Conformational and Structural Properties of High functionality Dendrimer-Like Star Polymers Synthesized from Living Polymerization Techniques[*]

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Abstract
The design, synthesis and solution properties of dendritic-linear hybrid macromolecules is described. The synthetic strategy employs living ring-opening polymerization in combination with selective and quantitative organic transformations for the preparation of new molecular architectures similar to classical star polymers and dendrimers. The polymers were constructed from high molecular weight poly(e-caprolactone) initiated from the surface hydroxyl groups of dendrimers derived from bis(hydroxymethyl) propionic acid (bis-MPA) in the presence of stannous 2-ethyl hexanoate (Sn(Oct)2). In this way, star and hyperstar poly(e-caprolactones) were elaborated depending on the generation of dendrimer employed. The ROP from these hydroxy groups was found to be a facile process leading to controlled molecular weight, low dispersity products (Mw/Mn) < 1.15. In addition to the use of dendrimers as building blocks to star polymers, functional dendrons derived from bis-MPA were attached to chain ends of the star polymers, yielding structures that closely resemble that of the most advanced dendrimers. Measurements of the solution properties (hydrodynamic volume vs. molecular weight) on the dendritic-linear hybrids show a deviation from linearity, with a lower than expected hydrodynamic volume, analogous to the solution properties of dendrimers of high generation number. The onset of the deviation begins with the polymers initiated from the second generation dendrimer of bis-MPA and becomes more exaggerated with the higher generations. It was found that polymerization amplifies the nonlinear solution behavior of dendrimers. Small angle neutron scattering (SANS) measurements revealed that the radius of gyration scaled with arm functionality (f) as $f^{2/3}$, in accordance with the Daoud-Cotton model for many arm star polymer.

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Introduction

The control of polymer properties through the synthesis of complex macromolecular architectures is central to many areas of science and advanced technological applications.[1] Accordingly, the synthesis of branched molecular architectures, such as hyper branched, dendritic, star, and combburst macromolecules has been the goal of many research groups. [2] The interest in these mesoscopic systems and nanostructures is driven by the potential interesting mechanical, rheological and solution properties. Dendrimers provide the standard of a material with a precisely defined structure, while hyper branched, dendri-graft and related architectures are less perfect elaborations of branched macromolecules. [3] With the rapidly growing interest in the synthesis of these materials coupled with advances in living controlled polymerization procedures, a significant number of building blocks for their construction have appeared. However, the use of ring-opening polymerization (ROP) to prepare polymers with unique topologies has been much less pervasive than other polymerization procedures and focused mostly on star-shaped polymers. [4] To this end, it seems plausible to combine the living ROP of cyclic esters with functional dendritic macromolecules to serve as initiators to produce polyesters with new macromolecular architectures. [5] In one example, Frechet et al. [6] reported the ROP of e-caprolactone from a dendron having an initiating site at the focal point to give hybrid dendritic-linear copolymers.

Here, we describe the design, synthesis and characterization of dendritic-linear hybrids from living ROP methods ill combination with selective and quantitative organic transformations for the preparation of new molecular architectures similar to classical star polymers and the most advanced dendrimers. Similar structures have been prepared by Frechet et al. by end capping a hydrophilic four-arm poly(ethylene glycol) star polymer with hydrophobic dendritic blocks. [7] In our case, the polymers were constructed from high molecular weight poly(e-caprolactone) with branching junctures derived from bis(hydroxylmethyl) propionic acid (bis-MPA), emanating radially from a central core. The choice of bis-MP A was based on the aliphatic structure as well as its documented use as building blocks in the synthesis of dendritic macromolecules. [8] The choice of polymerization reaction for growth of linear chains from dendritic polyesters was dictated by the presence of the numerous hydroxymethyl groups at the chain ends of the dendrimers. We have recently demonstrated that the living ROP of e-caprolactone from these hydroxyl groups is a facile process leading to controlled molecular weight, low polydispersity products. [9] The key to this synthesis is the use of catalytic amounts of stannous 2-ethylhexanoate ($Sn(Oct)_2$) to promote the polymerization. In this article, we review the design and synthesis of new macromolecular architectures using dendritic building blocks with controlled ROP in a modular approach to macromolecules. We also present structural properties, namely the radius of gyration R_g of the molecules in solution. Consideration of the molecular size of dendrimers and dendrimer-like star polymers to date has largely been of a theoretical nature. These studies have concluded that the growth in molecular size of a dendrimer molecule is approximately linear with the increase in generation number, scaling With the cube root of the number of monomers. Existing experimental study of the structural properties of dendrimer-like polymer systems is limited. [10] A study of poly(propyleneimine) dendrimers in aqueous solution demonstrated that the dimension of the dendrimer increased linearly with the dendritic generation number (roughly as $M^{1/3}$), independent of the character of the end

group and of the solvent used. However, in a previous study of the first three generations of caprolactone dendrimer-like star polymers synthesized from a six arm core, we have shown that the increase of R_g is nonlinear with generation number, increasing more significantly between the first and second generation than between the second and third. It was also shown that R_g is independent of the degree of polymerization of the arms (over the range studied), by reason of the increased flexibility of the arms permitting more folded molecular conformation. In this work, we focus on the structure of the star polymer (i.e., first generation dendrimer-like star) with respect to the star's functionality.

Experimental

Materials

Stannous-2-ethylhexanoate (Sigma) and all other chemicals (Aldrich) were purchased and used without any further purification except the Ii-caprolactone which was dried over CaH2 for 24 h and then distilled under high vacuum before use. The hydroxy-functional dendrimer were synthesized according to a procedure developed by Ihre et al.[7]

Techniques

^{1}H-NMR were recorded in $CDCl_3$ solution, on a Bruker AM 250 (250 MHz) apparatus with the solvent proton signal for reference. 13C-NMR spectra were recorded at 62.9 MHz on the same instrument using the solvent carbon signal as a reference. All polymer 13C-NMR spectra were recorded on 250 mg of sample using 16384 scans. The number average molecular weights of the polymers were calculated from the I H-NMR data. The molecular weight distributions were determined by size exclusion chromatography (SEC) using a Waters chromatograph connected to a Waters 410 differential refractometer and an UV -detector. Four 5µm Waters columns (300 x 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, 10^6 Å) were used with THF as solvent at 25 °C. Poly(styrene) standard samples were used for calibration.

Small angle neutron scattering (SANS) was performed at beamline NG1 at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD. The incident wavelength of the neutrons was λ = 0.6nm, and the energy resolution of the source was $\Delta\lambda/\lambda$ ~0.15. The liquid samples (2% polymer by weight in deuterated toluene), were contained in quartz cells which had an active path length of 1 mm. Data were collected on a 2-dimensional multiwire detector which was positioned 3.6m away from the sample holder, providing a q range: $0.05nm^{-1} < q < 1nm^{-1}$. These data were corrected for background scattering and scattering from the empty quartz cell.

2,2-Bis(phenyldioxymethyl)propionic acid [5].

Bis-MPA (50.0 g, 347 mIDoi), benzaldehyde dimethylacetal (85.1 g, 560 mIDol) and p-TSA (1.39 g, 7.46 mIDol) were dissolved in aceton. The mixture stirred for 14 h. NH4OH (aq, 30%)/EtOH (1:1) (8 mI) was then added to neutralize the p-TSA. The acetone was evaporated and the crude product was diluted in CH2Cb and extracted with water. The organic phase was separated, dried (MgSO4) and recrystallized from CH2Cb to yield of93.1 g (90%) of white crystals. 'H-NMR (CDCI3) 15 1.09 (s, 3H, -CHJ), 3.66-4.64 (q, 4H, --(ClliO)2CH-), 5.47 (s, IH, -CHPh), 7.31-7.47 (m, 5H, -Ph). 13C-NMR (aceton-d6) 15 18.14,42.61,73.96, 102.04,127.12, 128.67,129.35,139.81, 175.70.

2,2-Bis(methylol) benzyl propionate [6].

Bis-MPA (75.0 g, 521 mIDol) and KOH (31.8 g, 567 mIDoi) were dissolved in 100 ml dimethylformarnide (DMF). After I h at 110 °C benzyl cWoride (75.05 g, 592 mIDol)

was slowly added. The mixture was allowed to react for 14 h. DMF was distilled of and the residue was dissolved in CH2CI2 and extracted with water (3 x 75 ml). The crude product was purified by recrystallization from toluene. The toluene was then evaporated and the rest of the product was purified by column chromatography (silica gel, hexane/EtOAc as eluent the concentrations were 5,10,20,40,60,80, 100% eTOAc) to yield a total of 68.8 9 (60%) of white crystals. lR-NMR (COCh) 15 1.06 (s, 3R, -C~), 3.69-3.94 (q, 4R, -ClliOR), 5.18 (s, 2R, -ClliPh), 7.34 (s, 5R, -PhH). 13C-NMR(COCI3)15 17.20,49.49,66.55,66.63,127.82, 128.35,128.61,135.81,175.64.

2,2-Bis(tert-butyldimethylsiloxane) benzyl propionate-gl (- TBDMS, -CO~7n7) [7].

4 (49.8 g, 222 mmol), tert-butyldimethylsilyl cWoride (TBOMSC1) (80.5 g, 535 mmol) and imidazole (37.8 g, 533 mmol) were dissolved in CRJCN (150 mI). the mixture was stirred for 12 h and the solvent (CRJCN) was then evaporated. The crude product was dissolved in hexane and extracted with R2O. The organic phase was separated and dried (MgSO4). The hexane was evaporated to a yield of 95.2 9 (94%) of a colorless liquid. I R-NMR (COCI3) 6 0.00 (s, 12R, -Si(C~h), 0.83 (s, 18R, -C(C~)J), 1.12 (s, 3R, -C~), 3.64-3.77 (q, 4R, -ClliO -),5.10 (s, 2R, -CRr), 7.32 (s, 5R, -Ph).

2,2-Bis(tert-butyldimethylsiloxane) propionic acid-gl (TBDMS, -coon) [8] and a generafprocedure for the removal of the benzyl and benzylidene group.

5 (210 mmol, 95.2 g) was dissolved in EtOAc (100 mI) and Pd/C (10 wt%) (1.5 g) was added. The apparatus for catalytic hydrogenolysis was evacuated &om air and filled with R2(g). The apparatus for catalytic hydrogenolysis was evacuated &om air and filled with Rig). The reaction mixture was shaken. The deprotection was followed by I R-NMR and stopped after completion (approximately 4h) and the Pd/C was filtered off. The solvent was evaporated to yield 94.2 9 (99%) of a colorless liquid. I R-NMR (COCI3) 15 0.00 (s, 12R, -Si(C~h), 0.82 (s, 18R, -C(C~h), 1.07 (s, 3R, -C~), 3.60-3.69 (q, 4R, -ClliO-). 13C-NMR (COCI3) 6 -5.62,17.05,18.18,25.77,49.69,64.39,179.44.

g2(-TBDMS), -CO2C7H7) [9].

4 (23.3 g, 104 mmol), 6 (79.0 g, 218 mmol) and OPTS (4.87 g, 15.5 mmol) were dissolved and stirred in CR2Cb. OCC (55.7 g, 0.270 mmol) was then added and the mixture was left to react for 12 h. The mixture was filtered and the filtrate was purified by column chromatography (silica gel, hexane/EtOAc 95:5 as eluent). The yield was 30 9 (32%) ofa viscous and colorless liquid. J H-NMR (CDCI3) b 0.00 (s, 24H, -Si(CH3)2), 0.84 (s, 36H, -C(Clli)3), 1.09 (s, 6H, -(Clli)2), 1.23 (s, 3H, -Clli), 3.56-3.70 (q, 8H, -ClliO-), 4.15-4.30 (q, 4H, -ClliO-), 5.13 (s, 2H, -CHL), 7.33 (s, 5H, -Ph). 13C-NMR(CDCI3)b -5.58, 16.93, 17.58, 18.20, 25.83, 46.94,50.38,64.04,65.31,66.77,128.03, 128.30,128.60,135.57, 172.51,174.19.

g2(-TBDMS, -COOH) [10].

7 (30.0 g, 32.9 mmol) and Pd/C (1.5 g) were dissolved in EtOAc (100 mI) and hydrogenolyzed according to the general procedure for the removal of the benzyl group. The yield was 26.2 9 (97%) of a viscous and colorless liquid. 1 H-NMR (CDCI3) b 0.00 (s, 24H, -Si(Clli)2), 0.84 (s, 36H, -C(Clli)3), 1.06 (s, 6H, -C(Clli)2), 1.25 (s, 3H, -CH3), 3.57-3.72 (q, 8H, -ClliO-), 4.06-4.29 (m, 4H, -ClliO-), 5.28 (s, 2H, -CHL). 13C-NMR (CDCI3) 6 -5.59, 16.96, 17.55, 18.18,25.81,46.59,50.41,64.07,64.92, 174.17,178.84.

g3(-TBDMS, -CO2C7H7) [11].

8 (13.9 g, 16.9 mmol) was dissolved in CH2Ch. 4 (1.65 g, 7.36 mmol), OPTS (0.69 g, 2.21 mmol) and DCC (3.94 g, 19.14 mmol) was then added in that order into the stirred

solution. After 14 h, the mixture was filtered and rinsed with CH2Ch. Ch2Ch was then evaporated and an extraction with hexane and H2O was made. The organic phase was separated, dried (MgSO4) and purified by column chromatography (silica gel, hexane/EtOAc 96:4 as eluent). The yield was 84% of a colorless viscous oil IH-NMR (COCI3) b 0.00 (s, 48H, -Si(Clli)2), 0.84 (s, 72H, -C(Clli)3), 1.04 (s, 12H, -Clli), 1.09 (s, 6H, -Clli), 1.24 (s, 3H, *CH.,),* 3.59-3.72 (q, 16H, -ClliO-), 4.13-4.28 (q, 12H, -C(Clli)3). 5.13 (s, 2H, -CH2-), 7.33 (s, 5H, -Ph).13C-NMR (COCI3) 6 -5.58, 17.00, 17.48 18.20,25.84,46.78,50.32,64.00,64.81,66.19,67.14,128.38,128.45,128.65,135.42, .80,174.03.

A general procedure for polymerization of e-caprolactone, 1a.
0-1 (5.00 g, 7.64 mmol) was dried over MgSO4 in warm THF, and filtered into the pre-flamed reaction flask, which after filling was sealed. The solvent was then evaporated under vacuum at 90 °C. Dry toluene (2 mI) was added and evaporated to remove residual H2O. This process was iterative done three times. The reaction flask was now filled with N2(g) and dry toluene (2 ml) to dissolve the initiator. e-caprolactone (75.0 g, 658 mmol) was added and the temperature was increased to 110 °C before a catalytic amount of Sn(OCt)2 (32 mg, 0.08 mmol) was added. The ratio of catalyst/initiator was 1/400. The polymerization was stirred for 24 h, diluted with THF and precipitated into cold MeOh to give 72.0 9 (Yield: 90%) of a white crystalline powder. IH-NMR(CDCI3)15 1.30-1.42 (111, poly, -Cfu-), 2.26-2.32 (t, poly, -CfuO-), 3.60-3.65 (t, 18H, -CfuOH-), 4.01-4.07 (t, poly, -CfuCO-), 4.33 (s, 12H, -CCH3(CfuO)2-), 6.88-7.24 (dd, 12H, Ph-). 13C-NMR CDCI3) 15 17.74, 24.50,25.45, 28.27, 32.20, 34.03, 46.69, 51.58, 62.38, 64.05, 65.07, 120.67, 129.64, 146.22, 148.60, 171.37, 172.78, 173.65.

*General Procedure for the Derivitization of Poly(Caprolactone} Star Polymer* , *15.*
la (8.00 g, 0.538 mmol), g2(-TBDMS, -COOH) (3.98 g, 4.84 mmol), TPP (1.69 g, 6.46 mmol) and DIAD (1.30 g, 6.46 mmol) were dissolved in THF (15 mI) according to the general procedure. After 12 h, the mixture was precipitated into cold MeOH. The yield was 10.56 9 (99%) of a white crystalline powder. I H-NMR (CDCI3) 15 0.00 (s, 144H, -Si(Clli)2), 0.84(s, 216H, -{Clli)3), 1.05 (s, 36H, -Clli), 1.20 (s, 18H, -Clli), 1.30-1.42 (111, poly, -Cfu-), 1.57-1.69 (111, poly, -Cfu), 2.26-2.32 (t, poly, -CfuO-), 3.57-3.72 (q, 48H, -CfuO-), 4.01-4.07 (t, poly, -CfuCO-), 4.10-4.26 (m, 24H, -CfuO-), 4.33 (s, 12H, -CfuO-), 6.91-7.09 (q, 12H, -Ph). 13C-NMR(CDCL3)15 -5.59,17.00, 17.59, 18.18,24.55,25.50,25.81,28.33, 34.09,46.77,50.38,64.11,64.89,65.27, 120.72, 129.70, 146.26, 148.65, 171.40, 172.61, 172.83, 173.50,174.15.

A general procedure for the removal of the TBDMS group from the star polymer.
15 (10.03 g, 0.52 mmol) was added to a flask which was sealed. The flask was evacuated and filled with N2(g) (3x) to create an inert atmosphere. Dry CH2Cl2 (30 mI) and BF3EtO2 (0.37 g, 2.6 mmol) was then added in that order. The mixture was stirred for 12 h at 40 °C before it was precipitated into cold MeOH. The filtered, dried product was 7.1 9 (yield: 80%) of a white crystalline powder. IH-NMR(CDCb)15 1.04 (s, 36H, -Clli), (1.20 (s, 18H, -Clli), se NMR» 1.32-1.42 (111, poly, -Cfu), 1.57-1.69 (m, poly, -CfuCfu-), 2.26-2.32 (t, poly, -CfuO-), 3.63-3.84 (111, 48H, -CfuOH), 4.01-4.06 (t, poly, -CfuCO-), 4.13-4.24 (t, 48H, -ClliOCO-), 4.29-4.44 (m,36H, -ClliO-), 6.91-7.09 (q, 12H, -Ph). 13C-NMRCDC13)t5 17.03, 17.71, 18.00,24.47,25.43,28.24,34.01,46.29,46.68, 49.82,64.04,64.79,65.13, 66.84,120.66,129.62, 146.21, 148.59,171.36, 172.77, 172.94,173.45,174.89.

Results and Discussion

The first through the fourth generation dendrimers of bis-MPA were synthesized by procedures developed by Hult et al. [8] (Scheme 1). Fortuitously, e-caprolactone and lactide, once melted, dissolve the dendritic initiators allowing bulk polymerizations. In some cases, approximately five percent toluene was added to mediate the viscosity and prevent crystallization of the cyclic lactide, and the concentration of (Sn(OCt)2) relative to the initiating alcohol was held as low as possible. [9] Shown in Table 1 are selected data for the 6 to 48 arm star polymers. For each initiator and cyclic ester combination surveyed, the initiation of either e-caprolactone or lactide from the dendrimers proved to be extremely facile and gave the desired star-shaped polymers with accurate control of molecular weight, according to the monomer to initiator ratio, and extremely narrow polydispersities. For example, the polymerization of 960 molar equivalents of e-caprolactone with the fourth generation dendrimer (G-4), which has 48 hydroxyl groups at the chain ends, was carried out in bulk at 110 °C for 20h to give the star-shaped polymer, 4b, in 96% yield (M_n = 115 000 g/mol; M_w/M_n = 1.18) (Scheme 2).
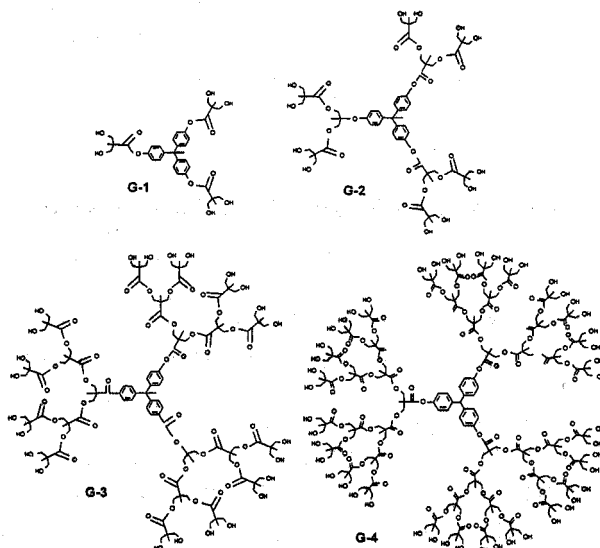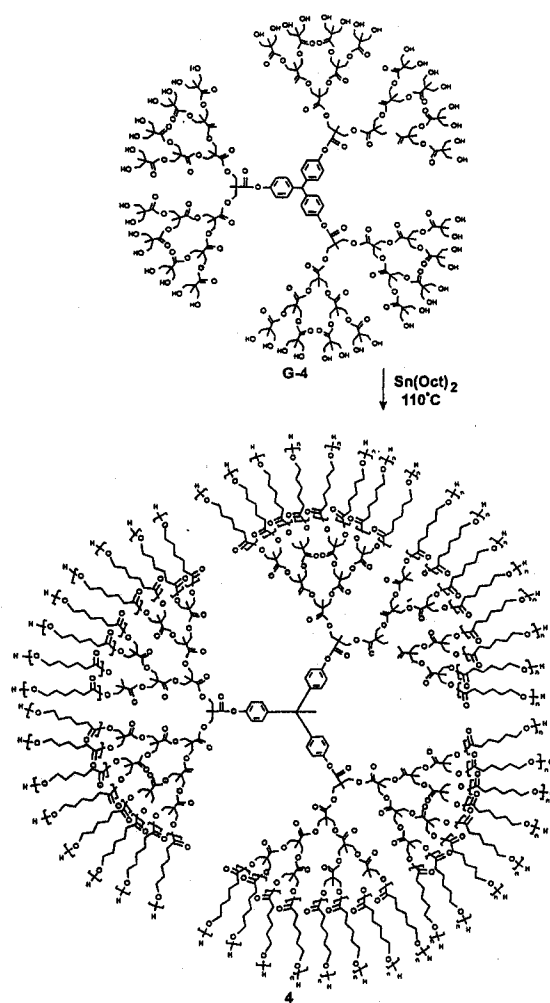

Scheme 1

Table 1. Characteristics of Star-shaped Polyesters

Sample Entry	Initiator Generation	Monomer	$\overline{M}_n$ (g/mol)			M_w/M_n	T_g °C	T_m °C
			Theory	SEC	¹H-NMR			
1a	G-1	ε-CL	17,000	29,000	16,100	1.09	−55	55
1b	G-1	ε-CL	39,000	47,500	3,700	1.14	−55	55
1c	G-1	L-lactide	17,900	32,900	17,000	1.04	55	143
1d	G-1	rac-lactide	17,900	3,100	17,900	1.05	40	—
2a	G-2	ε-CL						
2b	G-2	L-lactide	35,900	44,000	37,600	1.05	53	142
2c	G-2	rac-lactide	35,900	40,000	36,700	1.09	43	—
3a	G-3	ε-CL	69,000	—	71,135	1.18	−55	58
4a	G-4	ε-CL	33,600	31,400	31,200	1.18	−50	54
4b	G-4	ε-CL	96,000	115,200	114,900	1.17	−55	55

GPC analysis of **4b** showed a single monomodal peak with a polydispersity of 1.18, and the average degree of polymerization per arm was determined by 1 H-NMR. In this case, the analysis is greatly facilitated by the symmetrical and regular nature of the dendrimeric core, and comparison of the integration values for the methylene protons of the poly(e-caprolactone) with those for the core revealed a degree of polymerization per arm of 21 or a total molecular weight of 115 200 g/mol.

Scheme 2

This compares favorably with the target value of 20, and similar data was generated for each initiator/cycle ester combination. In addition to accurate control of molecular weight, control of the end groups and initiation was demonstrated. IJC-NMR was used to investigate whether all the hydroxyl groups have initiated polymerization.9

This was possible since the quaternary carbons of bis-MPA have distinctive resonances if they are mono- di- 01 unsubstituted.9 Shown in Figure I is the quaternary carbon region of IJC-NMR spectra of polymer 4b, and only a single peak (46.5 ppm) is observed consistent with only one type of substitution present or quantitative initiation. These data combined with the SEC results confirm that the hydroxyl groups of the different initiators have initiated polymerization Consistent with this data, near quantitative monomer consumption was observed and the molecular weight buildup was linear with monomer conversion9 Shown in Figure 2 is a I H-NMR spectra of **4b** which shows the four major peaks of poly(e-caprolactone) and dendritic initiator with no evidence of monomer or side reactions. The polymers were capable of film formation and manifested semicrystalline morphologies.
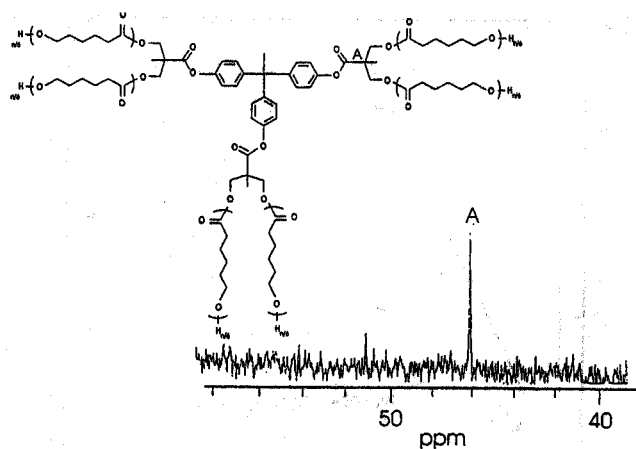
Figure 1. ^{13}C-NMR spectra of **1a**.
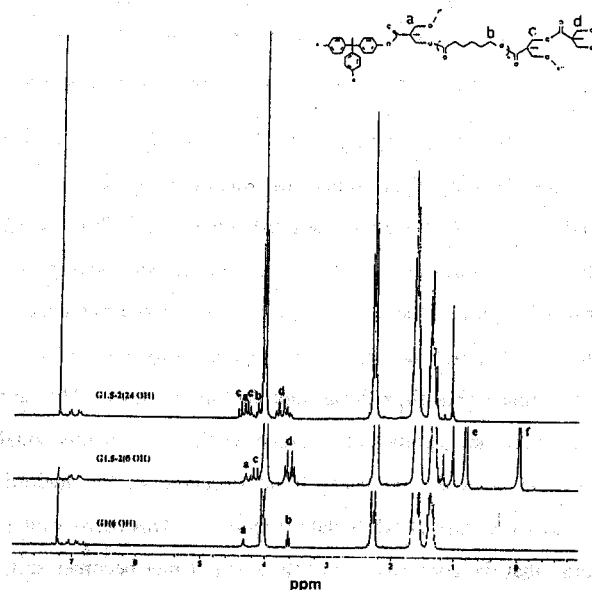
Figure 2. ^{1}H-NMR spectra of **1a** (bottom), **15** (protected) and **15** (deprotected), top.

A closer look at the SEC data of the different star polymers revealed some interesting differences in the hydrodynamic volumes of the polymers with increasing arm

number. A plot of the molecular weight as measured by SEC versus the molecular weight from 1 H-NMR clearly shows significant deviation from the expected linear behavior (Figure 3). This nonlinear trend has been reported earlier for dendrimers, however, in dendrimers the derivation from linearity occurs between the fourth and fifth generations. [11] In this case, polymerization amplifies the nonlinear behavior observed in dendritic polymers. The deviation begins with the twelve arm polymer and becomes significantly more exaggerated with the twenty-four and forty-eight arm polymers from the third and fourth generation bis-MPA initiator. The lower than expected hydrodynamic volume clearly indicate that these polymers assume a compact structure, and that the polymer arms playa significant role in this phenomena.
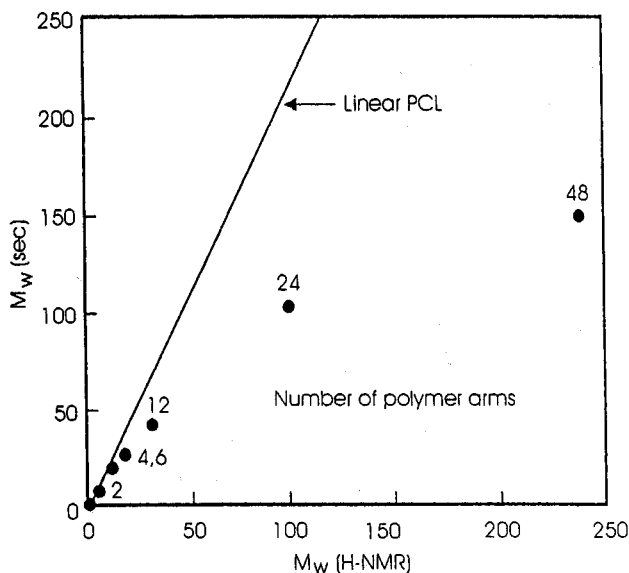
Figure 3. M_n(SEC) vs. M_n(^{1}H-NMR) for the star polymers with varying arm number.

Guinier plots of the SANS data revealed radius of gyration measurements R_g as shown in Figure 4 for the variable arm star polymers, each of which is comparable to the first generation versions of the dendrimer-like star polymers studied previously.9h For the six arm case, the measurement of R_g = 24Å compares favorably with the earlier measurement of R_g = 25Å. Figure 4a shows that the scaling of the radius of gyration R_g with arm number f is with a lower power than that for a linear polymer, arid thus implies, consistent with intuition, that the structures are more compact than their linear caprolactone analogs. The deviation from the predicted linear trend becomes significantly marked at the 12-arm functionality case. This observation is consistent with the nonlinear trend observed in the hydrodynamic volume measurements calculated from the ^{1}H-NMR data (Figure 3). This corroborates the implication of the ^{1}H-NMR data: that the conformation of the star polymer becomes sufficiently compact at the 12-arm case as to no longer be appropriately modeled by a linear analog, and thus both the hydrodynamic volume measurements and the R_g values deviate below the linear relation as the functionality of the star increases (Figure 4a). For consideration of the scaling of R_g with arm number f, we consider the Dauod-Cotton model for many arm polymers,12 which translates successfully in the modeling of micellar structures. 13.14.IS For a good solvent

$v = 3/5$ and thus we find that R_g scales with $f^{2/3}$, and Figure 4b shows a good fit of this model to the data from the multifunctional caprolactone star polymers.
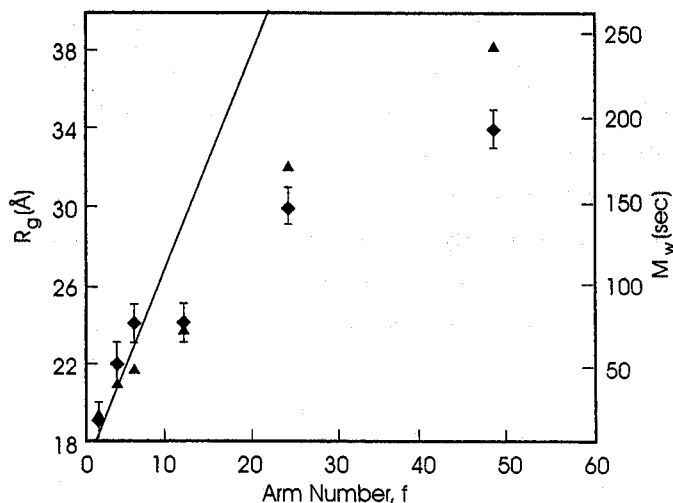

Figure 4a. Radius of gyration (♦) measured by SANS on left ordinate (Å) and M_w (▲) measured by SEC on right ordinate against functionality f for six first generation dendrimer-like caprolactone star polymers. The solid line indicates the predicted trend in M_n for a linear caprolactone polymer.
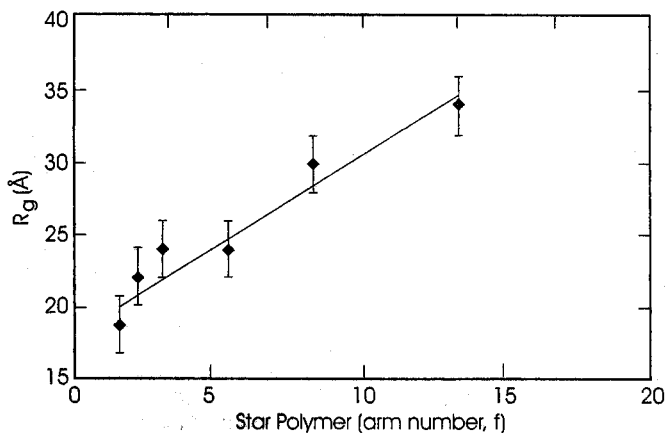

Figure 4b. Radius of gyration R_g(Å) versus $f^{2/3}$, where f denotes the functionality of the star polymer. The solid line indicates the predicted trend of the Daoud-Cotton model for many arm polymers in a good solvent.

In addition to the use of dendrimers as "building blocks" to star polymers, functional dendrons were attached to the chain ends of the star polymers to obtain molecular architectures that more closely resemble that of the most advanced dendrimers (Scheme 3). In this way, the functionality and hydrophilicity of the star polymers can be tailored with the generation of the dendron employed. The benzylidene-protected bis-MPA, **5**, was synthesized in one step from the reaction bis- MP A and benzaldehyde dimethyl acetal according to a literature procedure [9a] (Scheme 4). The tert-butyldimethylsilyl protected bis-MP A and the second and third generation acid functional dendrons derived from it were also used to modify the surface functionality of the star polymers. The
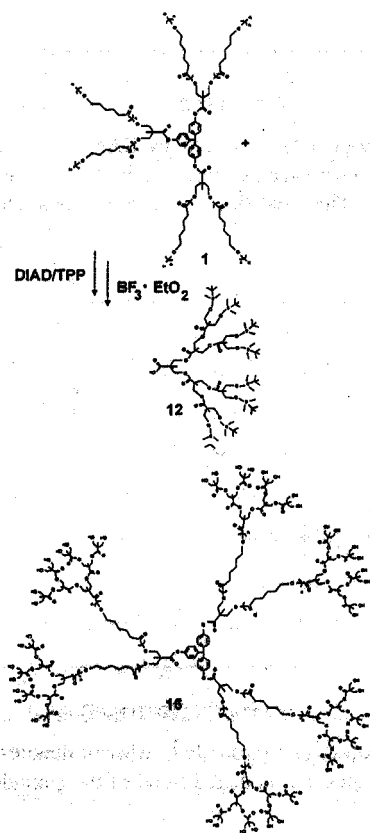
Scheme 4
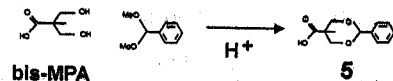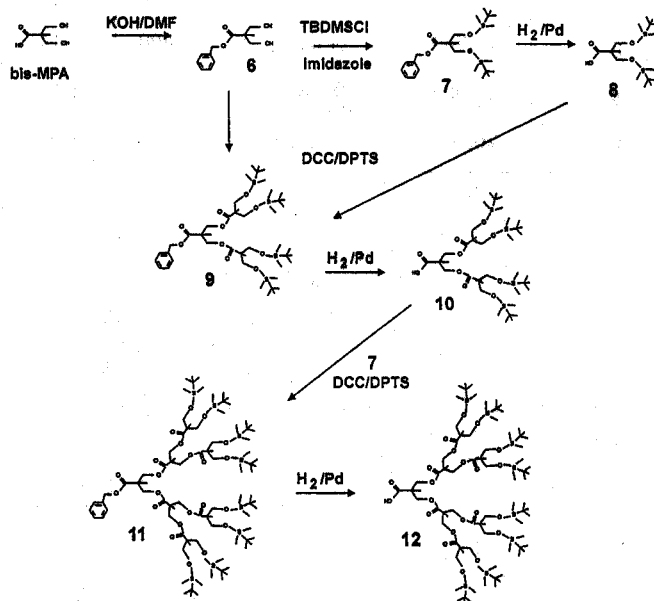
Scheme 5

Scheme 3

dendrons were synthesized by the convergent growth approach (Scheme 5).% The hydroxyl groups of the benzyl ester **6** were protected with tert-butyldimethylsilyl

chloride (TBDMSCI) to give **7**. The benzyl group could then be selectively removed by catalytic hydrogenolysis to give the free acid **8**, which was then coupled with **6** to afford the second-generation dendron **9**. This in turn could be readily hydrogenolyzed to give **10**. The third-generation dendron **12** was synthesized by the coupling of **6** with **10**. Deprotection by hydrogenolysis gave the requisite dendron **12**. The structures of the dendrons were confirmed by ^{1}H and ^{13}C-NMR. Mitsunobo conditions [16] were used to couple the hydroxyl-functional starpoly(e-caprolactone) to the acid-functional dendrons to produce star polymers with 12, 24 or 48 functional groups (Scheme 3). The extent of coupling was followed by ^{1}H and ^{13}C-NMR spectroscopy and SEC. The ^{13}C-NMR spectra for the six arm star polymer and the copolymer with the second generation dendron are shown in Figure 5. Quantitative functionalization is confirmed by the shift in the CH_2OH signal from $\delta = 62$ to 65 ppm upon esterification of the hydroxyl groups.

Table 2. Characteristics of Functionalized Star Polymers

Sample Entry		$\overline{M}_n$ g/mol			M_w/M_n	T_g °C	T_m °C
		Theory	SEC	^{1}H-NMR			
13	—	15,000	23,400	14,700	1.16	–50	53
14	g^1	15,900	24,000	15,600	1.14	–50	47
15	g^2	17,000	26,900	16,700	1.13	–50	48
16	g^3	20,000	35,300	19,700	1.09	–50	44
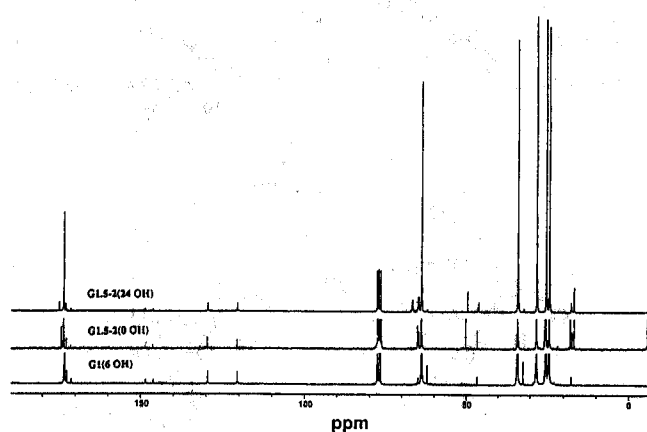
Figure 5. ^{13}C-NMR spectrum of 15.

Figure 6 shows the quaternary carbon region of the second generation dendron and the coupled product. The functionalized star polymer has four peaks in this region that are the combined signals of the star poly(e-caprolactone) and the second generation dendron. The peak denoted as C can be assigned to the outer layer of the dendron. Similar spectra were generated for the first and third generation coupled products. ^{1}H-NMR was also used to investigate the esterification of the dendrons to the chain ends of the star polymer (Figure 2). The peak b, assigned to the methyl protons adjacent to the hydroxyl chain ends, is quantitatively shifted to the ester region, consistent with the ^{13}C-NMR data. The tert-butyl dimethylsilyl protecting groups were removed with BF3.EtO$_2$, while the benzildene groups were removed by hydrogenolysis to give the requisite 12, 24 and 48 surface hydroxyl groups (Scheme 3). The ^{13}C-NMR spectrum of the deprotected product is free from the peaks associated with the protecting group, consistent with quantitative deprotection (Figures 5 and 6). The transformation is also observed in the quantitative shift in the peak denoted as C from the quaternary carbon in the outer layer of the dendron layer. Likewise, the peaks denoted as e and f in the ^{1}H-NMR spectra which are assigned to the protecting group disappear completely (Figure 2).
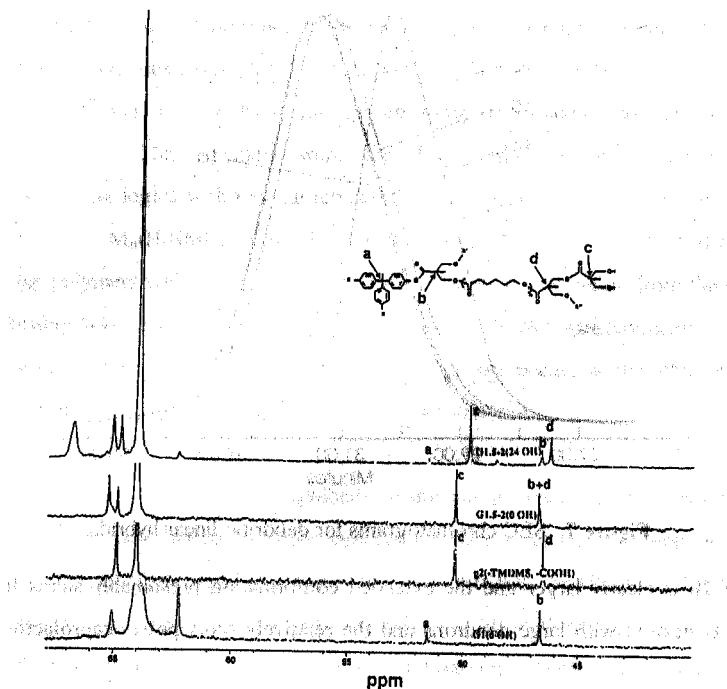
Figure 6. ^{13}C-NMR spectrum of **15**.

The theoretical and experimental number average molecular weights, as measured by SEC and ^{1}H-NMR and polydispersities, are shown in Table 2. As expected, the polydispersities of the six arm star polymers are lower when esterified with the monodispersed dendrons, and follow the expected trend (i.e., the higher the generation dendron employed, the lower the dispersity). The molecular weights obtained by ^{1}H-NMR are in good agreement with the theoretical values. Conversely, the SEC values, relative to polystyrene standards, show somewhat different behavior. Shown in Figure 7 are the SEC chromatograms for the six-arm star polymer and the functionalized star polymers. A clear shift to higher elution volumes is observed for the functional star polymers between the second and third generation dendron. The hydrodynamic volume of **16** is clearly larger and the extended conformation presumably sterns from steric crowding associated with large dendrons and the relatively short poly(e-caprolactone) block lengths.
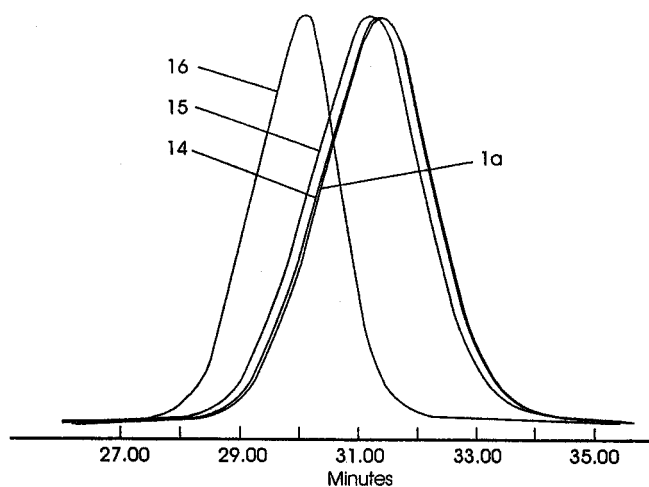
Figure 7. SEC chromatograms for dendritic-linear hybrids.

The star poly(e-caprolactone)s and poly(L-lactide)s as well as the functionalized star polymers were semicrystalline as measured by dynamic scanning calorimetry (DSC). A single T 9 was observed in the proximity of -55 °C for the poly(e-caprolactone) star polymers and ~ 55 °C for the poly(lactide) star polymers. The melting points for the star polymers were similar to that of the linear analog of comparable molecular weight. However, the functionalized star polymers showed a depression in the melting point with increasing chain end functionality. Presumably the bulky dendrons at the chain ends coupled with restricted mobility of the initiating core minimized the degree of crystallinity and reduced the melting point. Nonetheless, the polymers were film forming and somewhat opaque due to their semicrystalline morphology. Moreover, the films showed improved hydrophilicity and would swell in water.

SUMMARY
The synthesis and solution properties of dendritic-linear hybrids were described. The synthesis involved the living *ROP* of e-caprolactone initiated from the surface hydroxyl groups of dendrimers of bis-MPA in the presence of ($S_n(Oct)_2$). Poly(e-caprolactone) star and hyperstar macromolecular architectures were formed with polymers having 6 to 48 arms. The ROP of e-caprolactone was found to be a facile process affording controlled molecular weight, low dispersity products. The polymers were capable of film formation and manifested semicrystalline morphologies with melting temperatures comparable to their linear analogs. A plot of Mn(SEC) vs. Mn(H-NMR) revealed some interesting differences in the hydrodynamic volumes of the polymers with increasing arm number. Significant deviation from the expected linear relationship was observed which was corroborated by SANS measurements. Although this phenomena has been observed in dendrimers, it typically occurs at the fifth generation. Here, polymerization was found to amplify this nonlinear response. Alternatively, the functionality and hydrophilicity of the star polymers could be modified with dendrons of different generations to obtain molecular architectures that resemble dendrimers. Mitsunobo conditions were used to

couple the acid function dendrons to the hydroxyl terminated six-arm star to produce star polymers with 12, 24 or 48 surface hydroxyl groups. Molecular weights obtained by ^{1}H-NMR were in good agreement with the theoretical values, however, the SEC chromatograms of the star polymers with the third generation dendron showed a clear shift to higher elution volumes. The hydrodynamic volume is clearly larger for this sample and the extended conformation presumably stems from steric crowding associated with the large third generation dendron on the relatively short poly(e-caprolactone) arms. All polymers were capable of film formation and semicrystalline. However, the melting points of the polymers with the higher generation dendrons were somewhat lower than the linear analog.

ACKNOWLEDGMENTS

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