1076 – 1078; d) D. H. R. Barton, G. Bashiardes, J.-L. Fourrey, *Tetrahedron* **1988**, *44*, 147 – 162.

[3] a) J. A. Rechka, J. R. Maxwell, *Tetrahedron Lett.* **1988**, *29*, 2599 – 2600; b) A. B. Charette, J. Lemay, *Angew. Chem.* **1997**, *109*, 1163 – 1165; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1090 – 1092.

[4] P. D. Bailey, S. R. Baker, A. N. Boa, J. Clayson, G. M. Rosair, *Tetrahedron Lett.* **1998**, *39*, 7755 – 7758; P. D. Bailey, A. N. Boa, G. A. Crofts, *Tetrahedron Lett.* **1989**, *30*, 7457 – 7460.

[5] R. C. Neuman, M. L. Rahm, *J. Org. Chem.* **1966**, *31*, 1857 – 1859.

[6] J. E. Lyons, *J. Chem. Soc. Chem. Commun.* **1975**, 418 – 419.

[7] a) P. Armas, C. G. Francisco, E. Suárez, *Angew. Chem.* **1992**, *104*, 746 – 748; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 772 – 774; b) P. Armas, C. G. Francisco, E. Suárez, *J. Am. Chem. Soc.* **1993**, *115*, 8865 – 8866; c) R. Hernández, E. I. León, P. Moreno, E. Suárez, *J. Org. Chem.* **1997**, *62*, 8974 – 8975; d) C. G. Francisco, R. Freire, C. C. González, E. Suárez, *Tetrahedron: Asymmetry* **1997**, *8*, 1971 – 1974; e) C. G. Francisco, C. C. González, E. Suárez, *J. Org. Chem.* **1998**, *63*, 2099 – 2109; f) C. G. Francisco, C. C. González, E. Suárez, *J. Org. Chem.* **1998**, *63*, 8092 – 8093.

[8] J. L. Courtneidge, J. Lusztyk, D. Pagé, *Tetrahedron Lett.* **1994**, *35*, 1003 – 1006.

[9] J. Rodriguez, J.-P. Dulcère, *Synthesis* **1993**, 1177 – 1205.

[10] C. H. Marzabadi, C. D. Spilling, *J. Org. Chem.* **1993**, *58*, 3761 – 3766.

[11] M. Smietana, V. Gourverneur, C. Mioskowski, *Tetrahedron Lett.* **2000**, *41*, 193 – 195.

[12] W. Korytnyk, S. Valentekovic-Horvath, C. R. Petrie III, *Tetrahedron* **1982**, *38*, 2547 – 2550.

[13] G. Excoffier, D. Gagnaire, J.-P. Utille, *Carbohydr. Res.* **1975**, *39*, 368 – 373.

[14] Crystallographic data (excluding structure factors) for the structure **28** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155002. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] T. Okazoe, K. Takai, K. Utimoto, *J. Am. Chem. Soc.* **1987**, *109*, 951 – 953.

[16] The 3-deoxy-D-glucal precursor of **31** was prepared in two steps by BF$_3$-catalyzed rearrangement of commercially available tri-*O*-acetyl-D-glucal and LiAlH$_4$ reduction of the hex-2-enopyranoside formed (84 % overall yield): R. J. Ferrier, *Methods Carbohydr. Chem.* **1972**, *6*, 307 – 311; B. Fraser-Reid, S. Y.-K. Tam, B. Radatus, *Can. J. Chem.* **1975**, *53*, 2005 – 2016. A one-step method is available as well, also starting from tri-*O*-acetyl-D-glucal, although in lower yield (58 %): N. Greenspoon, E. Keinan, *J. Org. Chem.* **1988**, *53*, 3723 – 3731.

[17] For example, D. Meng, Q. Tan, S. J. Danishefsky, *Angew. Chem.* **1999**, *111*, 3393 – 3397; *Angew. Chem. Int. Ed.* **1999**, *38*, 3197 – 3201; C. M. Blackwell, A. H. Davidson, S. B. Launchbury, C. N. Lewis, E. M. Morrice, M. M. Reeve, J. A. R. Roffey, A. S. Tipping, R. S. Todd, *J. Org. Chem.* **1992**, *57*, 5596 – 5606; R. Baker, J. L. Castro, *J. Chem. Soc. Perkin Trans. 1* **1990**, 47 – 65.

[18] Recently, the use of DIB/I$_2$ for the deprotection of carbohydrate benzyl ethers was described: J. Madsen, C. Viuf, M. Bols, *Chem. Eur. J.* **2000**, *6*, 1140 – 1146.

A Schizophrenic Water-Soluble Diblock Copolymer**

Shiyong Liu, Norman C. Billingham, and Steven P. Armes*

Recently we reported the first example of a water-soluble diblock copolymer capable of existing in three states in aqueous solution, namely, as conventional micelles, reverse micelles, and molecularly dissolved (non-micellar) chains.[1] This diblock copolymer was based on two tertiary amine methacrylates, 2-(diethylamino)ethyl methacrylate (DEA) and 2-(*N*-morpholino)ethyl methacrylate (MEMA), and was synthesized using group transfer polymerization,[2, 3] a type of anionic polymerization which is particularly well suited to the living polymerization of methacrylates at room temperature. Formation of micelles with DEA cores was achieved merely by adjusting the solution pH value, but formation of the reverse micelles with MEMA cores required the addition of a large amount of electrolyte to selectively "salt out" the MEMA chains. To date, this remains the only well-documented example of such a "schizophrenic" block copolymer.[4]

Since its discovery in 1995,[5] atom-transfer radical polymerization (ATRP) has proved to be a reliable and versatile method for the synthesis of functional, controlled-structure copolymers.[6] This free-radical polymerization chemistry is "pseudo-living" and particularly tolerant of monomer functionality; it has been used to polymerize a wide range of hydrophilic monomers with narrow molecular weight distributions and controlled architectures.[7]
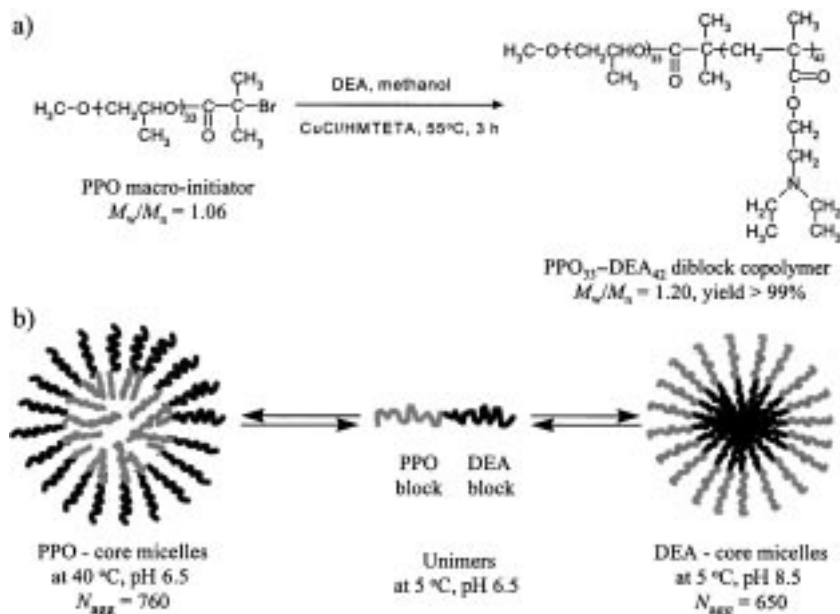
Herein we describe the facile ATRP synthesis of a new diblock copolymer based on poly(propylene oxide) (PPO) and DEA (Scheme 1 a). This diblock copolymer dissolves molecularly in cold aqueous solution but undergoes reversible micellar self-assembly to give either PPO-core micelles or DEA-core micelles. Unlike the DEA – MEMA diblock copolymer reported previously, both types of micelles can be formed solely by the judicious selection of solution pH value and solution temperature.

It is well known that PPO with an M_n of around 2000 dissolves in cold, dilute aqueous solution but becomes insoluble at 20 °C; its lower critical solution temperature (LCST) lies between 10 °C and 20 °C, depending on the solution concentration.[8] Similarly, we have recently shown that DEA homopolymer is soluble in acidic solution as a weak cationic polyelectrolyte (due to protonation of the tertiary amine residues), but precipitates from solution at around neutral pH. We have recently published several papers

[*] Prof. S. P. Armes, Dr. S. Liu, Prof. N. C. Billingham
School of Chemistry, Physics and Environmental Science
University of Sussex
Falmer, Brighton, E. Sussex, BN1 9QJ (UK)
Fax: (+44)1273-677-196
E-mail: s.p.armes@sussex.ac.uk

Scheme 1. a) Synthesis of the poly(propylene oxide-block-2-diethylamino)ethyl methacrylate (PPO – DEA) copolymer by atom-transfer radical polymerization. b) Schematic representation of the formation of micelles and reverse micelles by this diblock copolymer in aqueous solution. HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine.

assembly was completely reversible: Addition of acid resulted in instantaneous micellar dissolution, as judged by the disappearance of the characteristic bluish color of the micelles. Static light scattering (SLS) studies of these micellar solutions gave a high-quality Zimm plot (Figure 3 a) which yielded an average radius of gyration $\langle R_g \rangle$ of 35 nm and a micelle mass of approximately $7.6 \times 10^6 \, g\,mol^{-1}$. Taking the M_w of the PPO$_{33}$–DEA$_{42}$ diblock copolymer to be 11 700, this indicates a mean micelle aggregation number N_{agg} of approximately 650. The $\langle R_g \rangle / \langle R_h \rangle$ ratio is 0.875, which is only slightly larger than the value of 0.774 predicted for non-draining, uniform spheres. Analysis of transmission electron microscopy (TEM) images of DEA-core micelles (see Figure 5 of the Supporting Information) indicated a mean number-average radius of about 25 – 30 nm, which, allowing for hydration and probable "flattening" of the surface-adsorbed micelles, as well as polydispersity effects, is in reasonable agreement with the intensity-
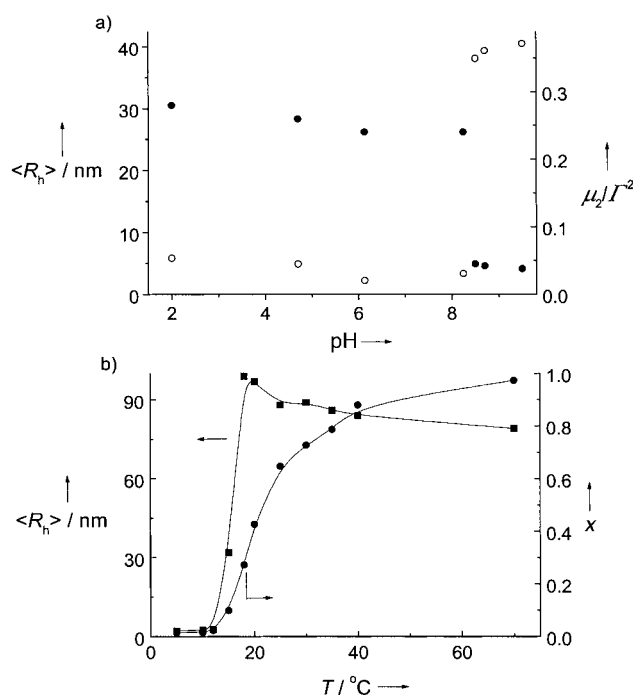
describing the pH-induced micellization of DEA-based diblock copolymers.[1, 9]

The aqueous solution behavior of the PPO$_{33}$–DEA$_{42}$ diblock copolymer proved to be complex and fascinating, as expected. Thus this copolymer dissolved molecularly in dilute aqueous solution at pH 6.5 and 5 °C (confirmed by both ^{1}H NMR studies in D$_2$O and dynamic light scattering measurements on 0.5 w/v % solutions), since both the PPO and DEA blocks are hydrophilic under these conditions. On addition of a small amount of NaOH to this molecular solution at 5 °C, micellization occurred at a solution pH of 8.5 or higher, as indicated by the dramatic increase in hydrodynamic radius (see Figure 1 a). On the basis of chemical intuition, the deprotonated DEA chains should form the hydrophobic micelle cores, with the still-solvated PPO chains forming the micelle coronas (see Scheme 1 b). The ^{1}H NMR studies confirmed this to be the case. The NMR spectrum of the PPO$_{33}$–DEA$_{42}$ copolymer molecularly dissolved in CDCl$_3$ is shown in Figure 2 a and was used to calculate the block composition. For the spectrum in Figure 2 b the copolymer chains are also molecularly dissolved, this time in D$_2$O at 5 °C and pH 6.5. Comparing Figure 2 b and d, it is clear that the signals due to the DEA residues at $\delta = 1.2$ and $\delta = 3.1$ have almost disappeared, indicating much lower mobility and decreased solvation for this block. On the other hand, the signals due to the PPO block at $\delta = 1.0$ and $\delta = 3.4$ are still prominent, indicating that this block forms the solvated micellar corona. Dynamic light scattering (DLS) studies indicated an intensity-averaged hydrodynamic micelle radius $\langle R_h \rangle$ of 40 nm and a polydispersity index (μ_2/Γ^2) as low as 0.04 by cumulants analysis. Previously we reported that DEA-based diblock copolymers become insoluble above pH 7.1 – 7.3 at 20 °C.[9] However, at 5 °C the critical pH for micellization of the DEA – PPO diblock increased to about pH 8.5. Self-

Figure 1. a) Variation of hydrodynamic radius $\langle R_h \rangle$ (○) and polydispersity index μ_2/Γ^2 (●) as a function of solution pH value for the PPO$_{33}$–DEA$_{42}$ diblock copolymer at 0.5 wt % and 5 °C. b) Variation of light scattering intensity X (●) and hydrodynamic radius (■) as a function of temperature for the PPO$_{33}$–DEA$_{42}$ diblock copolymer at 0.5 wt % and pH 6.50.

average radius of 40 nm obtained from DLS studies. The DLS data also supports the formation of spherical micelles since $\langle R_h \rangle$ is almost independent of scattering angle.

Reverse micelles with PPO cores were obtained by heating the same dilute solution of PPO – DEA diblock copolymer
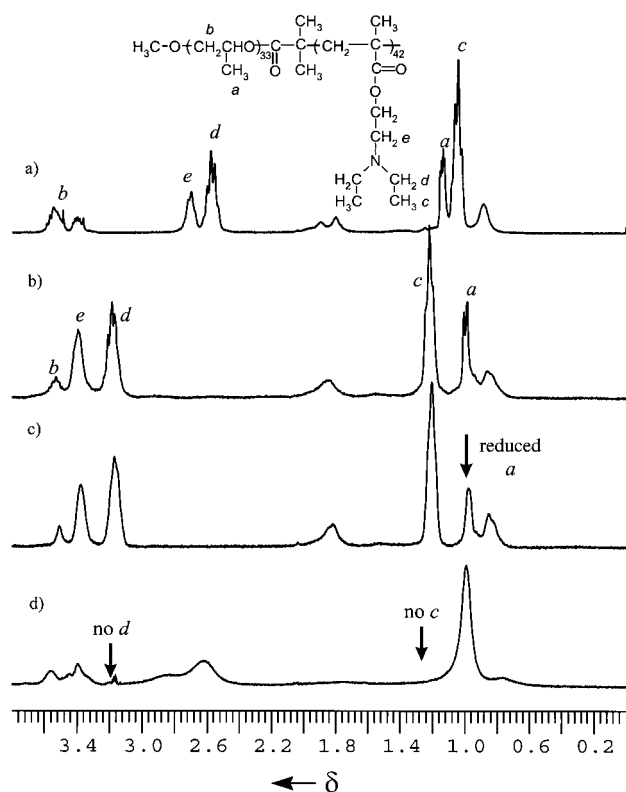
Figure 2. ^1H NMR spectra recorded for the $PPO_{33}-DEA_{42}$ diblock copolymer a) in $CDCl_3$ at 20 °C (both blocks solvated), b) in D_2O at pH 6.5 and 5 °C (molecularly dissolved copolymer), c) in D_2O at pH 6.5 and 40 °C (PPO-core micelles), and d) in D_2O at pH 8.6 and 5 °C (DEA-core micelles).
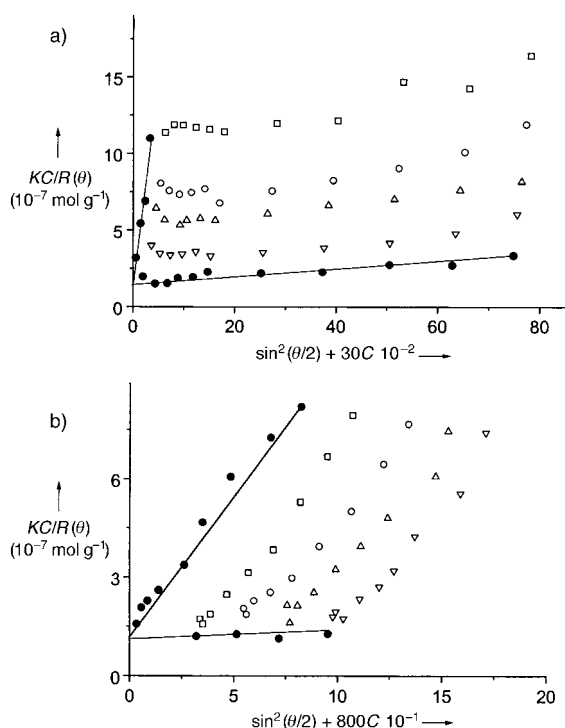

Figure 3. a) Typical Zimm plot of the $PPO_{33}-b-DEA_{42}$ micelles in aqueous solution at pH 8.50 and 5 °C, where concentration C ranges from 2.074×10^{-4} to 1.109×10^{-3} gmL^{-1}. b) Typical Zimm plot of the $PPO_{33}-b-DEA_{42}$ micelles in aqeueous solution at pH 6.50 and 40 °C, where C ranges from 4.012×10^{-4} to 1.190×10^{-3} gmL^{-1}. K is optical scattering constant, R is Rayleigh ratio at an angle θ.

prepared by dissolution at 5 °C and pH 6.5. Figure 1b shows the variation of light scattering intensity and intensity-averaged hydrodynamic radius as a function of solution temperature. The PPO block becomes progressively more insoluble at higher temperatures, leading to large, polydisperse, partially dehydrated aggregates initially being formed at 20 °C. At higher temperatures more compact, well-defined micelles are formed with more dehydrated PPO cores, as judged by ^1H NMR spectroscopy (see Figure 2c). The DEA block remained solvated under these conditions (note the prominent signals at $\delta = 1.2$ and $\delta = 3.1$), whereas the relative intensity of the signal due to the PPO block at $\delta = 1.0$ is reduced. However, this PPO signal does not completely disappear even at 70 °C (not shown), suggesting that the micelle cores remain partially hydrated. Dynamic light scattering measurements at a scattering angle of 15° indicated hydrodynamic micelle radii of 84 nm (polydispersity index 0.08) and 79 nm (polydispersity index 0.05) at 40 °C and 70 °C, respectively. Zimm plots yielded molar masses of approximately 8.9×10^6 gmol^{-1} and 1.2×10^7 gmol^{-1} (see Figure 3b), and the corresponding micelle aggeugation numbers N_{agg} were determined to be 760 and 1020 for micelles formed at 40 °C and 70 °C, respectively (Table 1). These N_{agg} values are quite

Table 1. Light-scattering characterization of micelles and reverse micelles formed by $PPO_{33}-b-DEA_{42}$ diblock copolymer under different conditions.

Conditions	$M_{w,micelles}$	$\langle R_g \rangle$ [nm]	$\langle R_h \rangle /$ [nm]	$\langle R_g \rangle / \langle R_h \rangle$	N_{agg}	$< \rho >$ [g cm^{-3}]
DEA-core micelles pH 8.5, 5 °C	7.6×10^6	35	40	0.875	650	0.047
PPO-core micelles pH 6.5, 40 °C	8.9×10^6	86	84	1.02	760	0.0060
PPO-core micelles pH 6.5, 70 °C	1.2×10^7	74	79	0.937	1020	0.0096

low given the relatively large micelle radii, but this probably reflects the partially hydrated nature of the PPO micelle cores, suggesting rather loosely packed aggregates. In this context, it is noteworthy that the micelles at 70 °C are significantly more compact (i.e., smaller in size but with a higher aggregation number and micelle density) than those formed at 40 °C; the $\langle R_g \rangle / \langle R_h \rangle$ ratio of micelles formed at 70 °C is 0.937, which is smaller than the value of 1.02 obtained for the micelles formed at 40 °C; presumably this is due to the increased dehydration of the PPO block, as indicated by the ^1H NMR studies.

For the PPO-core micelles formed, a rather large micelle radius of around 80 nm in water was observed. Even if the DEA units are fully stretched, the block copolymer could not possibly give a spherical micelle with an $\langle R_h \rangle$ of 80 nm. This unusually large micelle size is not consistent with a simple core-shell structure. At this stage, we cannot exclude the possibility that these PPO-core aggregates may be actually compound micelles or vesicles. Regardless of the precise morphology of these aggregates, the temperature-induced self-assembly process is fully reversible: Molecularly dissolved copolymer solutions are obtained on cooling to 5 °C.

In summary, we report the second fully verified example of a "schizophrenic" diblock copolymer which can self-assemble to form either micelles or reverse micelles in aqueous solution. This new class of diblock copolymer surfactant is particularly easy to synthesize and its two micellar phase transitions are dictated solely by the solution temperature and the solution pH value. In view of this, we expect that the rich phase behavior of this new diblock copolymer will be of particular interest to theoreticians for testing the validity of the various theories of micellization.[10]

Experimental Section

Synthesis of the PPO–DEA diblock copolymer: The diblock copolymer was synthesized by ATRP using a macro-initiator approach. A monohydroxy-capped poly(propylene oxide) (PPO-OH; mean degree of polymerization, Dp = 33 by ^{1}H NMR; M_w/M_n = 1.06 by gas-phase chromatography (GPC) with THF eluent) was kindly donated by Laporte Performance Chemicals (Hythe, UK). This PPO-OH was converted into an ATRP macro-initiator, PPO-Br, by allowing the terminal hydroxy group to react with 2-bromoisobutyryl bromide in the presence of triethylamine in toluene. ^{1}H NMR spectroscopy confirmed that the degree of chain-end functionalization was 100 %. The PPO macro-initiator (1.5 g, 0.75 mmol, 1 equiv), DEA (5.55 g, 30 mmol, 40 equiv), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 172 mg, 0.75 mmol, 1 equiv) and methanol (7 mL) were added to the reaction flask; the solution was degassed by two freeze–thaw cycles. After the solution temperature was increased to 55 °C, CuCl (74 mg, 0.75 mmol, 1 equiv) was introduced as a solid into the reaction flask to start polymerization at this temperature. The reaction solution became dark green and more viscous as polymerization proceeded. After about 3 h the conversion was close to 100 % as judged by ^{1}H NMR spectroscopy; the reaction mixture was diluted with methanol and passed through a silica column to remove residual ATRP catalyst. After solvent evaporation, the products were extracted with ice-cold water (0 °C, pH 9) several times to remove any traces of unchanged PPO macro-initiator and then dried under vacuum at room temperature. The mean Dp of the DEA block was calculated to be 42 using ^{1}H NMR spectroscopy. The GPC studies (THF eluent, PMMA standards, refractive index detector) of the diblock copolymer indicated a relatively narrow polydispersity (M_w/M_n) of 1.20.

Dynamic light scattering (DLS) studies were conducted with a Brookhaven model BI-200SM and 9000AT correlator using a solid-state laser (50 mW, λ = 532 nm) at a fixed scattering angle (θ) of 15º with both cumulants and CONTIN software. The dn/dc of the PPO$_{33}$–DEA$_{42}$ diblock copolymer was determined to be 0.128 in aqueous solution at pH 6.5 and 20 °C, using an Optokem differential refractometer operating at λ = 632.8 nm. Static light scattering studies (SLS) were conducted at 5 °C (DEA cores) as well as 40 °C and 70 °C (PPO cores) using the same instrument at scattering angles ranging from 15° to 135°. The M_w and R_g data were obtained using standard Zimm plot analyses, assuming that the effects of temperature and pH on the dn/dc were negligible. Variable-temperature ^{1}H NMR spectra were recorded on 1.0 w/v % copolymer solutions in D$_2$O using a Bruker Avance DPX 300-MHz spectrometer. Transmission electron microscopy studies were conducted using a Hitachi 7100 instrument operating at 75 kV and employing OsO$_4$ as a staining agent.

[1] V. Bütün, N. C. Billingham, S. P. Armes, *J. Am. Chem. Soc.* **1998**, *120*, 11818.

[2] O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. RanjanBabu, *J. Am. Chem. Soc.* **1983**, *105*, 5706.

[3] I. B. Dicker, G. M. Cohen, W. B. Farnham, W. R. Hertler, E. D. Langanis, D. Y. Sogah, *Macromolecules* **1990**, *23*, 4034.

[4] We recently reported another apparent example of a diblock copolymer which can form both micelles and reverse micelles in

aqueous media (V. Bütün, M. Vamvakaki, S. P. Armes, N. C. Billingham, *Polymer* **2000**, *41*, 3173). However, in this case we were unable to obtain any NMR evidence to support this hypothesis, which remains unverified at present.

[5] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.

[6] T. E. Patten, K. Matyjaszewski, *Adv. Mater.* **1998**, *10*, 901.

[7] a) M. Kato, M. Kamagaito, M. Sawamoto, H. Higashimura, *Macromolecules* **1995**, *28*, 1721; b) D. M. Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek, A. J. Shooter, *Chem. Commun.* **1997**, 683; c) M. Sawamoto, M. Kamagaito. *Trends Polym. Sci.* **1996**, *4*, 371.

[8] P. Alexandridis, T. A. Hatton. *Colloids Surf.* **1995**, *96*, 1.

[9] a) V. Bütün, N. C. Billingham, S. P. Armes. *Chem. Commun.* **1997**, 671; b) A. S. Lee, A. P. Gast, V. Bütün, S. P. Armes, *Macromolecules* **1999**, *32*, 4302; c) V. Bütün, S. P. Armes, N. C. Billingham, Z. Tuzar, A. Rankin, J. Eastoe, R. K. Heenan, *Macromolecules*, in press.

[10] a) A. Halperin, M. Tirrell, T. P. Lodge, *Adv. Polym. Sci.* **1992**, *100*, 31; b) M. Moffit, K. Khougaz, A. Eisenberg. *Acc. Chem. Res.* **1996**, *29*, 95; c) A. P. Gast, *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 258; d) G. E. Yu, Z. Yang, M. Ameri, D. Attwood, J. H. Collett, C. Price, C. Booth, *J. Phys. Chem. B* **1997**, *101*, 4394.

σ-Bond Metathesis of Alkanes on a Silica-Supported Tantalum(V) Alkyl Alkylidene Complex: First Evidence for Alkane Cross-Metathesis**

Christophe Copéret, Olivier Maury,
Jean Thivolle-Cazat,* and Jean-Marie Basset*

Here we report on direct evidence for the stoichiometric cross-metathesis of several alkanes (ethane, propane, and butanes) with the hydrocarbyl ligands of the surface complexes [($\equiv$Si–O)$_x$Ta($=$CHCMe$_3$)(CH$_2$CMe$_3$)$_{(3-x)}$] (**1**: x = 1, **2**: x = 2), and the catalytic activity of **1**+**2** in alkane metathesis.[1]

We have shown that the silica-supported tantalum hydride [($\equiv$SiO)$_2$TaH] (**3**) catalyzes the metathesis of alkanes (Scheme 1).[2, 3] The key steps proposed for the reaction mechanism are: a) activation of the C$-$C bond of an incoming alkane on the surface Ta alkyl complex **4** leading to the evolution of an alkane and the formation of a new surface complex **5**; and b) regeneration of **4** in an alkyl-exchange reaction (C$-$H bond activation).[4]

The related structures of **1**+**2** and **4/5**, the two key intermediates of the proposed mechanism for alkane metathesis, is noteworthy. This analogy led us to investigate the relative reactivity towards alkanes of **1**+**2**, a formal d^0 10-e metal center, and **3**, (the precursor of **4/5**) a formal d^2 8-e metal center.

[*] Dr. J. Thivolle-Cazat, Dr. J.-M. Basset, Dr. C. Copéret, Dr. O. Maury
Laboratoire de Chimie Organométallique de Surface
UMR 9986 CNRS – ESCPE Lyon
43 bd du 11 Novembre 1918
69626 Villeurbanne Cedex (France)
Fax: (+33) 4-72-43-18-11
E-mail: basset@mulliken.cpe.fr