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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 (TOF > 840 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 = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$] 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 $RhCl_3\cdot 3H_2O$ 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.

Keywords: Hydrogenation; Rhodium; TPPTS; Mixed micelles; Aqueous media

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 [$TPPMS = PPh_2(C_6H_4\text{-}m\text{-}SO_3Na)$] 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 $PPh_2(CH_2)_n–COONa$ ($n = 5,7$) 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 $Rh/PPh_2(CH_2)_n–COONa$ ($n = 5,7$) 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 $Rh/P(C_6H_4\text{-}m\text{-}SO_3^-)_3$, 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 procedure was repeated several times. $RhCl_3·3H_2O$ 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%. $^{31}P\{^1H\}$NMR (121 MHz, 25 °C, D_2O): 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 10^3–10^6 Å) and a Waters 410 differential refractometer, operated at 40 °C. The instrument was calibrated with both linear polystyrene and PEO standards. $CHCl_3$ 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 $CDCl_3$ at 30 °C.

2.3. Typical hydrogenation procedure

$RhCl_3·3H_2O$, 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 (2 l) 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 $^{31}P\{^1H\}$NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recordered on a Varian Unity Plus 300/54 spectrometer. The conversions of PB-*b*-PEO were determined by quantitative ^1H NMR analysis in $C_6D_5CD_3$ or $CDCl_3$; 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.