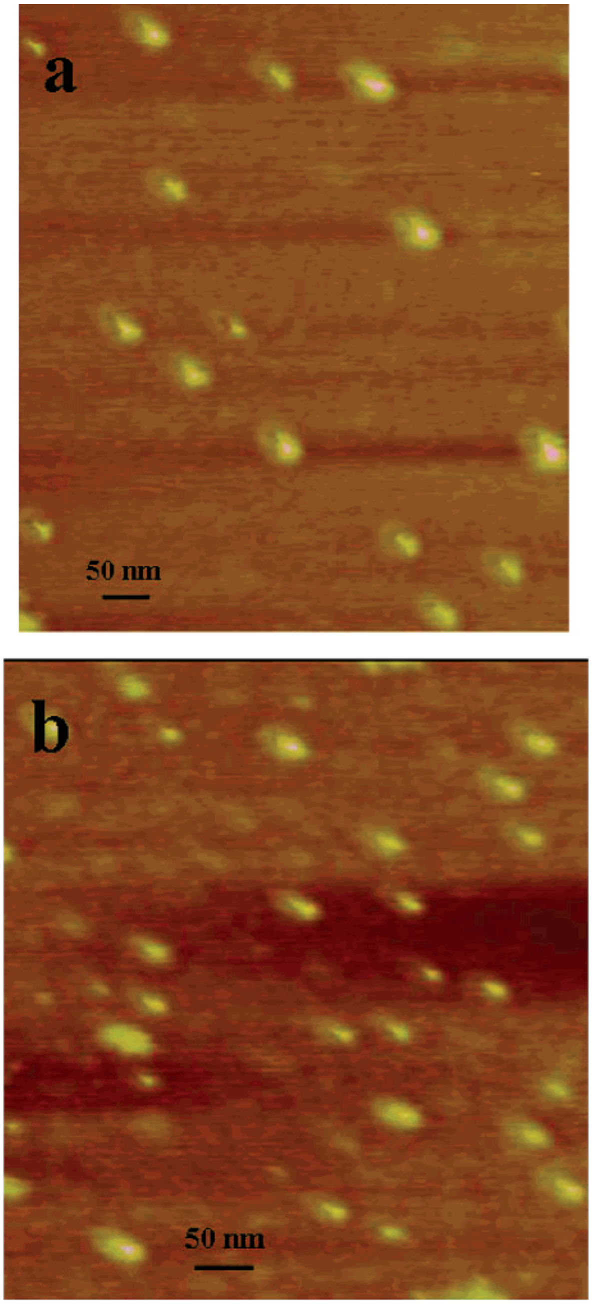
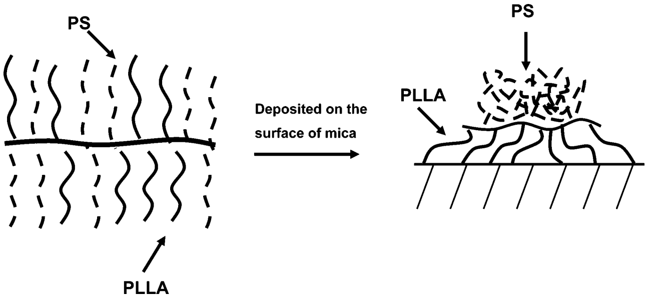


Figure 6. Tapping mode atomic force microscopy (AFM) micrographs of two mixed molecular brushes adsorbed on the surface of mica: (a) single molecules of 0.46-PLLA$_{36}$-PS$_{36}$ brush; (b) single molecules of 0.71-PLLA$_{26}$-PS$_{29}$ brushes.

Scheme 2. Formation of Starlike Morphology of PS and PLLA Mixed Macromolecular Brushes upon Casted from Diluted Chloroform Solution on the Surface of Mica



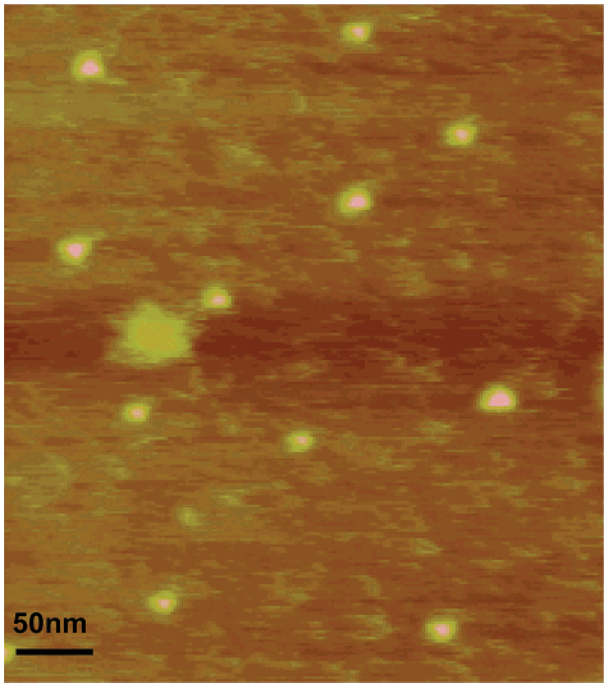


Figure 7. An tapping mode AFM image of 0.46-PLLA$_{36}$-PS$_{36}$ single molecular brushes after annealed at 110 °C.

side chains tend to aggregate at a high temperature. Inside a globular structure, PLLA phase and PS phase get smaller after thermal treatment, and the interfacial energy between PS and PLLA is further reduced after thermal treatment.

Conclusions

PS and PLLA mixed macromolecular brushes were prepared by using a combination of AGET ATRP and ring-opening polymerization. The glass transition temperature of PLLA is determined by side chain length. With the increase of side chain length, the glass transition temperature shifts to higher temperature. The crystallization of PLLA is greatly affected by PLLA and PS side chain lengths. The melting temperature of PLLA decreases with increasing PS chain length and increases with increasing PLLA chain length. Inside a molecular brush due to the unfavorable interaction between PLLA brushes and PS brushes phase separation occurs, and starlike morphology with core−shell structure can be observed. At a high-temperature molecular brushes tend to make globular conformation.

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