Poly(ether amide) Dendrimers via Nucleophilic Ring-Opening Addition Reactions of Phenol Groups toward Oxazolines: Synthesis and Characterization

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ABSTRACT: The synthesis of aliphatic−aromatic poly(ether amide) dendrimers via ring-opening addition reaction of phenol groups toward oxazoline up to generation 3 is presented. The first and second generation could be prepared both by convergent and divergent approaches. The ring-opening addition reaction was carried out in bulk at temperatures between 140 and 190 °C, followed by hydrogenation of the protecting benzyl ether units with palladium catalyst. The dendrons and dendrimers were characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI−TOF MS, SEC, and DSC. The synthetic scheme applied allowed to prepare perfect dendrimers having identical structure and end groups as previously described hyperbranched polymers which enabled a direct comparison of the properties. Melt rheology measurements on the dendrimers revealed a predominantly elastic behavior with a relatively high viscosity at low frequency, as was found also for the hyperbranched analogues. The second generation of one of the poly(ether amide) dendrimers was mixed with linear polyamide 6 (PA6) in melt up to an amount of 1 wt % in order to evaluate the influence of dendrimers on the properties of the matrix. The dendrimer was fully miscible with the matrix, but in contrast to the hyperbranched polymers of higher molar mass, it had no influence on the melt rheological behavior of the PA6.

Introduction

Dendritic polymers, both the perfectly branched dendrimers and the less perfect hyperbranched molecules, have attracted much attention over the past decade.[1,2] Amide junctions within the dendritic structure are often used, starting with the very well-known aliphatic PAMAM dendrimers reported by Tomalia,[3] up to aliphatic−aromatic and fully aromatic amide dendrimers[4,8] and several hyperbranched polyamides.[9−14] Whereas for example the PAMAM dendrimers found application in pharmaceuticals[15−20] and gene therapy,[21−23] hyperbranched polyamides have been discussed as blends components in combination with linear polymers[24] or as additives and processing aids.[25,26]

In preceding work[27] we reported the synthesis and modification of hyperbranched aliphatic−aromatic poly(ether amide)s based on oxazoline chemistry with phenolic end groups. We investigated their thermal and rheological properties for potential application as a rheological modifier in linear polyamide 6.[25,26] As expected for hyperbranched polymers, an imperfect branched structure and a broad molar mass distribution were achieved; thus, analysis of the exact molar mass of these highly branched poly(ether amide)s by size exclusion chromatography (SEC) was difficult.[28] Similarly, exact correlation of structure/molar mass and the properties of these molecules was not possible. Therefore, we were interested in studying analogous perfectly branched poly(ether amide) dendrimers to compare the properties. Aromatic−aliphatic poly(ether amide) dendrimers are known from the literature;[4−7] however, since all of them were synthesized by a convergent approach via amidation using activation methods and protective group techniques of peptide synthesis, the resulting terminal groups are either carboxylic acids or amines. Since the nature of the terminal groups determines to a large extent the material as well as the solution properties of dendritic polymers, we need for an adequate comparison perfect dendritic aliphatic−aromatic structures having not only identical repeating units but also the same end groups as our phenol-terminated hyperbranched poly(ether amide)s. For this reason, the dendrimers were synthesized by nucleophilic ring-opening addition reaction of phenols toward oxazolines, which followed the same synthetic approach as used for the synthesis of our previously[27] described hyperbranched poly(ether amide)s. This allows us to prepare exact dendritic analogues to our hyperbranched molecules and will contribute significantly to the structure property relationship studies in branched molecules as it was started by Fréchet et al.[29] when he compared structural identical linear, hyperbranched, and dendritic polyesters.

The synthesis and modification of polymers using the 2-oxazoline group has been intensively studied for several years.[30,31] Beside the cationic ring-opening polymerization using alkylation reagents as initiators,[30,32] the ring-opening addition reactions of oxazolines with thiol, phenol, or carboxylic acid groups to generate thioetheramides, etheramides, or esteramides were explored.[33−35] These reactions can be used to enhance molar mass by chain extension of polycondensates, to cross-link, or to prepare linear polymers.[33,36−40]

Experimental Part

Materials. All substances were used as purchased from Aldrich, Fluka, or Merck in >99% purity (p.a.) quality without further purification. All reactions were carried out under an argon atmosphere. 2-(3,5-Dihydroxyphenyl)-1,3-oxazoline (**3**) was prepared from *N*-(2-hydroxyethyl)-3,5-dihydroxybenzamide (**2**) as described previously.[27] The linear PA6 supplied by BASF AG, which was used as a matrix polymer, had a

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molar mass of $\bar{M}_w$ = 76 000 g/mol ($\bar{M}_n$ = 17 400 g/mol) as determined by SEC performed in hexafluoro-2-propanol + 0.05% trifluoroacetic acid potassium salt using a column combination of Shodex HFIP precolumn, Shodex HFIP 803, and Shodex HFIP 805 and calibration with poly(methyl methacrylate) standards from Polymer Standard Services PSS (0.5 mL/min, Kontron HPLC pump, detectors: UV photometer GAT LCD 503 at 230 nm; differential refractometer ERC 7510). The relation of the end groups was 53 mmol/kg:57 mmol/kg ($COOH:NH_2$) which was determined by titration (data supplied by BASF). The polyamide had a viscosity number VN = 149, measured with an Ubbelohde viscosimeter (Schott) at 25 °C in 96% H_2SO_4 ($VN = (t_1/t_0 - 1)(1/c)$; t_1, t_0 = flow times of solution and solvent, c = 0.005 g/mL of PA6 in sulfuric acid, ISO307).

Blend Preparation. The blend preparation of polyamide 6 with dendrimers was carried out at 250 °C in a DACA twin-screw microcompounder (DACA Instruments, model 20000) with a mixing compartment volume of approximately 5 mL. Both the matrix polymer PA6 and the dendrimer were added as dry powders at the same time at a screw speed of 100 rpm, and the components were mixed for 5 min. For comparison reasons, the pure matrix PA6 was treated in the same way before thermal and rheological analysis. The prepared mixtures contained an amount of 0.1 (**PA6/GII-OH/01**) and 1 wt % (**PA6/GII-OH/1**) of the dendrimer **GII-OH**. All blends were stored in a desiccator over silica gel after mixing to keep the material dry.

Measurements. Melting points were determined on a Mettler FP 62 melting point instrument (scan rate 2 K/min) and are uncorrected. The NMR spectra were recorded in 5 mm o.d. sample tubes with a Bruker DRX 500 NMR spectrometer at 500.13 MHz for ^{1}H NMR spectra and at 125.75 MHz for ^{13}C NMR spectra. DMSO-d_6 was used as solvent for all NMR experiments. For internal calibration the solvent peaks of DMSO were used: δ (^{13}C) = 39.70 ppm, δ (^{1}H) = 2.5 ppm. The signals were assigned by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC techniques using the standard pulse sequences provided by Bruker. FT-IR spectra were recorded with a Bruker IFS66V/s spectrometer with a Golden Gate Unit (crystal: diamond, single reflection, ATR technique). SEC measurements were performed with a modular chromatographic KNAUER equipment with an RI detector. A column set with two ZORBAX columns PSM 60 and PSM 300 (silica microspheres 6 μm, mol wt range 300−300 000 g/mol Rockland Technologies Inc.) was used. The experiments were carried out at 25 °C in distilled *N*,*N*-dimethylacetamide with 3 g/L LiCl and 2 vol % H_2O (calibrated with polystyrene (PS) or polyvinylpyridine (PVP) standards, flow rate of 0.5 mL/min). The MALDI−TOF mass spectra were recorded by a HP G2025A MALDI−TOF MS system equipped with a N_2 laser (337 nm) and a TLF unit. As matrix materials were used 2,5-dihydroxybenzoic acid or sinapinic acid (0.1 M THF solution) and Na^+, Li^+, or Cs^+ as modifier. The concentration of the sample solution was about 10^{-3} M. Mixtures of these solutions (10:1 matrix solution/sample solution) were placed on the target and dried in a vacuum.

The thermal behavior was investigated using a Perkin-Elmer DSC 7 with Pyris-Software. The measurements were carried out in aluminum pans under nitrogen in a temperature range from −10 up to 250 °C with a scanning rate of ±10 K/min as cycles consisting of first heating−cooling−second heating scans. The glass transition temperatures were determined from the second heating run by the Δc_p half-step method. The temperature and heat transitions were calibrated with In and Pb standards. The melt rheological measurements were performed using a Rheometrics ARES with plate−plate geometry in oscillation mode under a nitrogen atmosphere at 250 °C. The plate diameter was 25 mm, and the gap ranged from 0.6 to 1.3 mm. A frequency range between 0.1 and 100 rad/s and a strain within the linear viscoelastic range were used. The blend samples were investigated as extruded strands and the dendrimers as powders.

Synthesis of the Monomer. 2-(3,5-Bisbenzyloxyphenyl)-1,3-oxazoline (**4**): A mixture of 2-(3,5-dihydroxyphenyl)-1,3-oxazoline (**3**) (4.41 g, 24.60 mmol), benzyl chloride (6.26 g, 49.40 mmol), dried potassium carbonate (8.51 g, 62.00 mmol), and 18-crown-6 (1.32 g, 5.00 mmol) in dry acetone was heated at reflux and stirred vigorously under argon for 48 h. The mixture was allowed to cool and was evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2, and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were then dried over sodium sulfate, and the solvent was evaporated to dryness. The crude product was purified by column chromatography, eluting with ethyl acetate. The recrystallization from ethyl acetate/hexane gave **4** as white crystalline solid: yield 60%; mp 107.5 °C.

^{1}H NMR: δ = 7.42 (d, 4H, H^{10}), 7.38 (t, 4H, H^{11}), 7.32 (t, 2H, H^{12}), 7.08 (d, 2H, H^2), 6.84 (t, 1H, H^4), 5.12 (s, 4H, H^8) 4.37 (t, 2H, H^7), 3.93 ppm (t, 2H, H^6).

^{13}C NMR: δ = 162.82 (C^5), 159.53 (C^3), 136.90 (C^9), 129.58 (C^1), 128.57−127.73 (C^{10}−C^{12}), 106.76 (C^2), 105.31 (C^4), 69.61 (C^8), 67.59 (C^7), 54.50 ppm (C^6).

FT-IR−ATR: ν = 2970, 2900 (s, C−H), 1649 (w, C=N), 1594 (s, C=C), 1449 (m, C−H), 1165, 1059 cm^{-1} (s, C−O−C).

MALDI−TOF MS (5.96 μJ): m/z = 360 (M + H$^+$), 382 (M + Na$^+$).

General Procedure for the Ring-Opening Addition Reaction of Phenol Groups toward Oxazoline. *Method A***.** A mixture of the appropriate oxazoline (2 equiv) and *N*-(2-hydroxyethyl)-3,5-dihydroxybenzamide (**2**) (1 equiv) was placed into a Schlenk flask under argon. The flask was placed in an oil bath preheated to 190 °C. The substances melted completely after about 2 min, and the melt was stirred for 5 h at 190 °C. After cooling, the crude product was purified as outlined in the following text.

*Method B***.** A mixture of the appropriate phenol and 2 equiv per phenol group of 2-(3,5-bisbenzyloxyphenyl)-1,3-oxazoline (**4**) was placed into a Schlenk flask under argon. The flask was placed in a preheated oil bath. The substances melted completely after about 2 min, and the melt was stirred for 10 h at appropriate temperature. After cooling, the crude product was purified as outlined in the following text.

General Procedure for Cleavage of the Benzyl Ethers. A solution of benzyl ether (1.00 mmol) in 10 mL of dry ethyl acetate was added to a prehydrogenated suspension of 0.1 g of dry 10% palladium−charcoal per available benzyl ether protective group in dry methanol, and the mixture was stirred vigorously at room temperature under hydrogen for 24 h. The reaction mixture was then filtered through Celite and the filtrate evaporated to dryness under reduced pressure. The crude product was purified as outlined in the following text.

Convergent Synthesis. $HOCH_2CH_2NHCO$-[G1]-$(OBn)_4$ **(G1a-Bn):** This compound was prepared from 2-(3,5-bisbenzyloxyphenyl)-1,3-oxazoline (**4**) according to method A and purified by column chromatography on silica gel eluting at first with ethyl acetate to remove the byproducts. Subsequently, ethyl acetate/methanol (5%) as eluent was used to give **G1a-Bn** as white solid: yield 55%; mp 159.7 °C.

^{1}H NMR: δ = 8.65 (t, 2H, NH), 8.40 (t, 1H, NH), 7.44−7.30 (m, 20H, benzyl aryl-H), 7.13 (d, 4H, H^{12}), 7.04 (d, 2H, H^2), 6.82 (t, 2H, H^{14}), 6.68 (t, 1H, H^4), 5.11 (s, 8H, benzyl-CH_2), 4.71 (t, 1H, OH), 4.13 (t, 4H, H^8), 3.60 (q, 4H, H^9), 3.47 (q, 2H, H^7), 3.28 ppm (q, 2H, H^6).

^{13}C NMR: δ = 166.11 (C^5), 165.83 (C^{10}), 159.60 (C^3), 159.56 (C^{13}), 136.96 (C$^{\text{benzyl aryl}}$), 136.86 (C^1), 136.47 (C^{11}), 128.63−127.90 (C$^{\text{benzyl aryl}}$), 106.51 (C^{12}), 106.13 (C^{14}), 104.87 (C^2), 104.11 (C^4), 69.70 (C$^{\text{benzyl}-CH2}$), 66.41 (C^8), 59.88 (C^7), 42.39 (C^6), 38.98 ppm (C^9).

FT-IR−ATR: ν = 3294 (br, N−H), 3064, 3033 (w, aryl−H), 2931, 2872 (s, C−H), 1630 (w, NHC=O), 1590, 1529 (s, C=C), 1437 (m, C−H), 1305 (s, O−H), 1163, 1058 cm^{-1} (s, C−O−C).

MALDI−TOF MS (2.83 μJ): m/z = 923 (M + Li$^+$), 939 (M + Na$^+$), 955 (M + K$^+$).

$HOCH_2CH_2NHCO$-[G1]-$(OH)_4$ (**G1a-OH):** This compound was prepared from $HOCH_2CH_2NHCO$-[G1]-$(OBn)_4$ (**G1a-Bn)** following the general method for the benzyl ether cleavage. The product was dried in a vacuum to give **G1a-OH** as white solid: yield 89%; mp 140.9 °C.

^{1}H NMR: δ = 9.44 (s, 4H, OH), 8.38 (t, 3H, NH), 7.02 (d, 2H, H^2), 6.67 (d, 4H, H,^{12} 1H, H^4), 6.33 (t, 2H, H^{14}), 4.67 (t, 1H, OH), 4.10 (t, 4H, H^8), 3.56 (q, 4H, H^9), 3.48 (q, 2H, H^7), 3.29 ppm (q, 2H, H^6).

^{13}C NMR: δ = 166.93 (C^{10}), 165.83 (C^5), 159.57 (C^3), 158.44 (C^{13}), 136.82 (C^1), 136.63 (C^{11}), 106.09 (C^2), 105.58 (C^{12}), 105.31 (C^{14}), 104.06 (C^4), 66.38 (C^8), 59.86 (C^7), 42.36 (C^6), 38.86 ppm (C^9).

FT-IR−ATR: ν = 3381 (br, N−H), 3231 (br, O−H), 2942 (s, C−H), 1710 (w, NHC=O), 1588, 1544 (s, C=C), 1444 (m, C−H), 1330 (s, C−O), 1160, 1065 (s, C−O−C),1005 cm^{-1} (s, C−OH).

MALDI−TOF MS (4,05 μJ): m/z = 556 (M + H$^+$), 562 (M + Li$^+$), 578 (M + Na$^+$).

Ox-[G1]-(OBn)$_4$ **(G1Ox-Bn): G1a-Bn** (0.50 g, 0.55 mmol) was suspended in 2 mL of methylene chloride and cooled to 0 °C. Then thionyl chloride (0.1 mL, 1.3 mmol) was added dropwise under stirring. After an additional 1.5 h, the ice bath was removed and the solution was stirred at room temperature until gas development was completed. The solution was poured into ice water, and the organic layer was separated. The organic layer was washed with sodium hydrogen carbonate solution and water, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate to give mainly the chloroethyl derivate (besides a small amount of **G1Ox-Bn).** The chloroethyl derivate reacts with KOH to the oxazoline: KOH (0.043 g, 0.770 mmol) and 2-chloroethyl derivate (0.24 g) were dissolved in consecutive order in 3 mL of methanol and then refluxed for 1.5 h. After cooling the solution was put into water, and the resulting suspension was neutralized with aqueous acetic acid and filtered. The solid was dried in a vacuum to give **G1Ox-Bn**: yield 51%; mp 146 °C.

^{1}H NMR: δ = 8.59 (t, 2H, NH), 7.43−7.30 (m, 20H, benzyl aryl−H), 7.11 (d, 4H, H^{12}), 7.00 (d, 2H, H^2), 6.81 (t, 2H, H^{14}), 6.72 (t, 1H, H^4), 5.11 (s, 8H, benzyl−CH$_2$), 4.34 (t, 2H, H^7), 4.13 (t, 4H, H^8), 3.91 (t, 2H, H^6), 3.59 ppm (q, 4H, H^9).

^{13}C NMR: δ = 166.09 (C^{10}), 162.80 (C^5), 159.69 (C^3), 159.50 (C^{13}), 136.92 (C$^{\text{benzyl aryl}}$), 136.49 (C^{11}), 129.58 (C^1), 128.56−127.82 (C$^{\text{benzyl aryl}}$), 106.56 (C^2), 106.51 (C^{12}), 104.83 (C^{14}), 104.53 (C^4), 69.67 (C$^{\text{benzyl−CH2}}$), 67.57 (C^7), 66.42 (C^8), 54.51 (C^6), 39.03 ppm (C^9).

FT-IR−ATR: ν = 3295 (br, N−H), 3095, 3059 (w, aryl-H), 2987, 2901 (s, C−H), 1636 (w, NHC=O), 1592 (s, C=C), 1542 (s, C=C),1438 (m, C−H), 1157, 1059 cm^{-1} (s, C−O−C).

MALDI−TOF MS (4.28 μJ): m/z = 899 (M + H$^+$), 921 (M + Na$^+$), 937 (M + K$^+$).

HOCH$_2$CH$_2$NHCO-[G2]-(OBn)$_8$ **(G2a-Bn)**: This compound was prepared from Ox-[G1]-(OBn)$_4$ (**G1Ox-Bn)** according to method A and purified by column chromatography on silica gel eluting with methylene chloride/methanol (5%) for several times. However, it was not possible to receive the product **G2a-Bn** absolutely pure.

Divergent Synthesis. MeO$_2$C-[G1]-(OBn)$_4$ **(G1-Bn)**: This compound was prepared from methyl-3,5-dihydroxybenzoate (**1**) according to method B at 160 °C and purified by column chromatography on silica gel eluting at first with ethyl acetate to remove the excess of **4**. Subsequently, chloroform/ethanol (1%) as eluent was used several times to give **G1-Bn** as white solid: yield 51%; mp 160.4 °C.

^{1}H NMR: δ = 8.60 (t, 2H, NH), 7.43−7.30 (m, 20H, benzyl aryl−H), 7.11 (d, 4H, H^{11}), 7.08 (d, 2H, H^2), 6.83 (t, 1H, H^4), 6.81 (t, 2H, H^{13}), 5.11 (s, 8H, benzyl−CH$_2$), 4.15 (t, 4H, H^7), 3.80 (s, 3H, H^6), 3.60 ppm (q, 4H, H^8).

^{13}C NMR: δ = 166.10 (C,^{5} C^9), 159.84 (C^3), 159.51 (C^{12}), 136.92 (C$^{\text{benzyl aryl}}$), 136.47 (C^{10}), 131.79 (C^1), 128.57−127.82 (C$^{\text{benzyl aryl}}$), 107.86 (C^{13}), 106.52 (C^{11}), 106.32 (C^4), 104.83 (C^2), 69.68 (C$^{\text{benzyl−CH2}}$), 66.57 (C^7), 52.39 (C^6), 39.01 ppm (C^8).

FT-IR−ATR: ν = 3321 (br, N−H), 3065, 3032 (w, aryl−H), 2944, 2879 (s, C−H), 1717 (s, ROC=O), 1640 (w, NHC=O), 1588, 1522 (s, C=C), 1437 (m, C−H), 1344, 1299 (s, C−O), 1157, 1053 cm^{-1} (s, C−O−C).

MALDI−TOF MS (2.35 μJ): m/z = 888 (M + H$^+$), 910 (M + Na$^+$), 926 (M + K$^+$)

MeO$_2$C-[G1]-(OH)$_4$ **(G1-OH)**: This compound was prepared from MeO$_2$C-[G1]-(OBn)$_4$ (**G1-Bn)** following the general method for the benzyl ether cleavage. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (1%) and dried in a vacuum to give **G1-OH** as white solid: yield 98%; mp 194.7 °C.

^{1}H NMR: δ = 9.40 (s, 4H, OH), 8.38 (t, 2H, NH), 7.01 (d, 2H, H^2), 6.82 (t, 1H, H^4), 6.67 (d, 4H, H^{11}), 6.34 (t, 2H, H^{13}), 4.13 (t, 4H, H^7), 3.82 (s, 3H, H^6), 3.56 ppm (q, 4H, H^8)

^{13}C NMR: δ = 166.93 (C^9), 165.97 (C^5), 159.84 (C^3), 158.38 (C^{12}), 136.66 (C^{10}), 131.79 (C^1), 107.79 (C^{13}), 106.27 (C^4), 105.62 (C^{11}), 105.28 (C^2), 66.55 (C^7), 52.41 (C^6), 38.83 ppm (C^8).

FT-IR−ATR: ν = 3381 (br, N−H), 3253 (br, O−H), 3088, (w, aryl−H), 2924, 2854 (s, C−H), 1697 (s, ROC=O), 1643 (w, NHC=O), 1589, 1541 (s, C=C), 1441 (m, C−H), 1344 (s, C−O), 1305 (s, O−H), 1158, 1061 (s, C−O−C), 1005 cm^{-1} (s, C−OH).

MALDI−TOF MS (2.70 μJ): m/z = 527 (M + H$^+$), 549 (M + Na$^+$), 565 (M + K$^+$).

MeO$_2$C-[G2]-(OBn)$_8$ **(G2-Bn).** This compound was prepared from MeO$_2$C-[G1]-(OH)$_4$ **(G1-OH)** according to method B at 180 °C and purified by column chromatography on silica gel eluting at first with ethyl acetate to remove the excess of **4**. Subsequently, chloroform/ethanol (1%) as eluent was used several times to give **G2-Bn** as colorless glass: yield 57%; T_g 73 °C.

^{1}H NMR: δ = 8.61 (t, 6H, NH), 7.42−7.28 (m, 40H, benzyl aryl−H), 7.12 (d, 8H, H^{18}), 7.06 (d, 2H, H^2), 7.05 (d, 4H, H^{11}), 6.81 (t, 5H, H,^{4} H^{20}), 6.69 (t, 2H, H^{13}), 5.10 (s, 16H, benzyl-CH$_2$), 4.12 (t, 12H, H,^{7} H^{14}), 3.77 (s, 3H, H^6), 3.59 ppm (q, 12H, H,^{8} H^{15}).

^{13}C NMR: δ = 166.07 (C^{16}), 166.02 (C,^{5} C^9), 159.60 (C^3), 159.50 (C,^{12} C^{19}), 136.90 (C$^{\text{benzyl aryl}}$), 136.44 (C,^{10} C^{17}), 132.29 (C^1), 128.54−127.79 (C$^{\text{benzyl aryl}}$), 106.50 (C,^{11} C^{18}), 106.45 (C^4), 106.19 (C,^{13} C^{20}), 104.83 (C^2), 69.56 (C$^{\text{benzyl−CH2}}$), 66.40 (C,^{7} C^{14}), 52.27 (C^6), 39.03 ppm (C,^{8} C^{15}).

FT-IR−ATR: ν = 3325 (br, N−H), 3065, 3033 (w, aryl−H)), 2943, 2880 (s, C−H), 1719 (s, ROC=O), 1645 (w, NHC=O), 1590, 1529 (s, C=C), 1439 (m, C−H), 1342, 1300 (s, C−O), 1155, 1055 cm^{-1} (s, C−O−C).

MALDI−TOF MS (3.75 μJ): m/z = 1965 (M + H$^+$), 1987 (M + Na$^+$), 2003 (M + K$^+$).

MeO$_2$C-[G2]-(OH)$_8$ **(G2-OH)**: This compound was prepared from MeO$_2$C-[G2]-(OBn)$_8$ (**G2-Bn)** following the general method for benzyl ether cleavage. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (20%) and dried in a vacuum to give **G2-OH** as colorless glass: yield 83%; T_g 140 °C.

^{1}H NMR: δ = 9.44 (s, 8H, OH), 8.65 (t, 2H, NH), 8.42 (t, 4H, NH), 7.06 (d, 2H, H^2), 7.03 (d, 4H, H^{11}), 6.82 (t, 1H, H^4), 6.67 (d, 10H, H,^{13} H^{18}), 6.33 (t, 4H, H^{20}), 4.13 (t, 4H, H^7), 4.10 (t, 8H, H^{14}), 3.80 (s, 3H, H^6), 3.58 (q, 4H, H^8), 3.55 ppm (q, 8H, H^{15}).

^{13}C NMR: δ = 166.91 (C,^{5} C,^{9} C^{16}), 159.62 (C^3), 158.38 (C,^{12} C^{19}), 136.64 (C,^{17} C^{10}), 136.42 (C^1), 106.14 (C^{13}), 106.27 (C,^{4} C^{13}), 105.60 (C,^{18} C^{20}), 105.28 (C^2, C^{11}), 66.50 (C^7), 66.40 (C^{14}), 52.39 (C^6), 38.97 (C^8), 38.87 ppm (C^{15}).

FT-IR−ATR: ν = 3254 (br, O−H, N−H), 2952 (s, C−H), 1705 (s, ROC=O), 1641 (w, NHC=O), 1587, 1539 (s, C=C), 1444 (m, C−H), 1340 (s, C−O), 1302 (s, O−H), 1160, 1061 (s, C−O−C), 1005 cm^{-1} (s, C−OH).

MALDI−TOF MS (3.90 μJ): m/z = 1244 (M + H$^+$), 1250 (M + Li$^+$), 1266 (M + Na$^+$).

MeO$_2$C-[G3]-(OBn)$_{16}$ (**G3-Bn):** This compound was prepared from MeO$_2$C-[G2]-(OH)$_8$ (**G2-OH)** according to method B at 190 °C. After cooling, the melt was stirred with methanol for some hours to dissolve the excess of monomer **4**. The crude product was filtered off and purified by column chromatography on silica gel eluting with chloroform/ethanol (3%) several times to give **G3-Bn** as colorless glass: yield 32%.

^{1}H NMR: δ = 8.63 (t, 14H, NH), 7.40−7.27 (m, 80H, benzyl aryl−H), 7.10 (d, 16H, H^{25}), 7.04 (d, 14H, H^2, H,^{11} H^{18}), 6.79 (t, 9H, H,^{4} H^{27}), 6.67 (t, 6H, H,^{13} H^{20}), 5.07 (s, 32H, benzyl−CH$_2$), 4.09 (t, 28H, H,^{7} H,^{14} H^{21}), 3.58 ppm (q, 28H, H,^{8} H,^{15} H^{22}); H^6 could not be detected.

^{13}C NMR: δ = 166.07 (C,^{9} C,^{16} C^{23}), 159.60 (C^{26}), 159.49 (C^{3}, C,^{12} C^{19}), 136.88 (C,^{10} C,^{17} C^{24}), 136.43 (C$^{benzyl\ aryl}$), 128.52−127.77 (C$^{benzyl\ aryl}$), 106.50 (C,^{11} C,^{18} C^{25}), 106.19 (C,^{4} C,^{13} C,^{20} C^{27}), 104.83 (C^{2}), 69.64 (C$^{benzyl-CH2}$), 66.40 (C,^{7} C,^{14} C^{21}), 39.03 ppm (C,^{8} C,^{15} C^{22}); C^{1}, C^{5}, and C^{6} could not be detected.

FT-IR−ATR: ν = 3279 (br, N−H), 2933 (s, C−H), 1719 (s, ROC═O), 1639 (w, NHC═O), 1589, 1526 (s, C═C), 1437 (m, C−H), 1299 (s, C−O), 1155, 1054 cm^{-1} (s, C−O−C).

MALDI−TOF MS (6.94 μJ): m/z = 4119 (M + H^{+}), 4455 (M + 337 (monomer **4**)).

[G1]-(OBn)$_6$ (**GI-Bn):** This compound was prepared from phloroglucinol (**5**) according to method B at 200 °C and purified by column chromatography on silica gel eluting at first with ethyl acetate to remove the excess of **4**. Subsequently, chloroform/ethanol (1%) as eluent was used for several times to give **GI-Bn** as white solid: yield 61%; mp 150.4 °C.

^{1}H NMR: δ = 8.58 (t, 3H, NH), 7.43−7.30 (m, 30H, benzyl aryl−H), 7.12 (d, 6H, H^{11}), 6.81 (t, 3H, H^{13}), 6.16 (s, 3H, H^{2}), 5.10 (s, 12H, benzyl−CH$_2$), 4.06 (t, 6H, H^{7}), 3.56 ppm (q, 6H, H^{8}).

^{13}C NMR: δ = 166.06 (C^{9}), 160.46 (C^{1}), 159.51 (C^{12}), 136.92 (C$^{benzyl\ aryl}$), 136.48 (C^{10}), 128.56−127.81 (C$^{benzyl\ aryl}$), 106.52 (C^{11}), 104.83 (C^{13}), 94.33 (C^{2}), 69.68 (C$^{benzyl-CH2}$), 66.14 (C^{7}), 39.02 ppm (C^{8}).

FT-IR−ATR: ν = 3391 (br, N−H), 3064, 3032 (w, aryl−H), 2936, 2873 (s, C−H), 1638 (w, NHC═O), 1586, 1520 (s, C═C), 1438 (m, C−H), 1152, 1054 cm^{-1} (s, C−O−C).

MALDI−TOF MS (6.33 μJ): m/z = 1211 (M + Li^{+}), 1227 (M + Na^{+}).

[G1]-(OH)$_6$ (**GI-OH**): This compound was prepared from [G1]-(OBn)$_6$ (**GI-Bn**) following the general method for benzyl ether cleavage. The crude product was dissolved in a small amount of *N*,*N*-dimethylacetamide, precipitated into water, filtered off, and dried in a vacuum to give **GI-OH** as white solid: yield 84%; mp 160.3 °C.

^{1}H NMR: δ = 9.39 (s, 6H, OH), 8.36 (t, 3H, NH), 6.67 (d, 6H, H^{11}), 6.34 (d, 3H, H^{13}), 6.14 (s, 3H, H^{2}), 4.03 (t, 6H, H^{7}), 3.52 ppm (q, 6H, H^{8}).

^{13}C NMR: δ = 166.88 (C^{5}), 160.46 (C^{1}), 158.38 (C^{12}), 136.67 (C^{10}), 105.62 (C^{11}), 105.27 (C^{13}), 94.26 (C^{2}), 66.12 (C^{7}), 38.85 ppm (C^{8}).

FT-IR−ATR: ν = 3286 (br, O−H, N−H), 2944 (s, C−H), 1698 (w, NHC═O), 1588, 1541 (s, C═C), 1451 (m, C−H), 1305 (s, O−H), 1156, 1069 (s, C−O−C), 1005 cm^{-1} (s, C−OH).

MALDI−TOF MS (4.43 μJ): m/z = 664 (M + H^{+}), 670 (M + Li^{+}), 686 (M + Na^{+}).

[G2]-(OBn)$_{12}$ (**GII-Bn**): This compound was prepared from [G1]-(OH)$_6$ (**GI-OH**) according to method B at 180 °C and purified by column chromatography on silica gel eluting with chloroform/ethanol (1%) for several times to give **GII-Bn** as colorless glass: yield 85%; T_g 74 °C.

^{1}H NMR: δ = 8.64 (t, 9H, NH), 7.41−7.27 (m, 60H, benzyl aryl−H), 7.12 (d, 12H, H^{18}), 7.05 (d, 6H, H^{11}), 6.81 (t, 6H, H^{20}), 6.68 (t, 3H, H^{13}) 6.13 (s, 3H, H^{2}), 5.09 (s, 24H, benzyl−CH$_2$), 4.12 (t, 12H, H^{14}), 4.03 (t, 6H, H^{7}), 3.59 (q, 12H, H^{15}), 3.54 (q, 6H, H^{8}).

^{13}C NMR: δ = 166.31 (C^{16}), 166.24 (C^{9}), 160.64 (C^{1}), 159.83 (C^{12}), 159.74 (C^{19}), 137.14 (C$^{benzyl\ aryl}$), 136.67 (C,^{10} C^{17}), 128.78−128.03 (C$^{benzyl\ aryl}$), 106.75 (C^{18}), 106.42 (C^{11}), 105.06 (C^{20}), 104.42 (C^{13}), 94.51 (C^{2}), 69.89 (C$^{benzyl-CH2}$), 66.64 (C^{14}), 66.35 (C^{7}), 39.28 (C^{15}), 39.22 (C^{8}).

MALDI−TOF MS (5.11 μJ): m/z = 2827 (M + Li^{+}).

[G2]-(OH)$_{12}$ (**GII-OH**): This compound was prepared from [G2]-(OBn)$_{12}$ (**GII-Bn**) following the general method for benzyl ether cleavage. The crude product was dissolved in a small amount of *N*,*N*-dimethylacetamide, precipitated into water, filtered off, and dried in a vacuum to give **GII-OH** as white solid: yield 79%; T_g 149 °C.

^{1}H NMR: δ = 9.42 (s, 12H, OH), 8.61 (t, 3H, NH), 8.38 (t, 6H, NH), 7.03 (d, 6H, H^{11}), 6.67 (d, 15H, H,^{13} H^{18}), 6.34 (t, 6H, H^{20}), 6.14 (s, 3H, H^{2}), 4.10 (t, 12H, H^{14}), 4.05 (t, 6H, H^{7}), 3.56 ppm (q, 18H, H,^{8} H^{15}).

^{13}C NMR: δ = 166.93 (C^{16}), 166.04 (C^{9}), 160.42 (C^{1}), 159.63 (C^{12}), 158.41 (C^{19}), 136,63 (C^{17}), 136.43 (C^{10}), 106.15 (C^{11}), 105.58 (C^{18}), 105.30 (C^{20}), 104.15 (C^{13}), 94.28 (C^{2}), 66.40 (C^{14}), 66.11 (C^{7}), 39.0 (C^{8}), 38.87 ppm (C^{15}).

MALDI−TOF MS (4.02 μJ): m/z = 1746 (M + Li^{+}).

Coupling of Dendrons. C(O$_2$C-[G1]-(OBn)$_4$)$_2$ **(DG1-Bn)**: A mixture of MeO$_2$C-[G1]-(OBn)$_4$ (**G1-Bn)** (0.60 g, 0.68 mmol), 1,4-bis(hydroxymethyl)benzene (**6**) (23.30 mg, 0.17 mmol), and di-*n*-butyltin oxide (20.00 mg, 0.08 mmol) was put into a Schlenk flask under argon. The flask was placed in an oil bath preheated to 180 °C. The substances melted completely after about 2 min, and the melt was stirred for 5 h at 180 °C. After cooling, the crude product was purified by column chromatography on silica gel eluting with chloroform to give **DG1-Bn** as white solid: yield 67%; mp 85.2 °C.

^{1}H NMR: δ = 8.59 (t, 4H, NH), 7.43−7.28 (m, 20H, benzyl aryl−H; 4H, H$^{6'}$), 7.11 (d, 8H, H^{11}), 7.08 (d, 4H, H^{2}), 6.84 (t, 2H H^{4}), 6.81 (t, 4H, H^{13}), 5.29 (s, 4H, H^{6}), 5.09 (s, 16H, benzyl−CH$_2$), 4.14 (t, 8H, H^{7}), 3.59 ppm (q, 8H, H^{8}).

^{13}C NMR: δ = 166.08 (C^{9}), 165.27 (C^{5}), 159.87 (C^{3}), 159.49 (C^{12}), 136.90 (C$^{benzyl\ aryl}$), 136.44 (C^{10}), 136.08 (C$^{6''}$), 131.68 (C^{1}), 128.57−127.82 (C$^{benzyl\ aryl}$), 128.23 (C$^{6''}$), 108.01 (C^{13}), 106.51 (C^{11}), 106.20 (C^{4}), 104.82 (C^{2}), 69.66 (C$^{benzyl-CH2}$), 66.60 (C^{7}), 66.18 (C^{3}), 39.99 ppm (C^{8}).

FT-IR-ATR: ν = 3269 (br, N−H), 3065, 3033 (w, aryl−H), 2940, 2873 (s, C−H), 1713 (s, ROC═O), 1642 (w, NHC═O), 1590, 1522 (s, C═C), 1441 (m, C−H), 1300 (s, C−O), 1153, 1055 cm^{-1} (s, C−O−C).

MALDI−TOF MS (2.27 μJ): m/z = 1849 (M + H^{+}), 1871 (M + Na^{+}).

C(O$_2$C-[G2]-(OBn)$_8$)$_2$ **(DG2-Bn)**: A mixture of MeO$_2$C-[G2]-(OBn)$_8$ (**G2-Bn)** (1.34 g, 0.68 mmol), 1,4-bis(hydroxymethyl)-benzene (**6)** (23.30 mg, 0.17 mmol), and di-*n*-butyltin oxide (40.00 mg, 0.16 mmol) was placed into a Schlenk flask under argon. The flask was placed in an oil bath preheated to 180 °C. The substances melted completely after about 2 min, and the melt was stirred for 9 h at 180 °C. After cooling, the crude product was purified by column chromatography on silica gel eluting with chloroform/ethanol (2%) to give **DG2-Bn** as colorless glass: yield 20%; T_g 77 °C.

^{1}H NMR: δ = 8.65 (t, 12H, NH), 7.43−7.28 (m, 80H, benzyl aryl−H), 7.39 (4H, H$^{6''}$), 7.16 (d, 16H, H^{18}), 7.11 (d, 4H, H^{2}), 7.09 (d, 8H, H^{11}), 6.84 (t, 8H H^{20}), 6.83 (t, 2H, H^{4}), 6.72 (t, 4H, H^{13}), 5.29 (s, 4H, H^{6}), 5.10 (s, 32H, benzyl−CH$_2$), 4.15 (t, 24H, H,^{7} H^{14}), 3.63 (q, 24H, H,^{8} H^{15}).

^{13}C NMR: δ = 166.00 (C^{16}), 165.96 (C^{9}), 165.16 (C^{5}), 159.72 (C^{3}), 159.50 (C^{12}), 159.40 (C^{19}), 136.79 (C$^{benzyl\ aryl}$), 136.34 (C,^{10} C^{17}), 134.31 (C$^{6'}$), 131.68 (C^{1}), 128.42−127.68 (C$^{benzyl\ aryl}$), 127.93 (C$^{6''}$), 107.85 (C^{2}), 106.41 (C^{18}), 106.10 (C^{11}), 106.02 (C^{4}), 104.72 (C^{20}), 104.11 (C^{13}), 69.56 (C$^{benzyl-CH2}$), 66.46 (C^{7}), 66.31 (C,^{14} C^{6}), 38.95 (C^{15}), 38.87 (C^{8}).

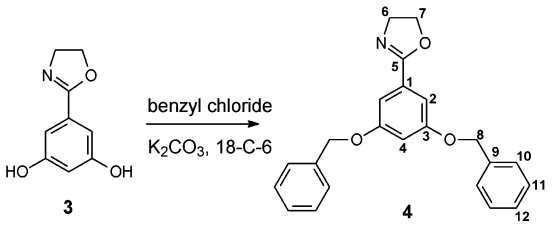
FT-IR−ATR: ν = 3290 (br, N−H), 3065, 3033 (w, aryl−H), 2940, 2873 (s, C−H), 1713, 1643 (w, NHC═O), 1590, 1522 (s, C═C), 1441 (m, C−H), 1153, 1054 cm^{-1} (s, C−O−C).

MALDI−TOF MS (2.27 μJ): m/z = 4008 (M + Li^{+}), 4027 (M + Na^{+}).

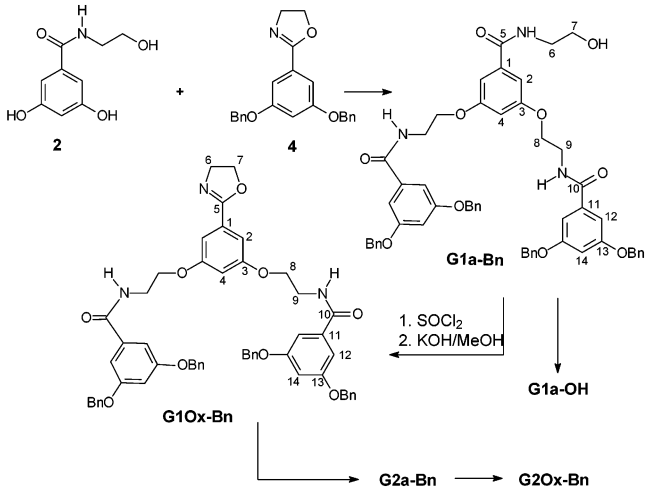
Results and Discussion

Monomer Synthesis. The aim of this work was to synthesize ether amide dendrimers via ring-opening addition of phenol groups toward oxazolines as described previously for hyperbranched poly(ether amide)s.[27] Both the convergent and the divergent growth approach are possible with the same AB$_2$ monomer 2-(3,5-dihydroxyphenyl)-1,3-oxazoline (**3**), but it is necessary to protect the reactive phenol groups. For this we used the benzyl ether protective group as described by Hawker and Fréchet[41] for the synthesis of 3,5-bis(benzyloxy)benzyl bromide since deprotection by catalytic hydrogenation can be performed under specific and mild conditions. The etherification was carried out with benzyl chloride in dry acetone and K_2CO_3 as base in the presence of 18-crown-6 (Scheme 1) to yield the protected monomer **4.**

Scheme 1



Scheme 2

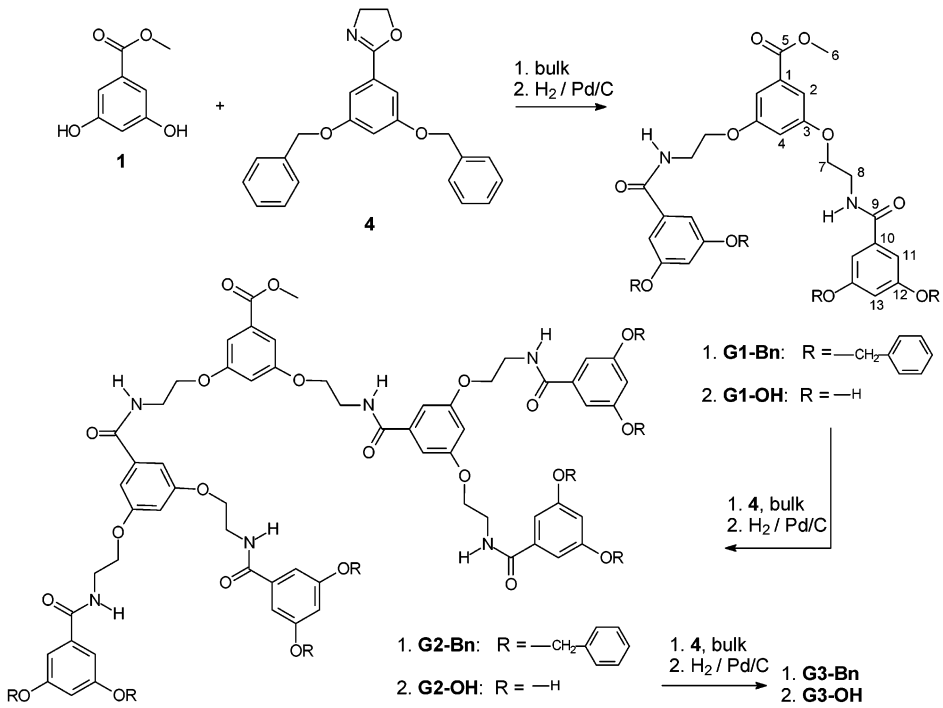


Convergent Growth Approach. The convergent synthesis is based on a focal group that is able to form the oxazoline unit. We used the known[27] *N*-(2-hydroxyethyl)-3,5-dihydroxybenzamide (**2**) as focal group to react with **4** in a ring-opening addition reaction, forming the first generation **G1a-Bn** in bulk at 190 °C (Scheme 2). The purification by column chromatography was difficult since **G1a-Bn** shows limited solubility in solvents like ethyl acetate or chloroform, and the focal *N*-hydroxybenzamide group leads to a high polarity of the compound. However, the mixture ethyl acetate/methanol (5%) as eluent (Rf = 0.15) gave **G1a-Bn** in 55% yield and high purity. The following ring formation to oxazoline **G1Ox-Bn** was not possible in one step as described for monomer **4**. The reaction of **G1a-Bn** with thionyl chloride gave first chloroethyl benzoic acid amide **10**, which formed the oxazoline ring with KOH/methanol. Reaction of **G1Ox-Bn** with the monomer unit **2**, as above, gave the second-generation **G2a-Bn** of ether amide dendron with focal *N*-hydroxybenzamide group. But it was not possible to fully purify **G2a-Bn** by column chromatography. Therefore, the divergent growth approach was investigated in order to have a more versatile approach to this ether amide system.

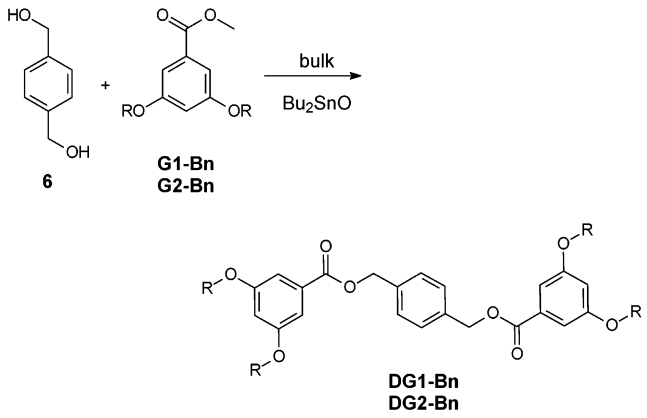
Divergent Growth Approach. The divergent growth approach is based on a two-step ring-opening addition reaction/hydrogenation procedure (Scheme 3). Starting from methyl-3,5-dihydroxybenzoate (**1**) treated with an excess of **4** at 190 °C gave the first generation of benzyl protected dendron in 51% yield after purification by column chromatography. Hydrogenation of **G1-Bn** gave the desired phenol-terminated dendron **G1-OH**. Similarly, benzyl-terminated second- and third-generation **G2-Bn** and **G3-Bn** were prepared from the phenol-terminated dendrons **G1-OH** and **G2-OH**. Please note that the convergently prepared dendrons **G1a-Bn** and **G2a-Bn** have nearly the identical structure as **G1-Bn** and **G2-Bn**, just having a different focal unit. Up to the second generation all dendrons are fully characterized by ^{1}H and ^{13}C NMR spectroscopy. Only for the third generation the focal methyl benzoate group was not detected whereas the other structural characteristics were as expected. In this third generation a growing spherical shape and thus lower distances between the functional groups could be the reason for a transamidation side reaction induced by the high reaction temperature. Therefore, the exact structure of **G3-Bn** could not be completely verified.

Coupling of the benzylic-terminated dendritic fragments via transesterification of the focal methyl benzoate was examined with a variety of cores (pentaeryth-

Scheme 3



Scheme 4



ritol, phloroglucinol (**5**), 1,4-bis(hydroxymethyl)benzene (**6**)) using a variety of catalysts (pyridine,[42] *p*-toluenesulfonic acid,[42] dibutyltin oxide, and with boron tribromide as described by Yazawa et al.[43]). But only the coupling with the bifunctional core molecule **6** as shown in Scheme 4 produced the dendrimers **DG1-Bn** and **DG2-Bn** in good yields after purification by column chromatography.

To obtain dendrimers with a trifunctional core, the divergent growth synthesis starting from the trifunctional phloroglucinol (**5**) core molecule as shown in Scheme 5 was explored. A similar set of reaction steps (ring-opening addition reaction/hydrogenation) as described above was used to synthesize the first (**GI-Bn, GI-OH**) and second (**GII-Bn, GII-OH**) generation.

Characterization: NMR Spectroscopy. The structures of all described compounds were fully established by ^{1}H and ^{13}C NMR spectroscopy. The signals in the ^{1}H NMR spectra start to broaden significantly at the third-generation dendrimer **G3-Bn**. Figure 1 shows the ^{1}H NMR spectra of the second generation of the monodendron **G2-Bn**, the coupled monodendron **DG2-Bn**, and the divergently grown dendrimer **GII-Bn**. All spectra show characteristic signals of the poly(ether amide) dendrimers, like for the aliphatic amide group at 8.61 ppm and for the aliphatic CH_2 groups at 4.1 and 3.6 ppm. Further characteristic chemical shifts were observed for the protons of the benzylic protective group at 5.1 and 7.3−7.43 ppm and for the protons of the core unit of **DG2-Bn** (H^6 and $H^{6''}$) and **GII-Bn** (H^2). Additionally, it is possible to distinguish the aromatic protons of the dendritic unit (7.07 ppm for H^{11} and 6.7 ppm for H^{13}) from the ones of the terminal unit (7.14 ppm for H^{18} and 6.82 ppm for H^{20}).

To compare the proton spectrum of a perfectly branched ether amide dendrimer with that of a hyperbranched poly(ether amide) prepared in a one-pot reaction from the monomer **3**[27] (Scheme 1), we used the divergently grown unprotected dendrimer **GII-OH** (Figure 2). The dendrimer exhibits identical chemical shifts for the protons as the hyperbranched polymer, with the exception of the signals for the linear units (9.66 ppm for O−H, 8.56 ppm for N−H, 6.9 and 6.5 ppm for aromatic protons) which are only present in the hyperbranched molecule and an additional signal at 6.14 ppm for the core unit. The interior part of the dendrimer corresponds to the dendritic unit and the exterior part to the terminal unit of the hyperbranched polymer.

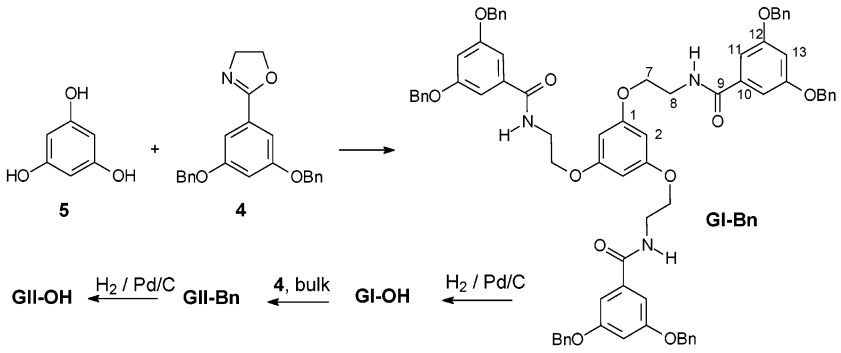
Table 1. Theoretical Molar Masses of the Poly(ether amide) Dendrimers Compared to the Molar Masses Determined by MALDI−TOF MS and SEC

dendrimer	MM_{calcd} (g/mol)	MALDI−TOF MS[a] *m/z*	$SEC_{PS-Stand}$[b] (g/mol)	$SEC_{PVP-Stand}$[b] (g/mol)
G1a-Bn	916.03	917	1600	1800
G1a-OH	555.54	556	1600	1800
G1Ox-Bn	898.02	899	1200	1400
G1-Bn	887.01	888	1100	1300
G2-Bn	1964.19	1965	3000	3200
G3-Bn	4134.72	4136[c]	6650	7450
G1-OH	526.49	527	1100	1400
G2-OH	1243.20	1244	3300	3400
DG1-Bn	1848.07	1849	2400	3100
DG2-Bn	4002.47	4004	5200	6100
GI−Bn	1204.38	1205	1600	1800
GII-Bn	2820.18	2821	4000	4900
GI-OH	663.63	664	1650	1900
GII-OH	1738.69	1740	4400	5200

[a] Matrix: 2,5-dihydroxybenzoic acid or sinapinic acid. [b] Solvent: DMAc/H_2O/LiCl, RI detector. [c] Additional peaks in SEC.

SEC and MALDI−TOF MS. Table 1 shows the results of MALDI−TOF MS and SEC of our dendrons and dendrimers in comparison with the calculated theoretical molar masses. Polystyrene (PS) and polyvinylpyridine (PVP) were used for SEC calibration. The results show that it is not possible to achieve the correct molar masses for dendritic molecules using linear standards as described also by Lederer et al.[28] for the analogous hyperbranched poly(ether amide)s. For hyperbranched polymers with molar masses higher than 10 000 g/mol, we obtained SEC molar mass values that were much lower than those obtained by, for example, light scattering methods. We explain this fact with the different solubility and solvation behavior of the linear standard and the hyperbranched polymer in the employed solvent *N*,*N*-dimethylacetamide. The dense globular structure of the hyperbranched polymers leads to smaller molecule dimensions compared with the loosely coiled linear standard molecules, and thus apparent

Scheme 5



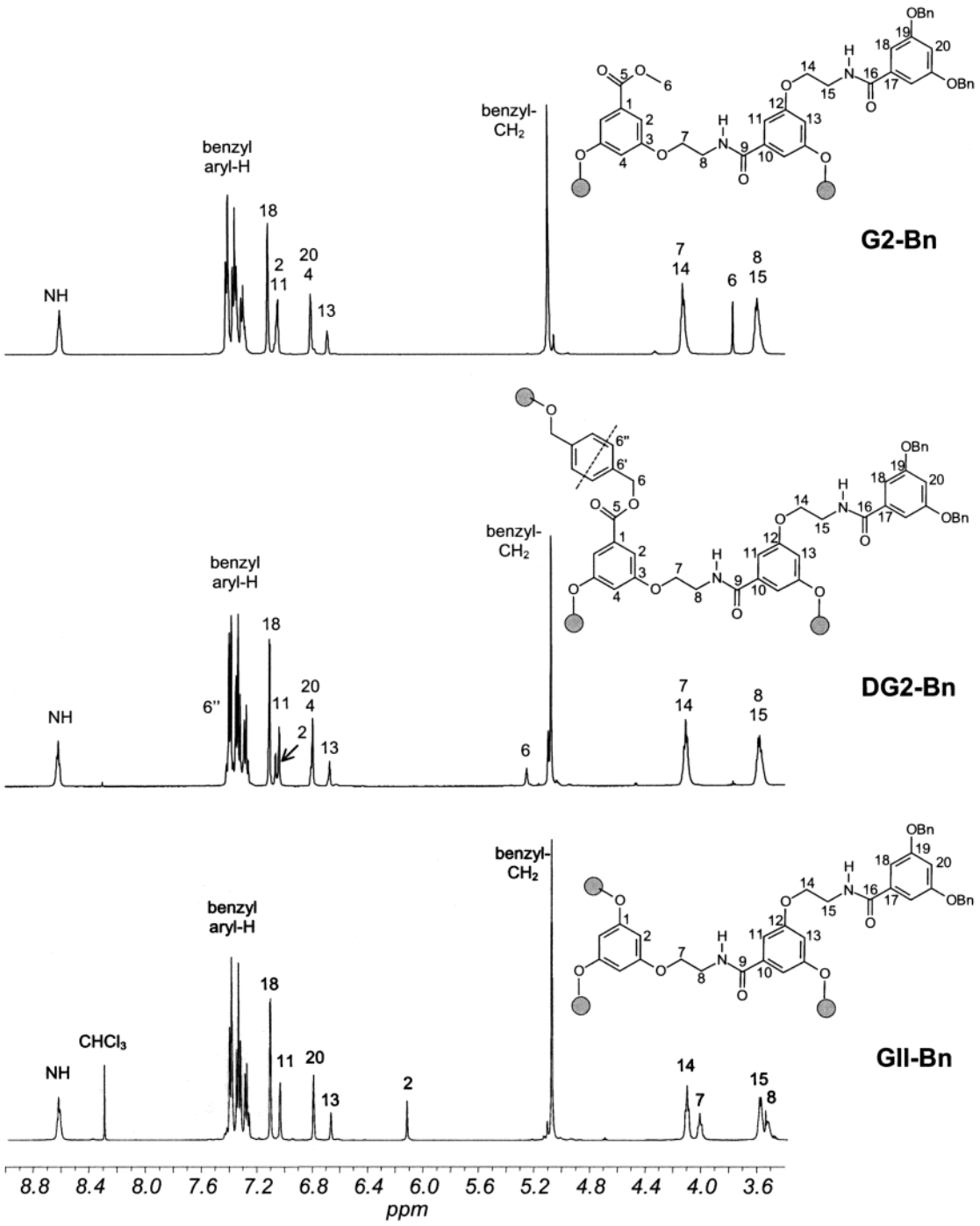


Figure 1. ^{1}H NMR spectra of **G2-Bn**, **DG2-Bn**, and **GII-Bn**.

lower molar masses were calculated. But in the case of the first- and second-generation dendrimers, we obtained molar masses determined by SEC that were higher than the calculated ones. This observation could be explained by assuming that low-generation dendrimers have more an open fractal than a dense collapsed structure with a strong influence of the functional terminal units on the solvation behavior. A dense, compact structure is reported mainly for dendrimers at or above generation 4.[2] In our case, on average the SEC molar masses M_n of the dendrimers are 2 times higher than the molar masses determined by MALDI−TOF MS or the calculated ones. With increasing molar masses of dendrimers the differences between SEC and MALDI−TOF MS decrease. Also, because of the polar end-group effect, the differences in molar masses of protected and unprotected dendrimers are not represented in the SEC values. MALDI−TOF mass spectrometry, however, proved nicely the existence of the attempted dendrimers and also the purity of the samples. Figure 3 shows a series of MALDI−TOF MS spectra for **GI-Bn**, **GI-OH**, **G1-Bn**, **G1-OH,** and **G2-Bn**. Only the different adducts of the pure product with H, Li, and Na ions are shown for **GI-Bn** and **GI-OH** (Figure 3a), whereas in **G1-Bn**, **G1-OH,** and **G2-Bn** (Figure 3b) small amounts of impurities can be detected.

Differential Scanning Calorimetry. Differential scanning calorimetric analysis revealed different thermal transition for the dendritic molecules. All of the first generation dendrimers melted between 100 and 160 °C in the first heating. But it was not possible to recrystallize the material (Figure 4), as observed also previously

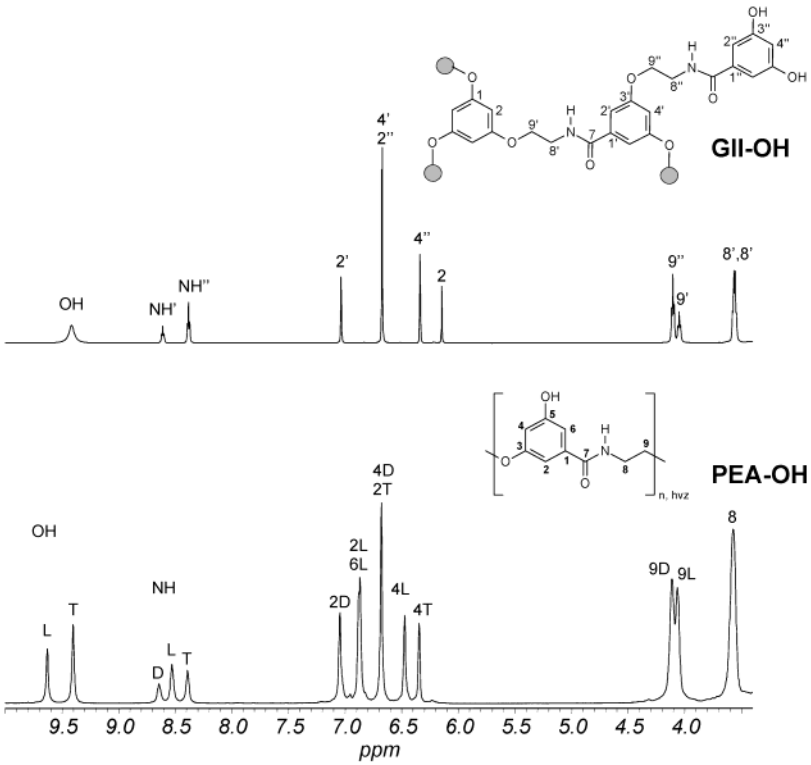


Figure 2. Comparison of ^{1}H NMR spectra of dendrimer **GII-OH** and hyperbranched polymer **PEA-OH**.

Table 2. Results of DSC Measurements

	T_m (first heat), °C		T_g (second heat), °C	
compound	R = Bn	R = OH	R = Bn	R = OH
G1a-R	158	136	56	127
G1-R	160	165	47	110
G2-R	*a*	*a*	73	140
DG1-R	86		61	
DG2-R	*a*		77	
GI-R	137	109	54	105
GII-R	*a*	*a*	74	149

[a] No melting.

for other poly(ether amide) dendrimers[6] and by Newcome et al.[44] for polyamide cascade dendrimers.

Two trends could be observed for the glass transition temperatures comparing dendrimers of increasing generation and with different terminal groups (Table 2). The T_g of all benzylic-terminated first-generation dendrimers (**G1a-Bn**, **G1-Bn**, **DG1-Bn**, **GI-Bn**) range from 47 to 61 °C, increasing with the molar mass. The T_g of the analogous hydroxy-terminated dendrimers (**G1a-OH**, **G1-OH**, **DG1-OH**, **GI-OH**) are approximately twice as high due to the increased number of possible hydrogen bonds. Up to the third generation the T_g increases with the generation number, reaching 149 °C for **GII-OH**. The literature[45,46] describes higher generation dendrimers reaching a T_g plateau value. Comparison with the T_g of the analogous high molar mass (M_n > 10 000 g/mol) hyperbranched poly(ether amide) **PEA-OH**, which is between 150 and 160 °C, allows the assumption that for the samples **G2-OH** and **GII-OH** (M_n = 1243/1738 g/mol; T_g = 140 °C/149 °C) this plateau value is almost reached.

Melt Rheology of Divergent Grown Dendrimer GII-OH. For having a direct comparison of the material properties between hyperbranched polymers and dendrimers, it was interesting to investigate their melt rheological behavior as well as the effect of the dendrimers in a linear matrix polymer. In previous work, the effect of the hyperbranched **PEA-OH** on the melt rheology and mechanical properties of polyamide 6 was intensively studied.[25] Would dendrimers show the same influence to the flow properties of linear polyamide 6 as the hyperbranched analogue?

First, the melt rheological behavior of the pure ester amide dendrimer was studied. For this, melt rheological measurements (frequency sweep) on **GII-OH** (M_n = 1738 g/mol) were performed at 250 °C. The dendrimer was stable under these conditions and repeated measurements resulted in identical curves. Figure 5 shows the result. As expected for the low molar mass sample, the melt viscosity of the sample was in a rather low range compared to the linear polyamide sample (see also Figure 5). However, the dendrimer shows an increase of the melt viscosity at lower frequency as observed previously[25] for hyperbranched polymers of identical chemical structure. This indicates a predominately elastic behavior of the sample as bulk material which has been related to the polar end groups and their possibility to form hydrogen bonds within the polymer chain as well as toward other polymer chains resembling a polymer network.

The dendrimer sample **GII-OH** was also added in 0.1 and 1 wt % concentration to a linear polyamide 6 matrix by melt mixing in a minicompounder. Similarly as the hyperbranched samples, at this low amount the dendrimer additive did not change the crystalline properties of the polyamide matrix: T_c and T_m remained uneffected, and the corrected melt enthalpy even increased slightly (Table 3). However, the glass transition temperature T_g of the mixture increased considerably from 54 to 57 °C, indicating first a complete miscibility between matrix polyamide and the dendrimer (only a single T_g was observed) and second the preferential incorporation of the dendritic additive in the amorphous part of the polyamide 6. Using hyperbranched poly(ether

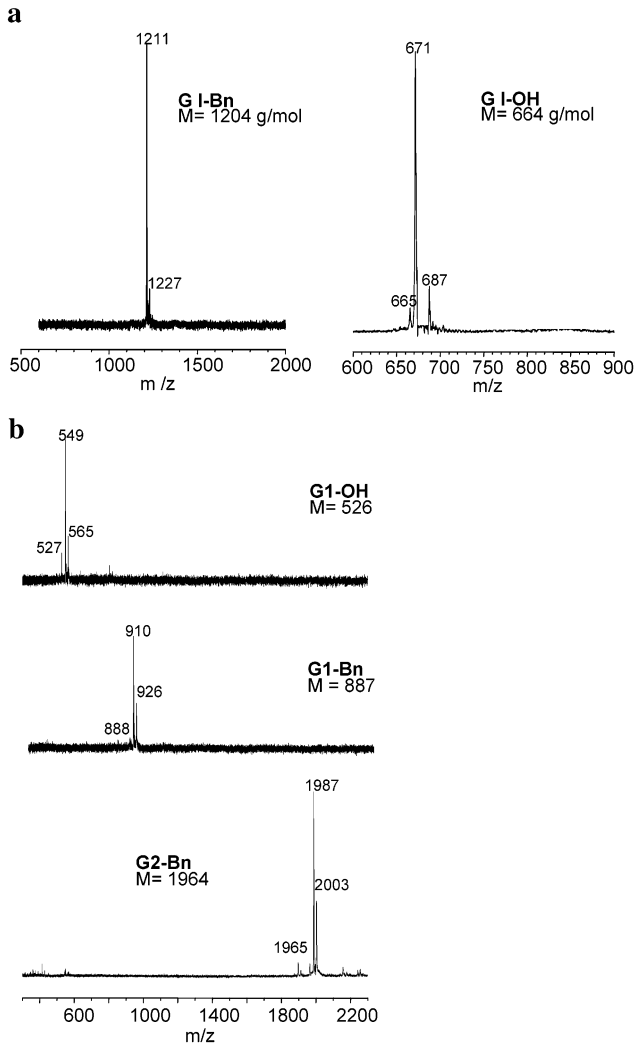


Figure 3. MALDI−TOF mass spectra of (a) **GI-Bn** and **GI-OH** and (b) **G1-OH**, **G1-Bn,** and **G2-Bn**.

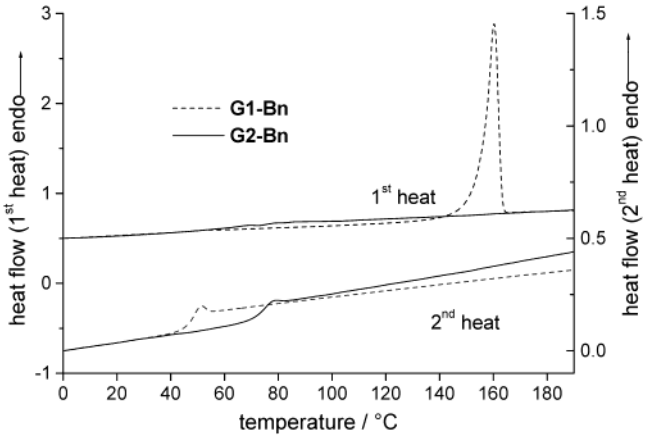


Figure 4. Plot of first and second heat of first- and second-generation dendrons **G1-Bn** and **G2-Bn**.

amide)s,[25] even this low content of a highly branched additive resulted in a decrease of the melt viscosity of the linear matrix. As shown in Figure 5, the dendrimer sample had no effect on the matrix viscosity. However, the hyperbranched polymer used before had a much higher molar mass (M_n > 20 000 g/mol), and the effect on melt viscosity was also lower when lower molar mass hyperbranched samples had been used.[26] Thus, we assume that the molar mass of the dendrimer was too

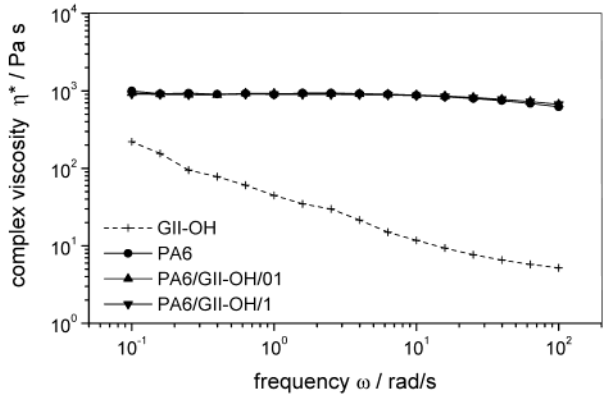


Figure 5. Plot of complex viscosity against frequency for blends of PA6 and 0.1 and 1 wt % of **GII-OH** in comparison with the pure blend components.

Table 3. Thermal Transitions in Blends of PA6 and Second-Generation Dendrimer GII-OH

sample	T_c[a] (°C)	$T_{c,0}$[b] (°C)	ΔH_c[c] (J/g)	T_m[d] (°C)	ΔH_f[e] (J/g)	T_g[f] (°C)
PA6	188.8	192.3	−62.3	220.6	62.8	54
PA6/GII-OH/01	188.5	192.1	−65.1	220.6	67.6	57
PA6/GII-OH/1	189.1	192.6	−66.5	220.1	66.3	57

[a] Crystallization temperature, peak maximum. [b] Onset crystallization temperature. [c] Heat of crystallization transition. [d] Melting temperature, peak maximum, second heat. [e] Heat of melting transition, second heat, corrected for PA6 matrix content. [f] Glass transition temperature.

low to observe an effect at this low concentration. For a more detailed study, larger amounts of the dendrimers are necessary as well as higher molar mass samples. Nevertheless, it is noteworthy that the melt rheology behavior of the plain dendrimer shows the same general tendency as hyperbranched samples of identical structure with a strong interaction of the highly polar end groups. Up to now only few melt rheology studies on bulk dendrimers exist. But a complex viscosity-thinning behavior dependent on shear rate, temperature, and number of generations of poly(benzyl ether)[47] and PAMAM[48] dendrimers in bulk was reported before whereas in concentrated solution of dendrimers mainly Newtonian behavior was observed.[49]

Conclusions

Aliphatic−aromatic poly(ether amide) dendrimers were synthesized up to generation 3 via ring-opening addition of phenol groups toward oxazoline in bulk between 140 and 190 °C. The first and second generations were prepared in both convergent and divergent approaches. The dendrons and dendrimers were characterized by ^{1}H and ^{13}C NMR spectroscopy and MALDI−TOF MS, and the purity and the perfect structure of the products were verified, indicating that the addition reaction is quite selective even at these high reaction temperatures. The products were compared to chemically identical hyperbranched poly(ether amide)s prepared in a one-step process from AB_2 monomers. DSC measurements indicated that the model dendrimers of lower generation are still able to crystallize, but the higher generations are amorphous with a T_g approaching the values of the high molar mass hyperbranched materials with identical end groups. Melt rheology measurements on the dendrimers revealed a predominantly elastic behavior with a relatively high viscosity at low frequency as found for the hyperbranched ana-

logues. Model blend studies proved that the second generation of a poly(ether amide) dendrimer is fully miscible with a linear polyamide matrix, but in contrast to effects observed in mixtures between PA6 and a hyperbranched material no influence on the melt rheological behavior of the PA6 was observed. This indicates that the molar masses of the model dendrimers had been too low to yield the same interactions between branched and linear molecules as observed previously for hyperbranched poly(ether amide)s.

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