

# Selective Hydrogenation of Nitrile-Butadiene Rubber Catalyzed by Thermoregulated Phase Transfer Phosphine Rhodium Complex

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**ABSTRACT:** Hydrogenation of polymer having C=C double bond can be carried out with the metal-organic complex as catalyst, which has the property of thermoregulated phase transfer. In this study, a new complex RhCl[PPh[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>5≤n≤6</sub>CH<sub>3</sub>]<sub>2</sub>]<sub>3</sub> (Rh/AEOPP) was synthesized with a good yield, which was further used as catalyst to selectively hydrogenated nitrile-butadiene rubber (HNBR). This is the first time that Rh/AEOPP complex was synthesized and applied in nitrile-butadiene rubber (NBR) hydrogenation. The result shows that hydrogenation degree of product (HNBR) can be extended to 90%, when the condition is [Cat] = 3% (based the weight of

NBR), L<sub>2</sub>: Cat (Weight Ratio) = 2, [NBR] = 5% (based on the weight of xylene solution), P (H<sub>2</sub>) = 1.5 MPa, T = 155°C, and t = 8 h. Also, by adjusting temperature, the catalyst could be easily separated from products with 89% catalyst complex recovery. In addition, <sup>1</sup>H-NMR and infrared (IR) spectra showed that C=C double bonds in NBR was successfully hydrogenated without causing reduction of the CN group. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1040–1046, 2012

**Key words:** metal-polymer complex; metal-organic catalysts; catalysts; rubber; selectivity

## INTRODUCTION

Homogeneous catalytic hydrogenation is a very useful method for modification of unsaturated polymers to get a desired chemical, physical, and mechanical property.<sup>1,2</sup> The homogeneous catalytic hydrogenation of nitrile-butadiene rubber (NBR) has been extensively studied during the past three decades. Many transition metal complexes, generally containing a group VIII transition metal from the second and third rows of the periodic table, were used as homogeneous catalysts for this process.<sup>3–6</sup> Particularly, for the hydrogenation of olefins, the Wilkinson catalyst, RhCl (PPh<sub>3</sub>)<sub>3</sub>,<sup>7</sup> was the most popular catalyst employed for this process.<sup>3,4,8–10</sup> Due to the fact that it is a highly active catalyst capable of providing an excellent hydrogenation degree and without

reduction of nitrile group.<sup>8</sup> But separating catalyst from substrates has being the major obstacles in the industrialization.

Several methods have been proposed to solve these problems. The most promising one is to use water soluble metal complex catalyst in aqueous-organic biphasic systems, in which catalysts and substrates can be easily separated from each other by a phase barrier. Many catalytic reactions have been carried out by this way, among them hydroformylation<sup>11</sup> and hydrogenation<sup>12</sup> of olefins were two of the representative examples.

However, a major disadvantage related to this method is the reduced catalytic activity resulted from the mass transfer limitation. A new concept, metal-organic complexes catalysis, which can hydrogenate in organic phase at higher temperature, has been proposed. Especially the metal-organic complex can be separated from substrates by adding water at lower temperature. This method has been proposed to achieve efficient catalyst recovery while maintaining good reactivity and selectivity of homogeneous catalysis.<sup>13</sup> A series of polyether-substituted triphenylphosphines, with an inverse temperature-dependent solubility in water, have been reported.<sup>14–16</sup> Because of its extraordinary solubility, it can be used as thermoregulated phase transfer

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ligand on complex catalysts. Recently, this kind of catalyst has been successfully applied to hydroformylation<sup>14–18</sup> of olefins. But only a few articles mentioned about hydrogenation for olefins,<sup>19–22</sup> especially much less for unsaturated polymer.

In this article, the Rh/AEOPP<sup>23</sup> complex was synthesized. NBR hydrogenation was explored using this new Rh/AEOPP complex as catalyst under different conditions, such as the catalyst concentration, rubber concentration, hydrogen pressure, and reaction temperature.

## EXPERIMENTAL

### Materials

Hydrogen gas with 99.99% purity was obtained from Electronic Factory of Beijing. Polyethylene glycol (PEG; Mw, 200), *n*-heptane, and xylene (>99%) were purchased from Beijing Chemical Factory. NBR (N230S) was provided by JSR (Japan). Chlorobenzene, ether, and ethanol, with reported purity of 99%, were purchased from Beijing Chemical Factory. RhCl<sub>3</sub>·3H<sub>2</sub>O, and PPh<sub>3</sub> were reagent-grade products of Aldrich Chemical Company. The phosphine ligand, AEOPP, was synthesized as described in the literature.<sup>21</sup> Stainless steel high pressure autoclave GS-0.1, 0.1 L (with stir and temperature controller), is manufactured by WeiHai Chemical Equipment Plant, China

### Preparation of the catalyst

Hot ethanol (40 mL) was added to the mixture of AEOPP (3.00 g) and rhodium trichloride trihydrate (0.30 g). The reaction mixture was kept refluxing for 2 h. The catalyst was separated from solution by distillation under nitrogen condition. The yield was about 90%.

### Hydrogenation of NBR

All the hydrogenation experiments were carried out in 100 mL autoclave reactor. The NBR (2.5 g) in xylene (50 mL) was added to autoclave and stirred vigorously under hydrogen for a couple of minutes, following by venting. This process was repeated five times to ensure that oxygen was completely removed. Then required the catalyst was transferred into the reactor. The autoclave was slowly heated to 145°C, and maintained at this temperature for 8 h with stirring. After reaction the autoclave was allowed to cool to room temperature.

### Separation of Rh/AEOPP complex

After the hydrogenation, PEG (Mw, 200) and *n*-heptane were added to the mixture of products [hydro-

genated nitrile-butadiene rubber (HNBR)] with stirring. The autoclave was cooled at room temperature. The mixture was clearly divided into two phases. The lower layer containing the Rh/AEOPP complex was easily separated from the mixture.

### Characterization

The structure of HNBR and NBR were characterized by <sup>1</sup>H-NMR spectroscopy and infrared (IR) spectroscopy. <sup>1</sup>H-NMR spectra were recorded on a Bruker AV 600-MHz spectrometer, with CDCl<sub>3</sub> as the solvent. IR spectra analysis was performed on a Bruker TENSOR 27 Fourier transform infrared spectroscopy (FTIR). The samples were analyzed as solution casting films from CHCl<sub>3</sub> solution of coagulated products on KBr plates.

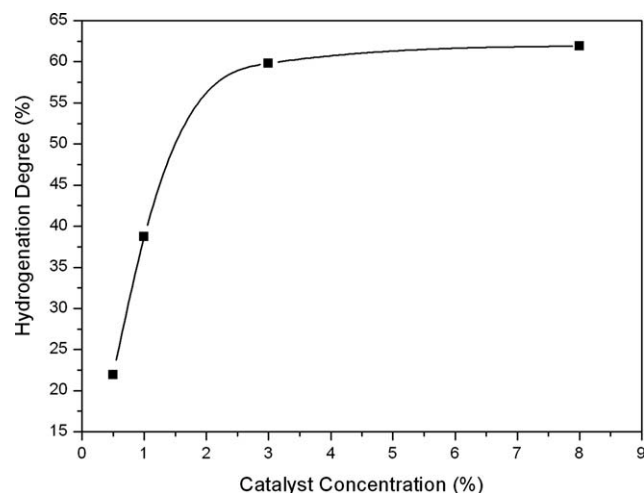
Typical <sup>1</sup>H-NMR spectrums of NBR sample (JSR N230S) and its hydrogenated product (HNBR, synthesized by our lab) are shown in Figure 8. For Figure 8(a), the main peaks are assigned as: 5.3–5.4 ppm (–CH=CH– 1,4 cis and trans units); 2.5 ppm (>CH–C≡N acrylonitrile units); 1.2–1.4 ppm (–CH<sub>2</sub>–CH< methylene units); 1.5–1.6 ppm (–CH<sub>2</sub>– methylene units); 0.8–0.9 ppm (–C–CH<sub>3</sub> methyl units).

For Figure 8(b) the main peaks are assigned as: 4.9–5.1 ppm (–CH=CH<sub>2</sub>, 1,2-vinylic units); 5.3–5.6 ppm (–CH=CH– 1,4 cis and trans units); 2.6 ppm (>CH–C≡N acrylonitrile units); 1.6–1.7 ppm (–CH<sub>2</sub>–CH< methylene units); 2.0–2.1 ppm (–CH=CH–CH<sub>2</sub>– methylene units); 2.2–2.3 ppm (>CH–CH<sub>2</sub>– methylene units); and 1.2–1.4 ppm (–CH<sub>3</sub> methyl units).

The FTIR spectrum of hydrogenated product (HNBR) is shown in Figure 9. The main peaks are assigned as: 2237 cm<sup>–1</sup> (–C≡N stretching); 2928 cm<sup>–1</sup> (–CH<sub>2</sub>– symmetric stretching); 2857 cm<sup>–1</sup> (–CH<sub>2</sub>– asymmetric stretching); 1463 cm<sup>–1</sup> (–CH<sub>2</sub>–, *n* ≥ 4 deformation vibration); 970 cm<sup>–1</sup> (–CH=CH– 1,4 cis and trans units). Hydrogenation degree was determined by Bromo-Iodometry method according to GB1676-81 (Chinese National Standards).

## RESULTS AND DISCUSSION

The metal–organic complex catalyst has been extensively used for hydrogenation of complex with C=C double bond. It is considered with good catalytic activity and easily separated from substrate by adjusting temperature.<sup>19</sup> However, the metal–organic complex catalyst with the themoregulated phase transfer function was seldom used for hydrogenation of unsaturated polymers because of the steric hindrance of ligands effect. In this article, the PPh[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>5≤n≤6</sub>CH<sub>3</sub>]<sub>2</sub> (AEOPP) as the ligand in catalyst was designed and



**Figure 1** Effect of catalyst concentration on hydrogenation degree.

synthesized to reduce steric hindrance, whereas still maintain a better separation from product by adjusting temperature.

#### The effect of catalyst concentration on hydrogenation degree

To explore the catalytic activity of Rh/AEOPP complexes, the catalyst concentration was first discussed. The effect of the catalyst concentration on NBR hydrogenation was investigated by changing the catalyst concentration from 0.5% to 8% based on the NBR at a constant reaction condition: [NBR] = 7% (based the weight of xylene solution),  $P(H_2) = 2$  MPa,  $T = 155^\circ\text{C}$  for 4 h. It is well known that when  $\text{RhCl}(PPh_3)_3$  is used for the hydrogenation of NBR in organic solvents, the conversion of hydrogenation increases with the increasing catalyst amount; once the catalyst amount used exceeded a certain level, part of the catalyst may not contribute to the reaction.<sup>24</sup> Figure 1 shows that increasing the amount of catalyst increases hydrogenation degree. However, an excess of the catalyst, e.g., 8% based on NBR, did not obviously improve hydrogenation degree compared with 3% based. This may indicate that when the C=C amount reaches a certain level, dimerization or other side reaction may occur. So the hydrogenation degree can not be enhanced further without optimizing other parameters.

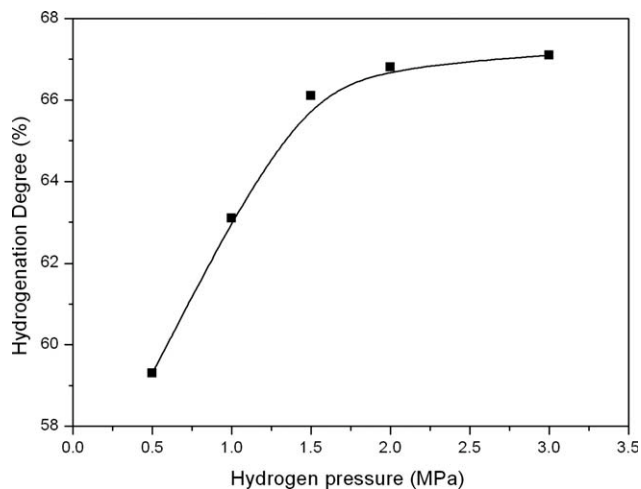
#### The effect of hydrogen pressure on hydrogenation degree

The effect of hydrogen pressure on hydrogenation degree was studied at mass fraction 3% catalyst based on the weight of NBR under  $145^\circ\text{C}$  for 8 h. With an increase in hydrogen pressure from 0.5 MPa to 1.5 MPa, as shown in Figure 2, the degree of hy-

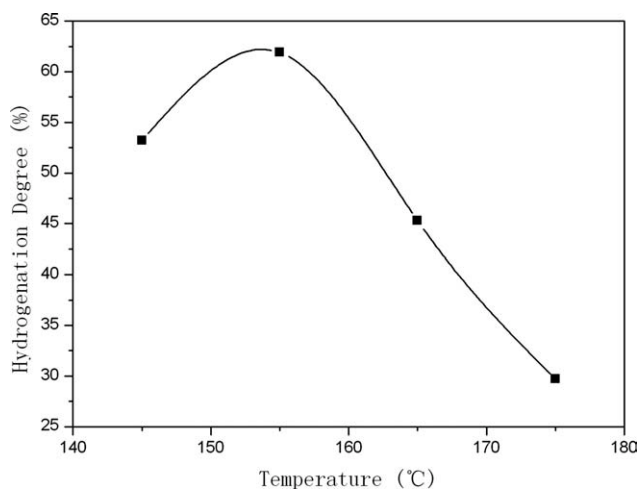
drogenation increases markedly, whereas for higher pressure ( $>1.5$  MPa), hydrogen pressure has no significant effect on the catalytic performance of Rh/AEOPP complex. According to previous study, the order of hydrogenation of NBR in the presence of  $\text{RhCl}(PPh_3)_3$  with respect to hydrogen pressure exhibited a first-to-zero-order dependence on the system pressure increased.<sup>25</sup> This conclusion is in good agreement with our data. These observations can be explained by invoking the hydride pathway mechanism for hydrogenation. Accordingly, hydrogen first reacts with  $\text{RhCl}(\text{AEOPP})_3$  to form a hydride complex,  $\text{RhClH}_2(\text{AEOPP})_3$ . This active species react with the double bond in the rate-determining step to form a metal alkyl complex; followed by the dissociation of metal alkyl complex lead to the formation of saturated polymer. At the lower hydrogen pressure ( $\leq 1.5$  MPa), the  $\text{RhClH}_2(\text{AEOPP})_3$  is not sufficient enough for the next reaction to reduce the C=C, hydrogenation degree increases with the increase of hydrogen pressure. At higher pressure like 1.5 MPa, total rate of hydrogenation of NBR might be determined by the rate-determining step. Thus hydrogenation degree is not much dependent on hydrogen pressure.

#### The effect of temperature on hydrogenation degree

According to previous studies of different kinds of Rh–Organic complex, it is clear that temperature plays a very important role in the hydrogenation reaction.<sup>26</sup> For  $\text{RhCl}(PPh_3)_3$ , the optimum reaction temperature for hydrogenation NBR is about  $145^\circ\text{C}$ .<sup>6</sup> Because of the increased steric hindrance effect of AEOPP, the catalytic activity of Rh/AEOPP complex may be lower than that of  $\text{RhCl}(PPh_3)_3$ . Therefore,  $145^\circ\text{C}$  was chosen as the starting point.



**Figure 2** Effect of hydrogen pressure on hydrogenation degree.



**Figure 3** Effect of temperature on hydrogenation degree.

A series of experiments were carried out over the temperature range 145–175°C, with catalyst concentration of 8% weight of NBR, NBR concentration of 7% weight of xylene solution, and hydrogen pressure of 2 MPa for 4 h. The results were shown in Figure 3. At lower reaction temperatures (from 145 to 155°C), the hydrogenation degree increases with the increase of temperature. However, with further increase in the reaction temperature ( $\geq 155^\circ\text{C}$ ) the hydrogenation degree decreases. This phenomenon can be explained on the basis that the catalyst was not active at lower temperature because of collisions of particles. As the reaction temperature increased, both the probability of collision and activity of the catalyst increased, resulting in enhancement of the hydrogenation degree of NBR. But it dramatically decreases when the temperature over 155°C. This was probably due to deactivation of the catalyst by dimerization or decomposition at higher temperature. It can be concluded that the hydrogenation degree was controlled by the collisions of particles at lower reaction temperature, while controlled by side reactions at higher temperature. The optimum temperature for the reaction was about 155°C.

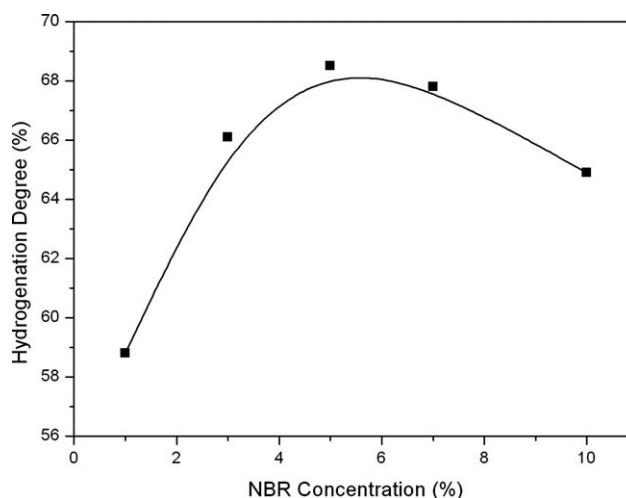
#### The effect of NBR concentration on hydrogenation degree

A series of experiments was carried out at different NBR concentration to examine the effect of NBR concentration on hydrogenation degree. The NBR concentration used ranged from 1% to 10% weight of xylene solution, whereas catalyst concentration (3% based on NBR), reaction temperature (155°C), hydrogen pressure (1.5 MPa), and reaction time (8 h) kept constant. The results are shown in Figure 4. It suggests that the hydrogenation degree increases with an increase in NBR concentration from 1% to 5%. In contrast, when the NBR concentration

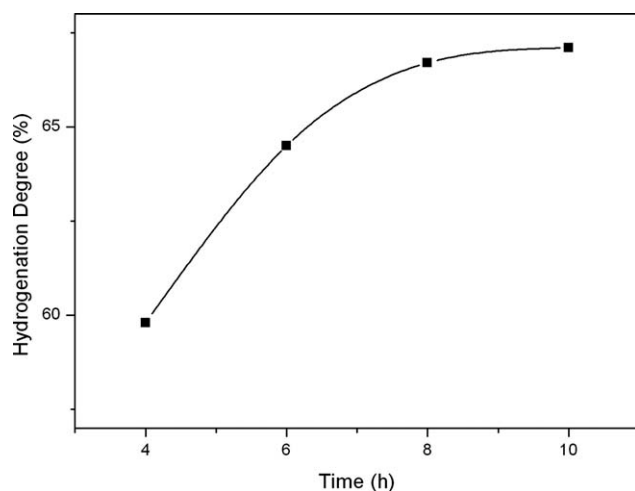
exceeds 5%, a decreased hydrogenation degree with higher rubber concentration was observed. The nitrile functional group in NBR is known to reversibly coordinate to metal complex catalyst as the nitrogen lone pair of electrons binding to the active center.<sup>27</sup> This behavior has also been reported for NBR hydrogenation catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$ <sup>28</sup> and  $\text{RhH}(\text{PPh}_3)_4$ .<sup>28</sup> So these two contrary rules might be explained in this lab. When NBR concentration is 1–5%, the C=C concentration play a decisive role, the higher C=C concentration, the faster reduce reaction. But for NBR concentration exceeds 5%, the nitrile functional group in NBR can bind to active center to prevent it from reacting with C=C bonds.

#### The effect of time on hydrogenation degree

The effect of reaction time on hydrogenation degree was examined at catalyst mass fraction 3% of weight of NBR under 155°C for 8 h. It can be seen from Figure 5 that the degree of hydrogenation NBR rise as reaction time increasing. However, these profiles do not have good linear response with respect to time. It can be seen that the curve has much higher slope at the beginning of 8 h than that of later period time. This suggests that the higher concentration of C=C at early stage of reaction than that of the later period. Because of the complexation and dissociation between active center and ligands, the active center of metal complex catalyst undergoes transforms of  $18e \rightarrow 16e \rightarrow 18e$  during catalytic reaction. The steric hindrance effect of AEOPP ligands lead to the low activity of catalyst during the low concentration of C=C. To further improve the catalytic efficiency, secondary ligand ( $L_2$ ) should be added to make an optimum complexation between active center and ligands.



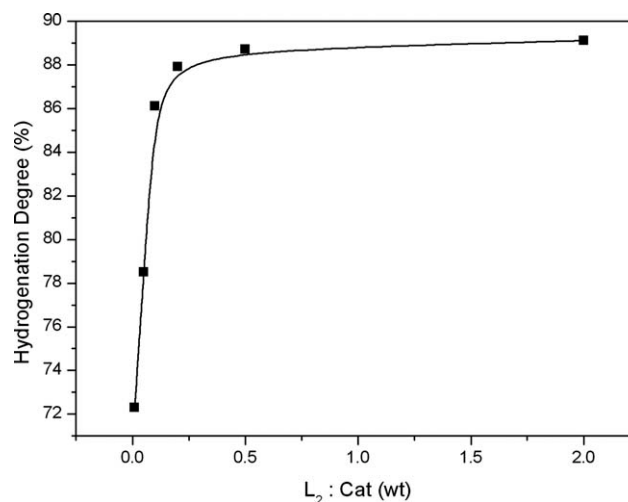
**Figure 4** Effect of NBR concentration on hydrogenation degree.



**Figure 5** Effect of time on hydrogenation degree.

### The effect of secondary ligand on hydrogenation degree

Some ligands have been used to enhance the catalytic activity of Rh complex for olefinic hydrogenation catalysts.<sup>29,30</sup> To improve the hydrogenation degree we choose a trivalent phosphine ligand as  $L_2$  to improve steric hindrance and the catalytic activity. A series of experiments were carried out at different weight ratio between  $L_2$  and catalyst to examine the effect of secondary ligand added on hydrogenation degree. The results are shown in Figure 6, which clearly indicate a dramatic increase of hydrogenation degree with the  $L_2$  added. When the ratio is less than 0.5, with  $L_2$  increases, the degree of hydrogenation also increases. But after that point the increase of  $L_2$  do not obviously contribute to hydrogenation degree. By comparing Figures 5 and 6, it can be seen that addition of the  $L_2$  did lead to higher hydrogenation degree. When catalyst concentration of 3% weight of NBR, NBR concentration of 5% weight of xylene solution, and hydrogen pressure of 2 MPa at 155°C for 8 h, hydrogenation degree of NBR can be increased from 67% to 88% by the addition of  $L_2$  at the ratio of 0.5, which shows that the  $L_2$  can help



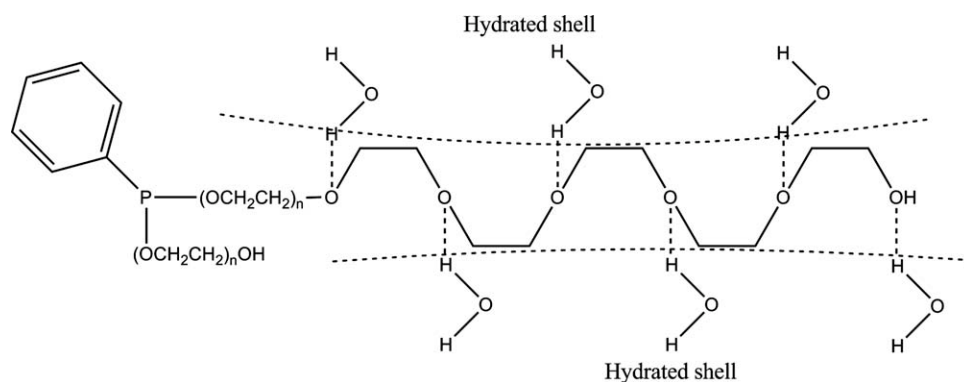
**Figure 6** Effect of secondary ligand on hydrogenation degree.

active species and ligands to maintain the best applicable complexation and lead the complexation go hydride pathway. The result shows that 90% hydrogenation degree of NBR can be approximately reached at the optimum condition with a 5% NBR xylene solution, catalyst 0.3% based on the weight of NBR, and 2 times of the ratio of the weight between  $L_2$  and catalyst under 1.5 MPa hydrogen pressure at 155°C for 8 h.

### Separation of Rh/AEOPP catalyst

The Rh/AEOPP complex has a desired property that can be easily separated from products by adjusting temperature. The mechanism of this thermoregulated phase transfer property is probably due to particular structure which form hydrogen bonds between the polyether chain and aqueous phase at lower temperature and be broken on heating, as Figure 7 shown.<sup>13</sup>

The recycling efficiency data of rhodium from this catalyst can be seen from Table I. The optimum value of recycling efficiency approximates 89%. The



**Figure 7** Hydrated shell and hydrogen bonds between polyether chain and aqueous phase for a nonionic surfactant.

TABLE I  
Recycling Efficiency of Rh/AEOPP Catalyst

Expt.	Hydrogenation degree (%)	Recycling efficiency (%)
1	67.8	88.9
2	72.3	80.4
3	78.5	73.6
4	86.1	64.5
5	87.9	40.2

result provides further evidence that the AEOPP has good transfer property in two-phase system. And the results show a different variation tendency of hydrogenation degree and recycling efficiency, which indicates that the appropriate molecular weight of ligand can provide better catalytic activity and separation efficiency.

### FTIR and $^1\text{H-NMR}$ spectroscopic characterization

A new catalyst, Rh/AEOPP complex, which has the property of themoregulated phase transfer, was synthesized. The hydrogenated products (HNBR), using Rh/AEOPP as catalyst, were characterized by  $^1\text{H-NMR}$  and IR spectroscopy. The results were shown in Figures 8 and 9.

From  $^1\text{H-NMR}$ , an enhanced intensity of the aliphatic protons at the expense of the olefinic ones by the comparison of (a) and (b) can be seen. There are no peaks for  $-\text{NH}_2$  or  $-\text{NH}$  units observed, which indicated that Rh/AEOPP catalyst for hydrogenation of NBR only took place on the  $\text{C}=\text{C}$  double bond saturated without causing reduction of the CN group.

IR (Fig. 9) shows that the characteristic peak ( $917\text{cm}^{-1}$ ) of 1,2-butadiene chains disappear. The peak of 1,4-butadiene ( $970\text{cm}^{-1}$ ) also exist but very small, which shows that when hydrogenation degree is higher than 84%, 1,2-butadiene structure of HNBR has been completely saturated, and only a small amount of trans 1,4-butadiene structure of  $\text{C}=\text{C}$  is

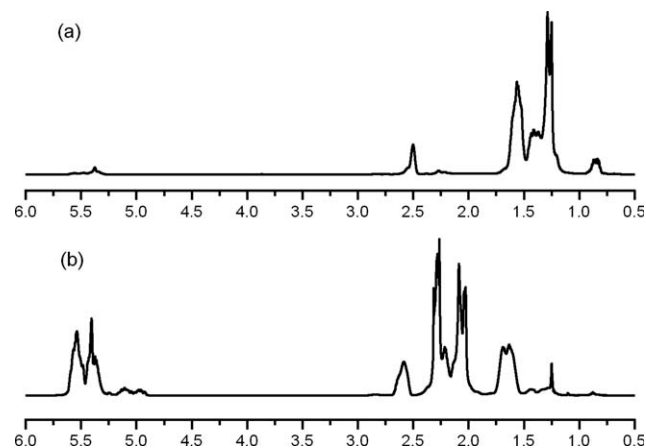


Figure 8  $^1\text{H-NMR}$  spectra of (a) HNBR and (b) NBR.

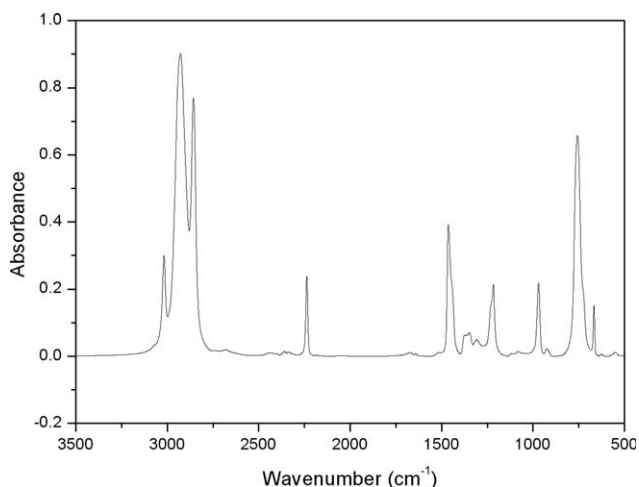


Figure 9 FTIR spectrum of HNBR.

still unsaturated. No peak around  $-\text{NH}_2$  ( $3400\text{--}3500\text{cm}^{-1}$ ) and  $-\text{NH}$  ( $3310\text{--}3450\text{cm}^{-1}$ ) observed suggest that Rh/AEOPP catalyst for hydrogenation of NBR only took place on the  $\text{C}=\text{C}$  double bond saturated without causing reduction of the CN group, which has good agreement with the results of  $^1\text{H-NMR}$ . These results suggest that Rh/AEOPP catalyst first hydrogenate the  $\text{C}=\text{C}$  double bond in 1,2-butadiene fraction, and then in 1,4-butadiene part.

### CONCLUSIONS

A new catalyst, the Rh/AEOPP complex, with themoregulated phase transfer property, was synthesized and was the first time applied to hydrogenation of NBR. The result shows that under the optimized conditions of  $[\text{Cat}] = 3\%$  (based the weight of NBR),  $\text{L}_2$ : Cat (Weight Ratio) = 2,  $[\text{NBR}] = 5\%$  (based the weight of xylene solution),  $P(\text{H}_2) = 1.5\text{MPa}$ ,  $T = 155^\circ\text{C}$ ,  $t = 8\text{h}$ , the hydrogenation degree of product (HNBR) can be approximately reached to 90%. After reaction, the Rh/AEOPP complex can be easily separated from substrates by controlling temperature, and the recycling efficiency can be over 88%. The spectra of  $^1\text{H-NMR}$  and FTIR confirmed that Rh/AEOPP catalyst can selectively hydrogenate NBR on the  $\text{C}=\text{C}$  group instead of the CN group.

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