Aqueous-phase hydrogenation of polybutadiene, styrene–butadiene, and nitrile–butadiene polymer emulsions catalyzed by water-soluble rhodium complexes

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Abstract

Hydrogenation of polybutadiene (PBD), styrene–butadiene (SBR), and nitrile–butadiene (NBR) polymers in aqueous/organic biphasic media catalyzed by the novel water-soluble complex $[RhCl(HEXNa)_2]_2$ **1**, (HEXNa = $Ph_2P–(CH_2)_5–CO_2Na$) at 100°C and 5.5 MPa H_2 was investigated. The results obtained under identical conditions with the previously known water-soluble catalyst $RhCl(TPPMS)_3$ **2**, (TPPMS = monosulphonated-triphenylphosphine) are also presented for comparison. Both complexes showed a reasonable catalyst activity toward polymer hydrogenation. Under the conditions employed in the present work the catalyst **1** was extracted into the organic phase during the reaction. This was attributed to the phase transfer properties of the complex which was rendered by the amphiphilic HEXNa ligand. The extraction of **1** into the organic phase was dependent on the nature of the organic co-solvent. Both **1** and **2** showed enhanced selectivity for hydrogenation of the 1,2 (vinyl) addition units over the 1,4 (internal) units in all the polymers studied in the present work.

Keywords: Water-soluble rhodium complexes; Catalytic hydrogenation; Polymer emulsions

1. Introduction

The chemical modification of unsaturated polymers via catalytic hydrogenation has attracted the attention of many researchers as an efficient synthetic route to novel polymers with desirable chemical, physical, and mechanical properties [1,2]. It offers a unique method for the synthesis of polymers which are inaccessible by direct polymerization, and also improves the elastomer properties such as resistance to oxida-

tive and ozonolytic aging, reduced gas permeability, and greater resistance to oils and fluids, especially at high temperatures [3–6]. Although catalytic hydrogenation has become a very important process for commercial production of specialty elastomers such as hydrogenated nitrile–butadiene rubber (HNBR), and hydrogenated styrene–butadiene rubber (HSBR), the high cost of the process, and hence the price of the end-product has remained as an open challenge to be tackled by rubber chemists and engineers. The use of Ru-complexes in catalytic hydrogenation has been studied as a practical alternative to the more expensive Rh and Pd

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based catalysts that are currently used in industrial processes [7–10].

A more economically viable approach is to hydrogenate the elastomers in the latex form. Because many of the elastomers are produced as an emulsion this approach would obviate many steps in the present commercial processes of polymer hydrogenation, such as the precipitation of the polymer from its emulsion, the drying process, and the redissolution of the polymer in an organic solvent. In addition, it would also facilitate processing and application of the end-product which is also in the form of an emulsion [11]. The few examples that are reported in this direction include hydrogenation of NBR latex using a stoichiometric diimide reagent [12], the catalytic hydrogenation of NBR latex using palladium acetate [13], and the catalytic hydrogenation of the SBR latex using the Wilkinson catalyst $RhCl(PPh_3)_3$ [14]; in these catalytic reactions an organic co-solvent was used to solubilize the catalyst. NBR latex has also been hydrogenated in emulsified form in methyl ethyl ketone using a Ru(II) catalyst [15]. An attractive variation of this is the catalytic hydrogenation of polymer latexes in aqueous media using water soluble metal complexes. Catalysis in the aqueous phase offer the advantage of the easy recovery of the products and catalyst from the reaction mixture, and in addition, it provides a safer, cheaper, and better environmental alternative to current industrial processes using organic solvents. There have been a number of reports on the hydrogenation [16–18] and hydroformylation [19–23] of low molecular weight olefins using water soluble catalysts. However, only a single report is available on latex hydrogenations; Singha and Sivaram hydrogenated NBR latex using water soluble analogs of the Wilkinson catalyst [24]. A major problem associated with such two-phase catalytic systems is poor reaction rates due to phase transfer limitations. As catalysis in such systems relies on the transfer of organic substrates into the aqueous catalyst phase, the problem becomes more dramatic when applied to

hydrogenation of large organic molecules. Several approaches have been used in the past to rectify this problem, which include the addition of phase transfer agents to the catalyst mixture [25], use of quaternary ammonium or phosphonium salts in place of the trisodium salt of the trisulphonated-triphenylphosphine (TPPTS) [26,27], the use of supported aqueous phase catalysts (SAP catalysts) [28,29], and the use of a 'promoter ligand' [30,31]. A more promising approach that we became interested in involves the use of catalysts containing surface active ligands; significant rate enhancements in hydroformylation of higher olefins have been observed in such systems [32–36].

We have recently reported the synthesis and characterization of two novel water-soluble Rh complexes bearing amphiphilic carboxylated phosphine ligands [37]; the catalytic activity of the two complexes, $[RhCl(HEXNa)_2]_2$ (HEXNa $= Ph_2P-(CH_2)_5-CO_2Na$) and $[RhCl(OCTNa)_2]_2$ (OCTNa $= Ph_2P-(CH_2)_7-CO_2Na$), in hydrogenation of a series of alkenes and polybutadiene in aqueous and aqueous/organic biphasic media were also reported [37]. In this paper we wish to report the activity of $[RhCl(HEXNa)_2]_2$ 1 in catalytic hydrogenation of NBR and SBR copolymers in aqueous/organic biphasic medium. The results are compared with those obtained with the previously known water soluble catalyst $RhCl(TPPMS)_3$ (TPPMS $=$ monosulphonated-triphenylphosphine) [38–40] under identical conditions.

2. Experimental

2.1. Materials

Distilled deionized water was used as the primary solvent for all the hydrogenation experiments. Analytical-grade toluene was used as supplied. Oxygen-free hydrogen gas was used as the hydrogen source. The polybutadiene used (from Scientific Polymer Products) contained

40% vinyl and 30% *trans*-1,4-units and had a $\overline{M}_n$ of 900. The acrylonitrile–butadiene copolymer (NBR, from Scientific Polymer Products) contained 90 mol% butadiene content with 18 mol% of pendent vinyl groups (of the total butadiene content), and had an approximate $\overline{M}_n$ of 6400. The styrene–butadiene copolymer (SBR) Finaprene-410 (from Petrofina) contained 68 mol% butadiene content with a 16 mol% vinyl groups (of the total butadiene content), and had an approximate $\overline{M}_n$ of 95,000. All the polymers were used without further purification. The synthesis and characterization of [RhCl(HEXNa)$_2$]$_2$ is previously reported [37]. RhCl(TPPMS)$_3$ was synthesized according to the procedure described in the literature [39].

2.2. Hydrogenation reactions

All the reactions were carried out in a stainless steel autoclave equipped with catalyst addition and sampling devices. In a typical run, 2 g of polymer dissolved in 10 cm^3 of toluene was added to 80 cm^3 water in a 250 cm^3 glass liner (SBR and NBR copolymers were stirred in toluene overnight to attain complete solubilization of the polymer). The catalyst was weighed into a glass bucket and placed in the catalyst addition device. The glass liner was then placed in the autoclave and the autoclave was assembled. After flushing with hydrogen three times, the mixture was degassed by bubbling H$_2$ for 15 min. The reaction system is then heated to the required temperature with agitation under 0.7 MPa hydrogen. After the temperature equilibrium is reached the bucket containing the catalyst is dropped to the solution by pressurizing the catalyst addition device to the reaction pressure. Hydrogen was introduced into the autoclave when required to maintain a constant reaction pressure throughout the reaction. Samples, withdrawn periodically from the reactor, were extracted with toluene or chlorobenzene. The organic extracts were dried under vacuum and the residue was dissolved in CDCl$_3$ and analyzed by ^{1}H NMR spectroscopy. The %

hydrogenation of the polymer was calculated from the NMR integrations as described in the literature [41].

3. Results and discussion

Prompted by the success in the hydrogenation of a series of olefins in aqueous medium, and polybutadiene (PBD) in aqueous/biphasic medium using the water soluble catalyst [RhCl(HEXNa)$_2$)]$_2$ 1, the studies were extended to test the performance of catalyst 1 in hydrogenation of SBR and NBR copolymers. The hydrogenations were carried out on the polymer emulsions formed by suspending a 16 wt% solution (in toluene) of the polymer in 80 cm^3 of distilled, deionized water; the resulting emulsion contained 2.2 wt% solids.

The most important qualitative difference observed in polymer hydrogenation by catalysts [RhCl(HEXNa)$_2$]$_2$ 1 and RhCl(TPPMS)$_3$ 2 is the distribution of the catalyst in the organic and aqueous phases after the reaction. In the hydrogenation experiments carried out with catalyst 2, the catalyst remained in the aqueous layer as evidenced by the pale orange aqueous phase and the colorless organic phase obtained after reaction. However, with 1, the catalyst was extracted into the organic layer during the reaction; the organic phase was orange–yellow and the aqueous phase was colorless after the reaction. This was in marked contrast to the hydrogenation of small organic molecules with 1 where the catalyst remained in the aqueous phase after the reaction; however with styrene and α-methylstyrene the catalyst was extracted into the organic phase. This difference in the distribution of catalyst 1 in the hydrogenation of polymers compared to that of small molecules is not something we expected; for the purpose of the present work the color of the two phases gave sufficient qualitative evidence for the distribution of catalyst at the end of the reaction, and further studies will focus on obtaining a quantitative measure via rhodium analyses.

Table 1
Effect of organic co-solvent and pH of the medium on distribution of the catalyst in aqueous/organic biphasic media in blank hydrogenation experiments [a]

Organic co-solvent [b]	pH of the medium [c]	Color after hydrogenation	
		Aqueous	Organic
Toluene	6 [d]	colorless	orange
Toluene	7	colorless	orange
Toluene	8	colorless	orange
n-Decane	6 [d]	yellow	colorless

[a] Conditions: as of Table 2, but without the use of polymer.
[b] 10 cm³.
[c] Controlled with 10 cm³ buffer.
[d] Normal pH of the medium (unbuffered).

However, the factors that can be thought of as contributing to this observed difference are: (a) complexation of the catalyst by organic substrate and/or product, (b) the pH of the medium; an acidic medium may convert the HEXNa ligand to the acid form and thereby render the complex organo-soluble, (c) solvent extraction of the catalyst from the aqueous phase by organic solvents. To ascertain which of these factor(s) is/are contributing to the observed behavior, a series of blank experiments were carried out under identical conditions to the polymer hydrogenation, but without the use of polymers. From the results of these experiments (Table 1) it is clear that the complex is extracted into toluene even without any substrate, as well as under both neutral and acidic media. But with n-decane the catalyst remained in the aqueous layer. Further, when an aqueous solution of 1 (~ 0.01 g in 9 cm³ H₂O) is stirred with toluene (1 cm³) under nitrogen at ambient temperature the catalyst is partially extracted into toluene over 16 h (toluene layer pale-orange and the aqueous layer pale-yellow); no such extraction was seen with n-decane. So it may be concluded that although 1 is readily soluble in water it preferentially is extracted into aromatic-organic, rather than into aliphatic-organic, solvents. This also explains the catalyst extraction into the organic phase observed in styrene and α-methylstyrene hydrogenation, but not in the hydrogenation of the other small molecules, all of which are aliphatic-organics;

the neat olefin was used as the substrate in all the small molecule hydrogenations, but in polymer hydrogenations the polymer was dissolved in toluene.

As described above, under the conditions used in the present work, polymer hydrogenation with catalysts 1 and 2 occur in organic and aqueous media, respectively. Therefore, our goal of evaluating the activity of the new catalyst 1 relative to that of the previously known catalyst 2 in polymer hydrogenation is not feasible. However, the results of the present work provide some useful information. From the results it is clear that the extent of hydrogenation with both catalysts follow the order PBD > NBR > SBR (Table 2). As the molecular weight of the polymer follows the exact reverse order (PBD < SBR), it could be argued that the observed trend in polymer hydrogenation is a manifestation of the polymer molecular weight. In support of this argument lies the observation that with 1 the extent of hydrogenation of SBR and NBR at any given time is roughly equal, whereas with 2 a significant difference in activity was observed in SBR and NBR hydrogenation. As hydrogenation with 1 occurs in the organic phase the reaction is insensitive to phase transfer limitations between the catalyst and the substrate, but

Table 2
Hydrogenation of PBD, SBR, and NBR Polymers with [RhCl(HEXNa)₂]₂ 1 and RhCl(TPPMS)₃ 2 complexes [a]

Polymer	Time (h)	% hydrogenation		% 1,2 addition units	
		with 1	with 2	with 1	with 2
PBD	0	0	0	40	40
	2	59	57	17	19
	4	72	65	6	16
	6	84	71	0	10
NBR	0	0	0	18	18
	2	37	47	8	0
	4	47	57	0	0
	6	53	62	0	0
SBR	0	0	0	16	16
	2	40	28	4	5
	4	46	34	0	0
	6	50	45	0	0

[a] Conditions: Rh = 2×10^{-5} mol; polymer = 2 g; solvent = 10 cm³ toluene + 80 cm³ water; $T = 100°C$; $P_{H_2} = 5.5$ MPa.

with **2** such effects become important as the catalysis occurs in the aqueous phase. Therefore, the common trend observed in the polymer hydrogenation by **1** and **2** could be attributed to the polymer molecular weight; the degree of hydrogenation is inversely related to the molecular weight of the polymers. With both catalysts **1** and **2** the 1,2 (vinyl) addition units are selectively hydrogenated over the 1,4 (internal) addition units in all the polymers. This is consistent with the observed selectivity of **1** in simple alkene hydrogenation where the terminal olefins are hydrogenated much faster than the internal olefins. However, unlike in hydrogenation of simple olefins by **1**, the presence of nitrile groups in NBR does not seem to enhance the degree of hydrogenation of the polymer compared to the non-activated double bonds in PBD; in hydrogenation of small molecules by **1** an enhanced activity was observed in hydrogenation of olefins containing nitrile groups (internal double bonds in *cis*-2-pentenenitrile and *trans*-3-pentenenitrile were hydrogenated much faster than both terminal and non activated internal olefins) [37]. Because of this observed difference in catalytic activity of **1** with small molecules and polymers it is interesting to characterize the nature of the catalyst at the end of the reaction in each of the systems. In addition, other aspects of the present system such as surface active properties of the ligands and rhodium complexes, possibility of formation of colloidal rhodium particles under hydrogenation conditions, feasibility of recycling of the catalyst in the hydrogenation of small molecules where the catalyst remained in the aqueous phase at the end of the reaction, were not studied in the present work. However, such aspects will be an essential part in continuation of the initial work presented in this paper.

4. Conclusion

The studies on the hydrogenation of PBD, SBR, and NBR polymers in aqueous/organic biphasic media catalyzed by water-soluble complex $[RhCl(HEXNa)_2]_2$ **1** with phase transfer properties were presented in this paper. Although the original goal of using water-soluble catalysts with phase transfer properties is to maximize the interaction with polymer/emulsion particles, in the present work the very nature of the HEXNa ligand causes the undesirable complete extraction of catalyst **1** into the organic phase. Rhodium loss to the organic phase during the reaction was found to be dependent on the nature of the organic solvent. Overall, the catalyst **1** shows a reasonable activity in polymer hydrogenation, especially for low molecular weight polymers, but does not satisfy the requirement of a two-phase catalyst system under the present experimental conditions. However, it has the potential in satisfying the ultimate aim of this work, which is to hydrogenate polymer emulsions from commercial polymerization processes without any added organic solvents.

Acknowledgements

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