

The Cyclization of Natural Rubber

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ABSTRACT: *The effects of solvent, temperature, time, weight percent of catalyst on the rate and mechanism of cyclization of natural rubber (NR) was studied in toluene and xylene solutions having tin tetra chloride catalyst (SnCl_4). Iodometric titration show, with 8% SnCl_4 (based on polymer weight) cyclization occurs, leaving 27.4% of the total unsaturation. Infrared spectra of cyclized NR show decreased absorption intensity at 840 and 780 cm^{-1} which are characteristic bands of the linear polymer and the appearance of absorption band at 890 cm^{-1} as cycles were formed. By using this chemical modification, NR is transformed into a resinous thermoplastic, hard, non rubbery cyclized material with much less unsaturation than the original rubber, which could find commercial applications as adhesives, printing inks, industrial and ship paints.*

KEY WORDS: *Cyclization, Natural rubber, Chemical modification, Ship paint, Cyclo-polyisoprene.*

INTRODUCTION

Cyclization reaction can occur when there are two neighboring units that can react together to yield cycles in the presence of appropriate reagents. The intramolecular cyclization of polyisoprene, involving two monomer units of the same kind, caused by various acids or Friedel-Crafts catalysts has been the subject of extensive investigation of many authors. [1-3].

Upon reaction with strong or Lewis acids such as BF_3 , TiCl_4 , SnCl_4 , FeCl_3 or variety of reagents such as sulfonyl chloride, NR can be transformed in to resinous thermoplastics, non rubbery hard materials with much less unsaturation than the original rubber and have found commercial applications as adhesives, inks and paints. The transformation from a

rubber to a resin is accompanied by a partial loss of the original unsaturation without any change in isoprene's empirical formula C_5H_8 . While the molecular weight remains high, the product is still soluble in rubber solvents so that cross-linking of the chains is rare. It has been concluded that intramolecular bonds are formed leading to ring structures within the chain and hence these products are called cyclized rubber or cyclorubber [4-11]. It has been proposed that pairs of adjacent isoprene units form six membered rings by a carbonium ion mechanism. In support of this structure the following changes on cyclization were observed, loss of about one half of the original unsaturation, complete disappearance of trialkyl substituted double bonds, $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$ according

to spectroscopic measurements [1,12].

Then, has been a controversy as to whether the product consists of monocyclic or polycyclic ring structures, suggesting the formation of polycyclic condensed ring structures by continuation of cyclization reaction after formation of the cyclic carbonium ion with successive addition to the double bonds of the adjacent isoprene units. However recent, evidence support the existence of an average tricyclic structure for cyclized rubber [13,14].

In the present work, NR was dissolved in solvent and the viscous cement was charged in to a jacketed reactor equipped with a reflux condenser and to it is added a catalyst such as SnCl_4 . In the course of reaction the viscosity is diminished and the degree of cyclization is controlled by the time and reaction conditions. Reaction is terminated by the action of alcohol which decomposes the addition compound to yield the final cyclorubber. We considered the effect of time, temperature, solvent and catalyst concentration on the remaining unsaturation.

This cyclized NR withstands water and exhibit resistance to weak and strong acids, alkalines, salts and other corrosive chemicals. Outstanding applications of cyclized NR are found in papercoatings. These products allow extremely low water-vapor transmission rates while providing good heatsealing compositions. The growth of usage of this product in the ink fields has been large primarily since it can be employed for production of instantaneously drying inks. An other application of cyclo NR is in reinforcement of natural and synthetic rubber compositions and in such uses it increases the tensile strength, elongation, hardness and abrasion resistance and improve resistance to impact. Paints produced from cyclorubber are used in applications requiring high resistance to chemicals like industrial and ship paints.

The aim of this work was chemical modification of NR for producing ship paints [21].

EXPERIMENTAL

Materials

Deproteinized NR [17] with $M_n = 2.73 \times 10^5$ was used. SnCl_4 was synthesized producing Cl_2 by

reacting HCl with KMnO_4 and passing the produced gas through H_2SO_4 , and then reacting it with Sn.

All chemicals were analytical grade obtained from Fluka (Diesenhofen, Germany) or Aldrich (Milwaukee, WI, USA) and used without further purification.

Instruments

IR-Spectra were obtained on a Jamasco (Japan) model spectrometer on purified thin polymer films casted on to NaCl plates.

METHOD

Cyclization procedure

Solutions of 10% NR in either xylene or toluene containing 5,8,10% by weight of SnCl_4 (based on NR weight) were heated in a 500ml, 3-necked flask equipped with a coiled condenser, stirrer and thermometer. Representative samples of each solution was kept at 80, 100, 120°C respectively (Table 1). After 3, 5, 8, 10, 12, 15, 20 hours, about 20-30 mL sample were taken from each reaction medium. The cyclized NR was isolated from the rest of solution by pouring the solution into methanol. Purified cyclized NR was obtained by washing it carefully with methanol during filtration. Finally purified cyclized NR was dried in vacuum at 40°C and kept for further analyses.

RESULTS AND DISCUSSION

The iodine value of the starting NR and each

Table 1: Conditions of each experiment

Number	Weight of catalyst (%)	Temperature of reaction (°C)
1	5	80
2	8	
3	10	
4	5	100
5	8	
6	10	
7	5	120
8	8	
9	10	

cyclized sample was determined via iodometric titration (Heap method) in order to assess the percentage

of unsaturation in the NR and the cyclized samples, Figs. (1-6).

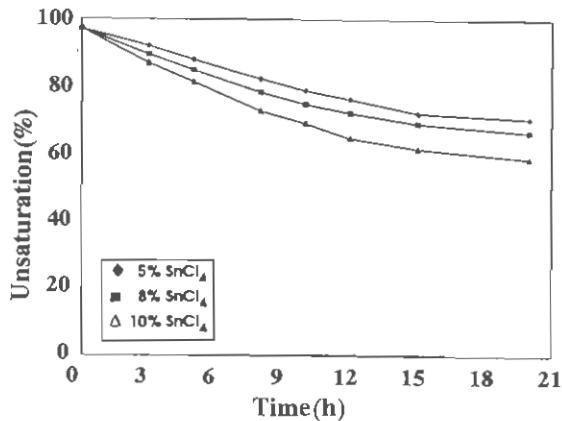


Fig. 1: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 80°C in Xylene

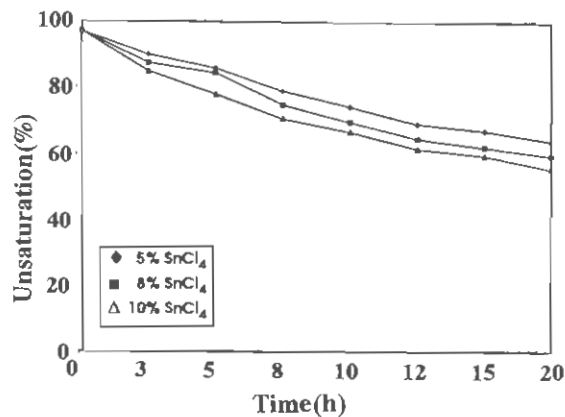


Fig. 4: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 80°C in Toluene

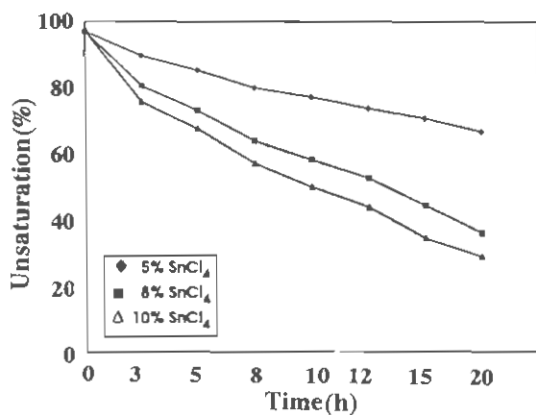


Fig. 2: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 100°C in Xylene

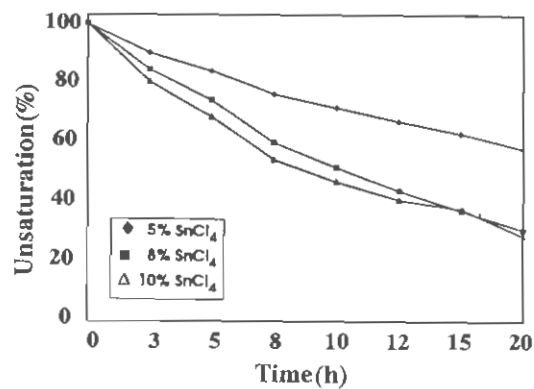


Fig. 5: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 100°C in Toluene

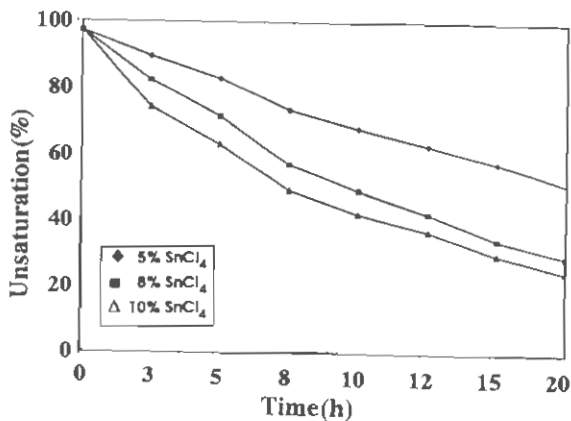


Fig. 3: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 120°C in Xylene

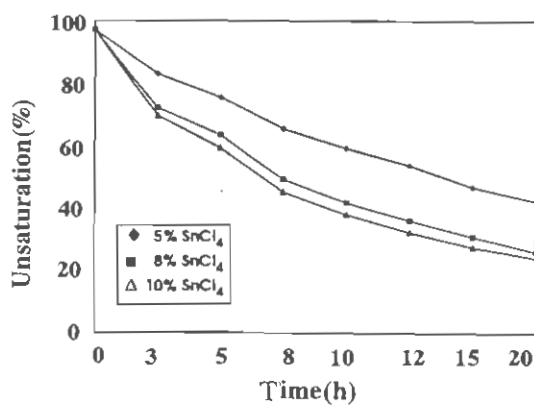
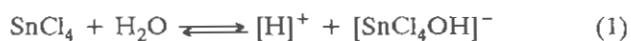


Fig. 6: Percentage of unsaturation in the NR cyclized with 5,8,10% SnCl₄ at 120°C in Toluene

The results at 80°C show that the concentration of SnCl₄ catalyst does not affect the cyclization process, and at the same time the cyclization reaction is incomplete. However, at 100°C under the same conditions as above, the concentration of catalyst has a very strong influence on the rate of cyclization; i.e., the cyclization proceeded very well and at 8% catalyst, an unsaturation of 36% and 27% can be achieved in xylene and toluene respectively. In other words at this temperature, the concentration of catalyst not only affects the process rate, but also changes the nature of the double bonds. The results at 120°C are indicative of the fact that at this temperature the rate of cyclization, is affected without any strong effect on the reaction mechanism. As for the influence of solvent, medium, a comparison of the results shown in Figs. 1-3, to those of 4-6, demonstrated that toluene is more effective than xylene, which may be due to better dissolution of NR in toluene; i.e. providing better conditions for the cyclization reactions.

A comparison of the IR spectra of NR before and after cyclization, Figs. 7 and 8, show the IR changes that occur during cyclization of NR. The major change being the disappearance of the 840 and 780 cm⁻¹ of trialkyl substituted double bond and the appearance of an absorption band at 890 cm⁻¹ which is indicative of the formation of cyclic entities. It is difficult to decide whether monocyclic, bicyclic, or polycyclic structures are formed simply on the basis of the determination of -C=C- double bond because of the unreliability of chemical methods of analysis and very meager data on absorptivities of -C=C- stretching vibrations in infrared analysis. Based on the results of cyclization of NR by SnCl₄ it appears that the type of cyclic structures formed depends on reaction conditions and the nature of the solvent.

According to Gordon and Bloonfield [12], Golub and Heller [1], the cyclization mechanism involves the protonation of the double bond in the chain, Eq. 1:



The addition of the proton probably proceeds in the Markownikoff sense to give an intermediate to which two or at least one hydrogen atom is attached, and the positive charge is localized on the carbon with

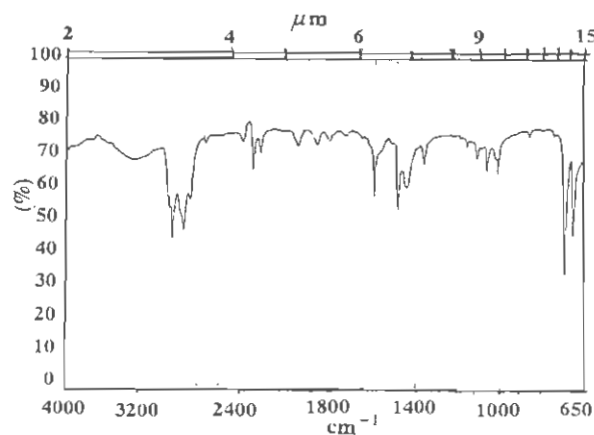


Fig. 7: IR spectra of NR

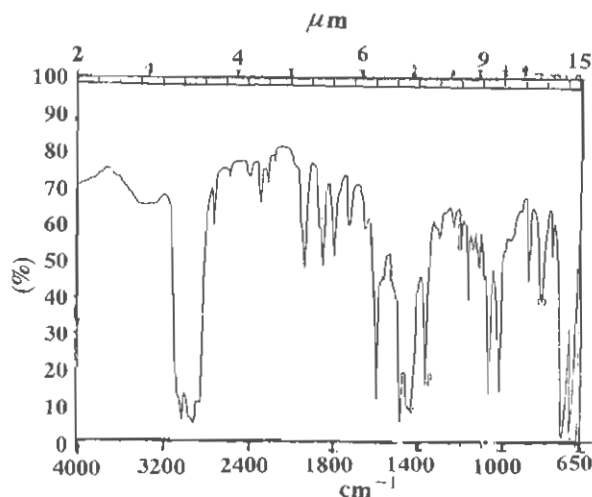


Fig. 8: IR spectra of NR after cyclization

no hydrogen [18,19]. The adjoining double bond in the chain is then polarized and a new bond, closing the ring, is formed. The positive charge then transfers to the carbon atom on this next double bond (Fig. 9).

CONCLUSION

It was shown that at 100°C in toluene solution, not only the rate, but also the mechanism of cyclization changes and that in the presence of 8% SnCl₄ at 100°C in toluene 27.4% of the total unsaturation remains in the cyclized NR which is a remarkable degree of unsaturation.

The degree of cyclization and the formation of mono-, bi-, or polycyclic structures can be estimated from the decrease of intensity of absorption bands characteristic of the original double bonds and from the decrease of the total amount of unsaturation.

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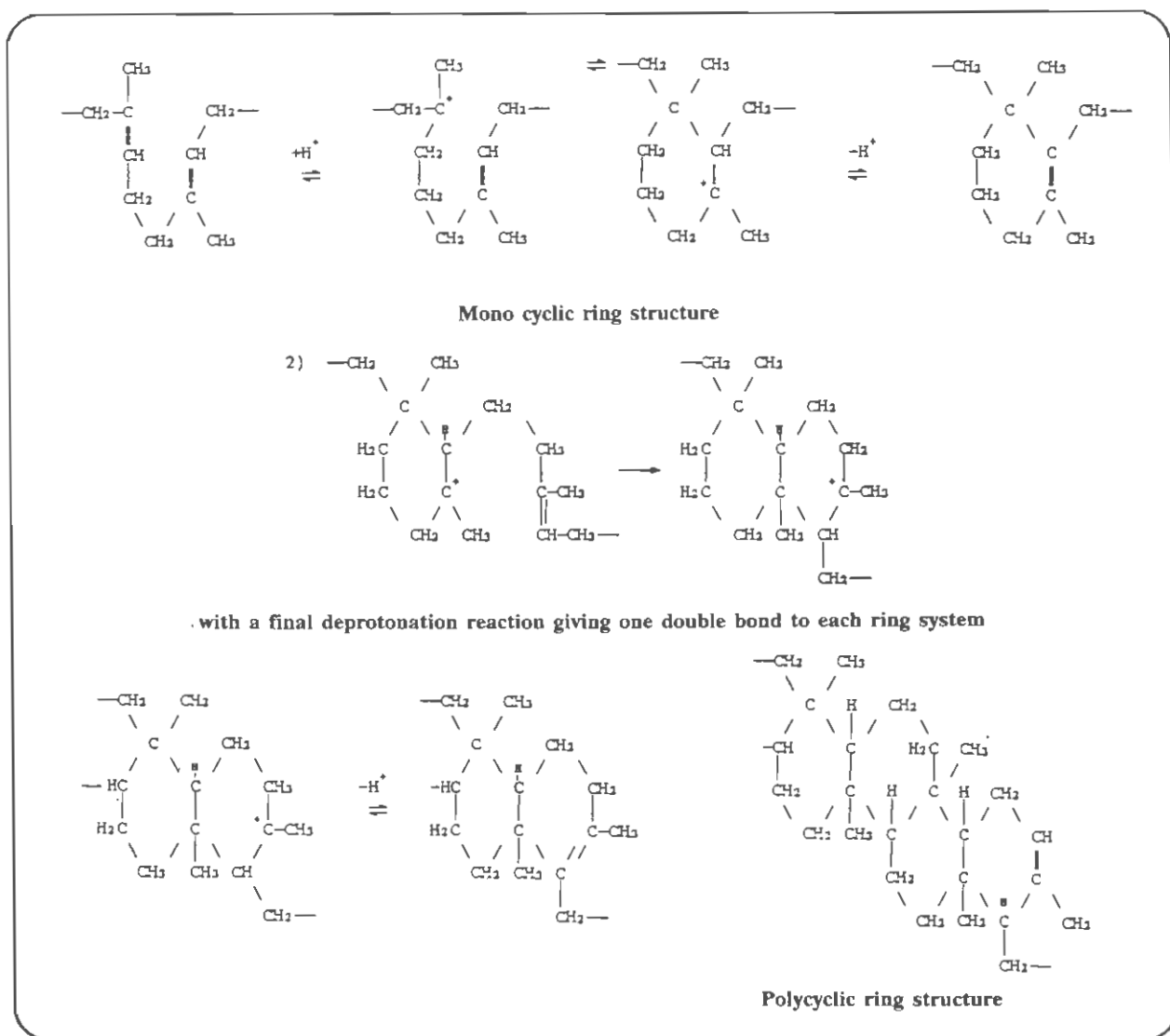


Fig 9: The cyclization mechanism

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