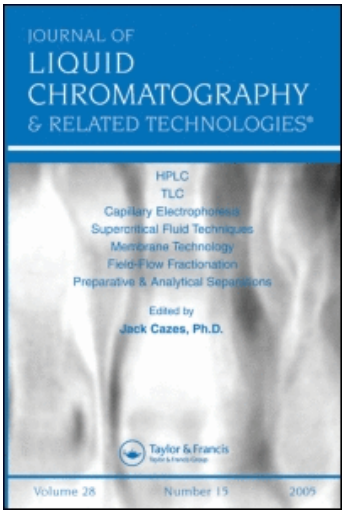

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László Garamszegi[a]; Tuan Q. Nguyen[b]; Christopher J. G. Plummer[a]; Jan-Anders E. Månson[a]
[a] Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland [b] Laboratoire de Polymères (LP), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

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Characterization of Hyperbranched Aliphatic Polyesters and Their Trimethylsilylated Derivatives by GPC-Viscometry

László Garamszegi,[1] Tuan Q. Nguyen,[2] Christopher J. G. Plummer,[1] and Jan-Anders E. Månson[1,*]

[1]Laboratoire de Technologie des Composites et Polymères (LTC) and [2]Laboratoire de Polymères (LP), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

ABSTRACT

Gel permeation chromatography (GPC) viscometry with universal calibration (UC) has been assessed as a means of characterizing the absolute molecular weight distribution of hydroxyl terminated hyperbranched aliphatic polyesters (HBPs) of aliphatic compounds. To generate a valid UC curve, it is necessary to work under conditions of strict size-exclusion separation. This requirement was met when both dimethyl formamide (DMF) and tetrahydrofuran (THF) were used as eluants. All the HBPs were highly soluble in DMF at room temperature, but its use may

*Correspondence: Jan-Anders E. Månson, Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; E-mail: jan-anders.manson@epfl.ch.

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necessitate special columns. Dissolution of the HBPs in THF, on the other hand, which is compatible with a variety of stationary phases, was relatively difficult, requiring prolonged heating above 50°C. As an alternative to direct characterization, the HBP hydroxyl end-groups were end-capped with trimethylsilane prior to the GPC measurements. Near quantitative replacement of the hydroxyl groups was achieved and the modified HBPs remained stable for several weeks under dry nitrogen. This permitted straightforward GPC analysis in THF at room temperature, giving results consistent with those obtained for the unmodified HBPs.

Key Words: Gel permeation chromatography (GPC); Hyperbranched; Polyesters; Solution properties; Universal calibration (UC).

INTRODUCTION

Dendrimer synthesis constitutes a significant breakthrough in the search for polymers with a precisely defined molecular weight (MW) and degree of branching.[1] Absolute control of polymer topology, nevertheless, requires a large number of synthetic steps in order to build up successive "generations" of monomer layers around a multifunctional core. As an alternative, schemes have recently been devised for producing dendritic macromolecules with a relatively narrow molecular weight distribution (MWD) by "one-pot" polymerization of AB_x monomers.[2] The resulting hyperbranched polymers possess comparable degrees of functionality and branching to those of dendrimers (Fig. 1), but their molecular structure is relatively poorly defined, being characterized by imperfect branching and cyclisation, as well as significant polydispersity.[3–5] Since HBPs are far less costly to produce, they may replace dendrimers in applications in which deviations from the ideal structure are tolerable, such as toughening by chemically induced phase separation in epoxy resins.[6,7] A rational approach to their exploitation, nevertheless, depends to a great extent on how well their molecular structure, and more specifically their MWD, can be characterized.

Molecular weight and MWD analysis of linear polymers is routinely performed by Gel Permeation Chromatography (GPC). Application of this technique to hyperbranched polymer systems poses a number of challenging problems, however:

1. Gel permeation chromatography separates molecules according to their hydrodynamic volume in solution. Measurement of the MWD in HBPs by classical GPC is made difficult by the large difference in hydrodynamic volume between the samples and the standards

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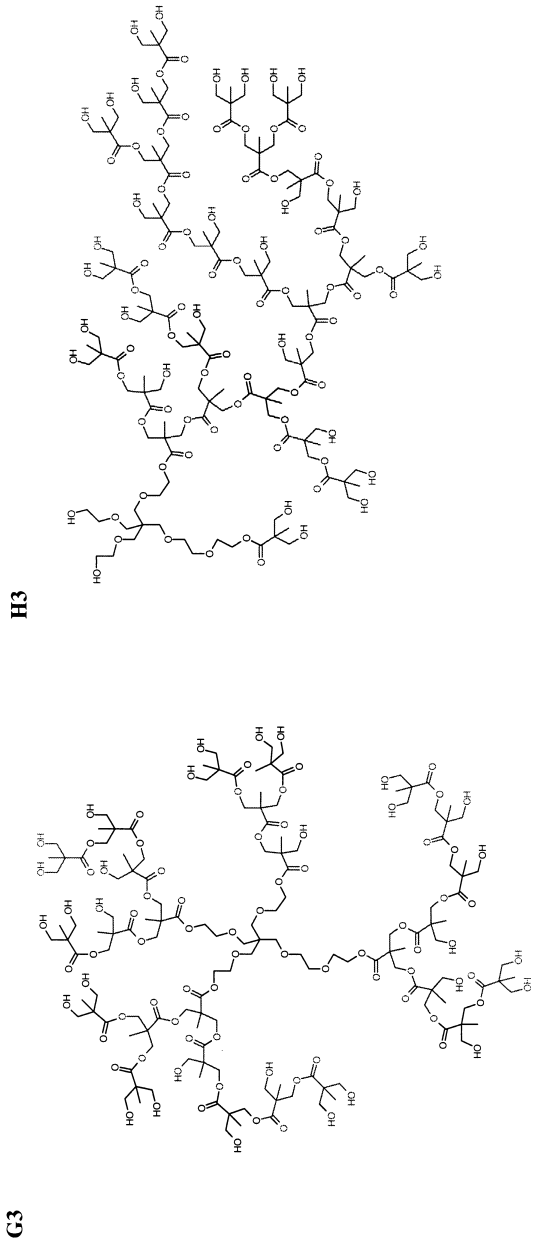

Figure 1. Chemical structure of a 3rd generation polyester dendrimer (G3) and one possible representation of an equivalent 3rd "pseudo-generation" hyperbranched polymer (H3) containing structural defects. The two structures have the same MW and number of —OH groups.

[generally polystyrene (PS) or polymethylmethacrylate (PMMA)] for a given MW. Modern GPC installations can now be equipped with MW-sensitive detectors, such as on-line viscometers and/or laser light scattering (LS) photometers, as well as the usual refractive index (RI) or ultraviolet detectors. Such set-ups are, in principle, sufficient to obtain absolute MW for linear and branched polymers, including HBPs. Dendritic polymers are highly compact with relatively low MW, and triple detection GPC with refractive index-viscometry and multiangle LS is currently the preferred method of MWD characterization.[8,9] Commercial availability of the appropriate detectors is recent, and currently only a limited number of laboratories are equipped for triple detection.

2. Even with optimum GPC instrumentation, reliable MW data can only be obtained if side-effects, such as aggregation and absorption or other interactions between the sample and the column packing are eliminated.[10] These problems are exacerbated in many dendritic polymers by the large numbers of polar functional groups per molecule.

The purpose of the present investigation is to explore the possibility of using GPC with differential viscometry to determine the MWD of highly polar hyperbranched aliphatic polyesters (HBPs) with the molecular structure depicted in Fig. 1.[11,12] It has been known since the late 60s, that GPC-viscometry can provide absolute MWD for polymers, given a valid universal calibration (UC), by which the hydrodynamic volume [proportional to (η)M] of a species is related to its elution time.[13] Since its inception, several groups have verified the "universality" of the hydrodynamic volume approach for linear polymers, polymers containing a few long branches and 3 and 4-arm star macromolecules.[14] The situation is much less clear when the UC is applied to macromolecules with molecular conformations markedly different from the random walk model. This is the case, for instance, for rods,[15] multiarm stars,[16] and compact spheroidal molecules.[17,18] HBPs, in spite of their compact structures, have nevertheless been reported to obey the UC.[4,5]

Regardless of these latter considerations, the UC concept is only valid under conditions of strict size-exclusion separation, and may be inappropriate to certain systems owing to the possibility of enthalpic interactions with the stationary phase. It follows, that a proper choice of eluant and separation medium is essential for successful GPC characterization with UC. In the HBPs considered here, the presence of numerous hydroxyl end-groups was anticipated to be particularly problematic in this respect. In order to verify the results, therefore, the HBPs were end-capped with trimethylsilane, this being a tried and tested technique for chemical transformation of —OH groups under

$$\text{HBP} \xrightarrow{\text{Cl–Si(CH}_3)_3} \text{TMS-HBP} \xrightarrow{\text{HCl/H}_2\text{O}} \text{HBP}$$

Scheme 1. End-group modification of the HBP.

mild experimental conditions. For the procedure to be applicable to GPC, chemical conversion should be high, reproducible, and not induce chemical degradation. The reliability of the procedure was investigated further by examining the effects of different degrees of trimethylsilylation, obtained by varying the ratio of the silylating reagent to the initial number of —OH end-groups. The trimethylsilylated HBP (TMS-HBP) was also converted back to its original hydroxyl-terminated form by hydrolysis in order to determine the extent of degradation (Sch. 1).

EXPERIMENTAL

Chemicals

All the chemicals were from Fluka AG (Switzerland). Anhydrous dimethyl formamide (DMF) and tetrahydrofuran (THF) were used in the present study to avoid possible artifacts. However, results obtained subsequently with standard puriss grade solvents showed no detectable differences with those presented here. Polystyrene and PMMA were MW standards from Polymer Laboratories (Shropshire, UK), with a polydispersity index <1.05. 2nd, 3rd and 4th "pseudo-generation." HBPs, referred to in what follows as H2, H3, and H4, respectively, were kindly provided by Perstorp Chemicals (Sweden).

Sample Preparation and Trimethylsilylation

The HBPs were dried at 80°C for 3 days under vacuum before GPC analysis and chemical transformation was carried out. A control experiment was run with 3rd generation HBP in order to check for possible chemical modification during the drying treatment. The material "as-received" and dried had identical molecular mass, but it took a longer time to completely dissolve the heat-treated (dry) sample. This is believed to be due to H-bond directed aggregation.

Preparative fractionation was carried out by dissolution of the "as-received" HBP in hot methanol, followed by precipitation in an excess of

diethyl ether. As will be discussed later, this simple treatment removed part of the oligomeric fraction responsible for the low MW tail observed in the GPC traces.

Trimethylsilylation was carried out in flame-dried vessels under purified nitrogen. About 2 g of HBP (equivalent to 15 mmol of reactive —OH) were introduced into a 250 mL three-necked vessel fitted with a reflux condenser and a magnetic stirrer. Fifty milliliters of dried THF were then added and the mixture heated, under reflux, until complete dissolution of the HBP (∼30–60 min). Depending on the required stochiometry, a predetermined amount of chlorotrimethylsilane was added, dropwise, in the presence of a 10% molar excess of triethylamine, used to neutralize the acid formed by the reaction. A white ammonium chloride precipitate appeared immediately on addition of the chlorotrimethylsilane. After cooling to room temperature, the solution was filtered, dried, and re-dissolved in 30 mL of *n*-hexane to remove any remaining ammonium salt. The final product was obtained by stripping off the *n*-hexane in a rotary evaporator and drying under high vacuum for 2 days at room temperature. Yield was typically about 80% by weight. At room temperature, the HBP changed from a solid to a paste, then to a viscous liquid with increasing degree of trimethylsilylation.

Instrumentation

Potentiometric titration for the determination of a hydroxyl number was carried out with an automatic burette (Metrohm Herisau Potentiograph E436). Proton NMR spectra were recorded in $CDCl_3$ on a Bruker DPX-400 instrument, using residual $CHCl_3$ ($\delta = 7.27$) as an internal reference. FT-IR spectra were obtained in attenuated total reflection (ATR) mode on a Nicolet Magna DSP 650, equipped with the Golden Gate® accessory and corrected for the wavelength-dependence of the penetration depth. Gel permeation chromatography was performed on a Waters 150CV modified for on-line differential viscometry. Previous studies have shown that the single capillary viscometer cannot provide a correct viscosity signal owing to flow rate perturbations ("Lesec's effect").[19] To correct for these baseline fluctuations, it is necessary to record the flow rate and the solution viscosity simultaneously, as a function of elution time. This was achieved by differential viscometric detection, that is by adding a second capillary viscometer between the Baseline Optimizing Box (BOB) and the injection system.[20,21] Different methods have been proposed for interdetector volume calibration, including the use of a broad standard and trial-and-error fitting until a correct Mark-Houwink exponent is obtained.[22] This approach, which has the advantages of taking axial dispersion into account, is difficult to apply to the present system, owing to the change in the slope of the viscosity law in the low MW range. We, therefore, relied on

the simpler method of calibrating with a uniform sample of sufficiently high MW for viscometric detection (Irganox 1035, an antioxidant from Ciba Specialty Chemicals with a MW of 642 g/mol). The density of the eluant, necessary for the calculation of polymer concentration and pump flow rate at the analysis temperature, was determined by pycnometry. The amount of injected polymer was 0.1 mL at a concentration of 5 mg/mL throughout.

RESULTS AND DISCUSSION

Materials characterization constitutes the essential part of the present investigation; chemical characterization and molecular characterization will be discussed in turn.

Chemical Characterization

Hydroxyl Titration

Determination of the hydroxyl number for the aliphatic polyester HBPs was carried out according to a normalized procedure (ASTM E322). The sample was acetylated under reflux for 60 min in an excess of acetic anhydride (1 part) and 10 parts pyridine as the solvent. The unreacted acetic anhydride was hydrolyzed with water and the acetic acid formed was titrated with 1.0 M NaOH. The hydroxyl number was calculated from the difference between the sample and a control. The procedure was repeated at least 3 times and the average values (standard deviation <3%) are given in Table 1. The conversion of OH group was checked by FT-IR after removal of excess reagents (pyridine and unreacted acetic anhydride) under high vacuum. A small, but measurable, quantity of residual OH groups was found, indicating that acetylation reaction

Table 1. End-group titration of the HBP.

	$H2^{ar}$	$H2^{fr}$	$H2^{sol}$	$H3^{ar}$	$H3^{fr}$	$H4^{ar}$	$H4^{fr}$
mg–OH/g	498.64	487.77	434.94	477.28	463.02	472.31	450.72
mmol–OH/g	8.87	8.69	9.53	8.51	8.25	8.42	8.03
mmol–OH/g^{de}	9.144	9.144	9.144	8.870	8.870	8.739	8.739

ar: as received.
fr: fractionated.
sol: remaining soluble fraction after precipitation.
de: dendrimer equivalent.

is not complete and that some error should be expected in the hydroxyl number determination.

^{1}H-NMR Spectroscopy

NMR spectroscopy provides a convenient absolute method for the microstructural characterization of HBPs and their derivatives.[23,24] In the case of the TMS-HBPs, the signal of the methylsilane protons [$-Si-(C\underline{H}_3)_3$, 0.08 ppm, broad s] was strong and well separated from the rest of the NMR spectrum. Since the signal from the $HO-C\underline{H}_2-$ and $-SiO-C\underline{H}_2-$ protons (3.8–3.7 ppm) overlapped strongly with that associated with $-O-C\underline{H}_2$ protons in the core (Fig. 2), the total number of the former was inferred from the $-C\underline{H}_3$ (1.3–1.0 ppm, m) and $-COO-C\underline{H}_2-$ (4.27 ppm, broad s) signals. This provided a quantitative measure of the degree of grafting (Table 2). Within experimental error, the values obtained by NMR were consistent with the stochiometric ratios (given in brackets in Table 2) used in the synthesis and will be retained in what follows.

FT-IR Spectroscopy

The FT-IR spectra, normalized with respect to the carbonyl absorption peak (Fig. 3), showed a gradual decrease in the strength of the hydroxyl band (3000–3650 cm^{-1}) and a corresponding increase in that of the siloxane peaks at 750 cm^{-1} (H_2C-OSi), 830 cm^{-1} (CH_3 rocking), 870 cm^{-1} ($Si-CH_3$ stretch), 1080 cm^{-1} (Si—O stretch), and 1250 cm^{-1} ($Si-CH_3$ symmetric bending) with increasing degree of trimethylsilylation.[25,26] However, even with a four-fold excess of chlorotrimethylsilane and a reaction time of 4 hours (the sample started to degrade after longer times), it was not possible to reduce the intensity of the —OH absorption peak to below about 11% of its initial value. Another striking feature of the spectra was the narrowing of the C═O band accompanied by an auxochromic shift from 1720 to 1734 cm^{-1} with increasing trimethylsilylation. Similar behavior was observed in the broad O—H stretching region, which in the unmodified HBP is characterized by a number of overlapping bands associated with various types of H-bonded structure. Trimethylsilylation decreases the extent of H-bonding, leaving free O—H groups, which absorbed at wavenumbers $>3400\ cm^{-1}$. The absorption strength may therefore, change with the extent of trimethylsilylation, in which case the band intensity will not provide a direct quantitative measure of the degree of trimethylsilylation. Indeed, the C═O and O—H bands have been used elsewhere to evaluate the number of hydrogen-bonded contacts in the same type of HBP.[27,28]

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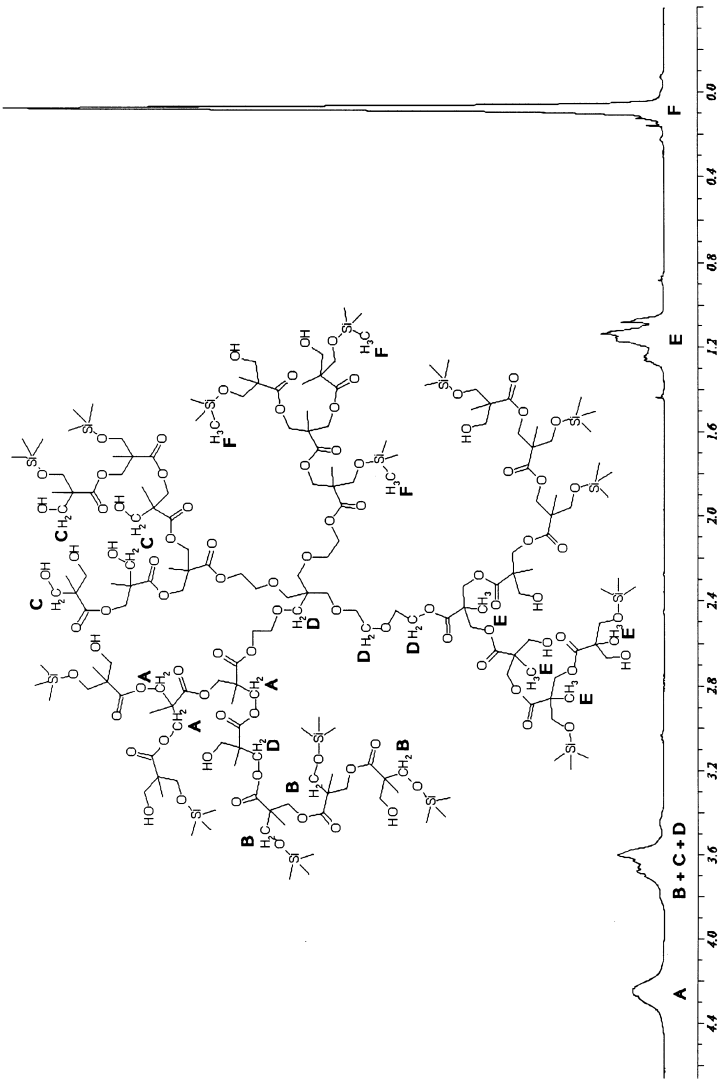

Figure 2. ^{1}H-NMR spectrum of a 48% grafted TMS-H3 polyester in $CDCl_3$. Proton positions associated with the chemical shifts are denoted by the corresponding letters on the spectrum and the drawing.

Table 2. ^{1}H-NMR characterization of TMS-H3 HBP (δ4.27 ppm set to 64).

	Integral values			
δ	TMS-H3^{fr} (25%)	TMS-H3^{fr} (50%)	TMS-H3^{fr} (75%)	TMS-H3^{fr} (100%)
4.27 ppm	64	64	64	64
3.8–3.7 ppm	91	102	89	92
1.3–1.0 ppm	99	97	98	97
0.08 ppm	65	141	212	277
Degree of grafting	21%	48%	71%	94%

fr: fractionated.

Molecular Weight Distribution Characterization

To investigate the consistency of data obtained under different experimental conditions, a comparative study was made using two different solvents, THF and DMF, which differ in polarity and in H-bonding capacity.

Gel Permeation Chromatography in *N*,*N*′-Dimethyl-Formamide

All the HBPs investigated were readily soluble in DMF at room temperature. The use of highly polar eluants with conventional PS/DVB based stationary phase frequently results in separation problems, such as early elution of the salt peak and peak distortion due to polymer adsorption. To minimize incompatibility problems, columns specifically designed for DMF are now available from most major column producers. In the present investigation, we selected the newly developed TSK-Gel Alpha columns (hydrophilic PMMA-type stationary phase) which, according to the manufacturer, should be compatible not only with water but also with a large range of polar organic solvents, including alcohols and DMF. To suppress polyelectrolyte effects, anhydrous lithium bromide was added to the eluant at a concentration of 0.03 M (a parallel study has indicated that the salt concentration has no influence on the elution behavior of the HBP within the investigated range of 0.01–0.05 M).

Gel permeation chromatography-viscometry traces for a series of TMS-H3, synthesized from a single fractionated H3 batch but with varying degrees of trimethylsilylation, are shown in Fig. 4. By applying the UC function established with PS standards, the MWD could be calculated along with the viscosity law from the RI and viscometry signals. The MWDs are given in Fig.5, and the

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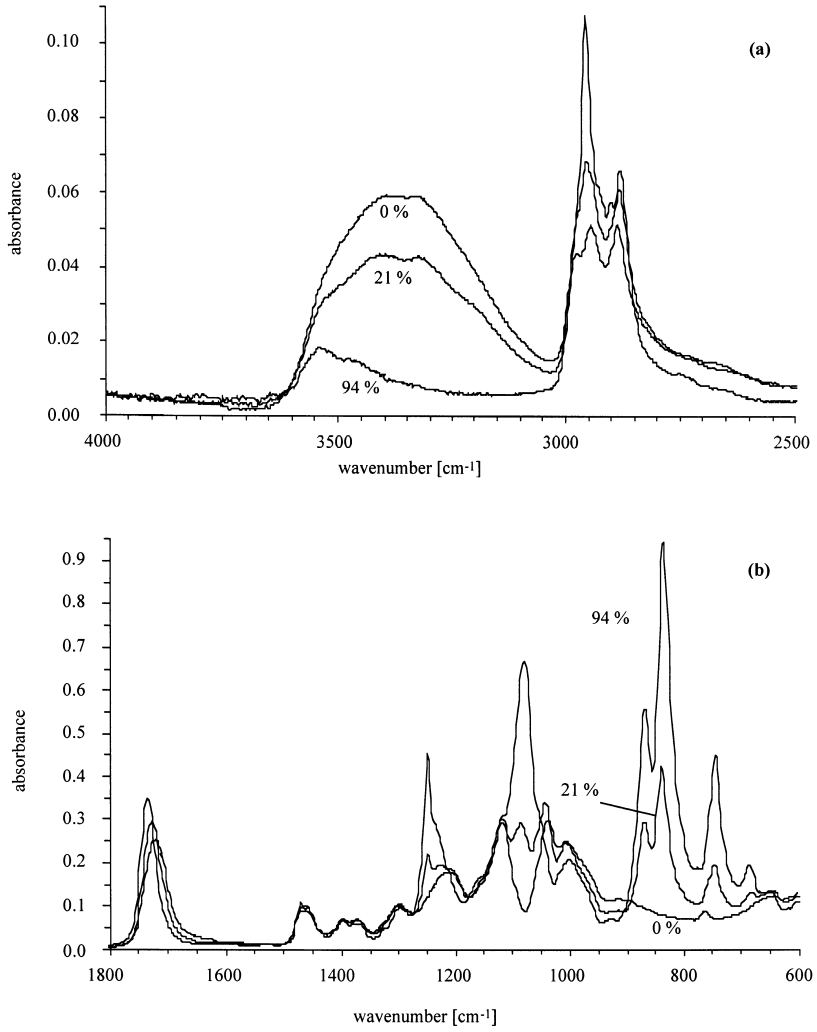

Figure 3. ATR-FTIR spectra of TMS-HBP samples with different degrees of trimethylsilylation (as determined by ^{1}H-NMR): (a) O—H and C—H stretch region; (b) C═O and fingerprint region.

corresponding MW averages and viscometry data are summarized in Table 3. Apart from the presence of low MW impurities detected as spurious peaks on the high elution volume side, the GPC traces for hydrolyzed 94% TMS-H3 were coincident with those for the unmodified polymer. This result confirmed the absence of degradation during trimethylsilylation.

The relative RI sensitivity, given by the surface constant A (proportional to refractive index increment dn/dc), decreased significantly with the degree of trimethylsilylation (Fig. 4 and Table 3). With proper calibration, measurement of the refractive index or the refractive index increment could therefore provide a simple method of determining the degree of trimethylsilylation. Another effect discernable in Table 3 was the sharp decrease in intrinsic viscosity with increasing degree of trimethylsilylation. Replacing the polar hydroxyl groups with hydrophobic trimethylsilane presumably led to a less expanded conformation in the polar solvent DMF. The resulting decrease in solubility of the TMS-HBP may have led to enthalpic interactions with the stationary phase. This could explain the observed decrease in M_w/M_n with increasing functionalization (Table 3). Nevertheless, given the precision generally attained by GPC, which rarely surpasses 7% for M_w and 15% for M_n,[29] the observed agreement between the experimental M_n and the theoretical values should still be considered satisfactory. It should also be borne in mind, that the number-average MW values in GPC are highly dependent on the lower integration limit.[30] In the evaluation of the GPC data, values below $\sim$300 g/mol (or $\log M < 2.5$) were excluded from the calculations in order to take into account the possible presence of unreacted core molecules.

The Mark-Houwink exponent of about 0.3 indicated a compact conformation in all the samples analyzed.

Gel Permeation Chromatography in Tetrahydrofuran

The TMS-HBPs were readily soluble in THF at room temperature, whereas the unmodified HBPs required heating to 50°C. Although THF is the preferred solvent for GPC analysis, this limited solubility may be associated with aggregation. Moreover, the presence of hydroxyl end-groups in the modified or partially trimethylsilylated HBPs may promote hydrophilic interactions with the stationary phase (Styragel™ HR) and interfere with the size-exclusion mechanism. Therefore, the validity of the UC concept must be carefully assessed.

Gel permeation chromatography traces and the corresponding MWD of TMS-H3 are given in Figs. 6 and 7, respectively, and the most relevant average MWs and viscometry data are summarized in Table 4. The GPC traces were normalized with respect to the RI peak maximum to emphasize the change in

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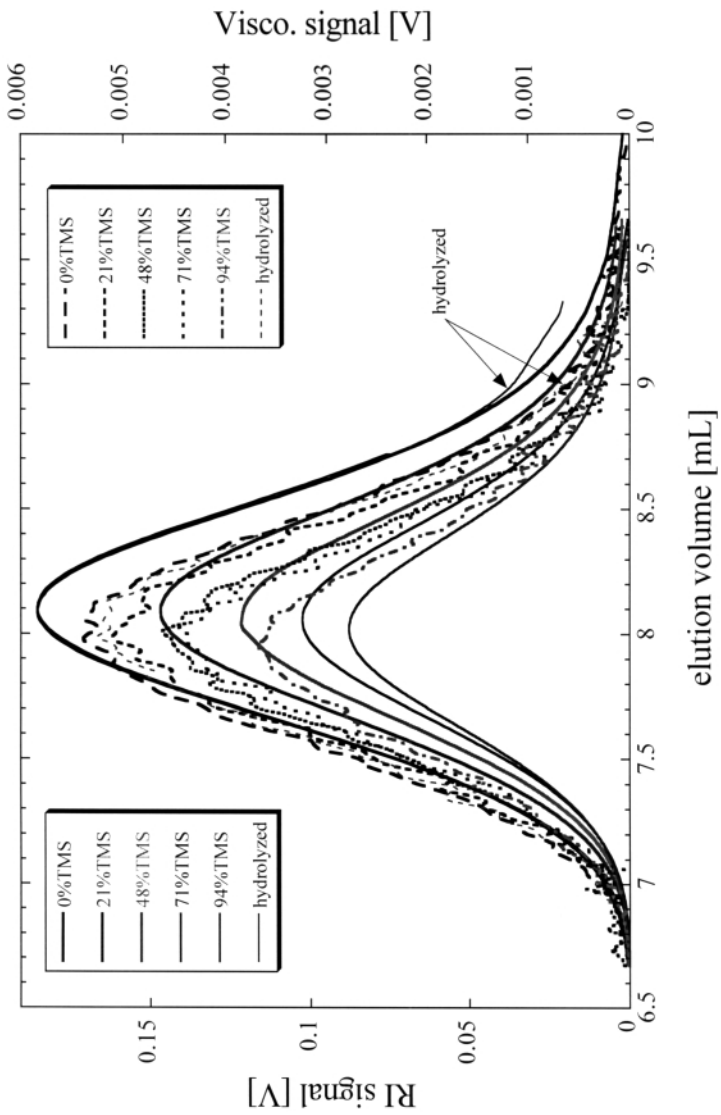

Figure 4. Gel permeation chromatography-viscometry traces of fractionated TMS-H3 in DMF (+0.03 M LiBr) at 60°C, recorded at identical polymer concentrations (5 mg/mL). RI signal: continuous lines, left scale; viscometry signal: broken lines, right scale.

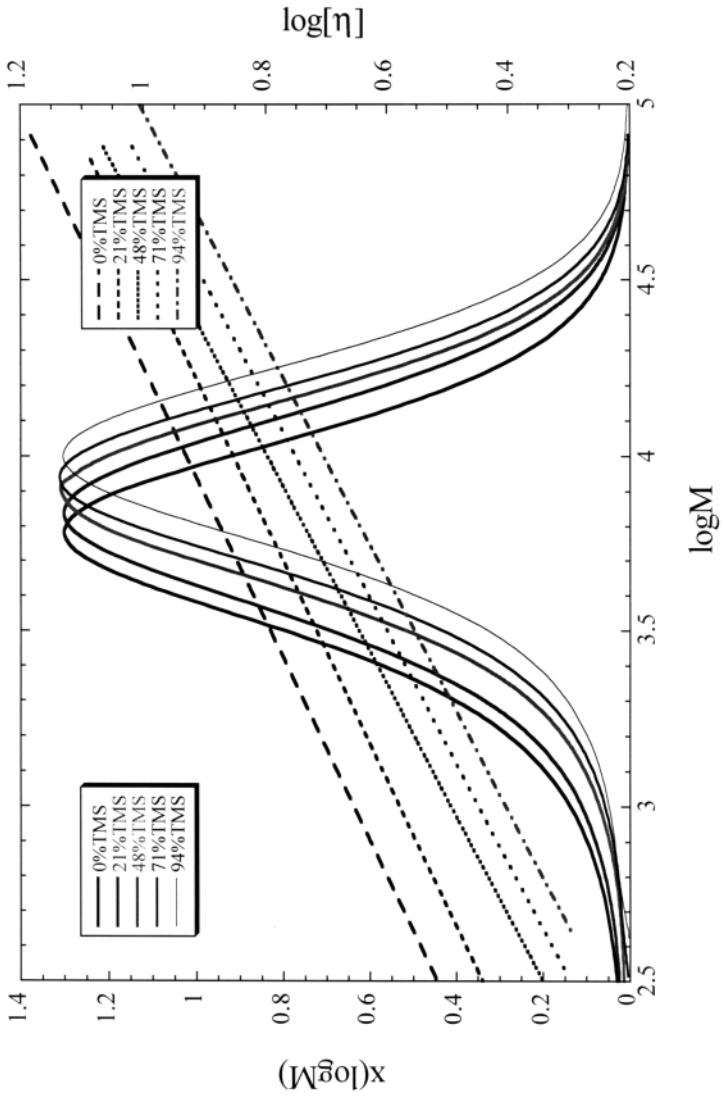

Figure 5. Molecular weight distribution (left scale) and Mark-Houwink plot (right scale) for TMS-H3 analyzed in DMF at 60°C, with the indicated degrees of trimethylsilylation. Experimental conditions: TSK-Gel Alpha 2500, 60°C, 0.8 mL/min, injected volme: 0.1 mL at 5 mg/mL.

Table 3. Gel permeation chromatography-viscometry results for TMS-H3 (fr) in DMF at 60°C.

	0% TMS	21% TMS	48% TMS	71% TMS	94% TMS	Hydrolyzed
M_n^{de} (g/mol)	3,608	4,093	4,716	5,248	5,779	3,608
M_p (g/mol)	5,620	6,530	7,750	8,290	9,700	5,360
M_n (g/mol)	3,510	4,280	5,140	5,560	6,570	3,320
M_v (g/mol)	5,790	6,640	7,830	8,380	9,850	5,430
M_w (g/mol)	7,140	8,120	9,350	9,970	11,800	6,880
M_z (g/mol)	12,370	13,540	15,040	15,660	19,140	12,290
M_w/M_n	2.03	1.90	1.82	1.80	1.80	2.07
(η) (mL/g)	−8.07	7.06	6.31	5.99	5.52	7.81
log K	−0.1316	−0.2023	−0.3837	−0.4113	−0.4601	−0.1045
a (MH)	0.276	0.275	0.304	0.303	0.301	0.267
A	2.41	2.00	1.50	1.12	0.96	2.39

de: dendrimer equivalent calculated using the formula $3608 + \% \cdot 32 \cdot 72.190$.

elution volume with the degree of trimethylsilylation. Again, given the precision of the technique, the agreement between the GPC data and the calculated theoretical values was satisfactory.

Comparison of Molecular Weight Distributions

After trimethylsilylation, the MW of the HBP increased by a factor F that varies with the grafting ratio and the mass concentration of the hydroxyl groups. Because the latter quantity may depend on the initial polymer MW (as, for instance, with dendrimers), the relationship between MW of the trimethylsilylated HBP and that of the original HBP can be written:

$$M(\text{TMS-HBP}) = \text{F}(M)M(\text{HBP})$$

For a randomly grafted linear polymer, F is essentially independent of MW. On the other hand, a dependence of F on M is expected if grafting occurs only at the chain ends, as in the dendritic polymers. Fortunately, this dependence, estimated using the perfect dendrimer structure, is negligible except for MW below ~1000 g/mol (Fig. 8). The MWDs of an unmodified HBP calculated from the trimethylsilylated derivative, using either the function F(M) or using a constant correction obtained from the average degree of functionalization, are almost undistinguishable for H3. The correction is more significant for the lower MW H2.

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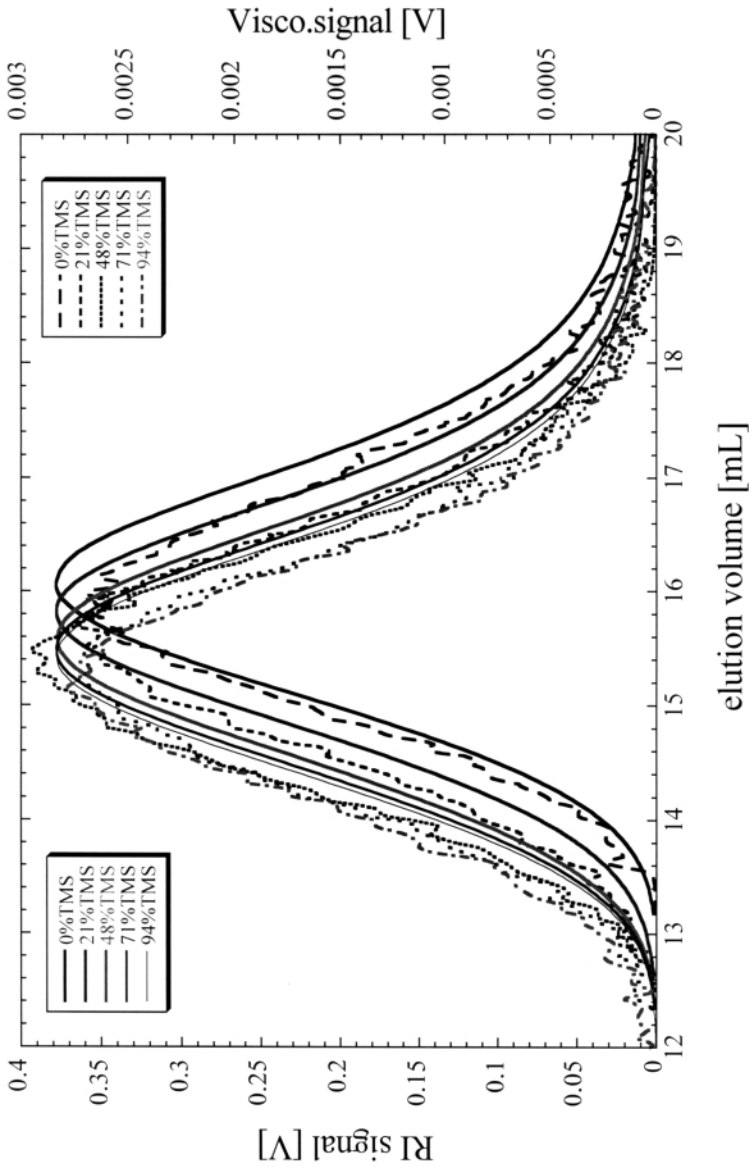

Figure 6. Gel permeation chromatography-viscometry traces for fractionated TMS-H3 in THF at 50°C, normalized with respect to the peak maximum.

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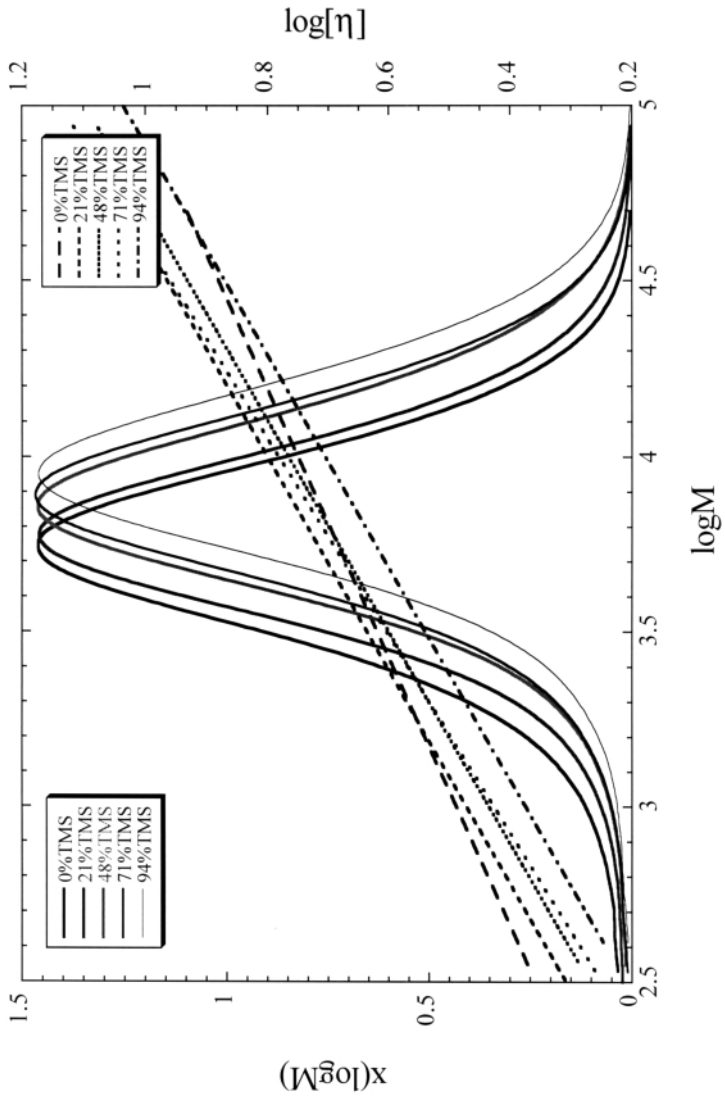

Figure 7. Molecular weight distribution (left scale) and Mark-Houwink plot (right scale) for TMS-H3 analyzed in THF, with the indicated degree of trimethylsilylation. Experimental conditions: Styragel HR-2 + HR-3, 50°C, 0.8 mL/min, injected volume: 0.1 mL at 5 mg/mL.

Table 4. Gel permeation chromatography-viscometry results for TMS-H3 (fr) in THF at 50°C.

	0% TMS	21% TMS	48% TMS	71% TMS	94% TMS
M_n^{de} (g/mol)	3,608	4,093	4,716	5,248	5,779
M_p (g/mol)	5,410	5,880	7,190	7,440	8,740
M_n (g/mol)	3,510	4,020	4,980	5,170	6,120
M_v (g/mol)	5,090	5,880	7,290	7,610	8,940
M_w (g/mol)	6,044	6,880	8,590	8,850	10,510
M_z (g/mol)	9,280	11,070	13,980	13,860	17,180
M_w/M_n	1.72	1.71	1.72	1.71	1.72
(η) (mL/g)	5.07	5.36	5.67	5.90	5.77
log K	−0.2662	−0.5072	−0.5250	−0.6070	−0.5467
a (MH)	0.262	0.328	0.331	0.355	0.331
A	2.40	2.22	2.03	1.91	1.63

de: dendrimer equivalent calculated using the formula $3608 + \% \cdot 32 \cdot 72.190$.

To assess further the variations engendered by different experimental conditions, we have replotted the experimental logarithmic MWDs for the different HBP samples analyzed in DMF and THF (Fig. 9). Any consistent GPC characterization should provide comparable MWDs for a given starting material, regardless of the eluant, stationary phase, or preparation technique employed. After translating with an appropriate constant along the log M axis, excellent superposition of the MWDs was obtained for samples analyzed with a given solvent. The fact that it is possible to superpose the MWD curves by simple translation along the log M axis indicates that the degree of trimethylsilylation is constant over the whole MWD. If this were not the case, a systematic change in width of the MWD would be observed.

More significant differences were apparent in the results obtained in DMF and in THF. In particular, the width of the MWD, characterized by the polydispersity index M_w/M_n, was larger in DMF than in THF. Such behavior may indicate deviations from the pure size-exclusion mechanism or increased axial dispersion in the DMF system. The increasing difference between $M_n^{(de)}$ and M_n measured in DMF with the percentage of TMS (Table 3), tends to support the first explanation. However, the role of axial dispersion may also be significant, because a single column was used for the analysis in DMF. An attempt to add a second TSK-Alpha 2500 column in series was unsuccessful owing to the partial incompatibility of this low porosity packing with DMF. Regardless of the exact source of discrepancies, the differences of $<10\%$ between the average MWs obtained in DMF and in THF are well within the usual precision range of GPC-viscometry referred to earlier.

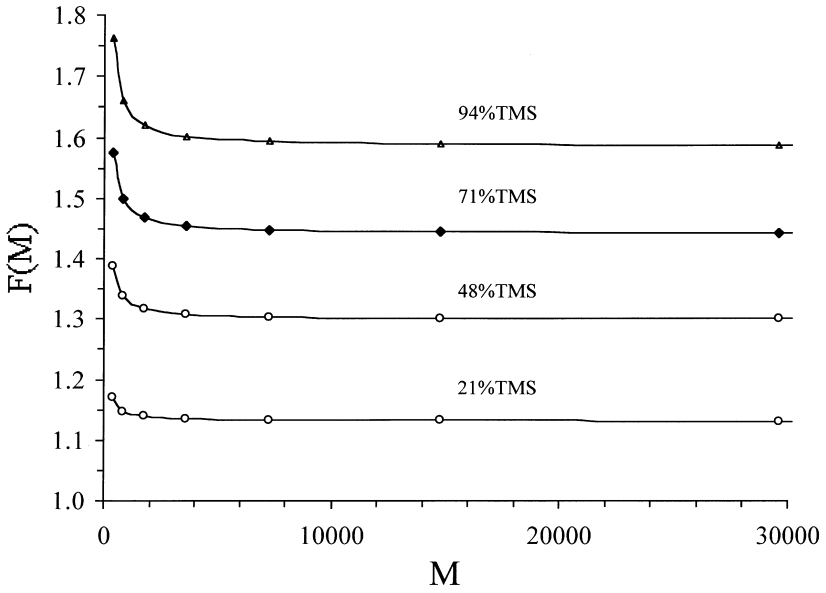

Figure 8. Fractional increase in MW after trimethylsilylation as a function of the unmodified polymer MW (calculations are based on perfect dendrimer structure, the abscissa values of the data points correspond to the dendrimer MW from generation 0 to 6).

The fractionation procedure removed some of the oligomers, giving products with sharper MWDs than those of the as received HBPs (Fig. 10). The M_n data for these latter were also significantly below the dendrimer equivalent values, in qualitative agreement with results obtained by other techniques for similar HBPs.[5] After fractionation, the experimental M_n were closer to the theoretical values and polydispersity indices decreased to about 2 (summarized in Table 5).

CONCLUSIONS

It is often reported that dendrimers display a maximum in the relationship between their intrinsic viscosity and MW and, hence, do not follow the Mark-Houwink-Sakurada (MHS) viscosity law.[31,32] With a single exception,[33] such behavior has not been observed in HBPs and it is generally believed that this class of polymer follows the linear $\log[\eta]$–$\log M$ relationship,[34–36] although some deviations may occur at high pseudo-generation numbers.[37]

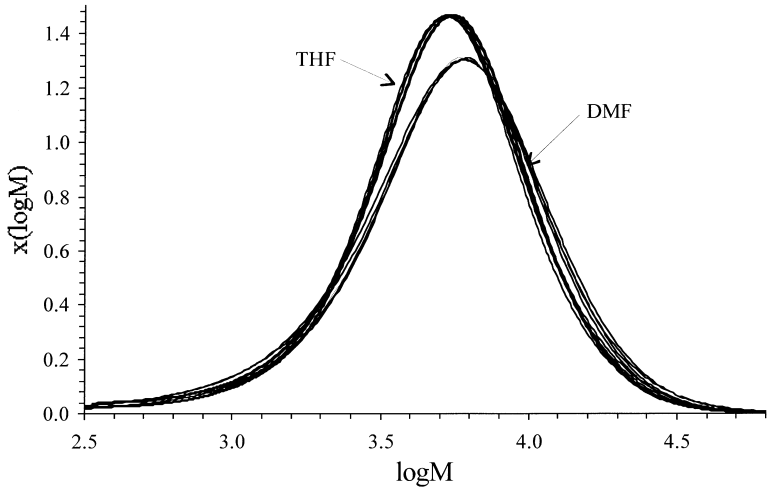

Figure 9. Superposed MWDs of fractionated H3 and TMS-H3 analyzed in DMF and in THF. Within experimental errors, the translation constants correspond to the values reported in Fig. 8.

The present study has demonstrated hyperbranched aliphatic polyesters to follow the MHS viscosity law with an exponent close to 1/3 characteristic of a compact space-filling molecular structure. It was further verified that the UC concept can be used to obtain absolute MWDs for these HBPs. To generate a valid UC curve, it is mandatory to work under conditions for which no secondary separation mechanism is present, including adsorption, thermodynamic partition, phase separation (precipitation), and ionic effects. Satisfying all these requirements is difficult in practice and enthalpic interactivity is invariably present to some extent, depending on the polymer/solvent/stationary phase combination, which has been employed.[38] For the systems studied, size-exclusion separation seems to be predominant for the systems HBP and TMS-HBP in THF on Styragel HR, and HBP in DMF on TSK-Gel Alpha columns. Some polar interactions may, however, be present for the system TMS-HBP/DMF/TSK-Gel Alpha.

Each of the eluant systems, DMF and THF, which have been employed in this investigation has its own drawbacks: DMF is a good solvent for polyesters, and HBPs from the core up the 6th "pseudo-generation", are readily soluble in this medium at room temperature, but special columns may be necessary when DMF is used as the eluant. Tetrahydrofuran THF, on the other hand, is compatible with a variety of stationary phases, but dissolution of the HBPs in THF is difficult and requires prolonged heating above 50°C.

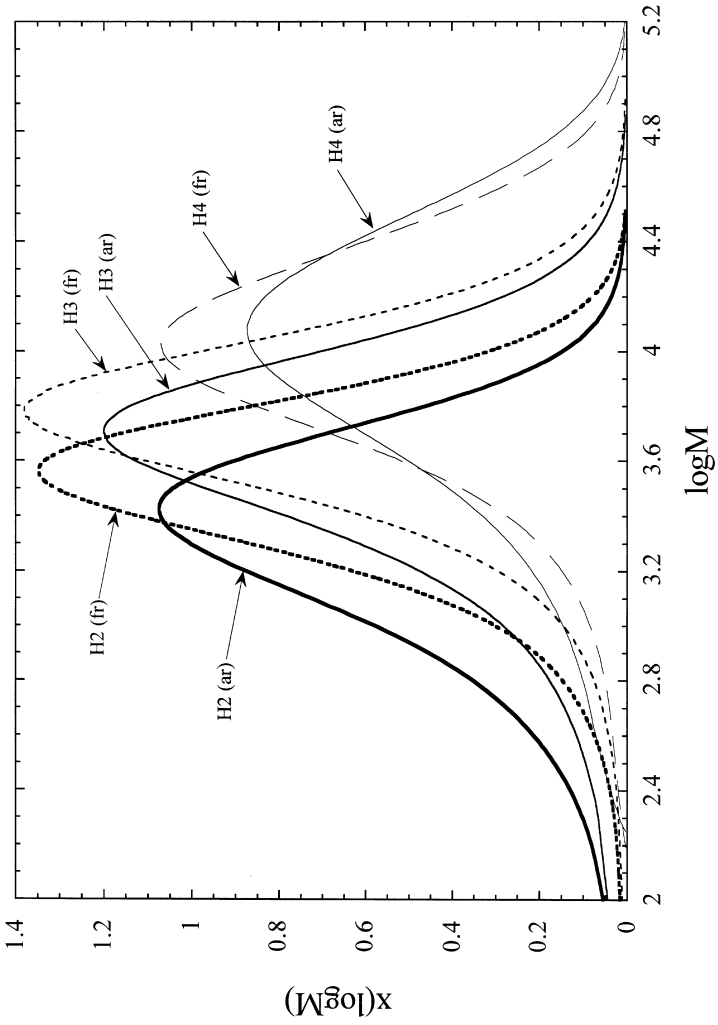

Figure 10. MWDs of H2, H3, and H4 before and after fractionation, analyzed in DMF at 60°C.

Table 5. Gel permeation chromatography-viscometry results for unfractionated and fractionated HBP in DMF at 60°C.

	$H2^{unfr}$	$H2^{fr}$	$H3^{unfr}$	$H3^{fr}$	$H4^{unfr}$	$H4^{fr}$
M_n^{de} (g/mol)	1,750	1,750	3,608	3,608	7,323	7,323
M_p (g/mol)	2,130	3,230	4,560	5,620	6,500	7,760
M_n (g/mol)	1,030	2,110	2,210	3,510	2,190	3,910
M_v (g/mol)	2,120	3,310	4,320	5,790	6,130	7,530
M_w (g/mol)	2,830	4,110	5,910	7,140	8,670	10,060
M_z (g/mol)	5,090	6,700	10,220	12,370	19,230	22,510
M_w/M_n	2.75	1.95	2.68	2.03	3.95	2.57
(η) (mL/g)	5.60	6.27	7.10	8.07	8.01	8.75
log K	0.0330	−0.0475	−0.0576	−0.1316	−0.3273	−0.2947
a (MH)	0.215	0.240	0.250	0.276	0.325	0.319
A	2.20	2.21	2.34	2.41	2.35	2.31

unfr: unfractionated.
fr: fractionated.
de: corresponding dendrimer equivalent.

Moreover, aggregation is thought to occur in THF for the higher MW polymers (5th and 6th "pseudo-generation"), resulting in spurious bimodal distributions.

Trimethylsilylation provides a convenient alternative method of analyzing the HBPs. Near quantitative replacement of the hydroxyl groups was achieved and the modified HBPs' remained stable for several weeks under dry nitrogen, permitting straightforward GPC analysis in THF at room temperature to give results consistent with those obtained for the unmodified HBPs.

Finally, it should be borne in mind, that the information obtained from a successful MWD analysis constitutes only one of the multiple facets of a complete structural characterization of an HBP. It is known from MALDI-TOF-MS, that chemical heterogeneity is present in most HBPs.[3–5] Even in the absence of chemical heterogeneity, a branched polymer requires measurement of two distributed properties, namely the overall degree of polymerization and the degree of branching corresponding to the number of monomer units between successive branch points.[39] Such a polymer system is known as "complex" and its characterization requires information from several detectors with at least one detector signal per property to be determined. In this respect, one may anticipate that the combined use of GPC with on-line LS (static and dynamic) and NMR spectroscopy should reveal additional features that are inaccessible to GPC alone. On-going work in our laboratory is aimed in this direction.

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