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Hyperbranched Poly(ϵ-caprolactone)s

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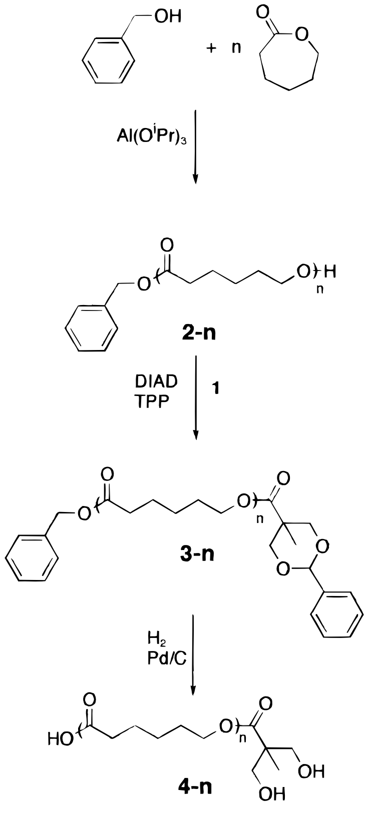
ABSTRACT: Novel hyperbranched poly(ϵ-caprolactone)s have been synthesized. The versatile synthesis utilizes AB_2 macromonomers and allows the thermo-physical properties of the polymers to be tailored. The ϵ-caprolactone-based AB_2 macromonomers were synthesized through living ring opening polymerization, using aluminum benzyloxide as the initiator. The aluminum benzyloxide initiated polymers were then functionalized with benzylidene-protected 2,2′-bis(hydroxymethyl) propionic acid and subsequently deprotected to form the α-carboxylic-ω-dihydroxy functional AB_2 macromonomers. The AB_2 polyesters were condensed into hyperbranched polymers through a room-temperature esterification synthesis using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS). All polymers were characterized by ^{1}H NMR, SEC, and DSC. The degree of branching in the hyperbranched polymers was found, by ^{1}H NMR, to be 0.37 ± 0.03, and to be independent of the macromonomer used. Significant flexibility exists in the new approach since the molecular weight and the type of macromonomer can be varied.

Introduction

The large number of end groups and low melt viscosities are examples of the unique properties of highly branched polymers that has given this group of materials significant attention.[1,2] The ultimate example of the effects of branching on the physical and solution properties of macromolecules is provided by dendrimers, which, however, are tedious to synthesize.[3] Hyperbranched polymers, first reported by Kim and Webster,[4] have a less perfect structure than dendrimers but have the advantage of being synthesized in only one step. Although this attractive feature has led to the development of many different architectures involving a large number of building blocks,[5] it is difficult to tailor-make the properties of hyperbranched polymers since only a few parameters can be varied. One modification includes the use of a core molecule with varying functionality which enables the molecular weight of the hyperbranched polymers to be controlled.[6] Most hyperbranched polymers are prepared through condensation methods,[5] but recent examples utilize chain polymerization techniques.[7] Noteworthy examples of hyperbranched polyesters have been reported by Hawker *et al.*[5a] and Johansson *et al.*[5c] in which the self-polymerizations of 3,5-dihydroxybenzoic acid[5a] and 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA)[5c] derivatives were demonstrated, respectively.

The use of ring-opening polymerization (ROP) methods to prepare highly branched polyesters with unique topologies has been much less pervasive than other polymerization procedures and has focused mostly on different block copolymers[8] and star-shaped macromolecules.[9] In addition, ROP of lactones have also been extensively surveyed in the area of telechelic polymers.[8g,10] Aluminum triisopropoxide is a well-known initiator for these polymerizations, and functional aluminum benzyloxides have been demonstrated to generate α-carboxylic-ω-hydroxy polyesters after polymerization and removal of the initiating benzylic group.[10f]

Scheme 1



If these polymers are functionalized with a protected bis-MPA at the ω-hydroxy chain end, a protected AB_2-functional α-carboxylic-ω-dihydroxy macromonomer, **4-*n***, would be formed, Scheme 1. This AB_2 macromonomer could then after deprotection be mildly condensed by a room-temperature esterification technique to produce a novel type of hyperbranched polyesters **poly(4-*n*)**, Scheme 2. This novel synthetic approach allows hyperbranched polymers to be produced with significant versatility, including variation of monomer, the size of the macromonomer, and the total molecular weight of

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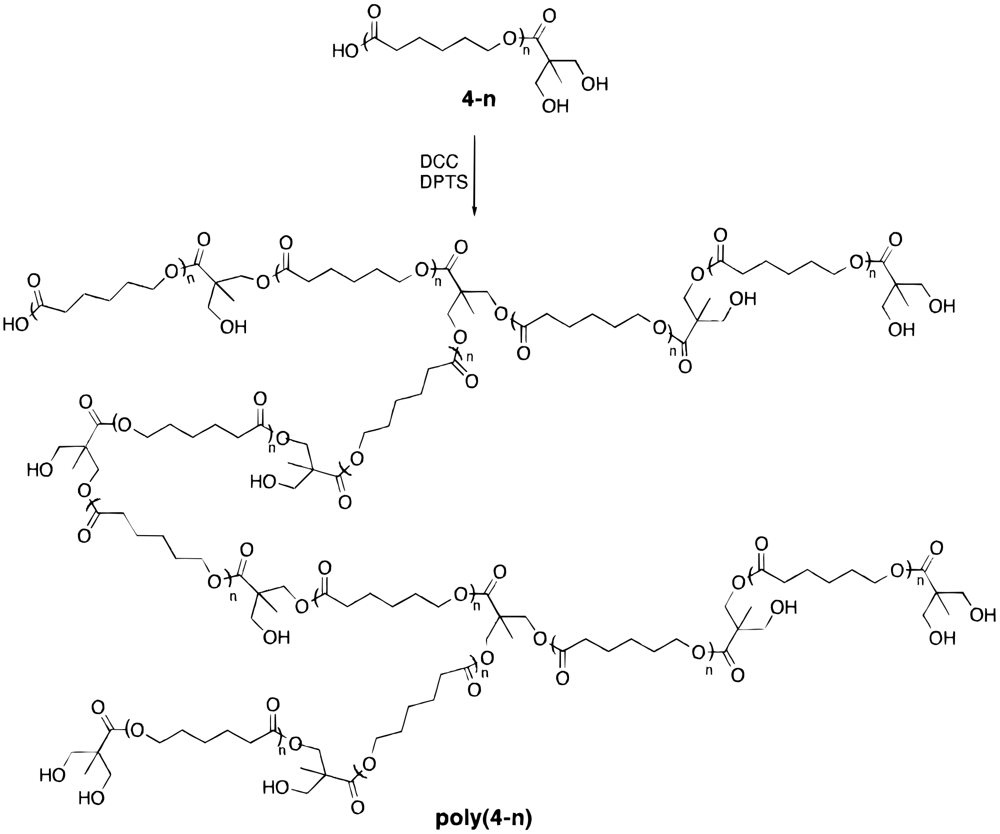
Scheme 2



the hyperbranched polyester. This paper reports the synthesis and the structural characterization of these novel polyesters. Furthermore, the thermophysical properties are discussed and related to the molecular architecture.

Experimental Section

Materials. Toluene was dried by refluxing over sodium and distilled just prior to use under nitrogen. The benzyl alcohol (Aldrich) was distilled under reduced pressure, and stored under a nitrogen atmosphere. The aluminum triisopropoxide (Aldrich) was sublimed and then dissolved in toluene under nitrogen. The concentration of this solution was measured by complexometric titration of the Al atom. 4-(Dimethylamino)-pyridinium 4-toluenesulfonate (DPTS) was synthesized according to a literature procedure.[11] G#4 Boltorn was kindly supplied by Perstorp AB. All other chemicals were purchased from Aldrich and used as delivered.

Characterization 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. ^{13}C NMR spectra were recorded at 62.9 MHz on the same instrument using the solvent carbon signal as a reference. The number average molecular weights of the polymers were calculated from the ^{1}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 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 at 25 °C. Poly(styrene) standard samples were used for calibration.

Synthesis. 2,2-Bis(phenyldioxymethyl)propionic acid (1). 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) (25.0 g, 187 mmol), benzaldehyde dimethyl acetal (42.6 g, 280 mmol), and *p*-toluenesulfonic acid (p-TSA) (0.69 g) were all dissolved and stirred in acetone (100 mL) at ambient temperature. After 2 h, a few drops of NH_4OH (aqueous, 30%)/EtOH (1:1) solution were added to neutralize the p-TSA. The reaction mixture was then diluted with 400 mL of CH_2Cl_2 and extracted once with H_2O (25 mL). The organic phase was separated, filtered, and concentrated. The residue was recrystallized from CH_2Cl_2 to give the product **1** as a white powder. Yield: 37.3 g (90%). Mp: 197−198 °C. ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 3H, $-CH_3$) 3.66−4.64 (2d, 4H, $-(CH_2O)_2CH-$, $J = 9.0$ Hz), 5.46 (s, 1H, $-CH$Ph), 7.31−7.47 (m, 5H, −Ph). ^{13}C NMR (DMSO-d_6): δ 22.75, 46.73, 77.81, 105.52, 131.25, 133.17, 133.85, 143.56, 180.71.

Polymerization of ϵ-Caprolactone (2-*n*). The initiating aluminum benzyloxide was formed by the reaction of aluminum triisopropoxide with benzyl alcohol. Azeotropic distillation of the mixture removed 2-propanol in the equilibrium reaction, favoring aluminum benzyloxide formation. Monomer and toluene were then added to a previously flamed glass flask, and the polymerizations were stirred for 24 h under nitrogen. Solvent, benzyl alcohol, and the catalyst were all added through a rubber septum with a syringe. The catalyst was added in a concentration of 1/5 relative to the amount of the initiating alcohols. The target degree of polymerizations was determined by the monomer-to-alcohol ratio. Quantitative yields were obtained. ^{1}H NMR ($CDCl_3$); δ 1.30 (m, poly, $-CH_2-$), 1.60 (m, poly, $-CH_2CH_2CH_2-$), 2.26 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 3.65 (t, 2H, $-CH_2OH$, $J = 5.6$ Hz), 4.01 (t, poly, $-CH_2O-$, $J = 5.3$ Hz), 5.06 (s, 2 H, $-CH_2$Ph), 7.24 (s, 5H, −Ph).

A General Procedure for Functionalization of α-Benzoate-ω-hydroxy Poly(ϵ-caprolactone) (3-*n*). The polymer **2-*n*** (5.00 g, 1.67 mmol) was dissolved in THF (5 mL) in a previously flamed flask, into which a solution of **1** (0.45 g, 2.17 mmol) in THF and triphenylphosphine (TPP) (0.87 g, 3.33 mmol) was added. Into this stirred solution was carefully mixed diisopropyl azodicarboxylate (DIAD) (0.67 g, 3.33 mol). After 12 h, the reaction mixture was precipitated into cold methanol, and the product was filtered to yield 4.00 g (75%) of functionalized polymer, **3-*n***. ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 3H, $-CH_3$), 1.32 (m, poly, $-CH_2$-), 1.61 (m, poly, $-CH_2CH_2CH_2$-), 2.27 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 3.58−4.64 (2d, 2H,

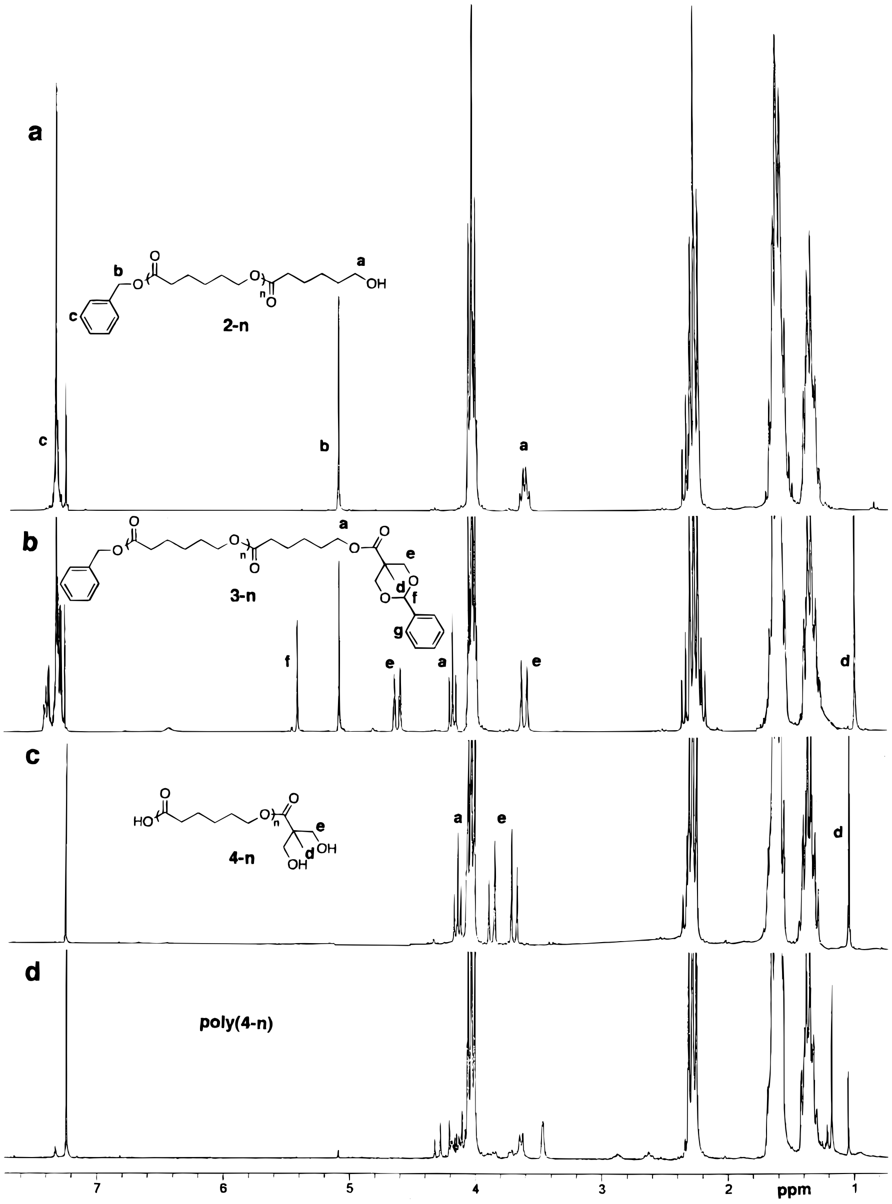


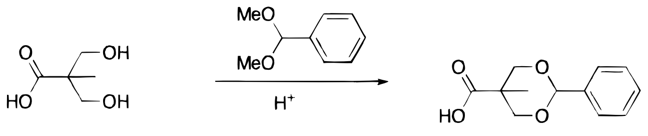
Figure 1. ^{1}H NMR spectra of (a) **2-*n***, (b) **3-*n***, (c) **4-*n*** and (d) **poly(4-*n*)**.

$-CH_2O-$, $J = 9.0$ Hz), 4.01 (t, poly, $-CH_2O-$, $J = 5.3$ Hz), 4.18 (t, 2H, $-CH_2O-$, $J = 5.2$ Hz), 5.08 (s, 2 H, $-CH_2Ph$), 5 0.41 (s, 1 H, $-CHPh$), 7.28−7.41 (m, 10H, 2 Ph).

General Procedure for Preparation of AB$_2$ Functional α-Carboxylic--dihydroxy Poly(ϵ-caprolactone) (4-*n*). Pd/C (0.40 g) was added to a solution of **3-*n*** (4.00 g) in THF (10 mL) and EtOAc (40 mL). The flask was first evacuated and then filled with H_2 (g). The reaction was stopped after 24 h, the Pd/C was filtered, and the clear solution was precipitated into cold methanol. The obtained macromonomer was a white crystalline powder. Yield: 3.00 g (78%). ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3H, $-CH_3$), 1.32 (m, poly, $-CH_2-$), 1.61 (m, poly, $-CH_2$-CH_2CH_2-), 2.27 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 3.66−3.88 (2d, 2H, $-CH_2O-$, $J = 8.9$ Hz), 4.01 (t, poly, $-CH_2O-$, $J = 5.3$ Hz), 4.14 (t, 2H, $-CH_2O-$, $J = 5.2$ Hz).

Polymerization of α-Carboxylic-ω-dihydroxy Poly(ϵ-caprolactone) (poly(4-*n*)). The macromonomer **4-*n*** (1.00 g, 0.33 mmol) was dissolved in CH_2Cl_2 (3 mL) in a previously flamed flask, into which a solution of DPTS (16.0 mg, 0.05 mmol) in THF and finally DCC (0.10 g, 0.50 mmol) was added. After 48 h, the reaction mixture was precipitated into methanol and filtered to yield 0.87 g (87%) of hyperbranched polymer **poly(4-*n*)**. ^{1}H NMR ($CDCl_3$), Figure 1d.

Scheme 3



bis-MPA

1

Results and Discussion

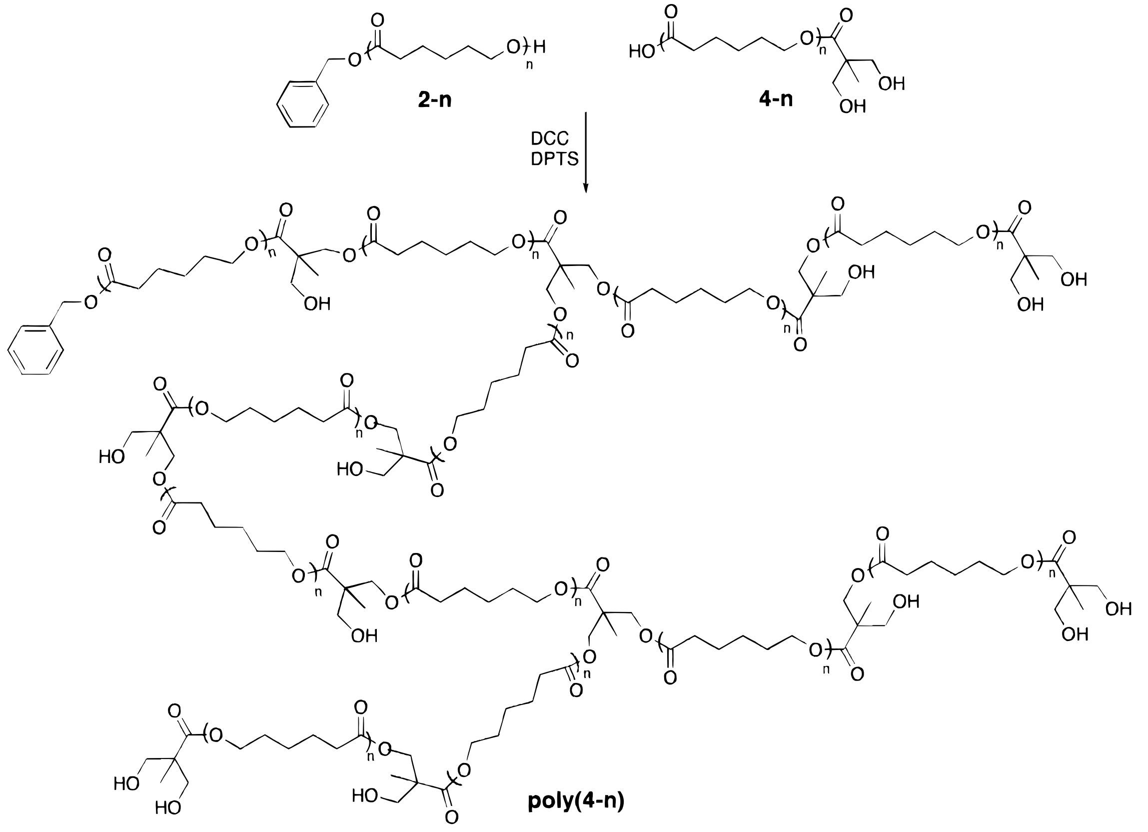
Design of the Hyperbranched Polymer. The novel polymers were developed in order to obtain a structure that combine classical properties of linear polymers such as entanglements and crystallinity with those of dendritic macromolecules, in particular the high functionality through the many end groups.[13] Poly(ϵ-caprolactone) was selected as the polymeric building block since it is possible to produce it with accurate control of molecular weight, molecular weight distribution, and end-group functionality. The selection of 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), as the branching point, was based on its aliphatic structure

Table 1. Theoretical and Experimental Molecular Weights and Thermal Transitions of the Different AB_2 Macromonomers

macromonomer	DP_{NMR}	DP_{target}	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n,GPC	T_m (°C)[a]	ΔH_m (J/g)[a]	T_c (°C)[b]	ΔH_c (J/g)[b]
4-8	8	10	1000	1900	1.12	43.3	87.7	8.9	82.8
4-12	12	10	1400	2400	1.14				
4-20	20	20	2500	4500	1.29	57.9	66.0	25.1	68.2
4-50	58	50	6700	11900	1.17	59.8	70.9	34.6	76.6

[a] DSC melting transition observed on second heating. [b] DSC crystallization transition observed on first cooling.

Scheme 4



as well as its documented use as building block in the synthesis of dendrimers[12] and hyperbranched polymers.[5c,6] The protecting groups were selected due to the mild conditions required for their removal from the highly sensitive poly(ϵ-caprolactone).

Synthesis and polymerization. The benzylidene-protected bis-MPA **1** was synthesized in high yields from bis-MPA and benzaldehyde dimethyl acetal, Scheme 3. This compound was essential in the synthesis of the AB_2 macromonomers **4-*n*** which is outlined in Scheme 1. Aluminum benzyloxide, prepared from benzyl alcohol and aluminum triisopropoxide, was used to initiate the polymerization of ϵ-caprolactone to form hydroxyl functional oligomers **2-*n***.[10f] The aluminum triisopropoxide undergoes rapid exchange reactions with the benzyl alcohol which allows the formed 2-propanol to be selectively removed through an azeotropic distillation, leaving the requisite aluminum benzyloxide as the sole initiating species.[14] During the polymerization a similar exchange reaction occurs between the propagating chain ends and the active aluminum atoms. Hydrolysis of the active metal alkoxide produces the requisite oligomers with hydroxyl-functional chain ends. The functional end group was then functionalized with the benzylidene protected bis-MPA, **1**, using Mitsunobo conditions.[15] The formed oligomer **3-*n*** was purified through precipitation into cold methanol or by column chromatography depending on their molecular weights. The benzylidene group and the benzyl ester of **3-*n*** were simultaneously removed using neutral conditions through catalytic hydrogenolysis to generate the requisite AB_2 α-carboxylic-ω-dihydroxy functional macromonomer, **4-*n***, in one step. The simple and mild deprotection performed under H_2 atmosphere over Pd/C occurred without affecting the acid- and base-sensitive poly(ϵ-caprolactone). The molecular weight, the molecular weight distribution, and the shape of the SEC chromatogram all remained unchanged, indicating that the macromonomers were intact. The resulting AB_2 oligomers **4-*n*** were finally self-condensed by an esterification procedure developed by Stupp and Moore using DCC and DPTS as reagents to give high molecular weight polymer **poly(4-*n*)**, Scheme 2.[11]

Shown in Table 1 are the general characteristics of the prepared macromonomers. In each case, the average degree of polymerization is in close agreement to the target value predicted from the monomer to benzyl alcohol ratio, and the molecular weight distributions are narrow. In addition, the required end groups were obtained as characterized by ^1H NMR spectroscopy. Figure 1a-d shows the ^1H NMR spectra of **2-*n***, **3-*n***, **4-*n***, and **poly(4-*n*)**. Figure 1a displays clearly the peaks derived from the two end groups $-CH_2OH$ (**a**) and $-CH_2Ph$ (**b**, **c**) of **2-*n***. Upon transformation of the chain

Table 2. Theoretical and Experimental Molecular Weights and Thermal Transitions of the Different Hyperbranched Polymers

macromer	**4-*n*/2-*n***	$M_{\mathrm{w,GPC}}$	$M_{\mathrm{n,GPC}}$	$M_{\mathrm{w}}/M_{\mathrm{n,GPC}}$	T_{m} (°C)[a]	ΔH_{m} (kJ/g)[a]	T_{c} (°C)[b]	ΔH_{c} (kJ/g)[b]
poly(4-8):1	10	32 300	13 700	2.36	38.9	48.8	−3.0	51.4
poly(4-8):2	20	37 900	16 600	2.29	38.6	50.5	−2.6	52.6
poly(4-8):3		47 900	25 400	1.89	38.2	47.8	−3.2	50.1
poly(4-12)	10	24 700	10 600	2.32	48.6	54.4	9.0	60.0
poly(4-20)		103 000	45 500	2.26	52.6	57.7	20.9	63.1
poly(4-50)		201 000	74 000	2.72	57.0	60.9	25.4	60.3

[a] DSC melting transition observed on second heating. [b] DSC crystallization observed on first cooling.

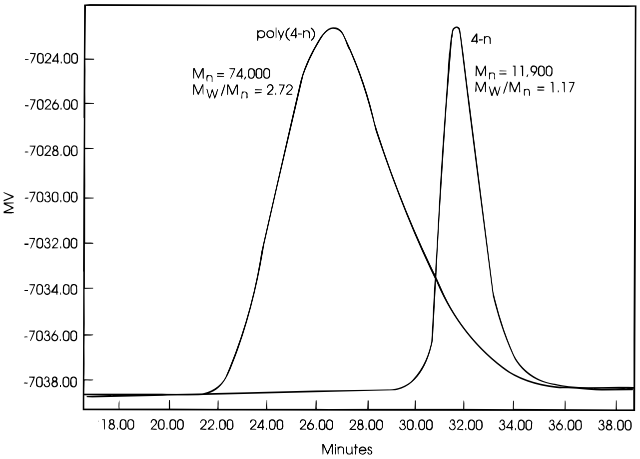


Figure 2. Size exclusion chromatogram of the AB_2 macromonomer **4-60** and the hyperbranched polymer **poly(4-60)**.

end from an alcohol into an ester (**3-*n***), the **a** peak shifts and a number of new peaks appear (**d**, **e**, **e**, **f**, and **g**) originating from the protected bis-MPA, Figure 1b. Deprotection of **3-*n*** removes the **b** and the **c** peaks derived from the benzyl group and the **f** and the **g** peaks originating from the benzylidene group, Figure 1c. In addition, the **e** ($-CH_2-$ in bis-MPA) and **d** ($-CH_3$ in bis-MPA) resonances are shifted in **4-*n***. Polymerization of **4-*n*** yields a less well-defined product, **poly(4-*n*)**. Figure 1d shows an end-capped **poly(4-*n*)**, Scheme 4.

The general characteristics of these hyperbranched poly(ε-caprolactone)s are shown in Table 2. The yields are between 80 and 90% which suggest that unreacted macromonomer might remain in the hyperbranched polymers. However, the SEC chromatogram shows only traces of macromonomer in the hyperbranched polymers, Figure 2. Possible macromonomer contamination was selectively removed from the hyperbranched polymer during the precipitation. Therefore, this technique is optimal for the lower molecular weight macromonomers (M_{n} < 5000 g/mol) since possible macromonomer contamination can be readily removed in the precipitation of the hyperbranched polymers.

It was also possible to synthesize hyperbranched polymers with different molecular weights using the same macromonomer, Table 2. These hyperbranched polymers with controlled molecular weight were synthesized by using various amounts of **2-*n*** as an end capper to restrict the polymer growth, Scheme 4. The different molecular weights of **poly(4-8)** were simply achieved by using different ratios of **2-8** relative to **4-8**. This technique is comparable to one, presented by Malmström et al.,[6] that uses a multifunctional core to control the molecular weight of hyperbranched polyesters.

Degree of Branching. The degree of branching (DB) is a often used method to reveal the structure of hyperbranched polymers. The most common definition used, reported by Frechet *et al.*,[5a] is

$$\mathrm{DB} = \frac{\sum \mathrm{D} + \sum \mathrm{T}}{\sum \mathrm{D} + \sum \mathrm{T} + \sum \mathrm{L}} \tag{1}$$

where ΣD is the number of dendritic units, ΣL is the number of linear units and ΣT is the number of terminal units. ^{13}C NMR and ^{1}H NMR are the most common techniques used to determine the degree of branching. The technique is usually based on low molar mass model compounds resembling the repeating units in the hyperbranched polymer. From these model compounds the different peaks in the spectra of the polymers can be assigned and the degree of branching can be calculated from the integrals of these peaks. In this study the ^{1}H NMR resonances of the $-CH_3$ protons in bis-MPA were used. The three peaks were assigned by the use of the monomer **4-*n*** (terminal unit) and two model compounds (**5** (linear unit) and **6** (dendritic unit)), Figure 3. **6** was synthesized according to ref 16, and **5**

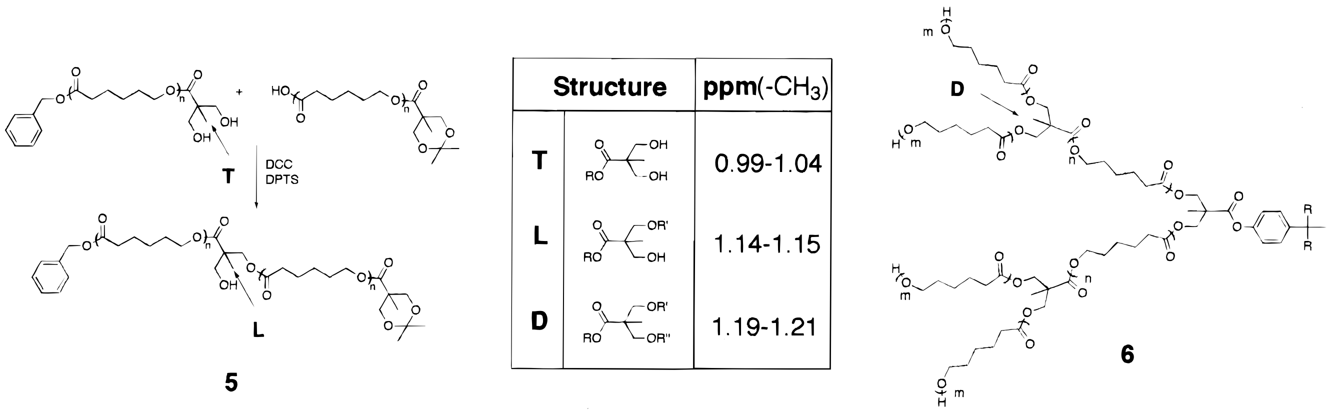


Figure 3. Chemical structures and the^{1}H NMR chemical shifts in $CDCl_3$ of the three possible repeating units in the hyperbranched poly(ε-caprolactone). **5** and **6** are model compounds that were used for the assignment of these shifts.

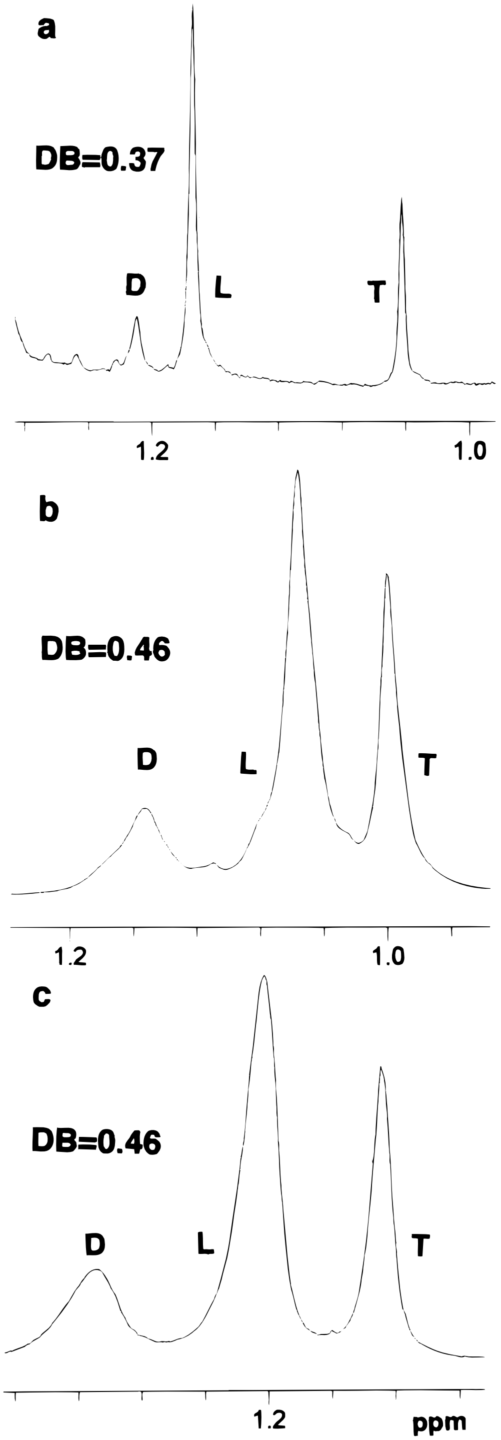


Figure 4. The enlarged $-CH_3$ region of the ^1H NMR spectra and the degree of branching of (a) **poly(4-*n*)** in $CDCl_3$, (b) G#4 Boltorn in DMSO-d_6, and (c) G#4 Boltorn in acetone-d_6.

was synthesized according to Figure 3. The chemical shifts of the linear, dendritic, and terminal units were found to be 1.14, 1.19, and 1.04, respectively, which correspond well to the values reported by Malmström et al.[6] Figure 4a shows that these three peaks clearly separate in the hyperbranched polymer. Using these peaks the DB was calculated to be 0.37 ± 0.03 for these new hyperbranched polymers. The DB was found to be independent of the molecular weight of both the macromonomer and the final hyperbranched polymer. To ensure the validity of this result, the ^1H NMR technique was employed to analyze the DB of a pure bis-MPA hyperbranched polymer, G#4 Boltorn.[6] The degree of branching was found to be 0.46 ± 0.015 and independent of the solvent used, which is comparable to the results obtained by ^{13}C NMR techniques.[6,17] Figure 4b shows the ^1H NMR spectra of G#4 Boltorn in DMSO-d_6, and Figure 4c shows the ^1H NMR spectra of the same polymer in acetone-d_6. These data demonstrate the utility of ^1H NMR as a technique to measure the degree of branching in hyperbranched systems based on bis-MPA.

Thermal Analysis. The hyperbranched polyesters and the macromonomers are all semicrystalline as measured by DSC, Table 2. The melting points and the transition enthalpies for the AB_2 macromonomers show markedly different values depending on the molecular weight. The same trend is seen for the hyperbranched polyesters **poly(4-8, 4-12, 4-20, and 4-50)** which indicates that the transition temperatures are strongly dependent on the DP of the macromonomer. In addition, the melting transitions of the three **poly(4-8)** moieties indicate that they are independent of the total molecular weight of the hyperbranched polymers. From these results, it can be concluded that the thermal behavior of the hyperbranched polymers are mainly dependent on the DP of the macromonomer.

Conclusion

Novel hyperbranched aliphatic polyesters have been developed. The hyperbranched polyesters were synthesized from well-defined AB_2 macromonomers obtained through a well-controlled ring opening polymerization. This novel synthetic strategy allows the preparation of hyperbranched polymers with significant variation in the architecture by simply altering the degree of polymerization or replacing ϵ-caprolactone with an alternative monomer. The DP of the macromonomer was found to have a large impact on the hyperbranched polymers thermal behavior. Hyperbranched polyesters having properties of thermoplastic elastomers should be possible through copolymerization of macromonomers of ϵ-caprolactone and for example 1,5-dioxepan-2-one.[10c]

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