Controlled Degradation of Natural Rubber and Modification of the Obtained Telechelic Oligoisoprenes: Preliminary Study of Their Potentiality as Polyurethane Foam Precursors

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ABSTRACT: Telechelic oligoisoprenes were successfully prepared by the selective controlled degradation of natural rubber, a renewable source, via epoxidation and cleavage reactions. The molar mass of the oligoisoprene product obtained depends on the degree of epoxidation of the starting materials. The chemically modified structures obtained via epoxidation, hydrogenation, and ring opening of epoxide groups were also studied, and the chemical structures and thermal properties of the oligoisoprene products were determined. Moreover, the preliminary study of preparation of hydroxytelechelic natural rubber (HTNR)-based polyurethane foam was performed. A novel HTNR-based polyurethane foam was successfully prepared and its thermal properties were investigated and the results indicated that the HTNR-based polyurethane foam has a good low temperature flexibility. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1279–1289, 2010

Key words: controlled degradation; telechelic; natural rubber; polyurethane foam oligoisoprenes

INTRODUCTION

The synthesis of reactive functional polymers from renewable sources has attracted considerable attention from polymer scientists throughout the world because of their potential attributed as substitute for petrochemical derivations. With petroleum production facing exhaustion day over day, scientists and technologists have recently started to focus their attention on the use of renewable materials as substitutes for raw materials for the manufacture of reactive polymers.[1]

Natural rubber (NR) is an interesting choice of natural polymer that can be modified to become a reactive functional polymer. Many reactions on the reactive double bonds of isoprene structure along the molecular chain such as epoxidation,[2,3] hydrogenation,[4–6] graft copolymerization,[7,8] and oxidative degradation reaction[9–13] have recently been investigated.

The chemical degradation of NR is a straightforward method of creating functional liquid NR that can be used for compatibilizer,[14,15] adhesive,[16] and coating[17,18] applications. Moreover, the specific functional groups at chain ends (telechelic liquid natural rubber, TLNR) are potentially reactive with other reagents via chain extension reactions to synthesize new polymer structures.[1,19–21]

Many techniques have been used to prepare TLNR. A phenylhydrazine-oxygen system was developed by French researchers[13,22] facilitated the synthesis TLNR of targeted molecular weight, however, suffered from the use of toxic reagents and hard to remove impurities that left the products a dark brown color. The oxidation of NR by hydrogen peroxide in tetrahydrofuran (THF) under UV irradiation was also performed; however, the degraded NR structure was complicated by secondary reactions.[23,24] Tangpakdee et al.[25] reported the degradation of deproteinised NR latex with (Potassium persulphate, $K_2S_2O_8$) but the occurrence of competitive

reactions between epoxidation and cleavage reactions meant that the degradation reaction was not completely controlled. The degradation of deproteinised epoxidized natural rubber latex (ENR) with periodic acid was similarly shown to occur in latex phase, but the epoxide content both before and after the degradation of the ENR were approximately the same.[10]

During the last decade, our research group has focused on selective degradation of synthetic cis-1,4-polyisoprene using well-controlled oxidative chain cleavage reaction leading to new carbonyl telechelic cis-1,4-polyisoprene.[9,19,20,26] Chemical modifications of carbonyl end-groups and carbon–carbon double bonds at various ratios have led to the development of new hydroxyl and amino telechelic cis-1,4-polyisoprenes.[19,20,26] Moreover, polyurethane films based on these precursors were found to present some interesting mechanical,[19] biological,[1] and thermal properties.[19,27] In recent years, the majority of precursors used as starting materials in the polyurethane foams are polyether polyol or polyester polyol; however, polyurethane foams from hydroxytelechelic polydienes (hydroxyl telechelic polybutadiene and hydroxyl telechelic polyisobutylene) have been reported in only a few publications.[28,29] Moreover, there are some reports that NR can act as the starting material to synthesize polyurethane materials[19–21] except foam applications. Therefore, the preparation of NR-based polyurethane foams was an interesting choice for the development of new materials with controlled properties and an interesting case study into the potential use of renewable sources to reduce a whole or partially usage of the petroleum precursors.

In this work, we report the preparation of hydroxytelechelic oligoisoprenes of differing molecular weights from NR and the chemical modifications thereof. The chemical structures and the thermal properties of these poly(isoprenes) were defined, and their feasibility to be used as polyurethane foam precursors was investigated.

EXPERIMENTAL

Materials

Field NR latex (Dry rubber content, DRC = 27%) was purchased from Pattani Industrial, Thailand. Formic acid (99%), hydrogen peroxide (35%), m-chloroperbenzoic acid (70–75%), and sodium borohydride (98%) were purchased from Acros organic. Nonionic surfactant, Sinnopal NP 307, was purchased from Cognis. Periodic acid (99%), lithium aluminum hydride (95%), 18% palladium on activated carbon, and dibutyl tin dilaurate (DBTL) were purchased from Aldrich. P-MDI (Polymethylene pol-

yphenylpolyisocyanate, 31.5% free NCO content, $\overline{f_n}$ = 2.7) and Dabco33LV (33% triethylenediamine in propylene glycol) were purchased by BASF and Air products, respectively. Silicon surfactant was obtained from Goldchmidt. Anhydrous magnesium sulfate was dried in an oven at 100°C before use. Dichloromethane, methanol, ether, ethyl acetate, and THF were distilled before use.

Synthesis

Controlled degradation of NR

Preparation of epoxidized natural rubber (ENR 2). Field NR latex (NR 1) was diluted with water to 20% DRC and stabilized by 3 phr (% weight of dry rubber) Sinnopal NP 307 at room temperature for overnight before epoxidation. The epoxidation was carried out in a 500 mL three-necked round bottom flask with a controlled stirrer speed of 300 rpm. The latex was heated to 60°C before slow addition of the constant amount of formic acid ([HCOOH]/[isoprene unit] = 0.3 mol mol^{-1}). The latex was stirred for 15 min before hydrogen peroxide ([H$_2$O$_2$]/[HCOOH] = 1 mol mol^{-1}) was slowly added. The reaction was allowed to occur for 4 and 8 h, respectively. The ENR 2 was coagulated in methanol, washed several times with water, and dried in a vacuum oven at 40°C for 2 days. The calculation of epoxide content of ENR has been described in previous works.[10,30]

^{1}H-NMR (CDCl$_3$) δ (ppm): 1.29 (s, CH_3COCH—), 1.67 (s,—CH_3isoprenic), 2.04 (m, —CH_2isoprenic), 2.70 (t, CH$_3$COCH—), 5.10 (t, =CHisoprenic).

^{13}C-NMR (CDCl$_3$) δ (ppm): 22.21 (CH$_3$COCH—), 25.90 (CH$_2$CH=C isoprenic), 31.70 (CH$_2$—C=CH isoprenic), 60.81 (CH$_3$COCH—), 64.50 (CH$_3$COCH—), 124.50 (C=CH isoprenic), 134.70 (C=CH isoprenic).

FTIR: $υ_{H—C=C}$ = 3035 cm^{-1}; $υ_{CH2, CH3}$ = 2900–2730 cm^{-1}; $υ_{C=O}$ = 1721 cm^{-1}; $υ_{C=C}$ = 1,664 cm^{-1}; $υ_{CH2, CH3\ cis-1,4-isoprene}$ = 1448, 1376 cm^{-1}; $υ_{C=C—H}$ = 834 cm^{-1}.

Preparation of carbonyl telechelic natural rubber (CTNR 3). This reaction was performed in a jacketed reactor with controlled temperature of 30°C. Periodic acid in THF (0.5 mol L^{-1}) was added dropwise to solution of ENR 2 in THF (0.4 mol L^{-1}). The oxidative reaction was allowed for 6 h at 30°C. The purification of product has been described in previous works.[9,19,20]

^{1}H-NMR (CDCl$_3$) δ (ppm): 1.67 (s, —CH_3isoprenic), 2.04 (m, —CH_2isoprenic), 2.13 (s, CH_3COCH$_2$), 2.25 (m, CH$_3$COCH$_2$CH_2), 2.34 (m, CH_2CH$_2$CHO), 2.43 (t, CH$_3$COCH_2CH$_2$), 2.49 (m, CH_2CHO), 5.10 (t, =CHisoprenic), 9.77 (s, CH$_2$CHO).

Disappearance δ (ppm): 1.29 (s, CH_3COCH—), 2.7 (t, CH$_3$COCH—)

^{13}C-NMR (CDCl$_3$) δ (ppm): 21.81 (CH$_3$COCH$_2$), 25.9 (CH$_2$CH=C isoprenic), 30.5 (CH$_2$CH$_2$OH), 31.7

(CH_2—C=$CH_{isoprenic}$), 41.88 (CH_2 CHO), 43.53 (CH_3-$COCH_2$), 124.5 (C=$CH_{isoprenic}$), 134.7 (C=$CH_{isoprenic}$), 201.61 (CH_2CHO), 208.21 (CH_3COCH_2).

FT-IR: $\upsilon_{H—C=C}$ = 3035 cm^{-1}; $\upsilon_{CH2, CH3}$ = 2900–2730 cm^{-1}; $\upsilon_{C=O}$ = 1721 cm^{-1}; $\upsilon_{C=C}$ = 1664 cm^{-1}; $\upsilon_{CH2,CH3\ cis\text{-}1,4\text{-}isoprene}$ = 1448, 1376 cm^{-1}; $\upsilon_{C=C—H}$ = 834 cm^{-1}.

Chemical modification of oligomers

Preparation of hydroxytelechelic natural rubber (HTNR 4). A solution of sodium borohydride (5 mol equiv) in THF (1 mol L^{-1}) was introduced into a jacketed reactor. A solution of CTNR 3 in THF was added dropwise, and the reaction was heated to 60°C for 6 h. The reaction mixture was then hydrolyzed with ice. The purification of product has been described in previous works.[19,20]

^{1}H-NMR (CDCl$_3$) δ (ppm): 1.20 (d, CH_3CHOH), 1.67 (s, —$CH_{3isoprenic}$), 2.04 (m, —$CH_{2isoprenic}$), 3.65 (t, CH_2OH), 3.80 (m, $CHOH$), 5.10 (t, =$CH_{isoprenic}$).

Disappearance: 2.04 (m, —$CH_{2isoprenic}$), 2.13 (s, CH_3COCH_2), 2.25 (m, $CH_3COCH_2CH_2$), 2.34 (m, CH_2CH_2CHO), 2.43 (t, $CH_3COCH_2CH_2$), 2.49 (m, CH_2CHO), 9.77 (s, CH_2CHO).

^{13}C-NMR (CDCl$_3$) δ (ppm): 25.9 (CH_2CH=$C_{isoprenic}$), 30.5 (CH_2CH_2OH), 31.7 (CH_2—C=$CH_{isoprenic}$), 39.0 ($CH_2CH(OH)CH_3$), 62.5 (CH_2OH), 67.5 (CH_3CHOH), 124.5 (C=$CH_{isoprenic}$), 134.7 (C=$CH_{isoprenic}$).

FTIR: υ_{OH} = 3350 cm^{-1}; $\upsilon_{C=C—H}$ = 3,035 cm^{-1}; $\upsilon_{CH2, CH3}$ = 2900–2730 cm^{-1}; $\upsilon_{C=C}$ = 1664 cm^{-1}; $\upsilon_{CH2, CH3\ cis\text{-}1,4\text{-}isoprene}$ = 1448, 1376 cm^{-1}; $\delta_{C=C—H}$ = 834 cm^{-1}.

Disappearance of $\upsilon_{C=O}$ at 1721 cm^{-1}.

Preparation of hydrogenated hydroxytelechelic natural rubber (HHTNR 5). HTNR 4 ($\overline{M_n}$ = 1050 g mol^{-1}, 0.83 g, 0.43 mmol) was dissolved in ethyl acetate (50 mL) in the presence of palladium on activated carbon (500 mg) and was then introduced into a catalytic hydrogenation device under 3.2 bar of hydrogen gas at room temperature. After 24 h, the pressure had dropped to 2.4 bar of hydrogen gas. The pressure was then released until normal atmospheric pressure was reached. The reaction mixture was filtered to remove the catalyst, and the solvent was evaporated to obtain the product.

^{1}H-NMR (CDCl$_3$) δ (ppm): 0.84 (s, CH_3CHCH_2) saturated unit), 1.20 (d, CH_3CHOH), 1.37 (s, CH_3CHCH_2), 1.67 (s, —$CH_{3isoprenic}$), 2.04 (m, —$CH_{2isoprenic}$), 3.65 (t, CH_2OH), 3.80 (m, $CHOH$), 5.10 (t, =$CH_{isoprenic}$).

^{13}C-NMR (CDCl$_3$) δ (ppm): 19.75 (CH_3CHCH_2) saturated unit), 25.9 (CH_2CH=$C_{isoprenic}$), 30.5 (CH_2CH_2OH), 31.7 (CH_2—C=$CH_{isoprenic}$), 32.80 (CH_3CHCH_2), 37.10 (CH_3CHCH_2), 39.0

($CH_2CH(OH)CH_3$), 62.5 (CH_2OH), 67.5 (CH_3CHOH), 124.5 (C=$CH_{isoprenic}$), 134.7 (C=$CH_{isoprenic}$).

FTIR: υ_{OH} = 3350 cm^{-1}; $\upsilon_{C=C—H}$ = 3035 cm^{-1}; $\upsilon_{CH2, CH3}$ = 2900–2730 cm^{-1}.

Intensity of the isoprene C=C bonds decreased after hydrogenation.

Preparation of epoxidized hydroxytelechelic natural rubber (EHTNR 6). HTNR 4 ($\overline{M_n}$ = 1,000 g mol^{-1}) was epoxidized by treatment with *m*-chloroperbenzoic acid (0.10, 0.20, and 0.30 mol equiv) in a three-necked round bottom flask at 0°C for 4 h. The purification of product has been described in previous works.[19]

^{1}H-NMR (CDCl$_3$) δ (ppm): 1.20 (d, CH_3CHOH), 1.29 (s, CH_3COCH—), 1.67 (s, —$CH_{3isoprenic}$), 2.04 (m, —$CH_{2isoprenic}$), 2.7 (t, CH_3COCH—), 3.65 (t, CH_2OH), 3.80 (m, $CHOH$), 5.10 (t, =$CH_{isoprenic}$).

^{13}C-NMR (CDCl$_3$) δ (ppm): 21.81 (CH_3COCH—), 25.9 (CH_2CH=$C_{isoprenic}$), 30.5 (CH_2CH_2OH), 31.7 (CH_2—C=$CH_{isoprenic}$), 39.0 ($CH_2CH(OH)CH_3$), 60.81 (CH_3COCH—), 64.50 (CH_3COCH—), 62.5 (CH_2OH), 67.5 (CH_3CHOH), 124.5 (C=$CH_{isoprenic}$), 134.7 (C=$CH_{isoprenic}$).

FTIR: υ_{OH} = 3350 cm^{-1}; $\upsilon_{C=C—H}$ = 3035 cm^{-1}; $\upsilon_{CH2, CH3}$ = 2900–2730 cm^{-1}; $\upsilon_{C=C}$ = 1664 cm^{-1}; $\upsilon_{CH2, CH3\ cis\text{-}1,4\text{-}isoprene}$ = 1448, 1376 cm^{-1}; $\delta_{C=C—H}$ = 834 cm^{-1}, $\upsilon_{C—O}$ (epoxide) = 870 cm^{-1}.

Preparation of multifunctional hydroxytelechelic natural rubber [HTNR 7 ($\overline{f_n}$ > 2)]. EHTNR 6 (11% epoxidation, 0.54 g, 0.50 mmol, or 23% epoxidation, 0.95 g, 0.90 mmol) in ether (50 mL) was added dropwise to a three-necked round bottom flask containing LiAlH$_4$ (5 mol equiv) in ether under nitrogen atmosphere and was left for 24 h. After this period had elapsed, the reaction mixture was hydrolyzed and the product was extracted with dichloromethane. The organic layer was dried with anhydrous MgSO$_4$, and the solvent was removed under vacuum to give the final product.

^{1}H-NMR (CDCl$_3$) δ (ppm): 1.15 (s, $CH_2C(OH)CH_2CH_3$), 1.20 (d, CH_3CHOH), 1.42 $CH_2C(OH)CH_2CH_3$), 1.67 (s, —$CH_{3isoprenic}$), 2.04 (m, —$CH_{2isoprenic}$), 3.65 (t, CH_2OH), 3.80 (m, $CHOH$), 5.10 (t, =$CH_{isoprnic}$).

Disappearance δ (ppm): 1.29 (s, CH_3COCH), 2.7 (t, CH_3COCH).

^{13}C-NMR (CDCl$_3$) δ (ppm): 25.9 (CH_2CH=$C_{isoprenic}$), 28.69 ($CH_2C(OH)CH_2CH_3$), 30.5 (CH_2CH_2OH), 31.7 (CH_2—C=$CH_{isoprenic}$), 39.0 ($CH_2CH(OH)CH_3$), 40.92 ($CH_2C(OH)CH_3CH_2$), 62.5 (CH_2OH), 67.5 (CH_3CHOH), 71.63 ($CH_2C(OH)CH_2CH_3$), 124.5 (C=$CH_{isoprenic}$), 134.7 (C=$CH_{isoprenic}$).

FT-IR: υ_{OH} = 3350 cm^{-1}; $\upsilon_{C=C—H}$ = 3035 cm^{-1}; $\upsilon_{CH2, CH3}$ = 2900–2730 cm^{-1}; $\upsilon_{C=C}$ = 1664 cm^{-1}; $\upsilon_{CH2, CH3\ cis\text{-}1,4\text{-}isoprene}$ = 1448, 1376 cm^{-1}; $\delta_{C=C—H}$ = 834 cm^{-1}.
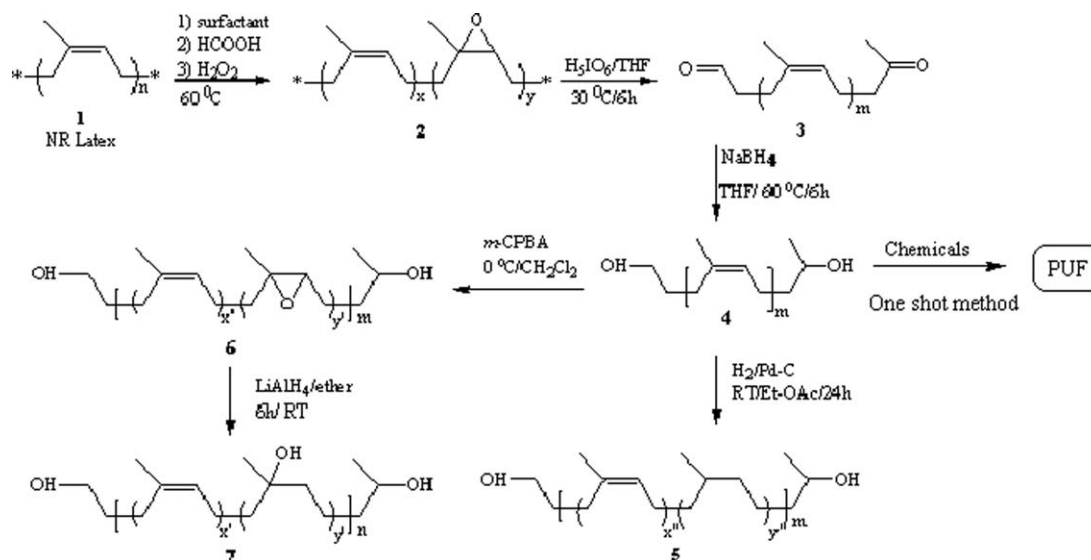
Figure 1 Preparation and chemical modification of natural rubber based oligomers.

Preparation of polyurethane foams

Polyurethane foams based on HTNR1000 ($\overline{M_n}$ = 1,000 g mol^{-1}) were prepared by the one-shot method (Fig. 1). HTNR1000 (4 g), water (0.16 g), silicone surfactant (0.034 g), Dabco 33-LV (0.006 g), DBTL (0.004 g), P-MDI (3.4 g), and dichloromethane (1 g) were mixed in a 250-mL beaker with a stirring speed of 11,000 rpm until a white liquid was observed. The white liquid was poured into molds and placed in an oven at 40°C for 48 h before testing.

Instruments

NMR analysis

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 400 Fourier transform spectrometer operating at 400.13 and 100.62 MHz, respectively. The samples were dissolved in CDCl$_3$, using tetramethylsilane as an internal standard.

FTIR analysis

FTIR spectra were recorded in a range of 4000–500 cm^{-1} on a Fourier transform Perkin-Elmer 1750 spectrophotometer equipped with a diamond attenuated total reflection (ATR) device.

Size exclusion chromatography

The average molecular weights ($\overline{M_n}$,$\overline{M_w}$) and molecular weight distributions (PDI) were measured using size exclusion chromatography (SEC) equipped with a spectra system AS1000 autosampler and a guard column (polymer laboratories, PL gel 5 μm Guard 50 × 7.5 mm) connected to the two columns (polymer laboratories, 2PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm). The system uses two detectors, that is, spectra system RI-150 and spectra system UV 2000. The eluent used was THF at a flow rate of 1 mL min^{-1} at 35°C. Polystyrene standards (580–483 × 10^3 g mol^{-1}) were used to calibrate the SEC. Polystyrene standardized molecular weights were corrected by the Benoit factor B according to a known formula.[31]

Maldi-TOF analysis

MALDI-TOF mass spectra (MS) was recorded on a Bruker Biflex III equipped with a nitrogen laser (λ337 nm). All MS were obtained in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH$_2$Cl$_2$ solutions using dithranol as matrix and silver trifluoroacetate (AgTFA) as doping agent. All data were processed using the Bruker XTOF software.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments (DSC Q 100) with a heating rate of 10°C min^{-1} in a range of −80 and 150°C under nitrogen atmosphere at a flow rate 50 mL min^{-1}. The sample weight was about 5 mg. Calibration was obtained by using indium as a reference material.

Thermogravimetric analyzer

Thermogravimetric analyzer (TGA) analysis was performed on a TA Instruments (TGA Q 100) with a heating rate of 10°C min^{-1} from room temperature

to 600°C under nitrogen atmosphere at a flow rate 90 mL min^{-1} using ~ 10 mg of sample for analysis.

Cell morphology

Cell dimension of polyurethane foams was determined according to BS 4443-Part I: 1988. Cell count is defined as the number of cell per centimeter of sample length. Cell size is defined as the average of dimension cell. The samples were magnified 22 times and photographed by optical microscope (Olympus model SZ-PT, Japan).

RESULTS AND DISCUSSIONS

Controlled degradation of NR

The controlled degradation reaction of NR was performed via a two-step procedure. The first step was the epoxidation of NR **1** which using *in situ* performic acid generated from a specific amount of formic acid and hydrogen peroxide with nonionic surfactant at 60°C, while the second step is the selective cleavage reaction via the epoxide group of ENR dissolved in THF with periodic acid (H_5IO_6) at 30°C, as shown in Figure 1.

It was found that the degree of epoxidation of ENR from field NR was 4.1% after 4 h and 10.0% after 8 h. Later, the ENR solution was modified by using a specific amount of periodic acid in THF at 30°C for a period of 6 h (Fig. 1). These isolated degradation products were both yellowish viscous liquids and were obtained in yields of more than 80% (Table I) The molecular weights obtained were:

$\overline{M_n} = 1980$ g mol^{-1} (Eq. PS), PDI = 1.92 for the CTNR from 10.0% epoxidation

$\overline{M_n} = 2670$ g mol^{-1} (Eq. PS), PDI = 2.02 for the CTNR from 4.1% epoxidation

The controlled selectively oxidative degradation of ENR in THF phase versus in latex phase with periodic acid in previous work[10] were compared. We found that the degraded NR obtained in solvent was better than that obtained in latex in terms of both molecular weight and microstructure control. These well-defined structures of telechelic NR are advantageous for the synthesis of novel block copolymers or branched polymers from natural polymers and for the introduction of other functional groups at chain ends or at the vinyl bonds, facilitating control over the properties of the degraded polymer. In addition, high yields of oligomers can be obtained from the direct use of field NR latex without the need for purification or deproteinization, and partial epoxidation (4 and 10%) allows the ENR to be dissolved in THF.

Chemical modification of oligomers

The carbonyl telechelic natural rubber (CTNR **3**) was modified into hydroxytelechelic natural rubber (HTNR **4**). By selection of the appropriate reagents and conditions, these oligomers may be developed into a variety of functional NRs, from difunctional hydrogenated hydroxytelechelic natural rubber (HHTNR **5**) to partially EHTNR **6**) and a multifunctional hydroxytelechelic natural rubber (HTNR **7** ($f_n > 2$)) as shown in Figure 1.

Synthesis of hydroxytelechelic natural rubber (HTNR 4)

The CTNR **3** was treated by NaBH$_4$ as shown in Figure 1, which specifically reduces the carbonyl groups (aldehyde and ketone) without affecting the vinyl bonds to give a yellowish-viscous liquid as product. As expected, the $\overline{M_n}$ of oligomers could be

TABLE I
Characteristics of Oligomers and Polyurethane Foam

| Samples | Yield (%) | $\overline{M_n}$ (NMR) | $\overline{M_n}$ (SEC)[a] | PDI | $\overline{f_n}$ (OH) | T_g (°C) | Thermal degradation steps | | | |
| | | | | | | | 1st step | | 2nd step | |
							T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
NR	–	–	–	–	–	–68	381	99	–	–
HTNR1000	83	1000	1330	1.92	2.00	–59	378	99	–	–
HTNR2000	85	2000	1790	2.02	2.00	–63	377	99	–	–
11% EHTNR1000	85	900	1000	1.70	2.00	–49	283	15	378	83
23% EHTNR1000	87	860	800	1.90	2.00	–41	248	18	398	78
33% EHTNR1000	77	1100	860	1.97	2.00	–36	278	13	400	83
98% HHTNR	70	1240	960	2.20	2.00	–59	462	99	–	–
HTNR $\overline{f_n}$>2 (11%E)	65	1230	*	*	2.70	–43	385	99	–	–
HTNR $\overline{f_n}$>2 (23%E)	60	950	*	*	4.30	–27	382	99	–	–
PUF (HTNR1000)	–	–	–	–	–	–52	321	21	371	68

[a] $\overline{M_{nSEC}}$ determined with polystyrene standards and corrected with Benoit factor (0.67 for polyisoprene) ($\overline{M_{nSEC}}$ PI = 0:67 × M_{nSEC}PS).
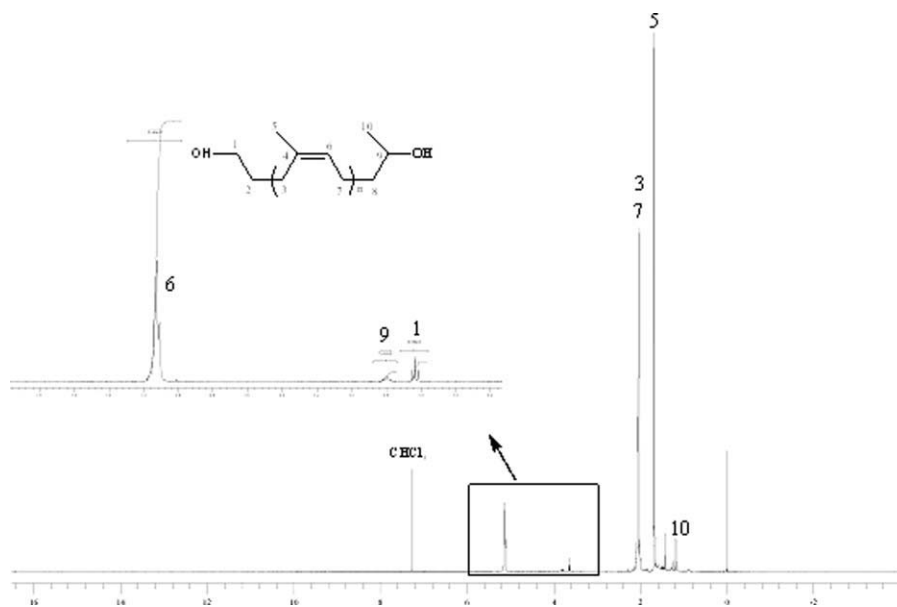* Not determined.

Figure 2 ^{1}H-NMR spectrum of HTNR **4.**

controlled by the amount of epoxide content of ENR (Table I, $\overline{M_n}$, and PDI data) with higher epoxide content of ENR used leading to lower molecular weight oligomers being formed.

Chemical modification of the polymer to demonstrate the presence of hydroxy functional groups at the chain ends was confirmed by NMR and FTIR. The ^{1}H-NMR spectrum in Figure 2 shows that the signal of vinyl proton (5.10 ppm) was unchanged whereas both signals of aldehyde protons at 9.80 ppm and methylic protons in ketone end group at 2.13 ppm, and the peak of CH_2 in α and β positions of carbonyl terminal functional groups between 2.20 and 2.60 ppm were completely disappeared. A new peak corresponding to aliphatic protons adjacent to secondary alcohol at 1.20 ppm and two peaks corresponding to CH (3.80 ppm) and CH_2 (3.68 ppm) adjacent to alcohol group at the terminal chain were observed. This ^{1}H-NMR analysis is in accordance with the FTIR spectrum where we observed the presence of strong peak of hydroxyl group at 3500 cm^{-1}, whereas the peak corresponding to the carbonyl group at 1720 cm^{-1} was absent (Fig. 3).

The average molecular weights ($\overline{M_n}$ and $\overline{M_w}$) and polydispersity index (PDI), as shown in Table I, were determined by SEC calibrated against polystyrene standards. Molecular weight values obtained from polystyrene equivalent were converted to
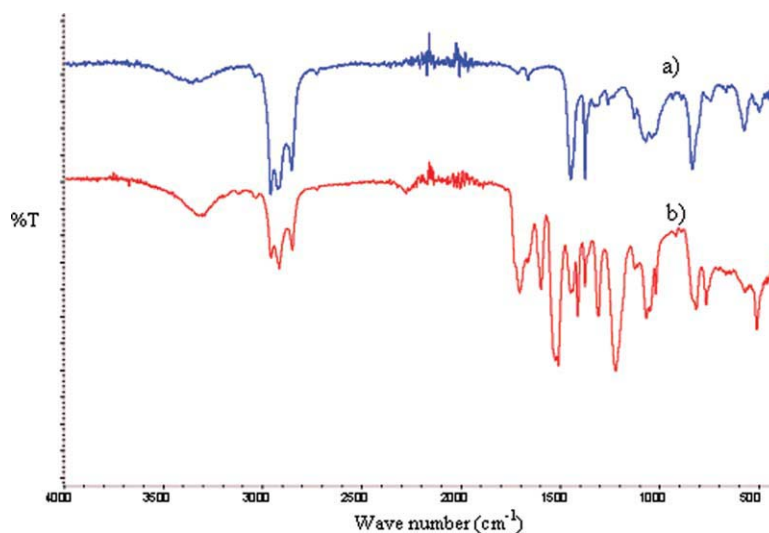

Figure 3 FT-IR spectrum of (a) HTNR and (b) polyurethane foam based on HTNR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
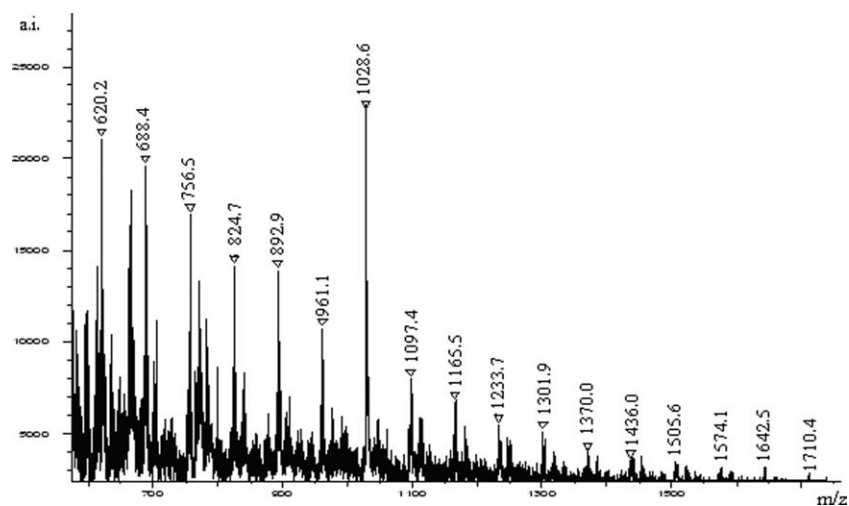
Figure 4 MALDI-TOF mass spectrum of HTNR1000.

actual values by using Benoit's factor, $B = 0.67$.[19,31] The relation of both values can be defined by $M_{PI} = B \times M_{PS}$ where M_{PI} corresponds to real molecular weights of cis-1,4-polyisoprene and M_{PS} is molecular weight obtained from standard polystyrene. These obtained values are comparable with those obtained by ^{1}H-NMR method. In addition, the average functionality of hydroxyl telechelic natural rubber was calculated in previously works[19,20] and is shown in Table I.

Moreover, the structure of HTNR was confirmed with MALDI-TOF analysis as shown in Figure 4 using Ditranol as a matrix and AgTFA doping agent. Sample peaks were identified with a mass corresponding to that of ionized HTNR molecules and silver (Ag). The theoretical masses (M) were calculated using the equation as shown below:

$$M = M(\text{end group}) + M(\text{Ag}) + nM(\text{repeating unit})$$

The isotopic distribution of observed peaks was identical to the simulation, as demonstrated in Figure 5. The different mass between these main peaks in spectrogram is equal to the repeating unit mass of polyisoprene ($M = 68$); therefore, the structure and the end functional groups of this oligomer were confirmed by this analysis method. In addition, the spectrogram (Fig. 4) shows two additional peaks at $M + 16$ and $M + 32$ corresponding to one and occasionally two epoxide groups, respectively, in the chain of few oligomers. However, these impurity products were not visible in the ^{1}H-NMR spectrum.

The average molecular weights ($\overline{M_n}$, $\overline{M_w}$) and polydispersity (PDI) were calculated from the MALDI-TOF spectrum as described in previous work.[32] The values of $\overline{M_n}$, $\overline{M_w}$, and PDI obtained are 960, 1050 g mol^{-1}, and 1.09 for HTNR1000; 1610, 1740 g mol^{-1}, and 1.08 for HTNR2000, respectively. These molecular weight values are comparable to those values obtained from the calculation of degree of polymerization by NMR. According to the results of some of our previous works,[1,19,20] the hydroxyl telechelic natural rubber has a well-controlled molecular weight, microstructure, and functionality at chain ends ($\overline{f_n} = 2$) and was obtained in high yield.
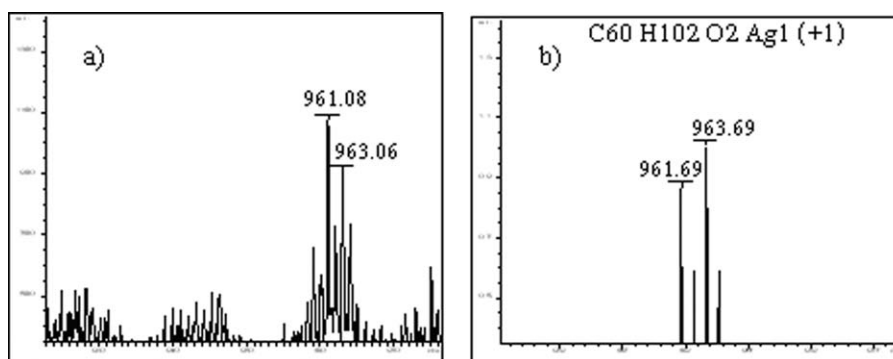

Figure 5 Isotopic distribution observed (a) and simulation (b) of HTNR molecule at $n = 11$ ionized of silver (Ag$^+$).
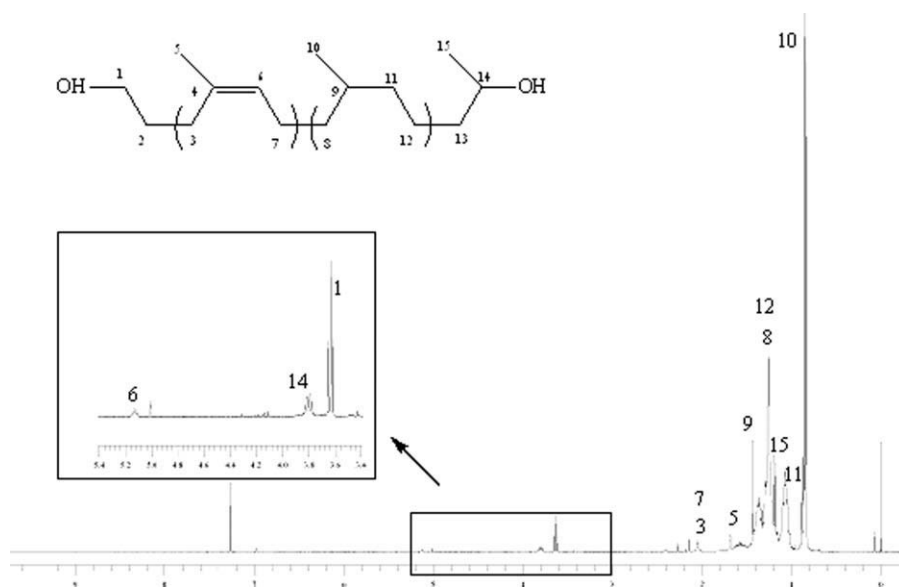
Figure 6 ^{1}H-NMR spectrum of HHTNR**5**.

Synthesis of hydrogenated hydroxytelechelic natural rubber (HHTNR 5)

Hydroxytelechelic natural rubber (HTNR), $\overline{M_n}$ = 1050 g mol^{-1} was hydrogenated as shown in Figure 1. Hydrogenation across the vinyl bonds was confirmed by NMR. The ^{1}H-NMR spectrum in Figure 6 shows that the intensity of the signal corresponding to the vinyl bonds of isoprene at 5.1 pm (C=CH) notably decreases, and new signals appear at 0.84 and 1.37 ppm corresponding to the aliphatic protons of the saturated chains unit. This confirms that the hydrogenation reaction occurs on hydroxytelechelic natural rubber structure, and the degree of hydrogenation calculated by ^{1}H-NMR to reach 98%.

Synthesis of epoxidized hydroxytelechelic natural rubber (EHTNR 6)

Hydroxytelechelic natural rubber with $\overline{M_n}$ = 1000 g mol^{-1} was reacted to 10, 20, and 30% epoxidation using m-chloroperbenzoic acid as reagent. This reaction, as shown in Figure 1, was performed at 0°C for 4 h. The results of ^{1}H-NMR analysis show the presence of the oxirane ring proton at 2.70 ppm and a
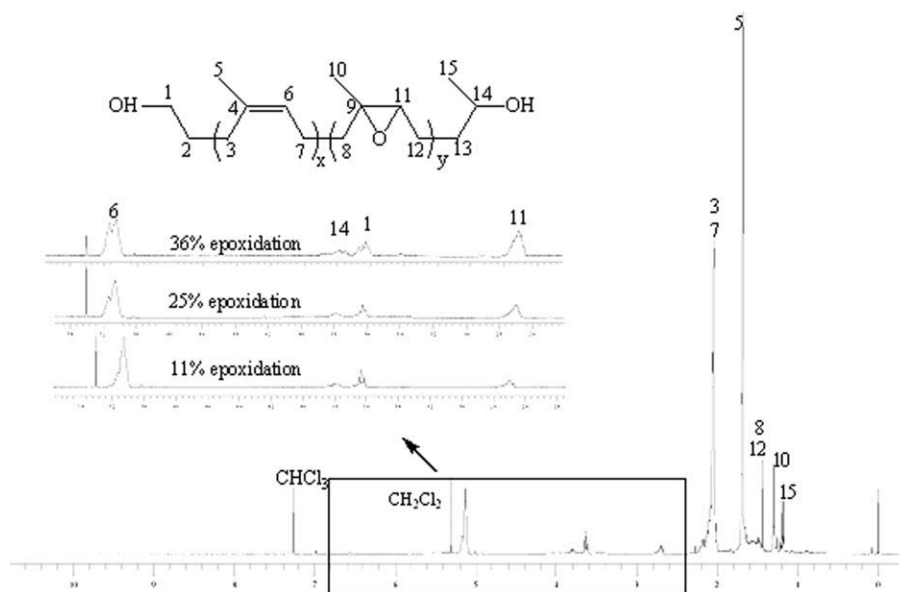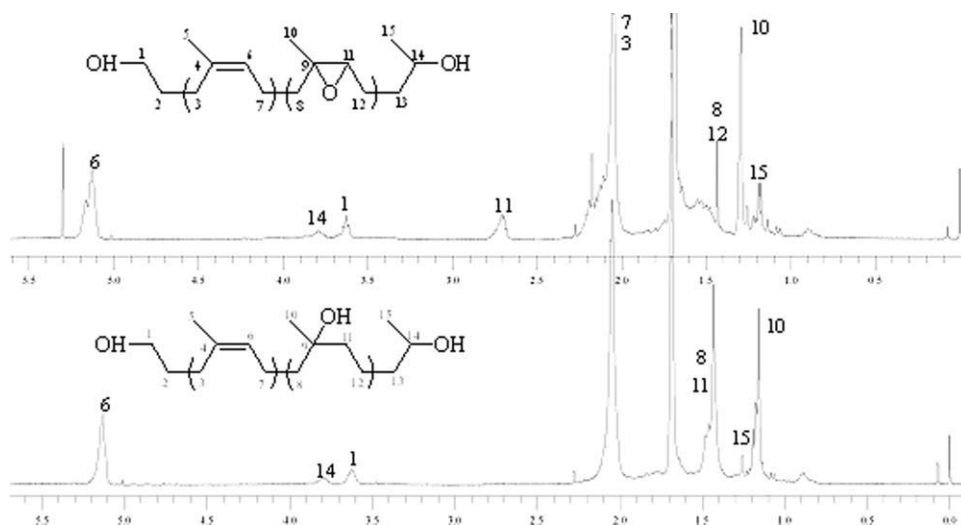

Figure 7 ^{1}H-NMR spectrum of EHTNR**6**.

Figure 8 ^{1}H-NMR spectrum of HTNR 7 ($f_n > 2$).

signal at 1.29 ppm corresponding to the methylic protons adjacent to the oxirane ring (Fig. 7).

Synthesis of multifunctional hydroxytelechelic natural rubber [HTNR 7 ($\overline{f_n} > 2$)]

The reduction of epoxide ring on EHTNR **6** ($\overline{M_n} = 1,000$) with $\sim$ 10 and 20% epoxidation was performed using lithium aluminum hydride (LiAlH$_4$) formed a telechelic natural rubber possessing tertiary alcohols throughout the backbone of the chain [HTNR **7** ($\overline{f_n} > 2$)] and with primary and secondary alcohols at the chain ends (Fig. 8). These reactions, as shown in Figure 1, were carried out for 6 h at room temperature. The yield of HTNR **7** ($\overline{f_n} > 2$) was 60%, which is the lowest of all oligomers studied. It is possible that this oligomer, which contains the most hydroxyl functionality, was partially retained in aqueous phase during the purification process thus limiting the yield.

The average functionality of oligomers was calculated from ^{1}H-NMR using the following relationship.

$$\overline{f_n} = [(I_{(CH3 \text{ tertiary alcohol})}) + I_{(CH3 \text{ secondary alcohol})} - 3\,I_{(CHOH)}/(3 \times I_{(CHOH)})] + 2$$

where

$I_{(CHOH)}$ = signal intensity of proton in α position of the secondary alcohol at 3.8 ppm

$I_{(CH3 \text{ tertiary alcohol})}$ = signal intensity of protons of methyl in β position of the tertiary alcohol at 1.15 ppm.

$I_{(CH3 \text{ secondary alcohol})}$ = signal intensity of protons of methyl in β position of the secondary alcohol at 1.18 ppm.

These functionalities and $\overline{M_n}$ of the modified hydroxytelechelic oligomers **7** through $\sim$ 10 and 20% EHTNR **6** are shown in Table I.

Thermal properties

DSC

The glass transition temperatures (T_g) of the oligomers HTNR1000, 2000 are slightly increased when compared with the T_g of NR because of the decrease of molecular weight and the presence of hydroxyl end-groups in the structure, as shown in Table I. The T_g of the oligomers (HTNR **4**, HHTNR **5**, EHTNR **6**, and HTNR **7** [$\overline{f_n} > 2$]) evaluated from second heating thermogram from DSC analysis.

A series of epoxidized hydroxytelechelic natural rubber (EHTNR **6**) with differing levels of epoxidation were degraded, and it was observed that increasing the epoxide content in the hydroxytelechelic natural rubber starting leads to an increase in
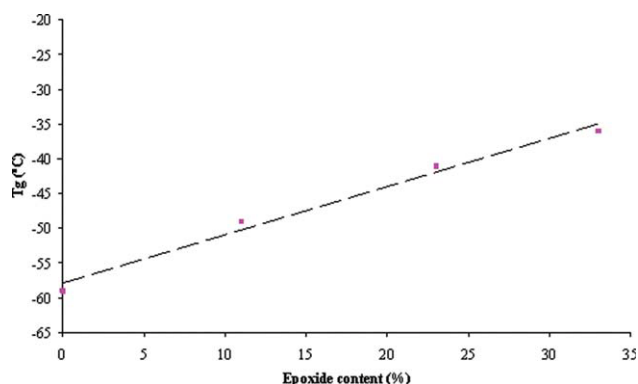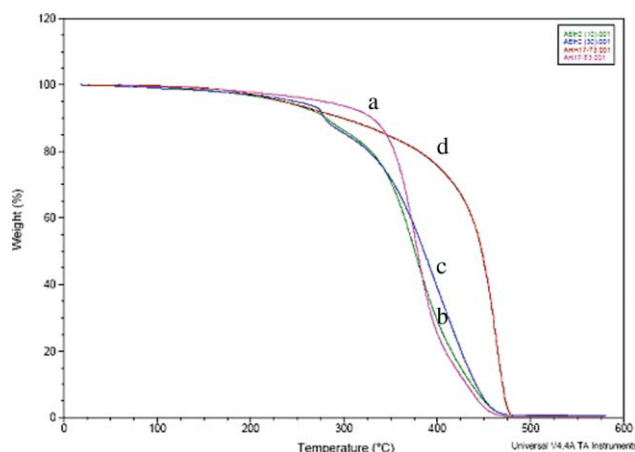

Figure 9 Tg versus epoxide content of HTNR1000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 10 TGA curves of (a) HTNR, (b) 10% EHTNR, (c) 30% EHTNR, (d) HHTNR. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the T_g of hydoxytelechelic oligoisoprenes formed by the degradation process (Table I and Fig. 9). Therefore, 33% EHTNR1000 has the highest T_g of all the epoxidized oligoisoprenes derived from HTNR1000 in this investigation. The increasing of epoxide groups on main chain leads to a more rigid backbone, inducing a decrease of backbone movement and an occurrence of chain interactions. This hypothesis was again supported by an increased of T_g of HTNR **7** ($\overline{f_n} > 2$), which was reduced from EHTNR **6** by LiAlH$_4$, when compared with the starting material (EHTNR **6**). These results are caused by chain interactions, which increase with increasing hydroxyl groups on polymer chains.

The T_g of HTNR based polyurethane foam tend to be higher than that of their starting oligomers (HTNR1000), because of the effect of physical crosslinks occurring between polymer chains via the urethane or urea groups. In addition, the HTNR based foam exhibited good flexibility at low temperature ($T_g = -52°C$) as shown in Table I.

Thermogravimetric analyzer

The thermal stability of oligomers with different molecular weights and microstructures were investigated under nitrogen atmosphere at a 10°C min^{-1} heating rate. All of the TGA results are summarized in Table I. Each characteristic temperature (T_{max}) corresponding to the maximum rate of degradation

and weight loss (%) were determined. It is worth mentioning that the thermal degradation of different HTNRs is not influenced by molecular weight.

The thermal degradation of HHTNR shows only one step [Fig. 10, curve (d)]. Its T_{max}, of more than 460°C, is noticeably the highest among these oligomers studied. This degradation step is because of oxidation, the contribution of which is higher than HTNR and other modified HTNRs. It is clear that the better thermal stability of HHTNR **5** is caused by the increased number of saturated units (98%) in polyisoprene backbone; therefore, we conclude that the thermal stability of hydroxytelechelic natural rubber can be improved by hydrogenation process.

In EHTNR **6** series, the thermal degradation curves of them show two steps of weight loss. The first step [i.e., 11% EHTNR1000 curve (b) and 33% EHTNR1000 curve (c)] likely corresponds to the degradation of epoxidized moieties located near the end-group of the oligomer chains or to the degradation of small molecules. An occurrence of intermolecular reactions between the remaining epoxide moieties lead to the increase in thermal stability observed in the secondary step (Fig. 10).

In the case of polyurethane foam based on HTNR, it was found that there are two steps degradation temperatures. The first step (321°C) corresponds to a degradation of the urethane group and the second step (371°C) corresponds to a further degradation of the oligoisoprenes (Table I). However, we can use other precursors (polyol, i.e., HTNR with $\overline{f_n} > 2$) or additives (chain extender such as diethanolamine and glycol) to improve the thermal stability of the polymer network.

Preparation of polyurethane foam

The chemical structures of polyurethane foam were determined by FTIR spectroscopy with measured using ATR technique. The IR spectrum (Fig. 3) showed the presence of absorption bands at around 3300, 1700, 1200 cm^{-1} corresponding to $N-H$, $C=O$ and $-C-O-$ stretching vibrations of urethane functional groups, respectively. The quasi disappearance of absorption peak at 2270 cm^{-1} shows a small residue of NCO function within the foam that might be the indication of incomplete reaction. However, this problem can be dissolved by keeping the samples in the oven more than 48 h to make sure the complete reaction. Other strong absorption peaks at 2700–3000

TABLE II
Some Physical Properties of Polyurethane Foam Based on HTNR1000

Precursor	Density (kg/m^3)	Cell count (cell in cm)	Cell size (mm)	Appearance	Cell characteristic
HTNR 1000	28.7 ± 4.3	24 ± 1.8	0.42	Light yellow	Open cell
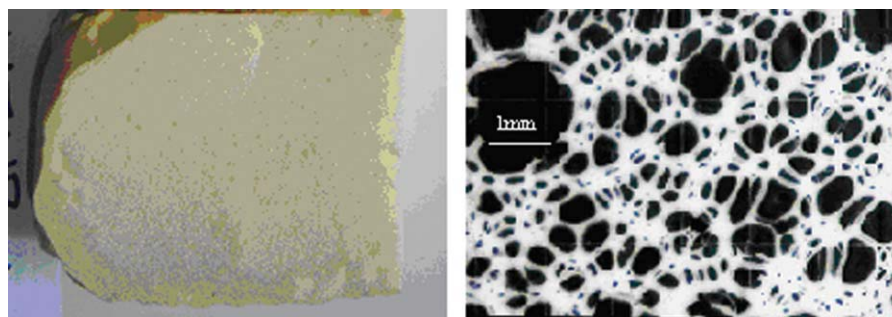
Figure 11 Sample of HTNR based polyurethane foam and optical microphotograph (×22). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and 1500 cm^{-1} were attributed to asymmetrical stretching of —CH$_2$ and —CH$_3$, and aromatic structure of isocyanates, respectively.

The physical properties of a HTNR based polyurethane foam are collected in Table II, and cell dimensions are shown in Figure 11. It was found that the cell size of foams based on HTNR was 0.42 mm, and spherical forms and regular size distribution were observed. Moreover, the obtained foams based on HTNR exhibit open cell structures.

CONCLUSIONS

In this work, the oligoisoprene with controlled molecular weight was successfully prepared by selective degradation of NR. It was shown that the oligomers with well-control of molecular weight and functionality were obtained with a good yield (80%). Well-controlled modified microstructures such as epoxide, saturated unit, and hydroxyl functionality of more than two were achieved. The HHTNR exhibits the highest maximum degradation temperature among all oligomers under this investigation. Moreover, the preliminary study of preparation of polyurethane foams based on HTNR was also investigated. It was found that this novel HTNR-based polyurethane foam that exhibited good low temperature flexibility can be successfully prepared. Therefore, this HTNR can be used as the starting material to replace the petroleum products for polyurethane foam synthesis.

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