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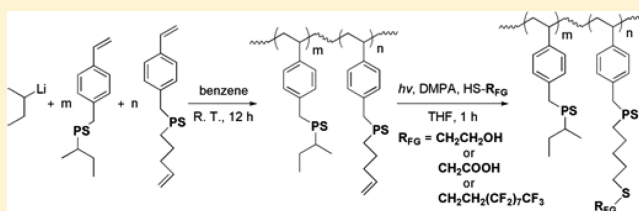
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S Supporting Information

ABSTRACT: A combination of living anionic polymerization and thiol–ene “click” chemistry provides an efficient and convenient method for synthesis of well-defined comb polystyrenes with precisely controlled architecture details and a wide selection of functionalities. ω -(*p*-Vinylbenzyl)-polystyrene macromonomer was synthesized by *sec*-butyllithium-initiated polymerization of styrene followed by termination with 4-vinylbenzyl chloride (VBC). For the synthesis of α -4-pentenyl- ω -(*p*-vinylbenzyl)polystyrene macromonomer, an unsaturated initiator, 4-pentenyllithium, was used followed by termination with VBC. To ensure successful living anionic polymerization of macromonomers, impurities present in the macromonomers and glass reactors were readily removed by titration with excess *sec*-butyllithium initiator right before initiation, resulting in polymacromonomers with controlled M_n (74 000, 130 000 g/mol) and narrow M_w/M_n . Living anionic copolymerization of mixtures of both types of macromonomers yielded a well-defined comb-shape precursor with controlled fractions of ω -vinyl branch end groups, which were subsequently subjected to facile and efficient functionalization by photoinitiated thiol–ene “click” reactions with diverse functional groups (–OH, –CO₂H, and –C₈F₁₇). Characterization by NMR, SEC, and MALDI-TOF mass spectrometry established their chemical structures and chain-end functionalities, which indicates precisely defined comb polystyrenes with controlled degrees of functionalization.



INTRODUCTION

The comb polymer is a special type of branched polymer with a high density of side branches along the backbone that has attracted considerable research interest due to its unusual architecture.^{1–8} The particular type of comb polymer of interest here is that in which every backbone repeat unit has one side branch. The properties of a comb polymer are very different from those of a linear polymer of the same molecular weight, in both solution and bulk state. For example, compared to its linear analogue, a comb polymer exhibits lower intrinsic viscosity,^{1,2} a nonlinear Mark–Houwink plot,³ a semiflexible molecular conformation in solution,^{4,5,7} a lower glass transition temperature,^{6,8} and greater difficulty in forming entanglements.^{5,6,8} The comb polymer is of particular interest with respect to our ongoing research on surface segregation of topologically diverse polymers.^{9,10} Wu and Fredrickson¹¹ have predicted that in a melt blend with linear polymers of equal molecular weight the comb polymers will be preferentially enriched at the surface.

It is convenient to synthesize comb polymers with extremely high side branch density by the polymerization of macromonomers. This macromonomer technique or “grafting through” technique has been comprehensively reviewed by multiple authors.^{1,12–15} Well-defined macromonomers with a polymerizable functional group at one end can be synthesized

by living polymerization methods.^{16,17} Alkylolithium-initiated living anionic polymerization is one of the most reliable methods for the synthesis of well-defined, chain-end-functionalized polymers with controlled molecular weights, narrow molecular weight distributions, and high end-group functionality.^{18–20} Polystyrene macromonomers functionalized with styryl end groups have been prepared by termination of living poly(styryl)lithium with 4-vinylbenzyl chloride (VBC).^{21,22} Living poly(styryl)lithium was end-capped with ethylene oxide, followed by reaction with methacryloyl chloride to afford macromonomer with a methacrylate end group.^{2,23,24} In most examples of comb polymers in the literature the combs are prepared by conventional radical polymerization of macromonomers.^{1,2,13,21,25} However, conventional radical polymerization has the limitations of poor molecular weight control, high polydispersity, and incomplete conversion. All of these limitations can be overcome with living or controlled polymerization methods, such as anionic polymerization,^{26–31} cationic polymerization,^{32,33} group transfer polymerization (GTP),³⁴ atom transfer radical polymerization (ATRP),^{35–40} reversible addition–fragmentation chain transfer polymer-

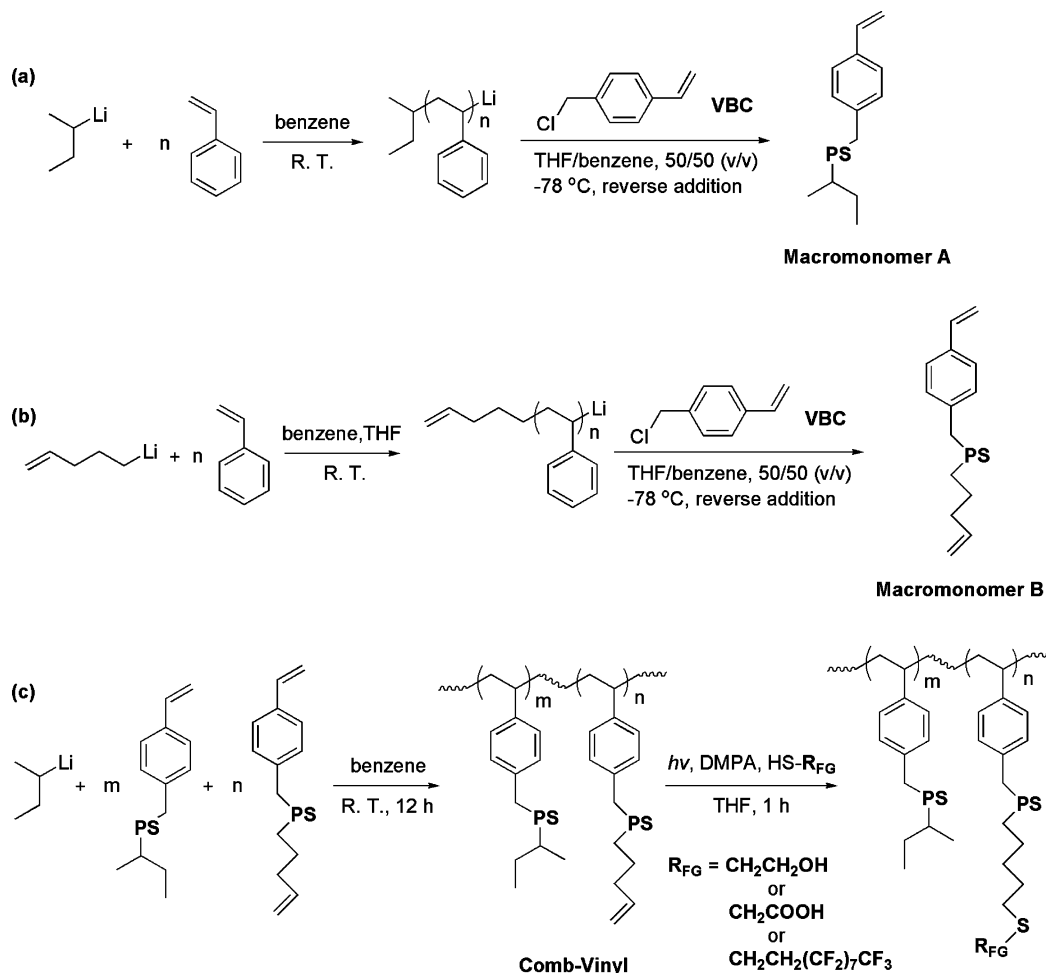
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Scheme 1. Reaction Pathway for the Synthesis of Functionalized Comb Polystyrenes: (a) Synthesis of Macromonomer A; (b) Synthesis of Macromonomer B; (c) Synthesis of Comb-Vinyl by Copolymerization and Subsequent Functionalization by Thiol–Ene “Click” Chemistry



ization (RAFT),^{41,42} nitroxide-mediated radical polymerization (NMP),⁴³ and ring-opening metathesis polymerization (ROMP).^{44–47}

Most of the branch end-functionalized combs reported in the literature have been prepared by ring-opening polymerization or conventional radical polymerization.^{48–57} There are a few examples applying controlled radical polymerization to synthesize such combs.^{58–61} However, no one has taken advantage of precise control and high efficiency provided by living anionic polymerization to prepare vinyl-based combs with functionalized branch ends. Macromonomers with functionalizable groups at one end and polymerizable groups at the other end are suitable building blocks to prepare branch end-functionalized comb polymers by living anionic polymerization. One of the best ways to synthesize such well-defined α,ω -difunctional macromonomers is to initiate a living anionic polymerization with a functional initiator and then terminate it with a functional terminating agent.¹⁰ The functionalizable end groups from the initiator should remain stable during anionic polymerization and should be amenable to various transformation chemistries in the subsequent functionalization step. The rapidly developing area of thiol–ene “click” chemistry⁶² provides an ideal option for functionalization of vinyl-functionalized comb polymers. Thiol–ene “click” reactions, which involve the photo- or thermally initiated radical addition

of thiols to vinyl groups, are highly efficient, rapid, regioselective (anti-Markovnikov addition), and insensitive to moisture and oxygen.^{63–78} Moreover, isolated vinyl groups reactive to thiol–ene reactions are inert during anionic polymerization. Recently, we have demonstrated successful incorporation of thiol–ene “click” chemistry reactions into the general functionalization methodologies (GFM) of anionic polymerization.⁷⁹

In this work a new, general method has been investigated for the preparation of well-defined, comb polystyrenes with controlled, variable amounts and types of branch chain-end functionalities by combining living anionic polymerization and thiol-end “click” chemistry as outlined in Scheme 1. 4-Pentenyllithium has been investigated as the initiator for the preparation of well-defined α -vinyl- and ω -styryl-functionalized macromonomers (macromonomer B) after termination with vinylbenzyl chloride (see Scheme 1). It was envisioned that these vinyl-functionalized macromonomers could be anionically copolymerized with different amounts of ω -styryl-functionalized macromonomers (macromonomers A, initiated by *sec*-BuLi) to form well-defined, comb polystyrenes with varying amounts of ω -vinyl functionality on branches. Subsequent photoinitiated, thiol–ene “click” reactions of substituted thiols with the pendant vinyl groups would then be used to introduce

diverse functionalities. The results of these investigations are reported herein.

■ EXPERIMENTAL SECTION

Materials. Benzene (EM Science, Certified ACS), heptane (EMD, 99%), styrene (Aldrich, 99%), diethyl ether (EMD, 99%), and tetrahydrofuran (THF, Fisher Scientific, >95%) were purified as previously reported.^{80,81} 5-Bromo-1-pentene (Aldrich, 95%) was fractionally distilled in vacuum, stirred over calcium hydride, and then distilled into a calibrated, flame-sealed ampule. 4-Vinylbenzyl chloride (VBC, Aldrich, >90%) was purified by passing through a column of activated basic alumina in cyclohexane, dried over calcium hydride, vacuum distilled into a sealed flask, and distributed into ampules in a drybox, and the ampules were flame-sealed on the vacuum line. Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distilling into ampules followed by flame-sealing. Lithium metal (FMC, stabilized, 1% Na), toluene (EMD, Certified ACS), dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99%), 1H,1H,2H,2H-perfluoro-1-decanethiol (Aldrich, 97%), mercaptoacetic acid (Acros Organics, 97%), and 2-mercaptoethanol (Aldrich, 99+%) were used as received. *sec*-Butyllithium (FMC, 1.4 M in cyclohexane) was used as received after double titration with allyl bromide.⁸²

Synthesis of ω -(*p*-Vinylbenzyl)polystyrene (M_n = 2500 g/mol, Macromonomer A). All polymerizations were carried out in sealed, all-glass apparatus using standard high-vacuum techniques.^{81,83,84} *sec*-Butyllithium (1.5 mL, 2.1 mmol, 1.43 M) was added to the A part of an all-glass reactor which consisted of two, connected reaction flasks. Reactor A was equipped with a styrene ampule (5.6 mL, 5.1 g, and 0.049 mol) and a THF ampule (41.5 mL, 36.9 g, 0.51 mol), and the other reactor (B) was equipped with an ampule containing VBC (5.0 mL, 5.42 g, 35.5 mmol)/THF (15 mL). Benzene (60 mL) was distilled into the reactor on the vacuum line. The reactor was then separated from the vacuum line by flame-sealing, and the styrene ampule break-seal was broken. After 3 h at room temperature the break-seal of THF ampule was broken. The VBC/THF ampule was broken in reactor B. All glassware was cooled to -78°C in an isopropyl alcohol/dry ice bath and poly(styryl)lithium in reactor A was slowly transferred into the VBC/THF solution in reactor B. Solvent was then removed by distillation under reduced pressure, toluene was added, and the resulting solution was precipitated into cold methanol (10 times solution volume) three times. The sample was dried in a vacuum oven overnight to afford a white powder.

Synthesis of 5-Lithio-1-pentene.⁸⁵ A 250 mL, Morton-creased, glass reactor equipped with ampules of diethyl ether (5 mL), 5-bromo-1-pentene (1.4 mL, 0.012 mol), lithium metal (0.82 g, 0.12 mol; 10-fold excess), and with a fritted glass filter connected to an empty ampule and a stir bar was placed under high vacuum. Heptane was distilled into the reactor, followed by flame-sealing from the vacuum line. The break-seals of the lithium metal and 5-bromo-1-pentene ampules were broken sequentially, and the reaction was stirred at room temperature for 3 days. The reactor and diethyl ether ampule were cooled to 0°C , and the ampule break-seal was broken. The reaction was stirred for 24 h at 0°C . The reactor was then connected to the vacuum line via a break-seal, solvent was removed by flash distillation, and 30 mL of heptane was added by distillation. The mixture was transferred through the glass filter into the empty ampule that was then flame-sealed from the reactor. The product was 0.19 M 5-lithio-1-pentene in heptane (48%) as determined by double titration.⁸²

Synthesis of α -4-Pentenyl- ω -(*p*-vinylbenzyl)polystyrene (M_n = 2300 g/mol, Macromonomer B). Macromonomer B was prepared using a procedure similar to that described for macromonomer A except for the following details. 5-Lithio-1-pentene (6.0 mL, 1.1 mmol, 0.19 M) was used as initiator, and the polymerization reactor A was equipped with a styrene ampule (3.1 mL, 2.8 g, 0.027 mmol), a THF ampule (A) (0.5 mL, 0.4 g, 6.2 mmol), and a second THF ampule (B) (22 mL, 19.6 g, 0.27 mol); reactor B was equipped with an ampule containing VBC (2.6 mL, 2.82 g, 18.4 mmol)/THF (8

mL). Benzene (30 mL) was distilled into the reactor after evacuation followed by breaking the break-seal for the THF ampule A before styrene addition. The contents of the second THF ampule (B) was added after 3 h. All other experimental procedures followed the details provided for macromonomer A.

Synthesis of Comb-Bu (M_n = 130 000 g/mol) and Comb-Vinyl (M_n = 74 000 g/mol). Comb-Bu. Macromonomer A (1.00 g) was placed in a flask equipped with a Rotoflo stopcock that was then connected to the vacuum line. Benzene (10 mL) was distilled into the flask followed by transfer to a drybox and dropwise addition of freshly diluted *sec*-butyllithium (0.0143 M in benzene) until a faint yellow color was observed. Then a calculated amount of diluted *sec*-butyllithium (0.6 mL, 0.008 mmol, 0.0143 M) was immediately injected into the flask, and the solution became orange. The polymerization was quenched by methanol after 12 h at room temperature. Polymer product was collected by precipitation of the solution into methanol and then freeze-dried from benzene.

Comb-Vinyl. The procedure for preparing Comb-Vinyl was similar to that for synthesizing Comb-Bu described above. Macromonomer A (0.76 g, 0.30 mmol) and macromonomer B (0.24 g, 0.10 mmol) dissolved in distilled benzene (10 mL) were well mixed in a flask equipped with a Rotoflo stopcock after the flask was attached to the vacuum line and evacuated. After titration of impurities with *sec*-butyllithium until a faint orange color was observed, the calculated amount of diluted *sec*-butyllithium (1.1 mL, 0.016 mmol, 0.0143 M) was added. Termination and work-up followed the procedure described for Comb-Bu.

Functionalization of Comb-Vinyl Using Thiol–Ene “Click” Chemistry.⁷⁹ Comb-vinyl prepared in the previous step was used as the precursor for functionalized comb polystyrenes: Comb-OH, Comb-COOH, and Comb- C_8F_{17} .

Comb-OH. Comb-Vinyl (M_n = 74 000 g/mol, 0.7 g, 85 μmol vinyl), 2-mercaptoethanol (24 mg, 307 μmol), and DMPA (4.1 mg, 16 μmol) were dissolved in 4 mL of THF. After irradiation with stirring for 1 h under a UV 365 nm lamp at room temperature, the solution was precipitated into cold methanol three times. The sample was dried in a vacuum oven overnight to obtain a white powder (Comb-OH, 0.63 g; yield 90%). It was further fractionated using toluene–methanol mixed solvents to obtain monodispersed product.

Comb-COOH. Comb-vinyl (M_n = 74 000 g/mol, 0.50 g, 61 μmol vinyl), mercaptoacetic acid (22 mg, 239 μmol), and DMPA (3.6 mg, 14 μmol) were dissolved in 3 mL of THF. After irradiation with stirring for 1 h under a UV 365 nm lamp at room temperature, the mixture was directly precipitated into aqueous NaOH solution (40 mL, pH = 10). The solid was collected, dissolved again in THF, and precipitated into aqueous HCl solution (40 mL, pH = 1). After precipitation again into distilled water (40 mL), the sample was collected by filtration and dried in a vacuum oven overnight to give a white powder (Comb-COOH, 0.32 g; yield 64%).

Comb- C_8F_{17} . Comb-Vinyl (M_n = 74 000 g/mol, 0.45 g, 55 μmol vinyl), 1H,1H,2H,2H-perfluoro-1-decanethiol (110 mg, 229 μmol), and DMPA (3.3 mg, 13 μmol) were dissolved in 2.5 mL of THF, followed by irradiation with stirring for 1 h under a UV 365 nm lamp at room temperature. The solution was precipitated into cold hexanes/methanol mixed solvent (v/v = 1/30) three times. The sample was dried in a vacuum oven overnight to give a white powder (Comb- C_8F_{17} , 0.36 g; yield 81%). It was further fractionated using toluene–methanol mixed solvents to obtain monodispersed product.

Characterization. Size exclusion chromatographic analyses (SEC) for the polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10³/10⁴ Å), mixed bed (10³, 10⁴, 10⁶ Å)], and a triple detector system, coupled of a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30°C . Samples were prepared in THF (10 mg/mL) and passed through a 0.45 μm Teflon filter before analysis.

¹H, ¹³C, and ¹⁹F solution NMR spectra were obtained on a Varian 500 spectrophotometer (500 MHz) using 40 mg of polymer dissolved

in 1 mL of CDCl_3 (Cambridge Isotopes). MALDI-TOF/TOF mass spectra were recorded on a Bruker Ultraflex-III MALDI-TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a Nd:YAG laser (355 nm). Solutions of DCTB (2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile) (20 mg/mL) (Alfa Aesar, 99+%), polymer sample (10 mg/mL), and silver trifluoroacetate (10 mg/mL) (Aldrich, 98%) were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix:cationizing salt:polymer (10:1:2), and 0.5–1.0 μL of the mixture was applied to the MALDI sample target and allowed to dry. To minimize polymer fragmentation, the intensities of the laser pulses were attenuated and adjusted to obtain the optimal signal intensity. Mass spectra were measured in the positive reflectron mode. The instrument was calibrated prior to each measurement with external PMMA standards at the molecular weight under consideration.

RESULTS AND DISCUSSION

Living Anionic Synthesis of (*p*-Vinylbenzyl)-polystyrene ($M_n = 2500$ g/mol, Macromonomer A). ω -(*p*-Vinylbenzyl)polystyrene was prepared by living anionic polymerization using the procedure described by Asami and co-workers²¹ with a slight modification of the reaction of poly(styryl)lithium (PSLi) with 4-vinylbenzyl chloride (VBC). PSLi initiated by *sec*-butyllithium in benzene was slowly added into 18 mol equiv of VBC in THF at -78°C . The reaction conditions used, including amount of VBC, reaction temperature, solvent, and addition mode, were based on previous investigations.^{21,28,86} The characteristic red color of the PSLi solution in THF disappeared in seconds once it was added to the VBC solution. The excess VBC was removed from the macromonomer samples by precipitation into methanol three times. Cold methanol was used to decrease the solubility of the macromonomers with low molecular weight ($M_n = 2400$ g/mol). The resulting macromonomer A had a *sec*-butyl group at the α -end and a polymerizable *p*-vinylbenzyl group at the ω -end. Its structure and purity were thoroughly characterized by SEC, NMR, and MALDI-TOF mass spectrometry. The SEC chromatogram of macromonomer A (Figure 1) exhibits a symmetric, monomodal distribution, and analysis of the chromatogram yielded $M_n = 2500$ g/mol (calcd $M_n = 2500$ g/mol) with PDI = 1.08. The ^1H NMR spectrum of macromonomer A in Figure 2 clearly shows characteristic peaks for vinyl protons from the *p*-vinylbenzyl group (H_a and H_b , 2 H, δ 5.2 and 5.7 ppm)²² and methyl protons from the *sec*-butyl initiator fragment (H_c , 6 H, δ 0.5–0.8 ppm),²² with an integral ratio of $H_a:H_c = 1:6.8$, which is close to the expected ratio of $H_a:H_c = 1:6$; this corresponds to a vinyl functionality of 88% and is in accord with previous studies.²² No proton peaks from VBC (sharp peaks at δ 4.5, 5.3, and 5.8 ppm)²² were observed in the spectrum, indicating that excess VBC was effectively removed in the precipitation step (see above). The MALDI-TOF mass spectrum (Figure 3) confirmed the uniformity and well-defined structure of macromonomer A with one narrow distribution of peaks corresponding to the proposed structure. A representative monoisotopic mass peak at m/z 2154.15 corresponds to the 18-mer of (*p*-vinylbenzyl)-polystyrene, $\text{C}_4\text{H}_9\text{-(C}_8\text{H}_8\text{)}_{18}\text{-C}_9\text{H}_9\text{Ag}^+$, with calculated monoisotopic mass $[57.0704(\text{C}_4\text{H}_9) + 18 \times 104.0626(\text{C}_8\text{H}_8) + 117.0704(\text{C}_9\text{H}_9) + 106.9051(\text{Ag}^+)] = 2154.17$ Da. Overall, no dimer peak was found in the SEC chromatogram, and the MALDI-TOF result did not show unfunctionalized species. These results, together with the NMR result, support the efficient synthesis of macromonomer A with controlled

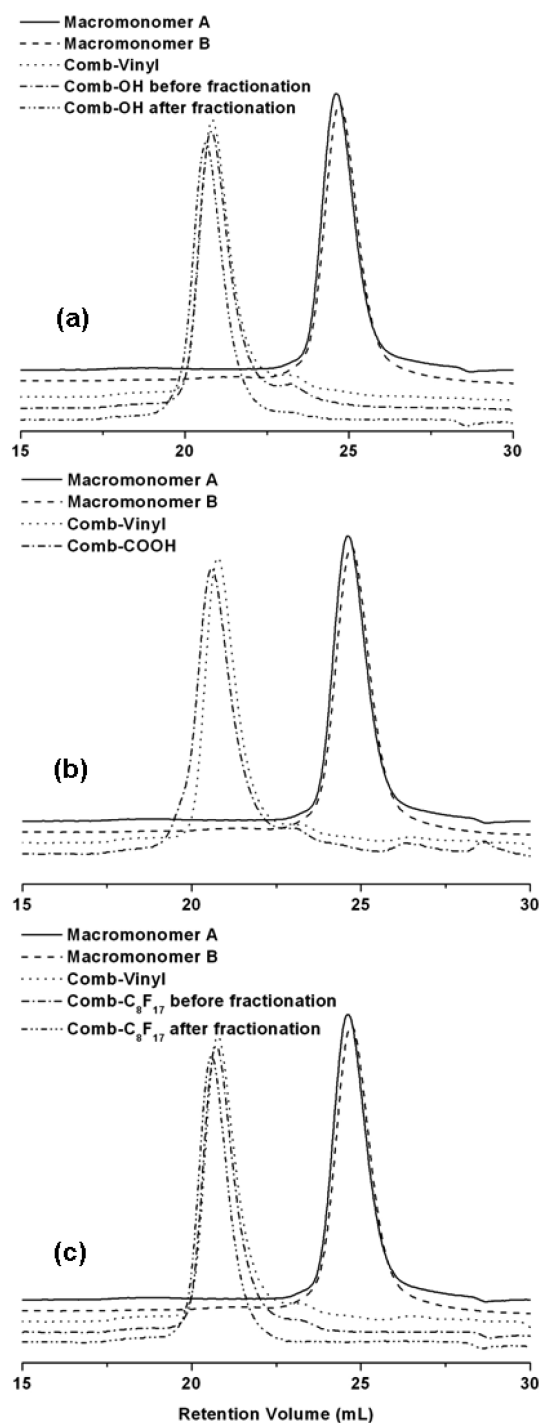


Figure 1. SEC overlays of the chromatograms for macromonomer A, macromonomer B, Comb-Vinyl, and functionalized comb polystyrene before and after fractionation for (a) Comb-OH, (b) Comb-COOH, and (c) Comb- C_8F_{17} .

molecular weight, narrow PDI, and high styryl chain end functionality.

Living Anionic Synthesis of α -4-Pentenyl- ω -(*p*-vinylbenzyl)polystyrene ($M_n = 2300$ g/mol, Macromonomer B). Living polymerization with a functional initiator ensures that every chain will have the functional group at the initiating, α , chain end.⁸⁷ The initiator 5-lithio-1-pentene was prepared using the procedure described by Takano and co-workers⁸⁵ by reacting lithium metal with 5-bromo-1-pentene in

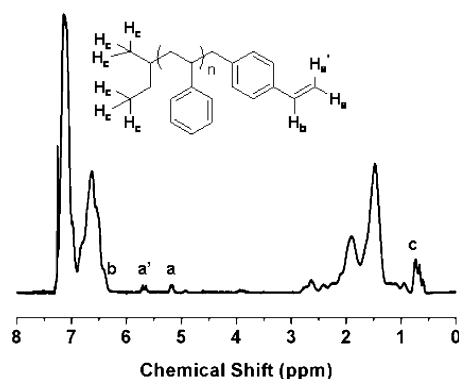


Figure 2. ^1H NMR spectrum of macromonomer A.

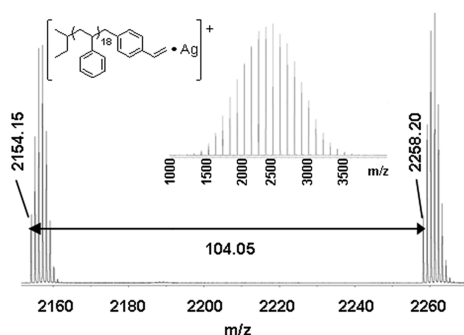


Figure 3. MALDI-TOF mass spectrum of macromonomer A.

heptane. 5-Lithio-1-pentene was then used to initiate the polymerization of styrene in benzene in the presence of 6 equiv of THF. As found in previous research,^{18,88,89} addition of Lewis base was required to promote dissociation of the primary alkylolithium initiator in hydrocarbon solvent and thus increase the rate of initiation relative to propagation, which was necessary to obtain a narrow molecular weight distribution product. The reaction of α -4-pentenylpoly(styryl)lithium prepared in this way with VBC followed the end-capping procedure for preparing macromonomer A described above.

The resulting product has a symmetric monomodal distribution as shown in Figure 1 and analysis of the SEC yielded $M_n = 2300$ g/mol (calcd $M_n = 2500$ g/mol) with PDI = 1.06. The ^1H NMR spectrum of the product is shown in Figure 4. Compared to that of macromonomer A, besides the peaks assignable to vinyl protons from the ω -(*p*-vinylbenzyl) group

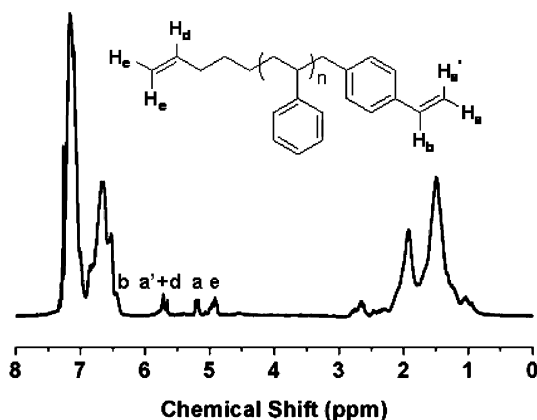


Figure 4. ^1H NMR spectrum of macromonomer B.

(H_a and $H_{a'}$, 2 H, δ 5.2 and 5.7 ppm), new peaks appear in the ^1H NMR spectrum which are attributable to protons from the 4-pentenyl initiator fragment (H_d , 1 H, δ 5.7 ppm, and H_e , 2 H, δ 4.9 ppm).¹⁰ The resonance peak for H_a overlaps with the peak for H_d at δ 5.7 ppm, which results in an integration ratio of 1.8:1.0:2.0 for peaks from vinyl protons at δ 5.7, 5.2, and 4.9 ppm, as expected.¹⁰ The vinyl carbons could also be observed in the ^{13}C NMR spectrum (Figure 5) at δ 114.0 and 139.0 ppm

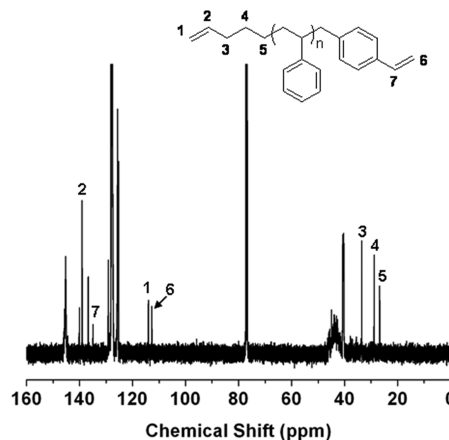


Figure 5. ^{13}C NMR spectrum of macromonomer B.

for α -4-pentenyl group and at δ 112.7 and 135.0 ppm for the ω -(*p*-vinylbenzyl) group, which are in good agreement with values reported in the literature.^{10,22,79} Thus, both ^1H and ^{13}C NMR spectral analyses confirm the structure of macromonomer B as α -4-pentenyl- ω -(*p*-vinylbenzyl)polystyrene. The MALDI-TOF mass spectrum of macromonomer B is shown in Figure 6. Only

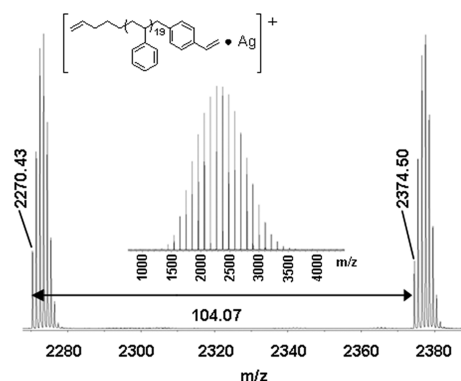


Figure 6. MALDI-TOF mass spectrum of macromonomer B.

one mass distribution is detected, with a representative monoisotopic peak at m/z 2270.43 corresponding to the 19-mer of α -4-pentenyl- ω -(*p*-vinylbenzyl)polystyrene, $\text{C}_5\text{H}_9\text{-(C}_8\text{H}_8\text{)}_{19}\text{-C}_9\text{H}_9\text{-Ag}^+$, with calculated monoisotopic mass $[69.0704(\text{C}_5\text{H}_9) + 19 \times 104.0626(\text{C}_8\text{H}_8) + 117.0704(\text{C}_9\text{H}_9) + 106.9051(\text{Ag}^+)] = 2270.24$ Da. Therefore, the MALDI-TOF mass spectrometry results combined with the SEC, and NMR results are consistent with efficient synthesis of macromonomer B with controlled M_n , narrow PDI, and high α -vinyl, ω -styryl chain-end functionality.

This α -vinyl functionalized macromonomer provides a unique ability to prepare comb polymers (polymacromonomers) with functionalized branch chain ends via a variety of postpolymerization functionalization reactions.

Synthesis of Comb-Bu ($M_n = 130\,000$ g/mol). Comb polystyrenes with extremely high branching density were prepared by living anionic polymerization of macromonomers with ω -styryl end groups. Since polystyrene macromonomers are solids, their purification in order to meet the demanding standards of living anionic polymerization is challenging. Impurities can also originate from glassware used as the reactor and from the solvent used for polymerization. These trace impurities significantly undermine or even completely disable the living anionic polymerization by quenching initiators and terminating growing macroanions, which is especially problematic when a high degree of polymerization is desired. For their kinetic studies Gnanou and Lutz²⁶ titrated impurities in the solvent with a small amount of *sec*-BuLi/styrene and then the copolymerization of macromonomer and styrene was initiated with poly(styryl)lithium. In Tsukahara's work,²⁸ macromonomers were dried with CaH_2 in benzene solution and freeze-dried several times under high vacuum. However, they reported that it was rather difficult to efficiently prepare poly-(macromonomer)s with a high degree of polymerization ($\text{DP} > 34$) because their procedure was unable to remove impurities in the macromonomers to the level required by living anionic polymerization. Later Yamashita and co-workers²⁹ reported the use of cross-linked polystyrene particles with pendant benzophenone sodium complexes as purging reagent in the purification of macromonomers. Living anionic polymerization of the purified macromonomers was able to produce combs with moderate degrees of polymerization ($\text{DP} \leq 10$). Hadjichristidis and co-workers^{30,31} bypassed the step of purifying macromonomers by performing the synthesis of macromonomers and the subsequent polymerization in the same reactor under high vacuum. Their strategy was successful for preparing combs with PS backbones and PI, PB, or PS-*b*-PI branches. However their strategy required a complicated reactor design and forfeited the convenience provided by synthesizing, characterizing, and polymerizing macromonomers in two separate processes. In this work, for purification purposes the benzene solution of macromonomers in the polymerization reactor was titrated with diluted *sec*-butyllithium initiator in a drybox filled with argon. Once impurities present in macromonomers and the reactor had been neutralized by *sec*-butyllithium, a faint yellow color appeared due to the formation of poly(styryl)lithium macroanions in the initiation step. Then the calculated amount of *sec*-butyllithium initiator was immediately added into the reactor to start the polymerization of macromonomers. It is also noteworthy that the excess VBC was efficiently removed from the macromonomers prior to their polymerization.

The SEC chromatograms of macromonomer A ($M_n = 2500$ g/mol) and its polymerization product Comb-Bu are compared in Figure S1; molecular weights were determined using SEC coupled with a light scattering detector. The peaks for macromonomer A have disappeared, and a new symmetric, monomodal peak at a lower retention volume has appeared, indicating successful polymerization. SEC analysis of the peak corresponded to $M_n = 130\,000$ g/mol with $\text{PDI} = 1.04$, which is slightly higher than the calculated $M_n = 120\,000$ g/mol. A very small shoulder next to the peak was observed at higher retention volume. It is possible that a small fraction of the macromonomers could have been initiated and even have been polymerized into macroanions with a low degree of polymerization ($M_n < 35\,000$ g/mol) before the titration was completed. However, these macroanions were soon terminated

by remaining impurities to form products corresponding to the shoulder.

Polymerization of macromonomers was also confirmed by evidence from ^1H NMR characterization. The peaks for protons from the *p*-vinylbenzyl group of macromonomer A (H_a and $\text{H}_{a'}$, 2 H, δ 5.2 and 5.7 ppm, Figure 2) disappeared in the ^1H NMR spectrum of Comb-Bu (Figure S2) due to polymerization. The broad peak at δ 0.5–0.8 ppm was attributed to methyl protons in *sec*-butyl groups originating from macromonomer A (H_c , 6 H, δ 0.5–0.8 ppm).

It is concluded from the characterization results by SEC and ^1H NMR analyses that impurities present in the reaction were efficiently removed with this titration purification procedure, and thus a relatively high degree of polymerization ($M_n = 130\,000$ g/mol; $X_n = 52$) for the resulting comb polymer Comb-Bu was achieved. It is also noteworthy that this high molecular weight comb also exhibited a narrow molecular weight distribution.

Synthesis of Comb-Vinyl ($M_n = 74\,000$ g/mol). The strategy of living anionic polymerization of macromonomer A purified by the *sec*-BuLi titration procedure, as demonstrated by the successful synthesis of Comb-Bu, was extended to copolymerization of macromonomers A and B for the preparation of Comb-Vinyl as the precursor for comb polymer with functionalized branch ends. The vinyl branch ends were introduced into comb polymer through the incorporation of macromonomer B. By simply varying the ratio of macromonomers A and B in the mixture before copolymerization, one can precisely control the fraction of vinyl branch ends in Comb-Vinyl and therefore the degree of functionalization in the final product. Since macromonomers A and B have the same styrene repeating unit, the same *p*-vinylbenzyl end group for polymerization, and similar molecular weights (2500 g/mol vs 2300 g/mol), the reactivity ratio for copolymerization of the two macromonomers should be close to unity, which is helpful for controlling the fraction of functionalizable vinyl chain ends and achieving their random distribution in Comb-Vinyl. For demonstration of this approach, Comb-Vinyl prepared from a mixture of macromonomers A/B = 76/24 (w/w) was selected.

Figure 1 shows the SEC chromatogram of the polymerization product. Complete conversion of both macromonomers was indicated by the disappearance of peaks for macromonomers A and B. A new monomodal peak, corresponding to the polymerization product Comb-Vinyl, appeared at retention volume lower than both macromonomers. SEC analysis of the peak yielded $M_n = 74\,000$ g/mol with $\text{PDI} = 1.09$, slightly higher than the calculated $M_n = 64\,000$ g/mol. A small amount of polymeric impurities ($M_n < 25\,000$ g/mol) presumably generated during the titration is present as a small shoulder next to the peak of Comb-Vinyl at higher retention volume.

The ^1H NMR spectrum of the resulting Comb-Vinyl is shown in Figure 7a. Comparison of ^1H NMR spectra for the two macromonomers (Figures 2 and 4) and Comb-Vinyl (Figure 7a) shows that the peaks for protons from the *p*-vinylbenzyl groups (H_a and $\text{H}_{a'}$, 2 H, δ 5.2 and 5.7 ppm)^{10,22} disappeared due to polymerization; peaks for protons from the 4-pentenyl initiator fragment of macromonomer B (H_d , 1 H, δ 5.7 ppm, and H_e , 2 H, δ 4.9 ppm)^{10,79} and protons from the methyl groups from the *sec*-butyl initiator fragment of macromonomer A (H_c , 6 H, δ 0.5–0.8 ppm)²² remained. The integral ratio of H_e and H_c from NMR analysis is 2.0:18.5 in the comb, which is close to the calculated ratio of 2.0:17.5 based on the weight ratio of macromonomers A/B (76/24)

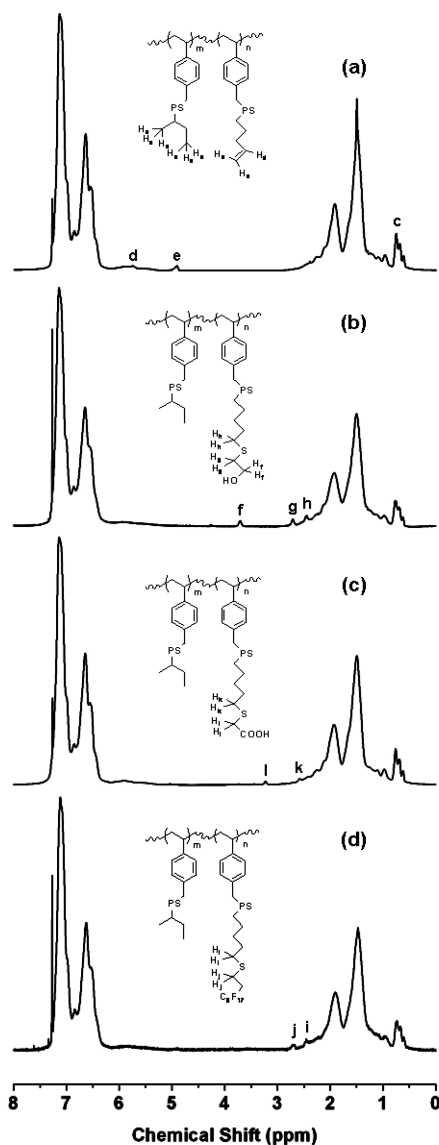


Figure 7. ^1H NMR spectra of (a) Comb-Vinyl, (b) Comb-OH, (c) Comb-COOH, and (d) Comb- C_8F_{17} .

before polymerization. The ^{13}C NMR spectrum of Comb-Vinyl is shown in Figure 8a. The most important observation is that peaks for carbons from the *p*-vinylbenzyl group (δ 112.7 and 135.0 ppm, see Figure 5) are gone, while peaks for carbons from the α -4-pentenyl group remain at δ 114.0 and 139.0 ppm.

On the basis of the SEC and NMR results, it is confirmed that macromonomers A and B were successfully copolymerized by living anionic polymerization and that the α -4-pentenyl groups from macromonomer B remained intact during the polymerization. These results once again demonstrate that the prepolymerization titration of impurities using *sec*-BuLi is an excellent method for anionic polymerization of macromonomers to form well-defined comb polymers.

Functionalization of Comb-Vinyl Using Thiol–Ene Chemistry. Comb-vinyl made by copolymerization of macromonomers A and B possesses pendent vinyl groups to which chain-end functionalities can be added. Thiol–ene “click” chemistry is an efficient and versatile process for functionalizing vinyl groups,^{63–79} making it ideal for bringing diverse functionalities to vinyl-functionalized combs. Three commer-

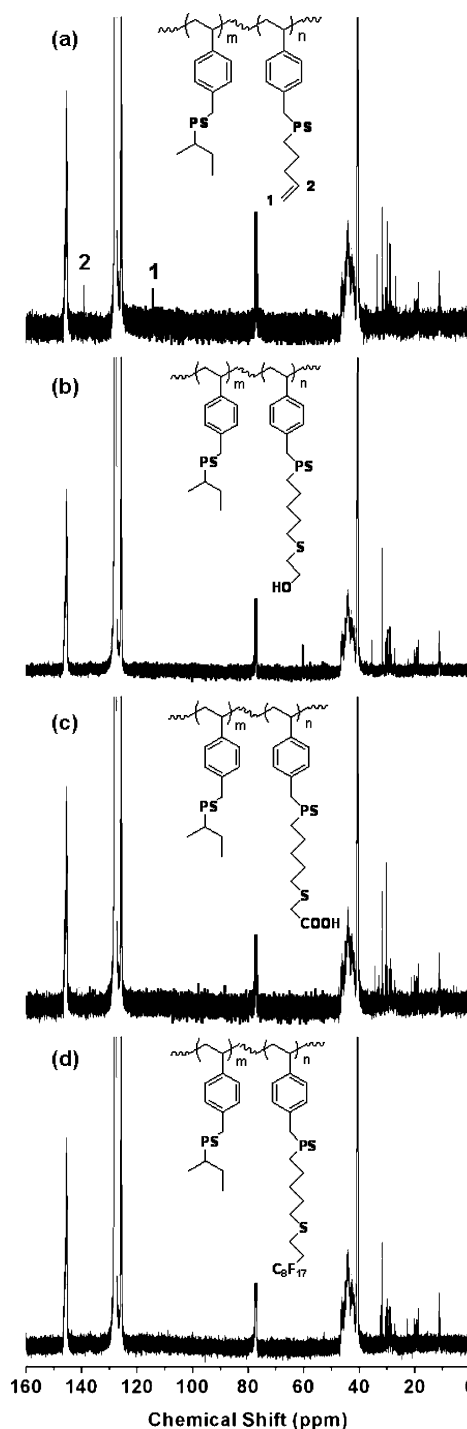


Figure 8. ^{13}C NMR spectra of (a) Comb-Vinyl, (b) Comb-OH, (c) Comb-COOH, and (d) Comb- C_8F_{17} .

cially available thiols with various functionalities were used: 2-mercaptoethanol, mercaptoacetic acid, and 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol. Our previous work⁷⁹ reported successful functionalizations of short linear model polystyrenes by thiol–ene “click” reactions. Herein a similar procedure was followed to functionalize Comb-Vinyl, except that a higher concentration ($[\text{thiol}]:[\text{C}=\text{C}] = 3.9:1$ vs $1.1:1$) and a longer reaction time (1 h vs 15 min) were used, due to the stronger steric hindrance effect expected for comb versus linear polymers. Major small molecule impurities, including excess thiol, initiator residue, and disulfide byproduct, were readily

removed by simple precipitation with no need for chromatographic separation. Fractionation was further applied here in order to remove polymeric impurities.

The SEC spectra of the functionalized combs are shown in Figure 1. The peak corresponding to each of the three functionalized combs overlapped with the peak of Comb-Vinyl very well, indicating the absence of side reactions causing molecular weight increases in the thiol–ene “click” reactions with all three thiols. For Comb-OH and Comb-C₈F₁₇, polymeric impurities were removed by fractionation, and thus better defined peaks were obtained after fractionation. However, attempts to fractionate Comb-COOH were unsuccessful. The strongly polar carboxyl groups at the chain ends greatly increased the solubility of Comb-COOH in methanol; therefore, a solution of Comb-COOH in mixed toluene/methanol solvent formed a stable emulsion and could not be readily separated into two clear layers. This observation supported the successful functionalization of Comb-Vinyl with carboxyl groups.

The ¹H NMR spectra of functionalized combs are shown in Figures 7b, 7c, and 7d. The peaks assignable to protons of the α -4-pentenyl group (H_d, 1 H, δ 5.7 ppm, and H_e, 2 H, δ 4.9 ppm) completely disappeared, which indicates complete reaction within 1 h. Complete reaction is also supported by the disappearance of the vinyl sp² carbon signals at δ 114.0 and 139.0 ppm in the ¹³C NMR spectra of all three functionalized combs (Figures 8b, 8c, and 8d). A broad peak attributed to methyl protons from the *sec*-butyl initiator fragment (H_j, 6 H, δ 0.5–0.8 ppm) was still observed. Because of the formation of thiol ether bonds, characteristic resonance peaks appeared in the NMR spectra as well. For Comb-OH, three peaks for methylene protons from the functionalized chain end can be clearly identified at δ 2.4 ppm for –SCH₂– (H_h), δ 2.7 ppm for –SCH₂CH₂O– (H_g), and δ 3.7 ppm for –SCH₂CH₂O– (H_f), respectively (Figure 7b).⁷⁹ The integral ratio of proton peaks by ¹H NMR analysis is H_f:H_g:H_h = 2.0:1.9:18.1, which is close to expected values of 2.0:2.0:18.5 based on the composition of Comb-Vinyl. For Comb-C₈F₁₇, the two peaks at δ 2.4 and 2.7 ppm in Figure 7d were attributed to protons (H_i and H_j) of the two methylene groups on each side of the thiol ether linkage.⁷⁹ The chemical shift of the methylene protons near CF₂ (–SCH₂CH₂CF₂–) could not be clearly identified since it overlapped with peaks from the polystyrene backbone protons in the ¹H NMR spectrum. ¹⁹F NMR signals from the long perfluorinated alkyl chain were clearly observed as a singlet peak at –80.7 ppm corresponding to methyl fluorines (CF₃–(CF₂)₇–) and multiple peaks from –121 to –126 ppm attributed to methylene fluorines (CF₃–(CF₂)₇–) in the ¹⁹F NMR spectrum of Comb-C₈F₁₇ (Figure S3). For Comb-COOH, the methylene protons (H_i) between the carbonyl group and sulfur (–CH₂SCH₂COOH) were observed at δ 3.2 ppm while the other methylene protons (H_k) near sulfur (–CH₂SCH₂COOH–) were evidenced by characteristic peaks at δ 2.6 ppm (Figure 7c).⁷⁹ The integral ratio of protons from thiol-functionalized chain ends and *sec*-butyl chain ends by ¹H NMR analysis was H_i:H_j = 2.0:23.6, which differed from the expected ratio of 2.0:18.1. The reason for the lower than expected fraction of thiol-functionalized chain ends in Comb-COOH is that lower molecular weight combs with branch chain ends functionalized with carboxyl groups are more soluble in polar solvents, which means that they are more likely to be removed from the products during precipitation. This explanation was supported by the fact that there was a lower

yield of polymers after purification for Comb-COOH (64%) than for Comb-OH (90%) and Comb-C₈F₁₇ (81%). TLC analysis of the purified Comb-OH, Comb-COOH, and Comb-C₈F₁₇ exhibited only one spot at the bottom of silica gel plate, consistent with a high yield of functionalized combs (unfunctionalized polymers <2%⁹⁰).

The combination of evidence from ¹H, ¹³C, and ¹⁹F NMR as well as TLC analysis shows that pendent α -4-pentenyl groups of Comb-Vinyl were efficiently functionalized with OH, COOH, or C₈F₁₇ groups by thiol–ene “click” reactions. No evidence for side reactions was observed, and impurities were easily removed. Therefore, well-defined comb polystyrenes with controlled amount and type of functionalized branch ends were successfully prepared using these methods.

CONCLUSIONS

Well-defined comb polystyrenes with three different ω -branch end-functional groups (OH, COOH, and C₈F₁₇) and precisely controlled degrees of functionalization were readily synthesized by combining living anionic polymerization and thiol–ene “click” chemistry. One macromonomer, ω -(*p*-vinylbenzyl)-polystyrene, was synthesized by termination of poly(styryl) lithium initiated by *sec*-butyllithium with 4-vinylbenzyl chloride. The other macromonomer, α -4-pentenyl- ω -(*p*-vinylbenzyl)-polystyrene, was prepared by using the unsaturated initiator, 4-pentenyllithium, followed by end-capping with 4-vinylbenzyl chloride. While living anionic polymerization of one macromonomer, ω -(*p*-vinylbenzyl)polystyrene, yielded well-defined comb polystyrenes with only *sec*-butyl branch ends, copolymerization of both macromonomers yielded well-defined comb precursors with pendent vinyl branch ends, which were subsequently functionalized by thiol–ene “click” reactions with various thiols. This strategy provides at least three synthetic advantages for synthesis of comb polymers: controlled molecular weight and narrow weight distributions; highly efficient functionalization; and facile control of the amount of functionalization. Work is in progress to develop strategies in combination with anionic polymerization to allow synthesis of more complex comb architectures, such as combs with two different functionalities in the same chain, and precisely controlling the spacing between two side branches of a comb. These model functionalized comb polystyrenes are also interesting targets for the study of modifying surface properties via surface segregation of branched polymers blended with linear polymers.

ASSOCIATED CONTENT

Supporting Information

SEC chromatogram and ¹H NMR spectrum of Comb-Bu and ¹⁹F NMR for Comb-C₈F₁₇. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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