

Hydrogenation of SBS Catalyzed by Immobilized Ru-TPPTS Complex in Polyether Molten Salt

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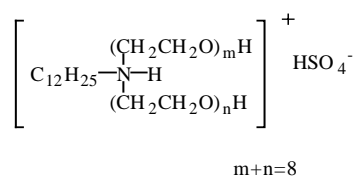
Abstract: Catalytic hydrogenation of SBS was performed for the first time in polyether molten salt with Ru/TPPTS complex as catalyst. Experimental results showed that the hydrogenation degree can be enhanced significantly by the addition of triphenylphosphine (TPP). When the molar ratio of TPP, TPPTS and Ru is 2:5:1, 89% hydrogenation degree can be achieved after 12 h under reaction conditions of 5.0 MPa and 150°C. The ionic liquid containing catalyst can be reused three times without obvious changes in the catalytic selectivity and activity.

Keywords: Hydrogenation, SBS, ruthenium complex, polyether molten salt.

The hydrogenation of polydienes is an important modification process for producing a variety of elastomers and thermoplastic polymers with improved chemical and mechanical properties. Heterogeneous hydrogenation, which was performed at drastic conditions, often results in side reactions like crosslinking or chain scission. Homogeneous catalytic hydrogenation has attracted attentions due to its high activity and selectivity under mild conditions. But the catalyst recovery and its separation from the product are major drawbacks of these catalytic processes. To solve these problems, one approach is to carry out the reaction in a two-phase catalytic system involving the ionic liquid (IL) as polar phase. At present few pioneer works have been reported for the hydrogenation of the polymers in organic /IL two-phase system^{1,2}.

Kong *et al*³ have synthesized a novel class of ionic liquid polyether molten salt (shown in **Scheme 1**), and successfully applied it for the Rh catalyzed hydroformylation of oleyl alcohol. In this paper, for the first time this ionic liquid was utilized for the hydrogenation of SBS catalyzed by Ru-TPPTS complex.

Scheme 1



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Experimental

All hydrogenation reactions were carried out in a 75 mL standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rates were kept constant for all experiments performance. Polyether molten salt, containing Ru/TPPTS catalyst, toluene, THF, TPP and SBS were placed in the autoclave and 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. Then the reactor was cooled to room temperature and depressurized. The organic phase, containing hydrogenated polymer, was separated by decantation from the catalyst and precipitated with ethanol and dried in vacuum.

Results and Discussion

The initial investigation of the biphasic hydrogenation was carried as follows: SBS was dissolved in toluene and THF solvent mixture and catalyst Ru/TPPTS was dissolved in polyether molten salt polar phase. When the reaction temperature was risen to 150°C, hydrogen pressure was 3.0 MPa, the hydrogenation degree of SBS was 25%. Attempts of prolonging the reaction time to 24 h or increasing the hydrogen pressure to 5.0 MPa have little effect on the hydrogenation degree SBS (less than 30 %). When TPP (molar ratio of TPP to Ru is 0.5) was added, the hydrogenation degree increased obviously from 25% to 75.2%. In the absence of TPP, due to the limitation of phase transference of two phases catalyst system, the reaction rate is poor. TPP in the organic phase will bind to the Ru-TPPTS catalyst, dissolved in ionic liquid, make the catalyst concentration at the interface to increase. The similar result was observed at the interface of a water-organic biphasic hydroformylation of octene catalyzed by Rh/TPPTS⁴ when TPP was added. The effect of the amount of TPP on hydrogenation degree was shown in **Table 1**. The result showed that increase the amount of TPP (TPP: Ru >5) can increase the hydrogenation degree in some extent but the color of organic phase changed from colorless into yellow and deep yellow, indicating the ruthenium loss to the organic phase.

Table 1 Effect of TPP on hydrogenation degree of SBS catalyzed by Ru-TPPTS complex

TPP/TPPTS/Ru (molar ratio)	Hydrogenation degree %	color after hydrogenation
		Organic phase
0:5:1	25.0	colorless
0.5:5:1	75.2	colorless
2:5:1	85.4	colorless
5:5:1	87.9	yellow
8:5:1	88.5	deep yellow

Conditions: [C=C]/[Ru]=2000 (molar ratio), [SBS]=5% (w/w), P=3.0 MPa, T=150°C, t=12h, polyether molten salt=1 g, solven=8.4 cm³ toluene +1.6 cm³ THF

Table 2 Recycling efficiency of Ru –TPPTS complex catalyst on hydrogenation of SBS

Entry	Hydrogenation degree %
1	89.0
2	88.0
3	89.4
4	85.4

Conditions: [C=C]/[Ru]=2000 (molar ratio), P=5MPa, t=12h, T=150°C, TPP/TPPTS/Ru=2:5:1, polyether molten salt=1 g, solven=8.4 cm³ toluene +1.6 cm³ THF

It is noteworthy that at the end of the hydrogenation reaction the product dissolved in organic phase can be separated from the ionic liquid and catalyst just by the decantation and the ruthenium catalyst is nearly completely retained in the ionic liquid phase. The catalyst can be recycled at least three times without reduce the catalytic activity and selectivity (see **Table 2**).

In summary, the two-phase hydrogenation of SBS has been performed in organic /polyether molten salt two-phase system using Ru/TPPTS complex. Addition of TPP into the system as ‘promoter ligand’ can enhance the catalyst activity. The inexpensive polyether molten salt, efficient separation of the product and recycling of catalyst make this system technologically attractive. Based on our observations in this study, the biphasic hydrogenation of the polymer SBS using Ru phosphine complexes might be valuable but the further work is needed for enhancing the hydrogenation degree, shortening reaction time and improving catalyst recycle efficiency.

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