Dendritic−Linear Miktoarm Star Polymers from Orthogonal Protected Initiators

Thierry Glauser,[†] Cheryl M. Stancik,[‡] Michael Möller,[†] Sarah Voytek,[†]
Alice P. Gast,[‡] and James L. Hedrick*,[†]

IBM Almaden Research Center, 650 Harry Rd. E1, San Jose, California 95120, and
Department of Chemical Engineering, Stanford University, Stanford, California 94305

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ABSTRACT: The synthesis of miktoarm dendritic−linear star copolymers in a tandem “core-in”/“core-out” approach is described. This synthetic approach is enabled by rational design and synthesis of an orthogonal protected compound containing six sites arranged in an alternating fashion for attachment of dendrimers and atom transfer radical polymerization of linear polymer chains. The judicious choice of the dendrimer surface functionality coupled with the properties of the monomer used in the linear chain allows the creation of amphiphilic molecules capable of supramolecular assembly. ^{1}H NMR and SEC studies of the block copolymers confirmed that the targeted polymer structures were achieved with low polydispersities and good yields. The nature and the size of the arms and dendrons had a significant influence on the hydrodynamic radii (R_h) measured by dynamic light scattering. Some of these macromolecules microphase-separated after annealing.

Introduction

The synthesis of block copolymers and new macromolecular architectures for advanced applications has been of scientific and technological interest for a number of years.[1] For instance, diblock copolymers, comprising two distinct polymers covalently bound at one point, are remarkable systems that can self-assemble into a variety of morphologies including lamellar sheets, hexagonally packed cylinders, and body-centered cubic arrays of spherical micelles.[2] The morphology of a self-assembled structure of diblock copolymers will depend on the relative volume fractions of the different monomer components, the interaction parameters (χ) within the system, and other external variables such as temperature. Although AB diblock copolymer investigations have focused on morphology due to the chemical composition of the polymer, more recent studies clearly demonstrate that the architecture of the polymer chain has a pronounced effect on the morphology and interfacial activity.[3] The importance of polymer architecture can be seen in dendritic−linear polymers[4] and in star polymer systems containing chemically different arms, which have been coined miktoarm star polymers.[5a] Because of their unique architecture, miktoarm star polymers manifest many interesting solution and solid-state properties.[5] Hadjichristidis et al. have studied A_nB_n star block copolymers and have found that their phase diagrams differ from their diblock analogues due to steric crowding near the central branching point, ultimately leading to high curvature at the interface of the microphase-separated domains.[6]

One general strategy for the synthesis of miktoarm stars is through the use of anionic polymerization techniques where the living chain ends are consecutively grafted onto a reactive multifunctional core.[7] This synthetically demanding procedure produces well-defined miktoarm stars, but with little control over the topological sequence, i.e., how the different arms alternate. Another approach utilizes the addition of anionically derived living polymers to a small amount of a difunctional monomer, such as divinylbenzene.[8] This leads to the formation of a star molecule with additional sites in the polymerizable core. Subsequent addition of another monomer capable of anionic polymerization yields the miktoarm star polymer. In this case, neither the exact number of arms nor their precise topological arrangement can be controlled. This general strategy has been extended to controlled radical polymerization techniques, where the active chain ends were reacted with a multifunctional monomer to form star copolymers.[9] In a different approach, new multifunctional initiators containing sites for the initiation of two different types of polymerization techniques, ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP), were arranged in an alternating fashion for the synthesis of miktoarm block copolymers.[10] These alternating arm block copolymers were prepared from the “core-out” utilizing consecutive ROP and ATRP processes.

In this paper, a similar concept in initiator design using orthogonally protected multifunctional compounds will be described as a novel route to dendritic−linear miktoarm copolymers. In this strategy to miktoarm systems, a building block containing a site for the initiation of ATRP and the attachment of a dendron is employed. Coupling of this building block, in a “core-in” fashion, to a multifunctional core leads to a multiarm compound with the transformation sites arranged in an alternating sequence. The dendritic−linear miktoarm star polymers can be prepared using a tandem “core-in”/“core-out” approach utilizing consecutive convergent dendron attachment and ATRP. These starlike macromolecules may form structures such as polymer-stabilized dendrimers, as shown in Scheme 1A, a homogeneous material in which the linear chains allow some degree of molecular interpenetration, or phospho-

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[†] IBM Almaden Research Center.
[‡] Stanford University.
* To whom correspondence should be addressed: e-mail hedrick@almaden.ibm.com; phone (408) 927 1632; Fax (408) 927 3310.

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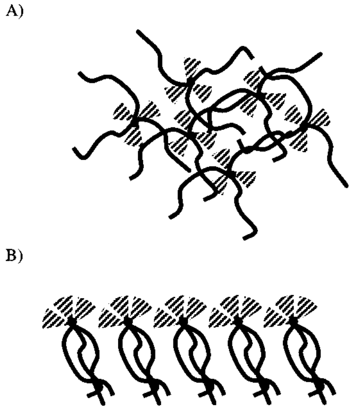
Scheme 1. Possible Conformations for the A_3B_3 Macromolecule Are as Homogeneous "Stabilized Dendrimers" (A), Where the Linear Chains Allow a Certain Degree of Entanglement and Film Formation, or in a Surfactant-like, Self-Organized Conformation (B)[a]



[a] In the sketches of the A_3B_3 the hydrophobic linear polymer chains are represented in bold lines, whereas the hydrophilic dendrons are represented by hatched wedges.

lipid-like macromolecules, as depicted in Scheme 1B, which can display properties such as phase separation in the bulk and self-assembly in solution under the appropriate conditions.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used without any further purification unless otherwise stated. The methyl methacrylate (MMA, Aldrich, 99%) and benzyl methacrylate (BMA, Aldrich, 96%) were freshly distilled under high vacuum prior to use. Copper bromide (CuBr, Aldrich, 99.999%) was washed with glacial acetic acid under protective atmosphere. The 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS)[11] and the dinonyldipyridine (dNbPy)[12] were prepared according to literature procedures.

Characterization. ^{1}H NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer using the solvent proton signal as an internal standard. The number-average molecular weight of the poly(methyl methacrylate) (pMMA)) and poly(benzyl methacrylate) (pBMA) were calculated from the ^{1}H NMR spectra from the ratio of the $-CH_3$ methylene proton signals ($\delta = 0.65$ and 0.85 ppm) to the aromatic $-CH-$ proton signals of the core ($\delta = 8.70$ ppm). ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer using the solvent carbon signal as internal standard. Size exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrene of known molecular weights as calibration standards. Four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6) were used with reagent-grade THF as solvent (25 °C, 1 mL/min flow rate). Analytical TLC was performed on commercial Merck plates coated with silica gel GF$_{254}$ (0.25 mm thick). For modulated differential scanning calorimetric (MDSC) measurements a TA Instruments 2920 MDSC was used. After annealing for 6 h at 220 °C, samples were scanned under nitrogen from −50 to 250 °C at a rate of 4 °C/min and a rate modulation of ±1 °C. T_g's were determined by the inflection point of the complex heat capacity (C_p). Thermal−mechanical analysis (DMA) was performed on a DMA 983 from TA Instruments. After annealing for 6 h at 220 °C, samples were scanned from −50 to 250 °C at a rate of 5 °C/min under nitrogen. The T_g was determined by the maximum of tan(δ). Dynamic light scattering (DLS) experiments allowed determination of the hydrodynamic radii of the A_3B_3 macromolecules and their micelles. The samples for the DLS experiments were prepared at 0.5 wt % in the chosen solvent and placed in an ultrasonic bath at low power to ensure complete dissolution. To reach complete dissolution, some samples required mild heating and overnight stirring. Samples were allowed to equilibrate after dissolution for at least a day. Each sample was passed through a 0.2 μm inorganic membrane filter prior to testing. The DLS experiments were conducted using a 2 W Lexel model 95 argon laser at a wavelength of 514.5 nm and with laser power ranging from 0.4 to 0.7 W. A Brookhaven Instruments BI-200 goniometer was used to select a scattering angle between 75° and 120°. The data were stored and processed on a Brookhaven Instruments BI-9000 correlator. All data were taken at a fixed temperature of 25 °C maintained by a Neslab circulating bath. Analysis of the autocorrelation data obtained from the DLS experiments was conducted using the CONTIN analysis program created by Provencher.[13] This program uses a constrained Laplace transform of the data to find the optimal size distribution that satisfies the experimentally obtained autocorrelation function. CONTIN is a powerful tool for investigating polydisperse polymer samples, particularly those with multimodal distributions, as is often the case in polymer micelles. For each sample, at least five data sets was collected and analyzed independently. We report the average value of R_h and the standard deviation of these measurements. Additionally, the average of the percent error obtained from the CONTIN analysis is reported. While the standard deviation of the R_h values gives a measure of the repeatability of the experiments, the average percent error gives an indication of the experimental error of the R_h values.

Initiator Synthesis. (5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-methanol, 2. The 1,1,1-tris(hydroxymethyl)ethane (92.0 g, 766 mmol) along with *p*-TSA (5.6 g, 29 mmol) was dissolved in 1.5 L of THF and stirred at room temperature for 2 h. Benzaldehyde dimethyl acetal (120.0 mL, 800 mmol) was added dropwise and allowed to react for 18 h. The solution was neutralized with NH_4OH/EtOH, diluted with 800 mL of CH_2Cl_2, and washed twice with 200 mL of water. The combined organic phases were dried over $MgSO_4$ and concentrated to yield 159.0 g (99%) of a colorless powder. The crude product was purified partially (15.0 g) by column chromatography on silica gel with ethyl acetate/hexane (1:1) to yield 11.1 g (50 mmol, 74%) of the desired product.

^{1}H NMR ($CDCl_3$): δ 0.71 (s, 3H, $-CH_3$), 3.57 (d, 2H, $-COCH_2-$, $J = 11.7$ Hz), 3.78 (s, 2H, CH_2OH), 3.99 (d, 2H, $-COCH_2-$, $J = 11.7$ Hz), 5.40 (s, 1H, $-CH$Ph), 7.30−7.503 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$): δ 16.9, 34.9, 65.3, 73.3, 101.8, 126.1, 128.3, 129.0, 138.6.

***tert*-Butyldimethyl-(5-methyl-2-phenyl-[1,3]dioxan-5-ylmethoxy)silane, 3.** Product **2** (105.0 g, 500 mmol), dissolved in 1.0 L of CH_2Cl_2, was added to dry triethylamine (77.5 mL, 550 mmol) and a stoichiometric amount of (dimethylamino)-pyridine (DMAP) (12.0 g, 98 mmol). The *tert*-butyldimethylsilyl chloride (115.0 g, 760 mmol) was added and stirred for 48 h. The reaction solution was diluted with 500 mL of CH_2Cl_2, washed with 200 mL (4×) of saturated NH_4Cl and with 200 mL of water (2×). The organic phase was dried over $MgSO_4$ and concentrated to yield 179.6 g of an orange transparent liquid. The crude product was purified partially by column chromatography on silica gel with ethyl acetate/hexane (1:40) to yield **3** as a transparent liquid in 77% yield.

^{1}H NMR ($CDCl_3$): δ −0.02 (s, 6H, $-SiCH_3$), 0.67 and 1.16 (s, 3*H*, $-CH_3$), 0.82 (s, 9*H*, $-CH_3$), 3.24 and 3.74 (s, 2*H*, $-CH_2O-$), 3.49−3.96 (m, 4*H*, $-CH_2O-$), 5.31 (s, 1H, $-OCH-$), 7.23−7.44 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$): δ −5.7, 17.2, 19.0, 25.8, 35.2, 65.3, 73.2, 101.9, 126.1, 128.3, 128.8, 138.6.

2-(*tert*-Butyldimethylsilanyloxymethyl)-2-methylpropane-1,3-diol, 4. Product **3** (11.2 g, 35 mmol) was dissolved in a THF/methanol (50:50) solvent mixture, and 1.0 g of palladium/carbon (10 wt %) was added under nitrogen. The apparatus for the catalytic hydrogenolysis was filled with H_2(g). The reaction mixture was shaken for 6 h, and afterward the Pd/C was removed by filtration. The solvent was concentrated to yield 8.2 g (35 mmol, 100%) of a colorless viscous liquid. No further purification was necessary, and the product (**4**) was used directly for subsequent reactions.

^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.00 (s, 6H, $-\mathrm{SiC}H_3$), 0.71 (s, 3H, $-\mathrm{C}H_3$), 0.82 (s, 9H, $-\mathrm{SiC(C}H_3)_3$), 2.28−2.35 (m, 2H, $-\mathrm{O}H$), 3.41 and 3.53 (s, 2H, $-\mathrm{C}H_2\mathrm{O}-$), 3.47−3.66 (m, 4H, $-\mathrm{C}H_2\mathrm{OH}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ −5.7, 16.8, 18.1, 25.8, 41.0, 67.9, 68.8.

3-(2-Bromoisobutyrate)-2-(*tert*-butyldimethylsilanyloxymethyl)-2-methyl-propan-1-ol, 6. Compound **4** (30.5 g, 130 mmol) was dissolved in dry triethylamine (40 mL, 286 g, 2.2 equiv) and cooled to 0 °C. 2-Bromoisobutyryl bromide (16.07 mL, 130 mmol, 1 equiv) was added dropwise. The reaction mixture was stirred for 4 h at room temperature. After dilution with 500 mL of $\mathrm{CH_2Cl_2}$, the mixture was extracted three times with 50 mL of a saturated solution of sodium bicarbonate. The organic phase was dried over magnesium sulfate. The solution was concentrated, and the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) to give 38.7 g (100.9 mmol, 78% yield) of product **6**.

^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.00 (s, 6H, $-\mathrm{SiC}H_3$), 0.81 (s, 3H, $-\mathrm{SiC(C}H_3)_3$), 0.83 (s, 9H, $-\mathrm{SiCH_2(C}H_3)_3$), 1.87 (s, 6H, $-\mathrm{C(C}H_3)_2\mathrm{Br}$), 2.28−2.35 (m, H, $-\mathrm{O}H$), 3.50 and 3.53 (s, 4H, $-\mathrm{C}H_2\mathrm{O}-$), 4.13 (s, 2H, $-\mathrm{C}H_2\mathrm{OH}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ −5.7, 8.5, 16.6, 18.1, 25.8, 30.8, 41.0, 45.2, 55.8, 67.5, 67.7, 128.4, 129.5, 171.8.

Benzene-1,3,5-tricarboxylic Acid 1,3,5-Tris-[3-(2-bromoisobutyrate)-2-(*tert*-butyldimethylsilanyloxymethyl)-2-methylpropyl] Ester, 8. Compound **6** (34.51 g, 99 mmol, 3.3 equiv) was dissolved in 100 mL of $\mathrm{CH_2Cl_2}$ and triethylamine (13.8 mL, 99 mmol, 3.3 equiv) at room temperature. The solution was stirred for 30 min, followed by the dropwise addition of 1,3,5-benzenetricarbonyl trichloride (**7**) (7.96 g, 30 mmol). The reaction mixture was stirred for 3 h, and 20 mL of ammonium chloride solution was added. After dilution with 200 mL of $\mathrm{CH_2Cl_2}$, the mixture was extracted three times with 50 mL of a saturated solution of ammonium chloride. The water phase was reextracted with $\mathrm{CH_2Cl_2}$, and the combined organic phases were dried over magnesium sulfate. The solution was concentrated, and the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:9) to give 26.5 g (20.29 mmol, 68% yield) of **8**.

^{1}H NMR: δ 0.00 (s, 18H, $-\mathrm{SiC}H_3$), 0.84 (s, 27H, $-\mathrm{C}H_3$), 1.08 (s, 9H, $-\mathrm{SiC(C}H_3)_3$), 1.89 (s, 18H, $-\mathrm{C(C}H_3)_2\mathrm{Br}$), 3.58 (s, 6H, $-\mathrm{SiOC}H_2-$), 4.16 (s, 6H, $-\mathrm{CC}H_2\mathrm{OOC}-$), 4.30 (s, 6H, $-\mathrm{CC}H_2\mathrm{OOCPh}$), 8.79 (s, 3H, −Ph). ^{13}C NMR: δ −5.6, 16.9, 18.2, 25.8, 30.8, 40.7, 55.6, 64.9, 67.1, 74.6, 131.5, 134.4, 164.8, 171.3.

Benzene-1,3,5-tricarboxylic Acid 1,3,5-Tris(3-(2-bromoisobutyrate)-2-hydroxymethyl-2-methylpropyl) Ester, 9. Compound **8** (11.1 g, 8.50 mmol) was dissolved in 200 mL of dichloromethane, and $\mathrm{Et_2O{\cdot}BF_3}$ (4.81 mL, 38.23 mmol, 4.5 equiv) was added dropwise and stirred at room temperature for 3.5 h. A saturated solution of ammonium chloride was added, and the mixture was diluted with 200 mL of chloroform and washed three times with 200 mL of a sodium bicarbonate solution and twice with 200 mL of water. The water phase was extracted with 50 mL of chloroform, and the combined organic phases were dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) to give 6.13 g (6.36 mmol, 75% yield) of product **9**.

^{1}H NMR: δ 1.11 (s, 9H, $-\mathrm{C}H_3$), 1.92 (s, 18H, $-\mathrm{C(C}H_3)_2\mathrm{Br}$), 2.20−2.50 (bs, 3H, $-\mathrm{O}H$), 3.60 (s, 6H, $-\mathrm{CC}H_2\mathrm{OH}$), 4.23 (s, 6H, $-\mathrm{CC}H_2\mathrm{OOC}-$), 4.36 (d, 6H, $-\mathrm{CC}H_2\mathrm{OOCPh}-$), 8.81 (s, 3H, $-Ph-$). ^{13}C NMR: δ 16.9, 30.7, 40.8, 55.6, 64.9, 67.2, 67.5, 131.2, 134.7, 164.7, 171.9.

Dendron Synthesis. Synthesis of generation 2 ($(\text{g-2})_\mathrm{p}$, **10**) and generation 3 ($(\text{g-3})_\mathrm{p}$, **11**) acetonide protected dendrons based on 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA) was performed according to the literature.[14] The subscript “p” indicates that the terminal hydroxyls of the dendrons are protected with acetonide groups.

Tri-ATRP Initiator with Three Protected Second Generation Dendrons, 12, and a General Procedure for DCC/DPTS Coupling. The core **9** (2.16 g, 2.2 mmol) and the $(\text{g-2})_\mathrm{p}$ dendrons **10** (4.5 g, 10.1 mmol) were dissolved in 100 mL of $\mathrm{CH_2Cl_2}$. 1,3-Dicyclohexylcarbodiimide (DCC) (2.08 g, 10.1 mmol) and DPTS (0.94 g, 3.02 mmol) were added and stirred for 18 h at 35 °C. The solution was filtered, diluted with $\mathrm{CH_2Cl_2}$, and washed three times with 50 mL of saturated $\mathrm{NH_4Cl}$ solution. The organic phase was dried over $\mathrm{MgSO_4}$, and the solvents were distilled off. The viscous oil was redissolved in ethyl acetate, cooled in liquid nitrogen, and cold filtered. Evaporation of the organic solvent yielded 5.3 g of a transparent, slightly yellow oil. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1). The column was neutralized with 10% triethylamine/hexane in order to prevent the cleavage of the acetonide protective group. 1.3 g (0.6 mmol, 27% yield) of **12** was obtained as a clear oil.

^{1}H NMR: δ 1.08 (s, 18H, $-\mathrm{C}H_3$), 1.17 (s, 9H, $-\mathrm{C}H_3$), 1.27 (s, 9H, $-\mathrm{C}H_3$), 1.30 (s, 18H, $(-\mathrm{OCH_2})_2\mathrm{C(C}H_3)_2$), 1.35 (s, 18H, $(-\mathrm{OCH_2})_2\mathrm{C(C}H_3)_2$), 1.89 (s, 18H, $-\mathrm{C(C}H_3)_2\mathrm{Br}$), 3.56 (d, 12H, $-\mathrm{COC}H_2-$, $J = 11.8$ Hz), 4.09 (d, 12H, $-\mathrm{COC}H_2-$, $J = 11.9$ Hz), 4.18 (s, 6H, $-\mathrm{CC}H_2\mathrm{OOC}-$), 4.20 (s, 6H, $-\mathrm{CC}H_2\mathrm{OOC}-$), 4.32 (s, 18H, $-\mathrm{CC}H_2\mathrm{OOC}-$), 8.77 (s, 3H, $-Ph-$).

^{13}C NMR ($\mathrm{CDCl_3}$): δ 17.7, 18.5, 22.1, 25.1, 30.6, 39.5, 42.0, 47.0, 55.4, 65.0, 66.0, 66.5, 98.1, 131.1, 134.6, 164.1, 171.0, 172.1, 173.5.

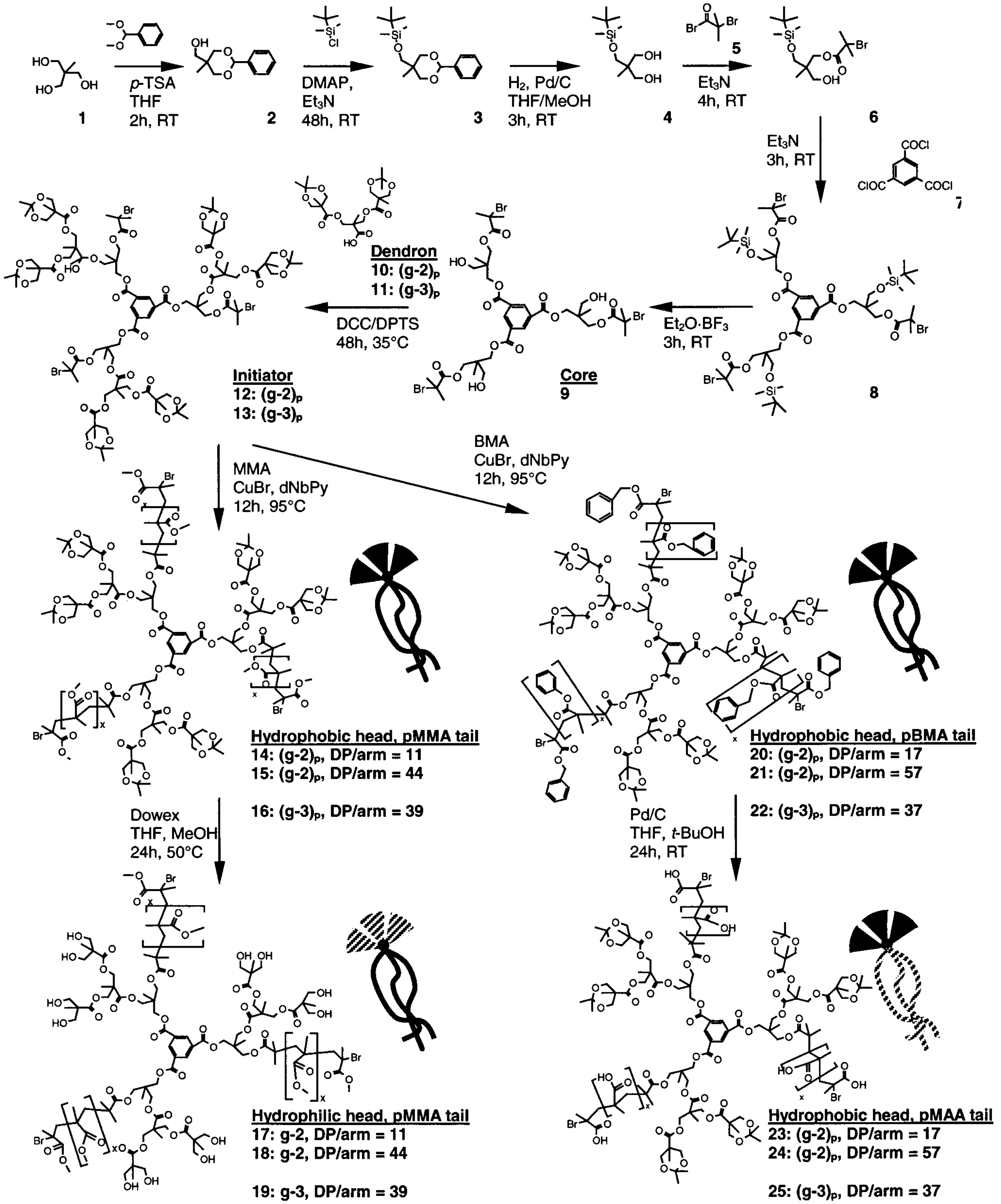
Polymerization of MMA (DP = 11) from a Triinitiator (12), 14, and a General Procedure for the Polymerization of Methacrylates by ATRP. The initiator **12** (0.37 g, 0.16 mmol) was dissolved in 15 mL of THF and degassed by freeze−thaw (3×). Before the last thaw, CuBr (23.0 mg, 0.16 mmol) and dNbPy (131.0 mg, 0.33 mmol) were added under argon. Once the THF removed, freshly distilled and degassed MMA (1.03 mL, 9.6 mmol) was added to the flask. The reaction proceeded for 16 h at 95 °C, resulting in a polymer with a high viscosity (solid in the case of higher molecular weights). The polymer was dissolved in THF and precipitated in methanol. 1.00 g (73% yield) of **14** was obtained as a white powder. The degree of polymerization per arm (DP/arm) was evaluated by scaling a peak of the MMA (^{1}H NMR δ 3.53 (s, 3H/monomer, $-\mathrm{COOC}H_3$)) to the protons of the aromatic core (^{1}H NMR δ 8.77 (s, 3H, $-Ph-$)). Many of the other peaks overlap in the ^{1}H NMR spectrum.

The same procedure was used for the polymerization of BMA, producing yields around 65%. The DP/arm was obtained by scaling a BMA peak (^{1}H NMR: δ 4.82 (s, 2H/monomer, $-\mathrm{COOC}H_2\mathrm{Ph}$)) to the protons of the aromatic core (^{1}H NMR: δ 8.77 (s, 3H, $-Ph-$)).

Macromolecule with 3 Hydrophilic Dendrons (g-2) and 3 Hydrophobic Tails (MMA, DP = 11), 21, and a General Procedure for the Deprotection of the Dendrons. Dowex 50WX8-200 ion-exchange resin (0.4 g) was added to **14** (0.5 g) dissolved in 10 mL of a THF/methanol mixture (1:1). The reaction mixture was stirred at 50 °C for 48 h to effect the deprotection reaction. The mixture was cooled, filtered to remove the Dowex, and concentrated (0.48 g, 95% yield). No further purification was necessary. The disappearance of the acetonide peak (^{13}C NMR ($\mathrm{CDCl_3}$) δ 98.1) indicated that the deprotection was complete. The amphiphilic nature and the polydispersity of the polymer did not allow for a well-resolved ^{1}H NMR spectrum.

Macromolecule with 3 Hydrophobic Dendrons ($(\text{g-2})_\mathrm{p}$) and 3 Hydrophilic Tails (MAA, DP = 17), 23, and a General Procedure for the Removal of the Benzyl Group. The macromolecule **20** (0.82 g, 0.07 mmol) was dissolved in 100 mL of a THF/*tert*-BuOH (50:50) solvent mixture. The dendron’s acetonide protecting group did not get cleaved using *tert*-BuOH. Under nitrogen, 1.0 g of Pd/C (10 wt %) was added into the reaction flask. The apparatus for catalytic hydrogenolysis was filled with $\mathrm{H_2(g)}$ at 30 psi, and the reaction mixture was shaken for 24 h. The Pd/C was removed by filtration (0.2 μm Teflon filters), and the solvents were evaporated to yield **23** (0.40 g, 49% yield) as a clear, brittle resin. No further purification was necessary. Deprotection was monitored by the disappearance of the peak of the benzyl ether (^{1}H NMR δ 4.82 (s, 2H/mer **(???)**, $-\mathrm{COOC}H_2\mathrm{Ph}$)). The presence of the acetonide was verified by NMR (^{1}H NMR: δ 1.30 (s, 18H, $(-\mathrm{OCH_2})_2\mathrm{C(C}H_3)_2$), 1.35 (s, 18H, $(-\mathrm{OCH_2})_2\mathrm{C(C}H_3)_2$); ^{13}C NMR: ($\mathrm{CDCl_3}$) δ 98.1).

Scheme 2. Synthesis of Dendritic–Linear Amphiphilic A_3B_3 Macromolecules, Composed of Polyester Dendrons and Linear Poly(methacrylates) Polymerized by ATRP[a]



[a] In the sketches of the A_3B_3 the hydrophobic part is in full, whereas the hydrophilic part is hatched.

Results and Discussion

The synthesis of the core, **9**, of the miktoarm star-polymer, which contains three hydroxyl groups that couple the focal point of the dendrons and three activated bromide sites for ATRP, is based on the orthogonal protection of 1,1,1-tris(hydroxymethyl)ethane, **1**, and the coupling to 1,3,5-benzyltricarbonyl trichloride, **7**, as shown in Scheme 2. Starting from compound **1**, two of the hydroxyl groups were protected as the benzylidene ketal, **2**, by a procedure described by Issidorides and Gulen.[15] The free hydroxyl group of **2** was protected with a *tert*-butyldimethylsilyl group (TBDMS) using standard

Table 1. Properties of A_3B_3 Macromolecules[a]

macromolecule A_3B_3	arms A	dendron B	^1H NMR DP/arm	^1H NMR M_n	SEC PDI	MDSC T_g [°C]	DMA T_g [°C]
		$_p$(g-2)$_p$		500	1.00	−23	
		$_p$(g- 3)$_p$		1100	1.01	1	
15	MMA	(g-2)$_p$	44	17 300			
17	MMA	g-2	11	5 800	1.16	2, 78	
18	MMA	g-2	44	17 100	1.10	7, 84	
19	MMA	g-3	39	16 700	1.16	0, 110	5, 120
20	BMA	(g-2)$_p$	17	11 900			
21	BMA	(g-2)$_p$	57	34 700			
23	MAA	(g-2)$_p$	17	7 300	1.17	*b*	
24	MAA	(g-2)$_p$	57	19 300	1.14	*b*	
25	MAA	(g-3)$_p$	37	15 000	1.15	*b*	0−180[b]

[a] The values for the dendrons ($_p$(g-2)$_p$ and $_p$(g-3)$_p$), measured on macromolecules with a protected focal point (benzyl ether) and terminal groups (acetonide), are given as comparison to the macromolecule. [b] These samples did not show a distinctive T_g.

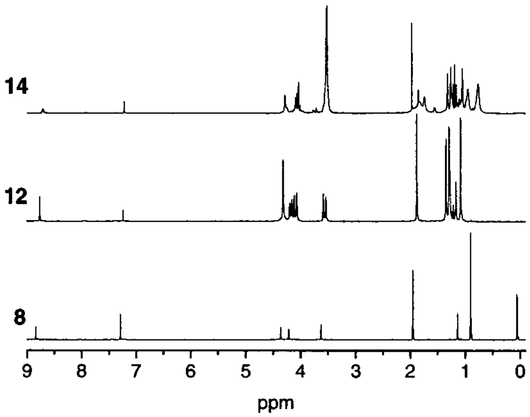


Figure 1. Stacked ^1H NMR spectra of macromolecules **8**, **12**, and **14**.

conditions with Et_3N, DMAP, and *tert*-butyldimethylsilyl chloride to obtain **3**. Deprotection of the benzylidene group was accomplished quantitatively by catalytic hydrogenolysis with Pd/C in a THF/MeOH (50:50) to yield **4**. Reaction of **4** with 1 equiv of 2-bromoisobutyryl bromide produced the targeted orthogonally protected compound **6** after column chromatography. Steric hindrance probably does not favor the disubstituted compound, so compound **6** is obtained in high yields. The sequence of the functionalization reactions is important since the activated bromide functionality is not compatible with the hydrogenolysis procedure. The protected core, **8**, was obtained by esterification of **6** with **7** in CH_2Cl_2 in the presence of Et_3N in 68% yield after column chromatography. The ^1H NMR spectrum of compound **8**, presented in Figure 1, shows the signals of the appended building block (TBDMS: δ 0.00, 1.08, 2-bromoisobutyrate: $\delta = 1.89$) together with the signal of the aromatic core. Selective removal of the TBDMS groups of **8** was accomplished with $Et_2O{\cdot}BF_3$, in 75% yield after column chromatography, to produce the core, **9**.

The judicious choice of the dendritic fragments provides an important design feature in the construction of the amphiphilic copolymers. Dendrimers derived from bis-MPA have been reported to be water-soluble owing to the abundant hydroxyl groups that decorate the surface.[16] Conversely, protection of the hydroxyl groups with the acetonide renders the dendrimers hydrophobic, providing versatility in the control of the amphiphilicity of the molecules. The second and third generation acetonide protected dendrons of bis-MPA were prepared by procedures developed by Hult et al.[14]

The hydroxyl groups of **9** were esterified in a “core-in”, or convergent approach,[4l] with either the second, **10**, or third generation, **11**, acid functional dendrons using DCC in the presence of DPTS in high yields. The ^1H NMR spectrum of **12** in Figure 1 clearly shows the peaks associated with the bis-MPA dendrimer ($\delta = 3.5-4.5$, 1.09, 1.17) together with the ATRP initiator ($\delta = 1.89$). The acetonide protective groups can clearly be seen ($\delta = 1.29$, 1.35), indicating that no deprotection took place during purification.

The controlled radical polymerization of either MMA or BMA from the activated alkyl bromide of **12** was accomplished using CuBr/dNbPy as a catalyst according to literature procedures.[17] Polymers derived from BMA are readily deprotected by hydrogenolysis to the poly(methacrylic acid) (pMAA) under neutral conditions, which allows the dendrimer functionality to be preserved. In this “core-out” procedure, bulk polymerization conditions were employed (95 °C, 12 h), since each of these monomers effectively dissolved the initiator, **12**, the catalyst, and the ligand. Modest molecular weights were investigated to allow molecular weight determination through end-group analysis and control of the ratio of hydrophobic to hydrophilic moieties. The characteristics of the A_3B_3 block copolymers are shown in Table 1. Narrow polydispersities, good yields, and predictable molecular weights were demonstrated for each of the targeted polymer architectures. It has been shown previously that star−star coupling can be minimized provided the catalyst concentration relative to initiator is low.[18] The ^1H NMR spectrum of copolymer **14** is shown in Figure 1, which confirms the targeted hybrid block copolymer structure of three pMMA chains (^1H NMR: δ 0.81, 0.99, 1.22, 3.57 ppm) and three acetonide-protected dendrons attached to an aromatic core. A small signal from noninitiating ATRP initiator (^1H NMR: δ 1.95) can be seen in samples with low molecular weights. It has been shown that quantitative initiation from multifunctional initiators is difficult for low molecular weights.[19]

The last step in the preparation of the A_3B_3 amphiphilic block copolymers was the deprotection of the acetonide-protected dendrimer. Mild conditions were required to remove of the acetonide protecting group and restore the dendrimer’s hydroxyl moieties. This transformation was accomplished by stirring the block copolymers, dissolved in a THF/methanol (50:50) mixture, with Dowex for 48 h at 50 °C. Dendrimers derived from bis-MPA have definitive ^1H NMR resonances due to the sensitivity of the neighboring $-CH_3$ groups to the hydroxyl group substitution, allowing these transformations to be carefully tracked. The ^1H NMR spectra clearly show a shift of this methyl group from 1.12 to

Table 2. Dynamic Light Scattering Results[a]

macromolecule		single molecule			assembly		
A_3B_3	solvent	R_h [nm]	std dev	avg error [%]	R_h [nm]	std dev	avg error [%]
15	THF	2.3	0.1	15.6			
20	THF	2.4	0.1	9.1			
21	THF	2.8	0.1	9.9			
23	H_2O	3.0	0.1	14.4	78.7	5.9	33.9
24	H_2O	3.0	0.1	31.4	47.1	3.0	28.0
24	PBS	2.7	0.1	9.0	29.3	2.1	12.2
					91.0	20.2	87.0

[a] THF is used as a nonselective solvent. The water-based solvents are selective solvents for the strongly hydrophilic pMMA giving a population of single molecules and one or two populations of micelles. The standard deviation (std dev) of the R_h values gives a measure of the repeatability of the experiments; the average percent error (avg error) from the CONTIN output gives an indication of the error in the R_h values.

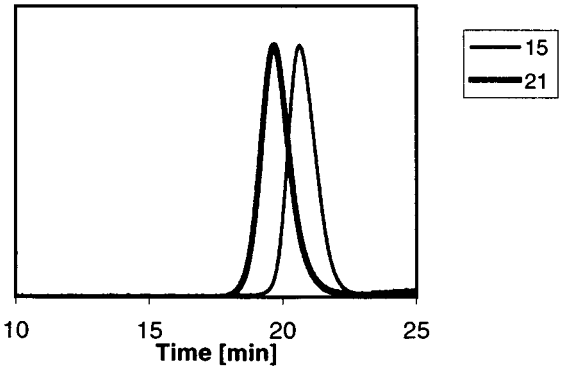


Figure 2. SEC traces of samples **15** and **21** showing narrow polydispersities.

1.05 ppm, consistent with the deprotection of the hydroxyl groups. Likewise, the quaternary carbon on the acetonide group at 98.1 ppm is no longer detectable after the deprotection transformation, indicating that the acetonide protection group has been removed from the dendrimer. Deprotection was performed cleanly and quantitatively with no detectable side reactions.

The use of pBMA provides additional opportunities in the design of unique amphiphiles. The benzyl ester group of pBMA was selectively and quantitatively removed by catalytic hydrogenolysis in a THF/*tert*-BuOH (50:50) mixture to give pMAA. This transformation was accomplished without affecting the acetonide-protecting group of the interior dendritic structure. ^{1}H NMR proved to be a useful technique to follow the transformation, as the benzyl ester peaks are distinct and well separated. Several molecular weights were investigated that showed narrow polydispersities with no evidence of star−star coupling (Figure 2). The bulk reaction is essentially kinetically quenched at high conversions owing to the dramatic increase in viscosity, which coupled with the low concentration of active species minimizes the risk of coupling of growing chain ends.

The hydrodynamic radii (R_h) of many of the A_3B_3 macromolecules including **15** **20**, **21**, **23**, and **24** were measured by DLS under different solvent conditions. A nonselective solvent, THF, was used to assess the R_h of single molecules while the self-assembly of **23** and **24** was studied in an aqueous solution. Of the molecules studied, each had a single molecule hydrodynamic radius of about 3 nm, although there is some variation of R_h due to the length of the polymer chains and quality of the solvent (Table 2). We estimated the contribution of the dendron volume to the overall volume of the molecule for samples **20** and **21** assuming that the dendron volume is not altered by the length of the polymer chain and that the molecule adopts a spherical shape of radius given by R_h. We accomplished this by comparing the incremental increase in R_h with chain length under the same solvent conditions for **20** and **21** (Appendix 1). In the case of the shorter pBMA chains (**20**), the dendrons contributed to 90% of the molecular volume while in the case of the longer pBMA chains (**21**), the dendrons only accounted for about 58% of the total molecular volume. These data indicate that the longer polymer chains could shield the dendrons much more effectively in a selective solvent environment.

The macromolecules with pMAA tails, **23** and **24**, were dissolved in deionized Milli-Q water, a selective solvent for pMAA, to investigate their solution properties. The analysis of the DLS data for both **23** and **24** showed a population of single molecules coexisting with a population of a larger species as evidenced by clearly resolved peaks in the CONTIN output. The relative area under each peak indicates the species population of the hydrodynamic size given by the peak position where the breadth of the peak gives some measure of polydispersity of the species. The larger species can be inferred to be self-assembled suprastructures of the single molecules. Although the population of the suprastructures is smaller than that of the single molecules, the peak indicating these structures was present and clearly resolved in all trials. The formation of suprastructures may occur as the pMAA chains that are compatible with the water environment shield the hydrophobic dendron moieties from the unfavorable interactions with water through self-assembly. The single molecule R_h of 3.0 nm for both **23** and **24** is consistent with the single molecule sizes for the precursors of these molecules (**20** and **21**) in THF. The R_h of the self-assembled structure of **23** was about 80 nm while that for **24** was only 47 nm. The large difference in the sizes of the self-assembled structures can be attributed to the differences in the composition of these two molecules: **23** has an average of 17 MAA units per tail, while **24** has an average of 57 units per tail. This difference in polymer chain length leads to different aggregation numbers in the self-assembly process. The bulky nature of the dendron moieties may also affect their ability to pack efficiently into the traditional spherical micelles that can form from diblock copolymers in selective solvents. The formation of elongated micellar structures, or “wormlike micelles”, would help relieve some of the packing constraints of the dendrons and may require less distortion of the molecules from their single molecule conformation.[20] Hence, the difference in the size of the molecules may also be due to differently shaped structures. Although these data cannot confirm the presence of anisotropic wormlike micelles, such structures would be consistent with these results. Further experiments are planned to investigate these self-assembled structures.

As pMAA has acrylic acid functionalities, further studies of **24** were performed in phosphate-buffered saline solution (PBS; 75 mM NaCl; 53 mM Na_2HPO_4; 13 mM NaH_2PO_4) at a pH of 7.4. The buffered solution helps to neutralize and screen acidic environments in the molecules. DLS experiments on **24** in PBS showed smaller self-assembled structures with a narrower size distribution than those in water. The single molecule R_h was 2.7 nm, the self-assembled structure's size was 29 nm, and a third R_h of about 90 nm was observed, but with a large distribution of sizes about the average. The average percent error of the hydrodynamic radius measured for the 29 nm assemblies is of the same order of that for the single molecules. The narrow distribution of these assemblies observed in this experiments indicate that stable structures form from closed association of the single molecules due to the selectivity of the solvent environment.

Phase separation of the miktoarm dendritic–linear block copolymers was studied in the bulk by MDSC and DMA. Samples **17**, **18**, and **19** (hydrophilic head/pMMA tail) each exhibited two distinct glass transition temperatures (T_g) upon annealing; a low-temperature transition is attributed to the dendrons and a high-temperature transition to the pMMA, indicative of a phase-segregated morphology. A comparison of the copolymers' T_g's with the values obtained for the dendrons (T_g: g-2 = −23 °C, g-3 = 1 °C) and linear pMMA (T_g: 120 °C) gives an evaluation of the extent of the segregation. As seen in Table 1, segregation increased mainly with dendrimer generation and somewhat with the degree of polymerization of the linear polymer. Samples **23**, **24**, and **25** (hydrophobic head/pMAA tail) each showed a single, broad T_g. Therefore, in the bulk these macromolecules can be seen as "stabilized dendrimers", where the linear chains allow for some interpenetration and presumably improve the bulk mechanical properties of the material.

In summary, the synthesis of miktoarm dendritic–linear block copolymers in a tandem "core-in"/"core-out" approach was achieved. The rational design of an orthogonally protected multifunctional compound containing sites for the attachment of dendrons in a convergent approach together with an initiator for ATRP enabled these syntheses. ^{1}H NMR and SEC studies confirm the versatility and efficiency of this approach, as illustrated by the control of the end-group functionality, molecular weights, and narrow polydispersities. Additionally, by adjusting the relative properties of the dendritic and linear blocks that comprise the molecules, unique polymer properties were observed including self-assembly into micellar structures as seen with DLS and phase separation shown with DSC. The ability to tune polymer properties through careful selection of monomer properties and design of unique macromolecular architectures will become increasingly important for development of advanced polymeric materials.

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Supporting Information Available: Calculations of the volume fraction of the dendron relative to the total hydrodynamic volume of the macromolecule as well as an example of data produced by the CONTIN software. This material is available free of charge via the Internet at http://pubs.acs.org.

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