Highly Functional Branched and Dendri-Graft Aliphatic Polyesters through Ring Opening Polymerization

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ABSTRACT: Highly branched poly(ϵ-caprolactones) with novel and well-defined molecular architectures have been synthesized by the use of new multifunctional initiators. The ring-opening polymerization methods used to prepare these new structures allowed accurate control of molecular weight and narrow molecular weight distributions. In addition, the synthesis of even more complex molecular architectures was possible by the use of 1,4,9-trioxaspiro[4.6]-9-undecanone as a comonomer with ϵ-caprolactone. After copolymerization, complete deacetalization of the polyester chains into the corresponding ketone groups followed by quantitative reduction formed polymers with hydroxyl pendant groups. With this synthetic strategy, significant additional functionality was introduced. In addition, the pendant hydroxyl groups along the chains can serve as macroinitiators for the further initiation of ϵ-caprolactone to prepare dendri-graft molecular architectures. The new polymers were characterized by ^{1}H NMR, ^{13}C NMR, and size exclusion chromatography (SEC). ^{13}C NMR spectra clearly showed that the hydroxyl groups of the initiators were fully substituted to give polymers with two, four, and six arms.

Introduction

Macromolecular engineering has assumed an increasingly important theme in polymer science. One approach to complex molecular architectures is through the preparation of block copolymers or two distinct homopolymers covalently bound at one point. The molecular architecture, block lengths, and composition of the copolymer can be designed to produce materials with a wide range of properties and morphologies.[1] Furthermore, since the two dissimilar materials are covalently bonded, miscibility is enhanced and phase separation, when it occurs, is restricted to dimensions on the order of 100−400 Å.[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 macromoelcules,[2] while hyperbranched and dendri-graft polymers are less perfect elaborations of such three dimensional structures.[2,3] Noteworthy examples of both hyperbranched and dendritic polyesters have been reported by Hult and co-workers[4a−c] and involves 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 dendritic polyesters were prepared by coupling dendrons of certain generations to a polyfunctional core. Alternate examples involve the preparation of 3,5-dihydroxybenzoic acid derivatives and their self-polymerization.[4d,e]

To expand the scope of new macromolecular architectures, possibly from controlled branching, reactive dendrons have been used as polymerization initiators. Fréchet and co-workers[5a] have prepared linear-dentritic hybrids from the anionic ring opening polymerization of ϵ-caprolactone from the potassium alkoxide of a fourth generation dendritic alcohol. This general methodology of dendritic initiators as a route to linear-dendritic hybrids was extended to "living" radical polymerizations of polystyrene initiated by a tempo group covalently attached at the focal point of a monodendron.[5b] A key advantage to a convergent dendrimer, containing a single reactive group at the "focal" point, is that the "focal" point is easily accessible to both large and small molecules, for subsequent transformation as demonstrated by successful copolymerization.[6a,b] It seems plausible to survey other dendritic macromolecules with significant functionality to serve as initiators to produce new multifunctional macromolecular initiators, polymers and possibly new AB_X macromonomers. For instance, dendritic macromolecules derived from bis-MPA and its derivatives should prove to be effective initiators for the ring-opening polymerization (ROP) of lactones and lactides.

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.[7] The exact mechanism of polymerization varies with the metal compound used, but most proceed through an insertion process.[8] The controlled synthesis of high molecular weight polyesters requires the minimization of side inter- and intramolecular transesterification reactions which broaden the molecular weight distribution. The degree of intramolecular side reac-

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tions or "back-biting" has been shown to depend on the metal compound used as the initiating species and generally follows the trend $Bu_2Sn(OR)_2 > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$.[9] To this end, much of our work on the synthesis of poly(ϵ-caprolactone) and related polyesters has been initiated with aluminum alkoxides, since the molecular weight of such polymers agrees closely to the monomer to initiator ratio, at least during the requisite time frame for monomer conversion, and narrow polydispersities are obtained.[10,11] Asymmetric functionality can be introduced in a controlled way through the use of aluminum alkoxides initiators bearing functional alkoxide groups.[12,13] After hydrolytic deactivation of the active aluminum alkoxide growing species, *a*-X, *ω*-hydroxyl poly(ϵ-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.[7,13,14]

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.[15] In this paper, we wish to report the controlled synthesis of poly(ϵ-caprolactone) initiated from dendritic macromolecules derived from bis-MPA and its derivatives; in some cases, 1,1,1-tris(hydroxyphenyl)ethane (THPE) was used as the core molecule. The initiating species contains anywhere from two to six hydroxyl-functional groups. ^{13}C NMR techniques will be discussed to survey the efficiency of initiation. In addition, we wish to report the synthesis of even more complex molecular architectures by using 1,4,9-trioxaspiro[4.6]-9-undecanone (TOSUO) as a comonomer. Jérôme and co-workers[16] have shown that random and block copolymerization is possible with TOSUO and ϵ-CL. Furthermore, complete deacetalization of these polyesters followed by a quantitative reduction allowed the preparation of polymers with hydroxyl groups. With this synthetic strategy, significant additional functionality can be introduced and provides the possibility to prepare macroinitiators and polyesters with dendri-graft molecular architectures.

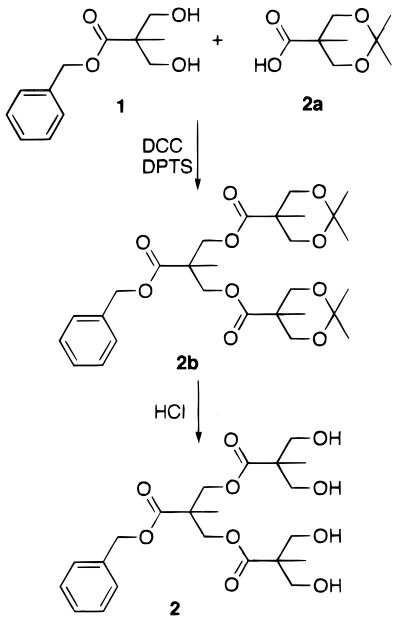
Experimental Section

Materials. Toluene was dried by refluxing over sodium and distilled under nitrogen prior to use. The ϵ-caprolactone (Aldrich) was dried over CaH_2, distilled under reduced pressure, and stored under a nitrogen atmosphere. The 2,2′-bis(hydroxymethyl) propionic acid was obtained from Aldrich and used without further purification. The aluminum triisopropyloxide (Aldrich) was sublimed and then dissolved in toluene under nitrogen. The concentration of this solution was measured by complexometric titration of the Al atom. The synthesis of 1,4,8-trioxaspiro[4.6]-9-undecanone (TOSUO) was described elsewhere (Scheme 1).[16] TOSUO was dried by repeated (three times) azeotropic distillation of toluene just before polymerization. Triphenylcarbenium tetrafluoroborate (ACROS) and sodium borohydride (Janssen) were used as received. The dimethylamino pyridinium 4-toluenesulfonate (DPTS) was synthesized according to a literature procedure.[17] All other chemicals were purchased from Aldrich and used without further purification.

Initiator Synthesis. Benzyl 2,2-Bis(hydroxymethyl)propionate, 1. Benzyl 2,2-bis(hydroxymethyl)propionate, **1**, was synthesized by a procedure similar to the one described in ref 4c. It differs only in that the purification of the crude product was done by recrystallization from toluene, instead of column chromatography.

2,2-Bis((2,2-propyl)dioxymethyl)propionic acid, 2a, was synthesized by reacting 2,2-bis(hydroxymethyl)propionic acid

Scheme 1



(bis-MPA) (10.0 g, 74.6 mmol), 2,2-dimethylolpropane (111 g, 112 mmol), and *p*-TSA (0.28 g) in 50 mL of acetone at room temperature. After 1 h, a few drops of a NH_4OH (aqueous, 30%)/EtOH (1/1) solution was added to neutralize the catalyst. The reaction mixture was then diluted with 400 mL of CH_2Cl_2 and extracted once with 25 mL of H_2O. The organic phase was separated, dried over $MgSO_4$, filtered and evaporated to yield 10.6 g (82%) of white crystals. ^1H NMR ($CDCl_3$): δ = 1.19 (s, 3H, $-CH_3$), 1.40−1.43 (d, 6H, $-C(CH_3)_2$), 3.64−4.19 (dd, 4H, $-C(CH_2O-)_2$). ^{13}C NMR ($CDCl_3$): δ = 18.35, 21.76, 25.41, 30.93, 41.68, 65.94, 179.0.

g2(−$CO_2C_7H_7$, −$(CH_3)_4$) (2b) and a General Esterification Procedure. 1 (3.68 g, 16.4 mmol), **2a** (6.00 g, 34.5 mmol), and DPTS (1.54 g, 4.90 mmol) were all dissolved in CH_2Cl_2. Dicyclohexylcarbodiimide (DCC) (8.79 g, 42.7 mmol) dissolved in CH_2Cl_2 (10 mL) was then immediately added and the mixture was stirred. After 24 h, the formed byproduct, urea, was filtered off, the solvent removed, and the remaining product was purified by column chromatography (silica gel, hexane/EtOAc as an eluent). The final product was isolated as a clear oil. Yield: 7.00 g (80%). ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6H, $-CH_3$), 1.23−1.27 (d, 6H, $-C(CH_3)_2$), 1.39 (s, 3H, $-CH_3$), 3.47−4.14 (dd, 8H, $-C(CH_2O-)_2$), 4.32 (s, 4H, $-C(CH_2O-)_2$), 5.08 (s, 2H, $Ph(CH_2-)$, 7.29 (s, 5H, *Ph*−). ^{13}C NMR ($CDCl_3$): δ = 17.71, 18.44, 22.20, 25.00, 42.00, 46.81, 65.32, 65.89, 66.95, 98.08, 128.21, 128.61, 135.45, 172.40, 173.52.

g2(−$CO_2C_7H_7$, −$(OH)_4$) (2) and a General Procedure for Removal of the Acetonide Group. 2b (5.0 g) was dissolved in a mixture of 30 mL of THF and 30 mL of 1 M HCl(aq). The reaction mixture was stirred for 2 h before the precipitated product was filtered and washed with water. The product was isolated as a white solid. Yield: 3.91 g (92%). ^1H NMR ($CDCl_3$): δ = 0.96 (s, 6H, $-CH_3$), 1.29 (s, 3H, $-CH_3$), 3.59−3.79 (dd, 8H, $-C(CH_2OH)_2$), 4.24−4.44 (q, 4H, $-C(CH_2O-)_2$), 5.16 (s, 2H, $PhCH_2-$), 7.33 (s, 5H, *Ph*−). ^{13}C NMR ($CDCl_3$): δ = 17.04, 18.10, 46.42, 49.65, 64.84, 67.14, 67.83, 128.35, 128.69, 135.29, 172.81, 175.12.

G1((−CH_3)$_6$) (3a). 1,1,1-Tris(hydroxyphenyl)ethane (1.70 g, 5.56 mmol), **2a** (3.00 g, 17.2 mmol), DPTS (0.72 g, 2.50 mmol), and dicyclohexylcarbodiimide (DCC) (4.47 g, 21.7 mmol) were reacted as described above (24 h). The final product was isolated as white crystals. Yield: 3.10 g (72%). ^1H NMR ($CDCl_3$): δ = 1.32 (s, 9H, $-CH_3$), 1.41−1.45 (d, 6H, $-C(CH_3)_2$), 2.13 (s, 3H, $-CH_3$), 3.71−4.32 (dd, 12H, $-C(CH_2O-)_2$), 7.29 (q, 12H, $-OPh-$). ^{13}C NMR ($CDCl_3$): δ = 18.53, 22.49, 24.87, 30.92, 42.29, 51.00, 66.05, 98.23, 120.82, 129.65, 146.18, 148.50, 173.00.

G1((−OH)$_6$) 3b (2.0 g) was reacted for 2 h according to the general procedure for the removal of the acetonide groups. The isolated product was a white solid. Yield: 1.50 g (89%). ^{1}H NMR (acetone-d_6): δ = 1.30 (s, 9H, −CH_3), 2.20 (s, 3H, −CH_3), 3.77−3.88 (m, 12H, −C(CH_2O−)$_2$), 7.04−7.16 (m, 12H, −O*Ph*−). ^{13}C NMR (acetone-d_6): δ = 17.37, 18.88, 51.59, 57.50, 65.83, 122.13, 130.22, 147.50, 150.90, 174.50.

Polymerization Techniques. Polymerization of ϵ-caprolactone (and/or TOSUO) was initiated with bis-MPA or its derivatives using a catalytic amount of Sn(Oct)$_2$ or Al(O^{i}Pr)$_3$.[18] The polymerizations were carried out in the melt at 110 °C (20 h). The polymers were then dissolved in THF and precipitated in cold methanol.

Deacetalization of TOSUO Containing Copolymers. ϵ-CL/TOSUO block copolymer (2.4 mmol of TOSUO) and triphenylcarbenium tetrafluoroborate (2.5 mmol) were dissolved under stirring for 30 min in 100 mL of dichloromethane (3 wt % copolymer). The copolyester was recovered by precipitation in cold methanol.

Reduction of Ketone Pendent Groups into Hydroxyl Groups. Copolyester A (1.2 mmol of ketone) and sodium borohydride (1.45 mmol) were dissolved under stirring in a CH_2Cl_2/ethanol (5/2 v/v) mixture (ca. 1.0 wt % copolymer) for 30 min. The polymer was isolated by precipitation in cold methanol.

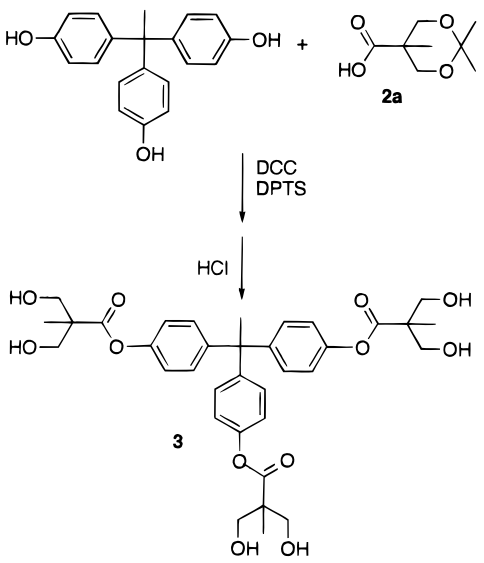
Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer. Size exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrene of known molecular weight as the calibration standards. 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 Å) were used with THF as solvent.

Results and Discussion

The initiators for this study are dendritic aliphatic polyesters based on 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and its derivatives, and in one case, 1,1,1-tris(hydroxyphenyl)) ethane (THPE) was used as the core molecule. Three initiators with varying degrees of functionality and architecture were surveyed. All initiators were prepared by procedures developed by Hult and co-workers.[4] The first initiator is the benzyl ester of bis-MPA (**1**) prepared by the nucleophilic substitution of the bis-MPA potassium salt with benzyl bromide. The second initiator **2** is the second generation of bis-MPA, a tetrahydroxy-functional dendron of bis-MPA. This initiator was prepared by reacting **1** with 2 equiv of the acetonide-protected bis-MPA (**2a**) in the presence of DCC and DPTS to form the second generation bis-MPA dendron **2b** in 85% yield (Scheme 1). The yield of **2b** was found to be dependent upon the amount of DPTS used, and it was concluded that the side reactions and byproducts were significantly lowered with higher DPTS content. The protected monomer, **2b**, was then deprotected with a 1/1 mixture of 1 M HCl-(aq) and THF to yield the crystalline tetrafunctional alcohol, **2**. The third initiator, **3**, is the first generation hexahydroxy-functional dendrimer of the bis-MPA. This dendrimer was prepared by the coupling of three equiv of **2a** with 1,1,1-tris(hydroxyphenyl)ethane using the same low temperature esterification reaction used for the preparation of **2b** (Scheme 2). The obtained product **3b** was deprotected for 2 h in a 1/1 mixture of 2 M HCl-(aq) and THF to yield the crystalline hexa-functional alcohol **3**.

The synthetic approach surveyed for the polymerization of ϵ-caprolactone from multifunctional initiators uses either Sn(Oct)$_2$ or Al(O^{i}Pr)$_3$ as catalyst.[18] A key feature in such a polymerization is the use of the organometallic compound in catalytic amounts so as to minimize complexation. In the latter approach, the Al(O^{i}Pr)$_3$ has been shown to undergo rapid exchange reactions with primary alcohols with the in situ formation of 2-propanol which can be selectively removed through an azeotropic distillation (i.e., 2-propanol/toluene), leaving the desired alcohol as the sole initiating species.[14] The growing alcohol chain ends can then undergo very rapid exchanges with the active aluminum alkoxide functions providing the "living" character to the polymerization reaction. Each of the initiators were readily soluble in ϵ-caprolactone producing homogeneous mixtures.

Scheme 2



Feijen and co-workers[19] have recently published the synthesis of ϵ-caprolactone and L-lactide block polymers by sequential addition of monomer using Sn(Oct)$_2$ in bulk, and polydispersities between 1.16 and 1.27 were obtained. Furthermore, quantitative conversion of monomer to polymer was observed. Kricheldorf et al. reported that minimal side transesterification reactions occurred at temperatures below 120 °C.[20a] Although the above examples show evidence of molecular control, no "living" character has been reported for lactone ROP catalyzed by Sn(Oct)$_2$. In the present work, ϵ-caprolactone has been polymerized in the bulk at 110 °C (16−20 h) initiated with the various multifunctional initiators in the presence of Sn(Oct)$_2$ (Scheme 3). In the initial study, the amount of Sn(Oct)$_2$ relative to the amount of initiating alcohols was investigated to determine the catalyst concentration for optimum molecular weight, molecular weight distribution and conversion control. The molar concentration of initiating alcohols relative to Sn(Oct)$_2$ ((M)/(Cat)) ranged from 1000 to 50, and markedly different results were produced. At ratios above 400, no polymer was obtained, presumably due to hydroxyl impurities which prevented polymerization. Conversely, catalyst concentrations in the ratio range of 400 to 150 produced polymer with extremely narrow molecular weight and exceptional molecular weight control. Shown in Figure 1 is a typical SEC trace which clearly shows the narrow and symmetrical molecular weight distribution. In selected bulk polymerizations at 110 °C, aliquots were periodically removed as a function of time and characterized. Several interesting results came from this study. First, plots of molecular weight as a function of monomer conversion were linear, suggesting some "living" character to these polymeriza-

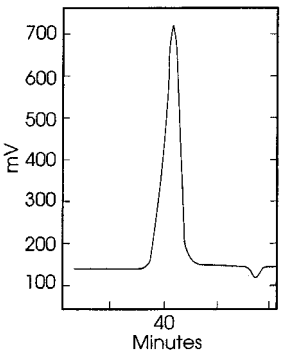
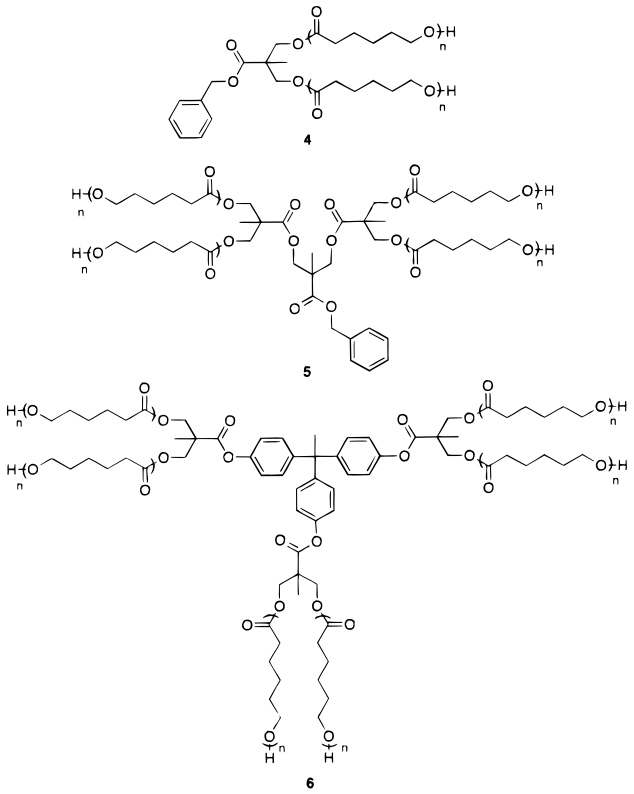


Figure 1. SEC trace of poly(caprolactone), **4d**, initiated with in the presence of $Sn(Oct)_2$ ($\langle M_w \rangle / \langle M_n \rangle = 1.14$).

Scheme 3



tions (Figure 2). Second, as in the case of $Al(O^iPr)_3$ alcohol exchange polymerization, an induction time is observed. Interestingly, at these catalyst concentrations, quantitative monomer conversions were observed for each of the polymerizations after just 16−20 h. Shown in Figure 3b is an ^1H NMR spectrum of an aliquot removed from the reaction vessel after 20 h of polymerization (110 °C). Clearly by this technique, no evidence of monomer or transesterification side reactions are observed, and the desired product is clearly obtained. Higher catalyst concentrations (M)/$Sn(Oct)_2$ < 150) resulted in a significant broadening of the molecular weight distribution (1.6−2.0), and molecular weight control was difficult.

These general polymerization procedures were applied to each of the multifunctional initiators **1**−**3** to generate polymers **4**−**6** (Scheme 3). In each case, the average degree of polymerization is in very close agreement to that of the monomer to alcohol ratio, irrespective of the catalyst used. Furthermore, the polydispersities are narrow. In addition to accurate molecular weight control, control of the end groups is possible,

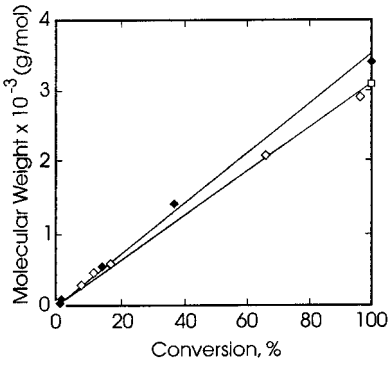


Figure 2. Molecular weight vs conversion for poly(caprolactone) initiated with **1** in the presence of $Sn(Oct)_2$.

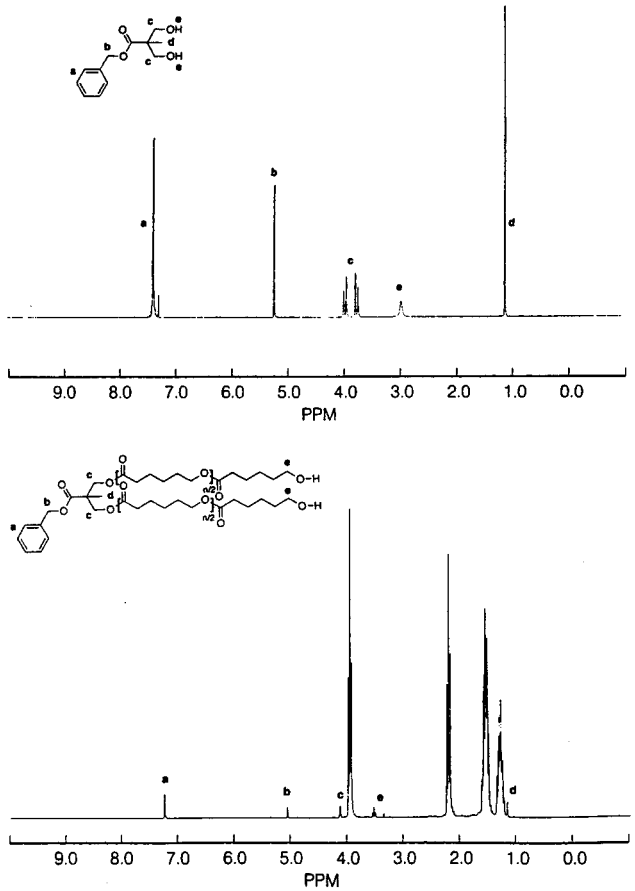
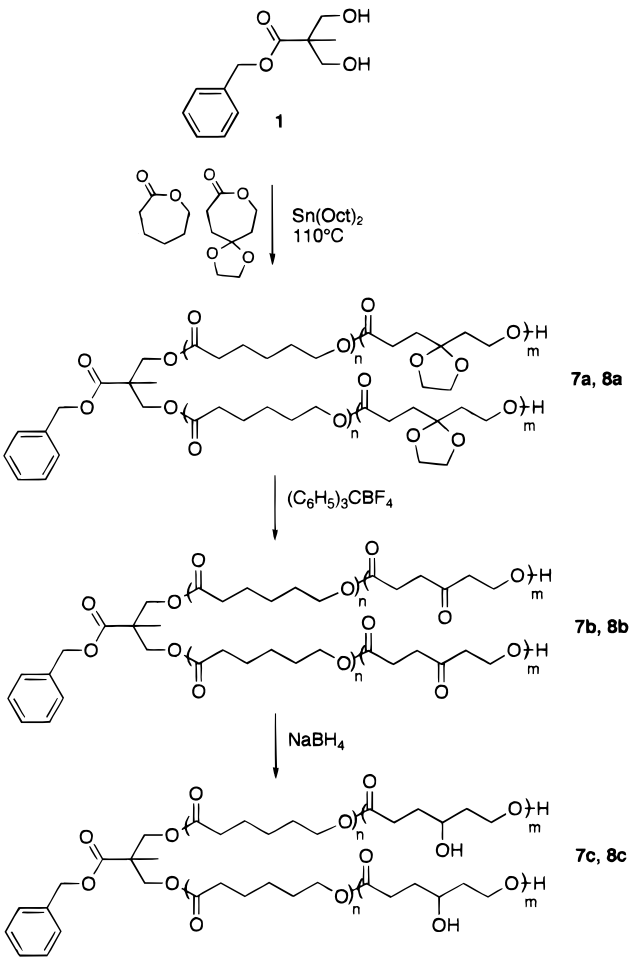


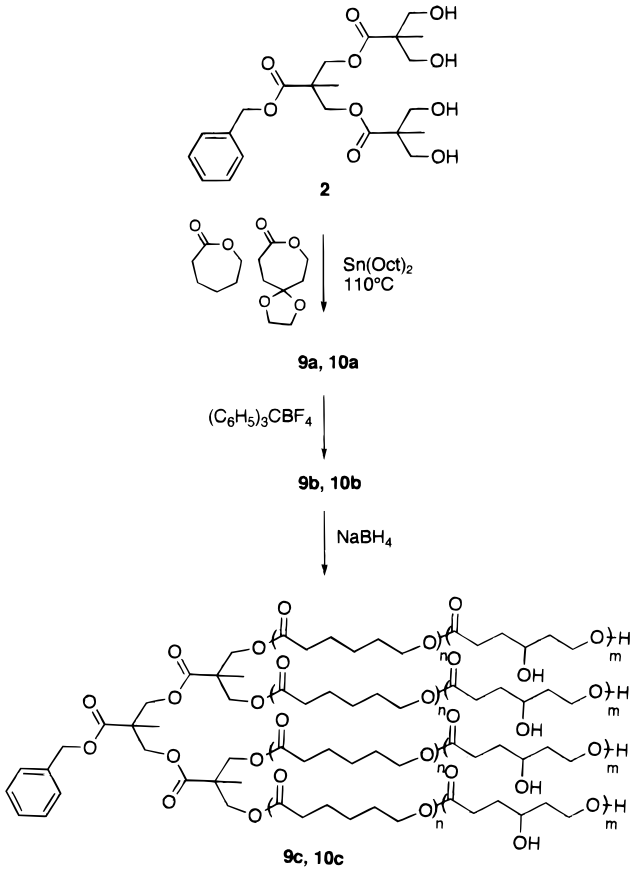
Figure 3. ^1H NMR spectra of initiator **1** (top) and poly(caprolactone) initiated with **4c** (bottom).

irrespective of the catalyst used. Figure 3 shows the ^1H NMR of the initiator **1** and the polymer **4c** which clearly shows the shifts of the peaks denoted as **c** and **d**, indicating that both of the hydroxyl groups have initiated the polymerization. If this was not the case, the $-CH_2-$ and $-CH_3$ groups in the bis-MPA would 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).[14(b)] We have recently reported the ^{13}C NMR spectrum of that region for polymers **4**−**6**.[20] In each case, only one peak, **A** (46.5 ppm), is detected indicating that there is only one type of substitution present, consistent with full substitution of each of the

Scheme 4



Scheme 5



hydroxyl groups. These data combined with ^{1}H NMR and SEC confirms that each of hydroxyl groups of **1** are substituted and, therefore, have initiated polymerization (i.e., quantitative initiation).

Recently Jérôme and co-workers[16] have demonstrated a straightforward and efficient pathway to introduce hydroxyl functionality along the poly(caprolactone) backbone. A new monomer, 1,4,8-trioxaspiro[4.6]-9-undecanone (TOSUO) has been homopolymerized and copolymerized with ϵ-caprolactone. The polymerizations are first order with respect to both monomer and initiator (aluminum isopropoxide), and end group analysis supports the expected coordination-insertion mechanism based on acyl−oxygen cleavage of the TOSUO ring. The deacetalization of the polyester chains has been reported to be quantitative as is the reduction of the ketone groups to the pendant hydroxyl groups. The use of TOSUO as a comonomer with ϵ-CL with the multifunctional initiator should produce a highly functional macromolecule. Polymerization of TOSUO and ϵ-CL initiated by either **1** or **2** was accomplished at 110 °C using bulk conditions in the presence of $Sn(Oct)_2$ (Schemes 4 and 5). TOSUO melts at ∼50 °C and was readily soluble in the ϵ-CL, and the combined monomer mixture dissolved the initiators. Quantitative monomer consumption was observed after 20 h. The molecular weight of the resulting polymers (**7a**−**10a**) showed good agreement to the initial monomer/initiator ratio (Table 2), consistent with the previous reports of Jérôme and co-workers. Furthermore, the polydispersities are narrow. The first step, i.e., the synthesis of chains bearing

Table 1. Characteristics of Branched Polyesters

sample entry	$\langle M_n \rangle_{,target}$	$\langle M_n \rangle_{,NMR}$	$\langle M_n \rangle_{,SEC}$	$\langle M_w \rangle / \langle M_n \rangle$
4a[a]	4560	4800	7700	1.18
4b[a]	11400	10000	14500	1.50
4c	4600	4700	7600	1.18
4d	8900	8300	13100	1.14
4	17900	18400	25000	1.13
5a	7200	8000	15700	1.15
5b	11400	11000	22800	1.21
6a	17000	16100	20000	1.09
6b	55400	59300	83200	1.08
6c	69000	71200	115000	1.06

[a] $Al(O^iPr)_3$-initiated polymerizations

various concentrations of acetal pendant groups, has proved the inertness of the acetal groups toward the active initiating and propagating species, at least under the experimental conditions used.

Deprotection of the ketone groups was carried out using triphenylcarbenium tetrafluororborate (**7b**−**10b**).[18] Owing to the sensitivity of the aliphatic polyesters, mild conditions were required to convert the pendant acetal groups into ketones. Jérôme and co-workers have shown that triphenylcarbenium tetrafluoroborate is an efficient reagent for the deacetalization in quantitative conversion. Shown in Figure 4 are the ^{1}H NMR spectra for the deacetalization of copolymer **7a**. Clearly, the acetal protons (δ = 3.95 ppm) have completely disappeared, consistent with quantitative deacetalization, **7b**. The molecular weight distribution is not affected by the deacetalization procedure, and the number average molecular weights, as determined by ^{1}H NMR end group analysis, are unaffected by the transformation. These combined data indicated minimal degradation of the polyester chain after the deacetalization step.

Table 2. Characteristics of Branched Poly(Caprolactone)s Containing TOSUO

		pendent groups														
		ethyleneacetal						ketone					hydroxyl			
initiator	sample entry	TOSUO content, mol %	M_w/M_n	target DP	DP, ^{1}H NMR	T_g, °C	T_m, °C	sample entry	M_w/M_n	DP, ^{1}H NMR	T_g, °C	T_m, °C	sample entry	M_w/M_n	DP, ^{1}H NMR	T_g, °C	T_m, °C
1	**7a**	10	1.2	20	22	−60	45	**7b**	1.2	22	−60	52	**7c**	1.73	14	−40	62
1	**8a**	2	1.19	20	20	−63	62	**8b**	1.21	22		43	**8c**	1.6	15	−40	62
2	**9a**	10	1.3	20	21	−60	54	**9b**	1.35	22		51	**9c**	1.36	15	−40	62
2	**10a**	15	1.4	20	17		43	**10b**	1.4	18		65	**10c**	1.32	15		45

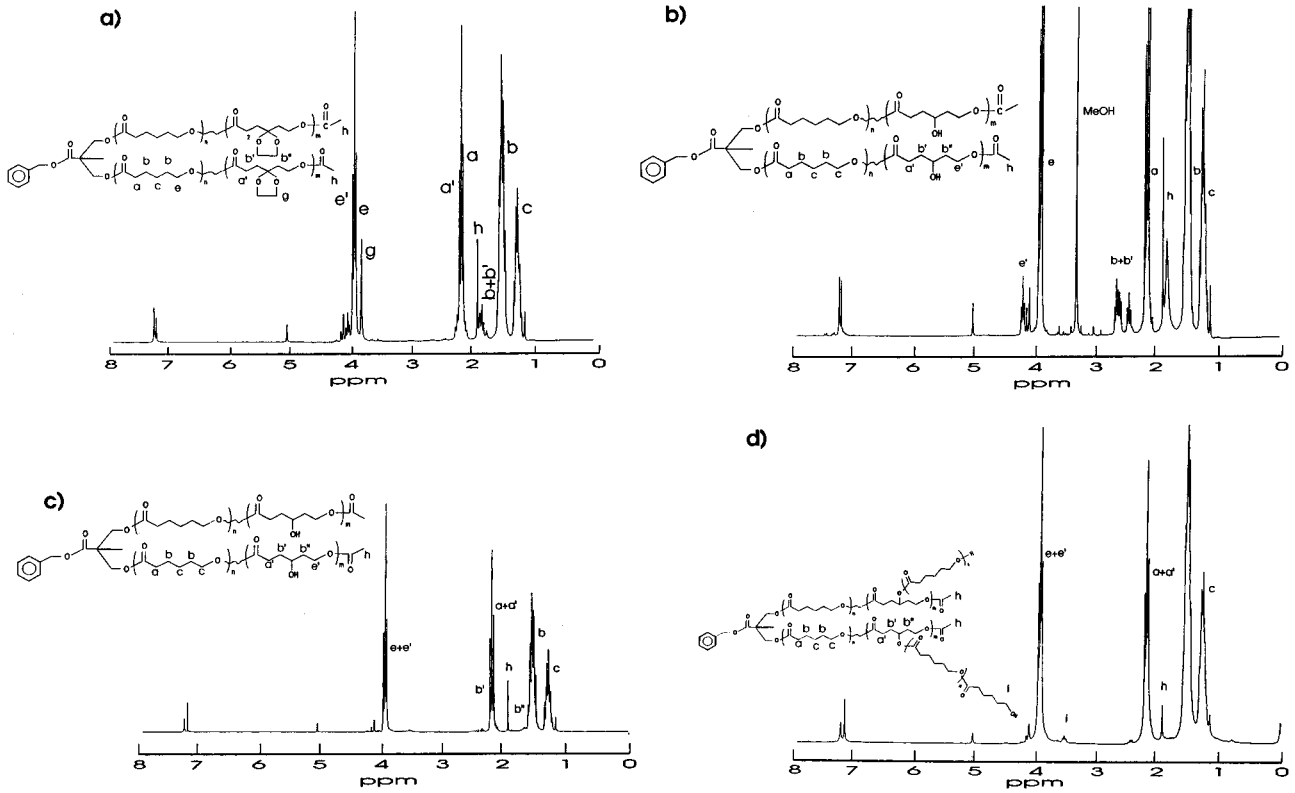


Figure 4. ^{1}H NMR spectra: (a) **7a**; (b) **7b**; (c) **7c**; (d) **7d**.

The reduction of the ketone on copolymers **7b**−**10b** into the hydroxyl pendant groups was accomplished using sodium borohydride by a procedure developed by Jérôme and co-workers (**7c**−**10c**). A methylene chloride/ethanol mixture solvent mixture was found to effectively solubilize the polyester and reducing agent. The ^{1}H NMR shows that the ketone pendant groups are completely reduced to the hydroxyl pendant groups, **7c** (Figure 4). However, of some concern is the peak at $\delta = 3.65$ which probably is due to a $-CH_2OH$ end group indicating some chain cleavage during the reduction. However, although the ^{1}H NMR data suggest partial degradation of the poly(ϵ-caprolactone) chains, the molecular weight distributions remain essentially unchanged after the reduction step and are narrow and symmetrical. These data are consistent with minimal or the absence of chain scission. The GPC peak is, however, shifted to lower elution volumes, and the chemical modification of the copolyester is believed to be responsible for changes in the polymer−solvent interactions, the elution volume, and the apparent molecular weight.[16]

Interestingly, further synthetic flexibility can be realized from these branched polymers containing the pendant hydroxyl groups by using these macromolecules themselves as initiators for the ROP of ϵ-CL (Scheme 6). In this way, successive grafting steps can be used to produce extremely complex molecular architectures. This scheme is analogous to that developed by Tomalia et al.,[3c] where successive grafting of reactive polymer chains formed dendritic graft polymers. The resulting macromolecules, termed "comb−burst," are prepared from functional linear chains. Tomalia[3c] demonstrated the synthesis of comb−burst poly(ethylene imines) by the repeated grafting of poly(oxazoline) onto poly(ethylene imines) followed by hydrolysis to regenerate the reactive amino groups. Similarly, Möller et al.[3b] used this stepwise approach in the synthesis of comb−burst polystyrene derivatives. Gnanou[15b] has reported the synthesis of similar graft-on-graft copolymers prepared by a stepwise synthesis containing a central polystyrene core with poly(ethylene oxide) as the outer layer. Likewise, Hawker, Fréchet, and co-workers[3a] have reported the synthesis of novel graft and dendrigraft systems via "living" free radical synthetic methods. In this case, a sequential two-step free radical approach based on an initial nitroxide-mediated "living" free radical polymerization followed by a "living" atom transfer radial polymerization was used to synthesize these complex molecular architectures.

In this study, initiator **1** was used to initiate the ROP of ϵ-CL and TOSUO (10 mol %) with a target molecular weight of 4000 per arm (~8200 total) (Scheme 6). The polymer chain ends were intentionally capped in the

Scheme 6

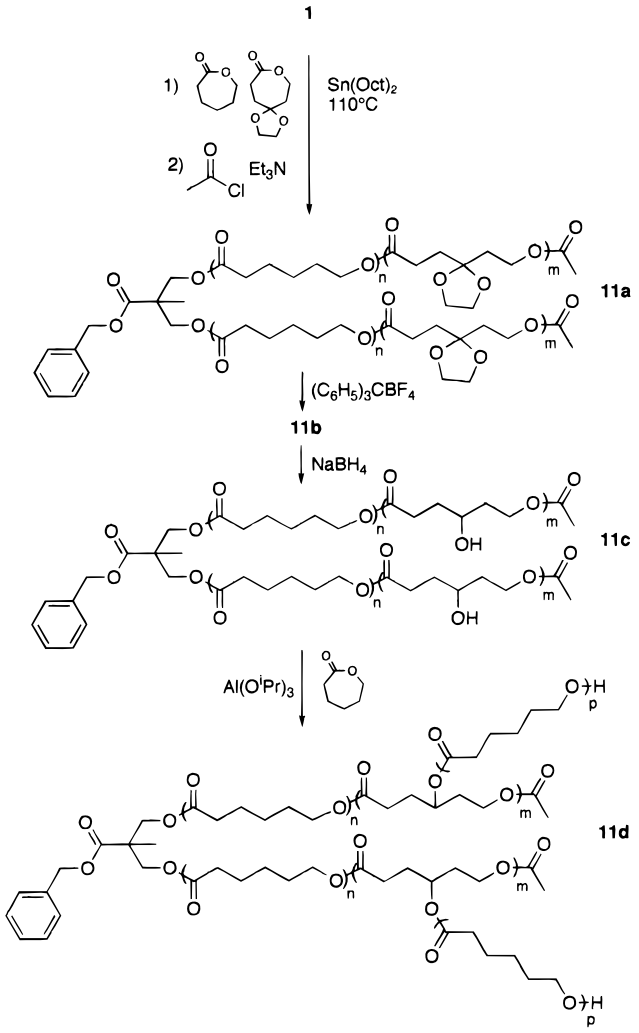


Table 3. Characteristics of Branched and Dendri-Graft Polyesters

sample entry	$\langle M_n \rangle$ target	$\langle M_n \rangle$ measured ^{1}H NMR	$\langle M_w \rangle / \langle M_n \rangle$
7a	8200	8100	1.13
7b	8200	7300	1.15
7c	8200	7400	1.17
7d	11500	10400	1.19

first step with acetyl chloride due to the reactivity difference between a primary polycaprolactone end group and secondary hydroxyl group generated by successive deprotection and reduction reactions of the functions to ROP, an important consideration if these macromolecules themselves will be used as initiators, **7a**. The deacetalization and reduction steps were accomplished as described above (Scheme 6). Figure 4 clearly shows the successful deprotection of the acetal groups followed by the reduction to form the pendant hydroxyl groups, **11b**. Furthermore, no evidence of transesterification side reactions or degradation was observed in the ^{1}H NMR spectra. The molecular weight and molecular weight distribution of the polymer remained essentially unchanged through these transformations (Table 3). The grafting polymerization from **7c** was accomplished using $Al(O^iPr)_3$ as a catalyst in toluene. The 2-propanol was selectively removed through azeotropic distillation, leaving the pendant alcohol group as the sole initiating species. The addition of ϵ-caprolactone produces the requisite dendritic graft polymer, **7d**, where one generation of grafted arms are clearly grown from the main chain (Scheme 6). Hydrolysis of the metal−alkoxide bonds produced a hydroxyl group at the growing chain ends. Clearly from ^{1}H NMR spectra of the grafted polymer, the methylene protons adjacent to the hydroxyl end groups are visible and can be used to calculate the molecular weight of the grafts (Figure 4d). The resulting graft or branched polymer showed an extremely narrow molecular weight distribution (Table 3). The number average molecular weight of the branches or grafts is somewhat lower than expected (DP of 6 as opposed to the target 10), and this discrepancy may simply result from insufficient polymerization time for the secondary alcohol initiated polymerization.

Summary

A general method for the preparation of branched and highly functional aliphatic polyesters has been demonstrated. We found that bis-MBA and its derivatives are efficient initiators for the ROP of lactones. The use of $Sn(Oct)_2$ as a catalyst allows accurate control of molecular weight and molecular weight distribution, as well as quantitative conversion of monomer to polymer. The use of TOSUO as a comonomer provides an additional means of introducing functionality along the chain. In this case, these polymers were used as macroinitiators for the preparation of dendrigraft and other complex molecular architectures. The new polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy and SEC. This represents one of the first examples of poly(caprolactone) synthesis which results in branched and more complex molecular architectures. Moreover, initiation from bis-MPA and its derivatives should prove effective with other monomers, providing a general methodology to highly branched and functional polymers.

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