# Cylindrical Core−Shell Brushes Prepared by a Combination of ROP and ATRP

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ABSTRACT: A molecular brush with block copolymer side chains, i.e., a crystalline poly($\epsilon$-caprolactone) (PCL) core with an amorphous poly(*n*-butyl acrylate) (PBA) shell, was synthesized by the "grafting from" approach using a combination of atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). The brush was prepared in the following steps. First, a well-defined poly(2-hydroxyethyl methacrylate) (PHEMA) was synthesized by ATRP in a methanol/anisole cosolvent. In the second step, PCL was grafted from the PHEMA macroinitiators by ring-opening polymerization (ROP) in the presence of tin(II) 2-ethylhexanoate ($Sn(EH)_2$) catalyst, and then the pendent hydroxyl groups in the resulting PCL brush were transformed to bromopropionyl ATRP initiating groups. Finally, the PBA chains were grafted from the PCL brush macroinitiators by ATRP. Gel permeation chromatography (GPC) analysis provided evidence for formation of a well-defined block copolymer side chain brush. The melting point and the heat of fusion of the homo-PCL brush and the PCL−PBA block copolymer side chain brush were measured by differential scanning calorimetry (DSC). According to the DSC results, the melting point of the PCL segments in the PCL−PBA block copolymer side chain brush was depressed when compared with a homo-PCL brush. This was due to the PCL crystalline domain being disturbed by the presence of the second PBA block. The crystalline core−amorphous shell structure of the brush was directly visualized by atomic force microscopy (AFM). On the basis of the AFM results, the polymer molecules obtained from the combined methods of ATRP and ROP were indeed well-defined brush macromolecules, indicating successful polymerization at each step.

## Introduction

Bottle brush macromolecules have attracted considerable attention over the past decade for their potential for intramolecular nanoengineering and development of novel material properties, such as supersoft elastomers.[1−3] Bottle brushes are special type of graft copolymers in which multiple polymer chains are grafted to a backbone polymer.[4−9] The side chains are attached densely enough so that they are stretched away from the backbone to form a brushlike conformation.[10−12] To better understand the structure−property relationship of these macromolecules, a series of well-defined polymers where the nature and the length of the side chains, architecture, composition, and the structure of the polymer backbone are systematically varied are required.

Since the establishment of facile methods of ATRP,[13,14] brushes with various molecular architectures, such as starlike multiarm structures,[15−17] cylindrical brush−coil block copolymers,[18,19] brushes with block copolymer side chains,[20−23] and brushes with a gradient in grafting density along the copolymer backbone,[24−27] have been synthesized. Brushes with block copolymer side chains have been studied extensively since intramolecular phase-separated core−shell structures are of great importance for many applications. These include block segment combinations of soft−hard[20] and hydrophilic−hydrophobic.[21,22]

While ATRP has been successfully used to prepare many types of copolymers, it still remains difficult and constraining to synthesize copolymers with different architectures using monomers which polymerize by fundamentally different mechanisms, such as ATRP and ring-opening polymerization (ROP). ROP is a successful procedure for controlled synthesis of aliphatic polyesters[28−30] such as polylactide, polyglycolide, polymandelide, polyvalerolactone, or poly($\epsilon$-caprolactone) (PCL), many of them crystallizable materials. These polymers, and their copolymers, are biodegradable and have been increasingly investigated as materials suitable for pharmacological, biomedical, agricultural, and environmental applications. In most of the reported studies, controlled radical polymerization (CRP) and ROP were studied independently, each preparing well-defined copolymers. However, both techniques can be combined for synthesis of well-defined architectures using either a sequential approach[31−37] or one exploiting simultaneous polymerization by two mechanisms.[31,38−43]

In this article, we demonstrate successful synthesis of brush macromolecules with block copolymer side chains of PCL and poly(*n*-butyl acrylate) (PBA) using a combination of ATRP and ROP. To our knowledge, a molecular brush with a crystalline core and an amorphous shell has not been reported. The crystalline PCL core was synthesized by ROP from a poly(2-hydroxyethyl methacrylate) (PHEMA) backbone. The resulting PCL brush macromolecule was functionalized to provide an ATRP initiator on each PCL chain end, and then an amorphous PBA shell was synthesized by ATRP. The crystallization behavior by DSC and molecular visualization by AFM for the tethered PCL core units, with and without the presence of a PBA shell, were studied.

## Experimental Section

**Materials**. All chemicals were purchased from Aldrich or Acros and used as received unless otherwise stated. 2-Hydroxyethyl

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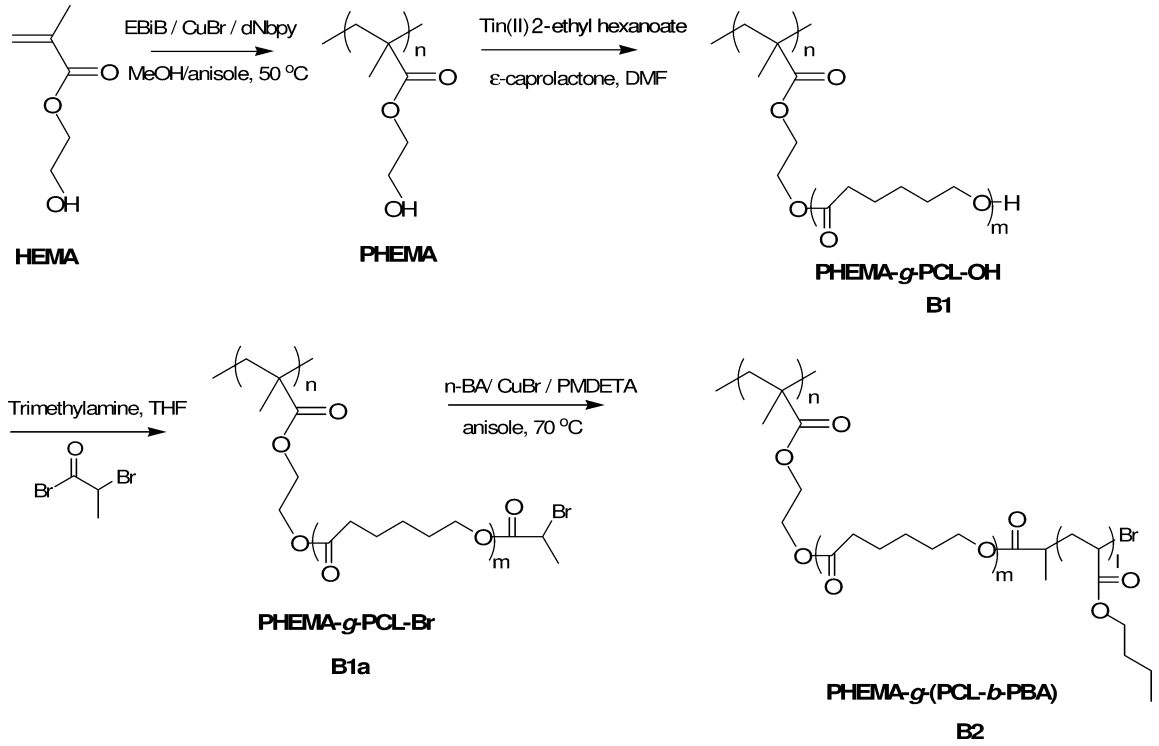
**Scheme 1. Synthesis of a Molecular Brush Containing 2-PCL and PBA in the Side Chains from a PHEMA Backbone**




methacrylate (HEMA) and *n*-butyl acrylate were purchased from Acros and distilled under vacuum prior to use. Caprolactone (99%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), ethyl 2-bromoisobutyrate (98%) (EBiB), 2-bromopropionyl bromide (98%), 4,4′-di-(5-nonyl)-2,2′-bipyridine (dNbpy), triethylamine (98%), dimethylformamide (DMF) (extra dry, less than 50 ppm of water), and tin(II) 2-ethylhexanoate ($Sn(EH)_2$) were purchased from Aldrich Chemical Co. CuBr was purified as described previously.[44] $\epsilon$-Caprolactone (CL), (Aldrich, 99%) was dried over calcium hydride under nitrogen at 25 °C, distilled under reduced pressure, and stored over molecular sieves.

**Equipment and Analysis**. The apparent molecular weight and molecular weight distributions of PHEMA were measured on a GPC system. It consisted of a Waters 510 HPLC pump, three Waters UltraStyragel columns (100, $10^3$, and $10^5$ Å), and a Waters 410 differential refractive index detector, with a DMF flow rate of 1.0 mL/min. Poly(methyl methacrylate) was used as a calibration standard employing WinGPC software from Polymer Standards Service. Apparent molecular weight and molecular weight distributions of the brush copolymers were measured on a GPC (Waters Microstyragel columns (guard, $10^5$, $10^3$, and $10^2$ Å), THF eluent at 35 °C, flow rate = 1.00 mL/min). The detectors consisted of a differential refractometer (Waters 410, $\lambda$ = 930 nm) and a multiangle laser light scattering (MALLS) detector (Wyatt Technology DAWN EOS, 30 mW, $\lambda$ = 690 nm). Apparent molecular weights were determined with a calibration based on poly(methyl methacrylate) (PMMA) standards using GPCWin software from Polymer Standards Service. Absolute molecular weights were determined with the d*n*/d*c* values of PCL (0.08 mL/g) and PBA (0.069 mL/g) using Wyatt ASTRA software. $^1$H NMR spectra were collected in deuterated chloroform at 30 °C using a Bruker 300 MHz spectrometer. Monomer conversion was determined by gas chromatography (GC) using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and ValcoBond 30 m VB WAX Megabore column. Thermal characterization of the PCL containing polymers, (4−7 mg) was carried out with the aid of Seiko DSC 220 (Seiko Instruments, Inc.) operated at a heating rate 10 °C/min. Dilute solutions of each brush sample were prepared using HPLC-grade chloroform from Fisher Scientific. Monolayer samples were prepared either by spin-casting using a spin-coater from Laurell Technologies Corp. (model WS-400A-6NPP/Lite) or by Langmuir−Blodgett deposition using a KSV-5000 with Milli-Q double-distilled water as the subphase (18.2 MΩ·cm) onto mica substrates (grade V-4 from SPI Supplier). A multimode atomic force microscope from Veeco Metrology group equipped with a Nanoscope IIIA control station and silicon cantilevers from Mikromasch USA with resonance frequencies of about 160 kHz, spring constants of 5.0 N/m, and radii less than 10 nm was used for visualization of the prepared films in the tapping mode. Custom computer software was used to obtain length measurements from the captured micrographs. Several images of ~300 molecules were analyzed to ensure a standard error below 2% and an experimental error below 5% in average length measurements.

**Synthesis. Poly(2-hydroxyethyl methacrylate) (PHEMA)**. 0.014 g (0.1 mmol) of CuBr and 0.082 g (0.2 mmol) of dNbpy were added to a 25 mL Schlenk flask and degassed by vacuum followed by nitrogen backfill three times. Solvent (65/35 v/v anisole/methanol, 6.0 mL) and HEMA (7.27 mL, 60 mmol) were degassed by bubbling with nitrogen for 30 min and then added to the Schlenk flask by syringe. An initial sample was taken by syringe, and then the initiator, EBiB (14.68 $\mu$L, 0.1 mmol), was added. The polymerization was conducted at 70 °C for 5 h. When monomer conversion reached 77.5%, the reaction was stopped by opening the flask to air, and the catalyst was removed by passing the solution through alumina. The resulting reaction mixture was precipitated into THF, filtered, and dried under high vacuum at room temperature for 12 h. The isolated polymer was reprecipitated from DMF into THF three times and dried under vacuum at 25 °C for 24 h (DP of PHEMA = 465, as determined GC). $M_n$(GPC) = 63 000 g/mol, $M_w/M_n$ = 1.22.

**Poly[2-hydroxyethyl methacrylate-*graft*-(ε-caprolactone)], PHEMA-*g*-PCL-OH (B1).** PHEMA with $M_n$ (GPC) = 63 000 g/mol and $M_w/M_n$ = 1.22 (0.10 g, $0.16 \times 10^{-2}$ mmol) was placed in a 25 mL Schlenk flask. The flask was sealed and purged with $N_2$ for 30 min. CL (5.26 mL, $4.61 \times 10^{-2}$ mol) and dry DMF (1.5 mL) were added to the flask followed by a solution of $Sn(EH)_2$ (5.0 $\mu$L, $1.5 \times 10^{-2}$ mmol) in dry DMF (1 mL). An initial sample was taken, and then the flask was placed in a thermostated oil bath at 90 °C and stirred. The polymerization was stopped after 90 h, exposed to air, and diluted with THF, and the PCL brush macromolecule was precipitated by addition of the solution to cold methanol. The solid polymer was dried under high vacuum (GPC: $M_n$ = 568 000 g/mol,

$M_w/M_n = 1.57$). $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ in ppm): 4.05 (2H, t, $-[CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$); 3.67 (2H, t, $-OCO-CH_2-CH_2-CH_2-CH_2-CH_2-OH$); 2.36 (2H, t, $-[CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$); 1.3−1.75 (6H, m, $-[CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$).

**Poly[2-hydroxyethyl methacrylate-*graft*-{(2-bromopropionyloxy)-ϵ-caprolactone}], PHEMA-*g*-PCL-Br (B1a).** A sample of the poly[HEMA-graft-(ϵ-caprolactone)] brush (PHEMA-*g*-PCL-OH) (0.6 g (assuming 0.15 mmol of OH groups)) was placed in a 50 mL round-bottom flask. The flask was sealed and purged with $N_2$, and then 20 mL of dry THF was added. Triethylamine (0.42 mL, 3 mmol) was added to the flask, followed by the slow addition of 2-bromopropionyl bromide (0.63 mL, 6 mmol). The reaction mixture was stirred for 48 h at room temperature, and then the functionalized polymer was precipitated by addition to methanol/ice (80/20 w/w). The precipitate was separated, redissolved in 10 mL of $CHCl_3$, reprecipitated into hexane, and dried under vacuum at room temperature for 24 h. $^1$H NMR confirmed complete conversion of the terminal OH groups (GPC MALLS: $M_n$ = 2 500 000 g/mol, $M_w/M_n = 1.25$). $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ in ppm): 4.40 (1H, quart, $Br-CH-CH_3$); 4.21 (2H, t, $-CH_2-CH_2-CH_2-OCO-CH(CH_3)-Br$); 2.36 (2H, t, $-[CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$); 4.07 (2H, t, $-[CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$); 1.85 (1H, quart, $Br-CH-CH_3$); 1.3−1.75 (6H, m, $-[CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-OCO]_n-$).

**Poly[2-hydroxyethyl methacrylate-*graft*-((ϵ-caprolactone)-*block*-*n*-butyl acrylate)], PHEMA-g-(PCL-b-PBA) (B2).** Poly[HEMA-*graft*-{(2-bromopropionyloxy)ϵ-caprolactone}] (0.06 g; assumed to contain 0.014 mmol of initiating groups), *n*-BA (2.88 g, 22.4 mmol), anisole (0.35 mL), and PMDETA (3 μL, 0.014 mmol) were added to a 10 mL Schlenk flask, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 0.5 h at room temperature, CuBr (0.0025 g, 0.014 mmol) was added under nitrogen, and the flask was placed in a preheated oil bath at 70 °C. The polymerization was stopped after 15 h by cooling the flask to room temperature and opening the flask to air. The resulting polymer solution was purified by passing through a column of neutral alumina. Solvent and the remaining monomer were removed under high vacuum (1 mmHg). The resulting product was dried at room temperature for 12 h ($DP_{sc}$ of *n*-BA = 110, as determined by gravimetry; GPC MALLS: $M_n$ = 10 900 000 g/mol, $M_w/M_n = 1.12$).

## Results and Discussion

**Synthesis.** The synthetic route for the preparation of block copolymer brushes with a PCL core and a PBA shell is outlined in Scheme 1. ATRP was used to directly prepare linear PHEMA with controlled molecular weight and low polydispersity. A CuBr/dNbpy catalyst system was used for the homopolymerization of HEMA using ethyl 2-bromoisobutyrate (EBiB) as initiator. Since PHEMA is soluble only in polar solvents, a mixed solvent system of anisole and methanol was employed to ensure a homogeneous reaction mixture throughout the polymerization of HEMA.[45,46] The molecular weight and molecular weight distribution of the linear macroinitiator were obtained on a GPC DMF line using PMMA standards ($M_n$ = 63 000 g/mol, $M_w/M_n$ = 1.22) (Figure 1). The apparent molecular weight obtained by GPC was in agreement with the theoretical molecular weight calculated by monomer conversion ($M_{n,th}$ = conversion × $MW_{HEMA}$ × $[HEMA]_0/[EBiB]_0$ = 60 500 g/mol). Purification of the resulting PHEMA was extremely important since PHEMA is directly used as a macroinitiator for ROP of ϵ-caprolactone (CL). If MeOH and HEMA, which were the reaction solvent and the monomer, respectively, are not completely removed, a linear PCL polymer initiated by MeOH or HEMA can be formed. If the trace of a PCL is formed from the residual HEMA monomer, then macromonomers will be created, which can be incorporated into the side chains on subsequent ATRP of BA. Therefore, the reprecipitation/purification cycle from DMF into THF was repeated several times to ensure that the PHEMA contained no MeOH and HEMA.

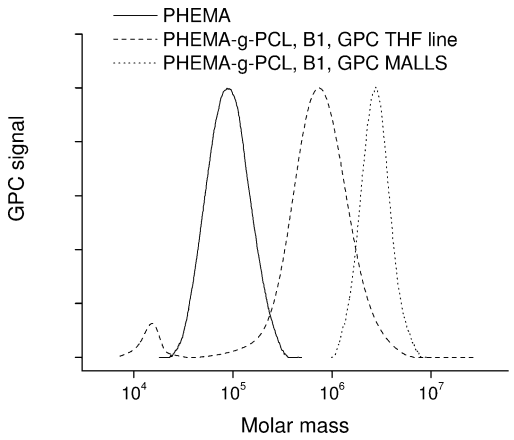



**Figure 1.** GPC traces of PHEMA and the resulting PHEMA-*g*-PCL-OH (**B1**) from GPC THF line and GPC MALLS.

**Table 1. Characterization of the PHEMA Backbone, PHEMA-*g*-PCL-OH (B1), PHEMA-*g*-PCL-Br (B1a), and PHEMA-*g*-(PCL-*b*-PBA) (B2)**

| entry | $DP_{conv}$ | $M_{n,theory}$[d] × $10^{-5}$ | $M_{n,absolute}$[e] × $10^{-5}$ | $M_{n,app}$ × $10^{-5}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| PHEMA | 465[a] | 0.60 | | 0.63[f] | 1.22[f] |
| **B1** | 36[a] | 19.2 | 24.6 | 5.68[g] | 1.26[g] |
| **B1a** | 35[b] | 19.2 | 25 | | 1.25[e] |
| **B2** | 120[a]/110[c] | 93.7 | 109 | | 1.12[e] |

[a] Calculated from conversion measured by gas chromatography. [b] Calculated from $^1$H NMR. [c] Calculated from conversion measured by gravimetry. [d] Calculated from conversion measured by gas chromatography assuming that polymer chains grow uniformly from the all initiating sites. [e] Absolute values determined by GPC MALLS in THF. [f] Apparent values determined by GPC in DMF with PMMA calibration. [g] Apparent values determined by GPC in THF with PMMA calibration.

In the next step, PHEMA was used as a multifunctional macroinitiator for ROP of ϵ-caprolactone. The reaction was carried out in dry DMF in the presence of $Sn(EH)_2$ catalyst at 90 °C. GPC traces of the macroinitiator and resulting brush with grafted PCL side chains are shown in Figure 1. The results confirm that a macromolecular brush was efficiently prepared. The small signal observed in the GPC traces after the second step indicates the presence of a small amount of low molecular weight homo-PCL, presumably initiated by traces of moisture or MeOH or HEMA. A signal from the low molecular weight homo-PCL was not observed, when a light scattering detector was used (Figure 1), since MALLS has poor sensitivity for low molecular weight species. Molecular weight measured by GPC equipped with a RI detector was much lower than when measured by GPC-MALLS (in Table 1: 568 000 vs 2 460 000 g/mol, respectively). This result is common for molecular brushes since the hydrodynamic volume is lower than linear polymers with equivalent molecular weight, giving a small apparent molecular weight.[8]

An esterification reaction was carried out in order to introduce an ATRP initiating group at the end of each grafted side chain. This was accomplished by reacting the PHEMA-*g*-PCL-OH brush (**B1**) with 2-bromopropionyl bromide in dry THF using triethylamine as a base. The isolated brush macroinitiator, PHEMA-*g*-PCL-Br (**B1a**), was characterized by $^1$H NMR spectroscopy. The spectrum provides evidence of complete transformation of the terminal hydroxyl groups to the bromopropionyl ATRP initiating groups. In Figure 2A, the peaks (a and b) at 3.67 and 4.05 ppm represent the methylene protons

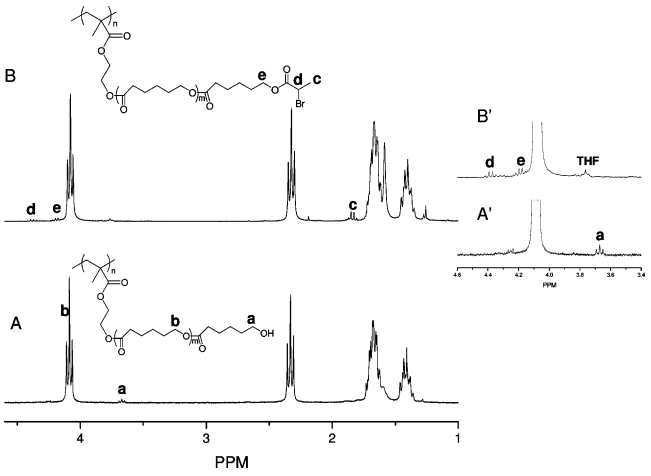



**Figure 2.** $^1$H NMR spectra of (A) PCL brush with the pendant hydroxyl groups, PHEMA-*g*-PCL-OH (**B1**), and (B) PCL brush with the pendant bromopropionyl groups, PHEMA-*g*-PCL-Br (**B1a**). The inset spectra show the expanded area from 3.4 to 4.8 ppm.

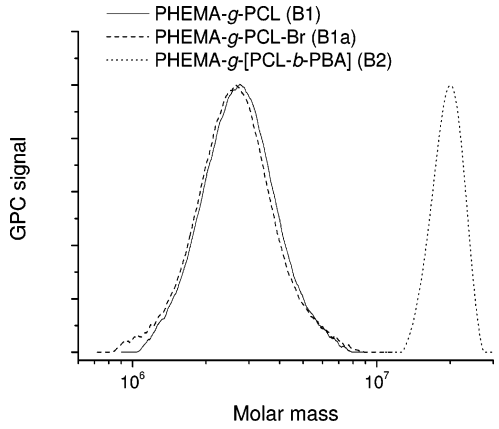



**Figure 3.** GPC MALLS traces for PHEMA-*g*-PCL-OH (**B1**), PHEMA-*g*-PCL-Br (**B1a),** and PHEMA-*g*-(PCL-*b*-PBA) (**B2**).

adjacent to the hydroxyl group and ester groups respectively from **B1**. The integral ratio for these two peaks was used to calculate the DP of PCL units, DP = 35. After transformation to **B1a**, the peak from the methylene protons adjacent to the hydroxyl group (a) at 3.67 ppm disappeared while new peaks (c, d, e) appeared as shown in Figure 2B, indicating a successful transformation. The esterified brush macroinitiator, **B1a**, was also characterized by GPC MALLS. No visible shift in MW was observed as **B1** was transformed to **B1a,** as shown in the overlaid GPC traces (Figure 3).

ATRP of *n*-BA was initiated with the well-defined brush macroinitiator, **B1a**. The polymerization was carried out in the presence of 15 vol % anisole to ensure complete dissolution of the macroinitiator. Since a relatively active PMDETA was used as a ligand, the ratio of [BA]:[**B1a**] was fixed at 1600:1 in order to ensure a low concentration of the active radicals. This provided well-defined block copolymer brushes with long side chains at very low conversion. The increase in the molecular weight of the graft copolymer **B2** is demonstrated by the complete shift of the GPC traces toward higher molecular weight (Figure 3). The molecular weight for the resulting brush was obtained by GPC MALLS. It is advantageous to use MALLS in order to obtain the true molecular weights of highly branched polymers, such as brushes, since it provides the absolute molecular weight of the macromolecule. The molecular weight was $1.1 \times 10^7$, and PDI was 1.12 for the final brush copolymer. The DP of the PBA units, based on measurement of monomer conversion, was determined to be 120 by GC and 110 by gravimetry.

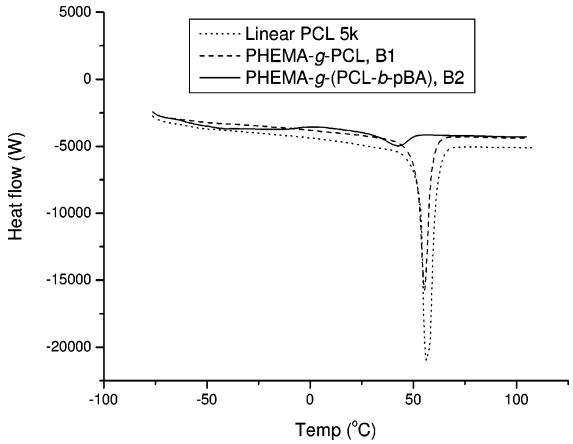



**Figure 4.** DSC thermograms for the series of PCL-containing polymers.

The DSC thermograms for a linear PCL (**L1**), PHEMA-*g*-PCL-OH (**B1**), and PHEMA-*g*-(PCL-*b*-PBA) **(B2**) are shown in Figure 4. The linear PCL (**L1**), which has a similar DP ($M_n$ = 5000) to the PCL incorporated in the side chains of **B1** and **B2**, was used to monitor the crystallization behavior of PCL in an unconstrained free state. While the melting points of **L1** and **B1** are almost the same, the melting point of **B2** was lower and heat of fusion was significantly smaller than that of **L1**. The decrease in the melting point for **B2** is due to a reduction in the ability of the PCL domain to crystallize by the presence of the second PBA block. This structural confinement of the PCL units between the backbone and the PBA phase of the second block can prevent folding of the PCL segments into lamellae of any appreciable size, increasing the disorder. This behavior was also observed from the heat of fusion, which was calculated by $\Delta H$ per unit amount of PCL for each polymer. The heat of fusion for **B2** was 2 times smaller than that for **B1**, which shows that the crystallinity of the PCL segments was greatly reduced after block extension with PBA.

**AFM Analysis of PHEMA-*g*-PCL-OH (B1) and PHEMA-*g*-(PCL-*b*-PBA) (B2).** Molecular visualization of both PHEMA-*g*-PCL-OH (**B1**) and PHEMA-*g*-(PCL-*b*-PBA) (**B2)** macromolecular brushes by AFM was undertaken after each polymerization to verify the success of the synthetic strategy for each step of the process. Visualization of densely grafted polymer brushes is facilitated by side chains, some of which are tightly adsorbed to a substrate while others desorb and segregate atop the backbone. The adsorbed side chains serve to separate each individual macromolecule while the desorbed side chains increase the topographic contrast between the surface and the molecule by creating a distinctly delineated backbone. In addition to separation and contrast enhancement, strong steric repulsion between the adsorbed chains results in the extension of the backbone.[7]

A monomolecular film of the PCL brush (**B1**) was prepared from a dilute chloroform solution and imaged using tapping-mode atomic force microscopy (TMAFM). As shown in Figure 5, the PCL brush copolymers were readily visualized and have a wormlike morphology similar to previously synthesized brushes.[7] With a backbone degree of polymerization $N = 450 \pm 40$ and a contour length $L_N$ of 97 ± 6 nm, the calculated length per monomeric unit, $l_m$, for the PCL brush is 0.22 ± 0.02 nm, very close to the value for a fully stretched all trans C−C−C bond conformation, $l_{max} = 0.25$ nm.[7] In addition, the length polydispersity index PDI ($L_w/L_n$) = 1.3 ± 0.3 is within

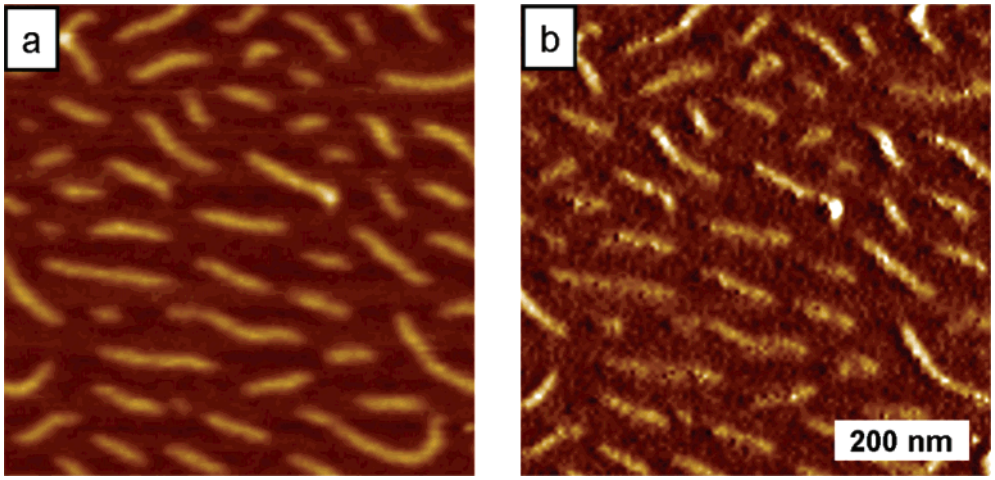



**Figure 5.** (a) Height and (b) phase image of the PHEMA-*g*-PCL-OH brushes (**B1**) adsorbed onto mica.

**Table 2. DSC Data for the Series of PCL-Containing Polymers.**

| | linear PCL 5K | PHEMA-*g*-PCL-OH B1 | PHEMA-*g*-(PCL-*b*-PBA) B2 |
|---|---|---|---|
| melting point (°C) | 56.4 | 55.4 | 42.7 |
| $\Delta H$ (mJ) | 105.3 | 68.6 | 10.8 |
| amount of sample tested (mg) | 6.3 | 3.8 | 4.9 |
| $\Delta H$/amount of sample tested (J $g^{-1}$) | 16.7 | 18.1 | 2.2 |
| weight % of PCL[a] | 100.0 | 96.9 | 20.0 |
| $\Delta H$/amount of PCL (J $g^{-1}$) | 16.7 | 18.7 | 11.0 |

[a] Calculated from the theoretical molecular weight in Table 1.

**Table 3. Summary of Results for Length and Molecular Weight Analyses for PHEMA-*g*-PCL-OH (B1) and PHEMA-*g*-(PCL-*b*-PBA) (B2)**

| brush sample | $L_N$ (nm)[a] | PDI[b] | $l_m$ (nm)[c] | $D$ (nm)[d] | $M_n$ (g/mol)[e] |
|---|---|---|---|---|---|
| PHEMA-*g*-PCL-OH (**B1**) | 97 ± 6 | 1.3 ± 0.3 | 0.22 ± 0.02 | 48 ± 3 | (2.5 ± 0.7) × $10^6$ |
| PHEMA-*g*-(PCL-*b*-PBA) (**B2**) | 100 ± 6 | 1.1 ± 0.3 | 0.22 ± 0.02 | 130 ± 8 | (1.2 ± 0.3) × $10^7$ |

[a] Number-average contour length. [b] Polydispersity index = $L_w/L_n$. [c] Length per monomeric unit = $L_n/N$. [d] Distance between molecules in a dense monolayer. [e] Number-average molecular weight by the AFM-LB technique.

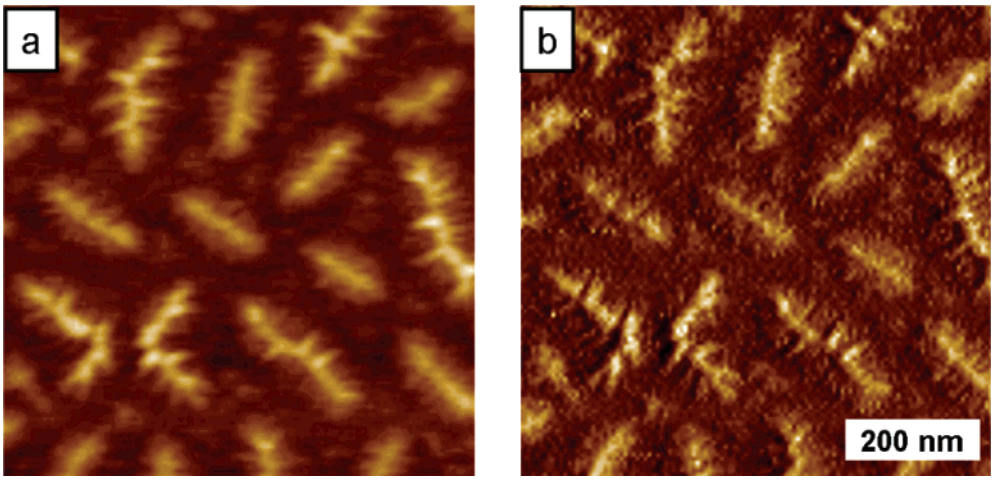



**Figure 6.** (a) Height and (b) phase image of the PHEMA-*g*-(PCL-*b*-PBA) brushes (**B2**) adsorbed onto mica.

statistical error of that obtained from GPC-MALLS ($M_w/M_n$ = 1.2). The distance $D$ between PCL brush molecules is $D$ = 48 ± 3 nm. The number-average molecular weight $M_n$ was calculated from the dense film using the AFM-LB technique,[47] and the result $M_n$ = (2.5 ± 0.7) × $10^6$ g/mol also agrees with that measured by GPC MALLS, $M_n$ = 2.46 × $10^6$ g/mol. The results are summarized in Table 3.

Unlike amorphous brushes, crystallization of the side chains in PCL brushes might hinder adsorption of the side chains and thus alter the molecular conformation, resulting in a globular conformation of brush molecules. However, AFM visualization of the fully extended backbone suggests that adhesion to the substrate is strong enough to prevent three-dimensional (bulk) crystallization of the PCL side chains.

Using the **B1a** as a precursor multifunctional macroinitiator, the living PCL side chains were further chain-extended with PBA via ATRP, thus creating brushes with block copolymer side chains. A monolayer film of the PHEMA-*g*-(PCL-*b*-PBA) (**B2**) was prepared, and the films were visualized using TMAFM. Similar to **B1**, the densely grafted **B2** macromolecules had clearly delineated and extended backbones resulting from side-chain desorption and repulsion (Figure 6). Both the height and phase images provide proof of chain extension. More importantly, one observes the presence of distinct stripes within

the corona. This unique feature is only seen with the block copolymer brushes **(B2)**. This morphological difference between the PHEMA-*g*-PCL-OH (**B1**) and the PHEMA-*g*-(PCL-*b*-PBA) brushes (**B2**) is quite striking, and the reason for this phenomenon is currently under investigation. The stripes are attributed to a very peculiar microphase separation of the crystalline PCL core blocks and amorphous PBA corona blocks. This system is very frustrated since the phase separation is confined within one molecule, and it is strongly constrained due to the covalent connectivity of the side chains. These constraints may result in adsorption of PBA blocks on the surface of the adsorbed PCL core blocks or crystallization of PCL blocks on top of the layer of PBA segments.

Because the PHEMA-*g*-(PCL-*b*-PBA) brushes (**B2**) used the PCL brushes as a precursor, the results from a length analysis of **B2** should be within experimental error of the **B1** brush, and that is indeed the case. With $L_n = 100 \pm 6$ nm, the calculated $l_m$ for the **B2** brush is also $0.22 \pm 0.02$ nm, which is identical to the PCL brush; i.e., PBA sections do not lead to additional extension or contraction of the backbone despite the morphological change. The length polydispersity is determined to be PDI $= 1.1 \pm 0.3$. For **B2** brush molecules in a dense monolayer, $D = 130 \pm 8$ nm, which is also consistent with $n$ calculated by gas chromatography ($n = 120 \pm 20$). Last, the $M_n = (1.2 \pm 0.3) \times 10^7$ g/mol calculated from the dense film also agrees with results from GPC MALLS ($M_n = 1.09 \times 10^7$ g/mol). All the results are summarized in Table 3.

Based on the results of the AFM studies, the polymeric materials obtained by combining ROP and ATRP for the sequential polymerization of two segments of a block copolymer from a multifunctional macroinitiator were indeed brush macromolecules, indicating that polymerization at each step was successful. This provides an opportunity for creating new materials by controlled polymerization procedures now that ROP of cyclic monomers such as $\epsilon$-caprolactone can be used in conjunction with ATRP and with one still able to maintain control over each step and create well-defined molecules.

## Conclusions

A bottle brush macromolecule with block copolymer side chains was synthesized employing ROP and ATRP for individual stages of the copolymerization. The PHEMA backbone was synthesized by ATRP in the initial step. Purification of the resulting PHEMA was extremely important since the PHEMA is directly used as a macroinitiator for ROP of CL. A crystalline PCL core was grafted from the PHEMA backbone by ROP. The hydroxyl groups on the active chain end of the resulting PCL brush polymer were transformed into bromopropionyl groups for further chain extension to form an amorphous PBA shell by ATRP. The DP of the PHEMA backbone, the PCL side chain, and PBA side chain were 465, 35, and 110, respectively, yielding brushes with $M_n = 1.1 \times 10^7$ and $M_w/M_n = 1.12$. DSC results showed that the melting point for the PCL segments in the block copolymer side chain brush, **B2**, was depressed when compared with the homo-PCL brush, **B1**. Based on the results of AFM studies of densely cast polymer films, the polymer molecules, obtained by combining ATRP and ROP for the controlled synthesis of individual polymer segments, were indeed brush macromolecules, indicating that the controlled polymerization procedures used at each step was successful.

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