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Articles

Copolymers of Glycidol and Glycidyl Ethers: Design of Branched Polyether Polyols by Combination of Latent Cyclic AB_2 and ABR Monomers

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ABSTRACT: Glycidol as latent branching AB_2 monomer was used in combination with glycidyl ethers as linear AB comonomers for the preparation of hyperbranched random copolymers with controlled degree of polymerization ($DP_n = 42-72$) and relatively low polydispersity ($M_w/M_n < 1.7$). Extending previous theoretical considerations, equations that permit to calculate the *DB* for AB_2/AB copolymerizations under slow monomer addition conditions were derived. The degree of branching (*DB*) for the random copolymers of glycidol and allyl glycidyl ether (AGE) as well as phenyl glycidyl ether (PGE) was controlled by the comonomer ratio ($DB = 9\%-58\%$). Furthermore, comparable block copolymers of glycidol and AGE, i.e., multiarm star polymers, have been prepared by sequential addition of the monomers. Thermal behavior of all materials has been investigated with respect to copolymer composition. Furthermore, reactions of the random glycidol/AGE copolymers have been developed: (i) cleavage of the allyl groups, leading to linear 1,3-glycerol units bearing primary hydroxy groups; (ii) dihydroxylation of the double bond, leading to hyperbranched polyglycerols with enhanced *DB*; and (iii) hydroformylation with subsequent reductive amination, making use of the orthogonality of the OH and allyl functionalities.

Introduction

Hyperbranched polymers are macromolecules with a random branch-on-branch structure based on AB_m subunits. These polymers represent an intriguing class of materials that can be expected to play an important role for the construction of complex polymer architectures in the future.[1] Well-defined multiarm star polymers[2] and inverted unimolecular micelles[3] on the basis of hyperbranched polymers represent first examples of such complex macromolecular topologies. Therefore, the development of principles to tailor hyperbranched polymers that are well-defined with respect to molecular weights, degree of branching (*DB*), and functionality is an important field.

In this context, recently new synthetic strategies based on latent AB_m structures have been explored as alternatives to the uncontrolled random polycondensation of AB_m monomers. Such monomers include the inimer-type structures used in the self-condensing vinyl polymerization (SCVP)[4] and cyclic monomers bearing additional B groups (e.g., hydroxyoxiranes,[5] hydroxyoxetanes,[6] hydroxycaprolactones,[7] aziridine[8]) that undergo self-condensing ring-opening. These approaches, however, do not lead to improved control of the abovementioned critical parameters molecular weight and *DB*, since self-condensing steps are involved in the polymerization mechanism. Suzuki et al. reported the only approach to date that is based on peculiar monomers that are unable to autopolymerize (i.e., cyclic carbamates). In this case, bulk polymerization in the absence of self-condensing steps is possible.[9]

Recently, it has been realized that on the basis of the slow addition of highly reactive, latent AB_m monomers (slow monomer addition, SMA) “pseudo-chain-growth” conditions can be achieved that permit control of molecular weights and enable to reduce polydispersity considerably.[10−12] Chain-growth-type kinetics is crucial to avoid self-condensing steps that lead to broad molecular weight distributions and intramolecular cyclization resulting in uncontrolled polymerization.[13] We have successfully employed this concept for the ring-opening multibranching polymerization of glycidol (ROMBP), obtaining hyperbranched polyether polyols with molecular weights between $M_n = 1000$ and $10\,000$ and polydispersities $M_w/M_n < 1.5$.[14] In addition, this synthetic strategy permits to prepare dendron-analogous structures with precisely defined, variable focal functionality.[15]

In recent years, progress has been made in both understanding and quantifying the branching density of hyperbranched polymers for the polycondensation approach[16,17] as well as SCVP.[18] In theoretical work, we have been able to show that copolymerization of branching AB_m-type monomers with linear AB monomers represents a promising strategy to lower the degree of branching of hyperbranched polymers in a predictable manner.[19] In addition, linear AB comonomers may bear a substituent R that should be inert under the polymerization conditions but permits postsynthetic modification of the hyperbranched structure (ABR monomers).

Random copolymerization of common epoxide monomers with glycidol for the preparation of branched

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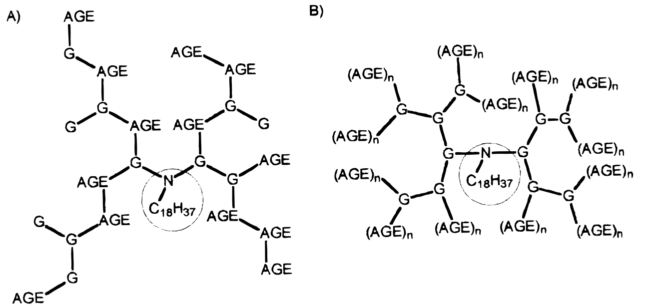
Scheme 1. Schematic Structure of (A) Random Glycidol (G)/Allyl Glycidyl Ether (AGE) Copolymer $P(G_{11}/AGE_{13})$ and (B) Glycidol/Allyl Glycidyl Ether Block Copolymer $P(G_{11}AGE_n)$[a]



[a] The initiator incorporated as core unit is circled.

polyether polyols has been mentioned, but no control of the reaction was achieved.[20] In previous work, we already reported block copolymerization of glycidol with linear epoxide comonomers leading to multiarm star polymers.[2d,21] In this paper, on the basis of theoretical considerations, we describe the copolymerization of glycidol (latent AB_2 monomer) with glycidyl ethers (ABR comonomers), i.e., allyl glycidyl ether (AGE) and phenyl glycidyl ether (PGE), as a versatile approach to tailor material properties with respect to molecular architecture, functionality, and thermal behavior. Scheme 1 illustrates the topology of the resulting random and block copolymers of glycidol and AGE investigated in this work. Furthermore, we show that AGE as a linear comonomer offers numerous possibilities for convenient further functionalization and structural design.

Experimental Section

Nomenclature. In accordance with our previous works, block copolymers are designated $P(G_xAGE_y)$, in which x indicates the degree of polymerization (DP_n) of the polyglycerol core and y the number of AGE units per hydroxyl end group, i.e., the DP_n of the arms attached to the hyperbranched core. Thus, $P(G_8AGE_1)$ describes a block copolymer with 8 glycidol units and 8 AGE units. Random copolymers are described by $P(G_x/AGE_y)$, in which x gives the DP_n of glycidol and y the DP_n of AGE. For instance, $P(G_8/AGE_8)$ describes a random copolymer that contains 8 glycidol and 8 AGE units, i.e., a linear comonomer fraction $x_{AB} = 50\%$. Thus, this abbreviation contains information concerning both the overall DP_n and the molar comonomer fractions.

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded in d_6-methanol with traces of $Cr(acac)_3$ at concentrations of 250 mg/mL on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively. SEC measurements were carried out on a Knauer microgel set C11, equipped with a Polymer Labaratories evaporative mass detector EMD 960, operating at 110 °C. We used DMF as an eluent at 45 °C. Poly(propylene oxide) samples with M_n in the range 1000−12 000 were used for calibration. Vapor pressure osmometry was carried out using a Knauer vapor pressure osmometer K7000 in DMF at 95 °C in a concentration range of 10−40 mg/mL. Glucose pentaacetate (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. The melting point of indium (156 °C) was used for calibration. IR measurements were performed on a Bruker IFS88 FT-IR spectrometer equipped with a Graseby Specac "golden gate" attenuated total reflection (ATR) unit.

Hydroxyl numbers were determined by a common titration method:[22] The esterification mixture consists of 0.45 L of anhydrous pyridine, 64.25 g of phthalic anhydride, and 10 mL of *N*-methylimidazole. 25 mL of this mixture was stirred with 25 mL of pyridine and 50 mL of water and after 15 min titrated with 1 N NaOH to give the blind volume V_{blind}. A polymer sample of a mass of m_{sample} g was then refluxed 15 min with 25 mL of the esterification mixture. 25 mL of pyridine and 50 mL of water were added to hydrolyze excess anhydride. The solution is titrated with 1 N NaOH to give V_{sample}. Each polymer was measured twice. The hydroxyl number HN is then given by $HN = (V_{blind} - V_{sample})(56.1/m_{sample})$.

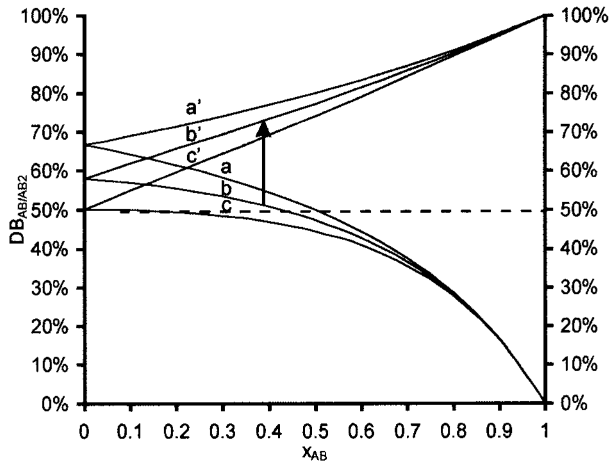


Figure 1. Degree of branching (DB_{AB/AB_2}) of random AB/AB_2 copolymers vs molar fraction of AB monomer for degrees of branching of homopolymers $DB_{AB_2} = 67\%$ (a), 58% (b), and 50% (c) (according to eq 12). The lines a′, b′, and c′ represent the same copolymers after transformation of all AB units into dendritic + terminal and linear + terminal AB_2 units (eq 16).

Materials. Glycidol (Aldrich) was distilled over a fractionating column prior to use. Allyl glycidyl ether (Fluka) and phenyl glycidyl ether (Merck) were distilled and dried with molecular sieves (4 Å), respectively, prior to use. Bis(2,3-dihydroxypropyl)octadecylamine was prepared by addition of 2 equiv of glycidol to octadecylamine (Fluka) according to literature procedure.[25] The product was purified by recrystallization from ethyl acetate.

Synthetic Procedures. a. Synthesis of Random Copolymers with AGE (exemplified for $P(G_{42}/AGE_{26})$). Polymerization was carried out in a reactor equipped with a mechanical stirrer and a dosing pump under argon atmosphere. 4.71 g (11.3 mmol) of bis(2,3-dihydroxypropyl)octadecylamine was partially deprotonated (10%) with 1.2 mL of a potassium methoxide solution (3.7 M in methanol, Fluka) by distilling off excess methanol from the melt. A mixture of 31.5 mL (0.47 mol) of glycidol and 34.8 mL (0.29 mol) of allyl glycidyl ether was slowly added at 120 °C over 12 h. After completed addition, the product was dissolved in 100 mL of methanol and neutralized by filtration over a cation-exchange resin (Fluka, Amberlite IR-120). Methanol was evaporated, and the residue was dried for 18 h at 120 °C in vacuo. The polymer was obtained as yellowish, viscous liquid in quantitative yield.

^1H NMR (300 MHz, CD_3OD): δ (ppm) = 5.95 (m, $C\mathit{H}{=}CH_2$), 5.24 (m, $CH{=}C\mathit{H_2}$), 4.8 ($O\mathit{H}$), 4.04 ($OC\mathit{H_2}{-}CH{=}CH_2$), 3.95−3.40 (polyether backbone), 3.32 ($RN(CH_2{-}C\mathit{H}(OR)CH_2OR)$, 2.58 ($N(C\mathit{H_2})_3$), 1.50 ($R{-}C\mathit{H_2}CH_2NR_2$), 1.31 ($R{-}(C\mathit{H_2})_{15}CH_3$), 0.92 ($C\mathit{H_3}$); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 136.5 ($\mathit{C}H{=}CH_2$), 117.6 ($CH{=}\mathit{C}H_2$), 82.0−81.5, 80.6−79.8, 74.7−73.9, 73.8−72.2, 71.8−70.7, 64.7, 63.1 (7 signals, polyether backbone, assignment cf. Figure 3B), 74.3 ($O\mathit{C}H_2CH{=}CH_2$), 33.3, 31.0, 30.7, 24.0 (4 signals, initiator), 14.8 ($\mathit{C}H_3$). IR (ATR): $\nu(cm^{-1})$ = 3450 (OH), 3080 (C=CH), 2890 (CH), 1645 (C=C), 1100 (C−O−C).

b. Synthesis of Random Copolymer $P(G_{25}/PGE_{23})$. Polymerization was carried out in a reactor equipped with a mechanical stirrer and a dosing pump under argon atmosphere. 4.71 g (11.3 mmol) of bis(2,3-dihydroxypropyl)octadecylamine was partially deprotonated (10%) with 1.2 mL of a

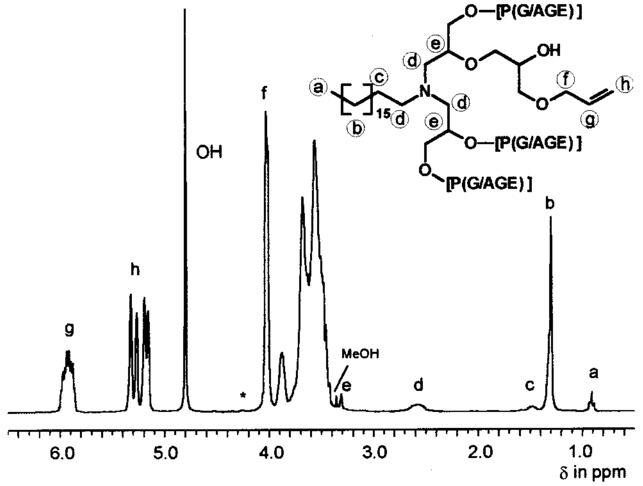


Figure 2. Assigned ^{1}H NMR spectrum of P(G_{24}/AGE_{31}) in CD_3-OD (proton of isomerized allyl ether is marked with an asterisk).

potassium methoxide solution (3.7 M in methanol, Fluka) by distilling off excess methanol from the melt. A mixture of 18.7 mL (0.28 mol) of glycidol and 35.3 mL (0.26 mol) of phenyl glycidyl ether was slowly added at 120 °C over 12 h. After completed addition, the product was dissolved in about 100 mL of methanol and neutralized by filtration over a cation-exchange resin (Fluka, Amberlite IR-120). Methanol was evaporated, and the residue was dried for 18 h at 120 °C in vacuo. The polymer was obtained as yellowish, viscous liquid in quantitative yield.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 7.24 (m-arH), 6.92 (o-arH, p-arH), 4.80 (O*H*), 4.10−3.30 (polyether backbone), 3.35 ($RN(CH_2{-}C\mathit{H}(OR)CH_2OR)$, 2.52 (($N(C\mathit{H_2})_3$), 1.41 ($R{-}C\mathit{H_2}CH_2$-$NR_2$), 1.28 ($R{-}(C\mathit{H_2})_{15}CH_3$), 0.92 ($C\mathit{H_3}$); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 160.4 (i-ar), 130.8 (m-ar), 122.2 (p-ar), 116.0 (o-ar), 82.2−81.3, 80.7−79.1, 74.7−73.7, 73.6−71.9, 71.8−70.1, 69.8−68.8, 64.7, 63.1 (8 signals, polyether backbone), 33.3, 31.1, 30.7, 24.0 (4 signals, initiator), 14.9 (*C*H_3).

c. Synthesis of Block Copolymers (exemplified for P(G_{48}-$AGE_{1.4}$). Glycidol was polymerized in the presence of bis(2,3-dihydroxypropyl)octadecylamine by the slow addition method described previously.[14] Without isolation, 12 g (3.1 mmol, 0.15 mol OH groups) of the obtained polyglycerol was again deprotonated to an extent of about 5% per OH group, using potassium hydride (Aldrich, dispersion in oil, 35 wt %). 24 mL (0.20 mol) of allyl glycidyl ether was slowly added to the reaction mixture at 120 °C over 12 h. The workup procedure was carried out as described for the random copolymers. The block copolymer was obtained as transparent, viscous liquid in quantitative yield.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 5.94 (m, C*H* =CH_2), 5.25 (m, CH=C$\mathit{H_2}$), 4.80 (O*H*), 4.04 ($OC\mathit{H_2}{-}CH{=}CH_2$), 3.95−3.40 (polyether backbone), 3.32 ($RN(CH_2{-}C\mathit{H}(OR)CH_2OR)$, 2.60 ($N(C\mathit{H_2})_3$), 1.58 ($R{-}C\mathit{H_2}CH_2NR_2$), 1.31 ($R{-}(C\mathit{H_2})_{15}CH_3$), 0.92 ($C\mathit{H_3}$); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 136.5 (*C*H=CH_2), 117.6 (CH=*C*H_2), 80.7−79.8, 74.8−74.2, 73.9−72.3, 72.0−70.7 (4 signals, polyether backbone, assignment cf. Figure 3D), 74.3 (O*C*H_2CH=CH_2), 33.3, 31.0, 30.7, 24.0 (4 signals, initiator), 14.8 (*C*H_3).

Cleavage of Allyl Ethers (exemplifed for P(G_{42}/AGE_{26}). *(A) Isomerization of the Allyl Ethers*: A suspension of 1.5 g (0.23 mmol, 6 mmol allyl groups) of P(G_{42}/AGE_{26}) and 1.0 g of Pd/C (Aldrich, 3 wt %) in 60 mL of methanol was refluxed under argon atmosphere for 2 days. The mixture was filtrated through a Celite pad. After evaporation of the solvent the product was obtained as pale yellow, viscous liquid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 6.23 (trans R(O)-C*H* =C(*H*)CH_3), 5.98 (cis R(O)C*H*=C(*H*)CH_3), 5.87 (residual $OCH_2C\mathit{H}{=}CH_2$), 5.19 (m, residual $OCH_2CH{=}C\mathit{H_2}$), 4.80 (OH), 4.73 (trans R(O)CH=C(*H*)CH_3), 4,32 (cis R(O)CH=C(*H*)CH_3), 3.98 (residual $OC\mathit{H_2}CH{=}CH_2$), 3.90−3.35 (polyether backbone), 3.25 ($RN(CH_2{-}C\mathit{H}(OR)CH_2OR)$, 2.56 ($N(C\mathit{H_2})_3$), 1.50 ($R{-}C\mathit{H_2}CH_2NR_2$), 1.24 ($R{-}(C\mathit{H_2})_{15}CH_3$), 0.86 ($C\mathit{H_3}$).

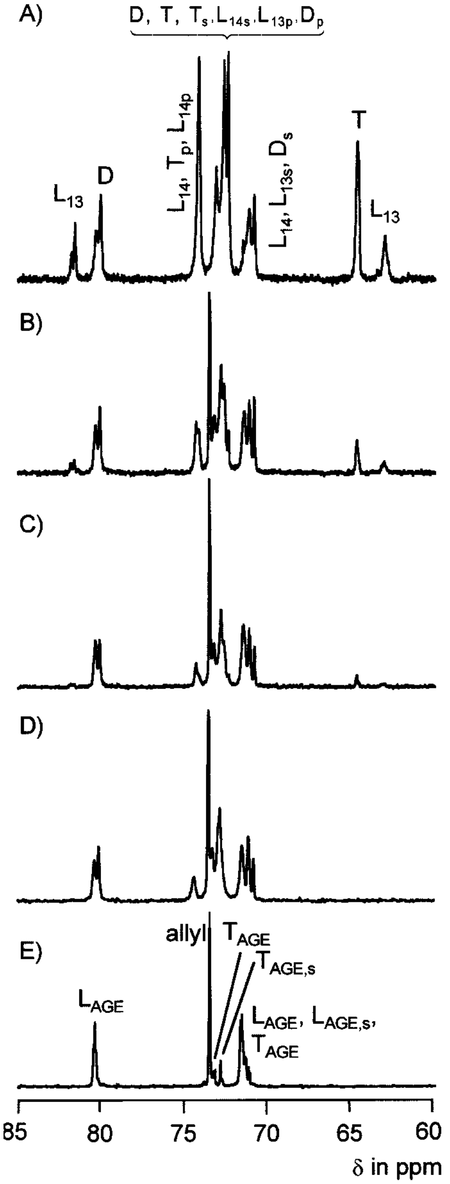


Figure 3. ^{13}C NMR IG spectra (CD_3OD) of copolymers (A) P(G_{72}) (x_{AGE} = 0%), (B) P(G_{42}/AGE_{26}) (x_{AGE} = 38%), (C) P(G_{24}/AGE_{31}) (x_{AGE} = 57%) (B, C: random copolymers), (D) block copolymer P($G_{48}AGE_{1.4}$) (x_{AGE} = 57%), and (E) P(G_2/AGE_{41}) (x_{AGE} = 95%). For assignment see Scheme 3 (allyl indicates the carbon at allyl position); assignment of the signals of the double bond and the initiator is given in the Experimental Section.

(B) Hydrolysis of Prop-1-enyl Ethers: To a solution of 1.5 g (0.23 mmol, 6 mmol prop-1-enyl groups) of the product of A in 50 mL of methanol was added 15 mL of 0.1 N hydrochloric acid. The mixture was stirred at room temperature for 1 day and subsequently neutralized by filtration over anion-exchange resin (Merck, strongly basic no. 3). The crude product was purified by dialysis in methanol (Sigma, MWCO 1000). After evaporation of the solvent the product was obtained as pale yellow viscous liquid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 5.94 (residual $OCH_2C\mathit{H}{=}CH_2$), 5.28 (m, residual $OCH_2CH{=}C\mathit{H_2}$), 4.80 (OH), 4.06 (residual $OC\mathit{H_2}CH{=}CH_2$), 3.95−3.40 (polyether backbone), 3.33 ($RN(CH_2{-}C\mathit{H}(OR)CH_2OR)$, 2.62 ($N(C\mathit{H_2})_3$), 1.50 ($R{-}C\mathit{H_2}CH_2NR_2$), 1.31 ($R{-}(C\mathit{H_2})_{15}CH_3$), 0.92 ($C\mathit{H_3}$); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 136.3 (residual $OCH_2\mathit{C}H{=}CH_2$), 117.8 (residual $CH_2CH{=}\mathit{C}H_2$), 82.0−81.3, 80.5−79.8, 74.6−

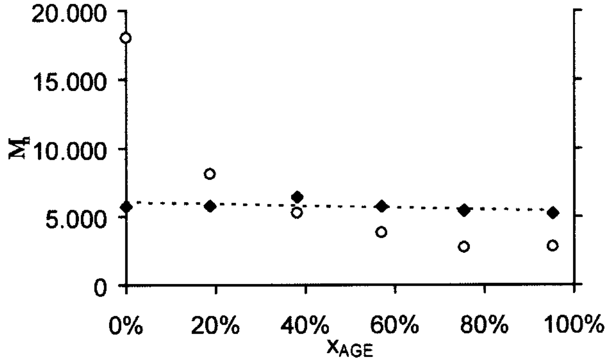


Figure 4. Molecular weights M_n of P(G_x/AGE_y) determined by NMR (◆) and SEC (○) vs copolymer composition x_{AGE}.

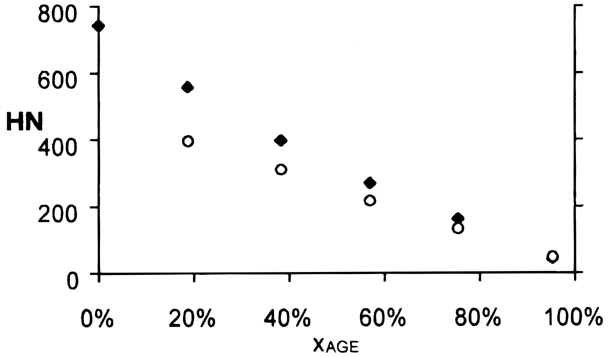


Figure 5. Hydroxyl number *HN* of P(G_x/AGE_y) calculated from NMR results (◆) and titrated (○) vs copolymer composition x_{AGE}.

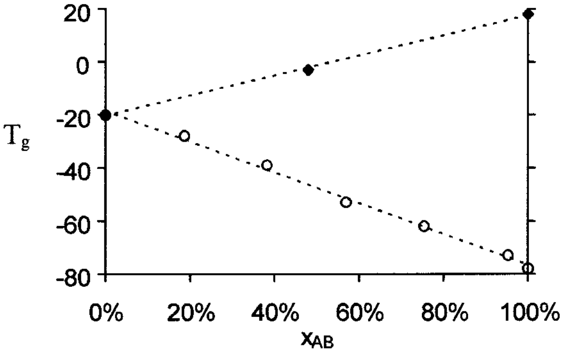


Figure 6. Glass transition temperature T_g of P(G_x/AGE_y) (○) and P(G_x/PGE_y) (◆) vs copolymer composition x_{AB}.

73.9, 73.8–72.0, 71.9–70.6, 64.6, 63.0 (7 signals, polyether backbone, assignment cf. Figure 7B), 74.5 (residual O*C*H$_2$CH=CH$_2$), 33.2, 31.0, 30.6, 23.9 (4 signals, initiator), 14.7 (*C*H$_3$).

Dihydroxylation of the Random Copolymers (exemplified for P(G_{42}/AGE_{26}). 1.0 g (0.16 mmol, 4 mmol allyl groups) of P(G_{42}/AGE_{26}) was dissolved in 25 mL of a 3:1 mixture of water:acetone. 0.65 g (4.8 mmol) of *N*-methylmorpholine-*N*-oxide·H_2O (Fluka) and 0.1 mL of an aqueous solution of osmium tetroxide (Aldrich, 4 wt %) were added and stirred in a water bath at room temperature for 2 days. The volatile compounds were removed in vacuo, and the brown residue was filtered and purified by dialysis in methanol (Sigma, MWCO 1000). After evaporation of the solvent, the product was obtained as a brownish viscous liquid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 5.91 (residual OCH$_2$C*H*=CH$_2$), 5.22 (m, residual OCH$_2$CH=C*H*$_2$), 4.8 (O*H*), 4.01 (residual OC*H*$_2$–CH=CH$_2$), 3.95–3.40 (polyether backbone), 3.30 (RN(CH$_2$–C*H*(OR)CH$_2$OR), 2.60 (N(C*H*$_2$)$_3$), 1.49 (R–C*H*$_2$CH$_2$NR$_2$), 1.27 (R–(C*H*$_2$)$_{15}$CH$_3$), 0.88 (C*H*$_3$). ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 136.5 (residual OCH$_2$*C*H=CH$_2$), 117.6 (residual OCH$_2$CH=*C*H$_2$), 82.0–81.5, 80.6–79.8, 74.6–74.0, 73.7–72.2, 71.9–70.7, 64.7, 63.1 (7 signals, polyether backbone, assignment cf. Figure 7C), 74.5 (residual O*C*H$_2$CH=CH$_2$), 33.3, 31.0, 30.7, 24.0 (4 signals, initiator), 14.7 (*C*H$_3$).

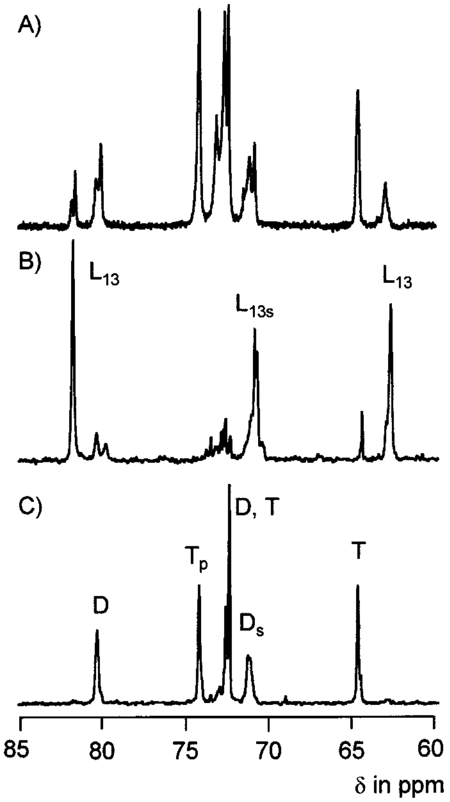


Figure 7. ^{13}C NMR IG spectra (recorded in CD_3OD) of (A) P(G_{72}), (B) cleaved P(G_2/AGE_{41}) = poly(L_{13}-glycerol), and (C) dihydroxylated P(G_2/AGE_{41}) = hyperbranched polyglycerol with *DB* = 100%.

Hydroformylation and Reductive Amination of P(G_{24}/AGE_{31}). *(A) Hydroformylation*: The reaction was carried out in an autoclave equipped with a mechanical stirrer. 5.0 g of P(G_{24}/AGE_{31}) (0.87 mmol, 27 mmol allyl groups), 80 mg (0.09 mmol) of Rh(PPh$_3$)$_3$(CO)H, and 600 mg (0.9 mmol) of triphenylphosphine (Fluka) were dissolved in 150 mL of anhydrous toluene and heated in the autoclave to 80 °C. The reaction was carried out for 16 h at 80 °C under hydrogen and carbon monoxide atmosphere (3:1) at 40 bar. After washing with toluene the cross-linked product (due to intermolecular semiacetal formation) was obtained as colorless crystals, which were dried at 120 °C in vacuo.

IR (ATR): ν(cm^{-1}) = 3450 (OH), 2890 (CH), 2730 (CHO), 1720 (C=O), 1100 (C–O–C).

(B) Reductive Amination: To a suspension of 20 mg of the hydroformylated product of A in 3 mL of methanol was added 2 mL (18 mmol) of benzylamine (Fluka). After stirring the mixture for 1 day at 50 °C under exclusion of water, the hydroformylated polymer dissolved. Without isolation of the product, 100 mg (1.6 mmol) of sodium cyanohydridoborate (Sigma) was added to this solution and stirred for 1 day at room temperature. Subsequently, methanol was evaporated, and the residue dissolved in 3 mL of water and three times extracted with 3 mL of chloroform. The organic phase was dried over $MgSO_4$, filtered, and purified by dialysis in chloroform (Sigma, MWCO 1000). After removal of the solvent, the product was obtained as a colorless viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.50–7.10 (arH), 4.50–3.00 (polyether backbone + Ph–C*H*$_2$–NR$_2$), 2.80–2.30 (BzN(H)C*H*$_2$R, BzN(H)C*H*(CH$_3$)–R, N(C*H*$_2$)$_3$), 1.70–1.40 (BzN(H)CH$_2$C*H*$_2$C*H*$_2$CH$_2$(OR)), BzNHCH(CH$_3$)C*H*$_2$CH$_2$(OR), RC*H*$_2$-CH$_2$NR$_2$), 1.23 (R–(C*H*$_2$)$_{15}$–CH$_3$), 1.10–0.90 (BzNHCH(C*H*$_3$)R), 0.86 ((CH$_2$)$_{15}$C*H*$_3$).

Results and Discussion

A. Theoretical Considerations. Although discussed already by Flory,[13] copolymerization of branching AB_m monomers with linear AB comonomers has been mentioned in few synthetic reports only and has been employed mainly in the context of self-condensing vinyl polymerizations (SCVP) to enhance the incorporated amount of the branching comonomer.[23] However, copolymerization of branching monomers with linear AB monomers is of considerable importance, since AB_m-type monomers are usually expensive compared to widely used linear AB monomers. In recent work we reported a general theoretical treatment of this random AB_m/AB_n polymerization with respect to the degree of branching (*DB*).[19] Independently, Müller et al. have derived analogous equations for the SCVP.[18] Both publications show that despite fairly large amounts of AB comonomer, a relatively high degree of branching is obtained. However, AB/AB_m copolymerization has not yet been investigated systematically as a method to vary the degree of branching and to tailor the properties of hyperbranched polymers. This is mainly due to the fact that hyperbranched polymers that are well-defined with respect to molecular weight and polydispersity were not accessible. A major prerequisite for the control of the polymerization of AB_2 or latent AB_2 monomers (i.e., monomers that possess inimer character) is the use of slow monomer addition (SMA) conditions.

Since it has been shown in both calculation[11] and simulation work[10] that this strategy affects the kinetics of hyperbranching polymerizations strongly, an expression for the degree of branching (*DB*) for AB/AB_2 copolymerizations under SMA conditions has to be derived in order to characterize the copolymers topologically. For AB/AB_2 copolymerizations in bulk (i.e., no SMA conditions) we already derived an equation for the *DB* based on statistical considerations.[19] For clarification reasons, the basic equations are

$$p(D) = x_{AB_2} p_A {p_B}^2 \tag{1}$$

$$p(L_{AB_2}) = 2x_{AB_2} p_A p_B (1 - p_B) \tag{2}$$

$$p(L_{AB}) = x_{AB} p_A p_B \tag{3}$$

$p(D)$, $p(L_{AB_2})$, and $p(L_{AB})$ give the incorporation probability of dendritic and linear units derived from AB_2 and AB monomers, respectively. p_A and p_B represent the conversion of A and B groups of the monomers, respectively. The complementary variables x_{AB_2} and x_{AB} assign the molar fraction of the AB_2 and AB monomers (eq 4), respectively. Using the previously derived definition of the *DB* (eq 5) and the relationship between p_A and p_B (eq 6),[19] a general equation for the *DB* in AB/ AB_2 bulk polymerizations (DB^{bulk}_{AB/AB_2}) can be derived (eq 7).

$$x_{AB_2} = 1 - x_{AB} \qquad x_{AB} = \frac{AB}{AB + AB_2} \tag{4}$$

$$DB_{AB/AB_2} = \frac{2p(D)}{2p(D) + p(L_{AB_2}) + p(L_{AB})} \tag{5}$$

$$p_B = \frac{p_A}{x_{AB} + 2x_{AB_2}} \tag{6}$$

$$DB^{bulk}_{AB/AB_2} = \frac{2x_{AB_2} p_A}{(x_{AB} + 2x_{AB_2})^2} = 2p_A \frac{1 - x_{AB}}{(2 - x_{AB})^2} \tag{7}$$

Equation 7 represents the degree of branching expected in bulk copolymerizations. For this case, the AB_2 homopolymerization leads to a maximum *DB* of 50%, i.e., a ratio of dendritic, linear, and terminal units of 1:2:1. Under ideal SMA conditions the *DB* equals 67%;[10,11] thus, this ratio in the AB_2 homopolymer changes to 1:1: 1. In other words, the probability of formation of a linear unit under SMA conditions is only half of the probability in bulk. Thus, for ideal SMA conditions the factor 2 in eq 2 is reduced to 1. For a more general treatment, this fit parameter will be assigned *f*, with $f = 2$ for bulk and $f = 1$ for SMA conditions (eq 8).

$$p(L_{AB_2}) = f x_{AB_2} p_A p_B (1 - p_B) \tag{8}$$

Using eq 8 for the same derivation as before based on eq 5, an expression for the degree of branching with *f* as adjustable parameter (DB^f_{AB/AB_2}, eq 9) is obtained.

$$DB^f_{AB/AB_2} = \frac{2(1 - x_{AB})p_A}{(f - 1){x_{AB}}^2 + ((f - 2)p_A - 3f + 2)x_{AB} + 2f + (2 - f)p_A} \tag{9}$$

In the case of ideal SMA conditions, i.e., $f = 1$ and full conversion $p_A = 1$ at all times, eq 9 simplifies to eq 10 to result in an expression for the degree of branching under SMA conditions (DB^{SMA}_{AB/AB_2}). Thus, the boundary conditions for both bulk and SMA conditions are treated correctly.

$$DB^{SMA}_{AB/AB_2} = \frac{2(1 - x_{AB})}{3 - 2x_{AB}} \tag{10}$$

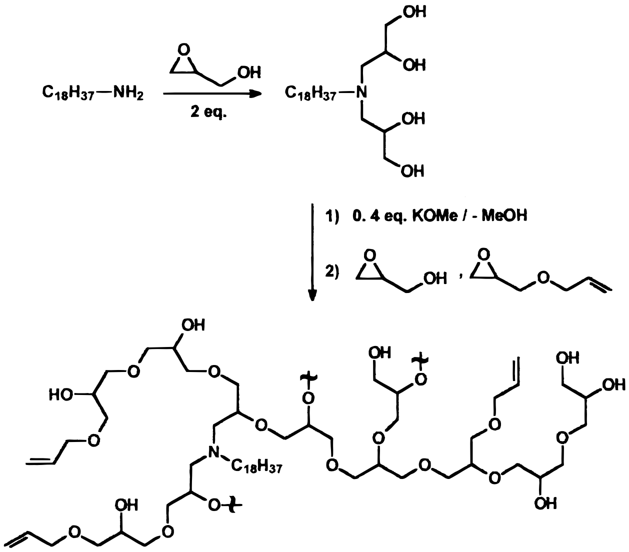
In many cases, these ideal conditions are not fulfilled. Even in the case of full conversion at all times ($p_A = 1$), the branching reaction might not be ideally random, which leads to a degree of branching between 50% and 67% for the AB_2 homopolymer, assigned DB_{AB_2}. Clearly, there is a relationship between DB_{AB_2} and the parameter *f*, which is derived from eq 5 (with $p(L_{AB}) = 0$) using the kinetic expressions eq 1 and eq 8 leading to eq 11.

$$f = \frac{2}{DB_{AB_2}} - 2 \tag{11}$$

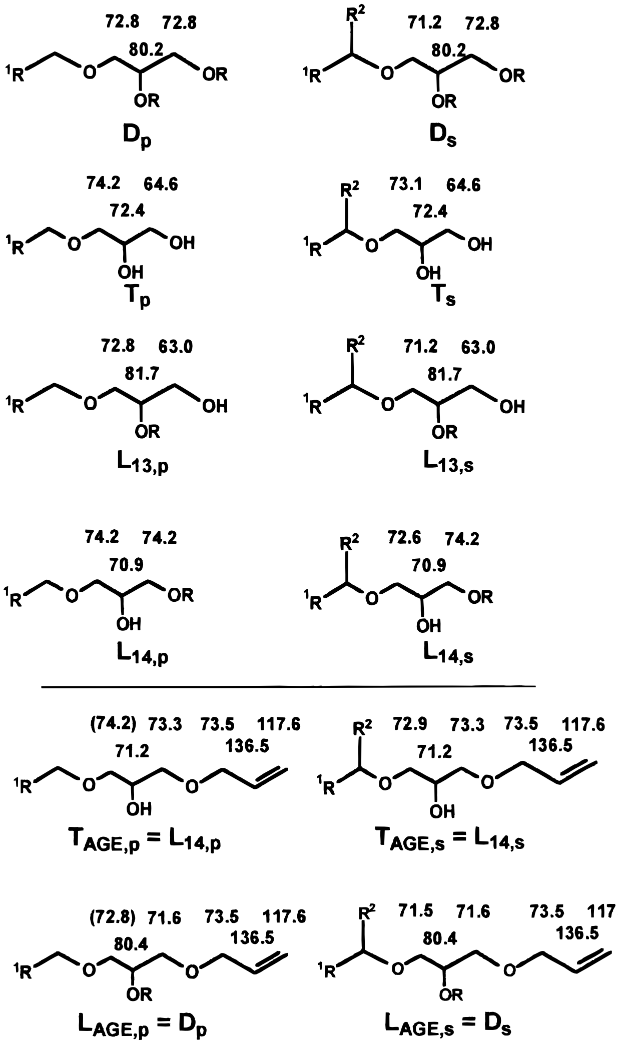
Assuming the efficiency of the branching reaction does not depend on the comonomer fraction, it is now possible to estimate the degree of branching in AB/AB_2 copolymerizations under experimental conditions. For a polymerization under nonideal SMA conditions maintaining full monomer conversion at all times, i.e., $p_A = 1$, eq 9 can be transformed into eq 12.

$$DB^f_{AB/AB_2} = \frac{2 - 2x_{AB}}{f(x_{AB} - 1)^2 + 2 - {x_{AB}}^2} \tag{12}$$

Scheme 2. Synthesis of the Initiator Bis(2,3-dihydroxypropyl)octadecylamine and Base-Catalyzed Random Copolymerization of Glycidol and AGE



Scheme 3. Assignment of ^{13}C NMR Signals (in ppm, Recorded in CD$_3$OD) for Each Structural Unit in Copolymers of Glycidol and AGE: Dendritic, Terminal, *L*inear 1,3 and Linear 1,4 Units Based on Glycidol and Linear and Terminal Units of *AGE*[a]



[a] Indices *p* and *s* indicate whether the respective unit is attached to a primary or secondary alkoxide.

The bottom half of Figure 1 shows a plot of $DB_{\mathrm{AB/AB_2}}$ versus the molar fraction of the linear comonomer x_{AB} for bulk (curve c, $DB_{\mathrm{AB_2}} = 50\%$, $f = 2$) and SMA conditions (curve a, $DB_{\mathrm{AB_2}} = 67\%$, $f = 1$). The degree of branching for the homopolymerization of glycidol is typically around $DB_{\mathrm{AB_2}} = 58\%$ ($f = 1.45$),[14] as shown in Figure 1, curve b.

In the following considerations an expression for copolymerizations with an ABR comonomer, such as AGE, will be derived that permits to calculate the enhancement of the *DB* as a result of postsynthetic modification. The respective syntheses are described in section D. If the allyl group is removed from the P(G_x-AGE_y) random copolymers, the *DB* is not affected, since the L_{AB} unit is simply transformed into a L_{13} glycerol unit, i.e., into $L_{\mathrm{AB_2}}$ (Scheme 4[4]). Nevertheless, this transformation is interesting, since it permits to maintain the polyglycerol structure and leads to polyglycerols with controlled DB. However, when the allyl group is dihydroxylated, each L_{AB} unit is transformed into a dendritic (D) and a pendant terminal unit (T), leading to an enhanced DB. Additionally, the terminal unit of the linear AB monomer (T_{AB}) is converted into a linear (L) and a pendant terminal unit (T). The incorporation probability of the T_{AB} unit is given in eq 13 (analogous to eqs 1−3).

$$p(\mathrm{T_{AB}}) = x_{\mathrm{AB}}p_{\mathrm{A}}(1 - p_{\mathrm{B}}) \tag{13}$$

Accordingly, $p(\mathrm{L_{AB}})$ has to be added to $p(D)$ (eq 14) and $p(\mathrm{T_{AB}})$ has to be added to $p(\mathrm{L_{AB_2}})$ as expressed in eq 15.

$$p(\mathrm{D}) = x_{\mathrm{AB_2}}p_{\mathrm{A}}{p_{\mathrm{B}}}^2 + x_{\mathrm{AB}}p_{\mathrm{A}}p_{\mathrm{B}} \tag{14}$$

$$p(\mathrm{L_{AB_2}}) = 2x_{\mathrm{AB_2}}p_{\mathrm{A}}p_{\mathrm{B}}(1 - p_{\mathrm{B}}) + x_{\mathrm{AB}}p_{\mathrm{A}}(1 - p_{\mathrm{B}}) \tag{15}$$

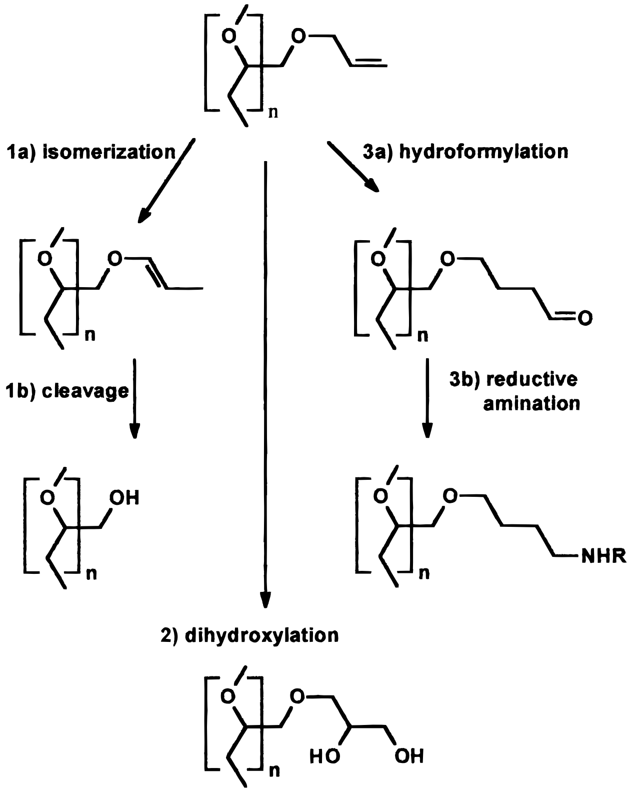
Using eq 14 and eq 15 for the transformation of eq 5 as before, eq 16 is derived which describes the *DB* of a random AB/AB$_2$ copolymer after a modification reaction that transforms all L_{AB} units in perfect dendritic units and all T_{AB} units into linear $L_{\mathrm{AB_2}}$ units, leading to an enhanced degree of branching ($DB^{f,\mathrm{enhanced}}_{\mathrm{AB/AB_2}}$).

$$DB^{f,\mathrm{enhanced}}_{AB/AB_2} = \frac{2 + 2x_{\mathrm{AB}} - 2{x_{\mathrm{AB}}}^2}{f(x_{\mathrm{AB}} - 1)^2 + 2 + 4x_{\mathrm{AB}} - 5{x_{\mathrm{AB}}}^2 + {x_{\mathrm{AB}}}^3} \tag{16}$$

The effect of this postsynthetic enhancement of the *DB* is illustrated in the upper part of Figure 1a′−c′). For example, a copolymer with 40 mol % AGE and 60 mol % glycidol possesses a degree of branching $DB = 51\%$. After dihydroxylation, this is enhanced to $DB = 73\%$ (indicated by the arrow in Figure 1, b → b′).

It needs to be mentioned that this modification is not a random process that affects all units of the polymers, since it is selective for L_{AB} units. Thus, the global parameter *DB* does not describe the topology appropriately anymore, e.g., the linear AB homopolymer ($DB = 0\%$) after modification consists of dendritic and terminal units only (formal $DB = 100\%$). Although the *DB* points to a fully branched dendrimer-type structure, obviously the polymer is a linear short-chain-branched

Scheme 4. Derivatization Reactions of Poly(allyl glycidyl ether) P(AGE): (1a) Pd-Catalyzed Allyl Isomerization and (1b) Subsequent Acidic Hydrolysis, (2) Dihydroxylation by *N*-Methyl Morpholine-*N*-oxide (NMO) and Osmium Tetroxide, (3a) Hydroformylation under Rhodium Catalysis, (3b) Reductive Amination with Benzylamine and NaBH$_3$(CN)



polyglycerol without extensive branch-on-branch topology.[24]

B. Random Copolymerization of Glycidol with Glycidyl Ethers. As described previously, glycidol can be polymerized to well-defined hyperbranched polyether polyols under anionic conditions.[14] The degree of polymerization is controlled by the monomer/initiator ratio employed. It is well-known that for linear polyethers random copolymerization can easily be realized by addition of a mixture of epoxide monomers to the active alkoxide polymerization mixture.[22] Thus, to prepare random copolymers, we used a mixture of glycidol with various amounts of a glycidyl ether, i.e., allyl glycidyl ether (AGE) and phenyl glycidyl ether (PGE), respectively, under SMA conditions. One important advantage of those readily available glycidyl ether comonomers is their structural similarity to glycidol with respect to reactivity and boiling point. We used a tetrafunctional initiator based on octadecylamine reacted with 2 equiv of glycidol forming the bis(2,3-dihydroxylpropyl) adduct[25] (Scheme 2). The initiator was partially deprotonated using potassium methoxide solution, distilling off excess methanol. Subsequently, the mixture of glycidol and glycidyl ether in the planned ratio was slowly added to the polymerization mixture at 120 °C. The random copolymerization of glycidol with AGE is shown in Scheme 2.

After completed addition, the random copolymers were neutralized by filtration over a cation-exchange resin, affording viscous oils whose solubility behavior depends strongly on the composition. Whereas the polyglycerol homopolymer is only soluble in very polar solvents, the homopoly(glycidyl ethers) are soluble in a broad variety of organic solvents (e.g., methanol, THF, toluene) with the exception of aliphatic hydrocarbons.

The degree of polymerization DP_n and the copolymer composition achieved can be calculated from ^{1}H NMR spectra. Figure 2 shows a representative spectrum of P(G$_{24}$/AGE$_{31}$). The signals of the aliphatic amine initiator are clearly distinguishable: methyl at 0.91 ppm, 15 methylene groups at 1.30 ppm, one methylene group in β-position to the nitrogen at 1.48 ppm. All three α-methylene groups surrounding the nitrogen atom exhibit a signal at 2.59 ppm. The two methine protons in β-position to the nitrogen show a resonance at 3.30 ppm. The signals of the polyether backbone overlap strongly to give a broad signal between 3.95 and 3.4 ppm. The allyl groups exhibit three resonances: the methylene group at 4.03 ppm and the three vinylic protons at 5.24 and 5.92 ppm. The ^{1}H NMR spectrum of P(G$_{25}$/PGE$_{23}$) is detailed in the Experimental Section.

Allyl ethers are known to form prop-1-enyl ethers under base catalysis;[26] thus, already during anionic polymerization a small fraction ($<$5%) of the allyl groups is isomerized, as evidenced by the signal at 4.23 ppm (Figure 2; assignment cf. Experimental Section). This reaction will be discussed in detail in section D. Since glycidol and AGE each contribute five protons to the backbone signal between 3.95 and 3.4 ppm, DP_n can be calculated from the integral ratio of backbone protons and initiator protons. The molar fraction of linear comonomer x_{AB} is calculated from the integral ratio of allyl protons and backbone protons (cf. eq 4).

Table 1 summarizes the results for various random copolymers of glycidol and AGE, as well as for one copolymer of glycidol and PGE. DP_n, x_{AB}, and M_n represent the values calculated from ^{1}H NMR. Since no polymer is lost during purification, the found values for the comonomer fraction x_{AB} and the DP_n correspond to the ratio of initiator, glycidol, and glycidyl ether. The third column of Table 1 lists the degree of branching DB calculated with eq 12, using $DB_{AB_2} = 58\%$ of the homopolymer (calculated from ^{13}C NMR, first row).

The polymer microstructure can be investigated by ^{13}C NMR. Figure 3 shows the ^{13}C NMR spectra (inverse gated (IG) measurements) of (A) P(G$_{72}$), (B) P(G$_{42}$/AGE$_{26}$), (C) P(G$_{24}$/AGE$_{31}$), and (E) P(G$_2$/AGE$_{41}$). The copolymer compositions are clearly reflected by the change of the signals. On the basis of results of dihydroxylated and cleaved P(AGE) (Figure 7B,C) and NMR investigation of perfect glycerol dendrimers,[27] we have to refine ^{13}C NMR assignments of the poly(glycerol) homopolymer as shown in Scheme 3, indicating that the three central signals are more complex than previously assumed. The core-closest methylene is sensible to the type of alkoxide next to it; thus, primary alkoxide neighboring methylene groups appear at 1−2 ppm lower field compared to the secondary alkoxide neighboring one. It should be emphasized that this improved assignment does not affect previously reported results,[14] since these carbons appear in the three overlapping peak regions at 73.5−74.5, 72.0−73.5, and 70.5−72.0 ppm which are not used for the calculation of DP_n and DB.

As shown in Scheme 3, the two possible incorporation modes of AGE, i.e., linear and terminal, are similar to the dendritic and linear 1,4 unit of polyglycerol. Thus, chemical shifts of the core-closest methylene and the methine group are almost identical with the resonances

Table 1. Characterization Data for Random Copolymers of Glycidol and AGE (P(G_x/AGE_y) and PGE (P(G_xPGE$_y$) from NMR, Vapor Pressure Osmometry (VPO), SEC, Hydroxyl Number Titration, and DSC

	^{1}H NMR				VPO^a	SEC^b		titration	DSC
sample	x_{AB} (%)	DB^c (%)	DP$_n$	M_n	M_n	M_n	PDI^d	HN^e	T_g (°C)
P(G_{72})	0	58^f	72.2^f	5760	n.d.	18060	1.5	n.d. (742)	−20
P(G_{54}/AGE_{12})	19	56	65.8	5790	5730	8110	1.5	396 (558)	−28
P(G_{42}/AGE_{26})	38	51	67.5	6450	6420	5290	1.7	311 (398)	−39
P(G_{24}/AGE_{31})	57	44	54.8	5730	5980	3820	1.6	218 (270)	−53
P(G_{12}/AGE_{36})	75	32	48.1	5440	5110	2770	1.5	134 (163)	−62
P(G_2/AGE_{41})	95	9	42.8	5220	5230	2810	1.2	49 (43)	−73
P(G_{25}/PGE_{23})	49	48	48.1	5770	n.d.	3670	1.6	231 (279)	−3

[a] Measured in DMF at 95 °C. [b] Performed in DMF at 45 °C with poly(propylene oxide) calibration. [c] Theoretical *DB* calculated by using eq 12 with $DB_{AB_2} = 58\%$. [d] Polydispersity index M_w/M_n. [e] Measured hydroxyl numbers (calculated hydroxyl numbers from NMR). [f] Calculated from ^{13}C NMR.[14] nd = not determined.

of the respective glycerol units. The methylene group next to the allyl ether exhibits a chemical shift of 73.3 ppm for a neighboring hydroxymethine unit (T_{AGE}) and 71.6 ppm for a neighboring methine ether unit (L_{AGE}). In the AGE homopolymer (Figure 3, spectrum E) all units are connected by secondary alkoxides ($L_{AGE,s}$ $T_{AGE,s}$). Therefore, the $L_{AGE,p}$ and $T_{AGE,p}$ units are only observed in the copolymers. Since the shifts of the respective methylene units are very similar to the related dendritic and linear 1,4 units of polyglycerol, their assignment is difficult. The allyl carbon leads to a signal at 73.5 ppm for both the T_{AGE} and L_{AGE} units, which overlaps with other glycerol signals.

In Figure 3 spectra A, B, C, and E reveal the gradual change from the polyglycerol homopolymer (A) to the poly(AGE) homopolymer (E) with increasing fraction of AGE comonomer. For example, the signals of the glycerol L_{13} and T units are reduced in intensity in (B) ($x_{AGE} = 38\%$) and are hardly visible in (C) ($x_{AGE} = 57\%$), supporting random incorporation of the two monomers as expected from statistics.

Unfortunately, the strongly overlapping signals of glycidol and AGE do not permit determination of the abundances of each of the 12 structural units (Scheme 3). Thus, the degree of branching cannot be calculated from the ^{13}C NMR spectra.

Further characterization data of the random copolymers are also summarized in Table 1. We used vapor pressure osmometry (VPO) in dimethylformamide (DMF) to verify molecular weights obtained from NMR. Polydispersities determined by SEC in DMF using poly(propylene oxide) (PPO) for calibration are low, ranging between 1.2 and 1.7. However, the number-average molecular weights M_n determined by SEC strongly depend on copolymer composition and resulting polarity (Table 1). Figure 4 shows M_n calculated from NMR and M_n determined by SEC vs copolymer composition. As reported previously, M_n is overestimated for large glycidol fractions incorporated ($x_{AGE} < 40\%$) due to polymer−solvent interactions.[14] Interestingly, for an intermediate composition of a molar fraction of AGE of about 40% values from NMR and SEC agree quite well; however, for higher AGE fractions SEC underestimates molecular weights. This is explained by the difference of hydrodynamic volume of poly(allyl glycidyl ether) and the PPO calibration due to the branched topology. It should be emphasized that the sample (P(G_2/AGE_{41}) is not a linear polymer but a four-arm star polymer, due to the functionality of the initiator employed.

The hydroxyl functionality of the copolymers was determined by end group titration. This is usually achieved by complete esterification of the hydroxyl groups, using a known excess of an anhydride. Unreacted anhydride is subsequently hydrolyzed, and the acid is titrated with aqueous base (e.g., NaOH). For the titration of polyols bearing secondary hydroxyl groups, cyclic anhydrides are preferred because of their high reacitvity. The parameter obtained is the so-called hydroxyl number (*HN*), which represents the mg of KOH equivalents per g polymer sample. A precise definition of this quantity is given in eq 17, in which *t* represents the hydroxyl functionality and M_n the molecular weight of the polymer.

Table 2. Characterization Data of Block Copolymers of Glycidol and AGE P($G_x$$AGE_y$) from NMR, SEC, and DSC

	NMR			SEC^a		DSC
sample	DP_n (G)^b	AGE:G (x_{AGE})^c	M_n	M_n	M_w/ M_n	T_g (°C)
P($G_{48}$$AGE_{1.4}$)	48.4	1.35 (57.4%)	11 450	8 990	1.6	−53^d
P($G_{72}$$AGE_{2.5}$)	72.2	2.45 (71.0%)	25 960	61 950	1.5	−78

[a] Performed in DMF at 45 °C with poly(propylene oxide) calibration. [b] Calculated from ^{13}C NMR. [c] AGE block length per OH end group, i.e., DP_n of glycidol + 4 (molar fraction of AGE), calculated from ^{1}H NMR. [d] Second T_g observed at −83 °C.

$$HN = \frac{t}{\bar{M}_n} \times 56100 \tag{17}$$

In the second to last column of Table 1 the experimental results for the end group titration are listed; the data in parentheses represent the values expected on the basis of the molecular weights and the functionalities calculated (DP_n of glycidol + 4) from the NMR data. With increased glycidol content, the titrated value deviates to an increasing extent from the expected value (Table 1, Figure 5). Since all titration experiments were carried out under identical conditions, with respect to the duration of the esterification reaction, this result points toward the increasing steric hindrance due to growing compactness of the polymers. This is in agreement with recent results for the propoxylated polyglycerols.[21]

To date, thermal properties of AB/AB_2 copolymers have been investigated to a very limited extent. DSC measurements show that the glass transition temperature T_g of the random copolymers depends linearly on copolymer composition (Table 2, Figure 6). Values for the respective P(AGE) and P(PGE) homopolymers were taken from the literature.[28] Since this linear relationship corresponds to that long known for linear, noncrystalline random copolymers, the branched architecture does not seem to have a peculiar influence on T_g. Copolymerization of glycidol with AGE leads to a lower T_g due to an increase in scaffold flexibility and a decrease in OH density. On the other hand, copolymerization with PGE leads to a higher T_g due to the incorporation of a more rigid, bulky monomer unit.

C. Block Copolymerization with Allyl Glycidyl Ether. In analogy to our previous work on propylene oxide,[21] block copolymers of glycidol and AGE have also been prepared by successive slow addition of both monomers. Two samples with relatively short P(AGE) blocks are described here; however, longer blocks are possible by the same synthetic approach. Polyglycerol was prepared by the previously reported procedure[14] using bis(2,3-dihydroxypropyl)octadecylamine as initiator. After complete addition of glycidol, the hydroxyl groups were deprotonated again to an extent of approximately 5%, using potassium hydride and AGE was slowly added at 120 °C. After neutralization, the block copolymers were obtained as transparent, viscous liquids. As expected, there is no difference in the ^{1}H NMR spectra of block and random copolymers; thus, the DP_n and the copolymer composition can be calculated from the spectra as described in the previous section (Table 2). Two block copolymers with different block lengths were prepared ($P(G_{48}AGE_{1.4})$, $P(G_{72}AGE_{2.5})$). Comparison of the ^{13}C NMR spectrum of $P(G_{48}AGE_{1.4})$ (Figure 3D) with the random copolymer $P(G_{24}/AGE_{31})$ of the same monomer composition $x_{AGE} = 57\%$ (Figure 3C) shows the topological difference. The random copolymer still exhibits signals of the glycerol units L_{13} and T, bearing hydroxyl groups, whereas these signals have completely disappeared in the block copolymer, since practically all glycerol monomers are present as perfect dendritic (D) units.

SEC measurements show that the elution behavior of the block copolymers differs from that of the random copolymers. At high AGE contents the molecular weight is *over*estimated, in accordance with the results on propylene oxide block copolymers.[21] The polydispersity remains unchanged after block copolymerization (compare $P(G_{72})$ and $P(G_{72}AGE_{2.5})$), being in the range of $M_w/M_n = 1.5$.

Interestingly, DSC measurements revealed a remarkable difference in the glass transition temperature of the block copolymers compared to the random copolymers. Whereas the block copolymer $P(G_{48}AGE_{1.4})$ exhibits a T_g at −53 °C according to the AGE fraction (cf. Figure 6), the block copolymer $P(G_{72}AGE_{2.5})$ already possesses the T_g of the P(AGE) homopolymer at −78 °C, while the comparable random copolymer $P(G_{12}/AGE_{36})$ exhibits a T_g at −62 °C. As observed for the propylene oxide block copolymers in previous work, a second T_g at very low temperature is observed for the sample with the short AGE block length $P(G_{48}AGE_{1.4})$. The analogous random copolymer $P(G_{24}/AGE_{31})$ does not exhibit this behavior. We conclude that the polyether backbone possesses a T_g of about −80 °C, but hydrogen bonding of the OH groups leads to increased rigidity, resulting in higher T_g's. Only in the case of high OH density *and* nonrandom distribution of the OH groups throughout the scaffold is "clustering" of the OH groups observed, leading to a second T_g at −53 °C. However, already a small increase in block length leads to a complete disappearance of these "domains", and only the T_g of the polyether backbone is detected. On the other hand, the random distribution of OH groups in the random copolymers leads to a more profound influence of hydrogen bonding on the rigidity and a linear decrease of T_g is observed with increasing AGE fraction.

D. Chemical Modifications of Random Glycidol/AGE Copolymers. In the previous two sections the linear AB type comonomer AGE was only used in order to vary branching density, polarity, and thermal behavior of the copolymers. Since AGE represents an ABR monomer, there are numerous possibilities for chemical modifications (Scheme 4): (i) The allyl group can be used as a protecting group that after removal leads to a linear 1,3-glycerol unit, bearing a primary hydroxy group. The synthesis of such poly(L_{13}-glycerol) homopolymers has already been described in the literature using various protecting groups.[29] (ii) The allyl group represents a latent glycerol unit, i.e., after dihydroxylation a dendritic glycerol unit with an attached terminal glycerol unit is formed (Scheme 4). This leads to hyperbranched polyglycerols, which possess an enhanced degree of branching (section A). (iii) The double bond allows further functionalizations orthogonal to the hydroxyl groups (e.g., hydroformylation). In the following, these three modification reactions will be discussed.

Cleavage of allyl ethers is performed by a two-step protocol. In the first step the allyl ethers are isomerized to form prop-1-enyl ethers (Scheme 4, 1a). This can be achieved by base catalysis,[26] while all hydroxyl groups present in the system have to be deprotonated. We employed this reaction successfully for the poly(AGE) star polymer $P(G_2AGE_{41})$ in DMSO using potassium *tert*-butyl alcoholate. Unfortunately, this route is not suitable for the random copolymers, since the respective polyalkoxides are insoluble in DMSO. However, this mechanism is responsible for the formation of isomerized allyl glycidyl ethers in the anionic polymerization (Figure 2). An alternative route is isomerization under palladium catalysis,[30] which yields more than 85% prop-1-enyl ethers. Vinyl ethers are known to hydrolyze quantitatively under acidic conditions (Scheme 4, 1b).[26] The poly(prop-1-enyl ether) from $P(G_2/AGE_{41})$ was allyl-deprotected to give a poly(1,3-glycerol) four-arm star polymer (Figure 7B). In analogy $P(G_{42}/AGE_{26})$ was cleaved in 87% yield to afford a hyperbranched polyglycerol with 42 glycerol units incorporated randomly and 26 glycerol units 1,3-linearly. The degree of branching is expected to be the same as for the uncleaved copolymer. Using the method established previously,[14] a DB of 60% was calculated for the deprotected product of $P(G_{42}/AGE_{26})$ from the ^{13}C NMR spectrum, while on the basis of the theory, one would expect 51% (Figure 1, curve b; Table 1). The deviation is most likely caused by the overlapping signals of the uncleaved ether resonances (Figure 7B).

For allyl-deprotected $P(G_2/AGE_{41})$ the calculated value is $DB = 36\%$ while theory would predict 9% (two dendritic units are incorporated already in the initiator). This deviation is due to the higher sensitivity of the DB at high linear comonomer fractions (Figure 1). Nevertheless, the results show that copolymerization and subsequent deprotection leads to a significant decrease in the degree of branching.

The second modification is dihydroxylation of the double bond (Scheme 4, 2). This can be carried out under OsO_4 catalysis using *N*-methylmorpholine-*N*-oxide (NMO) as cooxidant.[31] By this method all allyl ethers of linear AGE units (L_{AGE}) are transformed into terminal glycerol units attached to a dendritic glycerol unit. Allyl ethers of terminal AGE units (T_{AGE}) are transformed into terminal glycerol units attached to linear 1,4 glycerol units (L_{14}).

Hence, complete dihydroxylation of $P(G_2/AGE_{41})$ leads to a four-arm star−polymer in which the linear backbone consist of dendritic glycerol units, bearing one terminal unit as side chain each.

A topology of this kind with a $DB = 100\%$ has been proposed theoretically by Hobson and Feast.[24] The ^{13}C NMR spectrum of this polymer is shown in Figure 7C, exhibiting only signals of dendritic and terminal glycerol units (Scheme 4, assignment according to Figure 3A). It should be mentioned that this spectrum also agrees very well with that of the perfect glycerol dendrimer structure.[27] Dihydroxylation of $P(G_{42}/AGE_{26})$ only leads to a conversion of 71%; thus, from the ^{13}C NMR only a *DB* of 64% is calculated. For full conversion, theory would expect a degree of branching of 72% according to eq 16 (arrow in Figure 1). However, the enhancement of the degree of branching by dihydroxylation can clearly be seen.

Apart from architectural variations, the glycidol/AGE copolymers can be used to modify orthogonally hydroxyl and allyl functionality. Hydroxyl number titration, described in the previous section, already demonstrated the possibility of esterification reactions, leaving the allyl group unchanged. A third modification of the allyl group is hydroformylation, i.e., use of the allyl group as orthogonal functionality to the hydroxyl group (Scheme 4, 3a). The obtained poly(aldehyde) polyether polyols can subsequently be transformed into polyamino polyether polyols by reductive amination (Scheme 4, 3b). To this end, in the first step a toluene solution of $P(G_{24}/AGE_{31})$ was reacted with CO/H_2 in an autoclave in the presence of a rhodium catalyst.[32] Due to intermolecular semiacetal formation, the product was obtained as an insoluble gel. However, IR spectroscopy revealed the successful conversion into the aldehyde. Semiacetal formation was confirmed by facile dissolution of the gel in methanol under ultrasonication in the presence of catalytic amounts of *p*-toluenesulfonic acid (formation of the methanol semiacetal). The gel also dissolved in the presence of benzylamine, indicating the formation of the imine. Without isolation of the reaction product, the imine was reduced to the amine.[33] Careful NMR analysis showed that the transformation of the double bond into the secondary benzylamine was successful (>95%, cf. Experimental Section). Both possible isomers of the hydroformylation were found. In Scheme 4 the reaction product of 3a shown is only the addition product in the γ-position; addition in the β-position is also observed, indicated by the signal of the pending methyl group (γ-carbon, cf. Experimental Section).

Conclusions

On the basis of previous theoretical considerations, we have derived equations for the calculation of the degree of branching (*DB*) in random AB_2/AB copolymerization under slow-monomer-addition (SMA) conditions. These equations permit to predict the *DB* even in the case of a nonideal random branching reaction.

Using glycidol as latent branching AB_2 monomer and allyl or phenyl glycidyl ether as representative linear comonomers, we have been able to prepare hyperbranched random polyether copolymers with controlled DP_n, relatively low polydispersities ($M_w/M_n < 1.7$), and controlled *DB*, determined by the comonomer ratio. The synthetic results were in agreement with theory. In summary, we have developed conditions that enable us to use glycidol as branching comonomer in standard polyether chemistry in combination with a variety of common epoxides. In addition, the respective block copolymers (i.e., multiarm star polymers) have been prepared by sequential addition of glycidol and AGE. Investigation of the thermal behavior revealed interesting structure−property relationships of the polyether copolymers, based on their different block or random topologies.

In previous work, linear AB comonomers had only been used in order to vary branching density, polarity, and thermal behavior of the copolymers.[23] In the current paper we show additionally the potential of AGE as an ABR-type monomer, offering numerous design possibilities for hyperbranched polyethers. (i) The allyl group represents a protecting group, leading after cleavage to a linear 1,3-glycerol unit bearing a primary hydroxy group; (ii) the allyl group also represents a latent glycerol unit, leading to the formation of a dendritic glycerol unit with an attached terminal glycerol unit after dihydroxylation. This affords hyperbranched polyglycerols with an enhanced *DB* (section A). In the case of the P(AGE) homopolymer the linear isomer of the hyperbranched polyglycerol with $DB = 100\%$[27] is obtained. (iii) The double bond allows further functionalization reactions orthogonal to the chemistry of the hydroxyl groups, e.g., hydroformylation followed by reductive amination. The reaction products represent hyperbranched polyether polyols with additional multiple amino groups that are interesting coupling functionalities for biomolecules.

The present work reveals further aspects of the versatility of the controlled ring-opening multibranching polymerization. In contrast to dendrimer syntheses, properties can be tailored with respect to the targeted application by use of a modular approach,[1] combining suitable (functional) initiators, functional (co)monomers, and postsynthetic modification reactions.

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