An Approach to Core−Shell-Type Architectures in Hyperbranched Polyglycerols by Selective Chemical Differentiation

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ABSTRACT: In contrast to dendrimers, hyperbranched polymers show no distinguishable interior and periphery. Hyperbranched polyglycerol, however, possesses two types of OH functionalities (arising from linear and terminal glycerol units), which can be chemically differentiated. To generate a core−shell-type architecture in hyperbranched polyglycerol ($M_n = 5000$, $M_w/M_n = 1.5$), the 1,2-diols of the terminal glycerol units have been selectively converted into the corresponding acetals or ketals. This allows one to distinguish between interior (closer to the focal unit) and periphery (distant from the focal unit) of the macromolecule, since the remaining linear glycerol units remain unaffected by this transformation. In subsequent reactions, the linear units were functionalized with alkyl halides, such as allyl chloride or benzyl chloride, under phase transfer conditions to obtain the corresponding polyether polyketals. Selective deprotection of the 1,2-ketals was achieved with an acidic ion-exchange resin to give "core"-functionalized polyglycerols. By this procedure, hyperbranched polymers can be selectively tailored to contain hydrophobic substituents in the interior or in the periphery. Distribution coefficients ($CHCl_3/H_2O$), unusual thermal behavior, and spectroscopic properties of these macromolecules corroborate their core−shell-type architectures. Structural inversion of the architecture (apolar periphery with polar core vs polar periphery with apolar core) leads to striking changes in physical properties. Furthermore, the presented synthetic methods permit the preparation of a fully alkylated polyglycerol, which was obtained by phase transfer alkylation of polyglycerol. To demonstrate that the linear "core" units of polygylcerol are suitable for further selective functionalization, a polyglycerol pseudo-dendrimer, containing exclusively dendritic and terminal units, has been prepared by selective transformation of all linear into dendritic units.

Introduction

Multifunctional dendritic macromolecules have attracted interdisciplinary interest that is expected to lead to a variety of applications, ranging from supports for drugs or catalysts to highly functional cross-linkers, processing additives and rheology modifiers.[1] Due to their perfectly branched topology, dendrimers are commonly believed to be promising candidates for these applications.

One important peculiarity of the dendrimer topology is the clear differentiation between the interior branching scaffold, the *core*, and the end groups in the periphery, the *shell*. Because of the exponential growth of the number of end groups with each generation, there is a structural density gradient[2] from the core to the periphery (Figure 1A). The presence of an extremely dense periphery has been exploited for the permanent encapsulation and selective liberation of guests in the "dendritic box" by Meijer et al.[3] The dendritic core−shell architecture has also been used for the synthesis of molecules with polar periphery and apolar interior that show micelle-like behavior.[4] Dendritic liquid-crystalline polymers obtained by the attachment of mesogens to the periphery of dendrimers represent another example of core−shell-type materials with peculiar supramolecular order.[5] It should be noted, however, that in low generations backfolding of dendrimer end groups may occur for non-periphery-substituted dendrimers, leading to the absence of a density gradient.[6]

For many applications the difficult accessibility of dendrimers via costly multistep syntheses represents a major problem.[7] Hyperbranched polymers that can be obtained in one reaction step from the polymerization of AB_m or latent AB_m monomers are currently discussed as possible alternatives. Until recently, these polymers were considered as ill-defined, since they are characterized by a random branching pattern and broad molecular weight distribution.[8,9] We have been able to establish a synthesis for hyperbranched polyether polyols with controlled molecular weight and narrow polydispersities. The strategy is based on the ring-opening multibranching polymerization of glycidol using slow-monomer-addition conditions.[10] The resulting polyglycerols possess molecular weights between 1000 and 30 000 g/mol with polydispersities M_w/M_n typically below 1.5.[11] In contrast to perfect dendrimers, these hyperbranched polyglycerols exhibit a lower degree of branching (DB)[12] in the range 55−60% (Figure 1B).

We have already been able to demonstrate that some unusual properties typically associated with dendrimers (e.g., encapsulation of guest molecules) can also be achieved with unselectively functionalized hyperbranched polyglycerols.[13] It is an intriguing question, whether selectively functionalized hyperbranched polymers can exhibit further properties supporting a "core−shell" topology despite their random branching pattern. In dendrimers only dendritic and terminal units are present; thus, usually only the shell (i.e., terminal units) can be used for functionalization (Figure 1A). In hyperbranched polymers additional linear units are present throughout the structure (Figure 1B). Although randomly incorporated, they will predominate in the proximity of the focal or "core" unit of the macromolecule, when the polymers are prepared by slow monomer addition.[14] These struc-

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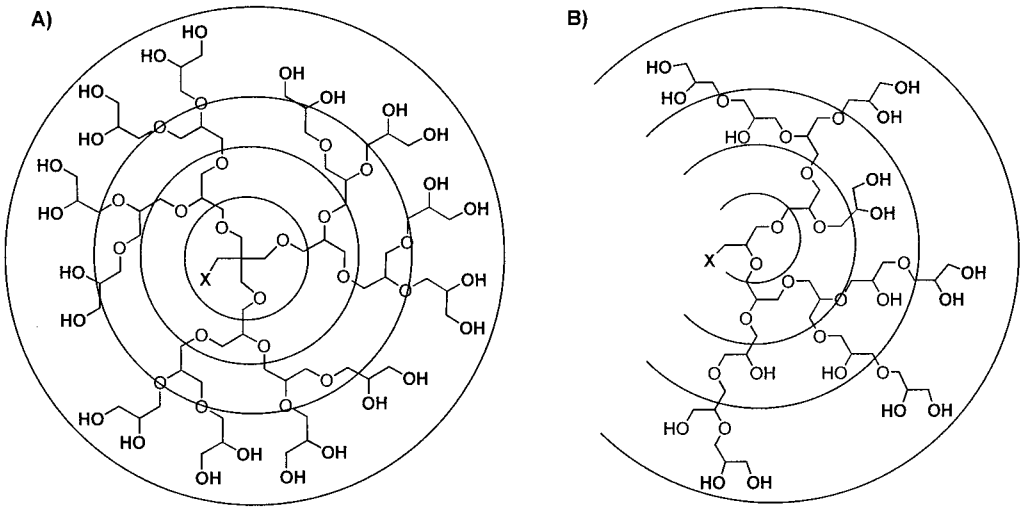


Figure 1. Schematic structures of (A) a perfect glycerol dendrimer [G3] possessing only dendritic and terminal groups[16] and (B) a hyperbranched polyglycerol with about 40% linear groups incorporated. Circles represent generations (A) and pseudogenerations[14] (B), respectively; the innermost circle encloses the focal unit (initiator).

tural considerations will be discussed in detail in section A.

It is the aim of the present paper to transfer the concept of core−shell architectures of dendrimers to the structural pecularities of hyperbranched polymers, i.e., the two types of building units that can be used for functionalization: (i) the focal-close linear units, the "core", and (ii) the "focal-distant" terminal units, the "shell". In section B we will present a "chemical differentiation" strategy to functionalize independently the "core" (linear units) and the "shell" (terminal units) of hyperbranched polyglycerols. The ensuing sections will then focus on how this core−shell-type architecture affects the properties of such materials.

Furthermore, the strategy of "chemical differentiation" permits to selectively modify the linear units, the "core" of a hyperbranched polyglycerol and to incorporate new functional groups. These can be modified independently of the "shell" functionality. In section E we will exemplify this possibility by the synthesis of a "pseudo-dendritic" polyglycerol, representing a selective synthetic alternative to the approach reported previously.[15,16]

Experimental Part

Materials. Polyglycerol **1** (M_n = 5000, M_n/M_w = 1.5) was prepared as described previously, using bis(2,3-dihydroxypropyl)stearylamine as initiator.[10] Acetone dimethylacetal, *p*-toluenesulfonic acid (PTSA), methyl iodide, benzyl chloride, Dowex 50, and tetrabutylammonium bromide (TBAB) were purchased from Fluka; osmium tetroxide (OsO_4) was from Acros. *N*-Methylmorpholine oxide (NMO), ethyl bromide (EtBr), NaOH, and all solvents (analytical grade) were purchased from Merck. Allyl chloride was received from Solvay. Reagents and solvents were used without any further purification.

General Directions. ^{1}H NMR and ^{13}C NMR spectra were recorded in [D_4]-methanol for polyglycerol and [D_1]-chloroform for modified polyglycerols at concentrations of 200 mg/mL on a Bruker ARX 300 spectrometer operating at 300 and 75.4 MHz, respectively. For the characterization and description of the polyglycerol backbone L, D, and T are used for linear, dendritic, and terminal units, respectively.[10] L_{13} and L_{14} describe the two different connectivities of linear glycerol units, primar/secondary and primary/primary ether linkage, respectively. DSC Measurements were carried out with a Perkin-Elmer DSC7 system in the temperature range of −100 to 30 °C at heating rates of 10 and 20 °C/min. The melting point of indium (156 °C) was used for calibration. IR spectra were recorded on a Bruker Vector 22 spectrophotometer, using thin polymer films on KBr disks.

Preparation of Functionalized Polyglycerols. Acetalyzation and Ketalization of Polyglycerol 1 (General Procedure I). To a mixture of polyglycerol **1** (10 g, 40 mmol of diol units) and 0.4 mol (10 equiv) of the respective dimethylacetal, 1 g (10 mol %) of PTSA was added. The reaction was performed under ultrasonication over 3 h at 25−40 °C. After about 15 min a homogeneous solution was obtained. The crude product was diluted in chloroform and then extracted three times with saturated Na_2CO_3 solution to remove the remaining PTSA. The organic phase was dried over $MgSO_4$. Dialysis in chloroform using a benzoylated cellulose membrane (MWCO 1000, Sigma) was performed for 1−2 days in order to remove traces of remaining dimethylacetal and PTSA. The purified product was dried under vacuum.

Polyacetal 2a. The reaction was performed according to general procedure I, using 1.0 g of polyglycerol, 25 mL of benzaldehyde dimethylacetal, and 0.1 g of PTSA. The resulting polyacetal **2a** (1.2 g, 85%) was obtained as a viscous, pale yellow transparent oil. IR (KBr): ν (cm^{-1}) = 3470 (OH), 3086, 3064, 3033, 3008 (aromatic), 2925, 2876, (alkyl), 1720, 1454, 1496, 1097, 1070, 1028, 758, 670 (aromatic: monosubstituted). ^{1}H NMR ($CDCl_3$): δ = 3.44 (m, C*H*, CH_2, polyether backbone), 3.90, 4.07, 4.25, (CHOCH_2O, C*H*OCH$_2$O), 5.80, 5.66, 5.56, 5.37 ($C_6H_5CH(OR)_2$), 7.25 (aromatic), 7.34 (aromatic). ^{13}C NMR ($CDCl_3$): δ = 66.7 (T), 70.9, 71.24 (D, T, L_{13}, L_{14}), 74.3 (L_{14}, T), 77.7 (D), 101.5, 102.8, 103.2 (acetal), 125.4, 125.7, 127.2, 127.3, 127.5 (C_3, C_5, aromatic), 128.1, 128.4, 128.7 (C_2, C_6, aromatic), 136.4, 137.1, 137.7 (C_1, aromatic).

Polyketal 2b. The reaction was performed according to general procedure I, using 10.0 g of polyglycerol and 50 mL of acetone dimethylacetal. The resulting polyketal **2b** (11.1 g, 95%) was obtained as a viscous, slightly yellow transparent oil. IR (KBr): ν (cm^{-1}) = 3448 (CHOH), 2985 (ketal: CH_3), 2925, 2876, 1117 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, CCH_3, ketal), 1.21 (s, CCH_3, ketal), 3.28 (m, C*H*, CH_2, polyether backbone), 3.52 (m, CHOCH_2O), 3.73 (s, O*H*), 3.85 (t, CHOCH_2O), 4.05 (m, C*H*OCH$_2$O). ^{13}C NMR ($CDCl_3$): δ = 25.8 (C−CH_3, ketal), 27.2 (C−CH_3, ketal), 62.4 (L_{13}), 67.1 (T), 71.9 (L_{13}, L_{14}, D), 72.9−73.2 (2 D, 2 T, L_{14}, L_{13}), 75.0 (2 L_{14}, T), 79.0 (D), 80.1 (L_{13}), 109.8 (*C*−CH_3, ketal).

Alkylation of All Remaining "Core" OH Groups (General Procedure II). Ether formation of all remaining linear OH groups in polyketal **2b** was performed with different alkylating agents under phase transfer catalysis conditions. 4 g of NaOH (100 mmol) was dissolved in 4 mL of deionized water. 0.435 g (1.35 mmol) of TBAB and the ketal protected polyglycerol **2b** (1 g, approximately 5 mmol of OH) dissolved

in 1 mL of toluene were added to the solution under vigorous stirring. The suspension was then heated at 40 °C, and the respective alkyl halide (3 equiv/OH group) was slowly added to the reaction mixture (1 equiv at the beginning, 2 equiv overnight) under vigorous stirring in order to reach full conversion. The alkylated ketal-protected polyglycerol **3** was then extracted with toluene, and the organic phase was concentrated and dried under vacuum. For further purification dialysis in chloroform or toluene using a benzoylated cellulose membrane (MWCO 1000, Sigma) was performed for 1−2 days.

Core-Methylation (3a). This product was obtained according to general procedure II. 500 mg of polyketal **2** dissolved in 1 mL of toluene was dispersed in 2 mL of water, 65 mg of TBAB, and 2 g of NaOH. Methyl iodide (1.0 mL, 16.0 mmol) was then added to the suspension over a period of 15 h. Purification of the final product was performed by dialysis in toluene. 307 mg of a pale yellow oil, polyether ketal **3a**, was isolated after concentration. IR (KBr): ν (cm^{-1}) = 2985 (ketal), 2929, 2876, and 1109 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 1.27 (s, CC*H*$_3$, ketal), 1.33 (s, CC*H*$_3$, ketal), 3.28 (s, OC*H*$_3$), 3.38−3.61 (m, C*H*, C*H*$_2$, polyether backbone), 3.66 (m, CHOC*H*$_2$O), 3.97 (t, CHOC*H*$_2$O), 4.18 (m, C*H*OCH$_2$O). ^{13}C NMR ($CDCl_3$): δ = 25.8 (C−*C*H$_3$, ketal), 27.2 (C−*C*H$_3$, ketal), 58.5 (CHO*C*H$_3$), 59.6 (CH$_2$O*C*H$_3$), 67.1 (T), 71.9 (L$_{13}$, L$_{14}$, D), 72.9 2 (2 D, 2 T, L$_{14}$, L$_{13}$), 75.1 (2 L$_{14}$, T), 79.7 (D), 109.7 (*C*−CH$_3$, ketal).

Core-Ethylation (3b). This product was obtained according to general procedure II. Polyketal **2** (2.96 g) dissolved in 1.7 mL of toluene were dispersed in 2.7 mL of water, 1.47 mg of TBAB, and 2.7 g of NaOH. Ethyl bromide (4.34 mL, 58.1 mmol) was slowly added to this suspension under vigorous stirring. Purification of the final product was performed by dialysis in $CHCl_3$, and 2.58 g of poly(ether ketal) **3b** was isolated after concentration as a pale yellow oil. IR (KBr): ν (cm^{-1}) = 2985 (ketal), 2981, 2871, 1114 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 1.11 (t, CC*H*$_3$), 1.28 (m, CC*H*$_3$, ketal), 1.34 (s, CC*H*$_3$, ketal), 3.41−3.57 (m, C*H*, C*H*$_2$, polyether backbone), 3.67 (m, CHOC*H*$_2$O), 3.97 (t, CHOC*H*$_2$O), 4.18 (m, C*H*OCH$_2$O). ^{13}C NMR ($CDCl_3$): δ = 14.2 (OCH$_2$*C*H$_3$), 25.8 (C−*C*H$_3$, ketal), 28.7 (C−*C*H$_3$, ketal), 64.8 (L$_{13}$), 66.6 (T), 69.6 (L$_{13}$, L$_{14}$, D), 71.5 (2 D, 2 T, L$_{13}$, L$_{14}$), 73.6 (2 L$_{14}$, T), 77.7 (D), 108.1 (*C*−CH$_3$, ketal).

Core-Benzylation (3c). Synthesis according to general procedure II. 500 mg of polyglycerol **2** dissolved in 1 mL of toluene was dispersed in 2 mL of water, 70 mg of TBAB, and 2 g of NaOH. Benzyl chloride (1.0 mL, 8.7 mmol) was slowly added to this suspension under vigorous stirring. Purification of the final product was performed by dialysis in toluene, and 420 mg of dry poly(ether ketal) **3c** was isolated after concentration as a pale yellow oil. IR (KBr): ν (cm^{-1}) = 3088, 3064, 3030 (aromatic), 2985 (ketal, CH$_3$), 2931, 2868, 1097 (alkyl), 1604, 1497, and 1453 (aromatic). ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, CC*H*$_3$, ketal), 1.32 (s, CC*H*$_3$, ketal), 3.21−3.73 (m, C*H*, C*H*$_2$, polyether backbone), 3.92 (t, CHOC*H*$_2$O), 4.13 (m, C*H*OCH$_2$O), 7.17−7.29 (m, aromatic). ^{13}C NMR ($CDCl_3$): δ = 24.4 (C−*C*H$_3$, ketal), 25.9 (C−*C*H$_3$, ketal), 65.8 (T), 70.7 (L$_{13}$, L$_{14}$, D), 71.5 (2 D, 2 T, L$_{13}$, L$_{14}$), 73.6 (2 L$_{14}$, T), 77.7 (D), 108.2 (*C*−CH$_3$, ketal), 126.6 (C$_3$, C$_5$, aromatic), 127.4 (C$_2$, C$_6$, aromatic), 137.3 (C$_1$, aromatic)

Core-Allylation (3d). Obtained according to general procedure II. 1 g of polyglycerol **2** dissolved in 1 mL of toluene was dispersed in 4 mL of water, 435 mg of TBAB, and 4 g of NaOH. Allyl chloride (3.1 mL, 38 mmol) was slowly added to this suspension under vigorous stirring. CAUTION: purification of the final product was performed by dialysis in chloroform, and 750 mg of dry poly(ether ketal) **3d** was isolated after concentration as a pale yellow oil. Caution: allyl groups are sensitive to oxidation and polymerization. Small amounts (0.1−1‰) of 2,6-di-*tert*-butyl-4-methylphenol (BHT) stabilizer were added to avoid polymerization. IR (KBr): ν (cm^{-1}) = 3079 (C=CH), 2985 (ketal), 2928, 2871 (alkyl), 1646 (C=C), 1108 (alkyl), 996 (C=CH$_2$), 924 (C=CH$_2$). ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, CC*H*$_3$, ketal), 1.34 (s, CC*H*$_3$, ketal), 3.20−3.80 (m, C*H*, C*H*$_2$, polyether backbone), 4.00 (m, CHOC*H*$_2$O), 3.10 (t, CHOC*H*$_2$O), 4.15 (m, C*H*OCH$_2$O), 5.18 (m, CH=CH$_2$), 5.85 (m, CH=CH$_2$). ^{13}C NMR ($CDCl_3$): δ = 24.4 (C−*C*H$_3$, ketal), 25.8 (C−*C*H$_3$, ketal), 65.8 (T), 69.2 (L$_{13}$, L$_{14}$, D), 70.0−71.5 (2 D, 2 T, L$_{14}$, L$_{13}$), 73.6 (2 L$_{14}$, T), 77.7 (D), 108.2 (*C*−CH$_3$, ketal), 115.7 (CH=*C*H$_2$), 134.0 (*C*H=CH$_2$).

Full Methylation of Polyglycerol (5). Preparation according to general procedure II. Polyglycerol **1** (3.0 g) was dissolved in 8 mL of water, containing 1.29 g of TBAB and 8 g of NaOH. Methyl iodide (2.8 mL, 44.4 mmol) was slowly added to this suspension under vigorous stirring. Purification of the final product was performed by dialysis in toluene. 2.11 g of the fully methylated polyglycerol **5** was isolated after concentration as a pale yellow oil. IR (KBr): ν (cm^{-1}) = 2958, 2923, 2854, and 1111 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 3.52 (s, OC*H*$_3$), 3.61−3.82 (m, C*H*, C*H*$_2$, polyether backbone). ^{13}C NMR ($CDCl_3$): δ = 58.3 (CH$_2$O*C*H$_3$), 59.5 (CHO*C*H$_3$), 69.8 (L$_{13}$, L$_{14}$, D), 72.1 (2 D, 2 T, L$_{13}$, L$_{14}$), 72.7 (2 L$_{14}$, T), 79.1 (D), 79.5 (L$_{13}$).

Deprotection (Acetal/Ketal Cleavage), General Procedure III. To a solution of the acetal-protected polyglycerols **2** or **3** (1.0 g) in 5 mL of methanol, 1.0 g of Dowex-50 resin was added. The mixture was stirred and heated at reflux for 15 h. The crude product was filtered, and the clear methanol solution was concentrated and dried under vacuum.

Core-Methylated Polyglycerol 4a. Prepared according to general procedure III. IR (KBr): ν (cm^{-1}) = 3386 (OH), 2924, 2878, and 1109 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 3.25 (s, OC*H*$_3$), 3.37−3.67 (m, C*H*, C*H*$_2$, polyether backbone), 4.79 (s, OH). ^{13}C NMR ($CDCl_3$): δ = 58.8 (CH$_2$O*C*H$_3$), 64.9 (T), 71.6 (L$_{13}$, L$_{14}$, D), 72.8 (2 D, 2 T, L$_{13}$, L$_{14}$), 74.5 (2 L$_{14}$, T), 80.3 (D), 81.3 (L$_{13}$).

Core-Ethylated Polyglycerol 4b. Synthesis according to general procedure III. IR (KBr): ν (cm^{-1}) = 3388 (OH), 2924, 2875, and 1111 (alkyl). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (m, OCH$_2$C*H*$_3$), 3.47−3.67 (m, C*H*, C*H*$_2$, polyether backbone), 4.79 (s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5 (OCH$_2$*C*H$_3$), 64.9 (T), 67.2 (CHO*C*H$_2$CH$_3$), 68.3 (CH$_2$O*C*H$_2$CH$_3$), 71.7 (L$_{13}$, L$_{14}$, D), 72.6−73.4 (2 D, 2 T, L$_{13}$, L$_{14}$), 74.5 (2 L$_{14}$, T), 79.4 (D), 80.4 (L$_{13}$).

Core-Benzylated Polygylcerol 4c. This product was obtained according to general procedure III. IR (KBr): ν (cm^{-1}) = 3386 (OH), 3087, 3063, 3029 (aromatic), 2924, 2862 (aliphatic), 1603, 1496, and 153 (aromatic).^{1}H NMR ($CDCl_3$): δ = 3.13−3.86 (m, C*H*, C*H*$_2$, polyether backbone), 4.41 (s, CHOC*H*$_2$C$_6$H$_5$), 4.49 (s, OH), 4.55 (s, CH$_2$OC*H*$_2$C$_6$H$_5$), 7.18 (s, aromatic), 7.28 (m, aromatic), 7.30 (m, aromatic). ^{13}C NMR ($CDCl_3$): δ = 71.2 (O*C*H$_2$C$_6$H$_5$), 126.7 (C$_3$, C$_5$, aromatic), 127.5 (C$_2$, C$_6$, aromatic), 137.3 (C$_1$, aromatic).

Preparation of a Polyglycerol Pseudo-Dendrimer. Dihydroxylation (3e). A mixture of poly(ether ketal) **3d** (200 mg, approximately 0.5 mmol of allyl groups), *N*-methylmorpholine-*N*-oxide (3.33 g, 25 mmol), acetone (0.8 mL), distilled water (0.2 mL), 1-butanol (0.2 mL), and 0.04 mL of a 4 wt % OsO_4 solution in water (CAUTION: OsO_4 is extremely toxic) were stirred for 20 h at 25 °C. After removal of all volatile compounds the obtained polyglycerol−polyketal **3e** was further purified by dialysis in chloroform. 210 mg of a pale yellow oil was obtained. IR (KBr): ν (cm^{-1}) = 3443 (OH), 2987 (ketal), 2876, 1083 (alkyl). ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, CC*H*$_3$, ketal), 1.31 (s, CC*H*$_3$, ketal), 2.6 (s, O*H*), 3.30−3.70 (m, C*H*, C*H*$_2$, polyether backbone), 3.75 (m, CHOC*H*$_2$O), 3.95 (t, CHOC*H*$_2$O), 4.20 (m, C*H*OCH$_2$O).

Polyglycerol Pseudo-Dendrimer 6. This product was obtained from the dihydroxylated polyglycerol polyketal after ketal cleavage according to general procedure III. IR (KBr): ν (cm^{-1}) = 3383 (OH), 2920, 2877, 1652, 1456, 1109, 1072 (alkyl). ^{1}H NMR (CD_3OD): δ = 3.38−3.92 (m, C*H*, C*H*$_2$, polyether backbone), 4.90 (s, OH). ^{13}C NMR (CD_3OD): δ = 64.9 (T), 71.7 (D), 72.6−73.4 (D, T), 74.4 (T), 80.3 (D).

Distribution Coefficients (H_2O/$CHCl_3$). The respective polyglycerol derivative **1**−**5** (100 mg) was dissolved in 10 mL of $CHCl_3$ and 10 mL of deionized water. Samples were shaken until total dissolution and phase separation occurred in 1−12 h, depending on the sample composition. The two phases were separated, dried under high vacuum, and weighed to determine the weight distribution of the polyglycerol derivatives between the two phases. Each distribution experiment was repeated twice (experimental error 5−10%).

Results and Discussion

A. Structural Considerations. To generate a core−shell-type structure in a hyperbranched polymer after the polymer synthesis, it is important to obtain information on the spatial distribution of the structural units. Hyperbranched polymers—in contrast to dendrimers—are characterized by a random distribution of dendritic, linear, and terminal units. This is illustrated schematically in Figure 1B, where the circles represent pseudogenerations[14] that give the distance to the focal unit in terms of monomer units. In a recent computer simulation, we analyzed the distribution of the different units for the slow monomer addition procedure,[14] which has been employed for the preparation of polyglycerol. Figure 2A,B was obtained with the computer simulation program developed in this work. Figure 2A indicates that the perfectly branched dendritic units are located preferentially close to the B_f-type initiator-core, which represents the focal unit in the hyperbranched macromolecule, whereas linear and terminal units are incorporated at increasing distances from the "core". Although the distribution curves of the building units with different structural perfection overlap, selective conversion of the linear or the terminal units, e.g., resulting in different polarity of these parts of the structure, should result in a differentiation of interior and periphery of the macromolecules. In the following discussion, we will use a simplified structural view, designating the linear units located closer to the focal unit as "core" and the more distant terminal units as "shell". Although—based on the simulation data shown—this approach represents a simplification of the real situation, the physical properties of the selectively "core"- or "shell"-modified hyperbranched polyglycerols presented in the final sections of this paper justify this topological view.

When all linear units are converted into dendritic units by an appropriate selective functionalization method, a fully branched structure is obtained that consists only of dendritic and terminal units, a so-called pseudo-dendrimer.[15,16] The distribution of units in dependence of the "core" distance is shown in Figure 2B. Perfectly branched units are located preferentially in proximity of the core, whereas the terminal units are located at larger average distance from the core. Figure 2C gives this distribution for an analogous, structurally perfect dendrimer molecule. As can be seen in Figure 2C, a similar, however, more pronounced separation of core and shell units is present.

B. Synthesis of "Core−Shell" Functionalized Polyglycerols. For the selective generation of "shell"-functionalized polyglycerols regioselective acetal/ketal formation (Scheme 1, **1** → **2**) was applied. This reaction converts all terminal 1,2-diols of polyglycerol **1** and results in the corresponding polyacetal **2a** or polyketal **2b**, respectively.[17] The reaction proceeds under mild conditions when dimethylacetals are used.[17b] The complete conversion (according to ^{13}C NMR) of all terminal 1,2-diols in polygylcerol **1** is observed after only 15 min, when acetone dimethylacetal and ultrasonication are employed. This selective ketal formation leaves approximately 40% of the OH groups unaffected, and the selective transformation of these linear ("core") functional groups (**2b** → **3**) results in a new type of bifunctional polymer. Complete conversion of these remaining OH groups into the corresponding ethers using classical Williamson's ether synthesis conditions

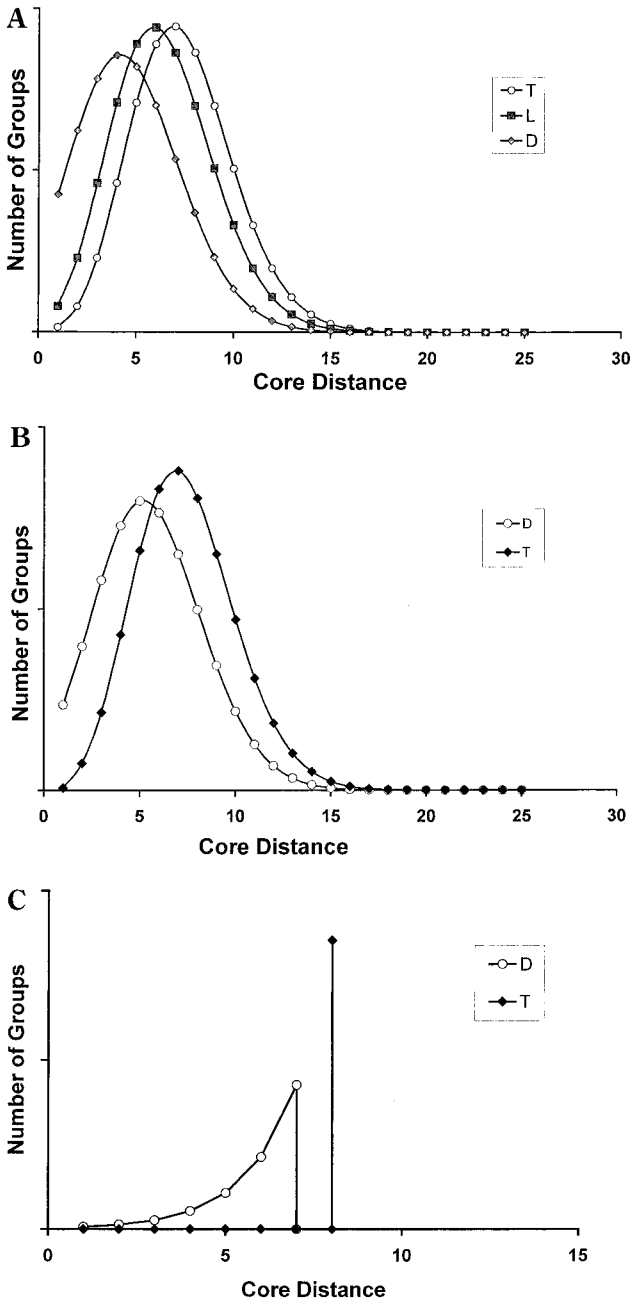
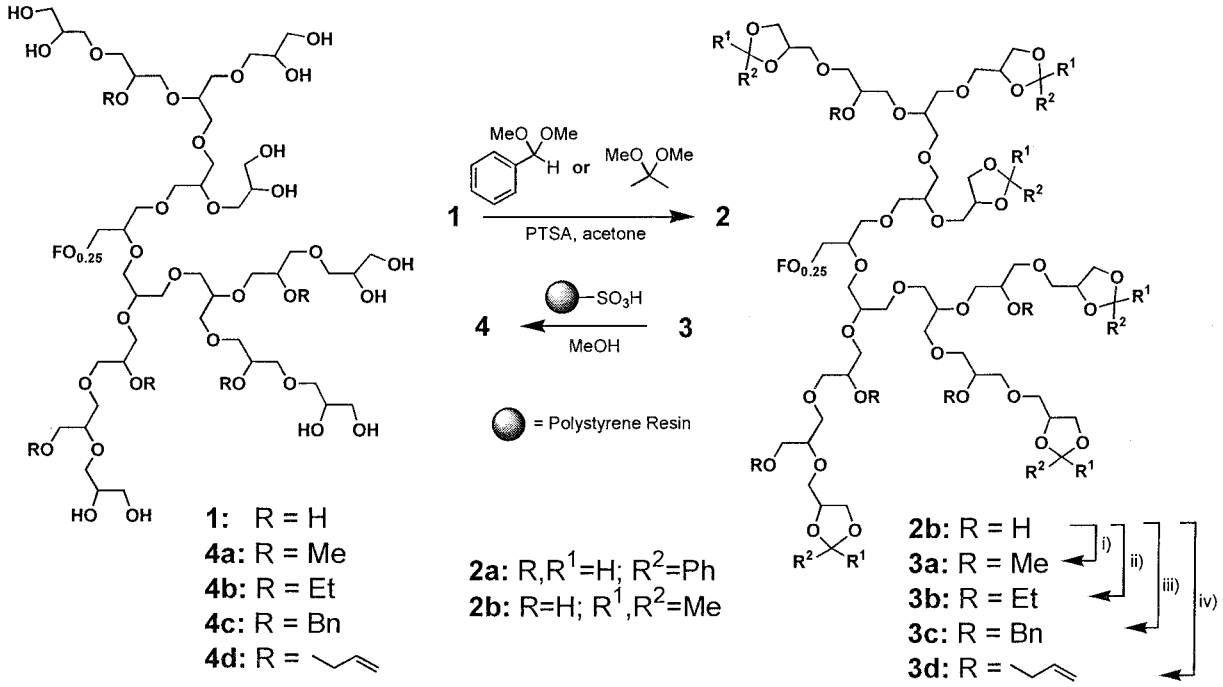


Figure 2. Distribution of dendritic (D), linear (L), and terminal (T) units in different dendritic polymer structures: (A) distribution of units in a hyperbranched polymer obtained by slow addition of AB_2 monomer to an initiator molecule; obtained from computer simulation; (B) distribution of units after transformation of this polymer into a pseudo-dendrimer; (C) distribution of dendritic and terminal units for an analogous, perfectly branched [G8] dendrimer.

(DMF, NaH, alkyl halide) was unsuccessful. Incomplete conversion (50−70%) was observed, when polyacetal **2b** was employed, clearly documented by the remaining OH band in the IR spectrum. To improve conversion, we used phase transfer conditions, which have been reported to be superior for the complete functionalization of polyols.[18] The alkylation of the remaining OH groups in the ketal-protected polyglycerol **2** proceeds quantitatively under these conditions, and the resulting polyether−polyketals **3a**−**d** do not exhibit an OH band in their IR spectra anymore (compare compound **3d** in Figure 4). Complete ether formation under phase transfer conditions was also achieved using the unprotected

Scheme 1. Selective Acetalization/Ketalization, Modification of All Linear OH Groups by Alkylation: (i) Methyl Iodide, NaOH, Bu_4NBr, H_2O, 40 °C (Phase Transfer Conditions); (ii) Ethyl Bromide, PT Conditions; (iii) Benzyl Chloride PT Conditions; (iv) Allyl Chloride, PT Conditions and Acetal Cleavage (F: Focal Unit)

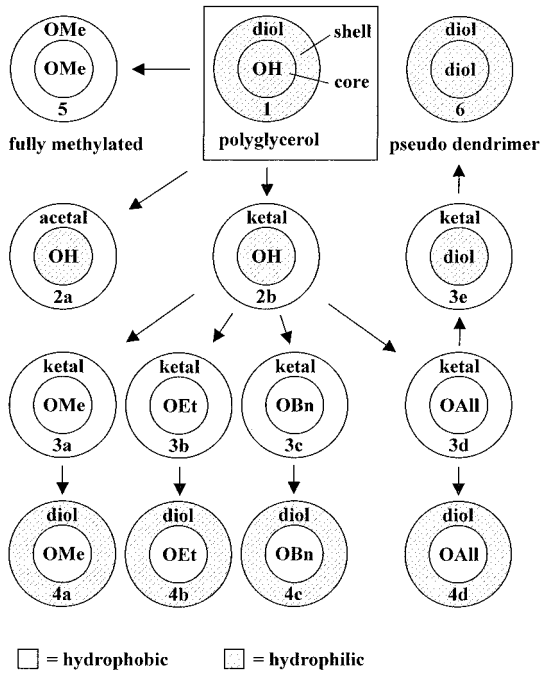


polyglycerol **1**, yielding a hydrophobic, fully methylated polyglycerol **5**. Again, the IR spectrum did not show any remaining intensity of the OH band, supporting complete conversion.

The orthogonal use of soluble and insoluble polymers in one chemical reaction has been reported previously.[19] We applied an insoluble, acidic Dowex-50 resin for the selective acetal cleavage in the fully protected polyglycerols **3a**−**c**. The acid-catalyzed cleavage of the acetal groups (**2** → **1**) or (**3** → **4**) proceeds with quantitative conversion (>95% according to ^{1}H NMR) and demonstrates the suitability of these dendrimer-like polymers as reversible, soluble polymer supports for carbonyl compounds.[17,20] Using combinations of acetal protection, etherification, and acid-catalyzed deprotection, different hyperbranched polyglycerols with "core" and "shell" of varying polarity have been prepared. The whole set of compounds prepared in this work is summarized in Scheme 2 which also illustrates the pathways to these materials.

C. Physical Properties of "Core−Shell" Functionalized Polyglycerols. *Distribution Coefficients in Chloroform / Water.* A series of experiments have been carried out to compare the core−shell-type hyperbranched macromolecules with respect to their solubility in water and organic solvents as well as their thermal behavior and peculiar topology-specific spectroscopic properties. The main issue addressed in this context is the effect of the different location of the hydroxyl groups, i.e., whether they are located preferentially in the "core" or the "shell" of the macromolecules. To assess the effect of apolar modification, the selectively functionalized macromolecules have been characterized with respect to their polarity on the basis of the distribution in a chloroform/water two-phase system under ambient conditions. Generally, the distribution coefficient of polymers in such organic solvent/water mixtures is a useful indicator of their polarity. In the case of core−shell-type architectures the distribution coefficient is expected to

Scheme 2. Overview of All Core−Shell-Type Architectures (1−6) Prepared in the Course of This Work and Distribution of Hydrophilic and Hydrophobic Substituents



be related to both the fraction of hydroxyl groups and the topology (Scheme 2). The results of the $CHCl_3$/water distribution experiments are summarized in Figure 3.

As described previously, polyglycerol **1** shows no solubility limit in water and was found only in the water phase (>99%). However, selective acetalization or ketalization of all terminal 1,2-diols (**2a,b**) was observed to enhance the solubility in the $CHCl_3$ phase dramatically (>99% and 95%, respectively). It should be noted that phase separation in the case of **2b** was slow due to the amphiphilic behavior of this polyketal polyol. Func-

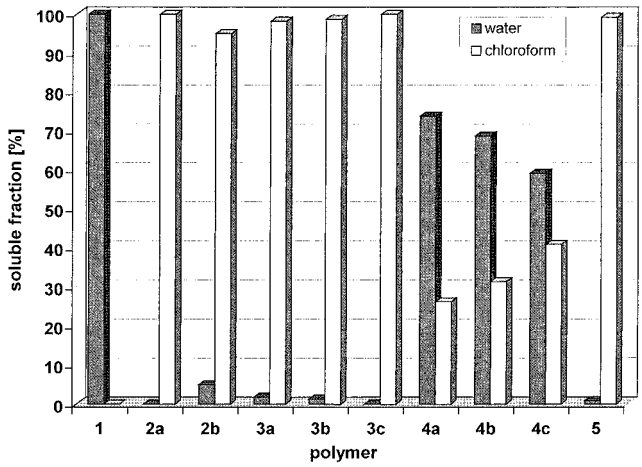


Figure 3. Distribution of selective "core" and "shell" modified polyglycerols **1**−**5** in a chloroform/water 1:1 mixture by their fraction in weight %.

tionalization of the remaining (40%) linear ("core") OH groups further decreases the solubility in water. The amount of all fully functionalized materials **3a**−**c** in the organic phase is influenced by the hydrophobicity of the corresponding ethers in the "core" (OMe = 98%, OEt = 99%, OBn = >99%).

While the fully methylated polyglycerol **5** is present exclusively (>99%) in the organic phase, the selectively "core"-methylated polyglycerol **4a** remains preferentially in the aqueous phase (75%). Again, the hydrophobicity of the alkyl groups correlated with the amount of polymer **4a**−**c** in the organic phase (OMe = 25%, OEt = 30%, OBn = 40%). These selectively "core"-alkylated polyglycerols also showed amphiphilic behavior, but nevertheless clean phase separation took place after several hours.

These solubilization studies clearly demonstrate that the functionalization of the terminal ("shell") 1,2-diols (approximately 60% of all OH-groups) in polyacetal and polyketal **2a,b** reduces the amount of polymer soluble in the aqueous phase to a much larger extent than functionalization of the linear ("core") OH groups (approximately 40% of all OH groups) in the series of polyethers **4a**−**c**.

The $CHCl_3$/water distribution studies indicate that not only the fraction of hydrophilic hydroxyl groups but also the architecture—location of hydroxyl groups in the "core" or the "shell"—controls the solubility and phase distribution of these compounds.

Thermal Behavior. It is an intriguing question, in which manner the presence of polar/apolar incompatible core−shell type structures affects the solid-state behavior of the hyperbranched polymers. Therefore, the thermal behavior of all compounds was studied by DSC. The glass transitions observed for the series of samples are summarized in Table 1. On the basis of these data, some interesting general conclusions on structure−property relationships can be drawn:

(i) Two glass transitions T_{g1} and T_{g2} at around −80 °C and −53 to −10 °C, respectively were observed for all samples possessing hydroxyl groups in the "shell", i.e., samples **1**, **6**, and **4a**−**c**. The glass transitions T_{g1} at approximately −80 °C clearly stem from the polyether scaffold of the compounds and are well-known for linear polyethers. We attribute the presence of a second glass transition in these samples to strong interaction and nanocluster formation of the hydroxyl groups present in the "shell" region of the polymers. Obviously, this leads to polar domains that are nanosegregated from domains that contain the polyether "core" structures. This structural view is supported by the observation that for the unmodified polyglycerol samples the T_{g1} indicative of an intrinsic core−shell-type superstructure was only observed at molecular weights exceeding 4000 and did not occur for a series of lower molecular weight samples studied.

Table 1. DSC Data of Functionalized Polyglycerols (Heating Rate: 20 °C/min)

compd	core	shell	T_{g1} [°C]	T_{g2} [°C]
1	OH	diol	−81 (weak)	−24
6	diol	diol	−79 (weak)	−32
2a	OH	benzacetal		−17
2b	OH	acetoneketal		−53
3a	OMe	acetoneketal		−40
3b	OEt	acetoneketal		−47
3c	OBn	acetoneketal		−53
5	OMe	OMe		−66
4a	OMe	diol	−78 (weak)	−54
4b	OEt	diol	−80 (weak)	−29
4c	OBn	diol	−78 (weak)	−31

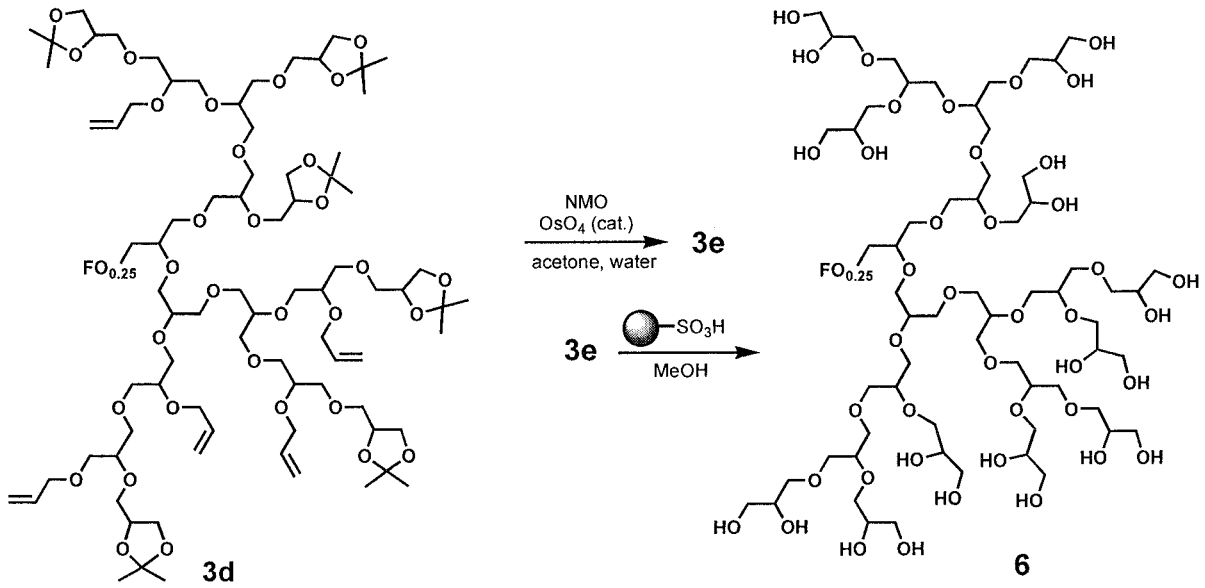
(ii) It is a striking observation that none of the samples **2a,b** with hydroxyl groups in the "core" showed a second T_{g1}, although the fraction of hydroxyl groups in these samples is similar to the materials **4a**−**c**. This demonstrates that the "core−shell" topology does have an effect on the bulk properties of these materials, i.e., that hydroxyl groups in the "shell" are considerably more important for the bulk behavior than hydroxyl groups in the "core" of the macromolecules.

(iii) In the case of the polymers **3a**−**c** with apolar ether "core" and ketalized, apolar "shell" only one T_g was observed. Thus, if hydroxyl groups are absent, the structure of the whole macromolecule determines the glass transition, no strong interactions leading to nanosegregation are possible, and both hydrophobic character and size of the substituents present in the "core" influence T_{g2}. The glass transitions for these materials are in the range −40 to −53 °C. Accordingly, full methylation (sample **5**) leads to the disappearance of polar interactions between polymer segments and results in further lowering of the T_g to −66 °C.

In summary, the thermal bulk behavior of the polymers is determined both by the fraction of interacting hydroxyl groups present and by their specific location in the proximity of the "core" or in the "shell". This conclusion is further supported by FTIR spectra discussed in section E.

D. Comparison between Structurally Inverted Polyglycerols. The synthetic strategy presented in section B also permits inversion of the polarity of "core" and "shell" structure, i.e., the preparation of structural analogues with reversed core−shell-type topology. To study the effect of this "structural inversion", we compared the physical properties of the "shell" functionalized polybenzylidene acetal **2a** and the "core"-benzylated polyglycerol **4c**. These polymers are suited for a direct comparison, since they carry approximately the same amount of phenyl groups, in the periphery **2a** and in the interior **4c**. This is corroborated by similar integral ratios (aromatic vs glycerol protons) in the ^1H NMR spectra of these materials. In addition, the hydrophilic lipophilic balance values (HLBs),[21] which do not contain any topological information and are calculated only on the basis of hydrophilic/lipophilic group

Scheme 3. Formation of a Pseudo-Dendritic Polyglycerol 6 by Selective Transformation of All Linear Glycerol Units into Terminal 1,2-Diols (F: Focal Unit)



ratio, does not differ significantly for both polymers **2a** and **4c** (6.6 and 7.8, respectively).

Comparison of samples **2a** and **4c**, however, reveals striking differences: the distribution coefficients in a chloroform/water mixture of both compounds are almost reciprocal. While the polybenzacetal **2a** is insoluble in water and is recovered exclusively in the organic phase (>99%), the "core"-benzylated polyglycerol **4c** shows significant water solubility (60%). Furthermore, the variation of the T_{g2}s (−17 °C (**2a**) vs −31 °C (**4c**)) as well as the presence of two glass transitions for **4c** can clearly be attributed to the different topology of these polymers.

In addition, the effect of the different location of the hydroxyl groups in the hyperbranched structure is supported by the OH band in the IR spectra of polymers **2a** and **4c**. Whereas the OH band maximum of the benzacetal **2a** is observed at 3470 cm^{-1}, the maximum of the OH band in the "core"-benzylated structure **4c** is observed at significantly lower wavenumber at 3386 cm^{-1}. This pronounced shift can only be explained by the different environment of the hydroxyl groups and is found throughout all "core−shell" structures (Table 2). It is generally known that isolated OH groups appear at higher wavenumbers (3600 cm^{-1}), whereas hydrogen-bonded OH groups appear at lower wavenumbers (3400−3200 cm^{-1}), depending on the strength of the hydrogen bonds. Apparently, only polymer **4c** with the OH groups in the periphery can form strong intra- and intermolecular hydrogen bonds, and hence its OH band maximum appears at a lower wavenumber. It should be emphasized that FTIR spectra were measured at ambient conditions; i.e., both samples were present above T_{g2} in the fully isotropic state.

In summary, the structural inversion of samples **2a** and **4c** leads to a pronounced change of all physical properties, supporting the postulated core−shell-type architecture. Similar effects caused by inversion of the polarity of a dendritic polymer structure have hitherto—to the best of our knowledge—not been observed.

E. Selective "Core"-Modification: Synthesis of Pseudo-Dendritic Polyglycerol. In previous work, we have demonstrated that hyperbranched polyglycerols can be transformed into fully branched structures with DB (degree of branching) = 100%, designated "pseudo-dendrimers", by applying one dendrimer synthesis step on a well-defined hyperbranched polyglycerol.[15,16] This synthetic modification affects all OH groups and thus is unselective without differentiating between linear and terminal units of the hyperbranched polymer. An alternative approach using the concept of selective "core−shell" differentiation in hyperbranched polyglycerols also leads to a pseudo-dendritic polyglycerol (DB = 100%). This can be achieved by the selective transformation of all linear into dendritic glycerol units, leaving terminal units unchanged. A polyglycerol pseudo-dendrimer—consisting only of dendritic and terminal units—is obtained by quantitative (>95% according to ^{1}H NMR) dihydroxylation of the allyl-substituted polyglycerol **3d**.[16] After selective cleavage of the ketals in the "core"-dihydroxylated polyglycerol **3e**, the completely branched structure **6** (Scheme 3) is obtained.

All steps of the conversion of the hyperbranched polyglycerol **1** (DB = 60%) into the pseudo-dendritic polyglycerol **6** (DB = 100%) were monitored by IR spectroscopy, confirming the unusual behavior of the OH bands in the "core−shell" structures (Figure 4, Table 2). The spectrum of polyglycerol **1** displays a wide OH band centered around 3384 cm^{-1} of high intensity. Protection of terminal diol units with acetone dimethylacetal leads to a significant decrease of the OH band intensity, as shown in the spectrum of the polyketal **2b**. It is also interesting to note the shift of the OH band maximum from 3384 to 3448 cm^{-1}, arising only from OH groups attached to linear "core" units in **2b**. This band shift is caused by the tendency of the OH groups to be present in nonassociated structures, as already discussed for the selectively benzylated structures (section D). In the spectrum of **2b** the peaks at 2985 and 1370 cm^{-1} are characteristic for the ketal protecting group. Reaction of compound **2b** with allyl chloride under phase transfer catalysis conditions leads to quantitative conversion of the remaining linear OH groups into allyl ethers, as indicated by the absence of the OH band (sample **3d**) and the presence of bands at 3079 and 1646 cm^{-1} from the allylic double bond. The subsequent dihydroxylation of the allyl groups generates diol groups in the "core" of the modified hyperbranched

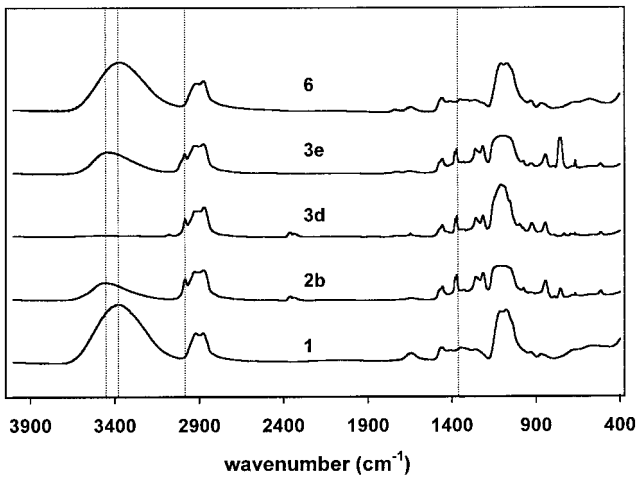


Figure 4. IR spectra of "core−shell" functionalized polyglycerols demonstrating the conversion of the hyperbranched polymer **1** into the pseudo-dendrimer **6** by selective "core" modification.

Table 2. OH Band Maxima in the IR Spectra of Core−Shell Functionalized Polyglycerols

compd	core	shell	OH band (cm^{-1})
1	OH	diol	3384
6	diol	diol	3383
2a	OH	benzacetal	3470
2b	OH	acetoneketal	3448
3e	diol	acetoneketal	3443
4a	OMe	diol	3386
4b	OEt	diol	3388
4c	OBn	diol	3386

polyglycerol, and spectrum **3e** confirms the presence of OH groups (broad band at 3443 cm^{-1}). Deprotection of the external diols by hydrolysis of the ketal groups leads to the "pseudo-dendritic" polyglycerol **6** as indicated by a significant increase (>50%) of the intensity of the OH band (3383 cm^{-1}) and by the disappearance of the ketal vibrations at 2985 and 1370 cm^{-1}.

The complete conversion of hyperbranched polyglycerol **1** into the fully branched polyglycerol **6** is also evident from the simplified NMR spectrum. ^{13}C NMR spectra of the hyperbranched polyglycerol **1** and pseudo-dendritic polyglycerol **6** are shown in Figure 5. The fully branched structure of the final "pseudo-dendrimer" is supported by the disappearance of three signals at $\delta =$ 63.0, 71.2, and 81.7 ppm, which are assigned to carbon atoms being part of the linear units. Furthermore, the intensity of the resonances at 74.4 and 72.6 ppm decreases due to the disappearance of the contribution of the linear units in these signals. Hence, the spectrum of the pseudo-dendritic polyglycerol only displays signals of carbon atoms from dendritic (71.7, 73.4, and 80.3 ppm) and terminal (64.9, 72.6−73.4, and 74.4 ppm) units. As expected, the spectrum of the pseudo-dendrimer **6** is in perfect agreement (chemical shifts and intensities) with that of the perfect [G3]-polyglycerol dendrimer.[16]

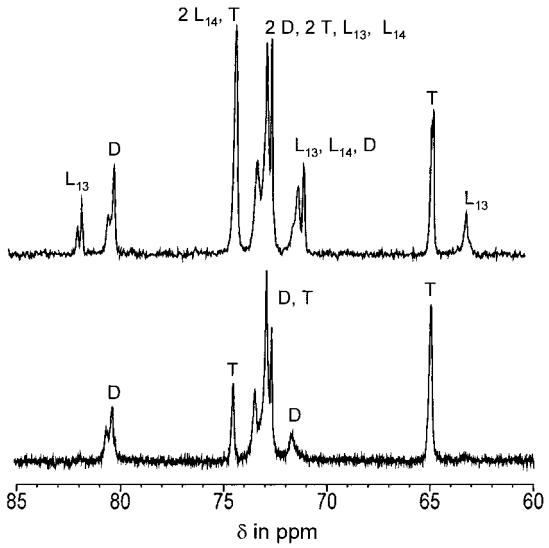


Figure 5. ^{13}C NMR spectra of hyperbranched polyglycerol **1** (top) and pseudo-dendritic polyglycerol **6** (bottom). D, L, and T refer to the dendritic, linear, and terminal glycerol units (detailed description of top spectrum is given in ref 10c).

Conclusions

We have presented a "chemical differentiation" strategy that permits in 1−3 synthetic steps—applied to hyperbranched polyglycerols—to generate macromolecules with clearly distinguished interior and periphery. The consequences of the resulting segmented nanostructures have been studied with respect to solubility and thermal and IR spectroscopic behavior in bulk.

Using this architectural control, it is possible to tune the materials' solubility and miscibility for various applications, e.g., for highly functional cross-linkers, processing additives, rheology modifiers, and homogeneous supports for organic substrates.[17] The obtained selectively functionalized aliphatic polyether polyols also possess great potential as supports for catalysts and drugs due to their inert building blocks. In addition, we have demonstrated that analogous, inverse "core−shell" structures with reversed polarity can be prepared, resulting in significant changes of all physical properties. Hyperbranched polymers certainly do not possess the structural perfection of discrete dendrimer molecules. However, we conclude from the presented results that the extensive branch-on-branch topology of these polymers leads to typical properties associated with core−shell architectures, i.e., nanosegregation depending on the polarity of the "core" and the "shell".

At present, we are investigating these selectively functionalized hyperbranched molecules with respect to the encapsulation of guest molecules or the creation of special microenvironments in the "core". Selective transport phenomena have already been observed for hyperbranched polyglycerols unselectively functionalized with fatty esters.[13] Similar behavior in both hydrophilic and hydrophobic media can be expected for these novel core−shell-type architectures.

Furthermore, the incorporation of new functional groups into the "core", as demonstrated for the "pseudo-dendritic" polyglycerol, can be extended to other "core"-modification reactions of polyglycerol, provided acidic cleavage of the acetal groups in the final step is tolerated.

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