Hyperbranched Polyether−Polyols Based on Polyglycerol: Polarity Design by Block Copolymerization with Propylene Oxide

Alexander Sunder, Rolf Mülhaupt, and Holger Frey*

Freiburger Materialforschungszentrum FMF und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

Received July 20, 1999; Revised Manuscript Received October 26, 1999

ABSTRACT: Multiarm block copolymers were synthesized via anionic ring-opening multibranching polymerization (ROMBP) of glycidol followed by addition of propylene oxide. The resulting polyether−polyols with molecular weights in the range 5000−12 000 g/mol possessed up to five propylene oxide units per end group and showed narrow molecular weight distributions (MWD < 1.7). Via propoxylation the polarity of the highly hydrophilic polyglycerols can be varied, resulting in versatile, highly functional branched polyether polyols. The hyperbranched polyglycerols with oligo(propylene oxide) segments were characterized by ^{13}C and ^{1}H NMR, demonstrating complete propoxylation of all end groups. ^{1}H NMR, SEC, vapor pressure osmometry, and hydroxyl number titration were used to determine molecular weights. The effect of the short poly(propylene oxide) blocks on the flexibility of the polyethers was studied by DSC. The T_g varied between −37 and −71 °C, depending on the length of the propylene oxide segments attached.

Introduction

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. Uncontrolled ring-opening polymerization and partial characterization of the branched polymers formed have been reported by Vandenberg et al.[1] as well as by Penczek and Dworak.[2] Recently, we reported the controlled synthesis of hyperbranched polyglycerols via the anionic ring-opening multibranching polymerization of glycidol[3] (ROMBP), using slow monomer addition conditions[4] in combination with partial deprotonation. In contrast to most previously reported syntheses of hyperbranched polymers that rely on the polycondensation of AB_m monomers,[5] this polymerization makes use of a controllable chain-growth process with dynamic exchange equilibrium between inactive hydroxyl and active alkoxide end groups. The polyether−polyols obtained in this chain-growth-like procedure possess polydispersities below 1.5 (mostly below 1.3), the degree of polymerization being controlled by the ratio of glycidol monomer to initiator.

Since most applications discussed for both dendrimers and hyperbranched polymers at present involve further functionalization, versatility of the structures regarding the functional group density and solubility in a wide range of solvents are important issues. However, due to the high density of hydroxyl groups, polyglycerol is insoluble in most common organic solvents. The few exceptions besides water are typically lower alcohols and dipolar aprotic media, such as pyridine, DMF, DMSO, or NMP, that are rather limited in preparative use. Previous work by various groups on hyperbranched polyesters as well as poly(ether ketone)s has shown that the attachment of apolar alkyl chains (e.g., by esterification) can be employed to modify the polarity as well as the glass transition temperature.[6−9] However, in this case the functionality of the hyperbranched polymers is affected (i.e., the number of functional groups is reduced) by the modification.

In this paper we wish to present a convenient approach that permits to tailor the polarity of the hyperbranched polyglycerol without reducing the functionality and without variation of the basic polyether structure, thus without change of the relative chemical stability of the hyperbranched scaffold. This is achieved by attaching short oligo(propylene oxide) segments to the hydroxyl end groups. The effect of this end group modification on the flexibility (i.e., the T_g) of the hyperbranched scaffold will also be investigated in detail.

Experimental Section

Polymerizations. Glycidol (Aldrich) was polymerized in the presence of 1,1,1-tris(hydroxymethyl)propane (TMP, Fluka) or diethylene glycol (Fluka) by the method described previously.[3] The obtained polyglycerol in the amount according to the desired monomer/ hydroxyl ratio was again deprotonated to an extent of ca. 5% per OH group using potassium hydride (Aldrich, dispersion in oil).

A 50 mL aliquot of propylene oxide (Fluka, distilled over CaH_2) was slowly added to the reaction mixture over 18 h, maintaining a reaction temperature of 95 °C at a bath temperature of 130 °C. After the addition was complete, the product was dissolved in methanol and neutralized by filtration over a cation-exchange resin. Methanol was distilled off and the residue dried for 15 h at 100 °C in vacuo. Block copolymers were obtained as transparent viscous oils.

NMR. ^{1}H 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.

SEC. The polymers were dissolved either in DMF or in chloroform at a concentration of 10 mg/mL. For measurements using DMF as eluent, a Knauer microgel set C11 at 45 °C equipped with a Polymer Labaratories evaporative mass detector EMD 960, operating at 110 °C, was used. Poly(propylene glycol) samples with M_n in the range 1000−12 000 were used for calibration.

VPO. Vapor pressure osmometry was carried out using a Knauer vapor pressure osmometer K7000 in chloroform at 40 °C in the concentration range 10−40 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

10.1021/ma991191x CCC: $19.00
Published on Web 12/28/1999

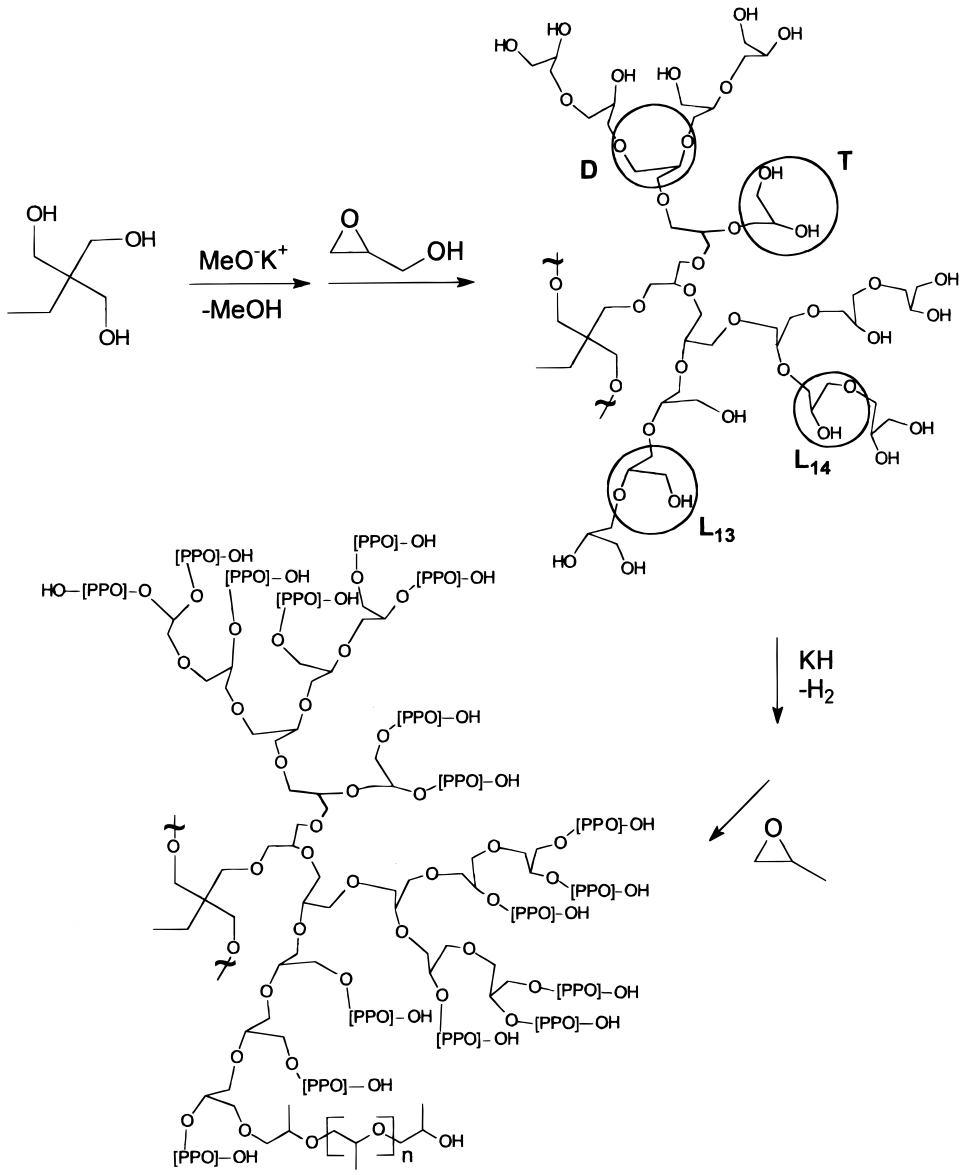

Figure 1. Synthesis of multiarm block copolymers. Step 1: anionic ring-opening multibranching polymerization (ROMBP) of glycidol using trimethylolpropane as initiator and potassium methylate as deprotonating agent; structural units (*T*erminal, *D*endritic, *L*inear-*1,3*, *L*inear-*1,4*) are indicated by circles. Step 2: anionic ring-opening polymerization of propylene oxide onto the polyglycerol core, reinitiated with potassium hydride (PPO = poly(propylene oxide) arms).

to 20 °C at heating rates of 9, 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.

Hydroxyl Number. Hydroxyl numbers were determined by a common titration method:[10] The esterification mixture consists of 0.45 L of anhydrous pyridine, 64.25 g of phthalic anhydride, and 10 mL of *N*-methylimidazole. A 25 mL aliquot of this mixture was stirred with 25 mL of pyridine and 50 mL of water and after 10 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 30 min with 25 mL of the esterification mixture. Both 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 $HN = (V_{blind} - V_{sample})(56.1/m_{sample})$.

Results and Discussion

As reported previously, glycidol can be polymerized under anionic conditions to hyperbranched polyether polyols.[3] The degree of polymerization can be controlled by the monomer/initiator ratio employed. It is well-known that, for linear chain polymers based on monofunctional epoxides, block copolymerization can easily be carried out by subsequent addition of a second monomer to the active alkoxide chain end.[11] In the present work we applied this concept to hyperbranched polyglycerol. To modify polyglycerol with propylene oxide, the living polyglycerol (polymerization carried out as described in ref 3) was deprotonated again in situ to a degree of approximately 5% per hydroxyl group, using potassium hydride, avoiding a workup procedure. A rapid, dynamic equilibrium between hydroxyl and alkoxide end groups ensures that all end groups propagate at the same rate. Since the anionic polymerization of propylene oxide (PO) proceeds slowly, this monomer had to be introduced into the mixture at high temperature. Propylene oxide (PO) was added slowly to the system at ambient pressure in such a manner that the reaction temperature did not exceed 95 °C at a bath temperature

Table 1. Characterization Data of the Polyglycerols Used as Hyperbranched Core Molecules

sample	dendritic[d]	linear 1,3[d]	linear 1,4[d]	terminal[d]	DP_n[a]	M_n[a]	M_n[b]	MWD[b]
$P(G_{38})$	27	28	11	34	38.2	2800	15 600	1.26
$P(G_{23})$	24	28	10	38	22.8	1800	7 400	1.20
$P(G_{52})$	28	27	11	34	51.9	4000	17 700	1.21
$P(G_{33})$[c]	27	28	12	33	33.0	2400	14 700	1.50

[a] Calculated from ^{13}C NMR (f_c(TMP) = 3); given in g/mol. [b] Apparent values from SEC in DMF, calibrated with PPO standards; g/mol. [c] Initiator: diethylene glycol (f_c = 2). [d] Given in mol %.

of 130 °C. Temperature rises once all gaseous monomer has been consumed (boiling temperature of PO: 34 °C), indicating that new monomer has to be added at that point. Polyglycerol possesses primary and secondary hydroxyl groups. Once all primary hydroxyl groups of the polyglycerol core are converted into secondary ones by propoxylation, all hydroxyl end groups in the system should possess similar reactivity and are therefore expected to propagate simultaneously. The preparation of the oligo(propylene oxide) terminated hyperbranched polyglycerols is schematically shown in Figure 1.

The multiarm block copolymers with short PO blocks are obtained as transparent, viscous oils whose solubility behavior is drastically different from the polar polyglycerol. Whereas the latter is only soluble in very polar solvents, the propoxylated polyglycerols become soluble in almost any organic solvent with the exception of purely aliphatic hydrocarbons, although the number of hydroxyl end groups remains unchanged, which represents a main advantage of this modification procedure.

Four different polyglycerols were prepared and used for the attachment of the oligo(propylene oxide) segments. Before addition of propylene oxide, in all cases samples were taken and the polyglycerol precursors fully characterized by NMR and SEC (cf. Table 1) with respect to both the degree of branching (DB) and molecular weight. The DB of all polyglycerol samples was in the range of 0.58.[3] A full assignment of all NMR signals to the four different units (dendritic (D), terminal (T), linear ($L = L_{13} + L_{14}$)) was achieved, as described previously.[3] The degree of polymerization could be calculated from the intensities of the ^{13}C NMR signals for the four different structural units and the core functionality f_C according to eq 1 and ranged between 23 ($P(G_{23})$)and 52 ($P(G_{52})$), i.e., molecular weights M_n between 1800 and 4000.

$$\overline{DP}_n(PGly) = \frac{T + L + D}{T - D} f_c \qquad (1)$$

The degree of polymerization also represents the hydroxyl functionality of polyglycerol, since on average each monomer unit contributes one hydroxyl group to the structure. SEC shows monomodal, narrow apparent molecular weight distributions with polydispersity between 1.2 and 1.5 for all polyglycerols employed.

NMR Characterization. ^1H as well as ^{13}C NMR yields valuable information on the degree of end group modification by oligo(propylene oxide) segments and will therefore be discussed in some detail in the following. Figure 2 shows ^1H NMR spectra of the polyglycerol sample $P(G_{52})$ and the resulting block copolymer $P(G_{52}PO_3)$ (characterization data in Tables 1 and 2). The polyglycerol spectrum shows the signals of the CH_x backbone between 3.2 and 3.9 ppm; the hydroxyl protons resonate at 4.8 ppm in methanol. If trimethylolpropane (TMP) is used as initiator core, the methyl and the methylene protons of the core unit are observed at 0.9

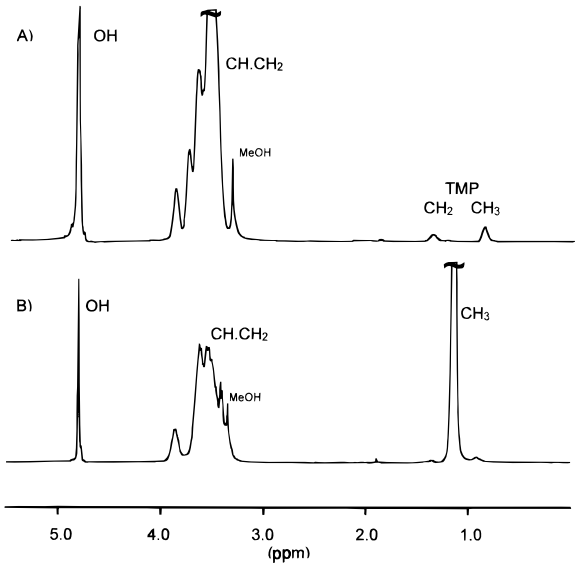

Figure 2. ^1H NMR spectra (CD_3OD, 50 °C) of (A) polyglycerol $P(G_{52})$ and (B) poly(glycerol-*b*-propylene oxide) $P(G_{52}PO_3)$.

and 1.4 ppm, respectively. It should be mentioned that, most probably due to shielding effects in the compact structure, molecular weights could not be calculated from the ratio of the signal intensities of the core unit and the polyether structure. After polymerizing propylene oxide onto the polyglycerol core, the signal of the methyl protons of poly(propylene oxide) (PPO) appears at 1.1−1.2 ppm. Additional methylene and methine protons from the oligo-PO segments overlap with those of polyglycerol. The resonance of the OH groups remains unchanged.

Interestingly, since the propoxylated multiarm block structure is different in polarity and functional group density, the relaxation behavior changes in comparison to polyglycerol. Integration of the signals is now possible, and since each glycerol unit of the hyperbranched core contributes on average one hydroxyl group, the degree of polymerization of PPO per end group can be calculated using eq 2.

$$\overline{DP}_n(PPO) = \frac{5}{3} \frac{I(CH_3)}{3(I(CH,CH_2) - I(CH_3))} \qquad (2)$$

$I(CH_3)$ and $I(CH,CH_2)$ represent the signal intensities of the methyl protons at 1.2 ppm and the methylene and methine protons between 3.2 and 3.9 ppm, respectively. The factor $^5/_3$ in eq 2 is due to the fact that the signals of the five protons of each glycerol unit overlap with the resonances of the three protons of propylene oxide. The results for the four different block copolymers are listed in Table 2.

Interpretation of the ^{13}C NMR spectra shown in Figure 3 is more complex. As published previously,[3] the signals of the polyglycerol core can be assigned unam-

Table 2. Characterization Data of the Multiarm Block Copolymers (NMR, Vapor Pressure Osmometry (VPO), SEC, and Hydroxyl Number Determination)

	NMR: PO:Gly[b]		NMR[c]	VPO	GPC			
sample[a]	^{1}H	^{13}C	M_n	M_n	M_n	MWD	hydroxyl no.[d]	T_g (°C)
P($G_{38}PO_1$)	1.07	1.29	5 600	4600	20 000	1.26	355 (384)	−36.9[e]
P($G_{23}PO_3$)	3.00	2.65	5 600	5000	12 400	1.19	229 (230)	−56.4
P($G_{52}PO_3$)	2.79	2.74	12 300	10500	45 300	1.24	234 (236)	−59.2
P($G_{33}PO_5$)	4.57	4.21	11 000	9200	37 800	1.66	160 (168)	−70.6

[a] P(G_xPO_y): x = DP_n of polyglycerol core; y = PO units per end group. [b] Ratio of monomer units propylene oxide/glycidol, calculated from NMR spectra. [c] Calculated from Table 1 and average ratio of ^{1}H and ^{13}C NMR data. [d] Measured (calculated) (cf. Experimental Section). [e] Second T_g at −72 °C observed.

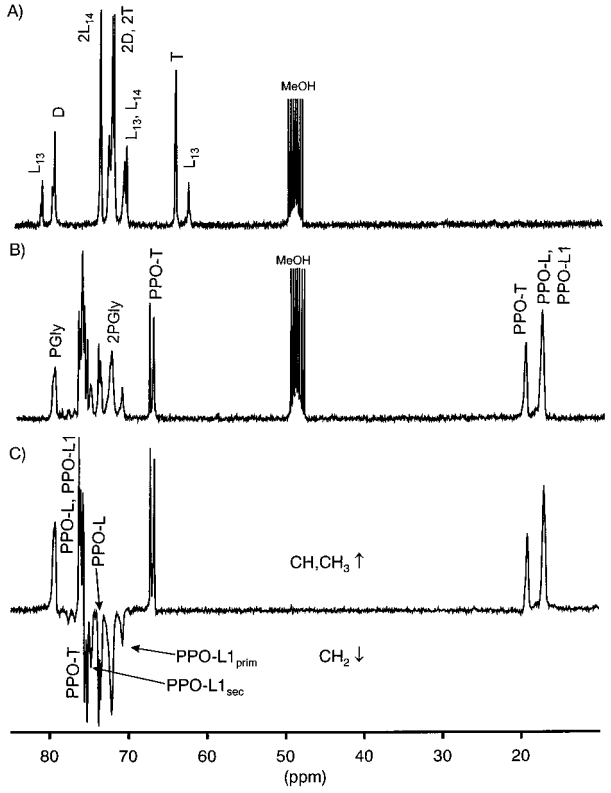

Figure 3. Assigned ^{13}C NMR spectra (CD_3OD, 50 °C, inverse gated pulse mode) of polyglycerol and poly(glycerol-*b*-propylene oxide). (A) P(G_{52}) initiated with 1,1,1-tris(hydroxymethyl)-propane (TMP): Carbons belonging to the terminal, dendritic, linear 1,3, and linear 1,4 units of polyglycerol are indicated by T, D, L_{13}, and L_{14}. (B) P($G_{52}PO_3$). (C) P($G_{52}PO_3$). DEPT spectrum: carbons belonging to polyglycerol and the different PPO units are designated as shown in Figure 4.

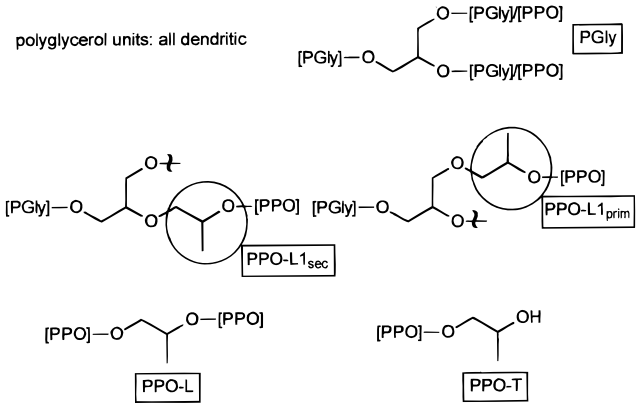

Figure 4. Structural units in poly(glycerol-*b*-propylene oxide): polyglycerol units (PGly); propylene oxide units at linear in-chain position (PPO-L) and at terminal position (PPO-T). The linear units directly attached to polyglycerol can be located next to either a primary or a secondary hydroxyl group of polyglycerol ($PPO\text{-}L1_{prim}$/$PPO\text{-}L1_{sec}$).

biguously (Figure 3A). Using DEPT, inverse gated (IG) NMR techniques, and the comparison of different degrees of polymerization of PO, a complete assignment of the spectrum of the star-block copolymer was achieved. Figure 3B shows the IG ^{13}C NMR spectrum and Figure 3C the corresponding DEPT spectrum. All structural units present are schematically shown in Figure 4. The spectra permit to distinguish between PO units incorporated in the short oligo-PO chains (PPO-L) in linear manner and the terminal PO units (PPO-T).

Summarizing these results, we conclude that all hydroxyl groups of the polyglycerol core have undergone propagation. This means that all monomer units of the polyglycerol core have been transformed into dendritic units, bearing glycerol and/or PO units, similar as in the case of postsynthetic modification of hyperbranched polycarbosilanes reported in recent work.[12] Interestingly, there is hardly any effect on the chemical shifts of the glycerol units by the PO attached; i.e., the dendritic polyglycerol signal remains at the same position.

From the spectra, detailed information on the structures formed can be extracted. All four possible types of PO units (Figure 4) can be observed: the first PO unit being directly attached to a glycidol unit may either have reacted with a primary or a secondary hydroxyl group ($PPO\text{-}L1_{prim}$, $PPO\text{-}L1_{sec}$). This only has an effect on the neighboring methylene carbon; thus, there are two distinguishable signals at 71.5 ppm for $PPO\text{-}L1_{prim}$ and at 75.6 ppm for $PPO\text{-}L1_{sec}$. Furthermore, the PO units incorporated in the short chains show distinct signals as assigned in Figure 3. Another special case is the terminal PO unit bearing the hydroxyl group. As can be confirmed from the well-known ^{13}C NMR spectra of linear PPO, the terminal group shows distinct signals at 20.1 ppm (methyl), 67.6−68.1 ppm (methine), and 76.0 ppm (methylene). The substructure of these peaks, also observed in linear PPO, is due to the possible triads of PPO. Another confirmation of this assignment is the fact that the terminal signals (PPO-T) change upon further functionalization.[13]

The signals for the terminal and the linear PO methyl carbons permit to calculate the degree of polymerization of oligo-PO per end group, which can be calculated using expression 3:

$$\overline{DP}_n(PPO) = \frac{I(\text{PPO-L}) + I(\text{PPO-T})}{I(\text{PPO-T})} \qquad (3)$$

I(PPO-L) and I(PPO-T) represent the intensities of the methyl group signal at 18 and 20 ppm, respectively. The results for the block copolymers are summarized in Table 2 and show excellent agreement with the data

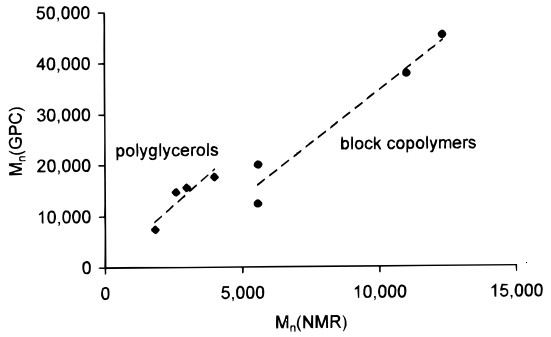

Figure 5. Correlation of number-average molecular weight (M_n) obtained from NMR and SEC measurements (DMF, 45 °C, poly(propylene oxide) calibration).

obtained from ^{1}H NMR. The planned ratios were 1.5 ($P(G_{38}PO_1)$), 3.0 ($P(G_{23}PO_3)$, $P(G_{52}PO_3)$), and 5.0 ($P(G_{33}PO_5)$). Loss of gaseous propylene oxide and dead volume effects in the reactor system provide the explanation for the fact that the actual average values observed are somewhat lower than expected. Since both values obtained from ^{1}H as well as ^{13}C NMR may show some experimental error, an average of both values for the PO/glycidol ratio is used for calculation of the molecular weights according to eq 4 (listed in Table 2).

$$\bar{M}_n = M(\text{initiator}) + \overline{DP}_n(\text{PGly})(74.1 + \overline{DP}_n(\text{PPO}) \times 58.1) \quad (4)$$

M(initiator), DP_n(PGly), and DP_n(PPO) represent the molar mass of the initiator used for glycidol polymerization and the degrees of polymerization for glycidol and PO per hydroxyl group as listed in Tables 1 and 2; 74.1 and 58.1 are the monomer masses of glycidol and PO.

SEC and Vapor Pressure Osmometry (VPO). As in the case of the unmodified polyglycerol samples, SEC in DMF using poly(propylene oxide) standards was carried out for all hyperbranched polymers with oligo-PO segments. As listed in Table 2, all polymers exhibit narrow apparent molecular weight distributions, M_w/M_n ranging from 1.2 to 1.7, which are comparable to those of the polyfunctional initiators (Table 1). As pointed out previously for aromatic polyesters[14] as well as polyglycerol,[3] SEC results for hyperbranched polyols have to be discussed with care. The globular topology of the polymers is different from common linear calibration standards, and the large number of hydroxyl end groups has been found to lead to a systematic overestimation of molecular weights.[14] At first glimpse, this is unexpected, since the hydrodynamic volume of highly branched polymers is smaller than that of their linear analogues, which should result in an underestimation of molecular weight. A probable explanation is interaction of the highly functional polymers with solvent and columns.

Figure 5 shows a plot of molecular weights determined by SEC with PPO standards versus the absolute molecular weights calculated from NMR. With respect to experimental errors, there is a linear relationship in the molecular weight range measured for both the polyglycerols and the propoxylated materials. However, due to the different copolymer compositions and hence differences in polarity, the values for the segmented star copolymers show some scattering. Nevertheless, the data make an estimate of molecular weights and polydispersity on the basis of standard SEC measurements possible.

To characterize the block copolymers with respect to their absolute molecular weights and to confirm the values calculated from NMR, vapor pressure osmometry (VPO) was carried out in chloroform. As shown in Table 2, the values obtained show good agreement with those calculated from NMR for all propoxylated samples, although generally they appear to be somewhat lower. This might be due to traces of low molar mass residues in the samples (most probably solvent traces).

Hydroxyl Number Determination. A common and convenient method for the characterization of the functionality of polyether−polyols is titration of the hydroxyl end groups. This is usually carried out by complete esterification of the hydroxyl groups, by using the reaction with 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 higher reacitvity. The parameter obtained is the so-called hydroxyl number (HN), which represents the milligram KOH equivalents per gram of polymer sample. A precise definition of this quantity is given in eq 5 in which f represents the hydroxyl functionality and M_n the molecular weight of the polymer.

$$\text{HN} = \frac{f}{\bar{M}_n} \times 56100 \quad (5)$$

In the second to last column of Table 2 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 (M_n, Table 2) and the functionalities calculated (DP_n, Table 1) from the NMR data. For $P(G_{23}PO_3)$, $P(G_{52}PO_3)$, and $P(G_{33}PO_5)$ excellent agreement and thus confirmation of the molecular weights determined by NMR and VPO were obtained. For $P(G_{38}PO_1)$ the measured hydroxyl number is somewhat lower than expected, which might be explained by the more compact structure of this sample with very short oligo-PO segment (DP_n(PPO) = 1.2), resulting in higher hydroxyl group density. This in turn can lead to incomplete conversion in the titration procedure due to sterical limitations. This explanation is supported by the similar behavior observed for unmodified polyglycerols, for which the end group titration method always resulted in molecular weights considerably lower than expected from other characterization techniques.

Thermal Behavior. In recent work we reported on the esterification of polyglycerol with rigid mesogenic units, which caused a strong increase of the glass transition temperature (T_g).[15] This increase is related to the liquid crystalline order of the materials induced by the mesogens. In the case of the propoxylation, it is an intriguing question as to how the oligo-PO segments affect the flexibility, i.e., the T_g of the hyperbranched polymer, since the PPO segments can be viewed as spacer units introduced between the hyperbranched scaffold and the hydroxyl end groups, leading to a decrease of the functional group density. In contrast to common end-functionalization techniques for hyperbranched polymers, the propoxylation does not affect the hydroxyl functionality of the polymers.

All polyglycerols with oligo-PO segments were investigated by DSC with respect to the T_g's. In the last column of Table 2 the respective data are given. The T_g's of unfunctionalized polyglycerols are in the range

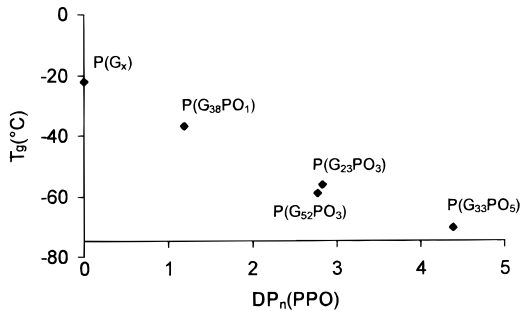

Figure 6. Glass transition temperatures (T_g) versus the degree of polymerization of PPO per hydroxyl group of the polyglycerol core (PG); abscissa intersects at T_g of PPO, −75 °C.

−20 to − 25 °C.[3] Linear PPO exhibits a T_g around −75 °C.[16] Noteworthy, only in the case of the lowest degree of polymerization of PO ($P(G_{38}PO_1)$), it is possible to observe two T_g's: one for the polyglycerol, decreased to −37 °C, and a second one for PPO at −72 °C, pointing to a nanophase separation due to clustering of the polar end groups.

For all other samples, one single T_g is observed, which gradually decreases with increasing length of the PPO block attached, approaching the T_g of linear PPO at −72 °C. In Figure 6 the T_g is plotted versus the block lengths, demonstrating this asymptotic behavior. In summary, the flexibility of polyglycerol is enhanced considerably by attachment of the oligo-PO blocks, approaching the T_g of PPO already at an arm length of 5 PO units.

Conclusions

Novel polyether multiarm star-block copolymers have been prepared by anionic ring-opening multibranching polymerization of glycidol, followed by anionic polymerization of propylene oxide in a one-pot procedure. The degree of polymerization of both the hyperbranched block and the linear segments attached can be controlled by the ratio of initiator:glycidol:propylene oxide. Molecular weights M_n of the polyglycerol cores employed range between 1800 and 4000 (DP_n, i.e., hydroxyl functionality: 23 to 52); molecular weights of the resulting block copolymers are in the range 5000−12 000 g/mol. A detailed assignment of the NMR spectra of the stars was achieved and permitted to calculate the molecular weights of the polymers. Characterization by SEC evidenced that the polydispersity of the hyperbranched polymers remained narrow after grafting of the oligo-PO segments. VPO and hydroxyl number determination were carried out to obtain molecular weights from two independent methods and showed excellent agreement with the results calculated from NMR.

Attachment of the oligo(propylene oxide) blocks represents a convenient method to tailor the polarity of the hyperbranched polyether from hydrophilic to hydrophobic without reducing the number of functional groups available for further modifications. Furthermore, by variation of the block lengths between 1 and 5, the flexibility of the hyperbranched scaffold can be varied in such manner that the T_g's range between that of polyglycerol and linear PPO.

In summary, it has been demonstrated that a convenient two-step one-pot reaction leads to a novel type of PO-terminated hyperbranched polyether−polyol. It should be emphasized that these materials can be easily prepared on a multigram scale, which permits the exploration of a wide range of further functionalization reactions aiming at a variety of unusual macromolecular architectures. For instance, the synthesis and characterization of poly(ethylene oxide)-based multiarm star polymers with narrow polydispersity has been accomplished on the basis of the PO-terminated polyglycerols and is the subject of a subsequent publication.[13] Various other possibilities for derivatization of the secondary hydroxyl end groups are currently under investigation.

Acknowledgment. H.F. thanks the GDCh for support in the context of a Hermann-Schnell award.

References and Notes

(1) Vandenberg, E. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23* (4), 915.
(2) (a) Tokar, R.; Kubisa, P.; Penczek, S.; Dworak, A. *Macromolecules* **1994**, *27*, 320. (b) Dworak, A.; Walach, W.; Trzebicka, B. *Macromol. Chem. Phys.* **1995**, *196*, 1963.
(3) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.
(4) Hanselmann, R.; Hölter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790.
(5) Kim, Y. H. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1685.
(6) Hawker, C. J.; Chu, F. K. *Macromolecules* **1996**, *29*, 4370.
(7) Malmström, E.; Johansson, M.; Hult, A. *Macromol. Chem. Phys.* **1996**, *197*, 3199.
(8) Malmström, E.; Hult, A.; Gedde, U. W.; Liu, F.; Boyd, R. H. *Polymer* **1997**, *38*, 4873.
(9) Brenner, A. R.; Voit, B. I.; Massa, D. J.; Turner, S. R. *Macromol. Symp.* **1996**, *102*, 47.
(10) Bailey, F. R.; Koleske, J. V. Alkylene Oxides and Their Polymers. In *Surface Science Series*; Schick, M. J., Fowkes, F. M., Eds.; Marcel Dekker: New York, 1990; p 96.
(11) Reference 10, p 94.
(12) Lach, C.; Frey, H. *Macromolecules* **1998**, *31*, 2381.
(13) Knischka, R.; Lutz, P.; Sunder, A.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 315.
(14) Burgath, A.; Hanselmann, R.; Hölter, D.; Frey, H. *PMSE Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *77*, 166.
(15) Sunder, A.; Quincy, M.-F.; Mülhaupt, R.; Frey, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2928.
(16) Peyser, P. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; J. Wiley & Sons: New York, 1989; p VI/209.

MA991191X