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Versatile and Controlled Synthesis of Star and Branched Macromolecules by Dentritic Initiation

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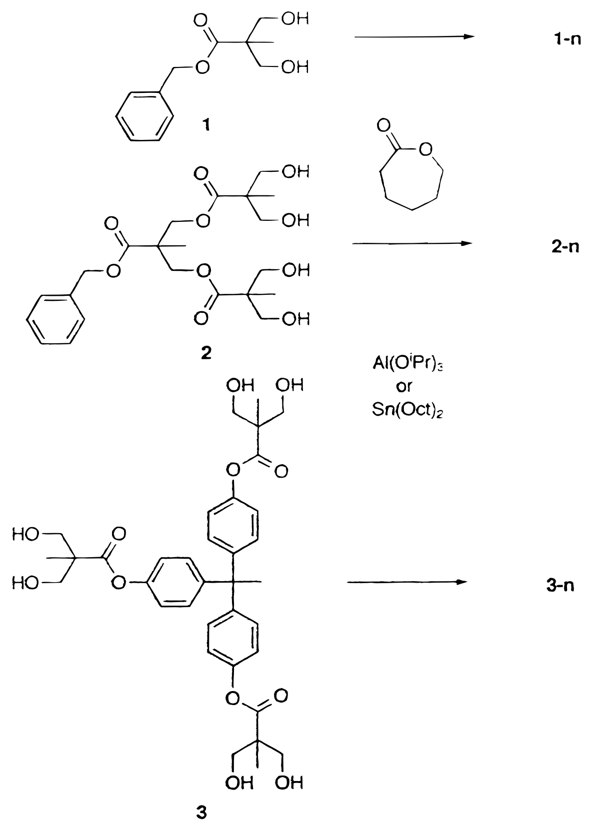
The renewed interest in ring-opening polymerization (ROP) of lactones, lactides, and glycolide stems, in part, from the discovery that many organometallic compounds, such as oxides, carboxylates, and alkoxides, are effective initiators for the controlled synthesis of polyesters.[1] The exact mechanism of polymerization varies with the metal compound used, but most proceed through an insertion process.[2] The controlled synthesis of high molecular weight polyesters requires the minimization of side inter- and intramolecular transesterification reactions that broaden the molecular weight distribution. The degree of intramolecular side reactions or "back-biting" has been shown to depend on the metal compound used as the initiating species and generally follows the trend $Bu_2Sn(OR)_2 > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$.[3] To this end, much of our work on the synthesis of poly(caprolactone) and related polyesters has been initiated with aluminum alkoxides, since the molecular weight of such polymers agrees closely with the monomer to initiator ratio, at least during the requisite time frame for monomer conversion, and narrow polydispersities are obtained.[4,5] Asymmetric functionality can be introduced in a controlled way through the use of aluminum alkoxide initiators bearing functional alkoxide groups ($Et_2Al(ORX)$, where X is bromine, amine, olefin, or methacrylate double bond).[6,7] After hydrolytic deactivation of the active aluminum alkoxide growing species, α-X-ω-hydroxylpoly(caprolactone) telechelic chains are quantitatively and selectively recovered. The coupling of the telechelic macromonomers through block copolymerization provides a precise methodology to controlled macromolecular architectures. For instance, polyimide nanofoams have been prepared from the selective thermolysis of the microphase-separated poly(caprolactone) component of polyimide-poly(caprolactone) copolymers.[8] The versatility of ROP as a means to macromolecular engineer aliphatic polyesters and related structures has resulted in the synthesis of many new block and graft copolymers.[1,5−7,9]

Scheme 1



The introduction of controlled branching provides an alternative methodology to controlled macromolecular architectures. Dendrimers provide the ultimate example of the effects of branching on the physical and solution properties of macromolecules,[10] while hyperbranched and dendrigraft polymers are less perfect elaborations of such three-dimensional structures.[10,11] The use of ROP to prepare polymers with unique topologies has been much less pervasive than other polymerization procedures and focused mostly on star-shaped macromolecules.[12] One example of a multifunctional or branched poly(caprolactone) prepared by ROP has been reported.[13] This synthesis uses 5-ethylene ketal caprolactone as a comonomer that is polymerized and subsequently deacelated and reduced to the hydroxyl group. Stoichiometric reaction of the pendent hydroxyl groups and triethylaluminum provides diethylaluminum alkoxide species and subsequently active multifunctional macroinitiators for controlled ROP of lactones.

Noteworthy examples of both dendrimers and hyperbranched polyesters, prepared by condensation methods, have been reported by Hult and co-workers[14a−c] and involve the self-polymerization of 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA). Hyperbranched polyesters were prepared in the melt via an acid-catalyzed polyesterification reaction, and the dendrimers were prepared by coupling dendrons of certain generations to a polyfunctional core. Alternate examples involve the preparation of 3,5-dihydroxybenzoic acid derivatives.[14d,e]

It seems plausible to combine the living ROP of caprolactone with dendritic macromolecules to serve as initiators to produce new multifunctional polymers and/or AB$_x$ macromonomers. Fréchet *et al.* have reported the ROP of caprolactone from a dendritic initiator to give hybrid dendritic-linear block copolymers.[14f] Here we describe several synthetic routes to new structures using dendritic initiators derived from bis-MPA and its derivatives (Scheme 1). The first initiator is the benzyl ester of bis-MPA prepared by the esterification of bis-

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Chart 1

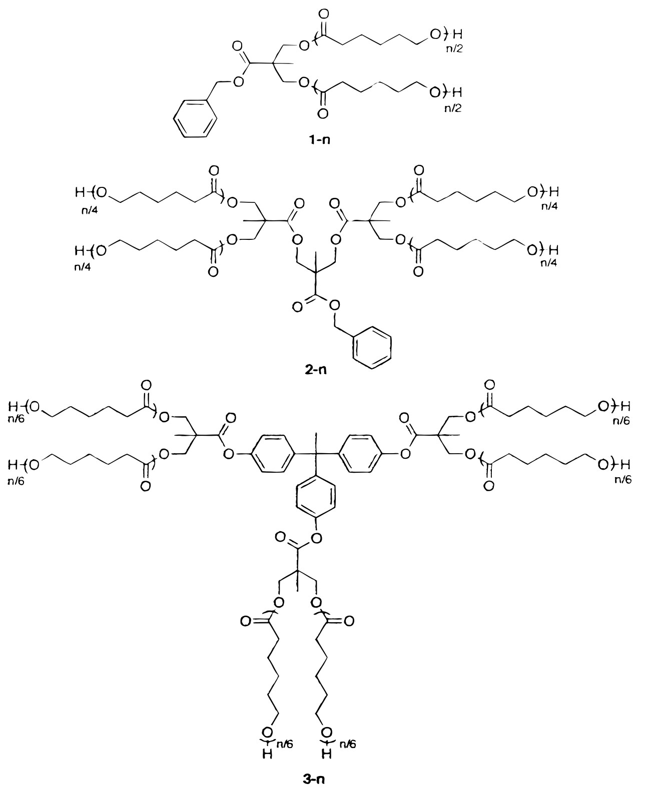

Table 1. Characteristics of Branched Polyesters

	$\langle M_n\rangle_{,\mathrm{target}}$	$\langle M_n\rangle_{,\mathrm{NMR}}$	$\langle M_n\rangle_{,\mathrm{SEC}}$	$\langle M_w\rangle\langle M_n\rangle$
1a	4 600	4 700	7 600	1.18
1b	8 900	8 300	13 100	1.14
1c	17 900	18 400	25 000	1.13
2a	7 200	8 000	15 700	1.15
2b	11 400	11 000	22 800	1.21
3a	17 000	16 100	29 000	1.09
3b	39 000	37 000	47 500	1.14

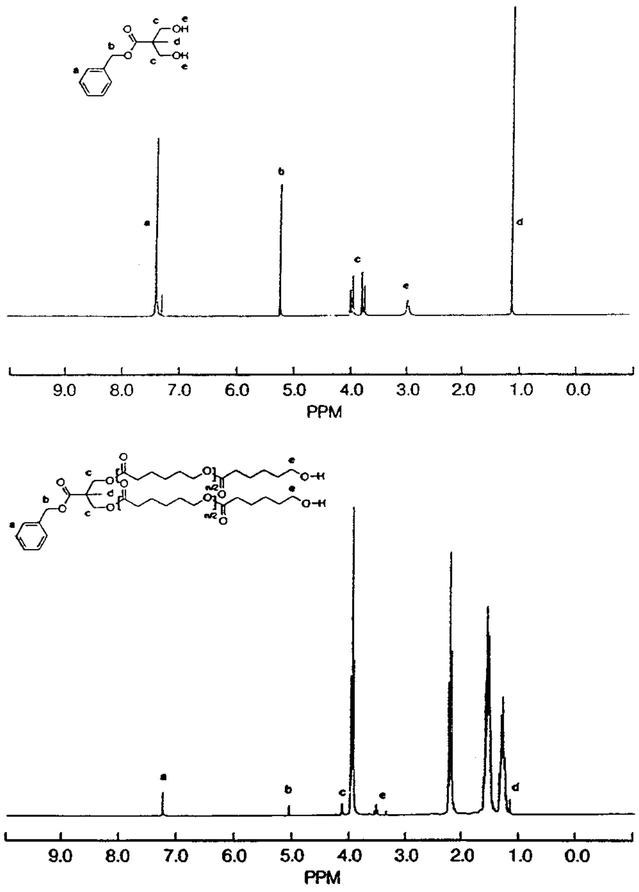

Figure 1. H NMR of **1** (top) and **1-n** (bottom).

MPA with benzyl bromide, **1**.[14a–c,15a] The second initiator is the second generation hydroxy functional dendron of the bis-MPA, **2**.[14,15b] The third initiator (**3**) was prepared by the esterification of bis-MPA with 1,1,1-tris(hydroxyphenyl)ethane to form the core of a star topology.[15c] All initiators were prepared by procedures developed by Hult and co-workers.[10i,14a–c] The initial attempt at preparing these multifunctional materials involved the reaction of **1** with triethylaluminum to form the bis(diethylaluminum alkoxide) initiator. The resulting dialkoxides showed high solution viscosity or even precipitation in both THF and toluene, probably due to significant complexation of the metal atoms and diols. Polymerization of caprolactone in the presence of the bis(diethylaluminum alkoxide) initiator produced polymers and molecular weight distributions in the 1.6–2.0 range, and the molecular weight did not follow the monomer to initiator ratio. In any respect, this conventional approach to the synthesis of poly(caprolactone) is not a viable approach to macromonomers of controlled molecular weight and functionality.

The second synthetic approach surveyed for the polymerization of caprolactone from multifunctional initiators uses either Sn(Oct)$_2$ or Al(O^{i}Pr)$_3$ as catalyst (Scheme 1). A key feature in such a polymerization is the use of the organometallic compound in catalytic amounts to minimize complexation. In the latter approach, Al(O^{i}Pr)$_3$ undergoes rapid exchange reactions with a dormant alcohol, and the 2-propanol can be selectively removed through an azeotropic distillation (i.e., 2-propanol/toluene), leaving the alcohol as the sole initiating species.[16] The growing alcohol chain ends can then undergo very rapid exchanges with the active aluminum alkoxide functions, leading to the living character of the polymerization reaction. Hydrolysis of the active metal–alkoxide bonds produces a hydroxyl chain end group. The polymerizations were performed in bulk at 110 °C (20 h). Interestingly, quantitative yields were obtained for both the Al(O^{i}Pr)$_3$ and Sn(Oct)$_2$ catalyzed polymerization. The catalyst was added in a concentration of 1/50 relative to the amount of initiating alcohols in the case of the Al(O^{i}Pr)$_3$ and in a concentration of 1/1000 for the Sn(Oct)$_2$.

This general polymerization procedure was applied to three multifunctional initiators, **1**–**3** (Scheme 1). Each of the initiators was readily soluble in caprolactone, producing homogeneous mixtures. In each case, the average degree of polymerization is in very close agreement to that of the monomer to alcohol ratio, and the polydispersities are narrow (Table 1).[17] In general, the use of Sn(Oct)$_2$ as the catalyst in ROP is not known to be of living character. However, the use of the di- and polyfunctional initiators in this study generates polymers with surprisingly narrow molecular weight distributions, molecular weight control, and quantitative yields. The "living" character of these polymerizations is currently under investigation. In addition to accurate molecular weight control, control of the end groups is possible, irrespective of the catalyst used. Figure 1 shows the ^{1}H-NMR of the initiator **1** and the polymer **1-n** which clearly shows the shifts of the peaks denoted as c and d, indicating that both the hydroxyl groups have initiated the polymerization. If this was not the case, the $-CH_2-$ and $-CH_3$ groups in bis-MPA would

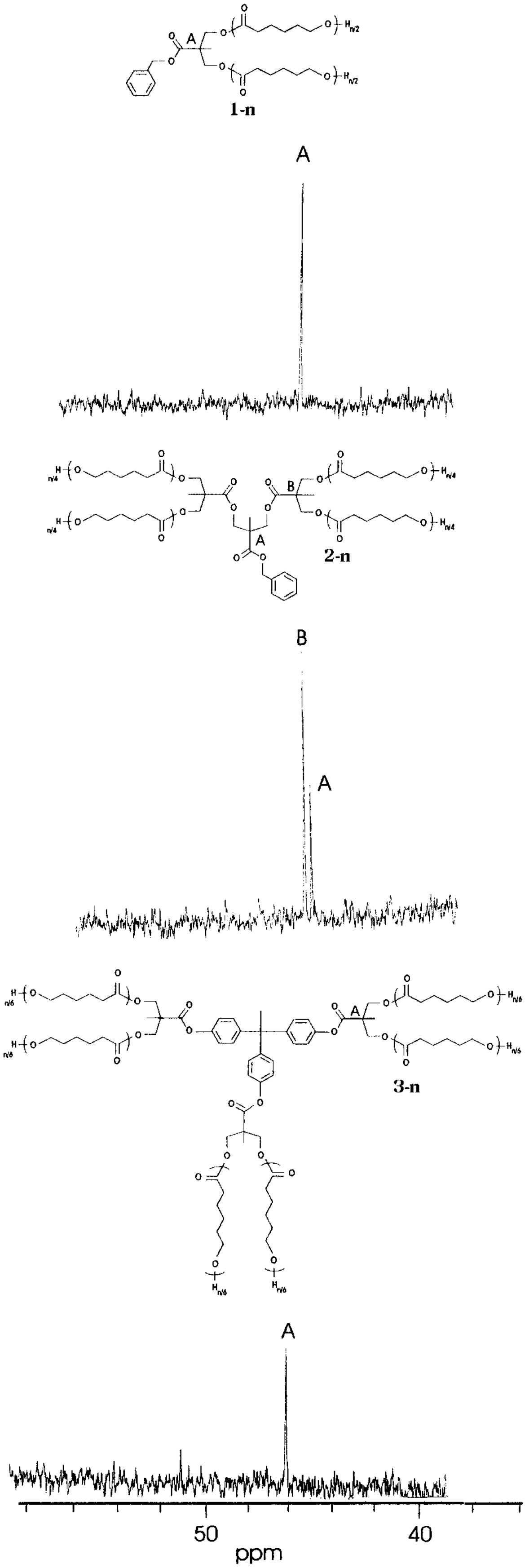

Figure 2. C-NMR of **1-n** (top, a), **2-n** (middle, b), and **3-n** (bottom, c).

be split and not appear as the singlets, c and d, as they do now. ^{13}C-NMR was used to investigate whether both the hydroxyl groups of **1** have initiated polymerization (i.e., the efficiency of initiation). The quarternary carbons of bis-MPA in $CDCl_3$ are known to shift if they are mono- (46.85 ppm), di- (48.85 ppm), or unsubstituted (50.65 ppm).[14b] Figure 2a shows the ^{13}C-NMR spectrum of that region for **1-n**. Only one peak, A (46.5 ppm), is detected, indicating that there is only one type of substitution present. These data combined with ^{1}H-NMR and SEC measurements confirm that each of the hydroxyl groups of **1** are substituted and therefore have initiated polymerization (i.e., quantitative initiation). The ^{1}H-NMR for **2-n**, and **3-n** do not allow a complete analysis since the spectra are complex and some of the peaks overlap. Figure 2b,c shows the ^{13}C-NMR spectrum of the quarternary region for **2-n**, and **3-n**, respectively. If **2-n** is fully substituted, it will manifest two types of substitution, and two singlets should appear in the region around 46.5 ppm. Since Figure 2b exhibits two singlets and no other peaks in the quarternary region, the ^{13}C-NMR spectrum provides clear evidence that **2-n** is fully substituted and quantitative initiation is achieved. In the case of **3-n**, only one type of signal should appear in the quartenary region of the spectra. Figure 2c shows a pronounced peak at 46.2 ppm, suggesting quantitative initiation from **3**. In addition, a peak at 51 ppm is observed, which is the quartenary carbon from the core.

The ultimate motivation in the preparation of highly functional aliphatic polyesters is to elaborate organic—inorganic hybrids with precise microphase or nanophase morphologies. Once the macromolecular species has organized or templated the inorganic component, the organic component can be selectively removed through thermolysis, leaving behind a nanoporous inorganic oxide. Similar investigations have been preformed by Chujo *et al.*[18] using “starburst” dendrimers to generate porosity in silica gel.[19] Poly(lactones) are ideally suited for this study since they are capable of significant interaction with the inorganic alkoxides and they thermally decompose quantitatively into nonreactive species via an unzipping mechanism.[16] Another promising class of materials are the hyperbranched poly(caprolactones) prepared by the self-polymerization of the deprotected AB_2 (**1-n**) and AB_4 (**2-n**) macromonomers.

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(15) ^{1}H-NMR ($CDCl_3$): (**1**) δ 1.00 (s, 3H, $\mathrm{C}H_3$), 2.97 (s, 2H, $-OH$), 3.62−3.87 (m, 4H, $-\mathrm{C}H_2\mathrm{OH}$), 5.12 (s, 2H, $\mathrm{ArC}H_2-$), 7.24 (s, 5H, *A*r); (**2**) δ 0.95 (s, 6H, $-\mathrm{C}H_3$), 1.29 (s, 3H, $-\mathrm{C}H_3$), 3.20 (s, 4H, $-\mathrm{O}H$), 3.59−3.78 (m, 8H, $-\mathrm{C}H_2\mathrm{OCO}-$), 5.16 (s, 2H, $\mathrm{ArC}H_2-$), 7.33 (s, 5H, *A*r−); (3) δ 1.24 (s, 9H, $-\mathrm{C}H_3$), 2.15 (s, 3H, $-\mathrm{C}H_3$), 3.78 (s, 12H, $-\mathrm{C}H_2\mathrm{OH}$), 6.98−7.10 (m, 12H, −*Ar*)−).

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(17) ^{1}H-NMR spectra were recorded in solution with a Bruker AM 250 (250 MHz) spectrometer, with the TMS proton signal as an internal standard. The number average molecular weight of the polymers were calculated from the ratio of the OCH_2 methylene proton signals ($\delta = 4.05$) and the $HOCH_2$ methylene proton signals ($\delta = 3.65$) in the ^{1}H-NMR spectra. ^{13}C-NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer with the solvent carbon signal as an internal standard. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). The silica gel for flash chromatography was Merck Kieselgel 60 (230−400 mesh). Size exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. 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 Å) were used with THF as solvent.

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