

Catalytic conversions in aqueous media: a novel and efficient hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) catalyzed by Rh/TPPTS complexes in mixed micellar nanoreactors

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Abstract

Exceptionally high catalytic activities ($\text{TOF} > 840 \text{ h}^{-1}$) were achieved in the aqueous phase hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) (PB-*b*-PEO) catalyzed by water-soluble Rh/TPPTS complexes [TPPTS = $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_3$] in mixed micellar nanoreactors formed by dodecyltrimethylammonium chloride along with PB-*b*-PEO especially when *n*-hexane was added to the reaction system. This is the first example of a catalytic hydrogenation of an unsaturated polymer using water-soluble transition metal TPPTS complexes in aqueous media. Using Rh/TPPTS catalysts high activities were observed in the hydrogenation of PB-*b*-PEO in mixed micelles whereas in single micelles the activities were lower. Dynamic light scattering experiments showed the presence of mixed nanomicelles with smaller hydrodynamic radii compared to the radii of single micelles. A model of a mixed micellar nanoreactor was proposed to rationalize the observed results. The hydrogenation reaction was shown to be homogeneously catalyzed by Rh/TPPTS complexes generated in situ from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and TPPTS under the reaction conditions. A recycling experiment showed that the catalytic activity remained high in a consecutive run even at a rhodium concentration of only 1 ppm in water.

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1. Introduction

There is increasing interest in catalysis in aqueous media employing water-soluble transition metal TPPTS and related complexes because of its broad range of potential applications [1]. The use of aqueous media facilitates recovery and recycling of the catalyst and circumvents the need for organic toxic solvents thereby providing substantial environmental and economical benefits. Furthermore, water is a non-toxic, non-inflammable, inexpensive, abundantly available and an environmentally friendly solvent [1]. Therefore, catalysis in

aqueous media fully implements the principles of “Sustainable/Green Chemistry” [2].

Catalytic hydrogenation of unsaturated polymers constitutes an important process because of the desirable properties of the materials obtained, which are not accessible or difficult to prepare by conventional polymerization methods [3]. Moreover, hydrogenation reactions improve the chemical, physical and mechanical properties of polydiene elastomers and impart excellent resistance to oxidative and ozonolytic ageing, improved resistance to oils and fluids, even at high temperatures, and reduced gas permeability to those materials. Nowadays, there are two industrial processes for the homogeneous hydrogenation of unsaturated polymers catalyzed by transition metal complexes in conventional organic media: (i) the Nippon Zeon Chemicals and Bayer/Polysar Rub-

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ber Corp. process for the selective hydrogenation of C=C in nitrile butadiene rubber (NBR) and (ii) the Shell process for the hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and block styrene butadiene rubber (SBR) [3a,3b]. However, the high cost of these processes and the price of the endproduct remains an important challenge for the future. The Dow Chemical Company is developing an industrial heterogeneous catalytic hydrogenation process of polystyrene (PS) to poly(vinylcyclohexane) (PVCH) used for the production of high-density (blue-laser) digital versatile discs (DVDs) with a storage capacity up to 30 gigabytes [4].

Recently, Wei et al. [5a] described the biphasic hydrogenation of SBS block copolymers catalyzed by Ru/TPPTS complexes in polyether modified ammonium salt ionic liquids. MacLeod and Rosso [5b] also reported the biphasic hydrogenation of PB, NBR and SBR catalyzed by RhCl(TPPTS)₃ in ionic liquids such as *N,N'*-butylmethylimidazolium tetrafluoroborate. Singha et al. [6] studied the hydrogenation of NBR latex using water-soluble RhCl(TPPMS)₃ catalysts [TPPMS = PPh₂(C₆H₄-*m*-SO₃Na)] in the presence of the non-ionic surfactant Triton-X-305 in order to stabilize latex in aqueous media. However, RhCl(TPPMS)₃ catalysts exhibited low catalytic activities (TOF = 4.0–9.3 h⁻¹) in such media [6]. Mudalige and Rempel [7] hydrogenated PB (*M*_n = 900; 60% 1,4-PB; 40% 1,2-PB), NBR (*M*_n = 6400) and SBR (*M*_n = 95 000) using water-soluble rhodium catalysts modified with the tenside ligands PPh₂(CH₂)_{*n*}-COONa (*n* = 5, 7) and RhCl(TPPMS)₃ catalysts in aqueous/organic two-phase systems. However, massive leaching of rhodium from the aqueous to the organic phase was observed with Rh/PPh₂(CH₂)_{*n*}-COONa (*n* = 5, 7) catalysts [7].

We have investigated the hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) (PB-*b*-PEO) in water catalyzed by Rh/TPPTS complexes in mixed micellar nanoreactors formed by the cationic surfactant dodecyltrimethylammonium chloride (DTAC), which interacts with the anionic catalytic system Rh/P(C₆H₄-*m*-SO₃⁻)₃, along with the amphiphilic PB-*b*-PEO starting material. To our knowledge, this is the first example of a catalytic hydrogenation of an unsaturated polymer using water-soluble transition metal TPPTS complexes in aqueous media.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Messer Hellas (Athens) and was used without further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this pro-

cedure was repeated several times. RhCl₃·3H₂O was purchased from Acros Organics. DTAC was purchased from Acros Organics and used without any further purification. TPPTS was prepared according to the procedure of Hoechst AG, Werk Ruhrchemie [8] and isolated with purity higher than 94%. ³¹P{¹H}NMR (121 MHz, 25 °C, D₂O): δ TPPTS = -5.4 ppm.

2.2. Synthesis of PB-*b*-PEO

The PB-*b*-PEO diblock copolymers were synthesized by anionic polymerization high vacuum techniques, according to well established procedures [9]. The polymerization was conducted in benzene using *s*-BuLi as initiator in the presence of a phosphazine base (phosphazine/Li = 0.9/1 molar ratio) to promote the anionic polymerization of ethylene oxide with lithium as the counterion [10,11].

The copolymers were analyzed by size exclusion chromatography (SEC) using a Waters SEC system composed of a Waters 600 Pump Controller, a set of four Styragel columns (continuous porosity range 10³–10⁶ Å) and a Waters 410 differential refractometer, operated at 40 °C. The instrument was calibrated with both linear polystyrene and PEO standards. CHCl₃ was the carrier solvent at a flow rate of 1 mL/min. Pure block copolymers without the presence of any extra peak were obtained in all cases [11]. Average composition of the copolymers was determined by ¹H-NMR spectroscopy using a Varian 200 MHz instrument in CDCl₃ at 30 °C.

2.3. Typical hydrogenation procedure

RhCl₃·3H₂O, TPPTS, PB-*b*-PEO aqueous solution, DTAC and the remaining amount of distilled deoxygenated water (see Table 1) were charged into a Hastelloy C autoclave (21) which was previously evacuated and filled with argon. After a number of pressurising–depressurising cycles with hydrogen to remove the last traces of argon, the autoclave was pressured and contents were heated with stirring. At the reaction temperature the pressure was 20 bar of hydrogen. After the reaction the autoclave was cooled to room temperature, vented of hydrogen and the reaction mixture removed. The reaction mixture was concentrated in vacuum and HPB-*b*-PEO products were precipitated in acetone, dried over vacuum for 1 week and analyzed by ¹H-NMR spectroscopy.

2.4. Product analysis

¹H NMR (300 MHz) and ³¹P{¹H}NMR spectra (121 MHz, referenced to external 85% H₃PO₄) were recorded on a Varian Unity Plus 300/54 spectrometer. The conversions of PB-*b*-PEO were determined by quantitative ¹H NMR analysis in C₆D₅CD₃ or CDCl₃; 5.35 ppm: olefinic protons from both *cis*- and *trans*-1,4-PB and olefinic protons of 1,2-PB; 4.95 ppm: vinylic protons of 1,2-PB units; 3.70 ppm: protons of the methylene groups of PEO.

Table 1
Micellar hydrogenation of PB-*b*-PEO diblock copolymers catalyzed by Rh/TPPTS complexes in the aqueous phase^a

| Entry | Diblock copolymer | Wt% PB | (M_n) _{diblock} | M_w/M_n | Catalyst precursor | P/Rh molar ratio | Cationic surfactant | Surfactant/TPPTS molar ratio | [Rh] (ppm) | C=C/Rh molar ratio | Temperature (°C) | Time (min) | Conversion (mol%) | TOF ^b (h ⁻¹) |
|-------------------|-------------------|--------|------------------------------|-----------|--|------------------|---------------------|------------------------------|------------|--------------------|------------------|------------|-------------------|-------------------------------------|
| 1 | PB- <i>b</i> -PEO | 16.3 | 26500 | 1.01 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 32 | 100 | 60 | 30 | 9.6 |
| 2 | PB- <i>b</i> -PEO | 16.3 | 26500 | 1.01 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | DTAC | 3 | 10 | 32 | 100 | 60 | 100 | 32 |
| 3 | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 100 | 100 | 60 | 94 | 94 |
| 4 | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 100 | 80 | 60 | 78 | 78 |
| 5 | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 100 | 100 | 60 | 92 | 92 |
| 6 | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl ₃ ·3H ₂ O | – | – | – | 10 | 100 | 100 | 60 | 100 | 100 |
| 7 | PB- <i>b</i> -PEO | 48.3 | 38000 | 1.04 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 95 | 100 | 60 | 0 | 0 |
| 8 | PB- <i>b</i> -PEO | 48.3 | 38000 | 1.04 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | DTAC | 3 | 10 | 95 | 100 | 60 | 80 | 76 |
| 9 ^c | PB- <i>b</i> -PEO | 89.0 | 15000 | 1.01 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 13 | 176 | 100 | 60 | 100 | 176 |
| 10 ^c | PB- <i>b</i> -PEO | 89.0 | 15000 | 1.01 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | DTAC | 3 | 13 | 176 | 100 | 30 | 81 | 285 |
| 11 ^{c,d} | PB- <i>b</i> -PEO | 89.0 | 15000 | 1.01 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | DTAC | 3 | 13 | 300 | 100 | 20 | 94 | 846 |
| 12 ^e | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl(TPPTS) ₃ | 3 | – | – | 10 | 100 | 100 | 60 | 100 | 100 |
| 13 | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | RhCl ₃ ·3H ₂ O/TPPTS | 3 | – | – | 10 | 100 | 80 | 60 | 100 | 100 |
| 14 ^f | PB- <i>b</i> -PEO | 50.0 | 3600 | 1.06 | Rh/TPPTS (recycled) | 3 | – | – | 1 | 100 | 80 | 60 | 100 | 100 |
| 15 ^g | NBR latex | 22.5 | Aparene N685 | – | RhCl(TPPMS) ₃ | 3 | Triton-X-305 | – | 3309 | 203 | 75 | 720 | 55 | 9.3 |

^a Reaction conditions: $P_{H_2} = 20$ bar; 7.89 mg (0.03 mmol) RhCl₃·3H₂O, 56.0 mg (0.09 mmol) TPPTS, a solution of PB-*b*-PEO (0.32 g of diblock copolymer dissolved and left overnight in 100 g deaerated distilled H₂O), 71.2 mg (0.27 mmol) cationic surfactant DTAC and addition of deaerated H₂O to give 308.2 g of aqueous reaction mixture.

^b Defined as mole of hydrogenated C=C units in the PB-*b*-PEO block copolymer per mole of rhodium per hour.

^c A two-phase system consisting of 231 g of aqueous phase and of 51 g of *n*-hexane (H₂O/*n*-hexane = 82/18).

^d 0.54 g of PB-*b*-PEO dissolved in 51 g of *n*-hexane.

^e 27.75 mg (0.03 mmol) of RhCl(PPh₃)₃ dissolved in 30 ml CH₂Cl₂ were extracted by an aqueous 100 ml solution of 56.0 mg (0.09 mmol) of TPPTS with intense stirring for 24 h. The two layers were separated and the aqueous phase containing RhCl(TPPTS)₃ after washing with CH₂Cl₂ was used as catalyst solution.

^f Twenty five grams of the reaction mixture of entry 13 was re-used after filtration over a 0.2 μm filter unit (Millex-FG of Millipore) with a solution of PB-*b*-PEO (0.026 g; 0.243 mmol of C=C units in 15 g of H₂O) and addition of deaerated H₂O for 265.9 g of reaction mixture.

^g The data of entry 15 were taken from Ref. [6].

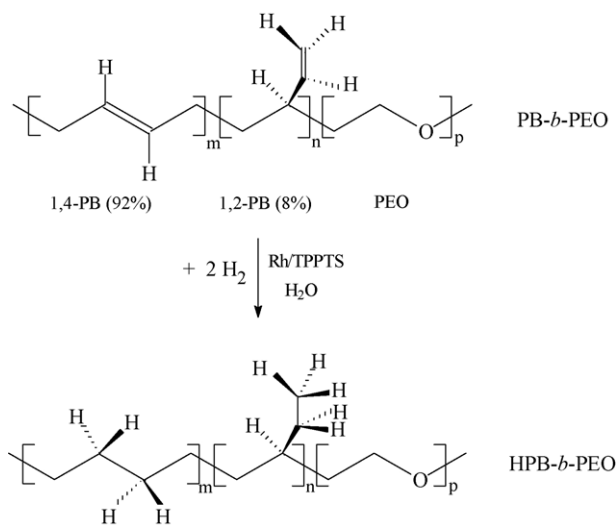
2.5. Dynamic light scattering

Measurements were conducted with a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar⁺ laser, operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit and a 192 channel correlator for the accumulation of the data. The correlation functions were analyzed by the cumulant method and CONTIN software. Measurements were carried out at 45°, 90° and 135°. The angular dependence of the ratio Γ/q^2 , where Γ is the decay rate of the correlation function and q the scattering vector, was not very important for the micellar solutions, due to their large sizes. Apparent translational diffusion coefficients at zero concentration, $D_{o,app}$ were measured using the equation: $D_{app} = D_{o,app}(1 + k_D c)$ (2); where k_D is the coefficient of the concentration dependence of the diffusion coefficient. Apparent hydrodynamic radii at infinite dilutions, R_h , were calculated by aid of the Stokes–Einstein equation: $R_h = kT/6\pi\eta_s D_{o,app}$ (3); where k is the Boltzmann's constant, T the absolute temperature and η_s the viscosity of the solvent.

3. Results and discussion

3.1. Effect of DTAC addition to Rh/TPPTS-catalyzed hydrogenation of PB-*b*-PEO

Typical results obtained in the micellar hydrogenation of PB-*b*-PEO to afford HPB-*b*-PEO (see Scheme 1) at 80–100 °C and 20 bar H₂ partial pressure in the presence of Rh/TPPTS catalysts and DTAC at very low rhodium concentrations ([Rh] = 10 ppm or even 1 ppm) in aqueous media are given in Table 1. Low catalytic activity (TOF = 9.6 h⁻¹) was observed in the hydrogenation of PB-



Scheme 1. Structures of PB-*b*-PEO diblock copolymers and of hydrogenated PB-*b*-PEO (HPB-*b*-PEO) catalyzed by Rh/TPPTS in aqueous micellar media.

b-PEO [(M_n)_{diblock} = 26 500, M_w/M_n = 1.01] with a short hydrophobic PB-chain (wt.%PB = 16.3) using Rh/TPPTS catalysts in water (entry 1). In contrast, when the cationic surfactant DTAC was added higher catalytic activity (TOF = 32 h⁻¹) was observed in the Rh/TPPTS-catalyzed hydrogenation of PB-*b*-PEO under the same conditions in water (entry 2).

We next turned our attention to the Rh/TPPTS-catalyzed hydrogenation of the amphiphilic diblock copolymer PB-*b*-PEO with a higher molecular weight [(M_n)_{diblock} = 38 000, M_w/M_n = 1.04] and a low *hydrophilic-lipophilic balance* (HLB) [1c] value, namely a longer hydrophobic PB-chain (wt.%PB = 48.3). High catalytic activity (TOF = 76 h⁻¹) was observed when DTAC was added to the Rh/TPPTS catalytic hydrogenation system of PB-*b*-PEO [(M_n)_{diblock} = 38 000, M_w/M_n = 1.04, wt.%PB = 48.3] at 100 °C, 20 bar H₂ pressure, a molar ratio of C=C unsaturation units of PB-*b*-PEO to rhodium of 95, within 1 h reaction time at a rhodium concentration of 10 ppm in the aqueous phase (entry 8). In sharp contrast, no catalytic activity (TOF = 0 h⁻¹) was obtained in the absence of DTAC in this hydrogenation reaction under the same conditions in aqueous media (entry 7).

In order to explain that the catalytic activity in the hydrogenation of PB-*b*-PEO, catalyzed by Rh/TPPTS in the aqueous phase goes through a maximum using cationic DTAC surfactants a simplified model of a Hartley ionic spherical mixed micelle [1b,1c,12–14] was proposed (Fig. 1). The micelle core is composed of the hydrophobic chain of the cationic surfactant DTAC where the hydrophobic PB-tail of PB-*b*-PEO with the C=C unsaturation units are located. Surrounding the core is the Stern layer where the charged head groups (NMe₃⁺ and SO₃⁻ of DTAC and TPPTS, respectively) are located together with the polar group(s) of the hydrophilic PEO-moiety of PB-*b*-PEO, along with the counter ions (Cl⁻ and Na⁺) of the ionic mixed micelle. The rhodium atom of the Rh/TPPTS catalyst is probably located on the polarity gradient between the Stern layer and the micelle core. Therefore, the position of the rhodium in the micelle should be dependent on the HLB value of PB-*b*-PEO itself and of the added surfactant. This dependence is in critical relationship between the length of the unsaturated hydrocarbon chain of PB-*b*-PEO and the length and nature of the added conventional surfactant for obtaining maximum reactivity. We used the cationic DTAC surfactant to create mixed micelles since one of us [15] as well as others [13a,1b] have found that the addition of only cationic surfactants to Rh/TPPTS catalytic systems accelerates the rates of catalytic reactions due to the attraction between the negatively charged Rh/TPPTS complex ions with the positively charged cationic end of the surfactant, therefore increasing the catalyst concentration in the micelle.

Dynamic light scattering experiments on aqueous solutions of PB-*b*-PEO [(M_n)_{diblock} = 26 500, M_w/M_n = 1.01, wt.%PB = 16.3] starting materials, at 0.06×10^{-3} M above their critical micellar concentration (cmc), showed the presence of micelles with an average hydrodynamic radius of

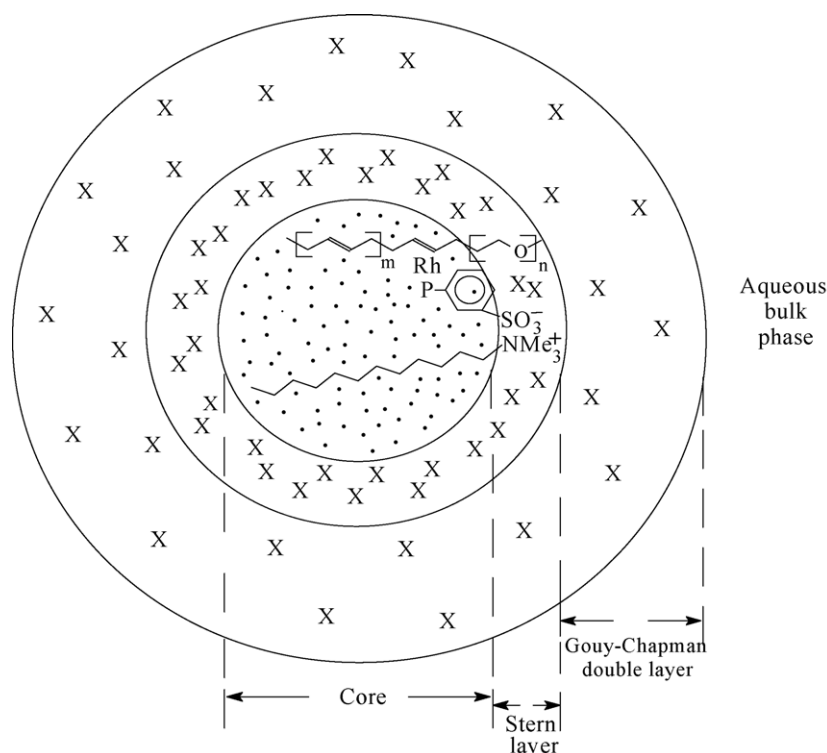


Fig. 1. Representation of a simplified proposed model of a spherical Hartley ionic mixed micelle containing the Rh/TPPTS catalyst, PB-*b*-PEO and DTAC. The hydrophobic tails of DTAC and of PB-*b*-PEO in the core of the mixed micelle (stippled part), the hydrophilic heads (NMe₃⁺) interacted with the SO₃⁻ groups of Rh/TPPTS catalyst in the Stern layer, the hydrophilic groups of PB-*b*-PEO in the Stern layer and Gouy–Chapman double layer, the counter ions (Na⁺ and Cl⁻ depicted as X) schematically indicate their relative locations and not the relationship to their molecular size, distribution, number or configuration.

55 nm (Table 2). In contrast, the observed hydrodynamic radius of the micelles of HPB-*b*-PEO in the hydrogenation mixture after the reaction using the same PB-*b*-PEO starting material in the presence of Rh/TPPTS and DTAC (Table 1, entry 2) was smaller, namely 31 nm (Table 2). The same

aggregation behaviour was observed by dynamic light scattering using an unsaturated amphiphilic diblock copolymer with a lower HLB value, PB-*b*-PEO [(M_n)_{diblock} = 38 000, M_w/M_n = 1.04, wt.%PB = 48.3]. The micelle of this unsaturated copolymer PB-*b*-PEO has an average hydrodynamic

Table 2
Dynamic light scattering measurements carried out on aqueous solutions^a of PB-*b*-PEO and HPB-*b*-PEO

| PB- <i>b</i> -PEO and HPB- <i>b</i> -PEO ^a | Concentration (M) | Average hydrodynamic radius (nm) |
|---|--------------------------|----------------------------------|
| PB- <i>b</i> -PEO (M _n = 26500, wt.%PB = 16.3) | 0.06 × 10 ⁻³ | 55 ^b |
| HPB- <i>b</i> -PEO (entry 2) ^c | 0.03 × 10 ⁻³ | 31 |
| PB- <i>b</i> -PEO (M _n = 3600, wt.%PB = 50.0) | 0.44 × 10 ⁻³ | 17 ^b |
| HPB- <i>b</i> -PEO (entry 3) ^c | 0.22 × 10 ⁻³ | 128 ^b |
| HPB- <i>b</i> -PEO (entry 4) ^c | 0.22 × 10 ⁻³ | 78 ^b |
| HPB- <i>b</i> -PEO (entry 5) ^c | 0.22 × 10 ⁻³ | 134 |
| HPB- <i>b</i> -PEO (entry 6) ^c | 0.22 × 10 ⁻³ | 69 |
| PB- <i>b</i> -PEO (M _n = 38 000, wt.%PB = 48.3) | 0.042 × 10 ⁻³ | 60 |
| HPB- <i>b</i> -PEO (entry 7) ^c | 0.021 × 10 ⁻³ | 66 |
| HPB- <i>b</i> -PEO (entry 8) ^c | 0.021 × 10 ⁻³ | 49 |
| HPB- <i>b</i> -PEO (entry 13) ^c | 0.02 × 10 ⁻³ | 77 |
| HPB- <i>b</i> -PEO (filtrated ^d mixture of entry 13 ^c) | 0.02 × 10 ⁻³ | 32 ^e |
| HPB- <i>b</i> -PEO (entry 14) ^c | 0.02 × 10 ⁻³ | 62 ^b |
| PB- <i>b</i> -PEO (M _n = 38 000, wt.%PB = 48.3) | 0.02 × 10 ⁻³ | 58 ^b |
| PB- <i>b</i> -PEO (M _n = 38 000, wt.%PB = 48.3)/TPPTS | 0.02 × 10 ⁻³ | 59 ^b |
| PB- <i>b</i> -PEO (M _n = 38 000, wt.%PB = 48.3)/TPPTS/DTAC | 0.02 × 10 ⁻³ | 41 |

^a All solutions investigated were blue-tinted indicating the presence of micelles.

^b Average value of a bimodal distribution.

^c The entry numbers refer to the entries of Table 1.

^d The solution was filtrated through Millex-FG filters of Millipore with pore size 0.2 μm.

^e The scattered light intensity was very weak.

radius of 60 (Table 2) whereas in the hydrogenated HPB-*b*-PEO after reaction in the mixture with Rh/TPPTS and DTAC (Table 1, entry 8) a smaller hydrodynamic radius of 49 nm (Table 2) was measured.

In order to confirm that addition of a cationic surfactant to an aqueous solution of PB-*b*-PEO decreases the hydrodynamic radius of the formed mixed micelle we measured the radius of the micelle of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 38\,000$, $M_w/M_n = 1.04$, wt.%PB = 48.3] at a different concentration (0.02×10^{-3} M) in the presence of TPPTS and DTAC. The radius of the single micelle of PB-*b*-PEO was 58 nm and after the addition of TPPTS slightly increased to 59 nm (Table 2). Indeed, addition of the cationic surfactant DTAC causes a decrease in the size of the mixed micelle formed with a hydrodynamic radius of 41 nm (Table 2).

Wang et al. [13c,13d] have found that addition of TPPTS to a cetyltrimethylammonium bromide (CTAB) micelle increased the molar mass of the micelle and that conversions obtained in the hydroformylation of the higher olefin *n*-dodecene-1 were higher in mixed micelles than in a single micelle of CTAB in aqueous media. Drexler et al. [14] showed that addition of the anionic surfactant sodium dodecylsulfate (SDS) to poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer micelles decreases the hydrodynamic radius of formed mixed micelles. These mixed micelles were used in the rhodium-catalyzed asymmetric hydrogenation of methyl (*Z*)- α -acetamidocinnamate. Addition of SDS to PEO-PPO-PEO amphiphilic solution increased the hydrogenation activity [14].

The decrease in size of the PB-*b*-PEO micelles after addition of DTAC would result in the formation of a higher number of mixed PB-*b*-PEO/DTAC micelles containing the Rh/TPPTS catalyst, under the same concentration. This higher number allows for a better solubilization of the hydrophobic PB-moiety of PB-*b*-PEO in the hydrophobic interior region of the mixed micelle and leads finally to a higher hydrogenation catalytic activity. This higher activity is probably due to the stabilization of the rhodium atom of the Rh/TPPTS catalyst in the polarity gradient between the Stern layer and the mixed micelle core (Fig. 1) and to the higher number of such mixed micellar nanoreactors. It should be noted that micelles are in dynamic equilibrium with individual surfactant molecules and are constantly being exchanged into and out of the micelle in a continuous disintegration and reformation process, which explains the quantitative conversion obtained in the hydrogenation of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 26\,500$, $M_w/M_n = 1.01$, wt.%PB = 16.3] (Table 1, entry 2) as well as the high conversion (80%) in the hydrogenation of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 38\,000$, $M_w/M_n = 1.04$, wt.%PB = 48.3] (Table 1, entry 8). Therefore, the application of mixed micelles represents another possibility to accelerate catalytic reactions in reactors with nanodimensions and may find a broad range of potential applications.

3.2. Rh/TPPTS-catalyzed hydrogenation of PB-*b*-PEO

The hydrogenation of low molecular weight PB-*b*-PEO [$(M_n)_{\text{diblock}} = 3600$, $M_w/M_n = 1.06$, wt.%PB = 50.0] proceeds smoothly in the presence of Rh/TPPTS catalysts. High catalytic activities (TOF = 78–94 h⁻¹) were observed in the absence of DTAC at 80 and 100 °C, 20 bar H₂ pressure, a molar ratio of C=C unsaturation units of PB-*b*-PEO to rhodium of 100, a rhodium concentration of 10 ppm and within 1 h reaction time, in the aqueous phase (see Table 1, entries 3–5). These results were rationalized by assuming that small micelles, probably with a low aggregation number [16] of amphiphilic PB-*b*-PEO molecules in a single micelle (defined as the number of individual polymer chains incorporated into the micellar structure) [16] are formed with the low molecular weight amphiphilic copolymer PB-*b*-PEO [$(M_n)_{\text{diblock}} = 3600$, $M_w/M_n = 1.06$, wt.%PB = 50.0]. Consequently, this small size of the micelles leads to the formation of a higher number of micelles with a low aggregation number and to a position of the rhodium atom of Rh/TPPTS catalyst on the polarity gradient between the hydrophobic interior region and the Stern layer, therefore giving an increase in catalytic hydrogenation activity. Indeed, dynamic light scattering studies on aqueous solutions of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 3600$, $M_w/M_n = 1.06$, wt.%PB = 50.0] demonstrated the presence of small micelles with an average hydrodynamic radius of 17 nm (Table 2). The micellar size of the HPB-*b*-PEO products (measured in the reaction aqueous mixture) increased and is consistent with the stronger hydrophobic interactions in the micelle due to the high degree of hydrogenation (78–94%) and also with the crystallinity of hydrogenated HPB-*b*-PEO products. The hydrodynamic radii of the aggregates were 128, 78 and 134 nm (Table 2) when the conversions in the hydrogenation were 94, 78 and 92%, respectively (Table 1).

Rh/TPPTS catalysts exhibited no catalytic activity in the hydrogenation of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 38\,000$, $M_w/M_n = 1.04$, wt.%PB = 48.3] in the absence of DTAC (Table 1, entry 7). The high aggregation number [16] of these amphiphilic PB-*b*-PEO molecules in a single micelle render the stabilization of the rhodium atom of Rh/TPPTS catalyst on the polarity gradient between the Stern layer and the core of the single PB-*b*-PEO micelle difficult. Another reason for the absence of catalytic activity might be mass transfer limitations resulting from the much lower water solubility of this starting material with a higher molecular weight at the reaction temperature of 100 °C, probably since the *critical temperature cloud point* (Tp) [1b] of PB-*b*-PEO was exceeded. We note that addition of SDS to PEO-PPO-PEO solutions increases the Tp [14]. The low catalytic activity (TOF = 9.6 h⁻¹) obtained in the hydrogenation of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 26\,500$, $M_w/M_n = 1.01$, wt.%PB = 16.3] by Rh/TPPTS catalysts in the absence of DTAC (Table 1, entry 1) could be explained by the lower aggregation number [16] of such amphiphilic PB-*b*-PEO molecules compared to the copolymer with the higher molecular weight in the single

micelle. This factor makes the approach and stabilization of the rhodium atom of Rh/TPPTS catalyst in the polarity gradient between the Stern layer and the core of the PB-*b*-PEO micelle easier.

3.3. Effect of *n*-hexane addition on the Rh/TPPTS-catalyzed hydrogenation of PB-*b*-PEO

Exceptionally high catalytic activities (TOF = 176–846 h⁻¹) were exhibited by Rh/TPPTS complexes in the micellar hydrogenation of the surfactant-like block copolymer PB-*b*-PEO [(M_n)_{diblock} = 15 000, M_w/M_n = 1.01, wt.%PB = 89.0], with a very low HLB value, in aqueous/organic (H₂O/*n*-hexane = 82/18) two-phase systems (Table 1). Rh/TPPTS catalysts showed high catalytic activity (TOF = 176 h⁻¹) in the biphasic hydrogenation of this PB-*b*-PEO starting material in the absence of DTAC probably due to the following parameters: (i) a not very high aggregation number in the single micelle, and (ii) the presence of the apolar solvent *n*-hexane, which is solubilized in the core causing the micelle to swell and facilitates the approach and stabilization of the rhodium atom of Rh/TPPTS catalyst on the polarity gradient between the Stern layer and the bulk hydrophobic interior region of this swollen micelle. Addition of DTAC to the biphasic catalytic system of the hydrogenation of PB-*b*-PEO [(M_n)_{diblock} = 15 000, M_w/M_n = 1.01, wt.%PB = 89.0] by Rh/TPPTS complexes created mixed micelles and considerably increased the catalytic activity from 176 to 846 TOFs per hour (Table 1, entries 9 and 11). It seems that the presence of apolar solvents like *n*-hexane is crucial for the enhancement of catalytic activity in single PB-*b*-PEO/Rh-TPPTS or mixed PB-*b*-PEO/DTAC/Rh-TPPTS micellar systems. This exceptionally high catalytic activity is even more remarkable when one considers that the concentration of rhodium is only 13 ppm in the aqueous medium.

Entry 15 of Table 1 compares typical results obtained by Singha et al. [6] in the hydrogenation of NBR latex catalyzed by RhCl(TPPMS)₃ in the presence of the non-ionic surfactant Triton-X-305 at a rhodium concentration of 3309 ppm where the catalytic activity was very low (TOF = 9.3 h⁻¹) in the aqueous medium.

3.4. Homogeneous or heterogeneous catalysis

RhCl₃·3H₂O catalysts precursors in the absence of TPPTS showed high activity (TOF = 100 h⁻¹) for the catalytic hydrogenation of PB-*b*-PEO [(M_n)_{diblock} = 3600, M_w/M_n = 1.06, wt.%PB = 50.0] in aqueous media (Table 1, entry 6). In this experiment a suspension of black particles was obtained, indicating that the reaction in the absence of TPPTS is probably heterogeneously catalyzed by Rh(0) particles prepared in situ by reducing RhCl₃·3H₂O with H₂ and stabilizing with the amphiphilic diblock copolymer PB-*b*-PEO starting material. Dynamic light scattering measurements on an aqueous solution of the reaction mixture as described in entry 6

(Table 1) showed the presence of micelles with an average radius of 69 nm (Table 2), which is consistent with the absence of TPPTS. Schulz et al. [17] prepared suspensions of Rh(0) nanoparticles by reducing RhCl₃·3H₂O with sodium borohydride and stabilizing with surfactant hydroxyalkylammonium salts, and used them as catalysts in hydrogenation reactions of various benzene derivatives in aqueous/organic two-phase systems.

The results of the experiments described above give rise to the question whether the hydrogenation of PB-*b*-PEO is actually homogeneously catalyzed by RhCl₃·3H₂O/TPPTS precursors. To verify whether the reaction proceeds homogeneously by Rh/TPPTS complexes in water, recycle experiments of the Rh/TPPTS catalyst were conducted after filtration over a 0.2 μm filter unit (Millex-FG of Millipore). First, hydrogenation of PB-*b*-PEO [(M_n)_{diblock} = 3600, M_w/M_n = 1.06, wt.%PB = 50.0] was carried out at 80 °C for 1 h in the presence of Rh/TPPTS catalysts in aqueous medium where the conversion of PB-*b*-PEO was 100% (Table 1, entry 13). 25 g of the aqueous reaction mixture of experiment described in entry 13, after filtration over a 0.2 μm filter unit, were re-used as catalyst in the hydrogenation reaction with additional water and PB-*b*-PEO starting material (Table 1, entry 14). In this recycle hydrogenation experiment the PB-*b*-PEO conversion at 80 °C after 1 h was 100% at a rhodium concentration of only 1 ppm (Table 1, entry 14). Therefore, we can conclude that the reaction in the presence of Rh/TPPTS catalysts is homogeneously catalyzed because if heterogeneous metallic Rh(0) nanoparticles were formed and catalyzed the hydrogenation reaction, then the HPB-*b*-PEO amphiphile would be absorbed on the Rh-nanoparticle surface [17b], the Rh/HPB-*b*-PEO aggregates would be separated off with the filter unit and the PB-*b*-PEO conversion would be 0% in the hydrogenation reaction, as described in entry 14. Dynamic light scattering studies were also carried out on the aqueous solutions of the reaction mixture in entry 13, of the filtrated mixture in entry 13, and of the product in entry 14 (Table 1). The micellar size of the product HPB-*b*-PEO obtained according to the conditions in entry 13, was 77 nm (Table 2). The filtrated reaction mixture of entry 13 was a clear solution and showed micelles with an average hydrodynamic radius of 32 nm (Table 2). However, the scattered light intensity was very weak, indicating that most of micelles in the reaction mixture of entry 13 were separated off and only fragments of these aggregates were passed through the pores of the filter unit. The micellar size of the HPB-*b*-PEO product obtained from the experiment as described in entry 14, was again larger, namely 62 nm (Table 2). A similar behaviour regarding the homogeneous or heterogeneous nature of catalytic reactions has been reported [19] with RuCl₃·*x*H₂O precursors in hydrogenation reactions in aqueous media. RuCl₃·*x*H₂O precursors heterogeneously catalyzed the hydrogenation of fructose in water, whereas RuCl₃·*x*H₂O in the presence of TPPTS, with formation of Ru/TPPTS complexes, homogeneously catalyzed the same reaction in aqueous media [19]. Further support that homogeneous Rh/TPPTS com-

plexes are capable of catalyzing PB-*b*-PEO hydrogenation in aqueous media was obtained from the following experiment. The RhCl(TPPTS)₃ complex was separately prepared and used as catalyst in the hydrogenation of PB-*b*-PEO [$(M_n)_{\text{diblock}} = 3600$, $M_w/M_n = 1.06$, wt.% PB = 50.0] at $T = 100^\circ\text{C}$, $P_{\text{H}_2} = 20$ bar, within 1 h at $[\text{Rh}] = 10$ ppm in aqueous media (Table 1, entry 12). RhCl(TPPTS)₃ catalysts, prepared separately, exhibited high catalytic activity (TOF = 100 h^{-1}) in the hydrogenation of PB-*b*-PEO (Table 1, entry 12). This behaviour is comparable with the catalytic activity (TOF = 94 h^{-1}) obtained by Rh/TPPTS complexes formed in situ from RhCl₃·3H₂O with TPPTS and H₂ in the PB-*b*-PEO hydrogenation under the same conditions in aqueous media (Table 1, entry 3).

Larpernt et al. [18] have reported the formation of RhCl(TPPTS)₃ from RhCl₃·3H₂O with TPPTS in the absence of H₂, where TPPTS acts both as a ligand and reducing agent to rhodium(III) chloride to afford RhCl(TPPTS)₃.

4. Conclusions

For the first time an efficient catalytic hydrogenation of an unsaturated polymer using water-soluble transition metal TPPTS complexes has been achieved in aqueous media. The procedure developed makes use of water-soluble Rh/TPPTS catalysts and performs the hydrogenation of PB-*b*-PEO in mixed micellar nanoreactors formed by the cationic surfactant DTAC and the amphiphilic PB-*b*-PEO starting material in the aqueous phase, under mild conditions. Exceptionally high catalytic activities have been achieved in the hydrogenation of PB-*b*-PEO employing water-soluble Rh/TPPTS catalysts in mixed PB-*b*-PEO/DTAC nanomicelles, especially in the presence of apolar *n*-hexane. From dynamic light scattering experiments it is evident that the sizes of the mixed PB-*b*-PEO/DTAC/Rh-TPPTS micelles in nanodimensions are smaller than the sizes of corresponding single PB-*b*-PEO micelles, thus resulting in a higher number of mixed micelles and a higher catalytic activity. Therefore, the application of mixed micelles represents another possibility for acceleration of reactions in nanoreactors and may find a broad range of potential applications (e.g. in catalytic reactions and micellar polymerizations). Aqueous phase hydrogenation in single PB-*b*-PEO micelles has also been achieved using Rh/TPPTS catalysts with small micelles and when low aggregation numbers of PB-*b*-PEO molecules were adjusted in the single micelles depending on the average molecular weight and on the HLB value of the amphiphilic PB-*b*-PEO starting materials. The nature of the PB-*b*-PEO hydrogenation reaction, catalyzed by Rh/TPPTS complexes generated in situ from RhCl₃·3H₂O and TPPTS in aqueous media, has been shown to be homogeneous. The use of homogeneous Rh/TPPTS catalysts in the hydrogenation of unsaturated polymers in micellar nanoreactors in aqueous media provides the means for catalyst recycling by separation of the hydrogenated polymer with a membrane. Thus, the Rh/TPPTS catalyst has been

recycled without any loss of catalytic activity. The exceptionally high catalytic activities in mixed nanoreactors coupled with the ease of catalyst recovery and recycling as well as the avoidance of organic solvents have obvious economic and environmental benefits and fully implement the principles of “Sustainable/Green Chemistry”. We are currently investigating the scope of this useful system.

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