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Spectroscopic Study of Di-Imide Hydrogenation of Natural Rubber

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Summary: The diimide hydrogenation of natural rubber (NR) was studied by using *p*-toluenesulfonylhydrazide (TSH) as a diimide-releasing agent. The microstructure and the percentage of hydrogenation were studied by Raman, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Quantitative measurements on fraction of hydrogenated part gave the results in good agreement by using these techniques. The results indicated that percent hydrogenation increased with increasing of reaction time and about 80-85 % hydrogenation was achieved when a two-fold excess of TSH was used. The vibrational characteristic of C=C bond of NR is strongly Raman active and noted at 1663 cm^{-1}. The decrease of this signal was clearly observed during the progress of hydrogenation but the vibrational frequency of the *cis* and *trans* structures of the trisubstituted olefin unit of NR can not be differentiated by this technique. While ^{1}H- and ^{13}C-NMR analysis showed that *cis-trans* isomerization of carbon-carbon unsaturation of NR occurred during hydrogenation.

Keywords: diimide hydrogenation; FT-IR; natural rubber; NMR; Raman spectroscopy

Introduction

Chemical modification of unsaturated polymers via hydrogenation is one of the most important methods for altering and optimizing the physical and mechanical properties of the macromolecules. The hydrogenation is also a potential method offering a polymer that can

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not be prepared by a simple conventional polymerization reaction. An example is the preparation of poly(ethylene-alt-propylene) which can be potentially obtained by fully hydrogenation of 1,4-polyisoprene.[1] Diimide (N_2H_2) is an inorganic reducing agent which has been progressively used for hydrogenation of unsaturated molecules.[2,3] It is considered as a noncatalytic reaction and found to be a convenient hydrogenation method since it can be performed under atmospheric pressure with relatively simple apparatus and procedure. In contrary, catalytic hydrogenation using hydrogen gas in the presence of a noble metal catalyst is rather difficult in handling the reaction, usually involving high pressure and temperature.[1,4]

Natural rubber (NR) which has been known as highly *cis*-1,4 polyisoprenic structure, has a primary drawback in thermal and oxidative stabilities and poor oxygen and ozone resistance. This is due to the presence of the unsaturation along the molecular chain. Therefore, reduction of the unsaturated units of NR should overcome some of these drawbacks. N.K. Singha *et al* reported that catalytic hydrogenation of NR using $RhCl(PPh_3)$ catalyst increased the thermal stability of the resulting product without affecting its glass transition temperature.[1] Utilization of a diimide hydrogenating agent generated from thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) for hydrogenation of polybutadiene and polyisoprene has been reported.[2,3] In both cases, an excess amount of TSH is required if complete hydrogenation is expected. The evidence of hydrogenation was examined by IR and NMR spectroscopy.

Generally, spectroscopic techniques i.e. Raman, infrared, ^{1}H- and ^{13}C-NMR can be used for characterization of the microstructure of the chemically modified products.[5,6] Hydrogenation of NR can be therefore extensively investigated by vibrational (i.e. Raman and infrared) and resonance spectroscopic techniques (i.e. ^{1}H- and ^{13}C-NMR) since the characteristic signal of the C=C bond of polyisoprene is very sensitive to its environment.[7,8] However, only a few work has been analyzed by Raman scattering and solid state NMR, including the quantification of the unsaturated units of NR. Therefore, these two techniques have been used for such purposes in this present work and compared to other spectroscopic technique i.e. ^{1}H-NMR in solution.

This article describes the hydrogenation of NR by using diimide as a reducing agent generated from the *in situ* decomposition of TSH. The progress of reaction was observed by

Raman, FT-IR and NMR both in solution and solid state spectroscopic techniques. The percentage of hydrogenation was determined by Raman, ^{1}H-NMR in solution and ^{13}C-NMR in solid state. The evidence of *cis-trans* isomerization as hydrogenation progress was also investigated by ^{1}H- and ^{13}C-NMR.

Experimental

Hydrogenation

Hydrogenation of NR was carried out as follows; about 1.0 g of rubber was dissolved in 100 ml of xylene (JT Baker). Two folds of *p*-toluenesulfonylhydrazide (TSH, Fluka) as compared to rubber unsaturated units ([TSH]/[C=C] = 2) was added to the solution. The mixture was then stirred and heated to 135°C under nitrogen atmosphere. Samples were taken at various reaction times and precipitated in methanol. The hydrogenated product was purified by dissolving in hexane and reprecipitating in methanol. Finally, the product was dried in vacuum at room temperature before analysis.

Characterization

Raman Spectroscopy

Raman spectra of all samples were recorded with a T64000 Jobin-Yvon multichannel spectrometer adjusted either in simple spectrograph configuration with a 600 lines/mm grating or in triple subtractive configuration for high resolution experiments. Samples were illuminated with a Coherent Argon-Krypton Ion Laser selecting the 647.1 nm lines in order to minimize luminescence contribution to spectra. To improve the signal/noise ratio, each spectrum was accumulated 20 times during 30 sec. The frequency range selected was 500-3200 cm^{-1}. Calibration of the spectrometer was precisely checked on the 520.2 cm^{-1} silicon band and the resolution of the spectra was estimated to be smaller than 1 cm^{-1}. All experiments were performed under microscope using an x 50 long work distance objective (Olympus B x 40 microscope).

FT-IR Spectroscopy

FT-IR spectra were carried out by using Perkin-Elmer system 2000 spectrometer by casting thin film of the sample on NaCl plate. All samples were recorded at 16 scans in the range of 500-4000 cm^{-1} with 4 cm^{-1} spectra resolution in order to obtain a good signal-noise ratio.

Nuclear Magnetic Resonance Spectroscopy in Solution

^{1}H-NMR and ^{13}C-NMR (Bruker DPX-300 NMR spectrometer) spectra were obtained from the samples dissolved in $CDCl_3$ using tetramethylsilane (TMS) as an internal reference.

Nuclear Magnetic Resonance Spectroscopy in Solid State

High resolution solid state experiments were recorded on a Bruker MSL 300 spectrometer operating at 75.47 MHz. The instrument is equipped with a high-power amplifier for proton decoupling. The experiments were carried out using a pulse width of 90° (4 μs) with a repetition time of 4 s. A spectral width of 20 kHz and 16 K data points were used for data collection. The spinning speed of MAS technique was applied at 10 kHz.

Results and Discussion

The diimide molecule (N_2H_2) is generated *in situ* from the thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) as shown in equation (1) in Figure 1. It can then release a hydrogen molecule directly to the carbon-carbon double bonds of isoprene units as represented in equation (2) in Figure 1.

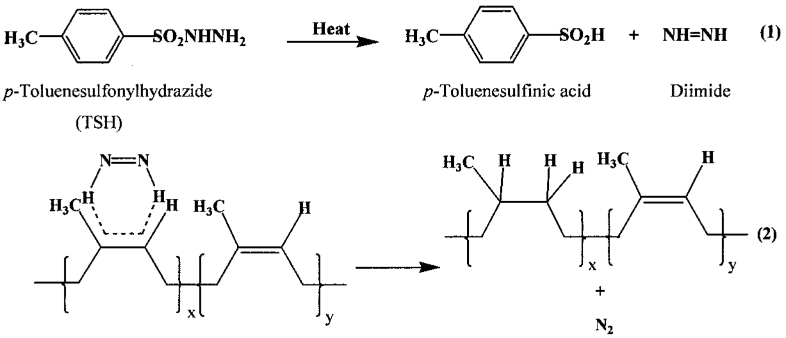

Figure 1. Hydrogenation of NR by using diimide generated from *p*-toluenesulfonylhydrazide.

Microstructure Analysis of Hydrogenated Rubber

Vibrational Spectroscopy

Non catalytic hydrogenation of NR in this study was carried out by using 2 moles of TSH as compared to the isoprene units. When one molecule of diimide reacted with the NR, one unit of the C=C should be disappeared as shown in Figure 1. The vibrational characteristic of the C=C of the isoprene unit can therefore be examined by Raman and Infrared (IR) spectroscopy. A comparison between the Raman spectra of the starting NR and that of hydrogenated NR (HNR) samples taken during hydrogenation at various reaction times is given in Figure 2. As hydrogenation reaction proceeded, the decrease of absorption band at 1664 cm^{-1} assigned to the C=C stretching modes can be clearly detected with increasing of the vibrational intensity of the band at 1432 cm^{-1}, attributed to the $-CH_2-$ deformation vibration. No alteration of the band at 1452 cm^{-1} which belongs to an asymmetric vibration of $-CH_3$ group in Raman spectra was noted after hydrogenation.

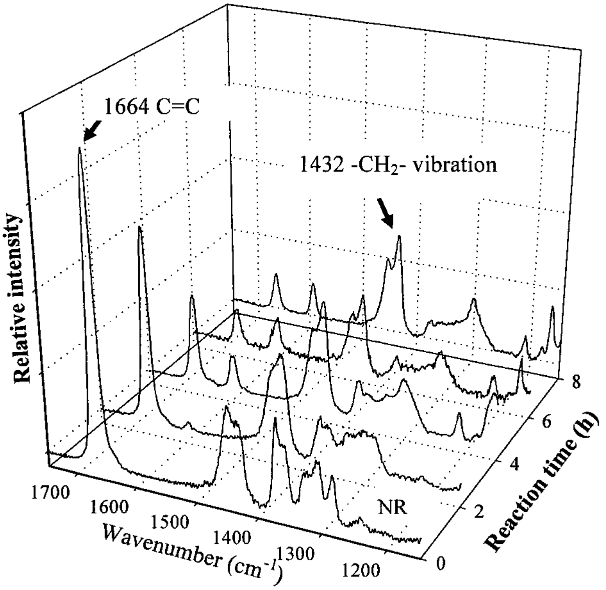

Figure 2. Raman spectra of natural rubber (NR) and hydrogenated rubbers at different reaction times.

It is not surprising that after 8 h of reaction the total disappearance of the peak at 1664 cm^{-1} is not observed as it has been reported that the complete reduction of unsaturation of butadiene polymers and of polyisoprene can be obtained with a five-fold excess of TSH.[2,3]

For IR analysis of the hydrogenated rubber, the decrease of two important characteristic peaks at 1665 and 836 cm^{-1}, attributing to C=C stretching and the C-H out of plane deformation of the trisubstituted olefin of polyisoprene, respectively, were observed as shown in Figure 3. The signal at 1375 cm^{-1} assigning to the C-H deformation and the signal at 735 cm^{-1}, being due to sequences of three continuous methylene units occurred after hydrogenation were also detected. It can be seen that the vibrational absorption modes obtained from IR spectrum is not as powerful as Raman mode. The intensity of the C=C absorption peaks at 1665 and 836 cm^{-1} are not strong for quantitative analysis of the percent of hydrogenation.

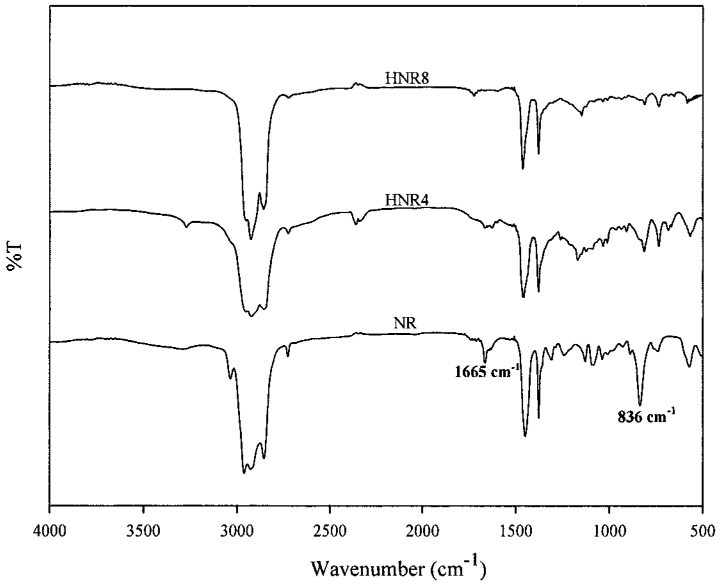

Figure 3. FTIR spectra of natural rubber (NR) and hydrogenated rubbers at 4h (HNR4) and 8h (HNR8) reaction times.

Resonance Spectroscopy

^{1}H-NMR analysis of NR in Figure 4 shows three main characteristic signals of proton adjacent to C=C, methylene and methyl protons of the unsaturated unit at 5.12, 2.03 and 1.67 ppm, respectively. ^{1}H-NMR spectra of the products of hydrogenation after 4 and 8 h of the reaction, symbolized as HNR4 and HNR8, respectively are also shown in Figure 4. The figure indicates that the intensity of proton signal adjacent to C=C bonds at 5.12 ppm decreases with the increased reaction time, as well as the decrease of signal at 1.67 ppm characteristic of methyl proton of *cis*-1,4 polyisoprenic units of NR. The methyl and methylene proton signals observed at 0.84 and 1.1-1.3 ppm, respectively showed a strong increment due to the transformation of double bonds into saturation moieties. The hydrogenation levels can be therefore determined by comparison of the integrals of signal at 5.12 ppm with the integrals for proton signal of saturated units.

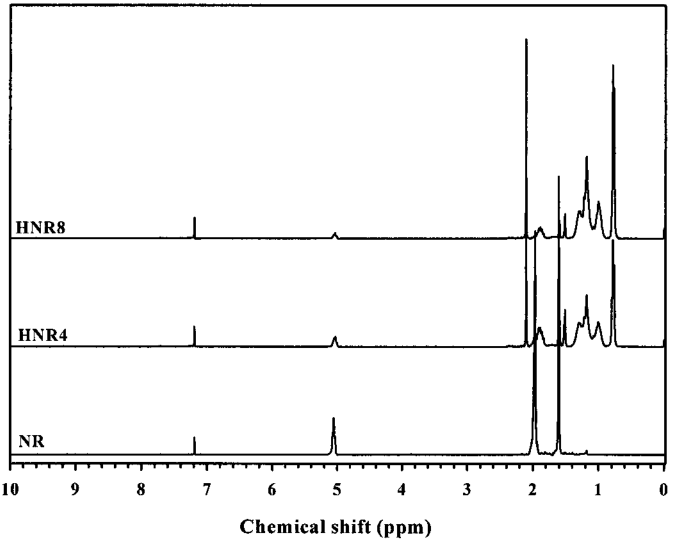

Figure 4. ^{1}H-NMR spectra of natural rubber (NR) and hydrogenated NRs at 4h (HNR4) and 8 h (HNR8) reaction times.

In the case of ^{13}C-NMR analysis in solution, the carbon signals of C=C of *cis*-structure of isoprene units of NR are positioned at 135.2 and 125.5 ppm. Three signals characteristic of methyl and two methylene carbons of the unsaturated unit were found at 23.4, 26.4 and 32.2 ppm, respectively. The extra peaks at 19.5, 33 and 37.1 ppm assigning to the methyl, methine and methylene carbons of saturated units in the hydrogenated rubbers are observed. The detected chemical shifts are in good agreement with those reported in the literatures.[1,9] The ^{13}C-NMR spectrum of the partially hydrogenated product reveals the evidence of the *cis-trans* isomerization of isoprene unit in the polymer chains as the signal at 134.9 and 124.7 ppm, corresponding to olefinic carbons of *trans*-polyisoprenic structure are detected for HNR.

The ^{13}C-NMR study in solid state of natural rubber and hydrogenated rubbers was carried out at room temperature, which is the temperature far above their glass transition temperatures (T_g). Under this condition, the dipolar interactions and chemical shift anisotropy that lead to line broadening are partially averaged by chain motion, and sharp lines are observed with high power decoupling and magic angle spinning. The motional averaging is such that high resolution signals of NR and HNR can be observed with spinning, and peak assignments can be established using the traditional solution methods (Figure 5).

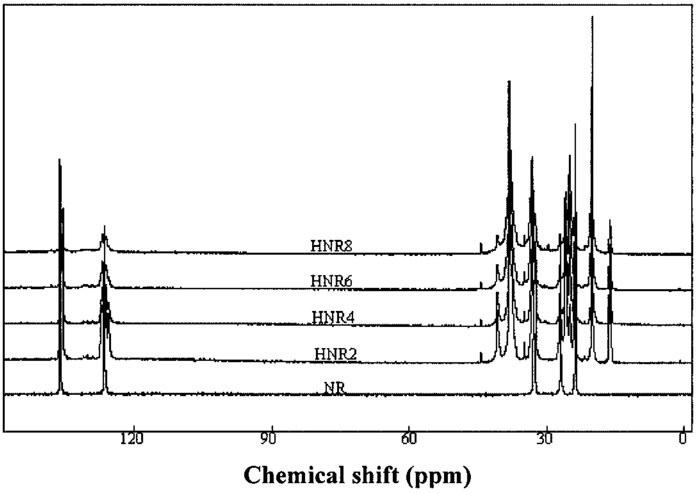

Figure 5. Solid state ^{13}C-NMR spectra of natural rubber (NR) and hydrogenated NR at 2h (HNR2), 4h (HNR4), 6h (HNR6) and 8 h (HNR8) reaction times.

The dominant peaks of NR spectrum at 23.6, 26.7, 32.5, 134.8 and 125 ppm observed were related to the five carbon atoms of the *cis*-1,4 polyisoprenic units, similar to the assignments using ^{13}C-NMR in solution. These characteristic peaks can be seen to diminish as the hydrogenation reaction proceeded. Then the significant peaks at 20.4, 33.3 and 38.1 ppm are found. Based on literature and by making comparison with the NMR spectra in liquid state, these peaks are assigned to the carbon signal of methyl, methine and methylene types, respectively.[1] Figure 5 shows also the characteristic *trans*-1,4-polyisoprene located at 16, 27 and 40 ppm, assigning to methyl and two methylene carbons.[10] This is the confirmation of *cis-trans* isomerization occurred simultaneously with hydrogenation. The extra resonances of trans-structural units allowed us to evaluate the amount of trans-isomer as increasing the reaction time.

Determination of Percent Hydrogenation

With the Raman scattering technique, it is possible to monitor the progress of saturated units in NR during hydrogenation. The percent hydrogenation of each sample can be estimated from the ratio of band areas arising from the stretching mode of C=C bond and the bending mode of CH_2, since each addition of hydrogen molecule on C=C bond gives rise to one new CH_2 unit.[11] The repeating unit of polyisoprene already presents two CH_2 groups. The CH_2 bending band appears to be moderately active near 1432 cm^{-1} as shown in Figure 2. The band intensity in Raman spectra can be roughly considered as proportional to the concentration of each species in the following:

$$A(C{=}C) = k_1[C{=}C]$$

$$A(CH_2) = k_2[CH_2]$$

where A(C=C) is the integrated intensity area of the band located between 1645 and 1685 cm^{-1} assigned to the C=C stretching vibrational band, $A(CH_2)$ is the integrated intensity area of the CH_2 bending band between 1415 and 1440 cm^{-1}, k_1 and k_2 are proportional constants associated with the considered C=C and CH_2 vibrational modes. If the starting rubber is composed of 100 repeating units, 100 C=C and 200 CH_2 units are then present, hence

$$k_1/k_2 = 2A_0(C{=}C)/A_0(CH_2)$$

Then, the ratio k_1/k_2 can be determined from the Raman spectrum of NR in Figure 2.

X is assigned for the concentration or number of the unit disappeared or formed, when X

C=C units disappear during hydrogenation, it can be noted that X of CH_2 units are created. For a partially hydrogenated product, X or the hydrogenation rate can then be calculated from the following equation :

$$X = 100\ [(K - 2\alpha)/(K + \alpha)]$$

where $K = k_1/k_2$ and $\alpha = A_0(C{=}C)/A_0(CH_2)$ of the partially hydrogenated compound.

From ^{1}H-NMR spectroscopy, the integrated areas of the signal at 5.12 and 0.84 ppm, corresponding to the proton adjacent to olefinic unit and methyl proton of saturated unit, respectively, were used for the determination of percentage of hydrogenation. The progress of hydrogenation by solid state ^{13}C-NMR was obtained by using the integrated areas of the signals of saturated methyl carbon at 20.4 ppm comparing to the methyl carbon of both cis- and trans-unsaturated units at 23.6 and 16 ppm, respectively. The results of percentage of hydrogenation at various reaction times of NR determined by different techniques are illustrated in Figure 6. It was found that the hydrogenation increased with the increase of reaction time. The maximal percentage of hydrogenation approximately 80-85 % was found by using all three techniques when a two-fold excess of TSH was used. Several publications reported that complete hydrogenation was obtained when 4-5 moles of TSH per mole of polyisoprene units were utilized for hydrogenation of homopolymer or copolymer containing polyisoprene units.[11,12] It was described that not only the syn form of the generated diimide can react with the C=C bonds of polyisoprene units, but it can also undergo disproportionation, giving nitrogen molecule and hydrazine.

Cis-trans Isomerization

It was reported that utilization of TSH as a diimide releasing agent for hydrogenation of *cis*-polybutadiene resulted in *cis-trans* isomerization.[13] Unfortunately, the *cis-trans* isomerization of the unsaturated units of NR during hydrogenation can not be detected by Raman spectroscopy as the vibrational frequency of the *cis* and *trans* structures of trisubstituted olefinic unit in Raman scattering are very close. While the ^{1}H-NMR spectra of the hydrogenated rubber exhibit the signal of methyl proton of the *cis*- and *trans*-1,4 polyisoprenic units at 1.67 and 1.60 ppm, respectively. The percentage of the remaining double bonds in *cis*- and *trans*- configurations of the hydrogenated samples at various reaction times can then be calculated and the results are shown in Figure 7 (a).

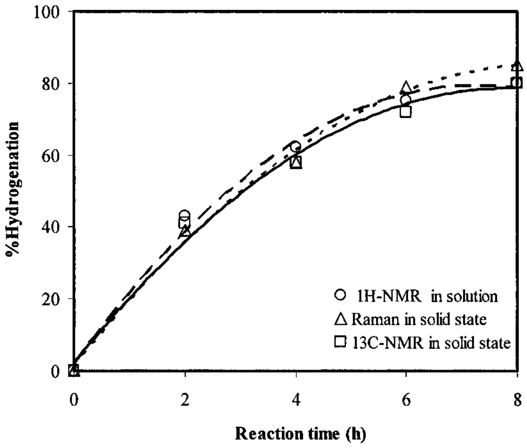

Figure 6. Results of percentage of hydrogenation at various reaction times of NR determined by ^{1}H-NMR in solution, Raman scattering and ^{13}C-NMR in solid state.

The ^{13}C-NMR spectrum in solution of the partial hydrogenated product reveals the evidence of the *cis-trans* isomerization. The carbon signals of *cis*-structure were located at 135.2 and 125.5 ppm while the signals at 134.9 and 124.7 ppm, corresponding to olefinic carbons of 1,4-*trans* polyisoprenic units were also detected for hydrogenated NR.

For solid state ^{13}C-NMR spectra, the signal of methyl carbon of *cis*- and *trans*- polyisoprenic structure can be clearly seen at 23.6 and 16 ppm, respectively. The results of the percentage of cis- and trans- isomers at various reaction times are illustrated in Figure 7(b). It seems likely that in this system the *cis-trans* isomerization is a reversible process. The thermal decomposition of TSH generates a diimide acted as a hydrogen-donor molecule as well as *p*-toluenesulfonic acid by-product. The formation of unstable complex between the double bonds and the *p*-toluenesulfinic acid by-product may be responsible for the *cis-trans* isomerization reaction.[13] No signal of the addition of the by-product onto the hydrogenated rubber was detected.

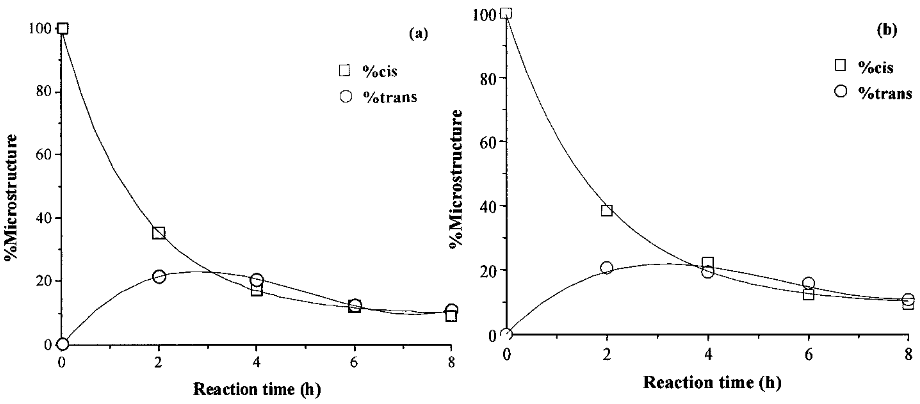

Figure 7. Progress of *cis-trans* isomerization rate during hydrogenation of NR determined by ^{1}H-NMR in solution (a) and ^{13}C-NMR in solid state (b).

Conclusion

Natural rubber (NR) was partially hydrogenated using two-fold moles of *p*-toluenesulfonylhydrazide (TSH) compared to the unsaturated unit. The microstructure of the hydrogenated products can be observed by using spectroscopic techniques i.e. Raman, FT-IR, ^{1}H- and ^{13}C-NMR. The quantitative measurements on fraction of hydrogenated part at different reaction times determined by Raman, ^{1}H- and ^{13}C-NMR gave similar results which indicated that percent hydrogenation increased with increasing of reaction time and about 80-85 % hydrogenation were obtained at 8h. ^{1}H-NMR and ^{13}C-NMR gave the evidence of the *cis-trans* isomerization during hydrogenation. These techniques were also used to monitor the progress of the isomerization.

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