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ORIGINAL PAPER

Poly(1,4-butadiene)-*graft*-poly(*L*-lactide) via the grafting-from strategy

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Abstract Poly(1,4-butadiene)-*graft*-poly(*L*-lactide) copolymers were efficiently prepared via the grafting-from strategy using a combination of ring-opening metathesis polymerization (ROMP) of a hydroxyl-functionalized cyclobutene monomer and organocatalyzed ring-opening polymerization (ROP) of *L*-lactide. The copolymers were characterized by NMR, MALDI-TOF, SEC, TGA, and DSC demonstrating that well-defined polyester-grafted poly(1,4-butadiene) were obtained through the reported methodology.

Keywords Graft copolymers · Polybutadiene · Poly(lactic acid) · Macroinitiator · Ring-opening metathesis polymerization (ROMP) · Ring-opening polymerization (ROP) · Organocatalyzed ROP

Introduction

Bottlebrush copolymers, which possess a very high density of polymer arms uniformly grafted to a backbone of a linear polymer, represent a unique class of polymers because of their interesting morphologies and properties [1]. The synthesis of densely grafted copolymers typically involves the use of one or more living/controlled polymerization methods [2]. Thanks to the orthogonality of ring-

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opening metathesis polymerization (ROMP) toward organocatalyzed ring-opening polymerization (ROP) and the highly active ruthenium-based olefin metathesis catalyst [3, 4], ROMP has emerged as an effective chemistry to reach narrowly dispersed graft copolymers based on polyenes and polyesters with high molar masses [5]. Indeed, numerous works have reported the synthesis of graft copolymers from "ROMP-able" (oxa)norbornene derivatives because of their high reactivity. Our group has developed a number of efficient synthetic strategies based on the cyclobutene ring as the "ROMP-able" functionality to prepare well-defined graft copolymers having a strictly poly(1,4-butadiene) (PBu) main chain with a high density of grafts [6]. These PBu-grafted copolymers have been synthesized using the grafting-from or the grafting-through approach [7–10]. Use of the grafting-from technique has allowed us to synthesize well-defined high molar mass PBu-*g*-poly(methyl methacrylate), PBu-*g*-poly(*tert*-butyl acrylate) and PBu-*g*-poly(ε-caprolactone) graft copolymers [9, 10].

In this work, we report the synthesis and characterization of bottlebrush PBu-*g*-poly(*L*-lactide) (PBu-*g*-P_LLA) copolymers obtained from the grafting-from strategy. Besides distinct properties among other polyesters, polylactide has a unique behavior related to stereocomplex crystallization between its two stereoisomers, i.e., P_LLA and P_DLA [11, 12]. In the literature, the few previous reports devoted to the synthesis of lactide-grafted ROMP polymers using the grafting-from approach started from a polynorbornene [13, 14], polynorbornene-*b*-polyoxanorbornene [15] or poly(norbornene-*stat*-cyclooctadiene) backbone [16, 17]. Herein, we expand this methodology to the grafting of PLA. PLA arms were synthesized from a PBu backbone containing one pendant hydroxyl in every repeating unit used as the initiating group for the organocatalyzed ROP of *L*-lactide (*L*-LA) mediated by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Thermal properties of the resulting PBu-*g*-P_LLA graft copolymers are reported.

Experimental

Materials

All chemicals were purchased from Aldrich unless otherwise noted. Acetic acid (98.0%, Merck), chloroform ($CHCl_3$, >99.8%), *n*-hexane (>97.0%), silica gel for chromatography (SiO_2, 0.035–0.070 mm, 60 Å, Acros Organics) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%) were used as received. *L*-Lactide (L-LA, 98%) was recrystallized in toluene three times prior to use. Dichloromethane (DCM, HPLC grade, Fisher Chemical) and toluene (HPLC grade, Fisher Chemical) were dried over dry solvent stations GT S100. Poly(1,4-butadiene)-based ring-opening polymerization (ROP) macroinitiators containing a pendant hydroxyl in each repeating unit (**PBu**) were synthesized according to the previously reported procedure [10].

General characterization

NMR spectra were recorded on an Advance DPX 200 spectrometer for ^{1}H NMR (200 MHz). Chemical shifts are reported in ppm relative to the deuterated solvent resonances. The average molar masses (Number-average molar mass $\overline{M_n}$, weight-average molar mass $\overline{M_w}$) and dispersity ($Đ = \overline{M_w}/\overline{M_n}$) values were measured by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF) as the eluent and carried out using a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 µm Guard column, 50 × 7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 µm MIXED-D columns, 2 × 300 × 7.5) and with a SpectraSYSTEM RI-150 detector. The instrument operated at a flow rate of 1.0 mL min^{-1} at 35 °C and was calibrated with narrow linear polystyrene (PS) standards ranging in molar mass from 580 to 483,000 g mol^{-1}. Matrix-Assisted Laser Desorption and Ionization Time Of Flight (MALDI-TOF) mass spectrometry analysis was performed on a Bruker UltraFlex II MALDI-TOF instrument equipped with a nitrogen laser operating at 337 nm, a 2 GHz sampling rate digitizer, a pulsed ion extraction source and a reflectron. The laser pulse width is 3 ns and the maximum power is 200 mJ. Spectra were recorded in the linear mode with an acceleration voltage of 19 kV and a delay of 200 ns. 100 single shot acquisitions were summed to give the spectra and the data were analyzed using Bruker FlexAnalysis and Polytools softwares. Samples were prepared by dissolving the matrix (trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTB) in DCM (30 mg mL^{-1}) and mixing with the polymer (2 mg mL^{-1}) in the ratio 1:50 (v/v). An aliquot of this solution (1 µL) was spotted directly onto a thin layer of sodium trifluoroacetate in acetone (concentration 19 mg mL^{-1}) that had been deposited to act as a cationizing agent. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 apparatus measuring the total mass loss on approximately 10 mg samples from 30 °C up to 600 °C at a heating rate of 10 °C min^{-1} in a nitrogen flow of 90 mL min^{-1}. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q100 connected to a computer in aluminum pans under nitrogen otherwise noted. Samples were heated from 20 to 100 °C, held at 100 °C for 20 min to erase any history effects, and then cooled to −80 °C, kept at −80 °C for 5 min, and heated again to 200 °C at a heating rate of 5 °C min^{-1}. Crystallization temperatures (T_c) were obtained from the cooling scan, while glass transition (T_g) and melting transition temperatures (T_m) were obtained from the second heating scan.

General procedure for ROP of L-LA from PBu

A dry 10 mL Schlenk flask equipped with a stirring bar, a vial, two rubber septums, PBu, *L*-LA and TBD were introduced into a glovebox. *L*-LA (0.500 g, 3.47 mmol) and the desired quantity of PBu were added into the Schlenk flask. The Schlenk flask was then capped with a rubber septum. TBD (20 mg, 144 µmol) was added into the vial and then capped with a rubber septum. The Schlenk flask and the vial were removed from the glovebox. 0.4 mL of degassed anhydrous DCM was then

Table 1 Characteristics of PBu-*g*-P_LLA graft copolymers synthesized upon ROP of *L*-LA mediated by TBD as the catalyst at 25 °C in DCM with a reaction time of 1 h

Run	Sample[a]	([*L*-LA]$_0$)/[OH]$_0$/[TBD]$_0$	$\overline{DP_{n,NMR}}$[b]	$\overline{M_{n,NMR}}$[c] (g mol^{-1})	$\overline{M_{n,SEC}}$[d] (g mol^{-1})	$Đ$[d]
1	PBu_{85}-*g*-P_LLA_9	16/1/0.16	9	127,604	97,500	1.07
2	PBu_{85}-*g*-P_LLA_{15}	35/1/0.35	15	201,044	194,600	1.07
3	PBu_{198}-*g*-P_LLA_9	35/1/0.35	9	297,104	231,300	1.32

[a] In the sample name, the first number denotes the number of 1,4-butadiene repeating units and the last number in subscript the number of *L*-LA repeating units determined by ^{1}H NMR spectroscopy

[b] $\overline{DP_{n,NMR}}$ of the grafts calculated from ^{1}H NMR spectra of the purified graft copolymer by comparing the peak areas of the aromatic protons of the benzyl group at δ = 7.10–7.45 ppm and the methyl protons of the P_LLA at δ = 1.35–1.50 ppm

[c] Determined by NMR analysis from $\overline{M_{n,NMR}} = \overline{M_{n,NMR}}(PBu) + (\overline{DP_{n,NMR}}(L\text{-LA}) \times M_{L\text{-LA}})$ with $M_{L\text{-LA}} = 144$ g mol^{-1}

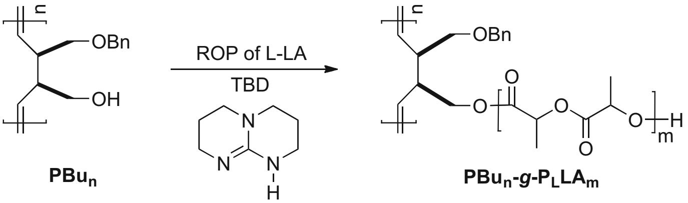
[d] Determined by SEC in tetrahydrofuran (THF) with RI detector, calibrated with linear polystyrene standards

introduced via a syringe into the vial ([TBD] = 359 mmol L^{-1}). 5 mL of degassed anhydrous DCM was then introduced via a syringe into the Schlenk flask and allowed to stir. When a homogeneous solution was obtained, the Schlenk flask was immersed in an oil bath preset at 25 °C and 100 μL of the TBD solution is added via a syringe to allow the polymerization to proceed (initial reaction time, $t = 0$). The polymerization was quenched after 1 h by the addition of acetic acid solution in toluene (0.2 mL, 16.5 mmol L^{-1}). The resulting mixture was then concentrated to dryness under vacuum. The crude polymer was then dissolved in DCM (2 mL) and precipitated into *n*-hexane (50 mL). The crude PBu-*g*-P_LLA copolymers were dissolved in $CHCl_3$ and passed through a short SiO_2 column (5 g for a 0.2 g PBu-*g*-P_LLA sample) using $CHCl_3$ as the eluting solvent. The resulting polymer solution volumes were reduced, and white copolymers were recovered by precipitating into *n*-hexane.

Poly(1,4-butadiene)-g-poly(L-lactide) ***PBu_{85}-g-P_LLA_{15}*** White plastic. [L-LA]$_0$/[OH]$_0$/[TBD]$_0$ = 35/1/0.35 (Table 1, run 2); $\overline{M_{n,NMR}}$ = 201,044 g mol^{-1}; $\overline{M_{n,SEC}}$ = 194,600 g mol^{-1}; $Đ$ = 1.07. ^{1}H NMR (200 MHz, CD_3COCD_3), δ (ppm): 7.25–7.10 (bs, 425H, CH_2–C_6H_5), 5.20–4.95 (t, J = 7.4 Hz, 2550H, C*H*–CH_3 of the P_LLA repeating unit), 1.52–1.30 (d, J = 7.2 Hz, 7650H, CH–CH_3 of the P_LLA repeating unit) (Fig. S3 in Supporting Information).

Results and discussion

The grafting-from approach was used to synthesize poly(1,4-butadiene) (PBu) backbones with poly(*L*-lactide) (P_LLA) grafts. Ring-opening polymerization (ROP) of *L*-lactide (*L*-LA) was performed following a procedure reported earlier [8] using



Scheme 1 Synthesis of poly(1,4-butadiene)-*g*-poly(*L*-lactide) graft copolymers according to the grafting-from strategy (Bn = CH$_2$-Ph)

PBu backbones containing pendant hydroxyl in every repeating unit as the ROP macroinitiator and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst (Scheme 1). TBD was chosen as the catalyst as it proved highly efficient in mediating the ROP of *L*-LA [18, 19].

The ROP of *L*-LA was carried out from PBu-based ROP macroinitiators with a number-average degree of polymerization ($\overline{\mathrm{DP}_n}$) of 85 and 198 containing pendant hydroxyl in every repeating unit with [*L*-LA]$_0$/[OH]$_0$ feed ratios ranging from 16/1 to 35/1 (Scheme 1; Table 1). The polymerization was performed at 25 °C in dichloromethane (DCM) for 1 h and then quenched by the addition of acetic acid. After precipitation in *n*-hexane, the crude copolymers were passed through a short column of silica to remove a small amount of linear P$_L$LA homopolymer presumably formed by adventitious initiation [17] and transesterification side reactions [20] (backbiting), as evidenced by the SEC profile showing a lower molar mass population (see Fig. S1 in Supporting Information) and Matrix-Assisted Laser Desorption and Ionization Time Of Flight (MALDI-TOF) mass spectrometry analysis applied to the low molar mass population (see Fig. S2 in Supporting Information). These side reactions lead to a lack of agreement between the monomer-to-initiator ratio and the experimental number-average degree of polymerization ($\overline{\mathrm{DP}_n}$) of the PLA grafts, determined from ^{1}H NMR analysis of the purified PBu-*g*-P$_L$LA copolymers (Table 1, run 2) by comparing the peak integration area of the methyl group of P$_L$LA at 1.35–1.50 ppm (labeled (b) in Fig. S3 in Supporting Information) with those of aromatic protons of the benzyl group at $\delta = 7.10$–7.45 ppm (labeled (c) in Fig. S3 in Supporting Information). Nevertheless, the experimental $\overline{\mathrm{DP}_n}$ values increased with increasing [*L*-LA]$_0$/[OH]$_0$ ratio (Table 1, run 1 vs 2). Furthermore, the clear shift of the SEC traces toward higher molar masses with increasing [*L*-LA]$_0$/[OH]$_0$ ratios and a narrow and unimodal elution peak with $Đ$ in the range of 1.07–1.32 (Table 1; Fig. 1 and Fig. S4 in Supporting Information) indicate that the P$_L$LA graft extension was effective to form well-defined PBu-*g*-P$_L$LA copolymers. The differences between $\overline{M_{n,\mathrm{NMR}}}$ and $\overline{M_{n,\mathrm{SEC}}}$ is the result of the difference in hydrodynamic volumes of the graft copolymers compared to linear polystyrene standards used to calibrate the SEC [7].

DSC analysis was used to determine the thermal properties of PBu-*g*-P$_L$LA graft copolymers and those of linear P$_L$LA homopolymer [8] (Fig. 2). The T_g of linear P$_L$LA homopolymer of similar $\overline{M_n}$ as the P$_L$LA grafts in the PBu-*g*-P$_L$LA copolymer was observed at 37 °C (see Fig. 2b). This value is close to those reported

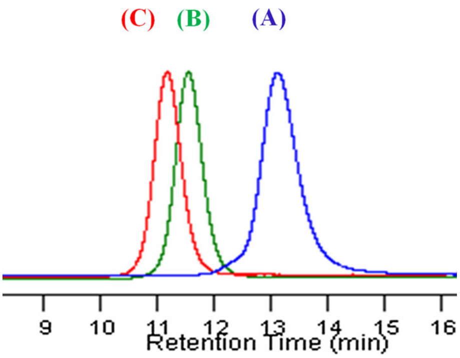


Fig. 1 SEC traces for the (*a*) **PBu_{85}**, (*b*) **PBu_{85}-*g*-P_LLA_9** (Table 1, run 1) and (*c*) **PBu_{85}-*g*-P_LLA_{15}** (Table 1, run 2) after purification

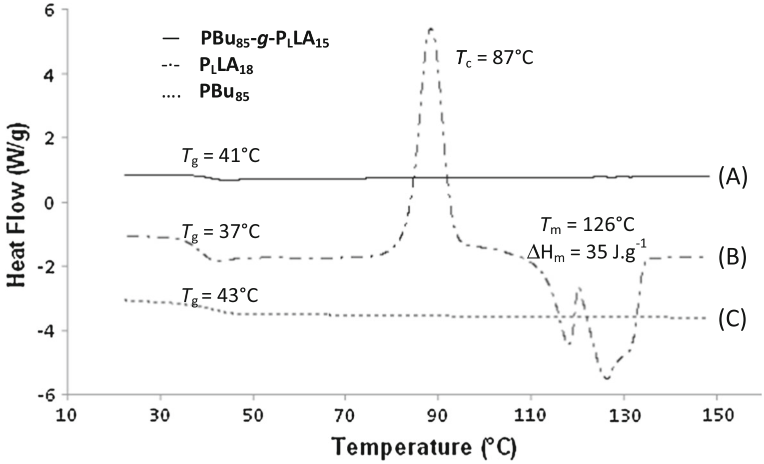


Fig. 2 DSC curves for (*a*) **PBu_{85}-*g*-P_LLA_{15}** (*full line*) (Table 1, run 2), (*b*) **P_LLA_{18}** (*dotted dashed line*) and (*c*) **PBu_{85}** (*dashed line*)

for linear P_LLA homopolymers with similar $\overline{M_n}$ and functionalized by norbornene or hepta-1,6-diyne chain end [21, 22]. The melting (T_m) and crystallization (T_c) temperatures of linear P_LLA are observed at 126 and 87 °C, respectively (see Fig. 2b), together with the well-known double-melting behavior of P_LLA [23]. The crystallinity of the samples, calculated by comparison with the reported enthalpy of fusion for the parent polymer crystal ($\Delta H_{\mathrm{f\ 100\%\ cristalline\ PLLA}} = 93\ \mathrm{J\ g^{-1}}$) [24], was 37%, and is similar with values reported in the literature for different linear P_LLA homopolymers [21, 22, 25]. DSC trace of **PBu_{85}-*g*-P_LLA_{15}** indicates a T_g at 41 °C but did not reveal any T_m (see Fig. 2a). A similar observation was reported in the literature [22, 25] for graft copolymers with short side chains of $P_LLA \leq 35$. This behavior can be ascribed to the confinement of the grafts that inhibits their mobility and capability for crystallization [22, 25].

The thermal decomposition profiles of copolymer **PBu_{85}-*g*-P_LLA_{15}** (Fig. 3c) and of the corresponding polymer precursors (Fig. 3a, b) were characterized via thermogravimetric analysis (TGA). The TGA curve of the **PBu_{85}-*g*-P_LLA_{15}**

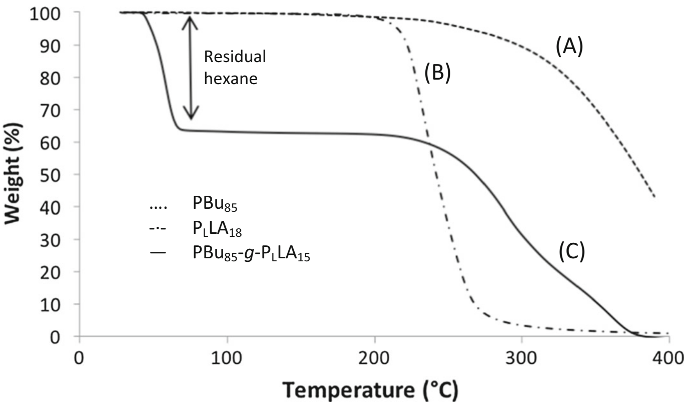


Fig. 3 TGA curves for (*a*) **PBu$_{85}$** (*dashed line*), (*b*) **P$_L$LA$_{18}$** (*dotted dashed line*), and (*c*) **PBu$_{85}$-*g*-P$_L$LA$_{15}$** (*full line*) (Table 1, run 2)

copolymer showed a two-step thermal decomposition: the first step can be caused by the decomposition of P$_L$LA in the range from 225 to 300 °C, and the second step is attributed to the decomposition of the PBu backbone. A similar observation was reported in the literature for polynorbornene-*g*-poly(*D*,*L*-lactide) copolymers [26]. This broad degradation temperature range for polylactide is a signature of the random chain scission accompanied by transesterification reactions [26].

Conclusion

In summary, PBu backbones bearing one pendant hydroxyl in every repeating unit have been successfully used as macroinitiators for the organocatalyzed ROP of *L*-LA by TBD to prepare original PBu-*g*-P$_L$LA copolymers through the grafting-from route. These polymers were thoroughly characterized by NMR, MALDI-TOF, SEC, TGA, and DSC to reveal their structure, sizes, molar masses, and thermal properties. The results are expected to be useful in the design and synthesis of complex hollowed nanostructures by taking advantage of the hydrolytic (bio)degradation P$_L$LA side chains of PBu-*g*-P$_L$LA.

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