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Synthesis and Thermal Behavior of Esterified Aliphatic Hyperbranched Polyether Polyols

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ABSTRACT: Hyperbranched polyglycerols ($DP_n = 23-83$; $M_w/M_n = 1.2-1.5$) as well as their propoxylated derivatives were esterified to different extents (23%−100%) with various carboxylic acids (C2 to C18, benzoic, biphenylcarboxylic, and benzoic acid). Composition and molecular weight of the hyperbranched polyether scaffolds were varied with absolute molecular weights (NMR) ranging from $M_n = 1800$ to 12 400 g/mol. Complete or partial esterification did not affect the narrow polydispersities of the hyperbranched polymers, which were in the range 1.2−1.5 for the esterified polyglycerol samples and 1.2−1.9 for the esterified propoxylated polyether polyols. The parameter a (fractional molecular weight increase) was introduced, which permitted to demonstrate that SEC separates the branched polymers according to hydrodynamic volume. Because of the narrow polydispersity, the samples could be studied systematically by DSC, showing that the flexibility, i.e., T_g, of the hyperbranched polymers is controlled mainly by two factors: (i) the extent of hydrogen bonding and (ii) the formation of order (mesophases, crystallization), which raises the T_g. T_g's of the esterified polyether polyols were in the range −58 to −22 °C, showing the scope and limitations of tailoring the thermal properties of hyperbranched polymers by means of derivatization.

Introduction

Both dendrimers, perfectly branched macromolecules and the randomly branched hyperbranched polymers are usually unable to crystallize due to their highly branched topology.[1] However, crystallization can be induced by the attachment of long alkyl chains to the cascade-branched molecular scaffold. For poly(propylenimine) dendrimers, this has been investigated by Meijer et al.,[2] who showed that these molecules, when substituted with long alkyl chains, form layered bulk structures, the branched core being expelled from the crystalline domains.

For hyperbranched polymers, to date crystallization has only been studied to a very limited extent. Hult et al. observed crystallization for aliphatic polyesters bearing alkyl chains with more than 12 carbons attached to the hyperbranched scaffold.[3]

With respect to potential applications for hyperbranched polymers, e.g., in coatings or as rheology modifiers, the glass transition temperature (T_g) represents a crucial parameter for the materials properties. Theoretical considerations for the thermal behavior of dendrimers showed that the T_g of a polarly functionalized cascade branched molecule mainly depends on the interaction of the end groups.[4] In contrast to linear polymers, their influence on the T_g does not vanish with increasing molecular weight, since the number of end groups depends on the degree of polymerization.

Several authors have described the influence of derivatization of hyperbranched molecules on their T_g.[3,5−8] In general, a decrease of the T_g was observed when the polymer was modified hydrophobically and an increase when polar groups were introduced. However, more detailed studies to date have been impeded by the broad polydispersities exhibited by hyperbranched polymers prepared by random polycondensation of AB_m monomers ($M_w/M_n > 3$).[1] In addition, these materials are likely to contain low molecular weight cyclic fractions.[9] Thus, softening effects caused by low molecular weight fractions cannot be excluded.

Recently, we described a strategy for the controlled synthesis of hyperbranched polyglycerols on the basis of a chain-growth reaction, i.e., the base-catalyzed ring-opening multibranching polymerization of glycidol (ROMBP).[10] With this technique, it is possible to obtain aliphatic polyether polyols with narrow polydispersities ($M_w/M_n < 1.5$, mostly < 1.3), controlled molecular weights up to 8000 g/mol, and hydroxyl functionality in the range 10−100. The highly flexible polyether structure ($T_g \sim -22$ °C) renders the polymers ideal compounds for a systematic study of the thermal and crystallization behavior of hyperbranched polymers upon derivatization with crystallizable substituents of varying size. In further work we have demonstrated that the polarity and flexibility of the hyperbranched polyglycerol can be varied, maintaining the overall functionality by "capping" polyglycerol with short oligo(propylene oxide) segments, which leads to multiarm block structures with very low T_g's between −37 and −71 °C.[11]

Esterification of polyglycerol with suitable carboxylic acids creates unusual phase-transfer properties, i.e., unimolecular inverted micelle-like behavior.[12] Furthermore, broad nematic liquid crystalline phases are observed upon esterification of the end groups with mesogenic acids.[13] In the current study we systematically investigate the thermal properties of end-functionalized hyperbranched polyglycerols, using samples of different molecular weights as well as the hydrophobically modified propoxylated polyglycerols. Partial and complete esterification with carboxylic acids of varying size was employed. Different esterification routes have been used. Thermal properties, i.e., glass transition and crystallization, of all samples have been investigated and compared with respect to (i) molecular weight, (ii) nature of the hyperbranched scaffold, (iii) alkyl substituent attached, and (iv) degree of substitution.

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Experimental Part

Materials. Preparation of the hyperbranched polyglycerols and capping with oligo(propylene oxide) segments was carried out using procedures described elsewhere.[10,11] All other reagents were purchased from Aldrich or Fluka and purified by standard procedures.

Syntheses. *1. Esterification via Acetic Anhydride.* In a typical experiment, 1.0 g of polyglycerol $\mathrm{P(G_{52})}$ was dissolved in 50 mL of a 1:1 mixture of pyridine/acetic anhydride and refluxed for 1 h. The volatiles were then removed under reduced pressure. The residue was dissolved in chloroform and washed three times with diluted aqueous acid. After drying of the organic layer over anhydrous $MgSO_4$ and filtration and removal of the solvent, 1.4 g of $\mathrm{P(G_{52}C2_{0.8})}$ was obtained as a yellowish viscous oil.

2. Esterification of Polyether Polyols via Acyl Chlorides: Exemplified Procedure for the Preparation of Sample $P(G_{84}\text{-}C16_{0.6})$. To a solution of 10.1 g (136 mmol of OH groups) of dried hyperbranched polyglycerol $\mathrm{P(G_{84})}$ and 0.5 mL of *N*-methylimidazole as catalyst in 200 mL of anhydrous pyridine, a solution of 25 mL (83 mmol, 0.6 mol equiv per OH group) of freshly distilled palmitoyl chloride in 100 mL of anhydrous toluene was added slowly at 80 °C. The mixture was refluxed overnight. IR measurements indicated complete conversion of the acyl chloride into the ester. After cooling to room temperature, 13 g of K_2CO_3 was added. Subsequently, 90% of the pyridine was distilled off. To remove remaining pyridine, 500 mL of degassed toluene was slowly added under distillative conditions. Inorganic salts were filtered off, and toluene was completely removed under vacuum. In case residues of free carboxylic acid were detected by ^{1}H NMR, the polymer was purified additionally by dialysis in chloroform, using a benzoylated cellulose membrane (MWCO 1000 g/mol). The esterified polyglycerols were obtained as waxy solids for C12 and C16 alkyl chains and as viscous oils for C8 and C11 alkyl chains.

3. Esterification via Free Carboxylic Acid. A solution of 1.5 g of propoxylated polyglycerol $\mathrm{P(G}_x\mathrm{PO}_y\mathrm{)}$, the calculated stoichiometric amount of carboxylic acid, and 0.1 g of *p*-toluenesulfonic acid was refluxed in 150 mL of toluene on a Dean–Stark trap until water evolution ceased (typically overnight). The reaction mixture was washed three times with a saturated solution of K_2CO_3 and NaCl. After filtration over anhydrous $MgSO_4$, toluene was removed, and the esterifed propoxylated polyglycerol $\mathrm{P(G}_x\mathrm{PO}_y\mathrm{R}_z\mathrm{)}$ was obtained as viscous oil, which in the case of the stearic acid esters crystallized slowly.

Characterization. NMR. ^{1}H NMR and ^{13}C NMR spectra were recorded in d_4-methanol (polyglycerols, propoxylated polyglycerols) and in d_1-chloroform or d_6-benzene (esterified polyethers) at concentrations of 100 g/L on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively.

Assignment of the ^{1}H NMR signals for the different substituents: acetic acid (C2): δ ($CDCl_3$) = 2.0 (CH_3); octanoic acid (C8): δ (C_6D_6) = 2.3 ($\mathrm{C}H_2\mathrm{COOP(G)}$), 1.7 (($\mathrm{C}H_2\mathrm{CH_2CO_2P(G)}$), 1.3 (($\mathrm{C}H_2)_4$), 1.0 ($\mathrm{C}H_3$); undecenoic acid (C11): δ ($CDCl_3$) = 5.8 ($\mathrm{CH_2{=}C}H$), 4.9 ($\mathrm{C}H_2\mathrm{{=}CH}$), 2.3 ($\mathrm{C}H_2\mathrm{COOP(G)}$), 2.0 ($\mathrm{CH_2{=}CHC}H_2$), 1.6 ($\mathrm{C}H_2\mathrm{CH_2CO_2P(G)}$), 1.3 (($\mathrm{C}H_2)_5$); dodecanoic acid (C12): δ ($CDCl_3$) = 2.3 ($\mathrm{C}H_2\mathrm{COOP(G)}$), 1.6 ($\mathrm{C}H_2\mathrm{CH_2CO_2P(G)}$), 1.3 (($\mathrm{C}H_2)_8$), 0.9 ($\mathrm{C}H_3$); hexadecanoic acid (C16): δ (C_6D_6) = 2.3 ($\mathrm{C}H_2\mathrm{COOP(G)}$), 1.7 (($\mathrm{C}H_2\mathrm{CH_2CO_2P(G)}$), 1.3 (($\mathrm{C}H_2)_{12}$), 1.0 ($\mathrm{C}H_3$); octadecanoic acid (C18): δ ($CDCl_3$) = 2.3 ($\mathrm{C}H_2\mathrm{COOP(G)}$), 1.6 ($\mathrm{C}H_2\mathrm{CH_2CO_2P(G)}$), 1.3 (($\mathrm{C}H_2)_{14}$), 0.9 ($\mathrm{C}H_3$); benzoic acid (Bz): δ ($CDCl_3$) = 8.0 (2H), 7.5 (1H), 7.3 (2H); 4-biphenylcarboxylic acid (Bp): δ ($CDCl_3$) = 8.1 (2H), 7.4 (3H), 7.6 (4H).

SEC. The polymers were dissolved in DMF at a concentration of 10 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. If the esterified polyethers were not soluble in DMF, SEC was carried out on a Knauer microgel set A22 at 35 °C, using chloroform as an eluent and polystyrene standards for calibration

DSC. Measurements were carried out on a Perkin-Elmer 7 series thermal analysis system in the temperature range −100 to 100 °C at heating rates of 3, 5, and 10 K/min. Melting points are extrapolated to heating rate 0. The melting point of indium (156 °C) was used for calibration.

Polarized Light Microscopy. An Olympus Vanox AH2 research microscope with a Linkam THM 600/TMS 90 hot stage with a cooling device was used.

Results and Discussion

Figure 1 shows the general synthetic scheme used for the preparation of the esterified polyether polyol samples. In the case of unmodified polyglycerol, aliphatic carboxylic acids ranging from acetic acid (C2) to palmitic acid (C16) have been employed as well as 10-undecenoic acid (C11). For the polyglycerols modified with oligo(propylene oxide) segments, attachment of varying fractions of stearic acid (C18) as well as benzoic acid (Bz) and 4-biphenylcarboxylic acid (Bp) has been investigated. For the esterification of polyglycerols two different methods were employed. To obtain the polyacetate (C2), the polymer was simply refluxed in a 1:1 mixture of pyridine/acetic anhydride. The higher alkyl esters (C8, C11, C12, C16) were synthesized by reaction with the acyl chlorides in pyridine. It should be mentioned that there is only a limited choice of suitable solvents for the transformation due to the high polarity of the polyglycerols. Pyridine turned out to be most convenient with respect to complete removal after the synthesis by acidic washing or azeotropic distillation with toluene. In case NMR indicated remains of free carboxylic acid due to hydrolysis of acyl chloride by traces of water in the polymer, an additional purification step was carried out by dialysis, using a benzoylated cellulose membrane. Purification by chromatographic methods was also possible but proved to be more tedious. The degree of substitution could be controlled by the OH/acyl chloride ratio. This indicates accessibility of all OH groups for functionalization, similar to low molecular weight compounds. We also attempted to carry out the esterification heterogeneously in toluene under acidic catalysis with the free carboxylic acid (polyglycerol is insoluble in toluene). However, since the heterogeneous reaction is very slow, water elimination from polyglycerol led to ether cross-linked products.

When the propoxylated polyglycerols were used as substrate for esterification, a much wider range of organic solvents could be used for the derivatization reactions due to the hydrophobic modification of the scaffold. In this case, we chose the acid-catalyzed esterification with free carboxylic acid unter constant water removal conditions in toluene as most convenient synthetic pathway. In the case of stearic (C18) and benzoic acid (Bz), the degree of substitution was controlled by the OH/carboxylic acid ratio with conversions exceeding 95%. When the sterically more demanding biphenylcarboxylic acid (Bp) was used for esterification, reaction times were considerably longer (5 days and more), and the degree of substitution even after prolonged reaction times did not exceed 70%. This is in accordance with results reported for esterification of polyglycerol with bulky mesogenic acids recently.[13]

In Table 1 all samples prepared are listed. Samples are designated using the following abbreviation scheme: $\mathrm{P(G}_x\mathrm{)}$, $\mathrm{P(G}_x\mathrm{PO}_y\mathrm{)}$, $\mathrm{P(G}_x\mathrm{R}_z\mathrm{)}$, $\mathrm{P(G}_x\mathrm{PO}_y\mathrm{R}_z\mathrm{)}$. G_x marks

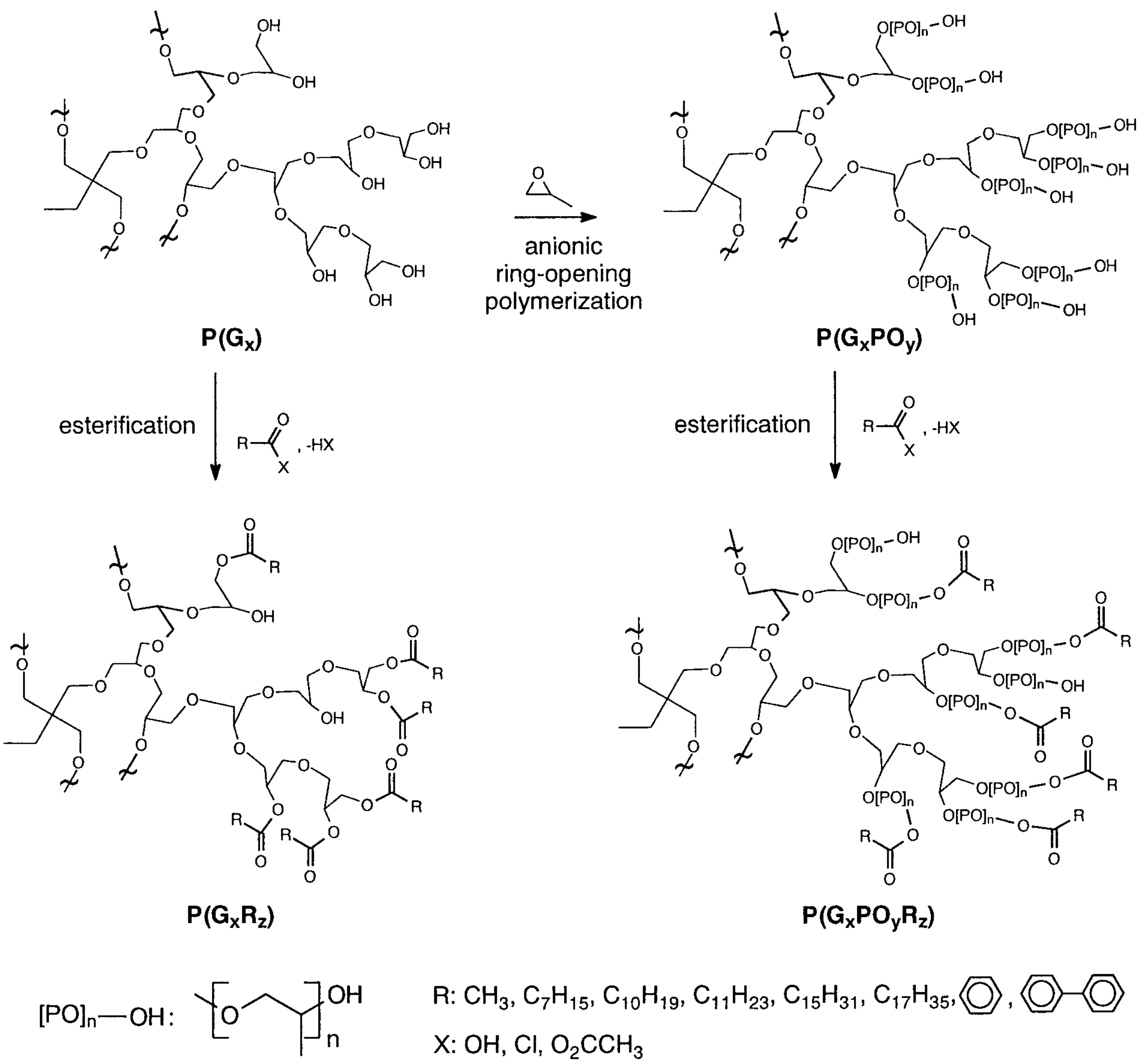

Figure 1. Esterification of polyglycerols and poly(glycerol-*b*-propylene oxides).

the degree of polymerization for the polyglycerol core, and PO$_y$ gives the degree of polymerization of propylene oxide per end group. R$_z$ names the type of ester substituent (R) and the degree of functionalization *f* per end groups (*z*). For example, the abbreviation P(G$_{33}$PO$_5$-C18$_{0.7}$) describes a sample with a polyglycerol core consisting of 33 glycidol units, five propylene oxide units on average being attached to each hydroxyl group of this core. Seventy percent of the hydroxyl groups of the poly(propylene oxide) segments are esterified with stearic acid (C18). To simplify the further discussion, variables *x*, *y*, or *z* are used when describing similar samples; e.g., all C18 esterified propoxylated polyglycerols are designated P(G$_x$PO$_y$C18$_z$).

NMR Characterization. Molecular weights for the polyglycerols P(G$_x$) and the propoxylated polyglycerols P(G$_x$PO$_y$) were calculated from ^{13}C NMR and ^{1}H NMR as described previously.[10,11] Several different hyperbranched polyether scaffolds were used (Table 1), varying both molecular weights and polarity. Degrees of polymerization (and thus hydroxyl functionality) for the polyglycerol cores ranged from DP$_n$ = 23 to 83 (=*x*) and for the oligo(propylene oxide) segments from DP$_n$ = 3−5 (=*y*). Thus, molecular weights of the polyether polyols employed ranged between M_n = 4600 and 12 400. The degree of functionalization by esterification was calculated from ^{1}H NMR spectra, using the signal intensities of the polyether scaffold and the signal intensities of the substituents. Figure 2 shows representative ^{1}H NMR spectra of P(G$_{23}$C16$_{0.9}$) and P(G$_{52}$PO$_3$C18$_{0.6}$). The methine protons of the esterified secondary hydroxyl group can be assigned at 5.2 ppm for polyglycerols P(G$_x$) and at 5.0 ppm for the propoxylated polyglycerol samples P(G$_x$PO$_y$). The methylene protons of the esterified primary hydroxyl group of polyglycerol show signals at 4.1 and 4.3 ppm. All other protons of methylene units of the polyether scaffold exhibit a broad signal between 3.0 and 4.0 ppm. The methyl group of the poly(propylene oxide) arms of the propoxylated polyglycerols P(G$_x$PO$_y$) resonates at 1.2 ppm. Remaining hydroxyl protons of these modified polyether polyols, in general, are not observed in CDCl$_3$ or benzene. The other signals originate from the substituents. (A detailed assignment for each substituent is given in the Experimental section.) Experimental results from ^{1}H NMR are listed in Table 1. In case a degree of substitution of 100% was achieved, the disappearance of the OH groups was confirmed by the absence of OH bands above 3200 cm^{-1} in the IR spectra (P(G$_x$R$_{1.0}$), P(G$_{33}$PO$_5$C18$_{1.0}$). The degrees of substitution achieved showed little deviation from the

Table 1. Characterization Data of the Underivatized $P(G_x)$ and $P(G_xPO_y)$, the Esterified Polyglycerols $P(G_xR_z)$, and the Esterified Propoxylated Polyglycerols $P(G_xPO_yR_z)$ (from NMR)

	underivatized sample		derivatized sample			
sample	DP_n G; PO	M_n	acid	f,[a] %	M_n	α_{abs}[b]
$P(G_{52}C2_{1.0})$	52	4000	C2	100	6200	
$P(G_{83}C8_{0.4})$	83	6300	C8	41	10600	
$P(G_{44}C11_{1.0})$	44	3400	C11[c]	100	10700	
$P(G_{44}C12_{1.0})$	44	3400	C12	100	11400	
$P(G_{23}C16_{0.6})$	23	1800	C16	56	4900	
$P(G_{23}C16_{0.9})$	23	1800	C16	87	6600	
$P(G_{83}C16_{0.6})$	83	6300	C16	56	17300	
$P(G_{33}PO_5C18_{0.2})$	33; 4.6	11000	C18	23	13400	0.22
$P(G_{33}PO_5C18_{0.7})$	33; 4.6	11000	C18	68	17400	0.58
$P(G_{33}PO_5C18_{1.0})$	33; 4.6	11000	C18	100	20200	0.84
$P(G_{52}PO_3C18_{0.6})$	52; 3.0	12400	C18	58	21100	0.70
$P(G_{33}PO_5Bp_{0.3})$	33; 4.6	11000	Bp[d]	33	13400	0.22
$P(G_{23}PO_3Bp_{0.7})$	23; 3.0	5700	Bp[d]	67	8600	0.51
$P(G_{23}PO_3Bz_{0.5})$	23; 3.0	5700	Bz[e]	50	7000	0.23

[a] Degree of substitution calculated from ^1H NMR. [b] Fractional increase of molecular weight $\alpha = M_n(\text{product})/M_n(\text{educt})-1$. [c] 10-Undecenoic acid. [d] 4-Biphenylcarboxylic acid. [e] Benzoic acid.

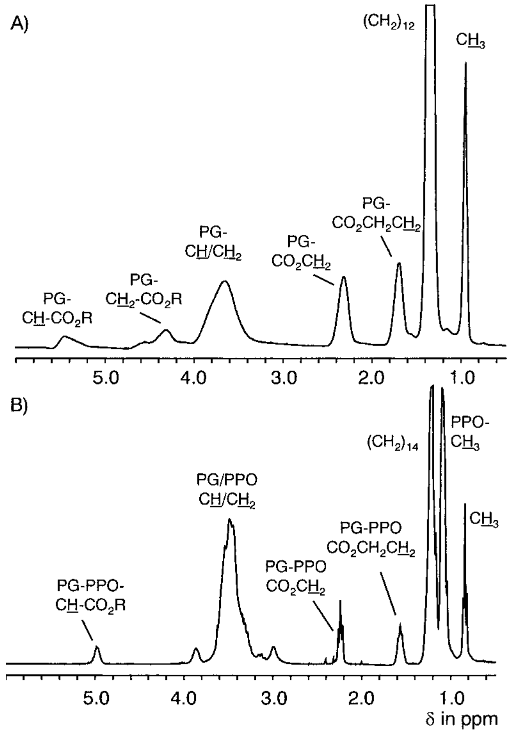

Figure 2. ^1H NMR spectra of (A) $P(G_{23}C16_{0.9})$ and (B) $P(G_{52}PO_3C18_{0.6})$.

Table 2. SEC Characterization of the Esterified Polyglycerols $P(G_xR_z)$ and the Esterified Propoxylated Polyglycerols $P(G_xPO_yR_z)$

	underivatized sample		derivatized sample		
sample	M_n[a]	M_w/M_n	M_n[b]	M_w/M_n	α_{SEC}[c]
$P(G_{52}C2_{1.0})$	23900	1.2	7100[a]	1.2	
$P(G_{83}C8_{0.4})$	26800	1.5	7400	1.5	
$P(G_{44}C11_{1.0})$	15200	1.2	10800	1.3	
$P(G_{44}C12_{1.0})$	15200	1.2	8400	1.3	
$P(G_{23}C16_{0.6})$	9300	1.2	4100	1.3	
$P(G_{23}C16_{0.9})$	9300	1.2	4900	1.2	
$P(G_{83}C16_{0.6})$	26800	1.5	6600	1.3	
$P(G_{33}PO_5C18_{0.2})$	15900b	1.7	16200	1.9	0.02
$P(G_{33}PO_5C18_{0.7})$	15900b	1.7	21800	1.6	0.37
$P(G_{33}PO_5C18_{1.0})$	15900b	1.7	24400	1.5	0.53
$P(G_{52}PO_3C18_{0.6})$	7800b	1.2	12200	1.2	0.56
$P(G_{33}PO_5Bp_{0.3})$	15900b	1.7	15900	1.8	0.00
$P(G_{23}PO_3Bp_{0.7})$	4600b	1.2	5700	1.2	0.24
$P(G_{23}PO_3Bz_{0.5})$	4600b	1.2	5000	1.2	0.07

[a] Measured in DMF (45 °C, PPO standards). [b] Measured in $CHCl_3$ (30 °C, PS standards). [c] Fractional increase of molecular weight $\alpha = M_n(\text{product})/M_n(\text{educt})-1$.

targeted values, with the exception of biphenylcarboxylic acid-substituted samples.

Since characterization of hyperbranched polymers remains a challenging issue, NMR and SEC measurements will be discussed in some detail in the following section.

SEC Measurements. Generally, molecular weight characterization of hyperbranched polymers possessing a large number of hydroxyl end groups is problematic and can lead to erroneous results, if common linear standards are employed.[14] Although the hydrodynamic volume of the compact hyperbranched macromolecules is smaller than for linear chain polymers, interaction of the highly polar end groups with solvent and/or column often leads to strong overestimation of molecular weights. However, it has been demonstrated recently that SEC carried out in DMF with poly(propylene oxide) standards is a suitable method for the characterization of polyglycerol samples,[10] since there is a systematic overestimation of molecular weights of a factor of approximately 5 compared with the results from independent, absolute methods (vapor pressure osmometry, NMR). In the case of the propoxylated species, chloroform could be used as an eluent. Surprisingly, the deviation between the apparent molecular weight obtained with polystyrene calibration and the absolute values calculated from NMR and measured by VPO is smaller for the propoxylated samples than for unmodified polyglycerol. The polyglycerol samples used exhibit apparent polydispersities below 1.5, with the propoxylated polyglycerols still below 1.7.[11]

Upon esterification of the highly polar polyglycerol samples a drastic change of their solubility behavior occurs. The samples esterified with longer carboxylic acids are not soluble in DMF any more. Therefore, all esterified polyglycerol samples $P(G_xR_z)$, except for the polyacetate $P(G_{52}C2_{1.0})$, were measured in chloroform with PS calibration. Unexpectedly, the apparent molecular weights found were close to the absolute values calculated from NMR (Table 2). Furthermore, the measurements confirm the narrow molecular weight distributions of the polyglycerols used as scaffolds.

Since the propoxylated polyglycerols and their esterified derivatives can be measured in the same eluent, additional information can be obtained. On one hand, as observed for the esterified polyglycerols, polydispersities remain almost unchanged after esterification of the propoxylated polymers $P(G_xPO_yR_z)$. Remarkably, the apparent M_n values for both substrates and products are quite close to the absolute values calculated from NMR. To investigate whether molecular weights from SEC show a systematic deviation from the absolute values, the parameter a is defined that gives the fractional increase of the molecular weight, according to eq 1 (values are listed in Table 1):

$$a = \frac{M_n(\text{product})}{M_n(\text{educt})} - 1 \tag{1}$$

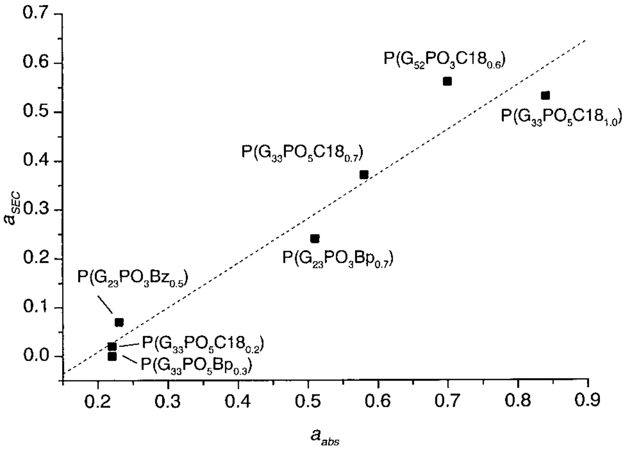

Figure 3. Correlation of fractional molecular weight increase from NMR and GPC for $P(G_xPO_yR_z)$.

The values of a from both NMR data (absolute molecular weights) and SEC are listed in the last column of Tables 1 and 2, respectively. In Figure 3, a_{SEC} is plotted versus a_{abs} for all $P(G_xPO_yR_z)$ samples. Interestingly, all values are located around one straight line, independent of the hyperbranched scaffold size, scaffold composition, substituent, and degree of functionalization. On the basis of these results, we conclude that the SEC columns fractionate these compounds according to hydrodynamic volume. Assuming similar density of the polymers investigated, this means separation according to molecular weight, which explains the linear relationship observed. In other words, the different topology and composition of the partially esterified polyether polyols does not lead to a change of the density of the structure; i.e., the ratio of molecular weight and hydrodynamic volume remains constant. Thus, in the investigated molecular weight range SEC can be used for the characterization of hyperbranched polyether polyols and their esters, when the apparent molecular weights are interpreted carefully and absolute molecular weights are accessible from independent methods for some of the compounds.

Thermal Behavior. The main objective of this work was a systematic study of the thermal behavior of esterified hyperbranched polymers, aiming at the influence of the parameters (i) molecular weight, (ii) nature of the hyperbranched scaffold, (iii) alkyl substituent attached, and (iv) degree of substitution. The results of the DSC measurements of all samples are listed in Table 3. A striking difference between polyglycerol and polyglycerol samples bearing oligo(propylene oxide) segments is noted immediately: generally, esterification of polyglycerol leads to a decrease of the glass transition temperature (T_g). On the contrary, a general increase of the T_g is observed for all propoxylated polyglycerols $P(G_xPO_yR_z)$ upon esterification.

The decrease of T_g in the former case appears to be independent of the scaffold size (i.e., the degree of polymerization) but depends to some extent on the length of the alkyl chain attached. If the chains attached induce crystalline order, the T_g drop is considerably smaller than for amorphous samples. For example, esterification of $P(G_{83})$ with 40% octanoic acid leads to a drop of the T_g from −21 to −39 °C ($P(G_{83}C8_{0.4})$; on the other hand, complete esterification of $P(G_{44})$ with dodecanoic acid hardly has an effect on the T_g (sample $P(G_{44}C12_{1.0})$), since the resulting material crystallizes. Complete esterification with acetic acid (sample $P(G_{52}C2_{1.0})$) leads to a T_g that is 9 K lower than that of the unmodified polyglycerol.

As reported previously, the T_g of −22 °C of the unsubstituted polyglycerols is considerably lowered upon attachment of oligo(propylene oxide) segments and approaches the T_g of poly(propylene oxide) at −75 °C with increasing length of the apolar, flexible PPO segments.[11] This is explained by a lowering of the density of the hydroxyl groups, causing a decrease of hydrogen bonding and a concurrent increase of the length of the flexible end groups, leading to enhanced flexibility of the polyether. However, when longer saturated fatty acids are used for esterification, the alkyl chains crystallize, thereby forcing the hyperbranched polyether core into a more rigid structure, causing an increase of the T_g. Thus, in the case of the esterified polyglycerols clearly two effects compete: reduced hydrogen bonding, lowering the T_g on one hand, and the tendency to crystallize with increasing alkyl chain length, raising the T_g somewhat on the other hand. We observed the maximum drops of T_g of −15 and −18 K for the samples $P(G_{44}C11_{1.0})$ and $P(G_{83}C8_{0.4})$. In both cases the scaffolds are hydrophobized with long alkyl chains, which are unable to crystallize.

For the propoxylated polyglycerols the situation is different, because intramolecular interaction due to hydrogen bonding is already lowered considerably by attachment of the apolar oligo(propylene oxide) segments, which represent the dominating structural element. For instance, $P(G_xPO_3)$ contains 70% propylene oxide and $P(G_xPO_5)$ 78%. The flexibility in this case is mainly determined by that of the poly(propylene oxide) segments; i.e., the T_g approaches the T_g of poly(propylene oxide).[11] When the end groups are esterified with stearic acid, the resulting further decrease in polarity by attachment of the alkyl chains has hardly any effect. However, the tendency of the long alkyl chains toward crystallization appears to be the dominating factor in this case, raising the T_g. Clearly, the effect depends on the degree of substitution, which is obvious from the comparison of the samples $P(G_{33}PO_5C18_{0.2})$ and $P(G_{33}PO_5C18_{0.7})$ and $P(G_{33}PO_5C18_{1.0})$, with T_g's of −58, −49, and −38 °C, respectively.

This behavior can be illustrated in a plot correlating the T_g drop (ΔT_g) for $P(G_xPO_yR_z)$ with the fractional molecular weight increase calculated from NMR (a_{abs}) as shown in Figure 4. For the stearic acid esters $P(G_xPO_yC18_z)$ and the benzoic ester $P(G_{23}PO_3Bz_{0.5})$ ΔT_g increases systematically with the fractional increase of the molecular weight. The latter is an indirect indicator for the degree of esterification. Esterification with biphenylcarboxylic acid $P(G_xPO_yBp_z)$ shows a stronger influence on T_g, although no crystallization is observed.

Crystallization. Hyperbranched polyglycerols in general do not crystallize. The attachment of small poly(propylene oxide) segments enhances the flexibility without inducing crystallinity. However, attachment of an aliphatic carboxylic acid with at least 12 carbon atoms induces crystallization. A typical DSC diagram obtained after repeated heating/cooling cycles is shown in Figure 5. Interestingly, in the cases of the C16 and the C18 esters the DSC curves showed a characteristic double peak, from which the more intensive upper peak was confirmed to be the melting peak by microscopy. It is known that multifunctional esters of long fatty acids tend to form ordered mesophases before crystallization,

Table 3. Glass Transition Temperatures T_g, Melting Temperatures T_m, and Melt Enthalpies ΔH_m for Esterified Polyglycerols $P(G_xR_z)$ and Poly(glycerol-*b*-propylene oxides) $P(G_xPO_yR_z)$

	underivatized sample	derivatized sample					
sample	T_g, °C	T_g, °C	ΔT_g, K	T_m, °C	ΔH_m, J/g	T_g/T_m[a]	comments
$P(G_{52}C21_{1.0})$	−23	−32	−9	nc[b]			
$P(G_{83}C8_{0.4})$	−21	−39	−18	nc			
$P(G_{44}C11_{1.0})$	−25	−40	−15	nc			
$P(G_{44}C12_{1.0})$	−25	−27	−2	8	44	0.88	
$P(G_{23}C16_{0.6})$	−23	−25	−2	48	78	0.76	double peak
$P(G_{23}C16_{0.9})$	−23	−26	−3	48	87	0.77	double peak
$P(G_{83}C16_{0.6})$	−21	−31	−10	46	76	0.76	double peak
$P(G_{33}PO_5C18_{0.2})$	−71	−58	+13	14	9	0.75	double peak
$P(G_{33}PO_5C18_{0.7})$	−71	−49	+22	22	41	0.76	double peak
$P(G_{33}PO_5C18_{1.0})$	−71	−38	+33	23	51	0.79	double peak
$P(G_{52}PO_3C18_{0.6})$	−59	−32	+27	22	43	0.82	double peak
$P(G_{33}PO_5Bp_{0.3})$	−71	−47	+24	nc			
$P(G_{23}PO_3Bp_{0.7})$	−56	−22	+34	nc			
$P(G_{23}PO_3Bz_{0.5})$	−56	−40	+14	nc			

[a] Using T_m and T_g in K. [b] Noncrystalline.

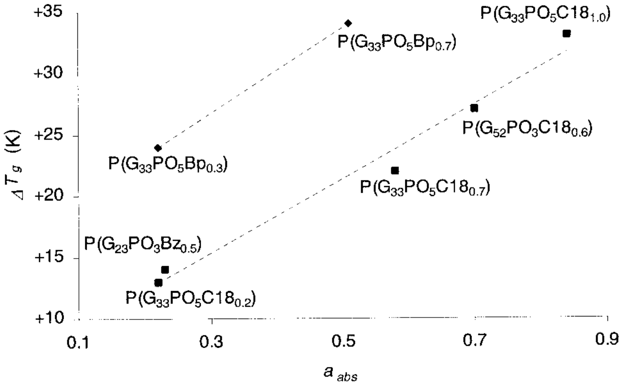

Figure 4. Correlation of ΔT_g and fractional molecular weight increase from NMR for $P(G_xPO_yR_z)$.

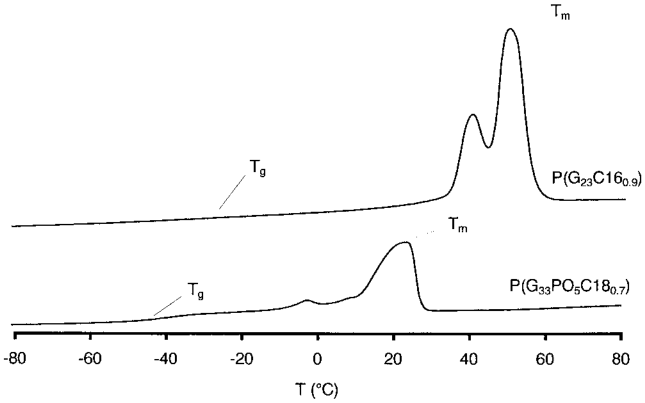

Figure 5. DSC diagrams of $P(G_{23}C16_{0.9})$ and $P(G_{33}PO_5C18_{0.7})$. T_g in upper DSC trace visible in enhanced image.

which may explain this observation. Another explanation might be the presence of different types of crystallites. The double-peak structure in the DSC diagram is observed at all heating rates and also upon cooling. Because of the small temperature interval, we have not been able to study the nature of the first endotherm in detail. Further investigations are in progress.

As seen in Table 3, melting points T_m depend only weakly on the degree of functionalization. For instance, comparing the samples $P(G_{23}C16_{0.6})$ and $P(G_{23}C16_{0.9})$, a melting point of 48 °C was observed for both polymers with different degree of alkyl substitution. Similarly, in the case of the propoxylated series $P(G_{33}PO_5C18_z)$ ($z = 0.2$, 0.7, and 1.0) T_m only varies in the range 14−23 °C for the fully C18-substituted $P(G_{33}PO_5C18_{1.0})$ sample.

However, the degree of substitution does have a strong influence on the melting enthalpy (ΔH_m). The two polyglycerols functionalized with 60% C16 esters possess a ΔH_m of 77 J/g ($P(G_xC16_{0.6})$); an increase of the degree of functionalization to 90% leads to a ΔH_m of 87 J/g. The same effect is observed for the four C18-esterified propoxylated polyglycerols ($P(G_xPO_yC18_z)$); i.e., for the same scaffold $P(G_{33}PO_5)$ a systematic increase of ΔH_m occurs with increasing degree of functionalization. A comparison of unmodified polyglycerol with the propoxylated scaffold reveals that the ester $P(G_{52}PO_3C18_{0.6})$ exhibits only half of the melting enthalpy value of the similar ester $P(G_{23}C16_{0.6})$ without poly(propylene oxide) segments. This indicates that propoxylation not only does enhance the flexibility of the backbone but also impedes crystallization significantly. Coupling of the rigid biphenyl units did not lead to crystalline order.

It is well-known that for linear, crystallizable polymers there is an empirical correlation between T_g and T_m, since both are influenced by the same factors. Typically, linear block copolymers exhibit a T_g/T_m ratio above 0.8.[15] Looking at the values listed in Table 3, one might consider the esterified polyglycerols as block copolymer analogues with the unfunctionalized and dendritic units representing one and the esterified units the other block.

To further investigate the growth of crystallites, some of the samples were heated to the melt, cooled slowly, and annealed well below their melting points. It should be emphasized that all materials were homogeneous on the length scale of the light microscope; no phase separation was observed, as noted in the case of common hyperbranched polymers (e.g., polyesters esterified with fatty acids) of broader polydispersity.[16] In Figure 6 micrographs obtained from the polarized light microscopy (crossed polarizers) are shown for two representative samples ($P(G_{23}C16_{0.9})$ at 20 °C and $P(G_{52}PO_3C18_{0.6})$ at −10 °C). The micrographs clearly demonstrate that the esterified polyglycerol forms crystallites of about 20 μm size. The propoxylated species, however, forms crystallites of about 2 μm size under comparable conditions. Larger spherulites were not formed even under very slow cooling conditions. The introduction of highly flexible poly(propylene oxide) segments between the crystallization inducing ester substituent and the hyperbranched polyglycerol core disturbs crystal formation considerably.

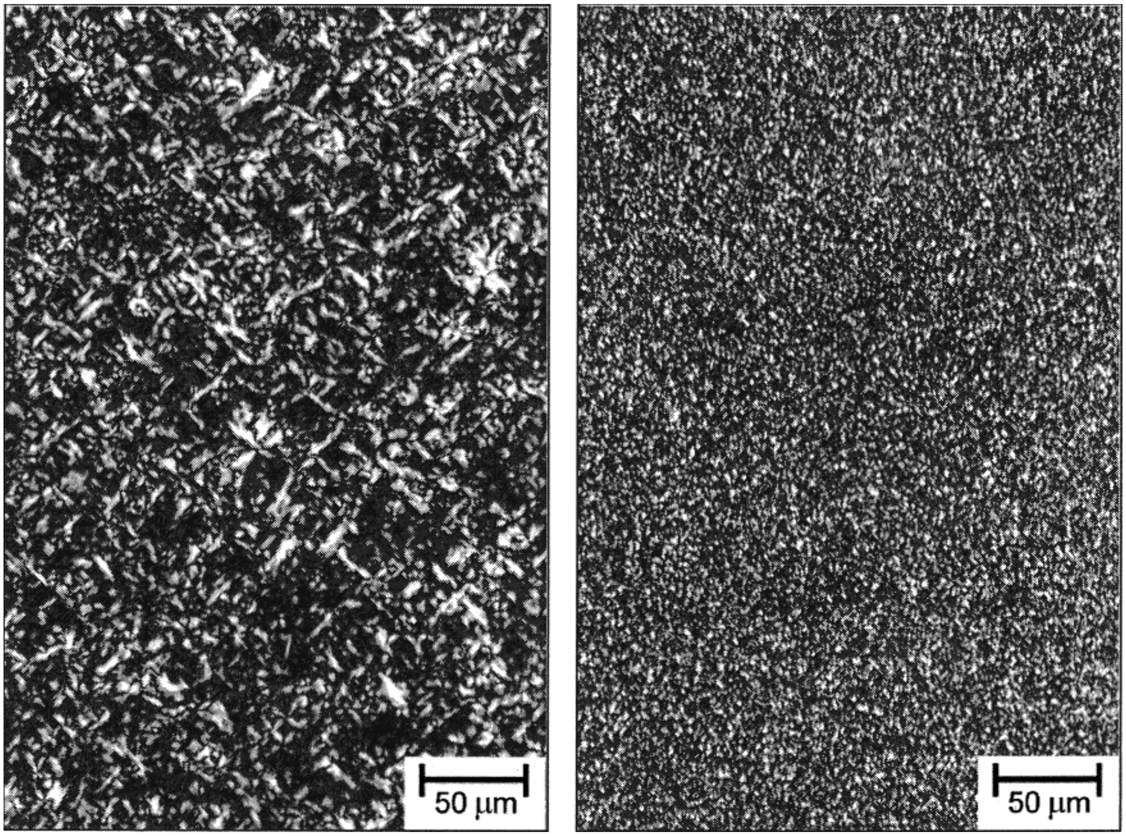

Figure 6. (A) P($G_{23}C16_{0.9}$) at 20 °C and (B) P($G_{52}PO_3C18_{0.6}$) at −10 °C; crossed polarizers.

Conclusion

Hyperbranched polyglycerols as well as their propoxylated derivatives have been esterified to different extents (20%−100%) with various carboxylic acids (C2 to C18, benzoic, biphenylcarboxylic). Three different synthetic approaches were used to covalently attach the acids onto the polyether scaffolds. Different compositions and molecular weights of the polyether scaffolds were used ranging in the degres of propoxylation from $DP_n = 0-5$ per hydroxyl group and in molecular weights from $M_n = 1800$ to 12 400 g/mol. Control of the reaction was achieved by the carboxylic acid/OH ratio employed. Only in the case of the bulky biphenylcarboxylic acid was a limiting degree of functionalization encountered.

The derivatization reaction did not affect the narrow polydispersities of the hyperbranched polyether structures, most esterified polyglycerols exhibiting apparent polydispersities M_w/M_n (SEC) considerably below 1.5. This rendered these compounds ideal materials for a systematic study of the thermal behavior of esterified hyperbranched polymers. Careful interpretation of the SEC results, using the parameter α (fractional molecular weight increase), offers valuable additional information on this type of polymer.

From the DSC measurements it was concluded that the flexibility, i.e., T_g, of a modified highly polar hyperbranched polymer with large number of hydroxyl end groups is controlled mainly by two factors: (i) hydrogen bonding of the end groups, increasing the rigidity of the molecules on one hand, and (ii) tendencies of the substituents to form higher ordered phases (mesophases, crystallization) on the other hand. To study this latter effect in more detail, polyglycerols with hydrophobic oligo(propylene oxide) segments were used as scaffolds, confirming that crystallization induced by the fatty esters raises the T_g.

The results of this study demonstrate scope and limitations of the tailoring of thermal properties of hyperbranched polyether polyols by means of derivatization. It is an important information that the degree of alkyl substitution has hardly any effect on T_m; however, there is a pronounced effect on the T_g. The versatile synthesis of the polyethers and their derivatives allows to control both functionality and solubility behavior. Flexibility and crystallization can then be further modified by a suitable choice of substituents. Further diffraction studies aiming at a detailed structural analysis are currently in progress.

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