Macromolecules **2001,** *34,* 5487−5493

^{1}H and ^{13}C NMR Spectra of a Hyperbranched Aromatic Polyamide from *p*-Phenylenediamine and Trimesic Acid

Hartmut Komber* and Brigitte Voit

Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany

Orietta Monticelli and Saverio Russo

Dipartimento di Chimica e Chimica Industriale, Università di Genova, via Dodecaneso 31, 16146 Genova, Italy

Received December 28, 2000; Revised Manuscript Received May 9, 2001

ABSTRACT: The structure of hyperbranched aromatic polyamides synthesized from different ratios of *p*-phenylenediamine and trimesic acid ($A_2 + B_3$ reagent pair) has been investigated by means of ^{1}H and ^{13}C NMR spectroscopy. On the basis of a detailed NMR signal assignment six 1,3,5-trisubstituted benzene moieties with different substitution patterns can be distinguished. The different monomer ratios influence the polymer architecture with respect to the content of these substructures, the degree of branching and the predominant functionalities (COOH or NH_2). An excess of B_3 results in a larger number of branches and a predominant COOH functionalization. ^{1}H NMR proves site-specific interactions between lithium cations and the polymer substructures. The observed chemical shift effects simplify the quantification of the spectra. Finally, acetylation of amino groups by acetic acid, an impurity in commercial trimesic acid, could be proven.

Introduction

In the past few decades, the synthesis of hyperbranched polymers has gained growing interest of many research groups which explored the preparation routes of a wide variety of polymers.[1,2] However, to be able to study their potential applications,[3] a good knowledge of the physical and chemical properties of hyperbranched polymers is necessary. One of the most crucial aspects of hyperbranched polymer characterization is the determination of its structure, namely the evaluation of the concentration of terminal (**T**), linear (**L**), and dendritic (**D**) units. The above values allow to calculate the degree of branching (DB), a parameter related to the polymer architecture. The degree of branching is generally calculated[4,5] according to the following equation: $\mathrm{DB} = (\mathbf{D} + \mathbf{T})/(\mathbf{D} + \mathbf{T} + \mathbf{L})$, where **T**, **L**, and **D** are the contents of terminal, linear, and dendritic units, respectively. More recently, Frey et al.[6] introduced a new definition ($\mathrm{DB} = 2\mathbf{D}/(\mathbf{L} + 2\mathbf{D})$) which takes also oligomers into account. Usually, the content of **T**, **L**, and **D** units is determined by NMR spectroscopy. Mostly, the NMR signal assignment was done on the basis of low-molecular-weight model compounds, which bear structures closely resembling linear, dendritic and terminal units in the corresponding hyperbranched polymers. The combination of one- (1D) and two-dimensional (2D) NMR techniques is a powerful approach to solve the polymer structure directly for hyperbranched polymer[7−9] without the use of model compounds.

In a previous paper,[10] we presented the synthesis and characterization of a hyperbranched aromatic polyamide, named pPDT, prepared from *p*-phenylenediamine (A_2) and trimesic acid (B_3), following the procedure suggested by Jikei et al.[11] As shown in Figure 1, the resultant polymer structure is characterized by 1,3,5-trisubstituted benzene (1,3,5-TB) moieties which can still contain nonreacted acid groups (**B**), and/or bonded *p*-phenylene moieties, named **A** when one amino group can still react and **A′** when both amino groups have already reacted.

A careful study of the influence of the reaction parameters (temperature, time, reactant concentration, etc.) on network formation has pointed out the high sensitivity of the system to reaction conditions. As compared to pPDT, hyperbranched aramide polymers prepared from the homologous AB_2 monomer show close similarities in terms of intrinsic viscosity and glass transition temperature but show higher molecular weights and peculiar differences in the relative ratios of the various structural units.

Up to the crucial point of gelation (i.e., due to the formation of networks) the polymers are well soluble and can be investigated by high-resolution NMR. First, ^{1}H and ^{13}C data for pPDT were reported by Jikei et al.[11,12]

In the present paper, the microstructure of pPDT has been extensively studied by ^{1}H and ^{13}C NMR spectroscopy using also 2D NMR methods. Namely, structural parameters of three pPDT samples, prepared from different reactant compositions will be discussed. Furthermore, ^{1}H NMR analysis has been employed in order to determine the presence of impurities in the polymer matrix. A comparison with NMR spectra, given in the literature[11,12] for the same material, has been performed. Finally, it is shown that specific interactions between pPDT substructures and Li^+ ions result in chemical shift effects which simplify the quantification of ^{1}H NMR spectra. The detailed interpretation of these effects is subject of a forthcoming paper.[13]

Experimental Section

Polymer Synthesis and Materials. The polymers were usually synthesized using equimolar amounts of *p*-phenylene-

---

* Corresponding author. Telephone: international code +351-4658-343. Fax: international code +351-4658-284. E-mail: komber@ipfdd.de.

10.1021/ma002223f CCC: $20.00

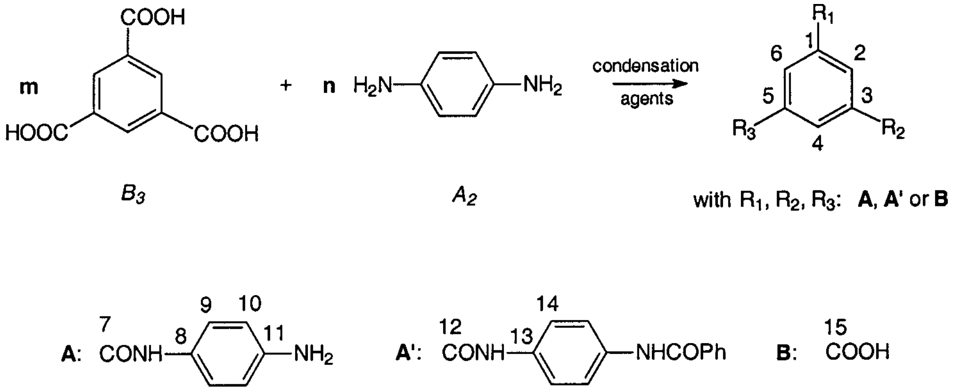


Figure 1. Synthesis of the hyperbranched aromatic polyamide (pPDT) from trimesic acid (B_3) and *p*-phenylenediamine (A_2) monomers and atom numbering for NMR signal assignment.

diamine (PPD) and trimesic acid (TMA). The TMA (Fluka) had a purity > 98% determined by NMR. According to the reaction in Figure 1, *m* and *n* are the same ($m/n = 1$), which corresponds to a ratio of functional groups $[COOH]/[NH_2] = 1.5$ (sample pPDT-2). Triphenyl phosphite and pyridine were used as condensation agents following the procedure described elsewhere.[11] Additionally, samples were prepared by using a ratio of functional groups $[COOH]/[NH_2]$ equal to 2 ($m/n = 1.33$, sample pPDT-1) and 1 ($m/n = 0.67$, sample pPDT-3), respectively. The reactions were carried out at 80 °C for 90 min. LiCl (Fluka) was dried in the vacuum oven before use. The inherent viscosities determined in dimethylformamide at 25 °C were 0.10 (pPDT-1), 0.33 (pPDT-2), and 0.21 dL/g (pPDT-3). The molecular weight M_w of sample pPDT-2 was 42 000 (GPC).

NMR Spectroscopy. The NMR measurements were carried out on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^1H and at 125.75 MHz for ^{13}C NMR spectra. DMSO-d_6 was used as solvent, lock, and internal standard ($\delta(^1H) = 2.50$ ppm, $\delta(^{13}C) = 39.60$ ppm). The spectra were measured at 303 K using 5 mm o.d. sample tubes. Quantitative ^{13}C NMR spectra were obtained using inverse gated decoupling, 30° pulses and a pulse delay of 8 s. The 1D NMR measurements were completed by $^1H-^1H$ shift correlated (COSY), 2D rotating frame Overhauser effect spectroscopy (ROESY), and $^1H-^{13}C$ one- and multiple-bond shift correlated (HMQC, HMBC) spectra using the standard pulse sequences provided by Bruker. The quantification of different structural units was done by integration and signal deconvolution of signal regions in the ^1H NMR spectra (with and without LiCl) and ^{13}C NMR spectra.

Results and Discussion

Structural Units of the Hyperbranched Aromatic Polyamide. Figure 2 gives a summary of the possible structures with focus on the functional groups bonded to the 1,3,5-trisubstituted benzene (1,3,5-TB) moiety. In the initial state of polycondensation, the reaction of B_3 and A_2 monomers results in the subsequent formation of the low-molecular-weight structures $\mathbf{AB_2}$, $\mathbf{A_2B}$, and $\mathbf{A_3}$ containing only one 1,3,5-TB moiety. The $\mathbf{AB_2}$ structure is described as starting monomer for the synthesis of hyperbranched aramide polymers.[10−12] The formed **A** unit still contains an amino group which can react with a **B** functionality (COOH). In this way, the **A** unit is transformed into an **A′** unit, which connects two 1,3,5-TB moieties. This is the predominant reaction at higher degrees of conversion and results in the formation of hyperbranched polymeric structures.

The 1,3,5-TB moiety acts as branching point. Its number of remaining carboxylic groups (2, 1, or 0) determines the assignment to terminal (**T**), linear (**L**), and dendritic (**D**) units. Nine structural units can be distinguished—two for the terminal unit **T**, three for the linear unit **L**, and four for the dendritic unit **D**. These structural units and their ratio to each other are well suited to follow structural changes when different molar adduct ratios are used, and therefore, they are used mainly in the forthcoming discussion.

However, also **A** units have to be considered in the definition of terminal, linear and dendritic structural units. It is obvious that an **A** unit still contains a free amino group as nonreacted functionality as the COOH group of the 1,3,5-TB moiety. Thus, a structural unit **AA′B** is considered linear with respect to **B** functions only but terminal when **A** and **B** are considered. Therefore, a second assignment (indicated by an slanted prime) of structural units to **T′**, **L′**, and **D′** is introduced based on the total number of **A** and **B** units on the 1,3,5-TB moiety (Figure 2). Only structures containing at least one **A′** unit (shown within the frame in Figure 2) where considered because the **A′** unit connects two 1,3,5-TB moieties as the smallest structure of a hyperbranched polymer. Structural units without an **A′** unit can be considered as nonpolymeric structures. When the total number of **A** and **B** units is two the 1,3,5-TB moieties terminate the polymer chain (**T ′**). Structural units containing only one of these units ($\mathbf{A'_2B}$, $\mathbf{AA'_2}$) result in a linear chain growth (**L′**) and only the $\mathbf{A'_3}$ unit introduces a new growth direction (**D′**). This assignment includes the structural units really observed for pPDT and is more useful to describe the structure of the polymer than the one which is based only on counting the **B** functions.

For hyperbranched polymers from AB_2 monomers it is assumed that each macromolecule has only one so-called "focal unit" containing an **A** functionality. This cannot be assumed for a soluble ($A_2 + B_3$) system because unreacted **A** and **B** functionalities are certainly a measure for the conversion of both functional groups, and at low conversion, branched molecules with more than one **A** functionality can be formed. However, at high degrees of conversion, an insoluble gel is formed.

^{1}H NMR Experiments. Figure 3 shows the ^1H NMR spectrum of a hyperbranched polyamide obtained from *p*-phenylenediamine (A_2) and trimesic acid (B_3) using a molar ratio 1:1 (pPDT-2).

Three signal regions can be assigned to the amide protons, to the protons of the substituted trimesic acid, and to the *p*-substituted phenylene moieties with one (**A**) and two (**A′**) amide groups, respectively. **A** units result in two signal groups at 6.70 and 7.51 ppm due to the protons ortho and meta to the remaining amino

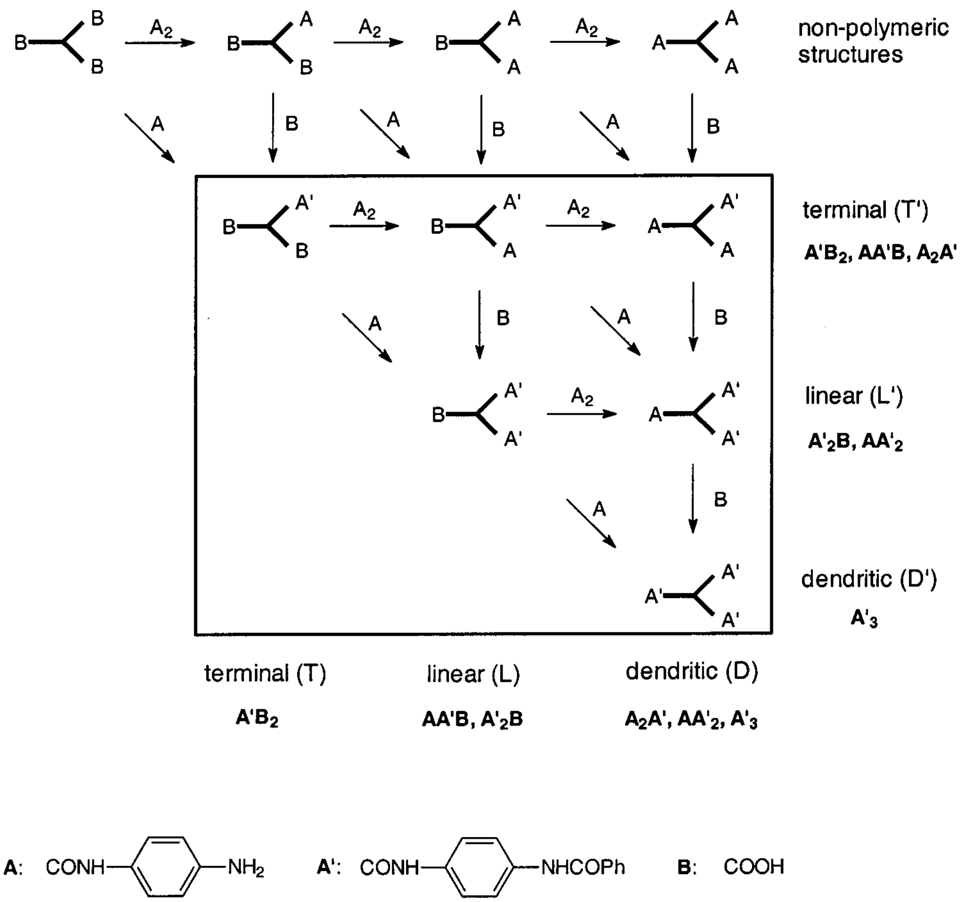


Figure 2. Structural units and reaction pathways for the polycondensation of *p*-phenylenediamine (A_2) and trimesic acid (B_3). Assignment to terminal (**T**), linear (**L**), and dendritic (**D**) units depending on the number of **B** functionalities (columns) and depending on the number of **A′** units (rows, indicated by an ′). The structural units within the frame were proven for our pPDT samples.

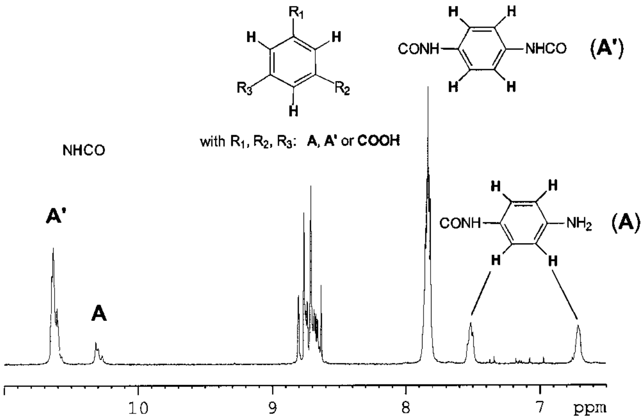


Figure 3. ^{1}H NMR spectrum of pPDT-2 (m/n = 1) in DMSO-d_6.

group. The amide protons appear as signal group at about 10.3 ppm. Starting with the low-field signal, the three signals can be assigned to the amide protons of **AA′B**, **AA′**$_2$, and **A**$_2$**A′** from a ROESY spectrum. The protons of the amino and carboxylic groups are in fast exchange, resulting in a very broad signal. It should be mentioned that increasing polymer concentration results in low-field shifts for all signals of **A** units. This should be caused by a higher degree of protonation. The effect of protonation on the proton chemical shift values of the **A** unit could be demonstrated by adding an excess of CF_3COOH to the sample. Large low-field shifts to 7.40, 7.95, and 10.78 ppm, respectively, were observed due to the high degree of protonation. In contrast, the chemical shift values for the **A** unit in pPDT correspond with data for 4-aminobenzoates. Both indicate that the degree of protonation of the amino groups in pPDT is low. The symmetric substitution of **A′** units results in signal groups at 7.84 ppm (aromatic protons) and at 10.63 ppm (NH) which are less sensitive to protonation. Both signal groups show splitting due to different substitution of the neighboring 1,3,5-TB moieties. However, the chemical shift differences are very low and a signal assignment was not possible.

In contrast, the finely resolved signal group of the protons of the substituted trimesic acid (Figure 4) reflects well the structure of the hyperbranched polymer with respect to the structural units given in the frame of Figure 2. Fortunately, the small $^4J_{HH}$ values (about 1.2 Hz) reduce signal overlapping. Using 2D NMR methods we were able to assign all signals. Furthermore, the substitution of **B** by **A** or **A′** units and of **A** by **A′** units result in characteristic substituent effects which confirm the assignments and allow to estimate also the ^{1}H chemical shifts of structures which were not found in the reaction product (**AB**$_2$, **A**$_2$**B**, **A**$_3$). The calculated values for **AB**$_2$ are in excellent agreement with the data determined for an authentic sample[10] (Table 1). Without synthesizing **A**$_2$**B** and **A**$_3$, we can prove that the purified polymer does not contain these structures. Table 1 summarizes both the ^{1}H chemical shifts of all possible 1,3,5-trisubstituted benzene moieties and the chemical shift effects due to changed substitution.

Because the chemical shifts of protons between amide groups show a slight concentration dependence (low-

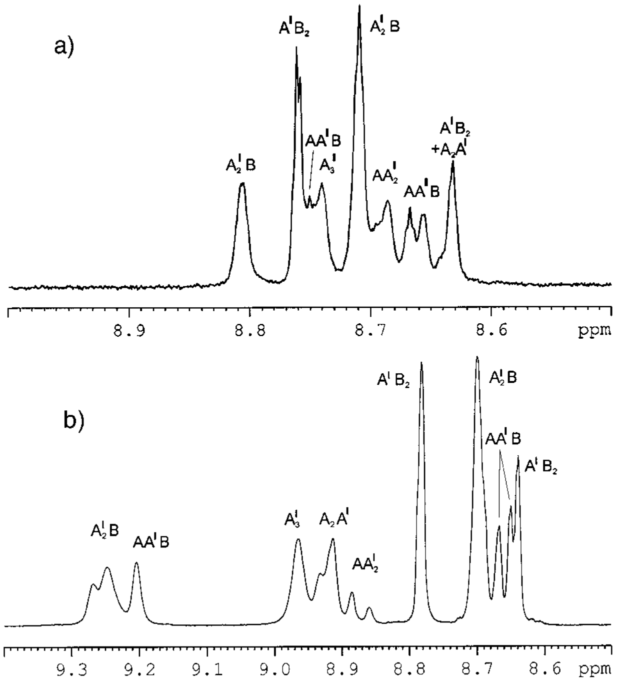


Figure 4. ^{1}H NMR spectra: enlarged region of the 1,3,5-trisubstituted benzene moiety of (a) 0.4 mg of pPDT-2 in 0.75 mL of DMSO-d_6 and (b) 20 mg of pPDT-2 and 4.5 mg of LiCl in 0.75 mL of DMSO-d_6.

Table 1. ^{1}H Chemical Shifts of the 1,3,5-Trisubstituted Benzene Moieties of pPDT in DMSO-d_6 with and without LiCl (Atom Numbering According to Figure 1)

struct unit	substitution			chem shifts (in ppm) without LiCl[a]			chem shifts (in ppm) with LiCl[b]		
	R$_1$	R$_2$	R$_3$	2	4	6	2	4	6
AB$_2$[c,d]	A	B	B	8.70	8.59	8.70			
A′B$_2$	A′	B	B	8.76	8.63	8.76	8.76	8.61	8.76
A$_2$B[c]	A	A	B	8.69	8.61	8.61			
AA′B	A′	A	B	8.75	8.66	8.67	9.49	8.62	8.64
A′$_2$B	A′	A′	B	8.81	8.71	8.71	9.53	8.66	8.66
A$_3$[c]	A	A	A	8.58	8.58	8.58			
A$_2$A′	A′	A	A	8.64	8.62	8.64	8.98	8.95	8.98
AA$_2$′	A′	A′	A	8.70	8.69	8.69	9.01	9.01	9.01
A′$_3$	A′	A′	A′	8.74	8.74	8.74	9.03	9.03	9.03

[a] 1 mg of pPDT-2 ($m/n = 1$) in 0.75 mL DMSO-d_6; concentration dependence of chemical shift values going from 0.4 to 40 mg polymer in 0.75 mL DMSO-d_6: protons between two amide groups, +0.035 ppm; all other, +0.01 ppm. [b] 5 mg of pPDT-2 ($m/n = 1$) and 40 mg LiCl in 0.75 mL DMSO-d_6. [c] Structures were not observed in the polymers. Chemical shifts were estimated from assigned structures based on the following shift effects (in ppm) determined from the experimentally assigned structures. $\Delta\delta$ (A′ → A): ortho, −0.06; para, −0.04. Further increments, $\Delta\delta$ (B → A′): ortho, +0.05 (varies between +0.03 and +0.08); para, −0.06. [d] Calculated chemical shifts correspond with experimentally determined values of the 1,3,5-TB moiety of **AB$_2$**: 8.59 (2/6) and 8.70 ppm (4).[10]

field shift up to 0.03 ppm with respect to the protons ortho to **B** groups) highly concentrated samples show more signal overlap. Therefore, we preferred low-concentration solutions for the quantification of structural units (<1.5 mg of polymer/mL of DMSO-d_6). The amide proton region (10.57−10.66 ppm) is not suitable for quantification due to concentration effects on chemical shifts and line widths. We have found that the chemical shifts of protons between two amide groups are very sensitive to addition of LiCl to the DMSO-d_6 solution. Obviously, **L** and **D** units of pPDT may act as bidentate ligands for Li$^+$. These interactions will be the topic of a forthcoming paper.[13] Nevertheless, Figure 4b depicts that this effect can be used to obtain a better separation of the signal groups. Table 1 gives signal assignments for a sample containing a *defined* content of LiCl. The induced low-field shifts are strongly dependent on the amount of LiCl added (compare Figure 4b—4.5 mg of LiCl—and data in Table 1—40 mg of LiCl). Therefore, the reproducibility of absolute chemical shift values is low but the sequence of signals due to different structural units remains unchanged. The overall content of **T**, **L**, and **D** units can be obtained quite easily also using spectrometers with lower resonance frequencies.

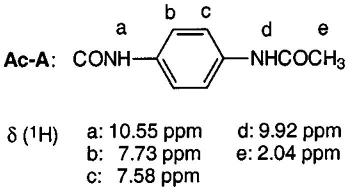


Figure 5. Acetylated **A** unit (**Ac-A**) and its ^{1}H NMR signals assignment.

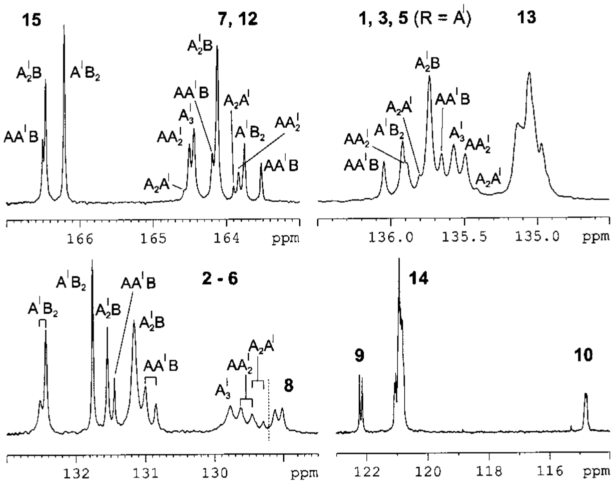


Figure 6. Regions of the ^{13}C NMR spectrum of pPDT-2 ($m/n = 1$) (the broadened signal of C$_{11}$ at 143.7 ppm is not shown), Atom numbering is according to Figure 1.

It should be mentioned that in the ^{1}H NMR spectra published by Jikei et al.[11,12] no signals which can be assigned to **A** groups could be identified. On the other hand, they observed signals at 10.52, 9.91 7.71, 7.69, and 7.58 ppm which are missing in our spectra. Surprisingly, these signals and an additional signal at 2.04 ppm were observed using a new sample of TMA for our polymer synthesis. Checking the quality of this TMA sample by ^{1}H NMR, we found a content of 10 mol % acetic acid. The additional signals could unequivocally be assigned to **Ac-A** units (Figure 5) formed by reaction of acetic acid with amino groups. Thus, the quality of the starting materials has to be checked very carefully to avoid side reactions in the polycondensation.

^{13}C NMR Experiments. ^{13}C chemical shifts are often more sensitive to structural changes than ^{1}H chemical shifts. Figure 6 shows signal regions of a ^{13}C spectrum of pPDT-2 ($m/n = 1$).

On the basis of the ^{1}H NMR results, ^{1}H−^{13}C shift correlated spectra (HMQC, HMBC) were used for signal assignment. Two subspectra were given as examples. Figure 7 depicts the HMQC subspectrum for the 1,3,5-TMB moiety. The CH carbons of this moiety can be assigned by its one-bond correlations to the corresponding protons. The carbonyl carbons can be assigned in

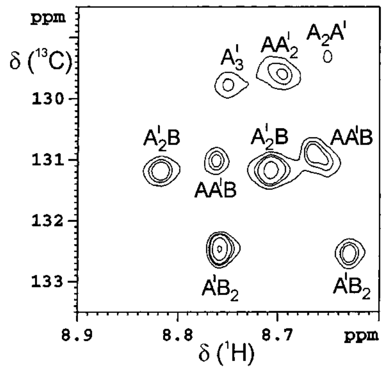


Figure 7. ^{1}H−^{13}C HMQC subspectrum of pPDT-2 (m/n = 1) showing the one-bond correlations for the 1,3,5-TB moiety.

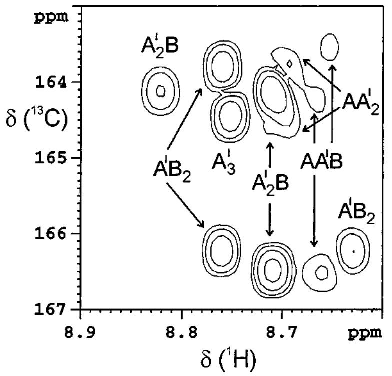


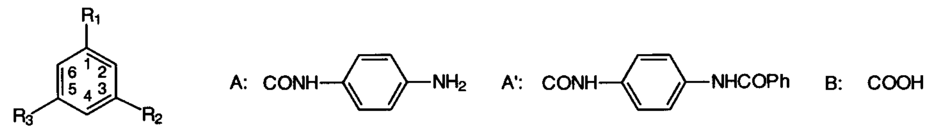
Figure 8. ^{1}H−^{13}C HMBC subspectrum of pPDT-2 (m/n = 1) showing the three-bond correlations between carbonyl carbons and protons of the 1,3,5-TB moiety.

the HMBC spectrum by its three-bond correlations to the protons of the 1,3,5-TMB moiety. This subspectrum is shown in Figure 8. The symmetric **A₃′** unit shows only one correlation. For **A′B₂** and **A₂′B**, the protons between an **A′** and **B** substituent show correlations to two different carbonyl carbons whereas the proton between two **A′** or two **B** substituents shows the expected correlation to only one carbonyl signal. For the units with lower signal intensity, the signal intensities in the quantitative ^{13}C NMR spectrum were additionally analyzed. In this way, a complete signal assignment is possible for the different substitution pattern of the 1,3,5-TB moiety (Figure 6). The signal splitting is caused only by the structural units assigned in the ^{1}H NMR spectrum but not by longer sequences All chemical shift values are given in Table 2. Characteristic substituent effects can be determined for the ring and carbonyl carbons. They confirm the assignments and allow the prediction of the chemical shifts of the structures **AB₂**, **A₂B**, and **A₃**. The calculated values for **AB₂** are in good agreement with the data determined for an authentic sample (Table 2).

The signals of the *p*-substituted phenylene units **A** and **A′** give less structural information. The carbon directly bonded to the NH₂ group of **A** (C_{11}) appears as broadened signal at 143.7 ppm (not shown in Figure 6). The other carbons show a splitting in two signals. From the intensity ratio we assign the signals of C_8, C_9, and C_{10} at 129.00, 122.23, and 114.75 ppm to the **AA′B** unit and at 129.11, 122.14, and 114.80 ppm to the **AA′₂** and **A₂A′** units.This assignment is confirmed by samples of different composition. The ipso-carbon of the **A′** units (C_{13}) and the protonated carbons (C_{14}) result in several signals at about 135 and 121 ppm, respectively. They are caused by the six possible **A′**-centered triads. The first and the last unit in these triads can be an **T**, **L**, or **D** unit. When these units are different, **A′** also becomes asymmetric, and so C_{13} and C_{14} can split up into two signals. This explains the large number of signals observed. On the other hand, we were not able to assign these signals to triads due to the very small chemical shift differences. Finally, our investigations confirm the assignment of five signal groups in the carbonyl region to **T**, **L**, and **D** units as given by Jikei et al.[12] with the exception of the high-field group at about 163.6 ppm. When the pPDT still contains **A** units besides the amide carbon signal of **A′B₂** (**T**) also amide carbon signals of the **L** unit **AA′B** and of the **D** units **A₂A′** and **AA′₂** appear in this region.

Structure of pPDTs Synthesized from Different *m*/*n* Ratios. Variation of the *m*/*n* ratio allows to change the composition of the resulting hyperbranched polyamide. The quantification of **A** and **A′** units and of different substituted trimesic units based on our NMR signal assignments allow to investigate these effects.

Table 2. ^{13}C Chemical Shifts of the 1,3,5-Trisubstituted Benzene Moieties of pPDT



struct unit	substitution			chemical shifts (in ppm)								
	R₁	R₂	R₃	1	2	3	4	5	6	C=O (R₁)	C=O (R₂)	C=O (R₃)
AB₂[a,b]	A	B	B	136.25	132.34	131.66	132.23	131.66	132.34	163.15	166.25	166.25
A′B₂	A′	B	B	135.92	132.44	131.76	132.52	131.76	132.44	163.75	166.21	166.21
A₂B[a]	A	A	B	135.95	130.83	135.95	130.68	131.34	130.68	163.60	163.60	166.55
AA′B	A′	A	B	135.65	131.00	136.05	131.00	131.44	130.85	164.20	163.52	166.51
A′₂B	A′	A′	B	135.74	131.17	135.74	131.17	131.55	131.17	164.12	164.12	166.47
A₃[a]	A	A	A	135.72	129.11	135.72	129.11	135.72	129.11	163.97	163.97	163.97
A₂A′	A′	A	A	135.41	129.28	135.80	129.44	135.80	129.28	164.57	163.90	163.90
AA′₂	A′	A′	A	135.50	129.44	135.50	129.60	135.89	129.60	164.51	164.51	163.83
A′₃	A′	A′	A′	135.57	129.77	135.57	129.77	135.57	129.77	164.44	164.44	164.44

[a] Structures were not observed in the polymer spectra. Chemical shifts were estimated from assigned structures based on the following shift effects (in ppm) determined from the experimentally assigned structures. $\Delta\delta$ (A′ → A): ipso, +0.31; ortho, −0.17; meta, −0.1; para, −0.32; C=O (A′, ipso), −0.6; C=O (B, meta), +0.04; C=O (A′, meta), +0.07; C=O (A, meta), +0.07. Further increments, $\Delta\delta$ (B → A′): ipso, +3.98; ortho, −1.4; meta, −0.17; para, −1.35; C=O (B, ipso), −2.05; C=O (B, meta), + 0.26; C=O (A′, meta), +0.34; C=O (A, meta), +0.3. [b] Calculated chemical shifts correspond to experimentally determined values of the 1,3,5-TB moiety of **AB₂**: 166.2 (C=O, $R_{2/3}$), 163.06 (C=O, R_1), 136.30 (1), 132.2 (2, 4) and 131.73 ppm (5). Further carbon signals: 145.42 (11), 127.85 (8), 122.35 (9), 113.72 ppm (10).

Table 3. Reactant Ratio (m/n), Characteristic Ratios of Structures and Functional Groups, Percentage of Structural Units,[a] and Degree of Branching (DB) for Three Different pPDT Samples

sample	pPDT-1	pPDT-2	pPDT-3
	Monomer Feed Data		
m/n	1.33	1	0.67
$[\mathrm{COOH}]/[\mathrm{NH_2}]$	2	1.5	1
	Polymer Data[b]		
m/n[c]	0.98	0.87	0.67
$[\mathbf{A}]/[\mathbf{A'}]$[c]	0.16	0.35	0.83
[COOH]/[CONH][c]	0.6	0.49	0.33
$[\mathrm{COOH}]/[\mathrm{NH_2}]$[c]	9.2	3.2	1.1
$\mathbf{A'B_2}$ (T, T′)	30.2	23.6	11.8
AA′B (L, T′)	6.1	14.0	23.7
$\mathbf{A'_2B}$ (L, L′)	45.4	38.4	24.6
$\mathbf{A_2A'}$ (D, T′)	0	3.3	9.3
$\mathbf{AA'_2}$ (D, L′)	6.1	10.5	22.8
$\mathbf{A'_3}$ (D, D′)	12.2	10.2	7.8
T	30.2	23.6	11.8
L	51.5	52.4	48.3
D	18.3	24	39.9
T′	36.3	40.9	44.8
L′	51.5	48.9	47.4
D′	12.2	10.2	7.8
DB (Frechet)[d]	0.48	0.48	0.527
DB (Frey)[d]	0.42	0.49	0.62
DB′ (Frey)[d]	0.32	0.29	0.25

[a] Nomenclature and assignment to **T**, **L**, and **D** and to **T′**, **L′**, and **D′**, respectively, according to Figure 2. [b] Determined from ^{1}H NMR spectra. [c] These values can also be determined from the content of structural units: $[\mathrm{COOH}] = 2[\mathbf{A'B_2}] + [\mathbf{AA'B}] + [\mathbf{A'_2B}]$; $[\mathbf{A}] = [\mathbf{AA'B}] + 2[\mathbf{A_2A'}] + [\mathbf{AA'_2}]$; $[\mathbf{A'}] = \{[\mathbf{A'B_2}] + [\mathbf{AA'B}] + 2[\mathbf{A'_2B}] + [\mathbf{A_2A'}] + 2[\mathbf{AA'_2}] + 3[\mathbf{A'_3}]\}/2$; $[\mathrm{CONH}] = [\mathbf{A}] + 2[\mathbf{A'}]$; $[\mathrm{NH_2}] = [\mathbf{A}]$; $n = [\mathbf{A}] + [\mathbf{A'}]$; $m = 100$ = sum of all structural units. [d] Determined from **T**, **L**, and **D** (DB) and **T′**, **L′**, and **D′** (DB′) according to the equations given in the text.

Three samples were prepared from different molar ratios of trimesic acid and *p*-phenylenediamine and their structure was analyzed by NMR spectroscopy (Table 3).

It is straightforward to determine the ratio of both reactants in the polymer, the ratio of *p*-phenylene units with one (**A**) and two (**A′**) amide groups and the ratio of carboxylic acid and amide groups from the integrals of signal groups which can be assigned to **A, A′**, and the 1,3,5-TB moiety (Figure 1). The content of the six structural units given in Table 3 was determined from the ^{1}H NMR spectra. The values obtained from the ^{13}C NMR spectra deviate only slightly from these values. The overall content of **T** (**T′**), **L** (**L′**), and **D** (**D′**) units was calculated from the content of the six structural units. Finally, from these contents, the degree of branching (DB) was calculated. Both, the well-known equation of Fréchet et al. ($\mathrm{DB} = (\mathbf{T} + \mathbf{D})/(\mathbf{T} + \mathbf{L} + \mathbf{D})$)[4] and also the equation published by Frey et al. ($\mathrm{DB} = 2\mathbf{D}/(\mathbf{L} + 2\mathbf{D})$)[6] were used for the calculation of DB.

In the following, we will discuss the data summarized in Table 3. It is obvious that the polymer composition with regard to the incorporated reactants B_3 and A_2 deviates from the monomer feed when no excess of A_2 is used. A m/n ratio of 0.89 was also found by Jikei et al. for a pPDT prepared from an equimolar ratio of A_2 and B_3 in the monomer feed.[11] We assume that during the purification procedure low-molecular-weight structures like unreacted B_3, $\mathbf{AB_2}$ and $\mathbf{A_2B}$ were removed from the crude reaction product. For this reason they were also not observed in the polymer spectra. As expected, the ratio of **A** units to **A′** units increases with decreasing excess of acid groups. In the same way the content of free acid groups decreases. Also the structural units reflect well these changes in composition. As compared to pPDT prepared by using an equimolar ratio of A_2 and B_3 (pPDT-2), an excess of acid groups decreased the content of dendritic groups **D** (pPDT-1) whereas an excess of amino groups promotes the formation of amide groups (pPDT-3) and, thus, the total number of remaining acid functions in **T** and **L** units was reduced. This offers possibilities to influence the $\mathrm{COOH/NH_2}$ ratio of the polymer which may be of importance for applications of pPDT. The degree of branching is a further important parameter for the characterization of hyperbranched polymers. The DB calculated according to Fréchet is found to be close to 50% but does not provide information on the structure development. For all samples the content of linear units is about 50% both when only the number of B units (**L**) and when the total number of **A** and **B** units (**L′**) is considered. The DB of Fréchet can be applied best for $m/n = 1$. In this case, the composition of the monomer feed results in the first reaction step at theoretical complete conversion in the formation of the classical AB_2 precursor for hyperbranched polymerization (structural unit $\mathbf{AB_2}$). When another monomer feed composition is applied the definition of Frey which compares the real number of actual growth directions with the number of possible growth directions should be used. We have calculated both the value based on the number of **B** units of the 1,3,5-TB moieties (DB(Frey)) and the value based on the total number of **A** and **B** units of the 1,3,5-TB moieties (DB′(Frey)). DB(Frey) increases with increasing content of A_2 in the monomer feed because more acid groups may be transformed to amide groups. However, the ratio of **A**/**A′** units shows that mainly the content of **A** increases which are also terminal units of the polymer. The terminal functionalities of the hyperbranched polymer change from a nearly 10-fold excess of COOH for $m/n = 1.33$ to a comparable amount of COOH and NH_2 for $m/n = 0.67$. Furthermore, the content of $\mathbf{A'_3}$ units which represent branches to three further 1,3,5-TB moieties decreases. This decrease in new growth directions is reflected by the decrease of DB′(Frey) with decreasing content of B_3.

It is obvious that different structural aspects were highlighted by the different DB definitions. When this is taken into consideration they are helpful tools to check the polymer architecture.

Conclusions

The synthesis of soluble hyperbranched polyamides via the $A_2 + B_3$ approach using commercially available monomers presents an attractive alternative to the classical approach via AB_2 monomers. However, the intrinsic danger of cross-linking reactions leading to gel formation in this reaction requires a very careful control of both the reaction conditions and the ratio of the reactants. High-resolution NMR techniques were proven to be very suitable tools to characterize in detail the internal structure of these highly branched systems including polar interactions and to quantify the amount of different structural units in dependence on the reaction progress and the ratio of functionalities in the monomer mixture. In contrast to an AB_2 system, one has to consider in the $A_2 + B_3$ hyperbranched product **A** and **B** end groups of different ratio depending on the feed ratio of A_2 to B_3 and slight changes in the degree of branching with a deviatiation from 0.5 are observed due to variations in the internal structural units.

Varying the ratio of A_2 to B_3 can shift the gel point toward higher conversion. Thus, the information provided by NMR analysis on structural changes in dependence on the A_2/B_3 ratio offers the possibility to optimize the reaction conditions and to adjust the functionalization of these polymers with respect to special applications, e.g., as chromatography material or as enzyme support.

Acknowledgment. The collaboration between the Genoa and Dresden laboratories has been financially supported by the DAAD Vigoni program.

Supporting Information Available: Figures showing additional plots of 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

(2) Fréchet, J. M. J.; Hawker, C. J. Synthesis and Properties of Dendrimers and Hyperbranched Polymers. In *Comprehensive Polymer Science*; Aggarwal, S. L., Russo, S., Eds.; Elsevier Science Ltd.: Oxford, England, 1996; 2nd Supplement, p 71ff.

(3) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.

(4) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(5) Kim, Y. H. *Macromol. Symp.* **1994**, *77*, 21.

(6) Hölter, D.; Burgrath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.

(7) Huber, T.; Böhme, F.; Komber, H.; Kronek, J.; Luston, J.; Voigt, D.; Voit, B. *Macromol. Chem. Phys.* **1999**, *200*, 126.

(8) Schmaljohann, D.; Komber, H.; Voit, B. *Acta Polym.* **1999**, *50*, 196.

(9) Schmaljohann, D.; Komber, H.; Barratt, J. G.; Appelhans, D.; Voit, B. Manuscript in preparation.

(10) Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S. *High Perform. Polym.* **2001**, *13*, 545.

(11) Jikei, M.; Chon, S.-H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061.

(12) Jikei, M.; Kakimoto, M. *High Perform. Polym.* **2001**, *13*, 533.

(13) Komber, H.; Monticelli, O.; Russo, S.; Voit, B. Manuscript in preparation.

MA002223F