Hydrogenation of Low Molecular Weight Polymers in Ionic Liquids and the Effects of Added Salt

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Abstract: The biphasic hydrogenations of a number of polymeric materials, polybutadiene (PBD), nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR), were investigated in a toluene/*N,N′*-butylmethylimidazolium tetrafluoroborate, ($BMI^+BF_4^-$) system with a water-soluble analogue of Wilkinson's catalyst, $RhCl(TPPTS)_3$ (TPPTS = triphenylphosphine, trisulfonated) at 100 °C and 3.1 MPa. The catalyst shows reasonable activity within ionic liquids with PBD although it was necessary in the case of NBR and SBR to add water as a co-solvent to solubilize the catalyst within the ionic media. Both the extent of hydrogenation and the ratio of the internal 1,4-olefins to vinyl 1,2-olefins were monitored. A clear preference for the external olefins was observed even within NBR and SBR where functionalization on the polymer might enhance the degree of hydrogenation of the internal olefins. The effect of adding NaCl to the PBD system was also investigated. The addition of salt decreases the activity of the catalyst but has no effect on the preference for the hydrogenation of vinyl olefins.

Keywords: biphasic catalysis; hydrogenation; ionic liquids; nitrile-butadiene rubber; polymers; styrene-butadiene rubber

The direct modification of unsaturated polymers such as polybutadiene (PBD), and rubbers such as nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) by catalytic hydrogenation is of great interest to the chemical production industry. The ability to control the extent of hydrogenation allows fine-tuning of the physical, mechanical, and chemical properties of these materials in order to meet a specific function. For example, properties such as elasticity, resistance to aging by oxidation, heat and fluid resistance are improved by hydrogenation. This type of modification is inaccessible through direct polymerization and current methods involve the use of rhodium or ruthenium homogeneous catalysts within organic solvents under harsh reaction conditions (typically temperatures are well above 100 °C and hydrogen pressures are between 2 and 4 MPa). An attractive alternative to this would be the use of a two-phase solvent system.

Over the past several years the use of two-phase solvent systems within catalytic reactions has received much attention.[1] The majority of the focus in this area has been on aqueous systems and has involved a variety of transformations including asymmetric hydrogenation[2] and hydroformylation[3] of olefins. However, only one large-scale application, the hydroformylation of propene to *n*-butyraldehyde by Ruhrchemie/Rhône-Poulenc is currently utilized on an industrial scale.[4] Further application of such two-phase solvent systems toward higher molecular weight species is limited by their low solubility within an aqueous solution. Several ideas have been proposed to overcome this limitation, including but not limited to, the use of fluorous phases,[5] supported aqueous phase catalysis,[6] the addition of surfactants, and/or the development of specialized amphiphilic or surface-active ligand systems[7] to increase the solubility of olefins in aqueous solution.

Recently, the use of ionic liquids has received attention as possible media for biphasic catalytic reactions. These liquids are salts that melt at low temperatures (< 100 °C), have no appreciable vapor pressure, and possess excellent chemical stability.[8] The largest class of ionic liquids investigated to date for catalytic reaction media have been based upon *N,N′*-dialkylimidazolium and *N*-alkylpyridinium salts with weakly coordinating anions (BF_4^-, PF_6^-, $AlCl_4^-$, etc.). Many organic compounds will form biphasic systems with ionic liquids making the separation of the products a simple and cost effective process. In addition, since ionic liquids have virtually no vapor pressure, products that are soluble in the liquid can be easily separated by distillation. Many types of reactions have been investigated over the last few years including hydrogenation,[9] hydroformylation,[10] Friedel–Crafts,[11] and Diels–Alder[12] reactions. Many of these reactions display unusual or different reactivity than what is observed in organic or aqueous solutions. Herein, the initial investigations of the rhodium-catalyzed hydrogenation of polybutadiene, NBR and SBR with $RhCl(TPPTS)_3$, a water-soluble catalyst are presented.

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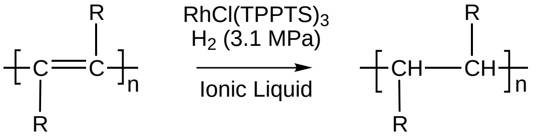
Table 1. Hydrogenation of polymeric materials under various reactions conditions.



R = H, alkyl, aryl, CN

Entry	Polymer	Olefin/Catalyst Ratio	mL $BMI^+BF_4^-$	mL toluene	mL H_2O	mL THF	% vinyl	Time [h]	% Total Hydrogenation
1	PBD	500	2	2	0	0	30	2	43
2	PBD	500	2	2	0	0	7	3	84
3	PBD	500	2	2	0	0	0	4	94
4	NBR	250	2	2	0	0	19	2	8
5	NBR	250	2	2	0.5	0	13	2	39
6	NBR	250	2	2	0.5	0	14	3	41
7	NBR	250	2	2	0.5	0	14	4	43
8	NBR	250	2	2	0.5	2	3	2	72
9	SBR	250	2	2	0.2	0	15	2	19

The initial investigation began with the biphasic hydrogenation of low molecular weight PBD ($\bar{M}_n \approx$ 900, 40% mol vinyl olefins, 30% *cis*-1,4-olefins and 30% *trans*-1,4-olefins) in toluene/BMI^+ BF_4^-. It can be seen from entries 1 through 3 in Table 1 that under given conditions, as the reaction proceeds, the ratio of vinyl olefins versus internal 1,4-olefins dropped over the time period studied. This selective hydrogenation of external olefins is not unexpected as the rate of hydrogenation of olefins by Wilkinson's catalyst is much greater for external than for internal olefins. This same preference has been seen in other biphasic studies.[13] Virtually complete hydrogenation of all olefins (94%) can be achieved within four hours.

In comparison to PBD the hydrogenation of low molecular weight NBR ($\bar{M}_n \approx 6{,}400$, 10% nitrile, 18% mol vinyl olefins of the total olefin concentration) initially proved more problematic. Under the similar reaction conditions for PBD only 8% total hydrogenation is observed within a two-hour time period (Table 1, entry 4). In addition, an orange precipitate was observed suspended between the ionic liquid and toluene phase suggesting that the catalytic species was precipitated during the reaction. Since properties of ionic liquids, such as solvent polarity, are sensitive to any impurities[14] the precipitation is attributed to a small amount of the NBR/toluene mixture dissolving in the ionic liquid thus changing the solubility of the catalyst within the liquid.

In order to increase the solubility of the catalyst, a portion of deionizied water (0.500 mL) was added to the ionic liquid. Under these conditions we observed that catalytic activity increased to a maximum total hydrogenation of 39% after two hours (Table 1, entry 5) with partial precipitation of the hydrogenated species from the mixture. Total isolation of the product is accomplished by extraction with THF or chlorobenzene.

SBR ($\bar{M}_n \approx 90{,}000$, 23% styrene, 18% mol vinyl olefins of the total olefin concentration) was hydrogenated for comparison purposes and resulted in a total hydrogenation of 19% after 2 hours. Even with the addition of water to the catalytic medium the activity of the catalyst follows the trend PBD > NBR > SBR. We attributed this decrease in activity to the decreased solubility of the polymers within the ionic liquid due to either the functional groups on NBR and SBR or their higher molecular weights. Similar results were reported for the hydrogenation of polymers with the catalyst $RhCl(TPPMS)_3$ (TPPMS = triphenylphosphine, monosulfonated) in a biphasic toluene/water mixture where decreased activity with increasing molecular weight of the polymer was attributed to the decreased solubility within the aqueous phase.[15]

Examination of the rate of hydrogenation for the internal versus terminal olefins for the three polymers reveals no enhancement for the rate of SBR or NBR over PBD due to functional groups on the polymer. One might expect a preference for the hydrogenation of internal olefins of SBR and NBR over that of unsubstituted PBD since generally, incorporation of such groups to simple olefins increases the rate of reaction.[16]

Table 2. Color of phases after hydrogenation.

Substrate	Ionic Phase	Organic Phase
PBD	orange	colorless
NBR	yellow	pale yellow to brown
SBR	orange	colorless

Table 3. Effect of added salt on the hydrogenation of polybutadiene.

$ClRh(TTPTS)_3$			$ClRh(TTPTS)_3 + NaCl$		
Time	% Vinyl	% Total Hydrogenation	Time	% Vinyl	% Total Hydrogenation
0 h	40	0	0 h	40	0
2 h	30	43	2 h	37	25
3 h	7	84	3 h	33	46
4 h	0	94	4 h	15	75

However, such a trend was not observed in this study or in the biphasic studies utilizing the aqueous phase.[15]

Attempts to further the total hydrogenation of NBR past the observed 39% proved problematic as the hydrogenated polymer precipitates out of the toluene phase and swells within the mixture preventing further hydrogenation from occurring (Table 1, entries 5, 6, and 7). The observed precipitation of the hydrogenated product may be a function of the sample of NBR used as it is not a reported observation within similar systems utilizing a neutral ruthenium catalyst and a different sample of NBR.[17] In order to overcome this limitation 2 mL of THF was added to the toluene-polymer phase during hydrogenation. Addition of THF allows the polymer to remain completely within the solution and the extent of total hydrogenation increased to 72% within two hours under the same conditions (Table 1, entry 8). The observed increase in hydrogenation is most likely due to better contact between the two phases as the ionic liquid itself has partial solubility within the toluene-THF mixture as observed by ^1H NMR. Although it was not quantitatively measured some of the rhodium complex is extracted into the organic layer as evinced by a change in color of the organic phase (Table 2). NBR was the only polymer to exhibit this property and only did so after the addition of THF. The presence of THF also contaminates the resulting polymer product with a small amount of ionic liquid, which can be removed by extraction with water from chlorobenzene.

The effect of adding a neutral salt to the ionic liquid was also investigated within the PBD system. Extent of hydrogenation and the ratio of terminal to internal olefins were monitored to determine if they were affected by the presence of an additional ionic species within solution. Table 3 summarizes the results of saturating the reaction mixture with NaCl, and it appears that there is little to no effect on the preference of olefin hydrogenation. However, a clear decrease in catalytic activity is observed between the two systems. This decrease in activity can be explained by competition between the chloride anion and the olefin of the active site on the catalyst; further it has been observed that ionic liquids that are contaminated with halides show decreased activity.[18] We are currently investigating the effects of other non-halide salts within this system.

We believe that, based on our observations within this study, the biphasic hydrogenation of the polymeric species PBD and SBR appears viable but several problems need to be addressed for practical use with NBR. Many of the problems we encountered may be dependent on the sample of NBR utilized, as similar studies do not report such observations. The advantage of this ionic liquid/organic system over other biphasic systems is the ability to fine tune the structure of the ionic liquid as well as the catalyst to meet the needs of a particular set of reaction conditions. A more detailed study of the NBR system is currently being investigated.

Experimental Section

A typical run involved dissolving previously prepared $RhCl(TPPTS)_3$[19] (0.0184 g, 1.00×10^{-5} mol) in *N,N′*-butylmethylimidazolium tertafluoroborate, ($BMI^+BF_4^-$) (2 mL) to create a 5×10^{-3} M solution in a glass-lined pressure vessel. For reactions that involved addition of water, distilled-deionizied water was used in all cases. The system was sealed and evacuated for several minutes. After addition of hydrogen gas at 1.4 MPa at elevated temperatures (90–100 °C) a homogeneous yellow-orange solution was obtained with the color change attributed to the formation of the catalytic species, $RhH_2Cl(TPPTS)_3$. A solution (2–4 mL) of toluene or toluene/THF containing the polymer was injected into the pressure vessel and the pressure was increased to 3.1 MPa. After a set time interval the reaction was stopped, the two-phase system was separated, the ionic phase was further extracted with toluene, THF or chlorobenzene and the extracts were combined. Removal of solvent yielded the polymeric material. All runs were examined by ^1H NMR spectroscopy in $CDCl_3$ and the extent of the hydrogenation of vinyl *versus* internal olefins of the polymer was measured by integration of the NMR peaks.[20]

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References

[1] a) B. J. Cornils, *Mol. Catal. A: Chem*. **1999**, *143*, 1; b) B. J. Cornils, W. A. Herrmann, in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2, (Eds.: B. J. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**.

[2] a) Y. Amrani, L. Lecomte, D. Sinou, F. Bakos, I. Toth, B. Heil, *Organometallics* **1989**, *8*, 542; b) J. Holz, D. Heller, R Stürmer, A. Börrner, *Tetrahedron Lett.* **1999**, *40*, 7059; c) W. Li, Z. Zhang, D. Xiao, X. Zhang, *J. Org. Chem.* **2000**, *65*, 3489.

[3] a) B. J. Cornils, E. G. Kuntz, *J. Organomet. Chem*. **1995**, *502*, 177; b) W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1524; c) W. A. Herrmann, C. W. Kohlpaintner, H. Bahrmann, W. Konkol, *J. Mol. Catal*. **1992**, *73*, 191.

[4] W. A. Hermann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524.

[5] a) S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 155; b) B. Betzemeir, P. Knochel, *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2623; c) R. Kling, D. Sinou, G. Pozzi, A. Choplin, F. Quignard, S. Busch, S. Kainz, D. Koch, W. Leiner, *Tetrahedron Lett.* **1998**, *39*, 9439.

[6] a) J. P. Arhancet, M. E. Davis, B. E. Hanson, *Catalysis Letters* **1991**, *11*, 129; b) J. P. Arhancet, M. E. Davis, J. S. Merola, B. E. Hanson, *Nature* **1989**, *339*, 454.

[7] a) T. L. Schull, L. R. Olano, D. A. Knight, *Tetrahedron* **2000**, *56*, 7093; b) B. E. Hanson, *Coord. Chem. Rev.* **1999**, *185*, 795; c) B. E. Hanson, H. Ding, C. Kohlpainter, *Catalysis Today* **1998**, *42*, 421; d) H. Ding, B. E. Hanson, J. Bakos, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 1728.

[8] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed. Eng.* **2000**, *39*, 3772.

[9] P. J. Dyson, D. J. Ellis, D. G. Parker, T. Welton, *Chem. Commun.* **1999**, 25.

[10] P. Wasserscheid, H. Waffenschmidt, *J. Mol. Catal. A: Chem.* **2000**, *64*, 61.

[11] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480.

[12] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965.

[13] D. C. Mudalige, G. L. Rempel, *J. Mol. Catal. A: Chem.* **1997**, *123*, 15.

[14] a) K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275; b) J. D. Holbrey, K. R. Seddon, R. Wareing, *Green Chem.* **2001**, *3*, 33.

[15] D. C. Mudalige, G. L. Rempel, *J. Mol. Catal. A: Chem.* **1997**, *123*, 15.

[16] D. C. Mudalige, G. L. Rempel, *J. Mol. Catal. A: Chem.* **1997**, *116*, 309.

[17] L. A. Müller, J. Dupont, R. F. deSouza, *Macromol. Rapid Commun.* **1998**, *19*, 409.

[18] Y. Chauvin, L. Mussmann, H. Oliver, *Angew. Chem. Int. Ed. Eng.* **1995**, *107*, 2941.

[19] W. A. Herrmann, J. Julpe, J. Kellner, H. Riepl, (Hoechst Aktiengesellschaft), *US Patent* 5,057,618, **1991**.

[20] N. A. Mohammadi, G. L. Rempel, *J. Mol. Catal*. **1989**, *50*, 259.