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Synthesis of Brush Copolymers Based on a Poly(1,4-butadiene) Backbone via the "Grafting From" Approach by ROMP and ATRP

**Gaëlle Morandi,[†] Sagrario Pascual,[†] Véronique Montembault,[†] Stéphanie Legoupy,[†]
Nicolas Delorme,[‡] and Laurent Fontaine*,[†]**

[†]*LCOM-Chimie des polymères, UCO2M, UMR CNRS 6011, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 09, France, and* [‡]*LPEC-Laboratoire de Physique de l'Etat Condensé, UMR CNRS 6087, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 09, France*

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ABSTRACT: The synthesis of brush copolymers based on a strictly 1,4-polybutadiene (PB) backbone is reported via the "grafting from" strategy by combining two highly controlled polymerization methods: ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP). ROMP of a *cis*-3,4-disubstituted cyclobutene derivative (inimer) containing two initiating sites for ATRP was first investigated with Grubb's first-generation catalyst ($((Cy_3P)_2RuCl_2(CHPh))$), leading to well-controlled polymerization for $\overline{DP_n}$ up to 75. The well-defined 1,4-polybutadiene backbones obtained ($\overline{M_{n,SEC}}$ ranging from 3600 to 25 200 g·mol^{-1}, PDI ≤ 1.16) were then used as macroinitiators in ATRP with styrene, methyl methacrylate, and *tert*-butyl acrylate. While styrene polymerization led to nonnegligible side reactions, well-defined PB-*g*-poly(methyl methacrylate) ($\overline{M_{n,SEC}}$ = 19 900−98 200 g mol^{-1}, PDI ≤ 1.20) and PB-*g*-poly(*tert*-butyl acrylate) ($\overline{M_{n,SEC}}$ = 36 600−140 000 g mol^{-1}, PDI ≤ 1.21) were obtained through this synthetic approach. In addition, the morphology of a PB-*g*-poly(*tert*-butyl acrylate) was studied through AFM measurements.

Introduction

Brush copolymers, composed of polymeric arms regularly and densely spaced along a polymeric backbone, are an interesting class of polymers that have complex geometries and properties.[1] The synthesis of densely grafted copolymers can be accomplished through three different approaches: the "grafting onto" (coupling reaction between end-functionalized preformed polymer grafts and reactive side chains of a polymer backbone), the "grafting from" (initiation of graft polymerization from a polymer backbone), and the "grafting through"[2−4] (polymerization of macromonomers) strategies. Controlled polymerization techniques have been widely employed to prepare well-defined brush copolymers.[5] Because of its high functional group tolerance, ROMP allows to synthesize polymers with reactive functional groups along the backbone.[6−9] ROMP is then an attractive method to synthesize primary polymer backbones containing initiating sites. Thus, a variety of brush copolymers have been synthesized via a "grafting from" strategy by combination of ROMP with ROP (ring-opening polymerization),[10,11] NMP (nitroxide-mediated polymerization),[12] RAFT (reversible addition−fragmentation chain transfer) polymerization,[13] or ATRP (atom transfer radical polymerization).[14−17] Because of their high reactivity, norbornene derivatives or oxanorbornene derivatives were used in all these studies as polymerizable units by ROMP. To our best knowledge, only one study has been reported on cyclobutene derivatives by Charvet et al. about the one-pot synthesis of graft copolymers by combination of ROMP and ATRP; however, this study was limited to poly(methyl methacrylate) (PMMA) grafts.[18]

In the present work we report the synthesis of brush copolymers, based on a 1,4-polybutadiene (PB) backbone, via the "grafting from" strategy by combination of ROMP and ATRP, using a *cis*-3,4-disubstituted cyclobutene derivative as inimer (a monomer capable of initiating ATRP). This approach provides final copolymers with a high density of grafts (two per repeat unit) and an exclusively linear polybutadiene backbone with a strictly 1,4-type microstructure. Such unsaturated-backbone polymers are either unattainable or have imperfect microstructure when made using radical or ionic polymerization techniques. The ROMP of inimer **1** provides an ideal platform for subsequent grafting reaction since ATRP gives access to grafts of various nature (polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(*tert*-butyl acrylate) (P*t*BA)). Lastly, this study constitutes an alternative to the synthesis of PB-*g*-(PS-*b*-PtBA) via the "grafting through" approach previously reported.[19−21]

Experimental Section

Materials. Styrene (St, 99%), methyl methacrylate (MMA, 99%), and *tert*-butyl acrylate (*t*BA, 99%) from Acros were distilled over 2,5-di-*tert*-butylhydroquinone under vacuum and stored at 4 °C after purification. *N*,*N*,*N'*,*N'*,*N''*-Pentamethylethylenetriamine (PMDETA, 99+%), anisole (99%), and toluene (99%) were purchased from Acros. Copper(I) bromide (CuBr, 99.99%) and Grubbs' first generation catalyst (Grubbs I) were respectively purchased from Aldrich and Strem Chemicals and used without further purification. *N*-*n*-Octyl-2-pyridylmethanimine was synthesized according to the literature.[22] The inimer *cis*-3,4-bis(2-bromo-2-isobutyrylmethyl)-cyclobutene (**1**) was prepared as previously described.[19]

Characterization. NMR spectra were recorded on a Bruker Avance 400 spectrometer for ^{1}H NMR (400 MHz). Chemical shifts are reported in ppm relative to the deuterated solvent resonances. Molecular weights and molecular weight distributions were measured using size exclusion chromatography

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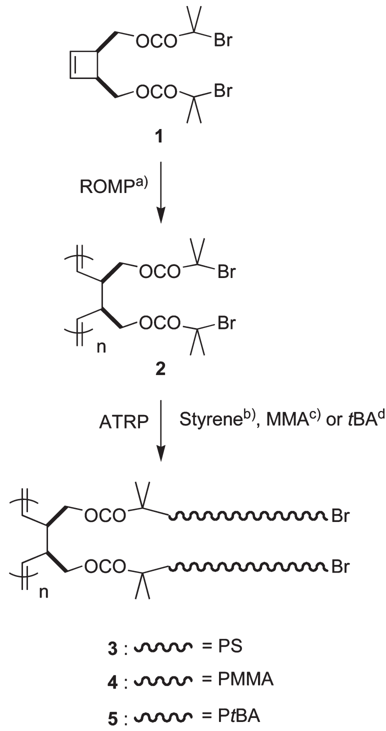
*Corresponding author: Tel +33 (0)2 43 83 33 30, Fax +33 (0)2 43 83 37 54, e-mail laurent.fontaine@univ-lemans.fr.

Scheme 1. Graft Copolymer Synthesis (PMDETA = *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine; MMA = Methyl Methacrylate; *t*BA = *tert*-Butyl Acrylate)[a]



[a] Reagents and conditions: (a) $[\mathbf{1}]_0$/[Grubbs I]$_0$ = 9−75, toluene, 50 °C. (b) $[\mathrm{S}]_0$:$[\mathbf{2}]_0$:[CuBr]$_0$:[PMDETA]$_0$ = 100*n*:1:*n*:*n*, toluene (50% v:v), 80−100 °C. (c) [MMA]$_0$:$[\mathbf{2}]_0$:[CuBr]$_0$:[*N*-*n*-octyl-2-pyridylmethanimine]$_0$ = 120*n*:1:2*n*:4*n*, toluene (50% v:v), 70−90 °C. (d) [*t*BA]$_0$:$[\mathbf{2}]_0$:[CuBr]$_0$:[PMDETA]$_0$ = 100*n*:1:*n*:*n*, toluene (70 % v:v), 60 °C.

(SEC) on 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), with a SpectraSYSTEM RI-150 detector. The eluent used was tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1} at 35 °C. Polystyrene standards (580−4.83 × 10^5 g mol^{-1}) were used to calibrate the SEC. MALDI-TOF analysis was realized on a Bruker Biflex III using a DCTB matrix. Atomic force measurements were recorded with an Agilent 5500 operating in the tapping mode. The measurements were performed at ambient conditions using silicon tip (Nanoworld-Arrow NCR) with a spring constant of 42 N m^{-1}. The samples were prepared by spin-coating on a rotating silica substrate at 2000 rpm of dilute solution of brush copolymers in solution in dichloromethane (C = 0.002 mg/L).

ROMP of Inimer 1. A 0.1 M solution of inimer **1** in toluene was degassed by three freeze−pump−thaw cycles. An exact amount of Grubbs I catalyst, in degassed toluene ($C = 10^{-2}$ mol L^{-1}), was then added to the solution of inimer to give the desired monomer-to-initiator ratio. The reaction mixture was then stirred in a thermostated oil bath at 50 °C during various times (depending on the initial monomer-to-initiator ratio). The polymerization was then quenched by the addition of ethyl vinyl ether, and the final polymer was obtained via filtration through a basic alumina column and precipitation in methanol. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.90 (s, 12 H, C(C*H*$_3$)$_2$Br), 2.50−3.50 (m, 2H, =CH−C*H*−), 4.25 (d, 4H, −C*H*$_2$−OCO), 5.60 (m, 2H, =C*H*−). ^{13}C NMR (CDCl$_3$): δ (ppm) 31 (C(*C*H$_3$)$_2$Br), 42 and 37 (=CH−*C*H− *trans* and *cis*), 53 (*C*(CH$_3$)$_2$Br), 65 (−*C*H$_2$−OCO), 130 and 129 (=*C*H− *trans* and *cis*), 170 (O−*C*=O).

ATRP. *Typical ATRP.* A Schlenk tube was loaded with copper(I) bromide, capped with a rubber septum, and cycled three times between vacuum and argon to remove oxygen. In another Schlenk tube, toluene, PB backbone **2** (Scheme 1), anisole (internal reference for St and *t*BA polymerization), and monomer were introduced. The resulting solution was degassed under vacuum by three freeze−pump−thaw cycles and was added to the CuBr contained in the first Schlenk tube via a cannula. The reaction mixture was degassed by another three freeze−pump−thaw cycles. The Schlenk tube was placed in an oil bath thermostated at the polymerization temperature. At $t = 0$, the ligand was added. Aliquots were taken periodically via a degassed syringe to follow the kinetic of the polymerization process. The final polymer was collected by filtration through a basic alumina column and precipitation in methanol.

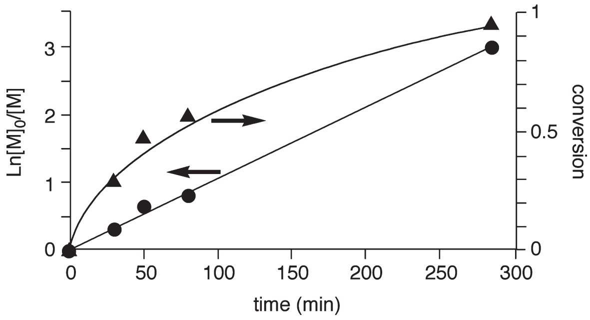


Figure 1. Evolution of ln([M]$_0$/[M]) vs time for ROMP of inimer **1** ($[\mathbf{1}]_0$/[Grubbs I]$_0$ = 10, toluene, 30 °C).

PB-*g*-PS **3**. [St]$_0$:[backbone unit]$_0$:[CuBr]$_0$:[PMDETA]$_0$ = 100:1:1:1, toluene: 50% v/v, anisole: 5% v/v, 80−100 °C. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.00−2.40 (m, C*H*$_2$ and C*H* of St units and C(C*H*$_3$)$_2$Br), 2.50−3.50 (m, =CH−C*H*−), 4.20 (m, C*H*$_2$−OCO), 5.30−5.60 (br m, =C*H*−), 6.80−7.30 (m, C$_6$*H*$_5$ of St units).

PB-*g*-PMMA **4**. [MMA]$_0$:[backbone unit]$_0$:[CuBr]$_0$:[*N*-*n*-octyl-2-pyridylmethanimine]$_0$ = 100:1:2:4, toluene: 50% v/v, 70−90 °C. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.75−2.10 (m, C*H*$_3$ and C*H*$_2$ of MMA units and C(C*H*$_3$)$_2$Br), 3.10−3.80 (m, OC*H*$_3$ of MMA units and =CH−C*H*−), 4.20 (m, C*H*$_2$−OCO), 5.30−5.60 (br m, =C*H*−).

PB-*g*-P*t*BA **5**. [*t*BA]$_0$:[backbone unit]$_0$:[CuBr]$_0$:[PMDETA]$_0$ = 100:1:1:1, toluene: 70% v/v, anisole: 5% v/v, 60 °C. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.80−2.30 (m, C*H*$_3$ and C*H*$_2$ of *t*BA units and C(C*H*$_3$)$_2$Br), 3.10−3.80 (m, =CH−C*H*−), 4.20 (m, C*H*$_2$−OCO), 5.30−5.60 (br m, =C*H*−).

Results and Discussion

Our strategy relies on the synthesis by ROMP of a PB backbone **2** (Scheme 1) bearing initiating sites for ATRP. To synthesize this backbone, the inimer **1** (Scheme 1), already involved in the "grafting through" strategy in previous studies,[19−21] was engaged in ROMP. This inimer (initiator−monomer) contains two α-bromoester functionalities (used as initiators sites for ATRP) and a cyclobutene unit (used as a monomer for ROMP); it was synthesized according to the procedure already described.[19]

Synthesis of the Poly(1,4-butadiene) Backbone by ROMP. ROMP of inimer **1** was performed using Grubbs' generation I catalyst ((Cy$_3$P)$_2$RuCl$_2$(CHPh)) (Grubbs I), which has already proved to be efficient to initiate the ROMP of *cis*-3,4-disubstituted cyclobutenes.[23] The polymerization of **1** was first investigated by ^{1}H NMR ($[\mathbf{1}]_0$/[Grubbs I]$_0$ = 10, toluene, 30 °C): a linear evolution of ln([M]$_0$/[M]) vs time, consistent with a pseudo-first-order kinetics, was observed (Figure 1), and a complete conversion was obtained after 6 h.

Polymerization of **1** was then studied with different monomer-to-initiator initial ratios ($[\mathbf{1}]_0$/[Grubbs I]$_0$) ranging from 10 to 500 (toluene, 50 °C). The results are gathered in Table 1.

For $[\mathbf{1}]_0$/[Grubbs I]$_0$ ratio ranging from 9 to 75 (Table 1, entries **2a**−**2g**), well-defined PB **2** were obtained with low

Table 1. Characteristics of PB Backbones 2 Synthesized by ROMP of Inimer 1 Using Grubbs I Catalyst at 50 °C (Solvent: Toluene)

entry	$[\mathbf{1}]_0$/ [Grubbs I]$_0$	time (h)	$\overline{M_{n,calc}}^a$ (g mol^{-1})	$\overline{M_{n,SEC}}^b$ (g mol^{-1})	PDI^c
2a	9	4	3 709	3 600	1.14
2b	10	4	4 121	4 100^d	1.20
2c	25	5	10 303	10 600	1.09
2d	37	8	15 248	14 400	1.08
2e	50	8	20 605	21 600	1.09
2f	75	8	30 908	24 300	1.10
2g	75	9	30 908	25 200	1.16
2h	100	24	41 211	25 000	1.89
2i	250	24	103 025	38 300	2.02
2j	500	24	206 050	29 100	1.80

[a] Number-average molecular weight calculated using: $\overline{M_{n,calc}}$ = 412.1 × $[\mathbf{1}]_0$/[Grubbs I]$_0$. [b] Number-average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards. [c] Polydispersity index measured by SEC. [d] $\overline{M_{n,MALDI}}$ = 4200 g mol^{-1} (see Figure 3).

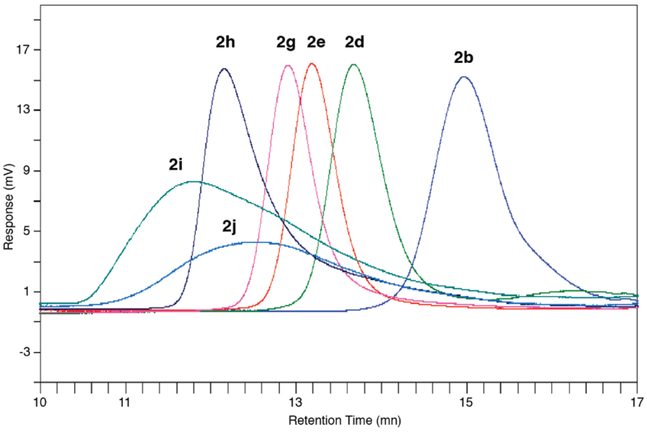


Figure 2. SEC traces of PB backbones **2** obtained by ROMP with $[\mathbf{1}]_0$/[Grubbs I]$_0$ initial ratios ranging from 9 to 500 (see Table 1; solvent: toluene, 50 °C).

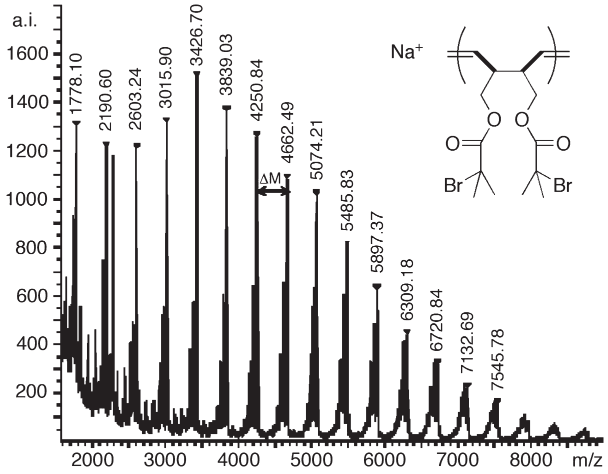


Figure 3. MALDI-TOF analysis of PB backbone **2b** obtained by ROMP of inimer **1** (conditions: see Table 1); $\overline{M_{n,MALDI}}$ = 4200 g mol^{-1}.

polydispersity indexes (≤1.20). For $[\mathbf{1}]_0$/[Grubbs I]$_0$ ratios upper than 75 (Table 1, entries **2h**−**2j**), very low conversions were observed (a high amount of unreacted inimer being detected by SEC) and highly polydisperse PBs **2** (PDI ≥ 1.80) were obtained, showing an important spreading of the SEC traces (Figure 2) revealing that the polymerization is no longer controlled in those experimental conditions. The long reaction times required to reach high conversion of **1** could favor "backbiting" phenomena and cause this loss of control.[6,8]

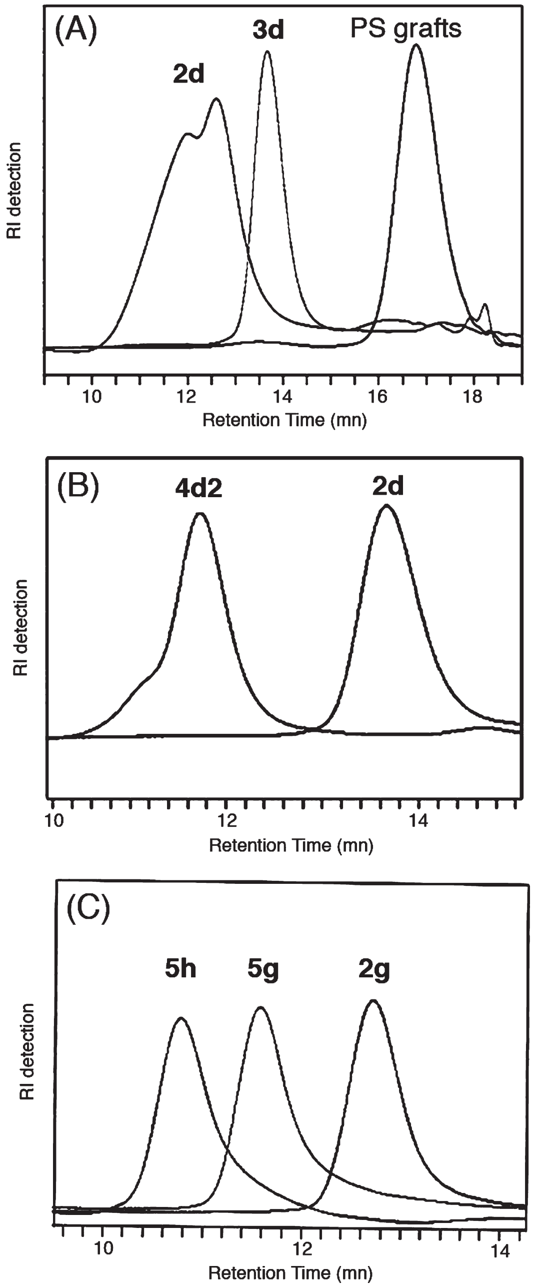


Figure 4. Size exclusion chromatography (SEC) traces of brush copolymers synthesized by ATRP of (A) styrene, (B) MMA, and (C) *t*BA (conditions: see Table 2).

The structure of PB backbone **2b** (Table 1) with $\overline{M_n}$ = 4100 g mol^{-1} and the low polydispersity index (PDI = 1.14) was confirmed by MALDI-TOF analysis. The MALDI-TOF spectrum showed a constant value between peaks of m/z = 412 (Figure 3), corresponding to one constitutive unit of **2b**, and $\overline{M_{n,MALDI}}$ = 4200 g mol^{-1} was thus determined, in good agreement with the SEC data.

Therefore, ROMP of inimer **1** using Grubbs I catalyst gives access to well-defined PB backbones **2** with $\overline{DP_n}$ up to 75. To our best knowledge, this is the first reported synthesis of such PB backbones obtained from ROMP that could be used as macroinitiators for ATRP.

Synthesis of Graft Copolymers by ATRP. In previous work, inimer **1**, precursor of PB **2**, has proved to be an efficient initiator for ATRP, leading to well-defined macromonomers with low PDI (≤1.20).[19,20] The PB backbones **2**,

Table 2. Brush Copolymers Synthesis by ATRP of Styrene (St), Methyl Methacrylate (MMA), and *tert*-Butyl Acrylate (*t*BA) Initiated from Poly(1,4-butadiene) (PB) Backbones 2

			PB backbone **2**			brush copolymers		
entry	monomer	temp (°C)	$\overline{M_{n,SEC}}$[a]	PDI[a]	conv[b]	$\overline{M_{n,SEC}}$[a]	PDI[a]	$\overline{M_{n,calc,{}^1H\,NMR}}$[f]
3e	St[c]	100	21 600	1.09		insoluble polymer		
3d	St[c]	80	14 400	1.08	0.10	bimodal SEC trace		50 800
4b	MMA[d]	90	4 100	1.20		insoluble polymer		
4d$_1$	MMA[d]	70	14 400	1.08	0.02	19 900	1.18	21 400
4d$_2$	MMA[d]	70	14 400	1.08	0.38	86 700	1.19	147 300
4d	MMA[d]	70	24 300	1.10	0.13	98 200	1.20	101 000
5a	*t*BA[e]	60	3 600	1.14	0.60	36 600	1.16	70 800
5e	*t*BA[e]	60	21 600	1.09	0.11	48 700	1.08	95 500
5g	*t*BA[e]	60	25 200	1.16	0.14	75 400	1.13	134 900

[a] Determined by SEC in THF calibrated with polystyrene standard. [b] Monomer conversion determined by ^{1}H NMR. [c] $[St]_0$:[backbone unit]$_0$:-$[CuBr]_0$:$[PMDETA]_0$ = 100:1:1:1, toluene: 50% v/v, anisole: 5% v/v; PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine. [d] $[MMA]_0$:[backbone unit]$_0$:$[CuBr]_0$:[*N*-*n*-octyl-2-pyridylmethanimine]$_0$ = 100:1:2:4, toluene: 50% v/v. [e] [*t*BA]$_0$:[backbone unit]$_0$:$[CuBr]_0$:$[PMDETA]_0$ = 100:1:1:1, toluene: 70% v/v, anisole: 5% v/v. [f] $\overline{M_{n,calc,{}^1H\,NMR}} = \overline{M_{n,SEC}}$(PB backbone) + $\overline{M_{n,{}^1H\,NMR}}$(grafts) = $\overline{M_{n,SEC}}$(PB backbone) + [$\overline{DP_{n,backbone\ unit}}$ × ([monomer]$_0$/[backbone unit]$_0$) × M_{unit} × conv], where $\overline{DP_{n,backbone\ unit}}$ is the degree of polymerization of the PB backbone and M_{unit} is the molecular weight of the monomer unit (St, MMA, and *t*BA).

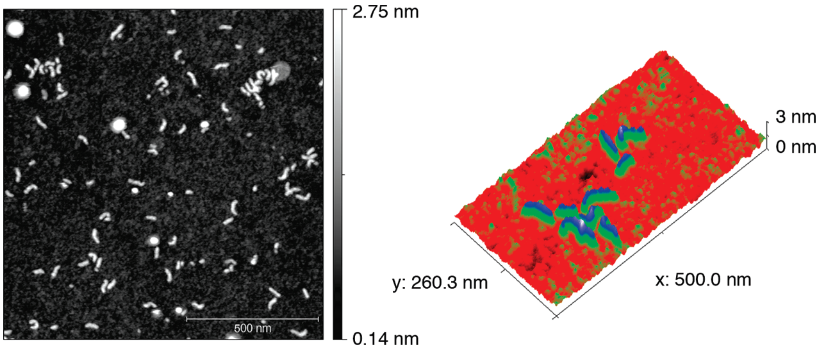


Figure 5. Tapping-mode AFM images of PB-*g*-P*t*BA **5h** ($\overline{M_{n,SEC}}$ = 140 000 g mol^{-1}, PDI = 1.21): (left) topography image of a freshly prepared solution (C = 0.002 mg L^{-1} in CH_2Cl_2) spin-coated on silica; (right) 3D view of the wormlike unimolecular macromolecules.

containing two initiating sites for ATRP per repeat unit, were then used as macroinitiators in ATRP to synthesize the grafts and obtain brush copolymers. The ATRP of three different monomers was studied: styrene (St), methyl methacrylate (MMA), and *tert*-butyl acrylate (*t*BA).

ATRP of St. The PB backbone **2** was engaged in copper-mediated ATRP of styrene with the CuBr/PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) catalytic system at 100 °C.[24] The first attempt, with PB **2e**, led to an insoluble polymer probably due to cross-linking reactions during ATRP, as already reported in the literature during ATRP of styrene initiated from polynorbornene or polymethacrylate backbones.[10,25] The effect of a temperature decrease was then studied, and the polymerization of styrene, initiated from PB **2d**, was conducted at 80 °C. The SEC analysis of the final copolymer revealed a bimodal trace (Mp_1 = 42 000 g mol^{-1}, Mp_2 = 73 000 g mol^{-1}). The structure of this copolymer was further investigated through cleavage of the grafts from the backbone: **3d** was submitted to KOH hydrolysis in refluxing methanol. SEC analysis of the final product shows a monomodal trace (Figure 4A) with a $\overline{M_n}$ of 1000 g mol^{-1}, in good agreement with the calculated $\overline{M_n}$ of the PS grafts (10% St conversion); thus, all PS arms have a homogeneous size. The bimodal SEC trace probably results from cross-linking coupling reactions involving the PB backbone. It should be noted that such graft copolymers have been successfully prepared using the "grafting through" strategy previously reported.[19]

ATRP of MMA. ATRP of MMA was conducted with the CuBr/*N*-*n*-octyl-2-pyridylmethanimine catalytic system in toluene at 90 °C.[22] As these conditions led to an insoluble polymer, the polymerization was then studied at 70 °C. This lower temperature allows the synthesis of a PB-*g*-PMMA **4d$_1$** with quite a low PDI (1.19) in spite of the presence of a high molecular weight shoulder on the SEC trace (Figure 4B). Although some side reactions seem to occur in that system, PB-*g*-PMMA **4** with relatively low PDI (≤1.20) were synthesized (Table 2, entries **4b**, **4d$_1$**, **4d$_2$**, **4f**). Interestingly, these PDI values are lower than those previously reported in the literature for one-pot-synthesized graft copolymers with PMMA arms (PDI ≥ 1.45).[14,18]

ATRP of *t*BA. We then focused our interest in *t*BA, which can be polymerized in a controlled way at lower temperature than the previous monomers. The *t*BA polymerizations were conducted with the CuBr/PMDETA catalytic system in toluene (70% v:v) at 60 °C.[26] The first attempt with the PB backbone **2a** of low molecular weight ($\overline{M_{n,SEC}}$ = 3600 g mol^{-1}) led to a well-defined PB-*g*-P*t*BA with $\overline{M_{n,SEC}}$ = 36 600 g mol^{-1}, a low PDI (1.16), and no residual macroinitiator on the SEC trace, indicating a complete conversion of **2a** into brush polymer.

PB backbones **2** of different sizes were then used in ATRP allowing the synthesis of well-defined PB-*g*-P*t*BA (PDI ≤ 1.16) with different backbone sizes and grafts lengths (Table 2, entries **5a**, **5e**, **5g**). Furthermore, initiation of a second ATRP of *t*BA from PB-*g*-P*t*BA **5g** led to a well-defined brush copolymer **5h** with an unimodal SEC trace, a low PDI (PDI = 1.21, $\overline{M_{n,SEC}}$ = 140 000 g mol^{-1}), and no trace of residual macroinitiator **5g** (Figure 4C). This experiment proves that a bromine group ends all the chains during the ATRP of *t*BA. ATRP of *t*BA initiated from PB backbones **2** are then well controlled with negligible transfer and termination reactions. Furthermore, P*t*BA chains are very interesting as we proved in previous work that the easy removal of the *tert*-butyl groups in acidic media yields poly(acrylic acid) side chains that have a number of important applications, without alteration of the ester linkages between the backbone and the grafted chains.[19,21]

Atomic Force Microscopy (AFM) Visualization. Further evidence for the nature of copolymer PB-*g*-P*t*BA **5h** ($\overline{M_{n,SEC}}$ = 140 000 g mol^{-1}, PDI = 1.21) was provided by direct AFM visualization of individual molecules on silica. A freshly prepared solution of **5h** (C = 0.002 mg L^{-1} in CH_2Cl_2) was spin-coated on silica. Tapping-mode observation revealed individual wormlike molecules lying flat on the substrate (Figure 5). This wormlike morphology is consistent with the relative lengths of the backbone ($\overline{DP_n}$ = 75) and the grafts ($\overline{DP_n}$ = 17). When the backbone is longer than the grafts, the steric hindrance among these grafts stiffens the backbone and forces the brush polymers to adopt a cylindrical morphology.[27−29] The polymeric brushes are on average 50 nm long, 10 nm wide, and 2 nm high, the asymmetric cross-sectional dimensions being due to the collapse of the polymer chains onto the surface after the removal of solvent. Since the $\overline{DP_n}$ of the backbone is 75 and the number-average length obtained from AFM is 50 nm, the length per monomer unit of the backbone is calculated to be l_{unit} = 0.67 nm, close to the value estimated for the *all-trans* conformation of the corresponding aliphatic chain (0.50 nm).[30]

Conclusion

In conclusion, the synthesis of well-defined PB based brush copolymers has been successfully carried out through the "grafting from" strategy by combination of ROMP and ATRP. Grubbs' first generation catalyst has proved to be efficient to initiate the ROMP of the cyclobutenyl inimer **1**, leading to well-controlled polymerization. A range of original well-defined PB backbones has been synthesized with $\overline{DP_n}$ up to 75, bearing two lateral ATRP initiating sites per repeat unit. ATRP of different monomers initiated from these original PB backbones was then studied. Although ATRP of styrene led to some cross-linking reactions, well-defined PB-*g*-PMMA and PB-*g*-P*t*BA with low PDI and quite high molecular weights were obtained through ATRP of MMA and *t*BA. This synthetic approach allows a high degree of control on the final brush copolymers structure and offers the possibility to tailor the backbone and graft lengths as well as the graft density through copolymerization of **1** with others monomers. The "grafting from" strategy constitutes an alternative to the macromonomers polymerization approach previously reported.[19−21] The "grafting from" process allows synthesizing polymers with molecular weights that are not easily attainable by the macromonomer approach. These results expand the range of attainable architectures by combination of ROMP and ATRP through the "grafting from" approach.

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