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Synthesis and Thermal Properties of Well-Defined Amphiphilic Block Copolymers Based on Polyglycidol

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ABSTRACT: A series of amphiphilic block copolymers functionalized with three different alkyl side chains (alkyl chain length = C_{12}, C_{14}, and C_{16}) were synthesized and analyzed via NMR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The block copolymers were obtained in a four-step synthesis. In the first step ethoxy ethyl glycidyl ether (EEGE) and *tert*-butyl glycidyl ether (*t*BuGE) were sequentially polymerized via an anionic mechanism. In the next step, the acetal protection groups of EEGE repeating units were selectively removed and the hydroxyl groups obtained were reacted with alkyl isocyanates. Finally, the *tert*-butyl ether protection groups were removed. All steps of the synthesis were controlled via ^{1}H NMR spectroscopy, GPC, and DSC analyses. All block polymers showed three thermal transitions regardless of the chain length of the isocyanate used: a glass transition characteristic for the polyglycidol backbone and two endothermic peaks, associated with melting of the aliphatic side chains and subsequent breakdown of the hydrogen bonds due to the urethane groups. This thermal behavior suggests that diblock copolymers self-assemble into microdomains whose stability (existence) can be tuned with temperature.

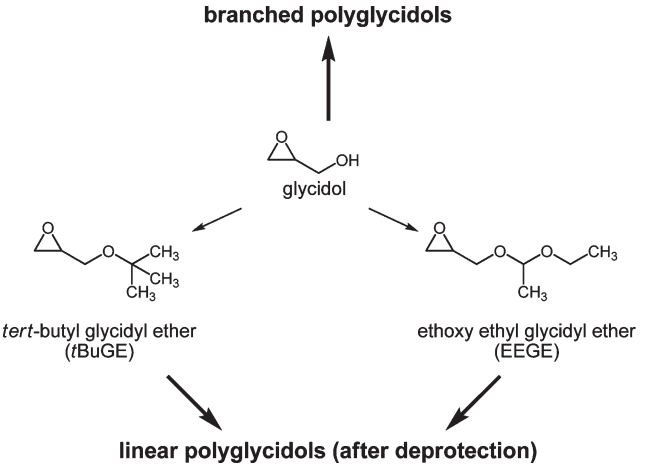
Introduction

Block copolymers based on glycidol can be synthesized with a variety of initiators. Although cationic polymerization with Lewis acids is known in the literature,[1,2] most publications focus on anionic ring-opening polymerization of glycidol or protected glycidols. The polymerization can be initiated either by alkali metal hydroxides[3,4] or by alkoxides.[5] Polymerization of unprotected glycidol leads to branched polyether structures,[3,6−8] while linear polyglycidols are obtained via polymerization of protected glycidols followed by the removal of the protection group (Scheme 1).[4,9]

Most suitable and frequently used protection groups for glycidol are tertiary butyl ether groups as in *tert*-butyl glycidyl ether (*t*BuGE) or acetal protection groups as in ethoxy ethyl glycidyl ether (EEGE). EEGE, the most used glycidol protected monomer, was first synthesized by Fitton et al.[10] Both monomers were polymerized via anionic mechanisms; the removal of the protection groups is achieved under mild acidic conditions for the acetal protection groups and strong acidic conditions for the tertiary butyl ether groups.

Since anionic polymerization of protected glycidols is a living polymerization, the microstructure of the polymer can be adjusted. Polymers with a random distribution of repeating units are obtained via polymerization of a mixture of the monomers while block copolymers are obtained by sequential addition of the monomers to the initiator. Although random copolymers made from EEGE and *t*BuGE were prepared in our group before,[11] it was not possible to selectively remove the acetal protection groups. The reason for this is that in a random copolymer after removal of the acetal protection groups under mild acidic conditions repeating units with tertiary butyl ether groups are randomly surrounded by glycidol units. The hydroxymethyl groups of glycidol repeating units interact with water via hydrogen bonds and accelerate the removal of adjacent *tert*-butyl ether groups via a zip reaction (Scheme 2). However, P*t*BuGE under these mild acidic conditions does not hydrolyze due to the hydrophobicity of the tertiary butyl groups.

Scheme 1. Synthesis of Linear and Branched Polyglycidols



In a block copolymer−P(EEGE)-*b*-P(*t*BuGE)−it should be possible to selectively remove first the acetal protection groups, as the *tert*-butyl groups form a closed hydrophobic domain excluding water and preserving cleavage of the *tert*-butyl ether protection groups. Once this selective deprotection is achieved, the hydroxyl groups can be functionalized, which in principle offers the possibility to produce a wide variety of functional polyethers via polymer analogous reaction.[12]

In the present work diblock copolymers based on linear polyglycidols were prepared comprising a hydrophilic polyglycidol block and a hydrophobic block consisting of a polyether backbone modified with alkyl side chains. The alkyl side chains

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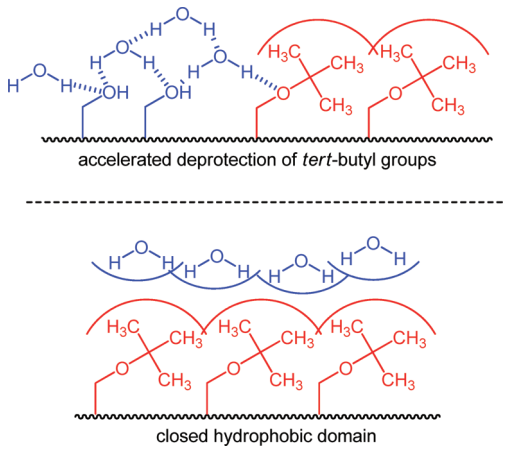
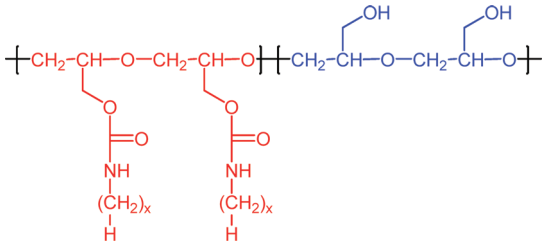
Scheme 2. Enhanced Rate of Hydrolysis in Random *tert*-Butyl Glycidyl Ether/Glycidol Copolymers (top) and Reduced Speed of Hydrolysis in a Poly(*tert*-butyl glycidyl ether) (below)



Scheme 3. Final Structure of the Designated Amphiphilic Diblock Copolymer



are linked via urethane groups to the polyether backbone (Scheme 3).

These block copolymers will be excellent candidates to investigate the interplay between side-chain ordering and hydrogen bonds as well as its impact on microphase separation. To that purpose the relative mass fraction of the hydrophobic to hydrophilic block was systematically altered. This can be done either by varying the degree of polymerization or by altering the length of the aliphatic side chain from C_{12} to C_{16}.

Results and Discussion

Amphiphilic block copolymers based on polyglycidol comprising a hydrophilic block with a polyether backbone and hydroxymethyl side chains and a hydrophobic block having a polyether backbone with C_{12}, C_{14}, and C_{16} alkyl side chains and a urethane spacer between backbone and side chain were prepared according to a four-step synthetic concept (Scheme 4). Sequential polymerization of EEGE and *t*BuGE will be studied using a potassium alcoholate as initiator. In a first attempt the control of the molecular weight and the molar ratio of repeating units in the block copolymer will be analyzed. In the second step the reaction conditions for a selective removal of the acetal protection groups have to be determined. Special emphasis has to be placed on the complete removal of the acetal protection groups without effecting the removal of tertiary butyl ether groups. In the third step the redundant (the free set) hydroxyl groups were reacted with alkyl isocyanates of different chain lengths. Also in this step special attention has to be given to a quantitative conversion of the hydroxyl groups. Finally in the last step, reaction conditions for a selective removal of the tertiary butyl protection groups have to be determined without affecting the hydrolysis of the urethane groups. Careful analysis is essential for the determination of the ratio of repeating units.

Sequential Polymerization of Ethoxy Ethyl Glycidyl Ether and *tert*-Butyl Glycidyl Ether. For the sequential polymerization of the two protected monomers 3-phenylpropanol was chosen as initiator and diglyme as solvent. For the first experiments a monomer-to-initiator ratio of 50−100 was adjusted, and 10% of the OH groups of the initiator were activated using potassium *tert*-butoxide as K^+ donor (Table 1, no. 1−4).[16] According to our synthetic strategy, EEGE is the monomer which is more easily deprotected, and therefore in the final diblock copolymers these repeating units will be functionalized with alkyl chains and thus will form the hydrophobic block. As a consequence EEGE was polymerized first and after full conversion the second monomer (*t*BuGE) was added.

Polymerization of different ratios of the two monomers ranging from EEGE/*t*BuGE from 10/40 to 10/90 resulted in block copolymers with a narrow molecular weight distribution (M_w/M_n ca. 1.2).

By adjusting a monomer-to-initiator ratio of 180 (experiment 5) and 10% monomer activation, no polymer was obtained. By increasing the activation to 40% (experiment 6), again good results were obtained.

^{1}H NMR analysis of P(EEGE)-*b*-P(*t*BuGE) copolymers reveals the signals of both repeating units and the initiator (Figure 1); however, not all signals are well resolved. For the initiator the methylene group in the benzyl position at $\delta = 2.67$ ppm (signal a) is well resolved and was used for the calculation of the number of repeating units *m* and *n* in Table 1. The EEGE repeating units have characteristic signals for the acetal proton c at $\delta = 4.70$ ppm; the methylene and methine protons of the EEGE and *t*BuGE repeating units are centered at $\delta = 3.5$ ppm, and the methyl groups of both repeating units are between $\delta = 1.16$ and 1.33 ppm. The number of EEGE repeating units *m* was calculated from the ratio of the integral of signal c to that of signal a. The number of repeating units *n* for *t*BuGE was calculated according to eq 1.

$$n\ (\text{number of } t\text{BuGE r.u.}) = \frac{I_{x,y,z} - 6I_c}{9}\frac{2}{I_a} \qquad (1)$$

Based on the values determined for *m* and *n*, the ratio of the repeating units in the block copolymers and the molar mass of the repeating units, M_n, was calculated (Table 1). These values differ from those obtained via GPC using THF as eluting solvent; however, it is known that for block copolymers the determination of absolute molar masses by using a refractive index detector only is not possible.[17] GPC analyses were mainly used for comparison of M_n and M_w/M_n of block copolymers with the same building blocks. As seen in Table 1, the changes of M_n determined via NMR and GPC are in agreement and M_w/M_n of ca. 1.2 was obtained.

Selective Deprotection of the Ethoxy Ethyl Glycidyl Ether Block. To remove the acetal protection groups and to keep the *t*BuGE block intact at the same time, the reaction conditions of hydrolysis had to be optimized. Besides the concentration of the acid, the reaction time was the critical parameter.

For deprotection the block copolymer were dissolved in THF. A calculated amount of hydrochloric acid, based on the number of EEGE repeating units in the block copolymer, was added. The mixture was stirred at temperatures between rt and 35 °C for a fixed period. Subsequently, the reaction was stopped by the addition of saturated sodium hydrogen carbonate solution.

When the reaction conditions were adjusted correctly, it was always possible to deprotect the EEGE block and at the

Scheme 4. Synthetic Concept for the Preparation of Amphiphilic Block Copolymers Based on Polyglycidol: (i) Sequential Polymerization of Ethoxy Ethyl Glycidyl Ether (EEGE) and *tert*-Butyl Glycidyl Ether (*t*BuGE); (ii) Selective Removal of the Acetal Protection Groups; (iii) Reaction of the Hydroxyl Groups with Alkyl Isocyanates; (iv) Removal of the *tert*-Butyl Ether Protection Groups

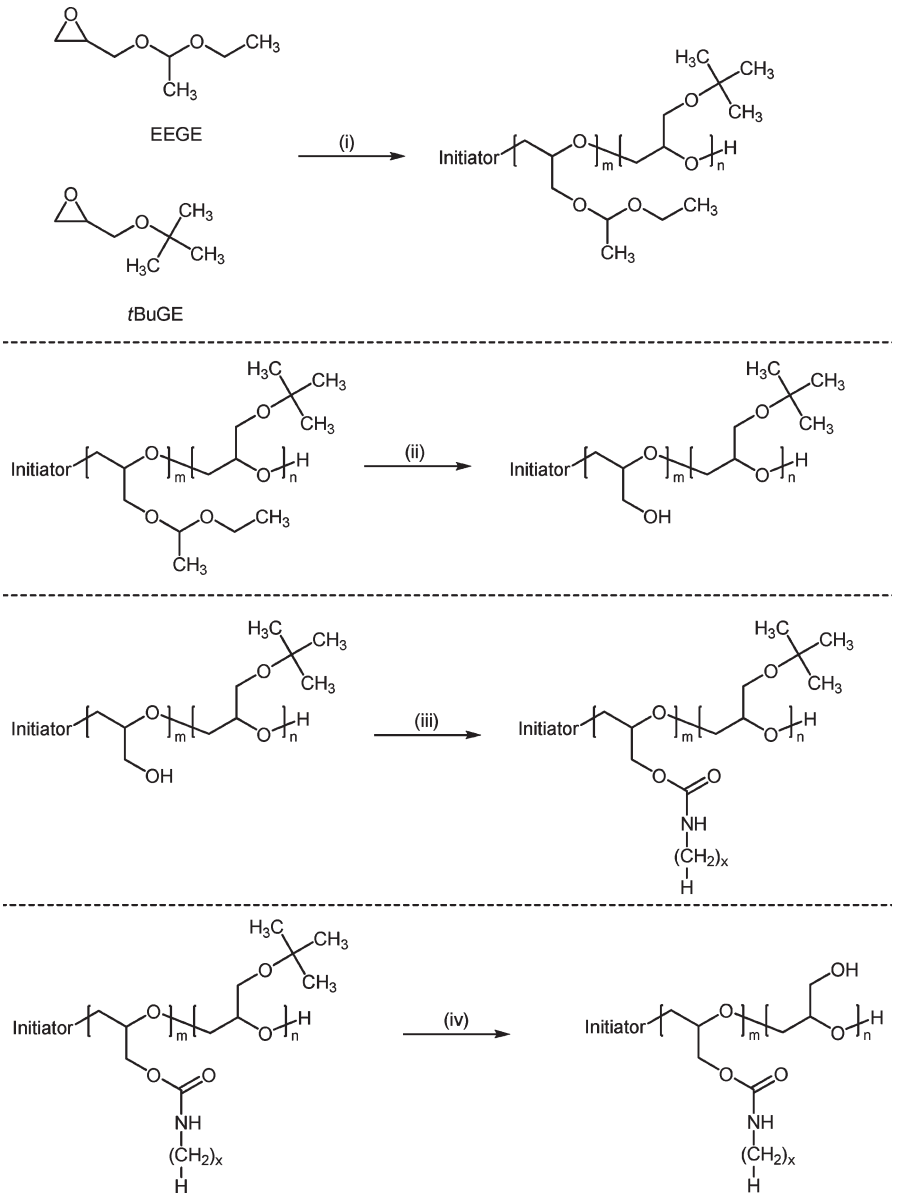


Table 1. Sequential Anionic Polymerization of Ethoxy Ethyl Glycidyl Ether (EEGE) and *tert*-Butyl Glycidyl Ether (*t*BuGE): Monomer Ratio in the Feed, Concentration of Active Species, Ratio of Repeating Units in the Block Copolymer, and Results of the GPC Analysis

					GPC[d]	
no.	EEGE/*t*BuGE[a]	concentration of active species (10^{-3}mmol/g)	P(EEGE)$_m$-*b*-P(*t*BuGE)$_n$[b] *m*:*n*	M_n (calcd)[c]	M_n	M_w/M_n
1	10:40[e]	7.98	8:35	5725	6200	1.19
2	10:60[e]	6.21	10:61	9403	6800	1.21
3	10:72[e]	5.64	10:77	11486	7000	1.26
4	10:90[e]	6.16	9:87	12641	9700	1.22
5	20:160[f]	3.08		n.d.	n.d.	n.d.
6	15:120[g]	16.24	16:133	19653	7700	1.28

[a] Monomer ratio in the feed. [b] Ratio of r.u. in the copolymer as determined from ^{1}H NMR spectroscopy. [c] Determined via end-group analysis. [d] THF as solvent. [e] (EEGE + *t*BuGE)/3-PP = 50−100; 10% activation. [f] (EEGE + *t*BuGE)/3-PP = 180; 10% activation. [g] (EEGE + *t*BuGE)/3-PP = 135; 40% activation.

same time preserve the *tert*-butyl ether groups intact. The reaction conditions and composition of the resulting product are summarized in Table 2.

^{1}H NMR analysis of P(G)$_m$-*b*-P(*t*BuGE)$_n$ clearly reveals complete removal of acetal protection groups (Figure 2). Direct comparison of the integral intensity of signal z at δ = 1.17 ppm and signal a of the initiator results in the number of *t*BuGE repeating units *n* while for the number of glycidol repeating units *m* eq 2 was applied; however, it should be mentioned that due to the low solubility of the

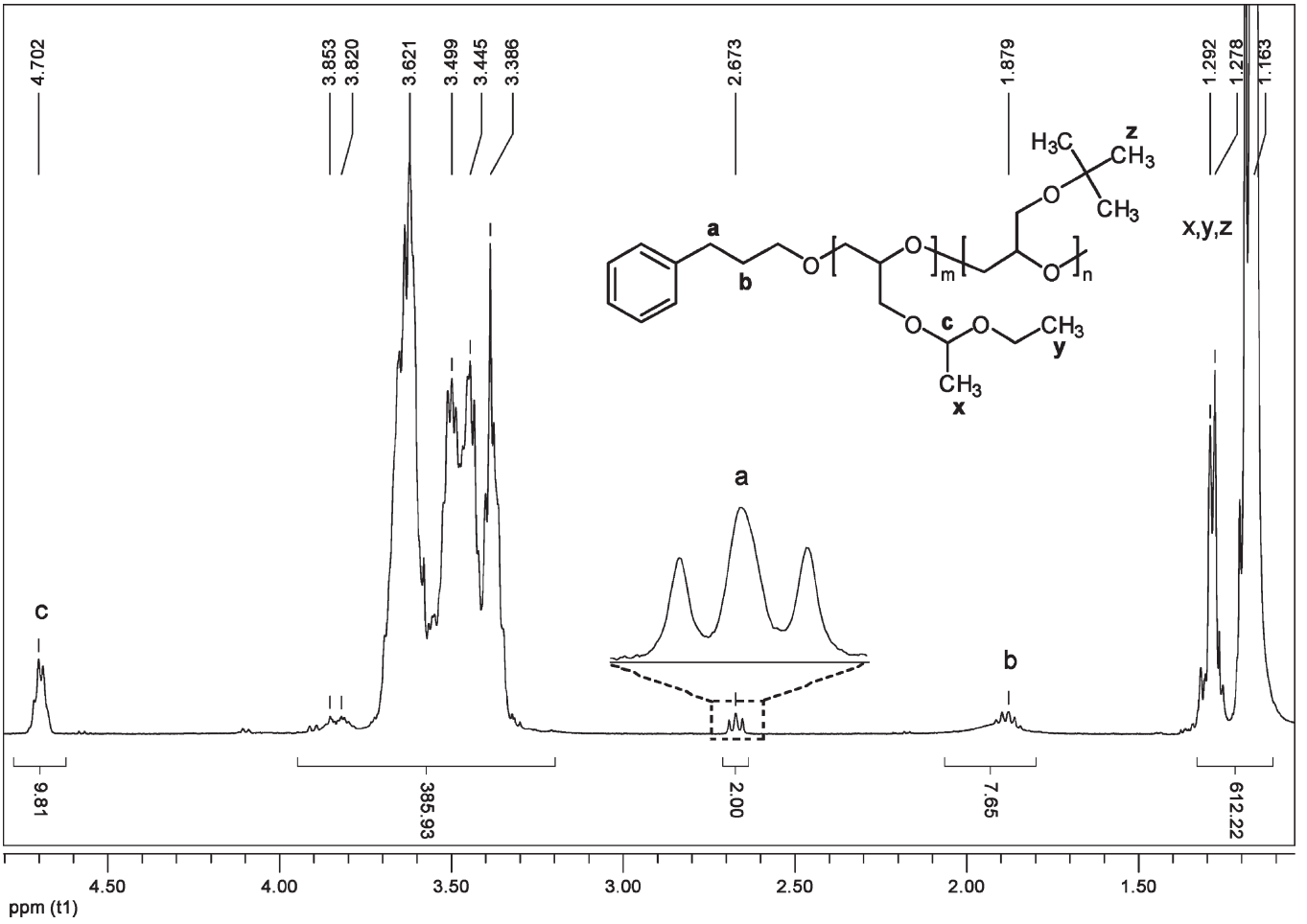


Figure 1. ^{1}H NMR spectrum of a poly(ethoxy ethyl glycidyl ether)-*b*-poly(*tert*-butyl glycidyl ether) block copolymer (no. 2 of Table 1) with 3-phenylpropanol as initiator.

Table 2. Selective Deprotection of Ethoxy Ethyl Glycidyl Ether Repeating Units in Poly(ethoxy ethyl glycidyl ether)-*b*-poly(*tert*-butyl glycidyl ether) Diblock Copolymers: Reaction Conditions, Concentration of Hydrochloric Acid, Reaction Time, Temperature, and the Number of Repeating Units after Deprotection

no.	P(EEGE)$_m$-*b*-P(*t*BuGE)$_n$ *m*:*n*	polymer/solvent (g/mL)	equiv of HCl	*t* (min)	temperature (°C)	P(G)$_m$-*b*-P(*t*BuGE)$_n$ *m*:*n*[a]
1	10:77	0.15	2.0	60	r.t.	9:56[b]
2	10:61	0.14	2.0	900	r.t.	12:55
3	10:61	0.13	2.0	420	35	15:57
4	9:87	0.15	2.0	90	35	12:61
5	9:87	0.17	1.5	60	35	15:72

[a] *m* and *n* were determined from ^{1}H NMR spectra. [b] One remaining EEGE group.

polyglycidol block in $CDCl_3$, the results are less precise.

$$m\ (\text{number of P(G) r.u.}) = \frac{I_{\text{backbone}} - 5n}{5}\frac{2}{I_{\text{a}}} \qquad (2)$$

Functionalization of the Hydroxyl Groups. The free hydroxyl groups can be functionalized with reactive molecules such as isocyanates,[18,19] acid chlorides, or chloroformiates. Potentially, variation of the side chains may lead to diblock copolymers with different properties. In the present report, the focus is on the insertion of long alkyl chain side groups. To link the alkyl chains to the OH groups of the polymer backbone, isocyanates were used. The working procedure was always the same regardless of the polymer or isocyanate used.

Poly(glycidol)-*block*-poly(*tert*-butyl glycidyl ether) was dissolved in 1,2-dichloroethane, and depending on the number of glycidol repeating units a given amount of isocyanate was added. Although primary OH groups like those in the glycidol repeating units are more reactive than secondary or tertiary ones, a tin catalyst was added to ensure full conversion. The mixture was stirred at 75 °C for several hours. In all cases the isocyanates were successfully linked to the polymer backbone. The obtained polymers were characterized via ^{1}H NMR spectroscopy and GPC analyses. The efficiency of functionalization and the average number of attached alkyl groups were calculated from the ^{1}H NMR spectrum (Figure 3) based on the ratio of the integrals of the CH_2 group (2) in the side chain and the CH_2 group (a) of the initiator.

The reaction conditions and the resulting diblock copolymer characteristics are summarized in Table 3.

Analysis of the ^{1}H NMR spectrum revealed characteristic signals for the polymers (Figure 3). The methylene group of the functionalized polyglycidol backbone centered

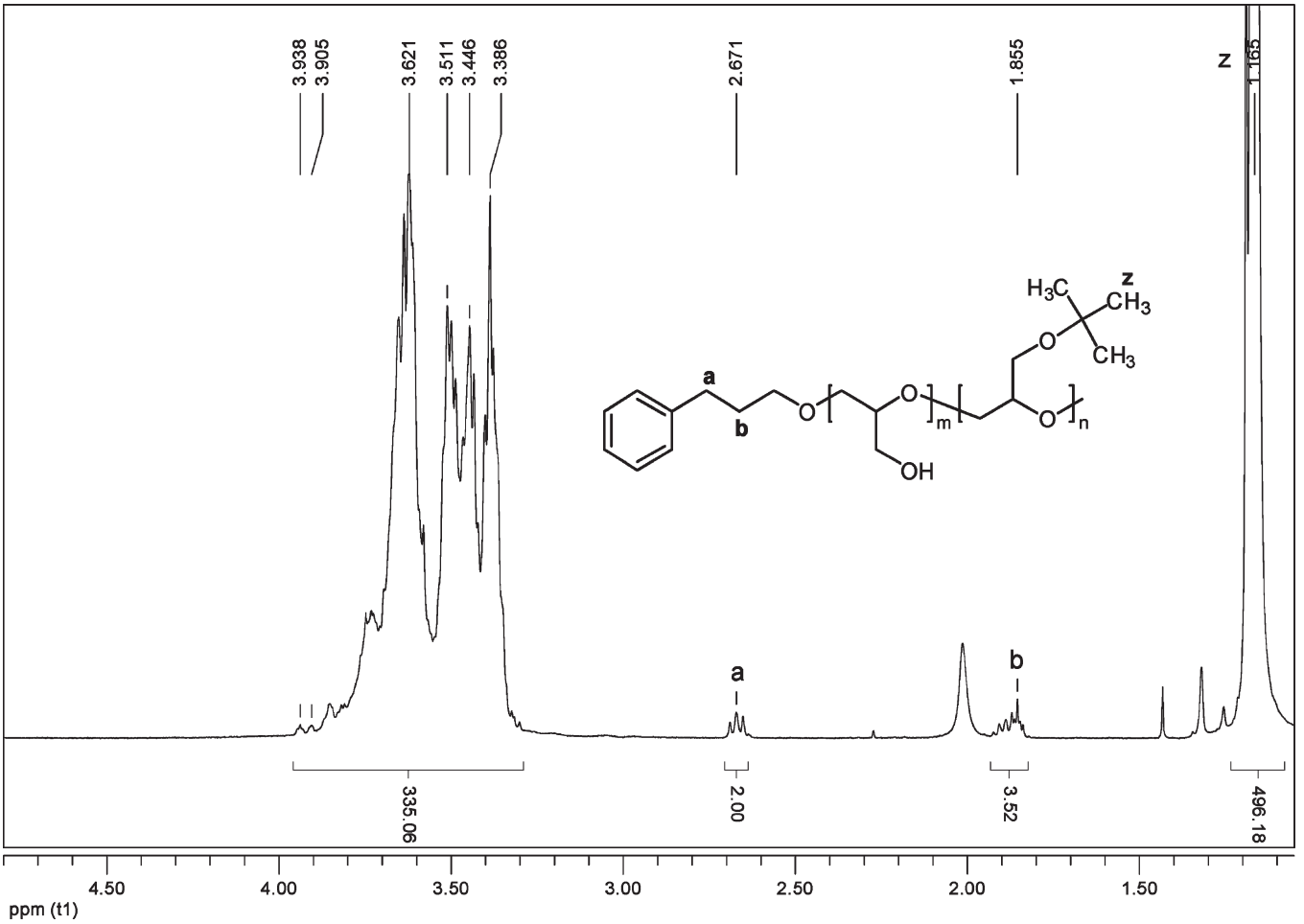


Figure 2. ^{1}H NMR spectrum of a selective deprotected poly(glycidol)$_m$-*b*-poly(*tert*-butyl glycidyl ether)$_n$ block copolymer (no. 2 of Table 2).

at δ = 4.1 ppm (signal 1), the α and β methylene groups of the alkyl side chain at δ = 3.12 and δ = 1.48 ppm (signals 2 and 3), and the methyl group at δ = 0.88 ppm (signal 4) are all well resolved. The remaining methylene groups of the alkyl side chains are centered at δ = 1.25 ppm and overlap with each other. The integral of the CH_2 group (a) of the initiator was again used as reference.

Cleavage of the *tert*-Butyl Ether Groups. In the last step the *tert*-butyl ether groups were removed by reaction with trifluoroacetic acid.[20] The urethane bonds formed in the previous step are stable under these conditions.

P(G-alkyl)$_m$-*b*-P(*t*BuGE)$_n$ was treated with trifluoroacetic acid, and the mixture was stirred for several hours leading to complete dissolution of the polymers. For purification the polymers were dissolved in THF, dialyzed against water, and freeze-dried afterward. The resulting polymers were characterized via ^{1}H NMR spectroscopy and GPC analyses. Because of the amphiphilic character of the block copolymers, no common solvent was found in which both blocks are well soluble. Therefore, the NMR spectra were measured in chloroform—a suitable solvent for the hydrophobic block—and in DMSO—a suitable solvent for the hydrophilic block. It must be taken into consideration that the integrals of signals belonging to different blocks cannot be compared due to the fact that one of the blocks is collapsed. However, a comparison with signals of the initiator should be possible. The ^{1}H NMR spectrum in chloroform revealed that all *tert*-butyl groups were removed (Figure 4, top). In addition, the number of repeating units in the hydrophobic block was determined by comparison of the integrals of signal 2 or 3 in the alkyl side chains with signal a of the initiator. These numbers are slightly lower than the numbers obtained before removal of the *tert*-butyl ether groups. The reason for this is not clear. The ^{1}H NMR spectrum in DMSO in which the polyglycidol block is well soluble shows the signals of the glycidol repeating units centered at δ = 3.50 ppm. Quantification of these signals is not possible. GPC analysis in DMF analysis showed that the block copolymers have a narrow distribution after dialysis; values between 1.06 and 1.19 were determined.

The mass fraction of the hydrophobic block was calculated from the number of alkyl chains found in the chloroform NMR spectrum after the last step. It varied between 30 and 44%. A list of obtained polymers is summarized in Table 4.

The chloroform NMR spectrum (4, on top) showed the characteristic signals of the aliphatic side chains. The methylene groups of the functionalized polyglycidol backbone centered at δ = 4.1 ppm (signal 1), the α and β methylene groups of the alkyl side chain at δ = 3.12 and δ = 1.48 ppm (signals 2 and 3), and the methyl group at δ = 0.88 ppm (signal 4) are all well resolved. The remaining methylene groups of the alkyl side chain are at δ = 1.25 ppm and overlap. The integral of the CH_2 group (a) was again used as reference. The polyglycidol backbone shows a broad signal centered at δ = 3.63 ppm. The block is too hydrophilic for the solvent; therefore, its resolution is low. A second spectrum of the copolymer was measured in DMSO. This spectrum also showed the characteristic signals (Figure 4, below). The methylene group of the functionalized polyglycidol backbone is centered at δ = 4.0 ppm, the α and β

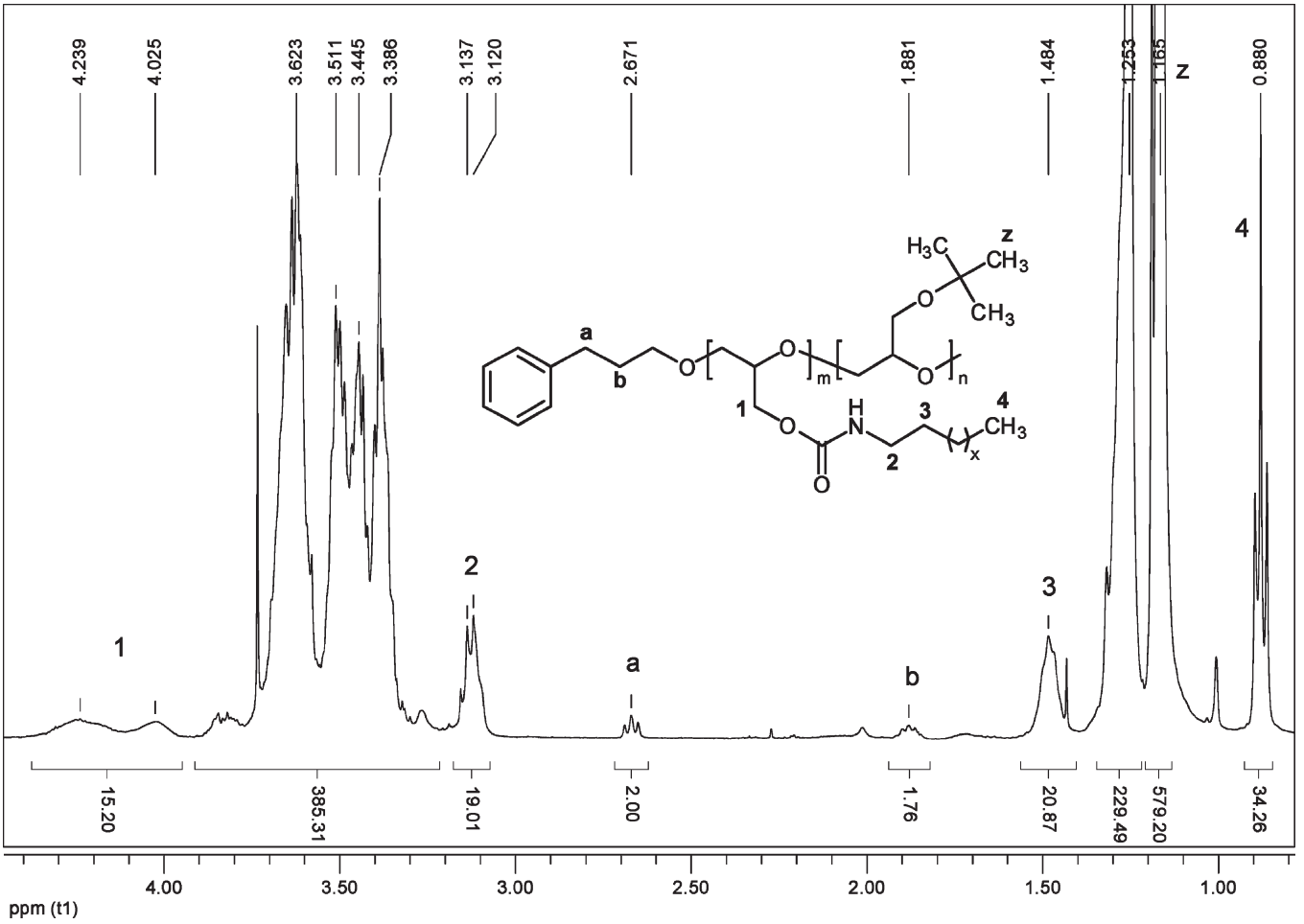


Figure 3. ^{1}H NMR spectrum of a poly(alkyl glycidol)$_m$-*b*-poly(*tert*-butyl glycidyl ether)$_n$ block copolymer (no. 2 of Table 3).

Table 3. Used Isocyanate, Number of Found Alkyl Chains and *tert*-Butyl Glycidyl Ether Repeating Units, and THF−GPC Results for the Functionalization of the Partial Deprotected Block Copolymer

			GPC[b]	
no.	isocyanate	P(G-alkyl)$_m$-*b*-P(*t*BuGE)$_n$[a] *m*:*n*	M_n	M_w/M_n
1	C_{12}	11:74	7800	1.48
2	C_{14}	10:64	7700	1.25
3	C_{16}	11:64	7600	1.18
4	C_{14}	15:99	n.d.	n.d.
5	C_{16}	10:98	11400	1.27

[a] Ratio of repeating units in the copolymer as determined from ^{1}H NMR spectroscopy. [b] THF as solvent.

methylene group of the alkyl side chain at δ = 2.94 ppm and δ = 1.36 ppm, and the methyl group at δ = 0.85 ppm. The remaining methlyene groups of the side chain are centered at δ = 1.23 ppm. However, it must be mentioned that this spectrum cannot be used for quantitative analysis. The CH_2 group (signal a) of the initiator, which was used to calculate the degree of polymerization and the number of attached alkyl side chains in the chloroform spectrum, overlaps with the signal of DMSO. Its integral cannot be used for calculations.

Thermal Properties of Poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$. The thermal properties of the block copolymers P(G-alkyl)$_m$-*b*-P(G)$_n$ were studied in detail by differential scanning calorimetry. The thermogramms of the second heating and cooling cycle are shown in Figure 5a,b. All samples show reversibly three thermal transitions:

(i) At low temperature below 0 °C small but systematic changes in the baseline were measured for all polymers. This was assigned to the glass transitions temperature T_g of the amorphous polyglycidol block.

(ii) The occurrence of the second transition (position and amplitude) depends on the length of the aliphatic side chains. Note that the transition temperature is defined as the maximum of the peak. For block copolymers with C12 side chains two weak transition temperatures around 24 and 38 °C are observed. However, upon cooling a single endothermic peak appears around 10 °C. For BC with C14 side chains a clear order−order transition was measured upon heating/cooling cycle and, it occurs at 39 and 26 °C, respectively, i.e. $T_{exo} - T_{endo} = \Delta T = 13$ °C. For longer side chain C16 the order−order transition occurs at 61 °C with ΔT = 15 °C.

(iii) The third thermal transition corresponds to an order−disorder transition which takes place around 100 °C regardless of the length of the aliphatic side chains. Except for the BC with C16, it has been observed that upon cooling the transition occurs at significantly lower temperature 84 °C instead of 102 °C.

In Table 5 the transition temperatures and the associated enthalpies are summarized.

In order to understand the thermal properties of the diblock copolymers, the transition temperature and the corresponding enthalpies are plotted depending on the number of carbon atom per alkyl chain. The graph (Figure 6a) shows that the order−order transition temperature increases monotonically with the length of the alkyl chain. These results agree with literature reports.[21−23] The new feature is the transition temperature from the mesomorphic to an isotropic phase which remains constant around 100 °C regardless of the length of the alkyl chain.

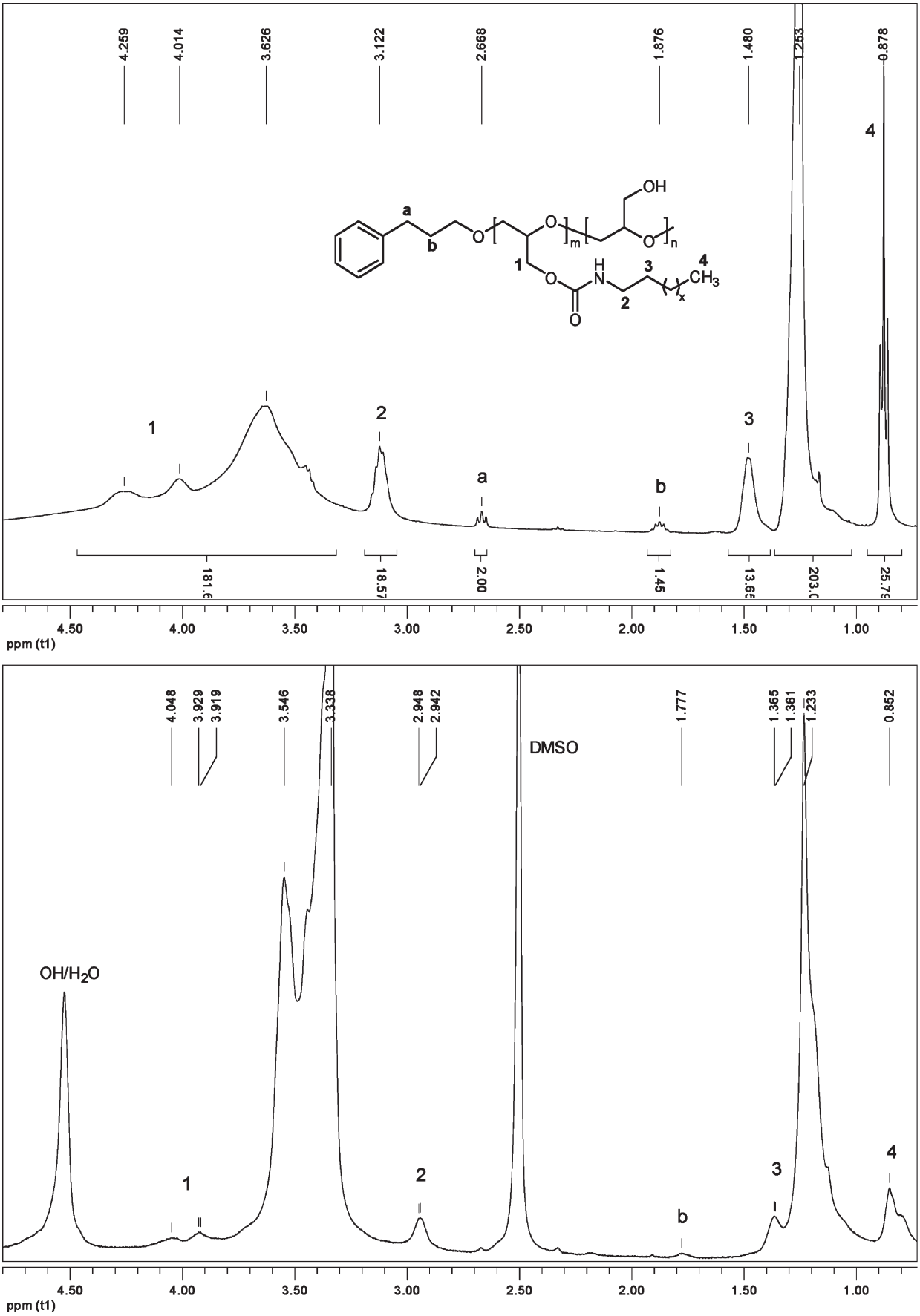


Figure 4. ^{1}H NMR spectrum of a poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ block copolymer (no. 3 of Table 4) in $CDCl_3$ (top) and in DMSO-d_6 (below).

These data first suggest that the hydrophilic polyglycidol segregates from the hydrophobic block to form microdomains, leading to defined glass transition temperatures regardless of the length of the aliphatic chains. Second, the high-temperature mesophases are assigned to ordering of the hydrophobic block—mainly to the aliphatic side chains as their lengths raise the transition temperature. It is well-known[24] that the aliphatic side chains organize into partially crystallized lamellar (or smectic) phases. Upon heating disordering of the aliphatic chains occurs, but in the present system the layered structure is preserved.[25,26] The reasons are the urethane moieties which anchor the alkyl chains to the flexible polymer backbone. These units are susceptible to form intramolecular hydrogen bonds imparting stability to the layered structure. Therefore, at high temperature, above 100 °C the hydrogen bridges are destabilized and the hydrophobic block undergoes mesomorphic-to-isotropic phase transition.

To better understand the interplay between hydrogen bond and the self-assembly of the aliphatic side chain, the molar enthalpies needed to melt the alkyl chain ΔH_m^{bulk} or to break the hydrogen bonds of the urethane moieties ΔH_i^{bulk} were plotted as a function of the number of carbon atoms per side chain (p). Figure 6b shows that the enthalpies are a monotonic function of p. The heat of fusion ΔH_m^{bulk} linearly increased from 0.8 kJ/mol for P(G-C_{12}-alkyl)$_{10}$-*b*-P(G)$_{77}$ to 8.6 kJ/mol for P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{62}$. Such

Table 4. Synthesized Poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ Block Copolymers: Number of Alkyl Chains, DMF−GPC Results, and Calculated Mass Fraction of the Hydrophobic Block

		GPC[a]		
no.	number of alkyl chains	M_n	M_w/M_n	mass fraction hydrophobic block (%)
1	10	5700	1.09	33.3
2	9	5600	1.06	38.0
3	9	5600	1.09	40.1
4	15[b]	n.d.	n.d.	43.9
5	8	7900	1.16	29.8

[a] DMF as solvent. [b] After functionalization.

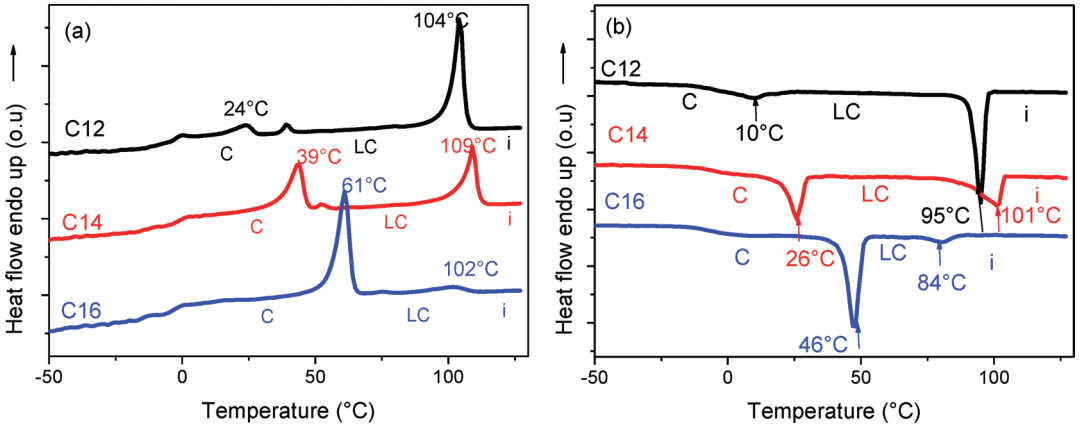


Figure 5. DSC thermograms of poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ diblock copolymers: (a) the thermograms are based on the second heating scan at a scan rate of 10 °C/min; (b) the first cooling scan at a scan rate of 10 °C/min (C: crystal; LC: liquid crystal; i: isotropic).

Table 5. Phase Transition Temperatures and Corresponding Enthalpies of Poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ Block Copolymers

P(G-alkyl)$_m$-*b*-P(G)$_n$	T_g (°C)[a]	ΔC_p (J/(g K))[a]	T_m (°C)[b]	ΔH_m^{bulk} (kJ/mol)[b]	T_i (°C)[c]	ΔH_i^{bulk} (kJ/mol)[c]
P(G-C_{12}-alkyl)$_{10}$-*b*-P(G)$_{77}$	−4	0.37	24	0.78	104	4.86
P(G-C_{14}-alkyl)$_9$-*b*-P(G)$_{62}$	−2	0.33	44	3.84	109	2.63
P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{62}$	−3	0.36	61	8.59	102	0.44

[a] The glass phase transition temperature (T_g) was determined from the second heating curve (heating rate of 10 °C/min). [b] The melting phase transition temperature (T_m) and the associated enthalpy (ΔH_m^{bulk}) were deduced from the second heating curve (heating rate of 10 °C/min). [c] The isotropic phase transition temperature (T_i) and the associated enthalpy (ΔH_i^{bulk}) were determined from the second heating curve (heating rate of 10 °C/min).

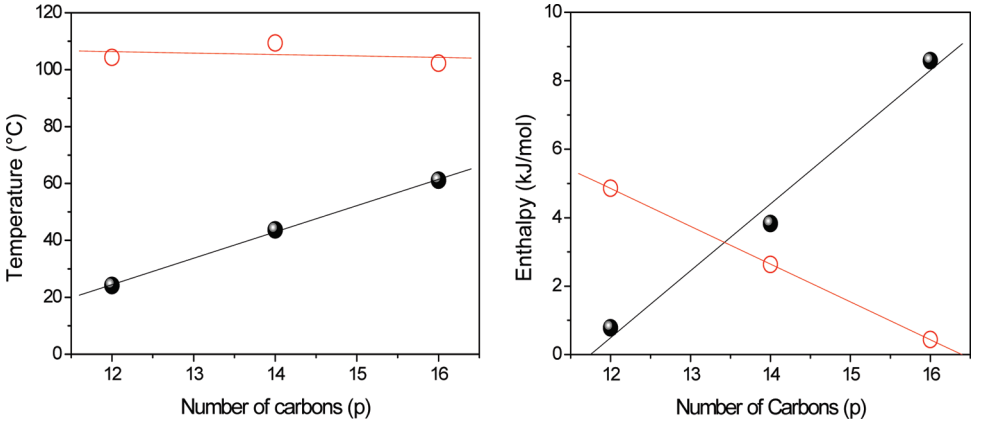


Figure 6. (left) Thermal transition temperature of poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ block copolymers (● mesomorphic thermal transition T_m and ○ isotropic thermal transition T_i) as a function of the number of carbon atoms per aliphatic side chain p. (right) Associated mesomorphic and isotropic enthalpies (● ΔH_m^{bulk}; ○ ΔH_i^{bulk}) as a function of the number of carbon atoms per aliphatic side chain p. The solid line is a linear fit of the data.

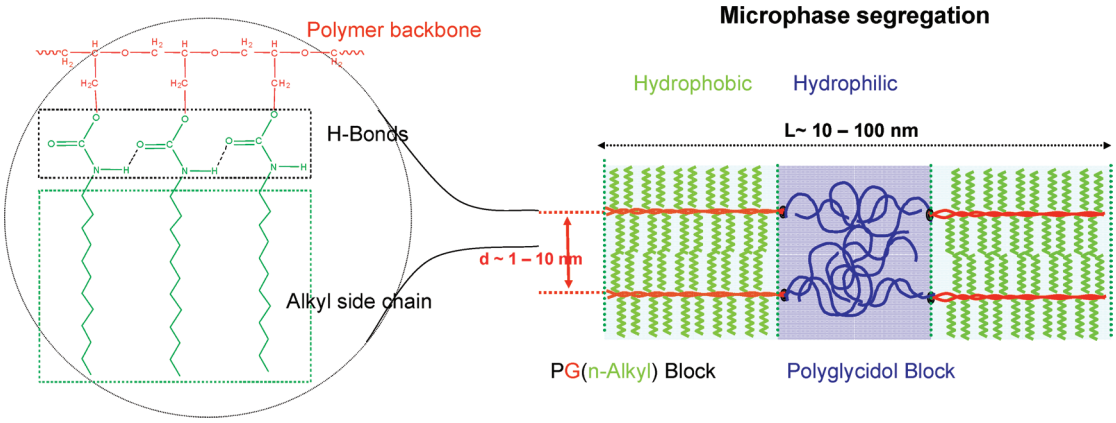


Figure 7. Schematic representation of H-bonding in poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ block copolymers (left).[31] Overview of the ordering of poly(alkyl glycidol)$_m$-*b*-poly(glycidol)$_n$ block copolymers (right).

linearity was observed for *n*-alkanes as well as for flexible polymer backbone with the corresponding *n*-alkanes side chain.[27,28] The linear dependence was represented by the following equation:

$$\Delta H_{\mathrm{m}} = pk + \Delta H_{\mathrm{m,e}} \tag{3}$$

where k is the contribution of each added methylene group to the enthalpy and $\Delta H_{\mathrm{m,e}}$ is a constant reflecting the contribution of the chain end to the enthalpy. The linear regression for the actual data $\Delta H_{\mathrm{m}}{}^{\mathrm{bulk}}$ is given by the following expression:

$$\Delta H_{\mathrm{m}}{}^{\mathrm{bulk}}\ (\mathrm{kJ/mol}) = 2.0p - 22.9 \tag{4}$$

The value of k evaluated from eqs 3 and 4 was 2.0 ± 0.2 kJ/mol per methylene group, and $\Delta H_{\mathrm{m,e}}$ was −22.9 ± 3.5 kJ/mol. The heat of fusion of alkyl chains is 2.9 kJ/mol per methylene group as they melt from the less densely packed ss phase.[29] Thus, the alkyl side chains are in less ordered state compared to the ss phase. In this study, the minimum number of crystalline CH_2 groups p_c in a side chain was also calculated using eq 3:[27]

$$p_c = \frac{\Delta H_{\mathrm{m}}}{k} \tag{5}$$

The value of p_c increased from 0.4 for P(G-C_{12}-alkyl)$_{10}$-*b*-P(G)$_{77}$ to 4.4 for P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{62}$. Based on this calculation, 10−11 methylene groups in a side chain were in the disordered state. This study leads to the conclusion that short side chains (p = 12) are less ordered than longer side chains (p = 16).

On the other hand, the systematic decrease of the enthalpy ΔH_{i} associated with the isotropic transition followed a linear regression given by the following expression:

$$\Delta H_{\mathrm{i}}{}^{\mathrm{bulk}}\ (\mathrm{kJ/mol}) = -1.1p + 18.1 \tag{6}$$

The extrapolation to p = 0 gives $\Delta H_{\mathrm{i}}{}^{\mathrm{bulk}}$ = 18.1 kJ/mol and corresponds to the enthalpy needed to dissociate the H-bond. This value is similar to the energy needed to break H-bond in polyether based polyurethanes (13−28 kJ/mol).[30,31] The slope of eq 6 is −1.1 ± 0.01 kJ/mol and suggests that the addition of each methylene group will reduce the energy needed to break the hydrogen bonds. On the basis of this calculation, one finds on average that only 26% of the urethane groups can form hydrogen bonds in the case of P(G-C_{12}-alkyl)$_{10}$-*b*-P(G)$_{77}$ and 15% for P(G-C_{14}-alkyl)$_9$-*b*-P(G)$_{62}$, whereas only 3% of urethane groups are involved in hydrogen bonds for P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{62}$.

The DSC study demonstrates that P(G-alkyl)$_m$-*b*-PG$_n$ block copolymers exhibited three reversible thermal transitions. First, the glass transition of the amorphous polyglycidol block appeared around 0 °C regardless of the length of the alkyl side chain (p), as expected for microphase-segregated block copolymers. Second, the order−order transition (melting transition) assigned to the hydrophobic block, showed a linear dependence on p. A minimum of 10−11 carbons was required to observe ordering of the alkyl chain, in agreement with the literature.[32] Ordering of the hydrophobic block was preserved above the melting temperature of the alkyl chains. The breaking of the hydrogen bonds occurred above 100 °C, corresponding to the isotropic state of the hydrophobic block. Figure 7 summarizes the results and gives a schematic view on ordering of the alkyl chain and intramolecular H-bonds pattern (left). In Figure 7 (right) the scheme gives an overview of the hierarchical ordering displayed by the studied block copolymers. The hydrogen bond model was adapted from the literature.[30,31,33] For our study, it was decided to draw predominant hydrogen bonds in urethane groups, as determined by Ren et al.[31] As shown in Figure 7, the ordering of alkyl side chains competes with hydrogen bonds.

Conclusions

Amphiphlic block copolymers based on polyglycidol were successfully synthesized via the sequential polymerization of EEGE and *t*BuGE. The degree of polymerization was calculated from ^{1}H NMR spectroscopy via end-group analysis. The EEGE block was deprotected selectively without affecting the *tert*-butyl ether groups. For each step the reaction conditions were optimized. The hydroxymethyl groups in P(G)-*b*-P(*t*BuGE) were converted quantitatively with alkyl isocyanates followed by removal of the *tert*-butyl protection groups with trifluoroacetic acid. The DSC study demonstrates that P(G-alkyl)$_m$-*b*-P(G)$_n$ block copolymers exhibit three reversible thermal transitions: the glass transition of the amorphous polyglycidol block, the melting transition assigned to the alkyl chains, and the breaking of the hydrogen bonds.

Experimental Part

Materials. *tert*-Butyl glycidyl ether (*t*BuGE) (Aldrich, 99%) was dried over calcium hydride, distilled, and stored on molecular sieves (3 Å) under a nitrogen atmosphere. 3-Phenylpropanol (Aldrich, 98%) and diethylene glycol dimethyl ether (diglyme) (Aldrich, 99%) were dried over sodium, distilled,

Table 6. Poly(ethoxy ethyl glycidyl ether)-*b*-poly(*tert*-butyl glycidyl ether) Preparation

$P(EEGE)_m$-*b*-$P(t\text{BuGE})_n$	entry	EEGE/mmol	*t*BuGE/mmol	3-PP/mmol	conversion/%
$P(EEGE)_8$-*b*-$P(t\text{BuGE})_{35}$	1	10.5	42.0	1.05	90.1
$P(EEGE)_{10}$-*b*-$P(t\text{BuGE})_{61}$	2	10.5	63.1	1.05	97.3
$P(EEGE)_{10}$-*b*-$P(t\text{BuGE})_{77}$	3	10.9	76.1	1.05	97.9
$P(EEGE)_9$-*b*-$P(t\text{BuGE})_{87}$	4	10.5	94.9	1.05	95.8
$P(EEGE)_{20}$-*b*-$P(t\text{BuGE})_{160}$	5	21.0	168	1.05	
$P(EEGE)_{16}$-*b*-$P(t\text{BuGE})_{133}$	6	15.8	126.1	1.05	96.1

Table 7. Selective Deprotection of Ethoxy Ethyl Glycidyl Ether Repeating Units in Poly(ethoxy ethyl glycidyl ether)-*b*-poly(*tert*-butyl glycidyl ether) Block Copolymers: Experimental Conditions and Yield

$P(G)_m$-*b*-$P(t\text{BuGE})_n$	entry	polymer/g	EEGE r.u./mmol	*t*BuGE r.u./mmol	HCl/mL	yield/g
$P(G)_9$-*b*-$P(t\text{BuGE})_{56}$	1	3.00	2.61	20.1	5.2	2.29
$P(G)_{12}$-*b*-$P(t\text{BuGE})_{55}$	2	3.07	3.26	19.9	6.5	2.61
$P(G)_{15}$-*b*-$P(t\text{BuGE})_{57}$	3	2.66	2.83	17.3	5.6	2.40
$P(G)_{12}$-*b*-$P(t\text{BuGE})_{61}$	4	3.00	2.14	20.7	4.3	2.72
$P(G)_{15}$-*b*-$P(t\text{BuGE})_{72}$	5	3.11	2.21	21.4	3.3	2.71

and stored on molecular sieves (3 Å) under a nitrogen atmosphere. 1,2-Dichloroethane (Merck, >99.5%) was stirred over calcium chloride, distilled, and stored on molecular sieves (3 Å) under a nitrogen atmosphere. Glycidol (Aldrich, 96%), ethyl vinyl ether (Aldrich, 99%), *p*-toluenesulfonic acid monohydrate (Fluka, ≥98.5%), potassium *tert*-butoxide (Acros, 1 M in THF), dodecyl isocyanate (Aldrich, 99%), tetradecyl isocyanate (Aldrich, 97%), hexadecyl isocyanate (Aldrich, 97%), dibutyltin dilaurate (Fluka, techn.), and trifluoroacetic acid (Aldrich, 99%) were used as received.

EEGE was prepared according to Fitton et al.,[10] stirred over calcium hydride, and stored on molecular sieves (4 Å) under a nitrogen atmosphere. The dialysis membrane (Spectra/Por 6 dialysis membrane, regenerated cellulose, molecular weight cutoff 1000) was washed with demineralized water several times before use.

Polymerization and postpolymerization reactions were performed under a nitrogen protective atmosphere.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer at 400 and 100 MHz, respectively. Deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents with tetrametylsilane as internal standard.

GPC analyses were performed on two different systems.

For THF as eluting solvent a high-pressure liquid chromatography pump (ERC HPLC 6420) and a refractive index detector (WGE Dr. Bures Eta 2020) were used at 30 °C with a flow rate of 1.0 mL/min. Four different columns with MZ gel were used: length of each column 30 cm, diameter of each column 8 mm, diameter of gel particles 5 μm, and nominal pore widths 50, 100, 1000, and 10 000 Å.

For DMF as eluting solvent a high-pressure liquid chromatography pump (Bischoff 2250) and a refractive index detector (Jasco 2040+) were used at 30 °C. The DMF contained 1 g/L LiBr and had a flow rate of 1.0 mL/min. Four different columns with PSS GRAM gel were used: length of each column 30 cm, diameter of each column 8 mm, diameter of gel particles 10 μm, and nominal pore widths 30, 1000, 1000, and 3000 Å.

For both systems the calibration was achieved using poly(methyl methacrylate) (PMMA) standards.

DSC measurements were carried out on a Netzsch DSC 204 differential scanning calorimeter under a nitrogen atmosphere. Samples were prepared in perforated closed aluminum pans using approximately 3−6 mg of sample. The samples were heated and cooled with a rate of 10 °C/min from −50 to 150 °C. The heat flow was measured as a function of the temperature. First-order transitions were reported as the maxima or minima of the endothermic and exothermic peaks during the second heating and the first cooling scans.

Synthesis. *Preparation of Poly(ethoxy ethyl glycidyl ether)$_{10}$-b-poly(tert-butyl glycidyl ether)$_{61}$.* In a Schlenk flask with a magnetic stirrer and septum 3-phenylpropanol (0.14 g, 1.05 mmol) was dissolved in diglyme (7 mL). Potassium *tert*-butoxide (0.11 mmol, 10 mol % of 3-phenylpropanol) was added, and the solution was stirred for about 40 min at room temperature. The formed *tert*-butanol was removed in vacuo. EEGE (1.54 g, 10.5 mmol) was added to the initiator solution and polymerized at 120 °C. After 4 h, *t*BuGE (8.21 g, 63.1 mmol) was added and the polymerization was continued for an additional 16 h. The reaction mixture was dissolved in of chloroform (70 mL). The crude product was washed three times with saturated sodium hydrogen carbonate solution (20 mL). The organic layer was dried over sodium sulfate and filtrated, and the solvent was evaporated. Yield (entry 2): 9.66 g (97.3% conversion).

^{1}H NMR (400 MHz, $CDCl_3$, TMS_{int}). Repeating units: δ = 1.16 (br, 9H, $C(CH_3)_3$), 1.25−1.33 (br, 6H, $OCHCH_3/OCH_2CH_3$), 3.20−3.96 (br, polyglycidol backbone), 4.70 (s, 1H, $OCHCH_3O$) ppm. End group: δ = 1.88 (m, 2H, $CCH_2CH_2CH_2O$), 2.67 (t, 2H, $CCH_2CH_2CH_2O$), 3.20−3.96 (br, 2H, $CCH_2CH_2CH_2O$), 7.17−7.29 (m, 5H, phenyl ring) ppm.

The experimental conditions for each reaction are listed in Table 6.

Selective Deprotection of the Ethoxy Ethyl Glycidyl Ether Repeating Units in Poly(ethoxy ethyl glycidyl ether)-b-poly(tert-butyl glycidyl ether). The block copolymer $P(EEGE)_{10}$-*b*-$P(t\text{BuGE})_{61}$, Table 6, entry 2) (2.66 g, with 2.79 mmol of EEGE and 17.0 mmol of *t*BuGE r.u.) was dissolved in THF (15 mL). The solution was heated to 35 °C, and hydrochloric acid (5.58 mmol) was added. After 420 min the reaction was stopped by addition of saturated sodium hydrogen carbonate solution. Chloroform (70 mL) was added, and the organic phase was washed three times with saturated sodium hydrogen carbonate solution. The organic layer was dried over sodium sulfate, and the solvent was evaporated. Yield of $P(G)_{15}$-*b*-$P(t\text{BuGE})_{57}$ (entry 3): 2.40 g.

^{1}H NMR (400 MHz, $CDCl_3$, TMS_{int}). Repeating units: δ = 1.16 (br, 9H, $C(CH_3)_3$), 3.39−3.85 (br, polyglycidol backbone) ppm. End group: δ = 1.85 (m, 2H, $CCH_2CH_2CH_2O$), 2.66 (m, 2H, $CCH_2CH_2CH_2O$), 3.39−3.85 (br, 2H, $CCH_2CH_2CH_2O$), 7.17−7.30 (m, 5H, phenyl ring) ppm. Concentration: 1 mol/L.

The experimental conditions for additional experiments are listed in Table 7.

Functionalization of Poly(glycidol)-b-poly(tert-butyl glycidyl ether) with Isocyanates. The deprotected polymer $P(G)_{15}$-*b*-$P(t\text{BuGE})_{57}$ (Table 7, entry 3, 2.40 g with 2.83 mmol of EEGE r.u.) from the last step was dissolved in 1,2-dichloroethane (10 mL) and placed in a Schlenk flask with a magnetic stirrer and a septum. Tetradecyl isocyanate (0.67 g, 2.80 mmol) and dibutyltin dilaurate (0.03 g, 0.05 mmol) were added. The solution was stirred at 75 °C for 20 h and then cooled to room temperature. Chloroform (70 mL) was added, and the organic phase was washed three times with saturated sodium hydrogen carbonate solution (20 mL) and dried over sodium sulfate. Evaporation of the solvent yielded $P(G\text{-}C_{14}\text{-alkyl})_{10}$-*b*-$P(t\text{BuGE})_{64}$. Yield (entry 2): 2.31 g.

Table 8. Functionalization of Poly(glycidol)-*b*-poly(*tert*-butyl glycidyl ether) Copolymers with Long Alkyl Chain Isocyanates: Experimental Conditions and Yield

P(G-alkyl)$_m$-*b*-P(*t*BuGE)$_n$	entry	polymer/g	EEGE r.u./mmol	isocyanate (mmol)	*t*/°C	yield/g
P(G-C_{12}-alkyl)$_{11}$-*b*-P(*t*BuGE)$_{74}$	1	2.29	2.61	C_{12} (2.57)	75	2.56
P(G-C_{14}-alkyl)$_{10}$-*b*-P(*t*BuGE)$_{64}$	2	2.40	2.83	C_{14} (2.80)	75	2.31
P(G-C_{16}-alkyl)$_{11}$-*b*-P(*t*BuGE)$_{64}$	3	2.61	3.26	C_{16} (3.31)	75	3.35
P(G-C_{14}-alkyl)$_{15}$-*b*-P(*t*BuGE)$_{99}$	4	2.71	2.14	C_{14} (2.35)	75	3.23
P(G-C_{16}-alkyl)$_{10}$-*b*-P(*t*BuGE)$_{98}$	5	2.72	2.21	C_{16} (2.32)	75	2.98

Table 9. Deprotection of the *tert*-Butyl Glycidyl Ether Repeating Units in Poly(alkyl glycidol)-*b*-poly(*tert*-butyl glycidyl ether)

P(G-alkyl)$_m$-*b*-P(G)$_n$	Entry	Polymer/ g	*t*BuGE r.u. / mmol	CF_3COOH/ mmol
P(G-C_{12}-alkyl)$_{10}$-*b*-P(G)$_{77}$	1	2.56	20.11	78.77
P(G-C_{14}-alkyl)$_9$-*b*-P(G)$_{62}$	2	2.31	17.26	96.42
P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{62}$	3	2.61	19.89	86.78
P(G-C_{14}-alkyl)$_{15}$-*b*-P(G)$_{81}$	4	3.23	21.40	106.1
P(G-C_{16}-alkyl)$_9$-*b*-P(G)$_{87}$	5	2.98	20.65	106.1

^{1}H NMR (400 MHz, $CDCl_3$, TMS_{int}). Repeating units: δ = 0.88 (br, 3H, alkyl chain−CH_3), 1.16 (br, 9H, C(CH_3)$_3$), 1.24−1.31 (br, methylen groups of the alkyl chain), 1.49 (br, 2H, NHCH$_2$CH_2), 3.08−3.18 (m, 2H, NHCH_2CH$_2$), 3.39−3.85 (br, polyglycidol backbone), 4.02 (br, 1H, CH_2CONH), 4.24 (br, 1H, CH_2CONH) ppm. End group: δ = 1.88 (m, 2H, CCH$_2$-CH_2CH$_2$O), 2.66 (m, 2H, CCH_2CH$_2$CH$_2$O), 3.39−3.85 (br, 2H, CCH$_2$CH$_2$CH_2O), 7.17−7.30 (m, 5H, phenyl ring) ppm.

The experimental conditions for additional experiments are listed in Table 8.

Deprotection of the tert-Butyl Glycidyl Ether Repeating Units. To P(G-C_{14}-alkyl)$_{10}$-*b*-P(*t*BuGE)$_{57}$ (Table 8, entry 2, 2.31 g, with 17.3 mmol of *t*BuGE r.u.) from the previous step trifluoroacetic acid (11.00 g, 96.42 mmol) was given, and the mixture was stirred at r.t. for 4 h. The excess acid was removed via oil pump vacuum. The crude product was dissolved in chloroform (70 mL) and washed three times with saturated sodium carbonate solution (20 mL). The organic phase was dried over sodium sulfate, and the solvent was evaporated. The crude product was purified via dialysis.

^{1}H NMR (400 MHz, $CDCl_3$, TMS_{int}). Repeating units: δ = 0.88 (m, 3H, alkyl chain−CH_3), 1.12−1.35 (br, methylen groups of the alkyl chain), 1.48 (br, 2H, NHCH$_2$CH_2), 3.12 (br, 2H, NHCH_2CH$_2$), 3.35−3.93 (br, polyglycidol backbone), 4.01 (br, 1H, CH_2CONH), 4.26 (br, 1H, CH_2CONH) ppm. End group: δ = 1.88 (m, 2H, CCH$_2$CH_2CH$_2$O), 2.67 (m, 2H, CCH_2CH$_2$-CH$_2$O), 3.35−3.93 (br, 2H, CCH$_2$CH$_2$CH_2O), 6.81−7.29 (m, 5H, phenyl ring) ppm. ^{1}H NMR (400 MHz, DMSO-d_6, TMS_{int}). Repeating units: δ = 0.85 (m, 3H, alkyl chain−CH_3), 1.12−1.31 (br, methylen groups of the alkyl chain), 1.36 (br, 2H, NH-CH$_2$CH_2), 2.94 (br, 2H, NHCH_2CH$_2$), 3.35−3.55 (br, polyglycidol backbone), 3.91 (br, 1H, CH_2CONH), 4.06 (br, 1H, CH_2-CONH) ppm. End group: δ = 1.70−1.83 (br, 2H, CCH$_2$CH_2-CH$_2$O), 2.61 (m, 2H, CCH_2CH$_2$CH$_2$O), 3.35−3.55 (br, 2H, CCH$_2$CH$_2$CH_2O), 6.81−7.29 (m, 5H, phenyl ring) ppm. Numbers are taken from Table 7.

The experimental conditions for additional experiments are listed in Table 9.

Dialysis of Poly(alkyl glycidol)-b-poly(glycidol). The polymer (200 mg) was dissolved in THF (15 mL), and the solution was transferred into a dialysis membrane. The polymer was stirred for several days in demineralized water, which was exchanged several times during this procedure. Afterward the cleaned polymer was freeze-dried.

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