

# POLYMERISATION OF DEC-1-ENE.

## II.\* EFFECT OF REACTION TEMPERATURE

By K. I. BEYNON, C. B. MILNE and D. SOUTHERN

The effect of temperature on the polymerisation of dec-1-ene has been studied, the catalysts used being (a) a catalyst prepared by mixing triethylaluminium and titanium tetrachloride at a molar ratio of 0.3:1 and (b) aluminium chloride. Polymers prepared at room temperature with triethylaluminium/titanium tetrachloride contain an average of one double bond per molecule. Increase in temperature from 20 to 150° produces saturated polymers of higher viscosity. The loss of olefinic unsaturation is due to cyclisation reactions, which produce aromatics and cycloalkanes, and to disproportionation reactions. An increase in reaction temperature from 20 to 150° with aluminium chloride as catalyst has little effect other than to reduce the viscosity of the polymer. The polymers produced at high temperatures by both catalyst systems are very similar. It is concluded that the active catalyst species in the triethylaluminium/titanium tetrachloride system at 150° is aluminium chloride or a complex containing it.

### Introduction

The polymerisation of dec-1-ene has been studied previously,<sup>1</sup> using catalysts prepared by mixing triethylaluminium and titanium tetrachloride. The properties of the polymers varied with the ratio of the two components of the catalyst. With triethylaluminium and titanium tetrachloride at molar ratios less than about 0.8:1 liquid polymers were obtained; with ratios greater than 1:1 waxy polymers were formed. The difference was considered to arise from a change in the reaction mechanism which was thought to be predominantly cationic at lower ratios (<1:1) and predominantly anionic at higher ratios (>1:1).

The effect of temperature on the polymerisation was also briefly studied, the mixed catalyst being used at a molar ratio of 0.3:1. The effects of an increase in reaction temperature from 20° to 150° were:

- (i) The melting point of the polymer was lowered from -43° to -52°.
- (ii) The bromine number of the polymer decreased from 16-17 to less than 1.
- (iii) The viscosity of the polymer at 100°F ( $V_K 100^\circ F$ ) increased from 58cS to 82cS. (This is unusual; in most cationic polymerisations the molecular weight of the product decreases as the reaction temperature is increased).
- (iv) The K.V.I. (kinematic viscosity index) of the polymer decreased from 144 to 129 (the K.V.I. is a measure of the change of viscosity with temperature and its significance has been discussed previously<sup>1</sup>).
- (v) Unpolymerised monomer was converted to paraffins and cyclo-paraffins.

The most noticeable effect of the increase in temperature is the decrease in the amount of unsaturation in the polymer as indicated by the bromine number and by infra-red spectroscopy. The effect of temperature on the polymerisation of dec-1-ene catalysed by  $AlEt_3/TiCl_4$  has now been studied in more detail in an attempt to explain this loss of unsaturation. The effect of temperature on polymerisations catalysed by  $AlCl_3$  has also been studied.

### Experimental

#### Materials

The purification of dec-1-ene and iso-octane and the sources of the catalyst components have been described previously.<sup>1</sup>

### Apparatus

The olefin was polymerised in a flask provided with a stirrer, dropping funnels to add reactants, a thermometer and a nitrogen inlet system. All operations were carried out in an inert atmosphere and the usual precautions were adopted to exclude moisture.

### Polymerisation procedure

The reactions at room temperature were carried out in iso-octane but no solvent was used in the reactions at elevated temperatures.

#### Polymerisations using $AlEt_3/TiCl_4$ at 20°

The order of the addition of the materials was iso-octane (2500 ml), dec-1-ene (1000 g), titanium tetrachloride (26.7 ml) and finally triethylaluminium (10 ml). The reaction temperature did not exceed 20° and the reaction was allowed to proceed for 20 hours. The molar ratio of triethylaluminium to titanium tetrachloride was 0.3:1.

#### Polymerisations using $AlCl_3$ at 20°

The order of the addition of the materials was iso-octane (200 ml), dec-1-ene (198 g), resublimed aluminium chloride (2 g). The reaction was allowed to proceed at about 20° for 20 hours.

#### Polymerisation using $AlEt_3/TiCl_4$ at 150°

A solution of titanium tetrachloride (9.8 ml) in dec-1-ene (188 g) was added to the reaction vessel at the same rate (approximately 10 ml/min) as another solution containing triethylaluminium (3.7 ml) in dec-1-ene (190 g). The reaction vessel was heated in an oil bath at 160°. After the completion of the addition of the reagents the reaction was allowed to continue for 20 hours at 150°. This simultaneous addition allowed greater control of the temperature of the reaction mixture during the initial stages. The concentrations of the solutions were such that the molar ratio  $AlEt_3/TiCl_4$  in the reaction vessel was always 0.3:1 and the concentration of catalyst relative to monomer was always the same as for the reaction at 20°.

#### Polymerisation using $AlCl_3$ at 150°

A mixture of dec-1-ene (201 g) and resublimed aluminium chloride (2 g) was heated at 150° for 18 hours.

#### Treatment of polymer with $AlEt_3/TiCl_4$ at 150°

A monomer-free polymer which had previously been prepared using this catalyst at 20° as described above, was treated with fresh catalyst at 150°. The polymer (170 g)

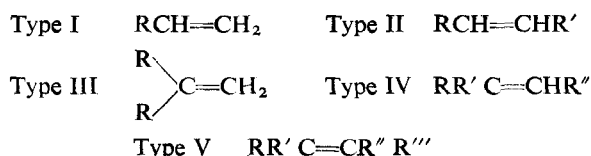
\*Part I: *J. appl. Chem., Lond.*, 1962, 12, 33

was heated to 120° in a stirred flask and titanium tetrachloride (4.5 ml) and triethylaluminium (1.7 ml) were then added. The temperature was then raised to 150° and maintained there for 20 hours.

The catalyst remnants and any solvent were removed in the manner described previously.<sup>1</sup> The unpolymerised material was removed from the polymers by distillation at a pressure between 10 and 70 mm Hg. This material was not dec-1-ene but a mixture of products which for convenience will be referred to as 'monomer fraction'. Samples of the polymers were subjected to further distillation at a pressure of about 1  $\mu$ m Hg to remove dimer and some trimer.

#### Analysis of the polymers

The methods used for the measurement of the bromine numbers, the viscosities, and the infra-red spectra of the polymers have been described previously.<sup>1</sup> The polymers were examined by ultra-violet spectroscopy and the more volatile products were examined in the mass spectrometer. The unsaturation in some of the polymers was measured by quantitative hydrogenation at room temperature using 10wt.-% platinum on charcoal as catalyst. In the subsequent discussion the following nomenclature of olefin types will be used:<sup>2</sup>



### Results

#### Monomer-free polymers

The polymers were obtained in high yield (> 90%) and their properties are listed in Table I. The effects of temperature on the polymerisation with  $AlEt_3/TiCl_4$  were similar to those found in the previous work<sup>1</sup> as summarised above. The effects of temperature on the polymerisations catalysed by  $AlCl_3$  were different from those on polymerisations catalysed by  $AlEt_3/TiCl_4$ . When  $AlCl_3$  was used as catalyst the increase in reaction temperature produced a decrease in the melting point of the polymer and also a decrease in the viscosity but unlike the case of the  $AlEt_3/TiCl_4$  system there was no change in the K.V.I. The unsaturation in the polymer

decreased but not in the same proportion as for the  $AlEt_3/TiCl_4$  system.

The polymer prepared at 20° with  $AlEt_3/TiCl_4$  was subsequently treated with the same catalyst at 150°. After this treatment the polymer properties were similar to those of the polymer prepared directly at 150°.

The olefin contents of the polymers as measured by infra-red analysis were lower than those measured by bromine number, the differences being due to the presence of olefin types II<sub>c</sub> (type II *cis*-olefin), IV and V. Such olefins are difficult to measure by infra-red techniques but types II<sub>c</sub> and IV generally react readily with bromine. From the two sets of results it is possible to calculate the percentage of olefinic groups in the polymer that are type II<sub>i</sub> (type II *trans*-olefin). In the polymer prepared at 20° with  $AlEt_3/TiCl_4$  the olefin is mainly type II<sub>i</sub>, but few of the olefin groups in the polymer prepared using  $AlCl_3$  at 20° are of this type. Appreciable amounts of hydrogen bromide were evolved during the determination of the bromine numbers probably owing to reaction between bromine and the allylic hydrogen of the polymers.

The analysis by ultra-violet spectroscopy showed that all of the polymers prepared at 150° contain substituted benzene rings and substituted naphthalene rings. No such groups were detected in the polymers prepared at room temperature. The polymer prepared using  $AlCl_3$  at 20° showed a strong band at 2475Å. This band is generally attributed to a cyclic conjugated diolefin or to a cyclic olefin with a double bond in a side chain that is conjugated with the double bond in the ring.

#### Recovered 'monomer fraction'

The properties of the 'monomer fractions' recovered from the polymers are given in Table II. There was no evidence for dec-1-ene in any of these fractions. From the results of the bromine number determinations and infra-red and mass spectroscopic analyses the following conclusions can be made about the composition of the recovered material.

#### Polymerisation using $AlEt_3/TiCl_4$ at 20°

The 'recovered monomer' contained 75wt.-% of type II<sub>i</sub> olefin and about 20wt.-% of a C<sub>10</sub> cycloalkane. Analysis by bromine number and infra-red spectroscopy gave almost the same figures for the olefin content. The remainder of the fraction was a mixture of a C<sub>10</sub> paraffin with a C<sub>11</sub> olefin or cycloalkane.

TABLE I  
Properties of monomer-free polymers

Catalyst	Reaction temperature, °C	Bromine no.	M.p., °C	V <sub>k</sub> 100°F, cS	V <sub>k</sub> 210°F, cS	K.V.I.	Type II <sub>i</sub> olefin concn. by infra-red†, moles/l	II <sub>i</sub> olefin groups, %	Ultra-violet analysis,* moles/kg
$AlEt_3/TiCl_4$	20	18	-37	46.0	8.68	148	0.9	86	(No evidence of aromatics or other specific absorbing material)
$AlEt_3/TiCl_4$	150	Nil	-56	103	14.0	130	Trace	—	Diaromatic > 0.05 Monoaromatic > 0.2
$AlCl_3$	20	12	-36	299	30.9	125	0.05	7	(Band at 2475 Å)
$AlCl_3$	150	8	-47	87.0	11.7	125	< 0.05	—	Diaromatics > 0.025 Monoaromatics > 0.22
$AlEt_3/TiCl_4^{**}$	150	Nil	-49	119	14.8	124	None	—	—

† No other functional groups were identified with any certainty in the infra-red spectrum

\* The figures for the aromatic contents are semi-quantitative owing to the presence of considerable background in the spectra.

The figures for the mono-aromatics may be as much as twice as high as the true values.

\*\* Reaction carried out with polymer which had been prepared using  $AlEt_3/TiCl_4$  at 20° instead of with dec-1-ene.

*Polymerisation using AlEt<sub>3</sub>/TiCl<sub>4</sub> at 150°*

The 'recovered monomer' fraction was a complex mixture of mainly C<sub>10</sub>—C<sub>17</sub> highly branched paraffins together with diolefins and triolefins.

*Polymerisation using AlCl<sub>3</sub> at 20°*

The 'recovered monomer' contained C<sub>10</sub> paraffin (80wt.-%) and a type II<sub>t</sub> C<sub>10</sub> olefin (20wt.-%).

Most of the olefins in these fractions were type II<sub>t</sub> and there was evidence for the presence of cycloalkanes, diolefins, triolefins and highly branched materials in some of the fractions.

**Dimer fractions**

The properties of the dimer fractions that were recovered are summarised in Table III. It is evident that some of these fractions also contained trimer.

*Polymerisation using AlEt<sub>3</sub>/TiCl<sub>4</sub> at 20°*

The dimer was almost entirely C<sub>20</sub> olefin of which 80wt.-% was of type II<sub>t</sub>.

*Polymerisation using AlEt<sub>3</sub>/TiCl<sub>4</sub> at 150°*

The dimer-trimer contained very little olefin. The products were mainly highly branched paraffins and alkylbenzenes. Hydrocarbons containing 27, 28 and 29 carbon atoms were observed.

*Polymerisation using AlCl<sub>3</sub> at 20°*

Only a very small amount of a dimer-trimer fraction was obtained under these conditions and it contained C<sub>20</sub> and C<sub>30</sub> olefins and there was evidence for substantial quantities of dienes.

*Polymerisation using AlCl<sub>3</sub> at 150°*

The bulk of the dimer-trimer fraction consisted of branched paraffins with a small amount of alkylbenzenes and olefins. Less than half of the olefins (42wt.-%) were type II<sub>t</sub>.

The dimer-free polymers were also examined but there were no new features of any significance and the results have not been recorded here.

**Quantitative hydrogenation**

The polymers prepared with AlEt<sub>3</sub>/TiCl<sub>4</sub> were hydrogenated quantitatively. A sample of dodec-1-ene absorbed the theoretical amount of hydrogen in 10—15 minutes. The polymer prepared at room temperature (16.95 g; bromine number 11) absorbed 337 ml of hydrogen in 15 hours at 762 mm and 20°. This agreed very well with the double bond content found by measurement of the bromine number. A polymer prepared at 150° (17.47 g, bromine number 0) absorbed 60 ml of hydrogen in 20 hours at 756 mm and 21.5°. The absorption was not complete after this time. The

TABLE II  
Properties of monomer fractions

Catalyst	Reaction temperature, °C	Yield of recovered 'monomer fraction' based on original monomers, wt.-%	Bromine no.*	Infra-red analysis: II <sub>t</sub> olefin, † moles/kg	Mass spectrometric analysis**
AlEt <sub>3</sub> /TiCl <sub>4</sub>	20	1.7	86	5.5	95% (approx.) mass number 140 and 5% (approx.) mixture of C <sub>10</sub> paraffin and C <sub>11</sub> olefin or cycloalkane.
AlEt <sub>3</sub> /TiCl <sub>4</sub>	150	1.3 (Two fractions obtained)	{ (Fr. 1) 3 (Fr. 2) 4	{ No unsaturation detected No unsaturation detected	C <sub>10</sub> —C <sub>14</sub> paraffins with small amounts of mono-olefins or cycloalkanes and di- and tri-olefins in C <sub>10</sub> —C <sub>14</sub> range. As Fr. 1 but aromatics may be present. Highly branched paraffins and olefins or cycloalkanes in C <sub>10</sub> —C <sub>17</sub> range are present. 80% C <sub>10</sub> paraffin and 20% mass number 140.
AlCl <sub>3</sub>	20	2.0	22	1.30	—
AlCl <sub>3</sub>	150	Nil	—	—	—

\* Dec-1-ene has a bromine number of 114, olefin content of 7.2 moles/kg and a mass number of 140.

† No other functional groups could be detected with any certainty by infra-red spectroscopy.

\*\* Mass spectroscopy was unable to differentiate between olefins and cycloalkanes in these systems.

TABLE III  
Properties of dimer fractions

Catalyst	Reaction temperature, °C	Yield of recovered dimer based on original monomer, wt.-%	Boiling range, °C and pressure, μm	Bromine no.*	Infra-red analysis: type II <sub>t</sub> olefin, moles/kg	II <sub>t</sub> olefin groups, %	Mass spectrometric analysis
AlEt <sub>3</sub> /TiCl <sub>4</sub>	20	14	130—190 at 0.1—0.4	50	2.3	78	Almost entirely hydrocarbon mass number 280. Evidence for small amounts C <sub>20</sub> diolefin and C <sub>22</sub> olefin.
AlEt <sub>3</sub> /TiCl <sub>4</sub>	150	12	{ Fr. 1 100—140 at 0.2 Fr. 2 140—160 at 0.2	< 1	Trace	—	Mainly C <sub>30</sub> branched paraffins with small amounts C <sub>10</sub> , C <sub>20</sub> paraffin. No olefins.
AlCl <sub>3</sub>	20	1	130—165 at 0.5	†	0.75	†	Mainly C <sub>30</sub> branched paraffin and C <sub>30</sub> alkylbenzene. Small amounts C <sub>27</sub> —C <sub>30</sub> paraffin and monoaromatics.
AlCl <sub>3</sub>	150	20	{ Fr. 1 < 90 at 4 Fr. 2 90—150 at 4—1.5 Fr. 3 150—208 at 1.5—0.9	7 8 9	0.05 < 0.05 < 0.05	12 < 12 < 12	Equal amounts of C <sub>20</sub> and C <sub>30</sub> olefins (or cycloalkanes) with substantial amounts of dienes. Almost entirely C <sub>20</sub> branched paraffins. A mixture of C <sub>20</sub> and C <sub>30</sub> branched paraffins. Traces of alkylbenzenes. No olefins observed. Mainly C <sub>30</sub> branched paraffins with some C <sub>30</sub> olefin.

\* Dimer of C<sub>10</sub> olefin has a bromine number of 57 and a mass number of 280

† Not measured

hydrogen uptake was very small and very slow and this was due to the hydrogenation of the aromatic groups known to be present in the molecule. A sample of xylene (0.692 g) subjected to hydrogenation under the same conditions absorbed 100 ml of hydrogen after 20 hours at 760 mm and 20° (theory, 471 ml).

### Discussion

#### Reactions occurring at elevated temperatures

The effect of an increase in temperature from 20 to 150° on the polymerisation of dec-1-ene with  $\text{AlEt}_3/\text{TiCl}_4$  (0.3:1) is to produce saturated polymers. The following explanations for this effect can be considered.

The absence of unsaturation may be only apparent. The olefin structures in the polymer are normally type II but at elevated temperatures it is possible that these isomerise in the presence of the catalyst to olefin types IV or V. Olefins of these types are difficult to detect by infra-red spectroscopy and type V may also be unreactive towards bromine. Raman spectroscopy can detect such olefins but this technique cannot be applied to coloured products. However, the results of quantitative hydrogenations indicate that the polymers prepared at elevated temperatures contain little, if any, olefinic unsaturation and this agrees with the measurements of unsaturation by bromine number and by infra-red spectroscopy. It may be concluded that the polymers prepared at elevated temperatures do not contain any significant proportion of olefinic groups.

It is possible that the disappearance of unsaturation at elevated temperatures is caused by hydrogen abstraction from the alkyl groups of triethylaluminium. However, calculations show that the amount of hydrogen available in this way is insufficient to saturate more than a small proportion of the polymer.

It is possible that the polymer undergoes cyclisation reactions to form cycloalkanes. It is difficult to obtain evidence for the presence of such structures in the polymers but they have been detected in the monomer fraction.<sup>1</sup> It has been shown<sup>3,4</sup> that cyclisation of carbon chains markedly increases the viscosity and decreases the K.V.I. Both of these effects occur when the reaction temperature is increased and it seems likely that they are due in part to cyclisation reactions.

The polymer may undergo cyclisation reactions to form aromatics. Aromatic groups have been identified in the polymers prepared at 150° (and in the distilled dimer fractions) but not in the polymers prepared at 20°.

It is possible that disproportionation reactions can occur between olefinic polymer and monomer, or between two polymer molecules, to form a saturated molecule and a diene. Such reactions have been recorded by Nametkin<sup>5</sup> in cationic polymerisations. Small amounts of diolefins have been detected in the 'monomer fractions' from the polymers prepared with  $\text{AlEt}_3/\text{TiCl}_4$  at 150° and it is likely that such disproportionation reactions are occurring in this system to a small extent. The 'monomer fraction', from the polymer prepared with  $\text{AlCl}_3$  at 20°, contained large amounts of  $\text{C}_{10}$  paraffin and the dimer contained considerable amounts of diene. It thus appears that disproportionation occurs in  $\text{AlCl}_3$  polymerisation at room temperature.

It may be deduced that the absence of olefinic unsaturation in the polymers prepared with  $\text{AlEt}_3/\text{TiCl}_4$  and  $\text{AlCl}_3$  at elevated temperatures is mainly due to cyclisation reactions

forming aromatics and cycloalkanes. The formation of  $\text{C}_{10}$  paraffin (in the recovered monomer) and other paraffins (in the dimer) can arise from hydrogenation of olefins by the hydrogen eliminated in the aromatisation or disproportionation reactions. The disproportionation reaction is probably only significant in those polymerisations involving  $\text{AlCl}_3$ .

Cyclisation is also accompanied by other isomerisation reactions. The  $\text{C}_{10}$  olefin which is recovered from polymerisations at room temperature is not dec-1-ene but mainly a type II olefin. At elevated temperatures isomerisation reactions occur to a greater extent; an increase in the amount of branching in the polymer can be seen in the infra-red spectrum and this is also shown by a decrease in K.V.I. The melting point of the polymer is lowered even though the viscosity of the polymer has greatly increased owing to further polymerisation or cyclisation reactions. There is also evidence for reactions involving the transfer of alkyl groups since products containing between 10 and 20 and between 20 and 30 carbon atoms have been detected in distillate fractions.

The mechanisms of these reactions are probably similar to the cyclisation, disproportionation and transfer reactions described in detail by Schmerling & Ipatieff<sup>6</sup> for polymerisations with  $\text{AlCl}_3$ . The evidence for such reactions has been deduced mainly from polymerisation reactions which proceed to give dimer and trimer only.

There are significant differences between the reactions occurring at room temperature with  $\text{AlEt}_3/\text{TiCl}_4$  (0.3:1) and those with  $\text{AlCl}_3$  which are reflected in the chemical and physical properties of the polymers. The former catalyst system gives a less viscous polymer of higher unsaturation, which is predominantly of type II; the K.V.I. is also higher which is indicative of a more regular, less branched, polymer. With  $\text{AlCl}_3$  as catalyst more viscous polymers are formed and the unsaturation is mainly of types II<sub>c</sub>, IV or V with possibly a trace of type III. The  $\text{AlCl}_3$  system is more active for cyclisation, isomerisation and disproportionation reactions at low temperatures. At elevated temperatures the differences in the properties of the products from polymerisations with  $\text{AlEt}_3/\text{TiCl}_4$  and  $\text{AlCl}_3$  largely disappear. In both cases the unsaturation is low or non-existent and there is direct evidence for cyclisation, aromatisation and isomerisation reactions.

#### Nature of the catalyst at high reaction temperatures

Because the behaviour of the  $\text{AlEt}_3/\text{TiCl}_4$  system shows a marked resemblance to that of  $\text{AlCl}_3$  at high polymerisation temperatures it seems reasonable to conclude that  $\text{AlEt}_3$  and  $\text{TiCl}_4$  undergo reactions in which  $\text{AlCl}_3$  is formed and that it is the  $\text{AlCl}_3$  (or a complex containing it) which is the active catalyst species at 150°. Arlman & de Jong<sup>7</sup> have studied the reaction between  $\text{AlEt}_3$  and  $\text{TiCl}_4$  at a molar ratio of 0.3:1. At 25° the reaction did not go beyond the conversion of  $\text{AlEt}_3$  to  $\text{AlEt}_2\text{Cl}$  but at 80°, 90% of the ethyl groups were replaced by chlorine within half an hour. Analysis of the precipitate showed it to consist of  $\beta\text{-TiCl}_3$  in which one out of six titanium atoms was replaced by aluminium. The aluminium compounds were firmly bound and could not be removed by washing. At higher temperatures (~170°) the precipitate had the same composition but the  $\text{TiCl}_3$  was in the purple ( $\gamma$ ) form.<sup>8</sup> The nature of the catalyst species formed from  $\text{AlEt}_3/\text{TiCl}_4$  (0.3:1) at room temperature will be discussed in a later paper but at high temperatures it seems likely to be  $\text{AlCl}_3$  or a  $\text{TiCl}_3\cdot\text{AlCl}_3$  complex.

The results of previous work<sup>1</sup> and of the present work show that when the reaction temperature in  $\text{AlEt}_3/\text{TiCl}_4$  polymerisations is increased, the viscosity of the product (and presumably the molecular weight) increases. This is unusual in cationic polymerisations and does not normally occur in polymerisations with  $\text{AlCl}_3$ . A co-ordination complex catalyst prepared from  $\text{Al}_2\text{Et}_3\text{Cl}_3/\text{TiCl}_4$  and propylene oxide has recently been shown<sup>9</sup> to have a similar effect in the polymerisation of oct-1-ene although in this case the polymerisation mechanism is claimed to be predominantly anionic. In the present case this effect can be explained by a change in the catalyst species. At room temperature the catalyst probably involves  $\text{TiCl}_3$  and  $\text{AlEtCl}_2$ ; this combination (like other Ziegler catalysts) is relatively unreactive towards the polymerisation of type II olefins and the unsaturation in the low temperature polymers is predominantly of this type. At high temperatures,  $\text{AlCl}_3$  (or a complex) is formed; this is reactive towards type II olefins and further polymerisation (together with cyclisation reactions) can occur giving higher molecular weight products with increased viscosities and reduced K.V.I. Evidence to support this hypothesis was obtained by taking a polymer which had been prepared at room temperature with  $\text{AlEt}_3/\text{TiCl}_4$  and subsequently treating it with the same catalyst for 20 hours at  $150^\circ$ . At the end of this period unsaturation in the polymer had disappeared, the melting point was lower, the viscosity had increased and the polymer was very similar to one prepared from dec-1-ene directly at  $150^\circ$  (Table I).

Polymers formed with  $\text{AlCl}_3$  at low temperatures generally contain little unsaturation and the unsaturation is mainly type II<sub>c</sub>, IV or V. Further polymerisation reactions are not likely to occur with this system and an increase in reaction temperature brings about a decrease in the viscosity of the polymer.

### Conclusions

Poly(dec-1-ene) prepared at room temperature with  $\text{AlEt}_3/\text{TiCl}_4$  as catalyst at a molar ratio of 0.3:1 contains one double

bond per molecule but at  $150^\circ$ , saturated polymers are formed. The loss of unsaturation is due mainly to cyclisation reactions and, to a lesser extent, to disproportionation reactions. With  $\text{AlCl}_3$  as catalyst a similar increase in reaction temperature has little effect other than to reduce the viscosity of the polymer.

The properties of the polymer prepared at  $150^\circ$  with  $\text{AlEt}_3/\text{TiCl}_4$  are very similar to those of the polymer prepared with  $\text{AlCl}_3$  at the same temperature. It is concluded that the active species in the  $\text{AlEt}_3/\text{TiCl}_4$  system at  $150^\circ$  is  $\text{AlCl}_3$  or a complex containing it.

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## POLYMERISATION OF DEC-1-ENE.

### III.\* THE NATURE OF THE CATALYST SPECIES USING TRIETHYLALUMINIUM AND TITANIUM TETRACHLORIDE UNDER CATIONIC CONDITIONS

By K. I. BEYNON, C. B. MILNE and D. SOUTHERN

The polymerisation of dec-1-ene, using several combinations of aluminium alkyls and titanium halides, has been studied to try to elucidate the nature of the active catalyst species in the system triethylaluminium/titanium tetrachloride at a molar ratio ( $\text{AlEt}_3/\text{TiCl}_4$ ) of 0.3:1. Polymers similar to those formed by the  $\text{AlEt}_3/\text{TiCl}_4$  system have been obtained using ethylaluminium dichloride in combination with titanium trichloride and titanium tetrachloride. The complexes formed from these combinations are the most likely catalyst in the  $\text{AlEt}_3/\text{TiCl}_4$  (0.3:1) system.

\* Part II: preceding paper