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

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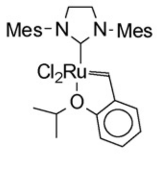
## Abstract

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 inisurf molecules for metathesis polymerization that are air-stable. Their ability to catalyze ring-closing metathesis in water has also been evaluated.

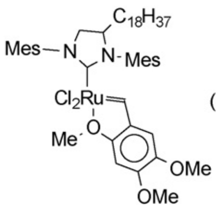
*Keywords:* Hoveyda's catalyst; Inisurf; Ring-opening metathesis polymerization; Ring-closing metathesis; Surfactant

## 1. Introduction

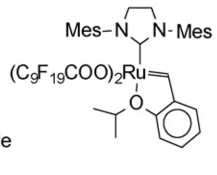
One of the biggest challenges in modern chemistry is to find environmentally friendly processes while carrying out already known chemical reactions. In this field, metathesis reactions were for a long time hampered because of chemical sensitivity of the catalysts versus oxygen or water. For one part, 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].



**1**



**2**



**3**

With such development, carrying out metathesis reactions in water with well-characterized catalysts is now feasible. Metathesis reactions have already be carried out in pure water, but mostly on non-preformed catalysts, like $RuCl_3$, $H_2O$ [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 $O_2$ content 25 ppm) or using Schlenk techniques connected to an argon line. Solvents were dried over $CaH_2$, 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

$^{1}H$ NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.13 MHz. $^{13}C$ 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. $^{19}F$ 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 $1.2\,mL\,min^{-1}$) on an apparatus equipped with a Waters refractive index detector, a Waters column pack (Ultrastyragel $10^4$, $10^3$, 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 ($2\,mmol\,Br_3^-\,g^{-1}$) were suspended. 2.54 g of 1-eicosene (9.05 mmol) in 10 mL $CH_2Cl_2$ 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%).

$^{1}H$ NMR: 0.91 ($t$ $^{3}J = 6.7$ Hz), 3H, Me); 1.25–1.6 (m, 32H, $-CH_2-$), 1.75–1.85 (m, 1H, $-CH_2-CHBr$), 2.08–2.22 (m, 1H, $-CH_2-CHBr$); 3.65 ($t$ $^{2}J = 10.2$ Hz $^{3}J = 10.2$ Hz, 1H, $-CH_2-Br$), 3.87 (dd $^{2}J = 10.2$ Hz $^{3}J = 4.6$ Hz, 1H, $-CH_2-Br$); 4.15–4.22 (m, 1H, $-CH-Br$).

$^{13}C$ NMR: 14.3 (Me–), 22.9, 27.0, 29.0, 29.6, 29.7, 29.8, 29.9, 32.1, 36.3 ($-CH_2-$), 36.6 ($-CH_2-Br$), 53.4 ($-CH-Br$).

Methane CI mass spectrum (relative intensity): 458 (13.7) $[M+CH_4]^+$, 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