

Article

A Structural Study of Epoxidized Natural Rubber (ENR-50) and Its Cyclic Dithiocarbonate Derivative Using NMR Spectroscopy Techniques

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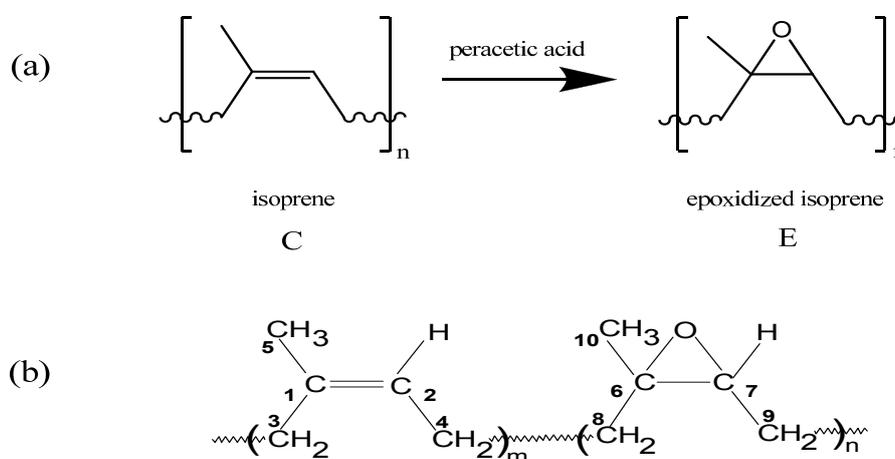
Abstract: A structural study of epoxidized natural rubber (ENR-50) and its cyclic dithiocarbonate derivative was carried out using NMR spectroscopy techniques. The overlapping ¹H-NMR signals of ENR-50 at δ 1.56, 1.68–1.70, 2.06, 2.15–2.17 ppm were successfully assigned. In this work, the ¹³C-NMR chemical shift assignments of ENR-50 were consistent to the previously reported work. A cyclic dithiocarbonate derivative of ENR-50 was synthesized from the reaction of purified ENR-50 with carbon disulfide (CS₂), in the presence of 4-dimethylaminopyridine (DMAP) as catalyst at reflux temperature. The cyclic dithiocarbonate formation involved the epoxide ring opening of the ENR-50. This was followed by insertion of the C–S moiety of CS₂ at the oxygen attached to the quaternary carbon and methine carbon of epoxidized isoprene unit, respectively. The bands due to the C=S and C–O were clearly observed in the FTIR spectrum while the ¹H-NMR spectrum of the derivative revealed the peak attributed to the methylene protons had split. The ¹³C-NMR spectrum of the derivative further indicates two new carbon peaks arising from the >C=S and quaternary carbon of cyclic dithiocarbonate. All other ¹H- and ¹³C-NMR chemical shifts of the derivative remain unchanged with respect to the ENR-50.

Keywords: ENR-50; 2D NMR; triad sequence; cyclic dithiocarbonate

1. Introduction

Epoxidized natural rubber (ENR) is a modified natural rubber (NR) [1]. A typical formation of ENR from NR, *cis*-1,4-isoprene, employing peracetic acid is shown in Scheme 1a [2]. The isoprene (C) and epoxidized isoprene (E) act as monomer units that are randomly distributed along the polymer chain [1]. Various degree of epoxidation of NR is commercially available. For examples, the isoprene units in the polymer chain are 25%, 50% and 75% epoxidized in ENR-25, ENR-50 and ENR-75, respectively. For the purpose of nomenclature, the general structure and the numbering of carbon atoms in ENR-50 is shown in Scheme 1b.

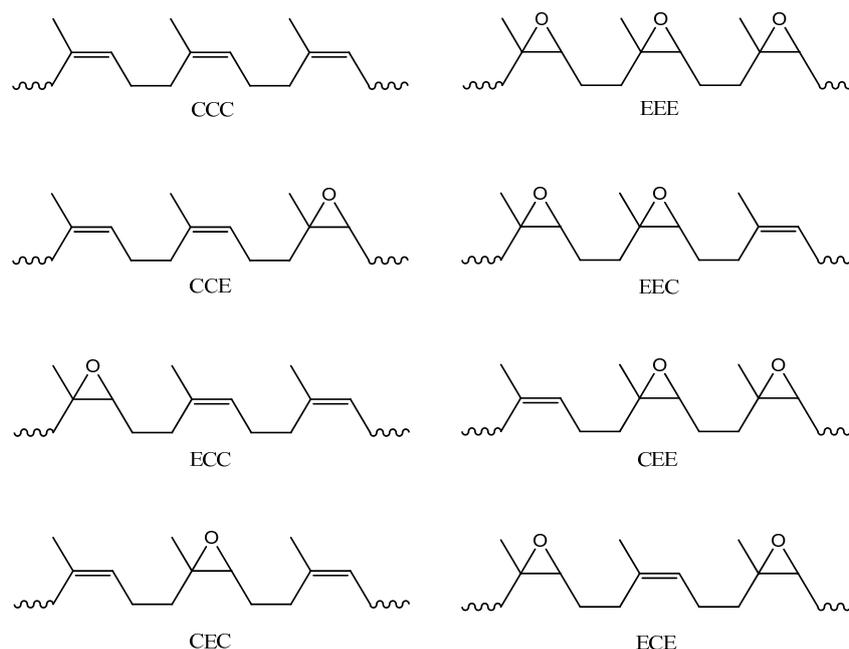
Scheme 1. (a) Modification of NR to ENR [2] and (b) the general structure and the numbering of carbon atom in ENR-50 employed in this work.



NMR spectroscopy techniques are widely used to characterize various polymers either in liquid or solid state. Characterization using 1D NMR gives structural elucidation on reactive groups and monomer units in the polymer chain. However, the 2D NMR extends detail structural arrangements of the monomer units within the polymer chain. Either or both of these techniques have been applied to ENR-25 [3], ENR-50 [4–9], and ENR-75 [6], and other ENR-related compounds [10]. However, most of these works fall short of full structural assignments due to the overlapping of signals arising from the randomly distributed C and E monomer units [11,12].

The random arrangement of C and E units within the ENR chains give rise to several probable sequences. This inevitably makes the structural interpretation via the NMR techniques difficult. To overcome this, Bradbury and Perera [12] have established a procedure of grouping the randomly located monomer units into triad sequence. A triad is made up of three possible monomer units. All possible triad sequences of ENR-50 are shown in Figure 1.

In a triad, the neighboring units may dictate the ¹H and ¹³C environments of the middle unit. It is the middle unit that will reveal the triad structure. For example, an ENR chain fragment may comprise of C unit attached to an E unit which in turn is attached to another E unit. Thus, this triad sequence is denoted as CEE. Triad comprising of similar unit is only denoted by a single unit. Triad CCC is denoted as C and triad EEE is denoted as E. The methyl of the middle unit in the CEE and CCC triads are referred to as CE¹⁰E and C⁵, respectively, and the methylene carbon of C³ refers to the third carbon in the ENR-50 structure as shown in Scheme 1b. This also applies to the proton in the ENR-50 structure.

Figure 1. The possible triad sequence of ENR-50.

Thus prior to the advent of the triad sequence, previous workers [6–9,12,13] were only able to ascertain the assignments of ^1H -NMR chemical shifts of the methine proton of C and E units but sporadically to either the methyl and or methylene protons of C and E of the ENR. Saito *et al.* [11] have reported the use of computer simulation [14,15] to predict chemical shifts of these protons and their triad assignments.

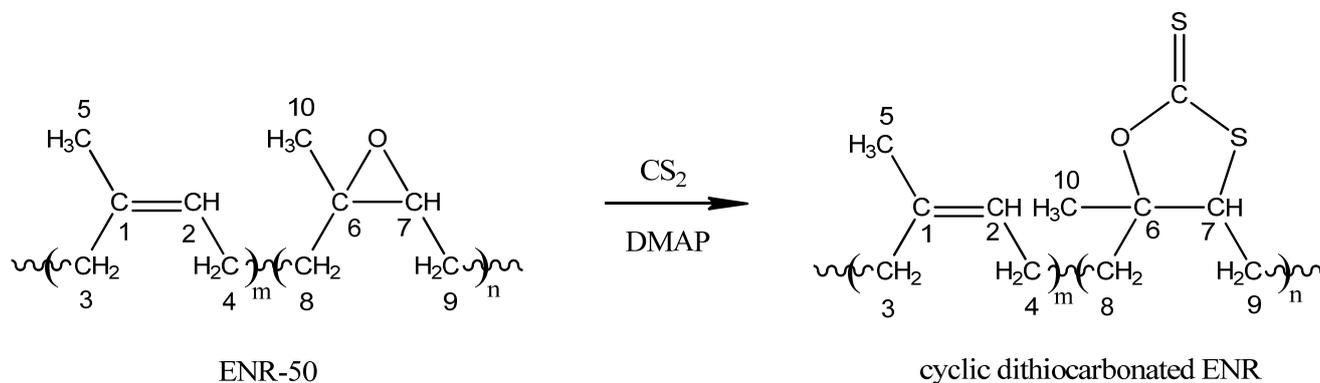
Gelling [2], on the other hand, has assigned the triad sequence based on ^{13}C -NMR chemical shifts for ENR-20. However, the assignment deals with certain triad sequences such as CEE, CEC, C, EEC, and ECE and the position of carbon represented by the triad sequences was found to be inconsistent. Consequently, Saito *et al.* [11] have successfully interpreted the ^{13}C -NMR spectra for the ENR related compounds and assigned their triad sequence as shown in Table 1, columns 2 and 4.

The increasing interests in the science and technology of ENR in various fields such as polymer blends [16], polymer modifications [17], polymer composites [18] and advanced green materials [19–21] makes it inevitable to understand the detail structure of ENR. This fundamental study is important to enable comprehensive structural characterization of the desired materials. Here we attempted a complete assignment of the commercial ENR-50 using the 1D and 2D NMR spectroscopy techniques. Our work differs from other reported works [11,22,23] in term of the degree of epoxidation and physical form of rubber. The ENR used is a low molecular weight fraction of ENR-50 obtained by solvent separation [19]. In this work, the results reported by Saito *et al.* [11] were used for comparison purposes. Apart from the above, this work also reported the structural elucidation of cyclic dithiocarbonate derivative of ENR-50 obtained from the reaction between purified ENR-50 with neat carbon disulfide, CS_2 [24]. The reaction is shown in Scheme 2. A complete ^1H - and ^{13}C -NMR chemical shifts assignments of the cyclic dithiocarbonate derivative of ENR-50 is given and the probable mechanism of formation was discussed.

Table 1. ^1H , ^{13}C -NMR chemical shifts and HMQC, HMBC and COSY spin coupling correlations of purified ENR-50.

^1H chemical shift δ (ppm)			^{13}C chemical shift δ (ppm)		HMQC	HMBC Coupling correlation		COSY Coupling correlation	
Ref: 14–15	Ref: 11	This work	Ref: 11	This work	Triad assignment	Middle unit δ (ppm)	Within same unit δ (ppm)	Middle unit δ (ppm)	Within same unit δ (ppm)
1.31	1.29	1.30	22.1	22.3	E ¹⁰	29.7 (E ⁸), 60.7 (E ⁶), 64.5 (E ⁷)	None	None	None
1.38	1.55	1.56	29.5	29.7	EE ⁸ C, E ⁸	22.3 (E ¹⁰), 60.7 (E ⁶), 64.5 (E ⁷)	24.7 (E ⁹), 64.5 (E ⁷)	None	1.68–1.70 (E ⁹)
			33.0	33.1	CE ⁸ C, CE ⁸ E	22.3 (E ¹⁰), 60.7 (E ⁶), 64.5 (E ⁷)	23.9 (C ⁴), 125.0 (C ²)	None	2.15–2.19 (C ⁴)
			26.9	27.0	CE ⁹ C, EE ⁹ C	60.7 (E ⁶), 64.5 (E ⁷)	28.7 (C ³), 134.7 (C ¹)	2.72 (E ⁷)	2.15–2.19 (C ³)
1.42	1.68	1.68–1.70	23.3	23.4	C ⁵	32.0 (C ³), 125.0 (C ²), 134.7 (C ¹)	None	None	None
1.38			24.6	24.7	CE ⁹ E, E ⁹	60.7 (E ⁶), 64.5 (E ⁷)	29.7 (E ⁸), 60.7 (E ⁶)	2.72 (E ⁷)	1.56 (E ⁸)
2.00	2.05	2.06	26.2	26.3	C ⁴ , EC ⁴ C	125.0 (C ²), 134.7 (C ¹)	32.0 (C ³), 134.7 (C ¹)	5.12–5.17 (C ²)	2.06 (C ³)
			32.0	32.0	C ³ , CC ³ E	23.4 (C ⁵), 125.0 (C ²), 134.7 (C ¹)	26.3 (C ⁴), 125.0 (C ²)	None	2.06 (C ⁴)
1.96	2.15	2.15–2.19	23.7	23.9	CC ⁴ E, EC ⁴ E	125.0 (C ²), 134.7 (C ¹)	33.1 (E ⁸), 60.7 (E ⁶)	5.12–5.17 (C ²)	1.56 (E ⁸)
			28.5	28.7	EC ³ C, EC ³ E	23.4 (C ⁵), 125.0 (C ²), 134.7 (C ¹)	27.0 (E ⁹), 64.5 (E ⁷)	None	1.56 (E ⁹)
-	-	-	60.3	60.7	E ⁶	-	-	-	-
2.51	2.70	2.72	64.0	64.5	E ⁷	22.3 (E ¹⁰), 24.7 (E ⁹), 29.7 (E ⁸), 60.7 (E ⁶)	29.7 (E ⁸), (None)	1.68–1.70 (E ⁹)	None
5.20	5.10	5.12–5.17	125.0	125.0	C ²	23.4 (C ⁵), 26.3 (C ⁴), 32.0 (C ³), 134.7 (C ¹) (NOT DETECTED)	32.0 (C ³)	2.06 (C ⁴)	None
-	-	-	135.0	134.7	C ¹	-	-	-	-

Scheme 2. Reaction of purified ENR-50 with carbon disulfide catalyzed by 4-dimethylaminopyridine (DMAP).



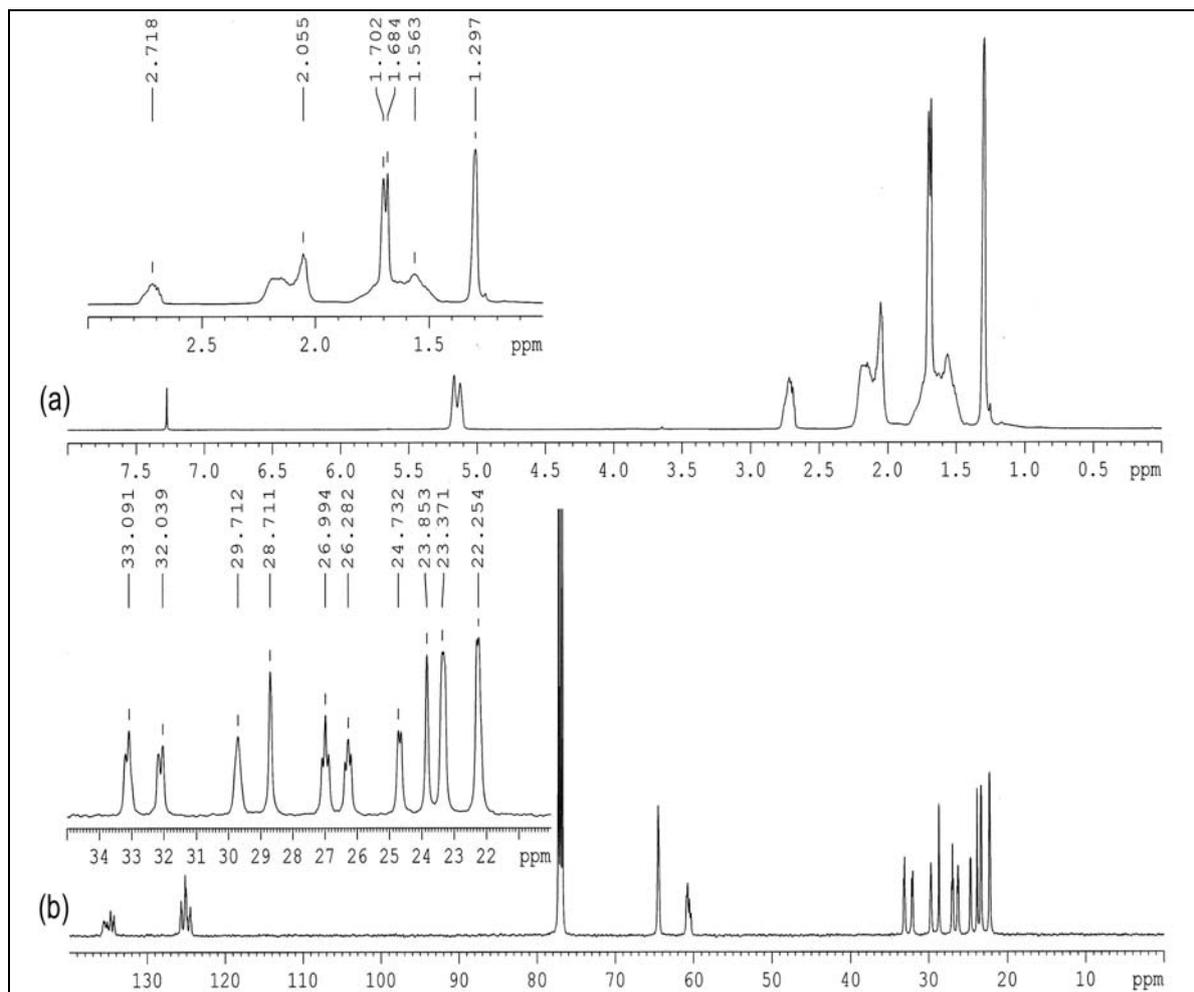
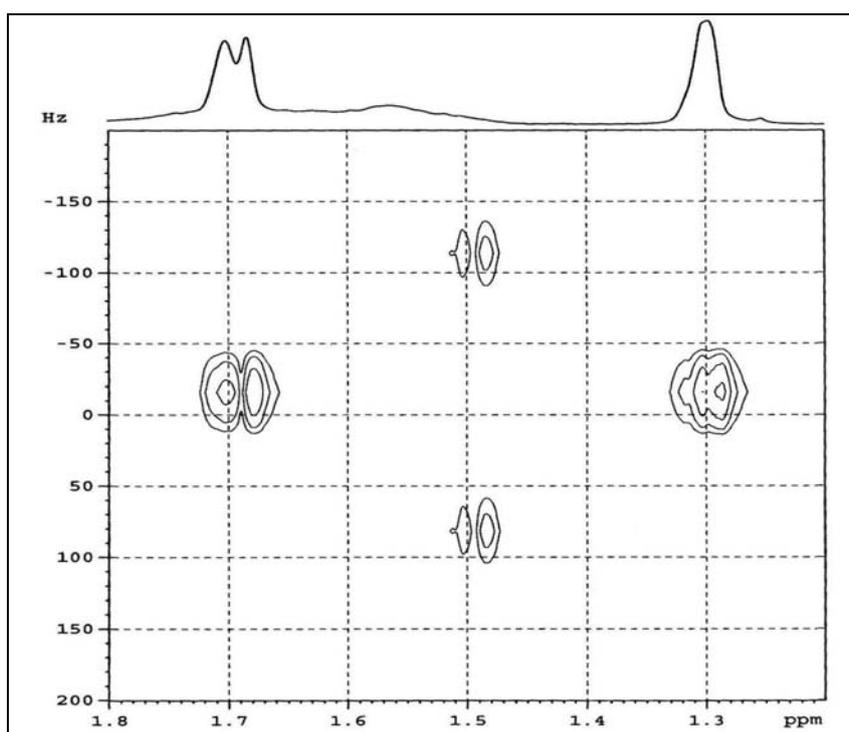
2. Results and Discussion

2.1. Epoxidized Natural Rubber

2.1.1. ¹H- and ¹³C-NMR Spectroscopy

The ¹H- and ¹³C-NMR spectra of purified ENR-50 are shown in Figure 2 and the respective chemical shifts are tabulated in Table 1. The respective observed chemical shifts were generally similar to those reported in previous works [11,14,15]. From Figure 2a, the ¹H-NMR chemical shift at δ 1.30 ppm is assigned to the methyl protons of E¹⁰, at δ 2.72 ppm to the methine proton of E⁷ and at δ 5.12–5.17 ppm to the methine proton of C². However, the chemical shift at δ 1.56 ppm overlapped with those at δ 1.68–1.70 ppm while the chemical shift at δ 2.15–2.19 ppm overlapped with those at δ 2.06 ppm. These overlapping signals may be due to the methylene protons of the ENR-50 chain. To confirm, a J-resolved spectroscopy (JRES) [25,26] experiment was conducted to specifically investigate the overlapping signals at δ 1.20–1.80 ppm region. Figure 3 shows the enlarged JRES spectra of δ 1.20–1.80 ppm region. The methyl of E¹⁰ is represented as a single contour at δ 1.30 ppm. The overlapping methylene signal in JRES was represented by a double contour located at δ 1.68 and 1.70 ppm, with coupling constant of 11 Hz. The multiple methylene protons signal is due to the different attachment modes of the epoxide to the isoprene which collectively form pairs of the enantiomers, stereoisomers and diastereoisomers that give rise to separate the resonances in the NMR spectrum [12].

The ¹³C-NMR spectrum of purified ENR-50 is shown in Figure 2b. The signals within δ 23.9 to 33.1 ppm represent the doublets of methylene carbons of C³, C⁴, E⁸ and E⁹. The methylene carbons of C⁴ and E⁹ are vicinal to the respective methine carbons of C² and E⁷. While the methylene carbons of C³ and E⁸ are vicinal to the respective quaternary carbons of C¹ and E⁶. The methine carbons of C² and E⁷ has greater electron density than the quaternary carbons of C¹ and E⁶ and therefore are more shielded causing the methylene carbons of C⁴ and E⁹ to be located in the upfield region compared to the methylene carbons of C³ and E⁸.

Figure 2. (a) ^1H and (b) ^{13}C -NMR spectra of purified ENR-50 (in CDCl_3).**Figure 3.** JRES spectra of purified ENR-50 (in CDCl_3).

The ^{13}C -NMR chemical shifts of the methylene carbons of C^4 and E^9 are also dependent on their vicinal neighboring units (*i.e.*, to the right (R)- or left (L)-hand side) in the triad. If E unit is on the R side of either C^4 or E^9 , the chemical shift is more shielded and upfield than those with neighboring C unit on the same R side. Thus the chemical shifts of CC^4E , EC^4E , CE^9E and E^9 triads will be upfield compared to C^4 , EC^4C , CE^9C and EE^9C triads. Similarly, when E is on the L side of C^3 and E^8 unit in the triad sequence, the chemical shifts of EC^3C , EC^3E , EE^8C and E^8 triads will be upfield compared to C when it is on the L side of C^3 and E^8 as in C^3 , CC^3E , CE^8C and CE^8E triads. In the case of C^1 , C^2 , C^5 , E^6 , E^7 and E^{10} triads, the ^{13}C -NMR chemical shifts of the E series are located in the upfield region while of the C series are located in the downfield region. This is due to the double bond in the latter causes deshielding.

2.1.2. HMQC

Figure 4 shows the HMQC spectra of purified ENR-50 and the identified triad assignments are tabulated in Table 1 (6th column). HMQC correlates the chemical shift of proton(s) directly bonded to carbon. The ^1H -NMR chemical shift depends on the type of carbon it is attached to. The σ bond formed between the carbon and a proton produce shielding effect [27]. Thus depending on the number of C-H bond, protons attached to the primary carbon is shifted more upfield compared to the secondary and tertiary carbons.

Figure 4. HMQC spectra of (a) purified ENR-50 and (b) enlargement of the boxed region in (a).

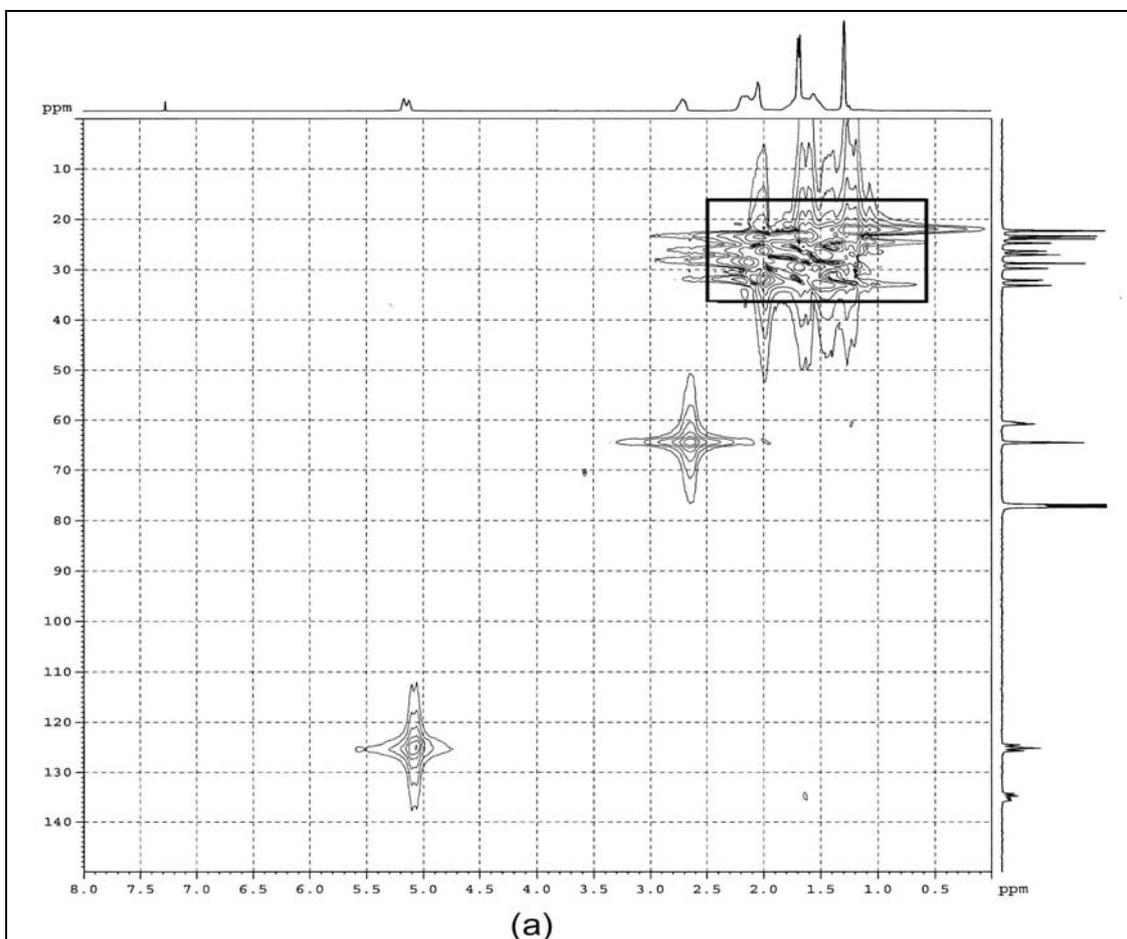
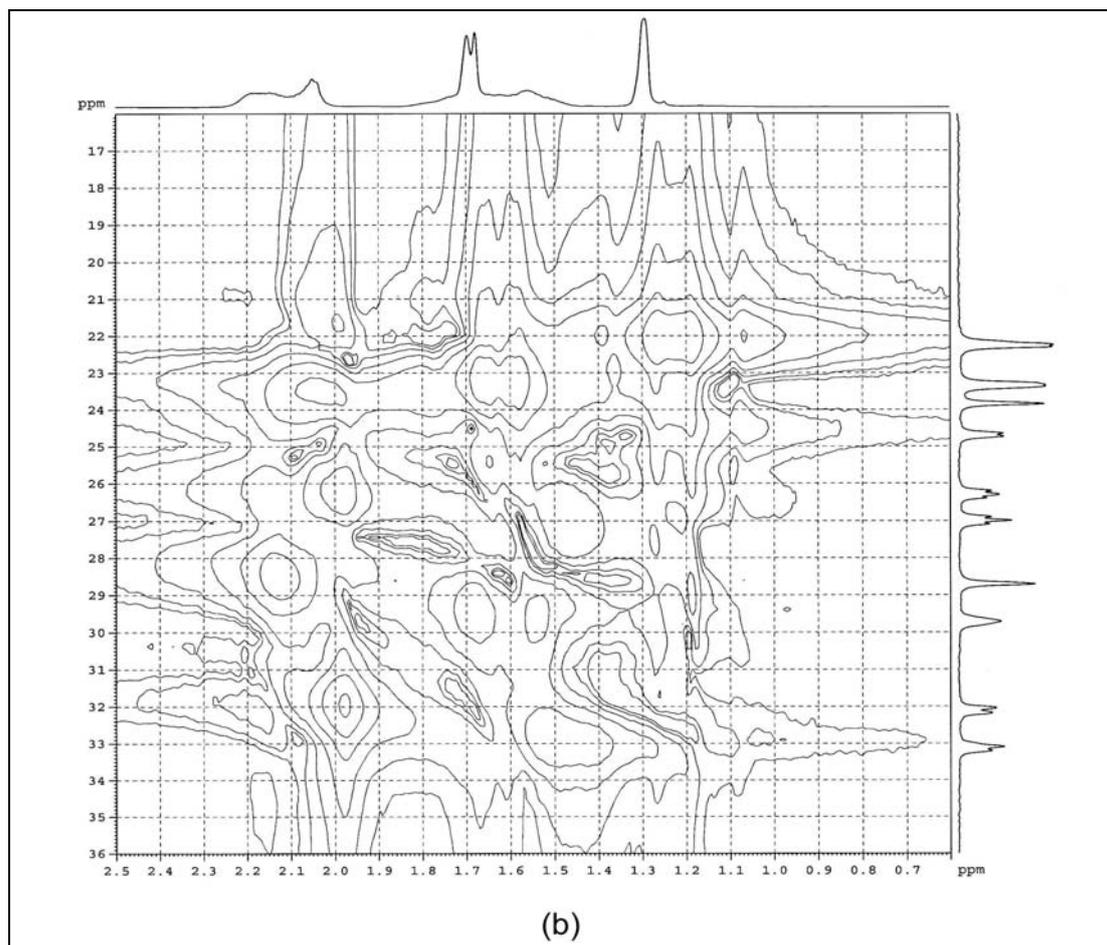


Figure 4. Cont.



The correlations of the methyls of E^{10} and C^5 are located upfield than the methylenes of C^3 , C^4 , E^8 , E^9 and methines of C^2 and E^7 . The correlations arising from the methyls of E^{10} and C^5 also depend on the types of vicinal quaternary carbon, *i.e.*, the epoxide (E^6) or the double bond (C^1). The methyl of E^{10} is vicinal to the quaternary carbon of E^6 while the methyl of C^5 is vicinal to quaternary carbon of C^1 . Thus the methyl of E^{10} is located upfield than that of methyl of C^5 . Similarly, the correlations of methines of E^7 and C^2 are influenced by the proximity of the epoxide or the double bond. The methine of E^7 is shielded by electron density of epoxide while the methine of C^2 is deshielded by the double bond. The methine of E^7 is therefore more upfield than the methine of C^2 . In the case of methines of E^7 and C^2 , their correlations are located downfield relative to the methylenes of C^3 , C^4 , E^8 and E^9 . The deshielding effects of the double bond caused the correlations of methylenes of C^3 and C^4 to be located downfield than the respective methylenes of E^8 and E^9 . Therefore C^3 is also downfield than E^8 while, C^4 is downfield than E^9 .

For the EC^3C and EC^3E triads, these correlations are located downfield than CC^4E and EC^4E in the ^{13}C -NMR spectrum. However, in the 1H -NMR spectrum, both appeared as overlapped peak. This is because the correlations of C^3 and C^4 superimpose those of CC^3E and EC^4C triads. Thus it can be similarly argued that the correlations of the triads CE^8C and CE^8E occur downfield than CE^9C , and EE^9C in the ^{13}C -NMR spectrum while in the 1H -NMR spectrum, those of EE^8C and CE^9E superimpose those of E^8 and E^9 .

2.1.3. HMBC

The HMQC results were further scrutinized using HMBC analysis. The HMBC correlation spectra of purified ENR-50 are shown in Figure 5. The ^1H - ^{13}C signals correlations are tabulated in Table 1 (7th and 8th column). The overlapping proton signals at δ 1.56, 1.68–1.70, 2.06 and 2.15–2.19 ppm were individually assigned through coupling correlations. The coupling correlation between neighboring units classifies and arranges the methylene carbons in the correct triad sequence thus confirmed the previous HMQC assignments. The methyls of E^{10} and C^5 , and methines of E^7 and C^2 were affirmatively assigned based on the deduced correlations and consistent with the previous study [11].

2.1.4. COSY

The COSY of purified ENR-50 is shown in Figure 6 and was conducted to evaluate the representations of ^1H -NMR signals at δ 1.56, 1.68–1.70, 2.06 and 2.15–2.19 ppm. The spin coupling correlations of the signals and the assigned triad sequences are as tabulated in column 9th and 10th in Table 1.

The signal at δ 1.56 ppm correlates with the signals at δ 2.72, 2.15–2.19 and 1.68–1.70 ppm. The signal of E^7 methine proton at δ 2.72 ppm correlates to the methylene protons of the middle unit of the triad sequences of CE^9C and EE^9C . The signal representing the methylene protons of CC^4E and EC^4E as well as EC^3C and EC^3E at δ 2.15–2.19 ppm correlates to the methylene protons of isoprene CE^8C , CE^8E , CE^9C and EE^9C . While the signal assigned to the methyl protons of C^5 , methylene protons of CE^9E and E^9 at δ 1.68–1.70 ppm correlates to methylene protons of the epoxidized isoprene of EE^8C and E^8 . The methyl proton of E^{10} at δ 1.30 ppm does not show any correlation as it is attached to the quaternary carbon, E^6 .

The signal that represents the methylene protons of the middle unit of C^4 and EC^4C as well as C^3 and CC^3E at δ 2.06 ppm correlates with the signals at δ 2.06 and 5.12–5.17 ppm. All these methylene protons are correlated to the methylene protons of isoprene with the same unit of triad at δ 2.06 ppm. However, for the triads C^4 and EC^4C , the correlation is to the methine proton of isoprene C^2 at δ 5.12–5.17 ppm.

The methylene protons of CC^4E and EC^4E at δ 2.15–2.19 ppm were correlated with the signals at δ 5.12–5.17 and 1.56 ppm. These are due to the methine proton of C^2 (δ 5.12–5.17 ppm) and the neighbouring methylene protons of epoxidized isoprene (δ 1.56 ppm) within the same unit. The methylene protons of EC^3C and EC^3E at δ 2.15–2.19 ppm are also correlated to the neighbouring methylene protons of epoxidized isoprene (δ 1.56 ppm) within the same unit of triad sequence.

Based on the COSY of purified ENR-50, the signal at δ 1.56 ppm represents the methylene protons of CE^9C , EE^9C , E^8 , EE^8C , CE^8C and CE^8E . The signal at δ 1.68–1.70 ppm represents the methyl protons of C^5 and the methylene protons of CE^9E and E^9 . The signal at δ 2.06 ppm arises from the methylene protons of C^4 , EC^4C , C^3 and CC^3E , while the signal at δ 2.15–2.19 ppm represents the methylene protons of CC^4E , EC^4E , EC^3C and EC^3E . These conformed to the HMQC results above.

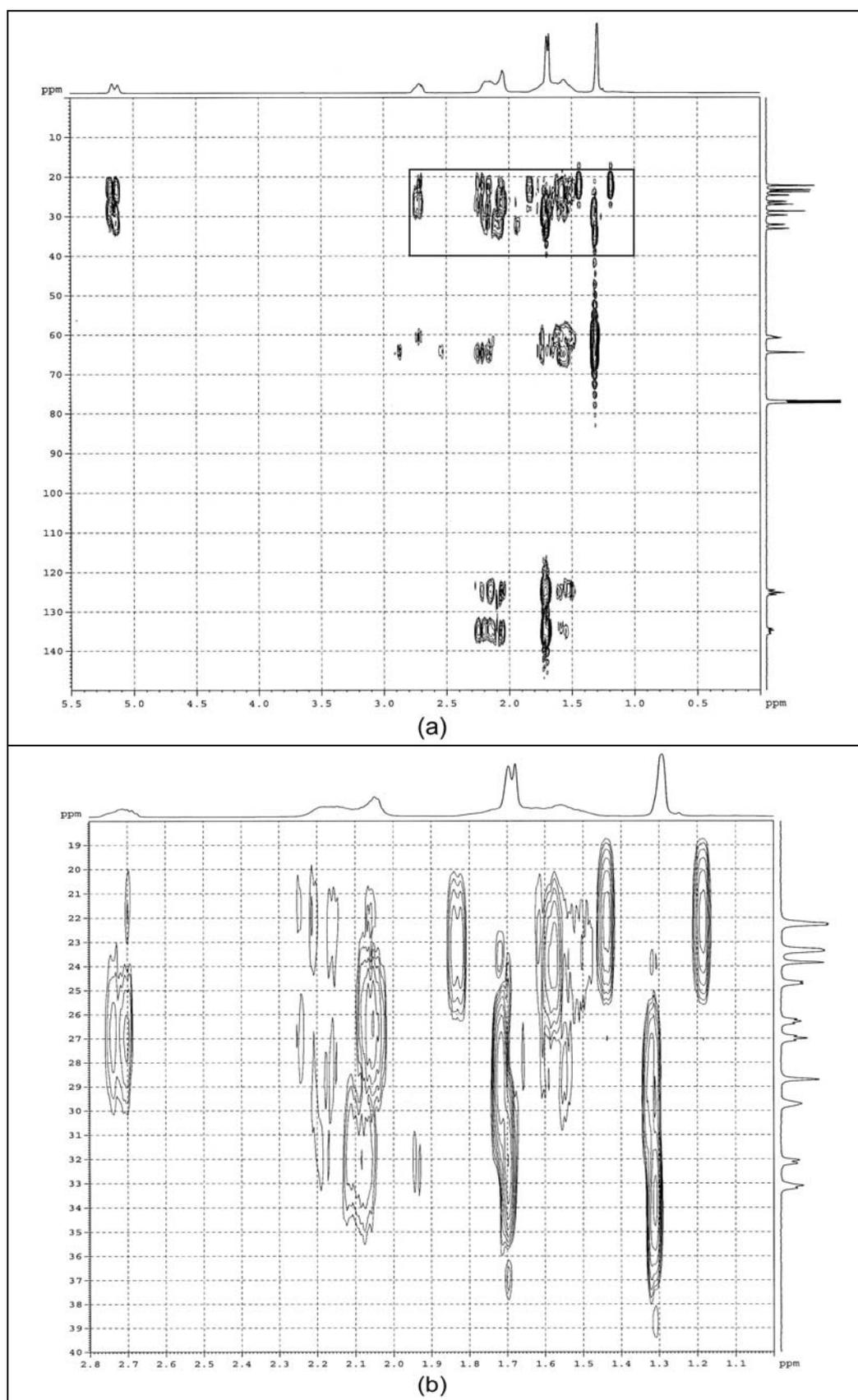
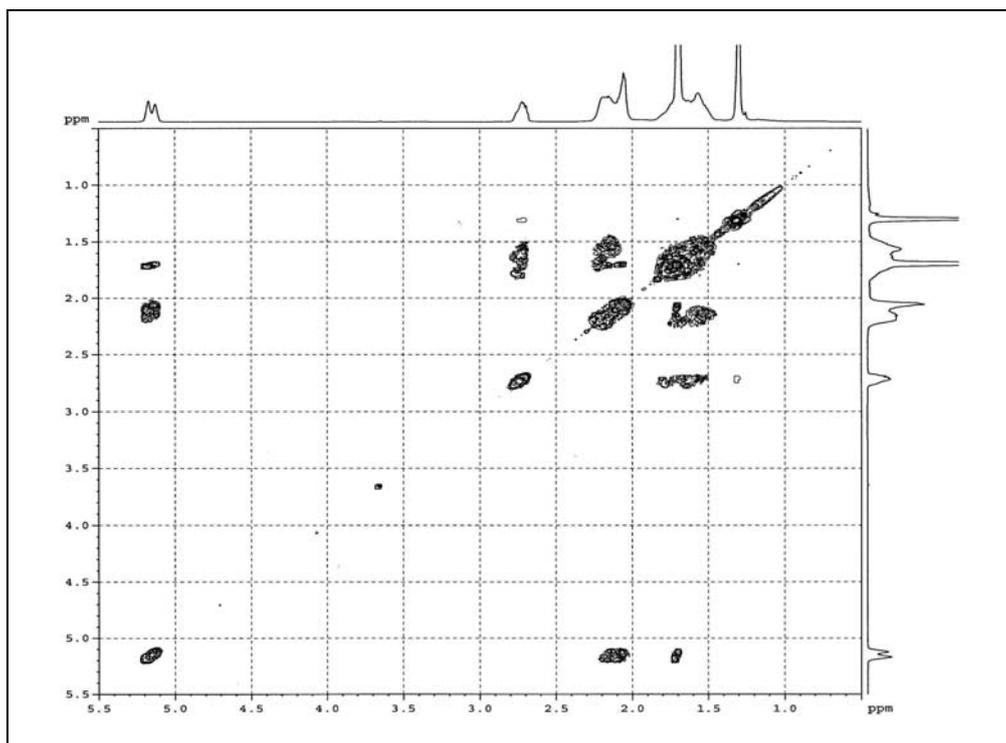
Figure 5. HMBC spectra of (a) purified ENR-50 and (b) enlargement of the boxed region in (a).

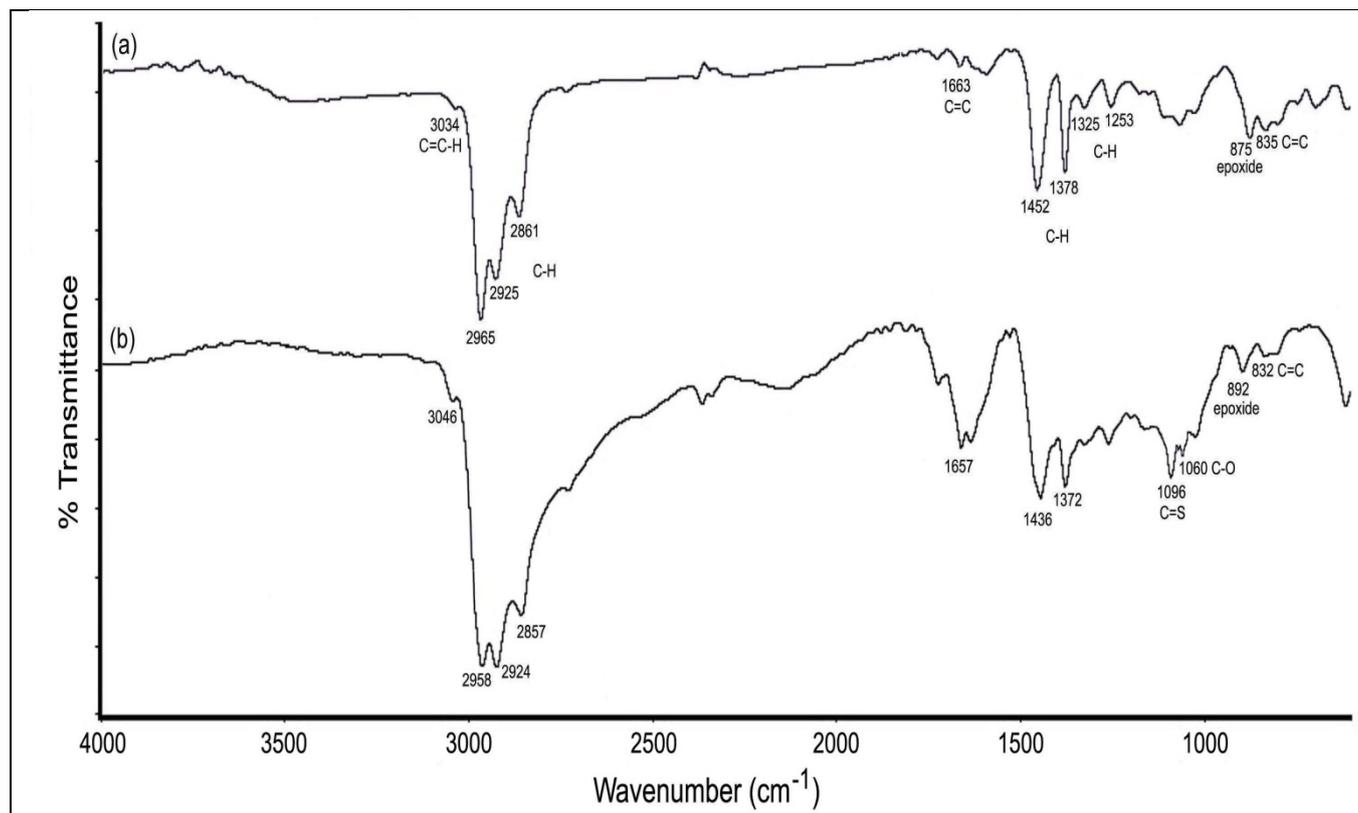
Figure 6. COSY spectra of purified ENR-50.

2.2. Cyclic Dithiocarbonate Derivative of ENR-50

The reaction of CS₂ with purified ENR-50 afforded the five-membered ring dithiocarbonate derivative of ENR-50 as shown in Scheme 2. The formation of cyclic dithiocarbonate is generally a Diels-Alder type of reaction [24]. In this work, a very dilute solution of purified ENR-50 was used with the aim to stretch the random coil conformation of ENR-50 polymer chains in order to expose the reactive epoxidized isoprene unit using dimethylaminopyridine (DMAP) as the catalyst. The C–S moiety of CS₂ is inserted into the epoxidized isoprene of the ENR-50. The reaction probably occurs via the S_N2 mechanism that involved the epoxide ring opening.

2.2.1. FTIR Spectroscopy

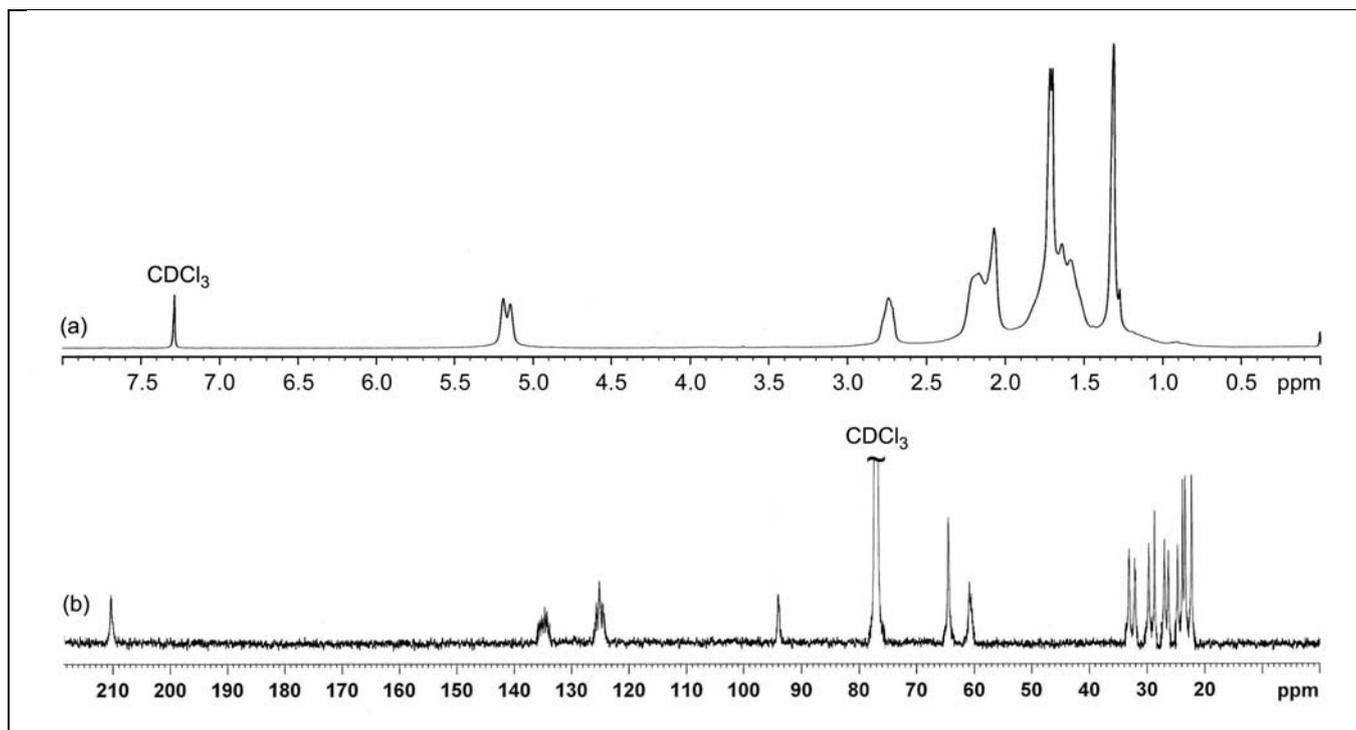
Comparison of the FTIR spectrum of purified ENR-50 (Figure 7a) with the FTIR spectrum of the reaction product (Figure 7b) revealed two new bands at 1096 and 1060 cm⁻¹ that are assigned to C=S and C–O functionalities, respectively [28,29]. The latter (ν_{C-O}) is located at lower wavenumber than the ν_{C-O-C} for cyclic ether at 1150–1070 cm⁻¹. The weak C–S stretching vibration in the range of 700–590 cm⁻¹ indicates bonding between sulfur from CS₂ and the carbon E⁷ [29]. The band attributed to the epoxide is shifted to higher wavenumber compared to purified ENR-50, *i.e.*, from 875 to 892 cm⁻¹. Other typical bands of C=C and C–H are also slightly shifted to a low wavenumber region. This is probably due to the intermittent presence of cyclic dithiocarbonate within the ENR-50 chains.

Figure 7. FTIR spectra of (a) purified ENR-50 and (b) cyclic dithiocarbonate derivative of ENR-50.

Comparison of the spectra of Figure 7a,b also indicates that there is a reduction in the epoxide band intensity after the reaction. The extent of dithiocarbonation reaction was estimated using semi-quantitative FTIR approach. This was based on the band area of the methyl, C=S and the epoxide functionalities before and after dithiocarbonation reaction. The band due to methyl at 1378–1372 cm^{-1} was used as the internal standard in this work [8]. Based on the FTIR approach, the percentage of epoxidation in the purified ENR-50 is $\sim 50.7\%$. It was also found that after the dithiocarbonation reaction, 47.9% of the epoxide has reacted with CS_2 while 52.1% were unreacted.

2.2.2. ^1H and ^{13}C -NMR Spectroscopy

The ^1H and ^{13}C -NMR spectra of cyclic dithiocarbonate derivative of ENR-50 are shown in Figure 8. The chemical shifts of the cyclic dithiocarbonate derivative of ENR-50 as well as the triad and carbon assignments are given in Table 2. From Figure 8a, with the exception for the splitting of peak at δ 1.58–1.63 ppm, the ^1H -NMR spectrum shows almost similar features compared to purified ENR-50 (Figure 2a). As discussed earlier, the split peak above represents the methylene protons of EE^8C , E^8 , CE^8C , CE^8E , CE^9C and EE^9C triads. The formation of cyclic five-membered dithiocarbonate within the ENR chain involves the E^6 and E^7 carbons as illustrated in Scheme 2. This, in turn, has affected the environment of E^8 and E^9 carbons. Therefore the split peaks observed at δ 1.58–1.63 ppm may be attributed to the methylene protons attached to the five-membered (cyclic dithiocarbonate) and three-membered (oxirane) rings, respectively. The methylene protons attached to the five-membered ring are slightly downfield at δ 1.63 ppm compared to those attached to the three-membered ring (at δ 1.58 ppm).

Figure 8. (a) ^1H and (b) ^{13}C -NMR spectra of cyclic dithiocarbonate derivative of ENR-50 (in CDCl_3).**Table 2.** ^1H and ^{13}C -NMR chemical shifts and triad assignments for purified ENR-50 and its cyclic dithiocarbonate derivative.

Chemical shift δ (ppm)				Triad assignment
^1H		^{13}C		
ENR-50 *	Cyclic dithiocarbonate derivative	ENR-50 *	Cyclic dithiocarbonate derivative	
1.30	1.31	22.3	22.4	E^{10}
1.56	1.58–1.63	29.7	29.8	EE^8C , E^8
		33.1	33.1	CE^8C , CE^8E
		27.0	27.0	CE^9C , EE^9C
1.68–1.70	1.70–1.71	23.4	23.5	C^5
		24.7	24.8	CE^9E , E^9
2.06	2.08	26.3	26.4	C^4 , EC^4C
		32.0	32.2	C^3 , CC^3E
2.15–2.19	2.12–2.19	23.9	24.0	CC^4E , EC^4E
		28.7	28.7	EC^3C , EC^3E
-	-	60.7	61.0	E^6
2.72	2.73	64.5	64.8	E^7 , E^7 of five-membered ring
-	-	-	94.0	E^6 of five-membered ring
5.12–5.17	5.15–5.19	125.0	125.1	C^2
-	-	134.7	134.9	C^1
-	-	-	210.5	CS_2 carbon of five-membered ring

* from Table 1.

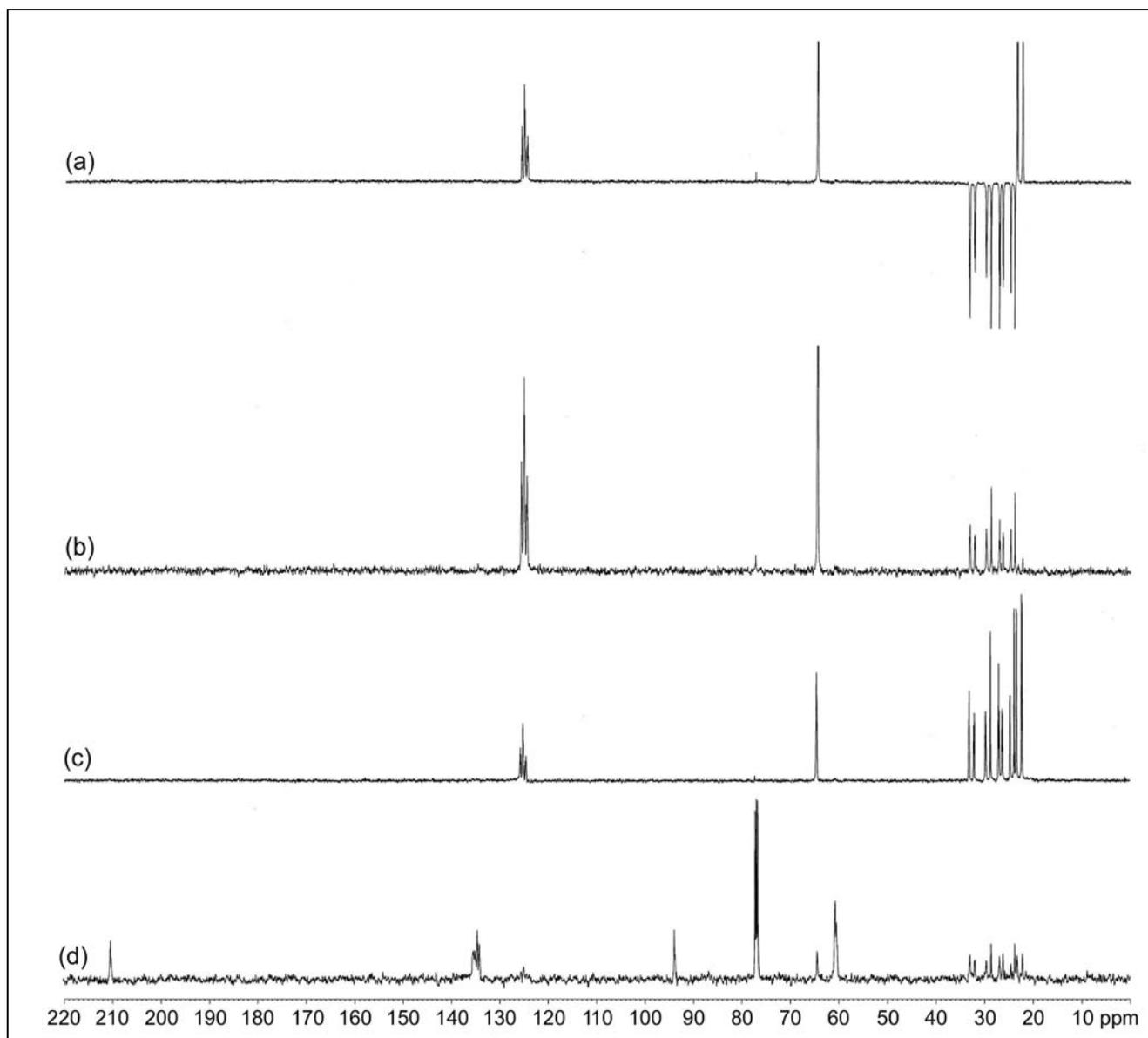
These methylene protons shows equal proton integrals compared to purified ENR-50. This is confirmed by the previous FTIR results where, approximately 1:1 ratio of reacted and unreacted epoxide is observed after the dithiocarbonation reaction. The formation of cyclic dithiocarbonate within the ENR chain however, does not produce any new peaks or change in the chemical shifts. Therefore it is expected that the ENR-50 polymer chains conformation was maintained upon dithiocarbonation.

The formation of cyclic dithiocarbonate also gives two new ^{13}C -NMR peaks at δ 210.5 and 94.0 ppm, respectively [24]. The peak at δ 210.5 ppm represents the carbon of $>\text{C}=\text{S}$ of the five-membered ring and is located at the most downfield region as this carbon is simultaneously bonded to the electronegative oxygen and sulfur. The carbon E^6 of the five-membered ring is located slightly downfield at δ 94.0 ppm because it is vicinally bonded to the carbon of $>\text{C}=\text{S}$. The chemical shift for carbon E^7 of the five-membered ring and the carbons of E^6 and E^7 of the three-membered ring (oxirane) however, remains unchanged, *i.e.*, similar to the purified ENR-50. The main difference between the cyclic dithiocarbonated ENR reported in this work and the previously reported cyclic carbonated NR [30] is the position of S atom in the former is replaced by O atom in the latter. This gives rise to the different chemical shifts due to the different in electronegativity of S and O atoms. In the cyclic carbonated NR, the ^{13}C -NMR chemical shift of quaternary carbon of $>\text{C}=\text{O}$ is at δ 151.0 ppm, the tertiary carbon of $>\text{C}(\text{H})-\text{O}-$ is at δ 75.0 ppm, and the quaternary carbon of $\equiv\text{C}-\text{O}-$ is at δ 74.0 ppm, respectively [30].

The ^{13}C -NMR quantitative analysis was carried out to evaluate the epoxidation level in the purified ENR-50 as well as its cyclic dithiocarbonate derivative. The epoxidation level in purified ENR-50 was found to be ~51.4%. In the cyclic dithiocarbonate derivative, 52.0% of the epoxide ring is unreacted while 48.0% has reacted with CS_2 . These results are consistent with the FTIR results discussed previously.

Figure 9 shows the various DEPT spectra for cyclic dithiocarbonate derivative of ENR-50. In DEPT-135, the signals of the methylene carbons are shown downward (negative) while the methyl and methine carbons are shown as the upward peaks (positive) [31]. The spectrum for DEPT-90 shows only the methine carbons [31]. However, spectrum for DEPT-45 shows the upward peaks for methyl, methylene and methine carbons. The peak at δ 64.8 ppm appears as upward signal in DEPT-135, DEPT-90 and DEPT-45 proved its assignment as a methine carbon for E^7 of the three-membered ring (oxirane) as well as carbon E^7 of the five-membered ring. DEPT quaternary only shows quaternary carbon as upward peak in the spectrum. The real signals of the quaternary carbons in this spectrum are at δ 60.1, 94.0, 134.9 and 210.5 ppm. While the rest of the peaks in this spectrum are not reliable because the signal to noise ratio is less than 5 and those peaks are proven previously as methyl, methylene and methine in DEPT-135, -90 and -45 except for the CDCl_3 peak which appear at 77.0 ppm. Thus the peaks at δ 94.0 ppm and 210.5 ppm are assigned for E^6 and CS_2 carbon of five-membered ring, respectively.

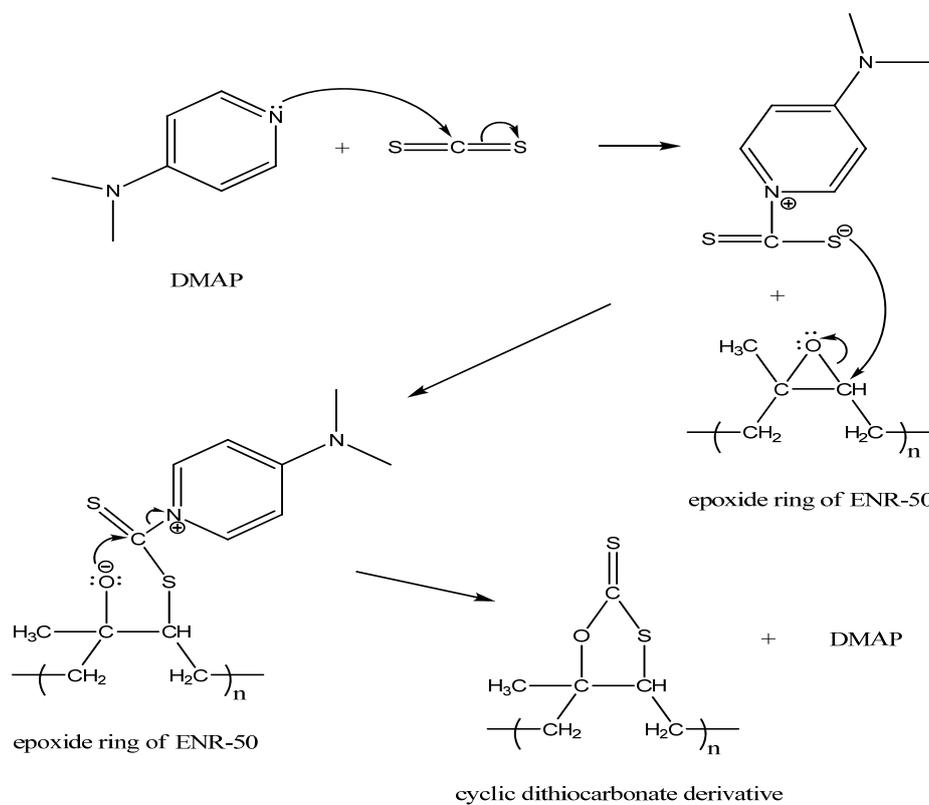
Figure 9. (a) DEPT-135; (b) DEPT-90; (c) DEPT-45 and (d) DEPT quaternary spectra of cyclic dithiocarbonate derivative of ENR-50 (in CDCl₃).



2.2.3. Proposed Mechanism for the Formation of Cyclic Dithiocarbonate

A proposed mechanism for the formation of cyclic dithiocarbonate from the reaction of ENR-50 with CS₂ is shown in Scheme 3. DMAP catalyst is well known as a strong nucleophile. The lone pair electrons of DMAP attack the carbon of CS₂ and form a [S₂C-DMAP] complex. The complex provides the condition for overall reaction to proceed via a S_N2 mechanism [32]. In this condition, the sulfur-centered nucleophile attacks the less substituted and less sterically hindered carbon E⁷ and ring opened the oxirane. The bond between oxygen and carbon E⁷ is severed and produced oxygen-centered nucleophile. This nucleophile attacks the CS carbon of [ENR-S(S)C-DMAP] intermediate with simultaneous detachment of a DMAP molecule and therefore affecting a ring closure via formation of O–C bond. The ring closure constitutes formation of cyclic dithiocarbonate derivative of ENR-50.

Scheme 3. Proposed mechanism for the formation of cyclic dithiocarbonate derivative of ENR-50 via oxirane ring opening.



3. Experimental

3.1. Materials

Carbon disulfide 99.7%, CS_2 (BDH Chemicals, Poole, UK), 4-dimethylaminopyridine 98%, DMAP and deuterated chloroform, CDCl_3 (Fluka Chemicals, Buchs, Switzerland) and *n*-hexane (System, Selangor, Malaysia) were all obtained commercially and used without further purification unless otherwise stated. Epoxidized natural rubber with 50% epoxidation (ENR-50) was purchased from the Rubber Research Institute (Kuala Lumpur, Malaysia).

3.2. Preparative Procedure

3.2.1. Purification of ENR-50 [19]

ENR-50 (about 20.00 g) was swelled in chloroform (400 mL) and stirred for 24 h at room temperature. The solution was then filtered through cotton gauze to separate the gel (high molecular ENR-50) from the extract (low molecular weight ENR-50). The later was precipitated in *n*-hexane and stirred using a glass rod. The white precipitate stuck to the glass rod was transferred to a Petri dish and was dried in a vacuum oven at 50 °C for two days. Mass of purified ENR-50 sample was recorded daily until a constant weight was achieved.

3.2.2. Reaction of Purified ENR-50 with CS₂ [24]

Purified ENR-50 (about 20 mg, 1.31×10^{-4} mol) was swelled in CS₂ (40 mL, 6.62×10^{-4} mol) under constant stirring. DMAP catalyst (about 16.44 mg, 1.32×10^{-4} mol) was added to the stirring solution. The mixture was then refluxed for 3 h and then left to cool to room temperature. The organic layer was washed with water (150 mL) to remove the catalyst. This procedure was repeated until the washing attained a neutral pH. The organic layer was then cast onto Teflon dishes before drying in a vacuum oven at 50 °C for 24 h.

3.3. Measurements and Characterization Techniques

FTIR spectra were recorded on a Perkin-Elmer 2000-FTIR using single beam transmittance onto a film of sample on ZnSe window in the range of 4,000–600 cm⁻¹. The FTIR samples were prepared by swelling sample (100.00 mg) with chloroform (5 mL). The sample solution was cast onto a Teflon mould and air dried. The thin film was dried in a vacuum oven at 50 °C for 1 h and was later transferred onto ZnSe window. 1D and 2D NMR spectra were obtained using a Bruker Avance 500 MHz instrument in CDCl₃ at 25 °C. A 10.00 mg sample was used for ¹H and J-Resolved Spectroscopy (JRES) while 50.00 mg were used for the ¹³C-NMR, distortion enhancement by polarization transfer (DEPT), heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple bond coherence (HMBC) and correlation spectroscopy (COSY) analyses. The respective range of the spectra and number of scan for ¹H and for ¹³C-NMR measurements were 15–0 ppm with 16 scans and 200–0 ppm with 15,000 scans, respectively. For quantitative ¹³C-NMR measurements, 1,000 scans were applied with 60 seconds relaxation delay. The number of scans applied for JRES, DEPT, HMQC, HMBC and COSY were 8, 2000, 128, 256 and 40 scans, respectively.

3.4. Theoretical Treatments

The FTIR semi-quantitative treatments were based on the band area of methyl, epoxide and C=S functional groups. The percentage of epoxide in purified ENR-50 and the percentage dithiocarbonation of the epoxide were determined using Equations (1) and (2), respectively. In Equations (1) and (2), N_{methyl} is the normalized band area of the methyl signal, $A_{\text{epoxide sample}}$ is the band area of epoxide functional group stretching peak for the sample, $A_{\text{C=S sample}}$ is the band area of C=S functional group stretching peak for the sample, and $A_{\text{epoxide ENR-50}}$ is the band area of respective functional group stretching peak in purified ENR-50:

$$\% \text{ Epoxide} = \frac{N_{\text{methyl}} \times A_{\text{epoxide sample}} \times 100\%}{A_{\text{epoxide ENR-50}}} \quad (1)$$

$$\% \text{ C} = \text{S} = \frac{N_{\text{methyl}} \times A_{\text{C=S sample}} \times 100\%}{A_{\text{epoxide ENR-50}}} \quad (2)$$

The ¹³C-NMR quantitative treatments were also used to determine the percentage of epoxidation in the purified ENR-50 and its five-membered ring cyclic dithiocarbonate derivative using Equations (3) and (4) below. In both equations, I_{C^1} is the integral of C¹ at δ 134.9 ppm, $I_{\text{E}^6 \text{ epoxide}}$ is the integral of E⁶ at δ 61.0 ppm, and $I_{\text{E}^6 \text{ cyclic}}$ is the integral of E⁶ at δ 94.0 ppm:

$$\% \text{ Epoxide} = \frac{I_{E6 \text{ epoxide}} \times 100\%}{I_{C1} + I_{E6 \text{ epoxide}}} \quad (3)$$

$$\% \text{ Cyclic dithiocarbonate} = \frac{I_{E6 \text{ epoxide}} + I_{E6 \text{ cyclic}} \times 100\%}{I_{C1} + I_{E6 \text{ epoxide}} + I_{E6 \text{ cyclic}}} \quad (4)$$

4. Conclusions

The overlapping $^1\text{H-NMR}$ signals of purified ENR-50 at δ 1.56, 1.68–1.70, 2.06, 2.15–2.17 ppm was successfully assigned to their respective triad sequences using the 2D NMR; HMQC, HMBC and COSY techniques. The signal at δ 1.56 ppm was assigned to methylene protons of epoxidized isoprene, δ 1.68–1.70 ppm to both methyl protons of isoprene and methylene protons of epoxidized isoprene. The signals at δ 2.06 and 2.17–2.19 ppm were both assigned to the methylene protons of isoprene. The $^{13}\text{C-NMR}$ chemical shifts were similar to those previously reported. However, the chemical shifts of methylene carbons were dependent on the types of vicinal neighbouring units in the triad sequence. The reaction of purified ENR-50 with CS_2 formed the cyclic dithiocarbonate derivative of ENR-50 involving ring opening of the oxirane and the insertation of the C-S moiety at the oxygen attached to the quaternary carbon and methine carbon of epoxidized isoprene unit respectively. FTIR analysis showed that the C=S and C–O absorption bands appeared at 1096 and 1060 cm^{-1} , respectively. $^1\text{H-NMR}$ spectrum of cyclic dithiocarbonate derivative of ENR-50 displays splitting at δ 1.58–1.63 ppm and was assigned to the methylene protons of the respective epoxide and five-membered dithiocarbonate rings. Meanwhile, $^{13}\text{C-NMR}$ showed two new carbon peaks assigned to the $>\text{C}=\text{S}$ and the quaternary carbon of five-membered cyclic dithiocarbonate ring. The FTIR semi-quantitative and $^{13}\text{C-NMR}$ quantitative calculations revealed that approximately half of the epoxide units in the ENR-50 were converted to the dithiocarbonate derivative.

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