

Efficient Synthesis of Narrowly Dispersed Brush Copolymers and Study of Their Assemblies: The Importance of Side Chain Arrangement

Yan Xia, Bradley D. Olsen, Julia A. Kornfield,* and Robert H. Grubbs*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received October 2, 2009; E-mail: jak@cheme.caltech.edu; rhg@caltech.edu

Abstract: Efficient, one-pot preparation of synthetically challenging, high molecular weight (MW), narrowly dispersed brush block copolymers and random copolymers in high conversions was achieved by ring-opening metathesis (co)polymerization (ROMP) of various macromonomers (MMs) using the highly active, fast-initiating ruthenium olefin metathesis catalyst $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$. A series of random and block copolymers were prepared from a pair of MMs containing polylactide (PLA) and poly(*n*-butyl acrylate) (P*n*BA) side chains at similar MWs. Their self-assembly in the melt state was studied by small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM). In brush random copolymers containing approximately equal volume fractions of PLA and P*n*BA, the side chains segregate into lamellae with domain spacing of 14 nm as measured by SAXS, which was in good agreement with the lamellar thickness measured by AFM. The domain spacings and order–disorder transition temperatures of brush random copolymers were insensitive to the backbone length. In contrast, brush block copolymers containing approximately equal volume fractions of these MMs self-assembled into highly ordered lamellae with domain spacing over 100 nm. Their assemblies suggested that the brush block copolymer backbone adopted an extended conformation in the ordered state.

Introduction

Brush polymers are a type of high molecular weight (MW) graft polymers with very dense and regularly spaced side chains. They possess an interesting worm-like structure due to the high steric crowding of sides chains.¹ Their nonspherical macromolecular geometries and lengths up to a few hundred nanometers afforded numerous potential applications in nanoscience, such as molecular actuators,² templates for inorganic particles,^{3–5} and as precursors for nanocapsules,⁶ nanotubes,⁷ and other carbon nanostructures.⁸

On the other hand, linear block copolymers have proven to be versatile, powerful tools in the “bottom-up” approach to create nanostructured materials with novel mechanical, optical, and electronic properties and with specific functionalities over

the last few decades.⁹ When two or more different types of side chains are attached to a linear polymer backbone to form brush copolymers, each side chain may behave like a block segment in a block copolymer: they can be long enough to drive segregation, due to selective solubility or enthalpically favored demixing, yet are constrained by covalent attachment onto a single molecule. The spatial arrangement of different types of side chains along the backbone and their relative ratio should dramatically affect the assembly of the copolymers. The assembly of brush copolymers may also be profoundly affected by the limited flexibility of the brush polymer backbone as a result of the high steric hindrance between densely grafted side chains. On the other hand, the densely grafted side chains and extended conformation of brush polymers give them reduced entanglement density compared to their linear analogs. The reduced entanglement is a favorable feature to overcome the kinetic barrier for self-assembly, especially for ultrahigh MW polymers. Bowden and co-workers and Rzayev have recently found that brush–coil and brush–brush block copolymers can self-assemble into exceptionally large structures with domain

- (1) Sheiko, S. S.; Möller, M. *Chem. Rev.* **2001**, *101*, 4099–4124. (b) Hadjichristidis, N. P., M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792. (c) Zhang, M.; Müller, A. H. E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3461–3481.
- (2) Li, C.; Gunari, N.; Fischer, K.; Janshoff, A.; Schmidt, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1101–1104.
- (3) Djalali, R.; Li, S.-Y.; Schmidt, M. *Macromolecules* **2002**, *35*, 4282–4288.
- (4) Zhang, M.; Drechsler, M.; Müller, A. H. E. *Chem. Mater.* **2004**, *16*, 537–543.
- (5) Zhang, M.; Estournes, C.; Bietsch, W.; Müller, A. H. E. *Adv. Funct. Mater.* **2004**, *14*, 871–882.
- (6) Cheng, C.; Qi, K.; Khoshdel, E.; Wooley, K. L. *J. Am. Chem. Soc.* **2006**, *128*, 6808–6809.
- (7) Huang, K.; Rzayev, J. *J. Am. Chem. Soc.* **2009**, *131*, 6880–6885.
- (8) Tang, C.; Dufour, B.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6199–6205.

- (9) (a) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32–38. (b) Klok, H.-A.; Lecommandoux, S. *Adv. Mater.* **2001**, *13*, 1217–1229. (c) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967–973. (d) Hamley, I. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1692–1712. (e) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A. *Prog. Polym. Sci.* **2005**, *30*, 725–782. (f) Ruzette, A.-V.; Leibler, L. *Nat. Mater.* **2005**, *4*, 19–31. (g) Cheng, J. Y.; Ross, C. A.; Smith, H. I.; Thomas, E. L. *Adv. Mater.* **2006**, *18*, 2505–2521. (h) Cui, H.; Chen, Z.; Zhong, S.; Wooley, K. L.; Pochan, D. J. *Science* **2007**, *317*, 647–650. (i) Tang, C.; Lennon, E. M.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. *Science* **2008**, *322*, 429–432.

spacing above 100 nm.^{10–12} Large domain structures are scientifically attractive and technically important with the potential to create periodic dielectric media to manipulate and control light, but have been challenging to achieve with linear block copolymers.^{13–16} However, self-assembly of brush copolymers has been much less explored relative to the vast number of reports on their linear copolymer analogs.^{10–12,17,18}

Well-defined macromolecular characteristics, such as the lengths of the backbone and side chains as well as the grafting density, are prerequisites to obtain ordered self-assembled structures. However, due to the complex architectures and demanding steric congestion, brush copolymers with controlled and high MW, low polydispersity (PDI), and complete side chain grafting remain challenging targets for polymer chemists. Current synthetic strategies to approach these targets normally involve multistep reactions and separations.

The most explored method to make brush polymers is “graft from”: the majority of previously reported brush block copolymers were synthesized by polymerizing different monomers from a diblock copolymer backbone using orthogonal polymerization mechanisms (i.e., radical polymerization and ring-opening polymerization).^{10–12,19,20} To grow distinct side chains from a given backbone requires orthogonal polymerization mechanisms and/or selective protection/deprotection and subsequent functionalization of the copolymer backbone. Furthermore, the initiation efficiency of the macroinitiators may be limited,^{12,21,22} and the monomer conversions must be kept low to avoid cross-linking due to the high density of initiating sites.^{2,6–8,10–12,19–22} Alternatively, preformed side chains can be “grafted onto” a polymer backbone to prepare brush polymers.^{23–25} Lanson et al. recently prepared brush block copolymers^{23,26} and random copolymers¹⁸ by grafting anionically prepared side chains onto polymers with pendent functional groups and by a combination of “graft from” and “graft onto” methods. However, purification to remove the unreacted side chains was required in each grafting step and repetitive protection and deprotection

of the backbone functional groups was required to synthesize brush block copolymers.

On the other hand, the macromonomer (MM) approach toward brush copolymers is highly desirable,²⁷ because (1) it does not require orthogonal, noninterfering chemistry for grafting different side chains; (2) the side chain and the graft polymer can be well characterized; and (3) it is the only approach that guarantees complete grafting on every repeating unit. However, the macromonomer (MM) approach toward brush block copolymers is exceedingly challenging due to steric hindrance at the propagating polyMM chain end. Brush-coil block copolymers and brush random copolymers have been reported using uncontrolled metallocene-catalyzed¹⁷ or radical²⁸ polymerizations and polycondensation²⁹ of MMs. As a result, the final graft polymers were polydisperse, and the MM conversion was limited. Neugebauer et al. reported copolymerization of MMs containing poly(ethylene oxide) and poly-(dimethylsiloxane) or octadecane side chains by atom transfer radical polymerization (ATRP) to produce random or gradient brush copolymers depending on the relative polymerization rates of MMs.^{30,31} However, the MMs used in those reports were relatively small and less hindered (MW ≤ 1100) and no brush block copolymers were reported.

Here we show that ring-opening metathesis polymerization (ROMP) can be used to overcome the obstacles to well-defined brush copolymers by taking advantage of the high ring strain of norbornene monomer and the high activity of Ru-based olefin metathesis catalyst. In contrast to prior reports of ROMP synthesis of short graft block copolymers using molybdenum-based catalyst that were limited to oligomers with 5–10 side chains per block (star-like rather than brush-like architectures),^{32,33} the present polymers have DP up to 200 per block. The present method builds on the highly efficient syntheses we recently demonstrated for a variety of ultrahigh MW brush polymers with controlled MW (up to 2600 kg/mol) and very low PDI (1.01–1.07) using the highly active, fast-initiating Ru olefin metathesis catalyst (H₂IMes)(pyr)₂(Cl)₂RuCHPh (**1**). Atomic force microscopy (AFM) revealed their worm-like structure and narrow PDI.³⁴

In this work, we utilized ROMP of MMs to efficiently prepare a library of high MW, narrowly dispersed brush copolymers with different side chains, including brush block copolymers and brush random copolymers, each in one pot. ROMP of MMs allowed for facile control of the side chain and backbone block lengths and virtually arbitrary selection of side chains. To the best of our knowledge, this report contains the first examples of high MW, narrowly dispersed brush block copolymers

- (10) Runge, M. B.; Bowden, N. B. *J. Am. Chem. Soc.* **2007**, *129*, 10551–10560.
- (11) Runge, M. B.; Lipscomb, C. E.; Ditzler, L. R.; Mahanthappa, M. K.; Tivanski, A. V.; Bowden, N. B. *Macromolecules* **2008**, *41*, 7687–7694.
- (12) Rzaev, J. *Macromolecules* **2009**, *42*, 2135–2141.
- (13) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals*; Princeton University Press: Princeton, 1995.
- (14) Edrington, A. C.; Urbas, A. M.; DeRege, P.; Chen, C. X.; Swager, T. M.; Hadjichristidis, N.; Xenidou, M.; Fetters, L. J.; Joannopoulos, J. D.; Fink, Y.; Thomas, E. L. *Adv. Mater.* **2001**, *13*, 421–425.
- (15) Park, C.; Yoon, J.; Thomas, E. L. *Polymer* **2003**, *44*, 6725–6760.
- (16) Kang, Y.; Walish, J. J.; Gorishnyy, T.; Thomas, E. L. *Nat. Mater.* **2007**, *6*, 957–960.
- (17) Neiser, M. W.; Muth, S.; Kolb, U.; Harris, J. R.; Okuda, J.; Schmidt, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3192–3195.
- (18) Lanson, D.; Ariura, F.; Schappacher, M.; Borsali, R.; Deffieux, A. *Macromolecules* **2009**, *42*, 3942–3950.
- (19) Runge, M. B.; Dutta, S.; Bowden, N. B. *Macromolecules* **2006**, *39*, 498–508.
- (20) Lee, H.-i.; Matyjaszewski, K.; Yu-Su, S.; Sheiko, S. S. *Macromolecules* **2008**, *41*, 6073–6080.
- (21) Neugebauer, D.; Sumerlin, B. S.; Matyjaszewski, K.; Goodhart, B.; Sheiko, S. S. *Polymer* **2004**, *45*, 8173–8179.
- (22) Sumerlin, B. S.; Neugebauer, D.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 702–708.
- (23) Lanson, D.; Schappacher, M.; Borsali, R.; Deffieux, A. *Macromolecules* **2007**, *40*, 5559–5565.
- (24) Schappacher, M.; Deffieux, A. *Macromolecules* **2005**, *38*, 7209–7213.
- (25) Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129*, 6633–6639.
- (26) Lanson, D.; Schappacher, M.; Borsali, R.; Deffieux, A. *Macromolecules* **2007**, *40*, 9503–9509.

- (27) Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H.; Pispas, S. *Macromol. Rapid Commun.* **2003**, *24*, 979–1013.
- (28) Stephan, T.; Muth, S.; Schmidt, M. *Macromolecules* **2002**, *35*, 9857–9860.
- (29) Deimede, V.; Kallitsis, J. K. *Chem.—Eur. J.* **2002**, *8*, 467–473.
- (30) Neugebauer, D.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8687–8693.
- (31) Neugebauer, D.; Theis, M.; Pakula, T.; Wegner, G.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 584–593.
- (32) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromolecules* **1997**, *30*, 4791–4798.
- (33) Nomura, K.; Takahashi, S.; Imanishi, Y. *Macromolecules* **2001**, *34*, 4712–4723.
- (34) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761–3766.

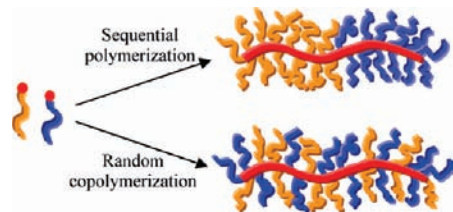
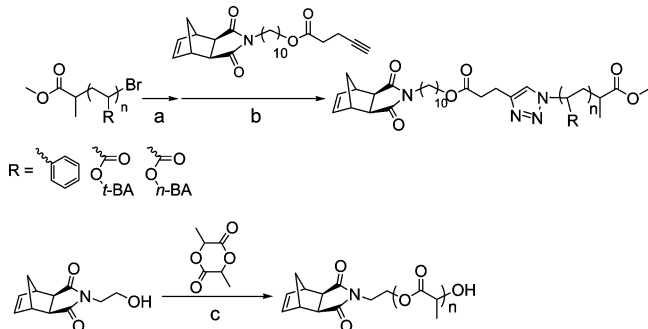


Figure 1. Schematic illustration of the synthesis of brush block copolymer through sequential addition (top) and brush random copolymer through random copolymerization (bottom) of MMs.

Scheme 1. Synthesis of Macromonomers^a



^a Conditions: (a) NaN₃, DMF, 25 °C. (b) CuBr, PMDETA, THF, 50 °C. (c) Sn[CH₃(CH₂)₃CH(C₂H₅)CO₂]₂, 120 °C.

prepared sequentially via living polymerization of MMs.³⁵ The well-defined molecular characteristics of these brush copolymers provided an excellent model system to study the effect of side chain arrangement on the backbone and the relative ratio of the MMs on the self-assembly of brush copolymers. Specifically, we compared brush block copolymers (Figure 1, top) to brush random copolymers (Figure 1, bottom), showing that they provide convenient routes to self-assembled nanostructures with the backbone either predominantly orthogonal to the “intermaterial dividing surface”³⁶ or localized to the “intermaterial dividing surface”, respectively.

Results and Discussion

Syntheses of Brush Copolymers. We have synthesized ω -norbornenyl MMs containing poly(*n*-butyl acrylate) (PnBA), poly(*t*-butyl acrylate) (PtBA), and polystyrene (PS) side chains, according to our reported procedure.³⁴ “Click” coupling of a norbornenyl group to the chain ends of polymers made by ATRP was used to prevent the unfavorable copolymerization of norbornene during ATRP.^{37,38} ω -Norbornenyl MMs containing polylactide (PLA) side chains were also synthesized from ring-opening polymerization of D,L-lactide using a norbornenyl alcohol as the initiator and stannous octoate as the polymerization catalyst (Scheme 1). All MMs were narrowly dispersed. A high degree of norbornenyl end group functionalization was confirmed from good agreement between the degree of polymerization (DP) calculated by end group analysis using ¹H NMR spectroscopy (DP_{NMR}) and the DP calculated from the absolute

Table 1. Characteristics of ω -Norbornenyl Macromonomers and Their Polymerization Rates

MM ^a	M_n^b (kDa)	PDI ^b	DP _{NMR} ^c	DP _{GPC} ^d	k_p (min ⁻¹) ^e	$k_{p,rel}^f$
NB(PS)6.6k	6.6	1.02	66	60	0.079	1
NB(PS)2.2k	2.2	1.03	19	17	0.092	1.2
NB(PtBA)4.7k	4.7	1.03	33	33	0.13	1.7
NB(PLA)7.0k	7.0	1.12	46	47	0.24	3.0
NB(PLA)4.7k	4.7	1.06	28	31	0.35	4.4
NB(PnBA)4.0k	4.0	1.06	29	28	0.33	4.2

^a Macromonomers were named using a format of NB(X)Y, with X designating the type of prepolymer and Y designating the M_n of macromonomer. ^b Determined by GPC in THF using refractive index (RI) and MALLS detectors. ^c Calculated by comparing the integrations of the norbornenyl olefin and polymer backbone proton signals from ¹H NMR spectra in CDCl₃. ^d Calculated by (M_n - molar mass of norbornenyl end group)/molar mass of monomer. ^e Conditions: [MM]₀ = 0.05 M in THF at room temperature, [MM/C]₀ = 200. ^f $k_{p,rel}$ is the relative rate constant with respect to k_p of NB(PS)6.6k.

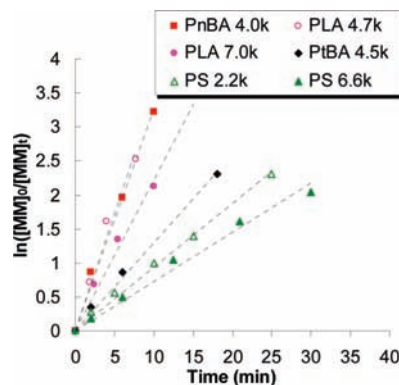


Figure 2. Dependence of $\ln([MM]_0/[MM]_t)$ on time for ROMP of MMs. Conditions: [MM]₀ = 0.05 M in THF at room temperature, [MM/C]₀ = 200. The dashed lines are best-fit lines.

MWs obtained from gel permeation chromatography (GPC) coupled with a multiangle laser light scattering (MALLS) detector (Table 1).

Polymerization of all these MMs using Ru catalyst **1** followed linear first-order kinetics (Figure 2). GPC analyses of the polyMMs each showed narrow, monomodal peaks, and MWs increased linearly with conversion while the PDI remained less than 1.1 throughout the entire polymerization (Supporting Information Figure S2a). Furthermore, all MMs reached greater than 90% conversion within 1 h at room temperature (Supporting Information Figure S2b). Although very weak signals that may correspond to MMs can be observed in the GPC traces of the crude polymer products, NMR spectroscopy of the reaction mixtures revealed the absence of the MM norbornene olefin signal. Therefore, the residual low MW peak may correspond to a small fraction of side chains with unfunctionalized chain ends in the MM. These observations collectively indicated the well-controlled character of ROMP of MMs and the extraordinary activity of catalyst **1**.

Due to the high activity of catalyst **1** and low critical monomer concentration of norbornene, the ROMP of MM can be performed at very low concentration ([MM]₀ = 0.05 M) to keep a relatively low viscosity of the solution throughout the polymerization. This is a distinct advantage over free radical polymerization of MMs.^{39–42} Therefore, the polymerization is unlikely to be diffusion controlled (at least until the very late

(35) We note that, during the preparation of this manuscript, we learned through personal communication that Karen L. Wooley and co-workers have also synthesized brush block copolymers using similar strategy.

(36) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *J. Chem. Phys.* **1991**, *95*, 9367–9375.

(37) Cheng, C.; Khoshdel, E.; Wooley, K. L. *Macromolecules* **2005**, *38*, 9455–9465.

(38) Patton, D. L.; Advincula, R. C. *Macromolecules* **2006**, *39*, 8674–8683.

(39) Tsukahara, Y. T., K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201–5208.

stage of the polymerization), in accord with the approximately linear first-order kinetics up to high conversions (>85%).

The polymerization rates, measured from the kinetic plot, depended weakly on both the MW and the structure of the MM (Table 1). In general, polyacrylate and polylactide MMs polymerized faster than polystyrene MMs. For example, NB(PLA)7.0k polymerized about 3 times faster than NB(PS)6.6k despite their similar MW. The nature of the effects of side chain structure and MW on the polymerization rate of MMs warrants further investigation. It may be the local steric congestion around the propagating metalocycle or different solvent quality for various polymers that is causing the observed difference in the polymerization rate. Although the relative polymerization rates of different MMs varied less than an order of magnitude, they are significant when statistical copolymerization is attempted, since the relative polymerization rates can determine the distribution of side chains along the backbone (i.e., random vs gradient).

The controlled nature of the ROMP of MMs and the very high conversions motivated us to prepare brush block copolymers via simple sequential addition of MMs: Polymerization was initiated by injecting catalyst from a stock solution into a solution of the first type of MM at room temperature. As soon as the MM has been all consumed and only unfunctionalized side chains remained, a solution of a second type of MM was injected into the reaction mixture. GPC was used to analyze the reaction mixtures before the injection of the second MM and after completion of the second block polymerization. The GPC peak had shifted from the first block homopolymer to a shorter elution time corresponding to the brush diblock copolymer. The peak shape remained narrow without significant tailing, and the PDI remained low (≤ 1.10) (Figure 3). The low PDI was also indicated by the complete overlap of the light scattering trace and refractive index trace from GPC. Only very weak signal was observed between 16 and 18 min in elution time, and this may correspond to unfunctionalized side chains in some of the MMs used. For example, in the brush PS and PnBA block copolymer, the intensity of the low MW peak remained similar in the first PS block and the diblock copolymer (Figure 3B), which may correspond to unfunctionalized side chains in the PS MM. The order of addition of different MMs did not affect the MW or the PDI of the final block copolymers. Therefore, different MMs were arbitrarily polymerized sequentially to give various brush block copolymers, and the DP of each block was easily controlled by the ratio of MM to catalyst ([MM]/[C]). With narrow PDIs less than 1.1, regardless of the MW and combination of MMs, the MW of the copolymers measured by GPC-MALLS is close to or slightly higher than the theoretical MW. GPC analysis of the reaction mixture revealed the final conversions of MM to be greater than 90% in all the copolymerizations, while NMR spectroscopy showed no MM norbornene olefin signal.

PnBA side chains in the brush block copolymers can be hydrolyzed into poly(acrylic acid) (PAA) using TFA in CH_2Cl_2 , leaving the other block and the backbone intact, as indicated by NMR spectroscopy (Supporting Information Figure S1). Thus, amphiphilic block brush copolymers were also easily obtained.

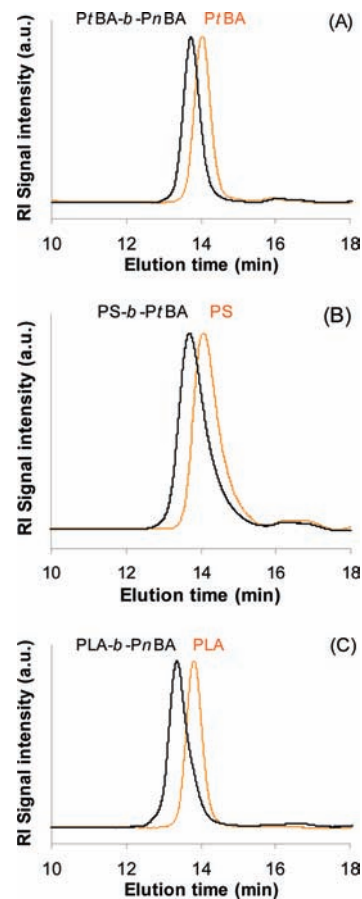


Figure 3. Representative GPC RI traces of the first block brush homopolymer (right) and the brush diblock copolymer (left) without any purification. (A) $(\text{PNB-g-PnBA})_{100}\text{-b-(PNB-g-PnBA)}_{100}$; (B) $(\text{PNB-g-PS})_{100}\text{-b-(PNB-g-PnBA)}_{50}$; (C) $(\text{PNB-g-PLA})_{100}\text{-b-(PNB-g-PnBA)}_{100}$.

The side chain distribution along the brush copolymer backbone can dominantly affect the macromolecular packing in order to minimize the interfacial energy while retaining relatively extended backbone conformation. In this report, we focus on the study of the melt state self-assembly of copolymers containing PLA and PnBA side chains. We chose MMs NB(PLA)4.7k and NB(PnBA)4.0k as the side chains, because they possess very similar MWs and polymerization rates, and their copolymers can be thermally annealed relatively easily due to their low T_g 's. These features allowed us to easily prepare a series of brush block and random copolymers with the same pair of side chains and matched backbone length, but varying the relative ratio of the two MMs (Table 2, entry 7–15). Brush block copolymers, $g\text{-[PLA}_x\text{-b-PnBA}_y]$, with varied block lengths and ratios were synthesized via sequential addition of MMs. Brush random copolymers, $g\text{-[PLA}_x\text{-ran-PnBA}_y]$, with varied total backbone length and side chain composition were synthesized via initiating a mixture of two MMs (Figure 3). Note that the subscripts x and y represent the number of side chains of each type—not the DP of the side chains, which was held fixed at approximately 30 for both the PLA and PnBA side chains (see the last two rows of Table 1). Since the ROMP of these MMs proceeded to very high conversions (>97%) and only a minute amount of catalyst was used (0.04–0.16 wt % to MMs used), no attempts to purify the polymer products were made. All polymer samples were simply dried under vacuum to remove solvent. These samples provided a model series to study how

(40) Dziezok, P.; Sheiko, S. S.; Fischer, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2812–2815.

(41) Roos, S. G.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8331–8335.

(42) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6243–6248.

Table 2. Characteristics of Brush Copolymers

entry	MM ₁	MM ₂	type of copolymer	[MM ₁ /C]:[MM ₂ /C] ^a	conv ^b	M _{n,theo} (kDa) ^c	M _{n,GPC} (kDa) ^d	PDI ^d
1	PS6.6k	PnBA4.0k	block	40:70	91%	540	730	1.04
2	PS6.6k	PnBA4.0k	block	40:200	91%	1060	1230	1.04
3	PtBA4.7k	PnBA4.0k	block	100:100	97%	870	890	1.05
4	PtBA4.7k	PnBA4.0k	block	100:200	98%	1270	1260	1.04
5	PS2.2k	PtBA4.7k	block	50:50	96%	345	340	1.03
6	PS2.2k	PtBA4.7k	block	100:50	94%	455	540	1.04
7	PLA4.7k	PnBA4.0k	block	20:180	98%	810	820	1.08
8	PLA4.7k	PnBA4.0k	block	40:160	97%	830	890	1.08
9	PLA4.7k	PnBA4.0k	block	100:100	97%	870	980	1.07
10	PLA4.7k	PnBA4.0k	block	200:200	96%	1740	1770	1.09
11	PLA4.7k	PnBA4.0k	random	50:50	98%	435	450	1.06
12	PLA4.7k	PnBA4.0k	random	100:100	97%	870	1050	1.05
13	PLA4.7k	PnBA4.0k	random	200:200	98%	1740	1880	1.10
14	PLA4.7k	PnBA4.0k	random	160:40	98%	910	1030	1.04
15	PLA4.7k	PnBA4.0k	random	130:70	98%	890	1030	1.05

^a Ratio of each MM to Ru catalyst. ^b Conversion of MM to brush copolymer is determined by comparing the peak areas of brush copolymer and residual MM from GPC measurement of the final crude product without any purification. ^c $M_{n,theo} = M_{n,GPC}(MM_1) \times [MM_1/C] + M_{n,GPC}(MM_2) \times [MM_2/C]$. ^d Determined by THF GPC using RI and MALLS detectors.

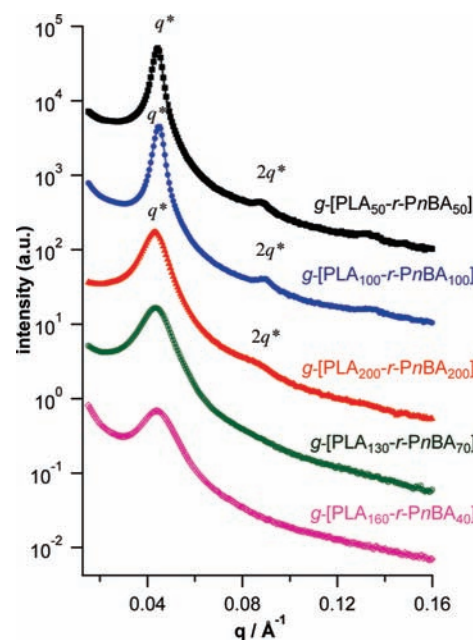
Table 3. Molecular and Morphological Characteristics of PLA-PnBA Brush Random and Block Copolymers

	f_{PLA}^a	$T_g, PLA/^\circ C^b$	d (SAXS)/nm ^c	d (AFM)/nm ^d	$T_{ODT}/^\circ C^e$
<i>g</i> -[PLA ₅₀ - <i>ran</i> -PnBA ₅₀]	0.49	38	14.2	18	80
<i>g</i> -[PLA ₁₀₀ - <i>ran</i> -PnBA ₁₀₀]	0.49	38	14.0	21	85
<i>g</i> -[PLA ₂₀₀ - <i>ran</i> -PnBA ₂₀₀]	0.49	38	14.6	17	75
<i>g</i> -[PLA ₁₃₀ - <i>ran</i> -PnBA ₇₀]	0.63	39	—	—	—
<i>g</i> -[PLA ₁₆₀ - <i>ran</i> -PnBA ₄₀]	0.79	42	—	—	—
<i>g</i> -[PLA ₁₀₀ - <i>b</i> -PnBA ₁₀₀]	0.49	49	116	—	—
<i>g</i> -[PLA ₄₀ - <i>b</i> -PnBA ₁₆₀]	0.19	49	—	—	—
<i>g</i> -[PLA ₂₀ - <i>b</i> -PnBA ₁₈₀]	0.09	—	64	—	—

^a Volume fraction of PLA calculated using densities $\rho_{PnBA} = 0.99$ g/mL, $\rho_{PLA} = 1.25$ g/mL. ^b T_g of PLA side chain, measured by DSC with heating rate of 15 °C/min. ^c Domain spacing determined by SAXS. ^d Lamellar thickness determined by AFM cross-sectional analysis. ^e Order–disorder transition temperature determined by SAXS.

side chain distribution along the brush copolymer backbone affects brush copolymer self-assembly in the melt state.

Thermal Analyses of Brush (Co)polymers. DSC analysis revealed the architectural effect of brush homopolymers and copolymers on the T_g of their side chains. For a PLA brush homopolymer (backbone DP=200) synthesized using NB(PLA)4.7k, a single thermal transition at 49 °C was observed in the temperature range of 0–200 °C scanned. This temperature corresponded to the T_g of amorphous PLA side chains and is close to the literature values. The T_g of the brush homopolymer was higher than that of the MM (42 °C), due to the increased MW and/or the increased molecular constraint resulting from linking the side chains along the formed polynorbornene backbone.⁴³ The T_g of PLA side chains in brush block copolymers was found to be about 49 °C, close to that of the PLA brush homopolymer, except for PLA₂₀-*b*-PnBA₁₈₀ whose signal was too weak to enable accurate T_g determination (Table 3). This is consistent with phase separation in the block copolymers to form two distinct domains. In contrast, the T_g of PLA was found to be lower in the brush random copolymers, and increasing the PnBA content resulted in further suppression of the T_g of PLA. However, the T_g 's of brush random copolymers were similar to that of the PLA MM, which indicated microphase separation of PLA and PnBA side chains. With equal amounts of PLA and PnBA in the brush random copolymers, the T_g was found to be 38 °C (Table 3). The lower

**Figure 4.** SAXS curves for brush random copolymers, *g*-[PLA-*ran*-PnBA].

T_g of PLA in random copolymers may be a result of smaller domain sizes than those in brush block copolymers.

Self-Assembly of Brush Copolymers in the Melt State. We investigated the self-assembly of brush copolymers in bulk using small-angle X-ray scattering (SAXS) and in thin films using AFM. These two techniques provide complementary information about the self-assembled morphology and domain spacing.

Brush random copolymers, *g*-[PLA-*ran*-PnBA], were thermally annealed at 100 °C for 12 h in order to achieve equilibrium, and prolonged annealing did not result in any further structural change. Brush random copolymers with an equal number of PLA and PnBA side chains (symmetric) exhibited a sharp principal SAXS peak at wavevector q^* along with peaks at integer multiples of q^* (Figure 4). This is indicative of a lamellar morphology, as expected due to the near symmetric volume fractions of the PLA and PnBA segments ($f_{PLA} = 0.49$). The domain spacing (d) calculated from q^* is very similar, 14.3 ± 0.3 nm, for all three symmetric random copolymers, independent of their backbone length. The inde-

(43) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315.

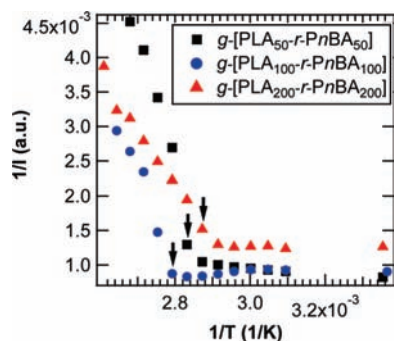


Figure 5. Inverse intensity of peak heights in the vicinity of the order–disorder transition for brush random copolymers, g -[PLA-*ran*-PnBA]. The arrows mark the T_{ODT} 's.

pendence of d -spacing on backbone length and the lamellar morphology suggests that the polynorbornene backbone is confined at the interface between PLA and PnBA layers, with the PLA and PnBA side chains segregated to opposite sides of the brush polymer backbone to minimize contact between dissimilar chains.

Furthermore, as the symmetric random copolymers were heated, they underwent a transition from an ordered lamellar phase into a microphase disordered regime. The order–disorder transition (ODT) temperature, T_{ODT} , can be evaluated using the discontinuity in the plot of inverse primary peak intensity vs inverse temperature (Figure 5), using SAXS patterns acquired in 5 °C step ramping with 5 min thermal equilibration at each temperature. This was accompanied by the disappearance of higher order peaks. The T_{ODT} was found to hardly change, giving 75–85 °C for g -[PLA₅₀-*ran*-PnBA₅₀], g -[PLA₁₀₀-*ran*-PnBA₁₀₀], and g -[PLA₂₀₀-*ran*-PnBA₂₀₀] as the MW increased from 450 to 1880 kDa. The broad scattering peak in SAXS that remained above the ODT originated from intramolecular correlations of block copolymers.⁴⁴ For a wide range of block copolymers, T_{ODT} is controlled by the product of the Flory–Huggins interaction parameter χ and the total degree of polymerization N .⁴⁴ The similar T_{ODT} 's observed for the brush random copolymers over a wide range of the brush backbone length suggested that the degree of polymerization N of the side chains dictates the T_{ODT} . This is consistent with side chain microphase separation with the backbones localized at interfaces between PLA and PnBA domains (Figure 6, top).

We studied the morphology of brush random copolymers in thin films using AFM. Based on the T_{ODT} determined using SAXS, these samples were annealed at 70 °C, which is below the T_{ODT} but still above the T_g of PLA. AFM showed that the films were featureless before annealing (Figure 7a). After annealing, a layer of islands with very uniform height was clearly observed for each of the symmetric random copolymers (Figure 7b–d). An island layer is formed if the natural repeat spacing of a parallel oriented block copolymer is incommensurate with the film thickness, and the film segregates excess material to the top surface to form an incomplete layer.^{45–47} The height difference between the thicker and thinner regions of the film is equal to the natural period of the block copolymer.

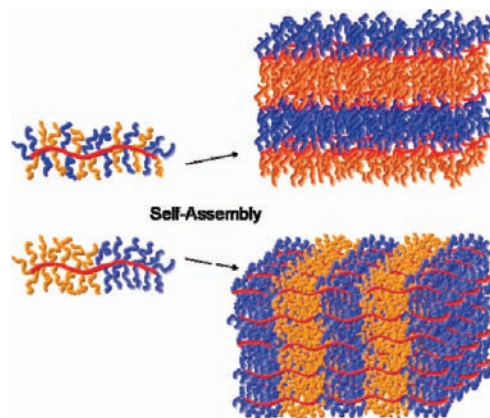


Figure 6. Proposed assembly of symmetric brush random copolymer and block copolymer.

Here the island layers are remarkably uniform across areas of tens of micrometers, with thickness of 17–20 nm for all three samples. The height values are very close to the bulk d -spacings measured by SAXS, indicating that the domain spacing of parallel oriented lamellae in the film is similar to domain spacing in the bulk.

Due to the independence of lamellar thickness on brush polymer MW, we propose that uniform lamellar structures can be obtained using polydisperse brush copolymer samples. Indeed, an indistinguishable “islands and holes” morphology with 17–20 nm in height was obtained from blends of any two of the symmetric random copolymers at arbitrary ratios after annealing. This further supports the complete dominance of the side chains in governing the self-assembly of these brush random copolymers.

In contrast to the symmetric random copolymers, when PLA and PnBA side chains were incorporated in uneven amounts (Table 2, entry 14 and 15), ordered microphase separation of the side chains was not observed: No structural features were observed in thin films by AFM after extensive annealing at temperatures ranging from 75 to 140 °C. SAXS of g -[PLA₁₆₀-*ran*-PnBA₄₀] and g -[PLA₁₃₀-*ran*-PnBA₇₀] showed only one broad peak with no higher order peaks; the single peak corresponds to intramolecular correlations between side chains of the block copolymers. Furthermore, the peak intensity continuously decreased upon heating, and no ODT was observed (Supporting Information Figure S5). As the side chains microphase separate to opposite sides of the backbone, the resulting asymmetric space filling on the backbone makes it impossible to assemble into lamellae. Meanwhile, the backbone of a brush polymer may be more difficult to coil than a linear polymer to adopt other morphologies, as a result of the high congestion of the segregated side chains.

We next investigated the self-assembly of brush block copolymers, g -[PLA-*b*-PnBA]. Due to the very large domain spacing in the assembled brush block copolymers, principal q^* was out of the q range obtainable by SAXS in some samples (Figure 8). For the symmetric block copolymer, g -[PLA₁₀₀-*b*-PnBA₁₀₀], multiple higher-order scattering peaks up to the 12th order were clearly observed. The even distribution of scattering peaks to $12q^*$ indicated remarkably well-ordered lamellar morphology with a d -spacing of 116 nm, consistent with the fact that principal q^* was out of the q range obtainable by SAXS. This length scale is close to the fully extended length of a polynorbornene brush homopolymer with backbone DP = 220

(44) Leibler, L. *Macromolecules* **1980**, *13*, 1602–1617.

(45) Coulon, G.; Collin, B.; Auserre, D.; Chatenay, D.; Russell, T. P. *J. Phys. (Paris)* **1990**, *51*, 2801–2811.

(46) Mayes, A. M.; Russell, T. P.; Bassereau, P.; Baker, S. M.; Smith, G. S. *Macromolecules* **1994**, *27*, 749–755.

(47) Olsen, B. D.; Li, X.; Wang, J.; Segalman, R. A. *Macromolecules* **2007**, *40*, 3287–3295.

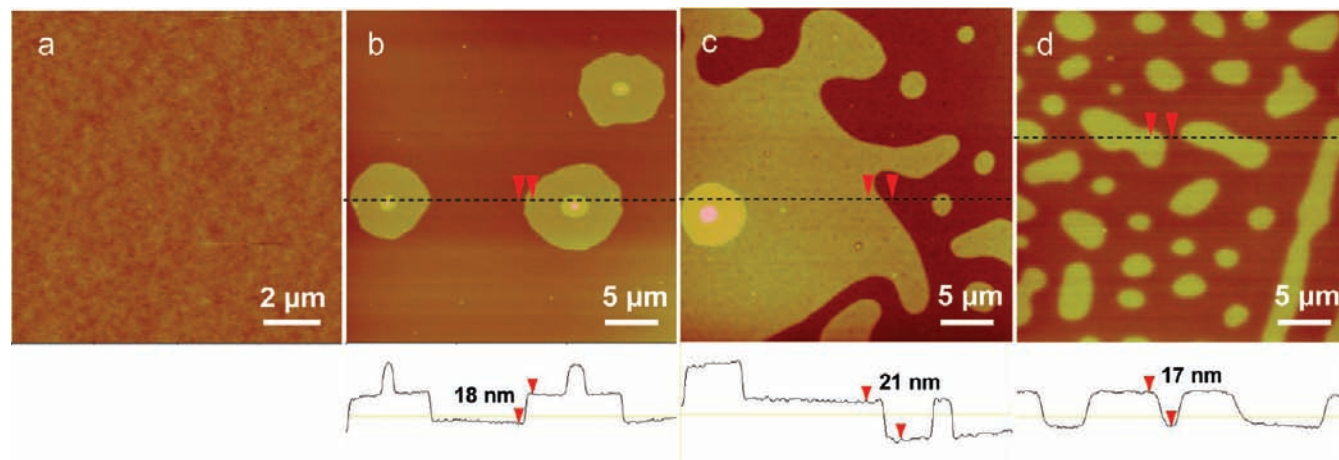


Figure 7. AFM height images of brush random copolymer thin films (120–150 nm) on silicon wafer and their cross sectional analysis. (a) g -[PLA₁₀₀-*ran*-PnBA₁₀₀] as cast, and after annealing (b) g -[PLA₅₀-*ran*-PnBA₅₀], (c) g -[PLA₁₀₀-*ran*-PnBA₁₀₀], (d) g -[PLA₂₀₀-*ran*-PnBA₂₀₀]. The vertical scale is 30 nm for (a) and 100 nm for (b–d).

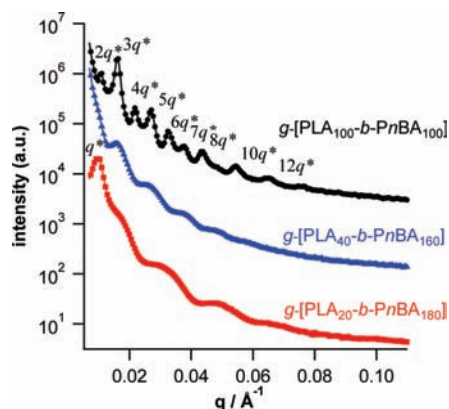


Figure 8. SAXS curves for brush block copolymers, g -[PLA-*b*-PnBA].

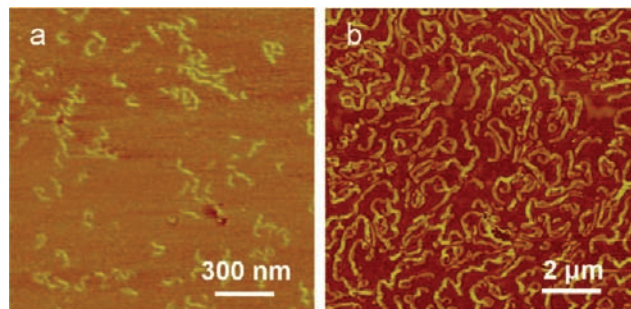


Figure 9. AFM phase images of (a) individual PLA brush homopolymers ($DP_{\text{backbone}} = 200$, MM NB(PLA)4.7k was used) on mica; (b) brush block copolymer, g -[PLA₁₀₀-*b*-PnBA₁₀₀], morphology in thin film (ca. 120 nm) as cast from 2.5% toluene solution onto silicon wafer.

and PS side chains of 6.6 kDa, as previously observed by AFM.³⁴ Although clear AFM imaging of individual g -[PLA₁₀₀-*b*-PnBA₁₀₀] polymers has been difficult due to the aggregation of molecules, AFM revealed worm-like shapes with contour lengths of ca. 110–130 nm for a PLA brush homopolymer with backbone $DP = 200$ prepared using the same MM as in the block copolymer (Figure 9a). Therefore, the large lamellar d -spacing of g -[PLA₁₀₀-*b*-PnBA₁₀₀] is dictated by the length of its highly extended polynorborene backbone and suggests interdigitated packing of the molecules in the lamellae (Figure 6 bottom). The highly ordered self-assembly structure also supports the well-controlled macromolecular characteristics of



Figure 10. Photograph of slowly dried g -[PLA₂₀₀-*b*-PnBA₂₀₀] (Table 2, entry 10) showing green color due to reflectance from the large self-assembled domains.

the brush copolymers obtained from ROMP of MMs. Notably, the larger symmetric block copolymer g -[PLA₂₀₀-*b*-PnBA₂₀₀] (Table 2, entry 10) appeared green spontaneously upon slowly evaporating the solvent (Figure 10). This indicates that the domain spacing in this ultrahigh MW sample is large enough to reflect green light.⁴⁸

On the other hand, highly asymmetric block copolymers, g -[PLA₂₀-*b*-PnBA₁₈₀] and g -[PLA₄₀-*b*-PnBA₁₆₀], formed non-lamellar morphologies. Both materials showed scattering peaks at very low q , a feature indicative of microphase separation, with q^* inaccessible for g -[PLA₄₀-*b*-PnBA₁₆₀] and q^* corresponding to a domain spacing of 64 nm for g -[PLA₂₀-*b*-PnBA₁₈₀]. Based on the domain spacing for g -[PLA₂₀-*b*-PnBA₁₈₀], it is clear that the backbone is not fully extended in its highly asymmetric polymer. In addition, both polymers show oscillations at higher q that originate from the form factor of the block copolymer aggregates.⁴⁹ Although the quality of fits is not sufficient to identify the specific shape of the aggregates, the period of the oscillations allows us to identify the characteristic size of the presumably spherical or cylindrical PLA domains with sizes of 38 and 67 nm in diameter, respectively,

(48) The wavelength of the reflected light at the interfaces of multilayer lamellae is governed by: $\lambda = 2(n_1d_1 + n_2d_2)$, where n and d are the refractive index and the thickness of each layer. In a rough estimate, taking $n_1 = n_2 = 1.5$ for both polymer layers and $\lambda = 500$ nm for green light, the domain spacing is calculated to be about 170 nm for a symmetric lamellar morphology presumably formed in the symmetric block copolymer g -[PLA₂₀₀-*b*-PnBA₂₀₀].

(49) Kinning, D. J.; Thomas, E. L. *Macromolecules* **1984**, *17*, 1712–1718.

irregularly distributed in a matrix of PnBA. In addition, the PLA domain size is consistent with the calculated result using the domain spacing of 64 nm obtained from q^* and 9% PLA volume fraction in g -[PLA₂₀- b -PnBA₁₈₀]. The nonlamellar morphologies formed from these asymmetric brush block copolymers suggest that the backbone is not as fully extended as in the symmetric brush block copolymer, g -[PLA₁₀₀- b -PnBA₁₀₀]. On the other hand, the decreased ordering in asymmetric block copolymers suggests frustrated packing when the backbone has to adopt nonlamellar morphologies due to its reduced flexibility. Similar packing frustration has also been suggested for asymmetric brush block copolymers with side chains of different MWs.¹²

Thin films of the block copolymer g -[PLA₁₀₀- b -PnBA₁₀₀] after spin-coating from toluene solution showed large cylindrical micellar structures of 200 nm wide and several micrometers long as imaged by AFM (Figure 10b), in sharp contrast to the featureless as-cast film from the random copolymer, g -[PLA₁₀₀- ran -PnBA₁₀₀], at the same MW and composition (Figure 7a). After annealing, the surface topology became rough, but clear phase separation was observed from the sharp contrast in the phase image, which derives from mechanical property differences between the PLA and PnBA blocks in the copolymers (Supporting Information Figure S7). Microphase separation in thin films of the asymmetric brush block copolymers was also observed from the AFM phase images. However, the structural assignment for the thin film morphologies of these brush block copolymers was unclear. This is because the film thickness is similar to the polymer domain spacing in bulk and corresponds to one layer of molecular packing. Therefore, the surface effect on the thin film morphology makes it difficult to correlate to the bulk morphology for large brush block copolymers.

Conclusions

ROMP of various MMs bearing polyacrylate, polystyrene, and polylactide chains using highly active, fast initiating Ru catalyst has shown typical characteristics of a living polymerization, such as first-order kinetics and linear MW growth with increasing conversion. The living nature of ROMP and very high conversion (>90%) of MMs have allowed facile one-pot preparation of a variety of high MW narrowly dispersed brush block and random copolymers in high conversions, which otherwise involve multiple steps to synthesize using different grafting techniques. The length of each block and the overall backbone can be easily controlled by the ratio of MM to catalyst.

By choosing MMs with the similar polymerization rates, we prepared a series of brush block and random copolymers from a pair of MMs, NB(PLA)4.7k and NB(PnBA)4.0k, varying their relative ratios. In symmetric brush random copolymers (equal number of PLA and PnBA side chains), the side chains were found to microphase separate into lamellar morphology with domain spacing of about 14 nm as determined by SAXS. AFM studies of thin film samples also revealed lamellar structures with similar thickness of 17–21 nm. The domain spacing and T_{ODT} were insensitive to the brush copolymer backbone length, suggesting microphase separation of side chains to opposite sides of the brush polymer backbone and that the side chains played a dominant role in the self-assembly. On the other hand, the brush block copolymer with the same number of PLA and PnBA side chains self-assembled into highly ordered, large lamellar domains over 100 nm as revealed by SAXS. The domain size was dictated by the backbone length.

Asymmetric brush copolymers containing different numbers of two types of side chains did not form well-ordered morphologies. This may be attributed to the reduced backbone flexibility of brush polymers and their increased difficulty to adopt coiled conformations.

Controlled ROMP of MMs greatly simplifies the syntheses of brush copolymers. The combination of facile synthesis and good structural control of brush copolymers with the functional group tolerant Ru catalyst opens the door to further studies of the self-assembly of these macromolecular architectures. Brush copolymers provide a unique macromolecular platform for bottom-up assembly to form nanostructures with large domain spacings and controlled intermaterial dividing surfaces.

Acknowledgment. This work was supported by the Department of Energy (DE-FG02-05ER46218). We gratefully acknowledge Professor James R. Heath for the use of the AFM, Brookhaven National Lab for the use of SAXS, Lixia Rong for assistance with SAXS measurement, and Edward H. Bramston-Cook for assistance with AFM measurement. BDO thanks the Caltech Beckman Institute for a postdoctoral fellowship.

Supporting Information Available: Experimental section, ¹H NMR spectra, GPC traces, and DSC traces of MMs and brush copolymers, conversion and MW growth profiles for ROMP of MMs, and additional AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA908379Q