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Synthesis of Dendron Functionalized Core Cross-linked Star Polymers

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ABSTRACT: The preparation of dendron functional initiators capable of initiating polymerization by atom transfer radical polymerization is described. Polyester dendrons up to the fifth generation were synthesized by the divergent route using acetonide-protected 2,2-bis(methoxy)propionic acid. These dendrons were functionalized, at the focal point, with a single α-bromoisobutyrate group, thus forming a dendron functional macroinitiator. A library of highly branched, 3-dimensional, dendron functional core cross-linked star (CCS) polymers were prepared from these macroinitiators by varying generation number and polystyrene chain length, followed by reaction with divinyl benzene, utilizing the "arm first" approach. The number of arms of the star polymer was shown to decrease with increasing dendron size; a generation 1 functional polymer prepared CCS polymers with 27 arms, and a generation 5 functional polymer prepared CCS polymers with 19 arms. The length of the polystyrene linear segment had a drastic effect on the formed CCS polymers; with as little as 5 styrene units attached to a generation 5 initiator, CCS polymers with 37 arms were produced, with 290 units of styrene, CCS polymers with 8 arms were prepared.

Introduction

One of the most versatile strategies for the preparation of star polymers involves the coupling of a preformed polymer with a difunctional monomer, forming a core cross-linked star (CCS) polymer.[1−9] This synthesis strategy, the "arm first" approach, is a powerful technique for the introduction of functional groups as it provides three discrete areas for functionalization: end functional star polymers can be prepared by initiating polymerization, in the arm-formation-step, with a functional initiator,[10,11] star polymers with pendant functionality can be prepared by polymerizing functional monomers,[2] and core functional star polymers can be synthesized by adding functional monomers and/or cross-linkers in the star-formation-step.[6−8]

This ability to design star polymers with spatial control over functional group location opens up possibilities for applications in areas such as drug delivery and medical imaging, where the interaction of reactive groups with the external environment can be mediated by their location.[12,13] For example, covalently stabilized polymer micelles with functionalities in the core for drug loading can be combined with specific binding molecules on the periphery (end functional) to prepare site-specific polymeric drug vehicles.[13]

A traditional drawback of end functional CCS polymers is the limitation of only one functional group per arm of the star; hence the functionality of the star will be equal (restricted) to the number of linear arms of the star. To overcome this restriction, initiators with multiple functionalities on the periphery may be envisaged. A promising strategy is to replace the starting linear polymers with hybrid dendron-*block*-linear copolymers, which have multiple chain end functionalities per macromolecule and have recently gained significant interest.[14−16] A convenient route to prepare such polymers is to synthesize a dendritic macroinitiator with a single functionality at the focal point capable of initiating polymerization.[14−16] The resulting hybrid dendritic-linear macromolecule can then be used in the usual manner to form star polymers by the "arm first" approach to give highly functionalized CCS polymers with a core−shell morphology. This unique type of star polymer has been reported using a fourth generation Fréchet-type block-polystyrene copolymer; however, these materials lacked any chain end functionality and a systematic study examining the synthetic variability and physical properties was not conducted.[6]

In this report, chain end functionalized dendrons up to the fifth generation based on 2,2-bis(methoxy)propionic acid (bis-MPA), pioneered by the groups of Hult[17,18] and Fréchet,[19−22] were prepared with a single alkyl halide at the focal point capable of initiating polymerization by atom transfer radical polymerization (ATRP). These dendritic initiators are used to initiate the polymerization of styrene and then to prepare dendron functionalized star polymers by the "arm first" approach. The synthetic procedure used to prepare dendron functional initiators and the preparation of dendron functional star polymers will initially be discussed and a systematic study to examine the effects of dendron generation and the length of the linear segment on the final star structure conducted. To the best of our knowledge, this is the first time a series of controlled dendron star structures with varying generation number and different arm lengths have been prepared and a variety of unique polymers with new and interesting architectures described.

Experimental

Materials. All chemicals were purchased from Aldrich. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%) and divinylbenzene (DVB, 80% mixture of isomers) were washed three times with 5% sodium hydroxide solution, once with distilled water, and then distilled over calcium hydride. Styrene (Sty, 99+%) was passed through a column of basic alumina and inhibitor remover and stored in a freezer. DOWEX-50-X2 was washed several times with methanol and then activated with 1 M HCl in methanol. Tetrahydrofuran (THF, HPLC grade), methanol (AR grade), anisole (anhydrous, 99+%), copper(I) bromide (99+%), 2,2-bis(methoxy)-

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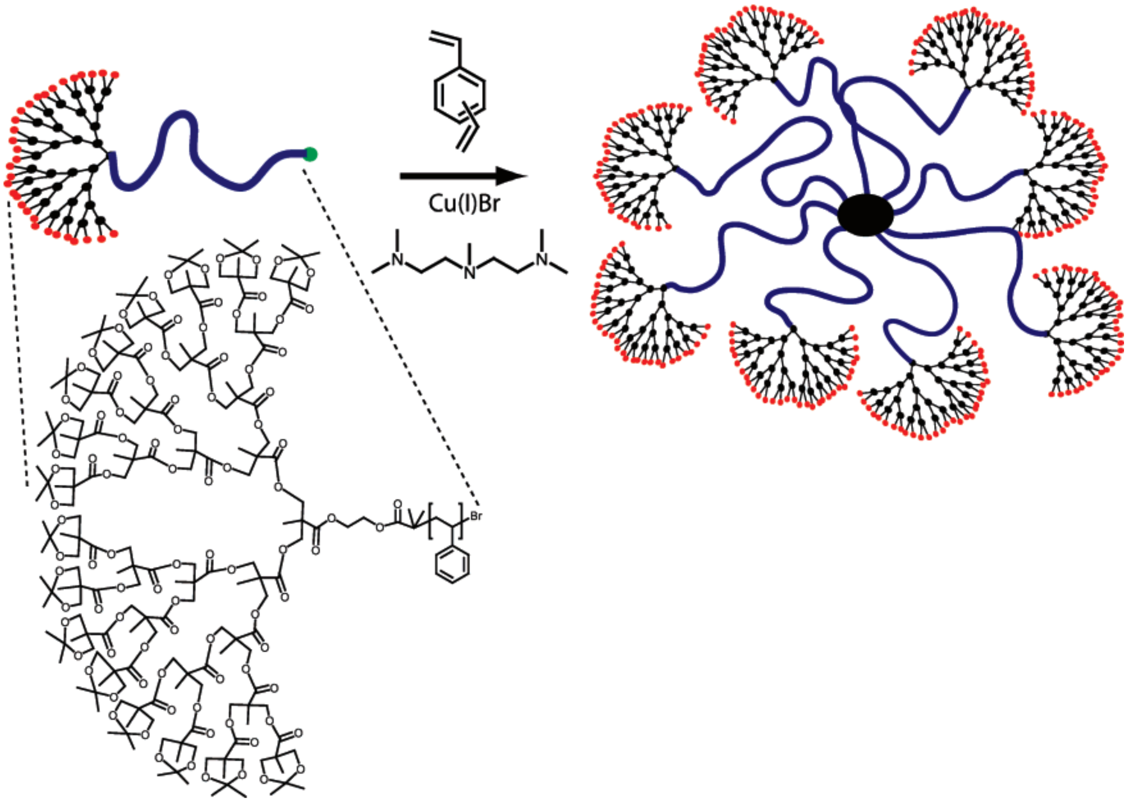
Scheme 1. Synthesis of Generation = 5 Functionalized Core Cross-linked Star (CCS) Polymers via the Arm First Approach

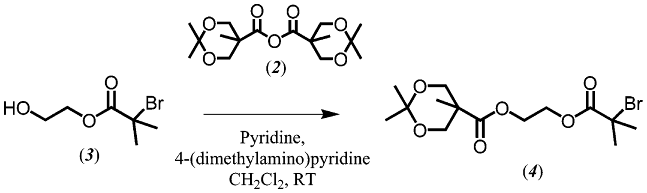


propionic acid (bis-MPA, 98%), 2,2-dimethoxypropane (98%), 2-bromoisobutyryl bromide (98%), ethylene glycol (99+%), triethylamine (99+%), benzyl bromide (98%), pyridine (anhydrous, 98%), 4-(dimethylamino)pyridine (DMAP, 99+%) and *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%) were used without further purification. 4-(Dimethylamino)pyridinium *p*-toluenesulfonate (DPTS),[23] acetonide-2,2-bis(methoxy)propionic acid (**1**),[22] 2-hydroxyethyl 2-bromo-2-methylpropionate (**3**),[24] benzyl-2,2-bis(methoxy)propionate (**5**),[22] acetonide-[G-2]-$CO_2CH_2C_6H_5$ (**6**),[22] acetonide-[G-2]-COOH (**7**),[22] $(HO)_4$-[G-2]-$CO_2CH_2C_6H_5$ (**9**),[22] acetonide-[G-3]-$CO_2CH_2C_6H_5$ (**10**),[17] acetonide-[G-3]-COOH (**11**),[17] $(HO)_8$-[G-3]-$CO_2CH_2C_6H_5$ (**13**),[17] acetonide-[G-4]-$CO_2CH_2C_6H_5$ (**14**),[17] and acetonide-[G-4]-COOH (**15**)[22] were synthesized by previously reported procedures.

Methods. NMR spectra were measured on a Varian Unity Plus 400 spectrometer, ^1H NMR operating at 400 MHz and ^{13}C NMR operating at 100 MHz. Spectra were run in deuterated chloroform or deuterated dimethyl sulfoxide using tetramethylsilane as a reference. Size exclusion chromatography was performed on a Shimadzu system with a Wyatt DAWN DSP multiangle laser light scattering detector (690 nm, 30 mW) and a Wyatt OPTILAB EOS interferometric refractometer (690 nm). THF was used as the eluent with three Phenomenex phenogel columns (500, 104, and 106 Å porosity; 5 μm bead size) operated at 1 mL/min with the column temperature set at 30 °C. Astra software (Wyatt Technology Corp.) was used to process the data using known d*n*/d*c* values to determine the molecular weight or an assumption of 100% mass recovery of the polymer where the d*n*/d*c* value was unknown. Monomer conversion was determined by gas chromatography using a Shimadzu GC 17-A gas chromatograph equipped with a DB-5 capillary column (30 m, 5% phenylsiloxane) and coupled to a GCMS-QP5000 mass spectrometer (injection temperature: 250 °C; initial column temperature: 40 °C; final column temperature: 250 °C heated at 10 °C min^{-1}). Monomer conversions were calculated from standard response versus concentration curves generated using pure monomers. Microanalysis was conducted by Chemical and Microanalytical Services Pty. Ltd.

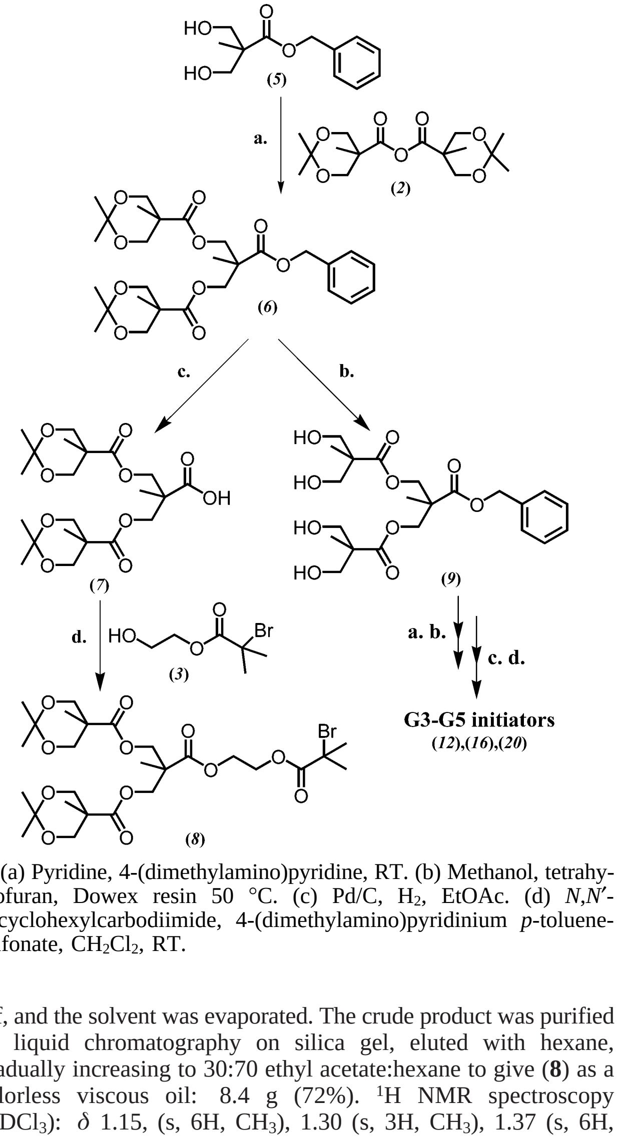
Preparation of Acetonide-[G-1]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (4). 2-Hydroxyethyl 2-bromo-2-methylpropionate (**3**) (10.0 g, 47.3 mmol) and DMAP (1.15 g, 9.47 mmol, 0.2 equiv) were dissolved in pyridine (45 mL). Acetonide-2,2-bis(methoxy)propionic anhydride (**2**) (23.45 g, 71.07 mmol, 1.5 equiv) was dissolved in 50 mL of dichloromethane and then added to the reaction mixture. The mixture was stirred at room temperature for 24 h and checked with NMR. The residual anhydride was quenched by reaction with 50 mL of water under rigorous stirring for 2 h. The reaction mixture was then taken up into 250 mL of dichloromethane and washed with $NaHSO_4$ (10%) (3 × 250 mL), $NaHCO_3$ (10%) (3 × 250 mL), and brine (250 mL). The organic layer was dried with $MgSO_4$, and the solvent was evaporated. The crude product was purified by liquid chromatography on silica gel, eluted with hexane, gradually increasing to 10:90 ethyl acetate:hexane. The product (**4**) was obtained as a white solid of 82% yield. ^1H NMR spectroscopy ($CDCl_3$): δ 1.18, (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.41 (s, 3H, CH_2), 1.90 (s, 6H, CH_3), 3.62 (d, 2H, $J = 12.0$ Hz, CH_2O), 4.27 (d, 2H, $J = 12.0$ Hz, CH_2O), 4.38 (S, 4H, CH_2O). ^{13}C NMR ($CDCl_3$): δ 18.67 ($-CH_3$), 22.90 24.47 ($-O-C-CH_3$), 30.70 ($Br-C-CH_3$), 41.90 ($-C-$), 55.45 ($Br-C-CO-$), 62.24 63.42 ($-CH_2-O-$), 65.91($-CH_2-O-$), 98.15 ($-O-C-CH_3$), 171.45 174.00 ($C{=}O$). Anal. Calcd for $C_{14}H_{23}BrO_6$: C, 45.79; H, 6.31. Found: C, 45.71; H, 6.44.

Scheme 2. Synthesis of Generation = 1 Dendron with Atom Transfer Radical Polymerization (ATRP) Initiating Moiety at the Focal Point



Preparation of Acetonide-[G-2]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (8). 2-Hydroxyethyl 2-bromo-2-methylpropionate (**3**) (5.74 g, 27.25 mmol) was added to a solution of acetonide-[G-2]-COOH (**7**) (8.1 g, 18.15 mmol) and DPTS (1.08 g, 3.6 mmol) in 30 mL of CH_2Cl_2. DCC (7.49 g, 36.3 mmol) was added to the mixture and stirred at room temperature for 24 h. The DCC-urea was filtered

Scheme 3. Synthetic Strategy for Production of 2,2-bis(methoxy)propionic Acid (bis-MPA) Based Dendrons with Atom Transfer Radical Polymerization (ATRP) Initiating Moiety at the Focal Point.



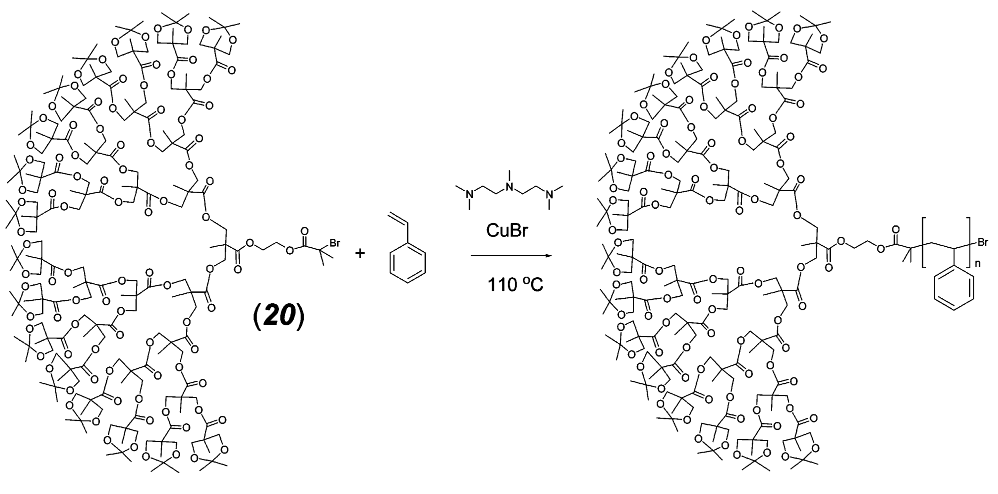
(a) Pyridine, 4-(dimethylamino)pyridine, RT. (b) Methanol, tetrahydrofuran, Dowex resin 50 °C. (c) Pd/C, H_2, EtOAc. (d) *N*,*N*′-Dicyclohexylcarbodiimide, 4-(dimethylamino)pyridinium *p*-toluenesulfonate, CH_2Cl_2, RT.

off, and the solvent was evaporated. The crude product was purified by liquid chromatography on silica gel, eluted with hexane, gradually increasing to 30:70 ethyl acetate:hexane to give (**8**) as a colorless viscous oil: 8.4 g (72%). ^{1}H NMR spectroscopy ($CDCl_3$): δ 1.15, (s, 6H, CH_3), 1.30 (s, 3H, CH_3), 1.37 (s, 6H, CH_3), 1.41 (s, 6H, CH_2), 1.90 (s, 6H, CH_3), 3.62 (d, 4H, $J = 12.0$ Hz, CH_2O), 4.27 (d, 4H, $J = 12.0$ Hz, CH_2O), 4.38 (S, 4H, CH_2O). ^{13}C NMR ($CDCl_3$): δ 17.62 (first generation $-CH_3$), 18.46 (second generation $-CH_3$), 21.86 ($-O-C-CH_3$), 25.32 ($-O-C-CH_3$), 30.67 ($Br-C-CH_3$), 40.02 (first generation $-C-$), 46.74 (second generation $-C-$), 60.64 ($Br-C-CO-$), 62.56 63.32 (focal point $-CH_2-O-$), 65.15 (first generation $-CH_2-O-$), 65.91(second generation $-CH_2-O-$), 98.08 ($-O-C-CH_3$), 171.85 (first generation $C{=}O$), 172.28 (second generation $C{=}O$), 172.91 (focal point $C{=}O$). Anal. Calcd for $C_{27}H_{43}BrO_{12}$ C, 50.71; H, 6.78. Found: C, 50.75; H, 6.82.

Preparation of Acetonide-[G-3]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (12). 2-Hydroxyethyl 2-bromo-2-methylpropionate (**3**) (4.59 g, 21.7 mmol) was added to a solution of acetonide-[G-3]-COOH (**11**) (14.4 g, 14.5 mmol) and DPTS (0.87 g, 2.9 mmol) in 40 mL of CH_2Cl_2. DCC (5.98 g, 29.0 mmol) was added to the mixture and stirred at room temperature for 24 h. The DCC-urea was filtered off, and the solvent was evaporated. The crude product was purified by liquid chromatography on silica gel, eluting with hexane, gradually increasing to 50:50 ethyl acetate:hexane to give (**12**) as a colorless viscous oil: 8.4 g (72%). ^{1}H NMR spectroscopy ($CDCl_3$): δ 1.15, (s, 12H, CH_3), 1.30 (s, 3H, CH_3), 1.37 (s, 12H, CH_3), 1.41 (s, 12H, CH_2), 1.90 (s, 6H, CH_3), 3.62 (d, 8H, $J = 12.0$ Hz, CH_2O), 4.27 (d, 8H, $J = 12.0$ Hz, CH_2O), 4.38 (S, 4H, CH_2O). ^{13}C NMR ($CDCl_3$): δ 17.60 (first generation $-CH_3$), 17.73 (second generation $-CH_3$), 18.55 (third generation $-CH_3$), 22.01 ($-O-C-CH_3$), 25.34 ($-O-C-CH_3$), 30.68 ($Br-C-CH_3$), 42.09 (first generation $-C-$), 46.67 (second generation $-C-$), 46.90 (third generation $-C-$), 55.37 ($Br-C-CO-$), 62.91 (focal point $-CH_2-O-$), 63.29 (focal point $-CH_2-O-$), 64.96 (first generation $-CH_2-O-$), 65.98 (second generation $-CH_2-O-$), 66.02 (third generation $-CH_2-O-$), 98.15 ($-O-C-CH_3$), 171.40 (first generation $C{=}O$), 171.33 (second generation $C{=}O$), 172.21 (focal point $C{=}O$), 173.56 (third generation $C{=}O$). Anal. Calcd for $C_{53}H_{83}BrO_{24}$ C, 53.76; H, 7.07. Found: C, 53.75; H, 7.12.

Preparation of Acetonide-[G-4]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**16**). 2-Hydroxyethyl 2-bromo-2-methylpropionate (**3**) (1.65 g, 7.8 mmol) was added to a solution of acetonide-[G-4]-COOH (**15**) (10.8 g, 5.2 mmol) and DPTS (0.31 g, 1 mmol) in 30 mL of CH_2Cl_2. DCC (2.14 g, 10.4 mmol) was added to the mixture and stirred at room temperature for 24 h. The DCC-urea was filtered off, and the solvent was evaporated. The crude product was purified by liquid chromatography on silica gel, eluting with hexane, gradually increasing to 50:50 ethyl acetate:hexane to give (**16**) as a colorless viscous oil: 9.0 g (76%). ^{1}H NMR spectroscopy ($CDCl_3$): δ 1.10, (s, 24H, CH_3), 1.23 (s, 18H, CH_3), 1.26, (s, 3H, CH_3), 1.30 (s, 24H, CH_3), 1.37 (s, 24H, CH_3), 1.89 (s, 6H, CH_3), 3.57, (d, 16H, $J = 6$ Hz, CH_2O), 4.10 (d, 16H, $J = 6$ Hz, CH_2O), 4.20−4.31 (m, 28H, CH_2) 4.35, (s, 2H, CH_2), 4.36, (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 18.70 (first generation $-CH_3$), 18.75 (second generation $-CH_3$), 19.54 (third generation $-CH_3$), 19.57 (fourth generation $-CH_3$), 23.12 ($-O-C-CH_3$), 26.28 ($-O-C-CH_3$), 31.65 ($Br-C-CH_3$), 43.07 (first generation $-C-$), 47.69 (second generation $-C-$), 47.75 (third generation $-C-$), 47.87 (fourth generation $-C-$), 56.46 ($Br-C-CO-$), 64.00 (focal point $-CH_2-O-$), 64.26 (focal point $-CH_2-O-$), 65.86 (first generation $-CH_2-O-$), 66.57

Scheme 4. Preparation of Generation = 5 Functional Polystyrene Using Atom Transfer Radical Polymerization (ATRP)



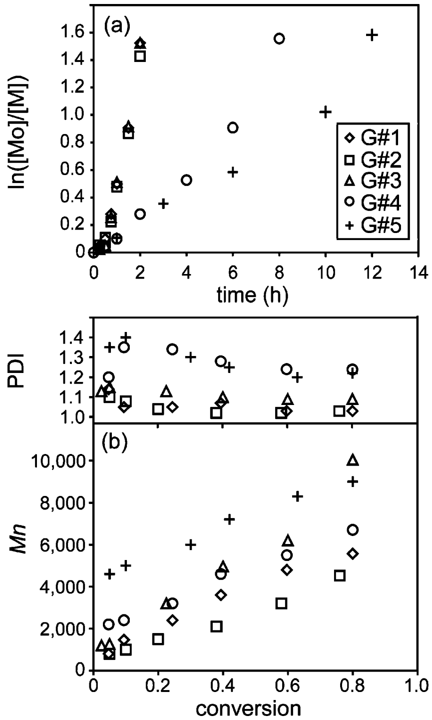


Figure 1. (a) Kinetic plots for polymerization of styrene (Sty) initiated by dendrons, (b) dependence of conversion on molecular weight (bottom section) and polydispersity (top section) of styrene polymerization. Reaction conditions: Bulk, 110 °C; $[\text{dendron}]_0$:$[\text{Sty}]_0$:[CuBr]:[*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine] 1:100:1:2. Initiated by: generation 1 (**4**) open diamonds, generation 2 (**8**) open squares, generation 3 (**12**) open triangles, generation 4 (**16**) open circles, generation 5 (**20**) crosses.

(second generation $-CH_2-O-$), 66.95 (third generation $-CH_2-O-$), 66.99 (fourth generation $-CH_2-O-$), 99.13 ($-O-C-CH_3$), 172.33 (first generation $C{=}O$), 172.42 (second generation $C{=}O$), 172.86 (focal point $C{=}O$), 172.89 (third generation $C{=}O$), 174.50 (fourth generation $C{=}O$). Anal. Calcd for $C_{105}H_{163}BrO_{48}$ C, 55.48; H, 7.23. Found: C, 55.39; H, 7.29.

Preparation of $(HO)_{16}$-[G-4]-$CO_2CH_2C_6H_5$ (17). Acetonide-[G-4]-$CO_2CH_2C_6H_5$ (**14**) (13.85 g, 6.4 mmol), was dissolved in THF:methanol, 3:2 (250 mL). Dowex, H^+ resin (10 g) was added, and the reaction mixture was stirred for 18 h at 50 °C. When the reaction was completed, the Dowex H^+ resin was filtered off in a glass filter and carefully washed with methanol. The methanol was evaporated to give (**17**) as colorless viscous oil: 12.74 g, (96%). ^1H NMR (DMSO-d_6): δ 1.03 (s, 24H, CH_3) 1.07 (s, 6H, CH_3), 1.10 (s, 12H, CH_3), 1.14 (s, 3H, CH_3), 3.42−3.50 (m, 32H, CH_2-OH), 4.01−4.10 (m, 16H, CH_2O), 4.15−4.20 (m, 16H, CH_2O), 4.26 (q, 4H, CH_2O, $J = 11.08$ Hz), 5.07 (s, 2H, CH_2Ar), 7.27 (m, 5H, ArH). ^{13}C NMR (DMSO): δ 18.71 (first generation $-CH_3$), 18.79 (second generation $-CH_3$), 19.59 (third generation $-CH_3$), 19.63 (fourth generation $-CH_3$), 43.18 ($Br-C-CH_3$), 48.32 (first generation $-C-$), 48.65 (second generation $-C-$), 48.87 (third generation $-C-$), 52.36 (fourth generation $-C-$), 66.46 ($-C-OH$), 66.80 ($-O-CH_2-Ar$), 66.87 (first generation $-CH_2-O-$), 66.98 (second generation $-CH_2-O-$), 67.06 (third generation $-CH_2-O-$), 68.53 (fourth generation $-CH_2-O-$), 129.07 (ArCH), 129.67 (ArCH), 129.84 (ArCH), 134.82 (ArC), 172.30 (first generation $C{=}O$), 172.42 (second generation $C{=}O$), 173.16 (focal point $C{=}O$), 174.50 (third generation $C{=}O$).

Preparation of Acetonide-[G-5]-$CO_2CH_2C_6H_5$ (18). $(HO)_{16}$-[G-4]-$CO_2CH_2C_6H_5$ (**17**) (11.58 g, 6.3 mmol) and DMAP (2.46 g, 20.0 mmol) were dissolved in 40 mL of pyridine. Acetonide-2,2-bis(methoxy)propionic anhydride (**2**) (49.6 g, 150 mmol) was dissolved in 150 mL of dichloromethane and then added to the reaction mixture. The reaction mixture was stirred for 18 h at RT and checked with NMR. The residual anhydride was quenched by reaction with 150 mL of water under rigorous stirring for 2 h. The reaction mixture was then taken up into 250 mL of dichloromethane and washed with $NaHSO_4$ (10%) (3 × 250 mL), $NaHCO_3$ (10%) (3 × 250 mL), and brine (250 mL). The organic layer was dried with $MgSO_4$, the solvent was evaporated, and the crude product was purified by liquid chromatography on silica gel, eluted with hexane, gradually increasing the polarity to 70:30 ethyl acetate: hexane to give (**18**) as colorless viscous oil (25.1 g, 78%). ^1H NMR ($CDCl_3$): δ 1.10, (s, 48H, CH_3), 1.24 (s, 42H, CH_3), 1.26, (s, 3H, CH_3), 1.30 (s, 48H, CH_3), 1.37 (s, 48H, CH_3), 3.57, (d, 32H, $J = 6$ Hz, CH_2O), 4.10 (d, 32H, $J = 6$ Hz, CH_2O), 4.20−4.31 (m, 28H, CH_2) 5.12 (s, 2H, CH_2Ar), 7.26−7.32 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$): δ 18.56 (first generation $-CH_3$), 18.77 (second generation $-CH_3$), 18.80 (third generation $-CH_3$), 19.54 (fourth generation $-CH_3$), 19.57 (fifth generation $-CH_3$), 23.14 ($-O-C-CH_3$), 26.27 ($-O-C-CH_3$), 31.77 ($Br-C-CH_3$), 36.00 (first generation $-C-$), 43.07 (second generation $-C-$), 47.72 (third generation $-C-$), 47.85 (fourth generation $-C-$), 56.86 (fifth generation $-C-$), 66.34 ($-O-CH_2-Ar$), 66.90 (first generation $-CH_2-O-$), 67.00 (second generation $-CH_2-O-$), 67.06 (third generation $-CH_2-O-$), 68.58 (fourth generation $-CH_2-O-$), 69.69 (fifth generation $-CH_2-O-$), 99.13 ($-O-C-CH_3$), 128.11 (ArCH), 128.39 (ArCH), 128.53 (ArCH), 135.43 (ArC), 172.45 (first generation $C{=}O$), 172.86 (second generation $C{=}O$), 172.89 (focal point $C{=}O$), 172.94 (third generation $C{=}O$), 174.42 (fourth generation $C{=}O$), 174.50 (fifth generation $C{=}O$).

Preparation of Acetonide-[G-5]-COOH (19). Pd/C (10%) 1.00 g was added to a solution of acetonide-[G-5]-$CO_2CH_2C_6H_5$ (**18**) (10.80 g, 2.5 mmol) in 50 mL of ethyl acetate. Air was removed from the apparatus and subsequently filled with H_2 (3 × 1 L) and allowed to stir over an 18 h period. The catalyst was filtered off in a glass filter and carefully washed with ethyl acetate. The filtrate was evaporated to give (**19**) as white crystals: 10.5 g, (99%). ^1H NMR ($CDCl_3$): δ 1.12 (s, 48H, CH_3), 1.26 (s, 24H, CH_3), 1.33 (s, 12H, CH_3), 1.35 (s, 6H, CH_3), 1.39 (s, 3H, CH_3), 3.61 (d, 32H, CH_2O), 4.12 (d, 32H, CH_2O), 4.20−4.36 (m, 60H, CH_2). ^{13}C NMR ($CDCl_3$): δ 17.15 (first generation $-CH_3$), 17.50 (second generation $-CH_3$), 17.67 (third generation $-CH_3$), 18.34 (fourth generation $-CH_3$), 18.46 (fifth generation $-CH_3$), 21.95 ($-O-C-CH_3$), 25.26 ($-O-C-CH_3$), 42.02 (first generation $-C-$), 42.14 (second generation $-C-$), 46.65 (third generation $-C-$), 46.79 (fourth generation $-C-$), 46.32 (fifth generation $-C-$), 64.77 (first

Table 1. Summary of Dendron Functional Polystyrene Synthesis[a]

entry	initiator	reaction time (h)	PDI[c]	M_n[c]	DP_n[c]
PS1	acetonide-[G-1]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**4**)	2	1.06	8000	73
PS2	acetonide-[G-2]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**8**)	2	1.08	9000	80
PS3	acetonide-[G-3]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**12**)	2	1.09	9400	80
PS4	acetonide-[G-4]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**16**)	5	1.21	10 000	75
PS5	acetonide-[G-5]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**20**)	2	1.22	5000	5
PS6	acetonide-[G-5]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**20**)	3	1.22	6200	17
PS7	acetonide-[G-5]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**20**)	8	1.23	12 400	77
PS8[b]	acetonide-[G-5]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**20**)	8	1.25	35 000	290

[a] Reaction conditions: bulk, 110 °C; $[\text{dendron}]_0$:$[\text{Sty}]_0$:[CuBr]:[PMDETA]: 1:100:1:2. [b] Bulk, 110 °C; $[\mathbf{20}]_0$:$[\text{Sty}]_0$:[CuBr]:[*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine]: 1:200:1:2. [c] polydispersity (PDI), number-average molecular weight (M_n), and degree of polymerization (DP_n) were measured by gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS).

Table 2. Summary of Polystyrene Stars Functionalized with Generation = 1 Dendrons[a]

	macroinitiator					core cross-linked star polymer			
entry	code	DP_n[b]	end group	$[PSt]_0$ (mM)[c]	r_0[d]	M_w star (GPC)[b]	PDI	no. arms[e]	arm. conv (%)[f]
SP1	**PS1**	73	Act-[G-1]	15	15	275 000	1.15	26	76
SP2	**PS1**	73	Act-[G-1]	20	15	300 000	1.17	30	60
SP3	**PS1**	73	Act-[G-1]	30	15	80 000	1.41	7	52
SP4	**PS1**	73	Act-[G-1]	15	5	90 000	1.20	10	68
SP5 (**SP1**)	**PS1**	73	Act-[G-1]	15	15	275 000	1.15	26	76
SP6	**PS1**	73	Act-[G-1]	15	20				

[a] Reaction conditions: $[PSt]_0 = [CuBr]_0 = [N,N,N',N'',N''\text{-pentamethyldiethylenetriamine}]_0/2$ and DVB, anisole, 100 °C, 40 h. [b] Degree of polymerization (DP_n) and weight-average molecular weight (M_w) were measured by gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS). [c] $[PSt]_0$ = overall initial concentration of dendron functionalized polystyrene macroinitiator. [d] r_0 = initial molar ratio of divinyl benzene (DVB) to polystyrene macroinitiator (PSt). [e] Number of arms calculated from the formula = $Wf_{arms} \cdot M_{w,star}/M_{w,arms}$. [f] Calculated from integration of GPC concentration detector (DRI).

generation $-CH_2-O-$), 65.35 (second generation $-CH_2-O-$), 65.47 (third generation $-CH_2-O-$), 65.87 (fourth generation $-CH_2-O-$), 65.96 (fifth generation $-CH_2-O-$), 98.11 ($-O-C-CH_3$), 171.38 (second generation $C{=}O$), 171.91 (third generation $C{=}O$), 173.14 (fourth generation $C{=}O$), 173.48 (fifth generation $C{=}O$), 173. 89 ($COOH$).

Preparation of acetonide-[G-5]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (20). 2-Hydroxyethyl 2-bromo-2-methylpropionate (**3**) (0.96 g, 4.5 mmol) was added to a solution of acetonide-[G-5]-COOH (**19**) (9.68 g, 2.3 mmol) and DPTS (0.27 g, 0.9 mmol) in 40 mL of CH_2Cl_2. DCC (1.15 g, 5.7 mmol) was added to the mixture and stirred at room temperature for 24 h. The DCC-urea was filtered off, and the solvent evaporated. The crude product was purified by liquid chromatography on silica gel, eluting with hexane, gradually increasing to 50:50 ethyl acetate:hexane to give (**20**) as a colorless viscous oil: 8.4 g (72%). ^1H NMR spectroscopy ($CDCl_3$): δ 1.10, (s, 48H, CH_3), 1.24 (s, 42H, CH_3), 1.26, (s, 3H, CH_3), 1.30 (s, 48H, CH_3), 1.37 (s, 48H, CH_3), 1.89 (s, 6H, CH_3), 3.57, (d, 32H, $J = 6$ Hz, CH_2O), 4.10 (d, 32H, $J = 6$ Hz, CH_2O), 4.20−4.31 (m, 28H, CH_2) 4.35, (s, 2H, CH_2), 4.36, (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 18.56 (first generation $-CH_3$), 18.77 (second generation $-CH_3$), 18.80 (third generation $-CH_3$), 19.54 (fourth generation $-CH_3$), 19.57 (fifth generation $-CH_3$), 23.14 ($-O-C-CH_3$), 26.27 ($-O-C-CH_3$), 31.77 ($Br-C-CH_3$), 36.00 (first generation $-C-$), 43.07 (second generation $-C-$), 47.72 (third generation $-C-$), 47.85 (fourth generation $-C-$), 56.86 (fifth generation $-C-$), 61.91 ($Br-C-CO-$), 65.78 (focal point $-CH_2-O-$), 66.34(focal point $-CH_2-O-$), 66.90 (first generation $-CH_2-O-$), 67.00 (second generation $-CH_2-O-$), 67.06 (third generation $-CH_2-O-$), 67.58 (fourth generation $-CH_2-O-$), 68.50 (fifth generation $-CH_2-O-$), 99.13 ($-O-C-CH_3$), 172.45 (first generation $C{=}O$), 172.86 (second generation $C{=}O$), 172.89 (focal point $C{=}O$), 172.94 (third generation $C{=}O$), 174.42 (fourth generation $C{=}O$), 174.50 (fifth generation $C{=}O$). Anal. Calcd for $C_{209}H_{323}BrO_{96}$ C, 56.39; H, 7.31. Found: C, 56.42; H, 7.29.

General Procedure for Polymerization of Styrene Using Dendron Functional Initiators. A mixture of styrene (2.00 mL, 19.2 mmol), CuBr (27.5 mg g, 0.2 mmol), PMDETA (80.2 μL, 0.4 mmol), and acetonide-[G-3]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$ (**12**) (227 mg, 0.2 mmol) was added to a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath at 110 °C and heated for 3 h. The reaction mixture was diluted with THF (10 mL), passed through a column of basic alumina and celite (4:1), and precipitated into methanol (**PS3**) and analyzed by GPC-MALLS (75% yield, $M_n = 9400$ Da, PDI = 1.09).

General Procedure for Preparation of Dendron Functional Core Cross-linked Star Polymers. A mixture of [G-3]-functionalized PSt macroinitiator (**PS3**) ($M_n = 9400$ Da, 0.3 g, 0.03 mmol), DVB (68.2 μL, 0.47 mmol), CuBr (5 mg, 0.03 mmol), PMDETA (12.5 μL, 0.06 mmol) in anisole (2.25 mL) was added to a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath at 100 °C and heated for 40 h, and a sample was then taken from the reaction mixture and analyzed directly by GC. The mixture was diluted with THF (10 mL), passed through a column of basic alumina and celite (4:1), concentrated and precipitated into methanol (100 mL), and collected by filtration to afford a colorless solid (**SP9**), which was analyzed by GPC-MALLS (M_n = 275 000 Da, PD = 1.13).

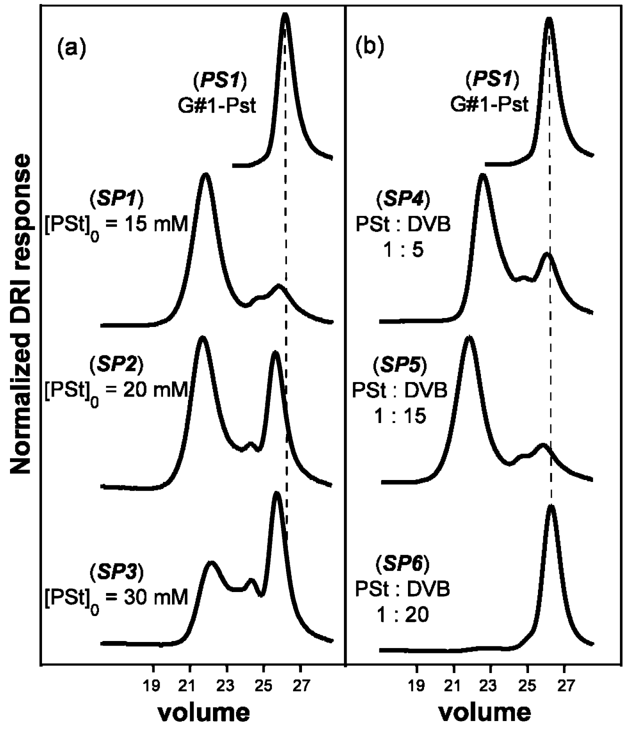


Figure 2. Normalized differential refractive index response from a series of generation = 1 functionalized polystyrene star polymers: (a) effects of initial macroinitiator concentration $[PSt]_0$, and (b) effects of cross-linker to macroinitiator ratio (r_0) on the structures formed.

General Procedure for Fractional Precipitation of Dendron Functional Core Cross-linked Star Polymers. A star polymer mixture (**SP9**) (100 mg) was dissolved in 10 mL of THF. Methanol was slowly added to this solution until a precipitate is formed, approximately 8 mL of methanol was added. The solid was allowed to settle and then filtered. This procedure was repeated to obtain multiple fractions. Quantitative assessment of star purity was made by GPC concentration detector (DRI) (yield = 35 mg, M_n = 275 000 Da, PD = 1.13).

General Procedure for Preparative GPC of Dendron Functional Core Cross-linked Star Polymers. Preparative GPC was performed (with the same GPC system as described above) on samples unable to be fractionated by precipitation methods. (**SP15**) was injected multiple times and fractions were taken in 30 s intervals, and star fractions were then consolidated to obtain pure star polymer.

Results and Discussion

Dendron functionalized star polymers were synthesized via the “arm first” approach with the initial dendritic macroinitiators

Table 3. Summary of Polystyrene Stars Functionalized with Different Generation Dendrons[a]

	macroinitiator					core cross-linked star polymer			
entry	code	DP$_n$[b]	end group	[PSt]$_0$ (mM)[c]	r_0[d]	M_w star (GPC)[b]	PDI	no. arms[e]	arm. conv (%)[f]
SP7	**PS1**	73	Act-[G-1]	15	15	280 000	1.14	27	78
SP8	**PS2**	80	Act-[G-2]	15	15	280 000	1.19	24	77
SP9	**PS3**	80	Act-[G-3]	15	15	275 000	1.13	21	55
SP10	**PS4**	75	Act-[G-4]	15	15	280 000	1.27	20	51
SP11	**PS7**	77	Act-[G-5]	15	15	300 000	1.31	19	60

[a] Reaction conditions: $[\mathrm{PSt}]_0 = [\mathrm{CuBr}]_0 = [N,N,N',N'',N''\text{-pentamethyldiethylenetriamine}]_0/2$ and DVB, anisole, 100 °C, 40 h. [b] Degree of polymerization (DP$_n$) and weight-average molecular weight (M_w) were measured by gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS). [c] $[\mathrm{PSt}]_0$ = overall initial concentration of dendron functionalized polystyrene macroinitiator. [d] r_0 = initial molar ratio of divinyl benzene (DVB) to polystyrene macroinitiator (PSt). [e] Number of arms calculated from the formula = $Wf_{\mathrm{arms}} \cdot M_{\mathrm{w,star}}/M_{\mathrm{w,arms}}$. [f] Calculated from integration of GPC concentration detector (DRI).

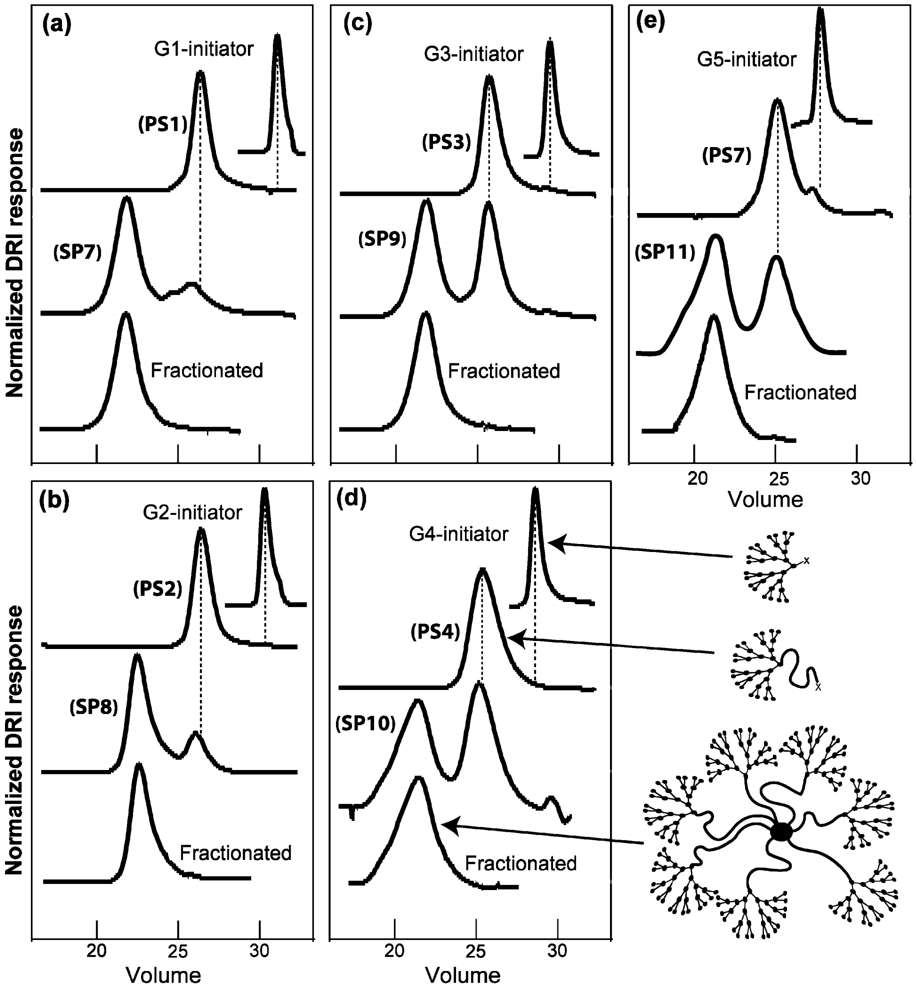


Figure 3. Normalized differential refractive index structures of star polymers made with varying generation initiators. First trace (top): dendron initiator; second trace: dendron functional polystyrene; third trace dendron functionalized star mixtures; fourth trace: pure dendron functionalized star structure (a) generation 1, (b) generation 2, (c) generation 3, (d) generation 4, (e) generation 5.

based on bis-MPA prepared via the divergent growth approach utilizing anhydride coupling chemistry.[17−21] Generations, [G = 1] to [G = 5] were functionalized at the focal point with an alkyl halide capable of initiating polymerization via ATRP followed by polymerization of styrene. Upon isolation, the resulting hybrid dendron-linear block copolymers were then used as macroinitiators, exploiting the "arm first" technique to couple with DVB to form dendron-functionalized core cross-linked star polymers. Scheme 1 shows an example of the synthesis of chain end functionalized star polymers with the fifth generation dendron attached to the periphery of the star.

Synthesis of Acetonide Protected Dendritic Initiators. The first generation dendron (**4**) was grown from 2-hydroxyethyl 2-bromoisobutyrate (**3**) by utilizing the anhydride of acetonide protected bis-MPA (**2**) (Scheme 2).[17−21] The bromoisobutyrate moiety is well-known to effectively initiate polymerization via ATRP.[25−27] Initially, this dendrimer (**4**) was used as the core moiety for divergent synthesis of higher generations, however, low yields and a mixture of products were obtained, most likely due to transesterification reactions at the bromoisobutyrate focal point under acidic conditions. To overcome these side reactions, it was decided to initially grow higher generation dendrons and introduce the ATRP initiating fragment in the final step.

As a result, the first generation bis-MPA dendron, protected at the focal point by a benzyl ester (**5**) was synthesized according to a literature method,[22] first by forming the potassium salt of bis-MPA, followed by treatment with benzyl bromide. This protected focal point derivative was then used to build up higher

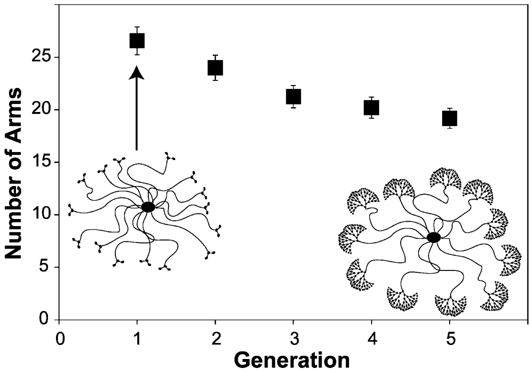


Figure 4. Effect of generation on the number of arms per star. All macroinitiators contained polystyrene with 70−80 repeat units.

generations, up to [G = 5]. The hydroxyl-functional benzyl-protected dendron (**5**) was reacted with the anhydride of acetonide bis-MPA (**2**) to afford acetonide functional groups at the periphery with a benzyl protected focal point (**6**), abbreviated to Act-[G-2]-$CO_2CH_2C_6H_5$. At this stage, the dendron was handled in two ways, deprotections were carried out at the focal point and at the periphery, separately. At the focal point, the benzyl ester of (**6**) was removed by catalytic hydrogenolysis to give the corresponding acid (**7**), Act-[G-2]-COOH. The desired acetonide protected derivative with an ATRP initiator at the focal point (**8**), Act-[G-2]-$CO_2(CH_2)_2CO_2C(CH_3)_2Br$, was then obtained by esterification of the acid (**7**) with 2-hydroxyethyl 2-bromoisobutyrate (**3**), using *N*,*N*′-dicyclohexylcarbodiimide (DCC) coupling and catalytic amounts of 4-(dimethylamino)-pyridinium *p*-toluenesulfonate (DPTS)[23] (Scheme 3). At the periphery of the benzyl protected dendron (**6**), the acetonide groups could be selectively removed and higher generation dendrimers obtained by repetitive acidic deprotections and coupling with the acetonide protected anhydride (**2**). Finally, at the core, the bromoisobutyrate moiety was coupled to the focal points via DCC couplings to yield acetonide protected dendrons, [G = 1] to [G = 5], with a bromoisobutyrate focal point (Scheme 3).

Polymerization Initiated from Dendron Functionalized Initiators. The kinetics of styrene polymerization (bulk) initiated by the dendron functional initiators was studied using CuBr/PMDETA as the catalytic system at a temperature of 110 °C, and Scheme 4 outlines the reaction for [G = 5] dendritic initiator.

Figure 1 displays the results of the kinetic analysis. Figure 1a shows the semilogarithmic plots displaying the variation of conversion with time for all five generations and is plotted over the entire reaction time, taken for the longest polymerization. This plot shows linear trends indicating a relatively constant concentration of active species. The molecular weight increases linearly with conversion (Figure 1b), characteristic of a living polymerization.[28] Interestingly, a large difference in reaction times is noted for low generations [G = 1] to [G = 3] as compared to the higher generation dendrimers [G = 4] to [G = 5]. For the lower generation dendrimers, 80% styrene conversion was reached in 2 h, whereas, for generations 4 and 5, a much slower polymerization was observed and 80% conversion required 8 and 12 h, respectively. The kinetic plots of generations 4 and 5 also show a slight upward curvature indicative of a slight loss of living character. A possible explanation for these deviations is that steric congestion at higher generation number may lead to a diminished rate of radical at the focal point and thus slowing down the rate of polymerization.

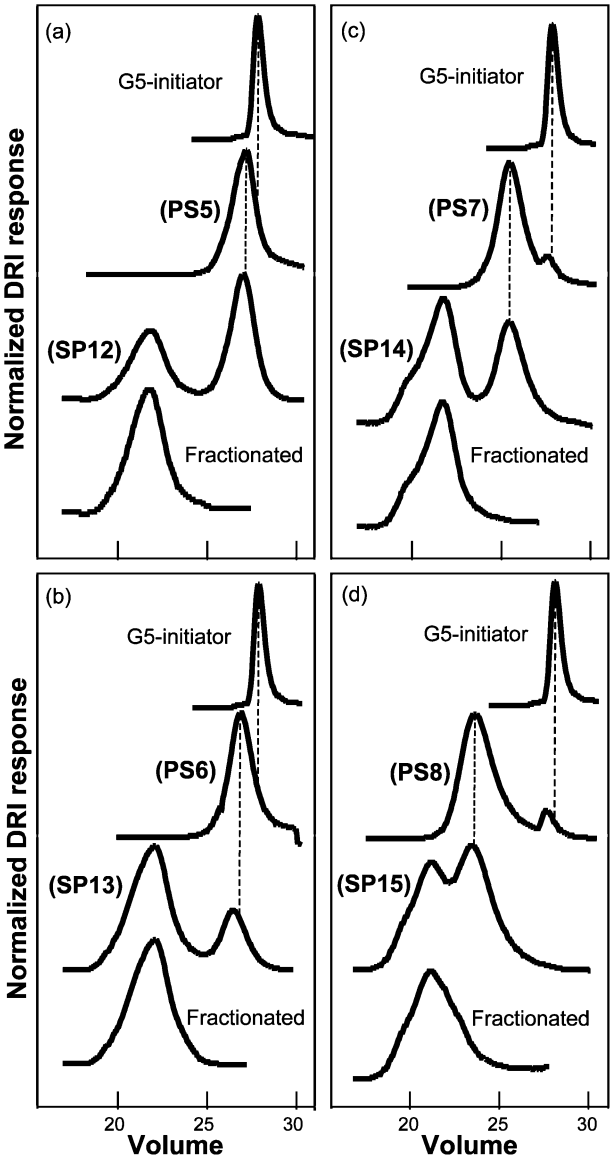


Figure 5. Normalized differential refractive index response of star polymers made from generation 5 functional polystyrenes with different degrees of polymerization (DP_n). First trace (top): dendron initiator; second trace: dendron functional polystyrene; third trace: dendron functionalized star mixtures; fourth trace: pure dendron functionalized star structure (a) $DP_n = 5$, (b) $DP_n = 17$, (c) $DP_n = 77$, (d) $DP_n = 290$.

A series of hybrid dendron-linear polystyrene block copolymers (PSt) were further prepared in order to construct a library of star polymers by the “arm first” approach (Table 1).

Formation of Star Polymers from Hybrid Linear-Dendron Copolymers: Optimizing Star Conditions. In order to optimize the conditions for star copolymer formation, the first generation polystyrene (**PS1**) derivative was used and the experimental conditions; concentration of macroinitiator in the reaction medium, $[PSt]_0$, and the molar ratio of macroinitiator to cross-linker, r_0, varied in order to obtain high yields of the desired star.

Initially, r_0 was kept constant at 15 and $[PSt]_0$ was varied from 15 to 30 mM (**SP1**−**3**, Table 2, and Figure 2). An increase in concentration caused an increase in star molecular weight, and at high PSt concentrations ($[PSt]_0$ = 30 mM, **SP3**), a large amount of insoluble gel was formed with only a low yield of star mixture. This may be due to the associated high concentration of cross-linker in the reaction solution. When $[PSt]_0$ was

Table 4. Summary of Polystyrene Stars Functionalized with Generation = 5 with Varying Length of Polystyrene Segment[a]

	macroinitiator					core cross-linked star polymer			
entry	code	DP_n[b]	end group	$[PSt]_{0(MF)}$ (g/mL)[c]	r_0[d]	M_w star (GPC)[b]	PDI	no. arms[e]	arm. conv (%)[f]
SP12	**PS5**	6	Act-[G-5]	0.13	15	350 000	1.14	37	43
SP13	**PS6**	17	Act-[G-5]	0.13	15	210 000	1.19	24	77
SP14	**PS7**	77	Act-[G-5]	0.13	15	290 000	1.13	16	38
SP15	**PS8**	290	Act-[G-5]	0.13	15	300 000	1.17	8	46

[a] Reaction conditions: $[PSt]_0 = [CuBr]_0 = [N,N,N',N'',N''\text{-pentamethyldiethylenetriamine}]_0/2$ and DVB, anisole, 100 °C, 40 h. [b] Degree of polymerization (DP_n) and weight-average molecular weight (M_w) were measured by gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS). [c] $[PSt]_{0(MF)}$ = overall initial concentration of dendron functionalized polystyrene macroinitiator. [d] r_0 = initial molar ratio of divinyl benzene (DVB) to polystyrene macroinitiator (PSt). [e] Number of arms calculated from the formula $= Wf_{arms} \cdot M_{w,star}/M_{w,arms}$. [f] Calculated from integration of GPC concentration detector (DRI).

held constant and r_0 varied, the molecular weight increased with increasing r_0 until, at $r_0 = 20$, when a large proportion of insoluble gel was formed (**SP4**−**6**, Table 2, Figure 2). For all samples, a low molecular weight, intermediate peak was also noted (Figure 2) that corresponded to ca. 2−3 polystyrene chains attached to a small core. From this analysis, the optimal conditions were found at $[PSt]_0 = 15$ mM in anisole with $r_0 = 15$ (**SP1**), giving a CCS polymer in 76% yield (270 kDa, 26 arms, PDI = 1.15).

Preparation of Star Polymers from Hybrid Linear-Dendron Copolymers: Effect of Generation. In order to effectively compare the structures formed from different dendron functionalized polystyrenes, a library of star copolymers were prepared. The number of styrene units were kept virtually constant (70−80), but dendron size was varied [G = 1] to [G = 5] (**PS1**−**PS4** and **PS7**, Table 1). The standard conditions developed in the previous section, obtained for [G-1]-PSt, were used to synthesize star polymers from these polystyrene macroinitiators (Table 3), and Figure 3 shows the molecular weight evolution of these star structures by GPC. The top trace shows the near monodispersed dendron functional initiator, the second trace the dendron functional PSt, and the third trace the dendron functionalized star polymers. It should be noted that there is a small amount of unconverted dendron functional linear-polymer in the crude reaction mixture, however, it is easily removed by fractional precipitation with the isolated pure dendron functionalized star polymers shown as the bottom trace. Star polymers from these macroinitiators displayed high molecular weights of around 300 kDa with low polydispersities. These results show that even using polymers functionalized with a steric bulky fifth generation dendron ($M_n = 4400$), the star coupling reaction was facile and a well-defined star structure could be obtained and purified.

As all macroinitiators end functionalized with dendrons, used in the coupling step, had 70−80 units of styrene and were low polydispersity, this precise control of the PSt chain length enables the effect of increasing the dendron generation on the final star structure to be studied in detail. Figure 4 shows that, with increasing dendron generation, the number of arms decreased, however, this effect is quite small. This may be due to the relatively long (70−80 units) polystyrene chain shadowing any significant effects of the dendron sizes.

Preparation of Star Polymers from Hybrid Linear-Dendron Copolymers: Effect of PSt Chain Length. A second design criteria in the preparation of dendron functionalized star polymers is the length of the linear polymer block, and to investigate this effect, a range of fifth generation hybrid polystyrene copolymers were prepared with chain lengths ranging from 6 styrene units to 290 (**PS5**−**PS8**, Table 1). The optimal conditions established for the [G = 1] series were then applied, and with a slight variation, the initial mass fraction of dendron functional polystyrene macroinitiator was held constant at $[PSt]_{0(MF)} = 0.13$ g mL^{-1} in anisole (rather than using a molar concentration $[PSt]_0$). If the molar concentration was held constant, unwanted insoluble gel was formed for the high molecular weight PSt macroinitiators.

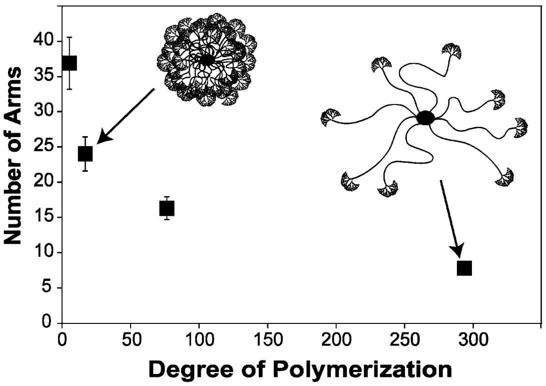


Figure 6. Effect of linear chain length of the macroinitiator on the number of arms formed on each star polymer. All macroinitiators were functionalized with fifth generation dendrimers.

Figure 5 shows the evolution of controlled architectures, from the starting fifth generation dendron (top trace), dendron functional polystyrenes (second trace), dendron functionalized star polymers (third trace), to finally isolated pure star polymers (bottom trace). By utilizing the ATRP technique, it was possible to polymerize as little as 6 styrene units or as many as 290 from the dendron initiators in a controlled fashion and then to couple these macroinitiators into high molecular weight star structures with low polydispersities (**SP12**−**15**, Table 4 and Figure 5). This allowed a library of macroinitiators to be prepared with a constant dendrimer size, [G = 5], but varying the PSt chain length.

Significantly, the degree of polymerization (DP_n) had a large effect on the structure of the stars formed. At low DP_n (6 styrene units), the stars produced had the highest number of arms, 37 (**SP12**), and as the DP_n was increased, the number of arms decreased exponentially with the highest molecular weight macroinitiator ($DP_n = 290$), producing a star with as few as 8 arms (**SP15**) (Figure 6). This result is similar to previous studies where an increase in the numbers of arms per star is noted as the molecular weight of the macroinitiator is decreased.[9,29−31] In this case, the presence of a highly branched dendron ([G = 5], $M_n = 4400$) attached to the end of the polystyrene macroinitiator has seemingly much less effect on the star formation than initially thought. For low DP_n (**SP12**) where the dendron comprises 90% of the total weight of the macroinitiator, a highly branched CCS polymer was still prepared. This result is somewhat surprising, indicating that a highly branched star polymer can still be successfully prepared with a large dendron attached to a relatively small linear segment.

Conclusions

Dendrons based on bis-MPA up to the fifth generation were synthesized and functionalized, at the focal point with a single alkyl halide, capable of initiating polymerization by ATRP. Polymerization kinetics catalyzed by CuBr/PMDETA system was studied and good control was established for all generations, with the higher generations displaying much slower reaction rates although still leading to low polydispersity materials. The precise control over the polymerization of styrene enabled the preparation of a range of hybrid dendron-linear block copolymers, controlling the styrene length from 6 to 300 units. These dendron functionalized polymers successfully formed CCS polymers even with a fifth generation dendron on the end of the macroinitiators. This controlled synthesis strategy enabled two studies to be conducted, first, the effect of generation number/molecular size and, second, the effect of PSt length of the macroinitiators on the star structures formed. The effect of generation number, although small, was as expected; by increasing the size of the dendron, the amount of arms attached to the star decreased. The effect of PSt length was more dramatic, with as little as 6 styrene units attached, a high molecular weight star structure produced stars with the greatest number of arms. When the PSt length was further increased, an exponentional decrease in the number of arms was observed. The large number of functional groups present at the chain ends of these high molecular weight star polymers offers significant potential to create polymers with specifically tailored surfaces. It is envisaged that these stars will show unique self-assembly properties, both in solution and in thin films; these properties will be investigated in subsequent publications.

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