Hyperbranched Poly(ϵ-caprolactone) Derived from Intrinsically Branched AB$_2$ Macromonomers

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Received February 2, 1998
Revised Manuscript Received May 4, 1998

Macromolecular engineering of complex molecular architectures through the preparation of block copolymers or through the introduction of controlled branching has assumed an increasingly important theme in polymer science. The interest is driven by the possible unique mechanical, rheological, and compatibility properties of these nanoscopically tailored materials. Dendrimers provide the ultimate example of the effects of branching on the physical and solution properties of macromolecules,[1] while hyperbranched polymers are less perfect elaborations of such three-dimensional structures.[2] Hyperbranched macromolecules are prepared in a single-step polymerization from AB$_x$ monomers, and polymers with irregular branching and broad molecular weight distributions are obtained.[2] Noteworthy examples of hyperbranched polyesters include those derived from 3,5-dihydroxybenzoic acid[2b] and 2,2-bis(hydroxymethyl) propionic acid (bis-MPA).[2f]

One limitation with hyperbranched macromolecules is that these highly branched molecules are densely packed and do not readily entangle which produces materials with brittle mechanical properties. Several synthetic strategies have been devised to avoid these problems, while maintaining the desired spherical symmetry and high functionality. The synthetic route used by Tomalia et al.[3] utilizes successive grafting of reactive polymer chains to form dendritic graft polymers. The resulting macromolecules, termed “comb-burst,” are prepared from functional linear chains. Tomalia 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.[4] used this stepwise approach in the synthesis of comb-burst polystyrene derivatives. Alternatively, Hawker and Fréchet have reported a tandem approach to graft and dendritic graft copolymers based on “living” free radical polymerizations.[5] In each of the above syntheses, a reiterative approach is used to prepare the dendritic graft or “comb-burst” polymer.

Recently, Hawker et al.[6] reported the first example of a hyperbranched equivalent to a “comb-burst” molecular architecture by a single-step polymerization of AB$_x$ macromonomers. A series of hyperbranched poly(ethylene glycol) derivatives were prepared containing linear chains with 3,5-dioxybenzoate branching units. We have recently reported the synthesis and self-polymerization of AB$_2$ macromonomers derived from aliphatic polyesters (Scheme 1).[7] The α-carboxylic-ω-dihydroxy functional poly(ϵ-caprolactone)s were prepared by living polymerization methods. Benzyl alcohol was used as the initiator in the presence of Al(O^{i}Pr)$_3$. Al(O^{i}Pr)$_3$ undergoes rapid exchange reactions with alcohols, and the liberated 2-propanol can be selectively removed, leaving benzyl alkoxide as the sole initiating species. Hydrolysis of the active chain end produces a ω-hydroxy functional end group. These polymers were functionalized with a protected bis-MPA at the ω-hydroxy chain end. The initiating benzyl group and the benzylidene protecting groups were concurrently removed by catalytic hydrogenolysis to give the desired ω-carboxylic acid−ω-dihydroxy-functional poly(ϵ-caprolactone). Polymerization of the AB$_2$ macromonomer was accomplished using a mild room-temperature esterification procedure (Scheme 1). This novel synthetic approach produces hyperbranched polymers with significant versatility in the monomer type, the size of the macromonomer and the molecular weight. High molecular weight polyesters were obtained with an average degree of branching of 0.37.[7a] This branching value is lower than that reported for hyperbranched polymers from bis-MPA 0.46−0.50.[7a,8,10] In principle, a living polymerization of an AB$_2$ monomer could lead to a perfect dendritic structure. However, this is never encountered. In the case of the bis-MPA or the bis-MPA functional polyesters, the initial reactivity of the two hydroxyl groups is essentially identical. However, the reactivity changes once one of the hydroxyl groups react to form the polymer-forming ester linkage. This results from steric constraints in the proximity of the unreacted hydroxyl group, lowering its reactivity. Likewise, the degree of branching in the hyperbranched polyesters prepared from the AB$_2$ macromonomers is lower than in the hyperbranched polyesters prepared from pure bis-MPA.

In this article we wish to report an alternative aliphatic AB$_2$ macromonomer in which the branching point is predefined and the reactive functionalities are less sterically hindered. We have recently reported the ring-opening polymerization of ϵ-caprolactone from derivatives of bis-MPA.[9] The polymerization of ϵ-caprolactone from the multifunctional initiators in the presence of a catalytic amount of Sn(Oct)$_2$ produced polymers with accurate control of molecular weight, molecular weight distribution and end-group functionality. After hydrolytic deactivation of the active alkoxide-growing species, multiarm ω-hydroxy poly(ϵ-caprolactone) semitelechelic chains were quantitatively and selectively recovered (Scheme 2). The acid functionality in the initiating bis-MPA derivatives was protected as a benzyl ester to allow polymerization. After polymerization, the benzyl ester can be readily removed by catalytic hydrogenolysis to give a novel AB$_2$ macromonomer capable of self-polymerization. In this approach, the polymer-forming functionalities are sufficiently separated such that the transformation of one does not effect the reactivity of the other. Furthermore, the degree of branching is inherently higher than the previously described route to hyperbranched polyesters, since the first branching point is predefined in the AB$_2$ macromonomer and is perfectly dendritic. This strategy is somewhat similar to that used by Malmström and coworkers[10] where they prepared and polymerized an AB$_4$ monomer derived from bis-MPA. The degree of branch-

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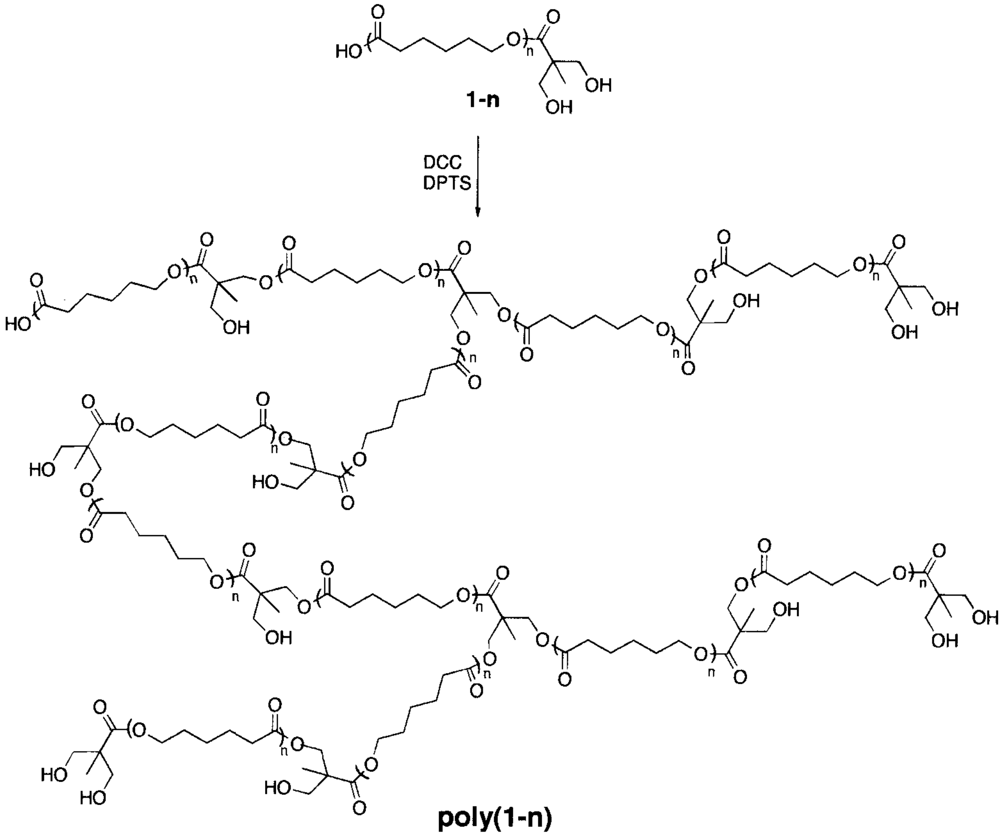
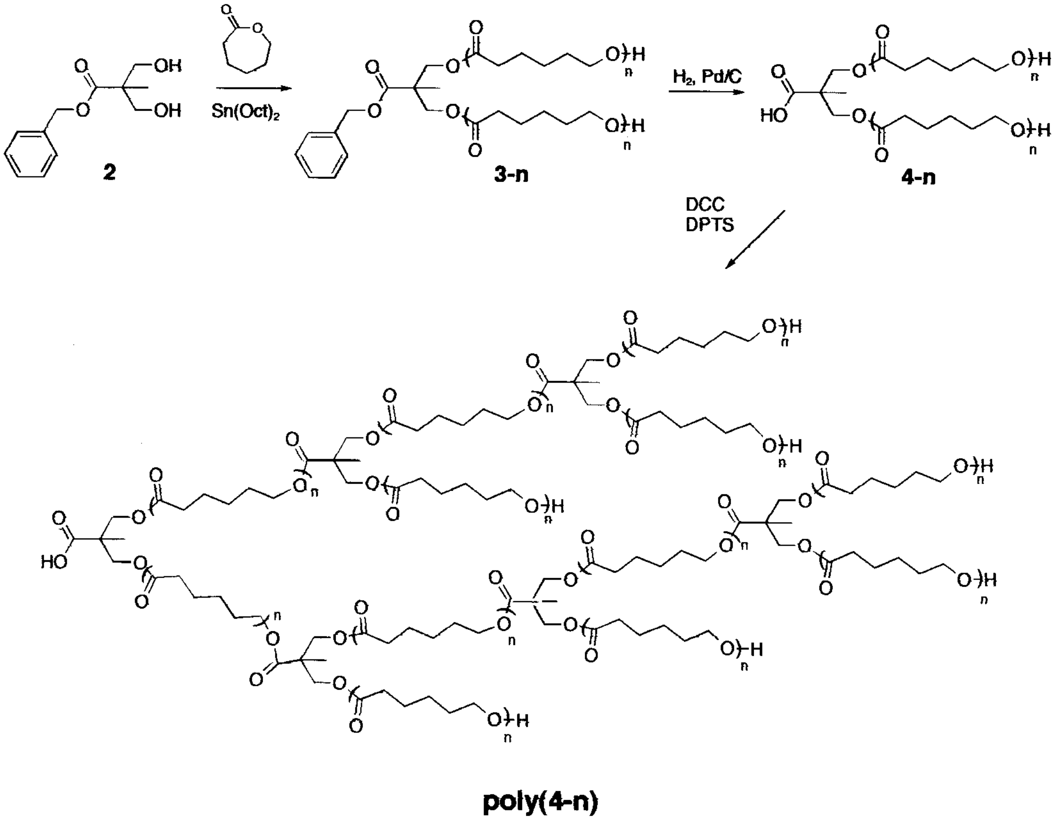
S0024-9297(98)00151-X CCC: $15.00

Scheme 1



Scheme 2



ing was found to be higher since dendritic units were predefined in the monomer. In this article, we will discuss the self-polymerization and characterization of the new AB$_2$ macromonomers.

In this study, ε-caprolactone was initiated from the benzyl ester protected bis-MPA, **2**, producing two arm polymers of various molecular weights **(3-*n*)**.[11] The polymerizations were carried out in bulk conditions at

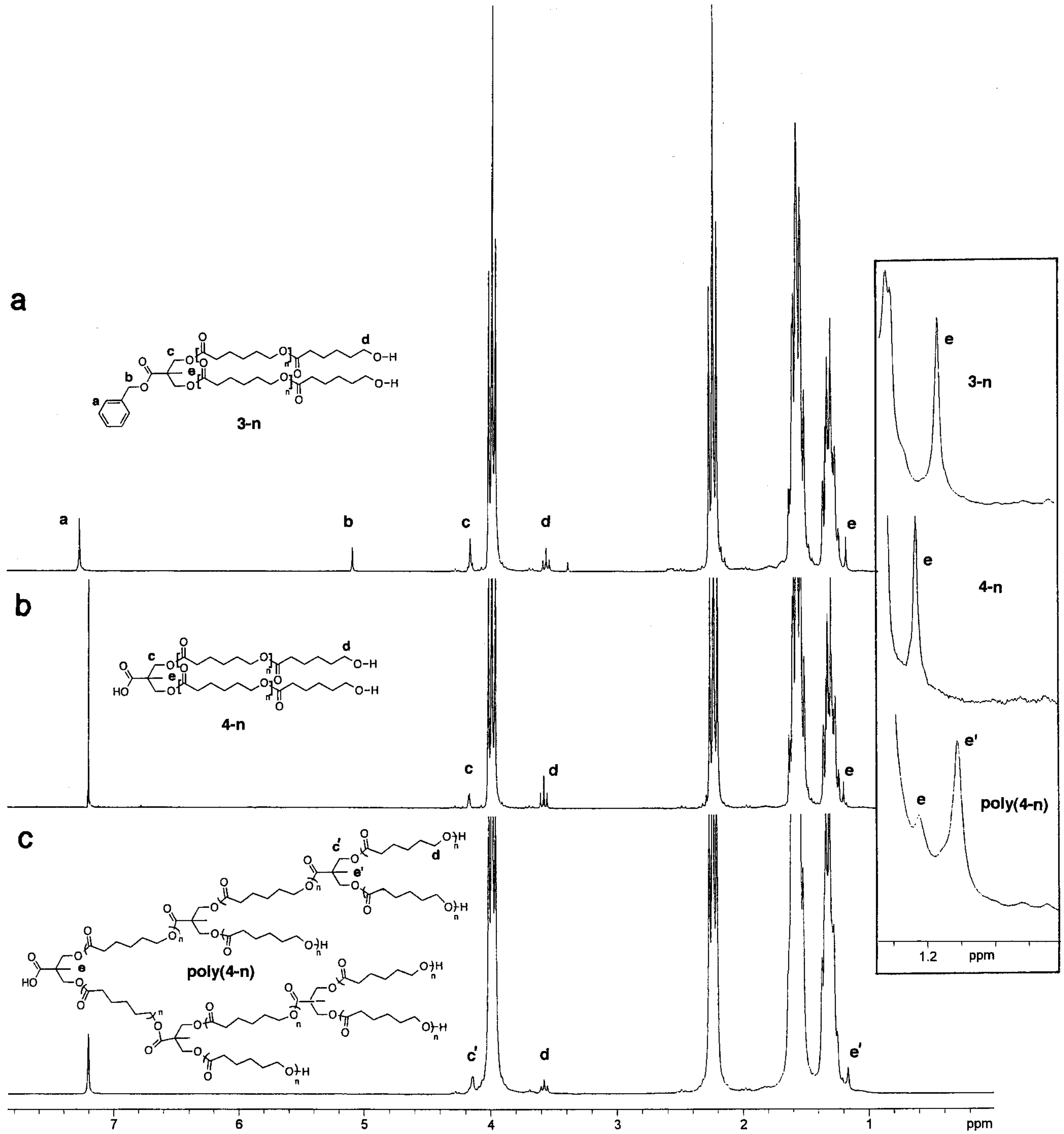


Figure 1. ^{1}H NMR spectra of (a) **3-*n***, (b) **4-*n***, and (c) **poly(4-*n*)**.

Table 1. Characteristics of Protected AB$_2$ Macromonomers

sample entry	target M_n	^{1}H NMR M_n	GPC M_w	GPC M_n	$\langle M_w\rangle/\langle M_n\rangle$
3-20	4 000	4 400	11 700	10 000	1.17
3-30	6 000	6 200	16 500	14 100	1.17
3-70	15 000	15 000	36 600	33 000	1.11

100 °C. Quantitative monomer consumption was observed after 20 h. The characteristics of the protected macromonomers, **3-*n***, are shown in Table 1, where **n** is the nominal degree of polymerization of each of the macromonomers. Accurate control of molecular weight, as predicted from the monomer-to-initiator ratio, and narrow polydispersities were demonstrated (Table 1).

Shown in Figure 1a is the ^{1}H NMR spectra of polymer **3-*n***.[12] The peaks denoted as c and e are the $-CH_2$- and $-CH_3$ groups of the bis-MPA initiator which exist as singlets, as previously reported.[9] The benzyl groups on the initiator were removed from the polymers by catalytic hydrogenolysis (Scheme 2).[13] This simple and mild transformation performed under H_2 atmosphere over Pd/C generated the requisite acid functionality and the α-carboxylic-ω-hydroxy AB$_2$ macromonomers, **4-*n***. Shown in Figure 1b is the ^{1}H NMR spectrum of **4-*n*** after deprotection, which clearly shows that the aromatic (7.31 ppm) and the benzylic (5.07 ppm) protons have disappeared during the deprotection reaction. Likewise, the peak denoted as e ($-CH_3$) is shifted downfield as

Table 2. Characteristics of Hyperbranched Polyesters

sample entry	macromonomer entry	GPC M_w	GPC M_n	$\langle M_w\rangle/\langle M_n\rangle$	DP[a]
poly(4-20)	4-20	80 700	37 000	2.18	19.8
poly(4-30)	4-30	55 300	35 000	1.58	8.0
poly(4-30)	4-30	87 900	47 000	1.87	9.2
poly(4-30)	4-30	98 700	52 500	1.88	15.2
poly(4-70)	4-70	68 100	52 000	1.31	1.9
poly(4-70)	4-70	139 000	93 000	1.49	5.0

[a] The DP values are obtained from ^{1}H NMR.

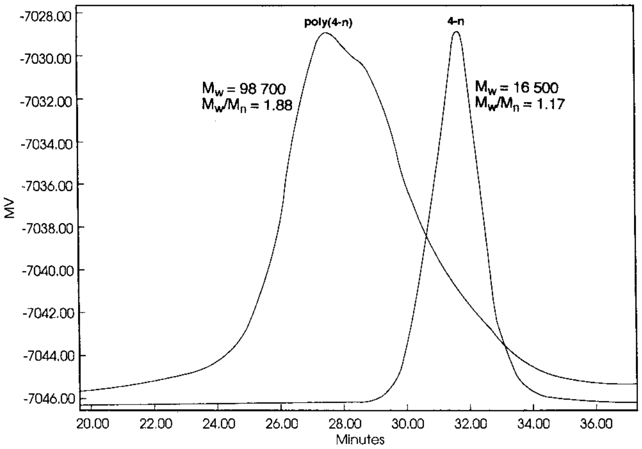


Figure 2. SEC traces for **4-*n*** and **poly(4-*n*)**.

can be seen in the expanded window of Figure 1. SEC measurements of **4-*n*** show no change of molecular weights or the molecular weight distributions before and after deprotection.

The polymerizations of the AB_2 macromonomers were carried out in CH_2Cl_2 using dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino)pyridinum 4-toluenesulfonate (DPTS) as reagents (Scheme 2).[14] The general characteristics of these hyperbranched poly(ϵ-caprolactone)s are shown in Table 2. Clearly, a significant increase in molecular weight (M_w) is observed and the molecular weight distribution broadens, as expected with a condensation polymerization. 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, indicating that most of the macromonomer contamination was selectively removed during the precipitation, Figure 2. The ^{1}H NMR spectra of one of these hyperbranched polymers (Figure 1c) shows a distinct decrease in the $-CH_2OH$ protons (peak d) and a shift of the $-CH_3$ protons in the bis-MPA from e to e'. This can be readily seen in the expanded region of the ^{1}H NMR (Figure 1). The remaining e peak arises from the focal point and from possible macromonomer contamination.

The ^{1}H NMR spectra of **4-*n*** and **poly(4-*n*)** were used to calculate the average degree of polymerization (DP) of the hyperbranched polymers. The DP was calculated from the following equation:

$$\mathrm{DP} = \frac{x}{2n - x} \qquad (1)$$

Here, x and n are the ratios of the integrated area of the peak corresponding to one of the repeating units of poly(ϵ-caprolactone) ($\delta = 2.15$, Figure 1) to the integrated area of the peak originating from the chain ends (d, Figure 1) for the hyperbranched polymer **poly(4-*n*)** and the macromonomer **4-*n***, respectively. This equation is related to branching theories discussed by Flory[15a] and Stockmayer.[15b] The results, listed in Table 2, show that it is possible to obtain an average DP of between 10 and 20 for lower molecular weight macromonomers. These values show a clear trend and are larger than the data from SEC, which indicate that the structures are highly branched and that the hydrodynamic volume of these polymers is not a linear relationship to the molecular weight. The SEC chromatogram for the two **poly(4-70)** display a bimodal distribution due to large macromonomer contamination, and hence these samples have low DPs and low molecular weight distributions. The reason is that the concentration of functional groups in this macromonomer is too low to react properly. In addition, they are too large to be removed by precipitation. Therefore, it can be concluded that this technique is optimal for the lower molecular weight macromonomers (M_n < 6000 g/mol) since they react faster and possible macromonomer contamination can be readily removed in the precipitation of these hyperbranched polymers.

Figure 3 shows the expanded $-CH_3$ region of the ^{1}H NMR spectra of the novel hyperbranched polymer, **poly(4-*n*)**, the previously reported hyperbranched poly(ϵ-caprolactone), **poly(1-*n*)**, with a degree of branching of 0.37, and a third class of branched poly(ϵ-caprolactone), **G-2(12 OH),** denoted as dendrimer-like star polymer.[16] The first polymer, **poly(1-*n*)**, is comprised of linear (denoted as peak b), terminal (denoted as peak c) and dendritic (denoted as peak a) bis-MPA units. The last polymer, **G-2(12 OH)**, was synthesized by a time-consuming divergent growth approach and contains only dendritic (denoted as peak a, Figure 3c) units of bis-MPA.[16] The bis-MPA units from the core are hidden underneath the large peak originating from one of the repeating units of the poly(ϵ-caprolactone). This polymer with controlled branching has a high molecular weight (M_n = 42 300) as measured by ^{1}H NMR, a narrow polydispersity (1.16), and 12 arms and end groups. A comparison of the three spectra shows that the spectrum of **poly(4-*n*)** resembles the spectrum of the dendrimer-like star poly(ϵ-caprolactone). That is, both polymers are mainly comprised of dendritic **poly(4-*n*)** bis-MPA units. In addition, the spectrum of **poly(4-*n*)** displays a small resonance at 1.24 ppm which arises from the acid-functional end group or focal point of the polymer and possible macromonomer contamination. Since the branching in the macromonomer **4-*n*** is predefined, it is no surprise that the spectra are similar. However, the ^{1}H NMR spectra manifest that **poly(4-*n*)** is dramatically different from **poly(1-*n*)** which is mainly comprised of linear (peak b) and terminal (peak c) bis-MPA units, characteristic of an irregular branched structure. In addition, the macromonomer is designed in such a way that the propagation should be independent of the transformation of the other alcohol. That the propagation is more statistically controlled in **poly(4-*n*)** than in **poly(1-*n*)** is not experimentally verified, however, as an example a "linear" trimer of **4** have four remaining hydroxyl groups which all have the same chemical environment, indicating that further propagation should be purely statistically controlled. This is completely different than a "linear" trimer of **1** where two of the remaining alcohols are terminal and two are immediately connected to the middle of the

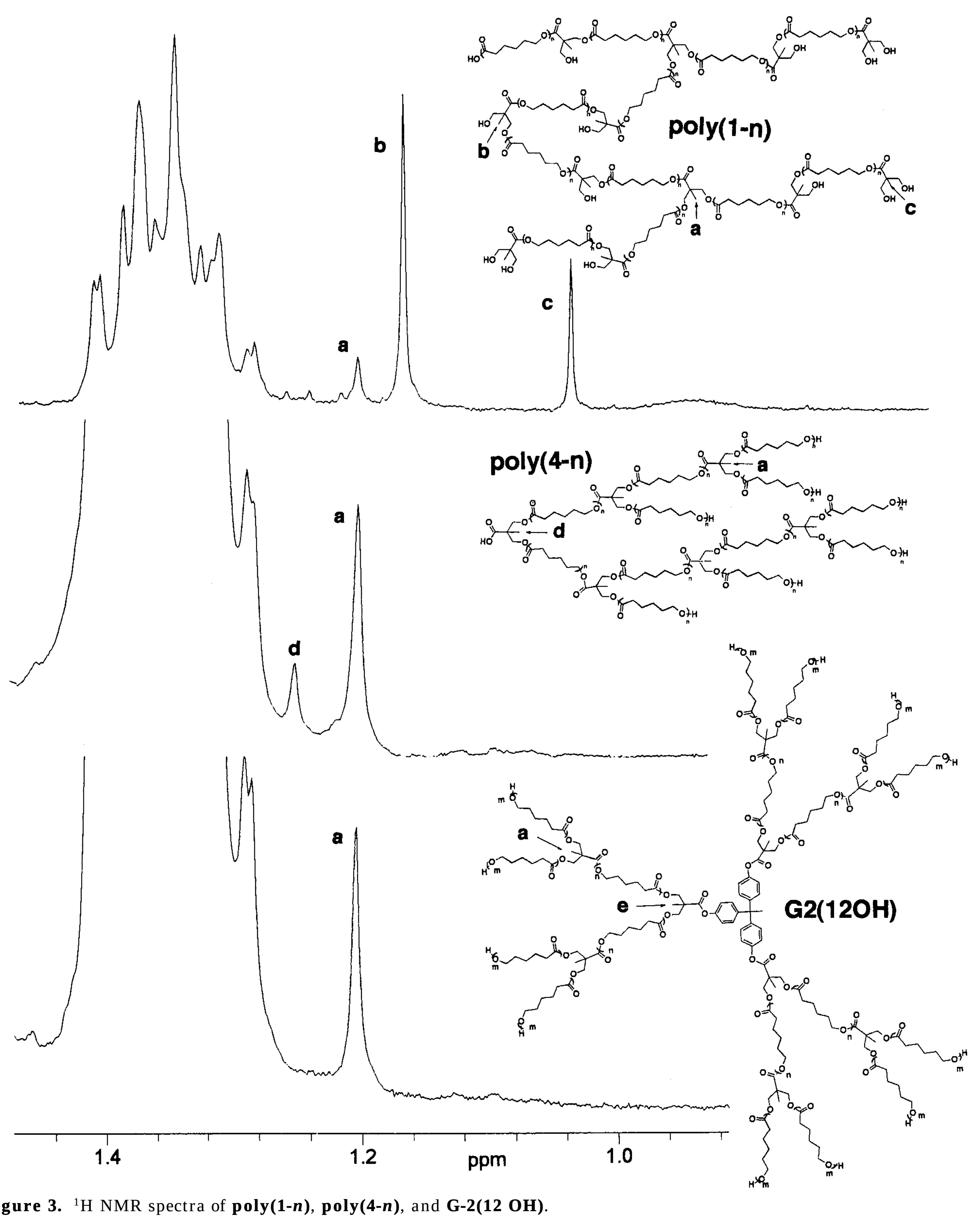


Figure 3. ^{1}H NMR spectra of **poly(1-*n*)**, **poly(4-*n*)**, and **G-2(12 OH)**.

polymer backbone. These two hydroxyl groups are less nucleophilic due to restricted mobility, and the propagation is in this case no longer statistically controlled. As mentioned, this is not experimentally verified and should only be true when the DP of the macromonomer is sufficiently high. The combined data from ^{1}H NMR and SEC suggest that the new hyperbranched polyesters have a highly branched structure which is analogous to that of the rigorously synthesized dendrimer-like star polymers. However, it cannot be excluded that some of the hyperbranched polymers consisting of only a few macromonomers have a more “linear” structure where all the second arms of the macromonomers are pending, analogous to a graft polymer. However, this type of structure seems to be statistically unlikely when the degree of polymerization is relatively high.

In conclusion, a new route to hyperbranched poly(ϵ-caprolactone) has been demonstrated. The novel approach of using a two armed macromonomer with a predefined branching point yields a statistically hyperbranched poly(ϵ-caprolactone). ^{1}H NMR analysis of the hyperbranched polymers showed a branching pattern which is similar to those polymers prepared by a tedious stepwise divergent growth process. In addition, this novel synthetic approach allows the hyperbranched polymers to be produced with significant versatility, including variation of the monomer type and the size of the macromonomer. These variations could generate hyperbranched polymers with a different degree of crystallinity as well as hyperbranched block copolymers.

Acknowledgment. J.L.H and M.T. gratefully acknowledge the NSF funded Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA) under Award No. DMR-9400354 for financial support. M.T. also thanks the Frans Georg and Gull Liljenroths Foundation and the Axel Wenner-Gren Foundation for financial support.

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(11) The polymerization of ϵ-caprolactone was initiated with bis-MPA using a catalytic amount of Sn(Oct)$_2$. The polymerizations were carried out in the melt at 110 °C (20 h). The polymers were then dissolved in THF and precipitated into cold methanol. The complete polymerization procedure and the synthesis of the initiator **2** are reported elsewhere.[17]

(12) ^{1}H NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer. The number average molecular weights of the macromonomers were calculated from the intensity ratios of the $-OCH_2$- methylene proton signals ($\delta = 2.21$) and the $-CH_2OH$ methylene proton signals ($\delta = 3.60$) in the ^{1}H NMR spectra. Size exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5 and 10^6) were used with THF as solvent.

(13) A general procedure for the preparation of AB$_2$ functional α-carboxylic-ω-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 evacuated and put under H$_2$ (g) atmosphere. The reaction was stopped after 24 h, the Pd/C was filtered off and the clear solution was precipitated into cold methanol. The obtained macromonomer was a white crystalline powder. Yield: 3.00 g.

(14) A general procedure for the 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 CH_2Cl_2 and then DCC (0.10 g, 0.50 mmol) were added. After 48 h the reaction mixture was precipitated into methanol and then filtered to yield 0.87 g (87%) of hyperbranched polymer **poly(4-*n*)**.

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MA980151A