

New Method for Hydrogenating NBR Latex

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ABSTRACT: A new hydrogenation system consisting of hydrazine hydrate and sodium periodate has been developed for hydrogenation of nitrile-butadiene rubber (NBR) latex by diimide reduction technique. The optimization of the reaction conditions was obtained. The influences of the concentration of reactants, reaction time, and temperature on hydrogenation degree were investigated. The results indicated that hydrogenation degree of the product (HNBR) can be extended to 95% through this new method. In addition, ¹H-NMR and infrared spectra confirmed that C=C double bonds in NBR were successfully hydrogenated without reduction of the CN group. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: nitrile-butadiene rubber latex; diimide; hydrogenation; sodium periodate

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INTRODUCTION

The hydrogenated elastomers, such as hydrogenated styrene-butadiene rubber (HSBR), hydrogenated styrene-butadiene-styrene block copolymer (HSBS), and hydrogenated nitrile-butadiene rubber (HNBR) have better thermal stability and aging properties than their parent polymers.^{1–4} Especially, HNBR provides heat resistance, oxidative stability, and chemical resistance compared to NBR, while still retains the oil resistance. These properties make it possible for HNBR to be widely used in automobile industry, aircraft industry, and oil exploration field.

Homogeneous catalytic hydrogenation is a well-known method for modification of NBR. It has been extensively explored during the past decades.^{5–9} But this method requires a large amount of organic solvent, high-pressure hydrogen, and especially the noble metal catalyst, which is difficult to be separated from product (HNBR). Therefore, the loss of noble metals is inevitable even using the most advanced method. A new method, hydrogenating NBR by diimide *in situ*, obtained a lot of attention, particularly at some occasion where NBR latex is needed to use directly. Since gaseous hydrogen, organic solvents, and expensive transition-metal catalysts are not necessary, it is more environmental friendly and economical. Wideman¹⁰ initially hydrogenated unsaturated polymer using diimide *in situ* and observed partly hydrogenation in 1984. But the hydrogenated products were heavily crosslinked. A lot of effort has been made to improve hydrogenation degree and overcome the problem of crosslinking. Belt et al.¹¹ discovered that using boric acid as catalyst instead of cop-

per ions could achieve higher hydrogenation degree and less crosslinking, and significantly reduce the amount of hydrazine hydrate. More than 80% hydrogenation degree of product (HNBR) without gel was obtained by Xie et al.¹² at further optimized reaction conditions. Rempel and coworkers studied the kinetics of this method to explore the reaction mechanism of hydrogenation by diimide *in situ*.^{13–15} Schulz et al. hydrogenated NBR latex using diimide by an innovative method by using selenium as catalysts under an oxygen atmosphere. And they studied the kinetics of this new hydrogenation system.^{16,17}

Currently, crosslinking is the major obstacle for HNBR latex to industrialization. It was proposed that adding inhibitors into latex can reduce crosslinking.¹² Also crosslinking can be broken and reduced by adding some substances, such as amines, hydroxylamine, imines, azine, hydrazine, and oxime.¹⁸ However, all these efforts cannot completely prevent crosslinking reaction.

In this article, a new hydrogenation system (hydrazine hydrate/sodium periodate) was first introduced to hydrogenate nitrile-butadiene latex under different conditions. We show that the hydrogenation process occurs by diimide, which is originated from hydrazine hydrate and sodium periodate.

EXPERIMENTAL

Materials

Nitrile-butadiene latex (NBRL-42F) with 45% total solid content, butadiene : acrylonitrile is 33 : 67 (w/w), was obtained from synthetic rubber plant of Petro China Lanzhou

Petrochemical Company. Sodium periodate, chloroform, isopropyl alcohol, potassium iodide, sodium thiosulfate, soluble starch, and polyvinyl alcohol were reagent-grade products of Beijing Chemical Factory. Sodium dodecyl sulfate (SDS) with reported purity of 90% was purchased from Beijing Chemical Factory.

Hydrogenation of NBR Latex

A certain amount of sodium periodate was dissolved in deionized water to obtain a certain concentration of the solution. NBR latex and hydrazine hydrate were added respectively to a 250-mL three-neck flask equipped with condenser and funnel, and then stirred for 15 min. After heating the mixture to a set temperature, sodium periodate solution was added dropwise at a rate. After completing the addition of sodium periodate solution, the mixture was kept at reaction temperature for 1 h. The hydrogenated product was separated from mixture by adding isopropanol for agglomeration.

Determination of Hydrogenation Degree

Hydrogenation degree was determined by Bromo-Iodometry method according to GB1676-81 (Chinese National Standards). The carbon double bonds in HNBR react with excessive iodine bromide (IBr) reagent. The residual (IBr) is consumed by 10% solution of potassium iodide (KI) to form iodine molecules which can be titrated with a standard solution of sodium thiosulfate. The unsaturation level before and after hydrogenation and the degree of hydrogenation are obtained by the following equations:

$$H_0 \text{ or } H_1 = (V_0 - V_1) \times C/2W \quad (1)$$

$$HD = (H_0 - H_1)/H_1 \times 100\% \quad (2)$$

HD represents the degree of hydrogenation.

Characterization

The structure of HNBR and NBR were characterized by $^1\text{H-NMR}$ spectroscopy and infrared (IR) spectroscopy. $^1\text{H-NMR}$ spectra were recorded on a Bruker AV 600-MHz spectrometer, with CDCl_3 as the solvent. IR spectra were performed on a Thermo Nicolet NEXUS 670. The samples were analyzed as solution casting films from CHCl_3 solution of coagulated products on KBr plates.

RESULTS AND DISCUSSION

In this article, a new hydrogenation system (hydrazine hydrate/sodium periodate), which was firstly used for hydrogenating NBR latex, was evaluated. The effects of reaction parameters on the hydrogenation degree including concentration of reactants, reaction time, reaction temperature, and drip speed of sodium periodate were explored in order to obtain optimum reaction conditions.

The Effect of Sodium Periodate on Hydrogenation Degree

The hydrogenation reaction, which using diimide *in situ*, can be divided into two steps. These reactions are listed as follows:

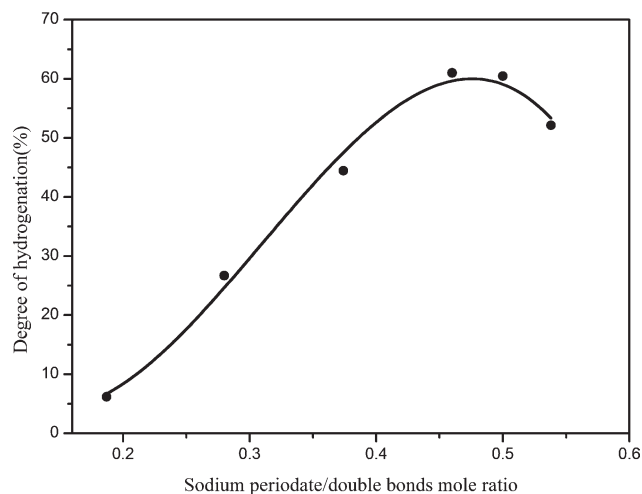
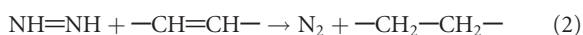
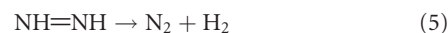
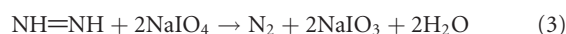


Figure 1. The effect of sodium periodate on hydrogenation degree.

As noted above, the unsaturated carbon–carbon double bonds can be hydrogenated by diimide *in situ*. The second step (reaction (2)) has the direct effect on hydrogenation reaction. However, the effect of sodium periodate on hydrogenation degree should be the first factor to be investigated, because its amount directly determined the diimide yield.

The effect of sodium periodate on hydrogenation degree was investigated by changing the ratio of $[\text{NaIO}_4] : [\text{C}=\text{C}]$ from 0.187 to 0.560 in a condition: $[\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}] : [\text{C}=\text{C}] = 6$, $T = 40^\circ\text{C}$ for 6 h. Figure 1 shows that the degree of hydrogenation increased with increasing the amount of sodium periodate, when the molar ratio of $[\text{NaIO}_4] : [\text{C}=\text{C}]$ changed from 0.187 to 0.46. This phenomenon can be explained according to the reaction (1). As the amount of oxidant in reaction system being constant, the concentration of diimide could be increased with increasing sodium periodate. Also, the probability of collision between diimide and $\text{C}=\text{C}$ group is indirectly enhanced. However, the hydrogenation degree dramatically decreases when the molar ratio of NaIO_4 and $\text{C}=\text{C}$ is more than 0.46. This is probably due to the three side reactions which are listed as follows:



This may indicate that when the amount of NaIO_4 increase and the amount of $\text{C}=\text{C}$ relatively decrease to a certain level, some side reactions may occur, which could decrease the concentration of diimide. Diimide could react with NaIO_4 directly as reaction (3). In addition, the more NaIO_4 added, the more diimide formed and the more chance for reaction (4) and (5) to occur. The optimum molar ratio between sodium periodate and $\text{C}=\text{C}$ for the reaction is about 0.46. At this optimum condition, the hydrogenation degree could reach at least 65%. From these reactions, it can be concluded that the parameters, that could affect the diimide yield, probably make a big difference to hydrogenation degree.

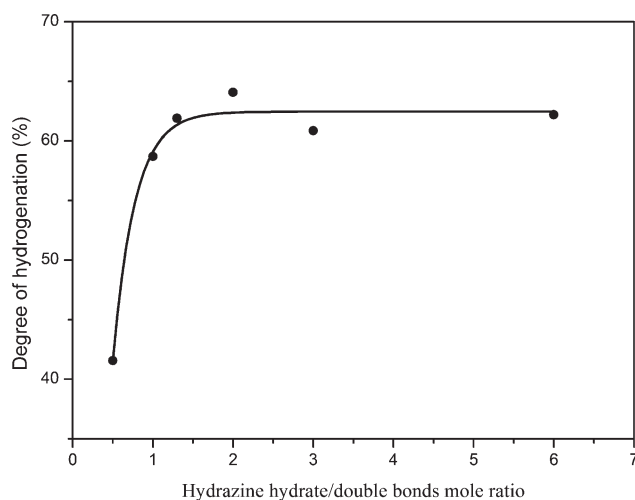


Figure 2. The effect of hydrazine hydrate on hydrogenation degree.

The Effect of Hydrazine Hydrate on Hydrogenation Degree

According to the reaction (1), the amount of hydrazine hydrate is another important factor in the hydrogenation reaction except sodium periodate. The amount of hydrazine hydrate could directly affect diimide yield. In order to investigate the effect of hydrazine hydrate on hydrogenation degree, a series of experiments were carried out over the molar ratio between N_2H_4 and $C=C$ from 0.5 to 6.0, with $[NaIO_4] : [C=C] = 0.46$ at temperature of $40^\circ C$ for 6 h. The results are shown in Figure 2. At low concentration of hydrazine hydrate ($[N_2H_4 \cdot H_2O] : [C=C] = 0.5-2.0$), the hydrogenation degree increased with the increase of hydrazine hydrate. However, with further increasing the concentration of hydrazine hydrate ($[N_2H_4 \cdot H_2O] : [C=C] \geq 2.0$), hydrogenation degree did not obviously increase. The results suggest the similar effect as sodium periodate on hydrogenation degree. At low concentration of hydrazine hydrate, it is improbable to trigger side reactions. While the concentration of hydrazine hydrate increased, the probability of collision increased, resulting in enhancement of the hydrogenation degree of NBR. When the concentration of hydrazine hydrate reached a certain point ($[N_2H_4 \cdot H_2O] : [C=C] \geq 2.0$), the hydrogenation degree did not obviously increase. This is probably because the side reactions (3), (4), and (5) were triggered.

The Effect of Temperature on Hydrogenation Degree

According to Arrhenius equation, temperature can directly affect the activation energy of reaction. Therefore, it plays a very important role in the hydrogenation reaction.

The effect of temperature on hydrogenation degree was studied in a condition: $[NaIO_4] : [C=C] = 0.5$, $[N_2H_4 \cdot H_2O] : [C=C] = 2.0$ for 6 h. And sodium periodate has been completely dripped off in 5 h. The results are shown in Figure 3. At lower reaction temperature (from $30^\circ C$ to $60^\circ C$), the hydrogenation degree obviously increases with the increase of temperature. These results can be explained that both the activity of the reactant molecules and collision probability of particles increased as the reaction temperature increased. And the hydrogenation degree was greatly increased because $NH=NH$ can easily get access to the latex particles. But the hydrogenation degree

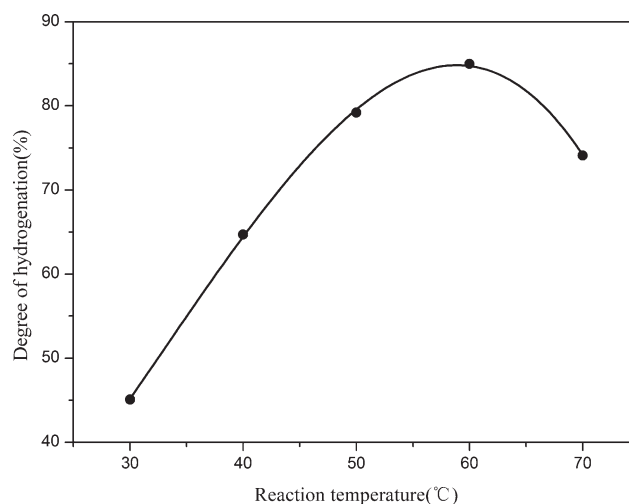


Figure 3. The effect of reaction temperature on hydrogenation degree.

dramatically decreases when the temperature was over $60^\circ C$. This was probably because the side reaction (4) was more likely to take place at higher temperature. In summary, the hydrogenation degree was controlled by the collisions of particles at lower temperature, while by side reactions at higher temperature. The appropriate temperature for this reaction was between $40^\circ C$ and $60^\circ C$. At the reaction temperature range of $30-50^\circ C$, the higher hydrogenation degree can be achieved by $H_2O_2/N_2H_4 \cdot H_2O$ system than $NaIO_4/N_2H_4 \cdot H_2O$ system,¹² probably due to $NaIO_4$ having more stability than H_2O_2 .

The Effect of Time on Hydrogenation Degree

The reaction time usually plays a very important role in the hydrogenation. A series of experiments were carried out from 2 h to 10 h with a constant condition, $[NaIO_4] : [C=C] = 0.5$, $[N_2H_4 \cdot H_2O] : [C=C] = 2.0$, at $60^\circ C$. It can be seen from Figure 4 that hydrogenation degree increased as reaction time increases. The increased level of hydrogenation at longer time is due to the reaction of larger number of double bonds with diimide. However, these profiles do not have good linear response with respect to reaction time. The curve has the highest slope

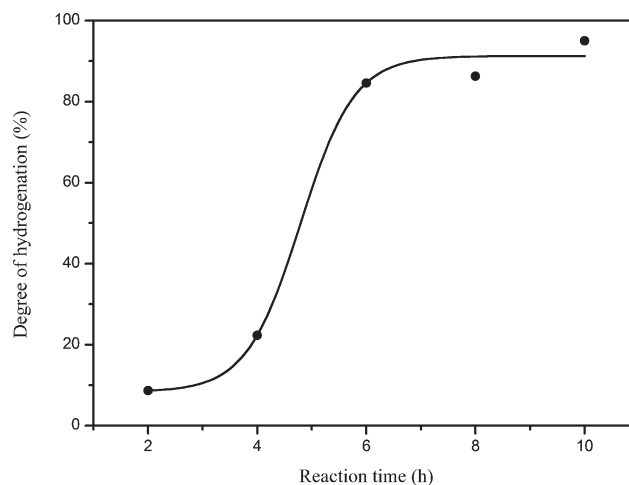


Figure 4. The effect of reaction time on hydrogenation degree.

from 4 h to 6 h through the whole reaction time. This may be possible because the concentration of diimide gradually increased and reached the highest value between 4 h and 6 h during reaction. On the other hand, the concentration of the double bonds gradually reduced with time and these side reactions (3), (4), (5) was more likely to be triggered in lower C=C concentration. In the reason of these side reactions, the concentration of diimide decreased and the hydrogenation degree tended to level off after 6 h. Thus, an appropriate reaction time is a critical factor to get products with high hydrogenation degree. At this optimum condition the hydrogenation degree is higher than 95%.

The Effect of the Drip Speed of Sodium Periodate on Hydrogenation Degree

From the reactions (1)–(5), we can guess not only the amount of sodium periodate but also the drip speed of sodium periodate solution affect the diimide yield and side reaction. The effect of the drip speed of sodium periodate on hydrogenation degree was examined from 9 mL/h to 80 mL/h in a condition: $[\text{NaIO}_4] : [\text{C}=\text{C}] = 0.46$, $[\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}] : [\text{C}=\text{C}] = 2.0$, at 40°C for 10 h.

It is observed from Figure 5 that the hydrogenation degree increases with the decrease in drip speed of sodium periodate and levels off when drip speed is slower than 15 mL/h. The slower drip speed needed for higher hydrogenation degree may be due to the relevant reactions of diimide. The higher drip speed is, the more diimide is produced in a short time. Before the diimide molecules diffuse from the aqueous phase to react with the double bonds inside of the latex particle, disproportionation of diimide itself takes place more easily according to side reaction (4). Hence, slower drip speed is necessary and the hydrogenation degree around 84.6% can be obtained at an average drop speed of 12 mL/h.

FTIR and ^1H -NMR Spectroscopic Characterization

A new hydrogenation method, hydrazine hydrate/sodium periodate, has been used to hydrogenate NBR. The hydrogenated product (HNBR) was characterized by ^1H -NMR and IR spectroscopy as shown in Figures 6 and 7.

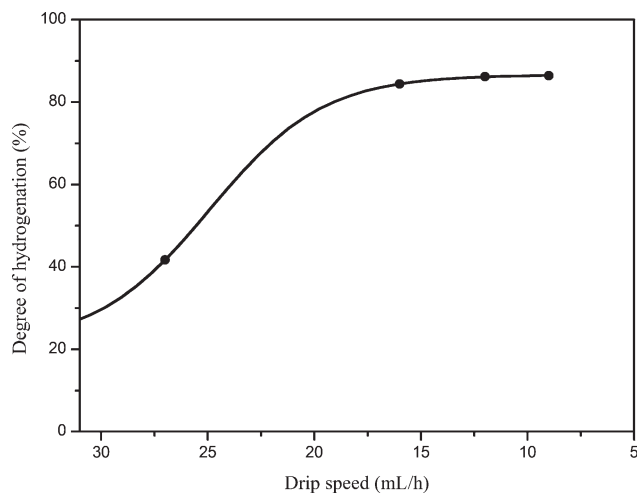


Figure 5. The effect of the drip speed of sodium periodate on hydrogenation degree.

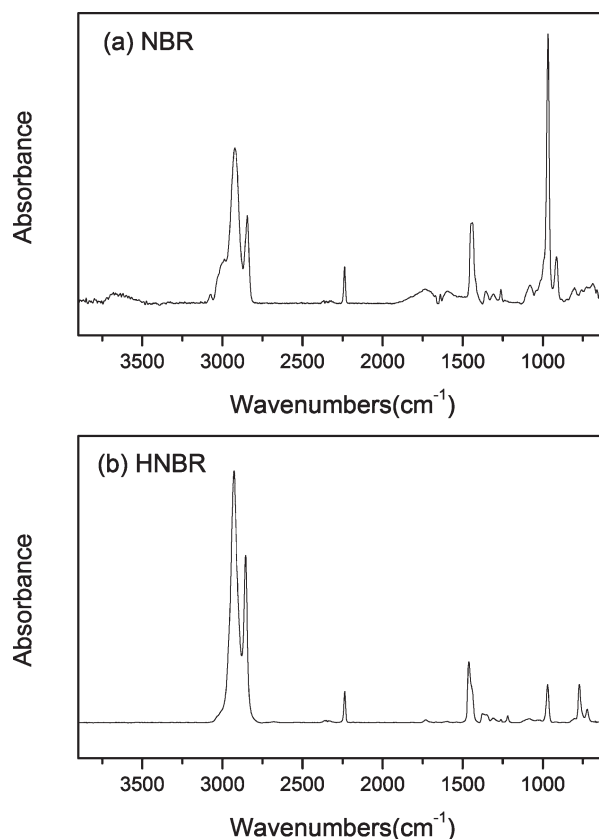


Figure 6. FTIR spectra of NBR (a) and HNBR (b).

FTIR spectra of NBR and HNBR were provided in Figure 6. For HNBR, the main peaks are assigned as: 2237 cm^{-1} ($-\text{C}[\text{tbond}]\text{N}$ stretching); 2928 cm^{-1} ($-\text{CH}_2-$ symmetric stretching); 2857 cm^{-1} ($-\text{CH}_2-$ asymmetric stretching); 1463 cm^{-1} ($-\text{CH}_2-$, $n \geq 4$ deformation vibration); 968 cm^{-1} ($-\text{CH}=\text{CH}-$ 1,4 *cis* and *trans* units); 724 cm^{-1} ($-\text{CH}_2-$, $n \geq 4$ vibration absorption). For NBR, the main peaks are assigned as: 2237 cm^{-1} ($-\text{C}[\text{tbond}]\text{N}$ stretching); 2928 cm^{-1} ($-\text{CH}_2-$ symmetric stretching); 2857 cm^{-1} ($-\text{CH}_2-$ asymmetric stretching); 1463 cm^{-1} ($-\text{CH}_2-$, $n \geq 4$ deformation vibration); 968 cm^{-1} ($-\text{CH}=\text{CH}-$ 1,4-*cis* and *trans* units); 917 cm^{-1} ($-\text{CH}=\text{CH}_2$ 1,2-vinylic units). The characteristic peak (917 cm^{-1}) of 1, 2-butadiene chains disappears. The peak of 1,4-butadiene (968 cm^{-1}) decreases, which shows that 1,2-butadiene structure of HNBR has been completely saturated, and only a small amount of *trans* 1,4-butadiene structure of C=C keep unchanged. No peak around $-\text{NH}_2$ ($3400\text{--}3500\text{ cm}^{-1}$) and $-\text{NH}$ ($3310\text{--}3450\text{ cm}^{-1}$) is observed, suggests that new hydrogenation system for hydrogenation of NBR only took place on the C=C double bond without causing reduction of the $-\text{CN}$ group.

Figure 7 illustrates ^1H -NMR spectra for NBR and HNBR. For HNBR, the main peaks are assigned as: 5.3–5.4 ppm ($-\text{CH}=\text{CH}-$ 1,4 *cis* and *trans* units); 2.5 ppm ($[\text{sbons}]\text{CH}-\text{C}[\text{tbond}]\text{N}$ acrylonitrile units); 1.2–1.4 ppm ($-\text{CH}_2-\text{CH}-$ methylene units); 1.5–1.6 ppm ($-\text{CH}_2-$ methylene units); 0.8–0.9 ppm ($-\text{C}-\text{CH}_3$ methyl units). For NBR, the

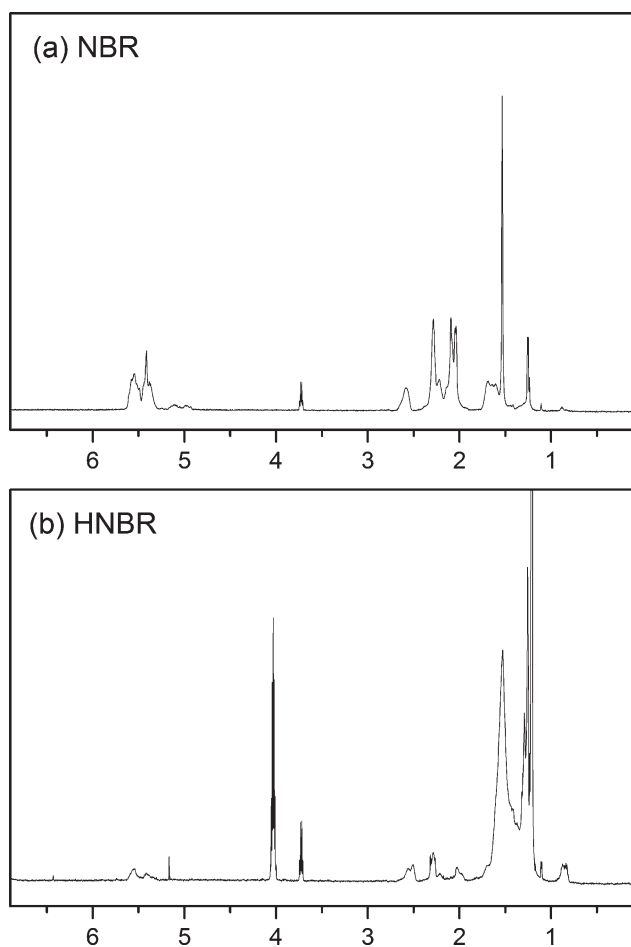


Figure 7. ^1H -NMR spectra of NBR (a) and HNBR (b).

main peaks are assigned as: 4.9–5.1 ppm ($-\text{CH}-\text{CH}_2$, 1,2-vinyl units); 5.3–5.7 ppm ($-\text{CH}=\text{CH}-$, 1,4 *cis* and *trans* units); 2.6 ppm ($-\text{CH}-\text{C}[\text{tbond}]\text{N}$ acrylonitrile units); 1.6–1.7 ppm ($-\text{CH}_2-\text{CH}-$ methylene units); 2.0–2.1 ppm ($-\text{CH}=\text{CH}-\text{CH}_2-$ methylene units); and 2.2–2.3 ppm ($-\text{CH}-\text{CH}_2-$ methylene units); 1.2–1.4 ppm ($-\text{CH}_3$ methyl units). An enhanced intensity of the aliphatic protons instead of the olefin ones by the comparison of NBR and HNBR can be seen from ^1H -NMR spectra. The peaks for $-\text{NH}_2$ or $-\text{NH}$ units were not observed, which indicated that for this new hydrogenation system hydrogenation of NBR only took place on the $\text{C}=\text{C}$ double bonds without causing reduction of the $-\text{CN}$ group, which has good agreement with the results of FTIR spectroscopic.

CONCLUSIONS

A new hydrogenation system (hydrazine hydrate/sodium periodate) was applied to hydrogenate NBR latex for the first time. The results show that under the optimized condition of

$[\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}]/[\text{C}=\text{C}] = 2$ (mole ratio), $[\text{NaIO}_4]/[\text{C}=\text{C}] = 0.5$ (mole ratio), $[\text{NaIO}_4] = 0.8$ g/mL, the drip speed of sodium periodate = 12 mL/h, $T = 60^\circ\text{C}$, $t = 10$ h, the hydrogenation degree of product (HNBR) can approximately reach to 95%. The spectra of ^1H -NMR and FTIR confirmed that this new method can selectively hydrogenate NBR on the $\text{C}=\text{C}$ group with no influence on the $-\text{CN}$ group.

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