ORIGINAL PAPER

Controlled degradation and functionalization of natural rubber by ozonolysis in organic solvent

Alireza Banan[1] · Hossein Mehdipour[1]

Abstract

Hydroxyl-terminated natural rubber can be used as an eco-friendly and renewable bio-based polyol for the production of sustainable polyurethanes. It can also have other advantages such as high elasticity and thermal stability over many other conventional polyols. Liquid natural rubber (LNR) with primary and secondary hydroxyl end-groups was prepared via ozonolysis of natural rubber (NR) in chloroform at 60 °C followed by the subsequent reduction with sodium borohydride. M_n and M_w of the prepared hydroxyl-telechelic liquid natural rubber were 2368 g/mol and 3949 g/mol, respectively. The prepared liquid natural rubber has a narrow unimodal molecular weight distribution and a relatively low polydispersity index of 1.9. The presence of terminal hydroxyl groups and *cis*-1,4-isoprenic microstructures of hydroxyl-telechelic liquid natural rubber were determined by FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The prepared hydroxyl-telechelic liquid natural rubber was successfully cured with toluene diisocyanate (TDI) and a polyurethane elastomer was obtained.

Keywords Ozonolysis · Telechelic polymer · Liquid natural rubber · Polymer degradation

Introduction

Natural rubber latex is an emulsion of natural rubber (NR) in water which typically consists of long and linear chains of poly(*cis*-1,4-isoprene), along with small amounts of protein, carbohydrates, neutral and polar lipids, minerals, amino acids, amides, etc., and about 50–70% (w/w) water [1–3]. NR is a high molecular weight renewable polymer (up to 1×10^6 g/mol) which is one of the most important raw materials in industrial applications due to its outstanding elasticity and thermal stability [4]. However, high molecular weight and low solubility of NR has hampered rubber processing and limited its applicationin some rubber industries.

Liquid natural rubber (LNR) is the modified form of natural rubber (NR), with average molecular-weight (M_w) below 20,000 g/mol and the ability to flow at room temperature. LNR usually has certain functional groups and is widely used in adhesives, coatings, plasticizers and compatibilizers [5–12]. LNR is synthesized by controlled degradation and chain cleavage of natural rubber [13]. In this process, the molecular weight of polymeric chains decreases and, in a mean time, specific functional groups are formed at the end of chains.

Degradation of natural rubber backbone and the control of parameters and conditions that could influence the modes of chain scission for production of LNR bearing specific types of reactive terminal groups have been developed from a wide variety of methods such as chemical, mechanical, thermal and photochemical degradation methods and LNRs with various end groups such as carbonyl, hydrazine, hydroxyl and carboxyl have been reported [13–17]. As a result, there has been a great deal of interest recently in the introduction of desired end-groups in natural rubber along with carbon–carbon double bond for further chain modification. Hydroxyl-telechelic liquid natural rubber has attracted much attention especially in the synthesis of block copolymers, interpenetrating networks (IPNs), polyurethane foams and elastomeric materials [18–23].

Various chemical reagents have been used for degradation of natural rubber and synthesis of end-functionalized natural rubber. The molecular weight and the type of functional groups of the degraded rubber depend on the chemical reagent and the condition of the reaction. Hydrogen peroxide, potassium persulfate and m-chloroperbenzoic acid/periodic acid are examples of the reagents that have been used for

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chemical degradation of natural rubber and synthesis of telechelic natural rubber [24–27]. Figure 1 depicts the degradation reaction of natural rubber with various chemical reagents and the products resulted from these reactions.

However, in most cases, the molecular weight of the rubber does not decrease to the extent that a liquid rubber can be obtained. Moreover, most of the previously introduced methods need to high temperature, long reaction time, and specific chemical reagents and it is difficult to control the molecular weight and functionality of the product. Formation of hazardous waste and laborious isolation and purification of the product are other problems encountered in the synthesis of telechelic natural rubber.

Among various chemical reagents used for degradation and functionalization of rubbers, ozone seems to be more promising reagent than the others. Ozone (O_3) is one of the most powerful oxidizing agents highly reactive toward double bonds and other functional groups with high electron densities. Ozone is readily available by in situ production from air or oxygen. Ozonolysis is considered as a clean and effective method for oxidation and degradation of organic compounds and can be regarded as a promising alternative for conventional oxidative degradations. Fragmentation of unsaturated polymers by ozone (ozonolysis) has been the subject of considerable researches owing to a decrease in the molecular weight accompanied with an increase in the functionality of the prepared materials [28]. Kodama et al. investigated the degradation of natural rubber in the latex phase with ozone gas [29]. They found that the molecular weight (M_w) of natural rubber decreased to a minimum value of about 50,000 g/mol after ozonolysis. But this molecular weight is not low enough to obtain a liquid rubber. Nor and Ebdon performed the ozonolysis of natural rubber in organic solvent and obtained a degraded natural rubber with

molecular weight (M_n) as low as 900 g/mol [28]. However, this degraded natural rubber can contain various functional groups and its functionality is not well-controlled.

The aim of this work is to prepare liquid telechelic natural rubber with controlled functionality and end-groups by ozonolysis and evaluate the structural characterization of the prepared material. Herein we described a simple method for preparing hydroxyl-telechelic liquid natural rubber by ozonolysis of naural rubber and subsequent reduction of end-groups. The reaction of the synthesized hydroxyl-telechelic liquid natural rubber with toluene diisocyanate (TDI) for preparation of polyurethanes was then investigated. The microstructure, molecular weight and polydispersity index (PDI) of the products in each step were determined by Fourier transform infrared (FT-IR), ^{1}H nuclear magnetic resonance (^{1}H-NMR), ^{13}C nuclear magnetic resonance (^{13}C-NMR) and gel permeation chromatography (GPC).

Experimental

Materials and apparatus

NR latex was supplied from Malaysia. All other reagents and solvents including tetrahydrofuran (THF), cyclohexane, chloroform, sodium borohydride ($NaBH_4$), periodic acid (H_5IO_6), toluene diisocyanate (TDI), formic acid and ethanol were purchased from Merck and used as received.

The ozone gas was generated using an ozone generator (Mahabzist, Iran) with flow rate of 10 g/h. Fourier transform infrared (FT-IR) spectra were recorded on pressed KBr pellets at the spectral range of 400–4000 cm^{-1} using a Perkin-Elmer spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on the samples dissolved in deuterated

Fig. 1 Degradation of natural rubber with various chemical reagents
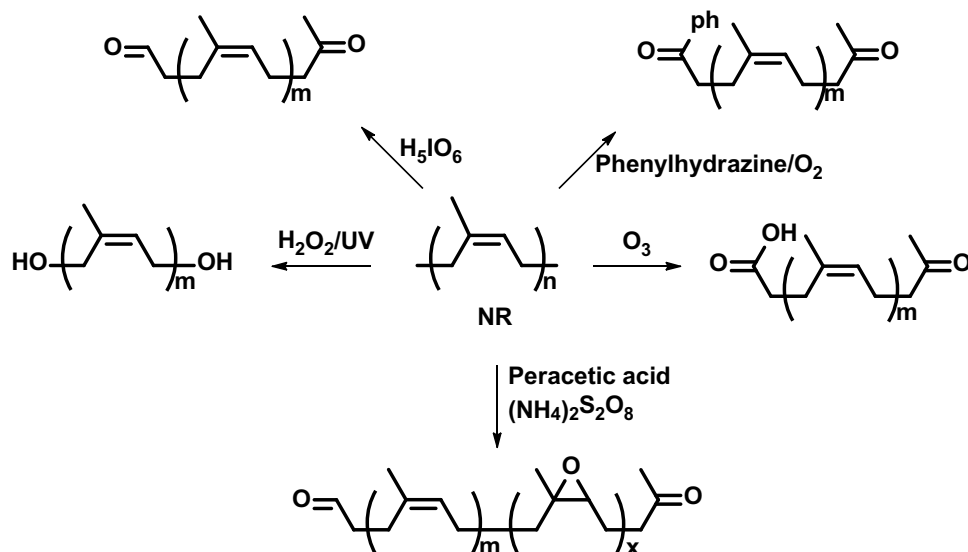
chloroform (CDCl$_3$) and analyzed using a Bruker DRX-500 spectrometer (500 MHz). Differential scanning calorimetry (DSC) was carried out by SDT–Q600 thermal analyzer (TA Instruments Inc., USA) with a heating rate of 10 ℃.min^{-1} under argon stream (100 mL.min^{-1}) at atmospheric pressure. The molecular weight distribution was determined using an Agilent series 1100 gel permeation chromatograph (GPC) with cross-linked polystyrene-packed column. Measurements were made using THF as an eluent monitored with a refractometer at 30 °C. Calibration was done using commercial standard polystyrenes.

Isolation and purification of natural rubber

A solution of formic acid (1%) was added dropwise to 100 mL NR latex while the mixture was magnetically stirring. The resulting coagulum (solid natural rubber) was washed twice by distilled water and three times with ethanol, and then dried in an oven at 60 °C for 24 h. (^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 1.68 (3H, -CH$_3$), 2.05 (4H, -CH$_2$-), 5.10 (1H, C=C-H).

Ozonolysis of natural rubber

Natural rubber (10 g) was charged into a two-necked flask equipped with a condenser and chloroform (200 mL) was added. For complete dissolution of natural rubber, the solution was heated overnight at 60 °C in an oil bath. Ozone stream from the ozone generator was passed into the solution at 60 °C for 2 h. The solvent was removed by rotary evaporator and the product was analyzed with FT-IR, NMR and GPC.

Synthesis of hydroxyl-telechelic liquid natural rubber

The resulting carbonyl-telechelicliquid natural rubber (6 g) from previous experiment was charged into a 100 mL flask equipped with a condenser. THF (50 mL) was added and the solution was heated at 60 °C in an oil bath with magnetic stirring until carbonyl-telechelic liquid natural rubber was completely dissolved. Then, sodium borohydride was added and the mixture was heated at 60 °C for 24 h. The excess sodium borohydride was hydrolyzed by adding water (3 mL). Afterwards, the solvent was removed at 80 °C *in vacuo* for 30 min. Cyclohexane (50 mL) was addedto precipitate residual salts. Then, the mixture was filtered through a fritted funnel. The solvent was removed at 80 °C *in vacuo* for 30 min and the product was analyzed by FT-IR, NMR, and GPC.

Ozonolysis of natural rubber in latex phase

Natural rubber latex (10 g) was charged into a two-necked flask equipped with a condenser. Water (50 mL) was added

and the mixture was magnetically stirred at 60 °C in an oil bath. Nonylphenol ethoxylates (0.08 g) was added as a nonionic emulsifying agent. Ozone stream from the ozonizer was injected into the solutionfor 6 h at 60 °C. The depolymerized NR was recovered by treatment of the mixture with methanol and purified by washing three times with distilled water and twice with methanol and then dried in an oven at 50 °C.

Synthesis of polyurethane

The polyurethane sample was prepared via the one-step route. A three-neck flask was charged with hydroxyl-telechelic liquid natural rubber as a polyol and was put in an oil bath at 40 °C. TDI (with 1:1 molar ratio to hydroxyl-telechelic liquid natural rubber) was added dropwise during 45 min under continuous stirring and nitrogen purging. The viscous liquid was casted into a silicone rubber mold and cured for 72 h at 50 °C.

Results and discussion

Synthesis of carbonyl-telechelic liquid natural rubber by ozonolysis

It has been established that the mechanism of ozone attack on olefinic compounds includes an initial addition of ozone to the carbon–carbon double bond forming an unstable adduct (molozonide) followed by a transformation to stable ozonide which subsequently will be cleaved by reducing or oxidizing agentsto a series of oxygenated compounds such as aldehydes, ketones, carboxylic acids and alcohols as proposed by Criegee (Fig. 2) [28, 30].

The functional groups that are desirable for the first step of our study are aldehyde and ketone groups because we aim to reduce and convert them to hydroxyl groups and prepare a hydroxyl-telechelic liquid natural rubber. Thus, the reaction conditions were optimized to obtain a carbonyl-telechelic
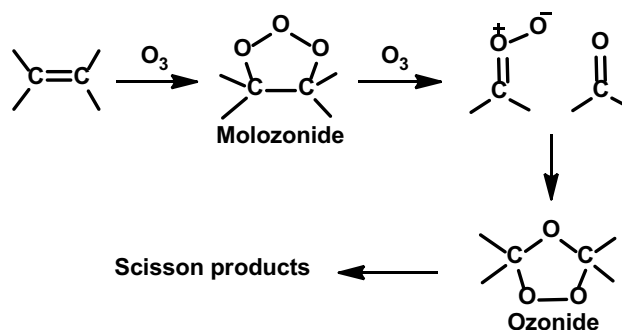

Fig. 2 Mechanism of ozonolysis of olefinic compounds

liquid natural rubber by fragmentation of NR by ozone. The effect of various parameters such as solvent, temperature and time of ozone treatment on oxidation of natural rubber, was investigated and the results are displayed in Table 1. The ratio of the area under the peak of aldehyde proton to the area under the peak of vinyl protons in ^{1}H NMR spectra were used as a measure of the aldehyde content formed at the end of degraded NR chains. A higher value of aldehyde to vinyl ratio indicates that NR chains were degraded more extensively and, simultaneously, low molecular weight NR with more carbonyl end-groups were obtained.

Fragmentation of natural rubber by ozone was examined in various solvents. The aldehyde content of the product obtained after 2 h ozonolysis of NR in dichloromethane at 0 °C was only 0.06% indicating that ozone cleavage of NR was not successful (Table 1, entry 1). High aldehyde content was not obtained in dichloromethane even at higher temperatures and after longer reaction times (Table 1, entries 2–4). These results show that a low molecular weight NR cannot be obtained by ozonolysis in dichloromethane which could be due to the poor solubility of NR in this solvent. The aldehyde content of the oxidized rubber does not change significantly by increasing the temperature and time of the reaction (Table 1, entries 1, 2). Higher aldehyde contents were obtained using THF, toluene and chloroform which are better solvents for NR. The aldehyde content of NR ozonolized

at 0 °C is 0.51%, 0.58% and 0.71% in toluene, THF and chloroform, respectively (Table 1, entries 5, 9, 13). Natural rubber is partially soluble in THF, toluene and chloroform at room temperature but the solubility is increased at higher temperatures. Thus, the ozonolysis was performed at higher temperatures to obtain a fully dissolved rubber. In all solvents, the aldehyde content of the ozonolized NR increased with raising temperature and extending the reaction time, indicating that higher degradation efficiency is obtained at higher temperatures and longer reaction time. The aldehyde content increases with raising temperature and reaches to 0.11%, 1.24%, 1.38% and 3.32% after 2 h ozonolysis at 60 °C in dichloromethane, toluene, THF and chloroform, respectively (Table 1, entries 3, 7, 11, 17). Comparing the aldehyde content of NR ozonolized in various organic solvents revealed that chloroform is the best solvent for obtaining a carbonyl-telechelic natural rubber by ozonolysis.

The product of the ozonolysis in different solvents was also characterized by FT-IR spectroscopy. FT-IR spectra of the products obtained from ozonolysis of NR in THF, toluene and chloroform are illustrated in Fig. 3. The sharp strong peak appeared at 1711 cm^{-1} in the spectrum of the product obtained in chloroform (Fig. 3a) is assigned to C=O stretching vibrations of carbonyl groups. Three peaks at 2963 cm^{-1}, 2924 cm^{-1} and 2858 cm^{-1} are attributed to aliphatic C-H stretching vibrations. The absorption bands at 1663 cm^{-1} and 3038 cm^{-1} are assigned to C=C and vinylic C-H stretching vibrations, respectively. There is also a broad peak at 3200–3700 cm^{-1} which is attributed to O–H

Table 1 Ozonolysis of natural rubber[a]

Entry	Solvent	T (°C)	Time (h)	Aldehyde to vinyl ratio[b] (%)
1	CH$_2$Cl$_2$	0	2	0.06
2	CH$_2$Cl$_2$	40	2	0.09
3	CH$_2$Cl$_2$	60	2	0.11
4	CH$_2$Cl$_2$	60	3	0.12
5	Toluene	0	2	0.51
6	Toluene	40	2	0.96
7	Toluene	60	2	1.24
8	Toluene	60	3	1.27
9	THF	0	2	0.58
10	THF	40	2	0.92
11	THF	60	2	1.38
12	THF	60	3	1.45
13	CHCl$_3$	0	2	0.71
14	CHCl$_3$	20	2	1.14
15	CHCl$_3$	40	2	2.32
16	CHCl$_3$	50	2	3.01
17	CHCl$_3$	60	2	3.32
18	CHCl$_3$	60	3	3.08
19	CHCl$_3$	60	4	1.46

[a]Reaction conditions: 10 g NR, 200 mL solvent, and 10 g/h ozone gas
[b]Calculated by ^{1}H NMR spectroscopy
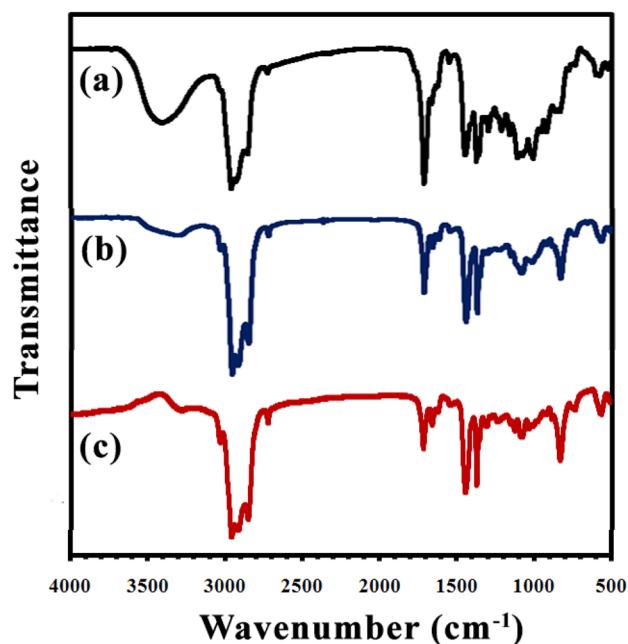
Fig. 3 FT-IR spectra of the products of ozonolysis of NR in **a**) toluene, **b**) THF, and **c**) chloroform
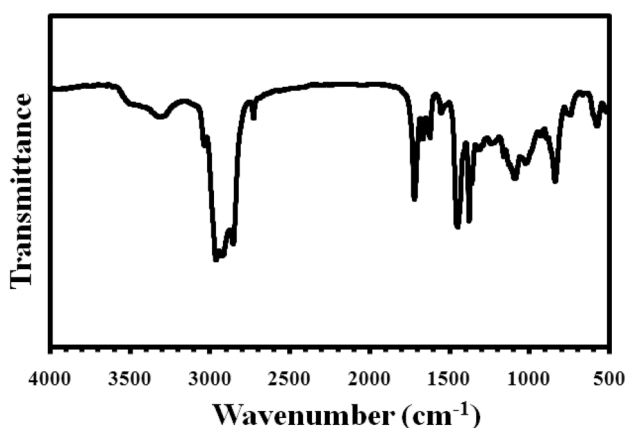
Fig. 4 FT-IR spectrum of NR treated with ozone in chloroform with prolonging the reaction time to 3 h

stretching vibrations of carboxylic acid groups. The presence of carboxylic acid groups could be due to the over-oxidation of rubber or due to the oxidation of toluene.

In the FT-IR spectrum of the product obtained in THF (Fig. 3b), the peaks appeared at 1717 cm^{-1} and 3300 cm^{-1} are attributed to C=O and O–H stretching vibrations, respectively. The lower intensity of these peaks compared with those appeared in the spectrum of the product obtained in toluene shows that over-oxidation of rubber or undesired oxidation of solvent is decreased in THF.

In the spectrum of the product obtained in chloroform (Fig. 3c), the intensity of C=O stretching vibration (1720 cm^{-1}) has decreased and the OH stretching vibration of carboxylic acid (3200–3500 cm^{-1}) is not observed. The results indicate that double bonds are oxidized and cleaved to terminal aldehyde and ketone by ozonolysis in chloroform. However, by prolonging the reaction time from 2 to 3 h, oxidation of terminal aldehydes occurs and terminal carboxylic acid groups are formed as confirmed by the appearance of the broad peak at 3300–3500 cm^{-1} (Fig. 4). This result is in agreement with the data obtained by ^{1}H NMR spectroscopy which indicated that the aldehyde content of ozonolized NR decreased from 3.32% after 2 h ozonolysis to 3.08% and 2.48% after 3 h and 4 h ozonolysis, respectively (Table 1, entries 17–19).

The results indicate that chloroform is not oxidized by ozone and over-oxidation of rubber does not take place in this solvent after 2 h. Thus, 2 h ozonolysis in chloroform at 60 °C was considered as the best reaction condition (Fig. 5).

^{1}H NMR spectrum of solid natural rubber coagulated and isolated from natural rubber latex is illustrated in Fig. 6. The signals attributed to the protons of methyl, methylene and vinylgroups are appeared at chemical shifts of 1.68, 2.05, 5.10 ppm, respectively.

The ^{1}H NMR spectrum natural rubber treated with ozone (chloroform as the solvent, 60 °C, 2 h), (Fig. 7) evidenced the presence of aldehyde functional groups in the chain of LNR. The signal appeared at 9.8 ppm is characteristic signal of aldehyde protons resulted from oxidation and cleavage of double bonds of rubber. The singlet at 2.13 ppm (3H) is assigned to methyl protons in alpha position to carbonyl carbon of ketone. Signals of other protons adjacent to carbonyl end-groups are also appeared in 2.10–2.60 ppm region (Fig. 7). The signal integration ratio of aldehyde to vinylic protons is 1:29 (3.32%). The results confirm that oxidation and cleavage of double bonds has been performed and carbonyl-telechelic liquid natural rubber has been successfully synthesized in chloroform as solvent.

^{13}C NMR spectrum of carbonyl-telechelic liquid natural rubber is depicted in Fig. 8. The signals of carbons in isoperenic repeating units are appeared at C_1: $\delta = 31$ ppm, C_2: $\delta = 134$ ppm, C_3: $\delta = 124$ ppm, C_4: $\delta = 25$ ppm and C5: $\delta = 22$ ppm. The signals at 41 ppm, 30 ppm and 43 ppm are assigned to carbons adjacent to aldehyde and ketone groups (C_7, C_8 and C_{10}). The signals at 202 ppm and 208 ppm are attributed to aldehyde and ketone carbons (C_6 and C_9, respectively).

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the original natural rubber were 380,000 g/mol, 680,000 g/mol and 1.8, respectively, as measured by GPC. It was found that by increasing the temperature and degradation time, the molecular weight of the product decreased due to higher oxidative degradation of NR chains. M_n and M_w of rubber after ozonolysis decreased to 2368 g/mol and 3949 g/mol, respectively. A remarkable decrease in molecular weight of the product confirmed degradation of polymeric chains by ozone. The molecular weight distribution curve showed a unimodal distribution similar to the molecular weight distribution of original natural rubber with a polydispersity index of 1.9 (M_w/M_n) that reveals a narrow molecular weight distribution.
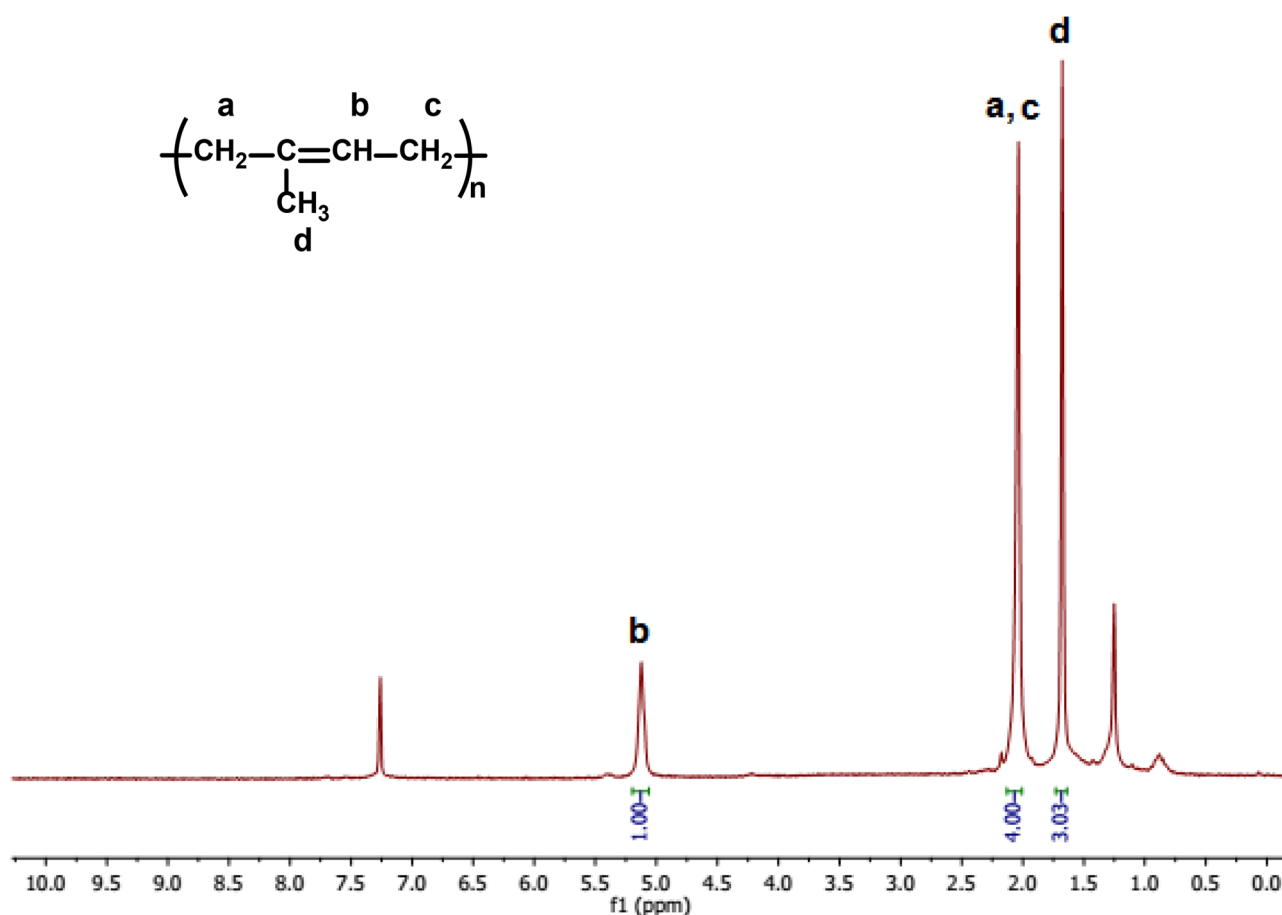
Synthesis of hydroxyl-telechelic liquid natural rubber

Synthesis of hydroxyl-telechelic liquid natural rubber was carried out by reduction of carbonyl-telechelic liquid natural rubber using sodium borohydride as the reducing agent (Fig. 9).

There are several parameters that have influence on the reaction such as reaction temperature, reaction time, solvent

Fig. 5 Synthesis of carbonyl-telechelic liquid natural rubber by ozonolysis of NR in optimum reaction condition
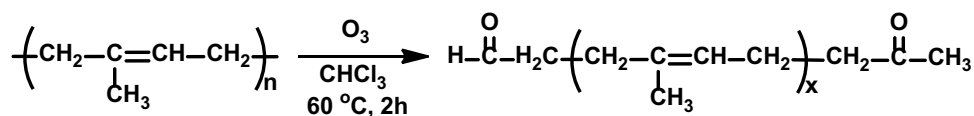
Fig. 6 ^{1}H NMR spectrum of solid natural rubber

and the amount of reagents. To optimize the reaction conditions for the reduction of terminal carbonyl groups in carbonyl-telechelic liquid natural rubber, the effects of various parameters were evaluated. The progress of the reduction was quantified by using the integrated intensity of the aldehyde proton signal at 9.8 ppm and its ratio to that of vinyl proton signal in the ^{1}H NMR spectra (Table 2).

THF, chloroform and cyclohexane were used as solvents and the extent of the reduction was evaluated (Table 2, entries 1–3). In chloroform and cyclohexane, a large content of aldehyde group was remained unreacted in the structure of the product even at high temperature, high dosage of NaBH$_4$ and long reaction time (Table 2, entries 1–6). THF was chosen as the best solvent considering time, reactants ratio and reduction yield. It is assumed that higher polarity of THF and better solubility of sodium borohydride in THF are responsible for better reduction of carbonyl groups in this solvent. The reduction in THF proceeds well even at shorter reaction time (Table 2, entries 11–13). Increasing the amount of sodium borohydride increased the yield of the reduction (Table 2, entries 14, 15). Decreasing the reaction temperature from 60 °C to 30 °C had a negative effect on

the yield of the product (Table 2, entries 15, 16). According to complete disappearance of aldehyde signal at 9.8 ppm in the ^{1}HNMR spectrum, the optimum conditions for this reaction were as follows: 8 mol % of NaBH$_4$:carbonyl ratio; THF as the solvent and reaction temperature of 60 °C (Table 2, entry 15). In this condition, the reduction was completed after 4 h and all carbonyl groups were converted to hydroxyl groups.

In the ^{1}H NMR spectrum of the product of the reduction of carbonyl-telechelic liquid natural rubber (Fig. 10), compared with that of raw material (Fig. 7), the signal at 9.8 ppm was completely disappeared after the reduction and two new signals were appeared at 3.64 ppm and 3.79 ppm. The signal appeared at 3.64 ppm (triplet) is attributed to two protons of methylene attached to terminal primary hydroxyl group and the signal at 3.79 ppm (multiplet) is attributed to one proton of methane attached to secondary hydroxyl group split by adjacent methyl and methylene protons (Fig. 10).

In the ^{13}C NMR spectrum of hydroxyl-telechelic liquid polyisoprene (Fig. 11), the signals at 202 ppm and 208 ppm related to carbons of aldehyde and ketone groups were disappeared (compared to the ^{13}C NMR spectrum of
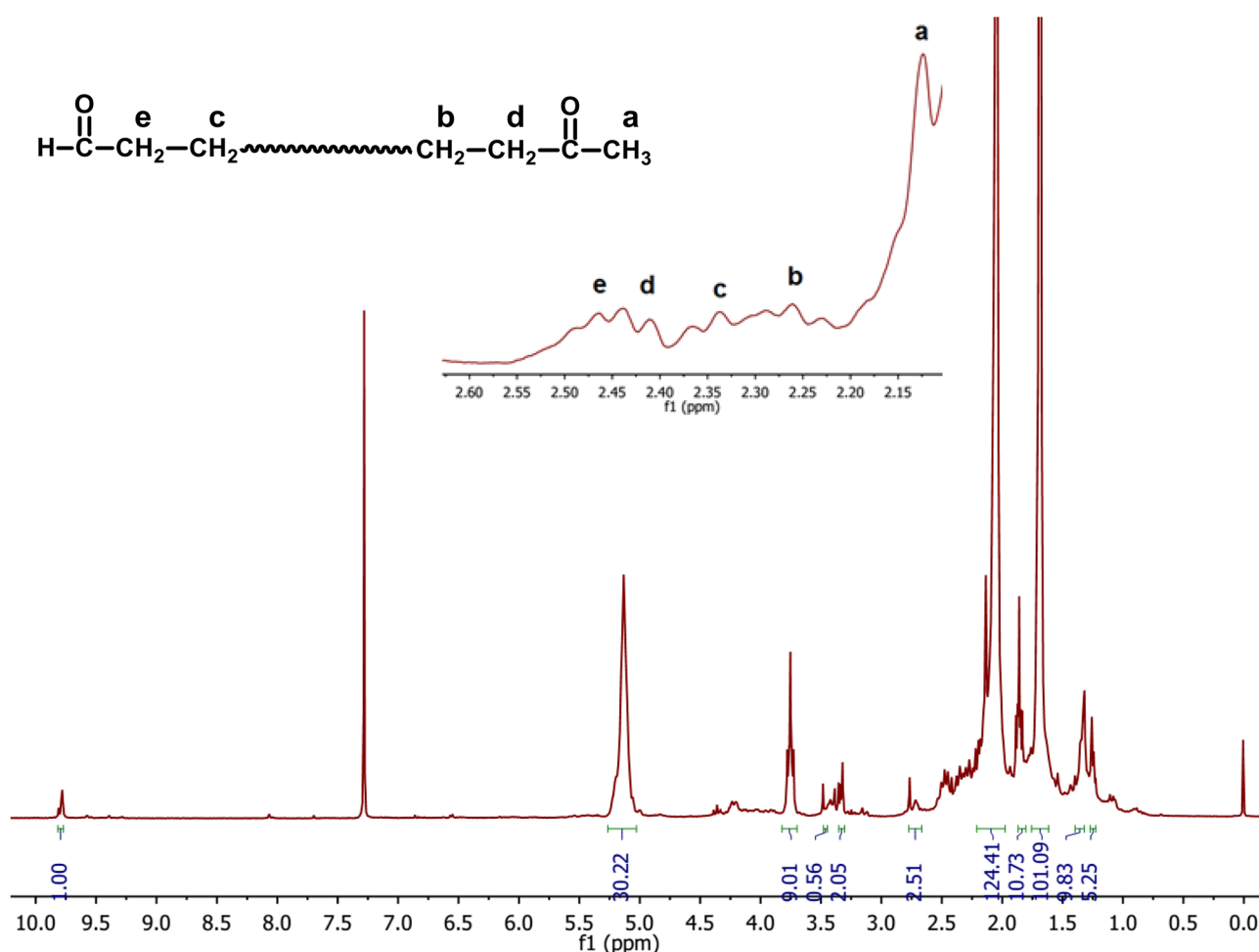
Fig. 7 ^{1}H NMR spectrum of the prepared carbonyl-telechelic liquid natural rubber in CDCl$_3$

carbonyl-telechelic liquid natural rubber, Fig. 8) and two new signals at 62 ppm and 67 ppm were appeared which are assigned to carbons attached to primary and secondary hydroxyl groups, respectively.

Since the properties of polyisoperene rubbers are significantly affected by its microstructures in polymer chains, it is important to determine the microstructure of the prepared liquid rubber. In the ^{13}C NMR spectrum of hydroxyl-telechelic liquid natural rubber, five signals of carbons present in the repeating unit of rubber were appeared at chemical shifts equal to that reported for poly(*cis*-1,4-isoprene) [31, 32]. This result shows that the microstructure of hydroxyl-telechelic liquid natural rubber is similar to that of NR (*cis*-1,4). The same result can be obtained from the ^{13}CNMR spectrum of carbonyl-telechelic liquid natural rubber. It can be concluded that the microstructure of NR does not change during ozonolysis process and subsequent reduction of carbonyl groups.

In the FT-IR spectrum of hydroxyl-telechelic liquid natural rubber, the characteristic peak of carbonyl groups at 1711 cm^{-1} was disappeared and a new broad absorption

band was appeared at 3200–3500 cm^{-1} which is related to O–H stretching vibrations (Fig. 12). This result indicates that the reduction of carbonyl-telechelic liquid natural rubber by sodium borohydride was successfully achieved and the resulting polymer has terminal hydroxyl groups. The FT-IR spectrum of hydroxyl-telechelic liquid natural rubber is similar to the reported spectrum of *cis*-1,4-polyisoprene [33]. The absorption band observed at 3038 cm^{-1}is assigned to C-H stretching vibrations in 1,4-units. While no peaks were observed at 3080–3070 cm^{-1} relating to C-H stretching vibrations in 1,2-units and 3,4-units. Moreover, C=C stretching vibrations of 1,4-unit were appeared at 1663 cm^{-1}. This peak in 1,2-units and 3,4-units is appeared at lower wavenumbers (1644 cm^{-1}) which is not observed in the spectrum of the prepared hydroxyl-telechelic liquid natural rubber. The presence of a band at 1377 cm^{-1} is attributed to bending vibrations of CH$_3$ with cis configuration. The peak related to trans configuration (1383 cm^{-1}) was not appeared in the FT-IR spectrum. These results confirm that the prepared hydroxyl-telechelic liquid natural rubber has 1,4-cis microstructure.
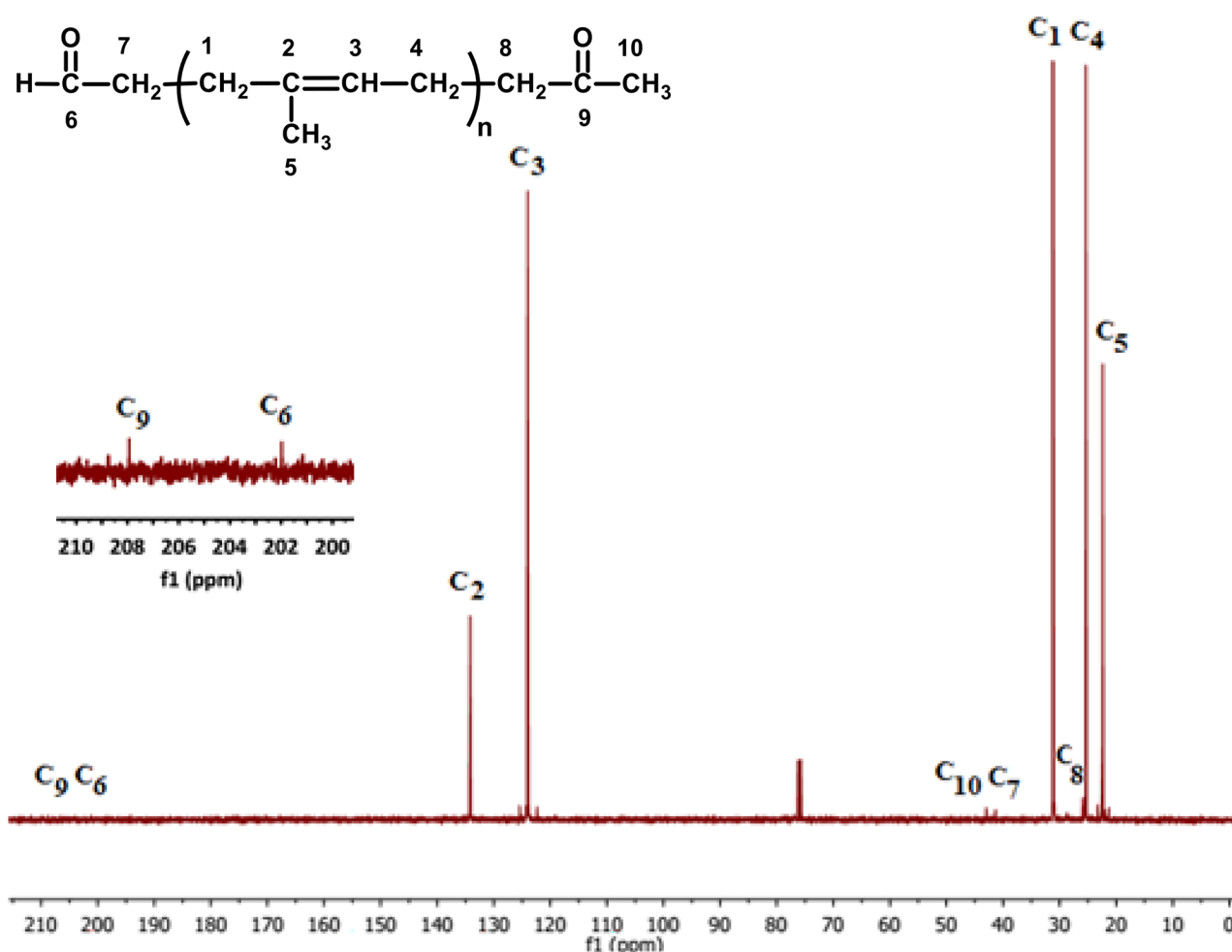
Fig. 8 ^{13}C NMR spectrum of carbonyl-telechelic liquid natural rubber

The number average functionality (f_n) of hydroxyl-telechelic liquid natural rubber was estimated by the following equation:
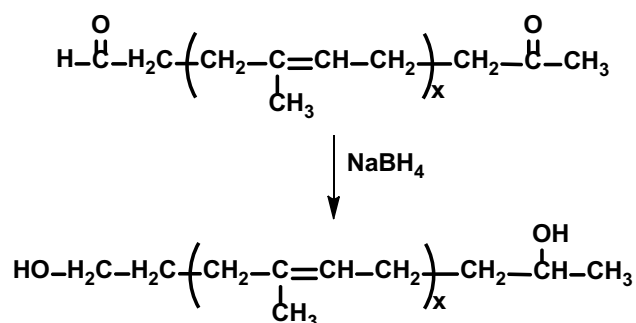
$$F_n = \frac{M_n \times OH_v}{56100}$$

Fig. 9 Reduction of carbonyl-telechelic liquid natural rubber by sodium borohydride

where M_n is number average molecular weight (g/mol) and OH_v is hydroxyl number of hydroxyl-telechelic liquid natural rubber (mgKOH/g).

M_n was measured by GPC and OH_v was determined by titration.

The calculated functionality of hydroxyl-telechelic liquid natural rubber is 2.3 which confirms the presence of primary and secondary hydroxyl groups at chain ends of polymer as confirmed by FT-IR and ^{1}H NMR data.

Degradation of natural rubber in latex phase

Degradation of natural rubber was also investigated in latex phase. It was observed that by the injection of ozone, the latex was coagulated. In order to increase the stability of the latex, nonylphenol ethoxylates was added to the latex as a nonionic emulsifying agent. The degradation of natural rubber in latex phase was carried out by injecting ozone gas into the mixture. The reaction was performed in various conditions as listed in Table 3.

Table 2 Optimization of the reaction of carbonyl-telechelic liquid natural rubber with sodium borohydride[a]

Entry	Solvent	NaBH$_4$: Carbonyl ratio	Temperature (°C)	Time (h)	Aldehyde to vinyl ratio[b] (%)
1	Chloroform	6	60	18	1.91
2	Chloroform	6	30	18	2.25
3	Chloroform	8	60	18	1.89
4	Cyclohexane	6	60	18	2.1
5	Cyclohexane	6	30	18	2.6
6	Cyclohexane	8	60	18	1.9
7	THF	6	30	18	0.098
8	THF	6	40	18	0.086
9	THF	6	50	18	0.078
10	THF	6	60	18	0.075
11	THF	6	60	6	0.078
12	THF	6	60	4	0.079
13	THF	6	60	3	0.084
14	THF	7	60	4	0.013
15	THF	8	60	4	0
16	THF	8	30	4	0.012

[a]Reaction conditions: 6 g carbonyl-telechelic liquid natural rubber, 50 mL solvent

[b]Calculated by ^{1}H NMR spectroscopy

Although the molecular weight of the oxidized rubber was decreased, a liquid product was not obtained. The isolated product was in the form of a solid material. The molecular weight of the rubber was decreased by increasing time of the ozone injection and temperature of the reaction. At the best condition, the molecular weight of
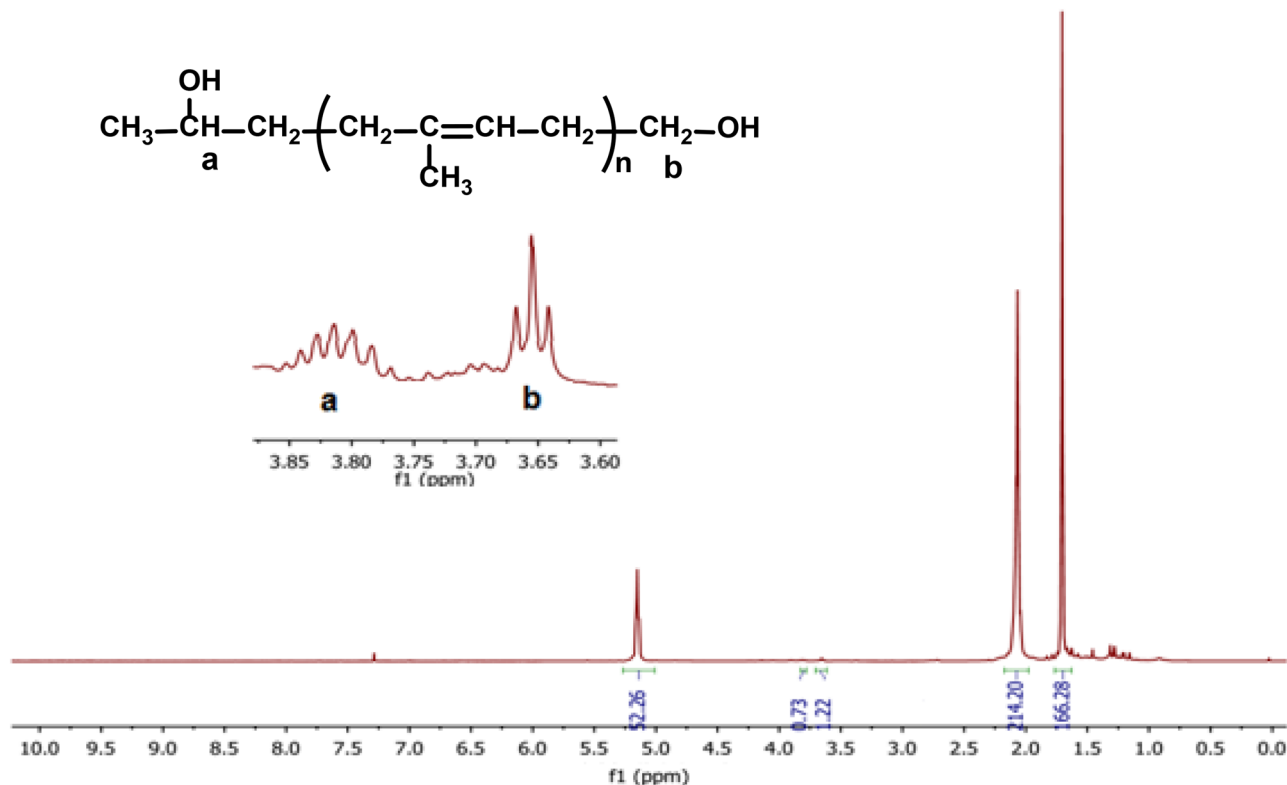
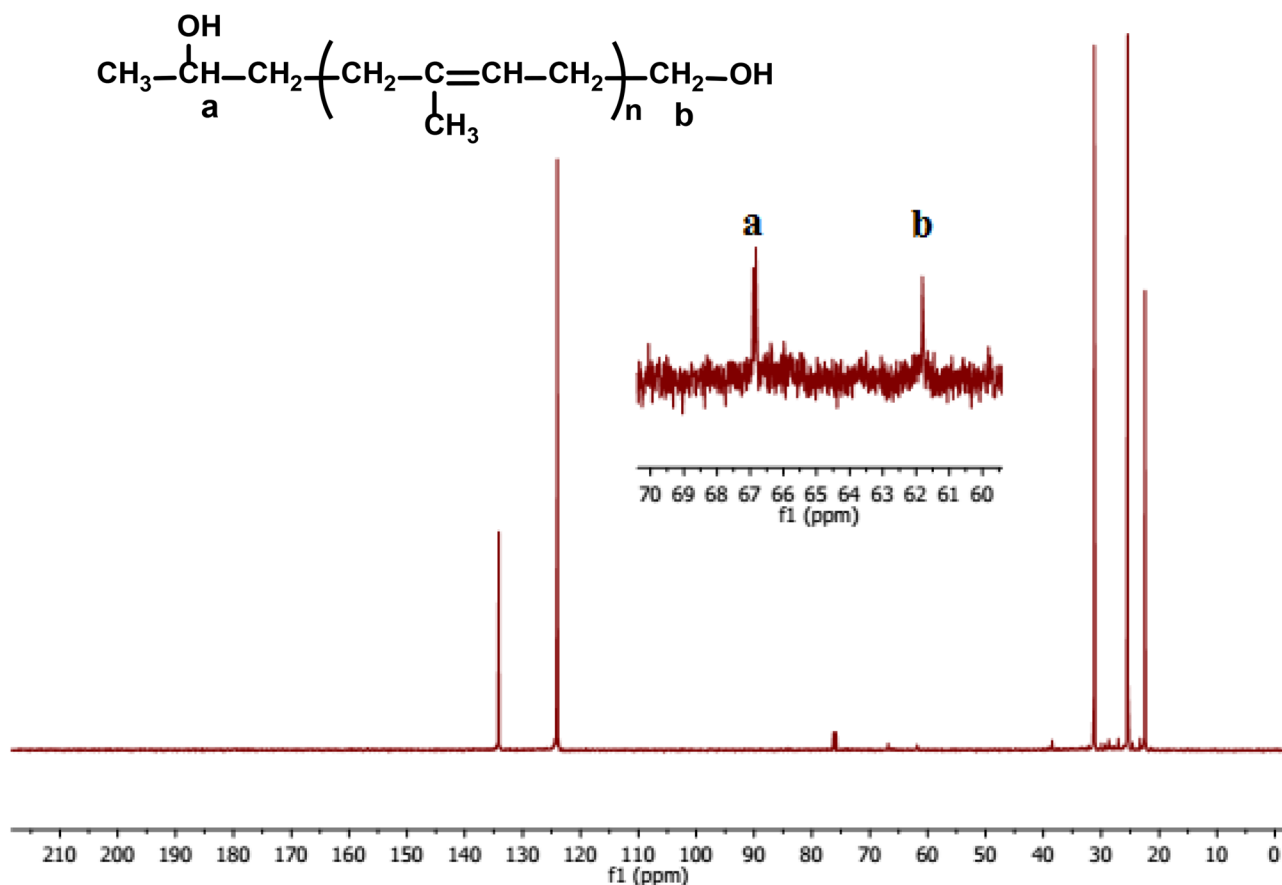**Fig. 10** ^{1}H NMR spectrum of hydroxyl-telechelic liquid natural rubber

Fig. 11 ^{13}C NMR spectrum of hydroxyl-telechelic liquid natural rubber

the oxidized rubber reached to 201,000 g/mol (Table 3, Entry 8). The results indicate that although degradation of natural rubber by ozonolysis in chloroform successfully

Fig. 12 FT-IR spectrum of hydroxyl-telechelic liquid natural rubber

provided liquid natural rubber, the same procedure is not successful in latex phase.

Synthesis of polyurethane

The synthesized hydroxyl-telechelic liquid natural rubber was further used as a polyol for preparation of a polyurethane elastomer. Since the synthesized telechelic liquid natural rubber contains active hydroxyl end groups, it can be used as a polyol for preparation of polyurethane materials. Hydroxyl-telechelic liquid natural rubber was reacted with TDI and an elastomeric material was obtained, according to the reaction shown in Fig. 13.

FT-IR spectrum of the prepared material is shown in Fig. 14. The peaks appeared at 1730 cm^{-1} and 3340 cm^{-1} are attributed to the stretching vibrations of urethane and -N–H groups, respectively. The absorption bands appeared at 1598 cm^{-1} and 1531 cm^{-1} are related to the bending vibrations of –N–H and stretching vibrations of C-N, respectively. These results indicate that urethane linkages were successfully formed. The other peaks appeared at 2919 cm^{-1} and
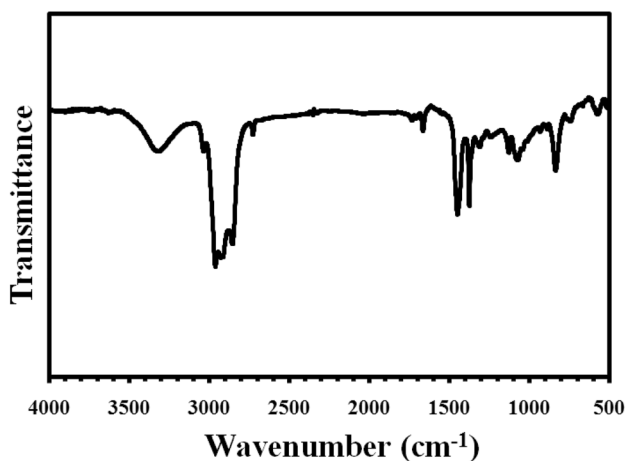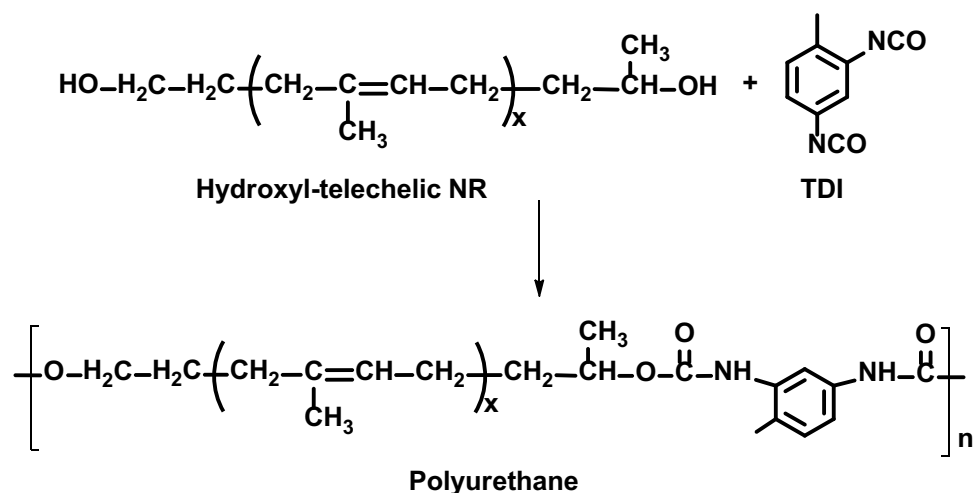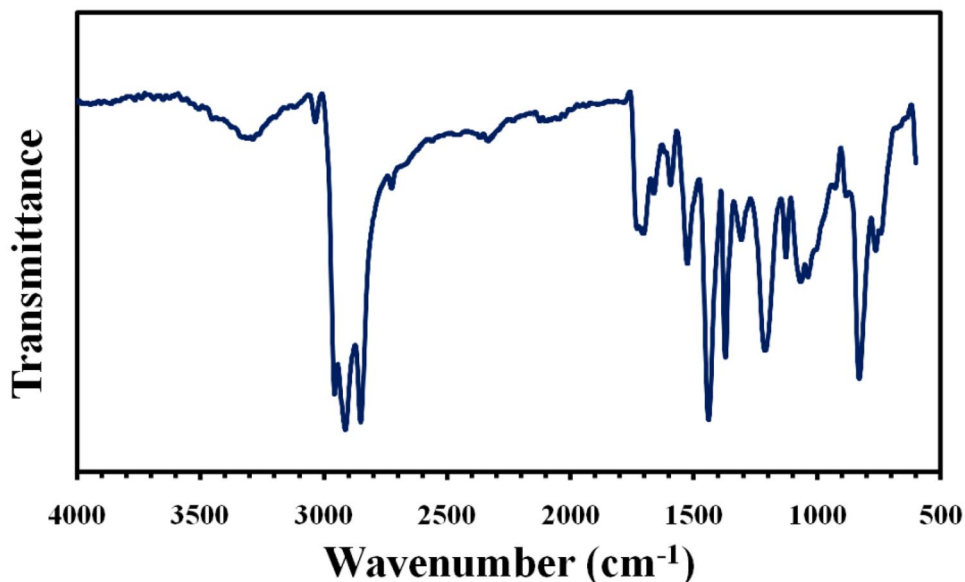
Table 3 Ozonolysis of natural rubber in latex phase[a]

Entry	Temperature (°C)	Time (h)	M_n (g/mol)
1	0	6	260,000
2	30	6	246,000
3	60	6	228,000
4	80	6	224,000
5	80	8	218,000
6	90	8	215,000
7	80	10	203,000
8	80	12	201,000

[a]Reaction conditions: 10 g NR latex, 0.08 g nonylphenol ethoxylates and a constant rate of ozone gas (10 g/h)

2850 cm^{-1} are related to the stretching vibrations of C-H bonds and the peaks appeared at 1375 cm^{-1} and 1445 cm^{-1} are related to the bending vibrations of methyl and methylene groups.

The DSC curve of the prepared polyurethane is shown in Fig. 15. The endothermic peak appeared at 325.74 °C and the exothermic peak appeared at 470.28 °C is related to the thermal decomposition of urethane linkages and the backbone of hydroxyl-telechelic liquid natural rubber, respectively. The results confirm that the synthesized hydroxyl-telechelic liquid natural rubber can be used as an alternative for traditional polyols in the production of polyurethane materials.

Fig. 13 The reaction of hydroxyl-telechelic liquid natural rubber with TDI

Fig. 14 FT-IR spectrum of the prepared polyurethane

Fig. 15 DSC curve of the prepared polyurethane
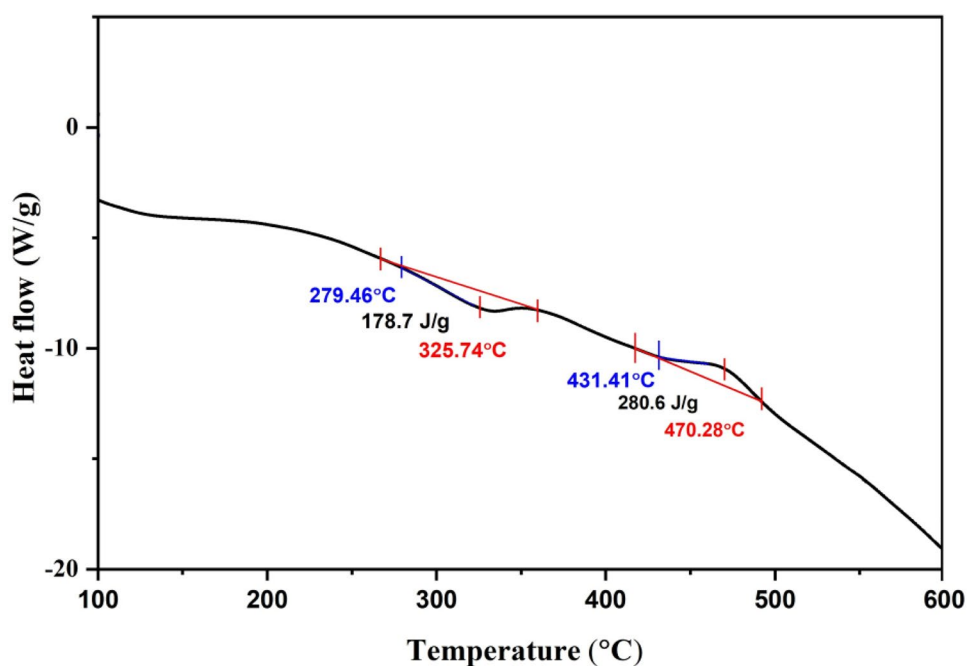
Conclusion

Oxidative cleavage of natural rubber (NR) by ozone in organic phase was studied. The FT-IR and NMR spectral data of the prepared liquid natural rubber confirmed the presence of terminal carbonyl groups in the structure of the fragmented rubber. The depolymerized natural rubber then was subjected to reduction using sodium borohydride and liquid natural rubber with terminal primary and secondary hydroxyl groups was prepared. At the optimum conditions, the molecular weight of NR was reduced to 2368 g/mol. The microstructure of the isolated liquid natural rubber is similar to that of natural rubber and contains *cis*-1,4-isoprenic unitsas determined by ^{13}C NMR and FT-IR spectroscopy. Direct ozonolysis of diluted samples of natural rubber in latex phase was also carried out, but an efficient decrease in molecular weights was not achieved.

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