# *Notes*

## Synthesis and Properties of ABA Amphiphiles

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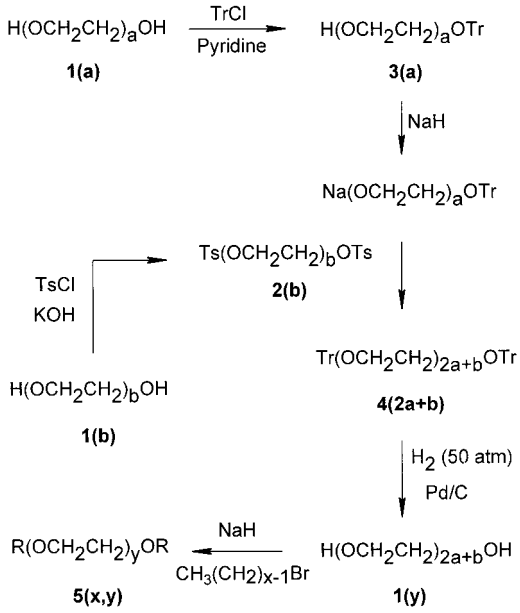
Neutral amphiphilic molecules have a broad range of applications ranging from nonionic surfactants[1,2] to templates for the synthesis of porous inorganic materials.[3−9] Some of the simplest and most versatile surfactants are combinations of linear alkyl and poly(ethylene glycol) (PEG) segments in an AB or ABA pattern, where A represents the alkyl portion and B corresponds to the PEG segment. We are particularly interested in amphiphilic molecules that have an ABA structure because they self-assemble to give ordered solid-state materials[10,11] and serve as models for understanding the ion−molecule complexes that are found in polymer electrolytes.[12] ABA amphiphiles also are important models for a series of recently synthesized $(AB)_n$ microblock copolymers.[13,14] A number of ABA surfactants are known, but it would be helpful to have a more complete series of ABA compounds so the trends in properties could be mapped in detail and related to those seen in polymers. To that end, we synthesized and characterized several families of ABA amphiphiles, and we report here their synthesis and some of their physical properties.

For ABA amphiphiles to be useful models for $(AB)_n$ microblock copolymers, they must replicate the solution- and solid-state properties of the polymers. Because the physical properties of the polymers are sensitive to distributions in the lengths of the blocks, we needed to prepare ABA model compounds where the length of each block was exact. Exact length alkyl segments are readily available, and thus the main synthetic challenge is obtaining the exact-length PEGs needed for the desired ABA structures. PEGs are commercially available in a variety of molecular weights, but only a limited number of exact-length glycols are available in high purity. Chromatographic separation of glycols from commercially available PEG mixtures was considered, but to ensure the purity of the glycols in the amounts needed (tens of grams), we opted for an iterative synthetic approach that allowed us to access a broad range of PEG lengths on large scales.

**Scheme 1**




### Results and Discussion

With the increased interest in using PEGs in polymer-supported solid-phase synthesis, cyclic ethers, and as elements of new materials, there have been several reports describing the synthesis of exact length PEGs. We adopted a modified version of the approach of Keegstra et al.[15] to prepare glycols where *y* is 6−10 and 14. The route to these PEGs is outlined in Scheme 1.

Success in any iterative synthesis demands that each step proceeds in high yield and that each intermediate be readily purified. Our work incorporated modified workup protocols designed to simplify product isolation and minimize the need for chlorinated solvents. For the preparation of the ditosylates, we used aqueous KOH instead of the powdered KOH/$CH_2Cl_2$ mixture used by Keegstra. We found the aqueous system easier to handle, and in our hands, it gave purer products. In addition, we noted that the conditions used by Keegstra (dry $CH_2Cl_2$/KOH) are very similar to those used for preparing

(1) Chu, B.; Zhou, Z. In *Nonionic Surfactants: Polyoxyalkylene Block Copolymers*; Nace, V. M., Ed.; Surface Science Series; Marcel Dekker: New York, 1996; Vol. 60.
(2) Sjoblom, J.; Stenius, P.; Danielsson, I. In *Nonionic Surfactants: Physical Chemistry*; Nace, V. M., Ed.; Surface Science Series; Marcel Dekker: New York, 1987; Vol. 23.
(3) Tanev, P. T.; Pinnavaia, T. J. *Science* **1996**, *271*, 1267−1269.
(4) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325−328.
(5) Eftekharzadeh, S.; Stupp, S. I. *Chem. Mater.* **1997**, *9*, 2059−2065.
(6) Goltner, C. G.; Henke, S.; Weissenberger, M. C.; Antonietti, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 613−616.
(7) Zhao, D. Y.; Huo, Q. S.; Feng, J. L.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024−6036.
(8) Raimondi, M. E.; Marchese, L.; Gianotti, E.; Maschmeyer, T.; Seddon, J. M.; Coluccia, S. *Chem. Commun.* **1999**, 87−88.
(9) Goltner, C. G.; Berton, B.; Kramer, E.; Antonietti, M. *Chem. Commun.* **1998**, 2287−2288.
(10) Matsuura, H.; Fukuhara, K. *J. Phys. Chem.* **1987**, *91*, 6139−6148.
(11) Matsuura, H.; Fukuhara, K.; Masatoki, S.; Sakakibara, M. *J. Am. Chem. Soc.* **1991**, *113*, 1193−1202.
(12) Frech, R.; Huang, W. W. *Macromolecules* **1995**, *28*, 1246−1251.
(13) Qiao, J.; Chen, Y.; Baker, G. L. Submitted to *Macromolecules*.
(14) Qiao, J.; Chen, Y.; Baker, G. L. *Chem. Mater.*, in press.
(15) Keegstra, E. M. D.; Zwikker, J. W.; Roest, M. R.; Jenneskens, L. W. *J. Org. Chem.* **1992**, *57*, 6678−6680.

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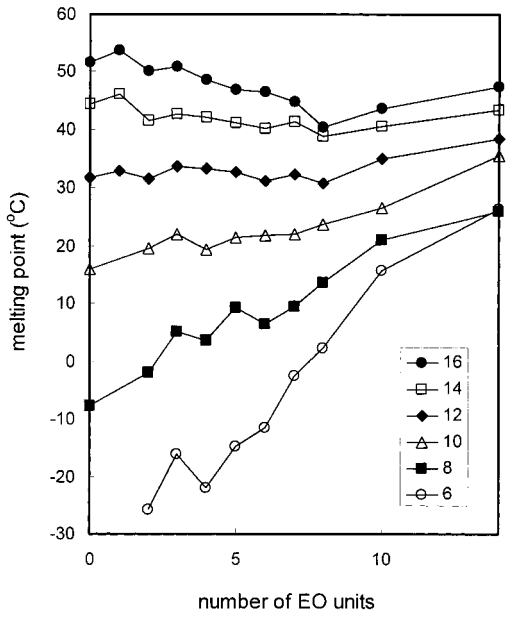


**Figure 1.** Melting points of $C_xEO_yC_x$ amphiphiles. The numbers in the inset are the values of $x$ for the compounds. The melting points were measured under helium by differential scanning calorimetry at a rate of 10 °C/min.

chain-extended poly(ethylene oxide) polymers. By switching to an aqueous system, we eliminated chain extension as a potential side reaction. The workup procedure for the monotritylates was also simplified, enabling us to obtain pure products in high yield. Both the monotritylate and ditritylate syntheses were modified to eliminate the need for $CH_2Cl_2$.

The ABA surfactants were prepared by treating the appropriate glycol with NaH and 2 equiv of the desired alkyl bromide. Depending on the molecular weight, the products ranged from viscous oils to waxy solids. Products with short chain length were initially purified by distillation, and all samples were also purified by low-temperature crystallization. Because the solubility of the amphiphiles changes with chain length, the short-chain compounds ($y = 2, 3$) were crystallized from acetone while the longer chain compounds ($y = 4-8, 10, 14$) were crystallized from methanol.

The melting points for the series of ABA amphiphiles were measured by differential scanning calorimetry (DSC), and the results are plotted in Figure 1. For alkyl groups with $x \geq 10$, the melting points of a series of ABA amphiphiles show a weak dependence on the length of the PEG segment. In contrast, increasing the length of the alkyl chain by two carbon atoms shifts the melting points for a series to higher temperatures. The trend in melting points is similar to that of the *n*-alkanes. For example, the melting points of $C_8EO_7C_8$ and $C_{10}EO_7C_{10}$ are 9 and 22 °C; the corresponding melting points for C16 and C20 are 18 and 38 °C.

Another feature of the melting point data is the oscillation of the melting points within a series, especially when $y \leq 6$. ABA molecules with odd values of $y$ have systematically higher melting points than those where $y$ is even. Odd−even effects are commonly seen in the melting points of *n*-alkanes and molecules such as liquid crystals, where chromophores or mesogens are linked with short alkyl chains in a planar zigzag conformation. In the ABA amphiphiles, the odd−even effect originates in the PEG segment, where an odd number of EO units correspond to an even number of oxygen atoms and a relatively high melting point. The odd−even effect can be understood by treating the oxygen atoms in the chain as defects in a linear alkane caused by the difference in the C−O−C bond angle relative to that of the C−C−C bond angle. Assuming the ABA chains adopt a planar zigzag conformation places successive oxygen atoms anti to each other, effectively canceling the distortions. Thus, ABA amphiphiles with odd values of $y$ are more linear and have higher melting points. Since the odd−even effect is related to the overall linearity of the amphiphile, increasing the length of either the alkyl or the ethylene oxide segments should result in a more linear structure. For long chains, the distortion introduced by an odd number of oxygen atoms can be accommodated by small changes in the conformation of the alkyl and ethylene oxide segments that restore the overall linear shape of the amphiphile. As shown in Figure 1, the odd−even effect becomes weak for $x \geq 12$ or $y \geq 6$.

## Experimental Section

**Preparation of Oligomeric Ethylene Glycol Ditosylates, 1,5-Bis(tosyloxy)-3-oxapentane [Ts(OCH$_2$CH$_2$)$_2$OTs, 2(2)].** A solution of diethylene glycol (130 g, 1.22 mol) and *p*-toluenesulfonyl chloride (701 g, 3.66 mol) in THF (1.5 L) was placed in a 3 L three-necked round-bottom flask and stirred with a mechanical stirrer. The flask was cooled with an ice/water bath, and a solution of KOH (450 g, 8.00 mol) in water (500 mL) was added slowly over a period of 1 h. The ice−water bath was removed, and the system was stirred for an additional 7 h. The resulting suspension was poured into a mixture of 1 L of $CH_2Cl_2$ and 500 mL of ice−water, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic solutions were washed three times with distilled water and dried over $MgSO_4$ overnight. After removal of $MgSO_4$ and solvent, the solid was recrystallized twice from methanol to give 89% yield of **2(2)** as a white crystalline product: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.76 (d, 4H), 7.33 (d, 4H), 4.07 (t, 4H), 3.59 (t, 4H), 2.43 (s, 6H); mp 87.5−88.5 °C (lit.[16] mp 87.0−87.5 °C)

**1,8-Bis(tosyloxy)-3,6-dioxaoctane [Ts(OCH$_2$CH$_2$)$_3$OTs, 2(3)]. 2(3)** was prepared similarly to give 87% yield of a white crystalline solid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.77 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.63 (t, 4H), 3.51 (s, 4H), 2.43 (s, 6H). mp 80−81 °C (lit.[16] 87.0−87.5 °C).

**Ditosylates for $y = 4-10$ [Ts(OCH$_2$CH$_2$)$_y$OTs, 2($y$)].** Ditosylates **2($y$)** for $y = 4-10$ were prepared the same way as diethylene glycol ditosylate. After the reaction was finished, ice−water was added, the solution was separated, and the aqueous layer was extracted with diethyl ether. The combined organic solutions were washed with saturated aqueous NaCl solution and dried over $MgSO_4$ overnight. After removal of $MgSO_4$ and solvent, a clear, colorless to light yellow viscous liquid was obtained. The product was pure enough for further use.

**1,11-Bis(tosyloxy)-3,6,9-trioxaundecane [Ts(OCH$_2$CH$_2$)$_4$OTs, 2(4)].** A clear, colorless oil[17] was obtained in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.57 (s, 4H), 3.54 (s, 4H), 2.43 (s, 6H).

**1,14-Bis(tosyloxy)-3,6,9,12-tetraoxatetradecane [Ts(OCH$_2$CH$_2$)$_5$OTs, 2(5)].** A clear, colorless oil[18] was obtained in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.57 (s, 4H), 3.55 (s, 8H), 2.43 (s, 6H).

**1,17-Bis(tosyloxy)-3,6,9,12,15-pentaoxaheptadecane [Ts(OCH$_2$CH$_2$)$_6$OTs, 2(6)].** A clear, colorless oil[19] was obtained in

(16) Ouchi, M.; Inoue, Y.; Kanzaki, T.; Hakushi, T. *J. Org. Chem.* **1984**, *49*, 1408−1412.
(17) Bartsch, R. A.; Liu, Y.; Kang, S. I.; Son, B.; Heo, G. S.; Hipes, P. G.; Bills, L. J. *J. Org. Chem.* **1983**, *48*, 4864−4869.
(18) Fenton, D. E.; Parkin, D.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 449−454.
(19) Newcomb, M.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6405−6410.

99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.58 (s, 4H), 3.55 (s, 12H), 2.43 (s, 6H).

**1,20-Bis(tosyloxy)-3,6,9,12,15,18-hexaoxaeicosane [Ts(OCH$_2$CH$_2$)$_7$OTs, 2(7)].** A clear, colorless oil[20] was obtained in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.56 (m, 20H), 2.43 (s, 6H).

**1,23-Bis(tosyloxy)-3,6,9,12,15,18,21-heptaoxatricosane [Ts(OCH$_2$CH$_2$)$_8$OTs, 2(8)].** A clear, colorless oil[15] was obtained in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.56 (m, 24H), 2.43 (s, 6H).

**1,29-Bis(tosyloxy)-3,6,9,12,15,18,21,24,27-nonaoxanonacosane [Ts(OCH$_2$CH$_2$)$_{10}$OTs, 2(10)].** A clear, colorless oil was obtained in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.56 (m, 32H), 2.43 (s, 6H).

**1,41-Bis(tosyloxy)-3,6,9,12,15,18,21,24,27,30,33,36,39-tridecaoxahentetracontane [Ts(OCH$_2$CH$_2$)$_{14}$OTs, 2(14)].** Ditosylate **2(14)** was prepared as described for tetraethylene glycol ditosylate except that the reaction time was extended to 16 h. After the reaction was finished, a mixture of 10/1 $CH_2Cl_2$ and ice−water was added to the reaction mixture until the solids dissolved. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic solutions were washed with saturated NaCl solutions and dried over $Na_2SO_4$ overnight. Removal of $Na_2SO_4$ and solvent gave a clear, colorless viscous oil in 97% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.78 (d, 4H), 7.32 (d, 4H), 4.12 (t, 4H), 3.65 (t, 4H), 3.56 (m, 48H), 2.43 (s, 6H).

**Ethylene Glycol Oligomer Monotritylates and Ditritylates. 7,7,7-Triphenyl-2,5-dioxaheptan-1-ol [Tr(OCH$_2$CH$_2$)$_2$OH, 3(2)].** A 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet was charged with diethylene glycol (106 g, 1.00 mol) and pyridine (11.9 g, 0.150 mol). With the mixture heated and maintained at 45 °C, powdered trityl chloride (27.9 g, 0.100 mol) was added to the reaction mixture under vigorous stirring. After being stirred at 45 °C for 16 h, the suspension was filtered, and the white solid was washed with distilled water. The crude product was recrystallized once from 2-propanol and twice from 2/1 EtOAc/hexanes to give a white crystalline solid: yield 71%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (d, 6H), 7.25 (m, 9H), 3.58−3.77 (m, 6H), 3.24 (t, 2H), 2.06 (t, 1H); mp 113.0−114.5 °C (lit.[15] mp 112.7−114.5 °C).

**10,10,10-Triphenyl-3,6,9-trioxadecan-1-ol [Tr(OCH$_2$CH$_2$)$_3$OH, 3(3)]. 3(3)** was prepared as described for diethylene glycol monotritylate. After the reaction was finished, the reaction mixture was poured into a separatory funnel, and an equal volume of distilled water was added. The mixture was shaken vigorously and allowed to settle for 2 h. The bottom layer was separated from the aqueous solution, and the aqueous solution was extracted with toluene. The product was dissolved in toluene and combined with the toluene extract. The toluene solution was washed with distilled water and dried over $MgSO_4$ overnight. Removal of the solid and solvent gave a yellow viscous gellike liquid[21] in 99% yield. The product was used for next reaction without further purification: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (d, 6H), 7.25 (m, 9H), 3.59−3.75 (m, 10H), 3.22 (t, 2H), 1.70 (s, 1H).

**13,13,13-Triphenyl-3,6,9,12-tetraoxatridecan-1-ol [Tr(OCH$_2$CH$_2$)$_4$OH, 3(4)]** was prepared and purified as described for **3(4)** to give a yellow viscous gellike liquid[22] in 99% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (d, 6H), 7.20−7.45 (m, 9H), 3.25−3.15 (m, 12H), 3.12−3.08 (t, 2H), 3.26 (t, 2H), 2.35 (s, 1H).

**General Procedure for the Preparation of Ditritylates. 1,1,1,24,24,24-Hexaphenyl-2,5,8,11,14,17,20,23-octaoxatetracosane [Tr(OCH$_2$CH$_2$)$_7$OTr, 4(7)].** A 500 mL Schlenk flask with an argon inlet was charged with NaH (3.00 g, 0.125 mol). A solution of diethylene glycol monotritylate (34.8 g, 0.100 mol) in 200 mL of THF was added dropwise, and the mixture was stirred for 24 h. Ts(OCH$_2$CH$_2$)$_3$OTs (23.0 g, 0.050 mol) in 150 mL THF was added dropwise, and the mixture was stirred for 96 h at room temperature. The solid was removed by filtration, and the organic filtrate was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated to give a quantitative yield of **4(7)** as a yellow gellike liquid:[15] $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45 (d, 12H), 7.18−7.30 (m, 18H), 3.59−3.69 (m, 24H), 3.19−3.25 (t, 4H).

**1,1,1,21,21,21-Hexaphenyl-2,5,8,11,14,17,20-heptaoxahenicosane [Tr(OCH$_2$CH$_2$)$_6$OTr, 4(6)].** A yellow, gellike liquid[15] was prepared by reacting Tr(OCH$_2$CH$_2$)$_2$OH with Ts(OCH$_2$CH$_2$)$_2$OTs: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45 (d, 12H), 7.18−7.28 (m, 18H), 3.62 (m, 20H), 3.20 (t, 4H).

**1,1,1,27,27,27-Hexaphenyl-2,5,8,11,14,17,20,23,26-nonaoxaheptacosane [Tr(OCH$_2$CH$_2$)$_8$OTr, 4(8)].** A yellow gellike liquid[15] was prepared by reacting Tr(OCH$_2$CH$_2$)$_2$OH with Ts(OCH$_2$CH$_2$)$_4$OTs: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.48 (d, 12H), 7.18−7.23 (m, 18H), 3.60−3.78 (m, 28H), 3.20−3.30 (t, 4H).

**1,1,1,30,30,30-Hexaphenyl-2,5,8,11,14,17,20,23,26,29-decaoxatricontane [Tr(OCH$_2$CH$_2$)$_9$OTr, 4(9)].** A yellow gellike liquid was prepared by reacting Tr(OCH$_2$CH$_2$)$_3$OH with Ts(OCH$_2$CH$_2$)$_3$OTs: yield 98%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45 (d, 12H), 7.18−7.30 (m, 18H), 3.58−3.69 (m, 32H), 3.19−3.25 (t, 4H).

**1,1,1,33,33,33-Hexaphenyl-2,5,8,11,14,17,20,23,26,29,32-dodecaoxatritriacontane [Tr(OCH$_2$CH$_2$)$_{10}$OTr, 4(10)].** A yellow gellike liquid was prepared by reacting Tr(OCH$_2$CH$_2$)$_4$OH with Ts(OCH$_2$CH$_2$)$_2$OTs: yield 99%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (d, 12H), 7.17−7.30 (m, 18H), 3.57−3.68 (m, 36H), 3.20 (t, 4H).

**1,1,1,45,45,45-Hexaphenyl-2,5,8,11,14,17,20,23,26,29,32,-35,38,41,44-pentatetracontane [Tr(OCH$_2$CH$_2$)$_{14}$OTr, 4(14)]** was prepared by reacting Tr(OCH$_2$CH$_2$)$_4$OH with Ts(OCH$_2$CH$_2$)$_6$OTs. Removal of the $MgSO_4$ and concentration of the solvent gave a brownish-yellow solution. The solution was refluxed over charcoal overnight and filtered to give a pale yellow solution. Removal of the solvent gave a viscous pale yellow liquid in 97% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (d, 12H), 7.17−7.30 (m, 18H), 3.57−3.68 (m, 52H), 3.20 (t, 4H).

**General Procedure for the Synthesis of Exact Length Ethylene Glycol Oligomers. 3,6,9,12,15,18-Hexaoxaeicosane-1,20-diol [H(OCH$_2$CH$_2$)$_7$OH, 1(7)].** A high-pressure Monel bomb with a glass insert was charged with 36.6 g (45.0 mmol) of heptaethyelene glycol ditritylate, 150 mL of $CH_2Cl_2$, and 0.677 g of 10% palladium on carbon. Hydrogenolysis was carried out at room temperature under 50 atm of $H_2$ for 48 h. Upon completion of the reaction, the catalyst (which can be reused) was filtered and washed with $CH_2Cl_2$. The filtrate was concentrated to give a mixture of a white solid (triphenylmethane) and an oil. The mixture was dissolved in boiling methanol, and the majority of the triphenylmethane crystallized when the solution was cooled to 0 °C. The mixture was filtered, and the filtrate was washed with hexanes six times to remove trace amounts of triphenylmethane. The solvent was removed to give a clear, colorless oil: yield 97%; bp 180−195 °C/50 mTorr (lit.[23] bp 200−208 °C/300 mTorr); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.67 (t, 4H), 3.66−3.61 (m, 20H), 3.60−3.55 (t, 4H), 2.9 (s, 2H).

**3,6,9,12,15-Pentaoxaheptadecane-1,17-diol [H(OCH$_2$CH$_2$)$_6$OH, 1(6)]:** clear, colorless oil; yield 99%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.67 (t, 4H), 3.66−3.61 (m, 16H), 3.60−3.55 (t, 4H), 2.9 (s, 2H); bp 197−205 °C/100 mTorr (lit.[24] bp 201−205 °C/700 mTorr).

**3,6,9,12,15,18,21-Heptaoxatricosane-1,23-diol [H(OCH$_2$CH$_2$)$_8$OH, 1(8)]:** clear, colorless oil;[15] yield 97%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.55 (m, 32H), 2.7 (s, 2H).

**3,6,9,12,15,18,21,24-Octaoxahexacosane-1,26-diol [H(OCH$_2$CH$_2$)$_9$OH, 1(9)]:** clear, colorless oil; yield 92%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.55 (m, 36H), 2.7 (s, 2H).

**3,6,9,12,15,18,21,24,27-Nonaoxanonacosane-1,29-diol [H(OCH$_2$CH$_2$)$_{10}$OH, 1(10)]:** clear light yellow oil; yield 96%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.56 (m, 40H), 2.58 (s, 2H).

**3,6,9,12,15,18,21,24,27,30,33,36,39-Nonaoxahentetracontane-1,41-diol [H(OCH$_2$CH$_2$)$_{14}$OH, 1(14)]:** white waxy solid;

(20) Weber, E. *J. Org. Chem.* **1982**, *47*, 3478−3486.
(21) Huszthy, P.; Bradshaw, J. S.; Zhu, C. Y.; Izatt, R. M.; Lifson, S. *J. Org. Chem.* **1991**, *56*, 3330−3336.
(22) Kaatsrichters, V. E. M.; Zwikker, J. W.; Keegstra, E. M. D.; Jenneskens, L. W. *Synth. Commun.* **1994**, *24*, 2399−2409.
(23) Warshawsky, A.; Kalir, R.; Deshe, A.; Berkovitz, H.; Patchornik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249−4258.
(24) Newkome, G. R.; Nayak, A.; McClure, G. L.; Danesh-Khoshboo, F.; Broussard-Simpson, J. *J. Org. Chem.* **1977**, *42*, 1500−1508.

yield 96%; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.72−3.56 (m, 56H), 2.58 (s, 2H); mp 37−39 °C.

**Preparation of ABA Amphiphiles [$CH_3(CH_2)_{x-1}(OCH_2CH_2)_yO(CH_2)_{x-1}CH_3$, $C_xEO_yC_x$].** Under Ar, the appropriate ethylene glycol oligomer (5.00 mmol) in 20 mL of dry THF was added dropwise to a 100 mL Schlenk flask charged with NaH (12.5 mmol). The reaction mixture was stirred for 24 h, and then the appropriate alkyl bromide (10.2 mmol) in 15 mL of THF was added and stirred for 72 h at room temperature or at reflux ($y$ = 2, 3). Upon completion of the reaction, 5 mL of water was added slowly, and the solution was stirred for 10 min. The layers were separated, and the water layer was extracted with ether. The combined organic solutions were washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The hexyl and octyl derivatives for $y$ = 2−5 were distilled under vacuum to give clear, colorless oils. All other compounds were recrystallized from acetone ($y$ = 2, 3) or methanol ($y$ = 4−8, 10, 14) at low temperature. Liquid products are clear and colorless, while the solid products are white and crystalline.

**Supporting Information Available:** Physical data ($^1$H NMR), yields, and melting and boiling points for $C_xEO_yC_x$ ($x$ = 6, 8, 10, 12, 14, 16; $y$ = 2−8, 10, 14). This material is available free of charge via the Internet at http://pubs.acs.org.

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