Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 8747–8754 **8747**
DOI: 10.1021/ma101869q

Renewable Rosin Acid-Degradable Caprolactone Block Copolymers by Atom Transfer Radical Polymerization and Ring-Opening Polymerization

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Received August 14, 2010; Revised Manuscript Received September 25, 2010

ABSTRACT: Renewable rosin acid-degradable caprolactone block copolymers were prepared by atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). Two-step sequential polymerization using either poly(2-acryloyloxyethyl dehydroabietic carboxylate)-OH (PAEDA-OH) or poly(ε-caprolactone)-Br (PCL-Br) as macroinitiators resulted in well-defined block copolymers with low polydispersity. One-pot polymerization was carried out with three different sequential feeds of AEDA and ε-CL monomers. The control of one-pot polymerization depended on the interactions of coexisting ATRP catalysts and ROP catalysts. While the minimal interactions between copper(I) and tin(II) catalysts produced well-defined block copolymers, excess copper(II) or tin(II) led to the formation of block copolymers with polydispersity > 1.5. It was suggested that the tin(II) catalysts reduced the persistent radicals copper(II) of ATRP, leading to a poorly controlled polymerization. PCL segments of the block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence of polymer compositions due to the possible crystallization of the PCL block.

Introduction

Synthetic plastics account for consumption of ~7% of fossil fuels worldwide.[1−3] Energy shortage and environmental concerns prompt opportunities to seek developing renewable resources for manufacturing of "green" plastics.[3−7] There are two major classes of natural resources. The first class of natural resources is biopolymers including cellulose, hemicellulose, and lignin.[5,6,8−10] These natural polymers have long been exploited without any modifications. Currently, common approaches involve physical blending and limited chemical modifications. Because of their complexity and already-existing macromolecular skeletons, these natural resources lack of the ability to expand precise macromolecular engineering toward diverse properties. In contrast, the second class of natural resources is small molecular biomass such as lactic acids and vegetable oils, which can be derivertized into monomers for polymerization. Particularly, lactic acid-derived polymers have achieved enormous success due to their ability to be molecularly engineered to allow precise and controlled polymerization. As one of the major classes of petroleum chemicals, cycloaliphatic and aromatic compounds offer rigidity and chemical stability to polymers derived from them. However, such important polymeric materials are largely missing or ignored in the communities of renewable polymers.

Gum rosin, whose major components are resin acids (or rosin acids as we refer below), has characteristic hydrocarbon-based hydrophenanthrene rings, similar in rigidity and chemical stability to petroleum chemical-based cycloaliphatic and aromatic compounds.[11−15] Therefore, it is reasonably expected that polymers with hydrophenanthrene building blocks have the potential to resemble many plastics derived from petroleum chemicals.[15−23] We have recently synthesized a series of rosin acid-derived model monomers and shown that they can be used to form well-defined vinyl polymers by atom transfer radical polymerization (ATRP).[24]

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Poly(ε-caprolactone) (PCL) is a hydrophobic, semicrystalline (bio)degradable polymer, which is generally prepared by ring-opening polymerization (ROP).[25,26] The use of PCL as degradable polymers has numerous advantages including nontoxicity, permeability, blend compatibility, controllable degradation kinetics and mechanical properties, and manufacturability. To be successful in new applications, it is desired that degradable polymers exhibit a broad spectrum of physical properties while retaining the degradability of the parent polymers. Common approaches used to tune the physical properties of degradable polymers include copolymerization, preparation of block copolymers, and synthesis of substituted degradable monomers.[27−38] From the perspective of energy concerns, it is more favorable, though much less explored, to combine caprolactone with renewable biomass, as caprolactone is usually a derivative of petroleum chemicals.

Although at the current stage gum rosin-derived vinyl polymers like many other vinyl polymers do not have noticeable degradability, the rosin moiety could be potentially degraded by microbials as reported in early work.[39,40] In addition, gum rosin obtained from pine trees is more compatible with the environment than petroleum-based chemicals. Therefore, integration of the rosin moiety holds new opportunities for the design of renewable degradable polymers. To the best of our knowledge, this is an area that has never been explored in the literature. We believe that it is possible to place renewable rosin acid moiety-containing segment and degradable caprolactone segment into a block copolymer through suitable functionalization and appropriate polymerization techniques (Scheme 1). Development of renewable rosin acid-degradable caprolactone-based block copolymers will have two major benefits: (1) increasing the use of renewable components in the degradable materials that are not renewable (e.g., caprolactone); (2) accessing novel properties originating from the rosin moiety. Herein, we report the first preparation of block copolymers containing a rosin acid-derived model monomer and caprolactone by a combination of ATRP and ROP.

Published on Web 10/13/2010

Scheme 1. A General Strategy toward Renewable Rosin Acid-Degradable Caprolactone Block Copolymers

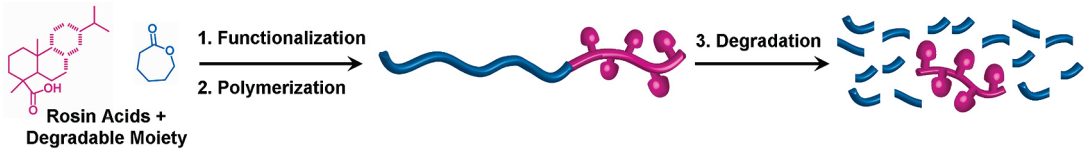


Table 1. Preparation of Block Copolymers of CL and AEDA by ROP and ATRP

entry	polymer	[monomer]/[inititaor]	monomer conv (%)	M_n (g/mol) (NMR)	PDI (GPC)
1	PCL-Br	[CL]/[HEBiB] = 50	82% (CL)	4.7K	1.25
2[a]	PCL_{41}-$PAEDA_{41}$-Br	[AEDA]/[HEBiB] = 100	41% (AEDA)	4.7K−16.4K	1.36
3	$PAEDA_{50}$-OH	[AEDA]/[HEBiB] = 100	50% (AEDA)	20K	1.30
4[b]	$PAEDA_{50}$-PCL_{500}-OH	[CL]/[HEBiB] = 556	90% (CL)	20K−57K	1.18
5[c]	$PAEDA_{52}$-PCL_{32}	[CL]/[HEBiB] = 100 [AEDA]/[HEBiB] = 100	52% (AEDA) 32% (CL)	20.8K−3.6K	1.24
6[c]	$PAEDA_{16}$-PCL_{320}	[CL]/[HEBiB] = 360 [AEDA]/[HEBiB] = 100	16% (AEDA) 89% (CL)	6.4K−36.5K	1.66
7[d]	$PAEDA_{20}$-$PCL_{\sim 2}$	[CL]/[HEBiB] = 349 [AEDA]/[HEBiB] = 100	20% (AEDA) <1% (CL)	8.0K−0.2K	1.51
8[e]	PCL_{200}-$PAEDA_{20}$	[CL]/[HEBiB] = 200 [AEDA]/[HEBiB] = 60	100% (CL) 22% (AEDA)	22.8K−8.0K	1.38

[a] Chain extension from PCL-Br (entry 1) to PAEDA. [b] Chain extension from PAEDA-OH (entry 3) to PCL. [c] One-pot simultaneous polymerization. [d] One-pot ADEA-first polymerization with sequential feeds from AEDA to CL. [e] One-pot CL-first polymerization with sequential feeds from CL to AEDA.

Experimental Section

Materials. Dehydroabietic acid (DA, ~90%) was obtained from Wuzhou Chemicals, China. Tetrahydrofuran (THF, Aldrich) and toluene (Aldrich) were refluxed with sodium and distilled out just before use under a nitrogen atmosphere. Oxalyl chloride, triethylamine, Sn(II) 2-ethylhexanoate ($Sn(Oct)_2$), and copper(I) bromide (99.999%) were used as received (Aldrich). ε-Caprolactone (CL, 97%, Aldrich) was dried with CaH_2 and distilled out before use. Tris(2-(dimethylamino)ethyl)amine (Me_6Tren) and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) were prepared according to reported literatures.[41] 2-Acryloyloxyethyl dehydroabietic carboxylate (AEDA) was prepared according to our recent report.[24]

Characterization. ^{1}H NMR spectra were recorded on Bruker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1 and HR2 (300 × 7.5 mm) from Waters. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples were filtered over a microfilter with pore size of 0.2 μm (Nylon, Millex-HN 13 mm syringes filters, Millipore). GPC was calibrated using polystyrene as standard. Fourier transform infrared spectrometry (FTIR) was conducted on a Shimadzu 8400 FTIR spectrometer. Thermal transitions were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from 0 to 200 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were collected during the second heating scan. The average sample mass was ~5 mg, and the nitrogen flow rate was 50 mL/min. Tapping mode atomic force microscopy (TMAFM) studies were carried out with the aid of a multimode NanoScope V system (Veeco Instruments, Santa Barbara, CA) equipped with a J-type vertical engage scanner. TMAFM observations were performed at room temperature in air using silicon cantilevers with a spring constant of 20−80 N/m and a resonance frequency of 292−333 kHz (standard silicon NCHV probes).

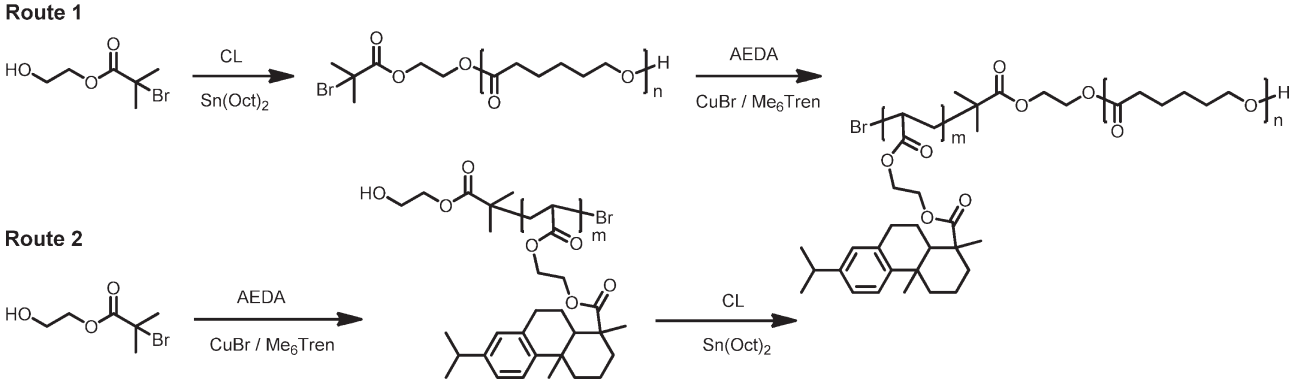
Synthesis. *Preparation of PCL-Br Macroinitiator by ROP (Table 1, Entry 1).* A mixture of CL (2.00 g, 1.75×10^{-2} mol), HEBiB (74.2 μL, 3.5×10^{-4} mol), $Sn(Oct)_2$ (14 mg, 3.5×10^{-5} mol), and toluene (2 mL) was introduced into a Schlenk flask. After three freeze−pump−thaw (FPT) cycles, the flask was placed into a preheated oil bath set at 120 °C. After an overnight reaction, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 4700 g/mol, PDI (GPC) = 1.25. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.0−4.2 (t, $-OCH_2-$); 2.2−2.4 (t, $-CH_2CO-$); 1.90−1.95 (s, $-C(CH_3)_2Br$), 1.3−1.8 (broad, $-CH_2CH_2CH_2-$). IR (neat): 3020−2820 cm^{-1} (CH stretching); 1723 cm^{-1} (C=O stretching).

Chain Extension To Prepare PCL-b-PAEDA-Br by ATRP (Table 1, Entry 2). A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me_6Tren (2.9 mg, 1.2×10^{-5} mol), PCL-Br macroinitiator (0.1 g, 2.5×10^{-5} mol; M_n (NMR) = 4700 g/mol, M_w/M_n (GPC) = 1.25), and THF (1 mL) was introduced into a polymerization tube. After three FPT cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by backfilling with nitrogen three times. The tube was placed into a preheated oil bath set at 90 °C. After 16 h, the tube was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 20 100 g/mol, PDI (GPC) = 1.36. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.8−7.2 (broad, aromatic, PAEDA); 4.1−4.3 (s, OCH_2CH_2O, PAEDA); 4.0−4.1 (t, $-OCH_2-$, PCL); 2.8−3.0 (s, protons next to aromatic ring, PAEDA); 2.2−2.4 (t, $-CH_2CO-$, PCL). IR (neat): 3070−2800 cm^{-1} (CH stretching); 1723 cm^{-1} (C=O stretching).

Preparation of PAEDA−OH Macroinitiator by ATRP (Table 1, Entry 3). A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me_6Tren (2.9 mg, 1.2×10^{-5} mol), HEBiB (5.3 μL, 2.5×10^{-5} mol), and THF (1 mL) was introduced into a polymerization tube. After three FPT cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by backfilling with nitrogen three times. The tube was placed into a preheated oil bath set at 90 °C. After 16 h, the tube was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 20 000 g/mol, PDI (GPC) = 1.30. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.7−7.2 (broad, aromatic); 4.0−4.4 (t, OCH_2CH_2O); 2.8−3.0 (s, protons next to aromatic ring). IR (neat): 3060−2790 cm^{-1} (CH stretching); 1732 cm^{-1} (C=O stretching).

Chain Extension To Prepare PAEDA-b-PCL-OH by ROP (Table 1, Entry 4). PAEDA-OH macroinitiator (0.24 g, 1.2×10^{-5} mol; M_n (NMR) = 20 000 g/mol, M_w/M_n (GPC) = 1.30), CL (0.76 g, 6.7×10^{-3} mol), $Sn(Oct)_2$ (0.5 mg, 1.2×10^{-6} mol), and toluene (1.2 mL) were mixed in a Schlenk flask. The mixture

Scheme 2. Preparation of Diblock Copolymers Containing CL and AEDA by Two-Step Sequential Polymerization



was degassed by conducting three FPT cycles. The flask was placed into a preheated oil bath set at 120 °C. After an overnight reaction, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 77 000 g/mol, PDI (GPC) = 1.18. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.9−7.2 (broad, aromatic, PAEDA); 4.1−4.4 (s, OCH_2CH_2O, PAEDA); 4.0−4.1 (t, −OCH_2−, PCL); 2.8−3.0 (s, protons next to aromatic ring, PAEDA); 2.2−2.4 (t, −CH_2CO−, PCL).

One-Pot Polymerization To Prepare PCL-b-PAEDA by ATRP and ROP

1. One-Pot Simultaneous Polymerization (*Table 1, Entry 5*). A mixture of AEDA (0.50 g, 1.25×10^{-3} mol), CL (0.14 g, 1.22×10^{-3} mol), Sn(Oct)$_2$ (0.5 mg 1.2×10^{-6} mol, Me_6Tren (1.4 mg, 6×10^{-6} mmol), HEBiB (2.5 μL, 1.2×10^{-5} mol), and toluene (1 mL) was introduced into a Schlenk flask. After three FPT cycles, CuBr (0.9 mg, 6×10^{-6} mol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by backfilling with nitrogen three times. The flask was placed into a preheated oil bath set at 120 °C. After 24 h, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 24 400 g/mol, PDI (GPC) = 1.24. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.9−7.2 (broad, aromatic, PAEDA); 4.2−4.4 (s, OCH_2CH_2O, PAEDA); 4.0−4.2 (t, −OCHH$_2$−, PCL); 2.8−3.0 (s, protons next to aromatic ring, PAEDA); 2.2−2.4 (t, −CH_2CO−, PCL).

2. One-Pot AEDA-First Polymerization (*Table 1, Entry 7*). A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me_6Tren (2.9 mg, 1.2×10^{-5} mol), HEBiB (5.3 μL, 2.5×10^{-5} mol), and toluene (1 mL) was introduced into a polymerization tube. After three FPT cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by backfilling with nitrogen three times. The tube was placed into a preheated oil bath set at 120 °C. After an overnight reaction, a deoxygenated mixture of of CL (1.00 g, 8.8×10^{-3} mol), Sn(Oct)$_2$ (4.0 mg, 9.9×10^{-6} mol), and toluene (1 mL) was added to the flask under nitrogen. After 16 h, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 8200 g/mol, PDI (GPC) = 1.51. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.9−7.2 (broad, aromatic, PAEDA); 4.0−4.4 (s, OCH_2CH_2O, PAEDA); 2.8−3.0 (s, protons next to aromatic ring, PAEDA).

3. One-Pot CL-First Polymerization (*Table 1, Entry 8*). A mixture of CL (1.00 g, 8.8×10^{-3} mol), Sn(Oct)$_2$ (9.0 mg 2.22×10^{-5} mol), HEBiB (9.0 μL, 4.27×10^{-5} mol), and toluene (1 mL) was introduced into a Schlenk flask. After three FPT cycles, the flask was placed into a preheated oil bath set at 120 °C. After the overnight reaction, a deoxygenated mixture of AEDA (1.00 g, 2.51×10^{-3} mol), CuBr (1.8 mg, 1.2×10^{-5} mmol), Me_6Tren (2.9 mg, 1.2×10^{-5}), and toluene (1 mL) was added to the flask under nitrogen. After 16 h, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 30 800 g/mol, PDI (GPC) = 1.38. ^{1}H NMR (300 MHz, $CDCl_3$, δ):[24] 6.9−7.2 (broad, aromatic, PAEDA); 4.1−4.4 (s, OCH_2CH_2O, PAEDA); 4.0−4.1 (s, −OCH_2−, PCL); 2.8−3.0 (s, protons next to aromatic ring, PAEDA); 2.2−2.4 (t, −CH_2CO−, PCL).

Degradation of Block Copolymers. A mixture of block copolymers (~23 mg), 3.0 M $HCl_{(aq)}$ (0.2 mL), and THF (2 mL) was introduced into a small vial. The solution was refluxed overnight at 65 °C. The solution was then evaporated to dryness.

Results and Discussion

Atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) were combined to prepare diblock copolymers containing 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) and ε-caprolactone (CL). Two strategies including five different synthetic routes were carried out to optimize the control of polymerization: two-step sequential polymerization and one-pot polymerization. All polymerizations involved the use of a difunctional initiator, 2-hydroxyethyl bromoisobutyrate (HEBiB), which allowed for both ROP and ATRP. The two-step synthesis of diblock copolymers employed the use of either PCL-Br or PAEDA−OH as a macroinitiator for chain-extension with PAEDA or PCL with the aid of CuBr/Me_6Tren or Sn(II) 2-ethylhexanoate (Sn(Oct)$_2$) as the catalyst system, respectively. The one-pot polymerization involved the use of monomers at different feeding sequences including simultaneous feeds of a mixture of CL and AEDA, sequential feeds from CL to AEDA and from AEDA to CL.

1. Two-Step Sequential Polymerization. *a. Chain Extension from PCL-Br to PAEDA: Diblock Copolymers PCL-b-PAEDA-Br*. The synthetic procedures of two-step sequential polymerizations are presented in Scheme 2. The −OH and −Br functional groups of the HEBiB initiator were used as initiating sites for ROP of CL and ATRP of AEDA respectively.

ROP of CL was carried out using HEBiB and Sn(Oct)$_2$ as the initiator and the catalyst respectively in the presence of dry toluene, yielding a bromine-terminated PCL-Br.[42,43] As shown in Figure 1, the ^{1}H NMR spectrum of PCL-Br polymers shows characteristic signals at 3.9−4.1 and 2.2−2.4 ppm, corresponding to the methylene protons of −CH_2O− and −$COCH_2$− in the ε-caprolactone unit, respectively. The peak at 1.9 ppm corresponds to the methyl protons of −C(CH_3)$_2$− from the initiator moiety at the end of polymer chain. The molecular weight based on ^{1}H NMR end-group analysis was in good agreement with the one calculated from reaction conversion by ^{1}H NMR, indicating all polymer chains retained the end group −Br. The molecular weight can be facilely tuned through adjustment of the molar ratio of monomers to initiators. GPC traces (Figure 2) show

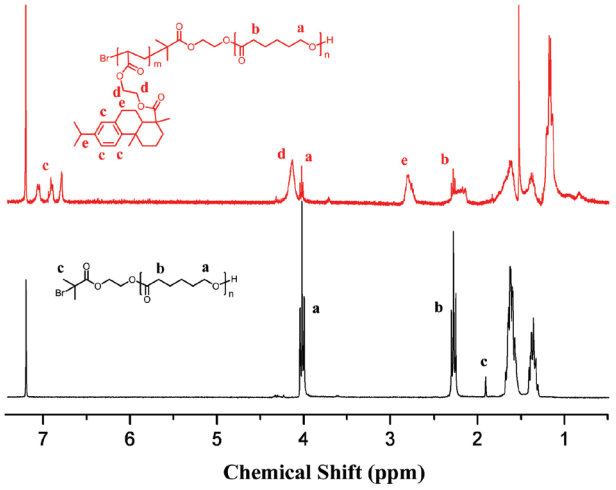


Figure 1. ^{1}H NMR spectra of PCL-Br and PCL-*b*-PAEDA-Br diblock copolymers prepared by sequential ROP and ATRP (entries 1 and 2 from Table 1).

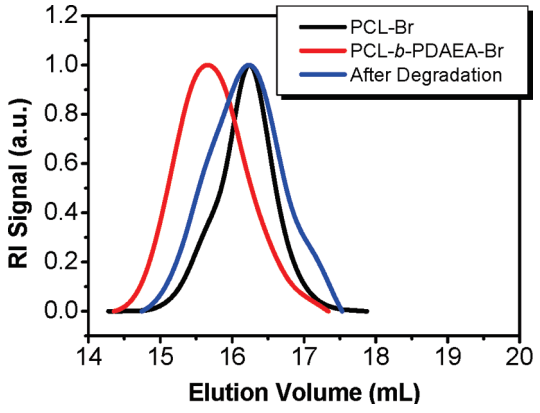


Figure 2. GPC traces of PCL-Br and PCL-*b*-PAEDA-Br prepared by sequential ROP and ATRP (entries 1 and 2 from Table 1) and polymers after acidic degradation.

unimodal peaks with PDI at 1.1−1.25 for all PCL-Br polymers synthesized although the GPC-based molecular weight was a little higher than those obtained from the NMR analysis. These well-defined PCL-Br polymers were then used as macroinitiators for chain extension with PAEDA.

ATRP of AEDA from the PCL-Br macroinitiator was carried out at a temperature of 90 °C in THF (50% v/v of the monomer) using CuBr/Me_6Tren as the catalyst system, as shown in Scheme 2. We have previously demonstrated the living homopolymerization of AEDA by ATRP using ethyl 2-bromoisobutyrate as an initiator in a similar reaction condition.[24] As shown in Figure 3, the kinetic study of the chain-extension from PCL-Br to PAEDA showed a linear semilogarithmic plot, indicating a controlled/living polymerization, consistent with AEDA homopolymerization. Figure 1 shows a typical ^{1}H NMR spectrum of the resulting PCL-*b*-PAEDA-Br diblock copolymer. Peaks at 2.6−2.9 ppm, 4.1−4.3 ppm, 6.7−7.1 ppm are assigned to the protons next to the phenyl ring, the methylene protons of $-OCH_2CH_2O-$ and aromatic protons of the PAEDA block respectively, while peaks at 4.0−4.1 ppm and 2.2−2.4 ppm from the PCL block. All other peaks of dehydroabietic side groups were nearly same as PAEDA homopolymers reported in our earlier work.[24] All these indicated that the PCL-Br has initiated the polymerization of AEDA. The compositions of block copolymers could be calculated

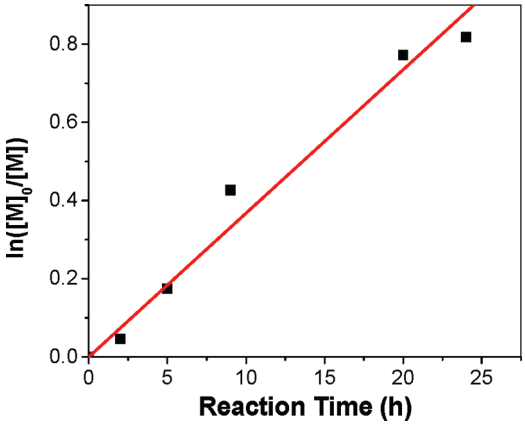


Figure 3. Kinetic plot of chain-extension reaction from PCL-Br to PAEDA by ATRP (entry 2 from Table 1). Reaction conversion was determined by ^{1}H NMR analysis.

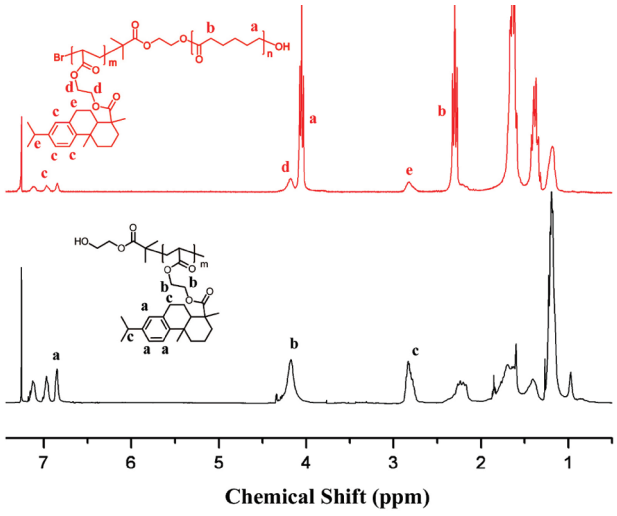


Figure 4. ^{1}H NMR spectra of PAEDA-OH and PAEDA-*b*-PCL-OH prepared by two-step sequential ATRP and ROP (entries 3 and 4 from Table 1).

by the integration areas of the characteristic protons from respective AEDA and CL blocks and are presented in Table 1. The GPC traces shifted clearly to a higher molecular weight with PDI ∼ 1.3 (Figure 2), indicating the successful chain-extension of PAEDA from the PCL-Br macroinitiator.

b. Chain Extension from PAEDA-OH to PCL: Diblock Copolymers PAEDA-b-PCL-OH. In parallel, PAEDA-OH prepared by ATRP was used as the macroinitiator for chain extension with PCL. PAEDA-OH was prepared using HEBiB as the initiator and CuBr/Me_6Tren as the catalyst system in the presence of THF, similar to the procedure reported in our earlier work.[24] The ^{1}H NMR spectrum (Figure 4) of PAEDA-OH shows characteristic signals of aromatic protons, methylene protons of $-OCH_2CH_2O-$, protons from $-CH_2-CH-$ backbone, and all other protons of dehydroabietic side groups. Hydroxyl-terminated PAEDA polymers were further utilized for ROP of CL using $Sn(Oct)_2$ as the catalyst in the presence of toluene, yielding PAEDA-*b*-PCL-OH diblock copolymers. The ^{1}H NMR spectrum clearly indicated the formation of PAEDA-*b*-PCL-OH block copolymers with characteristic protons from both blocks, similar to those from PCL-*b*-PAEDA-Br diblock copolymers. GPC traces (Figure 5) of the diblock copolymers shifted further into the higher molecular weight

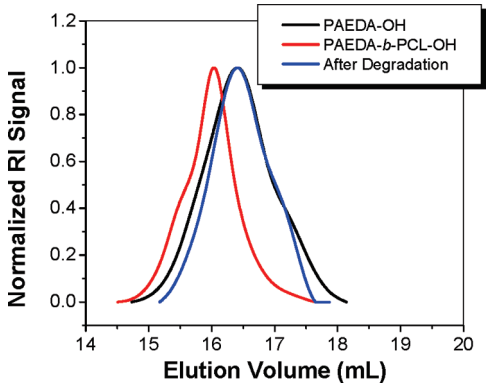
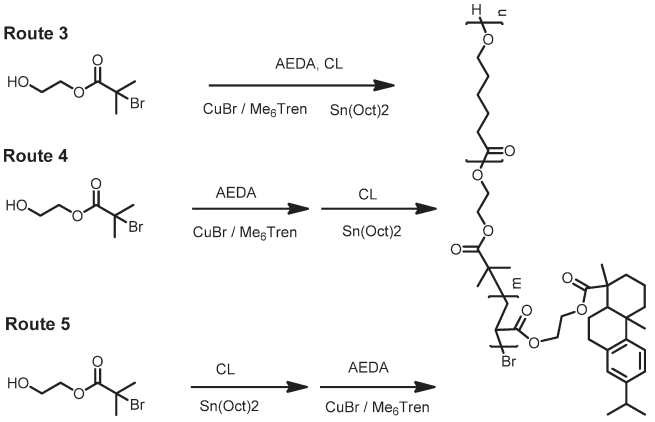


Figure 5. GPC traces of PAEDA-OH and PAEDA-*b*-PCL-OH prepared by two-step sequential ATRP and ROP (entries 3 and 4 from Table 1) and polymers after acidic degradation.

Scheme 3. One-Pot Polymerization of CL and AEDA To Prepare Diblock Copolymers by ROP and ATRP



with PDI ~ 1.3, indicating efficient chain extension. The chain length of the PCL block can be controlled by changing the molar ratio of monomers to macroinitiators. As high as DP = 500 was obtained for the PCL block, while keeping the PDI of PAEDA-*b*-PCL-OH block copolymers as low as 1.18.

2. One-Pot Polymerization. Although there are many precedent reports on the combination of ROP and ATRP in one pot,[42−47] the preparation of caprolactone-based renewable degradable block copolymers is rare. The two initiating sites of the HEBiB initiators have the potential to allow the synthesis of block copolymers in one pot without an intermediate work-up step.[42,43,47] We carried out the one-pot polymerization using three different routes, as shown in Scheme 3. Route 3 was used to polymerize CL and AEDA simultaneously in one pot. Routes 4 and 5 adopted a one-pot sequential feeding polymerization, in which one monomer was polymerized first followed by adding the second monomer into the first monomer reaction system without an extra work-up process.

a. One-Pot Simultaneous Polymerization. Route 3. The mixture of CL, AEDA, and HEBiB with same molar ratios of monomers to initiators ([CL]/[HEBiB] = [AEDA]/[HEBiB] = 100) in dry toluene was employed for simultaneous polymerization with $Sn(Oct)_2$ and $CuBr/Me_6Tren$ as the catalysts for ROP and ATRP, respectively. After 24 h polymerization, the ^1H NMR spectrum (Figure 6) shows a typical block copolymer composition distribution although the PCL block (DP = 32) was shorter than the PAEDA block (DP = 70). The GPC trace of the obtained block copolymers (Figure 7) shows narrow molecular weight distribution with the PDI = 1.24, indicating a good control on

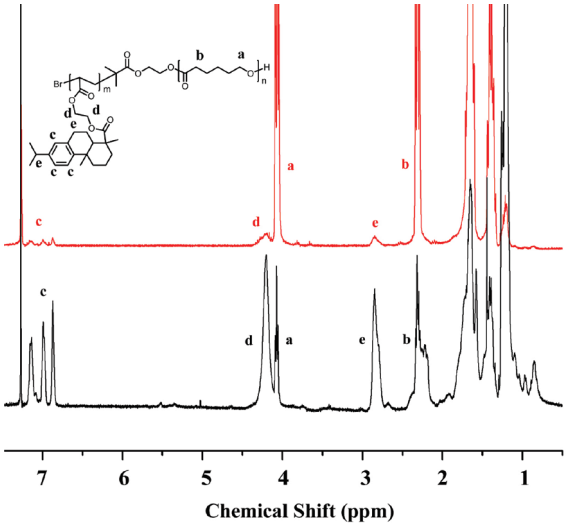


Figure 6. ^1H NMR spectra of AEDA and CL diblock copolymers prepared by one-pot simultaneous ATRP and ROP (entries 5 (bottom NMR) and 6 (top NMR) from Table 1).

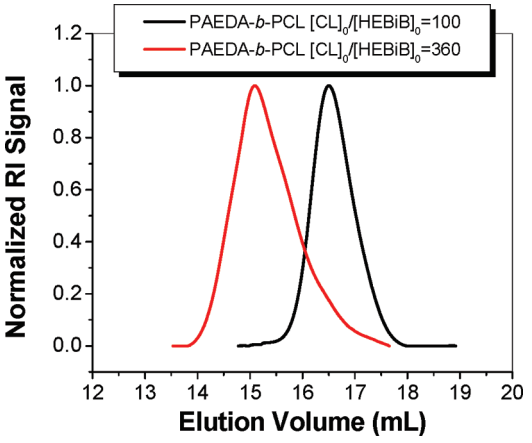


Figure 7. GPC traces of AEDA and CL diblock copolymers prepared by one-pot simultaneous ATRP and ROP (entries 5 (right trace) and 6 (left trace) from Table 1).

both blocks. When the molar ratio of CL to HEBiB increased ([$Sn(II)(EH)_2$] proportionally increased) with [AEDA]/[HEBiB] maintained at 100, the molecular fraction of CL in the block copolymers significantly increased. However, the PDI of block copolymers also increased. When the DP of PCL was 320 ([CL]/[HEBiB] = 360), the PDI was 1.66, while the DP of PAEDA was only 16. The increase of PDI indicated the increasingly poor control on polymerization, probably due to the undesirable interactions between the Sn(II) catalysts of the ROP system and the copper(II) catalysts of the ATRP system, which will be discussed in the later section of this paper.

b. One-Pot AEDA-First Polymerization. Route 4: from AEDA to CL. To further explore the effect of ATRP system on the ROP of CL, one-pot polymerization with sequential feeds from AEDA to CL was carried out. ATRP of AEDA was employed first with the use of $CuBr/Me_6Tren$ and HEBiB. After a 24 h reaction, a deoxygenated mixture of CL, $Sn(Oct)_2$, and toluene was added into the above reaction flask. As shown in Figure 8, the GPC trace shows a broad asymmetric distribution with a high PDI = 1.51 (Table 1, entry 7), indicating the poor control of polymerization. Surprisingly, ^1H NMR of the final polymers exhibited almost negligible signals from the PCL block, but most from

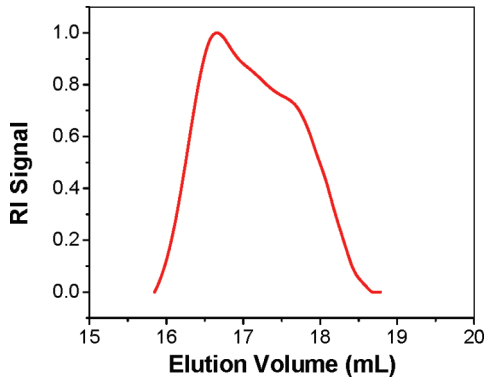


Figure 8. GPC trace of diblock copolymers prepared by one-pot AEDA-first polymerization (entry 7 from Table 1).

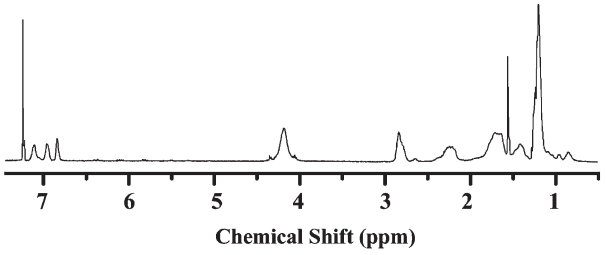


Figure 9. ^{1}H NMR spectrum of diblock copolymers prepared by one-pot AEDA-first polymerization (entry 7 from Table 1).

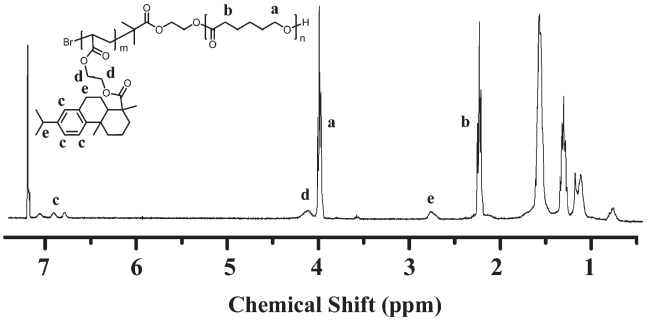


Figure 10. ^{1}H NMR spectrum of diblock copolymers PCL-*b*-PAEDA prepared by one-pot CL-first polymerization (entry 8 from Table 1).

the PAEDA block, as shown in Figure 9. These results indicated that the ROP of CL was almost completely suppressed, most likely due to the deactivation of Sn(II) catalysts by accumulated Cu(II) catalysts after prolonged ATRP of AEDA.

c. One-Pot CL-First Polymerization. Route 5: from CL to AEDA. To circumvent the influence of the ATRP copper catalyst on the ROP, CL was first added to carry out ROP in the presence of $Sn(Oct)_2$ using HEBiB as the initiator and toluene as the solvent. After 16 h, a deoxygenated mixture of AEDA, CuBr/Me_6Tren, and toluene was added into the above polymerization system to start the ATRP of AEDA. The ^{1}H NMR spectrum (Figure 10) shows that this strategy did allow the preparation of block copolymers with desirable lengths of PCL and PAEDA blocks. Even the PCL block has a DP as high as 200, a DP of 20 for the PAEDA block was achieved when the feed ratio of [AEDA]/[HEBiB] was 60, indicating that the end group −Br from the PCL chain was efficient to initiate the polymerization of AEDA. The GPC trace (Figure 11) shows a slightly asymmetric distribution, with a reasonable low PDI = 1.38. It also indicated that the tin-based catalyst had minimal impact on the ATRP

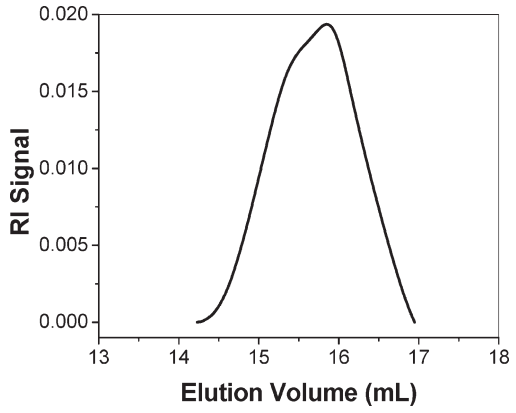
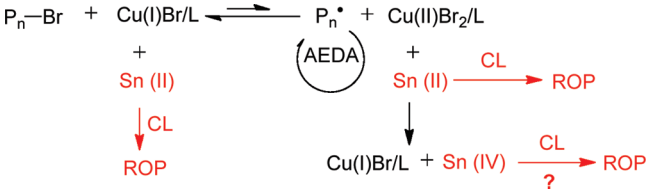


Figure 11. GPC trace of diblock copolymers prepared by one-pot CL-first polymerization (entry 8 from Table 1).

Scheme 4. A Proposed Mechanism for One-Pot Polymerization of CL and AEDA by ROP and ATRP



of AEDA. The higher DP of AEDA can be achieved by changing the feed ratio of [AEDA]/[HEBiB].

d. The Role of Tin Catalysts vs Copper Catalysts in One-Pot Polymerization. From the one-pot polymerization, it appeared that both the monomer feed sequence (therefore the catalyst feed sequence) and the catalyst amount played important roles in controlling the polymerization. The work of activator regenerated by electron transfer (ARGET) ATRP[48,49] indicated that Sn(II) can reduce Cu(II) catalysts of ATRP to form Sn(IV) and Cu(I). In the one-pot AEDA-first reaction system, prolonged ATRP of AEDA would produce significant persistent radicals Cu(II) species, which could oxide the newly added Sn(II) catalysts when CL was fed. From this perspective, it is not very unexpected that one-pot polymerization with sequential feeds from AEDA to CL was poorly controlled. The resulting Sn(IV) seemed to be problematic as a catalyst for ROP of CL in the current system. When CL and $Sn(II)(Oct)_2$ were proportionally increased (therefore the increase of molar ratio of $[Sn(II)(Oct)_2]$/[Cu(I)Br]) in the one-pot simultaneous polymerization system, a decrease of the AEDA block length and an increase of the CL block length were observed ($PAEDA_{16}$-PCL_{320}, Table 1, entry 6), also probably due to the undesirable reduction of persistent radicals Cu(II) by the large excess of Sn(II) species in the reaction system. The proposed mechanism of one-pot polymerization by ROP and ATRP is summarized in Scheme 4. Overall, the control of one-pot AEDA-first polymerization is limited toward well-defined block copolymers.

Degradability of Diblock Copolymers of AEDA and CL. Diverse diblock copolymers of AEDA and CL prepared from the above five routes were employed degradability tests. The block copolymers were dissolved in THF with a concentration of 30% HCl. After the hydrolysis of diblock copolymers PCL-*b*-PAEDA-Br in acidic solution, the GPC traces (Figure 2) show clear shift to lower molecular weight with symmetric distribution, presumably from the undegraded PAEDA-Br block. Additional evidence of PCL degradation is from the two-step chain extension from PAEDA-OH to PCL.

GPC traces (Figure 5) indicated that the macroinitiators PAEDA-OH had an identical trace with the undegraded polymers after the hydrolysis. ^{1}H NMR analysis indicated that undegraded polymers did not show any structures from the PCL block, but all characteristic signals originating from the PAEDA block, further confirming the complete degradation of the PCL block. It should be pointed out that most of rosin acid-derived polymers are not degradable to an appreciable extent under similar acidic conditions employed for PCL degradation tests. However, the rosin acid moiety is potentially biodegradable by microbials,[39,40] which is beyond the scope of current work.

Thermal Properties of Diblock Copolymers of AEDA and CL. The thermal properties of diblock copolymers of AEDA and CL were characterized with the aid of differential scanning calorimetry (DSC). As expected, homopolymers PCL-Br showed a characteristic strong endothermic melting peak at ~55 °C. Thermal behaviors of CL and AEDA diblock copolymers exhibited a strong correlation with the length and fraction of the PCL block in the block copolymers (Figure 12). Block copolymers with high fractions of PAEDA (PCL_{41}-*b*-$PAEDA_{41}$-Br) exhibited suppression of the PCL crystallization. The DSC curve shows only the T_g of the PAEDA block at ~50 °C, an amorphous block consistent with our earlier report.[24] No melting peak was observed, indicating the suppression of crystallization of the PCL block. However, a strong endothermic peak at ~55 °C was observed for block copolymers with high fraction of the PCL block ($PAEDA_{50}$-*b*-PCL_{500}-OH), corresponding to the melting of the PCL block. Although the T_g of the PAEDA block is also close to the melting temperature of the PCL block, it is not surprising that the glass transition was not observable in the spectrum, which is dominated by the strong endothermic peak in the almost same range of temperature.

Such thermal behaviors were further confirmed by AFM experiments on thin films (~50 nm thick) of diblock copolymers of CL and AEDA. Tapping-mode AFM imaging (Figure 13) was carried out at ambient conditions. AFM height images of block copolymers with high fractions of the PCL block ($PAEDA_{50}$-*b*-PCL_{500}-OH) revealed the formation of small crystals with an average size of a half micrometer and a roughness of ~20 nm. In contrast, thin films of block copolymers with a short length of the PCL block (PCL_{41}-*b*-$PAEDA_{41}$-Br) appeared to be very smooth with an average of roughness below 5 nm. No island-like morphology was observed, indicating the suppression of PCL crystallization, consistent with the DSC results.

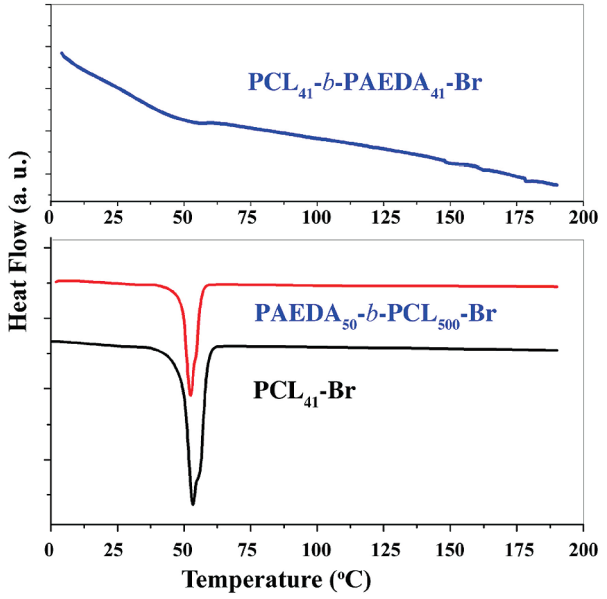


Figure 12. DSC curves of polymers PCL-Br, PAEDA-*b*-PCL-OH, and PCL-*b*-PAEDA-Br.

Conclusions

In conclusion, we have developed a versatile strategy to prepare novel well-defined renewable rosin acid-degradable caprolactone block copolymers. Two-step sequential polymerization and one-pot polymerization were used to prepare dehydroabietic acid-derived acrylate and CL diblock copolymers with the aid of atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). The two-step polymerization with either PCL or PAEDA as a macroinitiator yielded block copolymers with controlled molecular weight and compositions and narrow molecular weight distribution. The one-pot polymerization demonstrated that ROP of CL was greatly affected by the coexisting copper catalysts of ATRP, while ATRP of AEDA was also perturbed with the presence of the excess Sn(II) catalysts. A redox process between Sn(II) and Cu(II) catalysts was proposed to explain the control of one-pot polymerization. PCL segments of these block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence on polymer compositions. The successful synthesis of rosin acid−caprolactone block copolymers has the potential to be extended to other degradable polymers such as lactic acid polymers, opening a new avenue toward development of a variety of rosin acid moiety-containing renewable degradable polymeric materials for advanced applications.

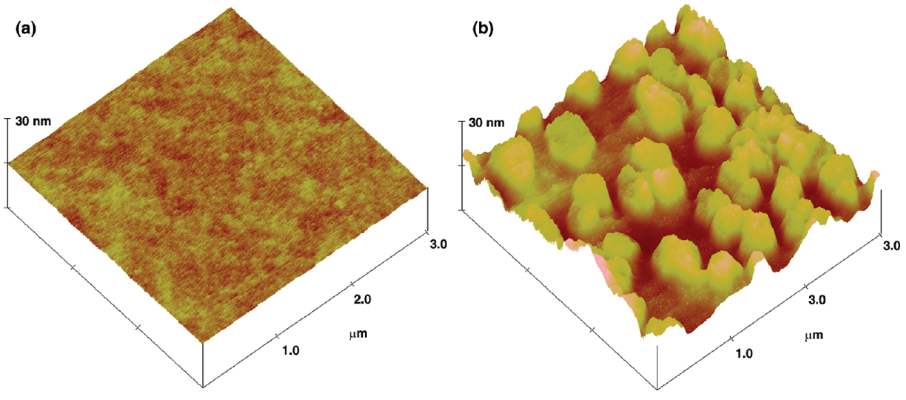


Figure 13. Tapping-mode AFM height images of diblock copolymers (a) PCL_{41}-*b*-$PAEDA_{41}$-Br and (b) $PAEDA_{50}$-*b*-PCL_{500}-OH.

Acknowledgment. We acknowledge the University of South Carolina Start-up Fund for financial support. P.W. acknowledges the Copenhaver Fellowship for support. Y.Z. acknowledges support from Peking University Graduate School Academic Exchange Fund. We thank Drs. Fuxiang Chu, Chunpeng Wang, and Jifu Wang at Chinese Academy of Forestry for providing raw rosin acid materials.

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