CYCLOPOLYMERIZATION OF CONJUGATED DIENES

NORMAN G. GAYLORD

Gaylord Associates Inc., Newark, New Jersey 07104, U.S.A.

ABSTRACT

The formation of essentially saturated polymers containing fused cyclohexane rings is a characteristic of the polymerization of conjugated dienes under the influence of all cationic or Lewis acid catalysts. The amount of cyclic structures and non-terminal linear unsaturation is dependent upon the electron accepting ability of the catalyst, which may be greatly influenced by the nature of the solvent. The cyclopolymerization generally proceeds to low conversion and then reaches a dormant state. Addition of monomer to the dormant mixture reinitiates polymerization which again attains a limiting equilibrium conversion. The molecular weight increases with conversion. Polymerization in aromatic solvents results in the incorporation of phenyl groups in the polymer structure. Polymers with low intrinsic viscosities have relatively high molecular weights as measured by light scattering. The proposed polymerization mechanism leading to a perhydrophenanthrene structure involves initiation by a 1,2 or 1,4 monomer cation-radical and propagation through a 1,3 polymer cation-radical.

INTRODUCTION

The polymerization of conjugated dienes with protonic or Lewis acids has been the subject of numerous investigations within the past 50 years. In general, the polymers from butadiene and isoprene were reported to be low molecular weight products, varying in appearance from viscous liquids to brittle solids. The microstructure consisted of predominantly trans-1,4 unsaturation, accompanied by 1,2 unsaturation, with little or no detectable cis-1,4 unsaturation. However, chemical analysis indicated that the total unsaturation was considerably lower than indicated by a normalized infrared analysis wherein the unsaturation was presumed to total 100 per cent. No identification of the structures responsible for the loss in unsaturation was made.

STRUCTURE OF CYCLOPOLYDIENES

In the course of an investigation of the polymerization of butadiene and isoprene with Ziegler-type catalysts consisting of alkyl or arylmagnesium bromide or triethyl aluminum with titanium tetrachloride, it was noted that the conversion and the nature of the polymer are dependent upon the Mg/Ti and Al/Ti molar ratios. The conversion curves contain two maxima (Figure 1), the first at an RMgX/TiCl₄ molar ratio of 0.5–1 or an AlR₃/TiCl₄ molar ratio below 1 and the second at an Mg/Ti ratio of 3–5 or Al/Ti ratio of about 1.
The influence of temperature on yield is also dependent upon the Mg/Ti mole ratio. As shown in Table 1, at an Mg/Ti ratio of 0.3, in the range of the first maximum, the yield of polymer from butadiene decreases with increasing temperatures. At an Mg/Ti ratio of 2.0, entering the region of the second maximum, the polymer yield increases with increasing temperature. This is considered indicative of the operation of different polymerization mechanisms.

### Table 1. Effect of temperature on polymerization of butadiene with C₆H₅MgBr—TiCl₄ catalyst (conversions after 1 h)

<table>
<thead>
<tr>
<th>Molar ratio, C₆H₅MgBr/TiCl₄</th>
<th>Temperature, °C</th>
<th>Yield, g</th>
<th>trans-1,4 configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>54</td>
<td>0.05</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>0.04</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.14</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.16</td>
<td>26</td>
</tr>
<tr>
<td>2.0</td>
<td>87</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

The infrared spectra of the polymers produced at the different ratios are distinctly different, as is the appearance of the polymers. The polymer formed at the first maximum is powdery and generally insoluble in common organic solvents and although its infrared spectrum may show some trans-1,4 content, it differs from those of 1,4 or 1,2-polydienes (Figure 2b). The polymer formed at the higher Mg/Ti or Al/Ti ratios is a soluble, non-resinous material whose infrared spectrum shows a preponderance of 1,4 units (Figure 2a).
Very few differences exist between the infrared spectra of the insoluble, powdery polymers prepared from the conjugated diene monomers and cyclized polyisoprenes prepared by cyclization of linear trans-1,4- (balata), cis-1,4- (Hevea) and 3,4-polyisoprenes. The spectra of the powdery butadiene polymers have the same characteristics as those of the powdery isoprene polymers and cyclized polyisoprenes.

Treatment of the powdery polymers which still contain some linear structures with sulphuric acid results in the disappearance of the absorption bands assigned to the linear forms (Figure 2c). The powdery polymers obtained directly from the monomers revert irreversibly to liquids at elevated temperatures in air. The reversion temperatures are 370° for the non-linear polyisoprene, 405° for the non-linear polybutadiene and 420° for the non-linear polychloroprene. The infrared spectra of the liquids are the same as those of their solid precursors except that the 1,4-units are absent in the former.

The similarity between the spectra of the polymers prepared from the conjugated diene monomers by the use of the Ziegler-type catalysts and the spectra of the cyclized polymers indicates that both types of polymers have the same polycyclic structure. The failure to cyclize 3,4-polyisoprene or cis-1,4-polyisoprene with the individual catalyst components or with the two component catalyst system under the conditions which are effective in the polymerization of the diene monomers to cyclopolymer confirms that the latter are formed directly from monomer and not as a result of the cyclization of initially formed linear polymers of these structures.

The exact structures of the cyclopolymer is not known. The infrared spectra are very simple and although structural assignments have been made to the various absorption bands which appear in the spectra, they
serve only as a basis for the postulation that the polymers contain fused cyclohexane rings. However, there is no direct evidence for the length of the blocks of fused rings. Examination of the spectra of cyclized polymers has led to the proposal that the blocks or segments contain 2–5 fused rings and are most probably tricyclic. By comparison the cyclopolymeres are considered more highly fused, i.e. at least 5 rings per segment.

Attempts to utilize nuclear magnetic resonance spectroscopy to confirm the cyclic character of the cyclopolymeres have been unsuccessful. The assignment of various peaks to the cyclic structure has been questioned.

The amount of cyclic structure but not the sequence length is obtained by difference after determining the absolute amount of unsaturation, i.e. the linear forms, by infrared analysis without the usual practice of normalizing so that the total unsaturation is 100 per cent and also, in the case of soluble polymers, by titration with iodine monochloride.

On the basis of spectral analyses and pyrolytic products, and particularly in consideration of the proposed mechanism of polymerization, which is discussed in a later section, the cyclopolymeres are presumed to contain perhydrophenanthrene (I) and/or perhydroanthracene (II) units, e.g. from butadiene:

![Diagram](https://via.placeholder.com/150)

**(I)**

**(II)**

**CYCLOPOLYMERIZATION AS A GENERAL CHARACTERISTIC OF DIENE POLYMERIZATION WITH CLASSICAL CATIONIC CATALYSTS**

The discovery that Ziegler-type catalysts RMgX–TiCl₄ and R₃Al–TiCl₄ containing an excess of the transition metal compound, and therefore presumably cationic initiators, catalyze the polymerization of butadiene, isoprene and chloroprene to cyclopolymeres, prompted an investigation of the extent of cyclopolymerization initiated by typical cationic catalysts. The probability of the occurrence of cyclic structures was enhanced by the low levels of unsaturation and the discrepancies between the infrared and chemical analyses of unsaturation reported in such polymers.

**Lewis acid catalysts**

The polymerization of isoprene to polymers with less than 20 per cent linear structures in the presence of ethyl aluminum dichloride and classical cationic catalysts, i.e. Lewis acids, is clearly shown in Tables 2 and 3.

The course of the reaction depends strongly upon the type of solvent used as the polymerization medium. Polymerization in n-heptane is charac-
**Cyclopolymerization of Conjugated Dienes**

**Table 2. Polymerization of isoprene in n-heptane medium***

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nature</th>
<th>Amount</th>
<th>Monomer conc., mmole</th>
<th>Time of Reaction, min</th>
<th>Conversion, %</th>
<th>Structure, %&lt;sup&gt;ab&lt;/sup&gt;</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIEtCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0-7</td>
<td>0-8</td>
<td>180</td>
<td>5</td>
<td>12</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>AIEtCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0-7</td>
<td>1-7</td>
<td>180</td>
<td>21</td>
<td>27</td>
<td>5</td>
<td>n.d.</td>
</tr>
<tr>
<td>AICl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0-8</td>
<td>0-8</td>
<td>120</td>
<td>6</td>
<td>2</td>
<td>1</td>
<td>n.d.</td>
</tr>
<tr>
<td>AlBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0-7</td>
<td>0-4</td>
<td>120</td>
<td>8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>TiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0-8</td>
<td>0-8</td>
<td>180</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0-8</td>
<td>0-8</td>
<td>180</td>
<td>6</td>
<td>2</td>
<td>1</td>
<td>n.d.</td>
</tr>
<tr>
<td>SnCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2-7</td>
<td>1-7</td>
<td>60</td>
<td>24</td>
<td>2</td>
<td>1</td>
<td>n.d.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0-8</td>
<td>0-8</td>
<td>60</td>
<td>28</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

— Catalyst in suspension
— 5 ml of moist n-heptane added

<sup>a</sup> 30 ml of solvent. 21 C.
<sup>b</sup> n. d. = not detectable.

Characterized by an extremely fast initial rate of polymerization followed by a period when the reaction practically stops. The conversion at that stage is very low and the polymers are powdery materials, insoluble in hydrocarbon and most common organic solvents. The infrared spectra generally do not indicate the presence of any absorption bands characteristic of common linear addition forms.

Although ethyl aluminum dichloride, aluminum bromide and stannic chloride behave in a similar manner, titanium tetrachloride is completely inactive unless moisture is introduced into the reaction mixture (Table 2). Nevertheless, the resultant cyclopolyisoprene contains less than 5 per cent residual unsaturation.

**Table 3. Polymerization of isoprene in aromatic solvents at 21 °C**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time, min</th>
<th>Yield, %</th>
<th>Microstructure, %&lt;sup&gt;ab&lt;/sup&gt;</th>
<th>Molecular weight&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Unsaturation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtAlCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Benzene</td>
<td>60</td>
<td>28.6</td>
<td>5</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>60</td>
<td>53.1</td>
<td>7</td>
<td>11</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Xylene</td>
<td>60</td>
<td>73.5</td>
<td>—</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Benzene</td>
<td>60</td>
<td>58.8</td>
<td>5</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>60</td>
<td>73.6</td>
<td>—</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>AlBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Benzene</td>
<td>60</td>
<td>79.5</td>
<td>7</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>60</td>
<td>91.3</td>
<td>4</td>
<td>8</td>
<td>0.5</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;TiCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Toluene</td>
<td>60</td>
<td>20.6</td>
<td>7</td>
<td>14</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>180</td>
<td>3.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TiCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Toluene</td>
<td>30</td>
<td>94.2</td>
<td>5</td>
<td>11</td>
<td>0.6</td>
</tr>
<tr>
<td>EtAlCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Toluene</td>
<td>60</td>
<td>26.5</td>
<td>8</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>SnCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Toluene</td>
<td>60</td>
<td>11.8</td>
<td>8</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

<sup>a</sup> [Isoprene] = 0.6-1.4 mole/l; 50 ml solvent; [catalyst] = 0.7-11 mole/ml except [SnCl<sub>4</sub>] = 12 mmole and [SbCl<sub>3</sub>] = 5 mmole.
<sup>b</sup> Light scattering.
<sup>c</sup> GPC.
The low conversion is not indicative of the termination of polymerization. As shown in Figure 3, the introduction of additional amounts of monomer results in further polymerization until a new limiting conversion or equilibrium is established. This process may be repeated many times, increasing the conversion at each step. When an equilibrium mixture is sealed off and stored, nearly 100 per cent conversion is attained after several weeks.

Polymerization rates in aromatic solvents are much higher than in $n$-heptane and the equilibrium conversion is also much higher (Table 3). The polymers are either white powders, tacky solids or oils depending upon the solvent and are very soluble in benzene. The molecular weight of the cyclopolyisoprenes produced in benzene range between 50,000 and 100,000 (light scattering).

The content of linear structures is higher than in cyclopolyisoprene prepared in heptane but does not exceed 30 per cent. independent of molecular weight (provided the product is not an oligomer). The use of aromatic solvents as reaction media results in the incorporation of high amounts of aromatic moieties, indicating that extensive chain transfer with the solvent takes place, a recognized characteristic of cationic polymerization. However, in contrast to conventional reactions of the latter type, wherein the transfer
reaction results in chain termination and the incorporation of only one phenyl group per chain, the cyclopolymerization yields polymers of high molecular weight containing more than one phenyl group per chain.

Polymerization rates and limiting conversions are much higher in halogenated solvents than in aromatic solvents and a higher concentration of linear forms, predominantly trans-1,4, is present in the cyclopolymerizers. Although no solvent residues are detectable in cyclopolyisoprene prepared in chlorinated benzenes, some chlorine is present in polymers prepared in methylene chloride or carbon tetrachloride\(^1\).

**Ethyl aluminum halide-titanium tetrahalide catalysts**

Cyclopolymerization of conjugated dienes is catalyzed not only by Lewis acids and \( \text{RMgX-\text{TiCl}_4} \) and \( \text{R}_3\text{Al-\text{TiCl}_4} \) combinations but also by Ziegler-type catalysts based on diethyl aluminum halides.

The polymerization of isoprene in \( n \)-heptane medium by the two component catalyst systems \((\text{C}_2\text{H}_5)_2\text{AlX-\text{TiCl}_4} \) (where X is fluoride, chloride or bromide), while maintaining a constant monomer concentration, is characterized by a strong dependence of the reaction rate on the Al/Ti ratio, accompanied by changes in the microstructure of the polymers (Tables 4 and 5).

### Table 4. Polymerization of isoprene with \((\text{C}_2\text{H}_5)_2\text{AlX + TiCl}_4\) catalyst\(^a\)

<table>
<thead>
<tr>
<th>((\text{C}_2\text{H}_5)_2\text{AlCl})</th>
<th>((\text{C}_2\text{H}_5)_2\text{AlF})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al/Ti Mole Ratio</strong></td>
<td><strong>Yield, g</strong></td>
</tr>
<tr>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>1.25</td>
<td>0.6</td>
</tr>
<tr>
<td>1.75</td>
<td>0.5</td>
</tr>
<tr>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td>2.5</td>
<td>0.1</td>
</tr>
<tr>
<td>2.75</td>
<td>0.2</td>
</tr>
<tr>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\(^a\) Catalyst components mixed for 60 min in heptane in absence of monomer at 21 C.

Isoprene content maintained constant during 3 h reaction period.

\(^b\) Yield after 2 h.

At certain ratios of the components of the catalyst the polymerization rate is practically zero, i.e. the catalyst is inactive. At ratios lower than these critical values, powdery, insoluble polymers are formed. Infrared analysis shows that these products are essentially all cyclic polysoprenes. At Al/Ti ratios higher than the critical value, the polymerization rate rises again and the polymers obtained are a mixture of linear and cyclic structures.

The maximum activity for the formation of cyclopolyisoprene occurs at
approximately the same Al/Ti molar ratio of 0.75, independent of the nature of the halogen. This corresponds to the reactions

\[(\text{C}_2\text{H}_5)_2\text{AlX} \rightarrow \text{C}_2\text{H}_5\text{AlX}_2 (100\%)\]

\[\text{TiCl}_4 \rightarrow \text{TiCl}_3 (75\%) + \text{TiCl}_4 (25\%)\]

The significantly lower activity of \(\text{C}_2\text{H}_5\text{AlCl}_2\), \(\beta\)-\(\text{TiCl}_3\), \(\text{AlCl}_3\), \(\beta\)-\(\text{TiCl}_3\)–\(\text{C}_2\text{H}_5\text{AlCl}_2\) and \(\beta\)-\(\text{TiCl}_3\)–\(\text{AlCl}_3\) and the inactivity of \((\text{C}_2\text{H}_5)_2\text{AlX}\) indicate that the active catalytic species is derived from the reaction of ethyl aluminum dihalide with titanium tetrachloride. The most active catalysts are obtained when the reaction of diethyl aluminum halide with titanium tetrachloride yields a 4:1 mixture of \(\text{C}_2\text{H}_5\text{AlX}_2\)–\(\text{TiCl}_4\).

### Table 5. Polymerization of isoprene with \((\text{C}_2\text{H}_5)_2\text{AlX} + \text{TiCl}_4\) catalyst

<table>
<thead>
<tr>
<th>((\text{C}_2\text{H}_5)_2\text{Al})</th>
<th>((\text{C}_2\text{H}_5)_2\text{AlBr})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield, g</strong></td>
<td><strong>Cyclic Structure, %</strong></td>
</tr>
<tr>
<td>Al/Ti Mole Ratio</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* Catalyst components mixed for 60 min in heptane in absence of monomer at 21°C. Isoprene content maintained constant during 3 h reaction period.

Polymerizations catalyzed by the diethyl aluminum iodide–titanium tetrachloride system (Table 5) are marked by a rapid consumption of monomer initially, cessation of the reaction at very low conversions and the formation of cyclopolyisoprenes at all Al/Ti ratios.

The very sharp minimum of polymerization rates at an Al/Ti ratio of 1.4 with the \((\text{C}_2\text{H}_5)_2\text{AlF}–\text{TiCl}_4\) system and the very broad region of minimum rates for systems containing the chloride and bromide are probably due to the decreasing reducing power and the increasing acidity of the complex in the series, F, Cl, Br.

The polymerization of isoprene with ethyl aluminum dichloride in heptane yields solid cyclopolyisoprene. The catalytic activity is markedly increased by the addition of titanium tetrachloride although the dry metal halide per se is not a catalyst for isoprene polymerization and titanium tetrachloride containing traces of moisture yields only small amounts of solid polymer.

Analogous to the observations described earlier with other catalyst systems, in polymerizations carried out while maintaining a constant isoprene partial pressure with a low concentration of catalyst components, the polymerization is characterized by a rapid initial stage, followed by a constant rate of monomer consumption and then a cessation of reaction.\(^{13}\)
Table 6. Polymerization of isoprene with EtAlCl$_2$ + TiCl$_4$ catalyst in heptane

<table>
<thead>
<tr>
<th>[TiCl$_4$] mmole</th>
<th>Al/Ti mole ratio</th>
<th>Yield, %</th>
<th>Cyclic structure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>—</td>
<td>0.25</td>
<td>91</td>
</tr>
<tr>
<td>0.22</td>
<td>3.18</td>
<td>0.5</td>
<td>87</td>
</tr>
<tr>
<td>0.44</td>
<td>1.59</td>
<td>0.8</td>
<td>87</td>
</tr>
<tr>
<td>0.8</td>
<td>0.87</td>
<td>1.1</td>
<td>98</td>
</tr>
<tr>
<td>1.3</td>
<td>0.54</td>
<td>1.7</td>
<td>91</td>
</tr>
<tr>
<td>4.1</td>
<td>0.17</td>
<td>2.9</td>
<td>94</td>
</tr>
<tr>
<td>7.1</td>
<td>0.1</td>
<td>4.1</td>
<td>88</td>
</tr>
<tr>
<td>8.1</td>
<td>0.086</td>
<td>3.6</td>
<td>93</td>
</tr>
<tr>
<td>16.2</td>
<td>0.043</td>
<td>2.7</td>
<td>93</td>
</tr>
</tbody>
</table>

Catalyst components mixed for 60 min in 35 ml heptane in absence of monomer at 21°C. Isoprene concentration maintained constant at 0.87 mole/l during 3 h reaction period.

The rate is dependent upon the initial concentrations of the catalyst components. The polymer yield after a fixed reaction period depends upon the initial concentration of either of the two catalyst components (Tables 6 and 7). Since both components are cationic initiators, cyclopolymer are produced irrespective of which component is present in excess.

Table 7. Polymerization of isoprene with EtAlCl$_2$ + TiCl$_4$ catalyst in heptane

<table>
<thead>
<tr>
<th>[EtAlCl$_2$] mmole</th>
<th>Al/Ti mole ratio</th>
<th>Yield, g</th>
<th>Cyclic structure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>—</td>
<td>—</td>
<td>93</td>
</tr>
<tr>
<td>0.7</td>
<td>1.59</td>
<td>0.8</td>
<td>93</td>
</tr>
<tr>
<td>1.35</td>
<td>3.1</td>
<td>2.6</td>
<td>92</td>
</tr>
<tr>
<td>2.7</td>
<td>6.1</td>
<td>2.7</td>
<td>92</td>
</tr>
<tr>
<td>4.05</td>
<td>9.2</td>
<td>2.6</td>
<td>86</td>
</tr>
<tr>
<td>7.5</td>
<td>18.7</td>
<td>1.7</td>
<td>95</td>
</tr>
</tbody>
</table>

Catalyst components mixed for 60 min in 35 ml heptane in absence of monomer at 21°C. Isoprene concentration maintained constant at 0.87 mole/l during 3 h reaction period.

The yield and rate of polymerization in the initial stage depends upon the time during which the two catalyst components react before the addition of monomer (Figure 4). On increasing the catalyst aging or reaction time, the polymer yield after 3 hours first increases and after reaching a maximum decreases (Figure 5). The position of the maximum depends upon the initial Al/Ti ratio.

It is apparent that the reaction of the two catalyst components yields an intermediate whose catalytic activity is higher than that of either
component. The cyclic structure of the polymers indicates that the active species are probably cations formed by dissociation of the reaction products. The concentration of the active species passes through a maximum in the course of the reaction between catalyst components indicating that the intermediate product is deactivated. The deactivation occurs in the absence of monomer, as shown by the effect of catalyst aging, as well as in the presence of monomer, as shown by the decrease in polymerization rate and finally cessation of polymerization. The electrical conductivity of the system after mixing the components first increases and after reaching a maximum decreases. The changes in conductivity parallel changes in polymerization activity.

The conversion of isoprene to cycopolymers increases with increasing temperature in n-heptane as well as in a mixture of n-heptane and benzene (Table 8). The apparent yield in benzene at times exceeds 100 per cent. owing to the chemically bonded solvent molecules. The cycopolymers
prepared in benzene have a higher solubility than those prepared in \( n \)-heptane. The greater solubility cannot be explained by low molecular weight since cyclopolyisoprene with a molecular weight of 3,000,000 has been found to be soluble in benzene.

\[
\begin{array}{cccccc}
\text{Benzene} & \text{Temp.} & \text{Yield.} & \text{Benzen} & \phi/100 \text{m.u.} & \text{Molecular} \\
\text{vol-%} & ^\circ\text{C} & \% & \text{Soluble.}\% & & \text{weight} \\
100 & 72 & 94 & 87 & 2:1 & 100,000 \text{L} \\
 & 63 & 94 & 100 & 1:9 & 3,000,000 \text{L} \\
 & 43 & 94 & 90 & 1:9 & \\
 & 25 & 91 & 90 & 3:0 & \\
 & 10 & 88 & 78 & 2:5 & 3,000,000 \text{L} \\
22 & 68 & 81 & 54 & 0:8 & 2300 \\
 & 25 & 53 & 62 & 1:0 & 7600 \\
 & 5 & 36 & 57 & 0:9 & \\
 & -15 & 27 & 67 & 1:1 & 3500 \\
\end{array}
\]

\* Total solvent 9: ml [isoprene] = 1:1 mole \( L \) \text{ reaction time 1 \( h \)}
\* Phenyl groups per 100 monomer units.
\* Ebulliometry except \( L \) = lightscattering.

In conventional cationic polymerization, benzene acts as a chain transfer agent and terminates chain growth. In the cyclopolymerization of conjugated dienes with the \( \text{C}_2\text{H}_5\text{AlCl}_2-\text{TiCl}_4 \) catalyst, benzene is incorporated into the polymer chain without terminating chain growth. In cyclopolyisoprene two phenyl groups are incorporated into the polymer structure per 100 monomer units, independent of molecular weight from \( 1 \times 10^4 \) to \( 2 \times 10^6 \) (Table 8), while cyclopolybutadiene contains as many as 7—9 phenyl groups per 100 monomer units (Table 9). The concentration of phenyl groups in the cyclopolymer depends on the solvent composition (Table 8) and the catalyst composition (Table 9).

\[
\begin{array}{cccc}
\text{[EtAlCl}_2\text{]} & \text{[TiCl}_4\text{]} & \phi/100 \text{m.u.} & \text{CH}_3 \text{ groups} \\
\text{mole/l} & \text{mole/l} & & \text{Relative} \\
0.027 & 0.20 & 7 & 17 & 48 \\
0.033 & 0.67 & 7 & 14 & 55 \\
0.050 & 0.033 & 9 & 22 & 63 \\
0.27 & 0.033 & 3 & 47 & 5 \\
\end{array}
\]

\* 20: 3 \( h \) [Butadiene] = constant = 1 mole/300 ml benzene
\* m. u. = monomer unit.

The concentration of double bonds in the cyclopolymer is essentially independent of temperature and benzene/heptane ratio. Cyclopolyisoprene contains one double bond per 3—5 monomer units, while cyclopolybutadiene
contains one double bond for 10 or more monomer units depending upon the ethyl aluminum dichloride concentration (Table 2). Infrared analysis shows that 10-40 per cent of the residual double bonds are not conventional ‘linear’ double bonds but are internal olefinic double bonds in a ring, i.e. cycloalkenyl.

Infrared analysis reveals the presence of methyl groups in the cyclopolymer. The content of methyl groups in cyclopolybutadiene is relatively high, increasing with increasing excess of titanium tetrachloride in the catalyst\textsuperscript{15}. On the other hand, the methyl groups are almost absent when the catalyst contains a large excess of ethyl aluminum dichloride (Table 2).

<table>
<thead>
<tr>
<th>Ti &gt; Al</th>
<th>Al &gt; Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>Rapid decrease of initial polymerization rate</td>
</tr>
<tr>
<td>Methyl groups in polymer</td>
<td>No methyl groups in polymer</td>
</tr>
<tr>
<td>10-12% of trans-1,4 units</td>
<td>24-26% of trans-1,4 units</td>
</tr>
<tr>
<td>2-3% of 1,2 units</td>
<td>Less than 0.4% of 1,2 units</td>
</tr>
<tr>
<td>Infrared spectrum had no band at 1360 cm\textsuperscript{-1}</td>
<td>Infrared absorption band at 1360 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>Aromatic solvents</td>
<td>Fragments of solvent in polymer</td>
</tr>
<tr>
<td>About 12% of trans-1,4 units</td>
<td>Up to 40% of trans-1,4 units</td>
</tr>
<tr>
<td>About 3% of 1,2 units</td>
<td>Less than 1% of 1,2 units</td>
</tr>
<tr>
<td>Large amount of methyl groups in polymer</td>
<td>Practically no methyl groups in polymer</td>
</tr>
</tbody>
</table>

These and other differences in the polycyclobutadienes, prepared with an ethyl aluminum dichloride–titanium tetrachloride catalyst, which result from the use of catalysts containing either excess titanium or excess aluminum, are summarized in Table 10\textsuperscript{16}. The differences may be explained on the basis of different active centres resulting in different initiation or propagation processes, as discussed in the mechanism section.

**CHARACTERISTICS OF COPOLYMERIZATION**

The characteristics generally observed in the cyclopolymerization of conjugated dienes are summarized in Table 11. The differences noted in butadiene polymerization with the $C_2H_5AlCl_2-TiCl_4$ catalyst system as a function of the Al/Ti ratio, i.e. the extent of incorporation of solvent moieties, only represent a minor deviation from the general characteristics.

Irrespective of the nature of the catalyst, the rate of polymerization of butadiene or isoprene at constant monomer pressure gradually decreases as the reaction proceeds. A rapid initial stage is followed by a constant rate of monomer consumption and then a cessation of reaction. Although in some cases, e.g. the polymerization of isoprene catalyzed by aluminum bromide in aromatic solvents\textsuperscript{17}, the stage of zero reaction rate is not reached for many hours, the reaction rate gradually decreases with time.
The reaction between ethyl aluminum dichloride and titanium tetra-
chloride in solution in the absence of monomer is relatively slow. Solid
 titanium trichloride appears only after about 15 minutes at \(20^\circ\). The appear-
ance of the solid phase is related to the formation of active centres. This
catalyst system is active only when the solid is present. However, a soluble
complex which appears simultaneously with the solid is also catalytically
active. Although isoprene slightly accelerates the reaction, the maximum
activity of the catalyst is attained only after one hour of polymerization.
No such induction period is observed with butadiene. By mixing the
catalyst components in the presence of butadiene an active catalyst forms
almost immediately. The solid phase of titanium trichloride also appears
within a few seconds after the addition of butadiene to a mixture of the
catalyst components. It follows that butadiene somehow participates in the
reduction of \(Ti^{4+}\) to \(Ti^{3+}\).

Table 11 Characteristics of cyclopolymerization

(a) Effective catalytic species are cationic in nature
(b) Polymerization proceeds to a low conversion
(c) An equilibrium exists between monomer, catalyst and polymer
(d) Addition of monomer to the dormant equilibrium mixture reinitiates polymerization which
again achieves a limiting equilibrium conversion
(e) The molecular weight increases with increased conversion
(f) The polymer contains non-terminal linear unsaturation as well as fused cyclic segments
(g) Polymerization in aromatic solvents results in the incorporation of phenyl groups in the
polymer structure
(h) Polymers with low intrinsic or reduced viscosities have relatively high molecular weights
as measured by light scattering

The polymerization of butadiene with ethyl aluminum dibromide–
titanium tetrachloride and aluminum tribromide–titanium tetrachloride
proceed in a comparable manner to the polymerization catalyzed by the
ethyl aluminum dichloride–titanium tetrachloride system.

The initial rate of polymerization of butadiene with the latter catalyst
is strongly influenced by the addition of cocatalytic amounts of iodine.
In equimolar proportions with respect to the catalyst, iodine increases the
initial rate of polymerization in heptane almost 30 times (Figure 6). However,
the addition of more than about 3 moles of iodine per mole of catalyst does
not cause any further increase in the rate of polymerization. The added
iodine is quickly consumed and the polymerization rate in the later stages
is the same as in the absence of iodine. The iodine can be removed from the
polymer at temperatures above 130\(^\circ\). The resulting polymer has a structure
similar to that obtained with the same catalyst without the iodine. The
iodine has little effect when the catalyst components are present in equimolar
amounts.

When the polymerization of isoprene is carried out in heptane with ethyl
aluminum dichloride as catalyst at \(20^\circ\), and the isoprene concentration is
maintained constant by the introduction of monomer at a rate equal to its
consumption, the limiting conversion is soon attained. However, the addition
of styrene monomer results in a renewed consumption of isoprene and
additional isoprene must be added to maintain a constant concentration. The isoprene consumption curve duplicates the initial curve and an equilibrium is again established. This process may be repeated again and the final isoprene consumption is identical with that in a homopolymerization of isoprene under the same conditions (Figure 7). The re-establishment of the polymerization activity of isoprene after the addition of styrene is apparently due to the liberation of the catalyst from the monomer–catalyst complex which is in equilibrium with free monomer\textsuperscript{18, 19}. The styrene is incorporated into the polymer chain in the form of a block copolymer in which the isoprene is present as saturated cyclic segments.
SOLVENT EFFECT ON CYCLOPOLYMERIZATION

The cyclopolymerization of isoprene in hydrocarbon solvents is initiated to a limited extent by Lewis acids which are dimeric in nature, e.g. aluminum tribromide and aluminum trichloride, or by Lewis acids in the presence of cocatalysts, e.g. titanium tetrachloride–water. However, the rate and extent of cyclopolymerization is greatly increased when Lewis acids such as antimony pentachloride, titanium tetrachloride, aluminum trichloride and phosphorus pentfluoride are used as catalysts in the absence of a cocatalyst with nitrobenzene as reaction medium.

Stable carbonium ion salts such as cycloheptatrienyl (tropylium) or triphenylmethyl (trityl) hexachloroantimonate have been shown to initiate the non-terminating cationic polymerization of cyclic ethers such as tetrahydrofuran and vinyl monomers such as alkyl vinyl ethers, N-vinylcarbazole and alkoxystyrenes, using methylene chloride or acetonitrile as reaction media.

Little or no polymerization occurs when tropylium hexachloroantimonate and trityl hexachloroantimonate are used as catalysts for the attempted polymerization of isoprene at 20°C in n-heptane, benzene, toluene, acetonitrile, methylene chloride or nitromethane. The cyclopolymerization of isoprene is readily effected when nitrobenzene is used as the reaction medium. n-Heptane and methylene chloride may be mixed with the nitrobenzene, the yield of polymer increasing in direct proportion to the nitrobenzene content of the solvent mixture (Table 12).

Table 12. Influence of solvent composition on isoprene polymerization initiated by tropylium and trityl salts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent (vol/vol)</th>
<th>Temp., °C</th>
<th>Conversion, %</th>
<th>[η] dl/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_3$CCl + SbCl$_5$</td>
<td>CH$_2$Cl$_2$</td>
<td>0</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$/φNO$_2$</td>
<td>0</td>
<td>6-9</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>20</td>
<td>51-5</td>
<td>0-057</td>
</tr>
<tr>
<td>$\phi_3$C*SbCl$_6$</td>
<td>n-C$<em>7$H$</em>{16}$</td>
<td>0</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>n-C$<em>7$H$</em>{16}$/φNO$_2$</td>
<td>20</td>
<td>22-0</td>
<td>0-040</td>
</tr>
<tr>
<td></td>
<td>3:7</td>
<td>20</td>
<td>44-0</td>
<td>0-056</td>
</tr>
<tr>
<td>C$_7$H$_7$SbCl$_6$</td>
<td>φNO$_2$</td>
<td>20</td>
<td>26-3</td>
<td>0-049</td>
</tr>
<tr>
<td></td>
<td>φNO$_2$</td>
<td>20</td>
<td>33-8</td>
<td>0-055</td>
</tr>
</tbody>
</table>

* [isoprene] = 3 mol/1.6 moles/l; [catalyst] = 1 mmole / 0-016 mole/l solvents, 50 ml; temperature 20°C; time 100 min.

At constant isoprene concentration, a limiting conversion is reached, although polymerization resumes on the addition of monomer, analogous to the behaviour in the cyclopolymerization of isoprene in benzene or heptane with ethyl aluminum dichloride or ethyl aluminum dichloride–titanium tetrachloride catalysts.

Triphenylmethyl groups are detected in the cyclopolyisoprene prepared.
with the trityl salt. However, no tropylium residues are detectable in polymers prepared with the tropylium salt catalyst. The content of triphenylmethyl groups in the cyclopolyisoprene is in inverse relation to the nitrobenzene content of the reaction medium.

The cyclopolymer is 10—45 per cent of unsaturation (trans-1,4 and 3,4). The unsaturation decreases with increasing trityl ion concentration but is independent of the tropylium ion concentration.

MECHANISM OF CYCLOPOLYMERIZATION

Several qualitative mechanisms have been proposed to account for the formation of cyclopolymer from conjugated dienes. The earliest proposal involved the cationic polymerization of the diene to tactic 1,2 (butadiene) or 3,4 (isoprene) polymer. Cyclization resulted from the reversal of the direction of the polymerization reaction or the copolymerization of additional monomer or a growing chain with the pendant 1,2 (or 3,4) groups.

The second proposal involved the dissociation of ethyl aluminum dichloride to the ion pair Al(C_2H_5)_2AlCl which reacted with the isoprene monomer to form a π-complex. Polymerization presumably proceeded in accordance with equation 1.

\[
\begin{align*}
(A) & \quad \text{or} \\
(A) & \quad \text{or} \\
\text{or} & \\
\text{or} &
\end{align*}
\]

Neither of these proposals satisfactorily explains the various observed characteristics of cyclopolymerization. The latter and the proposed structure of the cyclopolymer are consistent with a Diels—Alder charge transfer mechanism. A mechanism which adequately incorporated the experimental observations was proposed but modified since it led to a perhydroanthracene structure and did not account for the perhydrophenanthrene structure which is presently favored.

The active initiating species in the case of C_2H_5AlCl_2 is the ion pair resulting from the dissociation of the dimer, as shown in equation 2.
Cyclopolymerization of conjugated dienes

In the case of $\text{C}_2\text{H}_5\text{AlCl}_2 - \text{TiCl}_4$ or $(\text{C}_2\text{H}_5)_2\text{AlCl} - \text{TiCl}_4$ which produces the dichloride, the ion pair has the analogous structure shown in equation 3.

$$\text{C}_2\text{H}_5\text{TiCl}_3 + \text{AlCl}_3 \cdot \text{C}_2\text{H}_5\text{AlCl}_3$$

or

$$\text{(C}_2\text{H}_5\text{AlCl}_2)_2 + \text{TiCl}_4$$

$$\text{C}_2\text{H}_5\text{TiCl}_3 \cdot \text{AlCl}_2^+ + \text{C}_2\text{H}_5\text{AlCl}_3^-$$

(3)

While these reactions adequately provide for the formation of an electron-deficient particle which is capable of initiating cyclopolymerization in hydrocarbon solvents, the failure to initiate polymerization in these solvents with tropylium and trityl ion salts indicates that dissociation alone does not necessarily provide an active particle. In the latter cases, the interaction of the trityl or tropylium cation or the salt with the strongly electron-accepting nitrobenzene apparently produces a charge-transfer complex which is a better electron acceptor than the original ions and is the actual active species in the initiation. The active species in the Lewis acid–nitrobenzene system, e.g. antimony pentachloride, may be $\text{SbCl}_4^+ (\text{C}_6\text{H}_5\text{NO}_2)\text{Cl}^-$. The formation of titanium trichloride in catalyst systems containing titanium tetrachloride may be indicative of the presence of $\text{TiCl}_3^+$ as the active initiating species.

Notwithstanding the actual nature of the initiating species it is sufficient to indicate that it is an electron-deficient particle which is thus an electron acceptor. For the sake of simplicity in the following discussion, the catalyst-derived electron acceptor is represented as $A^+$ with the understanding that, assuming it is part of an ion pair, there is a counteranion which is intentionally omitted from the equation. Butadiene is shown as the monomer with the understanding that analogous reactions are proposed for isoprene and other conjugated dienes.

Formation of active species

The active centre results from the formation of a donor–acceptor charge transfer complex through a one-electron transfer from the diene monomer to the catalyst cation.

$$A^+ + \text{A} \rightarrow A^\circ$$

(4)

The monomer cation-radical may also exist in the allylic resonance form.

$$+\cdots+ \rightarrow +\cdots+$$

(5)
Initiation and ring formation

The 1,2 monomer cation-radical or its allylic resonance form, the 1,4 cation-radical, adds to one double bond of a diene monomer molecule, followed by addition to the residual double bond of the original monomer cation radical, resulting in ring closure and the generation of a 1,3 cation-radical, as shown in equations (6) and (7).

\[ \text{Equation (6)} \]

\[ \text{Equation (7)} \]

Propagation

The propagation step involves the 1,4 addition of the cation to the diene monomer followed by the 3,2 addition of the radical to the residual double bond. It is also possible that the radical undergoes the 1,4 addition while the cation undergoes the 3,2 addition. The resultant cyclodiene has a perhydrophenanthrene structure.
Residual unsaturation results from the 1,4 addition of monomer to the cation or radical species without the subsequent 3,2 addition step.

Phenyl groups are incorporated in the polymer when the reaction is carried out in aromatic solvents as a result of cationic alkylation and proton elimination. Methyl groups are formed when the 1,3 cation-radical undergoes intramolecular hydride transfer.

\[
\begin{align*}
\text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}} \rightarrow \text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}} \\
\text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}} \rightarrow \text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}}
\end{align*}
\]

The internal or ring unsaturation, which accounts for 10–40 per cent of the residual double bonds in a cyclodiene polymer, results from deprotonation at the carbon adjacent to the cation, a step well known in the cyclization of diene polymers.

\[
\begin{align*}
\text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}} \rightarrow \text{Cyclohexane}^* + \overset{\phi \text{H}}{\text{+}}
\end{align*}
\]

The residual linear or internal unsaturation in the polymer chain may react with activated monomer cation-radical in a reinitiation reaction. This results in the development of highly branched structures consistent with the brittleness of the cyclopolymer and the low intrinsic viscosities which are given by polymers whose molecular weights are quite high according to the light scattering measurements.
In the cyclopolymerization of butadiene with the $\text{C}_2\text{H}_5\text{AlCl}_2-\text{TiCl}_4$ catalyst, when Ti $>$ Al the cyclopolymer contains methyl groups and aromatic moieties when the reaction is carried out in an aromatic solvent. When Al $>$ Ti methyl groups and solvent moieties are essentially absent. The Ti $>$ Al catalyst is presumed to promote 1,3 cation-radical propagation with transoid monomer to yield the perhydrophenanthrene structure, as depicted in equations 6–8. The Al $>$ Ti catalyst is presumed to promote 1,2 cation-radical propagation with cisoid monomer to yield a perhydroanthracene structure, as shown in equation 13.

Although the reactions indicated in the above sequences imply that the sequence length of fused rings is infinite, the sequence is considered to be approximately five or six with connecting single bonds, due to reinitiation on the terminal vinyl groups shown in equations 8 and 13, or linear unsaturation.

The generation of active centres has been represented in equation 4 as a one-electron transfer to the catalyst-derived cation, producing a two-centre monomer cation-radical. The occurrence of a two-electron transfer, as in conventional cationic polymerization, would produce a conventional cationic species.

Monomer addition can take place in either a 1,2 and/or a 1,4 manner.
The carbonium ion at the end of the chain is a relatively stable allylic cation with reduced activity.

\[
\begin{align*}
\text{A}^+ \text{B}^- & \rightleftharpoons \text{A}^- \text{B}^+ \\
\end{align*}
\]

(17)

The resonance stabilization of the allylic cation accounts for the initial limiting conversion and the slow monomer addition over an extended period.

The reaction mixture, in the dormant state, contains monomer, polymer and catalyst. The low or negligible reactivity in this state is indicative of the tightness of the ion pairs \(\text{A}^+(-\text{monomer})\text{B}^-\) and \(\text{A}^+(-\text{polymer})\text{B}^-\) as compared to the catalyst, i.e. the reaction product of the catalyst components \(\text{A}^+\text{B}^-\).

On the addition of new monomer, i.e. an increase in the concentration of monomer, the tight ion pairs are loosened, possibly through solvation, and the \(\text{A}^+\text{B}^-\) ion pair is made available for the one-electron transfer monomer activation.

\[
\begin{align*}
\text{A}^+\text{B}^- + \text{M} & \rightarrow \text{A}^+(-\text{M})\text{B}^- \\
\text{A}^+(-\text{M})\text{B}^- + \text{M} & \rightarrow \text{A}^+\text{B}^- + 2\text{M} \\
\text{A}^+(-\text{P})\text{B}^- + \text{M} & \rightarrow \text{A}^+\text{B}^- + \text{P} + \text{M} \\
\text{A}^+\text{B}^- + \text{M} & \rightarrow \text{A}^+ \text{M}^- \\
\text{A}^+ \text{M}^- + \text{M} & \rightarrow \text{A}^+ \text{P}^+\text{B}^- \\
\end{align*}
\]

(18) \hspace{1cm} (19) \hspace{1cm} (20) \hspace{1cm} (21) \hspace{1cm} (22)

The participation of both two-electron and one-electron transfer reactions in diene polymerization is highly probable although the stronger the electron acceptor the greater the contribution of the one-electron transfer reaction. The \(\gamma\)-ray initiated polymerization of butadiene and isoprene at 20° and at \(-78^\circ\) yields polymers which are linear and of mixed linear and cyclic structures, respectively²⁹.

Due to steric factors the polymerization of 2,3-dimethyl-1,3-butadiene yields polymer containing monocyclic units and reduced unsaturation when the catalyst is ethyl aluminum dichloride or (\(i\)-\(C_4\text{H}_9\))₃\(\text{Al} - \text{TiCl}_4\) with \(\text{Ti} > \text{Al}\)³⁰. The monocyclic structure is also formed when the polymerization is initiated by \(\gamma\)-rays in bulk at \(-78^\circ\) or in a thiourea canal complex at 20° ²⁹.

CONCLUSIONS

The formation of essentially saturated polymers containing fused cyclohexane rings is apparently a characteristic of the polymerization of conjugated dienes under the influence of all cationic catalysts. The amount of cyclic structures and linear unsaturation is dependent upon the electron accepting ability of the catalyst although the interaction of the catalyst with the solvent, where the latter is a strong electron acceptor such as nitrobenzene, may greatly enhance the electron accepting ability of the catalyst.

The inability to detect the cyclic structures by either infrared analysis or nuclear magnetic resonance spectroscopy emphasizes the importance of
chemical analysis as an adjunct to instrumental analysis in the determination of microstructure in diene polymers. The need to utilize absolute values rather than normalized values in the infrared analysis is strongly indicated by the 100 per cent linear unsaturation reported for polymers which may contain less than 10 per cent unsaturation.

References