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An Efficient Synthesis, Evaluation of Parameters and Characterization of Nitro-Hydroxyl-Terminated Polybutadiene (Nitro-HTPB)

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Abstract: This article reports the nitration of Hydroxyl-Terminated Polybutadiene (HTPB) backbone by facile and efficient "one pot" procedure, resulting in the formation of conjugated nitro-alkene derivative of HTPB. The reaction was carried out with sodium nitrite and iodine. In order to optimization of the effective parameters on the synthesis of Nitro-HTPB, the proportional amounts of reactant, amount of solvent and temperature were investigated and the effect of these parameters on the nitration double bond on HTPB backbone was evaluated. The product Nitro-HTPB was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy as well as DSC, and TG.

Keywords: Hydroxyl-Terminated Polybutadiene (HTPB) · Nitro-Hydroxyl-Terminated Polybutadiene (Nitro-HTPB) · Functionalization of polymer · Conjugated nitro-alkene · Nitro olefine

1 Introduction

Nitro compounds, particularly conjugated nitro olefins, have great importance in synthetic organic chemistry [1]. Synthesis of nitro olefin *via* incorporation of a nitro group directly into the olefin is a powerful and preferred class of reactions. However, to obtain nitro olefins directly from olefins, different nitrating agents such as HNO_3/H_2SO_4[2a], $NaNO_2/HgCl_2$ [2b], $AgNO_2/I_2$ [2c], NO [2d], NO_2/O_3 [2e], $NaNO_2/Cu(II)-I_2$ [2f], $AgNO_2/CH_3COCl$ [2b], and $Fe(NO_3)_3$ [2h] have been employed so far [2]. Hydroxyl-terminated polybutadiene (HTPB) is a classic pre-polymer for the binder system of composite solid propellants, widely used for the propellant systems of military and space applications [3–12]. It is a low molecular weight telechelic liquid rubber, translucent liquid rubber which finds a wide range of applications. The presence of double bonds and hydroxyl end groups can be effectively utilized to chemically modify into various functional groups such as epoxy, urethane, urethane methacrylate, carboxylic acid, ester, amine etc. Further, terminal carbon atom can be also be functionalized. If HTPB is suitably functionalized with energetic groups, it is expected to contribute to the performance of the propellant in addition to its unique physico-chemical properties. Based on this philosophy some works have been reported in the literature in previous years to modify the HTPB by attaching energetic functionality into the backbone without destroying its excellent physico—chemical properties [13–15]. For example, the grafting of energetic polymers such as poly (glycidyl azide) onto HTPB [14], coordination of iron to the HTPB backbone to enhance the burn rate of the composite solid propellant [15], modification of HTPB by covalently attaching the 2, 4 dinitrochlorobenzene (DNCB) [16] and functionalization of HTPB by azide to impart energetic properties to the polymer by using two different synthetic approaches [17] has also been tried in the literature. Nitration of HTPB will impart greater energetic properties in HTPB, therefore in the current work efforts were made to functionalize HTPB with nitro groups.

There have been numerous attempts to nitration of the HTPB backbone by a few different reaction pathways: the classical method which employs a nitromercutation-demercutation route, or alternatively, by epoxidation of HTPB and the nitrating with dinitrogen pentaoxide. It has been observed that up to 10% nitration on the HTPB backbone gives a good balance of energy output, mechanical properties and miscibility with energetic plasticizers [13]. Also, Nitryl iodide (NO_2I) is the active reagent during the process of nitration of HTPB, generated in situ by reaction of $NaNO_2$ and iodine, has been reported in literature [18]. Herein, we report, the synthesis of Nitro-HTPB, optimization of the effective parameters and evaluation of the effect of these parameters on the nitration percentage of the double bond on HTPB and the yield of the product.

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2 Experimental Section

2.1 General

HTPB used for the synthesis was obtained from Shandong china (mainland). Its number average molecular weight and hydroxyl value were determined as 2550 g mol^{-1} (by Vapor Pressure Osmometer) and 44 mg KOH per g, respectively. All solvents and chemicals were of analytical grade, supplied by Merck Company and used as received without any further purification. Nuclear magnetic resonance (NMR) spectra of the polymers was recorded in a Bruker Avance 400 MHz spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz), using CDCl$_3$ as solvent. FT-IR spectra of the samples were performed by Bruker Vector 22, by preparing their potassium bromide (KBr) pellets. The $\bar{M}_n$ of the samples were measured by an GPC Agilent 1100 using tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 25 °C. Differential scanning calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) were performed with NETZSCH STA-409 in the temperature range of 50 to 600 °C at 10 °C/min under 20 mL/min N$_2$ flow. The viscosity determinations were measured with a LDVD-II Brookfield viscometer.

2.2 Synthesis

HTPB (51 g, 20.0 mmol), sodium nitrite, ethylene glycol and water were dissolved in ethyl acetate in a round-bottomed flaskin accordance with the examples listed in the Table 1 and Table 2. Reaction content was stirred for 10 min. Iodine was now slowly added for 15 min to the reaction flask and stirring continued for appropriate times at temperatures consistent with the Tables 1 and 2. At the end of the reaction, a solution of 10 % sodium thiosulphate was added to the reaction mixture until decolorize. Then, the organic layer was separated and evaporated under reduce pressure to get the reddish brown viscous liquid product. Finally, the crude product was washed with methanol until the impurities are separated and pure product is obtained.

**Table 1.** Evaluation of parameters for the synthesis of Nitro-HTPB at 0–25 °C.

Entry	EtOAc (ml)	NaNO$_2$ (mmol)	I$_2$ (mmol)	Nitration (%)	Time (h)	Yield (%)
1	300	640	240	3.2	96	84
2	600	640	240	7.3	96	84
3	1200	640	240	3.2	96	91
4	600	320	120	2.6	96	90
5	600	426.5	160	5.7	96	86
6	600	1280	480	16.2	96	78
7	300	320	120	5.8	96	93

Table 2. Evaluation of parameters for the synthesis of Nitro-HTPB at 25 °C.

Entry	EtOAc (ml)	NaNO$_2$ (mmol)	I$_2$ (mmol)	Nitration (%)	Time (h)	Yield (%)
1	600	640	240	8.0	144	85
2	300	320	120	4.0	144	85
3	600	320	120	5.1	144	89
4	600	426.5	160	5.8	144	92

3 Results and Discussion

The reported method provides a highly efficient mean for the synthesis of Nitro-HTPB following a one pot process. The synthesis procedure with optimized molar ratios of reactants and solvent to obtain a good energetic plasticizer for binder systems in energetic formulations is reported in this paper. Initially, one-pot reaction of HTBP (20.0 mmol), sodium nitrite (640.0 mmol), Iodine (240.0 mmol), ethylene glycol (25 ml), H$_2$O (60 ml) and EtOAc (300 ml) was performed under 0–25 °C. This reaction was regarded as the model reaction (Scheme 1). The model reaction was conducted for 96 h. With prolonged reaction time 3.2 % nitration on the HTPB backbone with 84 % yield was obtained (Table 1, entry 1). Increasing amount of EtOAc from 300 ml to 600 ml, did not significantly affect the yield, whereas double bond nitration percentage resulted in a remarkable increase (7.3 %) (Table 1, entry 2). However, increasing amount of EtOAc to 1200 ml, did not significantly affect the nitration but it was observed that the yield of the product was improved to 91 % (Table 1, entry 3).
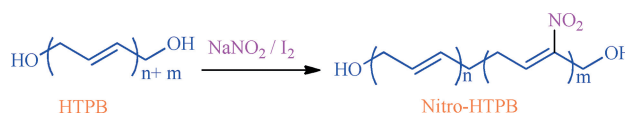
Scheme 1. Synthesis of Nitro-HTPB.

The scope of this process was illustrated by use of different amount of sodium nitrite and Iodine. It was found that by increasing the amount of sodium nitrite and iodine, the efficiency of the process decreases, but the percentage of nitration on the HTPB backbone increases (Table 1, entries 4, 5 and 6). Next, we decreased the amount of sodium nitrite, iodine, ethyl acetate, water and ethylene glycol by half under the same reaction conditions and investigated the effects of them on the product. It was observed that up to 5.8 % nitration on HTPB backbone in the highest yield (93 %) of the product (Table 1, entry 7).

In order to study the temperature effect, nitration on HTPB backbone was carried out at 25 °C and the effect of parameters was investigated. As indicated in Table 2, by increasing temperature the reaction time increases.

As indicated in Table 1 and Table 2, by increasing amount of sodium nitrite and I$_2$ the percentage of nitration on double bond on HTPB increases in both temperature conditions 0 °C and 25 °C. However, the best yield of the desired product was achieved by performing the reaction with the half amount of substrates and solvents relative to the model reaction at 0 °C and the mentioned reaction conditions in Table 2, entry 4 at 25 °C. The mechanism suggested for synthesis of Nitro-HTPB probably proceeds via in situ generation of NO$_2$I by reaction of NaNO$_2$ and iodine, followed by addition of NO$_2$I to the double bond in HTPB and forms nitro iodo derivative. Then, by elimination of HI under reaction condition to give conjugated nitro olefin derivative of HTPB.

Figure 1 indicates that by increasing temperature 0 °C to 25 °C in the EtOAc (600 ml) and sodium nitrite (320 mmol), the percentage of nitration on the HTPB backbone increases, whereas, by decreasing volume of EtOAc to 300 ml the percentage of nitration decreases. But a slight increase in percentage of nitration on the HTPB is observed in the EtOAc (600 ml) and sodium nitrite (426.5 mmol).
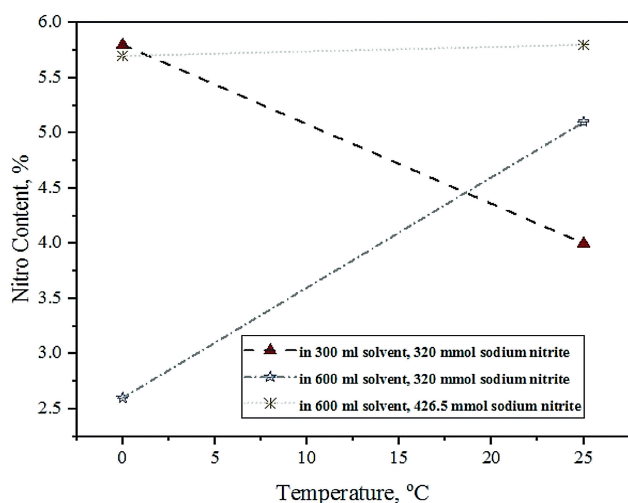

Figure 2. Variation of product yield in terms of temperature.

Figure 1. Variation of nitration in terms of temperature.

Figure 2 shows that by increasing temperature 0 °C to 25 °C in the EtOAc (600 ml) and sodium nitrite (426.5 mmol), the yield of the product increases, whereas by increasing temperature 0 °C to 25 °C in the EtOAc (300 ml) and sodium nitrite (320 mmol), the yield of the product decreases. But a slight decrease is observed in product yield in the EtOAc (600 ml) and sodium nitrite (320 mmol). It should be noted that all of the lines in the Figures 1 and 2 have been produced from a number of experiments and the rest of the points removed for the simplicity of the lines.

We have characterized the Nitro-HTPB sample using FTIR, ^{1}H and ^{13}C NMR. The FTIR spectra of Nitro-HTPB compound (Table 1, entry 7) along with HTPB is shown in Figure 3. The FTIR spectrum (Figure 3b) of the Nitro-HTPB com-
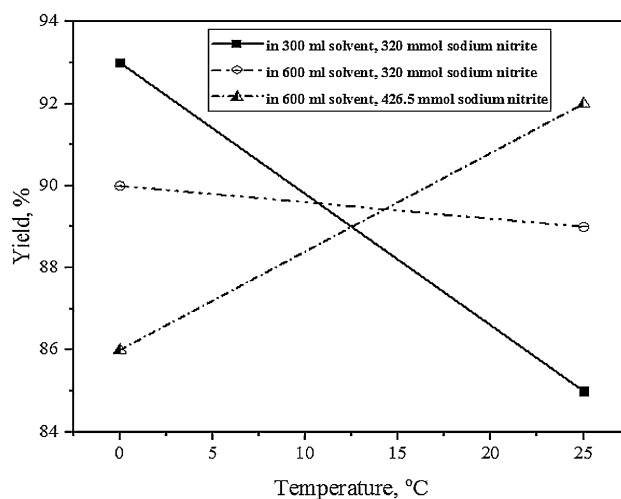
pound shows peaks for α,β-unsaturated nitro olefin at 1521 cm^{-1} and 1337 cm^{-1} belongs to the NO$_2$ asymmetric and symmetric stretch, which are absent in HTPB. Also, the other relevant peaks are in accordance with Pant et al. [18b]. Hence, the presence of OH stretching in the FTIR spectrum (Figure 3) of the Nitro-HTPB clearly proves that the modification of the HTPB backbone by nitration does not kill the availability of the free OH groups.

Figure 4 shows the ^{1}H NMR spectra of HTPB and Nitro-HTPB compound (5.8 %) in CDCl$_3$ solvent. ^{1}H NMR of Nitro-HTPB showed distinct signals at around δ = 7.1 ppm is due to the β-proton of α,β-unsaturated nitro olefin segment of the Nitro-HTPB and a signal at around δ = 2.6 ppm is due to deshielded aliphatic protons according to Pant et al. [18b], whereas these signals are absent in the HTPB backbone spectrum which further confirmed the formation of the product. The amount of NO$_2$ groups is determined by comparison of peak areas in ^{1}H NMR at δ = 7.1 ppm and δ = 4.9–5.6 ppm. Based on ^{1}H NMR studies it was found that approximately 5.8 % of the olefinic carbons were functionalized with NO$_2$ groups.

Figure 5 shows the ^{13}C NMR spectra of the HTPB and Nitro-HTPB (5.8 %) in CDCl$_3$ solvent. The peak in the δ = 151 ppm region corresponds to olefinic carbon bearing NO$_2$ of Nitro-HTPB. This peak is absent in the HTPB indicating the presence of NO$_2$ in the modified HTPB sample. The other chemical shift regions of the Nitro-HTPB compound are identical with the parent HTPB. Thus, we can conclude that FTIR, ^{1}H NMR, and ^{13}C NMR analysis revealed the covalent attachment of NO$_2$ onto the HTPB backbone.

Thermogravimetric analysis curves of Nitro-HTPB (5.8 % nitration) at a heating rate of 10 °C/min up to 600 °C are shown in Figure 6. TG thermogram of Nitro-HTPB showed distinct first step decomposition at 170 and 240 °C corresponding to 6.24 % weight loss, which represents loss of NO$_2$ groups.
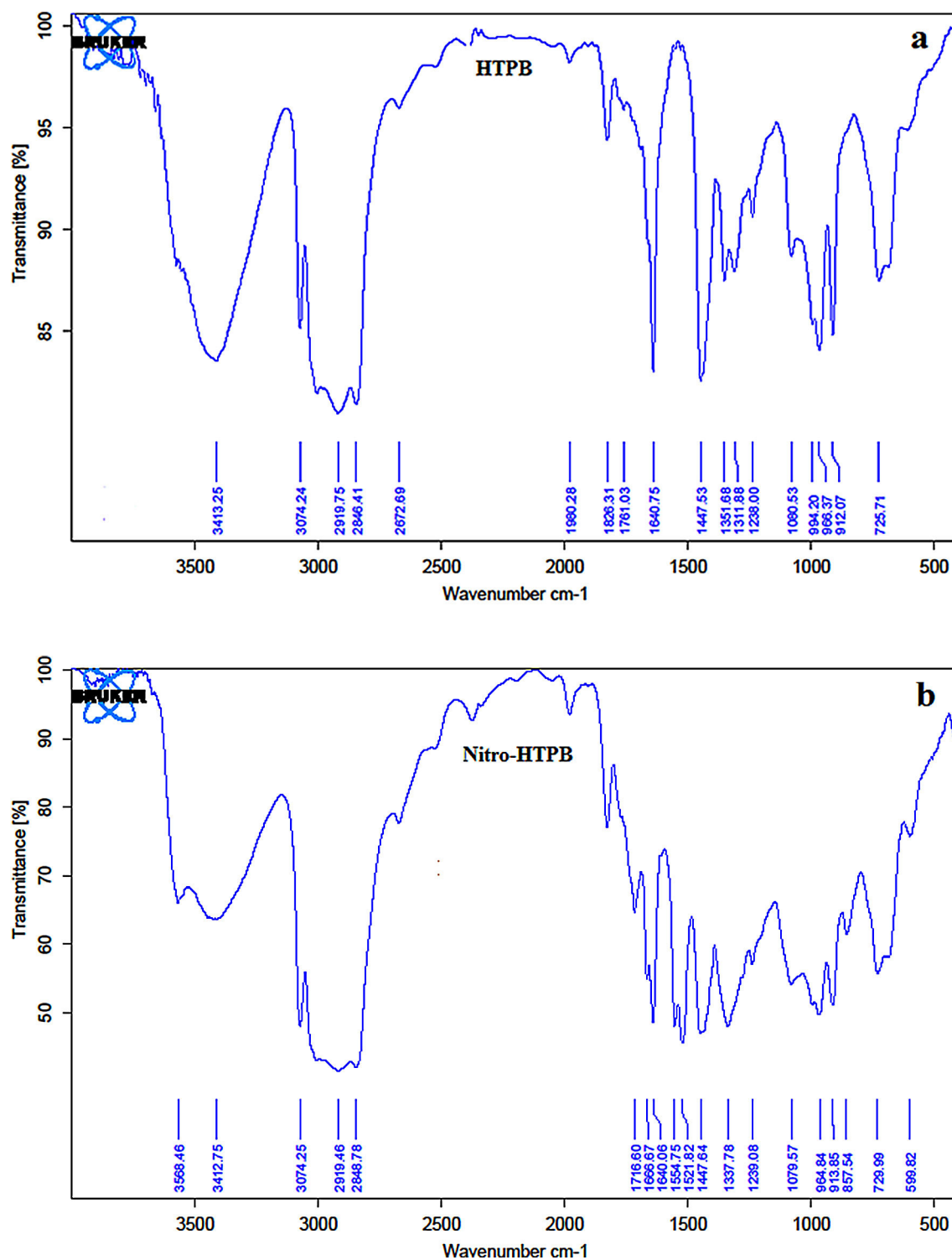
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Figure 3. FTIR spectra of the (a) HTPB and (b) Nitro-HTPB.

Figure 7 shows the DSC thermograms of HTPB and Nitro-HTPB samples heated at 10 °C min^{-1} up to 500 °C. Nitro-HTPB sample showed an exothermic decomposition with the peak temperature 170–240 °C.

The viscosity of the HTPB, Nitro-HTPB (Table 1, entry 7) and Nitro-HTPB (Table 2, entry 4) was measured with a viscometer and was found to be 6.1, 14.6, and 15 Pa s^{-1} at 30 °C, respectively. There was a significant rise in viscosity when
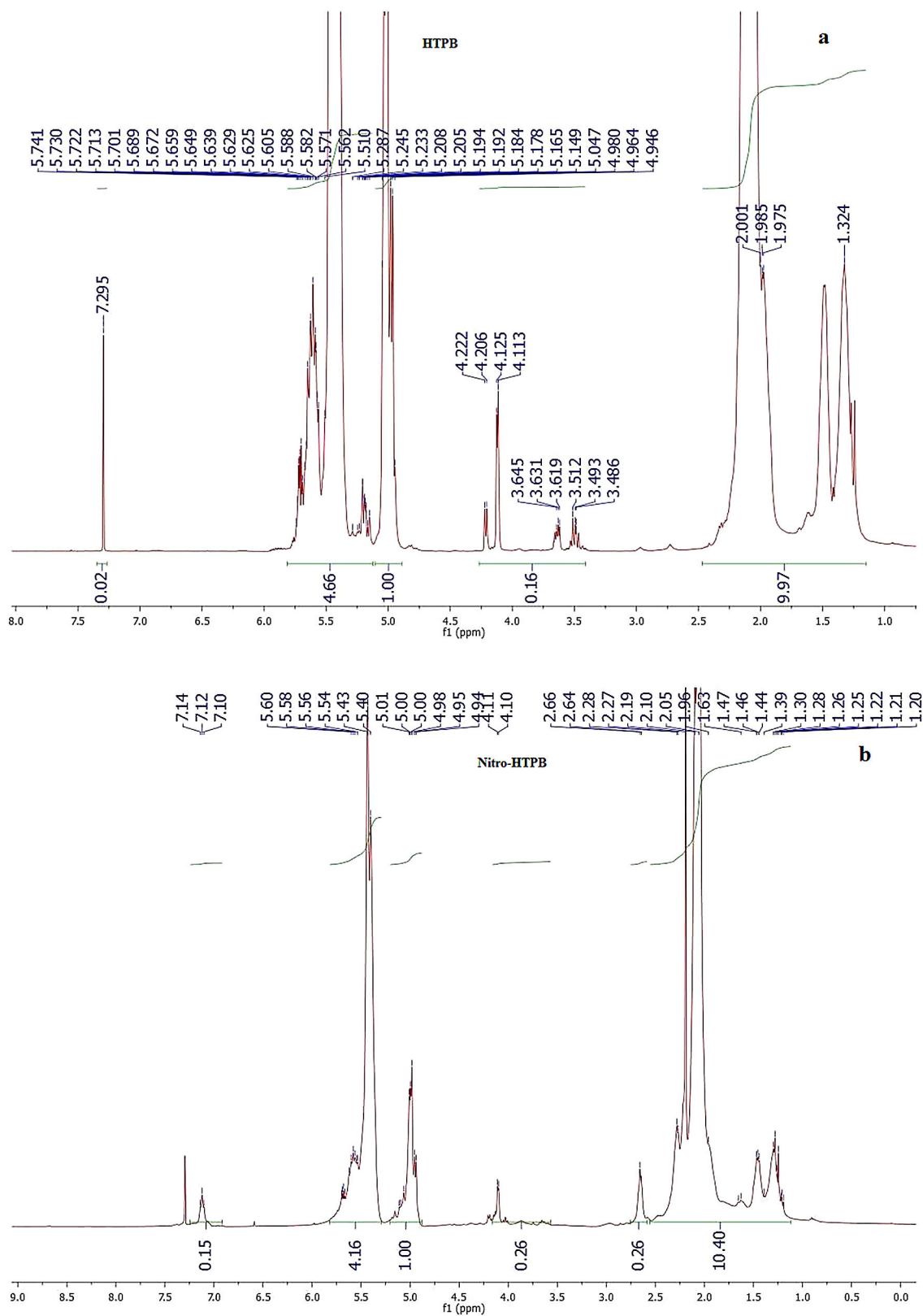
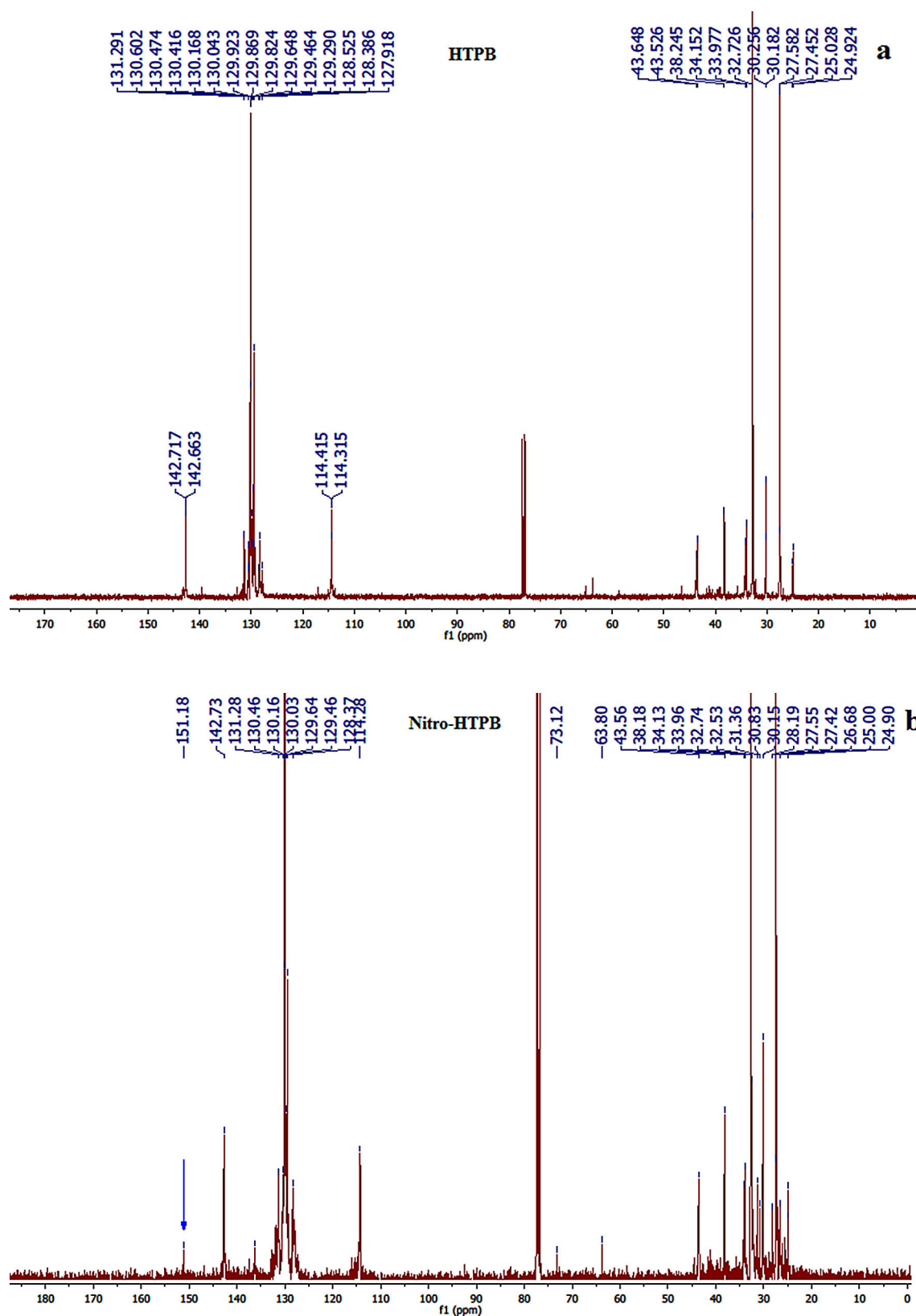**Figure 4.** ¹H NMR spectra of the (a) HTPB and (b) Nitro-HTPB.

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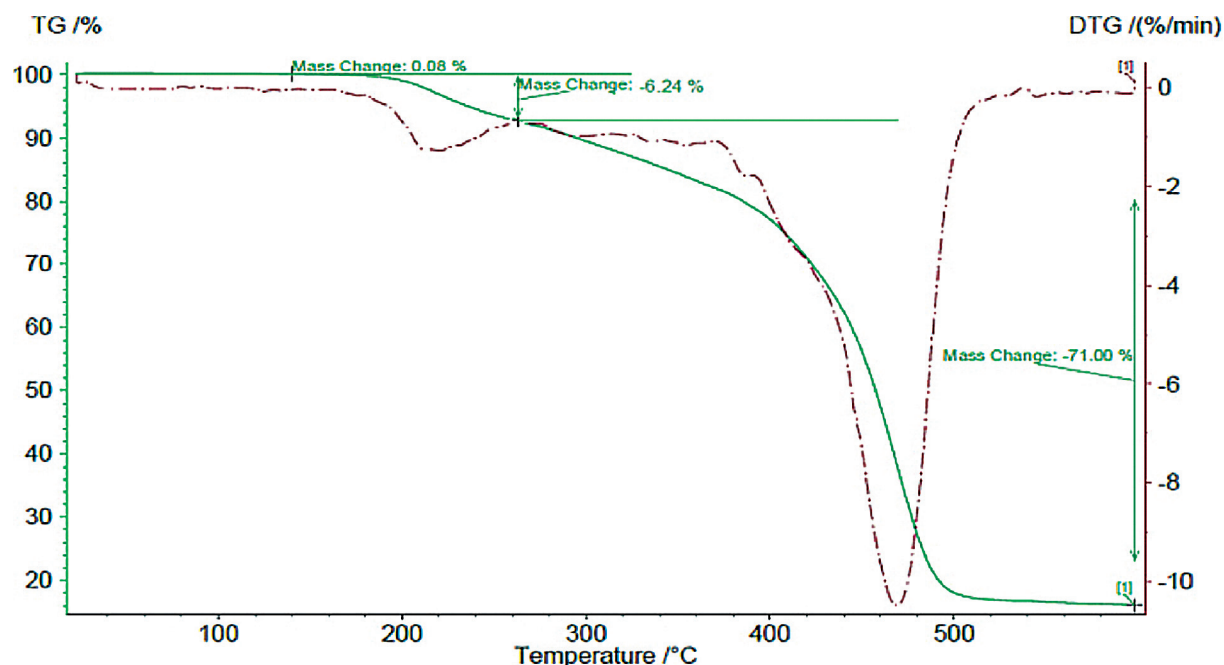**Figure 5.** ^{13}C NMR spectra of the (a) HTPB and (b) Nitro-HTPB.

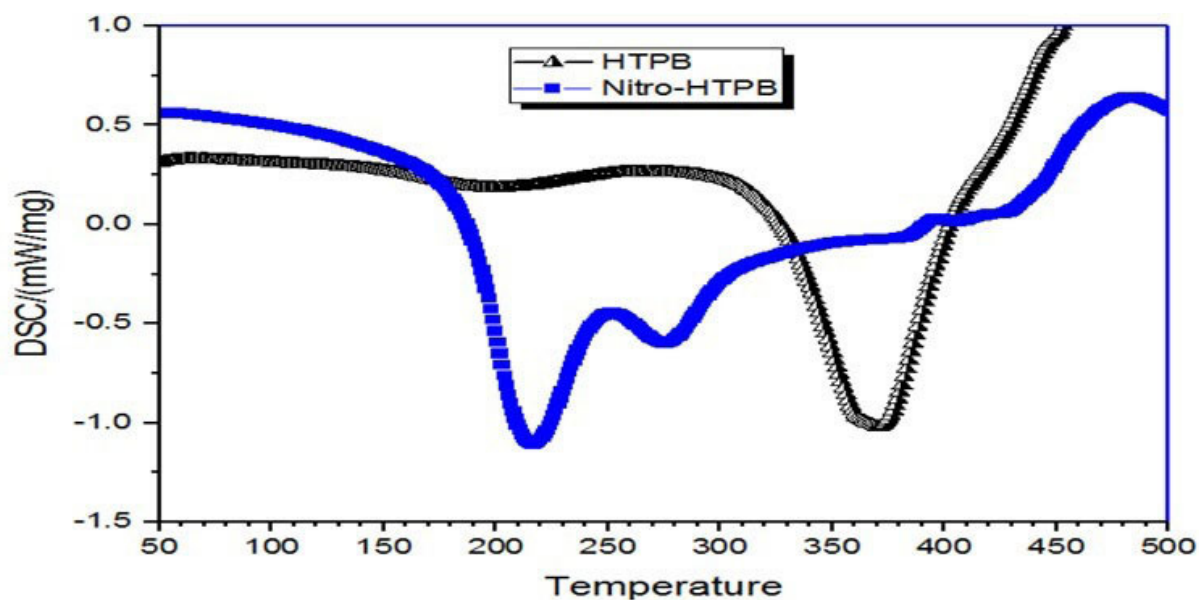**Figure 6.** TG thermogram of Nitro-HTPB with a heating rate at $10\,°C\,min^{-1}$.

Figure 7. DSC curves of HTPB and Nitro-HTPB with a heating rate at $10\,°C\,min^{-1}$.

nitration of double bonds of HTPB were carried out. An increase in viscosity after nitration of HTPB was expected because attaching polar group increases the viscosity of a polymer by strong polar interactions between the polymer chains. Number average molecular weight and specific gravity were measured as $2550\,g\,mol^{-1}$, $2740\,g\,mol^{-1}$ and $2780\,g\,mol^{-1}$, respectively (Table 3). Determination of hydroxyl value of the HTPB, Nitro-HTPB (Table 1, entry 7) and

Nitro-HTPB (Table 2, entry 4) was carried out by acetylation method and was found to be 38 mg KOH per g, 32 mg KOH per g and 30 mg KOH per g., respectively (Table 3).

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Table 3. Properties of HTPB and Nitro-HTPB.

Sample	Molecular weight, M_n/ g mol^{-1}	Viscosity at 30 °C/ Pa s^{-1}	Hydroxyl value/ mg KOH per g
HTPB	2550	6.1	38
Nitro-HTPB (5.8 %) at 0–25 °C	2740	14.6	32
Nitro-HTPB (5.8 %) at 25 °C	2780	15	30

4 Conclusions

We have functionalized the HTPB backbone by attaching the NO$_2$ group without destroying the unique physico–chemical properties of HTPB at 0–25 °C and room temperature. The best nitration percentage of the HTPB backbone (5.8 %) and Nitro-HTPB yield (93 %) were obtained when the reaction of HTPB (20.0 mmol) was carried out with sodium nitrite (320 mmol) and iodine (120.0 mmol) in EG (25 ml), EtOAc (300 ml) and H$_2$O (60 ml) for 96 hours at 0–25 °C. Also, the best conditions at room temperature with 5.8 % nitration and 92 % yield of the product were obtained when the reaction of HTPB (20.0 mmol) was carried out with sodium nitrite (426.5 mmol) and iodine (160.0 mmol) in EG (25 ml), EtOAc (600 ml) and H$_2$O (60 ml) for 144 hours. The functionalized polymer was analyzed for structural confirmation and determination of important physical and thermal properties. The FTIR, ^{1}H NMR, and ^{13}C NMR analysis revealed the covalent attachment of NO$_2$ onto the HTPB backbone. All of the effective parameters on the nitration double bond on HTPB were evaluated. TG thermogram of Nitro-HTPB represents loss of NO$_2$ groups. Nitro-HTPB obtained by nitration of 5.8 % double bonds of HTPB showed viscosity of 14.6 Pa s^{-1} and 15 Pa s^{-1}.

Acknowledgements

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