Controlled Synthesis of Hyperbranched Polyglycerols by Ring-Opening Multibranching Polymerization

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ABSTRACT: Glycidol represents a latent cyclic AB_2-type monomer that can be polymerized in a ring-opening multibranching polymerization (ROMBP). Hyperbranched aliphatic polyethers with controlled molecular weights and narrow molecular weight distribution have been prepared via anionic polymerization of glycidol with rapid cation-exchange equilibrium. 1,1,1-Tris(hydroxymethyl)propane (TMP) was partially deprotonated (10%) and used as initiator for the anionic polymerization carried out under slow addition conditions to minimize polymerization without initiator as well as cyclization. ^{13}C NMR spectra were employed to assess the degree of branching (DB), which was in the range 0.53−0.59. ^{13}C NMR, MALDI-TOF mass spectrometry, vapor pressure osmometry (VPO), and GPC were used to characterize molecular weights and polydispersities of the polyols formed, showing good agreement. $\overline{DP}_n$ for the polymers prepared was in the range 15−83 ($\bar{M}_n = 1250-6500$), and $\bar{M}_w/\bar{M}_n$ obtained was 1.13−1.47, being exceptionally low for hyperbranched polymers. MALDI-TOF spectra evidenced complete attachment of the hyperbranched structures to the TMP initiator and the absence of macrocyclics as well as hyperbranched macromolecules without initiator, due to the slow addition. The hyperbranched polyethers prepared showed T_g's between −20 and − 26 °C.

Introduction

Hyperbranched macromolecules possess a randomly branched structure, precisely one focal unit and at least two branching points. Such polymers are generally prepared by polymerization of AB_m-type monomers.[1] Recently, this class of polymers has become of increasing interest as a potential alternative for the perfectly branched dendrimers that have to be constructed in a usually tedious, stepwise approach.[2]

Two strategies for the preparation of hyperbranched polymers are currently employed, the most common method being polycondensation of AB_m monomers.[3] Pioneering efforts using this route were reported by Kim and Webster in 1988.[4] This type of polymerization can be carried out in concurrent mode or by slow addition of the branching AB_m monomer, which strongly affects the branching density and molecular weight distribution. A second elegant pathway to hyperbranched polymers was recently developed by Fréchet and coworkers[5,6] and is based on a vinyl monomer that bears an initiating group (inimer). Since in the polymerization the vinyl groups are consumed, but at the same time the polymerization shows the typical features of a polycondensation reaction, it was designated *self-condensing vinyl polymerization* (SCVP).

The main drawback of hyperbranched polymers prepared by AB_m homopolymerization via both pathways lies in the extremely broad molecular weight distributions, with polydispersities in the range of $\overline{DP}_n/2$. Recent theoretical work by Müller et al.[7] as well as simulation work by our group[8] has shown that copolymerization of a core molecule of the structure B_f (representing a polyfunctional initiator in the case of the SCVP and a poly-B-functional molecule for the AB_m-type polycondensation-type reaction) can be used to lower the polydispersity considerably. This has already been exemplified in a few reported synthetic studies.[9,10]

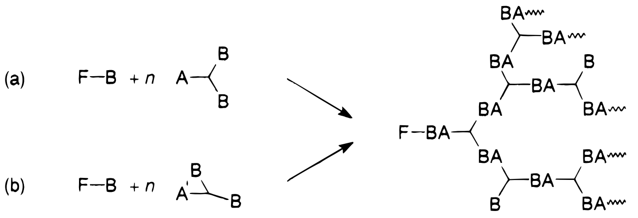

Figure 1. Analogy between formation of hyperbranched polymers by polycondensation and ROMBP: copolymerization of AB_2-type monomer with a monofunctional initiator F−B (F = focal unit, A, B = complementary reactive groups).

A third pathway to hyperbranched polymers, hitherto mentioned only in a few examples, is the ring-opening polymerization of cyclic latent AB_2-type monomers. In 1992, Suzuki et al. reported polymerization of a cyclic carbamate that may be classified under this third strategy. Suzuki referred to his concept as “multibranching polymerization”.[11] With respect to the ring-opening isomerization being the driving force of this type of reaction, in the further course of this article, this approach will be designated *“ring-opening multibranching polymerization”* (ROMBP). This synthetic strategy has been little explored so far, but it appears to possess promising potential for the controlled preparation of hyperbranched polymers. A general synthetic scheme of this type of reaction is shown in Figure 1, demonstrating the analogy between AB_2 polycondensation and the ROMBP approach.

Glycidol, a commercially available and highly reactive hydroxy epoxide, represents a latent AB_2 monomer that can be polymerized to hyperbranched polyethers with numerous hydroxyl end groups, “polyglycerols”. First attempts to polymerize glycidol were undertaken by Sandler and Berg.[12] Several groups polymerized glycidol to linear products in the presence of various catalyst systems but always considered branching as an undesired side reaction.[13] Vandenberg et al. characterized the

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branched structures formed to a certain extent.[14] Linear polyglycerol has been obtained from the polymerization of protected glycidols[15] and the polymerization of 3-hydroxyoxetane.[16] In summary, in these examples no controlled synthesis and comprehensive characterization of the hyperbranched polymer structure was achieved. Furthermore, glycidol has been polymerized cationically to branched polymers in elegant work by Penczek and Dworak.[17]

In this paper we describe the controlled anionic ring-opening polymerization of glycidol, making use of a partially deprotonated triol as alkoxide initiator. We demonstrate that anionic polymerization with rapid cation-exchange equilibrium, using slow monomer addition conditions can be employed to obtain hyperbranched polyols with polyether structure in a controlled manner. Furthermore, the degree of branching (DB) of the hyperbranched polyethers is determined, using previously derived expressions.[18]

Experimental Section

Polymerizations. Polymerizations were carried out in a reactor equipped with a mechanical stirrer and dosing pump under argon atmosphere. 1,1,1-Tris(hydroxymethyl)propane (Fluka) was partially deprotonated (10%) with potassium methylate solution (3.7 M in methanol, Fluka) by distilling off excess methanol from the melt. A 50 mL aliquot of glycidol (Aldrich) was slowly added at 95 °C over 12 h, choosing the initiator amount according to the monomer/initiator ratio.[19] After completion of the reaction (absence of excess epoxide) the product was dissolved in methanol and neutralized by filtration over cation-exchange resin. The polymer was twice precipitated from methanol solution into acetone and subsequently dried for 15 h at 80 °C in vacuo. Polyglycerol was obtained as a transparent, highly viscous liquid. Yields of isolated polymer ranged between 80% and 95%.

Caution: exposure of larger amounts of glycidol to alkoxides at elevated temperatures can lead to an explosive polymerization reaction.

NMR. ^1H NMR and ^{13}C NMR spectra were recorded in d_6-methanol at concentrations of 250 g/L on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively.

MALDI-TOF-MS. Measurements were performed with a Bruker Reflex II MALDI-TOF (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. α-Cyanohydroxycinnamic acid was used as matrix. Samples were prepared by dissolving the polymer in methanol at a concentration of 5 g/L. A 10 μL aliquot of this solution was added to 10 μL of a 20 g/L matrix solution and 1 μL of a LiCl solution (cationization agent). A 1 μL aliquot of the resulting mixture was applied to a multistage target to evaporate the methanol and create a thin matrix/analyte film. The ions were accelerated to 21.50 kV and measured in the reflectron mode of the spectrometer. Only lithium-cationized ions ($M + Li^+$) were detected. Poly(ethylene oxide) was used for an external calibration immediately before the measurement.

GPC. The polymers were dissolved in DMF at a concentration of 5 mg/mL. Measurements were performed with a Knauer microgel set C11 using DMF as an eluent at 45 °C and a Polymer Labaratories evaporative mass detector EMD 960 operating at 110 °C. Poly(propylene oxides) 1000, 2000, 4000 (Aldrich), 8000, and 12 000 (ARCO Chemical Co.) were used for calibration.

VPO. Vapor pressure osmometry was carried out using a Knauer vapor pressure osmometer in methanol at 45 °C in a concentration range of 5−10 mg/mL. Benzil (Merck) was used for calibration.

DSC. Measurements were carried out on a Perkin-Elmer 7 series thermal analysis system in the temperature range −100 to 20 °C at heating rates of 16, 25, and 36 K/min. The T_g was obtained by extrapolation to heating rate 0 from these measurements. The melting point of indium (156 °C) was used for calibration.

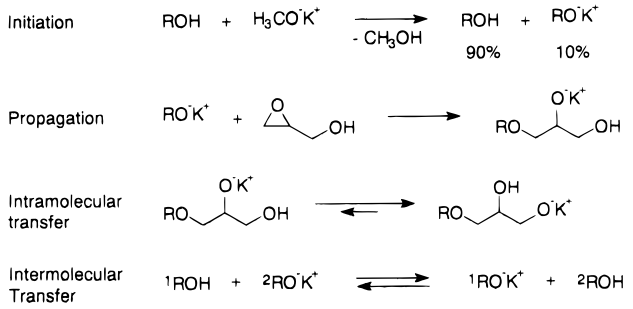

Figure 2. Mechanism of the anionic polymerization of glycidol.

Viscosimetry. Experiments were performed on a Schott AVS/6 Ubbelohde dilution viscosimeter at 20 °C using a capillary with a diameter of 0.46 mm and methanol as solvent.

Results and Discussion

Generally, the anionic polymerization of glycidol in the presence of alkoxides proceeds according to the mechanism shown in Figure 2, which is analogous to the polymerization of propylene oxide. However, as was first described by Vandenberg et al.,[14] intra- as well as intermolecular transfer steps after the ring-opening reaction can lead to the formation of a primary alkoxide as active site, which further propagates, resulting in branched structures.

Recently, intense research efforts are directed at “living“ polymerizations, which are based on a low concentration of active chain ends and a large number of dormant, i.e., potentially active, sites in combination with a rapid exchange equilibrium that leads to deactivation of active sites after a few propagation steps. In analogy to these concepts, particularly the ATRP concept, Inoue’s immortal polymerization,[20] and paralleling the technical strategy used for polymerization of propylene oxide,[21] we used an alcohol ROH that was only partially deprotonated as initiator. This enabled us to control the concentration of active sites (alkoxides) in the polymerization, leading to simultaneous growth of all chain ends and thus control of molecular weight and considerable narrowing of the polydispersity. By reaction of the alcohol used as initiator with a suitable deprotonating agent (e.g., potassium methylate followed by removal of excess methanol), only 10% of the hydroxyl groups were converted into the alkoxide.

In the subsequent propagation step the alkoxide initiator reacts with the epoxide ring on its unsubstituted end and thereby generates a secondary alkoxide. In contrast to cationic polymerization,[17] we did not observe nucleophilic attack on the substituted end of the epoxide ring. In the subsequent transfer the more stable and more reactive primary alkoxide is formed to a certain extent. When the polymerization proceeds, the initial concentration of 10% active species with respect to all hydroxyl end groups decreases, since incorporation of each one of the continuously added glycidol monomers generates a new hydroxyl group that represents a dormant chain end. After the polymerization, the polyglycerols were in all cases obtained as transparent, viscous liquids.

It was shown in recent theoretical work[7] as well as by computer simulation[8] that besides permitting control of molecular weights the use of a polyfunctional initiator

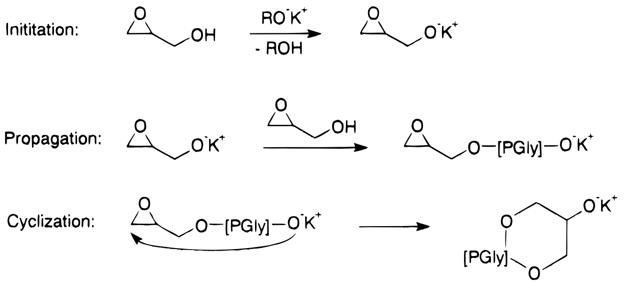

Figure 3. Formation of cyclics by intramolecular ring-opening at high glycidol/initiator ratios or in the polymerization of glycidol in the absence of initiator.

of the structure B_f in the synthesis of hyperbranched polymers results in considerable lowering of the polydispersity for both AB_m polymerization and SCVP. Additional slow monomer addition was calculated to result in even lower polydispersities and should result in complete control of the number-average molecular weights by the ratio monomer/initiator, as in this case every macromolecule formed is expected to be attached to the core unit.

In addition to the control of the concentration of active chain ends, a challenge in controlling glycidol polymerization lies in the supression of cyclization, since cyclization broadens polydispersity and lowers molecular weights achievable. In practically all theoretical approaches, cyclization is not considered due to theoretical difficulties.[22] Figure 3 illustrates the formation of (macro)cyclic products by the activated glycidol via proton abstraction from its primary hydroxyl group. Clearly, cyclization is expected only if no initiator is used or if the concentration of glycidol is considerably higher than that of the initiator, resulting in deprotonation of glycidol and initiation of polymerization by deprotonated monomer (Figure 3). Only in this case are macromolecules with an epoxide group as focal unit formed that may react intramolecularly with one of the hydroxyl end groups to form a cyclic structure.

Thus, in summary, the following reaction conditions were employed in order to (i) control molecular weights, (ii) lower the polydispersity, and (iii) suppress cyclization: 1,1,1-tris(hydroxymethyl)propane (TMP) used as trifunctional initiator was partially deprotonated (10%) using potassium methylate and the anionic polymerization was carried out under slow monomer addition conditions to minimize cyclization.

A schematic structure of the hyperbranched polyglycerol macromolecules prepared via this approach is shown in Figure 4. The initiator (a monofunctional alcohol or a polyol) is incorporated as core unit. (Figure 4 shows a monofunctional core unit F–B as an example.) Since all hydroxyl groups remain potentially active in the course of the polymerization, the resulting structure is hyperbranched and consists of perfect dendritic (D), linear (L), and terminal (T) units that can be incorporated at each position of the structure.

However, in contrast to common hyperbranched polymers obtained from the polycondensation of symmetrical AB_2 monomers, due to the unsymmetric glycidol structure, four structural units have to be distinguished, as shown in Figures 4 and 5. If the secondary hydroxyl group has propagated, the polymer chain is attached to a glycerol-like unit, and a linear 1,3-unit (L_{13}) is formed. If the primary hydroxyl group has undergone propagation, the corresponding linear 1,4-unit (L_{14}) is generated. If both hydroxyl groups have reacted with monomer, the result is a branched, i.e., dendritic, unit (D). If a monomer unit has been deactivated by proton exchange or by the final addition of acid, a terminal unit (T) with two hydroxyl end groups is formed.

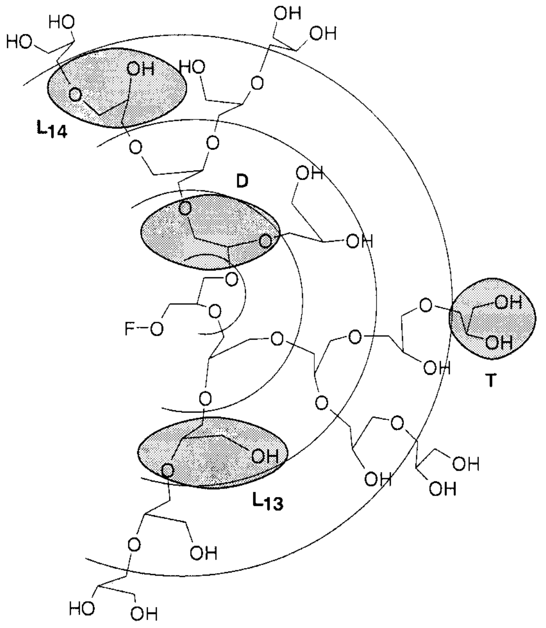

Figure 4. Schematic architecture of a hyperbranched polyglycerol. Examples of terminal (T), dendritic (D), linear 1,3 (L_{13}), and linear 1,4-units (L_{14}) are shaded, pseudogenerations are indicated by concentric lines, and F indicates the core unit attached to the focal monomer unit.

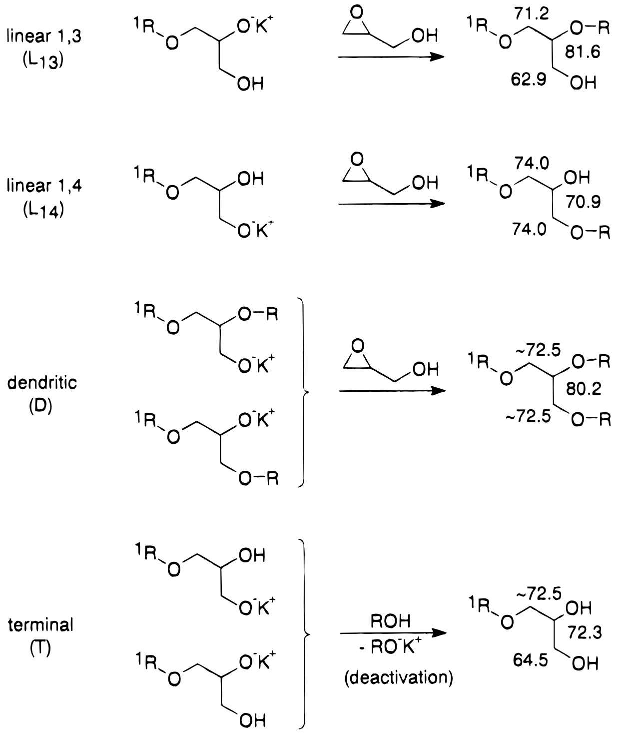

Figure 5. Formation of structural units and respective ^{13}C NMR shifts (in ppm).

NMR Experiments. NMR spectroscopy represents an important tool for the characterization of hyperbranched polymers since detailed analysis of the spectra permits to extract information on both the degree of polymerization and the extent of branching. Therefore, it is appropriate to discuss the results of this method in detail. Signal assignments for ^{13}C NMR spectra of

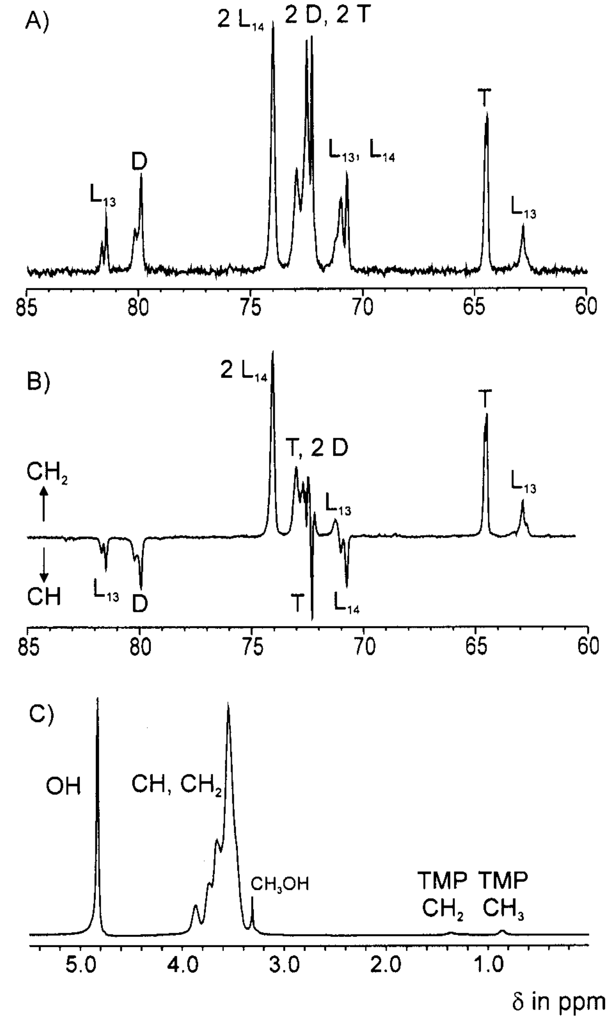

Figure 6. NMR spectra (CD_3OD, 50 °C) of polyglycerol PGly-3 ($\overline{DP}_n = 44$), obtained in the anionic polymerization initiated with 1,1,1-tris(hydroxymethyl)propane (TMP): (A) ^{13}C inverse gated spectrum, (B) ^{13}C DEPT spectrum. Carbons belonging to the terminal, dendritic, linear 1,3, and linear 1,4 units are indicated by T, D, L_{13}, and L_{14}, respectively. (C) ^1H spectrum.

Table 1. Interpretation of ^{13}C NMR Inverse Gated (IG) Spectra of Polyglycerol: Distribution of Structural Units, Degree of Branching (DB), and Degree of Polymerization (DP_n)

		relative integral			
region	shift (ppm)	PGly-1	PGly-2	PGly-3	PGly-4
L_{13}	81.0–82.0	1.00	1.00	1.00	1.00
D	79.5–80.5	2.31	2.59	2.58	2.63
2 L_{14}	73.5–74.5	6.02	5.90	5.55	5.04
2 D, 2 T	72.0–73.5	12.45	12.78	11.51	10.92
L_{13}, L_{14}	70.5–72.0	3.75	4.04	3.87	3.66
T	64.0–65.0	4.31	4.01	3.23	2.95
L_{13}	62.0–63.5	1.14	1.27	1.20	1.04

structural unit	relative abundance (%)			
terminal (T)	41	36	33	32
linear 1,3 (L_{13})	10	11	11	12
linear 1,4 (L_{14})	28	29	29	28
dendritic (D)	21	24	26	28

polyglycerol were first reported by Vandenberg[14] and extended by Penczek and Dworak.[17] To date, little attention has been paid to the branched structure of polyglycerol obtained from either anionic or cationic polymerization, and the degree of branching (i.e., the branching perfection of the structures) has not yet been characterized. The ^{13}C NMR spectrum of the branched polyglycerol possesses seven well-resolved peak regions between 60 and 85 ppm (Figure 6, spectrum A). DEPT spectra can be readily employed to distinguish methylene and methine carbons (Figure 6, spectrum B). Dworak et al. used a number of model compounds in order to assign most of the signals for the linear and terminal units quite unambiguously.

For a reliable signal assignment, two obvious prerequisites have to be proven by inverse gated (IG) NMR experiments that permit integration of the signal intensity: (i) IG ^{13}C NMR signal intensities correspond to the fact that each structural unit contains one methine and two methylene carbons; (ii) the number of terminal units equals the number of the initiating hydroxyl groups plus the dendritic units ($T = f_c + D$ for one molecule).[18]

With respect to the previously made assignments and our own results from NMR studies in various solvents (methanol, DMSO, pyridine), using information obtained from the DEPT NMR-spectrum, all signals can be assigned as given in Figure 5 as well as Figure 6A,B: (i) linear 1,3-unit (L_{13}): CH_2OH carbon at 62.9 ppm, CH_2 carbon at 71.2 ppm, and CH carbon at 81.6 ppm; (ii) linear 1,4-unit (L_{14}): both CH_2 carbons at 74.0 ppm, CHOH carbon at 70.9 ppm; (iii) terminal unit (T): CH_2OH carbon at 64.5 ppm, CHOH carbon at 72.3 ppm, and the CH_2 carbon at about 72.4 ppm; (iv) dendritic unit (D): CH carbon at 80.2 ppm, one CH_2 carbon at 73.0 ppm, and the other at about 72.4 overlapping with a CH_2 carbon of a terminal unit.

The substructure of the peaks, e.g., for the signal at 81.6 ppm for the L_{13} unit, is explained by the different possible triads. The results of the interpretation of the ^{13}C NMR spectra are summarized in Table 1, showing the signal intensities and assignments for the four different polyglycerol samples studied. Using the relative integrals from the IG ^{13}C NMR spectra, it is possible to calculate the relative abundance of each structural unit. The ratio of L_{13} and L_{14} units does not depend on molecular weight. The linear units (39%) are subdivided into 11% L_{13} units formed by the propagation of secondary hydroxyl groups and 28% L_{14} units formed by the propagation of primary hydroxyl groups. In accordance with Vandenberg's observations,[14] the higher reactivity due to lower sterical hindrance in combination with the higher stability of the primary alkoxide is responsible for the almost 3-fold larger fraction of linear 1,4-units in comparison to linear 1,3-units.

The degree of branching (DB) measures the suitability of a hyperbranching reaction to create dendritic structures, in other words, the perfection of a hyperbranched structure relative to the respective perfect dendrimer.[23] Thus, for linear structures the DB is 0, for homopolymerization of AB_2 monomers the DB assumes the value 0.5 in a random polycondensation reaction with equal reactivity of the B groups, and for a perfect dendrimer the DB is 1. The degree of branching can be calculated on the basis of the intensity of NMR signals from the fraction of structural units using a previously derived equation:[18a]

$$\mathrm{DB} = \frac{2D}{2D + L_{13} + L_{14}} \qquad (1)$$

in eq 1, DB represents the degree of branching, D, L_{13}, and L_{14} represent the fractions of dendritic, linear 1,3-units, and linear 1,4-units, respectively. The DB values

Table 2. Results from ^{13}C NMR, MALDI-TOF Mass Spectrometry, Vapor Pressure Osmometry (VPO), GPC, and DSC for Polyglycerols Obtained in the Anionic Polymerization of Glycidol, Initiated with 1,1,1-Tris(hydroxymethyl)propane:Potassium Methylate 10:3

	^{13}C NMR[a]			MALDI-TOF		VPO	GPC	DSC
sample	DB	$\overline{\mathrm{DP}}_n$	$\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g (°C)
PGly-1	0.53	15.0	1245	1298	1.15	1078	1.18	−19
PGly-2	0.55	22.2	1779	1571	1.19	1532	1.23	−26
PGly-3	0.57	44.4	3423	3583	1.15	3491	1.13	−25
PGly-4	0.59	83.4	6314	b		6494	1.47	−21

[a] Calculated from Table 1. [b] Not detectable.

(Table 2, first column) for the polyglycerol samples range between 0.53 and 0.59, slightly above the value expected for a random AB$_2$ polycondensation and below, however, the theoretical value for an AB$_2$ polymerization carried out in ideal slow addition mode, which would result in a DB of 0.66.[7] The increase of the DB with molecular weight is in agreement with theoretical expectations.[8,18b] This clearly illustrates that the polymerization of glycidol is comparable to common AB$_2$ polycondensation reactions with respect to the extent of branching of the polymers formed.

The number-average degree of polymerization $\overline{DP}_n$ can also be calculated from the distribution of structural units, on the basis of the prerequisite that only propagation onto the core unit has occurred (eq 2), i.e., that each macromolecule formed contains one TMP core molecule. Unfortunately, ^{13}C NMR cannot provide information on whether cyclization has occurred, since the cycles consist of linear and dendritic units and are thus indistinguishable from noncyclized species.

$$\overline{\mathrm{DP}}_n = \frac{T + L_{13} + L_{14} + D}{T - D} f_c \qquad (2)$$

$\overline{\mathrm{DP}}_n$ represents the number-average degree of polymerization, T designates the terminal monomer units, and f_c is the functionality of the core molecule. The $\overline{\mathrm{DP}}_n$ values calculated from the IG ^{13}C NMR spectra are also listed in Table 2 and range between 15 (PGly-1) and 83.4 (PGly-4). The $\overline{\mathrm{DP}}_n$ values correspond to monomer/initiator ratios of 15:1 (PGly-1), 30:1 (PGly-2), 60:1 (PGly-3), and 85:1 (PGly-4). Thus, the observed degrees of polymerization are commonly somewhat lower than the monomer/initiator ratios employed. We explain this by formation of a certain amount of low molecular weight cyclics due to initiation by deprotonated glycidol, as described above. These cyclic byproducts are lost upon precipitation of the polymer, which is manifested by the isolated polymer yields between 80% and 95% after precipitation. Nevertheless, the data demonstrate control of molecular weights by the monomer/initiator ratio employed.

^{1}H NMR spectra of polyglycerol (Figure 6 C) are less informative than the ^{13}C NMR spectra but clearly confirm incorporation of the TMP initiator. The signals of the methyl and the methylene group at 0.9 and 1.4 ppm, respectively, are due to TMP. The four methylene and one methine proton of polyglycerol appear as one broad resonance between 3.3 and 3.9 ppm. Hydroxyl protons give a signal at 4.8 ppm only in methanol.

MALDI-TOF MS. So far the only method that permits to investigate whether the TMP alkoxide employed as initiator has been incorporated into the hyperbranched macromolecules and allows to assess the extent of cyclization is MALDI-TOF mass spectrometry. In Figure 7A the MALDI-TOF spectrum of the polyglycerol sample PGly-1 is shown. The mass differences between the peaks represent precisely the molar mass of glycidol (M = 74.1). The exact peak mass of the peaks of the molecular weight distribution is the sum of the mass of the core unit 1,1,1-tris(hydroxymethyl)propane (M = 134.2), the respective number of glycidol repeating units, and the lithium counterion (M = 6.0). The number-average molecular weight $\bar{M}_n$ calculated from the MALDI-TOF spectrum is 1298, which is in good agreement with the value of 1245 obtained from the IG ^{13}C NMR spectra. Figure 7B depicts the MALDI-TOF spectrum of the higher molecular weight sample PGly-3. Also in this case, a monomodal molecular weight distribution is obtained. Again, $\bar{M}_n$ calculated from the MALDI-TOF spectra (3583 g/mol) is in good agreement

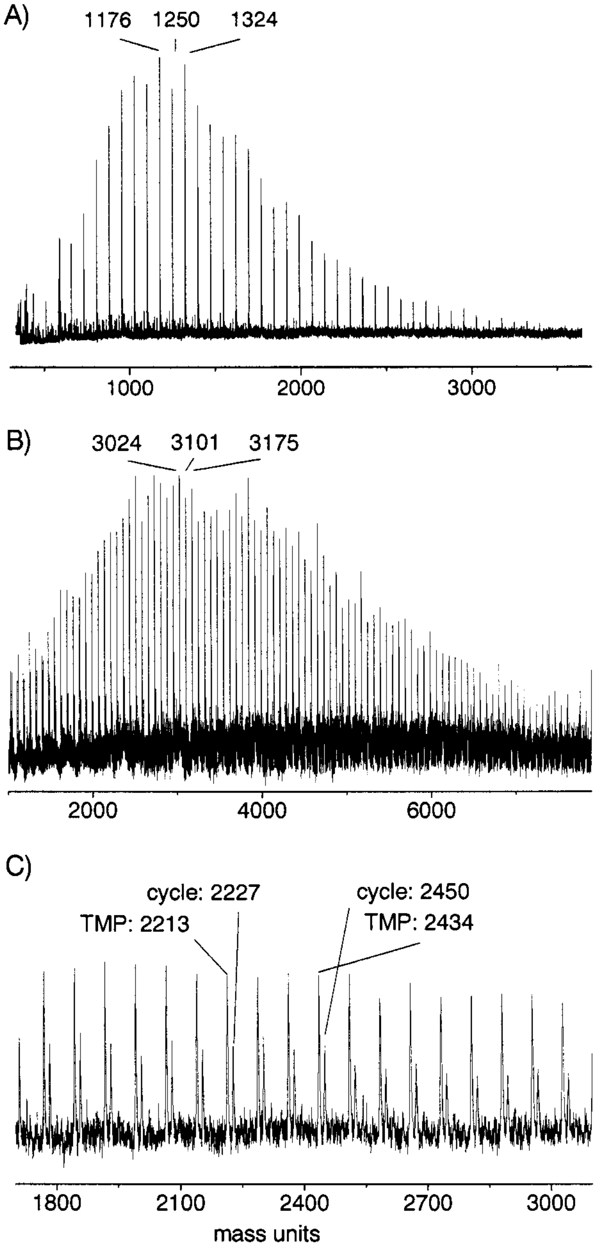

Figure 7. MALDI-TOF mass spectra of polyglycerols obtained in the anionic polymerization initiated with 1,1,1-tris(hydroxymethyl)propane: KOCH$_3$ 10:3 (A) PGly-1 and (B) PGly-(3) without side reactions, (C) with formation of cyclics in the case of rapid monomer addition.

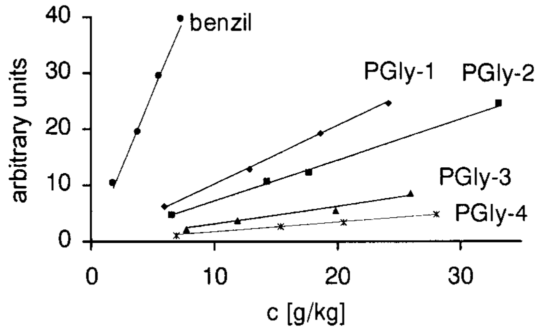

Figure 8. Results of vapor pressure osmometry of polyglycerols ($\bar{M}_n$ = 1100 [PGly-1], 1500 [PGly-2], 3500 [PGly-3], and 6500 [PGly-4]) in methanol at 45 °C, calibrated with benzil (M = 210.23 g/mol).

with the value determined from IG ^{13}C NMR spectra (3423 g/mol).

In Figure 7C the MALDI-TOF spectrum of a polyglycerol sample with a clearly discernible subdistribution shifted by 14−16 mass units is shown. The peak masses of the subdistribution peaks are the sum of the glycidol repeating units and the lithium counterion. MALDI-TOF spectra with additional distribution modes of this type were obtained in the case of rapid monomer addition and are due to hyperbranched macromolecules without TMP core formed concurrently with macromolecules initiated by deprotonated TMP. Thus, this subdistribution observed is most probably due to (macro)cyclic polyglycerol macromolecules, which lack the TMP core.

In summary, the values for number-average molar masses from the peak heights agree with the NMR results as shown in Table 1. To date, we have not been able to obtain reliable MALDI -TOF data for polyglycerols with masses exceeding 4000. For higher molecular weight samples such as PGly-4, the occurrence of cyclization can unequivocally be shown by MALDI-TOF; however, the molecular weight distributions observed do not represent the distribution actually present, as is often the case for MALDI-TOF spectra of higher molecular weights with a certain polydispersity.

Vapor Pressure Osmometry. In addition to ^{13}C NMR and MALDI-TOF, molecular weights of the polyglycerols have also been determined by vapor pressure osmometry (VPO) in methanol solution. Figure 8 shows the data obtained by vapor pressure osmometry. In case of aggregation due to hydrogen bonding, the slope of the concentration-dependent plots would be expected to decrease with increasing concentration. This behavior was not observed in methanol solution containing up to 3 wt % of polyglycerol, evidencing the absence of aggregation in this concentration range. Molecular weights were calculated by dividing the product of the slope of the benzil curve and the molar mass of benzil by the slope of the respective polyglycerol curve. The results of the VPO measurements are in excellent agreement with NMR and MALDI-TOF results for all four polyglycerol samples (Table 2).

GPC. Since the hydrodynamic volume of hyperbranched polymers is a function of the degree of polymerization, the degree of branching, and possible solvent/polymer interactions, GPC calibration in order to achieve quantitative molecular weight measurements is difficult. Furthermore, hyperbranched polymers (particularly polyols) often exhibit aggregation or interaction with the GPC columns due to their large number of end groups, leading to erroneous molecular weight characterization.[24] Provided no aggregation occurs, information on polydispersity can be obtained, when a suitable polymer standard is used for calibration. In contrast to the commonly used poly(styrene) standards, linear poly(propylene oxide) was employed for calibration of the GPC, since it possesses a structural backbone comparable to polyglycerol and is commercially available with low polydispersity (<1.1) in the molar mass range between 1000 and 12 000. Unexpectedly, the molecular weights of the polyglycerols measured for the four samples PGly-1 to PGly-4 by this method were 5 times higher compared to those obtained by the previous methods shown in Table 2, illustrating once more the problematic aspects of GPC for the analysis of hyperbranched polymers. This might be attributed to the difference of the repeating units as well as the difference in molecular architecture. Interestingly, the number-average molecular weights from VPO and GPC show a linear correlation, as seen from Figure 9. Due to the relatively low polydispersities as well as the monomodal molecular weight distributions found, formation of aggregates does not seem very likely. Furthermore, polydispersities measured by GPC show good agreement with the polydispersities calculated from the MALDI-TOF spectra (Table 2).

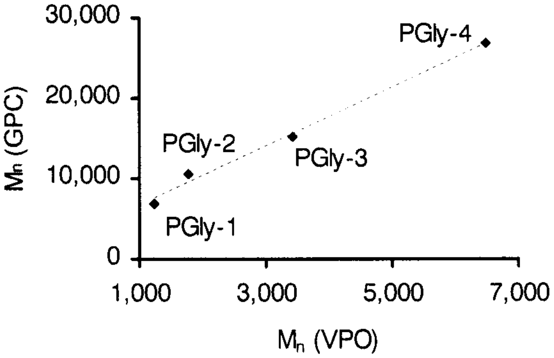

Figure 9. Correlation of number-average molecular weight (M_n) obtained from VPO (methanol, 45 °C) and GPC (DMF, 45 °C, poly(propylene oxide) calibration), showing a linear relationship.

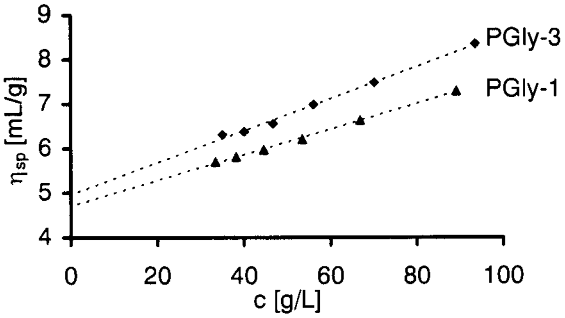

Figure 10. Specific viscosity (η_{sp}) of polyglycerols as a function of concentration in methanol at 20 °C. Intrinsic viscosities [η] are 4.71 mL/g for PGly-1 and 4.95 mL/g for PGly-3.

Viscosimetry. Figure 10 depicts the results of viscosity measurements of the polyglycerols PGly-1 and PGly-3 in methanol solution. The linear relationship between η_{sp} and concentration demonstrates that no aggregation occurs in the investigated concentration range, as already observed in the VPO measurements. However, concentrations used for viscosimetry were up to 3 times higher than for the VPO measurements.

DSC measurements show that all polyglycerols are flexible polymers, manifested by T_g's in the range −19 to −26 °C, which renders these polymers interesting multifunctional platforms for further functionalization.

Conclusions

Hyperbranched aliphatic polyethers with hydroxyl end groups, possessing a $\overline{DP}_n$ in the range 15−83, can be prepared in a controlled manner by anionic ROMBP-type polymerization of glycidol, making use of a fast proton-exchange equilibrium. Polydispersities below 1.5 (mostly below 1.25) were achieved by slow monomer addition conditions, which led to complete incorporation of the alkoxide initiator into the hyperbranched macromolecules. $\overline{DP}_n$ could be controlled reasonably well by the ratio of initiator and monomer, being somewhat lower for the polyglycerols than the monomer/initiator ratio, which is explained by the formation of a fraction of low molecular weight cyclic species. A detailed ^{13}C NMR spectroscopic study permitted to determine the degree of branching (DB), which was found to be enhanced (0.53−0.59) in comparison to the value of 0.5 expected for a random polymerization reaction, but still lower than the value expected under ideal core dilution/slow addition conditions (0.66).[7,8] As evidenced by MALDI-TOF mass spectrometry, careful control of polymerization conditions allows to suppress cyclization reactions.

We have developed various derivatization reactions for modification of the end groups of the novel hyperbranched polyols which will be discussed in forthcoming publications. The derivatives prepared, e.g., by esterification, show low polydispersities below 1.3, similar to the polyglycerols used, confirming once more the low polydispersities found for these polymers. We are confident that hyperbranched polyglycerols, prepared in a controlled manner in one step, may well become competitors for perfect dendrimers prepared in multistep syntheses.

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