

# Homogeneous Catalytic Hydrogenation of Natural Rubber Using $\text{RhCl}(\text{PPh}_3)_3$

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**ABSTRACT:** Hydrogenation is an important method of chemical modification, which improves the physical, chemical, and thermal properties of diene elastomers. It is also a useful method for preparation of polymers with unusual monomer sequences. Natural rubber (NR) could be quantitatively hydrogenated to a strictly alternating ethylene-propylene copolymer using a homogeneous  $\text{RhCl}(\text{PPh}_3)_3$  catalyst. The effect of concentration of rubber, catalyst and triphenyl phosphine, temperature, pressure, and solvent on the course of hydrogenation were evaluated. The thermal properties of the hydrogenated NR are compared with NR. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1647–1652, 1997

## INTRODUCTION

Chemical modification of polymers by hydrogenation is an active field of research since it leads to polymers with unusual and novel monomer sequences, which are otherwise inaccessible or difficult to prepare by conventional polymerization. Hydrogenation also improves the physical and chemical properties of diene-based elastomers.<sup>1–3</sup> There are reports of hydrogenation of poly(acrylonitrile-*co*-butadiene),<sup>2,4–6</sup> poly(butadiene),<sup>7,8</sup> poly(chloroprene),<sup>9</sup> and poly(styrene-*co*-butadiene)<sup>10,11</sup> using noble metal catalysts, such as Rh, Ru, and Pd. The advantage of these metal catalysts is that they can quantitatively and selectively hydrogenate the carbon-carbon unsaturation in the diene elastomers.

Poly(isoprene)s have been hydrogenated using noncatalytic reagents, such as using *p*-toluenesulfonyl hydrazide (TSH).<sup>12,13</sup> This reaction is known to lead to chain scission and incorporation of hy-

drazide fragments in the polymer, leading to deterioration of the elastomeric properties. Hahn<sup>14</sup> modified this method by adding tri-*n*-propyl amine in combination with TSH to eliminate the side reaction. The modification worked well for butadiene containing polymers. However, it had no effect on isoprene containing polymers. Hydrogenation of natural rubber (NR) had been studied using a homogeneous catalyst, namely,  $\text{RhCl}(\text{PPh}_3)_3$ , and a heterogeneous catalyst, namely, Pd supported on  $\text{CaCO}_3$ , by Shahab and Basheer.<sup>15</sup> Using  $\text{RhCl}(\text{PPh}_3)_3$  as catalyst in benzene as solvent and at 65°C/1atm  $\text{H}_2$  pressure, only 23 mol % hydrogenation of NR was reported. More recently,<sup>16</sup> hydrogenation of NR was studied using nickel-2-ethylhexanoate in combination with triisobutylaluminum. Quantitative hydrogenation was achieved in *n*-hexane solution at 30°C under an initial hydrogen pressure of 8.2 kg/cm<sup>2</sup>.

In view of our interest in the homogeneous hydrogenation of elastomers,<sup>6,9,11</sup> we undertook a re-examination of this reaction with a view to identify conditions capable of giving quantitative hydrogenation of NR. Quantitative hydrogenation of NR provides an easy entry to the alternating copolymer of ethylene-propylene, which is difficult

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to prepare by conventional polymerization. We report herein the results of this study.

## EXPERIMENTAL

All operations were conducted under dry nitrogen using standard bench top inert atmosphere techniques.

### Materials

RhCl<sub>3</sub> · 3H<sub>2</sub>O (Arora-Matthey Ltd. Calcutta), and triphenylphosphine (TPP) (E. Merck, Germany) were used as received. Toluene (Loba, AR grade) was purified by distillation under nitrogen from sodium benzophenone ketyl. NR (ISNR-5) was procured from Rubber Board, Kottayam, India. It was purified by dissolving in toluene and then reprecipitating by methanol. It had an intrinsic viscosity 5.38 dL/g (in toluene). The Wilkinson catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub>, was prepared according to the procedures outlined in literature.<sup>17</sup>

### Hydrogenation Procedure

Hydrogenation reactions were carried out using a 300 mL Parr reactor. The pressure drop due to the consumption of hydrogen was measured by the pressure transducer connected to the Parr reactor. In a typical hydrogenation procedure, NR (0.50g) was dissolved in 50 mL toluene in the reactor under nitrogen atmosphere. RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.087 g, 9.54 × 10<sup>-5</sup> mol) was introduced into the reactor. The reaction was carried out at 100°C and at a hydrogen pressure of 40 kg/cm<sup>2</sup> for 22 h. After the reaction, the product was precipitated by addition of methanol, filtered and dried under vacuum at 50°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ, ppm) conditions were as follows: 0.8 (—CH<sub>3</sub>), 1.2 (—CH<sub>2</sub>—), <sup>13</sup>C-NMR (CDCl<sub>3</sub>, δ, ppm) 20.00 (—C<sub>H</sub>—), 24.78 (—C<sub>H</sub>—, i.e. C<sub>ββ</sub>), 33.09 (—C<sub>H</sub>—), and 37.79 [—C(CH<sub>3</sub>)—C<sub>H</sub>—, i.e. C<sub>αγ</sub>]. Infrared (IR) (film, NaCl): 735 cm<sup>-1</sup> (—CH<sub>2</sub>— rocking vibration). Iodine value = 3.0.

### Analysis

<sup>1</sup>H- and <sup>13</sup>C-NMR of polymer were recorded on 90 and 200 MHz Bruker spectrometers, respectively, using CDCl<sub>3</sub> as the solvent. IR spectra were recorded on PC-16 Perkin-Elmer Fourier transform infrared (FTIR) spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-

Elmer TGA-7. Differential scanning calorimetry (DSC) analysis was carried out on Mettler-20 thermal analyzer. For DSC analysis, about 20 mg sample was first cooled to -100°C; then it was heated under nitrogen at the heating rate of 20°C min. Al<sub>2</sub>O<sub>3</sub> was used as the reference sample. The iodine value of the hydrogenated polymer was determined by the procedure outlined in the literature.<sup>8</sup>

## RESULTS AND DISCUSSION

Hydrogenation of NR in toluene was carried out using RhCl(PPh<sub>3</sub>)<sub>3</sub> as a catalyst in the temperature range of 40 to 100°C and with 10 to 40 kg/cm<sup>2</sup> of hydrogen pressure. Quantitative hydrogenation could be achieved after 22 h using 1.3 mol % catalyst at 100°C and 40 kg/cm<sup>2</sup> hydrogen pressure. This was confirmed by quantitative hydrogen absorption, IR, NMR and iodine value. <sup>1</sup>H-NMR of NR shows peaks at δ = 1.7, 2.0, and 5.1, which are attributed to —CH<sub>3</sub>, —CH<sub>2</sub>—, and olefinic protons, respectively. Upon hydrogenation, these peaks disappear, and new peaks appear at δ = 0.8 and 1.2, attributed to saturated —CH<sub>3</sub> and —CH<sub>2</sub>— groups. The characteristic IR peak at 840 cm<sup>-1</sup> due to trisubstituted olefinic C—H bending disappears in hydrogenated NR (HNR). A very intense peak appears at 735 cm<sup>-1</sup>, which is attributed to the —(CH<sub>2</sub>)<sub>3</sub>— group formed through hydrogenation.<sup>19</sup> Strictly alternating character was established by <sup>13</sup>C-NMR. The peaks at 135.36 and 125.20 for olefinic carbons (Fig. 1) vanished; and four new peaks emerged at 37.79, 33.09, 24.78, and 20.00, which are assigned for C<sub>αγ</sub>, —CH—, C<sub>ββ</sub>, and —CH<sub>3</sub> carbons, respectively (Fig. 1). The distortionless enhancement by polarization transfer (DEPT) spectrum confirmed this assignment (Fig. 2). The observed chemical shifts are in good agreement with those reported by Randall<sup>20</sup> for alternating copolymers of ethylene and propylene, as follows: —CH<sub>3</sub>—CH(CH<sub>3</sub>)—C<sub>αγ</sub>H<sub>2</sub>—C<sub>ββ</sub>H<sub>2</sub>—C<sub>αγ</sub>H<sub>2</sub>—CH(CH<sub>3</sub>)—CH<sub>2</sub>—CH<sub>2</sub>—.

The kinetics of hydrogenation of NR was studied by measurement of the pressure drop of hydrogen with reaction time (Fig. 3). A hydrogen consumption plot shows an apparent first-order rate dependence of hydrogenation on the [C=C], which is defined as the moles of C=C calculated as the ratio of the weight of NR taken divided by 68, the molecular weight of one isoprene unit. The reaction rate (*k*<sub>observed</sub>) was calculated from the

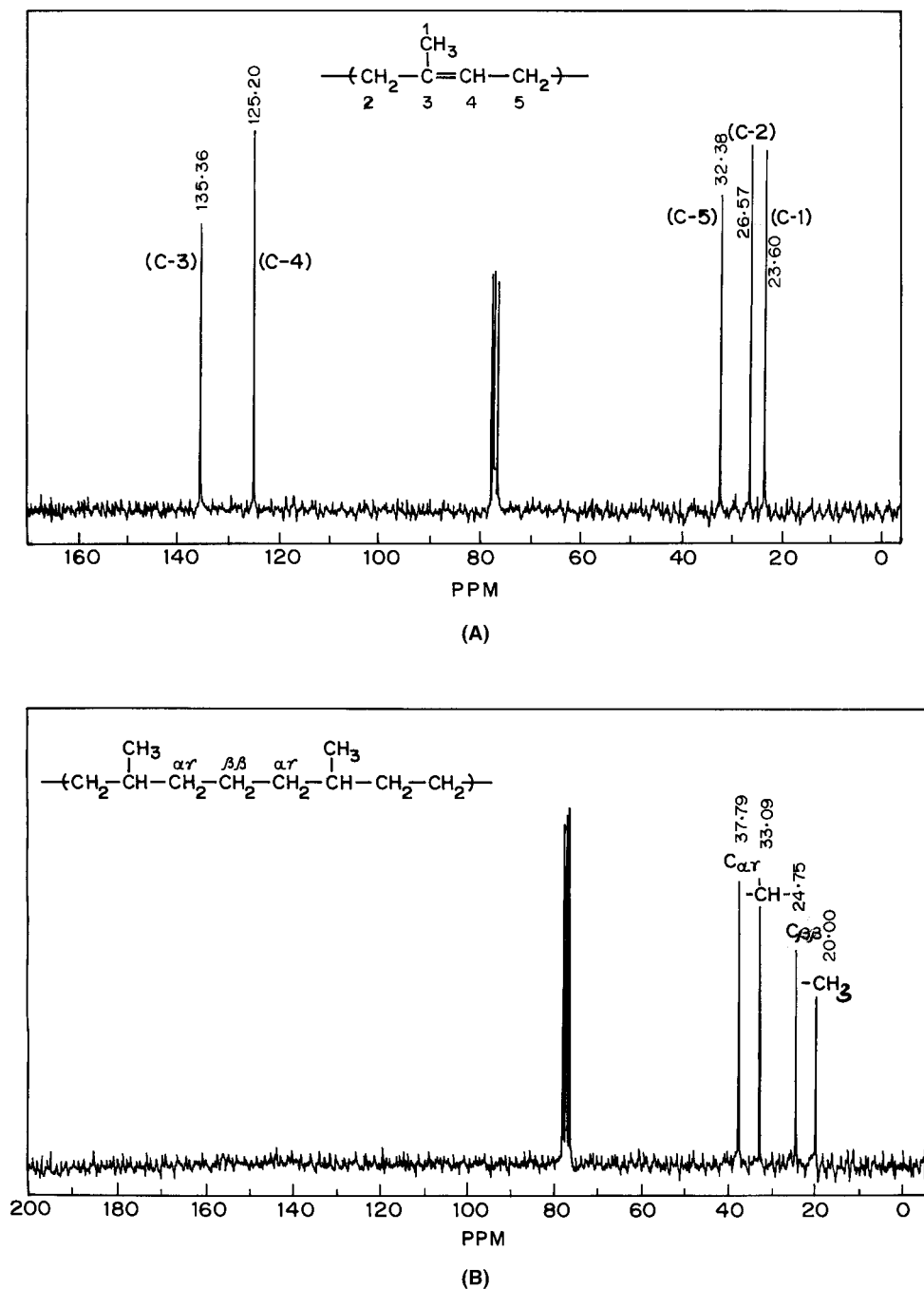


Figure 1 <sup>13</sup>C-NMR of NR (A) and HNR (B).

slope of the plot of  $\ln[\text{C}=\text{C}]$  versus time (Fig. 4). The rate of hydrogenation increases with increasing temperature (Fig. 5). The apparent activation energy of hydrogenation was calculated as 29.10 kJ/mol. This is similar to a value of 26 kJ/mol reported recently for hydrogenation using nickel-2-ethyl hexanoate and triisobutylaluminum.<sup>16</sup>

The effect of hydrogen pressure on the extent

of hydrogenation was studied at a catalyst concentration of 1.56 mM at 100°C and 22 h. With an increase in hydrogen pressure, the extent of hydrogenation increases; but after about 40 kg/cm<sup>2</sup>, it levels off. The extent of hydrogenation also increases with the increase in concentration of the catalyst. However, the rate of hydrogenation decreases with increasing concentration of triphenyl-

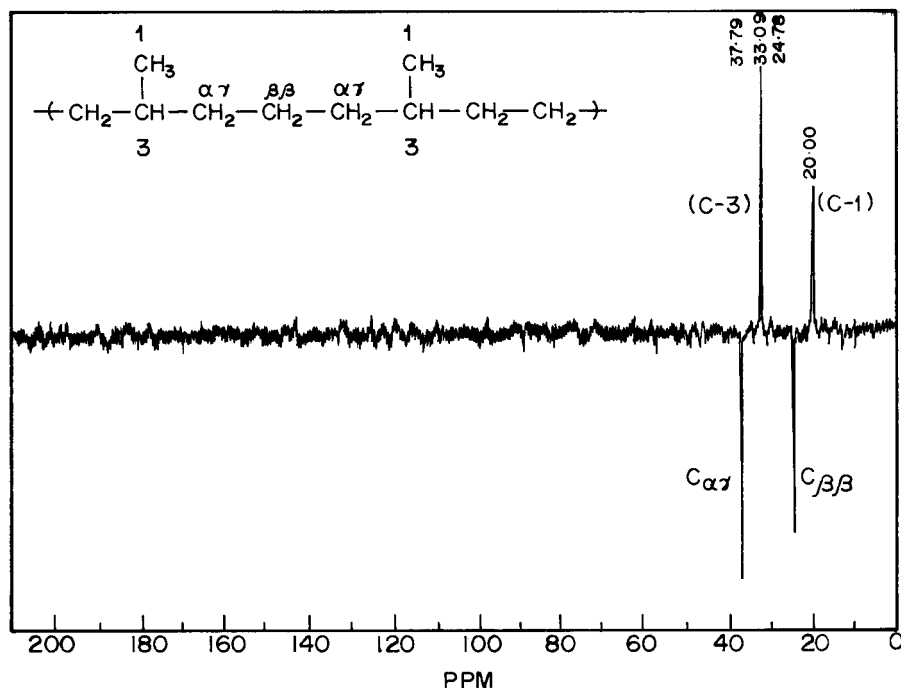


Figure 2 DEPT spectrum of HNR.

phosphine. These observations can be explained by invoking the hydride pathway mechanism for hydrogenation. Accordingly, hydrogen first reacts with  $\text{RhCl}(\text{PPh}_3)_3$  to form a hydride complex,  $\text{RhClH}_2(\text{PPh}_3)_3$ , which undergoes ligand exchange with solvent to form  $\text{RhCl}(\text{H}_2)(\text{PPh}_3)_2(\text{S})$  (where  $\text{S}$  is solvent). It has been confirmed by the observation that the rate of hydrogenation decreases with the addition of  $\text{PPh}_3$ . This active species re-

acts with the double bond in the rate-determining step to form a metal alkyl complex.<sup>7,10,21,22</sup> The metal alkyl complex undergoes dissociation, resulting in the formation of saturated polymer. The rate of hydrogenation of NR is slower than that of polybutadiene, presumably because of the tri-substituted nature of the olefinic unsaturation in NR.

The key features of hydrogenation of alkene using

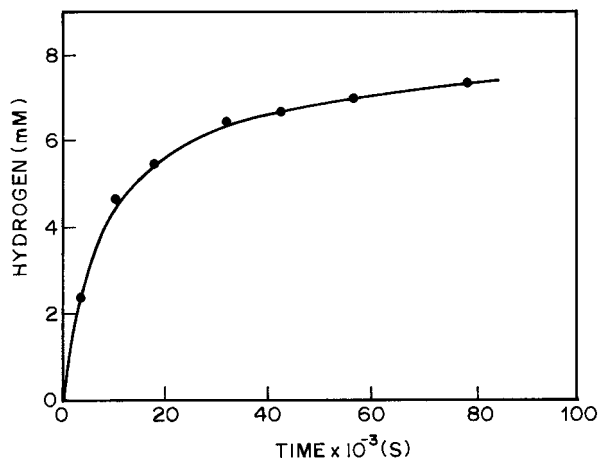


Figure 3 Representative hydrogen consumption plot for the hydrogenation of NR:  $[\text{C}=\text{C}] = 147$  mM,  $[\text{RhCl}(\text{PPh}_3)_3] = 1.89$  mM, time = 22 h, pressure = 30 kg  $\text{cm}^2$ , temperature = 100°C, and toluene = 40 mL.

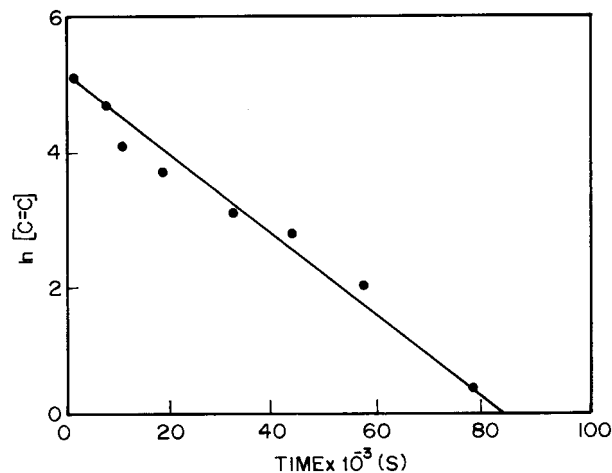
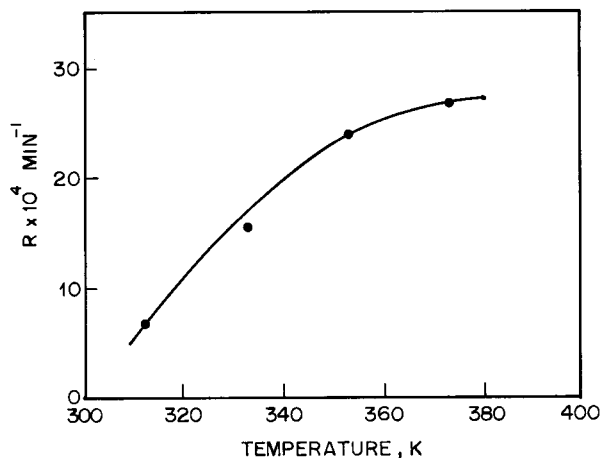


Figure 4 Plot of  $\ln[\text{C}=\text{C}]$  versus time for the hydrogenation of NR:  $[\text{C}=\text{C}] = 147$  mM,  $[\text{RhCl}(\text{PPh}_3)_3] = 1.89$  mM, time = 22 h, pressure = 30 kg  $\text{cm}^2$ , temperature = 100°C, and toluene = 40 mL.



**Figure 5** Effect of temperature on the rate of hydrogenation of NR:  $[C=C] = 147$  mM,  $[RhCl(PPh_3)_3] = 1.62$  mM, reaction time = 22 h, pressure = 30 kg/cm<sup>2</sup>, and toluene = 40 mL.

$RhCl(PPh_3)_3$  are the formation of  $RhCl(PPh_3)_2(S)$ ,  $RhClH_2(PPh_3)_2(S)$ , and  $RhClH_2(PPh_3)_2(C=C)$  (by the displacement of solvent molecule with an alkene); so it is obvious that solvent plays an important role in the hydrogenation reaction.<sup>23-25</sup> The coordinating power of the solvent is of importance. It should have sufficient coordinating power to displace the triphenylphosphine ligand, yet not be so strong to inhibit displacement by alkene. Solvation of halide and hydride ligand could also be important. Candlin and Oldham<sup>24</sup> reported that the solvent plays a key role not only in altering the rate of hydrogenation but also in the selectivity. Mohammadi and Rempel<sup>4</sup> showed that the selectivity of hydrogenation of terminal versus internal double bonds in acrylonitrile butadiene copolymer (NBR) was markedly influenced by the solvent. In methylethyl ketone (MEK), the catalyst did not exhibit selectivity for the hydrogenation of 1,2 over 1,4 units of the copolymer; whereas, distinct preference towards 1,2-unsaturation units was observed when the reaction medium was chlorobenzene. They also observed

complete hydrogenation of NBR in chlorobenzene using much higher reaction pressure and temperature than in MEK. Bhattacharjee et al.<sup>26</sup> observed that the extent of hydrogenation of NBR varied with the nature of solvent in this order: chlorobenzene > 1,2-dichlorobenzene > bromobenzene. In the present study, we observe that the extent of hydrogenation of NR decreases in the order of toluene > chlorobenzene > benzene (Table I). The nature of the solvated rhodium hydride complex, and also the interaction of the solvent with the polymer, may be the influencing factor.

TGA of NR and HNRs were measured under nitrogen at a heating rate of 10°C/min. The initial decomposition temperature (IDT) was determined from the intersection of two tangents at the onset of decomposition temperature. IDT increases with the degree of hydrogenation (Table II). The maximum decomposition temperature was calculated from the peak maxima of the derivative of TG curves. The integral procedural decomposition temperature (IPDT) were calculated from the normalized curves (with respect to residual weight) using Doyle's equation,<sup>27</sup> as follows:

$$T^* = 875A^* + 25$$

where  $T^*$  represents IPDT, and  $A^*$  is the total area under normalized curves from 25 to 900°C.

Both the  $T_{max}$  and IPDT increased with increasing reduction of carbon-carbon double bond in the elastomer.

The glass transition temperature ( $T_g$ ) was calculated from DSC thermograms. There is a slight increase in  $T_g$  on hydrogenation of NR (Table II). The calorific capacity ( $C_p$ ) is the characteristic of the rigidity of the chain in the macromolecular matrix.<sup>28</sup> For the determination of  $\Delta C_p$ , specific heat increment of NR and HNR samples temperatures are chosen in such a way that at least two data points are included in the glassy and rubbery regions. Table II shows that as there is slight in-

**Table I** Hydrogenation of NR Using Different Solvents<sup>a</sup>

Sr. No.	Solvent	$RhCl(PPh_3)_3$ ( $\times 10^5$ mol)	Hydrogenation (mol %)
1	Toluene	5.92	88
2	Chlorobenzene	5.92	65
3	Benzene	5.92	48

<sup>a</sup>  $[C=C] = 147$  mM; Temp = 100°C; Pressure = 30 kg/cm<sup>2</sup>; Time = 20 h.

**Table II TGA and DSC Analysis of NR and Hydrogenated NR**

Polymer	Hydrogenation (mol %)	IDT (°C)	$T_{\max}$ (°C)	IPDT (°C)	$T_g$ (°C)	$\Delta C_p^a$ (J/g/K)
NR	—	361	387	373	-59	0.28
HNR-1	45	380	400	375	-58	0.30
HNR-2	60	398	419	390	-58	0.31
HNR-3	80	412	437	403	-57	0.34
HNR-4	100	420	449	407	-56	0.37

<sup>a</sup>  $\Delta C_p$  = specific heat increment at  $T_g$ .

crease in  $\Delta C_p$  with the increase in the degree of hydrogenation.

In conclusion, NR can be quantitatively hydrogenated using  $\text{RhCl}(\text{PPh}_3)_3$  as a catalyst in toluene as the solvent.  $^{13}\text{C}$  NMR shows that quantitative hydrogenation of NR leads to an alternating copolymer of ethylene and propylene. Hydrogenation increases thermal stability of the hydrogenated NR without affecting its glass transition temperatures ( $T_g$ ).

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