Preparation of hydroxyl-terminated polybutadiene via oxidation-reduction method using alcohol catalysts

Ly Quoc Vuong[1*], Nguyen Manh Tuong[1], Doan Minh Khai[2]

[1]Institute of Materials, Biology and Environment, Academy of Military Science and Technology, 17 Hoang Sam, Nghia Do, Hanoi, Vietnam;
[2]Faculty of Special Equipment, Le Quy Don Technical University, 236 Hoang Quoc Viet, Nghia Do, Hanoi, Vietnam.
[*]Corresponding author: vuong.hvktqs@gmail.com
Received 6 Aug. 2025; Revised 3 Oct. 2025; Accepted 16 Oct. 2025; Published 18 Nov. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.IMBE.2025.70-75

ABSTRACT

Conventional methods for synthesizing hydroxyl-terminated polybutadiene (HTPB) with high cis-1,4 content typically involve multi-step oxidation-reduction processes, hindered by poor solubility of sodium borohydride in low-polarity solvents, resulting in low efficiency during the reduction of aldehyde-terminated polybutadiene. A one-pot synthesis approach that incorporates alcohol catalysts to enhance reduction performance is presented in this study. The study results show that ethanol significantly improved reduction efficiency, achieving near-complete conversion of carbonyl to hydroxyl groups within 15 minutes at 30 °C. The resulting HTPB possessed a cis-1,4 content of approximately 95%, with a molecular weight of ~4,880 g.mol^{-1}, a hydroxyl value of 0.78 mmol.g^{-1} and a glass transition temperature of T_g = -92.1 °C.

Keywords: Hydroxyl-terminated polybutadiene (HTPB); Alcohol catalyst; Sodium borohydride reduction.

1. INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is a liquid polymer characterized by reactive terminal hydroxyl groups, extensively utilized in both military and civilian applications. In defense systems, it serves as a binder in solid propellants and polymer-bonded explosives (PBXs), while in civilian industries, it functions as a key component in adhesives, coatings, sealants, and film-forming agents [1-3]. The microstructure of HTPB typically comprises three types of structural units: cis-1,4; trans-1,4; and vinyl-1,2 (figure 1). HTPB with a high cis-1,4 content (cis-HTPB) exhibits a low glass transition temperature (T_g = -104.7 °C for x ≥ 95%; T_g = -108 °C for x ≥ 98%), thereby enabling excellent resistance to low-temperature environments.

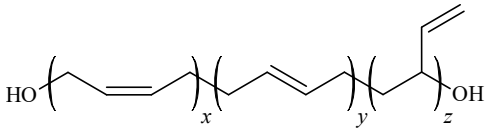

Figure 1. *Microstructure of HTPB.*

HTPB is typically synthesized from 1,3-butadiene via free radical polymerization [4] and anionic polymerization [5]. The microstructure, molecular weight, and molecular weight distribution of HTPB are influenced by factors such as the type of initiator, solvent polarity, and polymerization temperature. According to the literature [4], HTPB obtained through free radical polymerization exhibits a maximum 1,4-unit content of 79%, a functionality ranging from 2.1 to 2.3, and a polydispersity index (PDI) of approximately 2.0. In contrast, anionic polymerization yields HTPB with a higher 1,4-unit content of up to 90% (cis-1,4: 35.2%), a degree of functionality approaching 2.0, and a narrower PDI of around 1.0 [3, 5]. These findings indicate that accurately controlling the microstructure of HTPB remains challenging in conventional free radical or anionic polymerization processes.

Zhou et al. demonstrated that ATPB can be readily obtained through chain scission following

the reaction of cis-polybutadiene with H_5IO_6. Based on this approach, $NaBH_4$ was employed as a reducing agent to convert the aldehyde groups into hydroxyl groups, resulting in the formation of HTPB with a cis-1,4 structure content of 95% [3]. Each intermediate product must be separated after every step, rendering the overall process complex and relatively inefficient.

Deqian Meng et al. synthesized cis-HTPB from cis-polybutadiene via a one-pot method. The synthesis comprises two steps: step one involves the oxidative cleavage of double bonds using H_5IO_6 to form ATPB; step two reduces ATPB to HTPB using $NaBH_4$ [6]. However, $NaBH_4$ is almost insoluble in the chloroform/tetrahydrofuran (THF) solvent mixture employed for the reaction, which results in a prolonged reaction time required for the reduction of ATPB to HTPB. Tanemura studied the reduction of aldehyde and ketone functional groups of acetophenone with $NaBH_4$ using a small amount of methanol (MeOH) or ethanol (EtOH) as a catalyst, the process was easy to carry out [7]. Thus, a study on the cleavage of polybutadiene with the addition of MeOH or EtOH catalyst in the reduction of ATPB to HTPB has not been carried out.

In this study, cis-HTPB with a cis-1,4 content greater than 95% was synthesized via a one-pot method that incorporates a catalyst during the reduction of ATPB to HTPB. The effects of catalyst type and reaction time on the conversion of aldehyde groups to hydroxyl groups were proposed to achieve an efficient synthesis process for cis-HTPB.

2. EXPERIMENTAL

2.1. Materials

Cis-polybutadiene rubber (KBR-01, M_n = 500,000 g.mol^{-1}, Korea Kumho Petrochemical Co., Ltd), periodic acid (H_5IO_6; 99%, Shanghai Titan Technology Co., Ltd), sodium borohydride ($NaBH_4$; analytical grade, Shanghai Titan Technology Co., Ltd), and various solvents (chloroform, THF, MeOH, EtOH) were all sourced from China, with a purity of ≥ 99%.

2.2. Preparation of HTPB

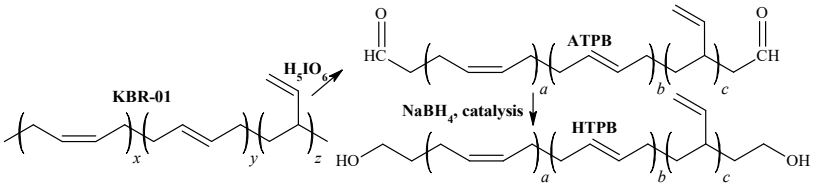

Figure 2. *Schematic diagram of HTPB preparation from KBR-01 rubber.*

The synthesis process of HTPB via the one-pot method was conducted as follows: 5 g of KBR-01 rubber was dissolved in 80 mL of a chloroform/THF mixture [50/30, (v/v)] in a 250 mL round-bottom flask and stabilized at 50 °C. The solution of periodic acid (H_5IO_6, 1.3 g) in 20 mL of THF was then added dropwise to the rubber solution over 30 minutes. The reaction was maintained at 50 °C with continuous stirring for 4.5 hours. Upon completion of the depolymerization reaction, the temperature of the reaction vessel was decreased to 30 °C. Finely powdered $NaBH_4$ (0.22 g; 5.79 mmol) was introduced into the reaction flask and dispersed uniformly within 5 minutes. Subsequently, 1.5 mL of catalyst (EtOH or MeOH) was added dropwise over approximately 5 minutes to prevent localized rubber agglomeration [7]. The reaction mixture was filtered to remove insoluble residues, followed by evaporation to eliminate the solvent. The resulting product was then dissolved in toluene and washed 3-4 times with deionized water in a separatory funnel to remove residual HIO_3 and excess $NaBH_4$. Finally, the product was washed multiple times with ethanol and dried at 40 °C for 12 hours. The HTPB synthesis process is illustrated in figure 2.

2.3. Molecular structure characterization

The FT-IR spectra of the samples were recorded using a PerkinElmer Spectrum 400 spectrometer in the range of 400 - 4000 cm^{-1}, with the samples being coated on KBr plates to form

thin films. NMR spectra were obtained using a Bruker Avance-III 400 (400 MHz) spectrometer with $CDCl_3$ as the solvent. The molecular weight (M_n) and the polydispersity index were determined by gel permeation chromatography (GPC) using a PL-GPC 50 Plus system, with polystyrene standards and chloroform as the eluent at a flow rate of 1 mL/min. The glass transition temperature (T_g) was measured using a TMA 450EM thermomechanical analyzer (TA Instruments, USA) at a heating (cooling) rate of 10 °C/min in a dry nitrogen atmosphere over a temperature range from -150 °C to 25 °C.

3. RESULTS AND DISCUSSION

3.1. The effect of the catalyst on the conversion rate of ATPB to HTPB

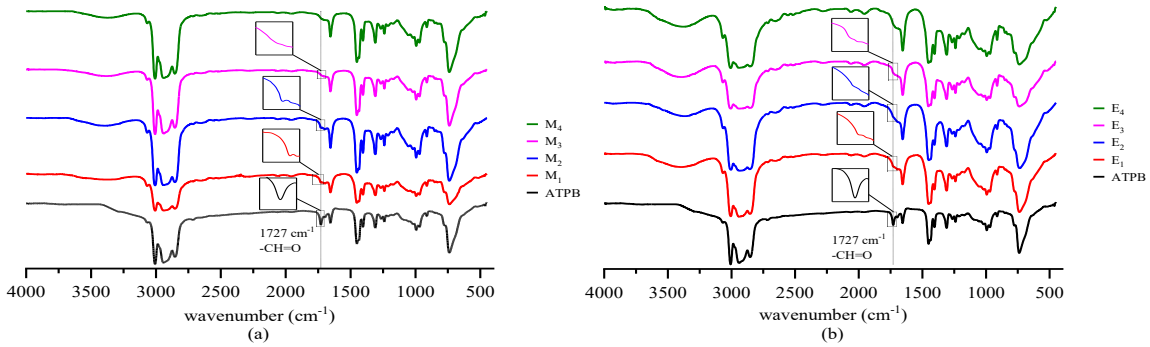

Figure 3. *The effect of reaction time on the reduction of ATPB under MeOH (a) and EtOH (b) catalytic conditions.*

When comparing the FT-IR spectra of ATPB and its reduced products over time using MeOH as a catalyst (figure 3a), it is observed that: after 10 minutes (M_1), the characteristic peak at 1727 cm^{-1} corresponding to the C=O stretching vibration appears quite clearly; after 30 minutes (M_2), the peak at 1727 cm^{-1} is significantly reduced but still present. After 50 minutes (M_3) and 70 minutes (M_4), the characteristic peak of the C=O group has disappeared. In figure 3b, when EtOH is used as the catalyst, the characteristic C=O peak almost completely disappears after 10 minutes (E_1), and is no longer observed at 30 minutes (E_2), 50 minutes (E_3), and 70 minutes (E_4) in the FT-IR spectra.

This phenomenon can be explained as follows: $NaBH_4$ is highly soluble in polar solvents. Upon the addition of a small amount of MeOH or EtOH to the reaction mixture, $NaBH_4$ dissolves in the alcohol, forming a homogeneous solution, and reduces ATPB according to the mechanism illustrated in figure 4. However, the proton in MeOH is more active than that in EtOH. As a result, $NaBH_4$ reacts with MeOH to generate hydrogen gas (H_2), reducing the amount of $NaBH_4$ available to react with the –CH=O groups [8]. When MeOH is replaced by EtOH, a similar reaction mechanism occurs. Nevertheless, due to the lower reactivity of the proton in EtOH, the generation of H_2 gas from the reaction between $NaBH_4$ and EtOH occurs more slowly, facilitating a more efficient reduction of the –CH=O group [9].

To further investigate the subsequent properties, HTPB was synthesized under conditions using EtOH as the catalyst for the reduction of ATPB over a reaction time of 10 minutes.

3.2. Structural analysis of HTPB

The molecular structure of HTPB is illustrated in the FT-IR spectrum (figure 5). The spectral band observed at 3300 - 3500 cm^{-1} is characteristic of the stretching vibrations of the terminal hydroxyl group. Additionally, distinct peaks appear at 736 cm^{-1}, 913 cm^{-1}, and 969 cm^{-1}, corresponding to the cis-1,4, vinyl-1,2, and trans-1,4 configurations, respectively. Among these, the peak at 736 cm^{-1} is the most dominant, followed by the peak at 969 cm^{-1}, with the peak at 913 cm^{-1} being the least intense.

The molecular structure of HTPB was further elucidated using ^{1}H-NMR and ^{13}C-NMR spectroscopy. The chemical shift at σ = 2.1 ppm corresponds to the protons of –C**H**$_2$–, while the signal at σ = 5.4 ppm corresponds to the proton of =C**H**–, and the shift at σ = 4.9-5.0 ppm is attributed to the protons of =C**H**$_2$. Additionally, a chemical shift at σ = 3.6 ppm, characteristic of the proton in the –C**H**$_2$OH group, is observed as a triplet, indicating the formation of a terminal -CH_2CH_2OH group resulting from the cleavage of a double bond in the 1,4-structure (figure 6). In the ^{13}C-NMR spectrum (figure 7), the chemical shifts at σ = 27.4 ppm and σ = 129.6 ppm correspond to the carbon atoms of =**C**H– and -**C**H_2– in the cis-1,4 isomer, respectively, while the shift at σ = 32.7 ppm is assigned to the –**C**H_2– carbon in the trans-1,4 isomer. The shift at σ = 62.6 ppm corresponds to the carbon atom in the –CH_2OH group.

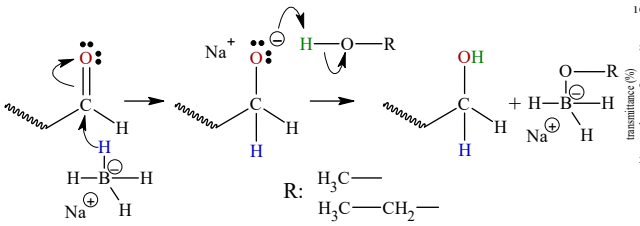

Figure 4. *Mechanism of ATPB reduction of $NaBH_4$ in the presence of EtOH or MeOH catalysts.*

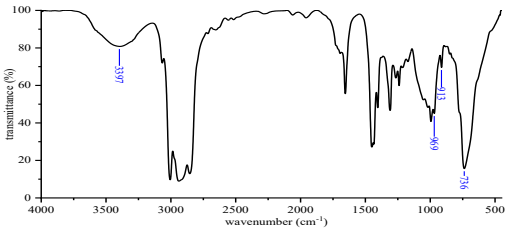

Figure 5. *FT-IR spectrum of HTPB (E1).*

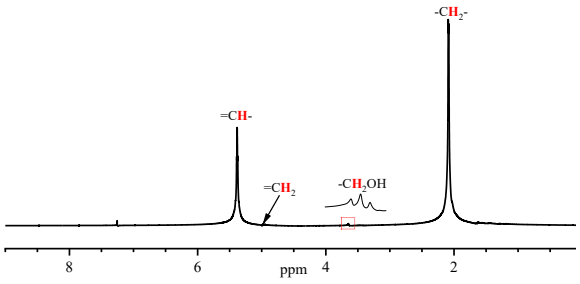

Figure 6. *^{1}H-NMR spectrum of HTPB (E1).*

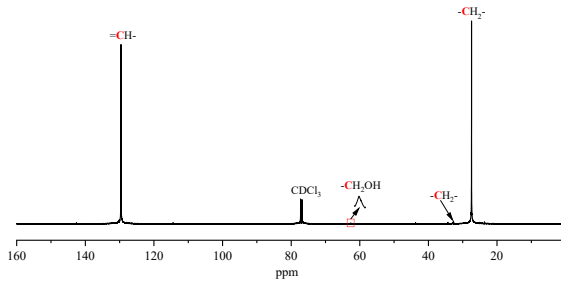

Figure 7. *^{13}C-NMR spectrum of HTPB (E1).*

The contents of the cis-1,4; trans-1,4; and vinyl-1,2 structures were calculated based on FT-IR and ^{1}H-NMR spectra using the following formulas [5, 10]:

According to FT-IR spectrum: $C_{cis\text{-}1,4}$ = 17667.D_{736}/A; $C_{trans\text{-}1,4}$ = 4741.D_{969}/A; $C_{vinyl\text{-}1,2}$ = 3674.D_{913}/A; in which: A = 17667D_{736} + 4741D_{969}+3674D_{913}) and D_{736}, D_{969}, D_{913} are the areas of the characteristic absorption peaks.

According to ^{1}H-NMR spectrum: $2C_{vinyl\text{-}1,2}/[C_{vinyl\text{-}1,2} + 2(1\text{-}C_{1,2})] = I_{4,94\text{-}5,00}/I_{5,38}$; $C_{trans\text{-}1,4}/(1\text{-}C_{vinyl\text{-}1,2}\text{-}C_{trans\text{-}1,4}) = I_{2,03}/I_{2,12}$; where I is the integral of the characteristic peak area. The results are presented in table 1. The data calculated from the FT-IR spectrum were in good agreement with those from the ^{1}H-NMR spectrum, and the cis-1,4 content of HTPB reached ca. 95%.

Table 1. *Molecular structure of HTPB (E1).*

Sample	$C_{cis\text{-}1,4}$		$C_{trans\text{-}1,4}$		$C_{vinyl\text{-}1,2}$		Hydroxyl value (mmol.g^{-1})*
E_1	FT-IR	^{1}H-NMR	FT-IR	^{1}H-NMR	FT-IR	^{1}H-NMR	0.78
	95.09	95.06	3.53	3.52	1.38	1.42	

**The hydroxyl value by the acetic anhydride-pyridine method.*

The above data demonstrated that HTPB with a high cis-1,4 content of more than 95% (cis-HTPB) was successfully prepared from KBR-01 rubber.

3.3. Determination of the molecular weight (M_n)

The number-average molecular weight (M_n) of HTPB (sample E_1) was determined using both gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy according to equation 1 [3]. The results are summarized in table 2 and figure 8.

$$M_n \frac{\text{I(5,4)} + \text{I(4,9-5,0)}}{\text{I(3,6)}} \times 2 \times 54 + 90 \quad (1)$$

Table 2. *Molecular weight of HTPB (E_1).*

Sample	M_n (g.mol^{-1})	
	^{1}H-NMR	GPC (PDI)
E_1	4,880	11,500 (1.59)

The M_n value obtained by ^{1}H-NMR was 4,880 g.mol^{-1}, which corresponds to the chain length estimated from the integration of terminal and internal protons. In comparison, the GPC analysis yielded a higher M_n of 11,500 g.mol^{-1}, with a polydispersity index (PDI) of 1.59, reflecting a moderate distribution of molecular weights in the polymer sample. The difference between these two methods arises from their measurement principles: while ^{1}H-NMR provides an average based on chemical structure and end-group analysis, GPC separates polymers based on their hydrodynamic volume in solution. When polymer chains associate through non-covalent interactions, they form larger aggregates that behave as single entities during chromatographic separation, leading to overestimation of molecular weight. These results confirm that the synthesized HTPB possesses a relatively narrow molecular weight distribution, suitable for use as a binder precursor in energetic composite formulations [3, 11].

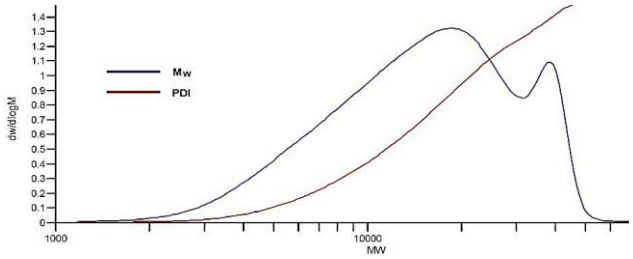

Figure 8. *GPC curves of HTPB (E1).*

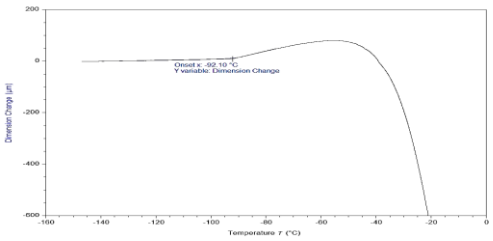

Figure 9. *TMA curves of HTPB (E1).*

3.4. Glass transition temperature of HTPB

To evaluate the thermal flexibility of the synthesized HTPB, thermomechanical analysis was performed under a constant applied load of 0.02 N and a heating rate of 10 ºC/min in a nitrogen atmosphere. The dimensional change of the sample was recorded as a function of temperature over the range from -150 ºC to 25 ºC. The resulting TMA curve is presented in figure 9. It clearly shows a noticeable shift in the dimension change rate at temperature -92.1 ºC, corresponding to the glass transition temperature (T_g) of the HTPB sample. The curve exhibits a smooth inflection typical of amorphous elastomers, and the relatively low T_g is consistent with a high cis-1,4 content. The T_g value obtained is in good agreement with previously reported data for cis-HTPB systems with cis-1,4 content above 95% [3].

4. CONCLUSIONS

In this study, a simplified one-pot synthesis of HTPB was successfully developed using an oxidation-reduction strategy. Oxidative cleavage of KBR-01 rubber with H_5IO_6 produced ATPB, which was subsequently reduced using $NaBH_4$ in the presence of alcohol catalysts. Ethanol demonstrated superior catalytic performance, achieving nearly complete conversion of aldehyde groups to hydroxyl within 15 minutes at 30 ºC. Comprehensive structural characterization via FT-

IR, NMR, and GPC confirmed a cis-1,4 unit content of approximately 95%. The synthesized HTPB exhibited a low glass transition temperature (T_g = -92.1 °C), indicating excellent flexibility at low temperatures, which is desirable for energetic binder applications. This approach offers a practical, time-efficient route for the synthesis of structurally controlled HTPB and may be extended to other functionalized rubbers.

REFERENCES

[1]. L. T. DeLuca et al., *"Characterization of HTPB-based solid fuel formulations: Performance, mechanical properties, and pollution"*, Acta Astronautica, 92(2), pp. 150–162, (2013).

[2]. V. Sekkar et al., *"Pot life extension of hydroxyl terminated polybutadiene based solid propellant binder system by tailoring the binder polymer microstructure"*, Journal of Macromolecular Science, Part A, 54(3), pp. 171–175, (2017).

[3]. Q. Zhou et al., *"Preparation of Hydroxyl-Terminated Polybutadiene with High Cis-1,4 Content"*, Industrial & Engineering Chemistry Research, 53(46), pp. 17884–17893, (2014).

[4]. J. C. Brosse et al., *"Hydroxyl-terminated polymers obtained by free radical polymerization - Synthesis, characterization, and applications"*, in Catalytical and Radical Polymerization, Springer Berlin Heidelberg, pp. 167–223, (1986).

[5]. J.-m. Chen et al., *"Synthesis of hydroxyl-terminated polybutadiene possessing high content of 1,4-units via anionic polymerization"*, Chinese Journal of Polymer Science, 28(5), pp. 715–720, (2010).

[6]. D. Meng et al., *"Preparation of Hydroxyl-Terminated Polybutadiene by the Pyrolysis Method and Its Application in Polyurethane"*, ACS Applied Polymer Materials, 6(14), pp. 8235–8243, (2024).

[7]. K. Tanemura, *"Reduction of aldehydes and ketones by a stoichiometric amount of $NaBH_4$ using a small amount of MeOH or EtOH"*, Results in Chemistry, 4, p. 100486, (2022).

[8]. K. Ramya et al., *"Hydrogen production by alcoholysis of sodium borohydride"*, International Journal of Energy Research, 37(14), pp. 1889–1895, (2013).

[9]. H. C. Brown et al., *"A Study of Solvents for Sodium Borohydride and the Effect of Solvent and the Metal Ion on Borohydride Reductions"*, Journal of the American Chemical Society, 77(23), pp. 6209–6213, (1955).

[10]. Y. Tanaka et al., *"Characterization of diene polymers. I. Infrared and NMR studies: Nonadditive behavior of characteristic infrared bands"*, Journal of Polymer Science Part A-2: Polymer Physics, 9(1), pp. 43–57, (1971).

[11]. D. Papp et al., *"A Complementary Multitechnique Approach to Assess the Bias in Molecular Weight Determination of Lignin by Derivatization-Free Gel Permeation Chromatography"*, Analytical Chemistry, 96(26), pp. 10612–10619, (2024).

TÓM TẮT

Tổng hợp hydroxyl-terminated polybutadiene bằng phương pháp oxy hóa-khử sử dụng chất xúc tác ancol

Các phương pháp truyền thống để tổng hợp hydroxyl-terminated polybutadien (HTPB) có hàm lượng cis-1,4 cao thường đòi hỏi các quá trình oxy hóa-khử nhiều bước, vốn bị hạn chế do khả năng hòa tan kém của natri borohydrid trong các dung môi có độ phân cực thấp, dẫn đến hiệu suất thấp trong quá trình khử aldehyde-terminated polybutadiene (ATPB). Nghiên cứu này giới thiệu phương pháp tổng hợp one-pot sử dụng chất xúc tác alcohol để nâng cao hiệu quả khử ATPB thành HTPB. Kết quả nghiên cứu cho thấy, ethanol cải thiện rõ rệt hiệu suất phản ứng khử, nhóm carbonyl chuyển thành hydroxyl gần như hoàn toàn trong 15 phút ở 30 °C. HTPB thu được có hàm lượng cis-1,4 khoảng 95%, với khối lượng phân tử khoảng 4.880 $g.mol^{-1}$, chỉ số hydroxyl là 0,78 $mmol.g^{-1}$ và nhiệt độ thủy tinh hóa T_g = -92,1 °C.

Từ khóa: Hydroxyl-terminated polybutadiene (HTPB); Xúc tác ancol; Khử natri borohydride.