SUPPORTING INFORMATION

Microwave-Ultrasound Simultaneous Irradiation: a Hybrid Technology for Ring Closing Metathesis.

Martina Sacco, a,b Clarence Charnay, c,* Francesco De Angelis, b Marilena Radoiu, d Frédéric Lamaty, a Jean Martinez, a Evelina Colacino, a,*

a Institut des Biomolécules Max Mousseron (IBMM) UMR 5247 CNRS – Université Montpellier - ENSCM, Green Chemistry and Enabling Technology Team, Place E. Bataillon, 34095 Montpellier Cedex 5, France. E-mail: evelina.colacino@univ-montp2.fr; webpage: http://www.greenchem.univ-montp2.fr

b Dipartimento di Scienze Fisiche e Chimiche Università dell’Aquila e Consorzio INCA, Via Vetoio, Coppito, 67100 L’Aquila, Italy

c Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2, CC1502, Université Montpellier, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France. E-mail: clarence.charnay@univ-montp2.fr

d SAIREM, 12, porte du Grand Lyon, BP 80214, 01702 Neyron Cedex, France.

General Experimental Procedures

Compounds. All reagents were commercially available and used without any further purification. 2-Methyl-tetrahydrofuran (2-Me-THF) was supplied by PennAKem (Memphis, USA). Glycerol was acquired from Alfa Aesar. The gemini dicationic surfactants 12-2-12 was synthesized according to the method reported by R. Zana et al. 57 NMR spectra were recorded at room temperature with the appropriate deuterated solvent (CDCl₃). Chemical shifts (δ) of ¹H NMR and ¹³C NMR spectra are reported in ppm relative to residual solvent signals (CHCl₃ in CDCl₃: δ = 7.27 ppm for ¹H and CDCl₃: δ = 77.04 ppm for ¹³C NMR, J values are given in Hz. ¹H and ¹³C NMR spectra were registered at 300 MHz. The identity of analytically pure RCM product 2 was assessed by comparison with its ¹H NMR spectrum, identical to that one previously described in the literature 44,58 and by their fragmentation in LC/MS. Yields were determined by ¹H NMR using CH₂Br₂ as internal standard (0.1425 mmol, 10 µL). LC-MS analysis were performed with HPLC Waters Alliance 2695 (UV Waters 2489), column Onyx C₁₈, (25 x 4.6 mm), flow 3 mL/min linear gradient CH₃CN in water 0-100% (+ 0.1% HCO₂H)
in 2.5 min. The reactions were followed by TLC (Petroleum ether/Diethyl ether 7:3 v/v) and revealed by iodine.

**Hybrid Microwave/Ultrasound Apparatus.** The experiments were performed with a modified monomode SAIREM Miniflow 200SS (www.sairem.com) apparatus equipped with ultrasound generator and optimized at the Institut des Biomolécules Max Mousseron, University of Montpellier II, France. The MiniFlow 200SS is based on Sairem’s semiconductor microwave generator, with power from 0 to 200 W adjustable by 1 W increment and controlled variable frequency from 2430 MHz to 2470 MHz manually or automatically adjustable by 0.1 MHz. The continuous control and monitoring of the forward power, reflected power and temperature were achieved via an integrated PLC/touch screen digital display. The temperature measurement and control of the reaction were performed via the built-in fibre optic thermometer. The absence of microwave leakage was verified and measured using a hand-held microwave leakage detector type IPF 5C, Sairem. The ultrasonic energy was generated by a transducer using a sonotrode (nominal power 200 W, Model Reus, Contes, France – www.etsreus.com) with a frequency of 25 KHz and resulted in an applied power of 1 W/mL, designed by REUS (France, www.etsreus.com). The emission of the ultrasound waves was made at the bottom of the reactor (diameter of transmission surface for the ultrasound plate: 74 mm). Reactions were performed in a cylindrical Pyrex vessel (capacity of 10-50 mL), in open vessel conditions at atmospheric pressure. The forwarded microwave power, the duration of microwave irradiation and the temperature were controlled with a programmer. A timer integrated in the generator controlled the ultrasound irradiation time separately.
Figure S1. SAIREM Miniflow 200SS, WR340 U-shaped waveguide.

Figure S2. Cooling jacket for the US.
Selected Graphics illustrating the Energy Absorbed by Reaction Mixtures under MW or SMUI.

The MiniFlow is a microwave equipment based on a solid state (semiconductor) generator which measures and displays continuously the forward power ($P_f$) and the reflected power ($P_r$). Equally, the MiniFlow has a device (sliding short circuit) that enables the tuning (minimization of the reflected power). The Microwave absorbed power by the reactor was measured as the difference between the forward power and reflected power. As the reflected power was tuned down to 0 W in all experiments, the absorbed power by the reactor was always equal to the $P_r$. Therefore, the total energy (J) absorbed by the reactor and reaction medium = $P_f(W) \times \text{time (s)}$. 

Figure S3. Scheme of the test-rig apparatus.
Figure S4. Table 1, entry 5: RCM using M2 catalyst a) under MW alone; b) under SMUI irradiation.

Figure S5. Table 1, entry 6: RCM using M2_0 catalyst a) under MW alone; b) under SMUI irradiation.
Figure S6. Table 1, entry 9: RCM using M5₂ catalyst a) under MW alone; b) under SMUI irradiation.