

Effect of Chain Unsaturation on the Self-Association of Tri- and Tetraethylene Glycol Octyl Ethers Obtained by Butadiene Telomerization

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2,7-Octadienyl ethers of tri- and tetraethylene glycol ($C_{8:2}E_3$ and $C_{8:2}E_4$) have been synthesized by the atom-economical butadiene telomerization of the corresponding poly(ethylene glycols). On one hand, this synthetic path is attractive because it is expeditious and environmentally benign, and on the other hand, it provides unconventional amphiphiles for which the lipophilic chains possess two double bonds. These two unsaturations increase the global hydrophilicity of the compound, which is also highlighted by the modelization of the compounds using the conductor-like screening model for real solvents (COSMO-RS). The behavior of $C_{8:2}E_3$ and $C_{8:2}E_4$ in binary amphiphile/water and ternary amphiphile/oil/water systems is therefore greatly modified compared to that of the conventional fully saturated homologues (C_8E_3 and C_8E_4) that are easily obtained after hydrogenation. This results in a lowered efficiency of the unsaturated compounds for oil solubilization. The usual Winsor-type microemulsion systems are formed, and for the same oil, the DLS investigation of the microstructure of the Winsor I microemulsion does not highlight any difference in the self-association between the unsaturated and saturated compounds.

1. INTRODUCTION

Poly(oxyethylene glycol) ethers of fatty alcohols $(C_i E_i)$ are a family of compounds that act as references in the physical chemistry of nonionic amphiphiles. Depending on (i, j), they cover a wide range of behaviors from weak to strong amphiphiles¹ and their phase behavior in water and oil/water systems is well documented.² They are also ubiquitous in industrial applications: the long-chain $C_i E_j$'s are the main nonionic surfactants on the market, and the short-chain $C_i E_i$'s, together with their homologues derived from propylene glycol (C_iP_i) , are often simply called glycol ethers and are used as solvents or additives in a number of large-scale formulations. Their main applications as solvents are in paints, inks, and cleaning fluids formulations, whereas other applications include anti-icing agents in jet fuel, fluids for hydraulic systems, and plasticizers.³ The world total consumption of glycol ethers was approximately 1.3 million metric tons in 2006.³ These glycol ethers are also often called hydrotropes, protosurfactants,⁴ or solvosurfactants⁵ because they

exhibit amphiphilicity, albeit limited, while still possessing the required properties to belong to the solvent family (low molecular weight, volatility). They are also sometimes named chameleonic solvents to express their good solubility both in organic solvents and in aqueous media. The shortest members of the series are banned for being reprotoxic,⁶ and that is why the scientific community tries to find biosourced alternatives to glycol ethers.⁷ However, compounds such as C₄E₁, C₆E₂, and C₈E₄ are considered to be safe and are still widely used because of their unique properties.

Industrially, $C_i E_j$'s are produced by reacting an anhydrous alcohol (e.g., *n*-butanol) with ethylene oxide, which gives rise to mixtures of compounds. Even if one can play on the reaction conditions to enhance the production of glycol monoethers, they

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Figure 1. Octadienylethers of tri- and tetraethylene glycol ($C_{8:2}E_3$ and $C_{8:2}E_4$).

are never formed as well-defined compounds and the commercial products are mixtures with an average degree of ethoxylation. To obtain well-defined compounds, an alternative synthetic path is based on the reaction of a given polyoxyethylene with a halogenoalkane under Williamson-type conditions.⁸ It is, however, unsatisfactory with respect to limited yields, the use of unwanted reactants (halogenated compounds, strong bases), the generation of side products (salts), and the required solvent extraction procedures to isolate the desired products.

The palladium-catalyzed telomerization of 1,3-dienes with nucleophiles was first discovered in 1967 by Smutny,⁹ and since then, it has received great attention from both the academic and industrial communities. This reaction pathway is indeed 100% atom-efficient and can avoid the use of organic solvents. 1,3-Butadiene has been the most studied diene, and monoalcohols are usually used as nucleophiles, as, for instance, in the industrially relevant reaction of 1,3-butadiene with methanol, which gives access to 1-octene after hydrogenation and methanol elimination. The use of polyfunctional nucleophiles raises issues of selectivity enhancement to avoid obtaining complex mixtures. Recent papers describe the butadiene telomerization with various polyols including ethylene glycol,^{10,11} 1,2-propanediol, 1,3propanediol, 1,2-butanediol, 1,4-butanediol,¹² glycerol,¹³ isosorbide¹⁴ or even more complex sugars or polyols as pentoses,¹⁵ sorbitol, or sucrose.¹⁶ The use of biphasic reaction systems increases the selectivity and allows catalyst recycling.¹¹

As well as being efficient, this synthetic pathway is also an expeditious way to obtain unconventional amphiphiles that possess a 2,7-octadienyl chain $(C_{8:2})$ with an inner double bond having a trans configuration (Figure 1). Subsequent hydrogenation gives way to the usual saturated homologues (C_8E_3 and C_8E_4). The effect of the presence of double bonds in the alkyl chain of amphiphiles, particularly the short ones, is not widely discussed in the literature.¹⁷ In this work, we have been interested in evaluating the effect of the presence of these double bonds on the behavior of tri- and tetraethylene glycol ethers obtained by butadiene telomerization with the corresponding poly(ethylene glycol). The self-association of $C_{8:2}E_3$ and $C_{8:2}E_4$ in water and oil/water has been evaluated in comparison with that of wellknown C_8E_3 and C_8E_4 . For C_8E_4 and $C_{8:2}E_4$, some DLS (dynamic light scattering) measurements have been performed in the microemulsion of Winsor I systems. The conductor-like screening model for real solvents (COSMO-RS) has also been used to model the compounds.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Triethylene glycol (99%) and tetraethylene glycol (99%) were purchased from Sigma-Aldrich, and palladium acetate (98%) was purchased from Strem. *n*-Octane and cyclohexane used for the construction of "fish" diagrams were obtained from Sigma-Aldrich or Fluka in the highest available grades. All chemicals were used as received.

For a comparison of DLS in the microemulsion phase, a sample of tetraethylene glycol decyl ether ($C_{10}E_4$) was synthesized and purified following known procedures.^{8,18}

2.2. General Methods. Analytical NMR spectra were recorded on Bruker AC spectrometers at 300.13 MHz for ¹H and 75.47 MHz for ¹³C. GC analyses were carried out on a Chrompack CP 9002 apparatus equipped with a flame ionization detector and a CP-Sil 5CB column with a 100% dimethylpolysiloxane internal phase (25 m \times 0.32 mm id). Undecane was chosen as the internal standard for GC analysis. Highresolution mass spectra were obtained at the Centre Universitaire de Mesures et d'Analyses de l'Université de Lille 2 on an Exactive instrument (Thermo Fisher Scientific).

2.3. Synthesis. The typical procedures are described below for $C_{8:2}E_3$ and its saturated homologue C_8E_3 . $C_{8:2}E_4$ and C_8E_4 are obtained through the same procedure.

2.3.1. Telomerization. Catalyst [Pd(OAc)₂] (11.2 mg, 0.05 mmol), phosphine ligand TPPTS (114 mg, 0.2 mmol), triethylene glycol (11.1 mL, 83 mmol), and a soda degassed aqueous solution (1 M, 0.8 mL) were introduced into a 100 mL stainless steel autoclave that was bolted and flushed with nitrogen. The base was dissolved in distilled water, degassed under nitrogen flow, and then transferred to the autoclave. The latter was cooled to -20 °C. A precise volume of butadiene (19 mL, 207 mmol) was condensed in a Schlenk tube with an acetone-dry ice mixture and transferred into the autoclave. Finally, the reactor was heated to 80 °C and vigorously stirred (at a rate of about 1000 rpm) with a magnetic stirrer for 3 h. After the reaction, the system was cooled and excess gaseous butadiene was vented. The crude product was homogenized by methanol addition, and 250 μ L of undecane was added. The conversion and selectivities were calculated from the GC analysis of the homogeneous mixture: 60% glycol conversion is achieved with a selectivity of up to 80% mono- $C_{8:2}E_3$ (linear + branched < 5%), 7% dialkylated dienols, and 13% octadienols.

2.3.2. Separation of the Telomers. Twenty milliliters of water were added, and the telomers were extracted with ethyl acetate (3 × 40 mL). The organic phase was dried by using Na₂SO₄ and evaporated to dryness. Telomers were purified by several distillations under reduced pressure (0.1 mbar). $E_b \approx 130$ °C for C_{8:2}E₃ and 145 °C for C_{8:2}E₄.

2.3.3. Hydrogenation. To get the saturated homologues (C_8E_3 and C_8E_4), hydrogenation was performed in an autoclave at 20 bars of hydrogen and at room temperature for 24 h in the presence of Pd/C. Total conversion was obtained, and filtration of the catalyst over Celite afforded the pure product.

The final products have 97-98% purity (GC and NMR) with 2 or 3% branched isomers as impurities.

2.4. $C_{8:2}E_{3.}^{1}$ ¹ H NMR (300 MHz, CDCl₃): δ 5.74 (ddt, 1 H, ${}^{3}J_{H-H}$ = 17.4 Hz, ${}^{3}J_{H-H}$ = 10.8 Hz, ${}^{3}J_{H-H}$ = 6.4 Hz, CH₂-CH=CH₂); 5.64 (dt, 1H, ${}^{3}J_{H-H}$ = 15.4 Hz, ${}^{3}J_{H-H}$ = 6.6 Hz, CH₂-CH=CH-CH₂O); 5.51 (dt, 1H, ${}^{3}J_{H-H}$ = 15.4 Hz, ${}^{3}J_{H-H}$ = 6.1 Hz, CH=CH-CH₂O); 4.95 (d, 1H, ${}^{3}J_{H-H}$ = 17.4 Hz, CH=CH₂); 4.90 (d, 1H, ${}^{3}J_{H-H}$ = 10.8 Hz, CH=CH₂); 3.92 (d, 2H, ${}^{3}J_{H-H}$ = 6.7 Hz, CH-CH₂O); 3.50 - 3.71 (m, 12H, triethylene glycol moiety): 2.92 (t, 1H, ${}^{3}J_{H-H}$ = 5.9 Hz, OH); 2.01 (dd, 4H, ${}^{3}J_{H-H}$ = 7.2 Hz, CH-CH₂-CH₂-CH₂-CH); 1.43 (tt, 2H, ${}^{3}J_{H-H}$ = 7.5 Hz, CH₂-CH₂ - CH₂); 1³C NMR (75 MHz, CDCl₃): δ 138.5 (1C, CH=CH₂); 134.4 (1C, CH=CH-CH₂O); 126.4 (1C, CH=CH-CH₂O); 114.5 (1C, CH=CH₂); triethylene glycol moiety: 72.5 (1C), 71.9 (1C), 70.6 (2C), 70.3 (1C), 68.9 (1C); 61.5 (1C, CH=CH-CH₂O); 33.1 (1C, CH₂-CH=CH₂CH₂O); 31.6 (1C, CH₂-CH=CH₂); 28.2 (1C, CH₂-CH₂-CH₂).

HRMS m/z: $[M + H]^+$ calcd for $C_{14}H_{26}O_4H$, 259.1904; found, 259.1905.

2.5. $C_{8:2}E_{4.}$ ¹H NMR (300 MHz, CDCl₃): δ 5.72 (ddt, 1 H, ${}^{3}J_{H-H}$ = 17.0 Hz, ${}^{3}J_{H-H}$ = 10.4 Hz, ${}^{3}J_{H-H}$ = 6.6 Hz, CH₂-CH=CH₂); 5.61 (dt, 1H, ${}^{3}J_{H-H}$ = 15.6 Hz, ${}^{3}J_{H-H}$ = 6.6 Hz, CH₂-CH=CH-CH₂O); 5.48 (dt, 1H, ${}^{3}J_{H-H}$ = 15.6 Hz, ${}^{3}J_{H-H}$ = 6.2 Hz, CH=CH-CH₂O); 4.92 (d, 1H, ${}^{3}J_{H-H}$ = 17.0 Hz, CH=CH₂); 4.87 (d, 1H, ${}^{3}J_{H-H}$ = 10.4 Hz, CH=CH₂); 3.88 (d, 2H, ${}^{3}J_{H-H}$ = 6.2 Hz, CH-CH₂O); 3.47-3.68 (m, 16H, tetraethylene glycol moiety); 2.81 (m, 1H, OH); 1.98 (dd, 4H,

 ${}^{3}J_{H-H} = 7.4$ Hz and ${}^{3}J_{H-H} = 6.6$ Hz, $CH-CH_{2}-CH_{2}-CH_{2}-CH)$; 1.40 (tt, 2H, ${}^{3}J_{H-H} = 7.4$ Hz, $CH_{2}-CH_{2}-CH_{2}$). ${}^{13}C$ NMR (75 MHz, CDCl₃): δ 138.5 (1C, $CH=CH_{2}$); 134.4 (1C, $CH=CH-CH_{2}O$); 126.4 (1C, $CH=CH-CH_{2}O$); 114.5 (1C, $CH=CH_{2}$); tetraethylene glycol moiety: 72.5 (1C), 71.9 (1C), 70.6 (2C), 70.5 (2C), 70.2 (1C), 68.98 (1C), 61.5 (1C, $CH=CH-CH_{2}O$), 33.2 (1C, $CH_{2}-CH=CH-CH_{2}O$), 31.6 (1C, $CH_{2}-CH=CH_{2}$), 28.2 (1C, $CH_{2}-CH_{2}-CH_{2}$).

HRMS m/z: [M + Na] calcd for C₁₆H₃₀O₅Na, 303.2166; found, 303.2158.

2.6. C_8E_3 . ¹H NMR (300 MHz, CDCl₃): δ 3.47–3.68 (m, 12H, triethylene glycol moiety); 3.36 (t, 2H, ³ J_{H-H} = 6.9 Hz, CH₂–CH₂O); 3.24 (m, 1H, OH); 1.49 (tt, 2H, ³ J_{H-H} = 6.9 Hz, CH₂–CH₂–CH₂O); 1.19 (m, 10H, CH₃–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–C

¹³C NMR (75 MHz, CDCl₃): triethylene glycol moiety: δ 72.5 (1C), 71.9 (1C), 70.4 (2C), 70.3 (1C), 69.0 (1C); 61.6 (1C, CH₂-CH₂-CH₂O); 31.8 (1C, CH₂-CH₂-CH₂O); 29.6 (1C, CH₂-CH₂-CH₂O); 29.4 (1C, CH₂-CH₂-CH₂-CH₂O), 29.3 (1C, CH₂-CH₂-CH₂-CH₂-CH₂O), 26.1 (1C, CH₃-CH₂-CH₂), 22.6 (1C, CH₃-CH₂), 14.2 (1C, CH₃).

HRMS m/z: $[M + H]^+$ calcd for C₁₄H₃₀O₄H, 263.2217; found, 263.2213.

2.7. C_8E_4 . ¹H NMR (300 MHz, CDCl₃): δ 3.46–3.67 (m, 16H, tetraethylene glycol moiety); 3.36 (t, 2H, ³ J_{H-H} = 6.9 Hz, CH₂–CH₂O); 2.91 (t, ³ J_{H-H} = 6.9 Hz, 1H, OH); 1.49 (tt, 2H, ³ J_{H-H} = 6.9 Hz, CH₂–CH₂–CH₂–CH₂–CH₂O); 1.18 (m, 10H, CH₃–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂); 0.79 (t, 3H, ³ J_{H-H} = 6.9 Hz, CH₃–CH₂). ¹³C NMR (75 MHz, CDCl₃): triethylene glycol moiety: δ 73.0 (1C),

¹³C NMR (75 MHz, CDCl₃): triethylene glycol moiety: δ 73.0 (1C), 71.6 (1C), 70.7 (2C), 70.6 (2C), 70.4 (1C), 70.1 (1C); 61.6 (1C, CH₂-CH₂-CH₂O); 32.1 (1C, CH₂-CH₂-CH₂O); 29.6 (1C, CH₂-CH₂-CH₂O); 29.4 (1C, CH₂-CH₂-CH₂O); 29.3 (1C, CH₂-CH₂-CH₂-CH₂-CH₂O); 26.1 (1C, CH₃-CH₂-CH₂); 22.7 (1C, CH₃-CH₂); 14.2 (1C, CH₃).

HRMS m/z: $[M + H]^+$ calcd for C₁₆H₃₄O₅H, 307.2479; found, 307.2477.

2.8. Surface Tension Measurements. The surface tension was measured with a Kruss K100 tensiometer equipped with a double dosing system for the automatic determination of the critical micellar concentration (cmc). Because of the high cmc values and the necessity to perform dilutions over a wide concentration range, individual measurements were also performed at given concentrations. The tension was measured by the plate method to an accuracy of ± 0.05 mN/m.

2.9. Interfacial Tension Measurements. The oil/water interfacial tension of pre-equilibrated Winsor III systems was measured with a Kruss Site 100 spinning-drop tensiometer. The heavy (water) phase was introduced into the thermostated capillary that was then rotated at a speed of about 6000 rpm to eliminate air bubbles. One drop of the light (oil) phase was then introduced, and the rotational speed was increased so that the deformation of the oil drop was sufficient. To avoid any destabilization processes, the sample, the tensiometer capillary, and the syringes used to extract each phase were thermostated at the same temperature (\pm 0.1 °C), that is, the optimal temperature of the system studied.

2.10. Determination of the Amphiphile/Water Miscibility Gaps. The binary diagrams of $C_{8:2}E_3$, $C_{8:2}E_4$, C_8E_3 , and C_8E_4 were determined visually by gradually increasing the temperature of individual samples and noting the temperature at which the solutions became cloudy. The experiments were performed on heating and cooling, and the discrepancy in the cloud-point temperature was usually lower than 0.1 °C. The cloud-point temperature was taken as the average.

For some samples, particularly at low concentrations, the visual observation was difficult; therefore, a transmission probe (Ocean Optics T200-RT-VIS/NIR) was used to have a reliable limit between clear and slightly turbid samples.

2.11. Solubilization of Sudan Red III. Aqueous solutions of the amphiphile to be tested were prepared at different concentrations, and disperse red 13 was added until reaching saturation. The solutions were stirred at room temperature for 24 h. After this period, the solutions were filtered by means of a syringe equipped with a 0.45 μ m pore-size filter. The amount of hydrophobic dye dissolved was determined by UV–visible absorption of the solutions at 503 nm (Varian Cary 50 spectrometer). Prior to the measurement, a calibration curve was established at this wavelength. The solutions were diluted in absolute ethanol before measurement.

2.12. Fish Diagrams. Ternary amphiphile/oil/water systems were prepared in 2 mL test tubes with the studied compound and chosen oil. Equal amounts (by weight) of water and oil were first introduced, and increasing amounts of amphiphile were added. After each addition, the test tubes were gently mixed and placed in a thermostated bath at the desired temperature (± 0.1 °C) until the attainment of equilibrium, which generally required 2 to 3 h. The types of Winsor systems (I–IV) were determined by visual observation.

2.13. Dynamic Light Scattering (DLS). Dynamic light scattering measurements were performed with a Malvern Zetasizer NanoZ using a 4 mW He-Ne laser operating at a wavelength of 633 nm with a detection angle of 173°. All samples were prepared with 100-nm-filtered Millipore water (resistivity $\approx 18.2 \text{ M}\Omega/\text{cm}$). Homemade sample cells were used to perform measurements in the microemulsion phase of fully equilibrated Winsor I samples at the desired temperature. These cells were made up of a 5 mm internal diameter glass tube in which the compounds were directly weighted (first water, then oil, and then amphiphile). The tube was then flame-sealed, and the sample was gently mixed and left to equilibrate in a thermostatted bath at the temperature required to get a Winsor I system. Once the sample was fully equilibrated, the test tube was placed in a 2 mL clear vial (typical vial for a GC autosampler) to allow for good positioning of the sample at the center of the Zetasizer measuring cell that was previously equilibrated at the same temperature. Previous control experiments were performed on pure solvents and polystyrene standards to make sure that the homemade sample cells did not disturb the DLS measurement.

3. RESULTS AND DISCUSSION

3.1. Atom-Economical Synthesis of C₈E₃/C_{8:2}E₃ and C₈E₄/ C_{8:2}E₄. The telomerization reaction has been applied to welldefined triethylene glycol and tetraethylene glycol as telogenic polyols. The reaction takes place under biphasic conditions, the catalyst remains in the aqueous phase thanks to the watersoluble ligand, and the monotelomers are extracted in the butadiene organic phase as they are formed.¹⁴ This favors the formation of monotelomers over ditelomers (only 1 to 2%). Apart from the butadiene dimer byproduct that is also formed in small amounts because of the biphasic conditions, the main impurities are the octadienols that result from the reaction with residual water.

In the monotelomer fraction, which is easily purified by distillation under reduced pressure, small amounts of branched products are also encountered (<3%) and cannot be separated from the main linear products. Hence, they must be considered to be inherent to the products under study (Figure 2).

After catalytic hydrogenation, saturated homologues C_8E_3 and C_8E_4 are obtained and also contain the same amount of branched isomers.

This synthetic path allows us to obtain in two steps using a very easy procedure around 50 g of pure products on a laboratory scale. It is thus a convenient and useful way to get polyethoxylated octyl ethers for physicochemical studies.



Figure 2. Simplified scheme of the catalytic cycle for the Pd-catalyzed synthesis of octadienylethers of tri- and tetraethylene glycol ($C_{8:2}E_3$ and $C_{8:2}E_4$) (left) and products obtained and studied in this work (right).



Figure 3. Cloud-point curves of the binary amphiphile/water systems of octadienylethers of tri- and tetraethylene glycol ($C_{8:2}E_3$ (\bullet) and $C_{8:2}E_4$ (\blacktriangle)) in comparison with those of their saturated homologues (C_8E_3 (\bigcirc) and C_8E_4 (Δ)).

Table 1. cmc and Cloud Points of C_8E_j (j = 3, 4) and $C_{8:2}E_j$ (j = 3, 4)^{*a*}

	cmc ($T_{\rm c}$ (°C)	
amphiphile	tensiometry	solubilization	cloud point
C ₈ E ₃	$10^{b} (8.5)^{c}$	11^b	$10.0 (11.0)^{c}$
$C_{8:2}E_3$ C_8E_4	$5^{b} (8.5)^{c}$	$\frac{38}{7^b}$	$40.5^{b} (40.8)^{c}$
$C_{8:2}E_4$	15^b	39^{b}	52.4 ^b

^{*a*} The cmc values were obtained either from dye solubilization experiments at 25 °C or surface tension measurements at 20 °C for the triethylene glycol derivatives and at 25 °C for the tetraethylene glycol derivatives. ^{*b*} This work. ^{*c*} Reference 25.

3.2. Binary Systems C_iE_j /Water (i = 8 or 8:2, j = 3 or 4). 3.2.1. *Miscibility Gaps for* $C_8E_3/C_{8:2}E_3$ and $C_8E_4/C_{8:2}E_4$. The miscibility gaps of binary systems $H_2O-C_8E_j$ and $H_2O-C_{8:2}E_j$ (j = 3, 4) are presented in Figure 3, and the coordinates of the critical points are reported in Table 1 in comparison to the literature data for C_8E_3 and C_8E_4 . The data reported by Schubert et al.¹⁹ are reference data because they have been obtained from ultrapure samples via a three-phase extraction technique (3PHEX). The data obtained in this work are in quite good agreement both for C_8E_4 and C_8E_3 , with a slightly higher discrepancy (1 °C) in the case of this latter compound.

Nevertheless, it is interesting that the small quantity of branched derivatives that are formed during the telomerization reaction (<3%) and that cannot be removed by distillation does not significantly impact the behavior in water, as far as the clouding



Figure 4. Optimized geometries and σ surfaces of C_8E_3 (left) and $C_{8:2}E_3$ (right).

phenomenon is concerned. Because this behavior is particularly sensitive to the presence of very small quantities of surface-active compounds, the branched derivatives do not show very different hydrophobicity.

The interesting point is to observe the large increase (more than 10 °C) in the cloud-point value for the doubly unsaturated samples. This increase should be related to the weakening of the lipophilicity of the chain when two double bonds are present, which tends to increase the global hydrophilicity of the compound. Usually, the evaluation of the effect of the presence of unsaturation in the alkyl chain of amphiphilic molecules focuses on the *cis*-ethylene bonds found in the fatty chain of natural fats. The general trend is that the presence of unsaturation lowers the lowest temperature at which fluid states may exist (Krafft temperature in the case of ionics). It was shown that the *cis* double bond in oleate has a profound effect on the Krafft boundary but the soap/water phase behavior is not very disturbed.¹⁷ The selfassembly of long-chain sugar-based amphiphiles in the form of liquid crystals is also modified by the presence of *cis* unsaturations in the alkyl chain.²⁰ However, the influence of chain unsaturation on liquid-liquid miscibility gaps in the case of polyethoxylated amphiphiles is not described and is generally assumed to be small.

To get an idea of the conformational change induced by the presence of the two unsaturations, the compounds were drawn using ArgusLab $4.0.10^{21}$ and optimized with Arguslab UFF. Next, DFT calculations were performed using Turbomole 5.1^{22} and DFT functional B88-PW86 with a triple- ζ valence polarized basis set (TZVP). Continuum solvation model COSMO²³ has been applied in order to simulate a virtual conductor environment for the molecule, and the COSMOconf extension²⁴ has been used to determine the most relevant conformers. In each case, only one conformer has been found, and the optimized geometries are presented in Figure 4 for C₈E₃ and C_{8:2}E₃, together with the COSMO surface (σ surface) generated for each compound showing the local positions of strongly polar sites. Similar results were obtained for the tetraethylene glycol derivatives.

In the σ -surface representation, green to yellow codes the weakly polar surfaces, blue represents positive polarity (δ^+), and red codes strongly negative polar surfaces (δ^-). In our case, the positive polarity (blue) is held by the terminal hydrogen of the polyethoxylate moiety, whereas the strongly negative polar groups (red) are the oxygen atoms of the polyethoxylate moiety.

As expected, the main differences are found in the alkyl chains of the compounds. For doubly unsaturated compounds $C_{8:2}E_{j (j=3,4)}$, the molecular shape is bent because of the *trans* double bond at carbon 2, and the two unsaturations increase the overall polarity of the alkyl chain, as shown by the yellow-to-orange segments at the location of the double bonds.



Figure 5. σ profiles of $C_{8:2}E_3(-)$ and $C_8E_3(--)$.

Both the bent conformation and the presence of more polar segments are responsible for the weakening of the hydrophobicity of $C_{8:2}E_i$ (j = 3, 4) compared to that of the corresponding C_8E_i .

The σ surface of the molecules can be expressed in a more convenient way by using the σ -profile representations, as presented in Figure 5. They express on a 2D graph the proportion of the surface with a given charge density σ . The comparison of the σ profiles of C₈E₃ and C_{8:2}E₃ shows that for both compounds the majority of the charge density is close to zero, expressing the low polarity of the carbon and hydrogen atoms of the skeleton. The oxygen atoms bear a negative polarity and are responsible for the secondary maxima encountered at around 0.01 e.Å⁻². The terminal proton imparts a slight hydrogen bond donor character to the molecules. The main difference between the σ profiles of C_8E_3 and $C_{8:2}E_3$ is the increase in density in the positive region for the octadienyl derivative due to the electron-rich parts of the hydrophobic chain (double bonds). The central peak is also slightly shifted to more negative σ because of the decreased number of hydrogen atoms in the skeleton compared to the number in the saturated homologue, which is also an indication of the decreased apolarity of the lipophilic chain.

3.2.2. Self-Association in Water by Surface Tension and Solubilization Experiments. The concentration dependences of the surface tension of aqueous solutions of the octadienyl ethers of tri- and tetraethylene glycols $C_{8:2}E_j$ (j = 3,4) in comparison to those of corresponding C_8E_j are presented in Figure 6a,b. For C_iE_3 (i = 8 or 8:2), the measurements were performed at 8 °C to be below the cloud point of C_8E_3 .

As expected for medium-chain amphiphiles, no clear break is observed at the aggregation concentration, which in this case cannot be properly called micellization. The decrease in the surface tension with concentration is rather smooth and is actually slightly more marked for the saturated compounds, which tends to show again a rather stronger amphiphilic behavior.

This point is confirmed by the value of the saturated surface tension that is also slightly higher for the octadienyl compounds than for the octyl homologues: 31.2 versus 28.9 mN/m for the triethylene glycol derivatives and 32.7 versus 27.9 mN/m for the tetraethylene glycol derivatives. For all compounds and particularly for the tetraethylene glycol derivatives, a minimum is observed at the cmc, which indicates the presence of one or several other surface-active compounds.

The concentration at which the saturated surface tension is reached is higher for the unsaturated compounds than for the



Figure 6. Surface tension vs concentration for aqueous solutions of octadienylethers of tri- and tetraethylene glycol ($C_{8:2}E_3 (\bullet)$ and $C_{8:2}E_4$ (\blacktriangle)) in comparison to their saturated homologues ($C_8E_3 (\circ)$ and C_8E_4 (Δ)) at T = 25 °C for tetraethylene glycol derivatives, and at T = 20 °C for triethylene glycol derivatives. The dotted vertical lines indicate where the cmc's are located, and the corresponding values are reported in Table 1.

usual saturated $C_i E_j$. To estimate more precisely the aggregation concentrations, solubilization experiments were performed, because the solubilization of a hydrophobic compound in aqueous surfactant solutions is known to increase strongly at the concentration at which the surfactants start to aggregate.

Figure 7a,b show these solubilization experiments performed with disperse red 13, a hydrophobic azo dye. They were carried out at 25 °C, a temperature higher than the cloud point of C_8E_3 , which explains the noisier results for this compound.

Nevertheless, for both the tri- and the tetraethylene glycol derivatives, it is clear from these results that aggregation takes place at higher concentrations for the unsaturated compounds. The aggregation concentrations can be clearly worked out from these data and are consistent with the surface tension curves. They are given in Table 1. The values for saturated C₈E₃ and C₈E₄ are in fairly good agreement with those obtained from the surface tension measurements and with the published values from Ohta et al.²⁵ For C_8E_3 , the value is slightly higher, but that can be due to the uncertainty in the data obtained once the solutions are cloudy. The values worked out for the unsaturated compounds are slightly higher than those obtained from the surface tension curves, but still the important point to stress is the increase in aggregation concentrations, which confirms the reduced hydrophobicity of these compounds. Ambrosone et al.²⁶ have studied even shorter amphiphiles and have shown that



Figure 7. Dye solubilization by aqueous solutions of octadienylethers of tri- and tetraethylene glycol $(C_{8:2}E_3 (\bullet) \text{ and } C_{8:2}E_4 (\blacktriangle))$ as a function of concentration, in comparison with their saturated homologues $(C_8E_3 (\bigcirc) \text{ and } C_8E_4 (\Delta))$ at T = 25 °C.

aggregation takes place at 0.00187 (molar fraction) for C_6E_3 and 0.00197 (molar fraction) for C_6E_4 , which correspond to approximately 104 and 109 mmol/L, respectively. If we compare these values to those determined in this work, then it appears that the loss in hydrophobicity for the octadienyl compounds compared to the octyl derivatives would thus correspond approximately to the loss of one carbon in the alkyl chain.

These experiments also show that the solubilization capacities of the aggregates formed are very similar for the octyl and octadienyl derivatives because the slopes of the straight lines obtained after aggregation are almost the same for the same polyethoxylated polar head.

Finally, it should be stressed that for $C_{8:2}E_3$ a zone of turbidity is found near the aggregation concentration (indicated as a gray zone in Figure 7a). The same behavior had been observed for C_6E_3 by Ambrosone et al.²⁶ and had been attributed to the "borderline" character of this compound, which has intermediate behavior between that of completely insoluble C_6E_2 and that of completely soluble and micellizing C_6E_4 .

3.3. Behavior in Oil/Water 1/1 Systems. It is well known that ternary mixtures of ethoxylated alcohols, *n*-alkanes, and water can separate into a maximum of three liquid phases at equilibrium, depending on the amphiphile, the alkane carbon number (ACN), and the temperature.²⁷ For a given oil and amphiphile, the three-phase systems (Winsor III) appear within a given temperature range, and the optimal temperature T^* is defined as the temperature at which the ethoxylated alcohol exhibits an equal affinity for the aqueous or oily phase. At T^* , the cosolubilization



Figure 8. Fish diagrams of octadienylethers of tri- and tetraethylene glycol ($C_{8:2}E_3$ (\bullet) and $C_{8:2}E_4$ (\blacktriangle)) in *n*-octane/water 1/1 systems in comparison with those of their saturated homologues (C_8E_3 (\bigcirc) and C_8E_4 (\bigtriangleup)).

of these two phases in the middle-phase microemulsion is maximized and the interfacial tension between the oily and aqueous phases is minimized.

The complete phase behavior of the $C_i E_j/n$ -alkane/water system is represented in a prism, but for the sake of simplicity and depending on the properties that need to be enlightened, 2D representations are preferred, namely, the delta (Δ) cut at constant temperature, the gamma (γ) cut with a constant water–oil ratio, and the chi (χ) cut at a constant surfactant concentration.²⁸

3.3.1. Fish Diagrams of C_8E_3 , $C_{8:2}E_3$, C_8E_4 , and $C_{8:2}E_4$ with *n-Octane/Water*. The γ cut at the 1/1 w/w water/oil ratio (also called a fish diagram) gives access to important parameters that allow the comparison of the amphiphilicity of various $C_i E_i$'s if the same *n*-alkane is chosen as the oil. Such diagrams have been drawn for the compounds under study in the n-octane/water system for which a number of literature data are available. They are presented in Figure 8. The three-phase region is encountered within the fish body in the $(T_l - T_u)$ temperature range and for $C_i E_j$ concentrations between C_0 and C^* . For concentrations higher than C^* , a one-phase microemulsion (Winsor IV) is obtained, and for concentrations lower than C_0 , two-phase systems are formed. In the $C_0 - C^*$ concentration range, for temperatures lower than T_{l} , Winsor I systems are formed, whereas for temperatures higher than T_{w} Winsor II systems are encountered. The coordinates of the X point of the fish diagram give the optimal temperature T^* and the efficiency C^* of the amphiphile.

The data are summarized in Table 2 in comparison with literature data on the same systems.

Table 2. Characteristic Data of the H₂O/*n*-Octane/C_iE_j γ Representations in Comparison with the Literature

amphiphile	<i>T</i> * (°C)	$T_1(^{\circ}C)$	$T_{\rm u}$ (°C)	$T_u - T_1$ (°C)	C* (%)	$C_{0}(\%)$	$C^* - C_0$ (%)
$C_6 E_3^{\ b}$	44.6	35.8	53.4	17.6	39.5	2.9	36.6
$C_6 E_4^c$	77.5	nd	nd	nd	53.7	nd	nd
$C_{8:2}E_3^{\ a}$	56.4	26.2	75.6	49.4	62.4	4.7	57.7
$C_8E_3^{a}$	15.2	10.4	20.0	9.6	21.5	1.8	19.7
$C_{8:2}E_4^{\ a}$	>80	49.1	>90		>60	2.5	
$C_8 E_4^{a}$	42.5	35.0	47.6	12.6	25.3	2.0	22.2
$C_8 E_4^{\ b}$	41.9	35.5	48.2	12.7	24.4	1.7	22.7
^{<i>a</i>} This work. ^{<i>b</i>} Reference 29. ^{<i>c</i>} Reference 30.							

The comparison of T^* indicates again that the unsaturated compounds exhibit very reduced hydrophobicity because for the same polar head (E_3 or E_4) the optimal temperature is increased by about 40 °C. For E_3 , it is interesting that T^* for $C_{8:2}E_3$ is even 12 °C higher than that of C_6E_3 , which indicates that the $C_{8:2}$ alkyl chain is even less hydrophobic than a saturated C_6 . Such a conclusion could not be anticipated from the data obtained with the binary systems C_iE_j /water. (See the comparison of aggregation concentration values in section 3.2.2.) The data presented in Table 2 for C_8E_3 and C_8E_4 are in good agreement with the literature values, which tends to indicate again that the presence of small amounts of branched byproduct do not affect the behavior in oil/water systems.

The second point that should be mentioned, which is linked to the weakening of the hydrophobic chain, is the lower efficiency of the unsaturated compounds, as indicated by the very high values of C*. This reduced efficiency has been confirmed by measuring the interfacial tension between excess oil and water phases in the optimal three-phase systems of the four compounds (next section).

The most characteristic feature that needs to be discussed in more detail is the large extension in temperature of the threephase region (fish body). Strey and co-workers^{29,31} have extensively studied the phase behavior of polyethoxylated alcohols ranging from weak to strong amphiphiles and have pointed out that in a homogeneous series of C_iE_j and for the same *n*-alkane the extension in temperature of the three-phase body is low for the shortest amphiphiles (C_4E_1), passes through a maximum for medium-chain amphiphiles (C_6E_3), and then diminishes again for long-chain amphiphiles ($C_{10}E_5$, $C_{12}E_6$). This maximum in the *T* extension of the fish body indicates the frontier between weakly and strongly structured mixtures, also named the Lifshitz line in other papers.³²

To evaluate the degree of structuration of the microemulsions formed by C_8E_4 and $C_{8:2}E_4$, some DLS (dynamic light scattering) experiments were performed (Table 3) in the amphiphile-rich phase of the different Winsor-type systems formed depending on the temperature. In parallel, the same measurements were carried out on similar systems formulated with a stronger amphiphile having the same hydrophilic head, namely, the decyl ether of tetraethylene glycol $C_{10}E_4$. The phase diagram of this compound in *n*-octane/water has already been studied in detail.²⁸ The fish diagram at 1/1 n-octane/water shows the existence of a three-phase system for $C_{10}E_4$ concentrations of between 0.9 and 10.8% in the temperature interval between 22.0 and 29.2 °C. In this work, as a point of comparison, DLS measurements were thus carried out at $1\% C_{10}E_4$ at 20, 35, and 30 °C for WI, WIII, and WII systems, respectively. In the same way,

Table 3. DLS Investigation of the Microemulsions of 10% C_8E_4 , 10% $C_{8:2}E_4$, and 1% $C_{10}E_4$ in *n*-Octane/Water 1/1^{*a*}

amphiphile	T (°C)	Winsor system	Z average (nm)	PDI
C_8E_4	25	WI	11	0.122
	40	WIII	23	0.131
	55	WII	22	0.167
C _{8:2} E ₄	25	WI	11	0.211
	55	WIII	20	0.220
$C_{10}E_{4}$	20	WI	49	0.292
	25	WIII	18	0.142
	30	WII	32	0.064
^{<i>a</i>} The Z avera	ge is the 1	nean hydrodynam	nic radius. PDI is	the poly
dispersity inde				

experiments were performed at 10% C_8E_4 and 10% $C_{8:2}E_4$ at temperatures chosen to scan the different Winsor systems (cf. Figure 8 and Table 3). Because of the extension of the fish body in the case of $C_{8:2}E_4$, the Winsor II system of this compound could not be investigated.

Only for $C_{10}E_4$ could the hydrodynamic radius worked out in the microemulsion of the WI system be consistent with the existence of discrete oil droplets (around 50 nm). For the C8E4 and C_{8:2}E₄ amphiphiles, average hydrodynamic radii close to 11 nm are found, which is too small compared to the molecular lengths of the compounds and indicates that no real structuration is found in this type of system. This was already pointed out by Bodet et al.³³ for similar systems formulated with C_4E_1 for which DLS showed the existence of short-living, diffusive microdomains but no real structuration. In the same way, all microemulsions in the WIII systems have an average hydrodynamic radius that is close to 20 nm, which is an indication of the fluctuating microstructuration. Again in the Winsor II systems, only in the case of C₁₀E₄ could the average hydrodynamic radius support the formation of discrete water droplets. Trying to establish a distinction between weak and medium-strength amphiphiles on the basis of the extension of the fish body or the DLS data is somewhat unwise. In our case, we can say that both C₈E₄ and C_{8:2}E₄ are fairly weak amphiphiles and no real structuration is observed.

The large extension of the three-phase body in the case of the unsaturated amphiphile might also be related to a loss of temperature sensitivity. In conventional C_iE_j , the temperature sensitivity is linked to the progressive dehydration of the polyethoxylated polar head on heating. In the case of the unsaturated compounds, a part, albeit small, of the hydrophilicity is held by the double bonds (σ surface in Figure 4) and does not undergo the same phenomenon when the temperature is increased.

Another alternative explanation of this enlargement of the fish body in temperature could be a modification of the individual solubilities of the amphiphiles in water and *n*-octane. The increased solubilities of the unsaturated compounds in water (higher cloud points, cp_{β}) have been established in the previous section. A lower solubility in oil (higher critical point of the miscibility gap, cp_{α}) has been verified in the case of the tetraethylene glycol derivatives: octylderivative C_8E_4 is completely soluble in *n*-octane down to -20 °C, whereas octadienyl derivative $C_{8:2}E_4$ presents a large miscibility gap in *n*-octane (Figure 9).

Kilpatrick et al.⁴ pointed out that there are two distinct patterns in which the three-phase system arises, depending on



Figure 9. Miscibility gap of the octadienyl ether of tetratethylene glycol $C_{8:2}E_4$ in *n*-octane.



Figure 10. Fish diagrams of the octadienylether of tetraethylene glycol $(C_{8:2}E_4(\blacktriangle))$ in cyclohexane/water 1/1 systems in comparison with that of its saturated homologue $(C_8E_4(\Delta))$.

the strength of the amphiphile, the relative sizes of hydrophilic and lipophilic moieties, the *n*-alkane chain length, and the temperature. In the case of low-molecular-weight C_iE_j such as the one under study (weak amphiphiles), they postulated that the third phase arises from the fusion of two different two-phase regions. We can assume that the reduced solubility of the unsaturated compounds in *n*-octane is responsible in this case for the enlarged three-phase region observed.

3.3.2. Fish Diagrams of C_8E_4 and $C_{8:2}E_4$ with Cyclohexane/ Water. To determine a complete γ plot for $C_{8:2}E_4$ in comparison with C_8E_4 in the experimentally available temperature range, *n*-octane has been replaced by cyclohexane, which has a lower equivalent alkane carbon number (EACN = 1.5^{18}). The corresponding γ plots for cyclohexane/water 1/1 are presented in Figure 10.

This system allows us to draw the same conclusions as in the *n*-octane systems regarding the values of T^* and C^* for the saturated and unsaturated compounds (i.e., a weakening of the hydrophobicity of the chain (higher T^*) and a lower efficiency of the unsaturated compounds).

With regard to the extension in temperature of the fish body, it can be noticed here as well that there is a widening of the temperature interval $(T_u - T_l)$ for $C_{8:2}E_4$ but this widening is far less important than in the case of *n*-octane.

Finally, to support the fact that the unsaturated amphiphiles present a reduced hydrophobicity and a lower amphiphilicity,

Table 4. Interfacial Tension between Excess Oil and Water Phases at the Optimal Formulation for the H_2O/n -Octane/ C_iE_3 and $H_2O/Cyclohexane/C_iE_4$ Systems

system	$T^*(^{\circ}C)$	γ (mN/m)
system	1 (0)	/ min (IIII (/ III)
C _{8:2} E ₃ / <i>n</i> -octane/water ^{<i>a</i>}	56.4	2
C_8E_3/n -octane/water ^a	15.2	$3 imes 10^{-2}$
C_8E_3/n -octane/water ^b	15.8	$2 imes 10^{-2}$
C _{8:2} E ₄ / cyclohexane/water ^a	43.0	$3 imes 10^{-1}$
C ₈ E ₄ /cyclohexane/water ^a	21.2	$2 imes 10^{-2}$
^a This work. ^b Reference 34.		

interfacial tension measurements were performed between the excess oil and water phases at the optimal formulation (corresponding to T^*). It is indeed at this point that the minimum interfacial tensions between the oil and water phases are encountered, when the affinity of the surface-active compound is the same for both phases.³⁴ The measurements were performed in the *n*-octane/water system for the triethylene glycol derivatives and in the cyclohexane/water system for the tetraethylene glycol derivatives (Table 4). For C_8E_3 , the results compare well with the literature data and are another proof of the convenient purity of the compounds prepared via the synthetic path presented here. In all cases, it is clear that the addition of two double bonds to the hydrophobic chain lowers the efficiencies of the amphiphiles because the interfacial tension at the optimal formulation is divided by approximately 100 in the case of the $C_i E_3/n$ -octane systems and by 10 in the $C_i E_4$ /cyclohexane systems.

4. CONCLUSIONS

Butadiene telomerization with polyols is a green atom-efficient way to graft an alkyl chain onto hydrophilic synthons and is thus convenient for obtaining amphiphilic species. The raw materials obtained by this method possess a 2,7-octadienyl alkyl chain with an inner double bond having a *trans* configuration. In this work, the reaction has been performed on tri- and tetraethylene glycols, leading to unconventional C_iE_j 's. Further hydrogenation leads to the well-known fully saturated homologues.

The behavior of these unsaturated derivatives in water and in oil/water systems shows a weakening of the hydrophobicity and a lower efficiency compared to that of the saturated homologues. In γ representations with *n*-octane as the oil, the extent of the fish body is greatly enlarged, which can be related to the weak amphiphile character of the compounds and to the decreased affinity of the unsaturated compounds with oil.

Even if this synthetic pathway cannot avoid the presence of a small amount of branched products (<3%), it seems that it does not strongly influence the physicochemical characteristics in either binary or ternary systems. This has been proven by comparison with the literature data on tetraethylene glycol and triethylene glycol octyl ethers.

Butadiene telomerization with polyols followed by hydrogenation is thus an interesting synthetic path to amphiphiles having an octyl alkyl chain. The hydrogenation step is mandatory to obtain the fully saturated compounds that are the real amphiphiles because it has been shown that the presence of two double bonds greatly impacts the efficiency of the compounds. Because this synthetic pathway can be easily scaled up, it could represent an efficient and more environmentally friendly way to obtain well-defined poly(ethylene glycol) ethers.

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REFERENCES

(1) Gradzielski, M.; Langevin, D.; Sottmann, T.; Strey, R. J. Chem. Phys. **1997**, *106*, 8232–8238. Kahlweit, M.; Strey, R.; Busse, G. Phys. Rev. E **1993**, *47*, 4197–4209.

(2) Sottmann, T.; Stubenrauch, C. In *Microemulsions*; Stubenrauch, C., Ed.; Wiley: Chichester, U.K., 2009; Chapter 1.

(3) Chinn, H. Chemical Economics Handbook Marketing Research Report, Glycol Ethers; SRI Consulting: Menlo Park, CA, November 2007.

(4) Kilpatrick, P. K.; Gorman, C. A.; Davis, H. T.; Scriven, L. E.; Miller, W. G. J. Phys. Chem. **1986**, 90, 5292–5299.

(5) Lunkenheimer, K.; Schroedle, S.; Kunz, W. Prog. Colloid Polym. Sci. 2004, 126, 14–20.

(6) The Toxicology of Glycol Ethers and Its Relevance to Man; Technical Report No. 64; European Center for Ecotoxicology and Toxicology of Chemicals: Brussels, 1995.

(7) Queste, S.; Bauduin, P.; Touraud, D.; Kunz, W.; Aubry, J. M. *Green Chem.* **2006**, *8*, 822–830. Zhu, Y.; Durand, M.; Molinier, V.; Aubry, J. M. *Green Chem.* **2008**, *10*, 532–540.

(8) Gibson, T. J. Org. Chem. 1980, 45, 1095-1098.

(9) Smutny, E. J. J. Am. Chem. Soc. 1967, 89, 6793-6794.

(10) Behr, A.; Urschey, M. Adv. Synth. Catal. 2003, 345, 1242-1246.

(11) Behr, A.; Urschey, M. J. Mol. Catal. A: Chem. 2003, 197, 101-113.

(12) Palkovits, R.; Parvulescu, A. N.; Hausoul, P. J. C.; Kruithof, C. A.; Klein Gebbink, R. J. M.; Weckhuysen, B. M. *Green Chem.* 2009, *11*, 1155–1160.

(13) Bigot, S.; Lai, J.; Suisse, I.; Sauthier, M.; Mortreux, A.; Castanet, Y. *Appl. Catal., A* **2010**, 382, 181–189.

(14) Lai, J.; Bigot, S.; Sauthier, M.; Molinier, V.; Suisse, I.; Castanet, Y.; Aubry, J. M.; Mortreux, A. *ChemSusChem* **2011**, *4*, 1104–1111.

(15) Hadad, C.; Damez, C.; Bouquillon, S.; Estrine, B.; Henin, F.; Muzart, J.; Pezron, I.; Komunjer, L. *Carbohydr. Res.* **2006**, *341*, 1938–1944.

(16) Desvergne-Breuil, V.; Pinel, C.; Gallezot, P. *Green Chem.* **2001**, 3, 175–177.Pennequin I.; Mortreux A.; Petit F.; Mentech J.; Thiriet B.

Fr. Patent 2,693,188, 1992. Pennequin, I.; Meyer, J.; Suisse, I.; Mortreux, A.

J. Mol. Catal. A: Chem. 1997, 120, 139. Hausoul, P. J. C.; Bruijnincx, P. C. A.; Klein Gebbink, J. M. K.; Weckhuysen, B. M. ChemSusChem 2009, 2, 855–858.

(17) Laughlin, R.G. In *The Aqueous Phase Behavior of Surfactants*; Ottewill, R. H., Rowell, R. L., Eds.; Academic Press: New York, 1994; Chapter 11.

(18) Queste, S.; Salager, J. L.; Strey, R.; Aubry, J. M. J. Colloid Interface Sci. 2007, 312, 98–107.

(19) Schubert, K. V.; Strey, R.; Kahlweit, M. J. Colloid Interface Sci. 1991, 141, 21–29.

(20) Jung, J. H.; Do, Y.; Lee, Y. A.; Shimizu, T. Chem.—Eur. J. 2005, 11, 5538–5544.

(21) Thompson, M. A. ArgusLab 4.0.1; Planaria Software LLC: Seattle, WA, 2004.

(22) Ahlrichs, R.; Baer, M.; Haeser, M.; Horn, H.; Koelmel, C. Chem. Phys. Lett. **1989**, *162*, 165.

(23) Klamt, A.; Schueuermann, G. J. Chem. Soc., Perkin Trans. 2 1993, 799–805.

- (24) Klamt, A.; Eckert, F.; Diedenhofen, M. J. J. Phys. Chem. 2009, 113, 4508–4510.
- (25) Ohta, A.; Takiue, T.; Ikeda, N.; Aratono, M. J. Sol. Chem. 2001, 30, 335–350.
- (26) Ambrosone, L.; Costantino, L.; D'Errico, G.; Vitagliano, V. J. Colloid Interface Sci. **1997**, 190, 286–293.

(27) Salager, J. L.; Rantón, R.; Andérez, J. M.; Aubry, J. M. Tech. Ing., Genie Procedes 2001, J2157/1–J2157/20.

(28) Pizzino, A.; Molinier, V.; Catté, M.; Salager, J. L.; Aubry, J. M. J. Phys. Chem. B **2009**, *113*, 1642–1650.

(29) Kahlweit, M.; Strey, R.; Busse, G. Phys. Rev. E 1993, 47, 4197-4209.

(30) Bouton, F.; Durand, M.; Nardello-Rataj, V.; Serry, M.; Aubry, J. M. *Colloids Surf.*, A **2009**, 338, 142–147.

(31) Koehler, R. D.; Schubert, K. V.; Strey, R.; Kaler, E. W. J. Chem. Phys. **1994**, *101*, 10843–10849.

(32) D'Arrigo, G.; Giordano, R.; Teixeira, J. Eur. Phys. J. E 2003, 10, 135–142.

(33) Bodet, J. F.; Davis, H. T.; Scriven, L. E.; Miller, W. G. Langmuir 1988, 4, 455–458.

(34) Sottmann, T.; Strey, R. J. Chem. Phys. 1997, 106, 8606–8615.