Morphology-Controlled Synthesis of Poly(oxyethylene)silicone or Alkylsilicone Surfactants with Explicit, Atomically Defined, Branched, Hydrophobic Tails

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Abstract: Silicone surfactants are widely used in commerce because of the unusual surface activity when compared with fluorocarbon or hydrocarbon surfactants. However, most silicone surfactants are comprised of ill-defined mixtures, which preclude the development of an understanding of structure-surface activity relationships. Herein, we report a synthetic strategy that permits exquisite control over silicone structure by using the B(C_6F_5)₃-catalyzed condensation of hydro- and alkoxysilanes. Six different, precise hy-

drophobes were then mated to hydrophilic poly(oxyethylene)s of three different molecular weights by a metalfree click cyclization to generate a library of explicit silicone surfactants. These compounds were calculated to have a relatively linear value range of the hydrophilic–lipophilic balance, ranging from about 8 to about 15. The

Keywords: click chemistry • poly-(oxyethylene) • silicone • surfactants • borane solubility of some of the compounds was too low to measure a critical micelle concentration (CMC). The others exhibited a broad range of surface tension values at the CMC that depend both on the length of the hydrophilic tail and, more importantly, the nature of the hydrophobic head group. Subtle distinctions in surfactant-related properties, which can be attributed to the three-dimensional structures, can be seen for compounds with comparable numbers of hydrocarbons and silicon groups.

Introduction

Poly(oxyethylene) monoalkyl ethers are the most widely used nonionic surfactants. These surfactants, both oligomeric and polymeric, find applications in consumer products, particularly personal-care products, and a wide variety of industrial processes.^[1] For surfactant design for specific purposes, advantage is taken of the well-established correlation between surface activity and sizes and structures of both the alkyl group and the poly(oxyethylene) hydrophile.

Silicone-based silicone surfactants, which have hydrophobes of much lower surface energy than alkanes, have remarkable surface-activity properties. For example, dilute aqueous solutions of superwetters (for an example see Scheme 1 A), which are commonly used to disperse agricultural chemicals on leaves, can rapidly spread across waxy leaves to 50 times the original droplet size.^[2,3] With the exception of some silicone surfactants that are based on small, well-defined siloxanes, most silicone surfactants involve illdefined mixtures of silicone polymers modified by oligo- or

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Scheme 1. Typical silicone surfactants: A) superwetters and B) rake co-polymers.

poly(ethylene glycol) (PEG) or propylene glycol (PPG) chains (Scheme 1 B).^[4] For the most part, this is because reliable syntheses for explicit silicones do not exist.

The nature of surfactant aggregates found in solution strongly depends on geometric constraints during self-assembly, which derive from structural parameters, such as the volume and length of the apolar constituent.^[5,6] Whereas the tailoring of the polar head groups of surfactants is a very widespread and usual feature in surfactant design, the finetuning of the hydrophobic tails has proven considerably more challenging. In the hydrocarbon series, functionalizedprecursors (such as, iodo or bromo, alkyne or alkene) that would allow the creation of branching units or the introduction of aromatic systems (e.g., phenyl groups) or reactive groups (such as, allyl groups) at precisely defined positions in the hydrocarbon chain are not always available. The silicone series has a similar problem regarding controlled synthesis of the hydrophobe. In addition, and more problemat-

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ic, is the fragility of silicone intermediates and products to acid- and base-catalyzed redistribution and other degradation reactions.^[7] Even in cases for which it is possible to assemble precise, larger silicone fragments, the preservation of these structures requires that subsequent steps are undertaken at neutral pH, which has proven challenging.^[8]

Recently, we^[9] and others^[10,11,12,13] have described the preparation of silicone polymers by using the Piers–Rubinsztajn reaction.^[14,15,16,17] Explicit silicone structures can be the result of such reactions.^[9] We have demonstrated the tolerance of $B(C_6F_5)_3$ to a variety of organic functional groups, including allyl, chloro-, and iodoalkanes.^[18] Equally important, additional functional groups can be incorporated into these silicones while their structures are preserved. For example, appropriately functionalized compounds will undergo click reactions, including metal-free addition of azides to alkynes and the thiolene reaction.^[19]

Herein we present a general, efficient, simple, and metalfree synthetic route to explicit silicone– or silicone–alkyl poly(oxyethylene) surfactants. The process relies on two separate, extremely efficient reactions: the Piers–Rubinsztajn reaction^[20] to create explicit silicone hydrophobes and the Huisgen 1,3-dipolar cycloadditions of azides to alkynes—metal-free click chemistry—used to link the silicone to a hydrophile. In addition to the syntheses, the critical micelle concentration (CMC) and the value of surface tension (ST) at the CMC were determined for the prepared surfactants, and related to the morphologies of the surfactants.

Results and Discussion

The surfactant synthesis required independent preparation of well-defined azidopropylsilicones and propiolate-terminated PEGs, respectively. The routes to each of these key intermediates is first outlined, followed by a description of the coupling process, which involved a low temperature, metal-free (and catalyst-free) cycloaddition of the hydrophobic azides to monopropiolate-terminated poly(oxyethylene)s of various molecular weights under almost solventfree conditions (Scheme 2).

The hydrophobic portion of the surfactant was prepared in two steps by starting from simple, commercially available chloro- or iodopropylalkoxysilanes. These were coupled with hydrosilanes by using $B(C_6F_5)_3$ as a catalyst to provide a small library of complex silicones that possessed a single alkyl halide-the Piers-Rubinsztajn reaction (Scheme 2 A).^[21] With the exception of azide 6-N₃, which was prepared from tris(trimethylsiloxy)silane 6-Cl, all azides 1-N₃ to 5-N₃ were prepared in high yields (typically ranging from 77 to 93%) by displacement of the alkyl halide by azide. It should be noted that the synthesis of such branched, explicit siloxane structures would be extremely tedious and, at the least, difficult with the use of conventional chlorosilane chemistry. The process permits the introduction of decreasing bulk and ramifications on the siloxane backbone, as shown by the comparison in the structures of azides



b) Silicone Fragments in



Scheme 2. a) Synthesis of explicit azidosilicones by using the Piers–Rubinsztajn reaction and/or nucleophilic displacement of halogens, followed by a click ligation. b) The explicit silicone fragments.

1-N₃, **3-N₃**, and **6-N₃**, with increasing numbers of trimethylsilyl groups. Moreover, the functional-group tolerance^[18,19] of the Piers–Rubinsztajn reaction permitted introduction of reactive groups, such as allyl (azide **5-N₃**) or a tunable amount of phenyl moieties (azides **2-N₃** and **4-N₃**; Scheme 2).

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Surfactant polar head groups were prepared from monopropiolate-terminated poly(oxyethylene)s, with average molecular weights of 350, 750 and 2000. The synthetic route to such derivatives involves a classical Fischer esterification of the corresponding monomethoxy-terminated poly(oxyethylene) derivative (Scheme 2B), followed by chromatographic purification (for the 350- and 750-molecular-weight precursors) or precipitation, for the highest-molecular-weight compounds.

Propiolate esters of poly(oxyethylene) were chosen due to the electron deficiency. We have shown previously that such activated alkynes undergo a metal-free click reaction (1,3-dipolar cycloaddition of azides to alkynes) at moderate (50 °C) or even room temperature, without the need of a copper catalyst.^[22,23,24]

The thermal cycloaddition of mono(propiolate) esters of poly(oxyethylene) proved to be extremely efficient; isolated yields that ranged from 79–99% were observed (Scheme 2 a C, Table 1). Moreover, the experimental procedure was straightforward: simple mixing of the two precursors in a small amount of toluene followed by mild heating allows the chemical ligation to proceed and gives the corresponding surfactants. The purification step benefits from two very interesting factors associated with the procedure. The first is inherent to this class of thermal cycloadditions; no byproducts are generated during the reaction. The second relies on the fact that a small excess of the azido derivative was used. This not only allowed the reaction to run faster and to ensure complete conversion of the poly(oxyethylene) propiolate into the surfactant, but also, due to the very large

Table 1. Summary of prepared surfactants.



| | Hydrophobic tail | Polar head group | п | Surfactant yield [%] ^[a] |
|----|------------------|------------------|----|-------------------------------------|
| 1 | 1-N ₃ | 7PEG-6 | 6 | 8PEG-6 (79%) |
| 2 | | 7 PEG-15 | 15 | 8PEG-15 (81%) |
| 3 | | 7PEG-44 | 44 | 8PEG-44 (83%) |
| 4 | 2-N ₃ | 7 PEG-6 | 6 | 9PEG-6 (89%) |
| 5 | | 7 PEG-15 | 15 | 9PEG-15 (90%) |
| 6 | | 7PEG-44 | 44 | 9PEG-44 (78%) |
| 7 | 3-N ₃ | 7 PEG-6 | 6 | 10PEG-6 (99%) |
| 8 | | 7 PEG-15 | 15 | 10PEG-15 (87%) |
| 9 | | 7PEG-44 | 44 | 10PEG-44 (84%) |
| 10 | 4-N ₃ | 7 PEG-6 | 6 | 11PEG-6 (83%) |
| 11 | | 7 PEG-15 | 15 | 11PEG-15 (88%) |
| 12 | | 7 PEG-44 | 44 | 11PEG-44 (93%) |
| 13 | 5-N ₃ | 7 PEG-6 | 6 | 12 PEG-6 (91 %) |
| 14 | | 7 PEG-15 | 15 | 12PEG-15 (90%) |
| 15 | | 7 PEG44 | 44 | 12 PEG-44 (87%) |
| 16 | 6-N ₃ | 7 PEG-6 | 6 | 13PEG-6 (88%) |
| 17 | | 7 PEG-15 | 15 | 13PEG-15 (84%) |
| 18 | | 7 PEG-44 | 44 | 13PEG-44 (93%) |

gap in polarity between the starting azidosiloxane (very nonpolar, running with the solvent front in TLC and chromatography) and the cycloaddition product (amphiphilic, thus more polar), allows easy isolation of the product from the reaction mixture (i.e., a simple "chromatographic" filtration over silica gel; elution with CH2Cl2 eluted the azide, followed by elution with a methanol:CH₂Cl₂ mixture to elute the product). Last but not least, the entire procedure was designed to respect the integrity of the siloxane hydrophobic moiety. Siloxane bonds are extremely sensitive to acid- and base-catalyzed redistribution and other degradation reactions.^[7] The isolated surfactants were analyzed by proton, carbon, and silicon NMR spectroscopy, which all indicate that the exact silicone structures of the starting azides were preserved in the corresponding surfactants. ²⁹Si NMR, in that respect, was essential as it proved, without any ambiguity, that every single M (monosiloxane R₃SiO-), D (disiloxane -OSiR2O-), or T (trisiloxane (RO)3Si-) unit was preserved during the synthetic process.

The structural diversity of the prepared surfactants is reflected in the aggregation properties and calculated hydrophilic–lipophilic balance (HLB^[25] and 3D-HLB)^[26] values, as shown in Table 2 and Figure 1. For example, surfactants **8PEG-6** to **13PEG-6**, based on the smallest poly(oxyethylene) **7PEG-6**, present HLB values that range from 5.41 to 8.79 (3D-HLB, oil component values that range from 2.18 to 10.48). Such low values indicate a highly hydrophobic character. Experimentally, the following was observed: these surfactants were not measurably soluble in water, and thus the CMCs could not be determined. However, this lack of aqueous solubility does not rule out other applications. These amphiphilic derivatives are extremely well suited for the development of water-in-oil emulsions (typical values of HLB

Table 2. CMC data for the prepared surfactants.

| | Surfactant | CMC [mM] | ST at CMC [mN m ⁻¹] | HLB ^[a] | 3D-HLB ^[26] |
|----|------------|----------------------|------------------------------------|--------------------|------------------------|
| 1 | 8PEG-6 | na | na | 5.41 | (5.41, 2.18) |
| 2 | 9PEG-6 | na | na | 5.93 | (5.93, 10.48) |
| 3 | 10 PEG-6 | na | na | 6.82 | (6.82, 2.76) |
| 4 | 11 PEG-6 | na | na | 7.10 | (7.10, 7.71) |
| 5 | 12 PEG-6 | na | na | 7.98 | (7.98, 6.12) |
| 6 | 13PEG-6 | na | na | 8.79 | (8.79, 3.55) |
| 7 | 8PEG-15 | na | na | 9.12 | (9.12, 1.70) |
| 8 | 9PEG-15 | na | na | 9.55 | (9.55, 7.78) |
| 9 | 10 PEG-15 | na | na | 10.58 | (10.58, 1.97) |
| 10 | 11 PEG-15 | 7.2×10^{-5} | 32.3 | 10.88 | (10.88, 5.45) |
| 11 | 12 PEG-15 | 6.1×10^{-5} | 25.0 | 11.82 | (11.82, 4.18) |
| 12 | 13PEG-15 | 5.7×10^{-5} | 23.7 | 12.59 | (12.59, 2.35) |
| 13 | 8PEG-44 | na ^[b] | na ^[b] | 13.92 | (13.92, 0.95) |
| 14 | 9PEG-44 | 8.3×10^{-5} | 48.0 | 14.29 | (14.29, 4.25) |
| 15 | 10 PEG-44 | 0.9×10^{-3} | 23.2 | 15.08 | (15.08, 1.02) |
| 16 | 11 PEG-44 | 4.0×10^{-5} | 46.7 | 15.30 | (15.31, 2.80) |
| 17 | 12 PEG-44 | 2.4×10^{-5} | 38.8 | 15.97 | (15.97, 2.06) |
| 18 | 13PEG-44 | 1.2×10^{-3} | 29.4 | 16.46 | (16.46, 1.12) |

[a] HLB values were calculated using Griffin's method. [b] Attempts to obtain the CMC value for this surfactant were unsuccessful, despite the excellent solubility in water.

[a] Isolated yield.

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Figure 1. ST data for two series of surfactants with different hydrophilic tails, **7PEG-15**, and **7PEG-44**.

range from 4 to 6) or the wetting of powders into oil (HLB range 7–9).

For the three water-soluble surfactants, **11PEG-15**, **12PEG-15**, and **13PEG-15**, extremely small CMC values were found, ranging from 57 (**13PEG-15**) to 72 μ M (**11PEG-15**). These values easily compete with existing explicit trisiloxane surfactants that possess various lengths of poly(oxyethylene) chains. For example, an explicit MDM trisiloxane surfactant with four ethylene-oxide units as the hydrophilic head group have a CMC of 79 μ M.^[2] Moreover, it is well known that the surface activities of siloxane surfactants decrease with increasing length of the poly(oxyethylene)

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chain. Indeed, long hydrophilic ethylene-oxide chains are not completely located in the bulk water, but can penetrate partially into the surfactant film, thus preventing the formation of a tightly packed surfactant film. The CMC of a MDM trisiloxane surfactant with a 16-ethylene-oxide-units hydrophilic head group was found to be 1 mm. Surfactants 11 PEG-15, 12 PEG-15, and 13 PEG-15 have similar hydrophilic components, yet their CMCs are more than two orders-of-magnitude lower than this value. Surfactant 13PEG-15 possesses a purely silicone hydrophobic tail, and accordingly, presents a ST value (23.7 mNm⁻¹) characteristic of silicone surfactants. The substitution of a methyl group by an allyl or a phenyl group produced an increase in the ST value at the CMC to 25.0 (12 PEG-15) and 32.3 mNm^{-1} (11 PEG-15), respectively. These results indicate that even a subtle manipulation in the morphology of the surfactants (e.g., an allyl moiety instead of a methyl) can be used to tailor the physical properties (Figure 1).

The ability to control the surfactant-related properties was further highlighted by the study of the aggregation of surfactants 8PEG-44-13PEG-44, based on the approximate 2000-molecular-weight poly(ethylene oxide) 7PEG-44. These surfactants presented HLB values in the range 13.92-16.46 (3D-HLB oil component values range 0.95-4.25), characteristic of surfactants with good aqueous solubility and high detergency power (i.e., able to strongly stabilize oil-inwater emulsions). The CMC values for surfactants 10 PEG-44 and 13PEG-44 are in the millimolar range, due to the reduced size of the hydrophobic moieties. On the other side, surfactants with a larger, hyperbranched hydrophobic tail, such as 9PEG-44, 11PEG-44, and 12PEG-44, have extremely low CMC values, ranging from 24 µm for 12 PEG-44 to 83 µm for 9PEG-44. Interestingly, surfactants 11PEG-44 and 12PEG-44, based on the 2000-molecular-weight poly(oxyethylene), exhibits CMC values (40 and 24 µм, respectively) that are approximately half of those of the analogues based on the 750-molecular-weight poly(ethylene)oxide 11 PEG-15 and 12 PEG-15 (72 and 61 µm, respectively). This behavior is unusual, as in the trisiloxane-oligo(ethylene oxide) surfactant series it was previously shown that CMC values increase with increasing hydrophilic chain length. However, this effect came with a large increase of the interfacial tension values at the CMC (from 25.0 to 38.8 mN m^{-1} , for 12PEG-15 and 12PEG-44, respectively). Although aggregation occurs at a lower concentration for higher-molecular-weight poly(oxyethylene)s, the interfacial stabilization between water and the surfactant is not as efficient; this effect could also reflect changes in the type of surfactant aggregates that form (micelles, worm-like micelles). Values of ST at the CMC are small for 10PEG-44 and 13PEG-44 and characteristic of silicone surfactants: increased alkyl or aryl character of the hydrophobic moieties also increases the ST at the CMC (with values as high as 48.0 mN m^{-1} for **9PEG**-44).

The surfactants based on the intermediate-chain-length poly(oxyethylene) **7PEG-15**, not surprisingly, presented an intermediate character. Whereas aqueous solubility and thus

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micellization could be observed for the more hydrophilic surfactants, such as **11PEG-15**, **12PEG-15**, and **13PEG-15** (HLB values of 10.88, 11.82, and 12.59, respectively, 3D-HLB (10.88, 5.45), (11.82, 4.18), (12.59, 2.35)), it was not possible to determine CMC values for **8PEG-15** to **10PEG-15**, due to the high hydrophobicity of the extended, ramified hydrophobic tail.

Conclusion

Taken together, all these results clearly show that this new class of hyperbranched, explicit silicone–ethylene oxide amphiphiles is extremely efficient surfactants. The methodology developed herein combines two extremely efficient coupling reactions that should allow the synthesis of tailor-made surfactants, at the wish of the experimentalist. This versatility allows for extensive tuning of surfactant morphology (alkyl versus silicone, degree of branching, size of the hydrophobic moiety), which leads to a great control over the aggregation properties and thus to a wide range of potential applications as detergents, oil-in-water or water-in-oil stabilizers, and so forth.

Experimental Section

Representative procedures for the synthesis of each type of building block used, explicit iodopropyl-modified silicones, the corresponding azido derivatives, monopropiolate-terminated poly(oxyethylene)s, and the surfactants prepared by metal-free click ligation, are given above. Detailed experimental procedures and spectroscopic characterizations of all synthesized compounds are provided in the Supporting Information. Synthesis of 3-iodopropyl(tris(allyldimethylsiloxy))silane: Allyldimethylsilane (1.55 g, 15.5 mmol) was added to a solution of iodopropyltrimethoxysilane (1.00 g, 3.4 mmol) in dry hexane (10 mL). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (40 µL of a 0.078 M solution in toluene, 3.1 µmol). After a short induction time (about 100 s), rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina to remove B- $(C_6F_5)_3$ (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were reaffording moved in vacuo, pure iodopropyl-(tris(allyldimethylsiloxy))silane (1.61 g, 86% yield). ¹H NMR (CDCl₃, 500 MHz): $\delta = 5.79$ (m, 3H; OSi(CH₃)₂CH₂CHCH₂), 4.86–4.91 (m, 6H; OSi(CH₃)₂CH₂CHCH₂), 3.19 (t, J=7.5 Hz, 2H; O₃SiCH₂CH₂CH₂CH₂I), 1.81-1.87 (m, 2H; $O_3SiCH_2CH_2CH_2I$), 1.59 (d, J=10.0 Hz, 6H; OSi-(CH₃)₂CH₂CHCH₂), 0.56–0.59 (m, 2H; O₃SiCH₂CH₂CH₂L), 0.12 ppm (s, 18H; OSi(CH₃)₂CH₂CHCH₂); ¹³C NMR (CDCl₃ 125 MHz): δ =134.15, 113.82, 28.29, 26.25, 16.18, 10.99, -0.16 ppm; ²⁹Si NMR (CDCl₃, 99 MHz, 1% w/v Cr(acac)₃): δ = 4.92 (M), -68.01 (T) ppm. HRMS (ES+): m/z: calcd for [M+Na]+: 565.0919; found: 565.0917.

Synthesis of 3-azidopropyl(tris(allyldimethylsiloxy))silane (5-N₃): A solution of 3-iodopropyl(tris(allyldimethyl-siloxy))silane (1.00 g, 1.8 mmol) in anhydrous DMF (2 mL) was added to a 10 mL round-bottomed flask equipped with a magnetic stir bar. Sodium azide (0.24 g, 3.7 mmol) was added, and the mixture was stirred at room temperature. The reaction was monitored by ¹H NMR spectroscopy; once full substitution of the iodo group was achieved (reaction was completed within 24 h), water (20 mL) was added. The desired product was then extracted with hexanes (25 mL), and the water phase extracted again with hexanes (3×10 mL). The organic layers were combined and dried over sodium sulfate (10 g).

The resulting solution was filtered and concentrated under reduced pres-(without heating) yield 3-azidopropylsure to (tris(allyldimethylsiloxy))silane (0.78 g, 92.5% yield). ¹H NMR (CDCl₃, 500 MHz): $\delta = 5.78$ (m, 3H; OSi(CH₃)₂CH₂CHCH₂), 4.86–4.91 (m, 6H; $OSi(CH_3)_2CH_2CHCH_2$, 3.23 (t, J=7.5 Hz, 2H; O₃SiCH₂CH₂CH₂N₃), 1.61–1.66 (m, 2H; $O_3SiCH_2CH_2CH_2N_3$), 1.59 (d, J=10.0 Hz, 6H; OSi-(CH₃)₂CH₂CHCH₂), 0.50-0.57 (m, 2H; O₃SiCH₂CH₂CH₂N₃), 0.12 ppm (s, 18H; OSi(CH₃)₂CH₂CHCH₂); ¹³C NMR (CDCl₃ 125 MHz): $\delta = 134.13$, 113.79, 54.07, 26.24, 23.29, 11.61, -0.19 ppm; ²⁹Si NMR (CDCl₃, 99 MHz, 1% w/v Cr(acac)₃): $\delta = 4.92$ (M), -67.21 (T) ppm. LRMS (ES+): m/z: calcd for $[M + K]^+$: 496.94; found: 496.3.

Synthesis of 7PEG-15: Propiolic acid (4.2 g, 60.0 mmol), toluene (90 mL), and a catalytic amount of p-toluenesulfonic acid (0.5 g, 2.6 mmol) was successively added in a round-bottomed flask containing monomethoxy poly(ethylene oxide) (av mol wt: 750, 15.0 g, 20.0 mmol). The flask, equipped with a Dean Stark apparatus, was heated with azeotropic removal of water. Completion of the reaction was monitored by ¹H NMR spectroscopy, by comparison of the three protons of the terminal methoxy with the appearance of the methylenic ester protons at 4.32 ppm (about 20 h). The solution was then cooled to room temperature, and washed three times with an aqueous potassium carbonate solution (50 mL). The organic phase was then dried over magnesium sulfate, concentrated in vacuo, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluent (up to 5% v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to afford pure monopropiolate, monomethoxy-terminated poly(ethylene oxide) (12.1 g, 77% yield). ¹H NMR (CDCl₃, 600 MHz): $\delta = 4.34$ (t, J = 6.0 Hz, 2H; -COOCH₂-), 3.74 to 3.55 (m, ≈ 60 H; -OCH₂CH₂O-), 3.37 (s, 3H; OCH₃), 2.89 (s, broad, 1H; HCCCOO); ¹³C NMR (CDCl₃, 125 MHz): $\delta = 152.68, 75.67, 74.56, 71.94, 70.57, 68.57, 65.24, 59.03$. HRMS (ES+): m/z: calcd for $[M + NH_4]^+$: 806.4749; found: 806.4768.

Synthesis of 12 PEG-15:



Prepared propiolate-terminated monomethoxy poly(ethylene oxide) (0.500 g, 0.63 mmol; av mol wt 750, mass calculated by HRMS 788.47 gmol⁻¹) and dry toluene (ca. 1 mL) was added to a 5 mL round bottom flask equipped with a magnetic stir bar and previously prepared azidopropyl(tris(allyldimethylsiloxy))silane (0.37 g, 0.82 mmol). The mixture was then stirred at 45°C and monitored by NMR spectroscopy for completion (typical time required is 64 h). The mixture was then concentrated in vacuo, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluent (up to 3% v:v). The fractions containing the desired compound were then evaporated under reduced pressure to affording pure pale yellow 12PEG-15 as two isomers, with a ratio of roughly 1:4. (0.712 g, 90.2% yield). Major isomer 1,4 (ca. 75 %): ¹H NMR (CDCl₃, 600 MHz): δ=8.05 (s, 1H; g), 5.73-5.78 (m, 3H; j), 4.82-4.88 (m, 6H; k), 4.50 (t, J=6.0 Hz, 2H; d), 4.36 (t, J=7.8 Hz, 2H; c), 3.79 (t, J=6.0 Hz, 2H; e), 3.59-3.68 $(m, \approx 60 \text{ H}; -\text{OCH}_2\text{CH}_2\text{O}-)$, 3.48–3.53 (m, 2 H; f), 3.36 $(s, 3 \text{ H}; \text{OCH}_3)$, 1.92–1.96 (m, 2H; b), 1.56 (d, J=12 Hz, 6H; i), 0.43–0.47 (m, 2H; a), 0.09 ppm (s, 18 H; h); ¹³C NMR (CDCl₃ 150 MHz): $\delta = 160.82$, 139.90, 138.22, 133.95, 127.45, 113.93, 72.07, 70.70, 69.08, 64.23, 59.15, 53.08, 26.16, 24.80, 11.34, -0.17 ppm; ²⁹Si NMR (CDCl₃, 119 MHz, 1 % w/v Cr- $(acac)_3$: $\delta = 5.80$ (M), -67.63 (T). HRMS (ES+): m/z: calcd for [M+

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NH₄]⁺: 1263.6818; found: 1263.6854; HLB value =20×(719.925/1245.79)=11.55. *Minor Isomer 1,5 (ca. 25 %)*: ¹H NMR (CDCl₃, 600 MHz): δ =8.15 (s, 1H; g'), 5.73–5.78 (m, 3H; j), 4.82–4.88 (m, 6H; k), 4.67 (t, *J*=9.0 Hz, 2H; c'), 4.44 (t, *J*=6.0 Hz, 2H; d'), 3.72 (t, *J*=6.0 Hz, 2H; e'), 3.59–3.68 (m, ≈24 H; −OCH₂CH₂O⁻), 3.48–3.53 (m, 2H; f), 3.36 (s, 3H; OCH₃), 1.89–1.91 (m, 2H; b'), 1.53 (d, *J*=12.0 Hz, 6H; i'), 0.43–0.47 (m, 2H; a), 0.07 ppm (s, 18H; h'); ¹³C NMR (CDCl₃ 150 MHz): δ =158.49, 139.90, 138.22, 127.45, 134.09, 113.77, 72.07, 70.70, 68.88, 64.70, 59.15, 52.87, 26.16, 24.71, 11.34, −0.23 ppm; ²⁹Si NMR (CDCl₃, 119 MHz, 1% w/v Cr(acac)₃): δ 5.80 (M), −67.63 (T); HRMS (CBC+): *m/z*: calcd for [*M*+NH₄]⁺: 1263.6818; found: 1263.6854; HLB value =20×(719.925/1245.79)=11.55.

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