# Hyperbranched Aliphatic Polyesters

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ABSTRACT: Hyperbranched, aliphatic polyesters of theoretically calculated molar masses 1200−44 300 were synthesized in the molten state from 2,2-bis(hydroxymethyl)propionic acid (repeating unit of $AB_x$ type) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (core molecule) using acid catalysis. The synthesis procedure was a pseudo-one-step reaction where stoichiometric amounts corresponding to each generation were added successively. The resulting polymers were glassy, slightly yellow solids at room temperature with hydroxyl groups as terminal groups. The degree of branching of the polyesters was determined with the help of model compounds using $^{13}C$-NMR and was found to be near 80%. The material exhibited good thermal stability as analyzed with TGA in a nitrogen atmosphere. Glass transition temperatures were determined using DSC and were found to be about 40 °C and to be relatively insensitive to variations in molar mass.

## Introduction

The field of nonlinear polymers such as hyperbranched or dendritic (dendritic, Greek = treelike) macromolecules has received considerable attention during recent years. A dendritic structure consists of a core molecule with two or more functional groups surrounded by several layers of repeating units which all contain one or more branch points ($AB_x$ type). Each layer is called a generation. A highly branched molecule is achieved even at quite a low molar mass, as each repeating unit increases the branching of the system. A low-generation molecule is to be regarded as linear or star-branched as far as its molecular shape is concerned. As the number of generations increase, it is believed to form a three-dimensional sphere if undistorted by the surrounding. This has been shown with energy-minimized computational molecular modeling[1] and also with Monte-Carlo simulations.[2] The generation at which the transformation to a spherical shape occurs is considered to be mainly dependent on the segmental mobility and geometry of the repeating unit. Due to their specific architecture, dendritic molecules are supposed to exhibit properties different from those of linear polymers of the same molar mass. The highly branched structure is also believed to introduce new or enhanced properties if mixed with commodity polymers.[3] Extensive reviews on dendrimers have been prepared by Tomalia *et al.*[1] and by Newkome *et al.*[4]

Dendritic macromolecules can be synthesized through convergent or divergent growth. Convergent growth starts at what will become the periphery of the final macromolecule and proceeds "inward". The last step is the attachment of the branched arms (=dendrons) to a polyfunctional central core. Divergent growth starts from a polyfunctional core and proceeds "outward". Regardless of which route is chosen for the dendrimer synthesis many protection/deprotection steps with extensive intermediate purification are needed. This makes dendritic polymers expensive and difficult to produce on a large scale.

If $AB_x$-type monomers are polymerized directly as first discussed theoretically by Flory in 1952[5] without full control over the growth process, the final product will be hyperbranched. A hyperbranched material contains a mixture of linearly and fully branched $AB_x$ repeating units and is supposed to exhibit properties resembling those of dendritic ones.[6] To be able to cope with the increasing industrial interest in highly branched materials, it seems that hyperbranched polymers might be a good alternative to dendrimers, as they can be produced on a large scale at a reasonable cost.

In recent years, several authors have published papers on hyperbranched polymers, using, e.g., 3,5-dihydroxybenzoic acid,[7,8] 3,5-diaminobenzoic acid,[9] 3,5-dihydroxybenzyl bromide,[10] 3,5-dihydroxybenzyl alcohol,[11] and 3,5-dibromophenylboronic acid.[12] Most of these studies have dealt with aromatic structures[13,14] in the absence of a certain core molecule.

In this paper, we present a new hyperbranched, aliphatic system based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) as an $AB_x$ monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) as a core moiety. The synthetic procedure is an esterification performed in the bulk using an acid catalyst and involves no purification steps. This facilitates large scale production. A similar system used in coating applications has already been reported.[15,16] Hyperbranched polyesters based on the same structure have been characterized by dielectric spectroscopy[17] in order to study the segmental mobility and thermal transitions. The polyesters have also been studied with respect to their rheological and mechanical properties.[18,19]

## Experimental Section

**General Directions.** Infrared spectra were recorded on a Perkin-Elmer 1725 infrared Fourier transform spectrometer (FTIR) as thin films using sodium chloride plates. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7, calibrated according to standard procedures, using a heating/cooling rate of 10 K $min^{-1}$. The glass transition temperature ($T_g$) was determined as the inflexion point of the curve showing heat capacity as a function of temperature (second heating). Thermogravimetric analysis (TGA) was made on a Perkin-Elmer TGA-7 using a heating rate of 10 K $min^{-1}$ in nitrogen. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 250 MHz or a Bruker 400 MHz using $CDCl_3$ or acetone-$d_6$ as a solvent and using the solvent signal as reference. Integrals in the $^{13}C$ spectra were obtained using the INVGATE experiment (D1 = 10 s) where the NOE effect is suppressed. Size exclusion chromatography (SEC) was performed on a Waters SEC system equipped with a WISP 710B automated injector and a Waters 410 differential refrac-

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**Table 1. Theoretical and Experimentally Found Values for the Hyperbranched Aliphatic Polyesters**

| polymer no. | molar ratio TMP/bis-MPA | theor gen | theor molar mass (g/mol) | SEC[a] $M_w$ (g/mol) | SEC[a] $M_n$ (g/mol) | SEC[a] $M_w/M_n$ | degree of branching (DB, %) | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|---|
| **5** | 1/9 | 2 | 1 179 | 1903 | 1400 | 1.36 | 96 | |
| **6** | 1/21 | 3 | 2 573 | 2616 | 1881 | 1.39 | 92 | 34.0 |
| **7** | 1/45 | 4 | 5 359 | 4472 | 3052 | 1.47 | 87 | 37.0 |
| **8** | 1/93 | 5 | 10 933 | 6905 | 4274 | 1.62 | 83 | 41.5 |
| **9** | 1/189 | 6 | 22 080 | 8545 | 4565 | 1.87 | 83 | 40.5 |
| **10** | 1/381 | 7 | 44 374 | 10765 | 5598 | 1.92 | 83 | 40.3 |

[a] As calibrated against linear polystyrene standards with low polydispersity index.

tometer. The columns used were $\mu$-Styragel with pore sizes of 500, $10^5$, $10^4$, $10^3$, and 100 Å, and the solvent was THF. Linear polystyrene standards with low polydispersity indices were used for calibration.

2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) were supplied from Perstorp Polyols AB, Sweden. All other chemicals were purchased from Aldrich and were used as received. All solvents were distilled prior to use.

**Synthesis of Model Compounds. Trimethylsilyl 2,2-Bis[(trimethylsiloxy)methyl]propanoate (1).** Hexamethyldisilazane (HMDS) (29.82 mmol, 4.81 g), bis-MPA (14.91 mmol, 2.0 g), and methylene chloride (6 mL) were mixed in a two-necked flask equipped with an argon inlet. The mixture was allowed to react for 24 h at 40 °C. IR spectroscopy verified that no carbonyl groups remained unreacted. The solvent and the excess of HMDS were removed on a rotary evaporator. $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) 3.54–3.68 (q, 4H, $-CH_2-$), 1.08 (s, 3H, $-CH_3$), 0.29 (s, 9H, $(CH_3)_3-Si-OOC-$), 0.08 (s, 18H, $(CH_3)_3-Si-O-$). FTIR (NaCl): 2959, 1714, 1253 cm$^{-1}$.

**Ethyl 2,2-Bis(methylol)propanoate (2).** To 5.0 g of **1** were added thionyl chloride (14.26 mmol, 1.69 g) and methylene chloride. After 3 h, FTIR showed the existence of three different carbonyl groups, and ethanol (excess) was added to the reaction mixture which was left for another hour. After purification with flash chromatography (silica gel, ethyl acetate/hexane), **2** was obtained. $^1$H-NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 4.17–4.26 (q, 2H, $-COO-CH_2-$), 3.66–3.93 (q, 4H, $-CH_2-OH$), ≈2.95 (m, 2H, $-CH_2-OH$), 1.27–1.33 (t, 3H, $CH_3-CH_2-$), 1.06 (s, 3H, $CH_3-C-$). $^{13}$C-NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 175.64 (1C, $-COO-$), 65.72 (1C, $-COO-CH_2-$), 60.57 (2C, $CH_2-OH$), 50.65 (1C, $-C-$), 17.30 (1C, $CH_2-CH_3$), 14.36 (1C, $-CH_3$).

**Ethyl 2-Methylol-2-(acetoxymethyl)propanoate (3) and Ethyl 2,2-Bis(acetoxymethyl)propanoate (4).** Model compound **1** (0.5 g, 3.08 mmol) and methylene chloride were added to a two-necked flask equipped with an argon inlet. Acetyl chloride (3.39 mmol, 0.27 g) in methylene chloride was added dropwise. The mixture was left to react overnight. The solvent was evaporated and the crude products were purified and separated using liquid chromatography (silica gel, hexane/ethyl acetate, standard gradient).

**3:** $^1$H-NMR (250 MHz, acetone-$d_6$) $\delta$ (ppm) 4.18–4.35 (m, 2H, $-CH_2-OOC-$), 4.17–4.24 (m, 2H, $-CH_2-CH_3$), 3.66–3.69 (d, 2H, $-CH_2-OH$), 2.08 (s, 3H, $CH_3-COO-$), 1.24–1.31 (t, 3H, $CH_3-CH_2-$), 1.18 (s, 3H, $CH_3-C$); $^{13}$C-NMR (400 MHz, acetone-$d_6$) $\delta$ (ppm) 174.36 (1C, $-COO-CH_2-$), 170.79 (1C, $CH_3-COO-$), 66.29 (1C, $-CH_2-CH_3$), 65.14 (1C, $-CH_2-OOC-$), 60.95 (1C, $-CH_2-OH$), 48.85 (1C, $-C-$), 20.55 (1C, $CH_3-COO-$), 17.82 (1C, $CH_3-CH_2-$), 14.35 (1C, $CH_3-C-$).

**4:** $^1$H-NMR (250 MHz, acetone-$d_6$) $\delta$ (ppm) 4.14–4.21 (q, 2H, $-COO-CH_2CH_3$), 4.21 (s, 4H, $-CH_2-OOC-CH_3$), 2.02 (s, 6H, $CH_3-COO-$), 1.24 (s, 3H, $CH_3-C$), 1.12–1.28 (t, 2H, $-CH_2-CH_3$); $^{13}$C-NMR (400 MHz, acetone-$d_6$) $\delta$ (ppm) 173.1 (1C, $-COO-CH_2-$), 170.4 (2C, $CH_3-COO-$), 65.8 (2C, $-CH_2-OOC-$), 61.4 (1C, $-CH_2-CH_3$), 46.8 (1C, $-C-$), 20.4 (2C, $CH_3-COO-$), 17.8 (1C, $-CH_2-CH_3$), 14.3 (1C, $CH_3-C-$).

**General Procedure for the Polycondensation of bis-MPA and TMP.** The different stoichiometric ratios between bis-MPA (repeating unit) and TMP (central core) used are presented in Table 1. A schematic representation of the synthesis of polyester no. **7** is outlined in Scheme 1. A mechanical stirrer was used instead of a magnetic bar for the synthesis of high-generation polymers because of the increasing viscosity of the polymer/monomer mixture. *p*-Toluenesulfonic acid (*p*-TSA) (0.5 wt %) based on bis-MPA was used in all reactions.

**Synthesis of Polyester 6.** Bis-MPA (50.0 mmol, 6.71 g), TMP (5.55 mmol, 0.745 g) (in stoichiometric correspondance to a perfect generation of second generation), and *p*-TSA (33.6 mg) were carefully mixed in a three-necked flask equipped with an argon inlet, a drying tube, and a stirrer. The flask was placed in an oil bath previously heated to 140 °C. The mixture was left to react under a stream of argon, removing the water formed during the reaction. After 2 h, the argon stream was turned off and the flask sealed and connected to a vacuum line (12 mbar, cooling trap) for 1 h. After the pressure was increased to atmospheric, bis-MPA corresponding to the third generation (66.7 mmol, 8.94 g) and *p*-TSA (44.8 mg) were added and the argon flow was started. After 2 h of reaction at normal pressure, vacuum was applied for 1 h before the reaction mixture was removed from the flask. FTIR (NaCl) showed no remaining carboxylic acid (1696 cm$^{-1}$, carbonyl) but only ester (1736 cm$^{-1}$, carbonyl).

All polyesters were synthesized according to this pseudo-one-step procedure.

## Results and Discussion

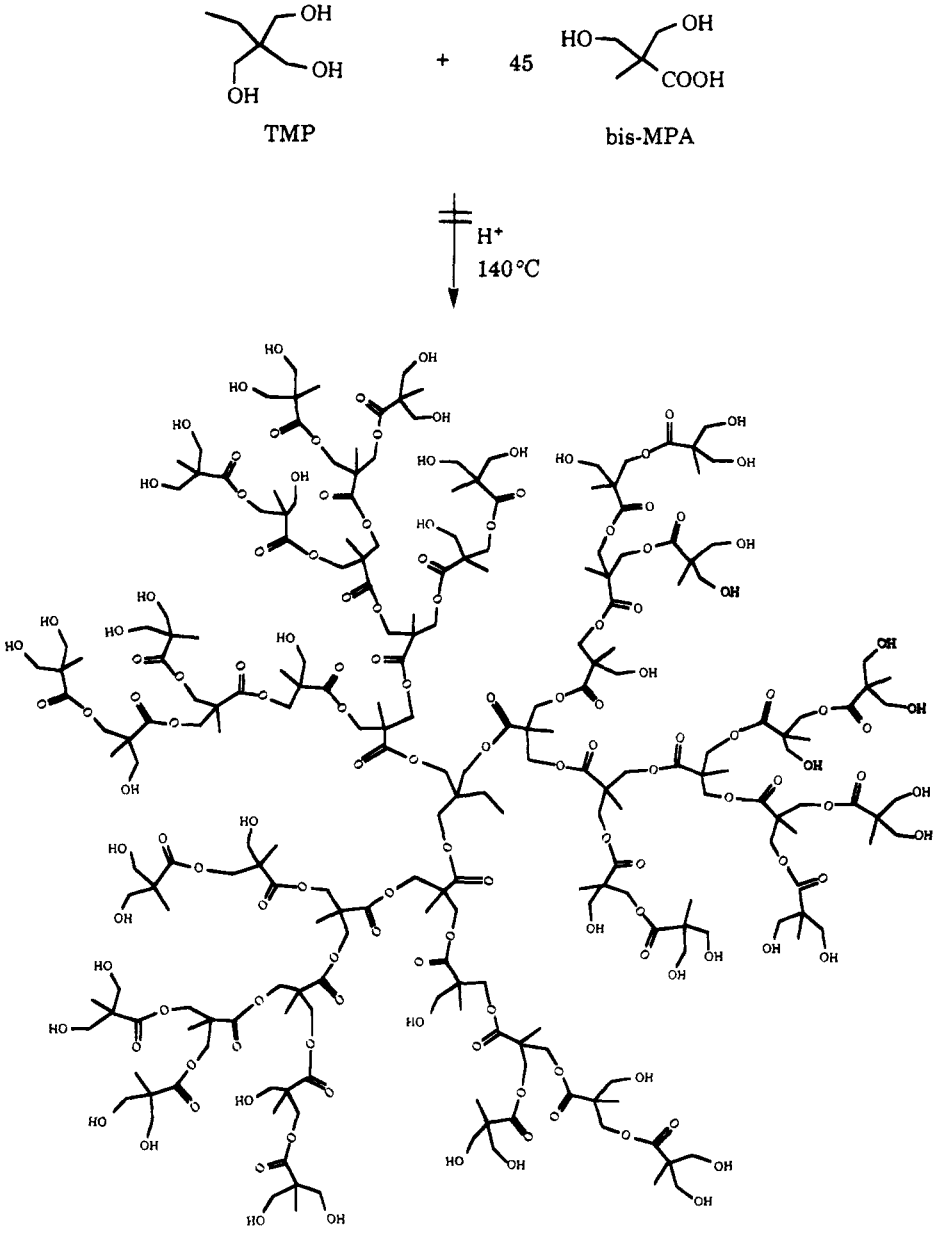
**Esterification Process.** The hyperbranched polyesters were synthesized according to common acid-catalyzed esterification procedures. The esterification reaction was carried out in bulk and driven toward high conversion as the water formed was removed continuously. Removal is essential to obtain high molar mass and was done with argon as the carrier gas at early stages of the polymerization and under reduced pressure as the condensation reached completion. In order to increase the probability that unreacted acid groups reacted with the hydroxy-functional hyperbranched skeleton and not with another free monomer, it was essential to keep the ratio of free bis-MPA to dendritic hydroxyl groups as low as possible. Therefore, bis-MPA was added in successive portions corresponding to the stoichometric amount for each generation; i.e. a pseudo-one-step procedure was used.

A relatively low esterification temperature, 140 °C, was chosen to suppress unwanted side reactions such as etherifications and trans-esterifications.

Common bimolecular acid-catalyzed hydrolysis of esters proceeds via a tetrahedral intermediate. If the carbonyl carbon were attached to a $R_3C$ group the transition state for the reaction would be very crowded and hence this is unlikely to occur. Acid-catalyzed hydrolysis is also possible via a unimolecular mechanism, but this occurs only in strongly ionizing solvents. The ester groups in these polyesters are attached to a quaternary carbon ($R_3C-$) which makes them much less susceptible to hydrolysis than linear polyesters.[20]

It is difficult to study the core in hyperbranched materials, as its percentage contribution to the final polymer rapidly decreases and soon becomes insignificant. We have not been able to assess the degree of

**Scheme 1. Two-Dimensional Theoretical Representation of the Synthesis of Hyperbranched Polymer No. 7 with a Degree of Branching about 80%**




conversion of the hydroxyl groups located on the central core of the molecule. When the same reaction was performed with no core molecule, the resulting polymer was very difficult to dissolve in any solvent, indicating that a high molar mass or cross-linked polymer was formed. This serves as indirect evidence of the importance of the core moiety.

**Molar Mass.** The architecture of hyperbranched and dendritic substances involves some characterization problems, mainly because many methods are based on calibration with linear polymer standards of known molar mass and polydispersity index. Dendritic or hyperbranched materials exhibit relationships between molar mass and hydrodynamic radius, $R_h$, or radius of gyration, $S$, different from those of their linear counterparts of the same molar mass. As $R_h$ is smaller for a branched polymer than for its linear counterpart of the same molar mass, it is expected that molar masses as determined with SEC, calibrated with, e.g., linear polystyrene standards, will be too low. Another problem is that, depending on how the hyperbranched molecule interacts with the solvent, it may occupy different volumes. Newkome *et al.*[21] have shown that the $R_h$ of carboxylic acid-terminated dendrimers in aqueous solution is strongly pH-dependent and may vary up to 50% merely by changing the pH of the solution. The hyperbranched polyesters reported in the present paper have been characterized by SEC using THF as solvent. The results are listed in Table 1. The experimentally determined $\bar{M}_n$ and $\bar{M}_w$ values expressed in relation to polystyrene standards differ pronouncedly from the theoretical values.

The polydispersity indices, Table 1, indicate a narrow distribution of hydrodynamic radius, but the radius of the hyperbranched polymer increases only moderately with increasing molar mass due to the specific architecture. The observed narrow distribution in molar mass may therefore be an artefact.

**Thermal Properties.** Glass transition temperatures, Table 1, were almost independent of theoretical molar mass. The increase in $T_g$ at lower generations is probably an effect of the skeleton buildup as the molar mass increases. These data were in accordance with earlier data of Kim and Beckerbauer.[22] The glass

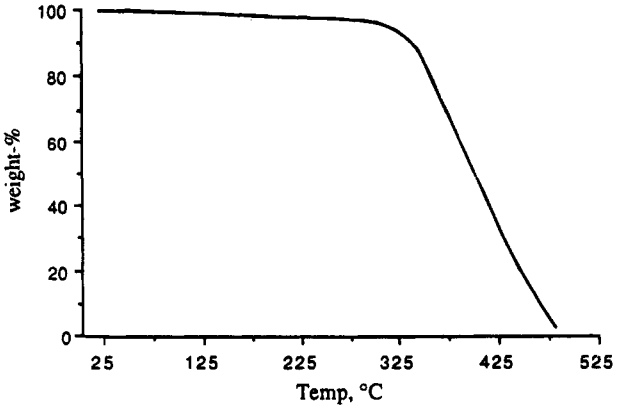



**Figure 1.** TGA thermogram of polymer no. **10** at a heating rate of 10 K $min^{-1}$ in nitrogen. The thermal degradation starts at 340 °C.

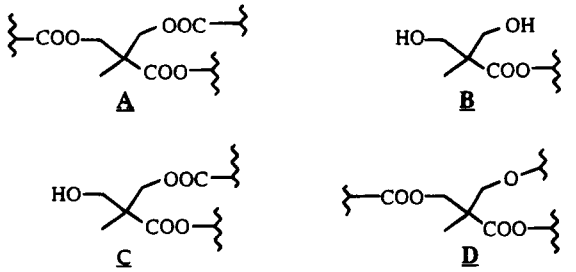



**Figure 2.** Possible repeating units in the hyperbranched polyesters.

transition temperature is strongly affected by the polarity of the terminal groups.[23] All polyesters in this study are hydroxyl-terminated and it is not surprising that the $T_g$ is unaffected by the theoretical molar mass as soon as the spherical, dendritic, shape has been formed. TGA analysis showed that these hyperbranched polyesters have good thermal stability, Figure 1. They lose about 3.5 wt % up to 340 °C due to loss of volatile compounds, before the thermal degradation starts.

**Degree of Branching and Characterization by NMR Spectroscopy.** The degree of branching (DB) of hyperbranched polymers is given by[8]

$$DB = \frac{\sum\text{dendritic units} + \sum\text{terminal units}}{\sum\text{dendritic units} + \sum\text{terminal units} + \sum\text{linear units}} \quad (1)$$

For an ideal dendritic substance, DB is equal to 1. A hyperbranched polymer takes DB values between 0 and 1. Fréchet *et al.*[8] used $^{13}$C-NMR and model compounds to quantify the different subunits appearing in their hyperbranched material based on 3,5-bis(trimethylsiloxy)benzoyl chloride, and it turned out that the same methodology was applicable to the hyperbranched polyesters here described.

The repeating unit, bis-MPA, in these hyperbranched polyesters can be incorporated into the polymer in three major ways, as shown in Figure 2, under the assumption that all acid groups have reacted. The fully esterified bis-MPA, A, is supposed to be the dendritic building block in the interior layers. Terminal units, B, at the outer layers have both hydroxyl groups on bis-MPA left unreacted. The linearly incorporated repeating unit, C, may be regarded as a defect as it does not contribute to branching. Bis-MPA can also be incorporated via an unwanted side reaction, yielding an ether, D. However, even though this reaction is a side reaction, it does not destroy the branching, as the repeating unit is still incorporated in the hyperbranched structure. In order to distinguish between these differently incorporated repeating units, low molar mass compounds, Figure 3, resembling the building blocks were synthesized. These were characterized by $^{13}$C-NMR, Figure 4, and their significant chemical shifts are reported in Table 2. The biggest difference in chemical shift was found for the quaternary carbons.

The $^{13}$C- and $^{1}$H-NMR spectra of polyester no. **10** dissolved in acetone-$d_6$ are illustrated in Figure 5. The $^{13}$C-NMR spectrum exhibits four distinct groups of peaks. The methylene peak found at 63–70 ppm

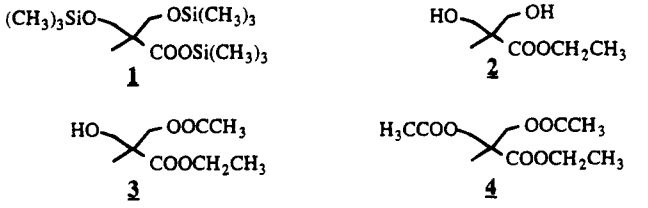



**Figure 3.** Compounds **1**–**4** synthesized and used as model compounds for determining the degree of branching.

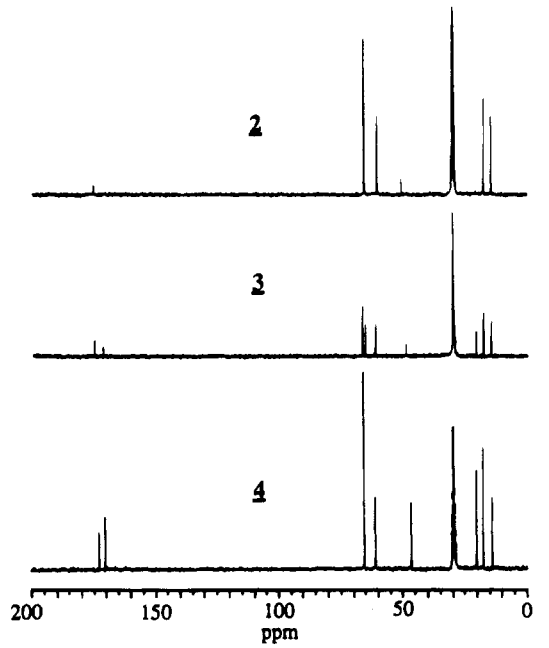



**Figure 4.** 400 MHz $^{13}$C-NMR spectra in acetone-$d_6$ of model compounds used for determining the degree of branching.

**Table 2. Chemical Shifts for Model Compounds in Acetone-$d_6$**

| Model Compound | $^{1}$H-NMR (ppm) | | $^{13}$C-NMR (ppm) | | |
|---|---|---|---|---|---|
| | $H_3C$-C< | -$CH_2$-< | -C< | -$CH_2$-< | $H_3C$-C< |
| 2 | 1.06 | 3.66-3.93 (q) | 50.65 | 60.57 | 14.36 |
| 3 | 1.18 | A) 3.66-3.69<br>B) 4.18-4.35 | 48.85 | A) 60.95<br>B) 65.13 | 14.35 |
| 4 | 1.12-1.28 | 4.21 | 46.80 | 65.82 | 14.34 |

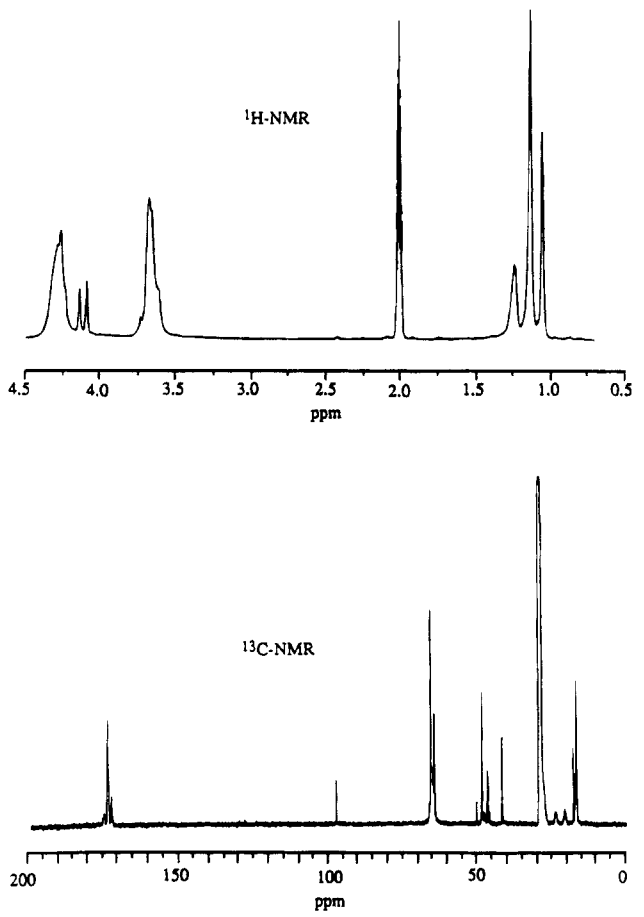



**Figure 5.** $^1$H-NMR (250 MHz) and $^{13}$C-NMR (400 MHz) of polymer no. **10** in acetone-$d_6$.

contains much fine structure due to the fact that carbons with the same chemical surrounding might be situated in different conformers. A distribution of relaxation times was revealed when this signal was studied with respect to spin–lattice ($T_1$) relaxation. Independently of where the methylene groups are situated, they will have the same number of surrounding $\beta$-protons and the differences in relaxation times will therefore depend only on the molecular motions. We have not yet been able to draw any conclusions from these measurements. The quaternary carbons give rise to signals in the region 42–52 ppm. Methyl groups are found at the lowest chemical shifts, around 20 ppm. The distinct peak at 98 ppm originates from methylene units adjacent to ether bonds. The branched structure gives rise to broad peaks in the $^1$H spectrum.

The spin–lattice relaxation time for the quaternary carbons was found to be approximately 3 s and the acquisition delay ($D_1$) was set to 10 s. With the help of these assignments it was possible to determine the content of each building block using a proton-decoupled $^{13}$C-NMR technique (INVGATE) suppressing the NOE-effect. A magnified spectrum of polymer no. **10** is shown in Figure 6. The degree of branching (eq 1) was calculated from the integral values found for building blocks *A*, *B*, and *C* and determined to be close to 0.8, Table 1, which shows that a highly branched structure is obtained; i.e. the kinetics of this reaction favors the formation of polyesters with a high degree of branching. The degree of branching seems to be almost independent of the stoichiometric ratio between the core molecule and the repeating unit.

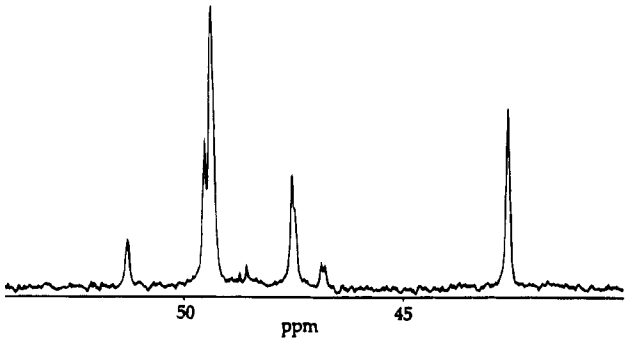



**Figure 6.** Magnification of the $^{13}$C-NMR spectrum of polymer no. **10** in acetone-$d_6$.

Hyperbranched systems, mostly based on aromatic building blocks without a core moiety, with a degree of branching of 50–70% are reported in the literature. Noteworthy, the hyperbranched aliphatic polyesters described herein exhibit a higher degree of branching than has hitherto been reported. There may be several reasons for this: The pseudo-one-step synthesis raises the probability for a monomer unit to react with the dendrimer skeleton instead of another free monomer over that in ordinary one-pot procedures. The reactivity of the remaining hydroxyl group on the repeating unit is almost the same as that of the first. This is a potential problem when using $AB_x$-substituted aromatics, due to changes in inductive effects and resonance. Aliphatic building blocks are more flexible than the corresponding aromatic ones. The steric hindrance is probably greater for an aromatic than for an aliphatic system.

## Conclusion

A new way of producing hyperbranched aliphatic polyesters has been presented, making it possible to produce larger quantities in an easy manner. Their degree of branching was found to be about 80%, indicating that the polymers are highly branched, although it has not been proven that all hydroxyl groups on the central core are consumed. The materials exhibit good thermal stability.

Our work with these hyperbranched polyesters is still in progress. Different aromatic and aliphatic cores and different terminal groups have been used in order to see how these affect the final properties. Work is also being carried out on perfect dendritic materials with the same chemical composition as the polyesters reported in this paper.

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