

# The Maleinization of Low Molecular Weight Guayule Rubber

S. F. THAMES,\* A. RAHMAN, and P. W. POOLE

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

## SYNOPSIS

The reactions of low molecular weight Guayule rubber (LMWGR) and maleic anhydride (MA) at varying mole ratios were studied in the polar solvent, cyclohexanone, and in *p*-xylene, a nonpolar solvent, by conventional free radical catalysis. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) were used to confirm product formation and identification. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Recent attention has focused on the plant Guayule (*Parthenium argentatum*), a rubber producing species which produces quality, high molecular weight natural rubber, and grows in the semiarid regions of the Southwestern United States. Given our nation's total dependency on imported natural rubber, a strategic material, the United States Department of Agriculture and the Department of Defense initiated a research and development program to develop a Guayule-based natural rubber industry<sup>1</sup> in America. The Guayule shrub is composed of several components with promise as commercial raw materials, including: (a) high molecular weight Guayule rubber (HMWGR), (b) low molecular weight Guayule rubber (LMWGR), (c) organic soluble resins, (d) water soluble extract, and (e) bagasse. This investigation focuses on the study and derivation of LMWGR. While the physical and mechanical properties of HMWGR are quite similar to those of Hevea (Malaysian rubber),<sup>2,3</sup> LMWGR holds particular interest as mastication is not required. In particular, LMWGR offers the opportunity for use in water-borne coatings technology. In an effort to prepare hydrophilic derivatives of LMWGR, thereby allowing for dispersion or solubilization, we have in-

vestigated the potential of grafting MA onto LMWGR. Maleic anhydride, a chemical of commercial importance,<sup>4</sup> is known to react with natural rubber<sup>5-9</sup> and to improve the properties of various polymers by its polarity, hydrophilicity, adhesion, and functionality for crosslinking. However, there are no reports of the maleinization of Guayule rubber, and this study reports on the potential utility of maleinized LMWGR in coatings.

## EXPERIMENTAL

### Extraction and Purification of LMWGR

Guayule resin was obtained from Dr. John Wagner and co-workers at the Texas A&M University Food Protein Research and Development Center. The extraction process to isolate LMWGR from its resinous medium involves its separation by dissolution and precipitation techniques. The resin fraction containing Guayule rubber is dissolved in xylene and precipitated into 90% ethanol in order to remove the majority of the contaminating waxes and hydrocarbons contained in the Guayule resin. The precipitated rubber is further purified by dissolution in carbon tetrachloride, followed by precipitation in 90% ethanol. The process is repeated until purified low molecular weight rubber is obtained. The purified rubber is dried *in vacuo* at room temperature

\* To whom correspondence should be addressed.

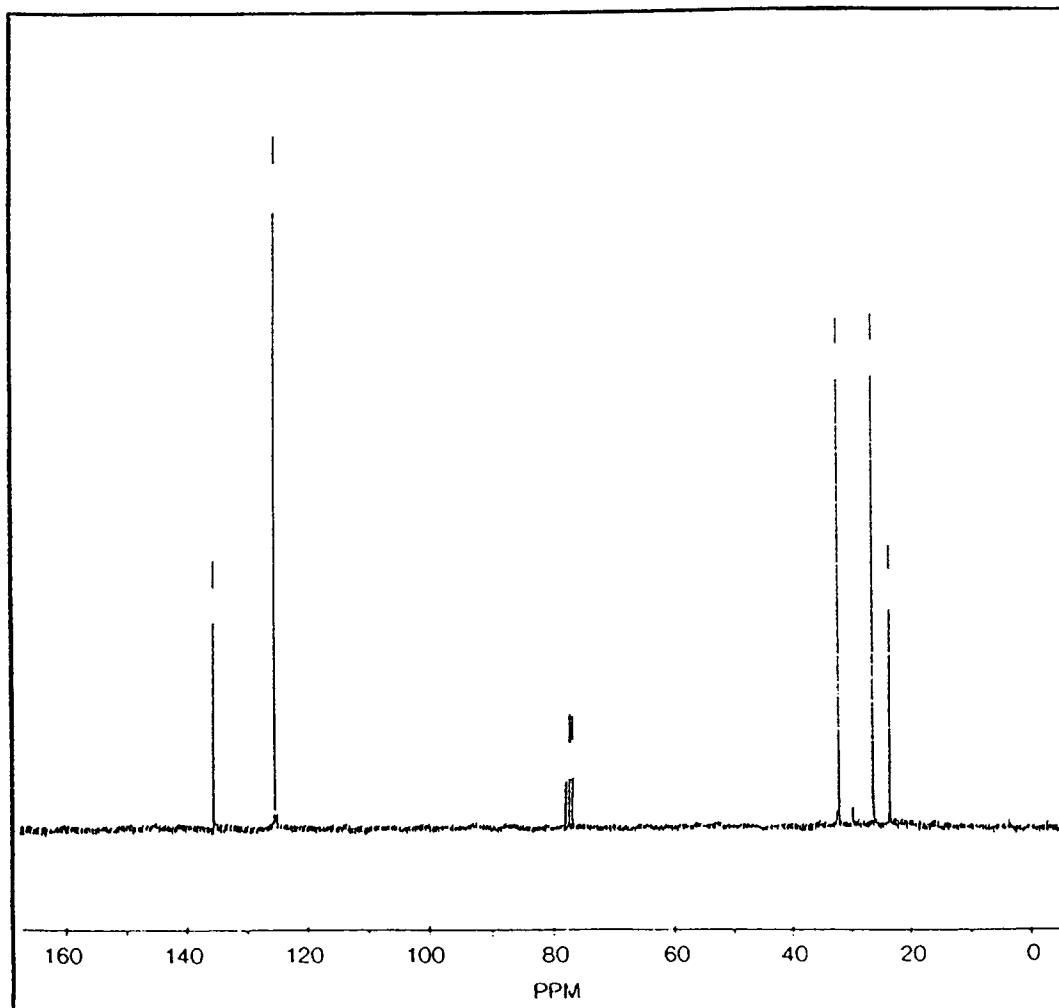


Figure 1  $^{13}\text{C}$ -NMR spectrum of LMWGR.

for 48 h, and its purity confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy (Fig. 1).

#### Maleinization of LMWGR

High purity maleic anhydride, benzoyl peroxide, *p*-xylene, and cyclohexanone were purchased from

Aldrich Chemical Company (Milwaukee, WI). They were used as received.

#### Method

The basic reaction technique was similar to that employed by Gaylord and others.<sup>10-13</sup> The reaction

Table I Reaction Condition of MA to LMWGR

Expt No.	LMWGR (mol %)	MA (mol %)	Solvent	Catalysts	Temperature (°C)
1	100	00	Cyclohexanone	BPO	80
2	100	25	Cyclohexanone	BPO	80
3	100	50	Cyclohexanone	BPO	80
4	100	100	Cyclohexanone	BPO	80
5	100	25	<i>p</i> -Xylene	BPO	115
6	100	50	<i>p</i> -Xylene	BPO	115
7	100	100	<i>p</i> -Xylene	BPO	115

**Table II Properties of the Product of MA to LMWGR**

Expt No.	Physical Appearance	Solubility	Acid Value Anhydride		Melting Point Anhydride		Diacid	$T_g$		$[\eta]_{int}$ (cc/g)	DP	MW
			1	11	1	11		1	11			
1	Brown-dark	Chloroform, THF, xylene carbon tet.	—	—	—	—	—	-58.0	-58.0	392	514	35,000
2	Off white	Acetone, DMF, THF, toluene-ethanol	131	122	140	135	155	-51.0	-64.1	251	264	43,795
3	Off white	Acetone, DMF, THF, toluene-ethanol	203	183	155	150	170	-51.8	-50.0	212	367	60,885
4	Off white	Acetone, DMF, THF, toluene-ethanol	243	235	180	182	194	-44.5	-46.7	189	453	75,191
5	Off white	Toluene and toluene-ethanol	130	136	130	130-40	150	-50.90	-59.88	—	—	—
6	White	Toluene-ethanol	186	203	190	187	210	-46.79	-48.08	—	—	—
7	White	Partly in toluene-ethanol	140	170	210	205	230	-37.92	-39.55	—	—	—

was conducted in cyclohexanone using benzoyl peroxide as the initiator. The reaction apparatus consisted of a 500-mL, four-necked round-bottom flask equipped with a dropping funnel, mechanical stirrer, and thermometer. The temperature of the flask, heated in an oil bath, was maintained with an accuracy of  $\pm 1^\circ\text{C}$ . A predetermined amount of MA and cyclohexanone was added to the reaction flask and heated at  $80^\circ\text{C}$  under a nitrogen atmosphere. A solution of LMWGR and benzoyl peroxide was added dropwise over a period of 20 min with continuous agitation and held for 45 min after addition was complete. The reaction mixture was cooled, the product was precipitated in 90% ethanol, and washed repetitively with 90% ethanol and dried to constant weight at  $40^\circ\text{C}$  *in vacuo*. This basic reaction was accomplished several times with varying molar ratios

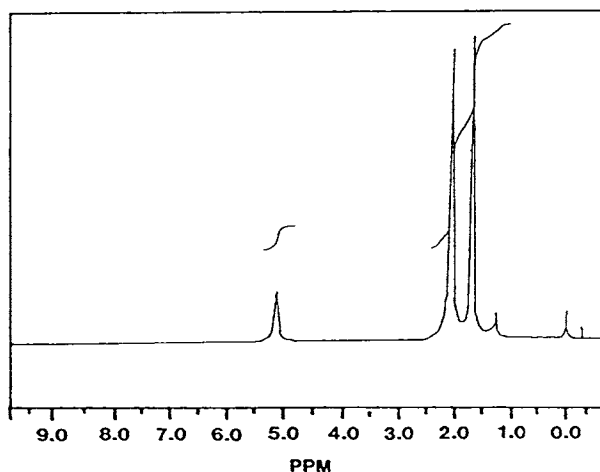
of MA to LMWGR (Table I). Similar reactions were conducted in *p*-xylene at a temperature  $115 \pm 1^\circ\text{C}$ .

### Copolymer Hydrolysis

The anhydride component of the copolymer(s) was hydrolyzed with either 1M sodium hydroxide or 1M ammonium hydroxide solution under a nitrogen atmosphere. After hydrolysis the acid salt was added to a large excess of aqueous dilute acetic acid. The products, grafts of maleic acid to LMWGR, were precipitated from solution, filtered, washed with water, and dried under reduced pressure at room temperature.

**Table III Elemental Analyses**

Expt No.	Theory (%)			Found (%)		
	C	H	O	C	H	O
1	—	—	—	—	—	—
2	65.10	6.59	28.31	70.30	7.76	21.94
3	71.80	8.47	19.73	72.91	8.38	18.71
4	77.84	10.16	12.00	75.96	8.96	15.08
5	65.10	6.59	28.31	63.39	6.90	29.71
6	71.80	8.47	19.73	67.33	7.30	25.37
7	77.84	10.16	12.00	74.48	8.49	17.03


**Figure 2**  $^{13}\text{C}$  spectrum of guayule LMWGR.

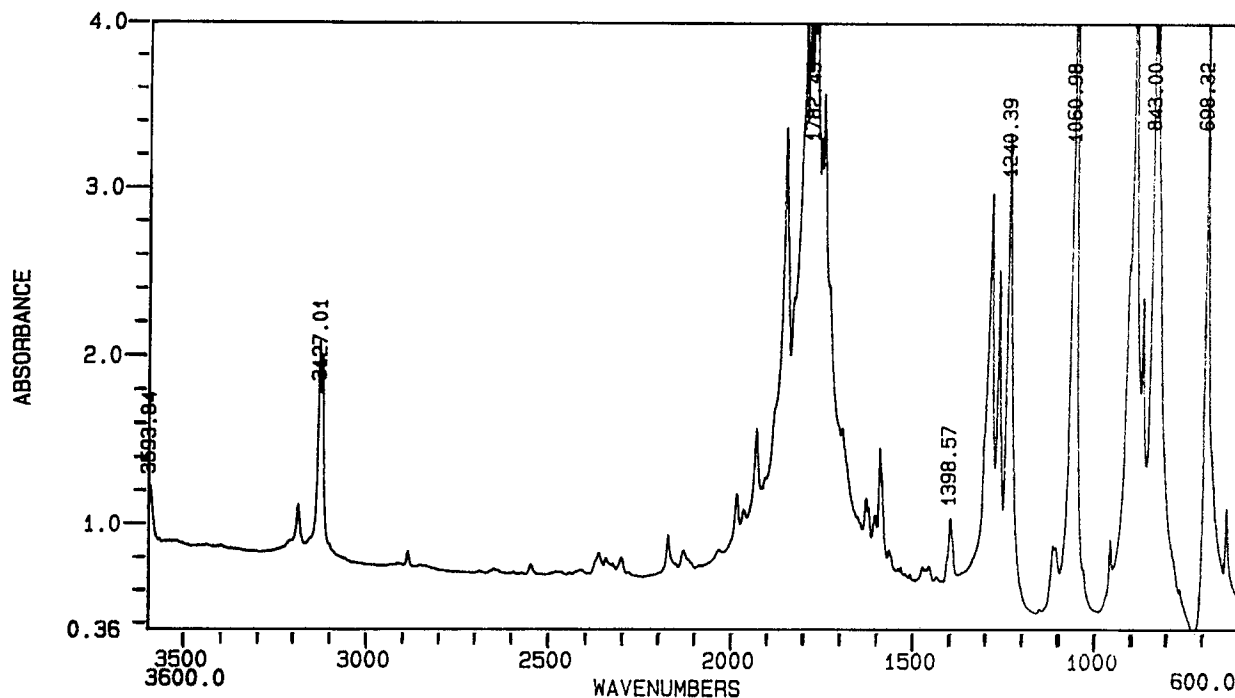


Figure 3 FTIR spectrum of maleic anhydride.

**Product Characterization**

The products were characterized by elemental analysis, Fourier transform infrared spectroscopy

(FTIR), nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and viscometry. Elemental analysis of the copolymers was

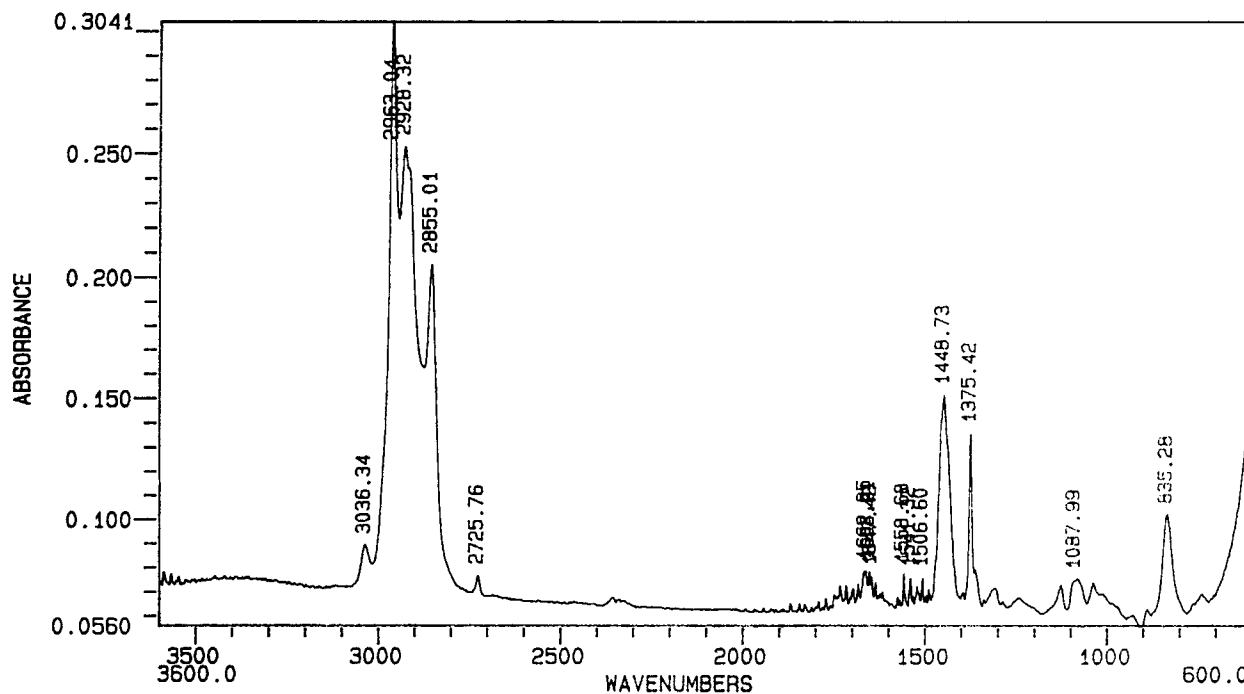


Figure 4 FTIR spectrum of LMWGR.

performed by MHW Laboratories. FTIR spectra were recorded from films cast from acetone solution and KBr pellets.

Glass transition temperatures were determined with a DuPont Model 9900 thermal analyzer in a nitrogen atmosphere. A heating rate of 10°C/min was maintained in all cases with indium used as a standard. Molecular weights of the copolymers were determined via GPC and Cannon-Fenske viscometry. Melting points of the products were determined with a Mel-Temp Device. Acid values were determined by the standard ASTM test method.<sup>14</sup>

## RESULTS AND DISCUSSION

The purification of LMWGR was affected and structural characterization was performed by peak assignment of NMR spectra (Fig. 2). The <sup>1</sup>H-NMR spectra of LMWGR contains three absorptions, 1.67 ppm (cis double bond methyl proton), 2.00 ppm (methyl proton), and 5.12 ppm (vinyl proton), and agree with literature values.<sup>15</sup> Moreover, a small peak was detected and represents impurity (ies).

### Reaction Mechanism

MA is known to add readily to polyisoprene at elevated temperatures or in the presence of free radical

catalysts.<sup>16,17</sup> These data strongly suggested that LMWGR would react in a similar, if not identical, fashion.<sup>7,8</sup> The malleinization of LMWGR should reduce its oxidative potential,<sup>18,19</sup> while at the same time rendering it water-dispersible.

The results of the experimental conditions, the product composition, and the characterization of the reaction products are summarized in Tables I, II, and III. The benzoyl-peroxide-initiated reactions were performed at 100°C, and, with its short life of 19.8 min,<sup>19</sup> the reactions proceeded swiftly and were exothermic.<sup>20</sup>

The IR spectra of MA, LMWGR, and the reaction product are shown in Figures 3, 4, and 5, respectively. The IR spectra confirms the presence of MA graft sites with reduced intensity of peaks at 3036, 1448, and 1375 cm<sup>-1</sup> all indicative of alkene absorptions. Comparison of the FTIR spectra of LMWGR and the product shows the characteristic absorption bands assignable at 1857 and 1780 cm<sup>-1</sup> and 922 cm<sup>-1</sup> to the anhydride presence. Moreover, the 1219 cm<sup>-1</sup> absorption corresponds band corresponds to the C—O stretching vibration of cyclic anhydrides.

The FTIR spectrum (Fig. 6) of hydrolyzed product (maleic acid-LMWGR) shows strong and broad carbonyl absorptions at 1641–1558 cm<sup>-1</sup> and 3100–2800 cm<sup>-1</sup>. The <sup>13</sup>C-NMR spectrum (Fig. 7) is characteristic of the maleinized products via absorptions at 173.29, 135.4, and 126.2 ppm, and 42.2–24.0 ppm

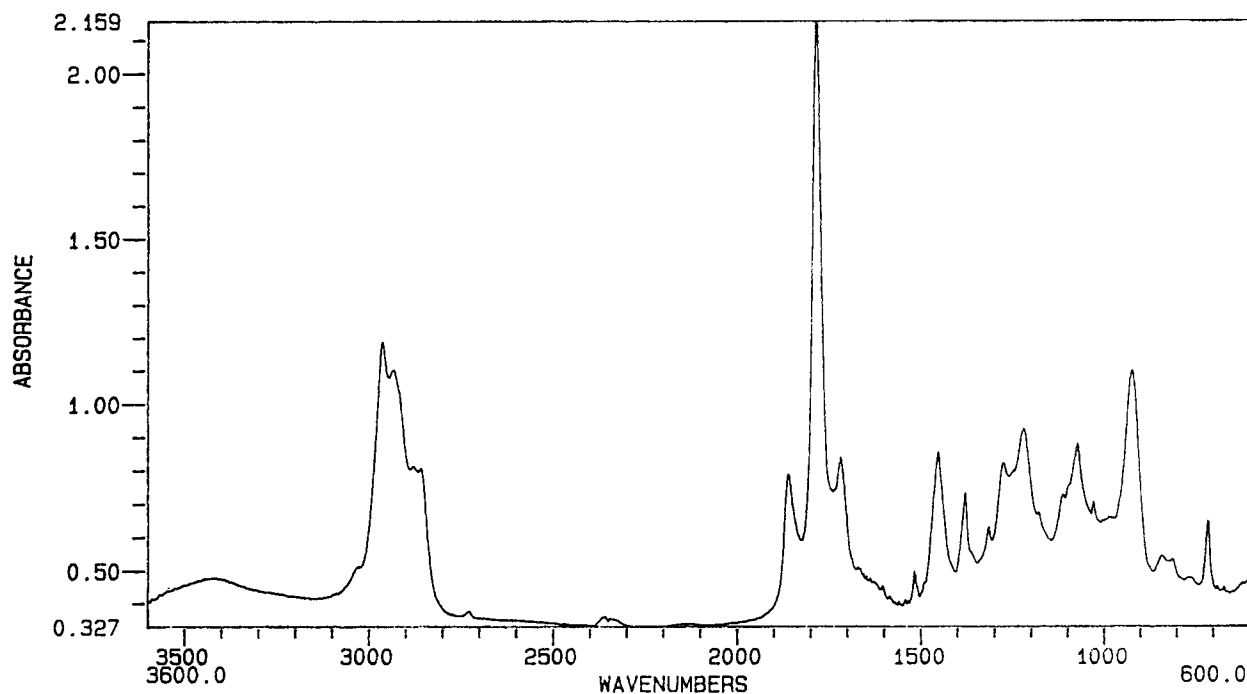


Figure 5 FTIR spectrum of maleinized guayule rubber.

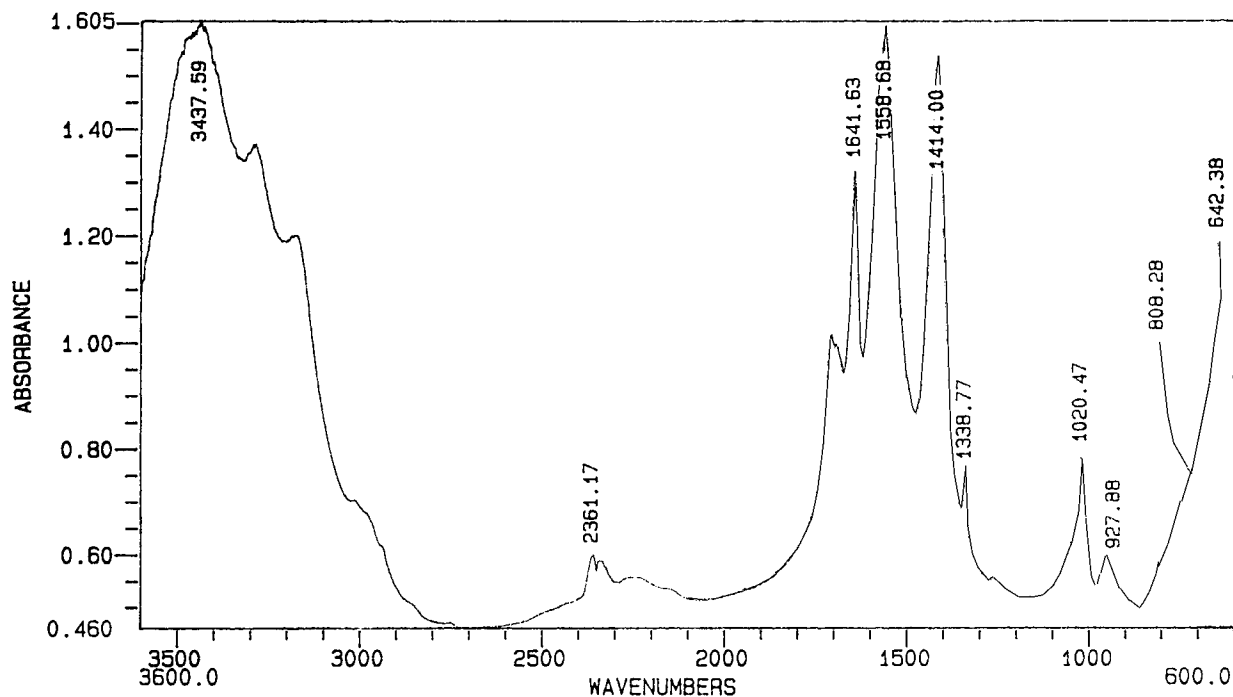


Figure 6 FTIR spectrum of MAGR upon ring opening.

representing the anhydride carbonyl group, the vinyl carbon, and the aliphatic carbons, respectively.

However, there were differences in product compositions from polar and nonpolar solvent. In the

former case, the product is soluble in dimethylformamide, dioxane, tetrahydrofuran, acetone, and in mixed solvents, such as toluene-ethanol, but insoluble in chlorinated hydrocarbons. In addition to

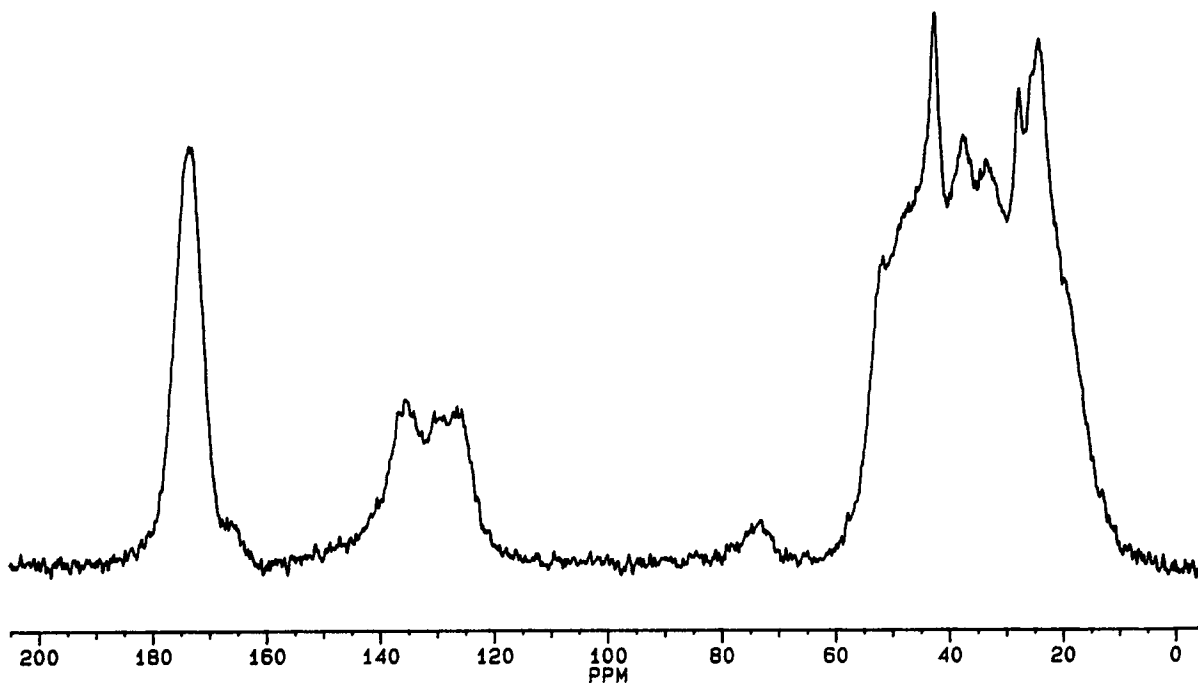


Figure 7  $^{13}\text{C}$  solid state NMR spectrum of MAGR.

maintaining reaction homogeneity throughout the reaction period, the polar solvents, dioxane, cyclohexanone, and tetrahydrofuran act to accelerate the rate of decomposition of the peroxide catalysts.<sup>17</sup>

At high molar ratios of MA to LMWGR, the product was insoluble in both polar and nonpolar solvents, suggesting that crosslinking becomes an important structural feature (Table II).

Glass transition data for LMWGR and its reaction products with MA are tabulated in Table II. The  $T_g$  of LMWGR ( $-58^\circ\text{C}$ ) increased to  $-39^\circ\text{C}$  as the maleic anhydride content increased. Indeed, the product's  $T_g$  and melting point were shown to be a function of the MA to LMWGR composition and increased with increases in MA grafting.

The intrinsic viscosity, calculated degree of polymerization, and molecular weight of LMWGR and its maleinized products are listed in Table II. The molecular weight of the product was determined by GPC using polystyrene standards. The data confirms an increase in molecular weight with the addition of increased amounts of MA. Additionally, elemental analysis supports the formation of MA grafted product (Table III).

## CONCLUSION

The reaction of MA and LMWGR, initiated by benzoyl peroxide, in polar and nonpolar solvents has been performed. The NMR, IR, DSC, and GPC of the products support the formation of the maleinized product. Anhydride ring opening was affected via the addition of sodium hydroxide or ammonium hydroxide solutions. The elemental analysis is consistent with the actual and theoretical composition of maleinized LMWGR and provides additional data supporting the tenet of a highly efficient, MA, grafting onto LMWGR.

Initial results indicate that the maleinized products can be utilized effectively in water-borne formulations and will be the subject of future communications.

The authors are grateful to the United States Department of Agriculture for the support of this work and to Mr. Darren Lowe for his unselfish cooperation and helpful advice.

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Received May 11, 1992

Accepted January 20, 1993