

Synthesis and Characterization of Maleinized-Silylated Low Molecular Weight Guayule Rubber (MASiGR)

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ABSTRACT: Maleinization followed by silylation of low molecular weight guayule rubber was accomplished for the first time via a two-step process. Maleinization was first effected by grafting maleic anhydride onto guayule rubber under the influence of benzoyl peroxide catalyst to give maleinized guayule rubber (MAGR). The maleinized rubber was then further derivatized via hydrosilylation with dichloromethyl silane and chloroplatinic acid (Speier's catalyst) to give maleinized-silylated guayule rubber (MASiGR). The silylated polymer (MASiGR) was further functionalized by reaction with ethanol or aqueous ammonia to produce ethoxysilane and silanol moieties, respectively. The products were characterized by Fourier transform infrared spectroscopy (FTIR), ^1H -, ^{13}C -, and ^{29}Si - nuclear magnetic resonance spectroscopy (NMR). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 754–761, 2001

Key words: guayule rubber; low molecular weight guayule rubber; maleinized guayule rubber; chlorosilane; chloroplatinic acid; maleinized-silylated guayule rubber; ethoxylated maleinized-silylated guayule rubber

INTRODUCTION

Guayule, *Parthenium argentatum gray*, is a shrub that grows in the semiarid regions of the southwestern United States and northern Mexico. During shrub processing, five major components are produced: high molecular weight guayule rubber (HMWGR), low molecular weight guayule rubber (LMWGR), organic soluble resins, water soluble extracts, and bagasse.^{1–4} While the physical and mechanical properties of HMWGR are quite similar to Hevea (Malaysian rubber),^{5,6} LMWGR holds specific interest, as mastication is not required for it to be useful. It is important to utilize all of the coproduct fractions in order to establish

a domestic guayule industry, and thus our interest in LMWGR.

Chemical modification or derivatization has emerged as a field of increasing importance and is considered an efficient synthetic route to novel polymers with desirable physical properties. Thus, we have investigated the potential for grafting maleic anhydride (MA) onto LMWGR followed by hydrosilylation. This modification has unique potential applications because MA provides hydrophilicity, polarity, and improved adhesion, while silicon is known to improve the polymer properties through its characteristics of high gloss, gloss retention, low viscosity, improved thermal stability, and enhanced water resistance.

EXPERIMENTAL

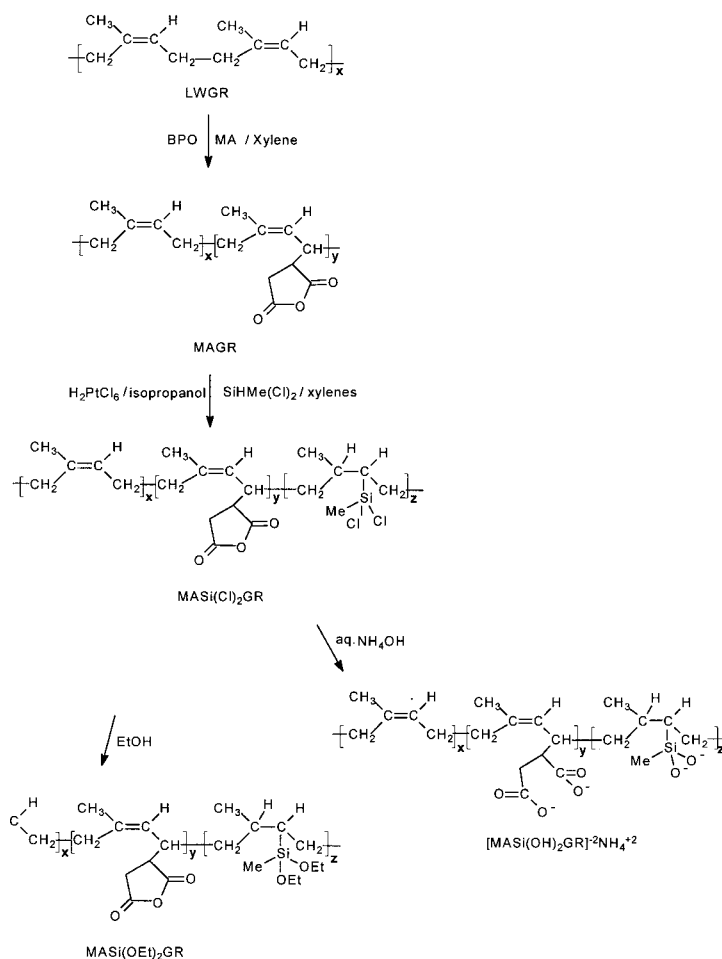
Materials

MA (99%), benzoyl peroxide (BPO), xylene, isopropyl alcohol, dichloromethylsilane (99.8%),

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Scheme 1 Syntheses are of MAGR, MASi(Cl)₂GR, MASi(OEt)₂GR, and [MASi(OH)₂GR]⁻²NH₄⁺².

hydrogen hexa-chloroplatinate(IV)-hydrate, anhydrous xylene, and anhydrous toluene were purchased from Aldrich Chemical Company (Milwaukee, WI), and were used as received. Guayule resin was obtained from Dr. J. Wagner and co-workers at the Texas A & M Engineering and Biosciences Research Center (College Station, TX). The LMWGR was isolated by continuous acetone extraction. The rubber was further purified by dissolving in toluene, filtering the solution through Gardco fine filter, and precipitating into 95% ethanol. The purified rubber was then dried in a vacuum oven to constant weight.

Synthesis of MA Grafted LMWGR (MAGR)

A known amount of purified rubber was dissolved in xylene in a four-necked round bottom flask

(RBF) immersed in an oil bath, equipped with a mechanical stirrer, reflux condenser, dropping funnel, and a thermometer.⁷ An inert atmosphere was maintained via a constant head pressure of nitrogen gas. BPO solution was added to the rubber solution, and the temperature of the reaction mixture was slowly raised to 85°C. At this point, a calculated amount of MA dissolved in xylene was added dropwise over a period of 45–60 min.

Table I Reaction Conditions for Maleinization

| % Grafting Desired | LMWGR (Moles) | MA (Moles) | BPO (Equivalents) |
|--------------------|---------------|------------|-------------------|
| 10 | 0.073 | 0.0073 | 0.02 |
| 25 | 0.073 | 0.0182 | 0.02 |

Table II Reaction Conditions for Hydrosilylation

| % Hydrosilylation Desired | 10% MAGR (Moles) | Dichloromethylsilane (mL) | Chloroplatinic Acid (ppm) |
|---------------------------|------------------|---------------------------|---------------------------|
| 10 | 0.0642 | 0.672 | 100 |
| 20 | 0.0642 | 1.342 | 100 |

The reaction was refluxed for 2 h and cooled. The polymer was precipitated into 95% ethanol and washed several times before drying *in vacuo*.

Synthesis of Dichlorosilane-Maleinized Guayule Rubber [MASi(Cl)₂GR]

A solution of MAGR in anhydrous xylene or toluene was taken in a three-necked RBF fitted with nitrogen inlet and a glass condenser. Speier's catalyst and the desired silylating reagent, dichloromethylsilane, were added dropwise. A mild nitrogen head was maintained throughout the reaction. The mixture darkened in 2 h. The reaction was continued for an additional 4 h, after which it was cooled to room temperature, concentrated, and stored under nitrogen awaiting further usage.

Derivatization

Synthesis of Diethoxysilyl-Maleinized Guayule Rubber [MASi(OEt)₂GR]

The concentrated MASi(Cl)₂GR was poured into a large excess of ethanol, whereupon the polymer

precipitated as a beige-colored product. The product was dissolved in methylene chloride and reprecipitated in ethanol.

Hydrolysis

Synthesis of the Ammonium Salt of Dichlorosilyl-Maleinized Guayule Rubber [MASi(OH)₂GR]⁻²NH₄⁺²

The concentrated MASi(Cl)₂GR was hydrolyzed by dropwise addition of 10% ammonium hydroxide solution with stirring. The hydrogen chloride gas was neutralized, and the pH was adjusted to 7 to give a cream-colored dispersion. The syntheses are shown in Scheme 1.

Analytical

Infrared analysis was performed with a Bio-Rad FTIR spectrometer. Samples were cast from dichloromethane onto sodium chloride polished discs, and analyzed after solvent evaporation. ¹³C- and ¹H-NMR were performed with a Bruker 300 MHz NMR spectrometer with deuterated

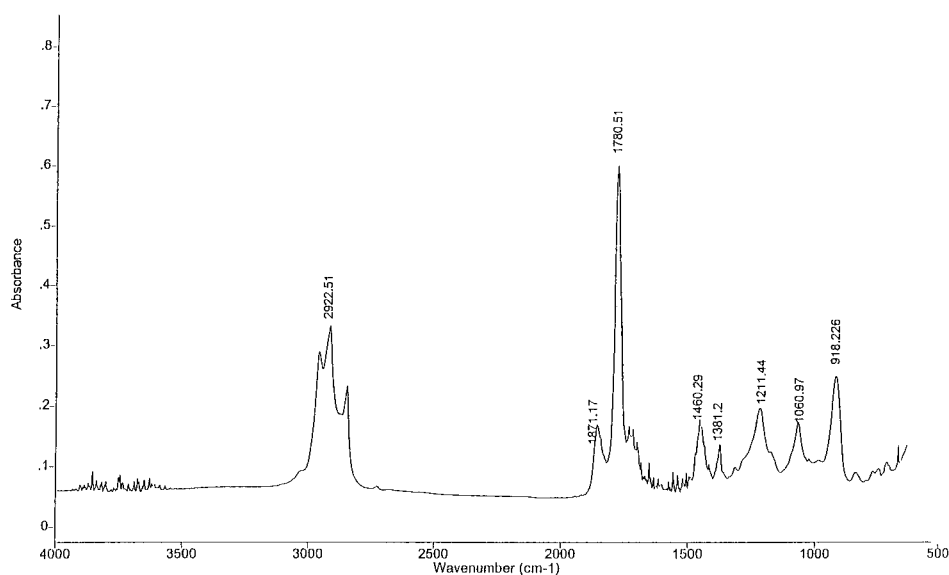


Figure 1 FTIR spectra of maleinized guayule rubber (MAGR).

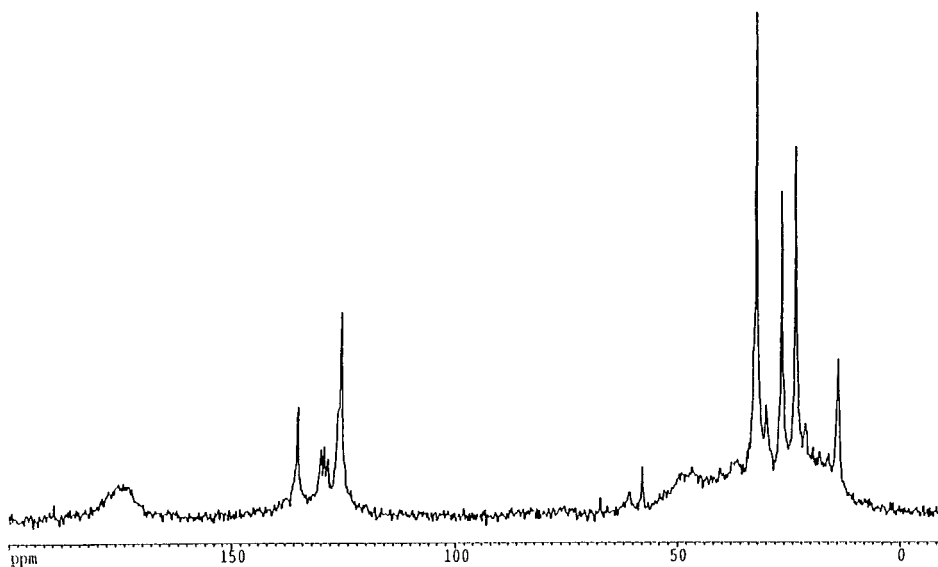
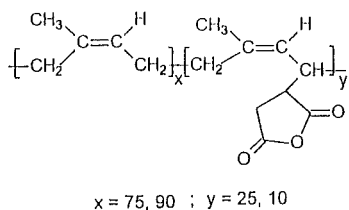


Figure 2 ¹³C-NMR spectra of maleinized guayule rubber (MAGR).

chloroform and tetramethylsilane as the internal reference, respectively. Solid state ²⁹Si- and ¹³C-NMR were performed with a Bruker 400 MHz

NMR spectrometer. The acid value of the polymer was determined using methanolic KOH titration via the ASTM D-1957-86 method.

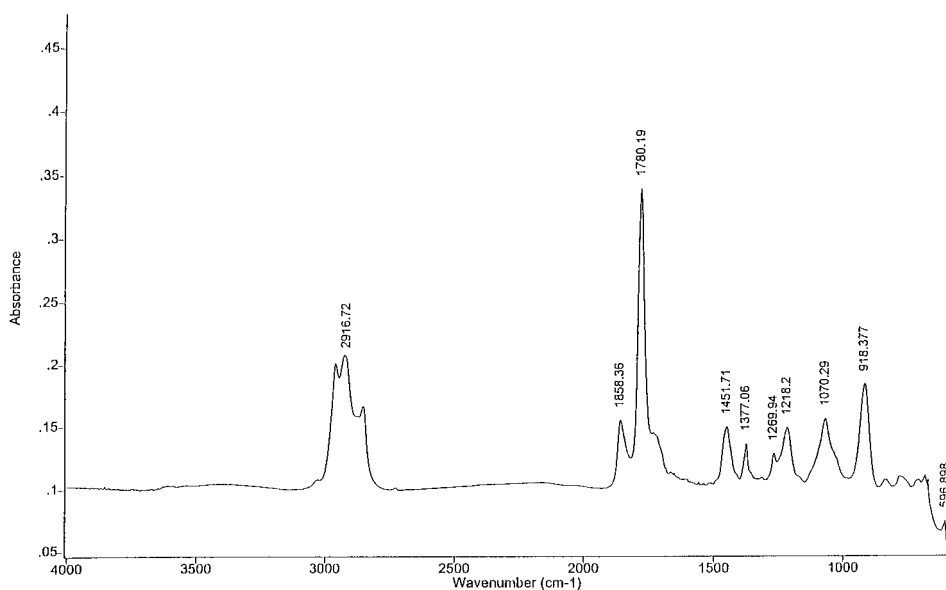


Figure 3 FTIR spectra of maleinized-silylated guayule rubber (MASiGR).

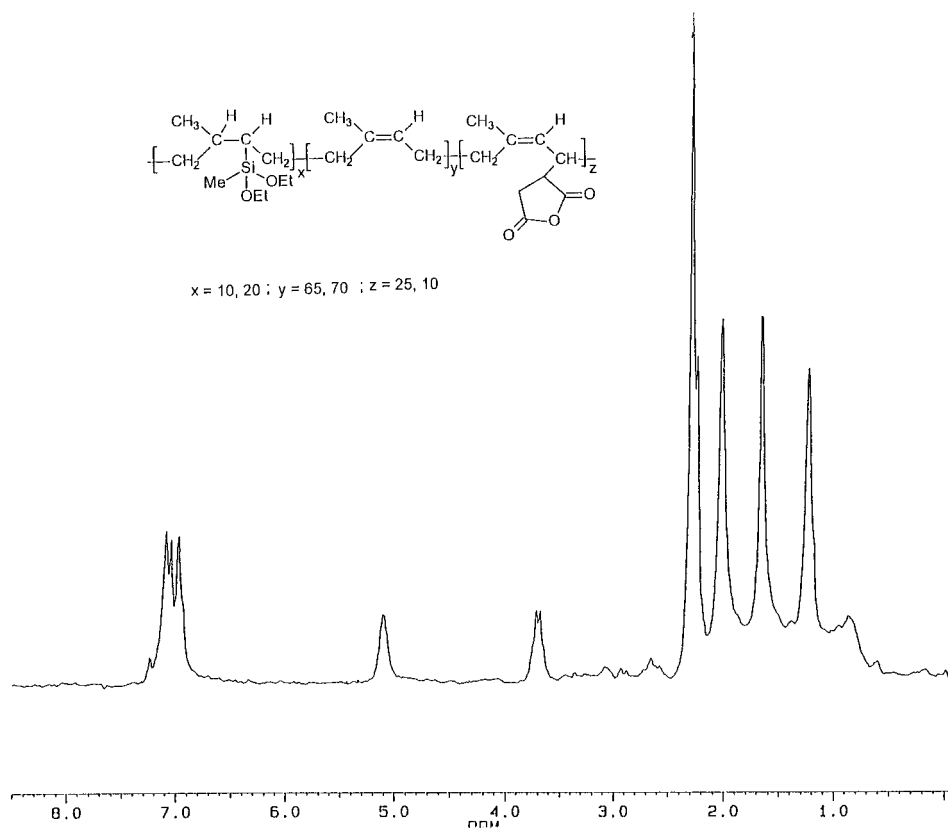


Figure 4 ^1H -NMR spectra of derivatized maleinized-silylated guayule rubber [MASi(OEt) $_2$ GR].

RESULTS AND DISCUSSION

The synthesis of anhydride functionalized hydrosilylated rubber (MASiGR) from guayule rubber has been accomplished. The synthesis was performed via a two-step process (Scheme 1). The first step involved free radical catalyst to effect anhydride grafting via the "ene" reaction.⁷⁻⁹ The molar ratios of LMWGR, MA, and BPO are given in Table I.

The second synthesis involved hydrosilylation of purified MAGR via dichloromethylsilane in the presence of chloroplatinic acid catalyst. The stoichiometric amounts of MAGR and methyldichlorosilane are cited in Table II.

All MAGR and MASi(OEt) $_2$ GR derivatives were soluble in chlorinated solvents or a mixture of toluene-ethanol or tetrahydrofuran. The ammonium salt formed a stable dispersion at room temperature. However, the MASi(Cl) $_2$ GR and MASi(OEt) $_2$ GR derivatives required storage under nitrogen. The MASi(OEt) $_2$ GR gelled upon exposure to atmosphere, presumably as a result of the

hydrolysis of the Si—OEt bond and subsequent formation of the corresponding Si—O—Si bonds.¹⁰

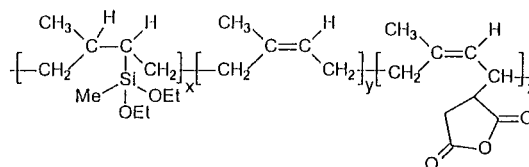
Characterization of MAGR

There have been many reports concerning the synthesis of MA grafted polyisoprene.¹¹⁻¹³ For instance, the MAGR derivatives were synthesized by MA grafting onto LMWGR backbone via BPO initiation. The structure of MAGR was confirmed via FTIR and ^{13}C -NMR, and the acid values were determined via methanolic KOH titration.

The FTIR spectrum (Fig. 1) of MAGR showed characteristic absorptions at 1871, 1780, 1211, and 918 cm^{-1} , indicative of the anhydride moiety. The ^{13}C -NMR spectrum (Fig. 2) showed absorptions at 174.3 ppm (anhydride carbonyl), 135 and 125.6 ppm (vinyl carbons), and 42–24 ppm (aliphatic carbons).

Characterization of MASi(OEt) $_2$ GR

The literature describes the hydrosilylation of polybutadiene^{10,14-16} and polyisoprene.^{17,18} More-



$$x = 10, 20 ; y = 65, 70 ; z = 25, 10$$

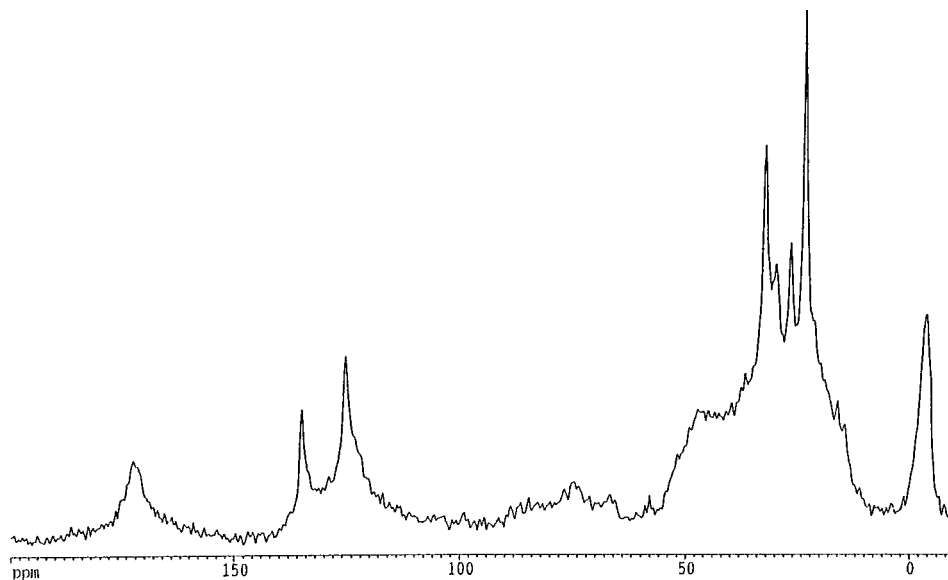


Figure 5 ^{13}C -NMR spectra of derivatized maleinized-silylated guayule rubber [MASi(OEt) $_2$ GR].

over, a wide range of catalysts for hydrosilylation have been reported.^{19,20} Most hydrosilylation reactions, however, are carried out in the presence of platinum complexes.^{19–22} In our reactions, chloroplatinic acid (Speier's catalyst)²³ was used for the synthesis of MASi(Cl) $_2$ GR, which was subsequently condensed with a large excess of 95% ethanol to give MASi(OEt) $_2$ GR.^{16,24}

MASi(Cl) $_2$ GR was hydrolyzed to its disilanol derivative by the dropwise addition of 10% ammonium hydroxide solution until a pH of 7 was reached, at which time a stable emulsion was formed. The dichlorosilyl derivative was unstable, unless stored under a dry nitrogen atmosphere.

Silylation was performed at two concentrations, i.e., at 10 and 20% of the available vinyl content. As expected, the 20% silylated product was found to be more easily crosslinked on exposure to the environment.

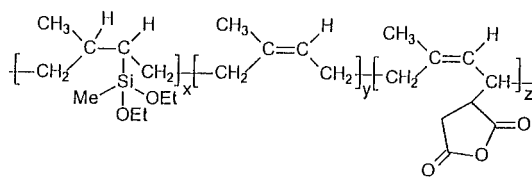
The structure of MASi(OEt) $_2$ GR was confirmed by FTIR and solid state ^1H -, ^{13}C -, and ^{29}Si -NMR. Analysis by FTIR (Fig. 3) showed absorptions at 1871, 1786 (anhydride), 1271 (Si—C bond), and

1074 Si(OEt) $_2$ cm^{-1} . The ^1H -NMR spectrum (Fig. 4) possessed absorptions at 5.11, 3.72, 0.86, and 0.60 ppm, corresponding to vinyl protons, methylene of —OCH $_2$ CH $_3$, methyl of —OCH $_2$ CH $_3$, and methyl of CH $_3$ —Si(OCH $_2$ CH $_3$) $_2$, respectively. Additional absorptions noted near 7.09 and 2.30 were due to residual xylene.

Accordingly, the solid state ^{13}C -NMR (Fig. 5) showed characteristic absorptions at 172.7 ppm (anhydride), 135.2 and 125.7 ppm (vinyl carbons of residual double bonds), and -2.9 ppm (methyl substituents bonded to silicon). The solid state ^{29}Si -NMR (Fig. 6) confirmed the presence of silicon via its absorptions at -58.01 and -65.19 ppm, frequencies indicative of the SiOR moiety.

CONCLUSIONS

Maleinization, followed by hydrosilylation, of LM-WGR was accomplished via a two-step procedure, and then the chlorosilane was functionalized ei-



$$x = 10, 20 ; y = 65, 70 ; z = 25, 10$$

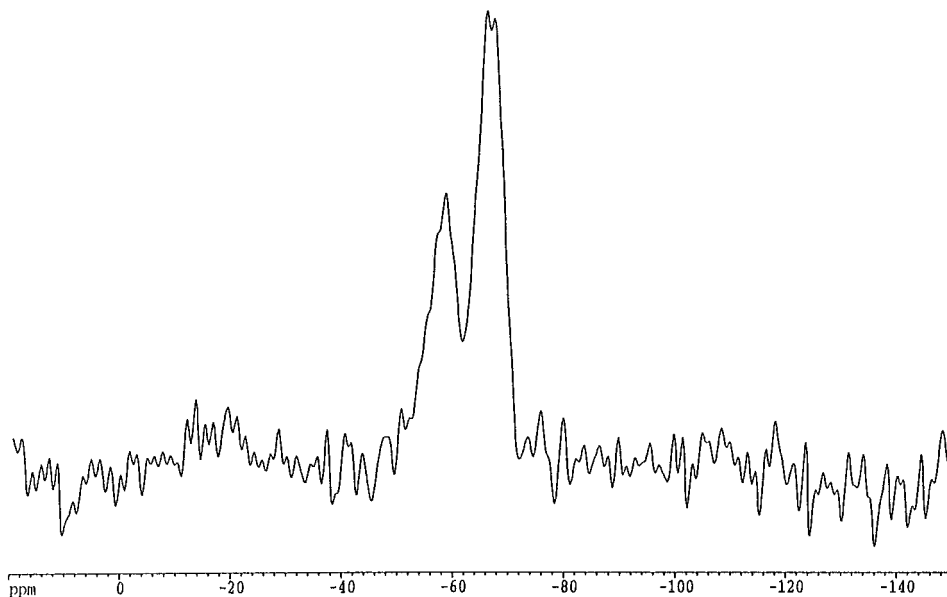


Figure 6 ^{29}Si -NMR spectra of derivatized maleinized-silylated guayule rubber [MASi(OEt) $_2$ GR].

ther with ethanol or ammonium hydroxide to give the silyl ether and silanol, respectively. Structural confirmation was accomplished via FTIR, ^1H -, ^{13}C -, and ^{29}Si -NMR spectroscopy.

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