Homogeneous Catalytic Hydrogenation of Hydroxyl-Terminated Liquid Nitrile Rubber

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ABSTRACT: It was difficult to obtain high degree of hydrogenation of hydroxyl-terminated liquid nitrile rubber (HTBN) by using homogeneous noble metal catalyst because the hydroxyl (—OH) in HTBN was likely to cause catalyst poisoning. In this study, with hexamethyl disilylamine protecting —OH, a good yields of hydrogenated HTBN was synthesized through the use of homogeneous metal catalyst. The effects of catalyst concentration, reaction time, hydrogen pressure, and temperature on the hydrogenation of HTBN were investigated and obtained the following optimum process parameter values: catalyst mass fraction of 0.8%, reaction time of 8 h, pressure of 1.6 MPa, and temperature of 100°C. Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy were used to characterize the hydrogenation product of the protected HTBN, indicating that under certain conditions a high degree of hydrogenation of HTBN can be achieved. Only the carbon–carbon double bonds (C=C), not the —CN bonds, are subject to hydrogenation. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1716–1722, 2012

Key words: hydroxyl-terminated liquid nitrile rubber (HTBN); Wilkinson's catalyst; protection; homogeneous hydrogenation; structure

INTRODUCTION

The molecular weight of NBR is hundreds of thousands. It has excellent features of oil resistance and thermal stability. On the contrary, the molecular weight of hydroxyl-terminated liquid nitrile rubber (HTBN) is about 3000. With hydroxyl end groups, HTBN can combine with bifunctional molecules in chain extension reactions to form large molecules with specific properties. It can also be used as adhesives for rubber, polyester, and metal, with the characteristic of curing at room temperature without solvent. Another use of HTBN is for the manufacture of corrosion-resistant coating that can be used in an acidic environment. The most important use of HTBN is as a toughening agent for the modification of epoxy resin. The hydroxyl groups (—OH) in HTBN react with not only epoxy groups but also with anhydride, connecting the rubber chain segments in HTBN and the epoxy resin chain segments to form a crosslink network or graft copolymer, thus improving the interface, creating a toughening effect, and significantly increasing the shear strength, impact strength, and fracture toughness of the epoxy resin.[1,2]

However, HTBN contains C=C bonds, limiting the application of the material and resulting in the degradation of heat resistance, aging resistance, ozone resistance, and other properties of the material. Hydrogenation is an excellent way for modifying unsaturated polymers, especially not by direct polymerization.[3–9] After hydrogenation, the products have excellent heat resistance, aging resistance, and ozone resistance.[10–13] Rempel and coworkers conducted a large number of studies on the hydrogenation of NBR, using different noble metal catalysts and different reaction conditions, and obtained a degree of hydrogenation of over 95%.[14,15] Meanwhile, using hydrazine hydrate to directly hydrogenate NBR can reduce the use of noble metals, and the method is simple and has become a research hotspot.[16–20] Bhattacharjee et al. reported the use of palladium complex catalyst in the hydrogenation of liquid carboxylated nitrile rubber and obtained a degree of hydrogenation of 60%.[21] The glass transition temperature of the hydrogenated product is lower than that of NBR, an indication of good low temperature resistance. However, there has been no report on the hydrogenation of HTBN. A lot of work

founded that the —OH group was likely to cause catalyst poisoning and a high degree of hydrogenation cannot be obtained.

In this study, a higher degree of hydrogenation of HTBN was obtained by using Wilkinson's catalyst.[22] The important factors on hydrogenation were discussed.

EXPERIMENTAL

Materials

HTBN: Lanzhou Chemical Industry Co, Ltd; anhydrous ethanol and xylene: analytically pure, Beijing Chemical Plant; triphenylphosphine and hydrated rhodium chloride: analytically pure, Aldrich Products, USA; chloroform: analytically pure, Beijing Yili Fine Chemicals Co, Ltd.

Preparation of catalysts

Ethanol solution was added to 30 g triphenylphosphine (PPh_3) at 90°C, back degassing for 20 min. Soluble rhodium chloride hydrated ethanol was added. 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%.

Terminal hydroxyl protection

A 2 g hexamethyl disilylamine and 10 g HTBN were dissolved in trimethyl amine. The reaction temperature was 60°C. The solvent was removed after 6 h and silyl-terminated liquid nitrile rubber was obtained.

Hydrogenation of HTBN

All the hydrogenation experiments were carried out in 100 mL autoclave reactor. Silyl-terminated liquid nitrile (7.5 g) in xylene (50 mL) was added to autoclave, and stirred vigorously under hydrogen for a couple of minutes, followed by venting. This process was repeated five times to ensure that oxygen was completely removed. Then the required catalyst was transferred into the reactor. The autoclave was slowly heated to different time, and maintained at this temperature for 8 h with stirring. After reaction the autoclave was allowed to cool to room temperature.

Condensation of hydrogenation product and removal of hydroxyl protection

The hydrogenation product was distilled at 70°C under vacuum until the product no longer contained xylene. After condensation, the product was dissolved in a mixed solution of chloroform and acetic acid. The ensuing reaction was allowed to proceed at 80°C for 60 min, resulting in removal of hydroxyl protection.

Analysis of degree of hydrogenation[23]

A 30 mg of the processed hydrogenated silyl-terminated liquid nitrile was accurately weighed and then added to a 250-mL iodine flask. Chloroform (20 mL) and BrI solution (2 mL) were added and allowed to stand for 30 min. Then 20 mL of 10% KI and 20 mL of water were added, followed by titration with $Na_2S_2O_3$ until the solution turned colorless. The degree of hydrogenation was calculated according to the following equation:

$$D = \frac{C_0 - C}{C_0} \times 100\%$$

where D represents the degree of hydrogenation, C_0 the degree of unsaturation before hydrogenation, and C the degree of unsaturation after hydrogenation.

Characterization

The changes in the structure of nonhydrogenated (parent) and hydrogenated polymer were determined by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (NMR). FTIR measurements were carried out by using the liquid film method on a Tensor 27 FRIR spectrometer (Bruker Optik GmbH, Germany). The spectra was taken in the range of wave numbers of 4000–600 cm^{-1} and used to estimate the changes in structure. NMR measurements were obtained from an AC600 spectrophotometer (Bruker Optik GmbH, Germany), with the use of CDCl$_3$ solution of about 3.5% w/v as solvent and TMS as internal standard. The changes in the structure of the polymers were confirmed by NMR measurements.

RESULTS AND DISCUSSION

Protection of —OH in HTBN

HTBN contains large amounts of —OH, which lead to poisoning of the Rh catalyst and lower catalytic activity. Using hexamethyl disilylamine for terminal hydroxyl protection can effectively prevent catalyst deactivation, leading to a degree of hydrogenation of 99%. The chemical equation given in Scheme 1 shows that the —OH groups at both ends of HTBN react with disilylamine, generating a hydroxyl-free polymer.

To further verify that the protected HTBN did not contain —OH, we used FTIR to analysis HTBN
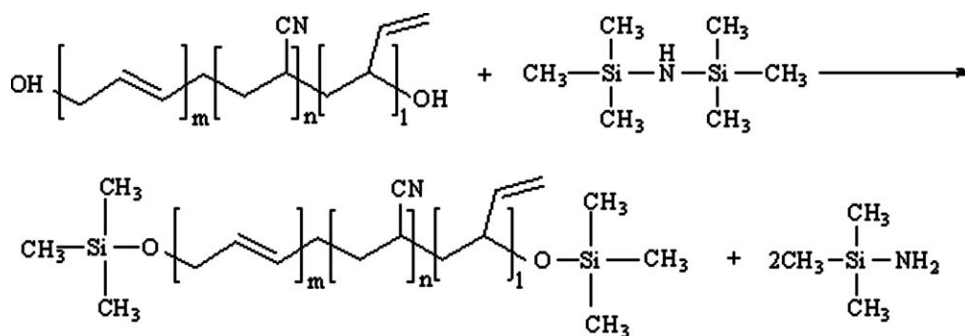
Scheme 1 Chemical equation depicting –OH.

before and after protection. Figure 1(a), the spectrum for the unprotected HTBN, shows a strong absorption peak for —OH at about 3500 cm^{-1}; there is no such peak in the spectrum for the protected HTBN [Fig. 1 (b)]. These results prove that the use of hexamethyl disilylamine results in complete terminal hydroxyl protection for HTBN.

Hydrogenation conditions

Scheme 2 shows that HTBN contains a large number of carbon–carbon double bonds and —CN bonds before reaction; after reaction, the C=C bonds in HTBN become —CH bonds, and the —CN bonds do not get involved in any reaction.

Effect of catalyst concentration on hydrogenation

The RhCl(PPh$_3$)$_3$ catalyst, which is highly active, was commonly used for NBR hydrogenation. Because HTBN has a similar structure to NBR, RhCl(PPh$_3$)$_3$ was selected as the catalyst for the

hydrogenation of HTBN. However, RhCl(PPh$_3$)$_3$ is a noble metal catalyst, which is expensive and air sensitive. Because noble metals are nonrenewable resources, we should reduce the amount of catalyst used provided that the degree of hydrogenation is not affected. Therefore, it is important to consider the effect of catalyst concentration on hydrogenation, as shown in Figure 2. As can be seen from Figure 2, the degree of hydrogenation increases with increasing concentration of the catalyst. But the increase in degree of hydrogenation slows down when the catalyst concentration reaches 0.8%. The higher the concentration of catalyst, the higher the number of catalytic active sites and the higher the rate of hydrogenation. As more C=C bonds are hydrogenated within a given period of time, the degree of hydrogenation increases. However, further increases in the concentration of catalyst result in hardly any change in the degree of hydrogenation because of the low concentration of C=C bonds relative to the concentration of catalytic active sites. Thus, the optimum catalyst concentration for the hydrogenation of HTBN is 0.8%.
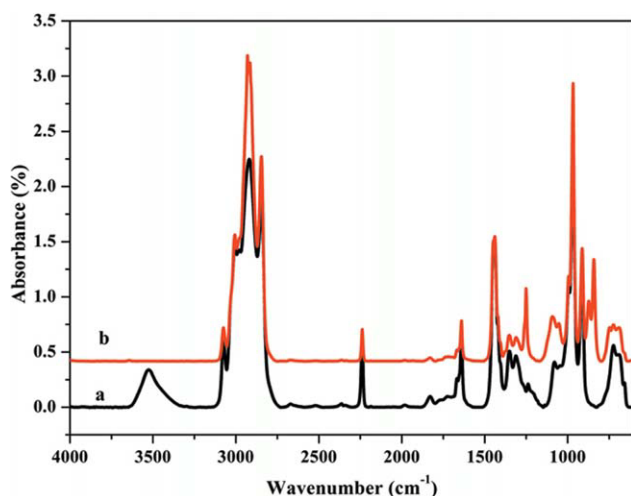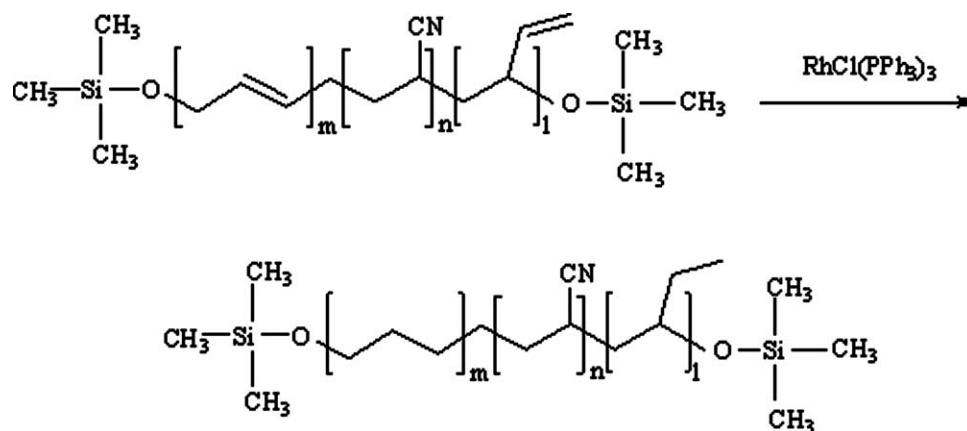
Effect of reaction time on hydrogenation

Figure 3 shows that the degree of hydrogenation increases with time early in the hydrogenation reaction (0–8 h) and then levels off after about 8 h. Initially, there was a high concentration of C=C bonds. After 8 h, most of the C=C bonds were converted to —CH bonds. With reduced concentration of C=C bonds, the rate of hydrogenation decreases and the degree of hydrogenation levels off. Therefore, the optimum reaction time for the hydrogenation of HTBN is about 8 h.

Effect of hydrogen pressure on hydrogenation

The hydrogenation of HTBN is carried out under high pressure. According to the kinetic theory of gases, with increasing pressure the reaction will go in the direction of reducing the pressure, namely the

Figure 1 FTIR spectra of (a) HTBN before protection and (b) HTBN after protection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2 Chemical equation for hydrogenation of HTBN.

direction of hydrogenation. Therefore, the hydrogen pressure has a significant effect on hydrogenation.

Figure 4 shows that the degree of hydrogenation increases rapidly with increasing hydrogen pressure between 0.4 and 1.0 MPa. When the hydrogen pressure exceeds 1.0 MPa, it has little effect on the degree of hydrogenation. Hydrogenation is a gas–liquid reaction. Hydrogen can come into contact with the catalyst and the C=C bonds only by dissolving in solution. With increasing hydrogen pressure, the hydrogen concentration in solution increases and so does the reaction rate. As a result, the degree of hydrogenation increases. However, at a given temperature, the solubility of hydrogen is fixed. When the solution is saturated with hydrogen, the solubility of hydrogen can no longer increase and the effect of hydrogen pressure on the degree of hydrogenation becomes increasingly small. As can be seen

from Figure 4, the optimum hydrogen pressure is about 1.6 MPa.

Effect of temperature on the hydrogenation

As shown in Figure 5, the degree of hydrogenation increases as the temperature gradually increases from 65 to about 100°C. The degree of hydrogenation reaches a maximum at about 100°C. It decreases with further increases in temperature. It drops to 58.3% at 145°C. From the kinetic point of view, raising the reaction temperature will speed up molecular motion and increase the probability of collision between molecules, thereby increasing the reaction rate. From the thermodynamic perspective, with increasing temperature, the energy barrier for the dissociation of the catalyst can be overcome more easily, resulting in an increase in the concentration of catalytic active sites. Thus, the reaction rate and
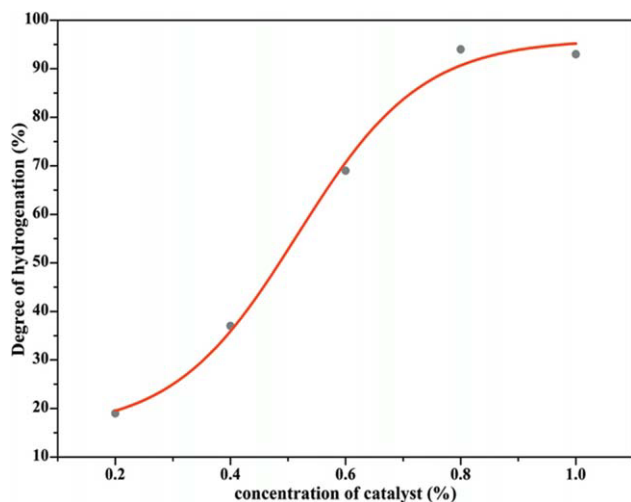

Figure 2 Effect of concentration of catalyst on hydrogenation of HTBN. w(HTBN) = 15%, 100°C, m(cat) : m(PPh3) = 1 : 8, 1 MPa, 8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

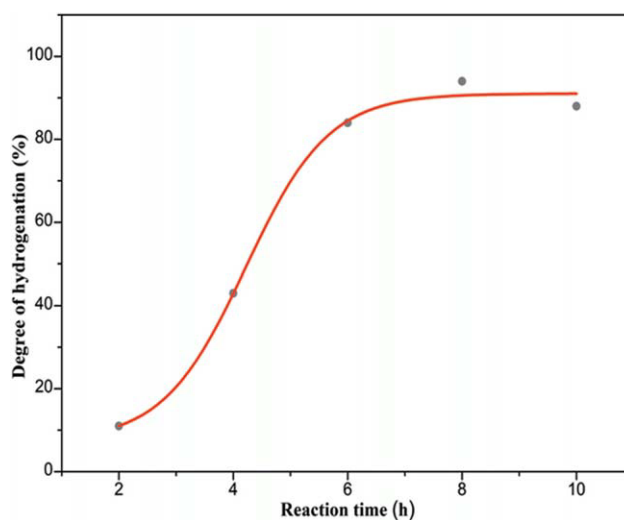**Figure 3** Effect of time on hydrogenation of HTBN. w(HTBN) = 15%, m(cat) : m(PPh3) = 1 : 8, 100°C, 1 MPa, w(cat) = 0.8%.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
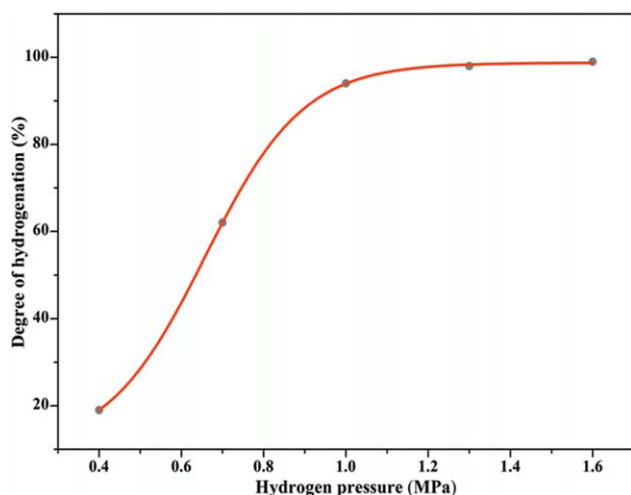
Figure 4 Effect of hydrogen pressure on hydrogenation of HTBN. w(HTBN) = 15%, m(cat) : m(PPh3) = 1 : 8, 100°C, 8 h, w(cat) = 0.8%.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the degree of hydrogenation increase. However, too high a temperature will lead to the decomposition of some protected HTBN, and the decomposition products will poison the catalyst. Too high a temperature will also cause the partial dissociation of the complex catalyst and hence loss of catalyst activity, resulting in a decrease in the degree of hydrogenation. According to Figure 5, the optimum hydrogenation temperature is about 100°C.

Removal of protection of ─OH

To avoid catalyst poisoning, it is necessary to protect the terminal hydroxyl groups before the hydrogenation of HTBN. However, the hydroxyl protection
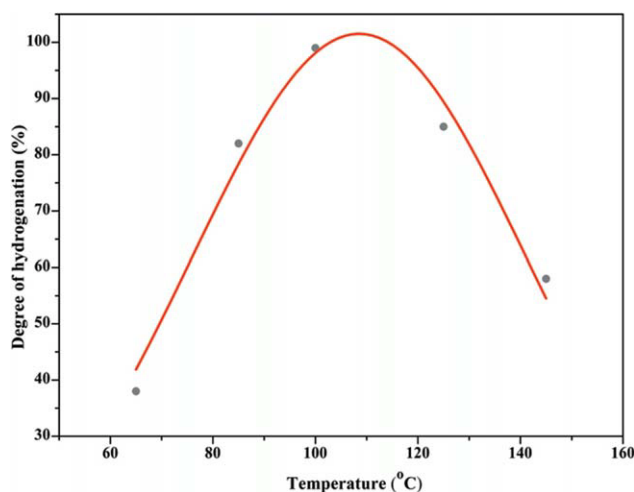

Figure 5 Effect of temperature on hydrogenation of HTBN. w(HTBN) = 15%, m(cat) : m(PPh3) = 1 : 8, 1.6 MPa, 8 h, w(cat) = 0.8%.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
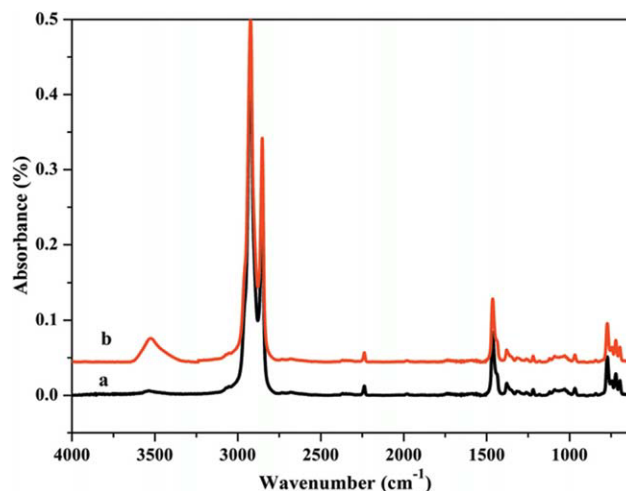

Figure 6 FTIR spectra (a) with protection of ─OH and (b) with protection of ─OH removed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

must be removed from the hydrogenation product for further hydrogenation of HTBN. The method involves dissolving the hydrogenation product in a mixed solution of chloroform and acetic acid and allowing the reaction to proceed at 80°C for 60 min. The hydroxyl protection in hydroxyl-terminated liquid nitrile is thus removed and saturated HTBN containing terminal ─OH obtained.

To verify the effectiveness of the process of protection removal, we carried out FTIR analysis of samples before and after protection removal. As shown in Figure 6, there is no ─OH absorption peak at 3525 cm^{-1} before protection removal [Fig. 6(a)], while a large ─OH absorption peak appears after
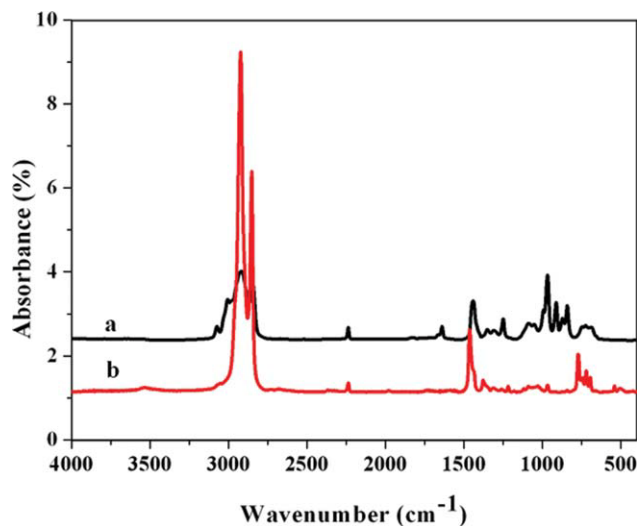

Figure 7 FTIR spectra of (a) HTBN and (b) H-HTBN* (98% hydrogenation). *Hydrogenation of HTBN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

protection removal [Fig. 6(b)]. This confirms that the method is effective in removing the protection of —OH and the structure did not change.

Structural characterization of HTBN hydrogenation

To verify that the hydrogenation of HTBN can reach high degree under certain conditions and that the reaction only involves C=C bonds but not —CN bonds, we performed FTIR and NMR analyses of samples before and after hydrogenation.

As can be seen from Figure 7, spectrum (a) for HTBN before hydrogenation has a strong absorption peak at 986 cm^{-1}, corresponding to the plane deformation vibration of the hydrogen; however, this peak does not appear in spectrum (b) for HTBN after hydrogenation, an indication that the C=C bond has been converted to a single bond. Meantime, the peak at 2237 cm^{-1} for —CN plane deformation vibration can be seen from both spectra. The position of this peak remains basically unchanged before and after hydrogenation, indicating that hydrogenation has no effect on the —CN bond, in agreement with the results of Wei et al.[15]

As shown in the ^{1}H-NMR spectra given in Figure 8, a chemical shift can be seen between 4.9 and 5.7 ppm in spectrum (a) for HTBN before hydrogenation, indicating strong carbon–carbon double bonds on the H peak before hydrogenation. However, spectrum (b) for HTBN after hydrogenation shows no peak in the same location. Meantime, the strong peak around 2.1 ppm basically disappeared, but a stronger -CH$_2$- absorption peak of hydrogen appeared at around 1.2 ppm after hydrogenation. The peaks at 2.6 ppm corresponding to H attached to carbon adjacent —CN group had no change, which proved the —CN untouched. Meantime, the
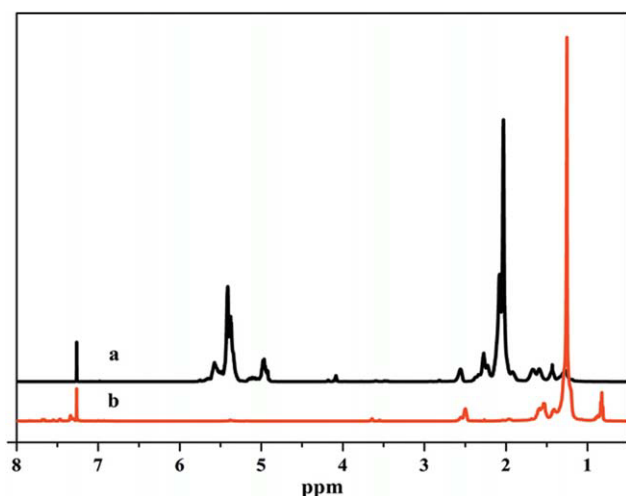

Figure 8 ^{1}H-NMR spectra of (a) HTBN and (b) H-HTBN (98% hydrogenation). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9 ^{13}C-NMR spectra of (a) HTBN and (b) H-HTBN (98% hydrogenation). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
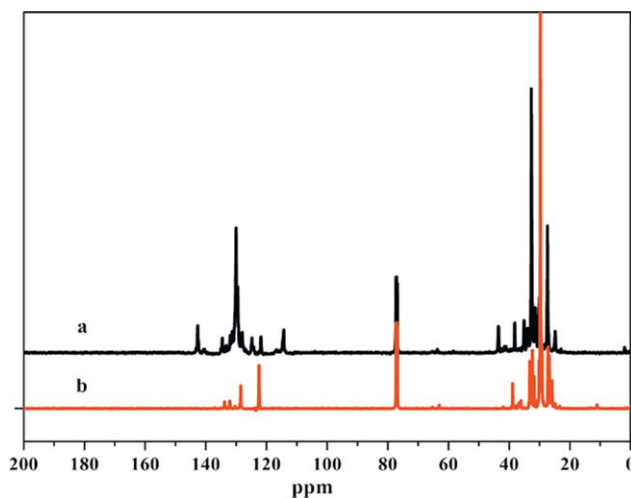
intensity of the peak for the -NH$_2$ groups was not found in NMR, which further proved that the —CN groups had no change. Figure 8 provides further evidence that by using RhCl(PPh$_3$)$_3$ as catalyst, a high degree of hydrogenation could be achieved on the C=C bonds, but not the —CN bonds.

To further verify that hydrogenation occurred on the C=C bond only and the —CN bond was not affected, we carried out ^{13}C-NMR analysis of materials before and after. As can be seen from Figure 9, the chemical shift between 125 ppm and 135 ppm in spectrum (a) for HTBN before hydrogenation shows a strong C peak for the C=C bond, while there is no such peak in spectrum (b) for HTBN after hydrogenation. On the other hand, the —CN absorption peak at 123 ppm appears in both spectra further proving that the hydrogenation involves only the C=C bond, not the —CN bond. These NMR results confirm the FTIR results obtained earlier. FTIR and NMR analyses show that under the right conditions, HTBN can be hydrogenated to a high degree to give H-HTBN with high structural integrity.

CONCLUSIONS

The use of hexamethyl disilylamine can protect the terminal hydroxyl groups in HTBN and has no effect on the hydrogenation of HTBN. The following optimum HTBN hydrogenation conditions were obtained: 0.8% catalyst concentration, reaction time of 8 h, pressure of 1.6 MPa, and temperature of 100°C. The degree of hydrogenation of HTBN can reach 99%. FTIR and NMR analyses showed that the hydrogenation process has no effect on the —CN bonds. Using acetic acid and chloroform can successfully remove the hydroxyl protection of the

hydrogenation product, and the structure of the product does not change.

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