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Metathesis degradation of natural rubber

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SUMMARY

Metathesis reaction of natural rubber was carried out using tungusten hexachloride and tetramethyl tin in chlorobenzene. The rubber had to be purified by several times precipitations before the reaction. Molecular weight decreased very much with the progress of reaction and with the increase of temperature. However, NMR studies indicated considerable decreases of carbon-carbon double bonds, which can not be explained by simple metathesis reaction. Some other reactions which consumed unsaturation have to be taken into account to elucidate the exact structure of resultant oligomers.

INTRODUCTION

Metathesis reaction is a catalytically induced reaction, in which carbon-carbon double bonds undergo cleavage and reforming processes as shown in Fig. 1. This reaction is induced by a wide range of transition metal complexes, but most important and practical catalysts are based on tungsten, molybdenum or rhenium with either tin or aluminum alkyl compound as cocatalyst (1,2).

In polymer chemistry, metathesis has been used for the polymerization of cyclic olefins to give poly(alkenamer)s (1-4). Recently, metathesis catalysts are noted for their ability to polymerize acetylene derivatives (5,6). Less known, but metathesis degradation of polymer having unsaturation was reported (7-9). Possibility of this type of reactions was extensively described by Strech (10,11) and by two (S. K. and A. A.) of the present authors (12).

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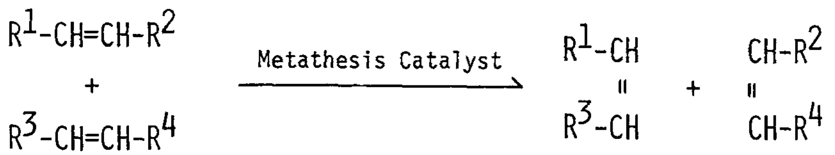

Fig. 1 General scheme of metathesis reaction

In this communication, metathesis degradation of natural rubber (NR) is described in comparison with that of synthetic cis-1,4-polyisoprene (IR) using tungsten hexachloride and tetramethyl tin. There have been few report on the metathesis reaction of natural rubber. In order to make full use of natural rubber, it may be very valuable if telechelic oligoisoprenes and/or block copolymers are prepared from natural rubber, which is a renewable hydrocarbon resource (12).

EXPERIMENTAL

NR (SMR 5, from Rubber Research Institute of Malaysia) and IR (JSR IR 2200) were purified by several times reprecipitations using benzene/methanol. Tungusten hexachloride and tetramethyl tin were purchased from Merck. Chlorobenzene was used as solvent for metathesis reaction after three times distillations over phosphorous pentoxide. NR (0.5 g) was dissolved in 200-ml chlorobenzene, followed by the injections of 2 ml of tungusten hexachloride solution and 100 ul tetramethyl tin. All manipulations were carried out in a vacuum and dry nitrogen line. After the reaction at a prescribed temperature, 2-ml methanol was added to stop the reaction.

Gel-permeation chromatography (GPC) was obtained on a Waters LC packed with Ultrastyragel using toluene as eluent. Infrared spectra were measured by Perkin Elmer Model 598, proton NMR and carbon-13 NMR by Varian XL-200 in deuterated chloroform using tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Decrease of Molecular Weight

An example of GPC traces of NR before and after the reaction is shown in Fig. 2. The molecular weight decreased considerably, and the shape of chromatogram also seemed to have been changed. However, due to very high viscosity of the rubbers, it was difficult to obtain fully reproducible results. We, therefore, used the molecular weight values at the peak position. They are nominal ones, because the molecular weights are those of standard polystyrenes. The molecular weight changes of NR and IR are shown in Table 1. Even at 28°C, NR was degraded with the elapse of time with drastic change of molecular weight from 1.2 million to 1.4 thousand. The higher was the temperature, the lower became the molelar weight of NR. IR seems to be degraded

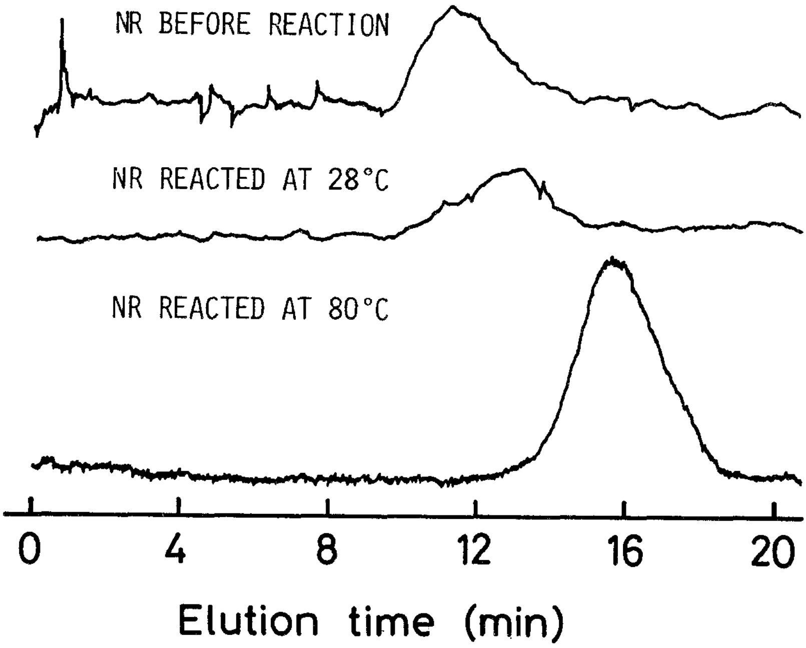

Fig. 2 GPC traces of NR before and after the metathesis reaction

similarly. Metathesis degradations of cis-1,4-polybutadiene as well as IR were already reported (9,13-15). But it was said very difficult to react natural rubbers (9). Our successful results on NR are based on purification of NR by several times reprecipitations, and selection of the catalyst system. Because metathesis catalysts are usually very sensitive to impurities, especially polar ones, it is difficult to conduct metathesis reactions on a naturally occurring substance very probably due to a lot of impurities, though their amounts might be extremely small. On this point, it is very interesting that we succeeded in the reaction of palm oil which was produced in Malaysia using the same catalyst system (16).

Table 1 Molecular weight changes of NR and IR by GPC.

Entry	Reaction Time (h)	Reaction Temp (°C)	Molecular weight $\times 10^{-3}$ by GPC
NR 1	0	-	1,200
NR 2	3	28	110
NR 3	5	28	100
NR 4	8	28	14
NR 5	3	50	42
NR 6	3	80	5.8
IR 1	0	-	900
IR 2	3	28	40

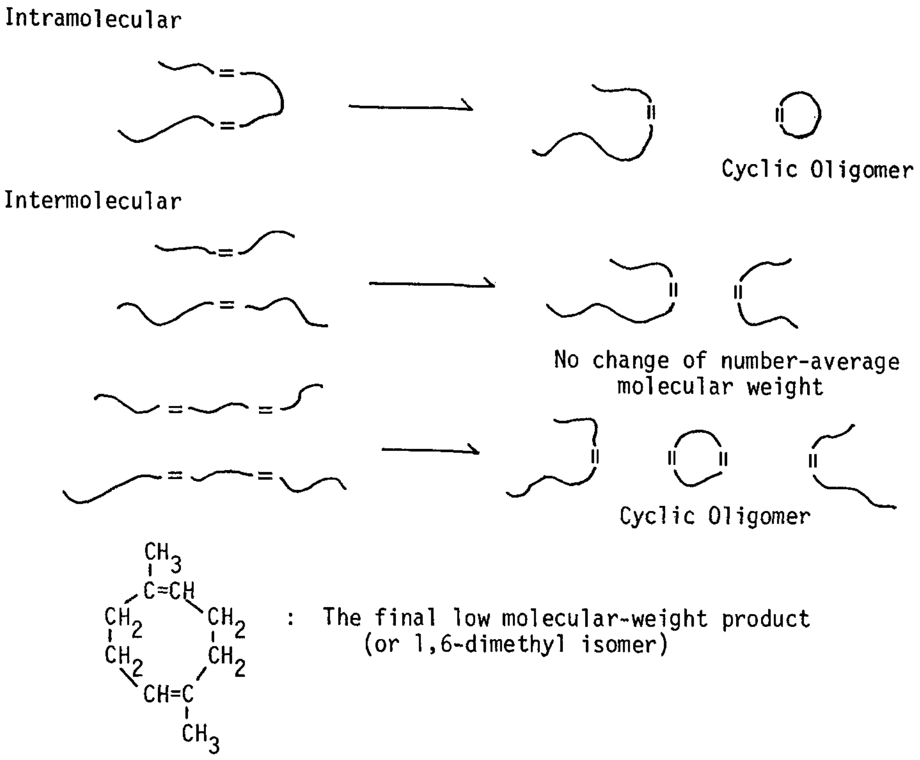

Fig. 3 The metathesis reaction scheme of NR

The decrease of molecular weight of NR by metathesis reaction should be interpreted by the reaction scheme shown in Fig. 3. Only cyclic products can explain the observed decrease, which are produced by either intramolecular or intermolecular metathesis. The final product of the metathesis degradation of NR is 1,5-dimethyl-1,5-cyclooctadiene and/or its 1,6-dimethyl isomer (DCOD). However, we did not observe the formation of it. The product, DCOD, is able to undergo the metathesis reaction very easily. In order to prove this mechanism, further experimental detection of cyclic polyisoprenes including DCOD is needed, which we plan to carry out.

Structural Changes of NR

It is important to know if the metathesis degradation of NR is accompanied by any structural changes in addition to molecular weight decreases. Fig. 4 shows proton NMR spectra of NR before and after the reaction. Considerable changes were observed by the reaction. Olefinic protons decreased very much, indicating that unsaturated bonds were involved. However, the protons between 0.7 and 2.3 ppm were not resolved well. From the decrease of olefinic protons, not only the reactions shown in Fig. 3 but also some other reactions were active in the present system.

In Fig. 5 are shown carbon 13 NMR spectra of NRs and trans-1,

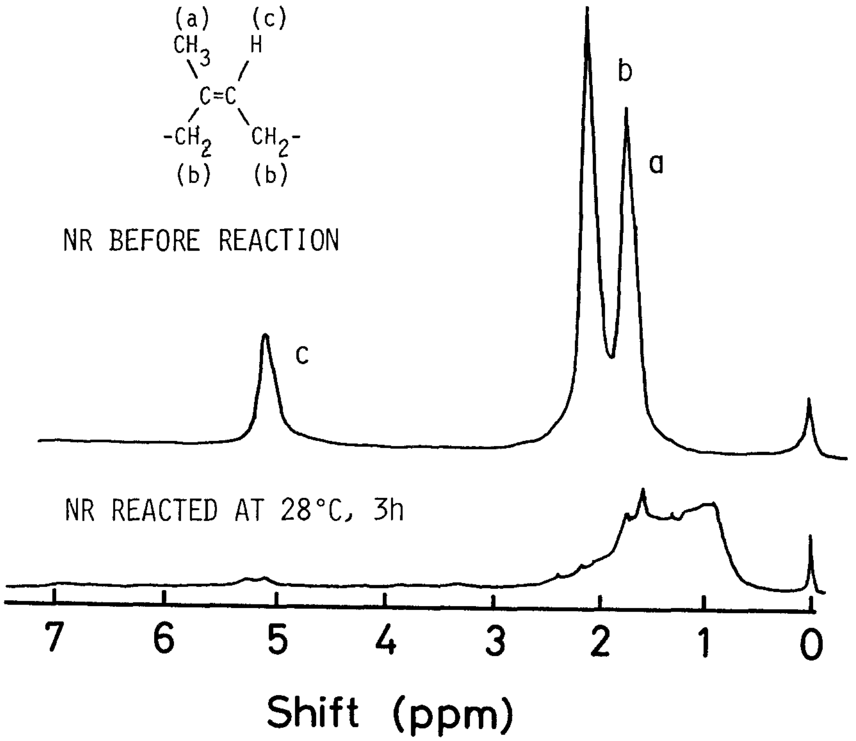

Fig. 4 Proton NMR of NR before and after the metathsis reaction

4-polyisoprene. Here also the same features were observed as in case of proton NMR, i.e., the height of peaks assignable to unsaturated carbons decreased much by the reaction. Due to the poor resolution in the saturated carbon area, it is not conclusive, but isomerization of cis-1,4 to trans-1,4 structure does not seem to be predominant. Both from proton NMR (Fig. 4) and carbon 13 NMR (Fig. 5), it is evident that some reactions leading to the decrease of unsaturation were active in the present reaction systems. For such reaction, cyclization by the other mechanism than metathesis is a most probable candidate. The acid catalyzed cyclization of natural rubber (17-19), which is shown in Fig. 6, is very well known in rubber chemistry. Although much attention was paid in our experiments, protonic species might have been produced by the reaction of tungusten hexachloride with adventituous moisture due to some Lewis acid nature of the metal halide. They seemed to initiate the intramolecular cyclization of cis-1,4-polyisoprene as depicted in Fig. 6.

Infrared specta revealed the presence of carbonyl groups in the reaction products. However, the spectra were again very broad and the carbonyl groups might have been introduced by oxidation after the metathesis reaction, i.e., oxidation in air during the handling of the polymers. Thermogravimetric measurements showed that 10-% weight loss temperature in nitrogen changed from 360°C for original NR to 410°C for NR 4 in Table 1. This result is in

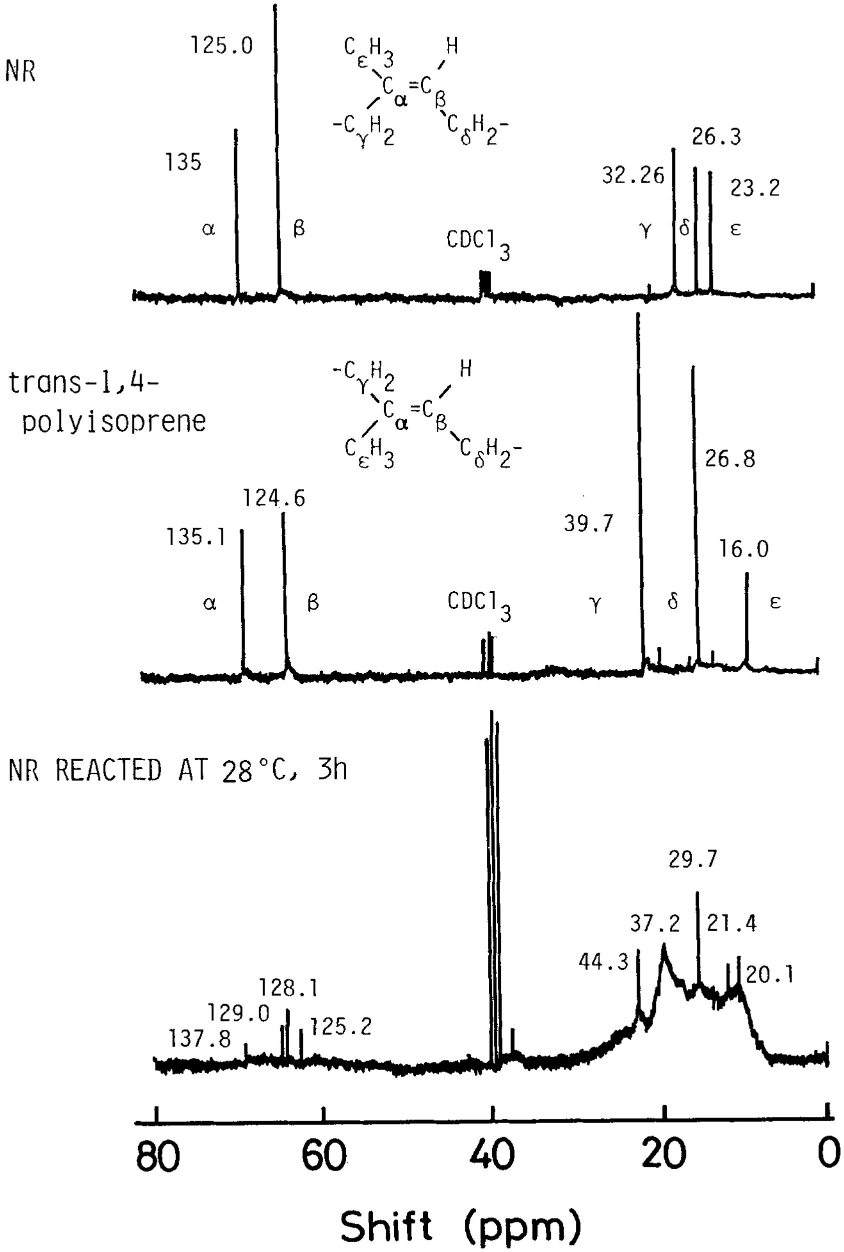

Fig. 5 Carbon 13 NMR spectra of NR (cis-1,4-polyisoprene), trans-1,4-polyisoprene, and NR after the metathesis reaction

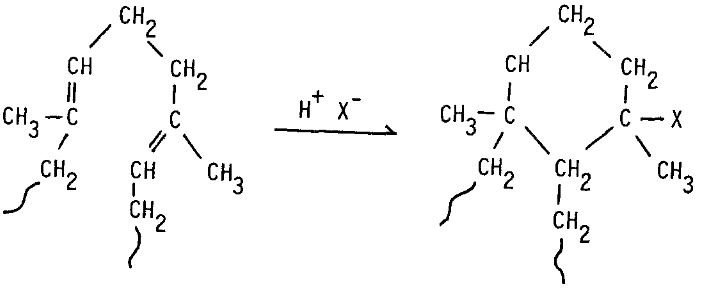

Fig. 6 Acid-catalyzed cyclization of NR

comformity with the assumption that cyclization products were in majorty. In other words, double bonds were consumed during the reaction of NR, which afforded much better heat resistance.

The structural informations on the reaction products were not enough at present. It seems to be probable that very complicated products were resulted from various reactions, i.e., inter- and intramolecular cyclizations, branching, gelation, and isomerization, to name a few. The last two may be of minor importance from our experimental observations.

Further investigations are now in progress including the isolation of DCOD from the metathesis reaction of natural rubber, and co-metathesis, i.e., metathesis reaction of natural rubber in the presence of olefinic compounds carrying functional groups to produce functionalized low molecular weight natural rubbers.

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