

Selective hydrogenation of SBS catalyzed by Ru/TPPTS complex in polyether modified ammonium salt ionic liquid

Li Wei, Jingyang Jiang*, Yanhua Wang, Zilin Jin

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, PR China

Received 31 March 2004; received in revised form 28 June 2004; accepted 1 July 2004

Available online 10 August 2004

Abstract

The hydrogenation of SBS catalyzed by Ru/TPPTS complex was performed in polyether modified ammonium salt ionic liquid biphasic system. It has been observed that the hydrogenation degree can be increased by addition of ‘promoter ligand’ TPP. Under the optimized conditions of $T = 150\text{ }^{\circ}\text{C}$, $t = 12\text{ h}$, $P = 5.0\text{ MPa}$, Ru/TPPTS/TPP = 1:5:2, the hydrogenation degree of the polybutadiene segments of SBS was 89%. In addition, no hydrogenation takes place on the benzene ring. The Ru catalyst immobilized in ionic liquid can be recovered simply by phase separation and recycled three times without significant changes in the catalytic activity.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrogenation; SBS; Ruthenium complex; Polyether modified ammonium salt ionic liquid

1. Introduction

Polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymers are an important class of the thermoplastic elastomers. Their formulating and processing flexibility have made them to be widely used in various applications [1]. However, SBS block copolymers do not have good long term heat, weather and UV stability owing to the presence of large amounts of unsaturated double bonds in their polybutadiene segments. By reducing the level of unsaturation via hydrogenation, the physical, mechanical and chemical properties of the copolymers can be modified to meet a specific demand. For hydrogenation of polymer it is important that mild conditions should be used to avoid unwanted side reactions such as crosslinking or chain scission, which may cause a catastrophic loss of the engineering properties of the polymer. So homogeneous catalytic hydrogenation has attracted much attention due to its high activity and selectivity under mild conditions. Hydrogenation of SBS block copolymers is typically practiced in cyclohexane solution us-

ing Ziegler-type nickel catalyst [2–4]. Recently, using of homogeneous metallocene catalysts [5] and noble metal complex catalysts [6–9] has been reported for polymer hydrogenation. However, the separation of catalysts from the reaction mixture has remained as a challenge to be tackled. One of viable approaches is the aqueous/organic biphasic hydrogenation catalyzed by water-soluble rhodium complex [10]. Ionic liquids have been demonstrated to be ideal immobilizing agents for organometallic catalysts in hydrogenation reactions [11]. However, only few papers have been reported about polymer hydrogenation in ionic liquids, including the hydrogenation of NBR using $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ as catalyst in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) [12,13] and the hydrogenation of SBR catalyzed by $\text{Rh}(\text{TPPTS})_3\text{Cl}$ in [BMIM][BF₄] [14]. Till now, there is no report about the hydrogenation of SBS in ionic liquid/organic biphasic system. In our previous work a novel class of ionic liquid-polyether modified ammonium salt ionic liquid was prepared and has been applied successfully for the Rh catalyzed hydroformylation of higher olefins [15,16]. Here, the above-mentioned ionic liquid was applied to the hydrogenation of SBS with Ru/TPPTS or Ru/TPPTS/TPP as catalyst.

* Corresponding author. Tel.: +41 188 993 854; fax: +41 188 993 854.
E-mail address: jjjiang@chem.dlut.edu.cn (J. Jiang).

2. Experimental

2.1. Materials

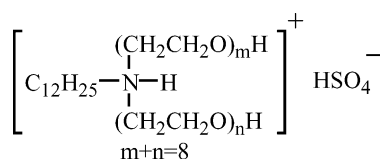
Solvents toluene and THF were distilled over *N*-benzophenone and stored under N_2 . Trisodium salt of tri (*m*-sulfophenyl) phosphine (TPPTS) was donated by Celanese GmbH (Germany). $RuCl_3 \cdot xH_2O$ (Ru 40 wt.%) and triphenylphosphine (TPP) were purchased from Aldrich. SBS block copolymer was obtained from Beijing Research Institute of Yanshan. The polymer has an average molecular weight of 6000 and a polystyrene content of 45 wt.%. The microstructure of the polybutadiene segments of the polymer comprise 35 % 1,2 unit, 40 % *cis*-1,4 unit and 25 % *trans*-1,4 unit. Polyether modified ammonium salt ionic liquid (shown in Scheme 1) was prepared according to previous work [15].

2.2. Preparation of Ru-TPPTS catalyst in polyether modified ammonium salt ionic liquid

The preparation of Ru-TPPTS catalyst was performed in a 75 mL stainless-steel autoclave immersed in a thermostatic oil bath. Appropriate amount of $RuCl_3 \times H_2O$, TPPTS and ionic liquid were placed in the autoclave and flushed three times with 2.0 MPa of hydrogen. The autoclave was pressurized up to 3.0 MPa with hydrogen and held at temperature of 150 °C with magnetic stirring for 8 h. After cooling to room temperature, the reactor was depressurized. The ionic liquid containing Ru-TPPTS catalyst was transferred into an Schlenk tube and stored under N_2 .

2.3. Hydrogenation reactions

All hydrogenation reactions were carried out in a 75 mL stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rates were kept constant for all experiments performed. Solid SBS, toluene, THF, TPP and the polyether modified ammonium salt containing Ru/TPPTS catalyst were placed in the autoclave. The autoclave was flushed three times with 2.0 MPa of hydrogen then pressurized up to the required pressure and held at the designated temperature with magnetic stirring for a fixed time. After reaction, the reactor was cooled to room temperature and depressurized. The organic phase containing hydrogenated polymer was separated from the catalyst by simple decantation. The product was precipitated with ethanol and dried in vacuum.



Scheme 1. The structure of the polyether modified ammonium salt ionic liquid.

2.4. Analysis of the product

The hydrogenation product was analyzed using Nicolet Avatar 360 infrared instrument. The hydrogenation degree of SBS was calculated as described in the literature [17]. The total hydrogenation degree was also checked by double bond bromination titration method. All results showed no hydrogenation of benzene ring. Gel formation has not been observed.

3. Results and discussion

3.1. Hydrogenation of SBS catalyzed by Ru/TPPTS complex and the promoting effect of TPP

The hydrogenation of SBS catalyzed by Ru/TPPTS complex in polyether modified ammonium salt ionic liquid/toluene-THF biphasic system was carried out and the results were listed in Table 1. The catalyst activity is low (hydrogenation degree of SBS is not higher than 30 %) in this biphasic system. It should be noted that the organic phase containing products could be easily separated by simple phase separation from the ionic liquid phase. The ruthenium catalyst is almost completely retained in the ionic liquid phase and can be reused.

It is well known that the major problem associated with the biphasic catalytic system is the poor reaction rate due to mass transfer limitation. It has been found that SBS is insoluble in polyether modified ammonium salt. The Ru/TPPTS complex immobilized in ionic liquid cannot transfer into toluene-THF phase. Therefore it is impossible for the reaction to occur in organic phase. Based on the above analysis, it is inferred that the reaction mainly occurs at the interface of biphasic system.

Chaudhari et al. [18] have reported that the addition of triphenylphosphine (TPP) can accelerate the water/organic biphasic hydroformylation of octene catalyzed by Rh/TPPTS complex. They have proposed that TPP ligand, which is soluble in the organic phase but insoluble in the aqueous, will bind to the water-soluble organometallic catalyst thereby increase the catalyst concentration at the interface. Enlightened by this idea, we attempted to test the effect of adding TPP on hydrogenation of SBS in ionic liquid/organic biphasic system. The results are shown in Table 2, which clearly indicate a dramatic increase of hydrogenation degree when TPP is added. When

Table 1
Effect of TPPTS on hydrogenation of SBS catalyzed by Ru/TPPTS complex

TPPTS/Ru (molar ratio)	Total hydrogenation degree (%)	Reaction time (h)
3:1	18	12
5:1	25	12
10:1	25	12
10:1	29	24

Conditions: $C = C/Ru = 2000$ (molar ratio); SBS = 1.3 g; $P = 3.0$ MPa; $T = 150$ °C; $t = 12$ h; Ionic liquid = 1 g and solvent = 8.4 mL (toluene) + 1.6 mL (THF).

Table 2
Effect of TPP on hydrogenation of SBS catalyzed by Ru/TPPTS complex

TPP/TPPTS/Ru (molar ratio)	Total hydrogenation degree (%)	Color after hydrogenation Organic phase
0.5:1	25	Colorless
0.5:5:1	75	Colorless
2:5:1	85	Colorless
5:5:1	88	Yellow
8:5:1	89	Deep yellow

Conditions: $C = C/Ru = 2000$ (molar ratio); $SBS = 1.3$ g; $P = 3.0$ MPa; $T = 150$ °C; $t = 12$ h, ionic liquid = 1 g and solvent = 8.4 mL (toluene) + 1.6 mL (THF).

the TPP/Ru molar ratio increases from 0 to 0.5, the hydrogenation degree is raised from 25 to 75%. Further increase of the TPP/Ru molar ratio will increase the hydrogenation degree also. But when the molar ratio of TPP to Ru is five or higher, the color of organic phase will change from colorless to yellow, which indicates the leaching of ruthenium catalyst to the organic phase. Thus, the optimized TPP/TPPTS/Ru molar ratio is 2:5:1.

3.2. Effect of reaction time on hydrogenation

Effect of reaction time on the hydrogenation of SBS with Ru/TPPTS/TPP complex as catalyst in the ionic liquid/organic two-phase system is shown in Table 3. Data in Table 3 indicate that the double bond in 1,2-unit is easier to be hydrogenated than that in *trans*-1,4 unit. The reason for this phenomenon is attributed to the steric hindrance of double bond. In addition, when the reaction time increases from 12 to 16 h, the hydrogenation degree increases only 1%. The results indicate that it is not advisable to enhance the hydrogenation degree simply by prolonging the reaction time.

3.3. Effect of reaction temperature on hydrogenation

The hydrogenation reaction was conducted at different temperatures ranging from 120 to 160 °C. The data in Table 4 shows that the hydrogenation degree of SBS increases with increasing of reaction temperature.

Table 3
Effect of reaction time on hydrogenation of SBS with Ru/TPPTS/TPP as catalyst

Reaction time (h)	Hydrogenation degree (%)			
	Total	1,2-unit	1,2-unit + <i>cis</i> -1,4 unit	<i>Tran</i> -1,4 unit
1	48	80	56	22
3	59	90	67	36
7	79	93	90	45
12	89	94	91	81
16	90	94	92	82

Conditions: $C = C/Ru = 2000$ (molar ratio), $SBS = 1.3$ g, $T = 150$ °C, $P = 5.0$ MPa, TPP/TPPTS/Ru = 2:5:1, ionic liquid = 1 g and solvent = 8.4 mL (toluene) + 1.6 mL (THF).

Table 4
Effect of reaction temperature on hydrogenation of SBS with Ru/TPPTS/TPP as catalyst

Reaction temperature (°C)	Hydrogenation degree (%)			
	Total	1,2-unit	1,2-unit + <i>cis</i> -1,4 unit	<i>Tran</i> -1,4 unit
120	68	81	72	55
130	72	86	76	60
140	81	89	85	68
150	85	93	91	70
160	86	93	91	71

Conditions: $C = C/Ru = 2000$ (molar ratio); $SBS = 1.3$ g; TPP/TPPTS/Ru = 2:5:1; $P = 3.0$ MPa; $t = 12$ h; ionic liquid = 1 g and solvent = 8.4 mL (toluene) + 1.6 mL (THF).

Table 5
Effect of hydrogen pressure on hydrogenation with Ru/TPPTS/TPP as catalyst

Reaction pressure (MPa)	Hydrogenation degree (%)			
	Total	1,2-unit	1,2-unit + <i>cis</i> -1,4 unit	<i>Tran</i> -1,4 unit
1	71	83	75	61
2	78	90	81	69
3	85	92	90	70
4	88	93	91	78
5	89	94	92	81

Conditions: $C = C/Ru = 2000$ (molar ratio); $SBS = 1.3$ g; TPP/TPPTS/Ru = 2:5:1; $T = 150$ °C; $t = 12$ h; ionic liquid = 1 g; solvent = 8.4 mL (toluene) + 1.6 mL (THF).

3.4. Effect of hydrogen pressure on hydrogenation

The effect of hydrogen pressure on the hydrogenation of SBS is listed in Table 5. Data in Table 5 show that the hydrogenation degree of SBS increases with increasing of pressure. In order to achieve a hydrogenation degree higher than 80%, the hydrogen pressure higher than 3 MPa is needed.

3.5. Recycling efficiency of Ru/TPPTS/TPP catalyst

It is worth to note that at the end of the hydrogenation reactions the catalyst immobilized in ionic liquid phase could be easily separated from organic phase and directly reused in the next reaction. When the catalyst being recycled for three times, almost no loss in the catalytic activity has been observed (see Table 6). In addition, the possible catalyst leaching in organic phase was checked. The hydrogenation reactions are conducted as usual. After reaction, the organic phase is separated and fresh SBS is added to it. The hydrogenation

Table 6
Recycling efficiency of Ru/TPPTS/TPP catalyst

Cycle numbers	Hydrogenation degree (%)
0	89
1	88
2	89
3	85

Conditions: $C = C/Ru = 2000$ (molar ratio); $SBS = 1.3$ g; $P = 5$ MPa; $t = 12$ h; $T = 150$ °C; Ru/TPPTS/TPP = 1:5:2; ionic liquid = 1 g and solvent = 8.4 mL (toluene) + 1.6 mL (THF).

reaction is repeated without the ionic liquid phase. After 24 h, no hydrogenation could be detected. The results show that the leaching of Ru catalyst to organic phase is not too much.

4. Conclusion

A polyether modified ammonium salt ionic liquid/organic biphasic system was applied to the hydrogenation of SBS with Ru/TPPTS complex as catalyst. The addition of TPP acting as promoter ligand can improve the hydrogenation degree of SBS. Under optimized reaction conditions, the hydrogenation degree of SBS is 89%. In addition, the hydrogenations of benzene ring and gel formation have not been observed. The products are easily separated from the reaction mixture by simple decantation and the catalyst retaining in the ionic liquid can be reused three times without significant loss in catalytic activity. The efficient separation and recycling of catalyst make this system technologically attractive. Meanwhile, the polyether modified ammonium salt is inexpensive and easy to be synthesized. Therefore, the hydrogenation of SBS with Ru/TPPTS/TPP as catalyst in ionic liquid/organic biphasic system appears feasible but more work should be done with the aim to enhance the hydrogenation degree, shorten reaction time and improve catalyst-recycling efficiency.

Acknowledgements

This work was supported by Fok Ying Tung Education Foundation (Grant No. 91071) and the Foundation of State

Key Laboratory of Fine Chemicals, Dalian University of Technology (Grant No. KF 02012).

References

- [1] H.L. Hsieh, R.P. Quirk, *Anionic Polymerization Principles and Practical Applications*, Marcel Dekker, New York, 1996.
- [2] R.J. Hoxmeier, US Patent 4, 879,349 (1989).
- [3] D.S. Breslow, A.S. Matlack, US Patent 3,113,986 (1963).
- [4] M.W. Wald, M.G. Quan, US Patent 3,595,942 (1971).
- [5] R.C. Tsiang, W.S. Yang, M.D. Tsai, *Polymer* 40 (1999) 6351.
- [6] K. Kato, K. Kishimoto, J. Kameda, Japan. Patent JP 01,289,805 (1989); CA 112:230685p.
- [7] X. Guo, P.J. Scott, G.L. Rempel, *J. Mol. Catal.* 72 (1992) 193.
- [8] J.W. Yang, L. Bao, R.Q. Xue, *China Synth. Rubber Indus.* 23 (1) (2000) 31.
- [9] N.K. Singha, S. Sivaram, *Polym. Bull.* 35 (121) (1995).
- [10] D. Chandrika Mudalige, G.L. Rempel, *J. Mol. Catal. A. Chem.* 123 (1997) 15.
- [11] J. Dupont, R.F. de Souza, P.A.A. Suarez, *Chem. Rev.* 102 (2002) 3667.
- [12] L.A. Müller, J. Dupont, R.F. de Souza, *Macromolecules, Rapid Commun.* 19 (1998) 409.
- [13] R.F. de Souza, V. Rech, J. Dupont, *Adv. Synth. Catal.* 344 (2002) 153.
- [14] S. MacLeod, R.J. Rosso, *Adv. Synth. Catal.* 345 (2003) 568.
- [15] F.Z. Kong, Dalian University of Technology, Doctoral dissertation, 2002.
- [16] F.Z. Kong, J.Y. Jiang, Z.L. Jin, *Catal. Lett.* 96 (2004) 63.
- [17] D.B. Chen, L. Zhong, X.H. Zhang, *China Synth. Rubber Indus.* 22 (1999) 216.
- [18] R.V. Chaudhari, B.M. Bhanage, R.M. Deshpande, H. Delmas, *Nature* 373 (1995) 501.