Synthesis and Characterization of Model Dumbbell Polymers

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ABSTRACT: High molecular weight dumbbell shaped polymers were prepared by atom transfer radical polymerization (ATRP) to grow branches from repeat units of end blocks of a symmetric triblock copolymer. The triblock copolymer itself was prepared by polymer−polymer coupling of a commercially obtained α,ω-end functionalized polystyrene as central block with end-functionalized poly(chloromethylstyrene) that we synthesized by nitroxide-mediated polymerization. Temperature gradient interaction chromatography (TGIC) enabled the estimation of the terminal hydroxyl functionality of the high molecular weight α,ω-difunctional polystyrene as 75%. Size exclusion chromatography (SEC) and ^{1}H NMR enabled the determination of molecular weights and verification of the structures of the intermediate and the cleaved products. Size exclusion chromatography coupled with light scattering (SEC-LS) and scanning force microscopy (SFM) were used to confirm that the desired dumbbell architecture was obtained.

1. Introduction

The design of novel architecture branched polymers has received a lot of attention due to their applications in rheology modification, mechanical performance, biomedical areas, and microelectronics.[1−4] In addition, polymers with controlled architecture provide opportunities toward a better understanding of the effects of topology on dynamics of complex macromolecules. Extensive investigations in the past have addressed the behavior of branched polymers such as star, comb, hyperbranched, H-shaped polymers, super-H-shaped polymers, and pompom polymers. For example, branched polymers display lower intrinsic viscosities due to their smaller size compared to linear polymers of comparable molecular weights.[5] They also provide opportunities for macromolecular architectures toward enhanced resistance to chain scission under strong flows of dilute solutions.[6,7] Multiarm star polymers show rich dynamic response such as exponential dependence of the relaxation time on arm length.[8−10] The dynamics of H-polymers and pompom polymer melts has been theoretically predicted by accounting for the relaxation behavior of both the arms and the connecting backbone.[11,12] Quantitative understanding of the rheology of branched polymers has been achieved by a systematic study of the linear rheological response of model comb polymers.[13,14] Experimental verification of the predicted, very interesting rheological behavior (such as molecular weight dependence and extensional thickening) has been facilitated by controlled synthesis of macromolecules with the corresponding architectures.[15−17] Recently, the viscoelastic properties have been evaluated for a series of well-defined dumbbell copolymers made up of star polybutadiene branches as the bells, linked with a polystyrene connector.[18] The relaxation dynamics of these dumbbells showed star-polymer-like strong dependence on the branch length for the dumbbells with large branches and dependence on the total molecular weight for the dumbbells with short branches. However the synthesis was limited to backbone molecular weights of ∼10 000 g/mol, comparable to the molecular weight of the branches. Widely different rheological behavior is expected if the central connector is much larger than the side branches.

This paper describes the synthesis and characterization of a series of dumbbell polystyrenes with connector molecular weights as high as 400 000 g/mol. To achieve this, we make use of a combination of nitroxide-mediated polymerization (NMP), polymer−polymer coupling, and atom transfer radical polymerization (ATRP), in addition to the living anionic polymerization used for the commercially obtained polystyrene connector. Polymer−polymer coupling is employed to overcome the constraint on the connector molecular weight.

The dumbbell shaped polymers can be best made by growing branches from side blocks of a symmetric triblock precursor, which are normally prepared by living polymerization of the involved two monomers in a sequential manner.[19,20] While such techniques are very effective for moderate molecular weights, extension of such techniques to very high molecular weights is hindered by limited reinitiation of the polymerization of the second monomer. Here, we couple a well characterized α,ω-difunctional polymer with end-functionalized macroinitiator for subsequent dense grafting. Such an opportunity for character-

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izing individual side blocks independently is not available in the sequential polymerization route.[21] Our triblock copolymer poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) is made from the central block of α,ω-dihydroxy polystyrene (DHPS) and the end blocks of hydroxy-terminated poly(chloromethylstyrene) (HTPCMS), the latter being synthesized by NMP of chloromethylstyrene (CMS) from an initiator carrying a hydroxyl functionality. Finally, the desired dumbbell polymers are obtained by using ATRP to graft polystyrene branches from the initiating sites on the PCMS end blocks of the triblock precursors.

2. Experimental Section

2.1. Materials. Styrene (99.9%, Aldrich) and chloromethylstyrene (CMS) (60/40 meta/para isomer mixture, 97%, Aldrich) were purified by passing through a column of activated basic alumina to remove inhibitor, stored over CaH_2, and then vacuum distilled before use. CuBr (98%, Aldrich) and CuCl (98%, Aldrich) were purified according to a literature procedure.[22] 4,4′-Di-*n*-nonyl-2,2′-bipyridine (d*n*Nbpy) (Aldrich, 97%) was recrystallized from absolute ethanol and dried in a vacuum oven at 40 °C overnight. α,ω-Dihydroxy-terminated polystyrenes (DHPS50 and DHPS400) were obtained from Polymer Source Inc. The sample DHPS50 has a number-average molecular weight $\overline{M}_n$ = 51 500 g/mol, and polydispersity $\overline{M}_w/\overline{M}_n$ = 1.05, while the sample DHPS400 has $\overline{M}_n$ = 345000 g/mol and $\overline{M}_w/\overline{M}_n$ = 1.12. The following chemicals were used as received: phosgene solution (20% in toluene, Fluka), pyridine (99+%, Acros), toluene (anhydrous, 99.8%, Aldrich), tetrahydrofuran (THF, AR stabilized with BHT, Biosolve), molecular sieves (pore diameter 3 Å, Fluka), potassium hydroxide solution in ethanol (0.1 N, Merck), chloroform-d_1 ($CDCl_3$, deuteration degree minimum 99.8% for NMR spectroscopy, Merck), methanol (AR stabilized, Biosolve), (2,2,6,6-tetramethyl-1-pipeidinyloxy) (TEMPO) (99%, Aldrich), and benzoyl peroxide (purum, 97%, Fluka). ***Caution!*** Phosgene is a very toxic compound and requires careful handling. The Drierite gas-drying unit was obtained from Aldrich. 1-Hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)-ethane (HTPTE) was prepared using a literature procedure.[23]

2.2. Measurements. Average molecular weights and radii of gyration were measured by size exclusion chromatography (SEC) and SEC coupled with light scattering (SEC-LS).

We used a Waters GPC equipped with a Waters 510 (SEC) or Waters 6000 A (SEC-LS) pump, Waters 410 differential refractometer (at 40 °C, wavelength = 930 nm), Waters WISP 712 autoinjector with injection volume of 50 μL (SEC) or 150 μL (SEC-LS). Columns for SEC measurements were: one PLgel (5 μm particle size) 50 mm × 7.5 mm guard column and two PLgel mixed-C (5 μm particle size, for 200 to 2 × 10^6 g/mol) 300 mm × 7.5 mm columns (40 °C). Columns for SEC-LS measurements were: a Waters Filter guard column and four Styragel 300 mm × 7.8 mm columns (HR5, HR4, HR3, and HR2 for 5 × 10^4 to 4 × 10^6, 5 × 10^3 to 6 × 10^5, 5 × 10^2 to 3 × 10^4, and 5 × 10^2 to 2 × 10^4 g/mol, respectively). Tetrahydrofuran (THF, Biosolve, stabilized with BHT) was used as eluent at a flow rate of 1.0 mL/min. SEC calibration was done using polystyrene (PS) standards (Polymer Laboratories). Data acquisition and processing (SEC) were performed using the Waters Millennium 32 (v3.2) software. For SEC-LS, a Dawn DSP−F multiangle laser light scattering detector (source is a 5 mV linearly polarized He−Ne laser at 632.8 nm) from Wyatt was used and data processed with the Wyatt Astra (v4.72.03) software, using refractive index increment (d*n*/d*c*) of 0.188 mL/g.[24]

Temperature gradient interaction chromatography (TGIC) analysis was carried out using an high performance liquid chromatography (HPLC) system equipped with an HPLC pump (LDC, CM 3200), a six-port sample injector (Rheodyne, 7125), and a variable wavelength UV/vis absorption detector (TSP, SC-100). For reversed-phase TGIC (RP-TGIC), a C18 bonded silica column (Kromasil C18, 150 × 4.6 mm i.d., 100 Å pore), and a mixture of CH_2Cl_2/CH_3CN (57/43 (v/v), with flow rate = 0.5 mL/min, were used as the stationary and mobile phase, respectively. For normal phase TGIC (NP-TGIC), a bare silica column (Nucleosil, 100 × 4.6 mm I.D., 100 Å pore) and a mixture of isooctane/THF (54/46 (v/v), (flow rate = 0.5 mL/min) were used. The temperature of the separation column was controlled during the TGIC elution by circulating fluid from a programmable bath/circulator (NESLAB, RTE-111) through a homemade column jacket.

^{1}H NMR spectra (400 MHz) were recorded on a Varian Mercury Vx400 spectrometer using $CDCl_3$ as the solvent.

Scanning force microscopy (SFM) images were taken on a Digital Instruments Dimension 3100 microscope operated in the tapping mode. The standard silicon nitride probes were driven at 3% offset below their resonance frequencies in the range of 250−350 kHz. The samples were prepared by either spin-coating or dip-coating using freshly cleaved mica as substrate. Highly diluted polymer solutions (2.5−4.0 mg/L) in THF or chloroform were used to avoid the aggregation of polymer molecules during sample preparation. Spin-coating was performed at 1000 rpm for 1 min. Dip-coating was carried out by dipping mica into a polymer solution for 15 s and then drying in air.

2.3. Polymerizations. HTPCMS by Nitroxide-Mediated Polymerization. A three-neck round-bottom flask, purged with argon and equipped with a reflux condenser, was charged with freshly distilled CMS (21 g, 0.14 mol) and HPTPE (0.36 g, 0.0013 mol) and heated to 125 °C in an oil bath for 2 h. The resulting polymer was dissolved in THF and precipitated with methanol. It was further fractionated by addition of methanol (64 mL) to a 7% solution (110 mL) of the polymer in THF to obtain HTPCMS (8.2 g) in the precipitate. The obtained precipitate was dried under vacuum. $\overline{M}_n$(SEC) = 12 000 g/mol; $\overline{M}_w/\overline{M}_n$ = 1.1. ^{1}H NMR ($CDCl_3$): δ 1.20−2.10 (b, aliphatic polystyrene H's), δ 4.40 (m, 2H, CH_2Cl), 6.40−7.25 (b, aromatic polystyrene H's).

PCMS−PS400−PCMS by Coupling of End-Functionalized Homopolymers. A three-neck round-bottom flask was charged with HTPCMS (0.24 g, 0.02 mmol) and toluene (15 mL), stirred with a magnetic stirrer, and purged for 30 min with argon that was predried by passing through the Drierite unit. A phosgene solution in toluene (0.5 mL, 1 mmol phosgene) was added under rapid stirring. The escaping phosgene and HCl were neutralized by passing the outgoing gases through aqueous NaOH solution. After reaction for 30 min, excess phosgene was removed by bubbling argon for 30 min. A solution (0.01 mL) of pyridine (1.2 mol /L) in toluene, which was predried by storing over molecular sieves, was added to this mixture. DHPS400 (1.0 g, 0.0028 mmol), predried under high vacuum (0.01 mbar) overnight in a 50 mL flask and stored under argon, was now added under argon purge. After 1 h, the reaction mixture was concentrated by argon flow to evaporate the solvent, reducing the reaction mixture volume to 0.5 mL. Further pyridine solution (0.011 mL, 1.2 mol /L) was added and the reaction was allowed to proceed for additional 5 h. The reaction mixture was diluted with THF, and the polymer was precipitated with methanol and dried under vacuum. The resulting polymer mixture of the coupled product and the excess end capped HTPCMS was fractionated as follows. The polymer was dissolved in THF to yield a 2 wt % solution (1.3 g/65 mL), and subjected to fractionation by gradual addition of methanol (50 mL). After fractionation, the coupled product PCMS−PS400-PCMS (0.95 g) was recovered from the precipitate while the excess of end capped HTPCMS remained in solution. The triblock copolymer thus obtained was dried under vacuum. $\overline{M}_n$(SEC) = 354500 g/mol; $\overline{M}_w/\overline{M}_n$ = 1.15. ^{1}H NMR ($CDCl_3$): δ 1.20−2.10 (b, aliphatic polystyrene H's), δ 4.40 (m, 2H, CH_2Cl), 6.40−7.25 (b, aromatic polystyrene H's).

PCMS−PS50−PCMS by Coupling of End-Functionalized Homopolymers. The triblock copolymer was synthesized in a similar way as the previous synthesis, except that DHPS50 (0.42 g, 0.0076 mmol) was reacted with phosgene and the HTPCMS (0.80 g, 0.066 mmol) was added after the excess phosgene was removed under argon bubbling. $\overline{M}_n$(SEC) = 727000 g/mol; $\overline{M}_w/\overline{M}_n$ = 1.10.

^{1}H NMR ($CDCl_3$): δ 1.20−2.10 (b, aliphatic polystyrene H's), δ 4.40 (m, 2H, CH_2Cl), 6.40−7.25 (b, aromatic polystyrene H's).

Dumbbell-Shaped Polymer by ATRP of Styrene from PCMS−PS400−PCMS. A three-neck round-bottom flask was charged with styrene (38 g, 0.37 mol), CuBr (0.15 g, 0.001 mol) and d*n*Nbpy (0.89 g, 0.002 mol), and then purged with Argon for 1 h under rapid stirring. In another flask, PCMS−PS400−PCMS (0.94 g, 0.36 mmol initiating sites) and styrene (19 g, 0.18 mol) were added and degassed for 1 h. The initiator mixture was then transferred to the monomer solution dropwise using a degassed syringe. The resulting mixture was placed in a thermostatically controlled oil bath at 80 °C. Samples were withdrawn at desired times. After 21 h, the reaction mixture was diluted with THF and passed through a basic alumina column to remove the catalyst. The polymer was precipitated from the resulting solution using methanol, and then dried under vacuum to get 1.5 g product. $\overline{M}_n$(SEC) = 637000 g/mol; $\overline{M}_w/\overline{M}_n$ = 1.16. ^{1}H NMR ($CDCl_3$): δ 1.20−2.10 (b, aliphatic polystyrene H's), 6.40−7.25 (b, aromatic polystyrene H's).

Cleavage of the Triblock or Dumbbell Polymers. The triblock copolymer PCMS−PS50−PCMS (0.0050 g, 6.8×10^{-5} mmol) was dissolved in THF (5 mL) and refluxed overnight with 1 mL of alcoholic KOH (0.5 mol/L in ethanol) at 100 °C. The resulting solution was evaporated to dryness, and the residue was dissolved in THF (5 mL) for SEC analysis. Bimodal SEC chromatogram: $\overline{M}_n$(SEC) = 55 000 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.05 and $\overline{M}_n$(SEC) = 12 000 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.1 respectively.

3. Results and Discussion

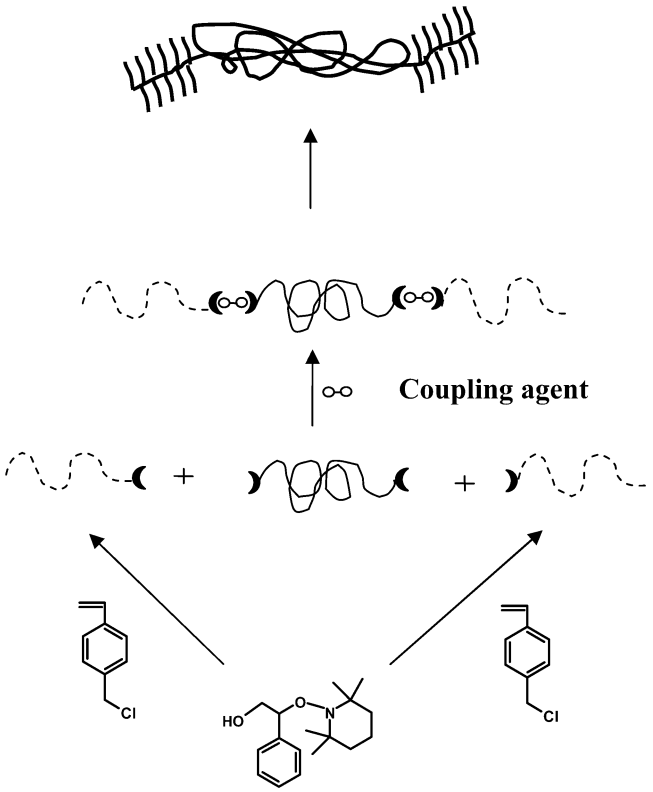
The goal of this work was to synthesize the dumbbell polymers by growing branches by ATRP from end blocks of a symmetric triblock copolymer made by polymer−polymer coupling of hydroxy-terminated poly(chloromethylstyrene) (HTPCMS) synthesized by NMP and commercially obtained α,ω-dihydroxy-terminated polystyrenes (DHPS).

An alternative route for the synthesis of the symmetric triblock is sequential living polymerization of the two monomers.[19] However, this has limitations when desiring a high molecular weight central block and short end blocks: chain transfer and limited reinitiation efficiency lead to lack of control, the extent of which is difficult to judge due to the impossibility to determine distribution of block lengths when one block is very large compared to the other. In comparison, our procedure (Scheme 1) provides independent characterization of both the central and the end blocks, prior to their coupling. Additionally, the possibility of cleavage of the coupling site provides the opportunity for separate analysis of the structure of the "bells" of the dumbbell product.

3.1. Synthesis of HTPCMS. A narrow polydispersity HTPCMS can be best synthesized by "living" polymerization. Since the CMS monomer has potential initiator sites for ATRP and terminating sites for anionic polymerization, HTPCMS must be synthesized by an alternative "living" radical polymerization technique, and we used nitroxide-mediated polymerization (NMP). The unimolecular initiator 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane (HPTPE) has been used in the past for synthesis of hydroxy-terminated polystyrene with controlled molecular weights and low polydispersities.[25] However, the original HPTPE synthesis is limited by its low yield, prolonged reaction time at elevated temperatures, strenuous product isolation and purification processes. Here we used the literature procedure of Gravert et al.[23] for the synthesis of the same initiator, and confirmed the structure of the initiator by using ^{1}H NMR.

Several attempts have been made for the synthesis of poly(chloromethylstyrene) (PCMS) by NMP in the past,[26,27] though

Scheme 1. Schematic Representation of Synthesis of Dumbbell Polymers



resulting in PCMS of high polydispersity (1.3−1.6), which can be attributed to transfer reactions to the chloromethyl groups that have been described by Lacroix-Desmazes et al.[28] Accordingly, our NMP of CMS from unimolecular initiator HPTPE resulted in the HTPCMS of a high polydispersity of around 1.4 (dashed line in Figure 1) determined from SEC chromatogram. We used precipitation fractionation from THF solution to obtain HTPCMS ($\overline{M}_n$ = 12 000 g/mol, SEC) of narrow polydispersity (1.1) (solid line in Figure 1).

3.2. Synthesis of Triblock Copolymers PCMS−PS50−PCMS and PCMS−PS400−PCMS. Coupling of end-functionalized polymers provides a versatile technique for block copolymer synthesis while retaining information and control over length distribution of the blocks. Cotiuga et al.[21] report an efficient one-pot coupling reaction for block copolymer synthesis using phosgene as a coupling agent. This is achieved by very efficient online removal of excess phosgene due to its distinctive high

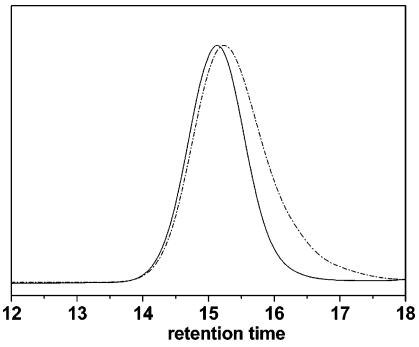
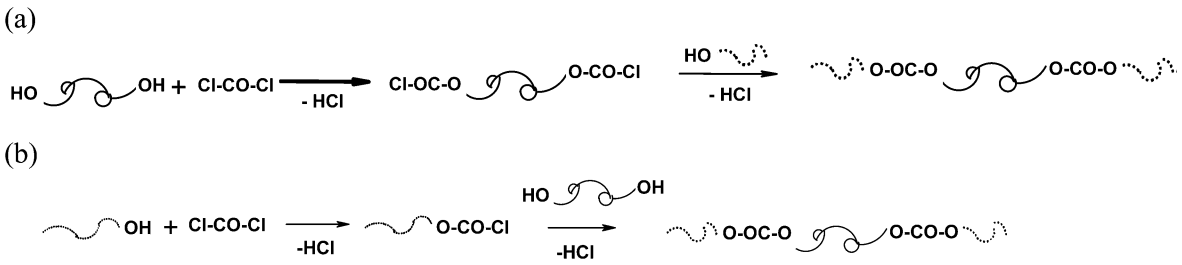


Figure 1. Size exclusion chromatography (SEC) traces of hydroxy-terminated poly(chloromethylstyrene) (HTPCMS) obtained by nitroxide-mediated polymerization of chloromethylstyrene with 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyl oxy) ethane (HPTPE) as initiator at 125 °C, before (dashed line) and after (solid line) precipitation fractionation.

Scheme 2. Coupling of α,ω-Dihydroxy-Terminated Polystyrene (DHPS) and Hydroxy-Terminated Poly(chloromethylstyrene) (HTPCMS) To Give Poly(chloromethyl Styrene-*b*-styrene-*b*-chloromethylstyrenes) (PCMS−PS−PCMS): (a) PCMS−PS400−PCMS and (b) PCMS−PS50−PCMS



volatility. This is facilitated by commercial availability of phosgene as a 20% toluene solution which can be safely dispensed with a syringe in a fume hood.[29,30]

We employed coupling of HTPCMS with $\overline{M}_n$ = 12 000 g/mol and commercially obtained α,ω-dihydroxy-terminated polystyrene (DHPS50 and DHPS400) to synthesize PCMS−PS−PCMS. In the PCMS−PS50−PCMS case (Scheme 2a), the hydroxyl functionality of DHPS50 is converted to the reactive chloroformate and HTPCMS is added after the removal of the excess phosgene. In the PCMS−PS400−PCMS case (Scheme 2b), we first modify the hydroxyl end-functionality of the HTPCMS with phosgene to highly reactive chloroformate, remove the excess of phosgene by Ar bubbling and then add the DHPS400. The latter procedure is more efficient since we used excess HTPCMS and the mobility of the minor component DHPS400 is perhaps limited by its high molecular weight. The excess of HTPCMS is removed by precipitation fractionation from THF solution using methanol. The SEC chromatograms of the triblocks before and after fractionation are shown in Figure 2 as dashed lines and solid lines respectively.

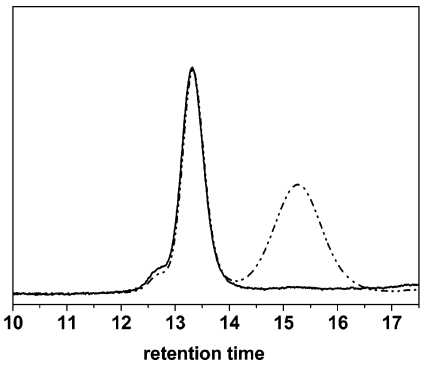


Figure 2. Size exclusion chromatograms of the triblock copolymers poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) (a) PCMS−PS50−PCMS and (b) PCMS−PS400−PCMS, formed by coupling of α,ω-dihydroxy-terminated polystyrenes (DHPS50 and DHPS400) with hydroxy-terminated polychloromethylstyrene (HT-PCMS); before (dashed lines) and after fractionation (solid lines).

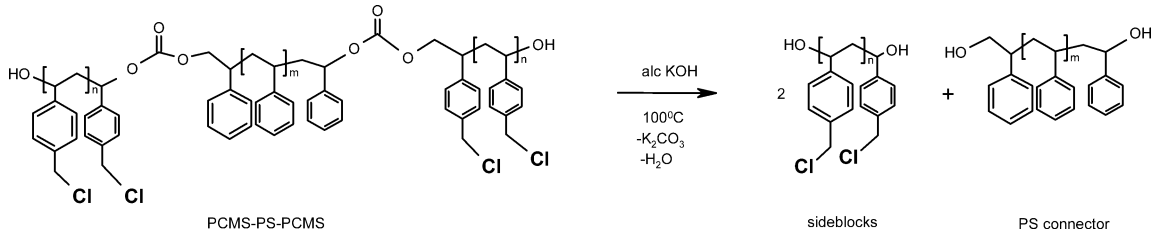
Table 1. Molecular Weight Characteristics (SEC) of the Triblock Copolymers Poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) Formed by Coupling of α,ω-Dihydroxy-Terminated Polystyrene (DHPS50 and DHPS400) with Hydroxy-Terminated Poly(chloromethylstyrene) (HTPCMS)

	$\overline{M}_n$ (g/mol)	PDI
PCMS−PS50−PCMS	72 700	1.10
PCMS−PS400−PCMS	354 500	1.15

The small shoulder on the high molecular weight side (low retention time) in the SEC peak (Figure 2a) is most likely due to the possible small extent of coupling of the DHPS molecules with each other. The DHPS50 is converted to the highly reactive chloroformate before the addition of HTPCMS and therefore more coupling in this case as can be inferred from the comparatively bigger shoulder in Figure 2a.

In the case of the coupling reaction of DHPS400, a small shoulder is also observed on the low molecular weight side ($\overline{M}_n \approx$ 200K) (Figure 2b), which is also present in the as received DHPS400. This can most likely be ascribed to the anionic polymerization proceeding from only one of the initiating sites during the synthesis of DHPS400 from a small fraction of the bifunctional initiator employed there. Thus, the high and low molecular weight shoulder in the coupled product SEC can be attributed presumably to PCMS−PS400−PS400−PCMS and PS200−PCMS created during the coupling reaction. The molecular weight characteristics of triblock copolymers obtained by SEC analysis are presented in Table 1.

Scheme 3. Hydrolytic Cleavage of Poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) into Backbone and Side Blocks, Obtained by Heating with Alcoholic KOH



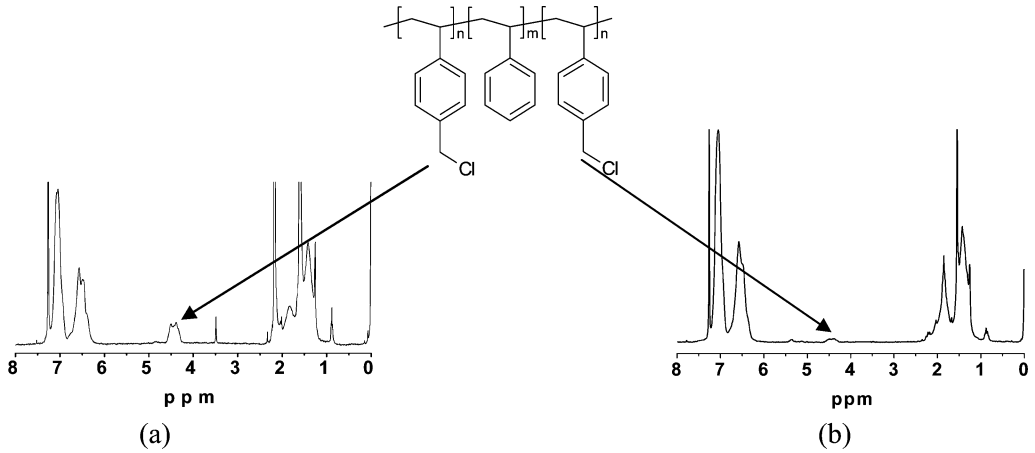


Figure 3. ^{1}H NMR spectrum of poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) (a) PCMS−PS50−PCMS $\overline{M}_n$(SEC) = 72700 g/mol and (b) PCMS−PS400−PCMS $\overline{M}_n$(SEC) = 354500 g/mol formed by coupling of α,ω-dihydroxy-terminated polystyrene (DHPS50 and DHPS400) with hydroxy-terminated poly(chloromethylstyrene) (HTPCMS). The peak at δ 4.4 ppm corresponds to the $-CH_2Cl$.

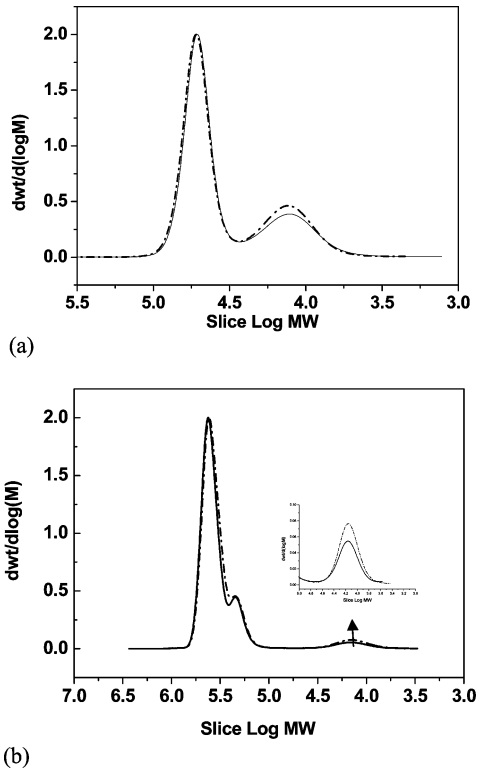


Figure 4. Size exclusion chromatograms of the cleaved product of triblocks poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) (solid lines) and of a physical mixtures (dashed lines) of α,ω-dihydroxy-terminated polystyrene (DHPS) and hydroxy-terminated poly(chloromethylstyrene) (HTPCMS) in molar ratio 1:2 as expected in the coupled product. The chromatograms display bimodal distributions, with the higher molecular weight peak corresponding to the DHPS and the lower molecular weight peak corresponding to HTPCMS. The chromatogram heights are adjusted so that the overlay results in equal area of the DHPS peak for cleaved products and the physical mixtures. Both (a) PCMS−PS50−PCMS and (b) PCMS−PS400−PCMS cases are shown. The inset in part b is a blow up of the peaks at (log MW = 4.10).

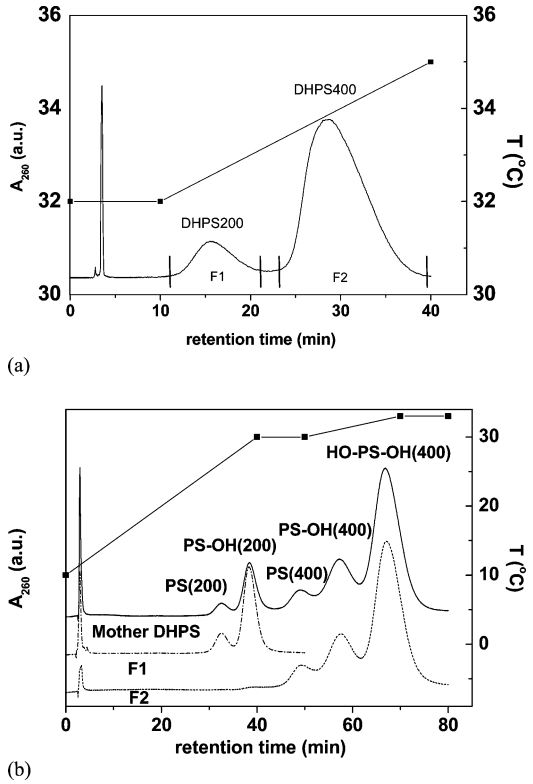
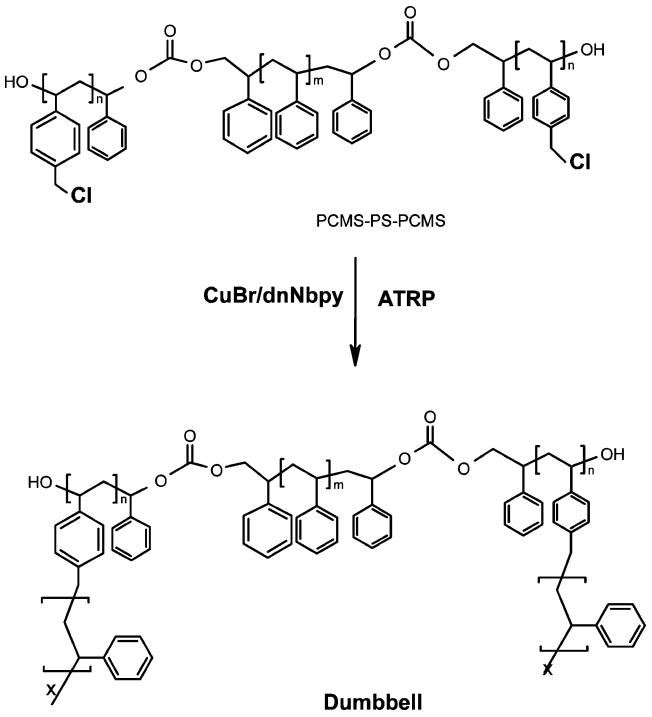


Figure 5. (a) Reversed phase temperature gradient isocratic chromatography (RP-TGIC) traces of the mother α,ω-dihydroxy-terminated polystyrene (DHPS). Small vertical bars indicate the range from which the fractions, F1 and F2 were collected. (b) Normal phase temperature gradient isocratic chromatography (NP-TGIC) traces of the mother DHPS sample and the two RP-TGIC fractions.

Even though the block copolymer $\overline{M}_n$ shown in Table 1 is calculated based on polystyrene calibration, it matches well with the expected value for PCMS−PS50−PCMS being $\overline{M}_n \approx$ 75500 g/mol. However the change in molecular weight for the high molecular weight DHPS400 on coupling with HTPCMS is very small, as expected. The block copolymers were further characterized by ^{1}H NMR (Figure 3). The area ratio (0.40) of the peak at δ 4.5 ppm ($-CH_2Cl$) in the CMS repeat units and the peak at δ 6.5 ppm, corresponding to 3 aromatic protons in the styrene repeat units of the PCMS−PS50−PCMS confirms the 2:1 molar ratio of PCMS to PS. However, in PCMS−PS400−PCMS, the peak at δ 4.5 ppm is too small to allow reliable area integration.

Thus, though ^{1}H NMR and SEC are very efficient in confirming the structure of PCMS−PS50−PCMS, we needed a more sensitive technique in the case of PCMS−PS400−PCMS. We therefore decided to perform alcoholic KOH assisted cleavage of the carbonate bond of the PCMS−PS−PCMS, resulting in the constituent blocks (Scheme 3). The subsequent SEC trace (solid line in Figure 4a) of the cleaved product of

Scheme 4. Dumbbell Synthesis from Poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS−PCMS) by Atom Transfer Radical Polymerization (ATRP) at 110 °C with CuBr/d*n*Nbpy as Catalyst/ligand System



PCMS−PS50−PCMS displays a bimodal distribution as the $M_p \sim 50$K peak (M_p = peak molecular weight) corresponds to the PS block and the $M_p \sim 12$K peak corresponds to the PCMS blocks. In Figure 4a, this chromatogram has been overlaid with the chromatogram (dashed line) of a physical mixture of DHPS50 and HTPCMS in molar ratio 2:1, the theoretical expected value in the case of precise coupling. In the case of PCMS−PS50−PCMS, the excellent match between the peak area ratios PS:PCMS (2.48 for physical mixture, 2.27 for cleaved product) confirms the desired structure of the triblock, that is, two PCMS blocks per PS50 block in the PCMS−PS50−PCMS. Similarly in the case of PCMS−PS400−PCMS the overlaid chromatograms of the cleaved product and the corresponding physical mixture are plotted in Figure 4b. The area of the PCMS peak (log M_p = 4.10) of the cleaved triblock is only 68% of the corresponding peak of the physical mixture when the areas of the PS400 peaks in the two samples are matched. This suggests a 91% efficiency of coupling of PCMS at the potentially available (75%) hydroxyl end groups of the DHPS400 (see further for the determination of end groups of DHPS400). This crucial measurement of the small concentration of available hydroxyl end groups in the high molecular weight DHPS400 sample was made possible by temperature gradient interaction chromatography (TGIC).[31]

TGIC makes use of a preprogrammed variation of column temperature during elution to control retention of polymeric solutes. The clear advantages of this method are the wide choice of detectors available owing to the isocratic condition, a better resolution than SEC, and excellent control of solute retention as compared to solvent gradient polymer elution chromatography.[32] Here we used a combination of reversed phase (RP) and normal-phase (NP) TGIC. The RP-TGIC is usually applied for MWD analysis of polymer mixtures, high molecular weight linear polymers, star-shaped polymers, etc. However NP-TGIC has more selectivity for separation of polymers based on their polar end groups. The DHPS sample was subjected to both RP−TGIC and NP-TGIC. The RP-TGIC chromatogram displayed in Figure 5a shows two fractions corresponding to two molecular weights present in the sample represented by PS400 ($\bar{M}_w \approx$ 400K from SEC) and PS200 ($M_w \approx$ 200K from SEC). A separation based on end groups cannot be expected since RP-TGIC is not sensitive to polar functionality.[32]

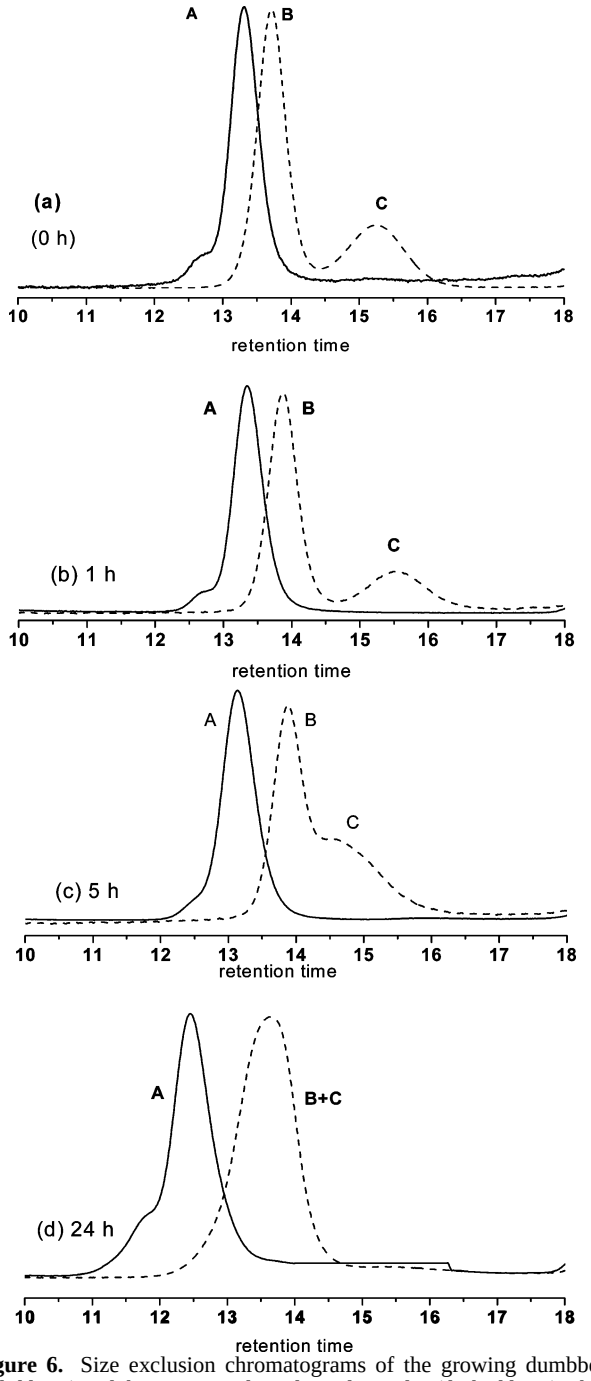


Figure 6. Size exclusion chromatograms of the growing dumbbell (solid lines) and the corresponding cleaved samples (dashed lines) taken during the atom transfer radical polymerization from the triblock initiator PCMS−PS50−PCMS to DB50 at various times (a) 0, (b) 1, (c) 5, and (d) 24 h. The solid line with peak A represents the growing dumbbell. The dashed lines represents the corresponding cleaved product, with peaks B corresponding to the central block PS50, and the peaks C corresponding to the growing side blocks (bells).

The NP-TGIC chromatogram of the DHPS mother sample is fully resolved into five peaks (Figure 5b). The NP-TGIC chromatograms of the two RP-TGIC fractions confirmed that the five peaks correspond to the five different species present in the sample namely the desired difunctional HO−PS400−

Table 2. Molecular Weight Characteristics of Dumbbell Polymers (DB50 and DB400) Prepared Using the Triblock Macroinitiators PCMS-PS50-PCMS ($\bar{M}_n = 7.7 \times 10^4$ g/mol, $\bar{M}_w/\bar{M}_n = 1.1$, 1 g) and PCMS−PS400−PCMS ($\bar{M}_n = 3.5 \times 10^5$ g/mol, $\bar{M}_w/\bar{M}_n = 1.15$, 1 g), Respectively

	[CuBr]:[dnNbpy]:[Cl]:[M]	T (°C)	time (h)	$\bar{M}_{n,SEC} \times 10^{-5}$ (g/mol)[a]	$\bar{M}_{w,SEC-LS} \times 10^{-5}$ (g/mol)[b]	yield (g)	PDI[c]
DB50	1:2:1: 1260	80	22	1.20	3.54	3.8	1.08
DB400-1	2:4:1:1500	80	21	4.03	5.46	1.3	1.16
DB400-2	3:6:1:1500	80	21	4.90	6.37	1.5	1.16
DB400-3	4:8:1:1500	80	21	6.08	11.6	2.7	1.16

[a] Number-average molecular weight determined by SEC in THF using polystyrene calibration. [b] Weight-average molecular weight determined by SEC equipped with a multiangle light scattering detector. [c] Polydispersity determined by SEC.

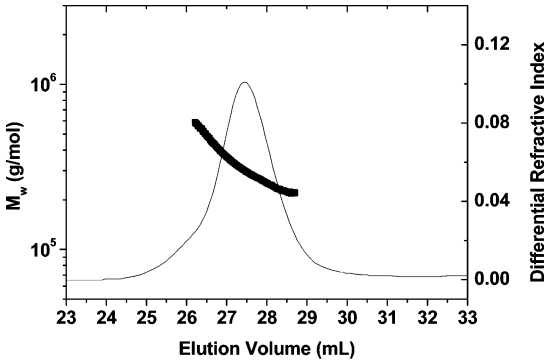


Figure 7. Size exclusion chromatography coupled with light scattering (SEC-LS) characterization of the dumbbell polymer sample DB-50 ($\bar{M}_n$(SEC-LS) = 120000) g/mol obtained by growing branches from poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS50−PCMS). Molecular weight (symbols) and concentration distribution (lines) vs elution volume.

OH, monofunctional PS400−OH, unfunctionalized PS400, monofunctional PS200−OH, and unfunctionalized PS200. From the area under the respective peaks, the percentages of these five species present in the mother sample were calculated as 54%, 21%, 10%, 10.8% and 2.2% respectively. The total hydroxyl functionality of DHPS can be estimated as 75% (defined as OH group per 200K molecular weight) by adding up all the functionalized species in the mother sample.

3.3. Dumbbell Synthesis from Triblock Copolymer PCMS−PS−PCMS. Several authors have used living polymerization to synthesize a variety of densely grafted or brush polymers by the "grafting from" approach.[33,34] The advantage of this method as compared to alternative methods like "grafting onto"[35,36] (attaching side chains to the backbone) and "grafting through"[37−39] (homopolymerization of macromonomers) approaches has been described widely.

We made use of ATRP to grow dense grafts from $-CH_2Cl$ initiating sites on the triblock copolymers PCMS−PS−PCMS, to obtain the desired dumbbell polymers (Scheme 4).

CuBr/d*n*Nbpy were used as the catalyst/ligand system and the reaction conditions are indicated in Table 2. Cu(II) salts are usually added[40] in densely grafted brush synthesis to suppress the radical coupling in anticipation of the persistent radical effect.

In our case, a high initial ratio of monomer to initiator sites and restricting to lower conversion gave well-defined dumbbell molecules. All the polymerizations were carried out at temperatures lower than the usual 110 °C for ATRP of styrene (Table 2). This helps to reduce the concentration of radicals during polymerization, and thus limit intermolecular coupling.

3.4. SEC and SEC-LS Characterization of the Dumbbell Polymers. The solid lines in Figure 6 are the SEC traces of the samples withdrawn during the ATRP reaction for the DB50 case. In going from Figure 6a−d with increasing reaction time, we notice the expected increase in the molecular weight (MW) of the dumbbells as indicated by the shift of the SEC peaks toward lower retention times. A narrow molecular weight distribution is indicative of minimal undesirable side reactions like chain transfer and intermolecular coupling. The increase in MW corresponds to increasing length of the branches on the side blocks. This is better illustrated by cleavage of the carbonate bond in these samples (section 3), leading to the separation of the central block and side blocks. The SEC traces of the cleaved samples are shown in Figure 6 as dotted lines to compare with the corresponding dumbbell samples (solid lines). For reaction times of 0−5 h, the cleaved samples display bimodal peaks, corresponding to the central block at retention time ~13.5 min and the growing side blocks at gradually reducing retention times (~15.2 to ~14.5 min). The area under the curves for the central block and side blocks is quantified by deconvolution into guassian peaks using Microcal Origin software and the known MW of the central linear block. This permits the determination of the molecular weights of the side blocks as $\bar{M}_n$ = 17 200 g/mol and $\bar{M}_n$ = 35 500 g/mol for the 1 and 5 h samples respectively. Knowing the number-average number of repeat units in the PCMS block as 79, the average $\bar{M}_n$ of PS grafts in

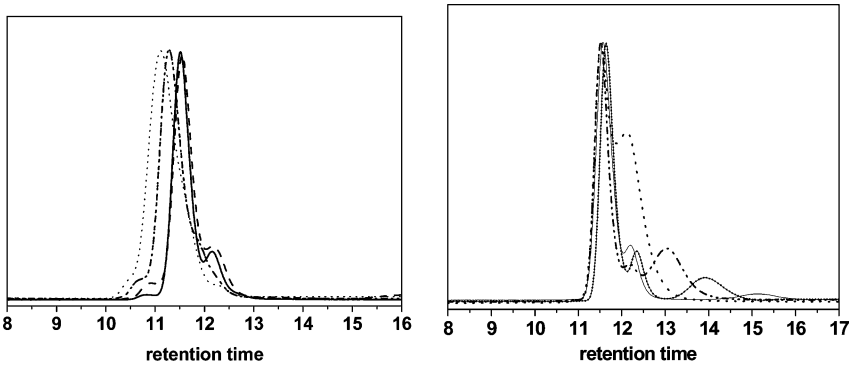


Figure 8. Size exclusion chromatograms of (a) the dumbbell samples obtained by growing branches from the macroinitiator poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS400−PCMS) and (b) the cleaved products obtained by reaction of dumbbells with aloholic KOH. DB400-1 (dashed line), DB400-2 (dashed-dotted line), DB400-3 (dotted line), and the starting triblock PCMS−PS400−PCMS (solid line).

Table 3. Molecular Weight Added on to the Side Blocks of the Triblock Copolymers

	$MW_{(side\ blocks)} \times 10^{-5}$ (g/mol)[a]	MW per graft (g/mol)[b]	MW per graft (g/mol)[c]
DB50	2.94	1875	
DB400-1	0.636	770	480
DB400-2	1.095	1520	1710
DB400-3	3.706	5122	

[a] From weight-average molecular weight of dumbbell samples determined using SEC-LS [b] Calculated from $MW_{(side\ blocks)}$ and number of initiating sites on the side blocks [c] From (SEC) analysis of cleaved products, using the area of central block as reference.

the 1 and 5 h sample is calculated as 110 and 226 respectively with this SEC area method. In the final sample (Figure 6d); the side block peak has moved so far to the left as to overlap with the central block peak. This overlap hinders the estimation of the side block MW from SEC. An alternative method of determination of graft MW is cleavage of branches from the backbone and their subsequent analysis by SEC. However the lack of cleavable ester groups in our graft initiating sites restricts this analysis for our dumbbell polymers. We employed an additional method that involves probing the shape of dumbbells with light scattering by simultaneous measurements of radius of gyration (R_g, *z*-average) and absolute molecular weight ($\bar{M}_w$, weight-average) of fractions eluting during SEC. Figure 7 shows a plot of the $\bar{M}_w$ and the concentration signals of DB50 obtained from SEC-LS measurements. From the distribution, the $\bar{M}_w$ of the final dumbbell is calculated as 3.5×10^5 (g/mol) as presented in Table 2. This, along with the $\bar{M}_w = 55\,500$ g/mol of the linear central block PS50, enables the determination of the molecular weight of the side blocks for the final sample of DB50 as 2.9×10^5 g/mol (Table 3). This corresponds to an average graft MW of 1875 g/mol in the final DB50 sample. ATRPs of styrene from side blocks of the higher MW triblock PCMS−PS400−PCMS were carried out in a similar way. To enhance the apparent polymerization rate and hence the graft length of the side blocks, we increased the CuBr and d*n*Nbpy concentrations compared to the initiator (Table 2).

The three dumbbells samples DB400-1, DB400-2, and DB400-3 prepared with different recipes (Table 2) differ in the graft lengths, but have the same central block as seen from the SEC traces of the dumbbells (Figure 8a) and their cleaved products (Figure 8b). We can notice a slight shoulder at both higher and lower retention times in Figure 8a for the dumbbells.

The shoulder at the lower retention time corrresponds to the densely grafted product from PCMS−PS400−PS400−PCMS (see also discussion in section 3.2 and Figure 4b). The shoulder at the higher retention time corresponds to the densely grafted product from PS200−PCMS (see also discussion 3.2 and Figure 4b). The molecular weight characteristics of the different dumbbell samples from PCMS−PS400−PCMS are also presented in Table 2.

Again, we monitored the dumbbell synthesis in the DB400 case by withdrawing intermediate samples during the reaction and subjecting them to cleavage into the constituent blocks and analysis by SEC and SEC-LS. We exemplify the DB400 case by describing the analysis done on samples withdrawn during ATRP to DB400-2 (Figure 9). Again, with increasing reaction time, we notice the expected shift of the SEC peaks (solid lines) toward lower retention times, while retaining narrow polydispersity. SEC traces of the cleaved samples of the dumbbells are also presented in the same figure as dotted lines. We can see that the SEC traces of the cleaved products are composed of three peaks: (A) central block PS400, (B) central block PS200 due to the contamination in the starting sample, and (C) growing side blocks which moves from 15.1 min (at 0 h) to 13.1 min (at 21 h). Using the SEC area method we calculated the corresponding MW of side blocks as 21K, 47K, and 109K for 1, 13, and 21 h samples respectively.

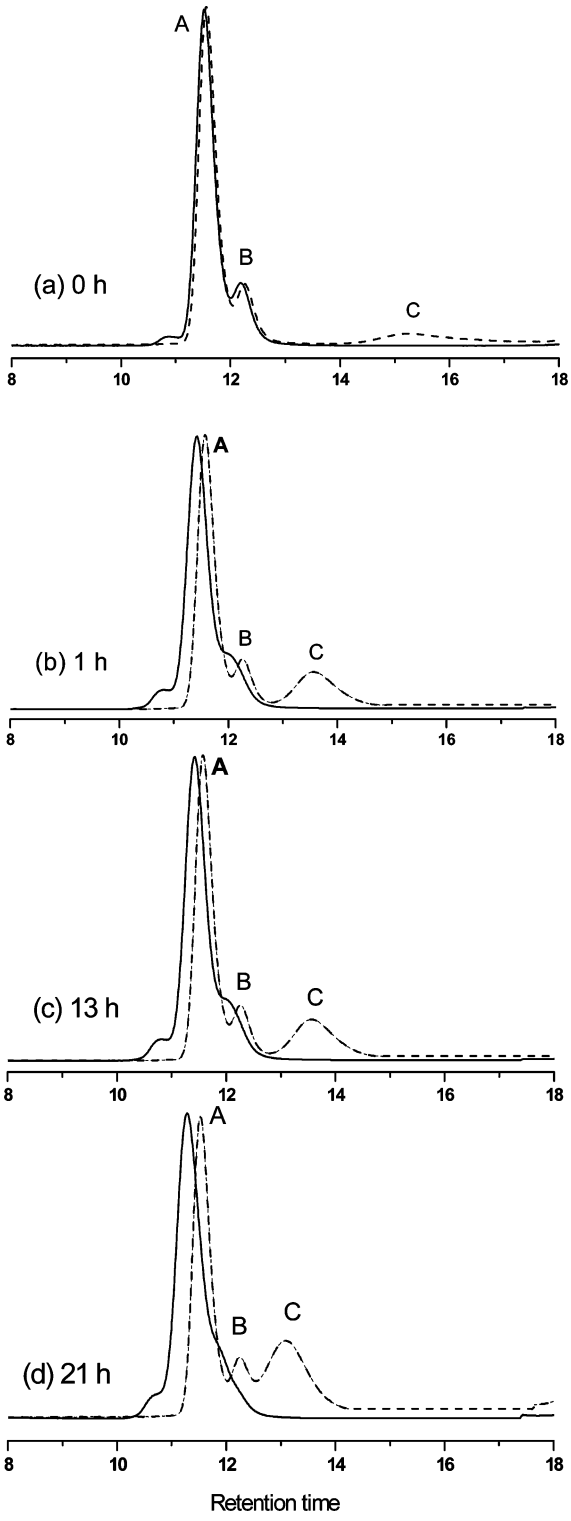


Figure 9. Size exclusion chromatograms of the growing dumbbell (solid line) and the corresponding cleaved samples (dashed line) during the atom transfer radical polymerization from the triblock initiator PCMS−PS400−PCMS to DB400-2 at various times (a) 0, (b) 1, (c) 13, and (d) 21 h. The indicated peaks in the dashed curves for the cleaved product represent the following constituents: (A) the central block PS400; (B) PS200 due to the contamination in the starting sample; (C) the growing side blocks.

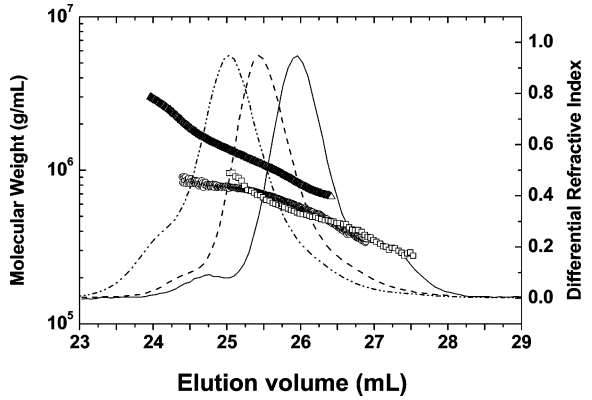


Figure 10. Size exclusion chromatography coupled with light scattering (SEC-LS) characterization of dumbbell samples (DB400) obtained by growing branches from the triblock macroinitiator poly(chloromethylstyrene-*b*-styrene-*b*-chloromethylstyrene) (PCMS−PS400−PCMS). Molecular weight (symbols) and concentration distribution (lines) vs elution volume. Solid line and squares represent DB400-1, dashed line and circles represent DB400-2, and dashed-dotted line and triangles represents DB400-3.

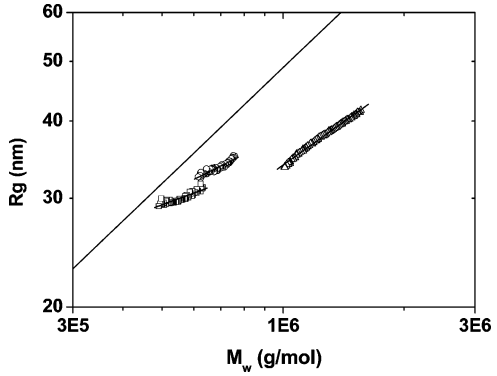


Figure 11. Radius of gyration vs molecular weight for the dumbbells (DB400 series) determined by SEC-LS. The solid line represent radius of gyration for linear polystyrene sample. Key: squares, DB400-1; circles, DB400-2; triangles, DB400-3.

The estimated molecular weights of the corresponding grafted branches for the three dumbbells of the DB400 series are shown in Table 3.

Figure 10 shows the MW and concentration vs elution volume plots of different DB400 dumbbells determined by SEC-LS analysis. We notice a change in MW vs elution volume slope at elution times corresponding to the shoulders in concentration curve, due to the dumbbells formed from PCMS−PS400PS400−PCMS and PCMS−PS200 formed during the coupling reaction. Figure 11 compares the R_g vs $\bar{M}_w$ data for dumbbell polymers and for linear polystyrene. The slope for the linear polystyrene is 0.6 corresponding to the Flory value, as commonly observed for linear flexible polymers in good solvents.[41]

For any given $\bar{M}_w$, the R_g values for the dumbbells are smaller than those for linear polystyrene due to the compactness of the dumbbell polymers. Among the dumbbell polymers, the R_g values are on the order of 28.7, 33.3, and 38.6 nm for the DB400-1, DB400-2, and DB400-3 samples, respectively.

The deviation of the R_g values of the dumbbells from that of linear PS appear to increase in the order DB400-1 ≤ DB400-2 < DB400-3 owing to the increasing compactness of the dumbbells with increasing graft length. The $R_g-\bar{M}_w$ relationship for all dumbbell samples (in the region of respective concentration peaks) displays a slope smaller than 0.6, due to compact structure of dumbbells.

3.5. Visualization of the Dumbbell-Shaped Polymers. SFM has been widely used to characterize branched polymers such as polymer brushes and star polymers.[6, 33, 34] Here we used SFM to visualize individual dumbbell molecules. Different solvents (THF and chloroform) and different sample preparation methods (spin-coating and dip-coating) were tried and consistent results were obtained. Figure 12a shows a typical SFM image of dumbbells on mica, and we notice here many nanosized bright spots, near circular in shape. The 3D image in Figure 12b further assists their visualization as concentrated masses of the polymer. Since several of these spots appear as pairs, these could correspond to pairs of (densely grafted) bells associated with individual dumbbell molecules, while we are unable to visualize the (linear) connectors corresponding to each pair of bells. We also visualize some spots that appear unpaired. These could result from the considerable amount of diblock copolymer (PS−PCMS) present in the triblock precursor (PCMS−PS400−PCMS). Cross-section analysis (Figure 12c) of the individual bells (along the vertical black line shown in Figure 12a) gives the average size of 36 ± 4 nm as diameter and 3.2 ± 0.3 nm as height. To evaluate the volume (V) of the visualized structures

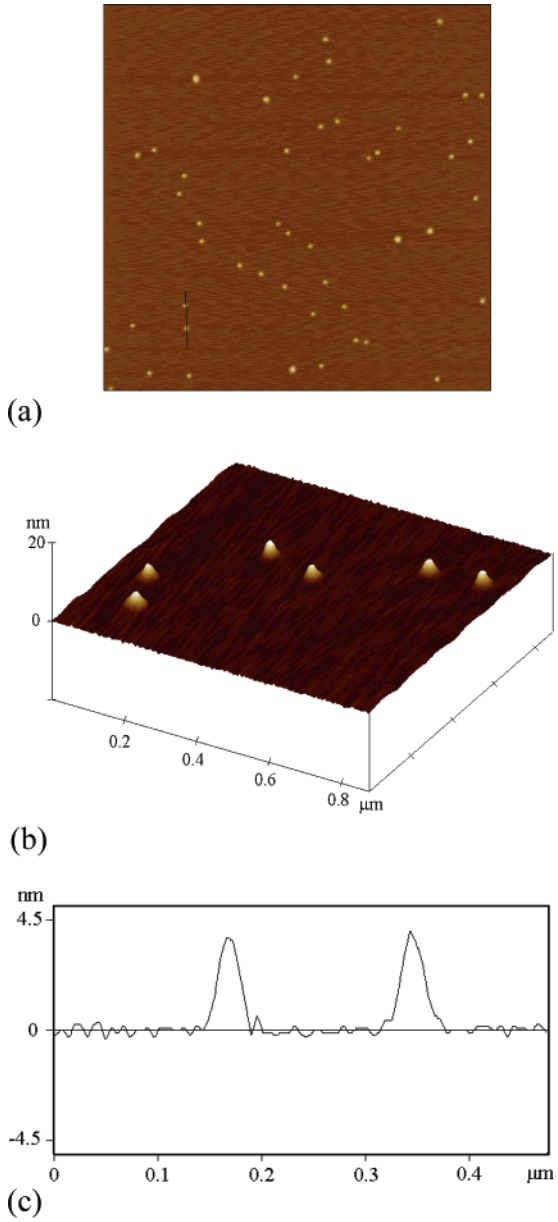


Figure 12. (a) Scanning force microscopy (SFM) height image (3 μm × 3 μm) of DB400-3 (z range: 10 nm). The sample was prepared by spin-coating of dilute DB400-3 solution (2.5 mg/L in THF) onto mica. (b) 3-D height image. (c) Cross-section along the black line in part a.

we assumed the cone shape for simplicity: $V_{SFM} = (1/3)\pi hr^2$, where h and $2r$ are the height and diameter of structures observed with SFM.[42] The calculated V_{SFM} is 1085 nm^3. If the bells of dumbbells were to have the same density as bulk PS (1 g/cm^3), based on its molecular weight (3.706 × 104 g/mol for DB400-3, Table 3) we can calculate the volume of each bell as $V_{cal} = 616$ nm^3, which is smaller than V_{SFM}. Taking into account that the lateral dimension (diameter) observed in SFM images may be significantly overestimated due to the scanning tip with a radius of about 10 nm,[43] the comparison between V_{cal} and V_{SFM} indicates that the visualized balls in SFM images may indeed correspond to individual bells of the dumbbells. In addition, while accounting for the overestimated linear dimension of the individual bells (diameter ~ 36 nm), it corresponds well with the expected stretched dimension perpendicular to the backbone (25 nm, twice the radially outward PS branches, each of average degree of polymerization ~50, Table 3) and along the backbone (18 nm from length of PCMS block of degree of polymerization = 72, and additional contribution due to bending branches). Because of the comparable dimensions along and perpendicular to backbone, the top projections of the resulting bells are circular rather than rodlike.[44]

4. Conclusions

Well-defined dumbbell polymers of different connector and branch lengths were prepared by grafting from specially synthesized triblock copolymers PCMS−PS−PCMS. This employed a combination of different techniques which include "living" radical polymerizations of the NMP and ATRP type, as well as polymer−polymer coupling. Synthesis of the required high molecular weight triblock precursor was made possible by the phosgene assisted coupling of the end-functionalized blocks, and the potential for cleavage of the thus formed carbonate bond between the blocks facilitated the reliable characterization of the dumbbells and the intermediates. Temperature gradient interaction chromatography enabled very sensitive quantitative detection of the terminal hydroxyl functionality of the polystyrene used as central block, and SEC and SEC-LS clearly and quantitatively demonstrated the progress of the compact grafting process. Finally, the dumbbell topology was directly visualized by SFM.

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References and Notes

(1) Schultz, D. N., Glass, J. E., Eds. *Polymers as rheology modifiers*; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991.
(2) Mecerreyes, D.; Jérôme, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1−59.
(3) Davis. K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 153−169.
(4) Agarwal, U. S. Polymer Properties. In *Handbook of Polymer Reaction Engineering*; Meijer, T., Keurentjes, J. T. F., Eds.; Wiley-VCH: New York. 2005; Vol. 2, pp 679−720.
(5) Knauss, D. M.; Huang, T. *Macromolecules* **2003**, *36*, 6036.
(6) Xue, L.; Agarwal, U. S.; Zhang, M.; Staal, B. B. P.; Muller, A. H. E.; Bailly, C. M. E.; Lemstra, P. J. *Macromolecules* **2005**, *38*, 2093−2100.
(7) Xue, L.; Agarwal, U. S.; Lemstra, P. J. *Macromolecules* **2005**, *38*, 8825.
(8) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(9) Vlassopoulos, D.; Fytas, G.; Paluka, T.; Roovers, J. *J. Phys. Condens. Matter* **2001**, *13*, R855.
(10) McLeish, T. C. B. *J. Rheol.* **2003**, *47*, 177. Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(11) Larson, R. G. *Macromolecules* **2001**, *34*, 4556−4571.
(12) McLeish, T. C. B.; Allgaier, J.; Bick, D. K.; Bishko, G.; Biswas, P.; Blackwell, R.; Blottiere, B.; Clarke, N.; Gibbs, B.; Groves, D. J.; Hakiki, A; Heenan, R. K.; Johnson, J. M.; Kant, R; Read, D. J.; Young, R. N. *Macromolecules* **1999**, *32*, 6734−6758.
(13) Kapnistos, M.; Vlassopoulos, D.; Roovers, J.; Leal, L. G. *Macromolecules* **2005**, *38*, 7852.
(14) Bailly, C.; Stephenne, V.; Muchtar, Z.; Schappacher, M.; Deffieux, A. *J. Rheol.* **2003**, *47*, 821.
(15) Archer, L. A.; Juliani. *Macromolecules* **2004**, *37*, 1076−1088.
(16) Roovers, J. *Macromolecules* **1984**, *17*, 1196−1200.
(17) Hadjichristidis, N.; Xeniduo, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; Garcia-Franco, C. A.; Sun, T.; Ruff, C. J. *Macromolecules* **2000**, *33*, 2424−2436.
(18) Houli, S.; Iatrou, H.; Hadjichristidis, N.; Vlassopoulos, D. *Macromolecules* **2002**, *35*, 6592−6597.
(19) Rajan. M.; Agarwal, U. S.; Bailly, C.; George, K. E.; Lemstra, P. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 575.
(20) Matyjaszweski, K.; Shipp, A. D.; Mcmurtry, G. P.; Gaynor, S. G.; Tadeusz, P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2023.
(21) Cotiuga, I. M.; Picchioni, F.; Agarwal, U. S.; Staal, B. B. P.; Vekemans, J. A. J. M.; Lemstra, P. J. *Macromol. Rapid Commun.* **2006**, *27*, 242.
(22) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.
(23) Gravert, D. J.; Janda, K. D. *Tetrahedron*, **1998**, *39*, 1513−1516.
(24) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989; Vol. VII, p 445.
(25) Hawker, J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993−2995.
(26) Devonport, W.; Michalak, L.; Malmstro, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. *Macromolecules* **1997**, *30*, 1929.
(27) Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, P. N. *Macromolecules* **1997**, *30*, 2228−2231.
(28) Lacroix-desmazes, P.; Delair, T.; Pichot, C.; Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3845−3854.
(29) Monsathaporn, S.; Effenberger, F. *Langmuir* **2004**, *20*, 10375.
(30) Nowick, J. S.; Holmes, D. L.; Noronha, G.; Smith, E. M.; Nguyen, T. M.; Huang, S.-L. *J. Org. Chem.* **1996**, *61*, 3929.
(31) Lee, W.; Cho, D.; Chun, B. O.; Chang, T.; Ree, M. *J. Chromatogr. A.* **2001**, *910*, 51−60.
(32) Chang, T. *Adv. Polym. Sci.* **2003**, *163*, 1−60.
(33) Beers. K. L.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 9413−9415.
(34) Cheng, G.; Boker, A.; Zhang, M.; Krausch, G.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 6883−6888.
(35) Subbotin, A.; Saariaho, M.; Ikkala, O.; ten Brinke, G. *Macromolecules* **2000**, *33*, 3447.
(36) Ruokolainen, J.; Saariaho, M.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Torkkelli, M.; Serimaa, R. *Macromolecules* **1999**, *32*, 1152.
(37) Djalali, R.; Hugenberg, N.; Fischer, K.; Schmidt, M. *Macromol. Rapid Commun.* **1999**, *20*, 444.
(38) Yamada, K.; Miyazaki, M.; Ohno, K.; Fukuda, T.; Minoda, M. *Macromolecules* **1999**, *32*, 290.
(39) Pantazis, D.; Chalari, I.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 3783.
(40) Borner, H. G.; Duran, D.; Matyjaszewski, K.; Da Silva, M.; Sheiko, S. S. *Macromolecules* **2002**, *35*, 3387−3394.
(41) Nakamura, Y.; Wan, Y.; Mays, J. M.; Iatrou, H.; Hadjichristidis, N.; *Macromolecules* **2000**, *33*, 8323−8328.
(42) Kiriy, A.; Gorodyska, G.; Minko, S.; Stamm, M.; Tsitsilianis, C. *Macromolecules* **2003**, *36*, 8704−8711.
(43) Xu, S.; Arnsdorf, M. F. *J. Microsc.* **1994**, *173*, 199.
(44) Zhang, M. T.; Breiner, H.; Mori, A.; Müller, H. E. *Polymer* **2003**, *44*, 1449.

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