

# One-step Synthesis of End-Functionalized Hydrogenated Nitrile-Butadiene Rubber by Combining the Functional Metathesis with Hydrogenation

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End-functionalized hydrogenated polymers obtained from nitrile-butadiene rubber (NBR) yield new materials with suitable properties for a number of applications as sealing material and adhesives. We investigated the one-step synthesis of ester end-functionalized hydrogenated nitrile-butadiene rubber (EFHNBR) by combining the functional metathesis with the hydrogenation of NBR in the presence of the 2<sup>nd</sup> generation Grubbs catalyst and a functionalized olefin as a chain transfer agent (CTA). We established the operating conditions for the effective

production of saturated functional polymers with a high degree of hydrogenation, high chemo-selectivity and moderate molecular weight. The structures of the products were confirmed by FT-IR and <sup>1</sup>H-NMR spectroscopy, rubber molecular weight, and distribution determined by using gel permeation chromatography (GPC); their thermal properties were determined by thermo-gravimetric analysis (TGA) and different scanning calorimetry (DSC).

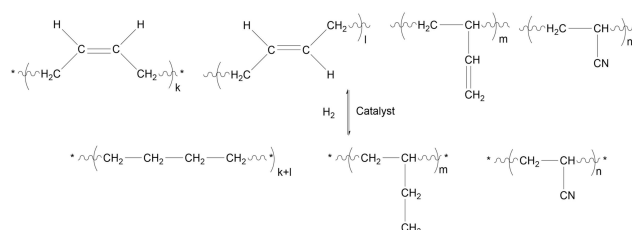
## 1. Introduction

Functional polymers are widely used in electronics, biology, and energy.<sup>[1–7]</sup> In recent years, the olefin metathesis reaction has received widespread attention for the synthesis of rubber due to its mild conditions, environment friendliness, high efficiency, and controllable performance.<sup>[8–11]</sup> The olefin metathesis reaction can be used for the chemical blending between unsaturated rubber and for the degradation of olefin unsaturated polymers,<sup>[12–14]</sup> such as polybutadiene (PBD), polyisoprene (PIp),<sup>[15]</sup> and poly(styrene-co-butadiene) (SBR). With the further development of olefin metathesis, adding different types of functional olefins in the olefin metathesis reaction sequence can conveniently introduce ester,<sup>[16]</sup> carboxyl hydroxyl,<sup>[17]</sup> and halogen groups at the end of the rubber molecular chain to form polymer materials with specific functions.<sup>[18–22]</sup> In addition, the olefin metathesis catalyst can be converted into a hydro-

genation catalyst under one atmosphere of hydrogen and be used for the catalytic hydrogenation reaction of unsaturated olefins.<sup>[23–25]</sup>

Nitrile butadiene rubber (NBR) is of primary interest in the automotive industry, on oil fields, and in aerospace due to its excellent oil and chemical resistance, low temperature flexibility, and high pressure and wear resistance.<sup>[26–28]</sup> Despite its many advantages, NBR has some disadvantages, including its swelling in aromatic and polar solvents and a maximum continuous operating temperature below 110 °C. To enable its use at higher temperatures (maximum 150 °C), we carried out the selective hydrogenation of NBR to prepare hydrogenated nitrile butadiene rubber (HNBR)<sup>[29]</sup> (Scheme 1). The most widely used methods to perform a selective hydrogenation of NBR are a homogeneous<sup>[30,31]</sup> and a heterogeneous<sup>[32]</sup> hydrogenation. However, the HNBR produced has a high viscosity relatively to the molecular mass of the macromere due to the limitation of the current production technology and natural aging of nitrile-butadiene rubber during storage.<sup>[33]</sup> This seriously affects its processing performance and restricts its widespread application.<sup>[34]</sup> The olefin metathesis reaction is a valuable new method to prepare moderate molecular weight HNBR.<sup>[35–40]</sup>

In the ongoing studies on the chemical modification of NBR by metathesis reaction, methyl methacrylate (MMA) is a



Scheme 1. Selective hydrogenation of nitrile butadiene rubber.

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valuable functional monomer to modify the molecular structure of NBR during hydrogenation. In this study, we combined the functional metathesis with the hydrogenation of NBR in the presence of a 2<sup>nd</sup> generation Grubbs catalyst and a functional olefin as a chain transfer agent (CTA). We first optimized the operating conditions of hydrogenation using a 2<sup>nd</sup> generation Grubbs catalyst to produce well-defined hydrogenated nitrile-butadiene rubber (HNBR) with a high degree of hydrogenation, high chemo-selectivity, and moderate molecular weight (Scheme 1, Table 1). A new approach combining the functional metathesis with the hydrogenation in one-step using a 2<sup>nd</sup> generation Grubbs catalyst in the presence of a functional monomer (MMA) was then implemented towards to produce ester end-functionalized hydrogenated nitrile butadiene rubber (EF-HNBR) (Scheme 2, Table 3). The structure of the modified polymer was confirmed by FT-IR and <sup>1</sup>H-NMR spectroscopy, as well as rubber molecular weight and distribution determined by using gel permeation chromatography (GPC) while the thermal properties were determined by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). So

far, there has been no report on a single-step synthesis of end-functionalized hydrogenated nitrile butadiene rubber.

## 2. Results and Discussion

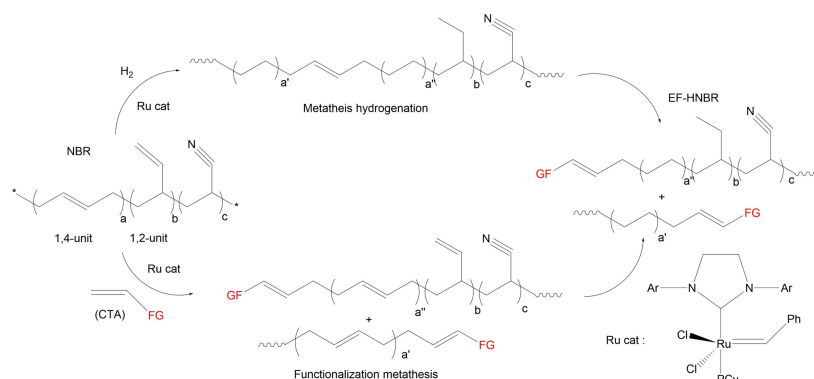
### 2.1. Synthesis and Characterization of HNBR

The degree of hydrogenation has a significant impact on the performance of the products. We evaluated the metathesis hydrogenation of NBR in the presence of 2<sup>nd</sup> generation Grubbs catalyst. The effects of various variables, such as the reaction temperature, the catalyst concentration, and the reaction time, on the hydrogenation degree (HD) were investigated. All reactions eventually had a quite good reproducibility. Some representative results are summarized in Table 1.

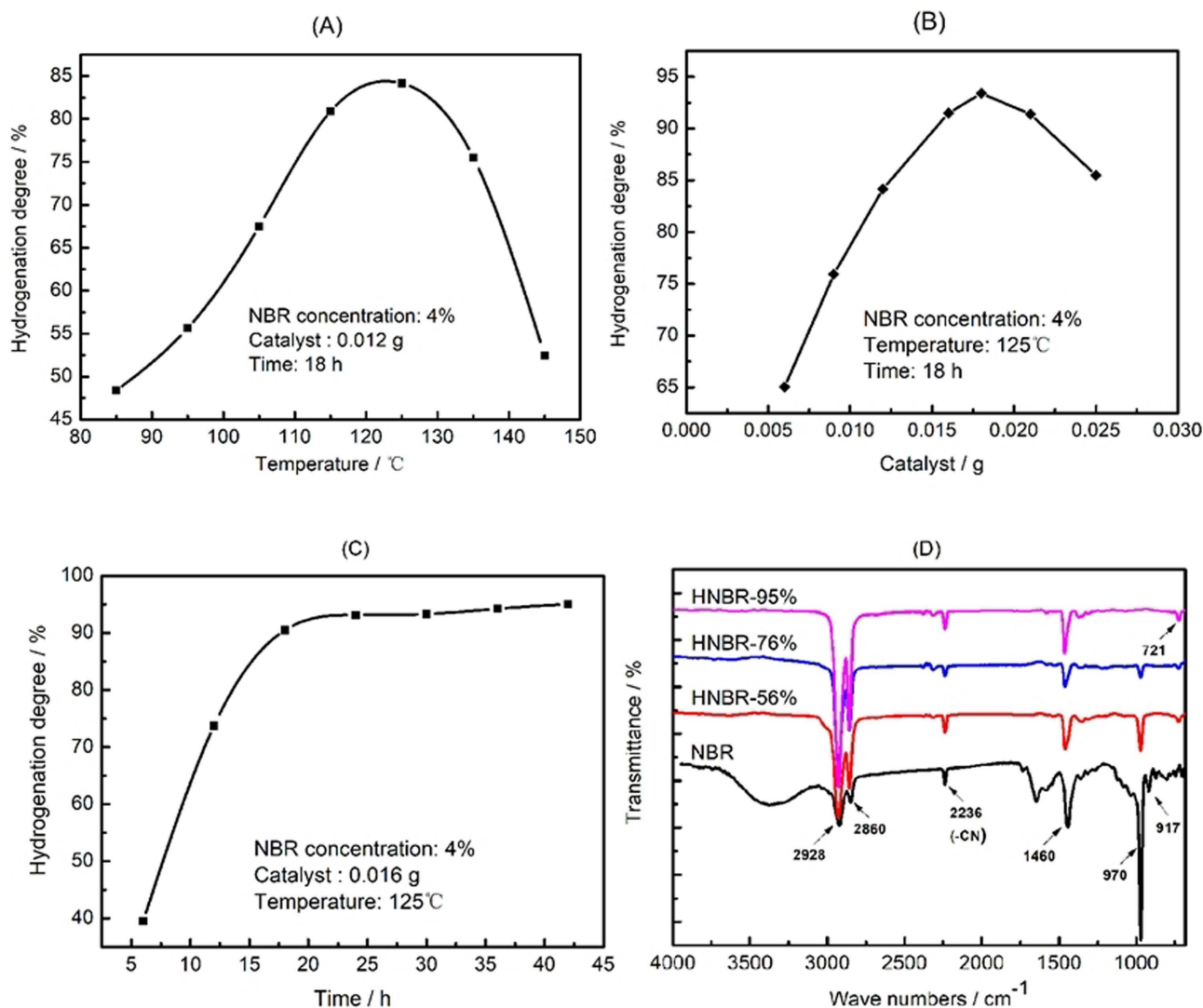
The reaction temperature usually plays a very important role in metathesis hydrogenation. First, the olefin metathesis hydrogenation of NBR was carried out at different reaction temperatures (entry 1–7, Table 1). The hydrogenation degree of the products is compared in Figure 1(A). The degree of hydrogenation first increases then decreases when the temperature increases. At lower reaction temperatures (from 85 °C to 125 °C), the hydrogenation degree increases significantly with the reaction temperature. This is because increasing the reaction temperature helps the dissociation of the tricyclohexylphosphine ligand (PCy<sub>3</sub>) from the 2<sup>nd</sup> generation Grubbs catalyst to form a 14-electron ruthenium active species (I) (Scheme 3).<sup>[41]</sup> Once the phosphine ligand dissociates, the carbon-carbon double bond coordinates with the active metal center to initiate the metathesis hydrogenation reaction. However, when the reaction temperature increases further, the hydrogenation degree decreases sharply. This is most likely because higher reaction temperatures lead to the decomposition of the catalyst. Overall, higher temperatures do not help the hydrogenation reaction and the polymer is cross-linking when the temperature exceeds a certain value (entry 8, Table 1). Our results show that the hydrogenation degree strongly depends on the reaction temperature and the optimal reaction temperature was 125 °C.

The loading of the Ru-catalyst was increased next to better assess the catalytic productivity and selectivity of the hydro-

Entry	Temperature/°C	Catalyst/g	Time/h	HD/%
1	85	0.012	18	48
2	95	0.012	18	56
3	105	0.012	18	67
4	115	0.012	18	81
5	125	0.012	18	84
6	135	0.012	18	76
7	145	0.012	18	52
8	175	0.012	18	Cross-linking
9	125	0.006	18	65
10	125	0.009	18	76
11	125	0.016	18	91
12	125	0.018	18	93
13	125	0.021	18	91
14	125	0.025	18	86
15	125	0.016	6	40
16	125	0.016	12	74
17	125	0.016	24	93
18	125	0.016	30	93
19	125	0.016	36	94
20	125	0.016	42	95



**Scheme 2.** One-step synthesis of ester end-functionalized hydrogenated nitrile-butadiene rubber (EF-HNBR) by combining the functional metathesis with the metathesis hydrogenation of NBR in the presence of the 2<sup>nd</sup> Grubbs catalyst and a functionalized olefin as a chain transfer agent (CTA).



**Figure 1.** Effect of various variables on the degree of hydrogenation: reaction temperature (A), catalyst concentration (B), reaction time (C), and FT-IR spectra of the NBR and H-NBR samples with a different HD (D).

generation reaction (entry 9–14, Table 1). Figure 1(B) shows that a high hydrogenation degree was achieved even with a very small amount of catalyst (0.006 g). This indicated that the 2<sup>nd</sup> generation Grubbs catalyst has an excellent activity for the metathesis hydrogenation reaction of NBR. Besides, the hydrogenation degree increased with the catalyst concentration. This is possibly due to the increase on 14-electron ruthenium active species (I) (Scheme 3) that leads to the gradual increase of the hydrogenation degree. The maximum hydrogenation degree was 93% when the catalyst dosage was 0.018 g. A further increase in the amount of catalyst did not increase the HD, but decreased it because the excess catalyst was deactivated by dimerization.<sup>[42]</sup> Finding an appropriate catalyst concentration is a critical factor to get products with a high hydrogenation degree.

A series of experiments was carried out over 6 h to 42 h with the other conditions kept constant (entry 15–20, table 1). Figure 1(C) shows that the hydrogenation degree increases

significantly from 40% to 95%. However, the hydrogenation degree grew only slowly with the reaction time after reaching 93% in 24 h. This may be because the concentration of double bonds was gradually reduced with time.

Figure 1(D) shows the FT-IR spectra of the NBR and HNBR samples with a different HD. The absorption peaks at 2929, 2860, and 1460 cm<sup>-1</sup> are attributed to the stretching vibrations and the deformation vibrations of the –CH<sub>2</sub>-group. All samples showed a distinct absorbance peak for the –C≡N group at 2230 cm<sup>-1</sup> and no new peak from the N–H stretching vibration appeared around 3500 cm<sup>-1</sup> after hydrogenation, indicating that the –C≡N groups had not reacted. Furthermore, the characteristic absorbance of 1,4-CH=CH– at 970 cm<sup>-1</sup> and 1,2-CH=CH<sub>2</sub> at 920 cm<sup>-1</sup> decreased remarkably when the hydrogenation degree increased. The peak of 1,2-CH=CH<sub>2</sub> at 920 cm<sup>-1</sup> almost disappeared implying that the hydrogenation reaction first occurred at 1,2-CH=CH<sub>2</sub> (920 cm<sup>-1</sup>), which is caused by the high reactivity of the terminal double bond. In addition, there

**Table 2.** Molecular weight of HNBR and comparison of the proposed approach with the reported works.

Entry	Catalyst	[Catalyst]/[NBR]	Temperature/°C	Time/h	HD/%	Mw × 10 <sup>4</sup>	Mw/Mn	Ref
1	Grubbs II	0.016 g/8 g	55	18	20	3.70	1.77	This work
2	Grubbs II	0.016 g/8 g	125	42	95	15.53	2.30	This work
3	Grubbs II	0.048 g/8 g	55	3	75	5.92	–	23
4	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	0.020 g/8 g	145	10	95	29.75	3.21	–

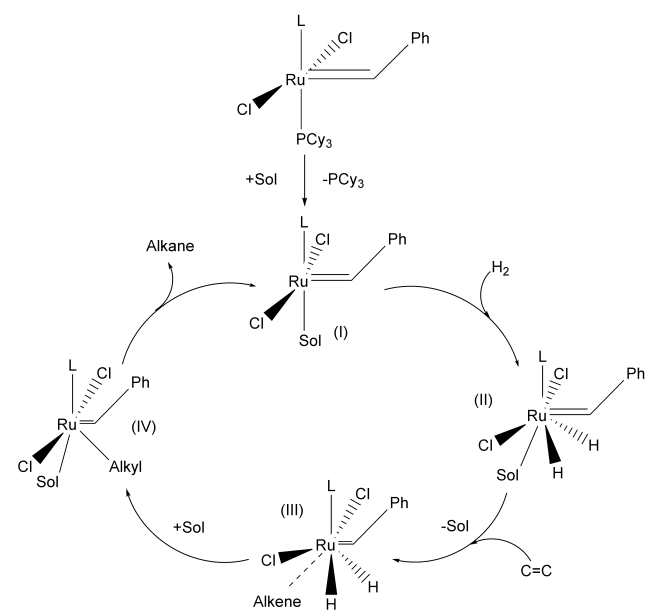
was a new peak at 730 cm<sup>-1</sup> after the hydrogenation. It was assigned to –CH<sub>2</sub>– vibration in the saturated carbon-carbon bond. Our results demonstrate that the –C=C– double bonds in both the 1,2- and the 1,4-units were successfully hydrogenated whereas the nitrile groups remained intact.

In addition, the molecular weight of the hydrogenation products obtained under different reaction conditions was measured (Table 2). At a low reaction temperature (55 °C), the molecular weight of the rubber was much lower ( $M_w = 3.70 \times 10^4$ ). The product was liquid, stuck to the wall, was difficult to process, and its degree of hydrogenation was very low (20%). At a higher temperature (125 °C), the rubber remained solid, with a higher molecular weight ( $M_w = 15.53 \times 10^4$ ) and higher degree of hydrogenation (95%). This was due to the fact that hydrogenation and metathesis reactions were competitively catalyzed by a Grubbs 2<sup>nd</sup> generation catalyst, which was consistent with a previous report on the hydrogenation of natural latex.<sup>[35]</sup> The catalyst dose used in this process was lower than that of the NBR hydrogenation route. The hydrogenation degree was high, the product molecular weight was appropriate, and it was easier to process. Based on the above experimental studies, the best processing conditions for the hydrogenation of NBR using the 2<sup>nd</sup> generation Grubbs catalyst in a homogeneous system were as follows: 0.016 g catalyst was added to a 4% NBR solution in 200 mL chlorobenzene, the

reaction temperature was 125 °C, and the reaction time was 24 h.

## 2.2. Synthesis and characterization of EF-HNBR

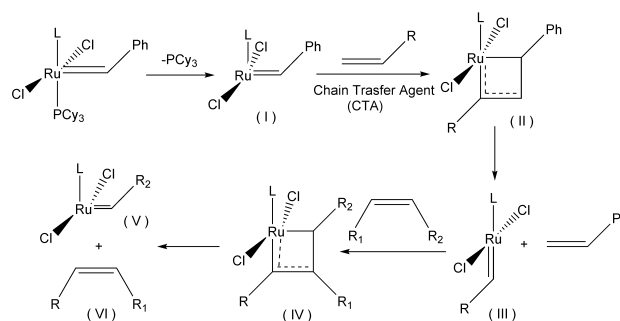
The objective is to prepare ester end-functionalized hydrogenated nitrile-butadiene rubber (EF-HNBR) that have a high degree of hydrogenation and a designated structure. We anticipated that combining the functional metathesis with the metathesis hydrogenation was a valuable approach. To our knowledge, no example of such a combined one-step functional metathesis and metathesis hydrogenation has been reported. Methyl methacrylate was chosen as the functional monomer in the present study due to its wide industrial availability. Then, the cross metathesis functionalized hydrogenation of NBR was investigated using 2<sup>nd</sup> generation Grubbs catalyst in the presence of methyl methacrylate as the CTA. The most relevant results are reported in Table 3. The mechanism of the olefin metathesis reaction has been reported by Chauvin et al.<sup>[41]</sup> (Scheme 4). The key step is the formation of a tetratomic-ring structure between the transition metal catalyst



**Scheme 3.** Proposed catalytic cycle for the olefin metathesis hydrogenation.

**Table 3.** Hydrogenation degree of the products obtained by the functional metathesis hydrogenation of NBR using the 2<sup>nd</sup> generation Grubbs catalyst in the presence of a functional olefin as CTA.

Entry	Temperature/°C	Catalyst/g	[CAT]/[NBR]	Time/h	HD/%
1	125	0.016	1:6	42	92
2	125	0.016	1:3	42	85
3	125	0.016	1:2	42	81
4	125	0.012	1:3	42	69
5	125	0.018	1:3	42	95



**Scheme 4.** Initiation step of the ruthenium complex bearing the N-heterocyclic carbene ligand.

and the carbon-carbon double bonds, through which new carbon-carbon double bonds are created.

Under the optimal hydrogenation reaction conditions, we studied the influence of [CTA]/[NBR] on hydrogenation degree (entry 1–3, Table 3). It was found that the degree of hydrogenation decreased with the increase of [CTA]/[NBR], which may have been due to the ability of the carbonyl oxygen of the excessive monomer to coordinate with the 14-electron Ru-alkylidene active center to form a stable complex, which impeded the metathesis hydrogenation reaction.<sup>[22]</sup> With the further increase of the amount of catalyst (entry 5, Table 3), the hydrogenation degree could reach 95%.

FT-IR and the <sup>1</sup>H-NMR spectroscopy of the functional metathesis hydrogenation products was carried out to confirm the formation of the well-defined modified polymer. Figure 2 shows the FT-IR spectra of NBR, HNBR, and EF-HNBR. The C=C double bonds were indeed hydrogenated, as evidenced by the disappearing peaks at 970 cm<sup>-1</sup> and 917 cm<sup>-1</sup> that are attributed to the 1,4-CH=CH- and 1,2-CH=CH<sub>2</sub> wagging vibrations. Instead, the bands of the saturated C-H in the methylene groups at 720 cm<sup>-1</sup> became much stronger. In addition, the absorbance peak of the -C≡N group at 2230 cm<sup>-1</sup> remained unchanged. The only difference in the spectra is the absorption at 1734 cm<sup>-1</sup>. It corresponds to the C=O stretching vibration of the acrylic ester. This provided sufficient evidence that the ester end-functionalized hydro-

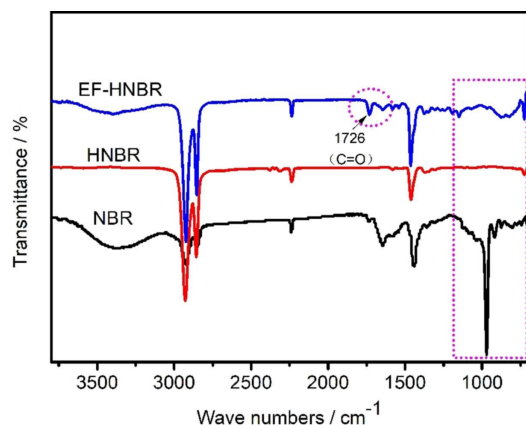


Figure 2. FT-IR spectra of the NBR, HNBR (entry 20, Table 1), and EF-HNBR (entry 5, Table 3).

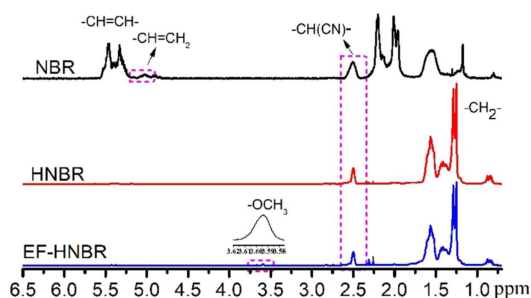


Figure 3. <sup>1</sup>H-NMR spectrum of NBR, HNBR (entry 20, Table 1), and EF-HNBR (entry 5, Table 3).

genated nitrile-butadiene rubber (EF-HNBR) was successfully prepared.

We thereby confirmed that the 2<sup>nd</sup> generation Grubbs catalyst reacts with CTA to form a new ruthenium carbene molecule (III, Scheme 4). This new catalyst (III, Scheme 4) undergoes metathesis hydrogenation with the double bonds of NBR to form the ester end-functionalized hydrogenated nitrile-butadiene rubber (EF-HNBR). Therefore, the one-step hydrogenation and functionalization reactions can continuously take place in a catalytic fashion.

Figure 3 shows the macromolecular structure of EF-HNBR confirmed by <sup>1</sup>H-NMR. The characteristic peaks at 5.4 ppm for the -CH=CH- protons and at 5.0 ppm for the protons of the 1,2-butadiene double bond (2H, -CH=CH<sub>2</sub>) decreased or disappeared after hydrogenation with the 2<sup>nd</sup> Grubbs catalyst. The chemical shift at 2.5 ppm for the protons adjacent to the nitrile (-C≡N) groups did not change, as reported previously. However, the chemical shift at  $\delta = 1.25$  ppm corresponding to the protons in the methylene units increased in intensity, indicating that the -C=C- double bonds in both the 1,2- and the 1,4-units were successfully hydrogenated whereas the nitrile groups remained intact.

After the functional metathesis hydrogenation of the NBR, we observed new peaks in the <sup>1</sup>H-NMR spectrum (Figure 3) at 3.6 ppm that were attributed to the methyl ester group (-OCH<sub>3</sub>). This indicates the successful end capping of the acrylic ester.

### 2.3. Thermal Properties of the functionalized polymer

The thermal properties of the materials are important for their practical applications. The glass transition temperature (T<sub>g</sub>) determines whether a material is an elastomer at the end-use temperature. As seen in Figure 4, the increase of the degree of hydrogenation and the introduction of CTA had little increases on the T<sub>g</sub> of the functionalized polymer. Moreover, neither of the three curves showed any crystallization peak, indicating that the functionalized polymer was still amorphous.

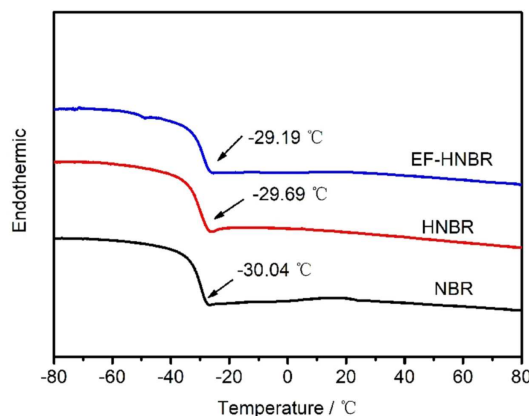


Figure 4. DSC thermograms of NBR, HNBR (entry 20, Table 1), and EF-HNBR (entry 5, Table 3).



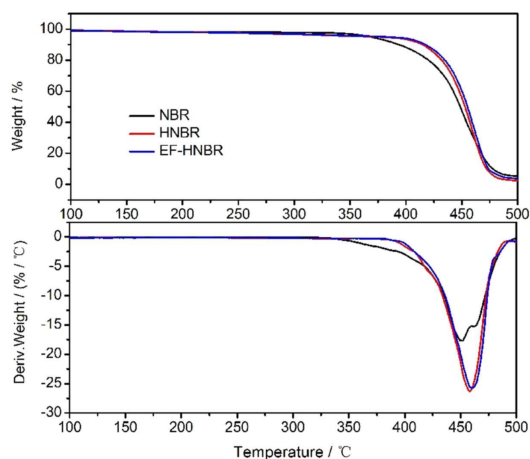


Figure 5. TGA curves of NBR, HNBR (entry 20, Table 1), and EF-HNBR (entry 5, Table 3).

The thermo-gravimetric analysis (TGA) of NBR, HNBR, and EF-HNBR was carried out in a nitrogen atmosphere (Figure 5). For all samples, the thermal degradation only occurred in one stage. By comparison with the functionalized polymer (HNBR and EF-HNBR), NBR decomposed more easily with a lower degradation temperature of 448 °C. Since all C=C double bonds in the functionalized polymer have been completely hydrogenated into saturated methylene groups, it had a better thermal stability with a higher degradation temperature at 460 °C. Besides, the thermal degradation of EF-HNBR was also slightly improved due to the existence of the ester groups.

### 3. Conclusions

We expose the first efficient one-step combination of a functional metathesis with metathesis hydrogenation of commercial nitrile butadiene rubber (NBR) using a ruthenium catalyst and a functional olefin as chain-transfer agent to produce ester end-functionalized hydrogenated nitrile butadiene rubber (EF-HNBR). The advantage of our method lies in the short synthesis path, the high yield, and of the compliance with green chemistry requirements. Under the optimal operating conditions, a hydrogenation degree of at least 95% was obtained in the modified polymer, which had a moderate molecular weight and a higher thermal stability. The highest catalytic activity and selectivity were simultaneously achieved using the ruthenium metathesis catalyst. The polymer obtained using this system has a lower Mooney viscosity compared with that obtained using a traditional catalytic hydrogenation process. In addition, it has overcome the low degree of hydrogenation and processing difficulties caused by the much lower molecular weight of the polymer obtained using the 2<sup>nd</sup> generation Grubbs catalytic hydrogenation. The use of the rubber products has been enhanced by the introduction of the polar ester group due to the improved adhesion properties between the rubber and the reinforcing materials, for instance. More importantly,

our results pave a new way for the precise synthesis of the end-functionalized saturated polymers in one single step.

## Experimental Section

### Materials

Nitrile butadiene rubber (NBR 3330F) was supplied by Lanxess (Germany) with an acrylonitrile content of 33%, ML (1+4) 100 °C 30 ± 3, Mw of 24.44 × 10<sup>4</sup>, and Mw/Mn of 2.47, to be used directly without any pretreatment.

Benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium (2<sup>nd</sup> generation Grubbs catalyst, 98%) was purchased from the Shanghai Coach Chem Technology Co., Ltd. Methyl methacrylate was purchased from the Shanghai Chemical Reagents Co. Ltd. and used without further purification. All other reagents were of analytical grade and were used directly without any pre-treatment. Deionized water, nitrogen gas (ultra-high purity), and oxygen-free hydrogen gas (99.99%) were used throughout this work.

### Analysis and Characterization

The FT-IR spectra of the polymers were recorded on a Nicolet 5700 spectrometer within 500–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> using KBr plates. The <sup>1</sup>H-NMR spectra were recorded on a Bruker 300 Fourier transform spectrometer at 300.13 and 100.62 MHz in CDCl<sub>3</sub> and by using tetramethylsilane (TMS) as the internal standard. The average molecular weight (Mw) and distribution (Mw/Mn) of the polymers were determined using a Viscotek TDA 302 GPC instrument with THF as the mobile phase with a flow rate of 1.0 ml/min at 30 °C, after calibration with polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo (Greifensee, Switzerland) DSC instrument under a nitrogen atmosphere at a heating rate of 10 °C/min from –100 to 100 °C. The thermo-gravimetric analysis (TGA) was carried out in a nitrogen atmosphere on a TA Q500 TGA analyzer. The samples were heated from 30 to 600 °C at a rate of 10 °C/min.

### Synthesis of Hydrogenated Nitrile Butadiene Rubber (HNBR)

The metathesis hydrogenation of nitrile butadiene rubber (NBR) was carried out in a 300 mL autoclave reactor. The desired amount of nitrile butadiene rubber was dissolved into a degassed chlorobenzene (200 mL) to obtain a solution with concentration of 4%. Then, a solution of the 2<sup>nd</sup> Grubbs catalyst in toluene (6 mL) was purged with nitrogen and stirred for 15 min. The mixed solution of 2<sup>nd</sup> Grubbs catalyst was then transferred into the NBR solution using a degassed syringe. The reactor was sealed and flushed with H<sub>2</sub> to remove N<sub>2</sub> for at least 1 h at room temperature and stirred at 1000 rpm. Then, the mixture was brought to the desired pressure and temperature. The hydrogenated product was precipitated in ethanol after the reaction was complete and allowed to cool down. Then, it was washed with ethanol three times and dried at 105 °C. The hydrogenation degree (HD%) was determined by bromo-iodometry according to GB1676-81 (Chinese National Standards), with an absolute deviation of iodine value < 0.15.

We investigated the effect of the reaction conditions, including the reaction temperature, the reaction time, and the concentration of catalyst, on the hydrogenation degree of the products.

## Synthesis of End-Functionalized Hydrogenated Nitrile Butadiene Rubber (EF-HNBR)

The ester end-functionalized hydrogenated nitrile-butadiene rubber (EF-HNBR) was synthesized in the presence of a functional olefin as a chain transfer agent (CTA) and the 2<sup>nd</sup> Grubbs catalyst. The conditions of the addition of the catalyst and the treatment of the reaction products are the same as mentioned above except that a certain amount of functional monomer (MMA) and 2<sup>nd</sup> generation Grubbs catalyst were added into the reactor sequentially using a syringe.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** nitrile-butadiene rubber · functional metathesis · hydrogenation reactions · end-functionalized saturated polymers · one-step synthesis

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