Supporting Information

"Grafting-from" synthesis of polyvinyl ether bottlebrush polymers via a combination of cationic polymerization and ATRP

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Materials

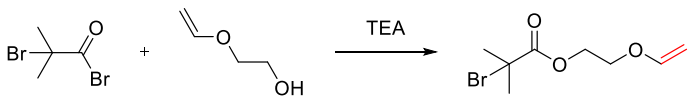
Methyl methacrylate (MMA), n-butyl acrylate (BA) and Styrene (St) were purchased from TCI chemicals. MMA was first degassed and dried over CaH_2 overnight, followed by vacuum distillation; then MMA was further purified by titration with neat tri(n-octyl)aluminum (Aldrich Chemical) to a yellow end point1 and distillation under reduced pressure. The monomer was deoxygenized by freeze-pump-thaw cycle three times, stored under a nitrogen atmosphere and sealed up. BA was degassed and dried over CaH_2, followed by vacuum distillation. St, and BA were purified by passing it through a plug of aluminum oxide (activated, basic) to remove the inhibitor, deoxygenized by freeze-pump-thaw cycle three times, backfilled with argon and sealed up. Subsequently, all of the purified monomers were stored under inert atmosphere at -20°C. Copper(I) bromide (Aldrich, 98%) was purified by steering over glacial acetic acid (Fisher Scientific), followed by filtration and washing of the solid three times with ethanol and twice with diethyl ether. The solid was dried under vacuum ($1*10^{-2}$ mbar) for 2 days. All other chemicals were purchased from Adamas-beta, Energy Chemical and Shanghai Chemical Reagents Co., Ltd. and used without further purification unless mentioned.

Characterisation

^1H NMR were recorded on Bruker AVIII 400 MHz or JEOL JNM-ECZ500R/S1 500 MHz in $CDCl_3$ with tetramethylsilane as the internal standard. The number-average molecular weight ($M_{n,GPC}$) and molecular weight distributions ($Đ$) of the obtained polymers were determined by a Waters 1515 series gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive-index detector, using a Styragel HR3THF (7.8×300 mm) Column and a Styragel HR4THF (7.8×300 mm) Column with measurable molecular weights ranging from 10^2 to 10^6 g mol^{-1} . THF was used as eluent at a flow rate of 1.0 mL/ min at 40 °C. GPC samples were injected manually and Shodex Polystyrene samples of known molecular weight were used as calibration standards for the experimental number-average molecular weight (M_n) and molecular weight distributions ($Đ$). DSC measurements were performed using a Mettler ToledoDSC3 calorimeter. Two scanning cycles of heating-cooling were performed in the temperature range from -40 to 180 °C with heating rates of 10 °C/min under nitrogen. T_g was determined from the second heating run. In scan assist mode, at Agilent 5500 scanning probe microscope, Agilent Technologies, Inc. Atomic Force microscope (AFM) images were obtained Using the Scan Asyst-air probe, the spring constant is 0.4N /m. The AFM samples were prepared by spin-casting from dilute dichloromethane solutions (0.01 mg/mL) on freshly cleaved mica substrates.

Synthetic Procedures

Synthesis of 2-vinyloxyethyl 2-bromoisobutyrate (VEBB)



VE (8.8 g, 100 mmol) and TEA (12.12 g, 120 mmol) were dissolved in 80 mL of anhydrous CH_2Cl_2 followed by cooling the solution with an ice bath for 40 min. Then, 20 mL of CH_2Cl_2 solution containing BIBB (25.8 g, 110 mmol) was slowly added, and the reaction system was allowed to warm to ambient temperature. After 5 h, CH_2Cl_2 was condensed and washed with saturated NaCl aqueous solution and deionized water three times to remove the byproducts. The organic phase was dried by anhydrous Na_2SO_4 and condensed to remove the solvent. VEBB was obtained after drying under vacuum for 2 days (22.5 g, 95% yield). ^{1}H NMR (200 MHz, $CDCl_3$, δ/ppm): 6.45 (q, 1H), 4.39 (t, 2H), 4.13 (dd, 1H), 4.08 (dd, 1H), 3.91 (t, 2H), 1.92 (6H).

General procedure for the synthesis of PVEBB via cationic polymerization

The preparation of reaction mixture was conducted in an inert nitrogen atmosphere in a glove box. VEBB (2 mmol, 25 eq, for the synthesis of PVEBB25) and toluene ([VEBB] = 0.4 M) were added to a flame-dried Schlenk bottle fitted with a magnetic stirring bar. The reaction mixture was then cooled in a dry ice/acetone bath (-78 °C) outside the glove box under positive argon pressure. Toluene solution of $HNTf_2$ (1 eq) was added through an airtight Hamilton syringe. To check the progress of polymerization, a sample was subjected to ^{1}H NMR analysis in $CDCl_3$ (0.6 ml) by quenching with a MeOH:TEA solution (10:1/20 μL). The completion of polymerization was determined by the disappearance of the C-H vinyl signal at 6.45 ppm (Conv > 99.9%, $M_{n,theo}$ = 4.2 kg mol^{-1}). A MeOH:TEA solution (10:1/50 μL, 0.34 eq TEA) was added to terminate the reaction after 20 minutes. PVEBB was isolated by precipitation in methanol twice and dried overnight in a vacuum oven. The PVEBB of different DP can be prepared by changing the ratio of [VEBB]/([$HNTf_2$]) by changing the dosage of $HNTf_2$ while keeping the molar concentration of VEBB unchanged.

General procedure for the synthesis of PVEBB-*g*-PMMA with ATRP

Samples of PVEBB (assuming a Br starting group of 0.02 mmol), MMA (2 mmol), anisole (0.212 mL), and PMDETA were added to a 10 mL Schlenk flask and degassed through three freeze pump-thaw cycles. CuBr ([MMA]/[CuBr]/[PMDETA] = 800/1/1) was then added under nitrogen. After stirring at room temperature for 0.5 h, the flask was placed in a preheated oil bath at 70℃. After 22 h, polymerization was stopped by cooling the flask to room temperature and opening the flask to contact with air. The resulting polymer solution was purified through a short neutral alumina column. The solution was then added to methanol to precipitate the polymer. The precipitation was separated, washed with methanol and dried in vacuum at room temperature for 24 h to afford the desired PVEBB-*g*-PMMA polymers.

Preparation of PVEBB-*g*-PBA

PVEBB (assuming a Br starting group of 0.02 mmol), BA (2 mmol), anisole (0.212 mL) and PMDETA were added to a 10 mL Schlenk flask and degassed through three freeze pump-thaw cycles. CuBr ([BA]/[CuBr]/[PMDETA] = 800/1/1) is then added under nitrogen. After stirring at room temperature for 0.5 h, the flask was placed in a preheated oil bath at 70℃. After 22 h, polymerization was stopped by cooling the flask to room temperature and opening the flask to contact with air. The resulting polymer solution was purified through a short neutral alumina column. The solution was then added to methanol to precipitate the polymer. The precipitation was separated, washed with methanol and dried in vacuum at room temperature for 24 h to afford the desired PVEBB-*g*-PBA polymers.

Preparation of PVEBB-*g*-PS

PVEBB (assuming a Br starting group of 0.02 mmol), St (2 mmol), anisole (0.212 mL) and PMDETA were added to a 10 mL Schlenk flask and degassed through three freeze pump-thaw cycles. CuBr ([St]/[CuBr]/[PMDETA] = 800/1/1) was then added under nitrogen. After stirring at room temperature for 0.5 h, the flask was placed in a preheated oil bath at 70℃. After 22 h, polymerization was stopped by cooling the flask to room temperature and opening the flask to contact with air. The resulting polymer solution was purified through a short neutral alumina column. The solution was then added to methanol to precipitate the polymer. The precipitation was separated, washed with methanol and dried in vacuum at room temperature for 24 h to afford the desired PVEBB-*g*-PS polymers.

Table S1. Summary of PVEBB-g-PBA bottlebrush prepared via grafting-from PVEBB backbone.

Entry	[BA]/[I]	$M_{n,theo}$ (kg mol^{-1})[b]	$M_{n,NMR}$ (kg mol^{-1})[a]	$M_{n,GPC}$ (kg mol^{-1})[c]	Đ[c]	BBP
1	20:1	16.2	12.8	11.4	1.3	PVEBB25-*g*-PBA2
2	30:1	19.2	21.6	20.1	1.2	PVEBB25-*g*-PBA4
3	40:1	25.0	29.3	23.3	1.19	PVEBB25-*g*-PBA7
4	50:1	36.1	46.1	36.3	1.18	PVEBB25-*g*-PBA10
5	80:1	41.5	46.9	42.1	1.17	PVEBB25-*g*-PBA12
6	200:1	63.2	57.5	55.8	1.17	PVEBB25-*g*-PBA19

Table S2. Summary of PVEBB-g-PS bottlebrush prepared via grafting-from PVEBB backbone.

Entry	[St]/[I]	$M_{n,theo}$ (kg mol^{-1})[b]	$M_{n,NMR}$ (kg mol^{-1})[a]	$M_{n,GPC}$ (kg mol^{-1})[c]	Đ[c]	BBP
1	25:1	12.2	12.9	13.4	1.14	PVEBB25-*g*-PS3
2	75:1	25.5	20.5	12.9	1.13	PVEBB25-*g*-PS8
3	100:1	40.5	40.7	40.1	1.12	PVEBB25-*g*-PS14

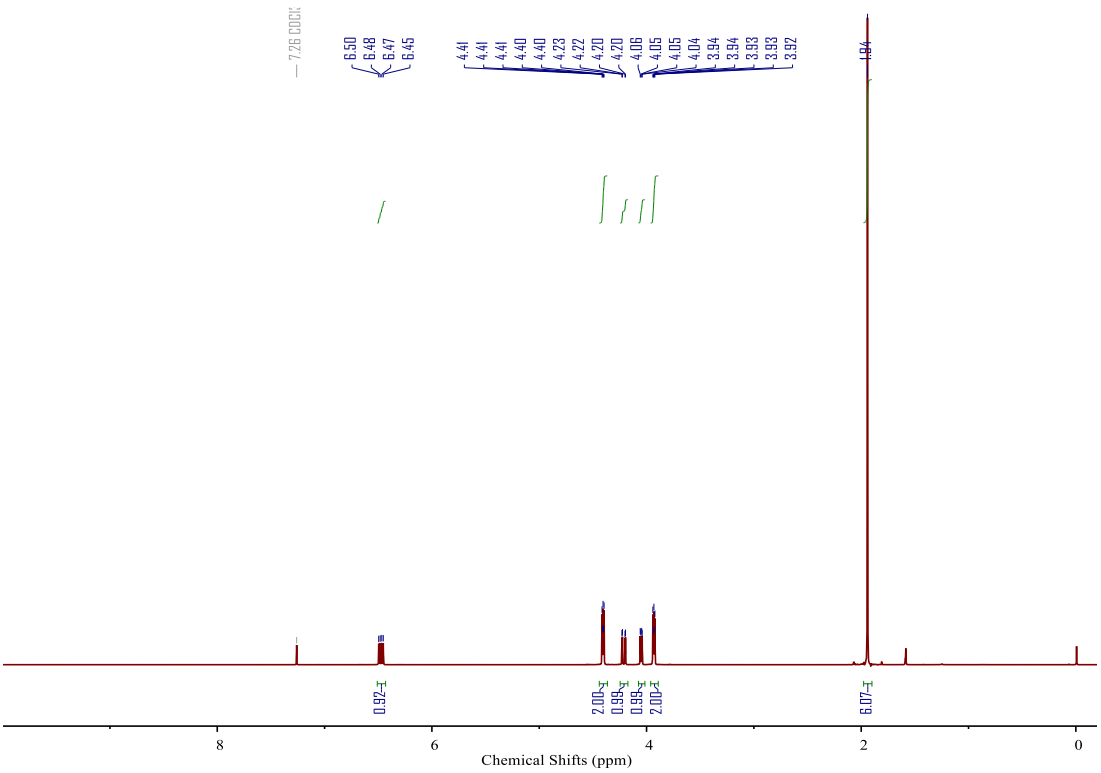


Figure S1: ^{1}H NMR spectrum of VEBB in $CDCl_3$

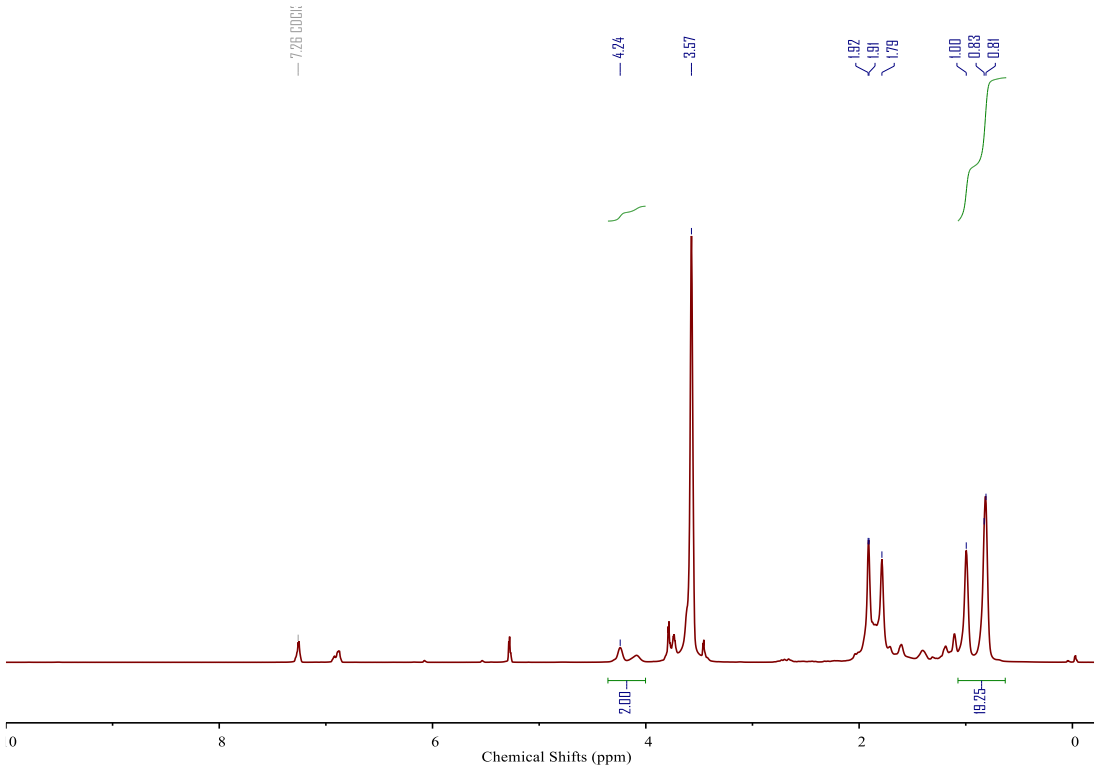


Figure S2: ^{1}H NMR spectrum of PVEBB25-*g*-PMMA6 in $CDCl_3$

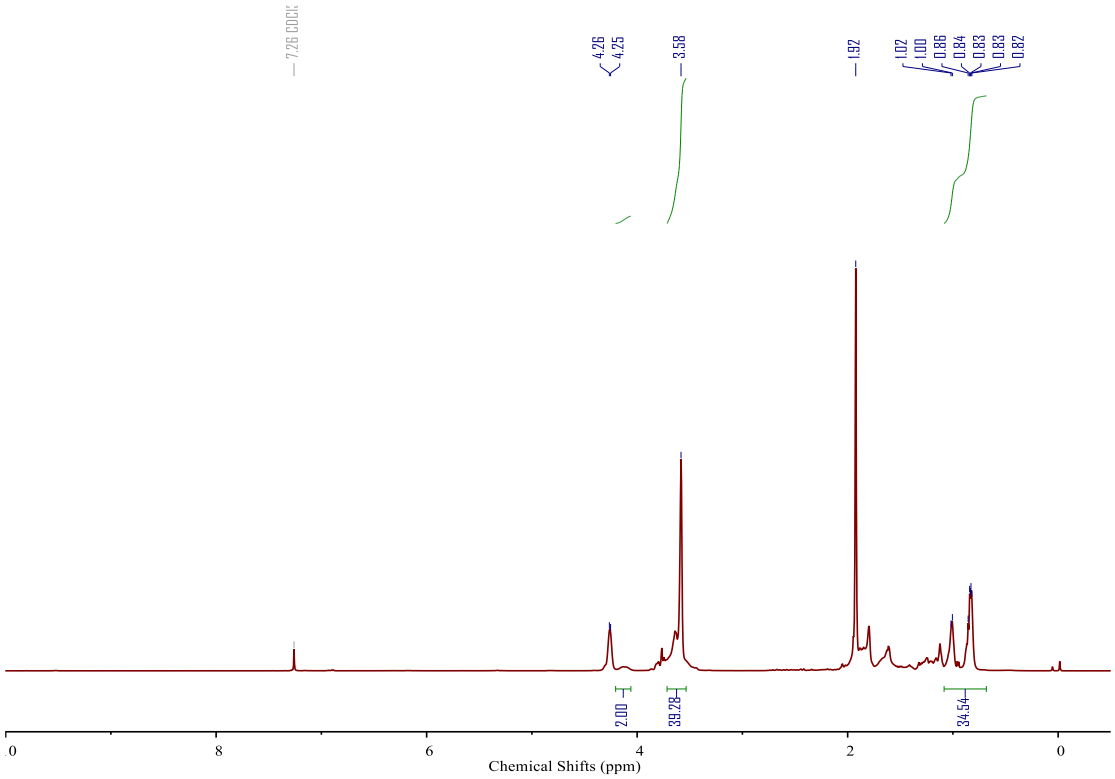


Figure S3: ^{1}H NMR spectrum of PVEBB25-*g*-PMMA13 in $CDCl_3$

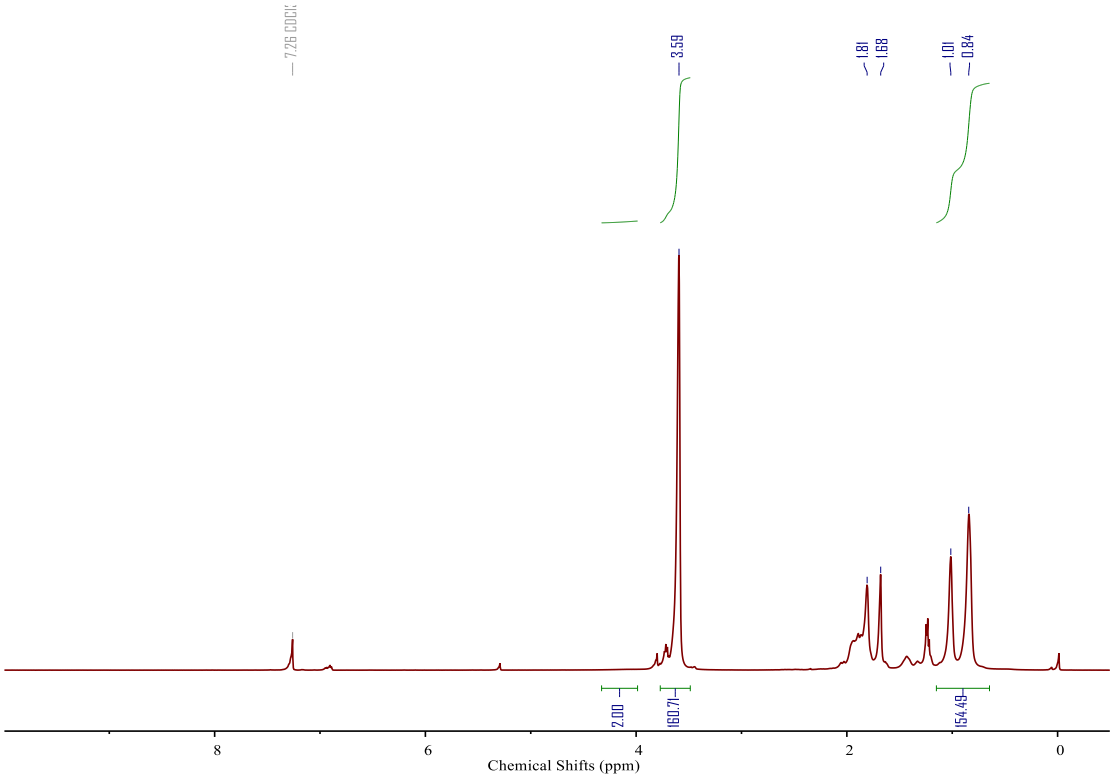


Figure S4: ^{1}H NMR spectrum of PVEBB25-*g*-PMMA53 in $CDCl_3$

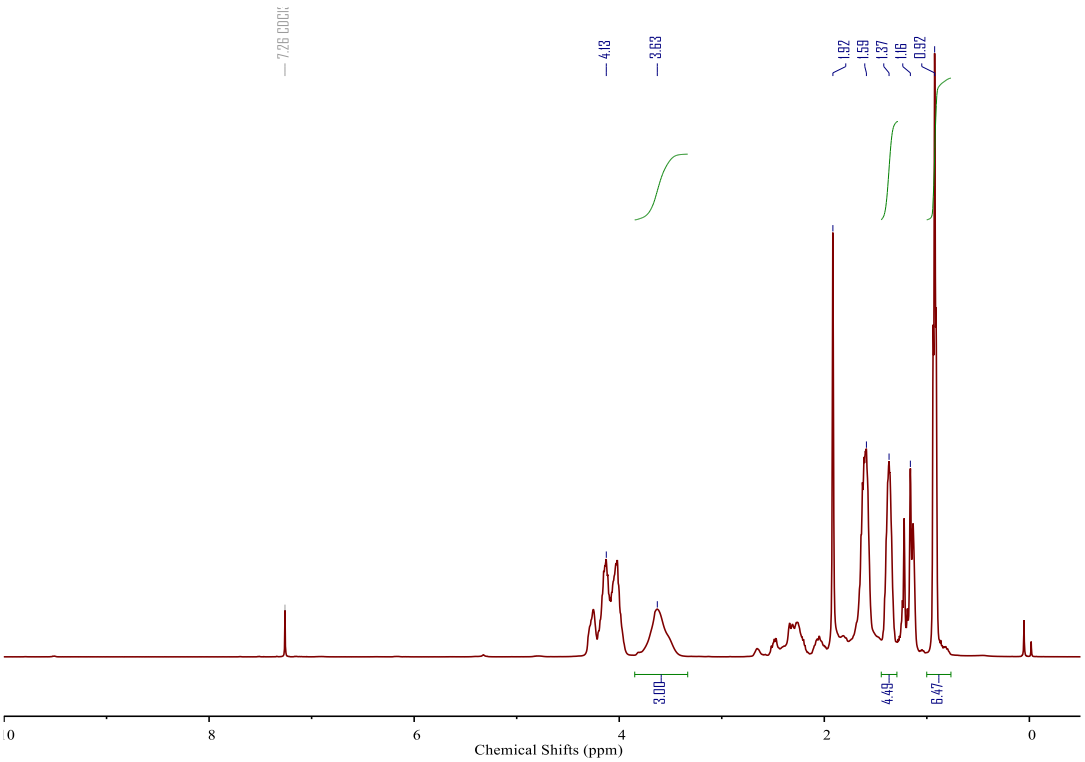


Figure S5: ^{1}H NMR spectrum of PVEBB25-*g*-PBA2 in $CDCl_3$

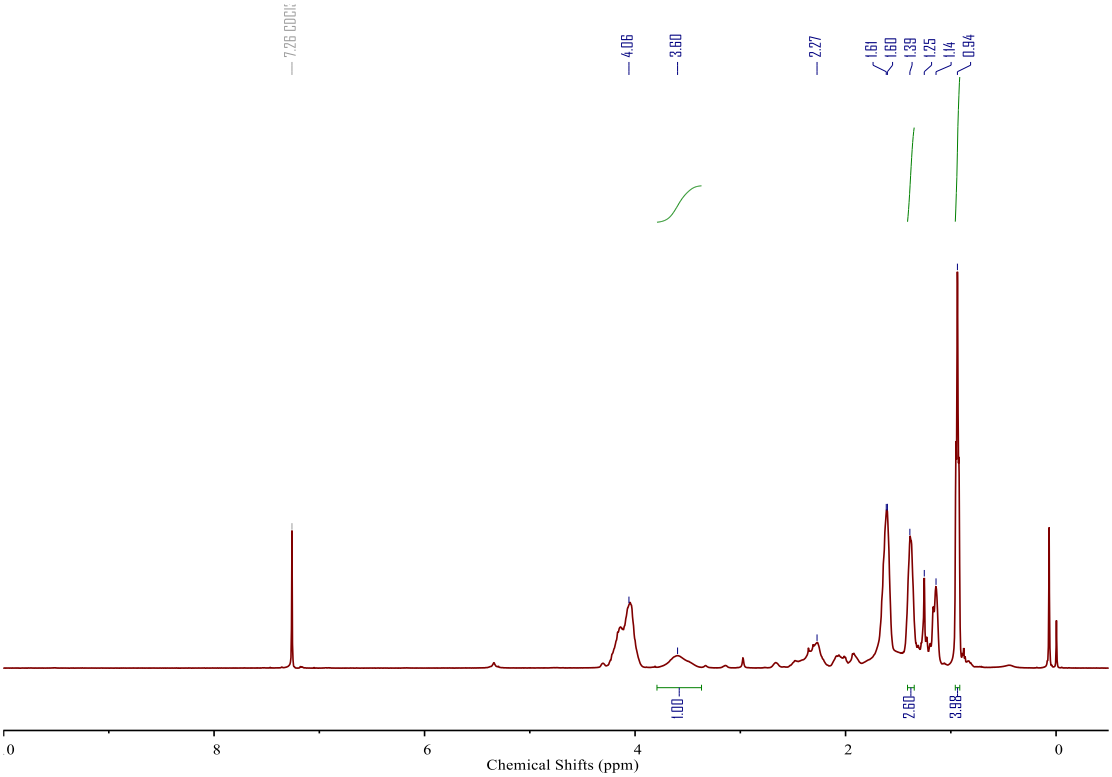


Figure S6: ^{1}H NMR spectrum of PVEBB25-*g*-PBA4 in $CDCl_3$

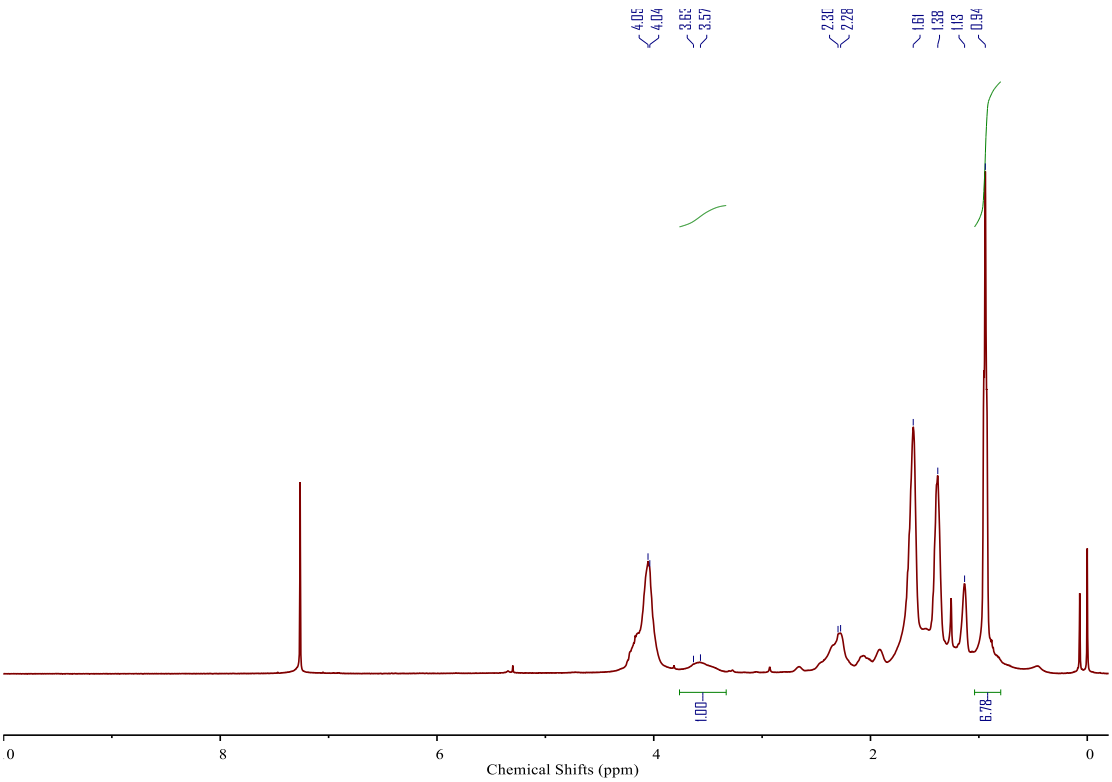


Figure S7: ^{1}H NMR spectrum of PVEBB25-*g*-PBA7 in $CDCl_3$

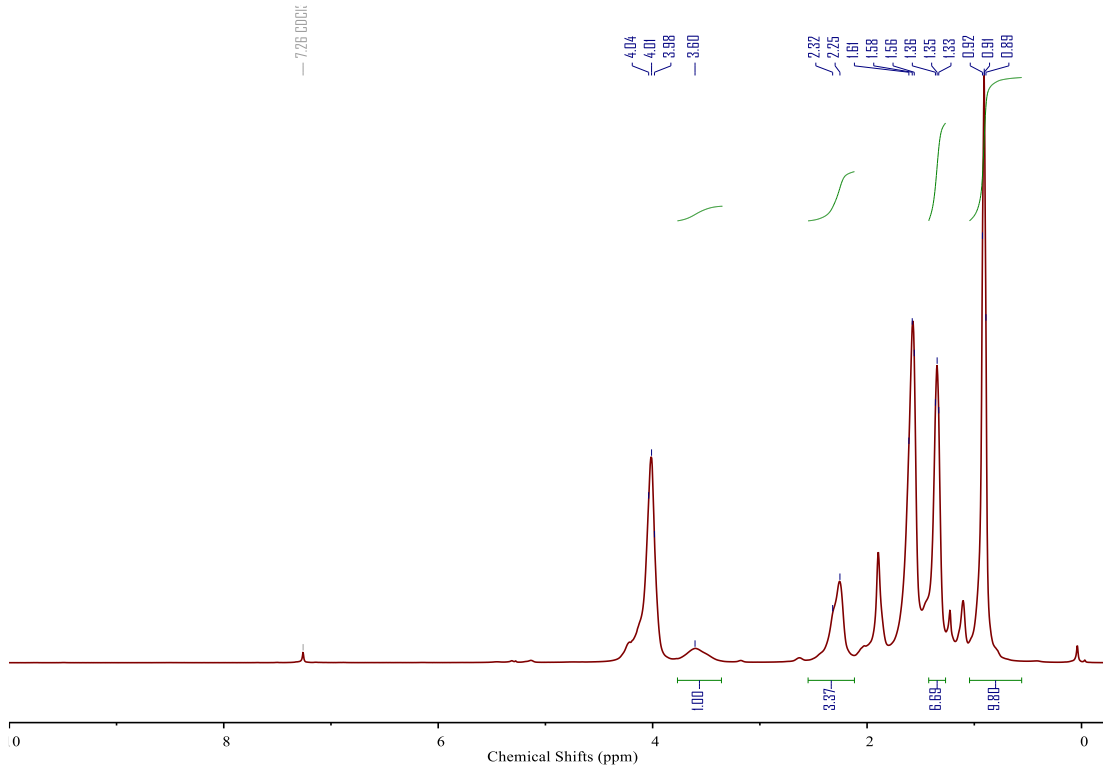


Figure S8: ^{1}H NMR spectrum of PVEBB25-*g*-PBA10 in $CDCl_3$

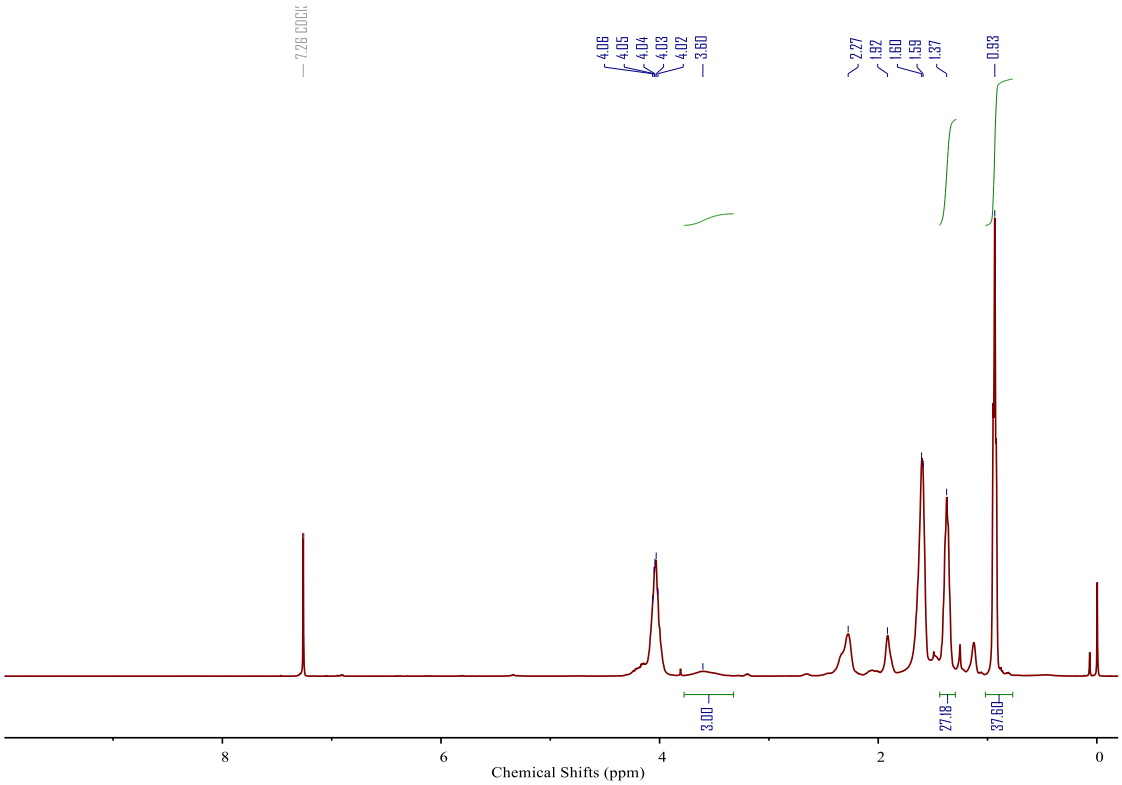


Figure S9: ^{1}H NMR spectrum of PVEBB25-*g*-PBA12 in $CDCl_3$

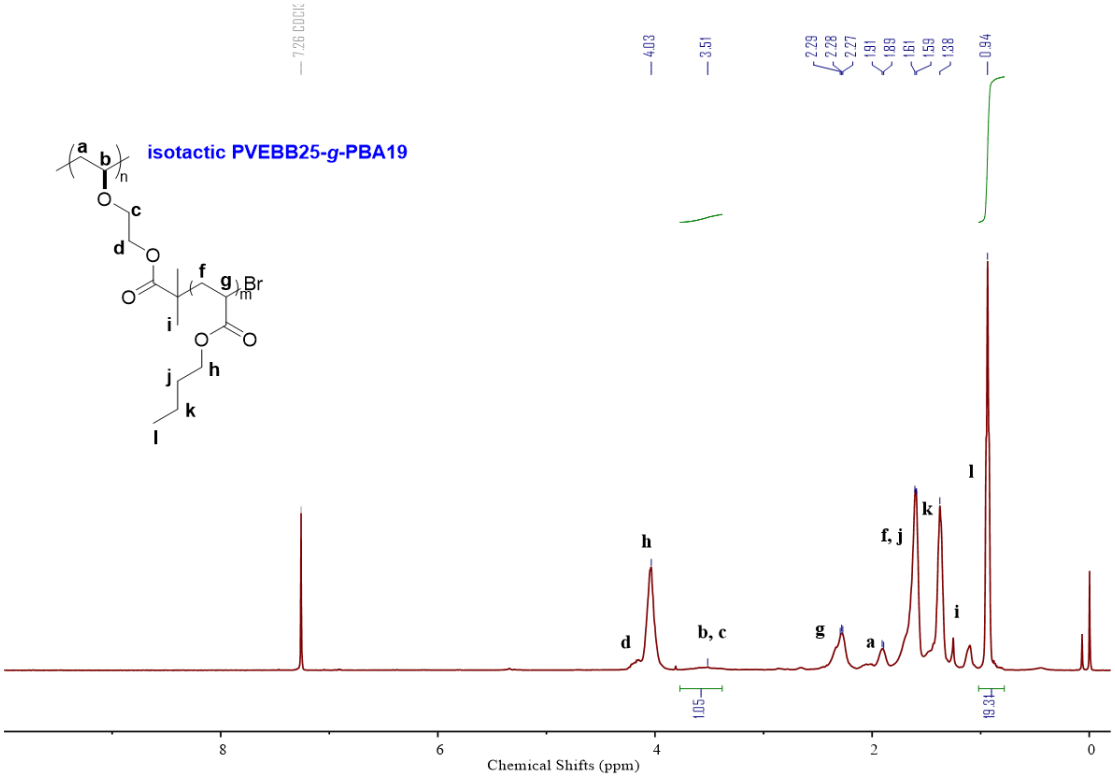


Figure S10: ^{1}H NMR spectrum of PVEBB25-*g*-PBA19 in $CDCl_3$

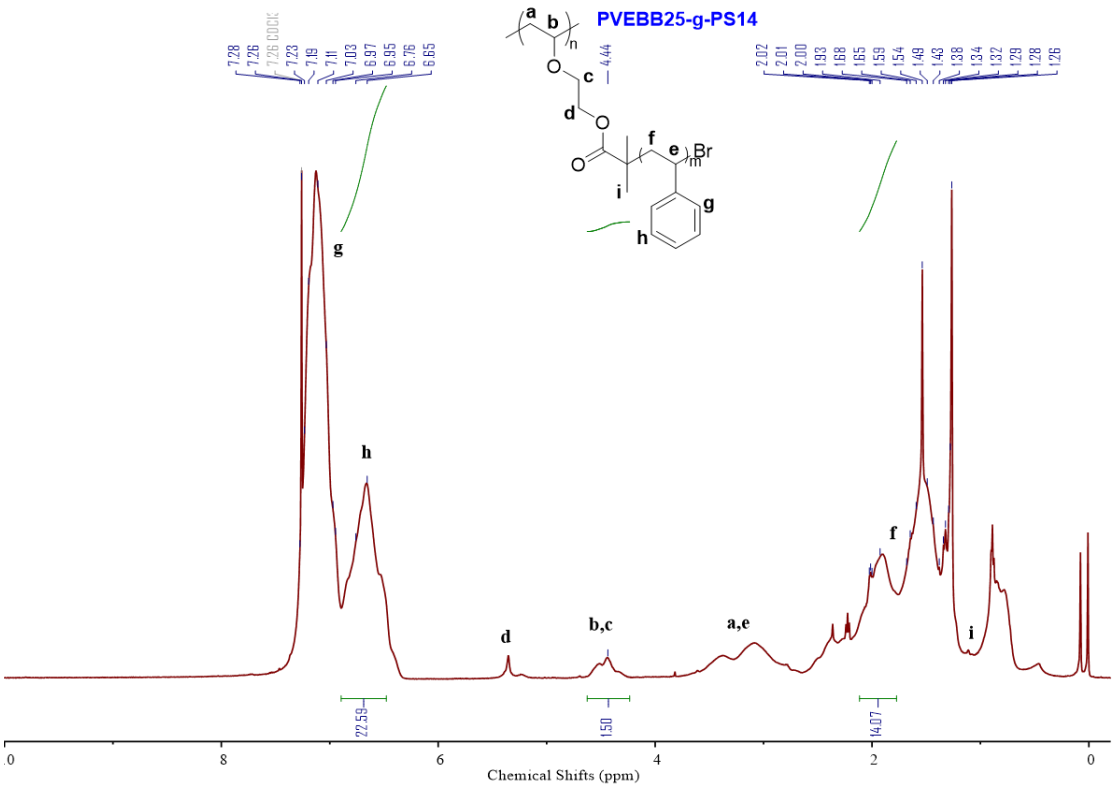


Figure S11: ^{1}H NMR spectrum of PVEBB25-*g*-PS14 in CDCl3

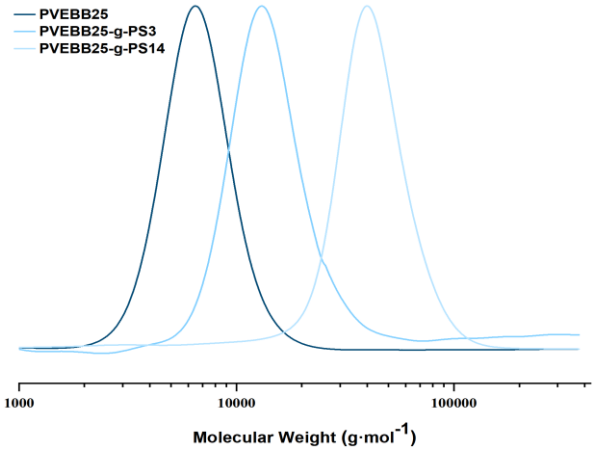


Figure S12: GPC traces of PVEBB25, PVEBB25-*g*-PS3, and PVEBB25-*g*-PS14

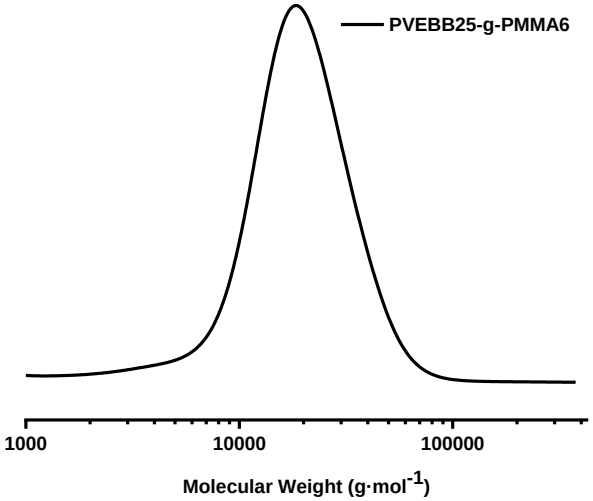


Figure S13: GPC traces of the subsequent synthesis of PVEBB25-*g*-PMMA6

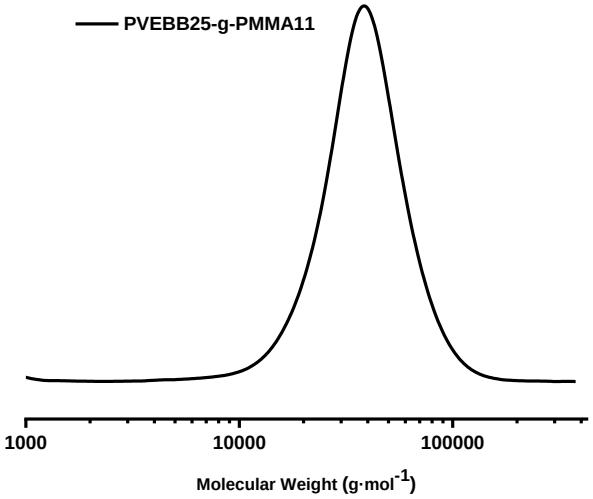


Figure S14: GPC traces of the subsequent synthesis of PVEBB25-*g*-PMMA11

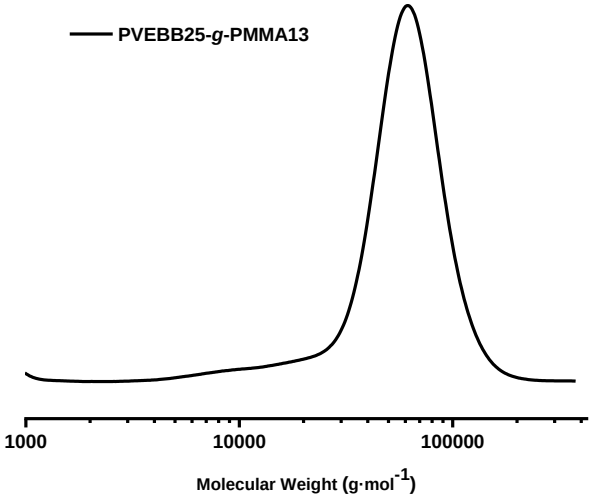


Figure S15: GPC traces of the subsequent synthesis of PVEBB25-*g*-PMMA13

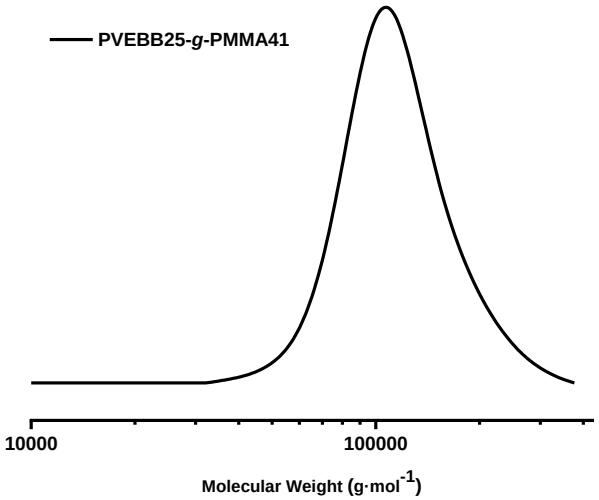


Figure S16: GPC traces of the subsequent synthesis of PVEBB25-*g*-PMMA41

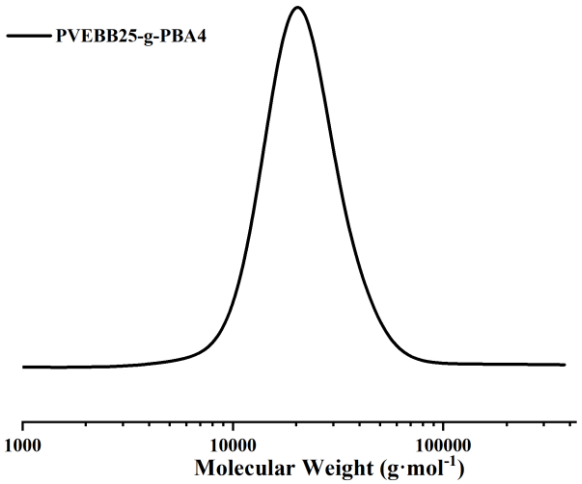


Figure S17: GPC traces of the subsequent synthesis of PVEBB25-*g*-PBA4

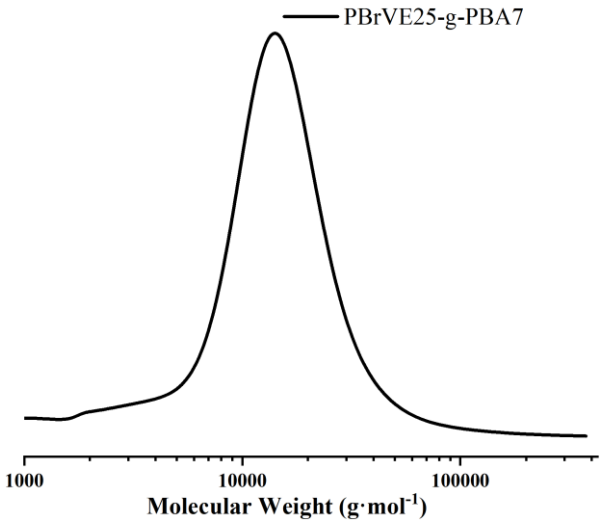


Figure S18: GPC traces of the subsequent synthesis of PVEBB25-*g*-PBA7

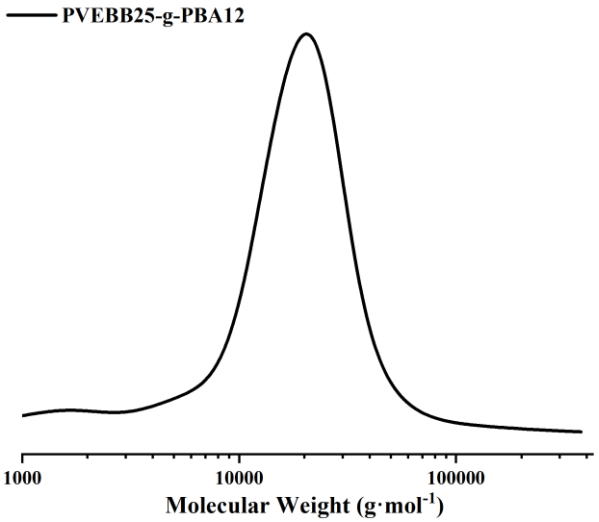


Figure S19: GPC traces of the subsequent synthesis of PVEBB25-*g*-PBA12

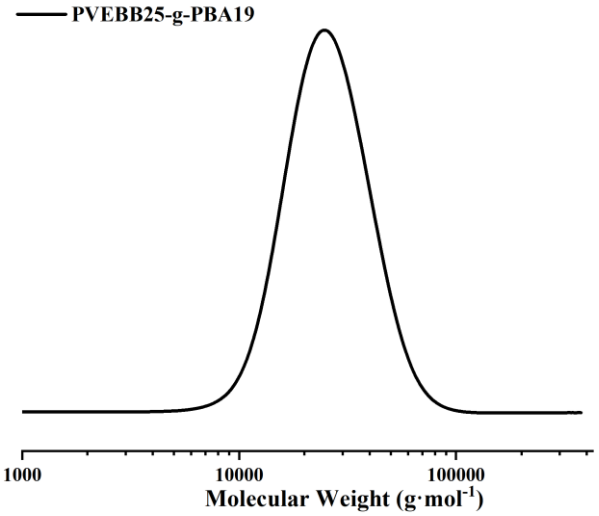


Figure S20: GPC traces of the subsequent synthesis of PVEBB25-*g*-PBA19

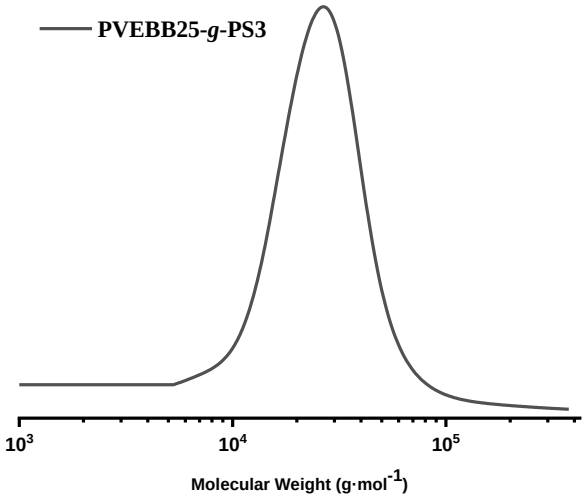


Figure S21: GPC traces of the subsequent synthesis of PVEBB25-*g*-PS3

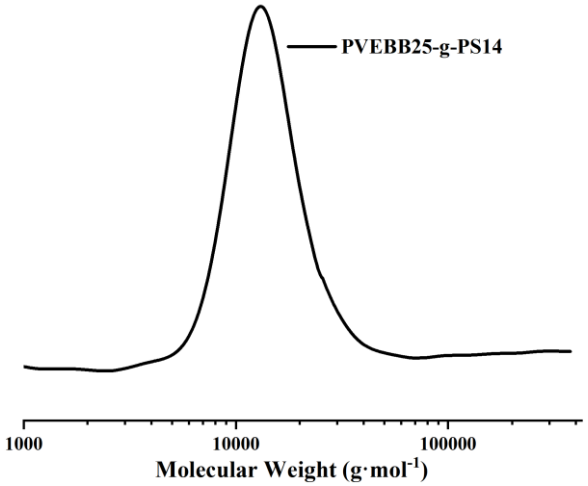


Figure S22: GPC traces of the subsequent synthesis of PVEBB25-*g*-PS14