

# Catalytic surfactants for ring-opening metathesis polymerization and ring-closing metathesis in non-degassed micellar solutions

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## Abstract

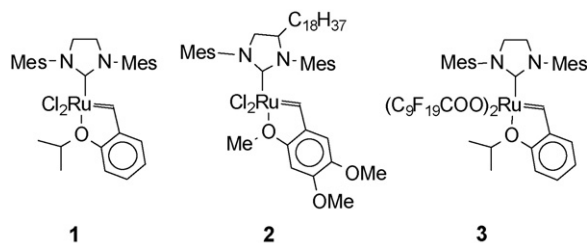
Metathesis catalysts bearing long alkyl chains and analogous to Hoveyda's catalyst have been synthesized. Their surface-active properties have been characterized by formation of Langmuir films at the air–water interface. They have been dispersed in micelles formed in non-degassed water and been used in polymerization of a hydrophilic monomer. These surfactants are therefore the first insurf molecules for metathesis polymerization that are air-stable. Their ability to catalyze ring-closing metathesis in water has also been evaluated.

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**Keywords:** Hoveyda's catalyst; Inisurf; Ring-opening metathesis polymerization; Ring-closing metathesis; Surfactant

## 1. Introduction

One of the biggest challenges in modern chemistry is to find environmentally friendly processes while carrying out already known chemical reactions. In this field, metathesis reactions were for a long time hampered because of chemical sensitivity of the catalysts versus oxygen or water. For one part, this drawback prevented the reactions to be carried out on functional molecules. Therefore, alkenes or cycloalkenes were the only molecules used in metathesis reactions. For another part, this also restricted the compatible solvents to hydrocarbons or chlorinated hydrocarbons. Since the last ten years, tremendous improvements have been made with the synthesis of new catalysts, either in organic synthesis or in polymerization. Grubbs' catalysts have enabled the use of metathesis reactions in the presence of functional groups [1,2]. Another essential step in the progress has then been achieved with the discovery of so-called Hoveyda's catalyst **1**, which is air-stable [3–5].



With such development, carrying out metathesis reactions in water with well-characterized catalysts is now feasible. Metathesis reactions have already been carried out in pure water, but mostly on non-preformed catalysts, like RuCl<sub>3</sub>, H<sub>2</sub>O [6,7]. In such systems, the carbene that is responsible for the reaction is formed *in situ* and therefore, its quantity is not always well controlled. Various studies have described the use of new catalysts such as Grubbs' first or second generation in protic media. For the first generation catalyst, Grubbs showed that polymerization close to a living one can be achieved, enabling the synthesis of block copolymers in mixed systems water/organic solvent in the presence of dodecyltrimethylammonium bromide [8]. For hydrophilic monomers, it was noted that the distribution in size exclusion chromatography (SEC) was bimodal. Other studies involved miniemulsion polymerization of norbornene in

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the presence of sodium dodecylsulfate (SDS) and hexadecane or pentanol [7,9]. In the first case, the obtained latex was not stable and in the second case, the conversion was not complete even after several hours. Claverie et al. and Grubbs and co-workers also described the use of hydrophilic catalysts that enabled the formation of latex [10,11]. In these systems, the use of organic solvent was still needed although in small quantity. Modification of the catalysts by polyethyleneglycol chain or grafting on a resin was also described [12,13]. For some catalysts, the addition of hydrochloric acid was mandatory to enable the reaction. As for ring-closing reactions, several studies report turnover numbers (TON) and turnover frequencies (TOF) in organic solvents for Grubbs and Hoveyda's catalysts [14–16]. Ring-closing metathesis (RCM) in water has been a challenge for a long time because of the instability of the formed carbene in water. Grubbs and co-workers first described this reaction on diethyldiallylmalonate (DEDAM) in methanol with a hydrophilic catalyst and stated that this was not feasible because of the reactivity of the carbene [17]. Connon and Blechert and also Davis and Sinou in 2002 assessed the same reaction with hydrophobic catalysts in methanol or water and showed that good yields could be obtained [18,19]. However, the reported TONs were still low (between 10 and 50). Two years ago, Zarka et al. published a study using a grafted version of Hoveyda's catalyst and presented a TON of 390 in water [20]. Yields were comprised between 40 and 90% depending on the conditions. During the writing of this article, a new study from Grubbs and co-workers described the synthesis of a Hoveyda's type catalyst bearing a polyethyleneglycol chain, enabling ROMP, RCM and cross metathesis to be carried out in water [21]. However, no TONs or TOFs were reported.

In the catalytic field, molecules that are at the same time catalysts and surfactants have proven to be valuable for the control of the reactions. For example, inisurf molecules [22–24] (for initiator and surfactant) have been well studied in radical polymerization to minimize the quantity of surfactant needed for the stabilization of latex. In metathesis reactions, no such study has been carried out. Therefore, in our continuing studies on controlling reactions along fluid interfaces [25,26], we report herein the synthesis of Hoveyda-type catalysts **2** and **3** that are surface-active and can be used without degassing the solutions. Our aim was to characterize whether these molecules would be helpful for two chemical reactions, namely ring-opening metathesis polymerization (ROMP) and RCM in water.

## 2. Experimental

### 2.1. Materials

Experiments with oxygen-sensitive ruthenium catalysts were carried out in a dry-box (maximum O<sub>2</sub> content 25 ppm) or using Schlenk techniques connected to an argon line. Solvents were dried over CaH<sub>2</sub>, distilled, and degassed before use when necessary. Column-chromatography was carried out on silica gel 60 (Merck, 0.04–0.063 mm). For ruthenium compounds, extra-pure silica (Merck, 0.063–0.2 mm) was used. Monomer **8** (Scheme 2)

was synthesized according to an already published procedure [27,28].

### 2.2. Characterizations

<sup>1</sup>H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.13 MHz. <sup>13</sup>C NMR spectra were recorded on a multinucleus Bruker ARX400 or Avance 500 spectrometer at 100.61 or 125.75 MHz. Attribution of the signals was made by COSY, HSQC and HMBC experiments. <sup>19</sup>F NMR spectra were recorded on a Bruker ARX400 spectrometer at 376.47 MHz. IR spectra were carried out on a Perkin Elmer FT-IR 1760× spectrometer. Unless noted, NMR measurements were carried out in deuterated chloroform and chemical shifts are given in ppm versus TMS.

The average molecular weight of the polymers was determined after termination with ethylvinylether by size exclusion chromatography (SEC) analysis in THF (flow rate 1.2 mL min<sup>-1</sup>) on an apparatus equipped with a Waters refractive index detector, a Waters column pack (Ultrastayragel 10<sup>4</sup>, 10<sup>3</sup>, 100 Å) and a Minidawn Wyatt light scattering detector. The refractive index increment for polynorbornene in THF at 25 °C was taken as 0.134 [29]. That for poly(**8**) was measured in THF at 25 °C and was found to be 0.096. The molecular weights were calculated after treatment by Corona software, enabling to extrapolate a calibration for the non-overlapping zones between LS and RI peaks. Owing to the relatively high concentration of dodecyltrimethylammonium chloride (DTAC) used in the dispersed experiments, the light scattering signal of SEC chromatograms presented in some cases a halo over the entire range of the elution time, causing erroneous calculation of molar masses. Therefore, for these experiments, only the refractometric signal was used and a polystyrene calibration curve was employed and corrected for poly(**8**) by a factor 1.17 that was determined from the initial analyses. Dynamic light scattering tests were carried out on a Malvern Zetasizer 3000HSA.

#### 2.2.1. 1,2-Dibromo eicosane

In 50 mL methylenechloride, 6.35 g of poly(4-vinylpyridinium tribromide) resin (2 mmol Br<sub>3</sub><sup>-</sup> g<sup>-1</sup>) were suspended. 2.54 g of 1-eicosene (9.05 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> were added and the solution was stirred at ambient temperature for 24 h. After filtration and evaporation of the solvent, 3.73 g of product was obtained (94%).

<sup>1</sup>H NMR: 0.91 (t <sup>3</sup>J=6.7 Hz), 3H, Me); 1.25–1.6 (m, 32H, –CH<sub>2</sub>–), 1.75–1.85 (m, 1H, –CH<sub>2</sub>–CHBr), 2.08–2.22 (m, 1H, –CH<sub>2</sub>–CHBr); 3.65 (t <sup>2</sup>J=10.2 Hz <sup>3</sup>J=10.2 Hz, 1H, –CH<sub>2</sub>–Br), 3.87 (dd <sup>2</sup>J=10.2 Hz <sup>3</sup>J=4.6 Hz, 1H, –CH<sub>2</sub>–Br); 4.15–4.22 (m, 1H, –CH–Br).

<sup>13</sup>C NMR: 14.3 (Me–), 22.9, 27.0, 29.0, 29.6, 29.7, 29.8, 29.9, 32.1, 36.3 (–CH<sub>2</sub>–), 36.6 (–CH<sub>2</sub>–Br), 53.4 (–CH–Br).

Methane CI mass spectrum (relative intensity): 458 (13.7) [M + CH<sub>4</sub>]<sup>+</sup>, 439 (66.9), 359 (100), 279 (51.1).

#### 2.2.2. N,N'-Dimesityl 1,2-eicosanediamine (**5**)

During 4 days, 1.56 g of 1,2-dibromo eicosane (3.54 mmol) and 4.8 g of 2,4,6-trimethylaniline (35.5 mmol) were stirred

together at 120 °C. After cooling to room temperature, 10 mL CH<sub>2</sub>Cl<sub>2</sub> and 3.6 mL NaOH aqueous solution (15 wt.%) were added. The organic layer was separated, washed with water (2 × 10 mL) and dried over sodium sulfate. The solvent was evaporated and the crude product (dark brown oil) was purified by column-chromatography (first column, eluent hexane/AcOEt 9/1; second column, eluent hexane/AcOEt 95/5). Yield: 1.75 g (90%).

<sup>1</sup>H NMR: 0.89 (*t*<sup>3</sup>*J* = 7.0 Hz, 3H, Me); 1.20–1.50 (m, 34H, –CH<sub>2</sub>–), 2.23 (s, 12H, CH<sub>3</sub> *ortho* Mes), 2.27 (s, 6H, CH<sub>3</sub> *para* Mes); 2.7–2.78 (m, 1H, –CH<sub>2</sub>–N), 3.18–3.24 (m, 1H, –CH<sub>2</sub>–N); 3.39–3.51 (m, 1H, –CH–N); 2.9–3.7 (br s, 2H, NH); 6.81 (s, 4H, Mes).

<sup>13</sup>C NMR: 14.2 (Me–), 18.1, 18.4, 19.3 (Me Mes); 22.8, 26.4, 28.9–29.9, 32.0, 34.1 (–CH<sub>2</sub>–), 53.0 (–CH<sub>2</sub>–N), 57.2 (–CH–N); 128.8, 129.5, 130.5, 131.1 (C<sub>Mes</sub>–Me); 129.0, 129.8 (CH<sub>Mes</sub>); 142.0, 143.8 (C<sub>Mes</sub>). Ammoniac CI mass spectrum (relative intensity): 549 (100) [MH]<sup>+</sup>, 400 (11.9), 149 (11.0).

IR (KBr)  $\bar{\nu}$  (cm<sup>–1</sup>): 3380 w (NH stretching), 2923 str (antisymmetric CH<sub>2</sub> stretching), 2853 (symmetric CH<sub>2</sub> stretching), 1483 m, 1466 m, 1376 1301 1231 w, 853 w (aromatic CH wagging), 734 w (CH<sub>2</sub> rocking).

### 2.2.3. 1,3-Bis(1-mesityl)-4,5-dihydro-4-octadecyl imidazol-3-ium tetrafluoroborate (6)

A solution containing 1.08 g of **5** (1.97 mmol), 0.79 g of triethylorthoformate (5.3 mmol) and 0.22 g of ammonium tetrafluoroborate (2.1 mmol) was stirred at 115 °C under argon during 8 h. The excess of triethylorthoformate was removed under vacuum and the product was purified by two successive precipitations by depositing AcOEt over a hexane solution of the product. Yield: 0.97 g (76%).

<sup>1</sup>H NMR: 0.89 (*t*<sup>3</sup>*J* = 7.0 Hz, 3H, Me); 1.20–1.30 (m, 32H, –CH<sub>2</sub>–), 1.71–1.82 (m, 2H, –CH<sub>2</sub>–CHN); 2.31–2.38 (5 s, 18H, CH<sub>3</sub> Mes), 3.9–3.97 (m, 1H, –CH<sub>2</sub>–N), 4.66 (*t**J* = 10.6 Hz, 1H, –CH<sub>2</sub>–N); 4.8–4.9 (m, 1H, –CH–N); 6.98–7.0 (2 s, 4H, Mes); 8.21 (s, 1H, –CH=N).

<sup>13</sup>C NMR: 14.3 (Me–), 17.8, 18.2, 18.9, 21.3 (Me Mes); 22.9, 25.6, 29.5–29.9, 32.1 (–CH<sub>2</sub>–), 33.4, (–CH<sub>2</sub>–CHN), 57.0 (–CH<sub>2</sub>–N), 64.6 (–CH–N); 129.0, 130.2, 135.6 (C<sub>Mes</sub>–Me); 130.3, 130.9 (CH<sub>Mes</sub>); 140.7, 140.9 (C<sub>Mes</sub>).

IR (KBr pellet)  $\bar{\nu}$  (cm<sup>–1</sup>): 3070 w (CH<sub>Ar</sub> stretching), 2921 s (antisymmetric CH<sub>2</sub> stretching), 2851 s (symmetric CH<sub>2</sub> stretching), 1631 s (C=N stretching), 1467 m, 1384 w, 1258 m, 1056 s (B–F stretching), 853 w (aromatic CH wagging), 720 w (CH<sub>2</sub> rocking).

HRMS calculated for C<sub>39</sub>H<sub>63</sub>N<sub>2</sub> (M–BF<sub>4</sub>): 559.4991. Found: 559.5164.

### 2.2.4. Hoveyda's complex analogue (2)

A suspension of 0.2 g of **6** (0.31 mmol) and 0.175 mL potassium *t*-amylate (1.7 M in toluene) in 6 mL hexane (distilled and degassed) was stirred in a glove box for 1 h. 0.204 g of first generation Grubbs' catalyst (0.25 mmol) was added and the red solution stirred at 65 °C during 30 min. The solution turned purple-brown. It was then added to a suspension containing 58 mg of  $\alpha$ -asarone (0.28 mmol) and 28 mg of CuCl (0.28 mmol)

in 10 mL CH<sub>2</sub>Cl<sub>2</sub> (distilled and degassed). The resulting solution was stirred at 40 °C during 1 h and turned brown-green. At this point, all manipulations were carried out in regular atmosphere with non-purified and non-degassed solvents. After evaporation of the solvent, the remaining product was dissolved in hexane/AcOEt 2/5 (v/v). The precipitating tricyclohexylphosphine was eliminated by filtration and the solvent removed. The product was purified by column-chromatography on ultra-pure silica gel (eluent hexane/AcOEt 7/3 then 1/1). 92 mg of green powder were obtained (40%).

<sup>1</sup>H NMR: 0.91 (*t*<sup>3</sup>*J* = 7.0 Hz, 3H, Me); 1.14–1.34 (m, 32H, –CH<sub>2</sub>–), 1.60–1.80 (m, 2H, –CH<sub>2</sub>–CHN); 2.36–2.5 (6 s, 18H, CH<sub>3</sub> Mes), 3.82 (s, 6H, MeO– 3,4); 3.85 (s, 3H, MeO– 6); 3.9 (m, 1H, –CH<sub>2</sub>–N), 4.19 (*t**J* = 10.0 Hz, 1H, –CH<sub>2</sub>–N); 4.40–4.47 (m, 1H, –CH–N); 6.38 (s, 1H, H<sub>2</sub>); 6.45 (s, 1H, H<sub>5</sub>); 7.07–7.27 (m, 4H, Mes); 16.0 (s, 1H, –CH=Ru).

<sup>13</sup>C NMR: 14.5 (Me–), 20.0, 21.5 (Me Mes); 24.0, 26.5, 29.6, 29.7, 31.9 (–CH<sub>2</sub>–); 33.9 (–CH<sub>2</sub>–CHN); 56.2 (MeO on C 3,4); 57.9 (–CH<sub>2</sub>–N), 58.9 (MeO– 6); 64.5 (–CH–N); 96.9 (C<sub>5</sub>); 106.6 (C<sub>2</sub>); 128.2–130.9 (CH<sub>Mes</sub> 9); 137.8 (C<sub>1</sub>); 138.4–138.9 (C<sub>7</sub>, 10 Mes); 139.9 (C<sub>8</sub> Mes); 144.6 (C<sub>3</sub>); 149.2 (C<sub>6</sub>); 150.7 (C<sub>4</sub>); 212.9 (C<sub>NHC</sub>); 290.9 (C=Ru).

IR (KBr pellet)  $\bar{\nu}$  (cm<sup>–1</sup>): 3000 w (CH<sub>Ar</sub> stretching), 2923 s (antisymmetric CH<sub>2</sub> stretching), 2852 s (symmetric CH<sub>2</sub> stretching), 1599 m, 1501 1466 1410 m, 1287 m, 1259 s, 1210 m, 1134 m, 1022 m (OMe stretching), 855 w (aromatic CH wagging), 754 w (CH<sub>2</sub> rocking).

Anal. Calcd. for C<sub>49</sub>H<sub>74</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>Ru %C 64.6, %H 8.2, %N 3.1; found %C 65.0, %H 8.0, %N 2.7. HRMS: adequate conditions could not be obtained for desorption.

### 2.2.5. Silver perfluorodecanoate (7)

A mixture of 0.5 g of perfluorodecanoic acid (0.97 mmol) and 0.134 g of silver carbonate (0.48 mmol) was stirred at 100 °C during 2.5 h. After few minutes, gas evolution occurred and the mixture solidified.

<sup>13</sup>C{<sup>19</sup>F} NMR (DMSO-*d*<sub>6</sub>): 108.5, 110.3, 110.9, 111.0, 111.1, 111.4, 111.8, 117.2, 159.0 (COO).

<sup>19</sup>F NMR: –49.6 (CF<sub>2</sub>–CF<sub>3</sub>); –46.3, –45.6, –45.1 (–CF<sub>2</sub>–); –38.5 (–CF<sub>2</sub>–COO); –4.2 (CF<sub>3</sub>).

IR (KBr pellet)  $\bar{\nu}$  (cm<sup>–1</sup>): 1613 s (CO stretching), 1419, 1372, 1337 m, 1236, 1211, 1147 s (CF<sub>2</sub> and CF<sub>3</sub> stretching), 1036 w, 931 830 m, 810 w, 637, 558, 529 m.

### 2.2.6. Fluorinated Hoveyda's catalyst (3)

A solution containing 0.2 g of **2** (0.32 mmol) and 0.1 g of Hoveyda's catalyst (0.16 mmol) in 10 mL THF was stirred under argon at 65 °C for 20 min. The green starting solution turned purple-gray and a white precipitate appeared. The solution was filtered and the solvent removed under vacuum. The product was purified by column-chromatography on ultra-pure silica gel (eluent hexane/AcOEt 8/2). Yield: 0.124 g (49%).

<sup>1</sup>H NMR: 1.01 (d <sup>3</sup>*J* = 6.0 Hz, 6H, Me<sub>IPr</sub>); 2.30 (s, 12H, CH<sub>3</sub> *ortho* Mes); 2.47 (s, 6H, CH<sub>3</sub> *para* Mes); 4.15 (s, 4H, –CH<sub>2</sub>–N); 4.54 (m, 1H, –CH<sub>IPr</sub>); 6.61 (d *J* = 8.5 Hz, 1H, H<sub>2</sub>); 6.94 (*t**J* = 7.2 Hz, 1H, H<sub>4</sub>); 7.14 (m, 1H, H<sub>5</sub>); 7.19 (s, 4H, Mes); 7.34 (m, 1H, H<sub>3</sub>); 17.6 (s, 1H, –CH=Ru).

$^{13}\text{C}\{^1\text{H}\}$  NMR: 18.1 ( $\text{Me}_{\text{Mes}}$  *ortho*), 20.0 ( $\text{Me}_{\text{iPr}}$ ); 21.1 ( $\text{Me}_{\text{Mes}}$  *para*); 51.5 ( $-\text{CH}_2-\text{N}$ ); 74.4 ( $-\text{CH}-\text{O}$ ), 110.9 (C2); 104.2–118.5 (m,  $-\text{CF}_2-$  and  $\text{CF}_3$ ); 122.8 (C4); 123.9 (C5); 129.8 (C9); 130.2 (C3); 140.0 (C7, 10 ?); 143.2 (C1); 153.2 (C6); 160.1 ( $t J_{\text{C}-\text{F}} = 25.4 \text{ Hz}$ ,  $\text{C}=\text{O}$ ); 210.3 ( $\text{C}_{\text{NHC}}$ ); 317.4 ( $\text{C}=\text{Ru}$ ).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR: 107.7, 108.6, 110.4, 110.8, 110.9, 111.1, 117.3, 117.35 ( $-\text{CF}_2-$  and  $\text{CF}_3$ ); 160.4 ( $\text{C}=\text{O}$ ).  $^{19}\text{F}$  NMR:  $-49.7$  ( $-\text{CF}_2-\text{CF}_3$ );  $-46.3$ ,  $-45.7$ ,  $-45.5$  ( $-\text{CF}_2-$ );  $-38.6$  (m,  $-\text{CF}_2-\text{CO}$ );  $-4.4$  ( $-\text{CF}_3$ ).

IR (KBr pellet)  $\bar{\nu}$  ( $\text{cm}^{-1}$ ): 3100–2840 broadband w (aliphatic and aromatic CH stretching), 1705 m (CO stretching), 1596 w (aromatic ring stretching), 1484 m, 1456, 1432 w, 1353 m, 1240, 1213, 1153 s ( $\text{CF}_2$  and  $\text{CF}_3$  stretching), 1026, 942 w, 853 w (aromatic CH wagging), 747, 645, 576 w.

Anal. Calcd. for  $\text{C}_{51}\text{H}_{38}\text{F}_{38}\text{N}_2\text{O}_5\text{Ru}$  %C 38.7, %H 2.4, %N 1.8; found %C 39.8, %H 2.6, %N 2.0.

### 2.2.7. Typical metathesis reaction in organic solvent

In an NMR tube, 25 mg of monomer **8** (0.118 mmol) was dissolved in 0.6 mL  $\text{CD}_2\text{Cl}_2$ , and 1.1 mg of catalyst **2** ( $1.2 \times 10^{-3}$  mmol) was introduced. The tube was vigorously hand-shaken and the reaction was followed by  $^1\text{H}$  NMR. At the end of reaction, 0.05 mL of ethylvinylether was added. The polymer was characterized by  $^1\text{H}$  NMR and SEC. The RCM reactions were carried out with the same protocol with a ratio  $[\mathbf{9}]/[\text{catalyst}]$  equal to 30.

### 2.2.8. Typical metathesis reaction in micellar solution

In 0.3 mL of chloroform, 1.5 mg of **2** ( $1.6 \times 10^{-3}$  mmol) and 46 mg of DTAC (0.174 mmol) were dissolved. The solvent was evaporated under a stream of argon. Non-degassed water (3 mL) was added and the resulting solution was added to another solution containing 68 mg of **8** (0.32 mmol), 46 mg of DTAC (0.174 mmol) in 4 mL water. The solution was stirred at room temperature during 18 h, at which time ethylvinylether was added in excess, followed by NaCl in order to destabilize the emulsion. The product was extracted with chloroform ( $2 \times 7 \text{ mL}$ ) and the solvent was evaporated.

### 2.2.9. Monolayers at the air–water interface

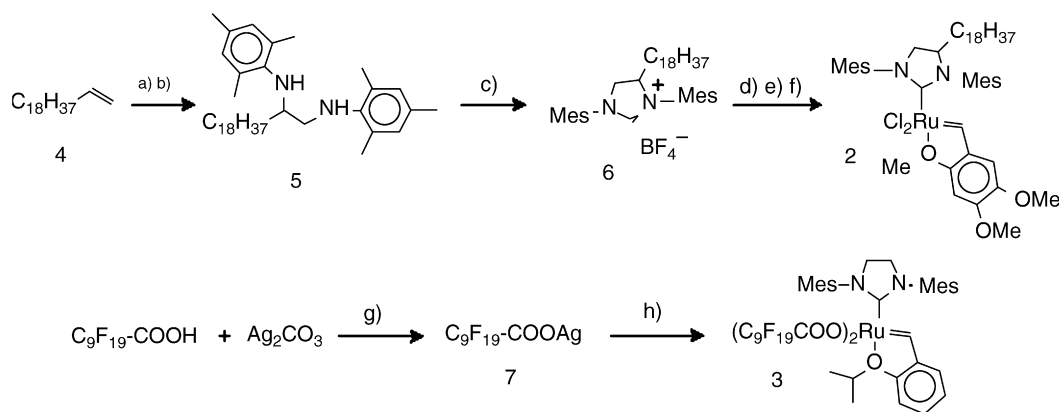
In order to measure the isotherms of the Langmuir films, a solution of the respective compound was spread on an aqueous surface. Chloroform (HPLC grade) was used as spreading solvent and the amphiphilic complex solutions were kept at  $-18^\circ\text{C}$  between experiments to limit solvent evaporation. Isotherms were obtained with a NIMA trough (type 601 BAM, maximum available surface ca.  $700 \text{ cm}^2$ ) equipped with a Wilhelmy plate and maintained at  $20^\circ\text{C}$ . The compression speed of the monolayer was  $10 \text{ cm}^2 \text{ min}^{-1}$ . A BAM2plus from NFT was used for the Brewster angle microscopy experiments.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the new catalysts

The new catalysts were synthesized according to Scheme 1. The first synthesis is based on modification of a known strategy [3,30,31] and started from eicosene **4**, which was transformed into 1,2-dibromo eicosane and its diamine analogue **5** (85% from **4**). Reaction with triethylorthoformate led to the imidazolium compound **6** in 76% yield. The ruthenium catalyst **2** was then obtained in a one-pot reaction through generation of NHC carbene and substitution of  $\alpha$ -asarone according to a method already described [31]. At this point, the compound was manipulated under air with non-degassed solvents. It was purified by classical column-chromatography on silica gel and was obtained in 40% yield as a green powder. The second catalyst was synthesized based on a method described by Buchmeiser and co-workers [16]. It first involved the synthesis of the silver salt **7** of perfluorodecanoic acid. Although several methods have been described [32,33], the best results were obtained by a bulk reaction with silvercarbonate at  $100^\circ\text{C}$ . The reaction of **7** with Hoveyda's catalyst led then to the desired compound **3**, which was handled and purified in the same manner than **2**. It was obtained in 49% yield as a purple powder.

Next, their potential as surface-active molecules was assessed. This was carried out by measuring their  $\pi = f(A)$



Scheme 1. Synthesis of catalysts **2** and **3**. (a) PVP-HBr<sub>3</sub>,  $\text{CH}_2\text{Cl}_2$ , r.t., 24 h, 94%; (b) 2,4,6-trimethylaniline,  $120^\circ\text{C}$ , 4 days, 90%; (c) triethylorthoformate,  $\text{NH}_4\text{BF}_4$ ,  $115^\circ\text{C}$ , 8 h, 76%; (d) potassium *t*-amylate, hexane, r.t., 1 h; (e) first generation Grubb's catalyst,  $65^\circ\text{C}$ , 30 min; (f)  $\alpha$ -asarone,  $\text{CuCl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $40^\circ\text{C}$ , 1 h, 40% from **5**; (g)  $100^\circ\text{C}$ , 2.5 h; (h) Hoveyda's catalyst, THF,  $65^\circ\text{C}$ , 20 min, 49%.

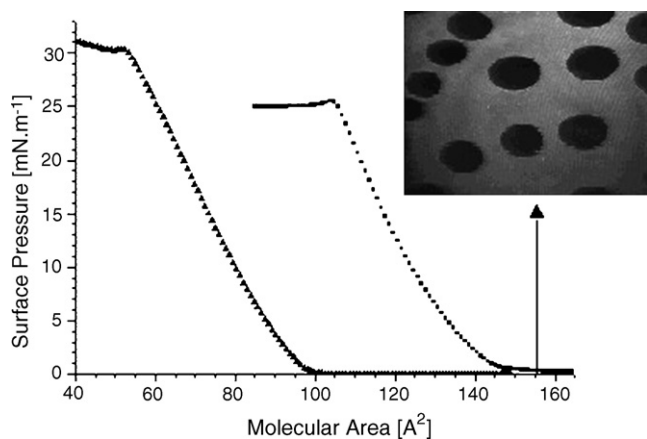


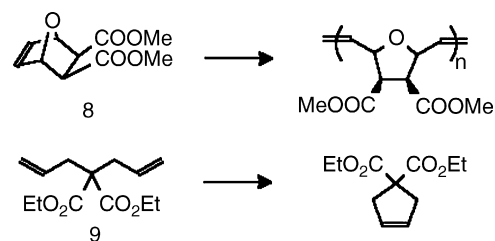
Fig. 1. Compression isotherms of catalysts **2** (left curve) and **3** (right curve) at the air–water interface at room temperature. (Inset) Brewster angle microscopy of catalyst **3**'s monolayer,  $\pi = 0.2 \text{ mN/m}$ , molecular area =  $155 \text{ \AA}^2 \text{ molecule}^{-1}$  (real size:  $430 \mu\text{m} \times 536 \mu\text{m}$ ).

isotherm in Langmuir monolayers at the air–water interface (Fig. 1). Monolayers of catalyst **3** presented an onset molecular area around  $148 \text{ \AA}^2 \text{ molecule}^{-1}$ . As the compression continues, a regular increase in the pressure was observed, up to the collapse at  $25 \text{ mN m}^{-1}$ . The isotherm for catalyst **2** exhibited a similar shape, with an onset molecular area of  $98 \text{ \AA}^2 \text{ molecule}^{-1}$  and a collapse pressure of  $30 \text{ mN m}^{-1}$ . These values are compatible with other already published ones for different ruthenium containing complexes [34–37]. The larger molecular area at the collapse for **3** compared to **2** could be attributed to the presence of the two fluorinated chains instead of one alkyl tail. The formation of monolayer was also confirmed by Brewster angle microscopy, which showed homogeneous monolayers at high surface pressure and the expected coexistence of liquid expanded domains and gaseous phase at low surface pressure (Fig. 1, inset). The formation of stable monolayers indicated without any doubt that these new catalysts are surface-active, meaning that the ruthenium moiety is polar enough to be close to the water surface.

Table 1  
RCM experiments on DEDAM

Catalyst	Solvent	[DEDAM] <sub>0</sub> (M)	[DEDAM] <sub>0</sub> /[catalyst]	T (°C)	Conversion (%)	Reaction time	TON	TOF (min <sup>-1</sup> )	
<b>1</b>	CH <sub>2</sub> Cl <sub>2</sub>	0.816	912	30	76	15 min	693	46.2	
		0.816	912	30	89	45 min	812	18.0	
	CD <sub>2</sub> Cl <sub>2</sub>	0.154	30	r.t.	40	6.9 min	12	1.7	
		0.83 <sup>a</sup>	5000	45	91	18 h	4550	4.2	
		0.83 <sup>a</sup>	2000	40	25	1 h	1500	420	
<b>2</b>	CH <sub>2</sub> Cl <sub>2</sub>	0.84	988	30	65	15 min	306	61.3	
		0.84	989	30	80	55 min	790	14.4	
	CD <sub>2</sub> Cl <sub>2</sub>	0.16	33	r.t.	40	17 min	13.4	0.8	
		D <sub>2</sub> O	0.038	195	r.t.	23	137 min	44.8	0.3
			0.038	195	r.t.	30	2 days	58.5	
<b>3</b>	CH <sub>2</sub> Cl <sub>2</sub>	0.83	1096	30	27	210 min	296	1.4	
		0.166	36	r.t.	17	150 min	6.1	0.04	
	D <sub>2</sub> O	0.036	203	r.t.	91	210 min	186	0.9	

<sup>a</sup> Values taken from Refs. [14,16].



Scheme 2. ROMP and RCM reactions.

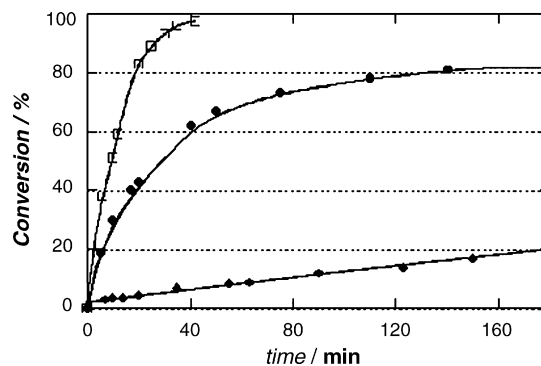
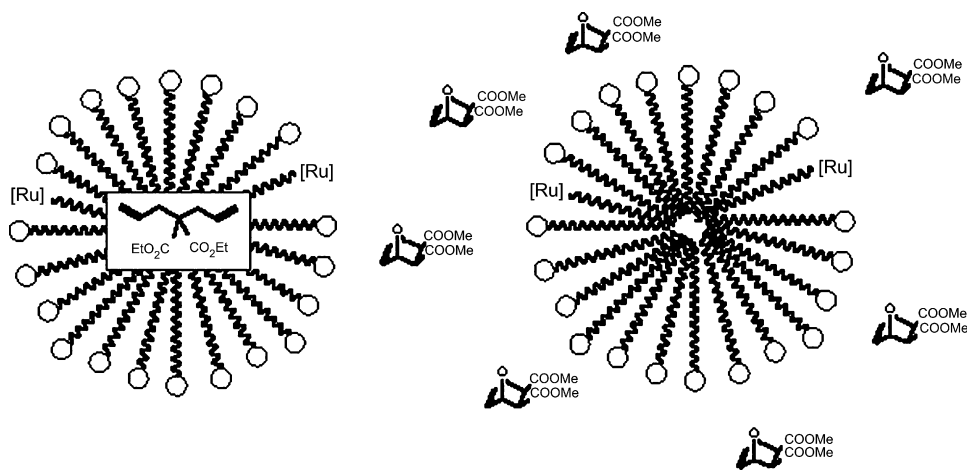


Fig. 2. Kinetics of RCM experiments. **1** (□), **2** (●) and **3** (◆). Determined by <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>, r.t., [diethyldiallylmalonate] = 0.16 M, [diethyldiallylmalonate]/[catalyst] = 30.

### 3.2. Ring-closing metathesis reactions

The new catalysts were studied both in homogeneous and micellar conditions on ROMP and RCM. Ring-closing metathesis experiments were carried out on DEDAM **9** (Scheme 2) and showed that Hoveyda's catalyst exhibited the highest activity in methylenechloride, closely followed by **2**, whereas catalyst **3** was the less active (Fig. 2). Turnover numbers and turnover frequencies were measured in order to compare these new catalysts with existing ones. Results are presented in Table 1. In homogeneous solutions, TONs of 800 were easily obtained for **1** and **2**, whereas TOFs up to  $60 \text{ min}^{-1}$  were measured. Compared to values reported by Buchmeiser, these were lower even for Hoveyda's catalyst. This can be explained by the difference



Scheme 3. Schematic localization of reagents for RCM and ROMP.

of experimental conditions (temperature and catalyst mole percent). As for catalyst **3**, lower TONs and TOFs are obtained. Buchmeiser also described a reduction of reactivity between Hoveyda's catalyst and a trifluoroacetate modified one [14]. In conclusion, the new catalysts exhibit an expected reactivity based on already known systems in organic solvents.

RCM reactions were then tested at room temperature in micellar solutions of dodecyltrimethylammonium chloride (DTAC). The concentration of DTAC was 0.048 M, which is higher than its critical micellar concentration (0.02 M at 25 °C [38]). Results are presented in Table 1. For catalyst **3**, an accelerating effect was clearly observed compared to homogeneous solutions and a turnover number of 186 was obtained. The solubility of DEDAM in pure water has been measured by <sup>1</sup>H NMR in the presence of known quantities of sodium trimethylsilylpropyl sulfonate and was found at  $8.7 \times 10^{-4}$  M. This solubility is in agreement with an estimated  $\log P$  value of 3.41 [39]. Consequently, in this case, the reagent is preferably localized in the micelles (Scheme 3), which is also the case of the cyclicized product based on a  $\log P$  value of 2.25 [39]. The accelerating effect observed might be due to *in situ* regeneration of Hoveyda's catalyst, owing to a ligand exchange between chloride ions from DTAC and perfluorocarboxylate moieties from **3**. This hypoth-

esis is corroborated by a change of color that has been observed during the initial mixing of DTAC and **3**. In the case of catalyst **2**, a decrease in reactivity was observed in micellar solution and TONs are not higher than 60, proving that catalyst and reactant are not in favorable positions. This is a further proof that the active site of catalyst **2** is in the hydrophilic part of the micelle and that DEDAM is mostly localized in the core of the micelle.

### 3.3. Ring-opening metathesis polymerization

ROMP was carried out using norbornene (NB) and diester **8** (Scheme 2) in methylenechloride. The results obtained for these monomers are presented in Table 2. Both synthesized catalysts were able to initiate the ROMP of both monomers, leading in all cases to conversions higher than 90%. In the case of NB, the polymerizations led almost instantaneously to very viscous solutions, due to the presence of high molecular weight chains. This is the sign of a rapid propagation step versus the initiation, as already observed in other ROMP systems [40–42]. In the case of diester **8**, the polymerization initiated by catalysts **2** and **3** behaved similarly to Hoveyda's catalyst. For catalyst **2**, the molecular weight of the obtained polymer was lower, indicating a more favorable process, although far

Table 2  
ROMP experiments

Monomer	Solvent	Catalyst	[M] <sub>0</sub> (M)	[M] <sub>0</sub> /[catalyst]	Conversion (%) <sup>a</sup>	% <i>cis</i> <sup>b</sup>	$\overline{M}_w^c$	$I = \overline{M}_w/\overline{M}_n^c$	$M_{th}$ at 100% conversion <sup>d</sup>
NB	CD <sub>2</sub> Cl <sub>2</sub>	<b>2</b>	0.28	110	95	55	492000	1.5	10400
	Tol- <i>d</i> <sub>8</sub> <sup>e</sup>	<b>2</b>	0.38	120	90	60	460000	1.7	11300
	CD <sub>2</sub> Cl <sub>2</sub>	<b>3</b>	0.31	100	100	n.d.	340000	1.6	9400
	Tol- <i>d</i> <sub>8</sub>	<b>3</b>	0.41	100	n.d.	n.d.	266000	1.6	9400
<b>8</b>	CD <sub>2</sub> Cl <sub>2</sub>	<b>1</b>	0.20	96	100	66	450000	1.6	20400
	CD <sub>2</sub> Cl <sub>2</sub>	<b>2</b>	0.19	98	100	65	140000	1.5	20800
	CD <sub>2</sub> Cl <sub>2</sub>	<b>3</b>	0.19	98	95 in 5 h	65	790000	1.3	20800

<sup>a</sup> At room temperature, time of reaction 5 min.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

<sup>c</sup> Determined by SEC.

<sup>d</sup>  $M_{th} = M_0[M]/[I]$ .

<sup>e</sup> Toluene-*d*<sub>8</sub>.

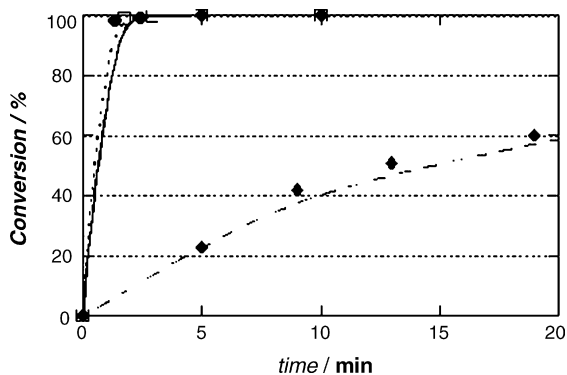


Fig. 3. Kinetics of ROMP experiments. **1** (□), **2** (●) and **3** (◆). Determined by  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$ , r.t.,  $[\mathbf{8}] = 0.2 \text{ M}$ ,  $[\mathbf{8}]/[\text{catalyst}] = 98$ .

from the theoretical molecular weight. Finally, with catalyst **3**, the reaction was slower, but the molecular weight was again very high. For all systems, the configuration of the new double bonds was found *cis* between 55 and 65%.

The kinetic differences are illustrated in Fig. 3 for monomer **8**. Hoveyda's catalyst and **2** are shown to have the same behaviour leading to 50% of conversion in less than 40 s and full conversion was attained after 3 min. Catalyst **3** resulted in a slower polymerization reaction for which 50% conversion was obtained after 13 min and 95% after 3 h.

Next, their use as catalytic surfactants was assessed for ROMP in micellar solutions. In such system, either water-soluble or insoluble monomers could be envisaged. In each case, the inisurf is by nature at the interface between hydrophobic and hydrophilic media. For water-soluble monomers, the system can be described as a dispersion polymerization, whereas for hydrophobic monomers, this is close to a suspension polymerization. Early experiments used micelles of oligoethyleneglycol ( $\text{C}_{12}\text{E}_4$ ). In this case, the polymerization seemed to be erratic, the repetition of same experimental conditions leading to non-reproducible conversions. This was surprising to us, since Grubbs' catalysts have been shown to be active in the presence of ethyleneglycol units [7,13]. This might be due to the more labile ligand in Hoveyda's catalysts compared to phosphine in the case of Grubbs' one. In this precise case, this could lead to a complexation of ethyleneglycol units to the ruthenium causing deactivation of the system.

Instead, when DTAC was chosen at a concentration higher than its critical micellar concentration (ca.  $2 \times 10^{-2} \text{ M}$  at  $25^\circ\text{C}$ ) [38], the reaction proceeded without any problem in non-degassed water. In the case of monomer **8**, such system is close from a dispersion polymerization since the reaction starts from a clear micellar solution. The solubility of monomer **8** in water was measured by  $^1\text{H}$  NMR in the presence of known quantities of sodium trimethylsilylpropyl sulfonate and was found at 0.1 M. Therefore, in all experiments presented here, the monomer is soluble in the aqueous solution, which is also consistent with an estimated  $\log P$  value of 0.47 [39] (Scheme 3). During the polymerization, the formed polymer remains dispersed in the solution through the presence of the surfactants. In the system described here, during the polymerization, no organic solvent was used. It was only employed as a common method for mixing the surfactant and the catalyst but it was eliminated under a stream of argon before adding water and obtaining the micellar solution.

The polymerization results are presented in Table 3 for monomer **8**. Under the conditions used here, all reactions yielded a quantitative conversion after 18 h in the presence of catalysts. Blank experiments without catalysts were also carried out to ensure that no uncontrolled polymerization of **8** occurred. Compared to experiments in homogeneous solution,  $\overline{M}_n$  values are much closer to theoretical ones for both new catalysts, showing a higher percentage of initiating catalyst. Previous studies reported that ROMP in water benefited the use of hydrochloric acid to optimize the exchange of ligands [13]. In our case, the reaction occurred even without any trace of acid since the ligand is more labile.

Kinetic follow-ups were carried out by  $^1\text{H}$  NMR by registering directly in the micellar solution the disappearance of monomer signal versus DTAC, since polymer signals could not be detected, as expected in the case of solid-like micelles. Parallel determination of conversion after extraction by chloroform gave similar results. These experiments showed that the polymerization was already finished after 30 min for catalyst **2** and 1 h with catalyst **3** that was much slower in organic homogeneous solution (Table 4).

TONs and TOFs were also calculated and values are reported in Table 4. These are only indicative values, since the calculation does not take into account the fact that only a fraction of catalyst actually leads to polymer chains. Having that in mind,

Table 3  
ROMP of **8** in non-degassed water at room temperature, after 18 h

Catalyst	$[\text{M}]_0$ (M)	$[\text{Catalyst}]_0$ (M)	$[\text{M}]_0/[\text{catalyst}]_0$	[DTAC] (M)	Conversion <sup>a</sup>	$\overline{M}_n^b$	<i>I</i>	$M_{\text{th}}^c$	$M_{\text{th}}/\overline{M}_n$
<b>2</b>	0.022	$2.3 \times 10^{-4}$	97	0.136	100	34470	1.3	20600	0.60
	0.022	0		0.136	0				
	0.0272	$2.32 \times 10^{-4}$	117	0.049	96	37330	1.4	23830	0.64
	0.0451	$2.32 \times 10^{-4}$	195	0.049	97	46980	1.4	40140	0.85
	0.0451	0		0.049	0				
<b>3</b>	0.0451	$2.3 \times 10^{-4}$	195	0.049	99	47010	1.6	41000	0.87

<sup>a</sup> Determined by  $^1\text{H}$  NMR.

<sup>b</sup> Determined by SEC with polystyrene standards, corrected for poly(**8**).

<sup>c</sup> Determined from  $[\text{M}]_0$  conversion/ $[\text{catalyst}]_0$ .

Table 4  
Characterization of ROMP of **8** at room temperature

Catalyst	Solvent	[M] <sub>0</sub> (M)	[M]/[catalyst]	Conversion (%) <sup>a</sup>	Reaction time (min)	TON	TOF (min <sup>-1</sup> )
<b>1</b>	CD <sub>2</sub> Cl <sub>2</sub>	0.188	94	99	1.75	91	52
<b>2</b>	CD <sub>2</sub> Cl <sub>2</sub>	0.188	99	99.3	2.40	97	40
	D <sub>2</sub> O	0.057	289	100	30	283	9.4
				83	5	240	48
<b>3</b>	CD <sub>2</sub> Cl <sub>2</sub>	0.188	99	42	9	41	4.6
				95	190	93	0.5
	D <sub>2</sub> O	0.041	232	90	25	210	8.3

<sup>a</sup> Determined by <sup>1</sup>H NMR.

the values are also presented for reactions in methylene chloride. Although the data cannot be compared directly because of different concentrations, these results show that the catalysts remain very active in the micellar system.

The presence of polymer aggregates has been analyzed by dynamic light scattering tests that revealed, at the beginning of the reaction with catalyst **2**, the formation of particles having a diameter of ca. 220 nm and a polydispersity index of 0.14 (see [Supplementary information](#)). The mean diameter remained stable for at least 18 h, that means well after the polymerization's end. However, the polydispersity index increased, showing a relative instability of the system. Further studies will be carried out to stabilize it. With catalyst **3**, the behaviour was similar but the particles were slightly smaller, having a diameter typically below 200 nm.

The polymerization of poorly water-soluble NB was also carried out and occurred in a quantitative yield but led to bimodal distributions in SEC, which is a sign of the presence of different sites for initiation. This system was not further characterized.

#### 4. Conclusion

Both catalysts presented here are able to catalyze efficiently metathesis reactions, even if catalyst **2** has a higher activity compared to **3**. Both form monolayers at the air–water interface, demonstrating their surface-active property. In preliminary experiments in micellar solution, we have shown that they are useful in surf molecules, enabling ROMP process to be carried out in non-degassed water with well-defined catalysts. The polymerization in this environment-friendly medium is furthermore better controlled compared to homogeneous solutions. RCM reactions also were shown to be very efficiently catalyzed by catalyst **3** when mixed in the micelles.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.08.015.

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