Cationic Cyclization of Purified Natural Rubber in Latex Form with a Trimethylsilyl Triflate as a Novel Catalyst

Sa-ad Riyajan,[1,4] Der-Jang Liaw,[2] Yasuyuki Tanaka,[1] Jitladda Tangpakdee Sakdapipanich[1,3]

[1]Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering, National Taiwan University of Science and Technology, Taipei, 106, Taiwan
[3]Institute of Science and Technology for Research and Development, Mahidol University, Salaya Campus, Nakornpathom 73170, Thailand
[4]Department of Polymer Science, Faculty of Science, Prince of Songkla University, Hat Yai 91400, Thailand

ABSTRACT: Cyclization of deproteinized natural rubber (DPNR) or purified natural rubber latex was effectively performed in latex phase by using trimethylsilyl-trifluoromethane sulfonate or trimethylsilyl triflate (TMSOTF) as a novel catalyst, which is still not reported in the case of natural rubber latex. Various cyclization conditions affecting the degree of cyclization were studied, such as dry rubber contents, temperature, TMSOTF concentrations, and time. The cyclized products were characterized by FTIR, Raman, ^{1}H-, and ^{13}C-NMR spectroscopies, as well as DSC and TGA. The degree of cyclization was estimated by ^{1}H-NMR spectrum. It was found that the degree of cyclization in NR was a function of cyclization conditions. The thermal stability of cyclized DPNR increased with the degree of cyclization. Solubility of the obtained rubber was good in chloroform, toluene, cyclohexanone, and cyclohexane, and bad in tetrahydrofuran. The average number molecular weight of cyclized DPNR with 76% degree of cyclization was about 4.2×10^4 g/mol. On the basis of FTIR, Raman, ^{1}H-, and ^{13}C-NMR, the C=C of cyclized DPNR dramatically decreased after prolonged reaction time. In addition, the topology of cyclization DPNR particles was rough on its rubber particle as analyzed by TEM. The mechanism for this reaction will also be discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 664–672, 2007

Key words: deproteinized natural rubber; cyclization; trimethylsilyl triflate; latex

INTRODUCTION

Polymer scientists have attempted to prepare cyclized rubber from natural rubber (NR), polyisoprene, and polybutadiene since the 1950s. Cyclized products are used in the formulation of adhesives, paintings, inks, and also in the compounding of NR to improve its mechanical characteristics.[1–5] Nowadays, new cyclized rubbers are synthesized with new catalysts and cyclization methods, and many applications have been devised and a lot of patents are being issued for which the cyclized rubbers are important components in the formulations.

For the preparation of cyclized rubber, NR, which is prepared in both solution and solid forms,[6] has been used as starting material. In a few cases, the reaction was carried out in latex state, attributing to the NR molecular chain confined to the internal scope of NR particles in a coiling state. Therefore, the catalyst molecules need to pass through the outer layer of the NR particles to contact the NR molecules and react with them. In solution state, the NR molecules are in a spreading state and can move freely, so the catalyst molecules can easily contact all parts of NR molecules.

As an example, G. J. Van Veersen et al.[6–9] have prepared cyclized rubber from latex by using catalysts such as hydrochloride, boron trifluoride, and sulfuric acid. They found that sulfuric acid was a good catalyst for preparation of cyclized NR in latex. However, the solubility of the cyclized NR obtained from this catalyst was very poor in common organic solvents.

Patterson and Koenig[10] have investigated the structure of cyclized NR obtained from p-toluenesulfonic acid in toluene solution by FTIR and NMR spectroscopies. They concluded that the cyclized portions contained both mobile and rigid domains due to crosslinking during the cyclization reaction. The cyclized samples showed a distribution of functionalities including some oxidation products and all three types of olefinic-segmented end groups were formed during cyclization (di-, tri-, and tetra-substituted olefins).

In 1983, Patterson and Beebe[11] also studied the microstructure of cyclized polyisoprene obtained from $TiCl_4/Cl_3COO_2H$, SbF_5/FSO_3H, or BF_3-diethyl etherate in cyclohexane solution by ^{1}H- and ^{13}C-NMR spectroscopy. They found the distribution of end-

group alkene segments among three structural types (di-, tri-, and tetra-substituted olefins) as well as did microstructural analysis of the remaining polyisoprene in partially cyclized samples by NMR analysis. In most instances, half or more of the end groups are tetrasubstituted alkene, and evidence was found for both *cis–trans* and positional isomerization (to the methyl carbon) of uncyclized 1,4-*cis* polyisoprene.

In this paper, TMSOTF was used as a new catalyst for cyclization of deproteinized NR (DPNR) in latex state. This catalyst is expected to enhance solubility of cyclized NR derived from latex form. Effects of TMSOTF concentration reaction, time, and temperature, as well as dry rubber content on the degree of cyclization were studied. Thermal properties of the cyclized DPNR were investigated. The structure of cyclized DPNR was also characterized by FTIR and NMR techniques. The molecular weight and intrinsic viscosity of cyclized DPNR were analyzed by gel permeation chromatography (GPC) and viscometry, respectively. In addition, its solubility in various kinds of organic solvents will be discussed.

EXPERIMENTAL

Materials

High-ammonia natural rubber latex (HANR-latex) was provided from Thai Rubber Latex (Thailand) Co. Ltd, and Terric 320 as a surfactant was supplied by East Asiatic (Thailand) Co. Trimethylsilyl triflate (Fluka, Switzerland), sulfuric acid (Lab-Scan, Thailand), and dodecylsulfonic acid (Fluka, Switzerland) were used as received. AR-grade solvents such as toluene, methanol were used without further purification. DPNR was produced from HANR latex by enzymatic deproteinization treatment.[12]

Preparation

Cyclized DPNR in latex form was prepared in two ways, i.e., with organic solvent and without organic solvent. Cyclization of DPNR in latex was carried out using DPNR latex at 50% dry rubber content (DRC) as starting material. DPNR latex was mixed with 2% w/w of surfactant. The prepared latex was heated to 90°C, followed by an addition of catalyst. After completion of the cyclization reaction, the resulting rubber was coagulated by acetone. The resulting rubber was purified by reprecipitation of the rubber solution in toluene with methanol twice and then, drying under vacuum in an oven at 50°C.

Characterization

FTIR spectra of cyclized DPNR, which was cast from chloroform solution, were recorded on a JASCO FTIR-460 spectrometer with 100 scans in the spectral range of 400–3600 cm^{-1}.

Raman spectra of all samples were recorded with a T64000 JOBIN-YVO multichannel spectrometer adjusted either in sample spectrophotograph configuration with a 600 lines/mm grafting or in triple subtractive configuration for high-resolution experiments. The ^{1}H- and ^{13}C-NMR spectra were obtained using $CDCl_3$ as solvent on a BRUKER DPX-300 at 300 MHz and 75 MHz, respectively.

Morphology of rubber was characterized by transmittance electron microscopy (TEM) by using HITACHI, H-7500, and osmium oxide was used as a straining agent. The diluted latex (DRC $\sim 0.02\%$) was mixed with the straining agent, cast on a copper grid, and stored at room temperature for 12 h.

Thermal gravimetric analysis was carried out with a Perkin–Elmer thermal gravimetric analyzer (TGA). The mass of the sample was about 8.00 mg. The carrier gas was either air or nitrogen with a flow rate of 60 mL/min. The temperature was scanned from 30 to 850 with rate at 20°C/min.

The intrinsic viscosities [η] of DPNR and cyclized product were evaluated by using an Ubbelohde viscometer. The measurement was 0.1–0.2 g/dL of the rubber in toluene solution at 30°C. The viscosity-average molecular weight was calculated from Mark–Houwink equation[13]

$$[\eta] = 1.90 \times 10^{-4} \, \overline{M}_v^{0.745}$$

The molecular weight and molecular weight distribution (MWD) of cyclized NR was determined by using a JASCO RI-1530 with THF at a flow rate of 0.5 mL/min at 35°C, monitoring with RI detectors. The exclusion limits of two columns packed with polystyrene gel were 2×10^8 and 5×10^2 g/mol. The calibration curve of molecular weight was made from *cis*-1,4-polyisoprene purchased from Polymer Service GmbH, Germany. Cyclized DPNR samples, adjusted at the concentration range of 0.25–0.4% w/v and filtered through 0.45-μm polyamide filter paper, were subjected to GPC analysis.

Determination of degree of cyclized DPNR

The degree of cyclization is estimated using ^{1}H-NMR based on two different methods. The first method is based on the following equation derived for cyclized NR.[14]

$$\text{Degree of cyclization} = \frac{\text{Area of } -CH_3 \text{ protons } (\delta = 0.86 - 1.0)}{[(\text{Area of } -CH_3 \text{ protons } (\delta = 0.86 - 1.0)) + 3(\text{Area of } -CH= (\delta = 5.16))]}$$

Temp (°C)	Degree of cyclization (%)	Appearance
27	0	Rubbery
50	0	Rubbery
75	2	Rubbery
90	70	Powdery
95	76	Powdery

Calculation of the residual unsaturation in cyclized DPNR

The second method for measuring of the degree of cyclization was based on quantitative analysis of residual isoprene units in cyclized DPNR using polyethylene oxide 6000 (PEG, $(—CH_2CH_2O—)_n$) as an internal standard. Cyclized DPNR sample 0.36 mg was mixed with 0.6 mg of PEG in a NMR sample tube and dissolved with $CDCl_3$. The percentage of residual isoprene units was determined based on the intensity ratio of the olefinic proton signals $=CH—$ at 5.16 ppm against the methylene proton signal of PEG at 3.46 ppm.

The intensity ratio between PEG (3.46 ppm) and $C=C$ (5.16 ppm) is calculated as follows;

$$\text{Ratio of (isoprene unit} = CH)/(PEG\ CH_2) = R_i$$
$$= \frac{\text{Intensity at 5.16 ppm}}{\text{Intensity at 3.46 ppm}}$$

Uncyclized DPNR was used for the measurement of the control R_i value, assuming the presence of 100% cis-isoprene units. The percentage of residual double bonds in isoprene units of cyclized DPNR was obtained by comparing the R_i value of cyclized NR with that of the control DPNR, using the following equation.

$$\%\ \text{Residual double bond} = \frac{R_i\ \text{of cyclized DPNR} \times 100}{R_i\ \text{of uncylized DPNR}}$$

RESULTS AND DISCUSSION

The factors influencing the degree of cyclization for the cyclized DPNR derived from TMSOTF as a catalyst are shown in Tables I–IV.

Effect of the reaction temperature

The cyclized DPNR was carried out at different temperatures ranging from 30 to 95°C. Table I represents the degree of cyclization obtained from DPNR latex, 34.0% w/w of TMSOTF for 5 h was 0, 0, 2, 70, and 76% at 30, 50, 75, 90, and 95°C, respectively. When the cyclization temperature was higher than 75°C, the reaction between the reactive sites on DPNR molecules were more pronounced. This result indicates that a high temperature favors the cyclization of DPNR with TMSOTF. The optimum temperature for preparation of cyclized DPNR in this system was 90–100°C. The cyclized DPNR containing 0–2% degree of cyclization was a rubbery material, while the cyclized sample containing 70–76% degree of cyclization was a powdery material.

Effect of TMSOTF concentration

Table II illustrates the results obtained from various TMSOTF concentrations using 50% DRC of DPNR, at 95°C for 5 h. The degree of cyclization of DPNR obtained from various concentrations, i.e., 0, 5, 10, 17, 34, and 50% (w/w) of TMSOTF was about 0, 2, 34, 76, and 80%, respectively. This result indicates that the cyclization of DPNR was obviously accelerated and degree of cyclization increased by increasing TMSOTF concentration. It could be expected that higher amount of TMSOTF would give higher carbonium species during cyclization reaction. The appearance of cyclized rubber derived from 5% w/w or less was rubbery material and the cyclized product obtained from 10.0 to 17.0% w/w of TMSOTF was leathery material. When TMSOTF concentration was up to 34.0% w/w, the modified rubber had a powdery appearance.

Effect of reaction time

Table III shows the influence of the reaction time on the degree of cyclization of DPNR. It was found that the degree of cyclization of DPNR increased as reaction time increased. The cationic cyclization reaction is gradually increased, thereby needing several hours.

It was found that the degree of cyclization of cyclized DPNR obtained from TMSOTF was higher than that of sulfuric acid and dodecylsulfonic acid. The degree of cyclization derived from TMSOTF, sulfuric acid, and dodecylsulfonic acid was 76, 40, and 2%, respectively, at 34.0% w/w of catalyst for 5 h of reaction time.

TMSOTF (% w/w)	Degree of cyclization (%)	Appearance
0	0	Rubbery
5	2	Rubbery
10	34	Leathery
17	54	Leathery
34	76	Powdery
50	80	Powdery

TABLE III
Effect of Reaction Time on Degree of Cyclization of DPNR Obtained from 50% DRC of DPNR, (a) 34% w/w of TMSOTF, and (b) 34% w/w of H_2SO_4, and (c) Dodecylsulfonic Acid at 95°C at Various Times

Time (h)	Degree of cyclization (%)			Appearance		
	(a)	(b)	(c)	(a)	(b)	(c)
0.5	6	0	0	Rubbery	Rubbery	Rubbery
1.0	7	0	0	Rubbery	Rubbery	Rubbery
1.5	10	5	0	Rubbery	Rubbery	Rubbery
3.0	15	15	1	Rubbery	Rubbery	Rubbery
4.0	60	38	1	Almost powdery	Leathery	Rubbery
5.0	76	40	2	Powdery	Leathery	Rubbery
9.0	77	40	3	Powdery	Leathery	Rubbery

It was clear that TMSOTF was an effective catalyst to accelerate the cyclization of DPNR latex, by observing the cyclized product obtained within 1.5 h of reaction time. From 0–3 h of reaction time, the appearance of cyclized product was still rubbery. When reaction time increased to 4 h, the appearance became almost powdery, corresponding to degree of cyclization of 60%. The largest part of the cyclization occurred within 5 h (or less), and the highest degree of cyclization value was observed after 9 h of reaction time. The degree of cyclization reached 60% at 4 h of reaction time.

In the case of sulfuric acid catalyst, it was found that degree of cyclization in cyclized DPNR was 0, 0, 5, 15, 38, 40, and 40% at 0.5, 1.0, 1.5, 3, 4, 5, and 9 h of reaction time, respectively. From 0–3 h of reaction time, the appearance of cyclized product was still rubbery. When reaction time continued to 4 h, the appearance became leathery, corresponding to degree of cyclization of 40%. The degree of cyclization was about 3% after 9 h of reaction time by using 34.0% w/w of dodecyl sulfonic acid as a catalyst and its appearance was still rubbery. By comparing these three catalysts (TMSOTF, sulfuric acid, and dodecylsulfonic acid), which affect the degree of cyclization, it can be seen that the maximum of degree of cyclization was observed in the case of TMSOTF at 9 h of reaction time.

Table III explains the effect of reaction time on degree of cyclization of DPNR obtained from 50% DRC of DPNR, (a) 34% w/w of TMSOTF, (b) 34% w/w of H_2SO_4, and (c) dodecylsulfonic acid at 95°C at various times

Effect of dry rubber content

Table IV shows the effect of DRC on degree of cyclized DPNR obtained from 34.0% w/w of TMSOTF at 95°C, for 5 h. It was found that the degree of cyclization increased as a function of DRC. The degree of cyclization obtained from 5, 10, 25, 35, 40, and 50% DRC was about 0, 2, 30, 54, 68, and 76%. The appearance of cyclized rubber derived from DRC 5 to 10%

was rubbery, when DRC of DPNR at 25–35% was used to prepare the cyclized rubber; the appearance of resulting product was leathery. If DRC at 40% was used, the appearance of cyclized NR was almost powdery. Up to DRC 50% of DPNR, the appearance of cyclized rubber became powdery. This result indicates that the efficiency of the catalyst is good at the higher DRC of DPNR. It is possible that the amount of acid catalyst that can penetrate into the rubber particle in the higher DRC was higher than that in the low DRC due to difference in surface area.

Comparison of degree of cyclization, unsaturation loss, and intrinsic viscosity of cyclized DPNR and uncyclized DPNR

Various methods have been used for the determination of residue unsaturation in the cyclized NR in the past 50 years.

For example, Lee et al.[15] investigated the unsaturation residual in cyclized NR by using peroxobenoic acid, followed by iodine titration. Gordon[5] estimated the extent of cyclization, which could be ascertained by determining the specific gravity of the reaction mixture. Gordon investigated the kinetics of the cyclization reaction between latex rubber and sulfuric acid and postulated a mechanism for the reaction favoring a copolymeric structure for cyclized rubber containing 86.55% of diisoprenic six membered rings with one double bond bold, and 13.5% of uncyclized isoprenic units. This data also substantiated the original statistical calculations for similar reactions involving adjacent units, made by Flory.[16] Gordon argued that if cyclization proceeded by a mechanism involving the interaction of adjacent isoprene units, but isolated pairs of isoprene units, then a certain proportion of those units will be left as "widow," which was unable to interact because they had no partners. It can be shown that, if all the isoprene units have an equal chance of reacting, then the proportion of unreacted units left at the completion of the reaction is (natural number) e^{-2}. Taking into account that the formation of each cyclohexane ring results in the loss of one olefinic double bond of the isoprene units from which it

TABLE IV
Effect of Dry Rubber Content of DPNR Latex on Degree of Cyclization of DPNR Using of DPNR, 34% w/w of TMSOTF, at 95°C for 5 h

DRC (%)	Degree of cyclization (%)	Appearance
5	0	Rubbery
10	2	Rubbery
25	30	Leathery
35	54	Leathery
40	68	Almost powdery
50	76	Powdery

was formed, the maximum extent to which the unsaturation of the product can be reduced should correspond to a residual unsaturation equal to a fraction $\frac{1}{2}(1-e^{-2}) + e^{-2}$ of the original, i.e., 56.8%.

In this present work, the degree of cyclization, and percentage of unsaturation loss were estimated from ^{1}H-NMR spectrum. It is clear that as the cyclization reaction progressed, the intensity of the signal at 0.86–1.00[17] ppm increased, while the intensity of the center signal at 5.16 ppm decreased. Thus, the degree of cyclization in NR could be then estimated.[14]

The percentage of unsaturation loss and degree of cyclization in the cyclized NR were estimated by internal standard (PEG). The results are shown in Table V. It was clearly observed that the degree of cyclization was directly proportional to the percentage of unsaturation loss. That is, the degree of cyclization at 0, 5, 33, 54, 70, and 76% corresponded to 0, 10, 40, 60, 80, and 89% of unsaturation loss, respectively.
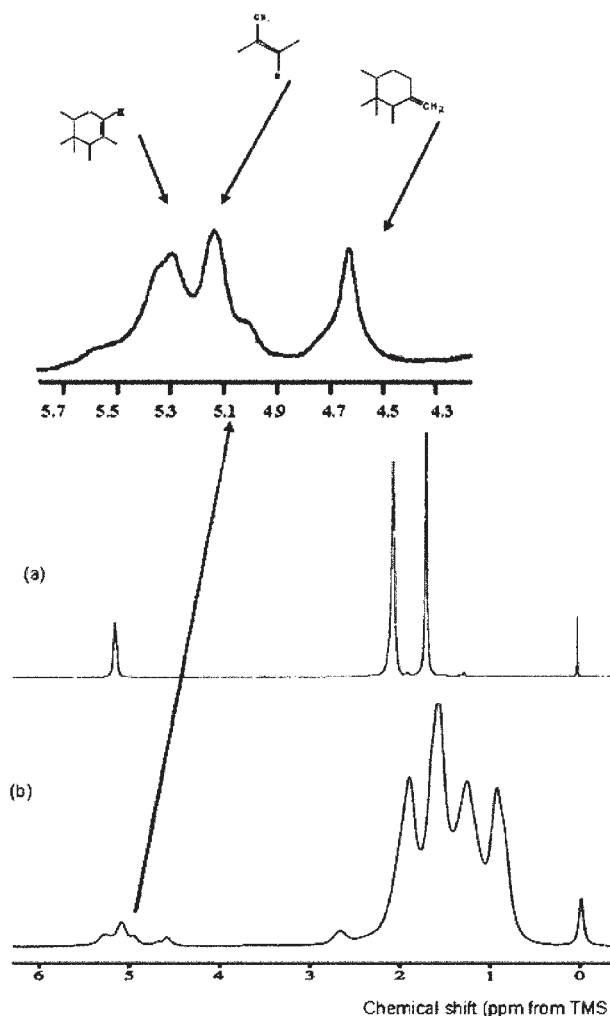
When TMSOTF was slowly dropped in DPNR latex, the cationic active species were formed. In the cyclization process, DPNR latex was white at first, and it became black when TMSOTF was added. The cyclization reaction occurred by the action of the catalyst attacking and opening the double bond of polyisoprene, then many cyclic structures were formed in the linear macromolecule chains. Therefore, high levels of cyclization are always accompanied by a sharp reduction in the intrinsic viscosity value of NR, as shown in Table V. The intrinsic viscosity of uncyclized DPNR or zero degree of cyclization, heated at 95°C for 5 h, without addition of TMSOTF was 2.0. When the cyclization reaction progressed, the intrinsic viscosity of DPNR containing 5, 33, 50, 70, and 76% exponentially decreased to be 1.7, 1.5, 0.9, and 0.4, respectively. It could be concluded that three parameters (degree of cyclization, unsaturation loss and intrinsic viscosity) showed the same tendency as given Table V.

Characterization of cyclization structure of the cyclized natural rubber

The ^{1}H-NMR spectra at 500 MHz of uncyclized and cyclized DPNR sample are shown in Figure 1. The

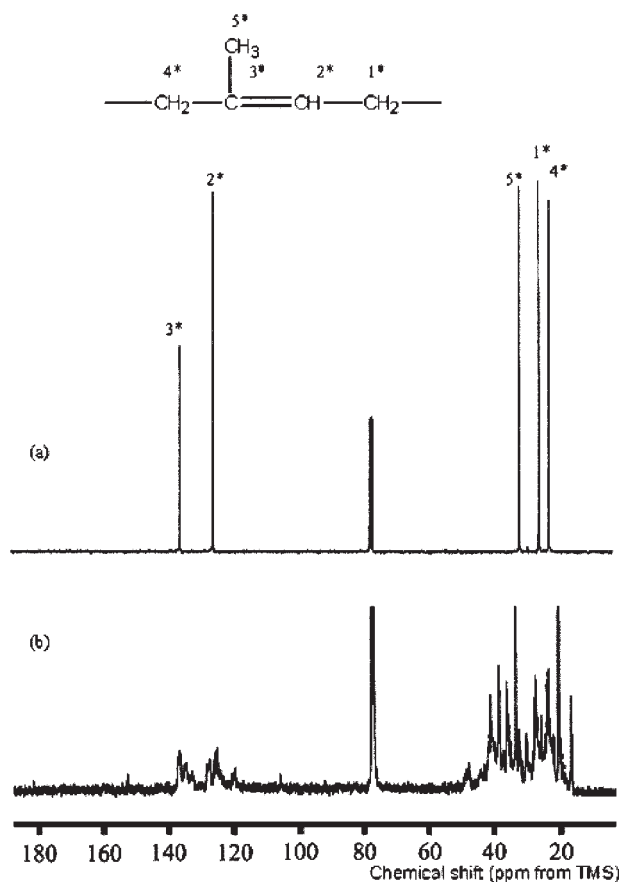
Figure 1 ^{1}H-NMR of cyclized DPNR having degree of cyclization (a) 0% and (b) 80% obtained from 50% DRC of DPNR, 34% w/w of TMSOTF at 95°C for 5 h.

unsaturation methylene proton shows singlet resonance center signal at 5.16 ppm. The center signal at 2.10 ppm may be attributed to the methylene protons and the singlet resonance signal of the methyl proton appears center signal at 1.70 ppm. The methyl protons attached to saturated carbons are observed as a triplet

TABLE V
Comparison of Degree of Cyclization (%), Unsaturation Loss (%) and Intrinsic Viscosity of Cyclized DPNR

Sample types	Degree of cyclization (%)	Loss unsaturation (%)	[η]
1	0	0	2.10
2	5	10	1.70
3	33	40	1.50
4	54	60	0.90
5	70	80	0.37
6	76	89	0.24

TABLE VI
Chemical Shift of Olefinic Protons in Cyclized Polyisoprene[11]

| Chemical shift*	5.16 4.78	4.72	4.64	5.32

*Solvent CDCl₃.

Figure 2 ^{13}C-NMR of cyclized DPNR having degree of cyclization (a) 0% and (b) 76% obtained from 50% DRC of DPNR, 34% w/w of TMSOTF at 95°C for 5 h.

signal showed center signal at 0.85 ppm. A center signal at 0.85 ppm is assignable to the methyl protons (CH$_3$) attached to the cyclic structure, which was not attached to the double bond.[17] A center signal at 1.3 ppm is due to the methylene protons attached to saturated carbons. These signals increased in intensity in return for the decrease of the methylene proton center
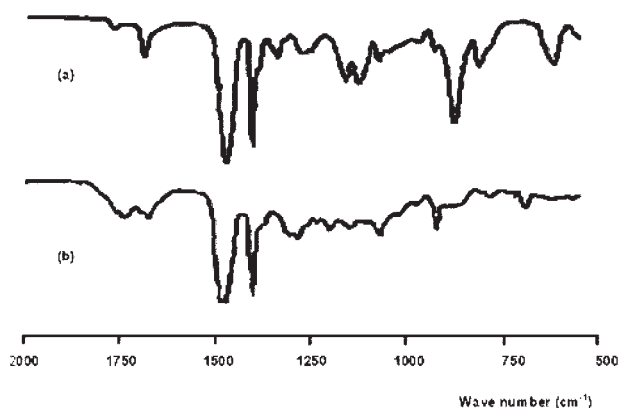
Figure 3 IR spectra of DPNR obtained from (a) uncyclized DPNR and (b) its cyclized DPNR with 76% degree of cyclization.

signal at 2.05 ppm, which is due to the methylene protons of original isoprene units. It is known that the methyl protons in the *cis*-1,4 and *trans*-1,4-isoprene units show overlapping signal at 1.61–1.68 ppm,
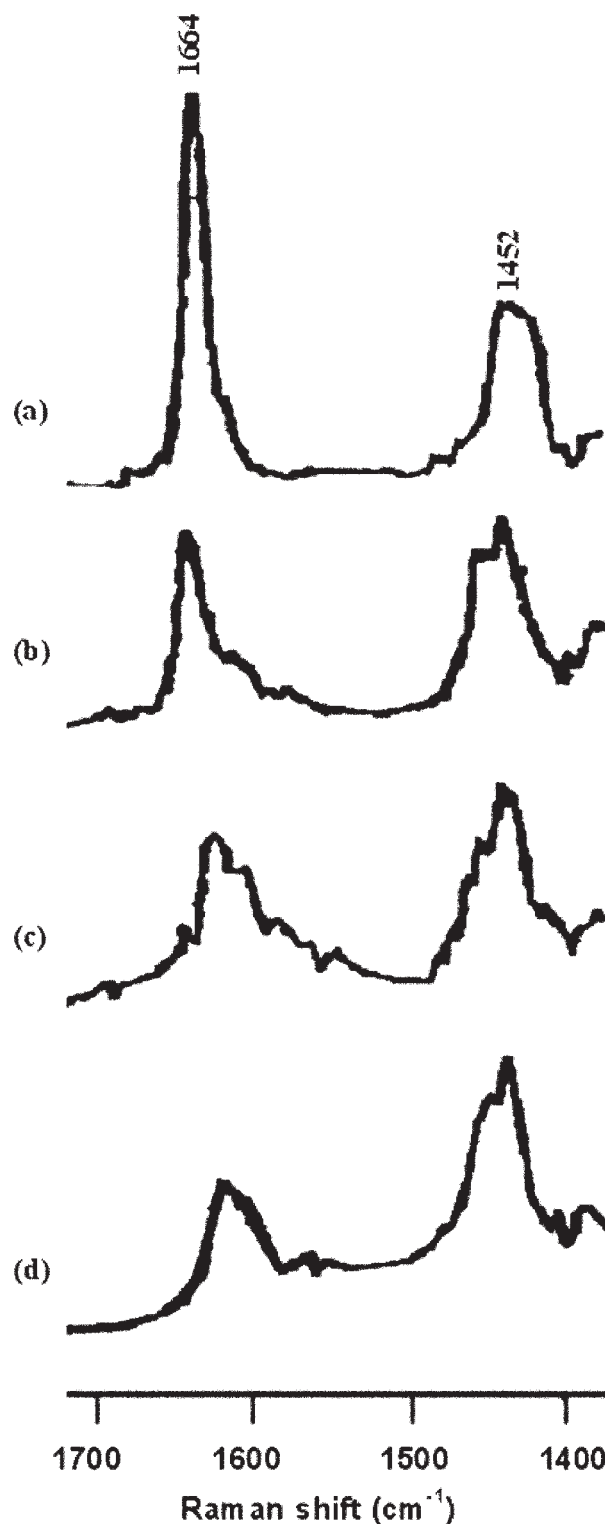
Figure 4 Raman spectra of (a) uncyclized DPNR and cyclized DPNR at different degrees of cyclization, (b) 34%, (c) 54%, and (d) 80%.

TABLE VII
Solubility of the Cyclized DPNR with Various Degrees of Cyclization

Degree of Cyclization (%)	Solubility (%)				
	Chloroform	Tetrahydrofuran	Cyclohexane	Cyclohexanone	Toluene
4	100	97	100	100	100
34	100	86	99	99	99
54	99	68	99	99	99
76	99	46	99	97	98

respectively, in CDCl$_3$. A new signal at 1.61–1.68 ppm is assignable to the methyl protons in the *trans*-1,4-isoprene units which formed by isomerization of *cis*-1,4 isoprene units. The methine proton at 2.70 ppm was observed in the side reaction product during cyclization. In previous work, it was assigned to the methine proton attacked to the oxirane ring[18–20] and the methine proton of the product occurring from hydrogen transfer.[17]

The center signals at 5.16, 5.32, and 4.64 ppm represent the olefinic structure of cyclized NR, as shown in Table VI.

These chemical shifts agree with those reported previously by Agnihotri et al.,[17] except that the use of higher magnetic fields (200 or 300 MHz), could allow the detection of 3, 4-polyisoprene and exocyclic structures.

In the case of ^{13}C-NMR analysis in solution state, the carbon signals of C=C of *cis*- structure of isoprene units of uncyclized DPNR were positioned at 135.0 and 125.0 ppm, as depicted in Figure 2. Three signal characteristics of methyl and two methylene carbons of the unsaturated unit were detected at 23.0 and 26.0 and 32.0 ppm, respectively. Figure 2 represents the ^{13}C-NMR of cyclized DPNR with 80% cyclization. It was seen that many overlapping signals were observed for the cyclized NR in aliphatic region. It was found that intensity of double bond is very low due to its opening double bond to cyclization structure. This result is in agreement with ^{1}H-NMR data, as described previously.

FTIR spectra of DPNR and the two partially cyclized DPNR samples are plotted in Figure 3. Two spectra regions were observed to undergo changes during cyclization; the carbon–carbon double bond stretching modes at 1600 cm^{-1}, the CH$_2$ deformation and C—C stretching mode region at 900–1200 cm^{-1}, and the C—H bending mode region at 800–900 cm^{-1}.[10,21] The band at 1664 cm^{-1} was due to the *cis*-1,4 carbon–carbon double bond stretching mode. This observation indicates that cyclization was incomplete. The band at 1718 and 1740 cm^{-1} is assigned to the C=O stretching of aldehyde and carboxylic acid groups, which are formed from oxidation reaction. The weak band at 1692 cm^{-1} is assigned to the C—C stretching of the tetra-substituted (endocyclic) species in the cyclized sequence.

The band at 884 cm^{-1} in the cyclized sample for 54.0% w/w of H$_2$SO$_4$ at 3 h was assigned to the C—H bending of the exocyclic species. The C—H out-of-plane deformation of the original *cis*-1,4-isoprene units was observed at 836 cm^{-1}. A band at the low frequency side of the 836 cm^{-1} bond shifted from 820 cm^{-1} to 815 cm^{-1}.

A comparison between the Raman spectra of the starting DPNR and that of cyclized NR samples taken during cyclization at various degrees of cyclization is given in Figure 4. As the cyclization reaction proceeded, the absorption band at 1664 cm^{-1} assigned to the C=C stretching modes clearly decreased with no alteration of the band at 1452 cm^{-1}, which belongs to an asymmetric vibration of —CH$_3$ group in Raman spectra.

The solubility of cyclized products using TMSOTF as a catalyst was analyzed. Cyclized DPNR (0.1 g) was dissolved in 25 mL of different solvents without stirring for 5 days and then the solutions were filtered through a G2 sintered glass filter. The insoluble fraction on glass filters was recovered and filtered under vacuum at 40°C for 24 h and weighed; the solubility was then calculated. Table VII shows the solubility of the cyclized DPNR then obtained from TMSOTF. It was found that the solubility of cyclized DPNR with 76% degree of cyclization was easily dissolved in chloroform, cyclohexane, cyclohexanone, and toluene, except in tetrahydrofuran. That is, the cyclized DPNR partially dissolved in tetrahydrofuran.

Figure 5 shows morphology of the cyclized DPNR obtained from TMSOTF. TEM has been used to study the micrograph of DPNR and cyclized DPNR. DPNR and cyclized DPNR particles were stained by osmium tetroxide as reagent, in which C=C content in DPNR
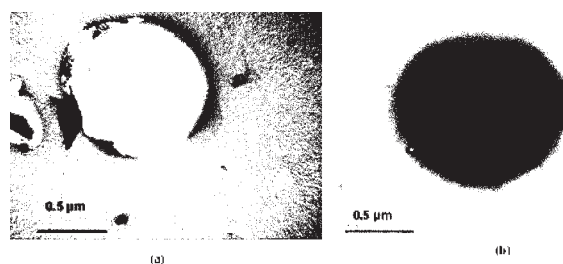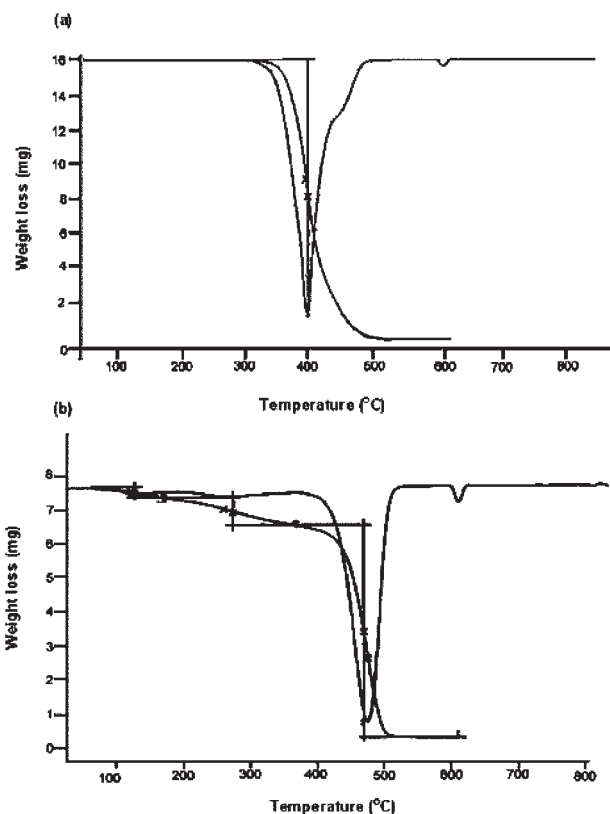

Figure 5 Topology of (a) uncyclized DPNR and (b) cyclized DPNR with 76% degree of cyclization obtained from TMSOTF, analyzed by TEM.
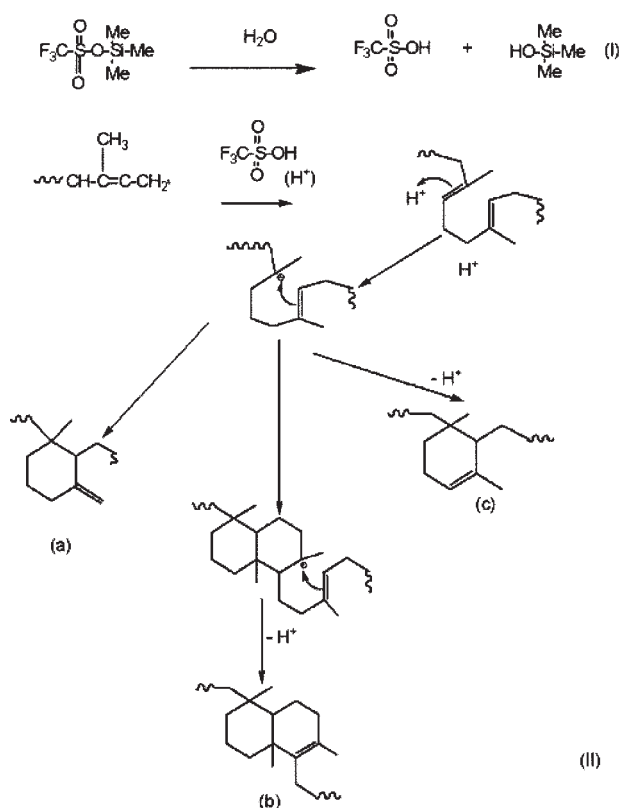
Figure 6 TGA of (a) uncyclized DPNR and (b) cyclized DPNR with 76% degree of cyclization obtained from TMSOTF.

Figure 7 Proposed mechanism of cyclized DPNR obtained from TMSOTF; (I) the reaction between TMSOTF and water and (II) the reaction between TMSOTF and DPNR particle.

and cyclized DPNR phase reacts with osmium tetroxide, leading to dark region. It is clear that the micrographs of the control DPNR and cyclized DPNR were different. That is, DPNR showed dark region, while cyclized DPNR showed light region due to the change of microstructure from polyisoprene to cyclic structure. From TEM results, it is confirmed that the lower amount of C=C content in cyclized DPNR comparing to DPNR sample.

Figure 6 shows TGA curves of the cyclized DPNR. The sample is heated in air at a linear rate of 20°C/min. It is clear that major reduction in weight loss of the cyclized DPNR with 80% cyclization at 467°C was observed. The 95% mass of uncyclized DPNR decomposed at 395°C as shown in Figure 6(a). This result implies that the thermal stability of the cyclized DPNR was more than that of the uncyclized DPNR,

which might be due to low double bond content in cyclized DPNR.

Table VIII shows the molecular weight of the cyclized DPNR obtained from latex by using TMSOTF as a catalyst. The number average molecular weight (M_n) of cyclized DPNR was about 4.2×10^4 g/mol and MWD was very broad. Therefore, the average molecular sizes measured by GPC may reflect the combination of results due to cyclization and the scission of the chains. These results corresponded with degree of cyclized DPNR obtained from ^{1}H-NMR.

Proposed mechanism

The possible mechanism of the cyclized DPNR is shown in Figure 7. There are two possible reactions both for TMSOTF and polyisoprene molecule.

The first step, the TMSOTF reacts with water to get the acid product, as shown in Figure 7(I). Next the acid catalyst reacts with the double bonds in polyisoprene thereby raising the cyclization. The products of this reaction are shown in Figure 7(II).

CONCLUSIONS

Cyclization of DPNR latex was carried out using TMSOTF as a new catalyst. Various cyclization condi-

TABLE VIII
Molecular Weight of Uncyclized DPNR and 76% Degree of Cyclization Obtained by GPC

Sample types	M_n (g/mol)	M_w (g/mol)	MWD
Uncyclized NR	1.93×10^5	4.4×10^5	2.2
Cyclized DPNR with 76% degree of cyclization	4.2×10^4	1.6×10^5	3.6

tions were studied such as dry rubber contents, temperatures, TMSOTF concentrations, and times. It was found that the degree of cyclization of natural rubber was a function with cyclization conditions. The optimum condition for preparing cyclized DPNR was 34.0% TMSOTF at 95°C for 5 h. The thermal stability of cyclized DPNR increases with the higher degree of cyclization, compared with the original one. The solubility of the obtained rubber was good in chloroform and cyclohexane, but it was low in tetrahydrofuran. Based on FTIR, Raman, ^{1}H-, and ^{13}C-NMR, the C=C of cyclized DPNR dramatically decreased after prolonged reaction time. From TEM results, it is confirmed that there is lower amount of C=C content in cyclized DPNR comparing with DPNR sample.

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