

# Hydrogenation of 1,3-Butadiene and Isoprene Prepolymers Having Carboxyl End Groups

YANMING LUO\*

Department of Chemistry, Staten Island College, City University of New York, Staten Island, New York 10301

## SYNOPSIS

The hydrogenations of butadiene and isoprene prepolymers having carboxyl and cyano end groups were investigated by two methods: Heterogenous hydrogenations were carried out at 45°C and 50 psi of hydrogen pressure with palladium on carbonate as catalyst. The best degree of saturation and carboxyl retention were 95 and 79% for butadiene prepolymers and 84 and 95% for an isoprene prepolymers, respectively. Diimide reduction was made in xylene at 130–140°C and normal pressure with *p*-toluenesulfonylhydrazide (TSH) as the diimide source. A nearly 100% degree of saturation for butadiene prepolymers and 91% for isoprene prepolymers were achieved. The effects of reaction conditions on the degree of saturation and the carboxyl retention, calculation of molecular weight before and after hydrogenation based on <sup>1</sup>H-NMR spectral data, and diimide reduction with TSH are discussed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

### Heterogeneous Hydrogenation of 1,3-Butadiene and Isoprene

Polybutadiene has been studied more thoroughly in hydrogenation processes than have any other synthetic unsaturated hydrocarbon polymers. In general, nickel or noble metal catalysts and lower reaction temperature are preferred for nondestructive processes. With these catalysts, it is possible to operate at sufficiently low reaction temperatures to avoid extensive degradation of the polymer chain.<sup>1–5</sup>

It was found, many years ago, that effective hydrogenation of polybutadiene could be achieved at atmospheric pressure and room temperature if sufficiently active catalysts were used.<sup>1</sup> For example, palladium on nickel, palladium on calcium carbonate, platinum black, and a mixture of platinized charcoal and chloroplatinic acid were shown to be satisfactory for this purpose. Palladium on calcium carbonate was reported to be particularly effective. It gave a product with a residual unsaturation of

only 2% when it was used for hydrogenation of polybutadiene at atmospheric pressure and room temperature.<sup>6,7</sup> More recently, Rachapudy et al.<sup>8</sup> further confirmed that catalysis by nickel on kieselguhr and palladium on calcium carbonate provided essentially complete hydrogenation without a remarkable change in molecular structure and without incorporation of interfering fragments of the catalyst. The reaction conditions were 700 psi H<sub>2</sub>, 160°C, 3–4 h and 500 psi H<sub>2</sub>, 70°C, 3–4 h, respectively, for the hydrogenation of anionically prepared polybutadiene containing about 8% vinyl double bonds.

Polybutadiene could be hydrogenated to a high level of saturation at atmospheric pressure by using very active catalysts, but the reaction rates were low. Therefore, most of the hydrogenations were carried out at 500–1000 psi H<sub>2</sub>. No remarkable effect of pressure on the reaction rate was found in or beyond this range.<sup>1</sup>

The amount of catalyst considerably affected the rate of hydrogenation and the level of saturation. For the hydrogenation of polybutadiene at 500 psi H<sub>2</sub> and 175°C with nickel on kieselguhr as the catalyst, the saturation degree of the product was as high as 99.3% if the catalyst level was 0.8 g/g polymer.<sup>1</sup> The nickel–kieselguhr catalyst should be activated prior to use by reduction of the oxide to

\* Present address: 4800 Berwyn House Road, #218, College Park, MD 20740.

**Table I** 1,3-Butadiene and Isoprene Prepolymers Having Carboxyl End Groups Used for Hydrogenation

Run No.	Temp (°C)	Time (h)	Monomer Conc <sup>a</sup> (M)	Initiator Conc <sup>b</sup> (mol %)	Yield <sup>c</sup> (%)	Carboxyl Content <sup>d</sup> (wt %)	Equivalent Weight <sup>e</sup>	$M_n$		Functionality	
								GPC	<sup>1</sup> H-NMR	GPC	<sup>1</sup> H-NMR
<u>1,3-Butadiene prepolymers</u>											
B-1	65	72	6.66	3.0	45	2.68	1680	3820	3440	2.27	2.05
B-2	65	72	6.66	3.0	40	2.59	1740	3760	3290	2.16	1.89
B-3	65	72	6.66	3.0	42	2.73	1650	3910	3320	2.37	2.01
B-4	65	72	6.66	10.0	35	4.06	1110	2820	2510	2.54	2.26
B-5	65	72	6.66	10.0	38	4.13	1090	2660	2420	2.44	2.22
B-6	65	72	6.66	10.0	29	4.09	1100	2600	2380	2.36	2.16
<u>Isoprene prepolymers</u>											
I-1	65	72	6.66	3.0	34	2.50	1800	4080	3970	2.27	2.21
I-2	65	72	6.66	3.0	29	2.47	1840	3920	3830	2.13	2.08
I-3	65	72	6.66	3.0	40	2.52	1790	4050	3740	2.26	2.09
I-4	65	72	6.66	3.0	33	2.62	1720	4170	3690	2.42	2.15
I-5	65	72	6.66	10.0	40	4.95	910	2480	2310	2.73	2.54
I-6	65	72	6.66	10.0	51	4.79	940	2510	2440	2.67	2.60

<sup>a</sup> All reactions were carried out in dioxane.

<sup>b</sup> Based on monomers.

<sup>c</sup> Yields of prepolymers purified by precipitation from methanol.

<sup>d</sup> Determined by titration with standardized KOH—CH<sub>3</sub>OH solution to a bromothymol blue endpoint in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>e</sup> Based on results obtained by titration.

<sup>f</sup> Cannot be precipitated from methanol.

metallic nickel with oxygen-free hydrogen at 315–415°C. The palladium on calcium carbonate (unpoisoned) could be used without activation or activated at 125°C with hydrogen before use.<sup>1,9</sup>

The hydrogenation rate and the ultimate saturation degree of butadiene polymers and copolymers were greatly dependent on their history and compositions. In general, synthetic polymers and natural rubber were quite readily hydrogenated. Gutta-percha was somewhat more difficult to be hydrogenated. Copolymers seemed to be less easily hydrogenated than were homopolymers.<sup>1</sup>

Hydrogenation of polyisoprene is a rather complex case of unsaturated polymer hydrogenations. Because the isopropenyl groups constituting the rubber macromolecules are trisubstituted ethylene derivatives, they should be hydrogenated at a lower rate than should di- and monosubstituted ethylenes. The process is further complicated by virtue of the high molecular nature of polyisoprene obtained from natural latex due to its less segmental mobility. This situation became worse as hydrogenation proceeded because increasing chain stiffness restricted the mobility. Therefore, the hydrogenation of polyisoprene required higher temperature and pressure, more catalyst, and longer reaction time.

Yakubchik et al.<sup>4</sup> studied the hydrogenation of natural rubber and synthetic *cis*-1,4-polyisoprene at 80–140°C and 80–100 atm H<sub>2</sub> for 150 min with nickel-kieselguhr as the catalyst. The synthetic polymer had a higher rate of hydrogenation because of its much lower molecular weight. They used large amounts of catalyst (rubber or polymer/catalyst = 1 : 2). The degree of hydrogenation increased with temperature, the amount of catalyst, and the reaction time.

*cis*-Polyisoprene was completely hydrogenated with Raney nickel at 240°C and 3600 psi H<sub>2</sub> in 48 h, but the molecular weight of the polymer was reduced by ca. 40%.<sup>10</sup> The hydrogenation of polyisoprene with a palladium catalyst has not been reported in the literature. A homogeneous catalyst, derived from alkyl or aryllithium and cobalt salts of 2-ethylhexanoic acid, was used for the hydrogenation of *cis*-1,4-polyisoprene at 50°C and 50 psi H<sub>2</sub>.<sup>11</sup>

Rachapudy et al.<sup>8</sup> investigated the homogeneous hydrogenation of polyisoprene by using alkylated transition-metal salts as catalysts. The metal alkyls were *n*-butyllithium and triethylaluminum and the metal salts were cobalt and nickel 2-ethylhexanoates and platinum and palladium acetylacetonates. The

**Table II Heterogeneous Hydrogenation of 1,3-Butadiene and Isoprene Prepolymers Having Carboxyl End Groups with Pd/CaCO<sub>3</sub> as the Catalyst**

Run No.	Temp (°C)	H <sub>2</sub> Pressure <sup>a</sup> (psi)	Time (h)	Catalyst/Double Bond <sup>b</sup> (mol %)	Prepolymer Conc <sup>c</sup> (M)	Saturation <sup>d</sup> (%)	Yield <sup>e</sup> (%)	Carboxyl Retention <sup>f</sup> (%)	<i>M<sub>n</sub></i>	
									Before Reaction <sup>1</sup> H-NMR	After Reaction <sup>1</sup> H-NMR
<b>1,3-Butadiene prepolymers<sup>g</sup></b>										
BH-1	80	600	4	1.0 <sup>h</sup>	0.20	76	84	69	3440	3600
BH-2	45	50	45	8.3	0.25	95	78	79	3440	3390
BH-3	45	50	72	2.5	0.25	64	82	94	3290	3590
BH-4	50	150	72	5.0	0.25	82	90	90	2420	2930
<b>Isoprene prepolymers<sup>g</sup></b>										
IH-1	70	500	4	1.0	0.20	6.8 <sup>i</sup>	93	97	3970	4050
IH-2	90	700	4	1.0 <sup>h</sup>	0.20	19.4 <sup>j</sup>	91	74	3670	3780
IH-3	120	800	4	25.0	0.60	92	71	40	3740	3900
IH-4	120	800	4	8.3	0.60	91	65	72	3740	4090
IH-5	50	300	43	8.3	0.60	89	73	58	3690	4130
IH-6	45	50	48	2.5	0.60	84	75	95	3690	4020

<sup>a</sup> Determined at reaction temperature.<sup>b</sup> Based on supported palladium.<sup>c</sup> All reactions were carried out in cyclohexane.<sup>d</sup> Based on <sup>1</sup>H-NMR data.<sup>e</sup> Yields of crude hydrogenated products obtained by filtration and evaporation.<sup>f</sup> Determination by titration with standardized KOH—CH<sub>3</sub>OH solution to a bromothymol blue endpoint in CH<sub>2</sub>Cl<sub>2</sub>.<sup>g</sup> See Table I for preparation and characterization.<sup>h</sup> Activated with hydrogen.<sup>i</sup> Initial saturation of isoprene prepolymer is 6.1%.<sup>j</sup> Initial saturation of isoprene prepolymer is 6.7%.**Table III Diimide Reduction<sup>a</sup> of 1,3-Butadiene and Isoprene Prepolymers Having Carboxyl End Groups with TSH**

Run No.	Temp (°C)	Time (h)	TSH/Double Bond (mol %)	Prepolymer Conc (M)	Saturation <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Carboxyl Retention <sup>d</sup> (%)	<i>M<sub>n</sub></i>		
								Before Reaction <sup>1</sup> H-NMR	After Reaction <sup>1</sup> H-NMR	
<b>1,3-Butadiene prepolymers<sup>e</sup></b>										
BD-1	130	4	200	0.20	~100	66	51	3590	<sup>f</sup>	
BD-2	130	4	200	0.26	~100	95	58	3440	<sup>f</sup>	
<b>Isoprene prepolymers<sup>e</sup></b>										
ID-1	130	4	200	0.15	89	96	65	3970	<sup>f</sup>	
ID-2	130	4	200	0.26	91	64	66	3740	<sup>f</sup>	

<sup>a</sup> All reactions were carried out in xylene under nitrogen.<sup>b</sup> Based on <sup>1</sup>NMR spectral data.<sup>c</sup> Yields of hydrogenated products purified by precipitation from methanol.<sup>d</sup> Determined by titration with standardized KOH—CH<sub>3</sub>OH solution to a bromothymol blue endpoint in CH<sub>2</sub>Cl<sub>2</sub> or DMF.<sup>e</sup> See Table I for preparation and characterization.<sup>f</sup> Cannot be calculated based on the <sup>1</sup>H-NMR spectral data.

**Table IV** Calculation of Molecular Weight of 1,3-Butadiene Prepolymers Having Carboxyl End Groups by <sup>1</sup>H-NMR Spectral Data (see Fig. 1)

Run No.	Initiator Concn (mol %)	Peak Area <sup>a</sup>					Calculation			
		A <sub>b</sub>	A <sub>b'</sub>	A <sub>c'</sub>	A <sub>d'</sub>	A <sub>g</sub>	$2(A_{b'} + A_{c'} + A_{d'})/3A_g$ n <sub>1</sub> + n <sub>2</sub>	A <sub>b</sub> /2g n <sub>3</sub> <sup>b</sup>	DP <sup>c</sup>	M <sub>n</sub> <sup>c</sup>
B-1	3.0	15.3	122	61.6	12.3	2.35	56	3	59	3440
B-2	3.0	24.7	151	77.9	16.6	3.14	52	4	56	3290
B-3	3.0	48.3	263	131	27.4	5.30	53	5	58	3400
B-5	10.0	29.9	152	82.7	18.5	4.62	37	3	40	2420
B-6	10.0	38.3	192	85.7	23.6	5.70	35	3	38	2380

<sup>a</sup> For peak assignments, see Figures 1 and 2. A<sub>a</sub>, A<sub>b</sub>, A<sub>c</sub>, A<sub>b'</sub>, A<sub>c'</sub>, A<sub>d'</sub>, and A<sub>g</sub> are areas of peaks a, b, a', b', c', d', and g, respectively.

<sup>b</sup> Rounded to the nearest whole numbers and DP = n<sub>1</sub> + n<sub>2</sub> + n<sub>3</sub> (degree of polymerization).

<sup>c</sup> Calculated by M<sub>n</sub> = 54.09 (n<sub>1</sub> + n<sub>2</sub>) + 56.09n<sub>3</sub> + 126.3 × 2 (1,3-butadiene prepolymers). Calculated by M<sub>n</sub> = 56.09 (n<sub>1</sub> + n<sub>2</sub>) + 54.09 (n<sub>3</sub> + n<sub>4</sub>) + 129.3 × 2 (hydrogenated 1,3-butadiene prepolymers).

hydrogenation was carried out at 70°C and 20 psi H<sub>2</sub> in cyclohexane for 4 h.

### Diimide Reduction of Polybutadiene and Polyisoprene<sup>12-17</sup>

Lenz et al.<sup>12</sup> and Hardwood et al.<sup>13</sup> studied this new method of polydiene hydrogenation early in 1973. The technique involved *in situ* generation of diimide by heating *p*-toluenesulfonylhydrazide (TSH) in a high-boiling aromatic solvent such as xylene. The transitory diimide hydrogenated polydienes *in situ* in the solution. Because the reaction was homogeneous and conducted at normal pressure, it was a convenient lab-scale method for hydrogenating a small amount of polymers.

Chen<sup>14</sup> found that the isomerization occurred in the hydrogenation of *cis*-1,4-polybutadiene by this technique. Nang et al.<sup>15</sup> studied the diimide reduction of *cis*-1,4-polyisoprene to clarify the effect of reaction conditions on the hydrogenation and of polymer consumption on the physical properties of the product. They found that the rate of hydrogen-

ation was directly proportional to the concentrations of polymers and TSH. *p*-Toluenesulfonic acid produced from TSH was partly converted to *p*-toluenesulfonic acid which caused the cyclization of polyisoprene and the acceleration of the thermal decomposition of the polymer. It was prevented by using a basic solvent such as pyridine. The degree of hydrogenation decreased by the order of *m*-xylene, dichlorobenzene, and pyridine. Several reviews were published on the hydrogenation of polybutadiene and polyisoprene.<sup>1,18-20</sup>

### NMR Determinations of Polybutadiene and Polyisoprene

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra have been studied in detail for both polybutadiene<sup>24-30</sup> and polyisoprene.<sup>30-38</sup> The <sup>1</sup>H-NMR spectrum of polybutadiene showed a clear separation of peaks which allowed one to determine *cis*, *trans*, and vinyl contents.<sup>21</sup> Spin decoupling of the olefin peaks gave triad distributions of *cis* and *trans* isomers.<sup>22</sup> At low fields, determination of only 1,2- and 1,4-units was possible

**Table V** Calculation of Molecular Weight of Hydrogenated 1,3-Butadiene Prepolymers Having Carboxyl End Groups by <sup>1</sup>H-NMR Spectral Data (see Fig. 2)

Run No.	Prepolymer No.	Peak Area <sup>a</sup>					Calculation				
		A <sub>a</sub>	A <sub>b</sub>	A <sub>b'</sub>	A <sub>c'</sub>	A <sub>d'</sub>	A <sub>g</sub>	$(A_a + A_b)/2g$ n <sub>1</sub> + n <sub>2</sub> <sup>b</sup>	$2(A_{b'} + A_{c'} + A_{d'})/3A_g$ n <sub>3</sub> + n <sub>4</sub> <sup>b</sup>	DP <sup>c</sup>	M <sub>n</sub> <sup>c</sup>
BH-1	B-1	17.5	157	31.6	9.00	1.80	1.86	47	15	62	3700
BH-2	B-1	7.20	77.8	2.89	0.23	0.04	0.80	53	3	56	3390
BH-3	B-2	21.2	237	104	42.3	8.46	3.83	36	30	66	3590
BH-4	B-5	14.3	155	22.3	8.59	1.72	2.22	38	10	48	2930

<sup>a-c</sup> See footnotes a-c to Table IV.

**Table VI** Calculation of Molecular Weight of Isoprene Prepolymers Having Carboxyl End Groups by <sup>1</sup>H-NMR Spectral Data (see Fig. 3)

Run No.	Initiator Concn (mol %)	Peak Area <sup>a</sup>							Calculation			DP <sup>c</sup>	M <sub>n</sub> <sup>c</sup>
		A <sub>a</sub>	A <sub>b</sub>	A <sub>a'</sub>	A <sub>b'</sub>	A <sub>c'</sub>	A <sub>d'</sub>	A <sub>g</sub>	(A <sub>a'</sub> + A <sub>b'</sub> + A <sub>c'</sub> + A <sub>d'</sub> )/2A <sub>g</sub> n <sub>1</sub> + n <sub>2</sub> <sup>b</sup>	2(A <sub>a</sub> + A <sub>b</sub> )/5A <sub>g</sub> n <sub>3</sub> <sup>b</sup>			
I-1	3.0	10.8	21.2	120	180	47.8	6.65	3.39	52	4	56	4070	
I-2	3.0	6.83	13.5	97.8	128	32.6	3.79	2.78	47	3	50	3670	
I-3	3.0	2.45	9.98	62.1	84.2	21.8	3.01	1.77	48	3	51	3740	
I-4	3.0	7.31	26.8	128	175	46.7	4.38	3.78	47	4	51	3690	
I-5	10.0	12.5	22.6	187	238	52.6	7.63	6.83	36	2	38	2840	
I-6	10.0	7.55	20.2	119	182	37.9	5.41	5.11	34	2	36	2700	

<sup>a</sup> For peak assignments, see Figures 3 and 4. A<sub>a</sub>, A<sub>b</sub>, A<sub>a'</sub>, A<sub>b'</sub>, A<sub>c'</sub>, A<sub>d'</sub>, and A<sub>g</sub> are areas of peaks a, b, a', b', c', d', and g, respectively.

<sup>b</sup> Rounded to the nearest whole numbers and calculated by DP = n<sub>1</sub> + n<sub>2</sub> + n<sub>3</sub> + n<sub>4</sub>, where DP is the degree of polymerization.

<sup>c</sup> Calculated by M<sub>n</sub> = 68.12 (n<sub>1</sub> + n<sub>2</sub>) + 70.12n<sub>3</sub> + 126.3 × 2 (isoprene prepolymers). Calculated by M<sub>n</sub> = 70.12 (n<sub>1</sub> + n<sub>2</sub>) + 68.12 (n<sub>3</sub> + n<sub>4</sub>) + 129.3 × 2 (hydrogenated isoprene prepolymers).

because of severe overlapping of the resonances.<sup>23</sup> The structure of polybutadiene<sup>24,27</sup> and hydrogenated polybutadiene were studied by <sup>13</sup>C-NMR spectroscopy.<sup>24-29</sup> The sequence distribution of *cis*- and *trans*-1,4-units in polybutadiene<sup>26,27</sup> and the sequence distribution of *cis*- and *trans*-1,4- and 3,4-units in polyisoprene<sup>31-37,39</sup> could be determined by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. The NMR assignments of polybutadiene and polyisoprene and their end groups were reported.<sup>30,38,40-43</sup> Strecker and French,<sup>42</sup> Gorbun,<sup>44</sup> and Szwarc and Rembaum<sup>45</sup> studied the termination mechanism for polymerizations of butadiene and isoprene.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Aldrich Chemical Co. except when specifically indicated. 1,3-Butadiene (99+%, inhibited with *p-t*-butylcatechol) was used without purification. Isoprene (99%, inhibited

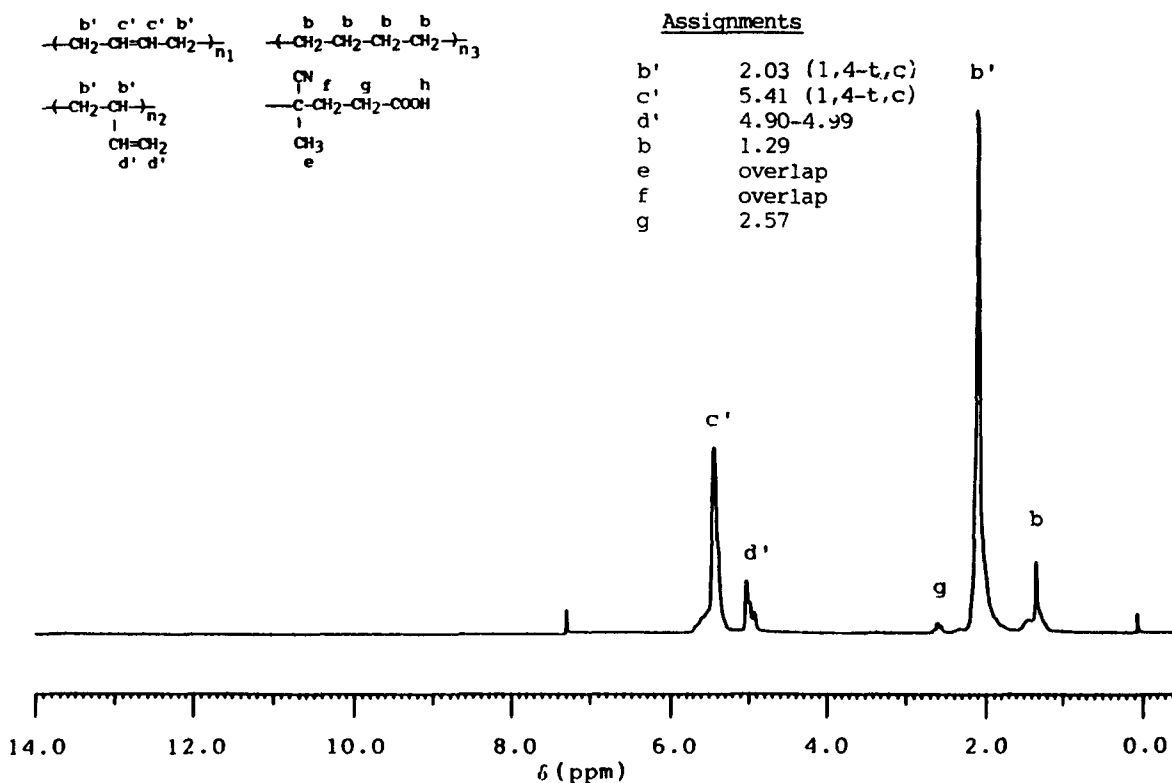
with *p-t*-butylcatechol) was distilled prior to use. 4,4-Azobis(4-cyanovaleric acid) (ACVA) and 2,2'-azobisisobutyronitrile (AIBN) were used as the initiator and dioxane as the solvent for polymerization of diene monomers.

The preparations of 1,3-butadiene and isoprene prepolymers having carboxyl end groups are described below. Palladium on calcium carbonate (5 wt %, unpoisoned) and Raney cobalt obtained from Strem Chemical Co. or Aldrich Chemical Co. were employed as catalysts for heterogeneous hydrogenation of these prepolymers. Hydrogen gas was purchased from Matheson Inc. Commercial *p*-toluenesulfonylhydrazide (TSH), obtained from Aldrich Chemical Co. (97%, mp 108–110°C dec.) or Pfaltz & Bauer Co., Inc. (98%, mp 108–110°C dec.), was purified by recrystallization from methanol and dried *in vacuo* or used as it was. Commercial cyclohexane (Aldrich, 99+%) was a solvent for catalytic hydrogenation of the prepolymers, and xylene (Aldrich, ACS reagent) was a solvent for their diimide reductions. Methyl chloride, 0.1N methanolic potassium hydroxide, and

**Table VII** Calculation of Molecular Weight of Hydrogenated Isoprene Prepolymers Having Carboxyl End Groups by <sup>1</sup>H-NMR Spectral Data (see Fig. 4)

Run No.	Prepolymer No.	Peak Area <sup>a</sup>							Calculation		DP <sup>c</sup>	M <sub>n</sub> <sup>c</sup>
		A <sub>a</sub>	A <sub>b</sub>	A <sub>a'</sub>	A <sub>b'</sub>	A <sub>c'</sub>	A <sub>d'</sub>	A <sub>g</sub>	2(A <sub>a</sub> + A <sub>b</sub> )/5g n <sub>1</sub> + n <sub>2</sub> <sup>b</sup>	(A <sub>a'</sub> + A <sub>b'</sub> + A <sub>c'</sub> + A <sub>d'</sub> )/2A <sub>g</sub> n <sub>3</sub> + n <sub>4</sub> <sup>b</sup>		
IH-3	I-3	87.7	184	8.44	12.7	3.06	0.27	2.31	47	5	52	3900
IH-4	I-3	116	258	16.1	24.2	4.38	0.83	2.91	51	8	59	4390
IH-5	I-4	130	300	23.9	35.9	6.15	1.23	3.51	49	10	59	4330
IH-6	I-4	68.4	143	15.5	23.3	4.38	0.45	1.97	43	11	54	4020

<sup>a-c</sup> See footnotes a–c to Table VI.



**Figure 1**  $^1\text{H}$ -NMR spectrum of butadiene prepolymer obtained at  $65^\circ\text{C}$  in dioxane for 72 h with ACVA as the initiator ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{B}]_0 = 6.66\text{M}$ ; ACVA = 3.0 mol %.

bromothymol blue for titration were purchased from Aldrich Chemical Co.

### Measurements

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of prepolymers and hydrogenated products were obtained on a Bruker WP-200-SY spectrometer. The content of carbon atoms was determined by an inverse-gated decoupling technique. GPC analysis was performed in a Waters gel penetration chromatograph with tetrahydrofuran as the eluent solvent.

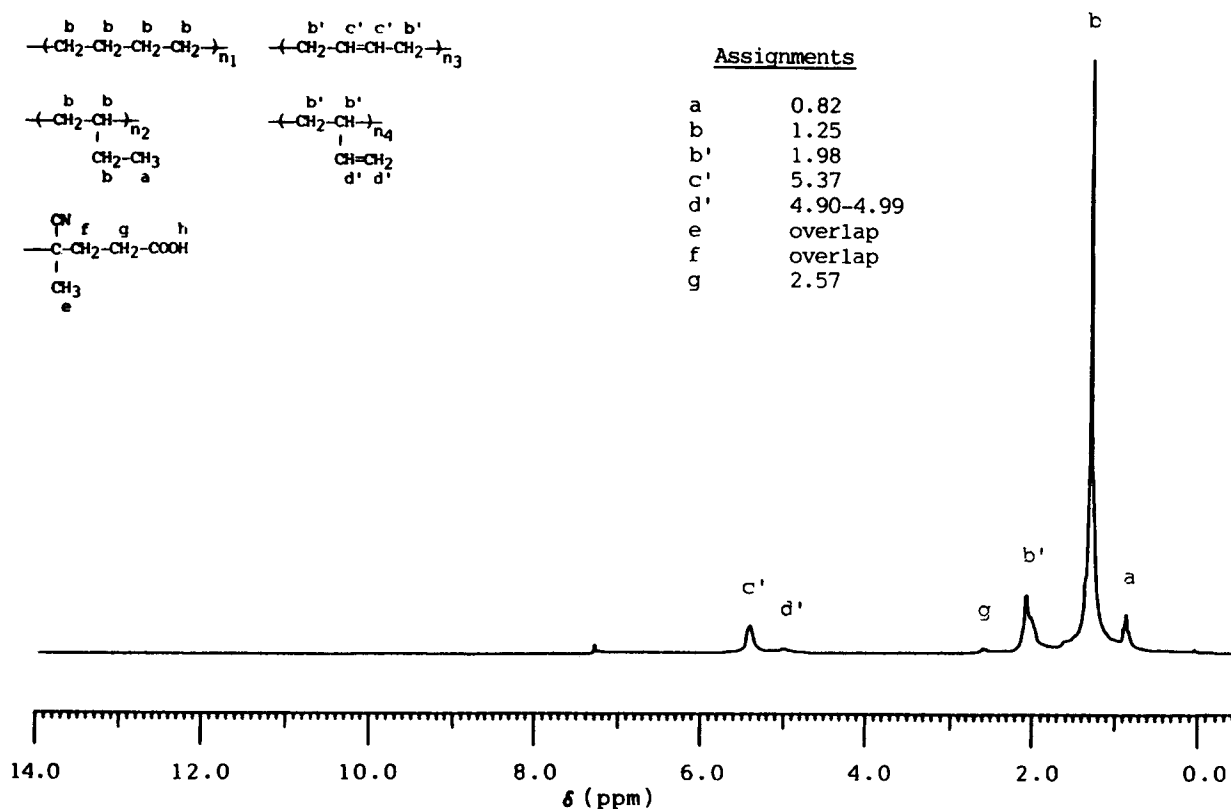
### Polymerization of 1,3-Butadiene Having Carboxyl End Groups<sup>46</sup>

In a 250 mL autoclave equipped with a glass container, a pressure gauge, a magnetic stirrer, an inlet, and a vent, 18.0 g (333 mmol) of 1,3-butadiene, 9.33 g of ACVA (33.3 mmol), and 50 mL of 1,4-dioxane were charged. The reactor was immersed in an oil bath. The polymerization was carried out at  $65^\circ\text{C}$  for 72 h. The pressure of the system was 60–70 psi. After the reaction was completed, unreacted butadiene and dioxane were removed by evaporation under reduced pressure. The initiator and remaining

dioxane were removed by dissolving the residue in 50 mL of diethyl ether and then adding the solution dropwise to methanol with vigorous agitation to precipitate the prepolymer. The precipitation was completed in a refrigerator overnight. The viscous precipitate was washed with methanol, and then the solvent was removed by evaporation under reduced pressure and dried in a vacuum oven at  $45^\circ\text{C}$  overnight, giving 5.15 g (29%) of viscous liquid as a butadiene prepolymer having carboxyl end groups (Table I).

### Polymerization of Isoprene Having Carboxyl End Groups<sup>46</sup>

In a 250 mL autoclave equipped with a glass container, a pressure gauge, a magnetic stirrer, an inlet, and a vent, 9.07 g (133.2 mmol) of isoprene, 3.73 g (13.32 mmol) of ACVA, and 20 mL of dioxane were charged. The reactor was immersed in an oil bath. The polymerization was carried out at  $65^\circ\text{C}$  for 72 h. After the reaction was completed, unreacted isoprene and dioxane were removed by evaporation under reduced pressure. The initiator and remaining dioxane were removed by dissolving the residue in 20 mL of diethyl ether and then adding dropwise



**Figure 2**  $^1\text{H-NMR}$  spectrum of hydrogenated butadiene prepolymer obtained at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 72 h with  $\text{Pd/CaCO}_3$  as the catalyst ( $\text{CDCl}_3$ ,  $35^\circ\text{C}$ ).  $[\text{PB}]_0 = 0.25\text{M}$ ; Cat. = 2.5 mol % (Strem).

the solution dropwise to methanol with vigorous agitation to precipitate the prepolymer. The precipitation was completed in a refrigerator overnight. The viscous precipitate was washed with methanol, and then the solvent was removed by evaporation under reduced pressure and dried in a vacuum oven at  $45^\circ\text{C}$  overnight, giving 7.17 g (40%) of viscous liquid as an isoprene prepolymer having carboxyl end groups (Table I).

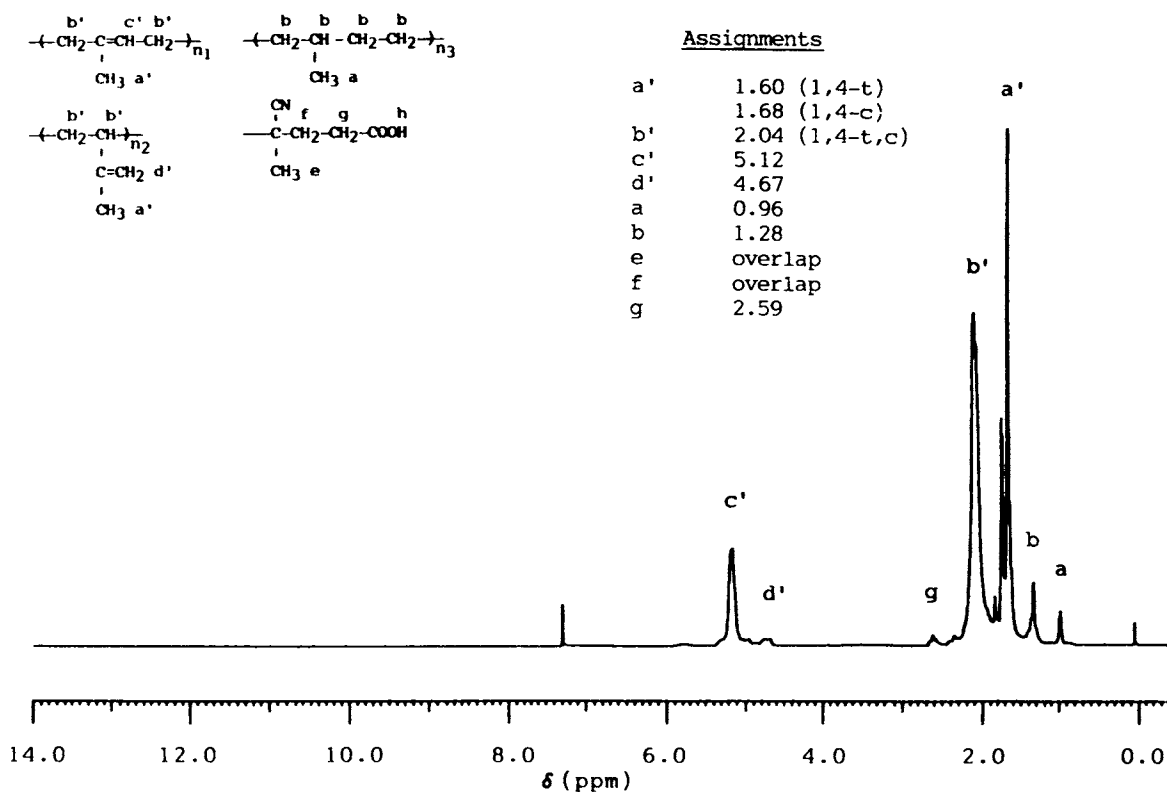
#### Heterogeneous Hydrogenation of 1,3-Butadiene Prepolymer Having Carboxyl End Groups with Palladium on Calcium Carbonate as the Catalyst<sup>8</sup>

A 400 mL autoclave (Parr Instrument Co.), equipped with a pressure gauge, a thermocouple, a mechanical stirrer, and a thermostatic heater, was used in this study. The catalyst was palladium on calcium carbonate (5 wt %, Strem Chemical Co., surface area  $10\text{ m}^2/\text{g}$ , or Aldrich Chemical Co.). Butadiene prepolymer, 2.70 g (50 mmol double bond), was dissolved in 200 mL of anhydrous cyclohexane ( $[\text{M}]_0 = 0.25\text{M}$ ). Then, 8.80 g of  $\text{Pd/CaCO}_3$  (4.16 mmol of Pd) was added to yield 0.083

mmol metal per mmol of the double bond. The reactor was purged with nitrogen and then with hydrogen. The hydrogenation was carried out at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 45 h. After the reaction was completed, fine particles of the catalyst were removed by filtration with a Millipore membrane filter (pore size  $0.25\ \mu$ ). Afterward, the solvent was removed by evaporating the filtrate at  $50^\circ\text{C}$  under vacuum, and the crude product was dried at room temperature *in vacuo* overnight. The hydrogenated product was obtained as a waxy solid. The yield was 2.21 g (78%), the degree of saturation was 95%, and the carboxyl retention was 79% (Table II).

#### Heterogeneous Hydrogenation of Isoprene Prepolymer Having Carboxyl End Groups with Palladium on Calcium Carbonate as the Catalyst<sup>8</sup>

The apparatus and procedure were similar to those used in the heterogeneous hydrogenation of 1,3-butadiene prepolymers. Isoprene prepolymer, 2.72 g (40 mmol double bond), was dissolved in 67 mL of anhydrous cyclohexane ( $[\text{M}]_0 = 0.60\text{M}$ ). Pd/



**Figure 3**  $^1\text{H-NMR}$  spectrum of isoprene prepolymer obtained at  $65^\circ\text{C}$  in dioxane for 72 h with ACVA as the initiator ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{I}]_0 = 6.66\text{M}$ ; ACVA = 3.0%.

$\text{CaCO}_3$  (1.0 mmol of Pd), 2.12 g, was added to yield 0.025 mmol metal per mmol of the double bond. The hydrogenation was carried out at 50 psi  $\text{H}_2$  and  $45^\circ\text{C}$  for 48 h. The hydrogenated product was obtained as a very viscous liquid. The yield was 75%, the degree of saturation was 84%, and the carboxyl retention was 95% (Table II).

#### Diimide Reduction of 1,3-Butadiene Prepolymer Having Carboxyl End Groups with *p*-Toluenesulfonylhydrazide<sup>8,12-14</sup>

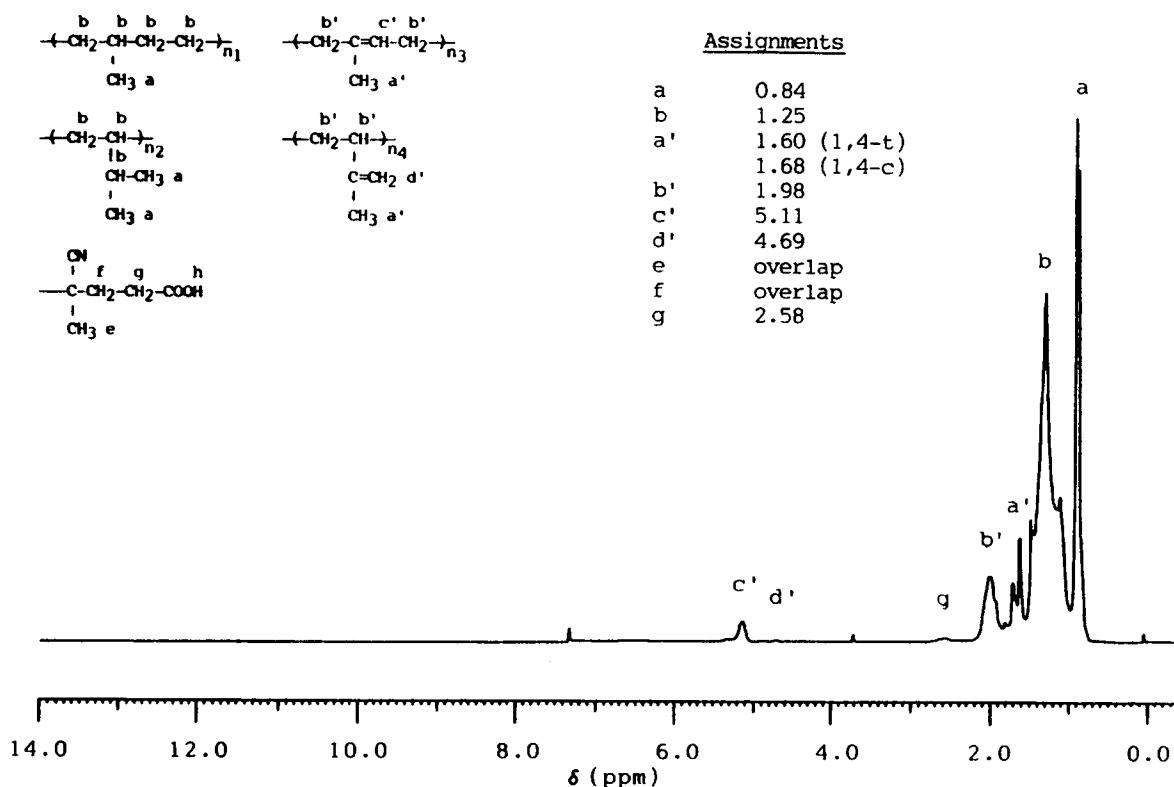
In a 500 mL three-neck round-bottom flask, fitted with a nitrogen inlet, a thermometer, and a magnetic stirrer, 3.52 g (65 mmol double bond) of the butadiene prepolymer was dissolved in 250 mL of xylene ( $[\text{M}]_0 = 0.26\text{M}$ ). The solution was heated under nitrogen with stirring to  $110\text{--}120^\circ\text{C}$ , at which time 24.20 g (130 mmol) of TSH was quickly added to yield 2 mmol of diimide per mmol of the double bond (100% excess). The solution was kept at  $130\text{--}140^\circ\text{C}$  under nitrogen for 4 h. During this time, TSH gradually decomposed to produce an active hydrogenating species: diimide. As the hydrogenation pro-

ceeded, nitrogen gas was evolved from the reaction mixture as fine bubbles, and a white powdery solid appeared as a precipitate. After the reaction was completed, xylene was removed by evaporating the reaction mixture at  $50^\circ\text{C}$  under vacuum. The hydrogenated product was obtained by dissolving the residue in 35 mL of benzene and then precipitating the polymer from 250 mL of methanol in a refrigerator overnight. Fine waxy particles of the polymer were suspended in a methanol-like milk and could be filtered out with a membrane filter. After being washed with methanol, hot water, and more methanol several times, the polymer was dried at room temperature *in vacuo* and obtained as a waxy solid. The yield was 3.58 g (95%), the degree of saturation was about 100%, and the carboxyl retention was 58% (Table III).

#### Diimide Reduction of Isoprene Prepolymer Having Carboxyl End Groups with *p*-Toluenesulfonylhydrazide<sup>8,15</sup>

The apparatus and procedure were similar to those used in the diimide reduction of 1,3-butadiene prepolymers. Isoprene prepolymer, 1.70 g (25 mmol





**Figure 4**  $^1\text{H-NMR}$  spectrum of hydrogenated isoprene prepolymer obtained at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 48 h with  $\text{Pd}/\text{CaCO}_3$  as the catalyst ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{PI}]_0 = 0.60\text{M}$ ; Cat. = 2.5 mol % (Strem).

double bond), was dissolved in 167 mL of xylene ( $[\text{M}]_0 = 0.15\text{M}$ ). The solution was heated under nitrogen with stirring to  $110\text{--}120^\circ\text{C}$  at which time 9.30 g (50 mmol) of TSH was quickly added to yield 2 mol of diimide per mol of double bonds (100% excess). The solution was kept at  $130\text{--}140^\circ\text{C}$  under nitrogen for 4 h. After the reaction was completed, xylene was removed by evaporating the reaction mixture at  $50^\circ\text{C}$  under vacuum. The hydrogenated product was obtained by dissolving the residue in 15 mL of benzene and then precipitating the polymer from 150 mL of methanol in a refrigerator overnight. After being washed with methanol, hot water, and more methanol several times, the polymer was dried at room temperature *in vacuo* and obtained as a very viscous liquid. The yield was 1.68 g (96%), the degree of saturation was 89%, and the percentage of carboxyl retention was 65% (Table III).

#### Preparation of 1,3-Butadiene and Isoprene Prepolymers with AIBN and Their Hydrogenation

Similarly, butadiene and isoprene prepolymers having cyano end groups could also be prepared by using AIBN as the initiator. The polymerizations were car-

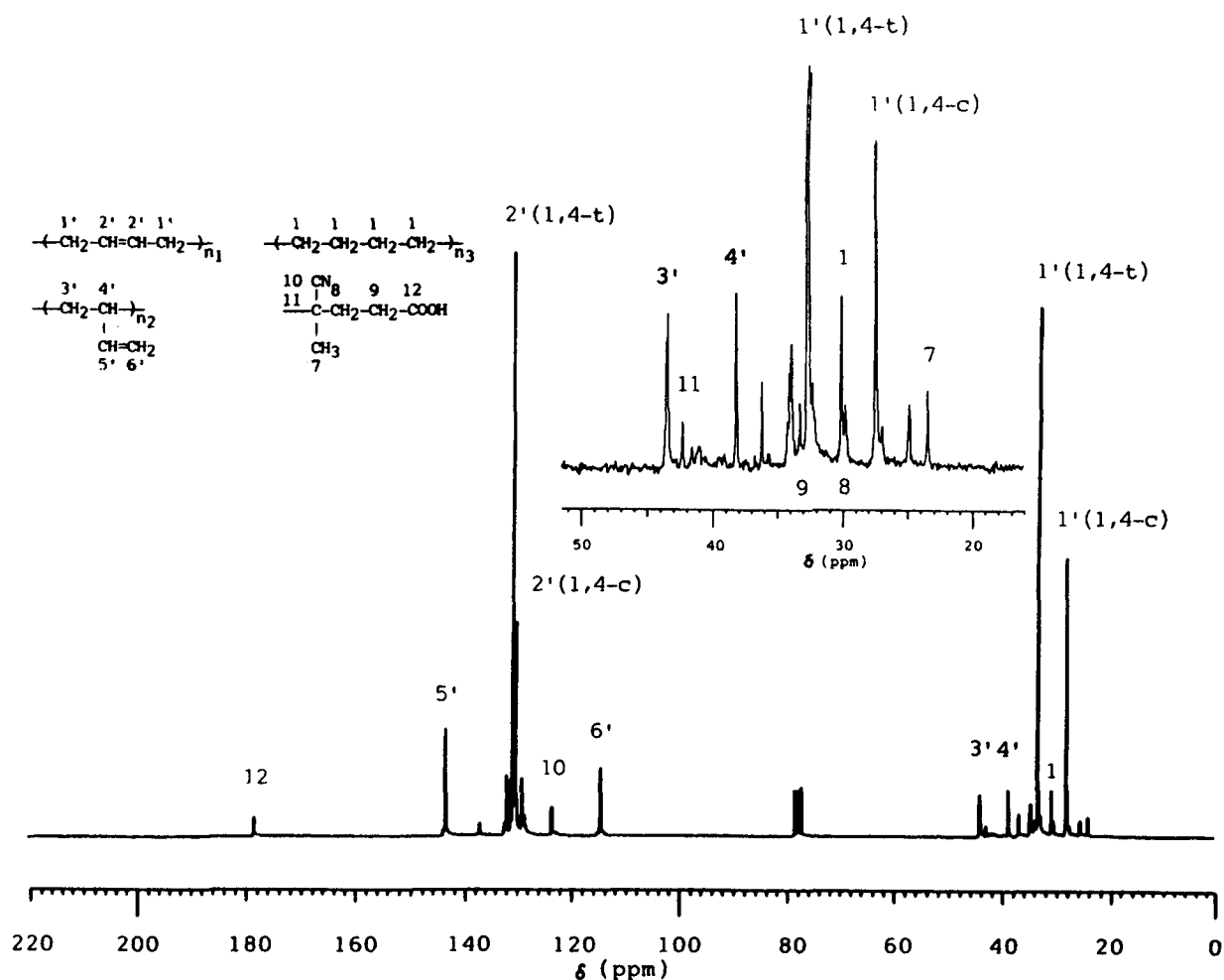
ried out in dioxane at  $65^\circ\text{C}$  for 72 h. These prepolymers were hydrogenated at  $60\text{--}80^\circ\text{C}$  and 300–600 psi  $\text{H}_2$  for 72 h with 2–5 mol% of  $\text{Pd}/\text{CaCO}_3$  as the catalyst.

#### Hydrogenation of 1,3-Butadiene and Isoprene Prepolymers Having Amino End Groups

If these prepolymers were obtained with AIBN as the catalyst, they could be hydrogenated in dioxane at  $150^\circ\text{C}$ , 700 psi  $\text{H}_2$  with Raney cobalt as the catalyst, giving butadiene and isoprene prepolymers having an amino end group.

#### Preparation of Potassium Salts of Butadiene Prepolymer

In a 500 mL flask, 3.24 g (1.2 mmol based on double bond) of a butadiene prepolymer was dissolved in 240 mL of methylene chloride, and then 0.10N methanolic potassium hydroxide solution was added dropwise to the above solution with vigorous stirring at room temperature. The necessary volume of the methanolic potassium hydroxide solution was calculated based on the titration data of the same prepolymer. The indicator was not used to avoid the



**Figure 5**  $^{13}\text{C}$ -NMR spectrum of butadiene prepolymer obtained at  $65^\circ\text{C}$  in dioxane for 72 h with ACVA as the initiator ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{B}]_0 = 6.66\text{M}$ ; ACVA = 3.0 mol %.

contamination of the product. The salt (ca. 100%) was obtained by evaporating methylene chloride and methanol.

#### Hydrogenation of Potassium Salts of Butadiene Prepolymer

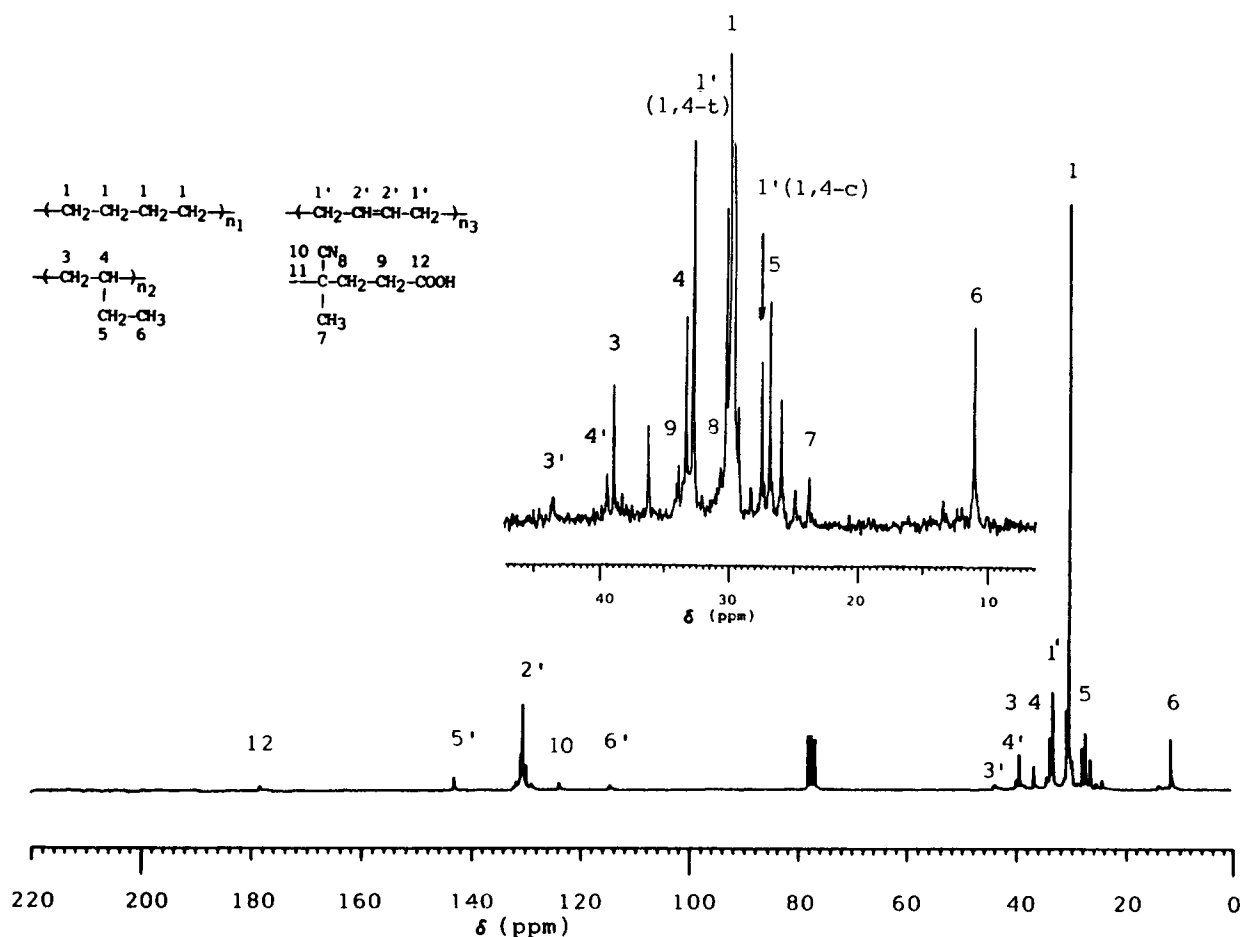
Potassium salt 1.08 g (20 mmol based on double bond), of a butadiene prepolymer was dissolved in 80 mL of methanol, and then 1.06 g (0.5 mmol of Pd, 2.5 mol % based on the prepolymer) of Pd/ $\text{CaCO}_3$  (5 wt %) was added to the solution as the catalyst. The mixture was charged in a 400 mL autoclave and purged with nitrogen and then with hydrogen. The hydrogenation was carried out at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 72 h. After the reaction was completed, very fine particles of the catalyst were removed with a Millipore membrane filter. The filtrate was evaporated to give a soaplike solid.

#### Titration of Carboxyl End Groups

Samples (0.10–0.20 g) of these prepolymers and their hydrogenated products were titrated to a bromothymol blue endpoint with 5–10 mN KOH– $\text{CH}_3\text{OH}$  solutions which were standardized with benzoic acid. Most of samples were titrated in methylene chloride to a dark green endpoint, but the hydrogenated butadiene prepolymers were titrated in DMF to a green point because they are insoluble in methylene chloride.

#### Determination of Amino End Groups of Hydrogenated Prepolymers

In a 50 mL flask, 0.10 g of a hydrogenated prepolymer were dissolved in 10 mL of toluene, and then 1 mL of benzoyl chloride was added as the acyl reagent and 1 mL of triethylamine as the base. The mixture was allowed to react at room temperature



**Figure 6**  $^{13}\text{C}$ -NMR spectrum of hydrogenated butadiene prepolymer obtained at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 72 h with  $\text{Pd}/\text{CaCO}_3$  as the catalyst ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{PB}]_0 = 0.25\text{M}$ ; Cat. = 2.5 mol % (Strem).

for 2 h. After the reaction was completed, the mixture was washed with water several times to remove unreacted benzoyl chloride. The upper organic layer was dried over magnesium sulfate. After filtration, the filtrate was added to 100 mL of methanol to precipitate the acylated polymer. It was dried at  $50^\circ\text{C}$  *in vacuo*. The amino end groups of the polymer were determined by  $^1\text{H}$ -NMR spectroscopy.

## RESULTS AND DISCUSSION

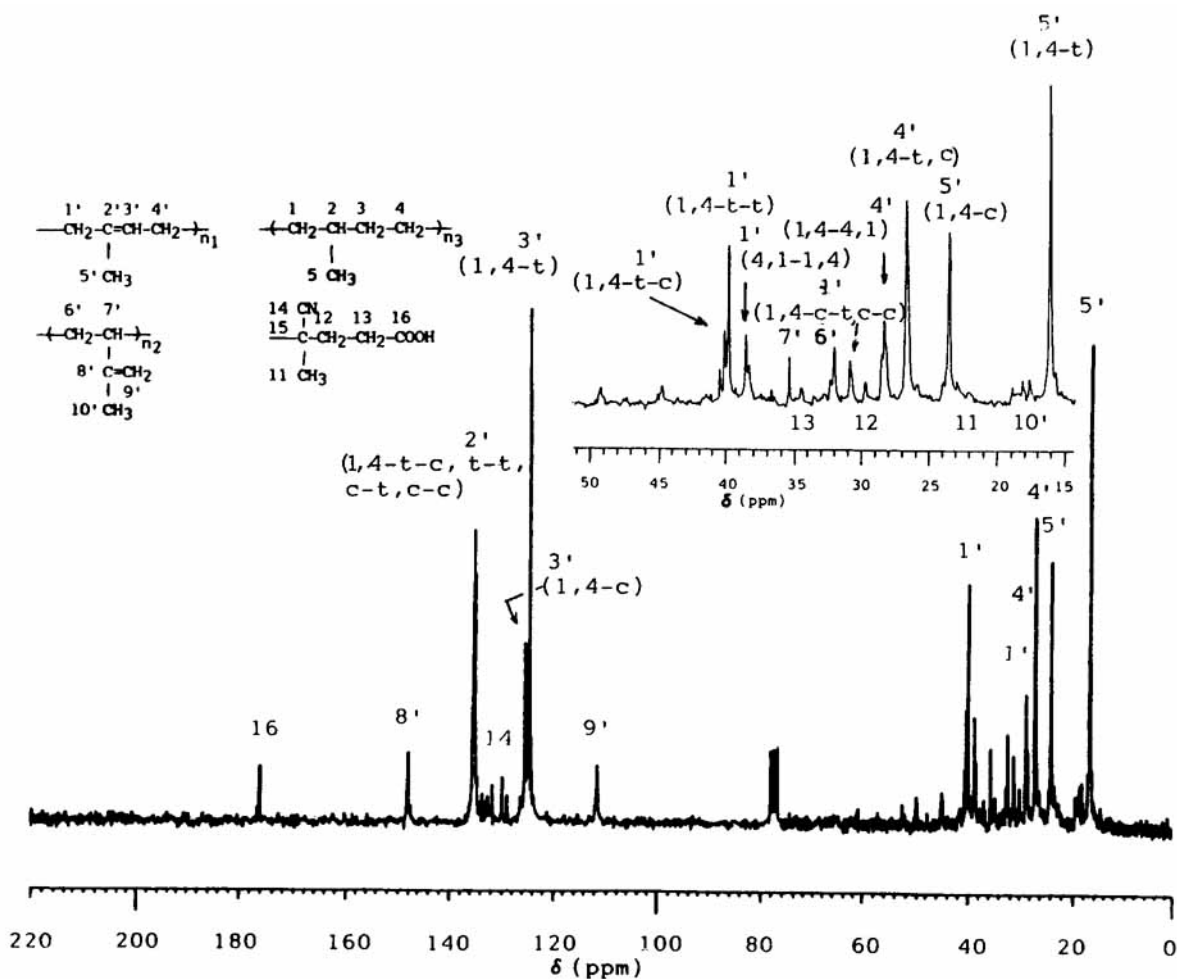
### Preparation of 1,3-Butadiene and Isoprene Prepolymers

1,3-Butadiene and isoprene were polymerized at  $65^\circ\text{C}$  in dioxane for 72 h in the presence of ACVA to prepare their prepolymers, respectively. The results are shown in Table I. Because the rate of solution polymerization of dienes initiated with free-

radical catalysts is relatively slow for most vinyl monomers, a longer reaction time is necessary for a higher yield of polymers. As shown in Table I, the yield ranges from 29 to 51% depending upon the reaction conditions. The initial initiator concentrations are at 3.0 and 10.0% levels. The carboxyl content increases and the molecular weight decreases with the initial initiator concentration. The molecular weight ranges from 2400 to 4000 and can be calculated based on  $^1\text{H}$ -NMR spectral data or determined by GPC. The choice of solvent is limited by the solubility of ACVA. DMF and acetonitrile can also be used as solvents. The carboxyl content, equivalent, and functionality, based on the titration data, are calculated by the following formulas:

$$C_{\text{COOH}} = 45.02NV_i/10W_s \quad (1)$$

where  $C_{\text{COOH}}$  is the content of the carboxyl group in the prepolymer (wt %); 45.02, the equivalent of the



**Figure 7**  $^{13}\text{C}$ -NMR spectrum of isoprene prepolymer obtained at  $65^\circ\text{C}$  in dioxane for 72 h with ACVA as the initiator ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{I}]_0 = 6.66\text{M}$ ; ACVA = 3.0%.

carboxyl group;  $N$ , the normal concentration of standardized solution ( $N$ );  $V_t$ , the volume of the titration (mL); and  $W_s$ , the weight of the sample (g).

$$E_{\text{COOH}} = 45.02 \times 100 / C_{\text{COOH}} \quad (2)$$

where  $E_{\text{COOH}}$  is the equivalent of the carboxyl group in the prepolymer; 45.02, the equivalent of the carboxyl group; and  $C_{\text{COOH}}$ , the content of the carboxyl group in the prepolymer (wt %).

$$F_{\text{COOH}} = M_n / E_{\text{COOH}} \quad (3)$$

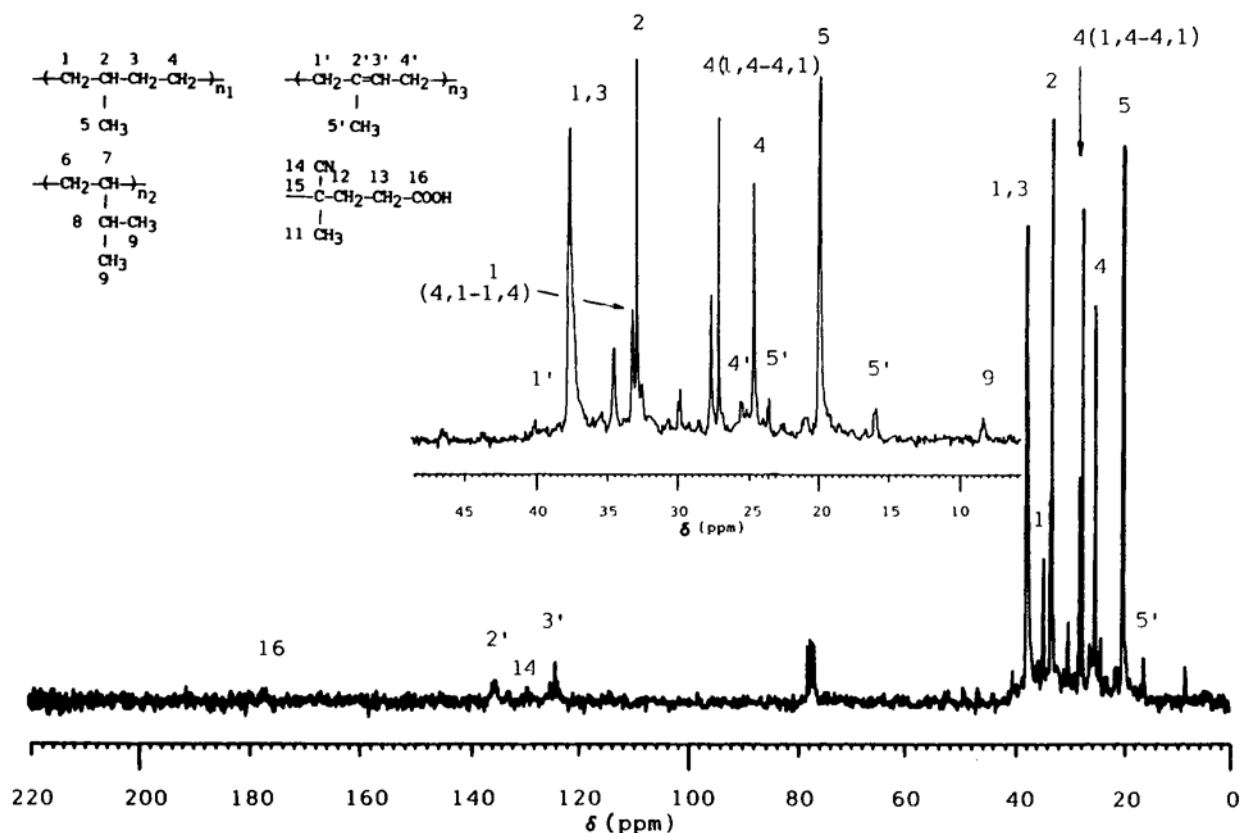
where  $F_{\text{COOH}}$  is the functionality of the carboxyl group in the prepolymer;  $M_n$ , the number-average molecular weight of the prepolymer; and  $E_{\text{COOH}}$ , the equivalent of the carboxyl group in the prepolymer.

The functionality of prepolymers can be calculated based on the  $M_n$  obtained by GPC or  $^1\text{H}$ -NMR

spectral data. Azo-type initiators with functional groups, such as ACVA and 5,5'-azobis(5-cyano-*n*-pentanol), were suitable for preparing carboxyl and hydroxyl-terminated butadiene and isoprene prepolymers. In our experiments, the functionalities greater than 2.0 can be contributed to the presence of transfer reactions and the accuracy of molecular weights based on the instrumental analysis.

#### Effects of Reaction Conditions on Hydrogenations

Previous studies concentrated on the hydrogenations of natural rubber, gutta-percha, and high molecular weight synthetic polybutadiene and polyisoprene. In general, the catalytic reactions were carried out at higher temperatures ( $160$ – $260^\circ\text{C}$ ) and hydrogen pressures ( $500$ – $3000$  psi) with nickel catalysts or at moderate temperature and hydrogen pressure ( $70^\circ\text{C}$ ,  $500$  psi) with palladium catalysts.



**Figure 8**  $^{13}\text{C}$ -NMR spectrum of hydrogenated isoprene prepolymer obtained at  $45^\circ\text{C}$  and 50 psi  $\text{H}_2$  for 48 h with  $\text{Pd}/\text{CaCO}_3$  as catalyst ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).  $[\text{PI}]_0 = 0.60\text{M}$ ; Cat. = 2.5 mol % (Strem).

Sometimes, these reactions could be conducted at ambient temperature and atmospheric pressure by using palladium or platinum catalysts, but the rate of hydrogenation was low. Under these severe conditions, the polydienes might undergo degradation or other structural changes.

The results of hydrogenation are affected by temperature, hydrogen pressure, kind and amount of catalyst, solvent, concentration of the polymer, reaction time, etc. Because the low molecular weight butadiene and isoprene prepolymers in our study have carboxyl and cyano end groups, it is preferred

to perform their hydrogenations at low temperatures and hydrogen pressures with very active catalysts, such as palladium on calcium carbonate. Cyclohexane is commonly used in the hydrogenations at low temperatures. It is also feasible to do these reactions under mild conditions because low molecular weight synthetic polydienes have more reactive double bonds and can be more readily hydrogenated than can natural rubber and high molecular weight polydienes. The solutions of prepolymers show much lower viscosities due to their low molecular nature; therefore, it is possible to accelerate the hydrogen-

**Table VIII**  $^{13}\text{C}$ -NMR Assignments for 1,3-Butadiene Prepolymers<sup>a</sup> ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )

Run No.	Initiator Concn (mol %)	Assignment												
		1	1'	2'	3'	4'	5'	6'	7	8	9	10	11	12
B-2	3.0	30.0	27.3 (c) 32.2 (t)	128.6 (c) 130.6 (t)	38.1	43.4	142.5	114.2	23.4	29.7	33.2	123.0	36.1	178.1
B-5	10.0	30.0	27.3 (c) 27.3 (t)	128.6 (c) 128.6 (t)	38.1	43.4	142.5	114.2	23.3	29.7	33.2	122.9	36.0	178.2

**Table IX**  $^{13}\text{C}$ -NMR Assignments for Hydrogenated 1,3-Butadiene Prepolymers<sup>a</sup> ( $\text{CDCl}_3$ , 25°C) (see Fig. 6)

Run No.	Initiator Concn (mol %)	Assignment														
		1	3	4	5	6	1'	2'	3'	4'	7	8	9	10	11	12
BH-2	3.0	29.7	38.8	36.1	26.7	10.9	32.7 (c) 33.2 (t)	128.9 (c) 130.0 (t)	43.5	38.2	23.7	<sup>b</sup>	<sup>b</sup>	123.4	33.8	178.2
BH-4	10.0	29.7	38.8	36.1	26.7	10.9	32.7 (c) 33.2 (t)	128.9 (c) 128.9 (t)	43.5	38.2	23.7	<sup>b</sup>	<sup>b</sup>	123.4	33.7	178.5

<sup>a</sup> For peak assignments, see Figures 5 and 6.<sup>b</sup> Overlapped.

ations by increasing the concentration of the polymers. Balancing these conditions, we can achieve a high degree of saturation and excellent retention of valuable carboxyl end groups.

Table II summarizes the heterogeneous hydrogenation of the butadiene and isoprene prepolymers. It is evident that both prepolymers can give very good results, i.e., a high degree of saturation and percentage of carboxyl retention under suitable conditions. For a butadiene prepolymer, 82% of saturation and 90% of carboxyl retention can be obtained at 50°C and 150 psi  $\text{H}_2$  in cyclohexane ( $[B]_0 = 0.25M$ ) for 72 h with 5.0 mol % (based on metal Pd) catalyst. For an isoprene prepolymer, 84% of saturation and 95% carboxyl retention can be obtained at 45°C and 50 psi  $\text{H}_2$  in cyclohexane ( $[I]_0 = 0.60M$ ) for 48 h with 2.5 mol % catalyst.

The increases in temperature, pressure, and amount of catalyst improve the saturation but reduce the carboxyl retention. At room temperature, the degree of hydrogenation becomes very low. For

a butadiene prepolymer, only 41% of saturation can be obtained at 25°C and 50 psi  $\text{H}_2$  in cyclohexane ( $[B]_0 = 0.25M$ ) for 72 h with 4.0 mol % catalyst. If the reaction time is too short (4 h) and the amount of catalyst is too small (1 mol %), very low saturations are obtained even at high temperatures and hydrogen pressures. These values are only slightly higher than are the initial saturations of the prepolymers. It is evident that lower temperatures and longer reaction times should be employed in order to achieve high carboxyl retention. The increases in the amount of catalyst and hydrogen pressure can accelerate the hydrogenation without a remarkable change in carboxyl retention, but also lead to a higher cost of equipment and production.

#### Diimide Reduction with TSH

The diimide reduction with TSH was proved to be a convenient and effective method for the hydrogenation of the butadiene and isoprene prepolymers.

**Table X**  $^{13}\text{C}$ -NMR Assignments for Isoprene Prepolymers<sup>a</sup> ( $\text{CDCl}_3$ , 25°C) (see Fig. 7)

Run No.	Initiator Concn (mol %)	Assignment										
		1'	2'	3'	4'	5'	6'	7'	8'	9'	10'	
I-2	3.0	31.9 (c-t)	134.3 (t-t)	124.2 (t)	25.6 (t, c)	15.9 (t)	32.1	35.2	147.4	111.2	18.0	
		30.7 (c-c)	134.6 (t-c)	125.0 (c)	28.2 (tail-tail)	23.4 (c)						
		39.7 (t-t)	134.8 (c-t)									
		39.9 (t-c)	134.9 (c-c)									
		38.2 (head-head)										
		Assignment										
		1	2	3	4	5	11	12	13	14	15	16
		37.4	32.8	37.4	24.5	27.5	<sup>b</sup>	29.7	34.3	129.5	<sup>b</sup>	177.4
		34.4 (head-head)	33.1		26.9 (tail-tail)							

<sup>a</sup> For peak assignments, see Figure 7.<sup>b</sup> Overlapped.

**Table XI**  $^{13}\text{C}$ -NMR Assignments for Hydrogenated Isoprene Prepolymers<sup>a</sup> ( $\text{CDCl}_3$ , 25°C) (see Fig. 8)

Run No.	Initiator Conc'n (mol %)	Assignment											
		1'	2'	3'	4'	5'	1	2	3	4	5		
I-2	3.0	31.9 (c-t)	134.3 (t-t)	124.0 (t)	25.5 (t, c)	15.9 (t)	37.4		32.8	37.4	24.5		19.7
		32.1 (c-c)	134.6 (t-c)	124.7 (c)	28.2 (tail-tail)	23.6 (c)	34.4 (head-head)	33.1			26.9 (tail-tail)		
		39.7 (t-t)	134.8 (c-t)										
		40.0 (t-c)	134.9 (c-c)										
		Assignment											
		6	7	8	9	11	12	13	14	15	16		
		b	b	b	b	b	b	b	129.5	b	177.8		

<sup>a</sup> For peak assignments, see Figure 8.

<sup>b</sup> Overlapped.

The degree of saturation was high, and the cost was also reasonable.

No appreciable differences were found between unrecrystallized and recrystallized TSH. Therefore, commercial TSH could be used without recrystallization.

As shown in Table III, the best combinations of the degree of saturation and the carboxyl retention are ca. 100 and 58% for a butadiene prepolymer and 91 and 66% for an isoprene prepolymer. The carboxyl retention may be improved by decreasing the temperature and reducing the amount of TSH.

According to the determination of the amino end group with benzoyl chloride, it is not recognized that the  $-\text{NHNH}_2$  group of TSH reacted with carboxyl end groups. A disadvantage of this method is the incorporation of a *p*-toluenesulfonic acid (TSA) fragment into the hydrogenated prepolymers, as shown by  $^1\text{H}$ -NMR spectra. It was reported in the literature,<sup>8,13,47</sup> but seems not to interfere with the determination of carboxyl end groups because TSA was very soluble in methanol and easily removed from the reaction mixture, and the incorporated fragment was not in the form of an acid.

As compared with the heterogeneous hydrogenation, the diimide reduction does not cause severe reduction of cyano groups. It is confirmed by the determination of amino end groups with benzoyl chloride. This observation is in agreement with previous works.<sup>16,17</sup>

After the solvent is removed from the reaction mixture by evaporation, a mixture of hydrogenated product, unreacted TSH, and TSA is obtained. The two impurities are readily removed by precipitating the polymer in methanol because of their good solubilities in methanol. The highly hydrogenated

products obtained by the diimide reduction are waxy solids, very similar in appearance to low molecular weight polyethylene.

#### Calculation of Molecular Weight by NMR Spectral Data

The number-average molecular weight,  $M_n$ , of butadiene and isoprene prepolymers and their hydrogenated products obtained with palladium on calcium carbonate as catalyst can be approximately calculated based on NMR spectral data. The results are shown in Tables IV–VII. For the hydrogenated products obtained by the diimide reduction, their molecular weights cannot be calculated based on  $^1\text{H}$ -NMR spectra because no relative data are available.

As shown in Tables IV–VII, no remarkable changes can be found before and after hydrogenation. For butadiene prepolymers, the molecular weights are ca. 3300–3400 at 3.0 mol % of ACVA and ca. 2400 at 10.0 mol % of ACVA, and the correspondent molecular weights of their hydrogenated products are ca. 3400–3700 and 2900, respectively. For isoprene prepolymers, the molecular weights are ca. 3700–4000 at 3.0 mol % of ACVA, and the correspondent molecular weights of their hydrogenated products are ca. 3900–4400.

The accuracy of this method is restricted by the integration data of the peak areas. Peak C usually has a long-tail portion, and peaks a and b sometimes overlap with peak a'. Peak g is small and must be carefully phased to avoid errors.

#### $^1\text{H}$ - and $^{13}\text{C}$ -NMR Determinations

$^1\text{H}$ -NMR spectra of butadiene and isoprene prepolymers and their hydrogenated products are shown

in Figures 1–8. The assignments are very close to the literature values.<sup>30,43</sup> <sup>13</sup>C-NMR assignments of butadiene prepolymers are shown in Table VIII and IX, and those of isoprene prepolymers, in Tables X and XI.

## CONCLUSION

1,3-Butadiene and isoprene prepolymers having carboxyl end groups were hydrogenated with palladium on calcium carbonate as the catalyst. The rate and degree of hydrogenation were dependent on temperature, hydrogen pressure, kind and amount of catalyst, initial concentration of polymer, the reaction time, etc. It was essential to balance these conditions to achieve the required high degree of hydrogenation and high carboxyl retention.

Palladium on calcium carbonate was a good catalyst for the hydrogenation of these prepolymers. By selecting a suitable initial concentration of the catalyst, the reaction could be carried out at low temperatures and pressures, e.g., 45°C and 50 psi H<sub>2</sub>. As shown by the NMR spectra, no appreciable structure changes were observed after hydrogenation. The very fine particles of the catalyst were readily removed with a Millipore membrane filter (0.25 μ).

The best combinations of the degree of saturation and the carboxyl retention were 95 and 79% for the butadiene prepolymers and 84% and 95% for the isoprene prepolymers, respectively.

The diimide reduction with *p*-toluenesulfonylhydrazide (TSH) was an excellent method for the hydrogenation of these prepolymers in the lab-scale experiments. No appreciable structure changes were found. The best combinations of the degree of saturation and the carboxyl retention were 100 and 58% for the butadiene prepolymers and 91% and 66% for the isoprene prepolymers.

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