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Linear-dendritic nonionic poly(propylene oxide)–polyglycerol surfactants

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Abstract—A new type of linear-hyperbranched surfactant has been prepared by anionic ring-opening multibranching polymerization of glycidol onto an end-functional poly(propylene oxide) (PPO) macroinitiator. A hyperbranched, highly hydrophilic polyglycerol block is obtained as the polar segment of the structure. Molecular weights of the nonionic amphiphiles obtained were in the range of 390 to 8,600 g/mol. For comparison, initiators bearing a C16 alkyl chain have also been employed. Furthermore, hyperbranched polyglycerol homopolymers were investigated with respect to amphiphilic properties. All linear-dendritic amphiphiles have been characterized by SEC, DSC, ^{13}C and ^{1}H NMR spectroscopy. A fluorescence-probe technique based on diphenyl hexatriene (DPH) as probe molecule was employed to determine the CMC (critical micelle concentration) of the samples in water. CMCs varied from 7.5×10^{-6} to 1.7×10^{-3} M and were found to depend on the copolymer architecture and the hydrophilic/hydrophobic balance. Measurements at pH 6.75 and 3.00 revealed an increase of the CMC by a factor of 10 for the amine containing copolymers upon lowering of the pH.

1. Introduction

The commercial triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), (PEO–PPO–PEO), commonly known under the trademarks Pluronics or Poloxamer, have attracted considerable attention due to their unique surface properties in combination with excellent biocompatibility. The interfacial properties of Pluronics have been investigated with respect to the formation of micellar solutions,[1] stabilization of emulsions[2] and the presence of ordered phases in micellar solutions.[3,4] Moreover, Pluronics are able to enhance the permeability of lipid membranes for various drugs.[5] The presence of PEO chains leads to biocompatibility and prolonged circulation time of Pluronics-based medical formulations, due to a reduced uptake by the mononuclear phagocytic system (MPS) as well as reduced adsorption on lipid surfaces.[6] Hydrophobically modified Pluronics-polymers have also been proposed as slow drug release systems.[7] Based on their properties, Pluronics are employed in a wide variety of applications from medical and pharmaceutical products to agricultural and photographic applications.[4]

The properties of linear surfactants have been studied in detail. Recently, the attention of researchers has turned to unusual amphiphilic polymer topologies. In several works, the synthesis of surfactants containing highly branched or dendritic polymer structures has been described and investigated.[8,9] A few examples of linear-dendrimer diblock copolymers have been synthesized and characterized with respect to their aggregation behavior.[10,11] Among the systems reported, only a small fraction consisted of a hydrophobic linear and a hydrophilic dendritic block.[8,12,13] In a recent study, the influence of the DB[14] on the aggregation behavior of hyperbranched polymers has been discussed.[15]

To date, well-defined amphiphilic block copolymers consisting of a linear and a hyperbranched segment have not been reported, most probably due to the large polydispersity of common hyperbranched polymers. However, recently we have described a synthetic strategy for the controlled synthesis of hyperbranched polymers based on slow monomer addition.[16] In the current paper we present a convenient synthetic route as well as the interfacial properties of various amphiphilic polyethers with a hydrophobic linear block and a hydrophilic hyperbranched polyglycerol segment.

2. Results and discussion

2.1. Synthesis

Linear-hyperbranched diblock copolymers have not been prepared to date, which is mainly due to the lack of a

Keywords: hyperbranched polymers; dendritic block copolymers; polyglycerol; surfactants; critical micelle concentration.

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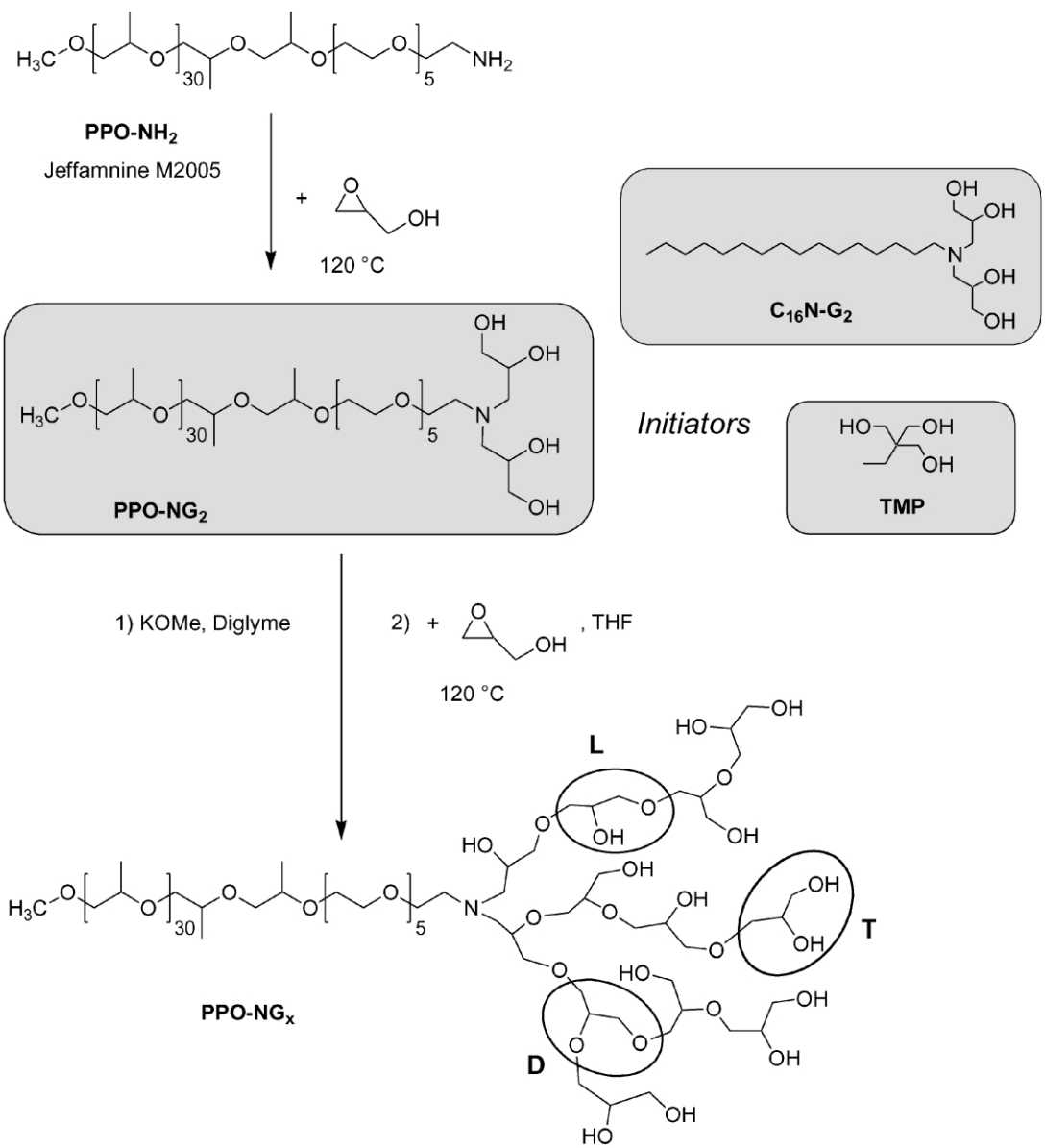
controlled synthetic procedure for the hyperbranched block. In the classic AB_2 polycondensation approach commonly employed for the preparation of hyperbranched structures, extremely broad molecular weight distributions are obtained. However, as has been described previously, glycidol can be polymerized under controlled conditions, incorporating the initiator employed as the core unit.[16] Consequently, linear polymers that are stable under these anionic polymerization conditions and elevated temperatures can be used as macroinitiators. PPO (poly(propylene oxide)) was selected as a suitable hydrophobic polyether macroinitiator for the polymerization of glycidol in our investigation. Since unmodified PPO contains only one terminal secondary alkoxide group, which would compete in reactivity with the primary hydroxyl groups of glycidol, a modified Jeffamine was used. Jeffamines are polyethers in which the terminal hydroxyl functionality has been substituted by a primary amine group (Scheme 1). Convenient reaction of this end group with 2 equiv. of glycidol leads to a bis(2,3-dihydroxypropyl) adduct, which can be further used as a tetrafunctional initiator-core for the polymerization of glycidol (PPO-NG_2). The Jeffamine used in this study consisted of 32 propylene oxide (PO) units and five additional EO units in the vicinity of the amine function with a polydispersity of 1.03, which was increased only slightly to 1.1 on reaction with glycidol (Table 1).

In order to assess the influence of the linear PPO-block on the amphiphilic properties of the linear-hyperbranched surfactants, two simple aliphatic units, bis(2,3-dihydroxypropyl) hexadecyl amine with a hydrophobic C16 alkyl chain and tris(hydroxymethylpropane) as a low molecular weight compound leading to polyglycerol homopolymers have also been used as core-initiators. The amount of glycidol added to these core-initiators in the hyperbranching ring-opening multibranching polymerization determines the molecular weight of the hyperbranched block of the resulting linear-hyperbranched diblock copolymer



Scheme 1. Structures of the linear-dendritic block copolymer surfactants studied. Species initiated by monofunctional poly(propylene oxide) (PPO-NG_x) is shown. Structural units (linear (L), dendritic (D) and terminal (T)) are highlighted.

structures. The degree of polymerization (DP_n) of the polyglycerol block was varied between 2 and 90, covering a wide range of block sizes. All branched surfactants investigated in this work and the general synthetic route are shown in Scheme 1.

2.2. Characterization

All polyglycerols studied were highly viscous liquids. Initiator molecules were either solid (C_{16}-NG_2, TMP) or liquid materials (PPO-NG_2) that were soluble in chloroform, ethanol and methanol. Molar mass data of the polymer samples was gathered by ^{1}H NMR and SEC (Table 1), showing good agreement with the theoretical values based on the amount of glycidol added to the macroinitiators. For all surfactants investigated, low apparent polydispersities in the range of 1.1 to 1.8 were obtained from SEC. Apparent molar masses obtained by SEC were overestimated by a factor of 5 through 9, which might be caused by aggregation phenomena. Furthermore, based on the elevated molar mass of the PPO-NG_2 macroinitiators, cyclized (i.e. non-attached) hyperbranched polyglycerol homopolymers formed during the monomer addition would be easily detectable as a separate distribution mode. However, all measurements showed monomodal, symmetrical molecular weight distributions, indicating that no or a neglectable amount of cyclization had occurred, in agreement with our previous observations.[16] ^{13}C NMR provided valuable information on the degree of branching (DB) of the polyglycerol blocks, which was around 0.58 for all polymers investigated ($DP_n(G)>10$).[16] The relative abundances of dendritic (28%), linear (40%) and terminal (32%) structural units (Scheme 1) could also be derived.

It is an important question, whether the hyperbranched polyglycerol blocks can be regarded as polar structures. Whereas, terminal monomer units are strongly polar due to the two hydroxyl groups, the perfectly branched dendritic moieties represent apolar structural elements. Whether the linear units add to this count as mainly polar or apolar does not strongly affect the hydrophilic/hydrophobic ratio of approximately 1:1. Based on these considerations and the distribution of units in the structure as obtained from detailed simulation studies,[17] a polarity gradient within the structure is already present in the hyperbranched polyglycerol homopolymers. As a consequence of the slow monomer addition, in the proximity of the core mainly dendritic apolar units are present, whereas at the borders of the macromolecule freely accessible, polar terminal units are most likely to occur. Prior investigation of amphiphilic esterified polyglycerols and selective core-shell differentiation agree with this picture.[18,19] In order to investigate whether the polyglycerol structure intrinsically represents an amphiphile, CMCs of the polyglycerol homopolymers with TMP-core have also been determined.

As expected, the solubility of all linear-branched surfactants was found to be strongly affected both by the nature of the linear hydrophobic segment and the degree of polymerization of the polyglycerol block. A polyglycerol block of moderate size (DP_n=10) resulted in an increased solubility in organic solvents: e.g. PPO-NG_2 was soluble within a wide range of solvents with different polarity. A further increase of the size of the polar block caused insolubility in apolar media, e.g. PPO-NG_{74} was only soluble in acetone, methanol and water. In addition to these findings, the opaque appearance of the copolymers PPO-NG_{74} and PPO-NG_{89} at room temperature pointed towards the formation of a phase-separated solid structure. This observation was confirmed by DSC. In the case of the Jeffamines and polyglycerol homopolymers, only one T_g is observed (Table 1, cf. PPO-NG_2 and TMP-G_{25}). In pronounced contrast, for PPO-NG_{74} two distinct glass transitions at −69 and −19°C were observed, clearly due to a phase-segregated supramolecular structure. The glass transitions can be assigned to the PPO- and the polyglycerol-block, respectively. A further increase of the size of the hydrophilic block (PPO-NG_{89}) results in only one detectable T_g, which indicates a decreasing influence of the PPO-chain on the solid phase properties of the diblock copolymers. For this compound, the polyfunctional hyperbranched block dominates the material properties which are based on multiple inter- and intramolecular hydrogen bonding. This observation is in line with the following results: C_{16}-NG_2 and C_{16}-NG_{10} were both soluble in ethanol, methanol and water. Hyperbranched polyglycerol homopolymers and block copolymers with a large polyglycerol fraction are only soluble in very polar media, such as methanol or water independent of the initiator used.

2.3. CMC results

A central objective of this paper was the investigation of the solution properties of the linear-branched surfactants in particular their dependence on the hydrophilic–lipophilic balance. Furthermore, the pH represents an interesting parameter, since the nitrogen atom at the linking site can be protonated. Critical micelle concentrations (CMC) of all branched surfactants in water have been determined by a common fluorescence-probe method, using diphenyl hexatriene (DPH) as probe molecule. DPH has also been used for the study of the micellation in Pluronics.[20,21] Within water or other polar solvents, DPH is quenched and exhibits practically no fluorescence, whereas the absolute intensity increases markedly with the hydrophobicity of the environment.[22,23] Since the fluorescence intensity of DPH is known

Table 1. Molar mass and thermal data for the linear-hyperbranched block copolymers

		TMP-G_{29}	TMP-G_{90}	C_{16}-NG_2	C_{16}-NG_{10}	C_{16}-NG_{82}	PPO-NG_2	PPO-NG_{74}	PPO-NG_{89}
	M_{theor}	2,000	6,000	389	1,100	6,000	2,200	7,000	9,000
SEC	M_n	14,500	n.d.	n.d.	9,800	23,700	10,000	52,000	65,000
	M_w/M_n	1.4	n.d.	n.d.	1.1	1.2	1.1	1.6	1.8
NMR	M_n	2,300	6,800	389	n.d.	6,500	2,200	7,500	8,600
DSC	T_g [°C]	−26	n.d.	n.d.	n.d.	n.d.	−69	−69/−19	−29

(n.d.=not determined).

Table 2. CMC values for the amphiphilic polyglycerols at varying pH (values M×10^{-5}; water solutions, 25°C)

	CMC [×10^{-5} M]								
		TMP–G_{29}	TMP–G_{90}	C_{16}–NG_2	C_{16}–NG_{10}	C_{16}–NG_{82}	PPO-NG_2	PPO-NG_{74}	PPO-NG_{89}
pH	6.75	170	180	0.8–4.6	4.8–19	6.2–28.0	4.2–14	6.6–98	28–130
	3.00	170	180	4.4–13	10–50	20–170	1.4–77	12–170	27–170

to vary with temperature, all measurements were carried out at 25°C. All sample solutions were kept for 20 h prior to the measurements. Table 2 lists the CMC results, which were determined from the crossing point between the straight lines that continue the fluorescence intensity vs log concentration curves before and after the inflection points. Each value is given as a range due to the error of assignment.

2.3.1. Polyglycerol homopolymers. Unexpectedly, for the polyglycerol homopolymers TMP-G_{25} and TMP-G_{90}, a CMC could also be determined. Although distinctively different in molar mass—2,300 compared with 6,800 g/mol—both samples exhibit nearly the same CMC value of 170×10^{-5} and 180×10^{-5} M, respectively, independent of the pH (6.75 or 3.00, cf. Fig. 1, Table 2). As pointed out before, due to the slow addition procedure employed, the macromolecular structure is of a gradient nature. The existence of a CMC for the polyglycerol homopolymers may be explained by the flexibility of the branched structure, permitting the formation of aggregates with a polar shell and a comparatively apolar core. The hydrophilic/hydrophobic balance seems to be independent of molar mass, resulting in the observed similar CMCs. For further clarification of the role of the structural subunits and in order to shed light on the polarity gradient within the hyperbranched polyols, samples with systematically varied DB are currently being synthesized and will be investigated. In summary, hyperbranched polyglycerol—albeit its large number of hydroxyl groups (93 in the case of $TMPG_{90}$!)—intrinsically behaves like an amphiphile.

2.3.2. C_{16}-Polyglycerol. In order to assess the effect of a size variation of the linear hydrophobic segment, a long alkyl chain (C_{16}) has also been introduced. Similar to the Jeffamine-based synthesis, glycidolized hexadecyl amine (C_{16}-NG_2) was used as tetra-functional starter molecule. The size of the hydrophilic block and the number of polar hydroxyl end groups has also been varied by the degree of polymerization of glycidol, ranging from 2 to 10 and 82, respectively. An increase of the size of the hyperbranched block from 2 to 10 glycerol units caused an increase of the CMC of 300% at pH 6.75. Increasing the degree of polymerization to 82 only lead to a further increase of the CMC of 50% (Table 2). Hence, CMCs of C_{16}-NG_x only show a small variation with the DP_n of polyglycerol. In comparison to pure polyglycerols these CMC values are smaller by a factor of about 10, which can be attributed to their decreased solubility.

2.3.3. pH-Variation. The presence of an amine functionality as the linkage between the linear PPO- and hyperbranched polyglycerol block renders pH-dependent measurements of the CMC interesting. The pH-dependent assembly of surfactants may be exploited for controlled release applications.

At a pH of 3, CMCs differ significantly from the values found at neutral pH. In this case, the CMC clearly increases with the size of the hyperbranched block (cf. Fig. 2). Since already at pH 6.75 almost all amine groups are protonated, we tentatively suggest that there is an additional influence of the counter-ion (Cl^-).

This trend unexpectedly plays an increasing role with the size of the polyglycerol block: for x=2 both values are

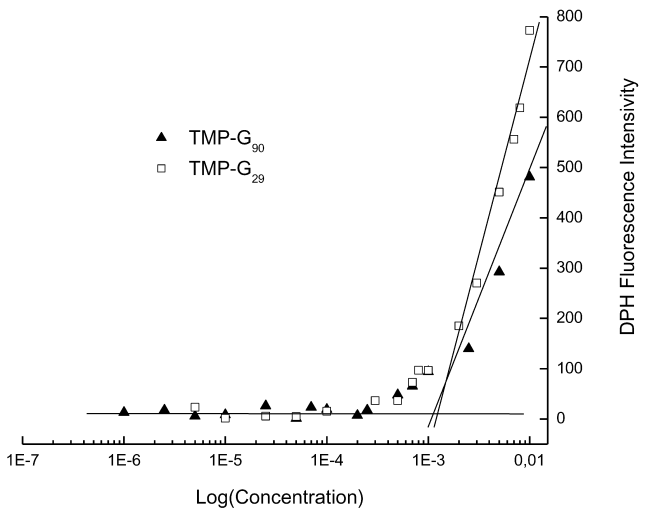


Figure 1. Fluorescence data for the polyglycerol homopolymers TMP-G_{29} (open squares) and TMP-G_{90} (filled triangles) in distilled water with DPH, measured at 25°C: the CMC is independent of molecular weight and pH (not shown).

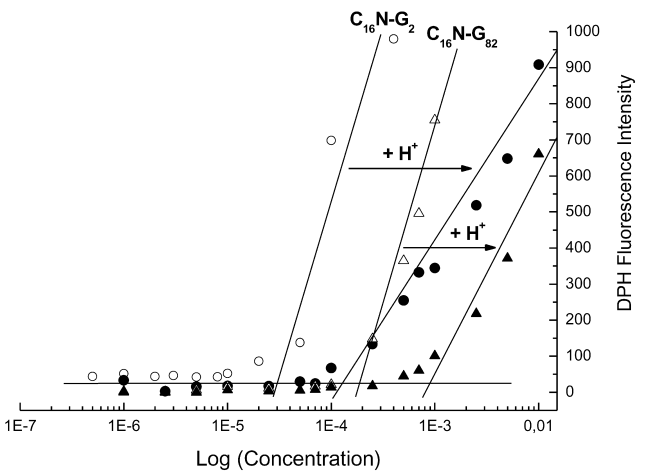


Figure 2. Fluorescence data for the alkylamine containing polyglycerol samples determined in distilled water with DPH at 25°C and two different pH values (6.75=open symbols; 3=filled symbols). Two molecular weights were chosen: 389 (C_{16}-NG_2, circles) and 6,500 g/mol (C_{16}-NG_{82}, triangles). The effects of polyglycerol fraction and pH are clearly recognizable.

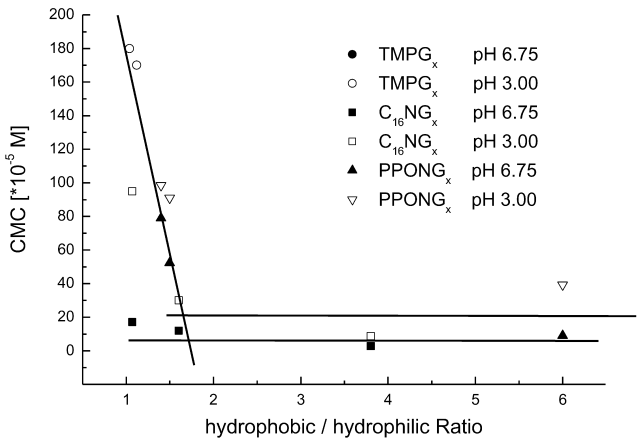


Figure 3. CMC vs hydrophobic/hydrophilic ratio for the investigated samples: filled symbols were determined at pH 6.75, open symbols at pH 3.00.

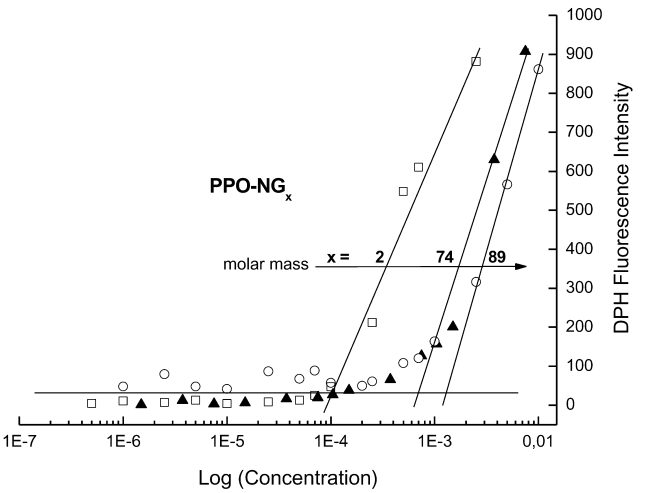


Figure 4. Fluorescence data for the PPO-block copolymers measured in distilled water with DPH at 25°C and pH 6.75: PPO-NG_2 (open squares), PPO-NG_{74} (filled triangles) and PPO-NG_{89} (open circles); the CMC increases with molar mass and polyglycerol content, respectively.

almost equal, for x=10 a factor of about 2.5 is observed and finally, for x=82 a 5-fold increase in CMC is detected, resulting in values almost comparable to polyglycerol homopolymers.

As a comparison of the hydrophilic and hydrophobic properties of all samples investigated, Figure 3 gives the CMC vs hydrophobic/hydrophilic ratio, calculated according to (1), considering only the fractional masses of the respective blocks. The abovementioned factor of 0.5 has been assigned to the polyglycerol block. For reasons of clarity, the average of minimum and maximum CMC value are plotted. For the C_{16}-NG_x systems (squares) the described trend is clearly visible. With the ratio approaching the value 1, a slight increase (pH 6.75) and a drastic increase at pH 3.0 of the CMC is obvious. For homopolyglycerols (circles) the highest CMC values are observed, with essentially no dependence on pH or molar mass.

$$\frac{\text{hydrophobic}}{\text{hydrophilic}} = \frac{m(\text{PPO}) + 0.5m(\text{PG})}{0.5m(\text{PG}) + m(\text{PEO})} \times [\text{PEO in the case of PPO}] \quad (1)$$

2.3.4. PPO–Polyglycerol. Starting from Jeffamine transformed into a starter macromolecule by reaction with glycidol, diblock copolymers with a linear segment of about 2,000 g/mol could be synthesized. As expected from the results for C_{16}-NG_x, the sample with the shortest polyglycerol part, namely PPO-NG_2, possessed the lowest CMC value with 14×10^{-5} M. Enlarging the number of glycerol units resulted in a significant further 7-fold increase of the CMC values going from PPO-NG_2 to PPO-NG_{74} (Fig. 3, Table 2). Although the increase from PPO-NG_{74} to PPO-NG_{89} is not very large, the values for polyglycerol homopolymers are almost obtained. In comparison to all other compounds studied here, PPO-NG_x are closest in chemical nature to Pluronics, although the structures do not match completely, since Pluronics possess a symmetric triblock structure with an interior PPO-segment. Based on an equal molar mass range, the CMC values for the Pluronics are approximately ten times larger than for the PPO-NG_x systems.[24]

An influence of the protonated amine function (pH 3.00) on the self-association behavior is detectable (Fig. 4; Table 2): the CMC increases by an approximately constant value to 40×10^{-5} to 70×10^{-5} M over the whole range of the hydrophobic/hydrophilic ratio. This might be attributed to shielding by the linear PPO-chain, as compared to the C_{16}-aliphatic chain. Two sterically demanding groups shield the amine from both sides: the linear, coiled PPO-chain on one side and the hyperbranched, globular polyglycerol on the other. In the case of the short alkyl chain the protonated amine is still accessible, despite the high degree of polymerization of the polyglycerol block, resulting in improved solubility and aggregation at higher concentrations.

3. Conclusions

Linear-hyperbranched block copolymer surfactants based on polyglycerol have been synthesized and studied with respect to their aggregation behavior in water, based on the determination of the CMC via the DPH fluorescence probe method. Tailoring of the various architectures was achieved by variation of the macroinitiator as well as the degree of polymerization of the polar polyglycerol segment. Adjusting the degree of polymerization led to the following conclusions.

Unexpectedly, polyglycerol homopolymers themselves showed surfactant properties with a CMC of approximately 180×10^{-5} M. This is important with respect to the surface activity of the polyglycerol-based surfactants with alkyl chains as well as PPO-chains. At sufficiently high degrees of polymerization, the CMCs of the diblock copolymers approach the value measured for the homopolyglycerol. Lowering the pH (3.00) enhances this trend, especially in the case of hexadecyl amine based systems. By altering the size of either initiator molecule or polyglycerol block, the CMC can be adjusted in the range from 10^{-6} to 10^{-3} M.

The influence of the protonated amine group decreases with the steric demand of the two polymeric substituents attached to it. In the case of a short alkyl chain, a strong influence on CMC is found, whereas for PPO-based samples only a small and constant increase in CMC was observed. At lowered pH, the quaternized amine appears to increase solubility and leads to hindered aggregation, thus resulting in increasing CMC values.

The periphery of hyperbranched polyglycerols obviously resembles the PEO-block of Pluronics in its polarity. Thus, it will be intriguing to study whether hyperbranched polyglycerol amphiphiles can show 'stealth' effects in biological systems or increase the permeability of lipid membranes. Work on this topic is currently in progress. Encapsulation of apolar guest molecules should also be favored by the presence of the hyperbranched block, forming the shell of the assumed micellar structure. The multiply branched structure should impose a steric barrier for embedded guest molecules, potentially allowing good release control.

At present, a detailed study on the influence of the branching structure of the hyperbranched block on aggregation is in progress. By systematic variation of the DB, additional evidence for the assumed gradient structure of polyglycerol will be obtained, while additional new and interesting amphiphilic diblock copolymer structures will be synthesized.

4. Experimental

4.1. Materials

The macroinitiators 1,1,1-tris(hydroxymethyl)propane (TMP; Fluka), hexadecyl amine (C_{16}-NH_2; Aldrich), Jeffamine M2005 (PPO-NH_2; Huntsman) as well as Diphenyl hexatriene (DPH; Aldrich) were used without further purification. Glycidol (G; Degussa) was distilled prior to polymerization. THF and diglyme were distilled from sodium; methanol and acetone were used as purchased.

4.2. Syntheses

The basic polymerization protocol has been described previously[16] for polyglycerol homopolymers and is based on the slow-monomer-addition principle: 10% deprotonated initiator was dissolved in diglyme using potassium methylate as a base, removing the liberated methanol by distillation. The amount of initiator was chosen according to the desired monomer/initiator ratio. Glycidol (50 mL, 0.75 mol), dissolved in THF, was slowly added to the initiator-core solution at 120°C over 12 h. After completion of the reaction the product was dissolved in methanol and neutralized by addition of cation-exchange resin, twice precipitated into cold acetone and subsequently dried for 72 h at 80°C under vacuum. Yields: 80 to 97%.

The macromolecular initiator-cores based on hexadecyl amine (C_{16}N-G_2) and Jeffamine M2005 (PPO-NG_2) were obtained by dropwise addition of a stochiometric amount of glycidol to a solution of the amine at 120°C within 30 min. The reaction was complete, when no excess glycidol could be detected. Dissolution in warm ethyl acetate and precipitation upon cooling was repeated twice, yielding pure bisglycidolized, tetra-hydroxyfunctional macro-initiators.

4.2.1. TMP-G_x. ^{1}H NMR spectrum (300 MHz, MeOH-d_4) δ 4.7 (s, ×1H, OH), δ 3.9, 3.2 (m, ×5H, PG-scaffold), δ 1.41 (m, 2H, CH_2–TMP), δ 0.93 (m, 3H, –CH_3TMP). ^{13}C NMR spectrum (75 MHz, MeOH-d_4) δ 82–81, 80.0–79.5, 74.5–73.5, 73.5–72.0, 72.0–70.5, 65.0–64.0, 63.5–62.0 (PG-scaffold), 45.46 (C_qTMP), 24.39 (–CH_2–TMP), 8.86 (–CH_3TMP). SEC (see Table 1).

4.2.2. C_{16}-NG_x. ^{1}H NMR spectrum (300 MHz, MeOH-d_4) δ 4.77 (s, ×1H, OH), 3.9, 3.3 (m, ×5H, PG-scaffold), 2.6–2.4 (m, 6H, –CH_2–N), 1.23 (m, 28H, –CH_2–), 0.84 (m, 3H, –CH_3). ^{13}C NMR spectrum (75 MHz, MeOH-d_4) δ 81.3, 79.5, 73.7, 72.7–71.7, 71.2–70.3, 64.1, 62.5 (PG-scaffold), 32.8 (–CH_2–CH_2–CH_3), 30.7–30.19 (m, –CH_2–), 23.46 (–CH_2–CH_3), 14.25(–CH_3). SEC (see Table 1).

4.2.3. PPO-NG_x. ^{1}H NMR spectrum (300 MHz, MeOH-d_4) δ 4.71 (s, OH), 3.9–3.2 (m, PG-scaffold), 1.09 (CH_3PPO). ^{13}C NMR spectrum (75 MHz, MeOH-d_4) δ 79.79, 78.73, 72.49, 71.23–70.77, 69.23, 62.94, 60.96, 57.75 (PG/PPO-scaffold), 17.22 (–CH_3PPO). SEC (see Table 1).

4.3. Characterization

^{1}H and ^{13}C NMR. NMR-Spectra were recorded in d_4-methanol at concentrations of 100 g/L on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively.

SEC measurements were carried out in DMF at concentrations of about 3 g/L. Measurements were performed with a Knauer microgel set C11 using DMF as an eluent at 45°C and a Polymer Laboratories evaporative mass detector EMD 960 operating at 110°C. Polystyrene standards were used for calibration.

(*MALDI TOF*) *mass spectrometry* could not be successfully performed on the products. This is due to the linear combination of the two molar mass distributions (PPO and PG) that adds up to a complex spectrum with overlapping peaks and low signal intensities, rendering it impossible to obtain useful results.

Fluorescence spectroscopy. Measurements were performed employing a luminescence spectrophotometer Perkin–Elmer LS50B using 1 cm path-length polystyrene cuvettes. The sample chamber was thermostated to 25°C using a Thermomix BM circulating water bath, which permitted precise temperature control within ±0.1°C.

CMC. The determination was carried out according to Schubert:[25] A stock solution of 11.62 mg DPH in 5 mL of THF (10 mmol/L) was prepared, of which 0.25 mL were taken for each measurement. THF was evaporated at room temperature and atmospheric pressure for 30 min, before high vacuum was applied for 10 min. 1 mL of distilled water was added and was tip sonicated for 1 min to suspend DPH

completely. After addition of another 4 mL of distilled water, the dispersion was tip sonicated for additional 3 min. 20 μl of this DPH dispersion were added to the polymer solutions (2 mL), which were afterwards homogenized using an ultrasound bath. The samples were allowed to equilibrate for 20 h in order to avoid relaxation processes previously observed for Pluronics.[20] Fluorescence spectra were recorded employing an excitation wavelength of 366 nm and an emission wavelength of 430 nm (slit size=7 nm).

pH. Measurements were made on a Knick 500 laboratory pH-meter. Polymer solutions at pH 3.00 were obtained by dropwise addition of 0.1 M HCl to the polymer solution until the correct pH was reached. Dilution of the polymer solutions with 10^{-3} M HCl afforded the different concentrations.

Thermal properties were measured on a Perkin–Elmer 7 Series Thermal Analysis System in the temperature range of −100 to 20°C at heating rates of 6, 16, 25 and 36 K/min. The melting point of indium (156°C) was used for calibration.

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