Structure of Ziegler-Natta Catalysts for the Polymerization of Isoprene

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Structural investigation was carried out by means of ^{1}H-NMR, ESR, and chemical ionization mass spectrometry on the complexes formed by the reaction of alkylaluminum with titanium(IV) *t*-butoxide or vanadium(IV) *t*-butoxide as a catalyst for polymerization of isoprene. The *t*-butoxide was monomeric in benzene, and reduced to form a bivalent complex *via* trivalent ones on addition of the alkylaluminum to the solution followed by the formation of two kinds of binuclear aluminum complexes. In the trivalent state the complexes caused polymerization of isoprene to form five kinds of polymers, 1,4-polymerization of isoprene being likely caused by tris[di-μ-t-butoxo-dialkyltitanium(III)]aluminum, or the corresponding vanadium(III) complex. The final product of the reduction of vanadium(IV) *t*-butoxide was bis(di-μ-alkyl-dialkylaluminum)vanadium(II), which exhibits no catalytic activity.

It is well-known that polymerization of isoprene is caused either by Ziegler-Natta catalysts or by organolithiums. Significant characteristics of the Ziegler-Natta catalysts lie in their ability to form stereoregular polymers, the chemical nature of the catalysts being ascribed to structure and electronic state of the complex composed of aluminum and one of transition elements. Since the pioneer work of Natta *et al.*[1] a number of investigations have been made in this field, but the stucture of the catalysts is not clear so that the mechanism of the catalytic reaction is still ambiguous. The original Ziegler-Natta catalysts, prepared by the reaction of alkylalumium with chloride of titanium or other transition elements, formed a heterogeneous system, which resulted in difficulty in structural study of the catalysts. The polymerization mechanism of isoprene with the catalyst of organolithiums, however, was studied in detail by Morton *et al.*,[2] who examined the propagating chain end of polyisoprene by means of ^{1}H NMR.

Alkylaluminums react with alkoxides of titanium(IV) or vanadium(IV) to form a homogeneous system.[3–6] Natta *et al.*[3] examined polymerization of butadiene and isoprene with the catalysts prepared by the reaction of the alkylaluminums with the titanium(IV) alkoxides by measuring the infranred absorption and X-ray diffraction of the reaction products, and by determining the structures of the 1,2- and the 3,4-polymers. Angelscu *et al.*[4] measured the ESR spectra of the reaction mixture of triethylaluminum and titanium(IV) *t*-butoxide to detect a titanium(III) complex containing two aluminum nuclei. Hirai *et al.*[5,6] also studied the ESR spectra of the reaction mixture of triethylalumium and titanium(IV) butoxide as a catalyst for the polymerization of butadiene, penta-1,3-diene and isoprene to determine the molar ratio of aluminum and titanium in the resulting polynuclear complexes. However, they could not throughly correlate the structure of the Ziegler-Natta catalyst to the reaction mechanism.

We have tried to determine the structure and electronic state of the Ziegler-Natta catalysts prepared by the reaction of trimethyl-, triethyl- or triisobutylaluminum with titanium(IV)- or vanadium(IV) *t*-butoxide as a catalyst for the polymerization of isoprene. The paramagnetic and the diamagnetic species were examined by means of ESR and ^{1}H-NMR, respectively. The evaluation of the *g* factor was performed on the basis of the ligand field theory. Chemical ionization mass spectrometry was utilized in dtermination of the molecular weight of the catalytic complexes.

Experimental

Reagents. Trimethyl-, triethyl-, and triisobutylaluminum were obtained from Ethyl Co. Titanium(IV) chloride was manufactured by Kishida Chemical Co., vanadium(IV) chloride by Wako Pure Chemical Industries, Ltd., and butyllithium by Mitsuwa Chemical Co. These reagents were used without further purification. Aluminum chloride (Kanto Chemical Co.) was ground into powder, and dried *in vacuo* at 25 °C for 20 h. Organic reagents were purified by using dehydration reagents as the occasion demanded. Aluminum-, titanium(IV)- and vanadium(IV) *t*-butoxides were synthesized in diisopropyl ether according to the following reactions,[7,8] and purified by distillation under reduced pressure.

$$\mathrm{LiBu + HNEt_2 \rightarrow LiNEt_2 + BuH}$$

$$\mathrm{MCl}_n + n\mathrm{LiNEt_2} \rightarrow \mathrm{M(NEt_2)}_n + n\mathrm{LiCl}$$

$$\mathrm{M(NEt_2)}_n + n t\text{-}\mathrm{BuOH} \rightarrow \mathrm{M}(t\text{-}\mathrm{BuO})_n + n\mathrm{HNEt_2}$$

where M denotes aluminum, titanium or vanadium.

Preparation of Samples. Samples were prepared under nitrogen atmosphere. The alkylaluminum and the metal alkoxide were separately dissolved in benzene or toluene, and the solutions were mixed to form the catalyst. Aging of the catalyst and polymerization of isoprene were carried out in a reaction tube made of stainless steel for 0.5 and 20 h, respectively. Molar ratios of the transition elements, isoprene and the solvent were fixed at 1.00 : 100 : 300.

Spectral Measurements. ^{1}H-NMR spectra were measured with a Varian Associates HA-100 high resolution spectrometer operating at 100 MHz. ESR spectra were taken on a Japan Electron Optics Laboratory JES-ME3 spectrometer operating in the X-band with 100 KHz modulation. *g*-Values and hyperfine coupling constants were determined by using the ESR signal of manganese dioxide as a standard. Liquid nitrogen was used to measure the ESR spectra at −196 °C. Mass spectra were recorded on a Finnigan 3300F quadrupole spectrometer equipped with a chemical ionization system. Isobutane was used as a reactant gas for the chemical ionization.

Results and Discussion

Polymerization of Isoprene. Experiments of isoprene polymerization were performed in benzene at

80—140 °C with the catalysts prepared by the reaction of trimethyl-, triethyl- or triisobutylaluminum with titanium(IV)- or vanadium(IV) *t*-butoxide. Structure of the reaction products was studied by ^{1}H-NMR spectra. It was found that five types of reactions take place to form 1,4-polyisoprene, 3,4-polyisoprene, 2,6-dimethyl-1,3,6-octatriene, 1-methyl-4-isopropenyl-1-cyclohexene, or 2-methyl-4-isopropenyl-1-cyclohexene. The molar ratio of *cis*- and *trans*-1,4 bonds in 1,4-polyisoprene was *ca.* 1 : 2 showing dependence neither upon the species of the transition element nor upon the present reaction conditions. Three kinds of isoprene dimers, 2,6-dimethyl-1,3,6-octatriene, and 1- and 2-methyl-4-isopropenyl-1-cyclohexenes, could be distilled out from the reaction mixture under reduced pressure, but it was difficuot to separate the two high polymers, 1,4- and 3,4-polyisoprenes, from each other. For convenience, the symbol *A* is used to show the added molar ratio of the alkylaluminum and titanium(IV)- or vanadium(IV) *t*-butoxide.

Aging of the catalytic system at 100—140 °C for 20—30 min was required to reproduce the reactions. Yield of the reaction products varied in accordance with the value of *A*, and the catalytic reaction system containing vanadium was higher in conversion of isoprene as well as in selectivity of the reactions than the system containing titanium. Experimental data with the catalysts composed of trimethylaluminum and titanium(IV)- or vanadium(IV) *t*-butoxide are shown in Figs. 1 and 2, respectively. All the reactions took place mainly in the region *A*=1—7. This suggests that the transition element of the catalytic complex is active at the trivalent state, but not at the tetra- or the bivalent state. Titanium and vanadium are supposed to produce the active complexes with a similar stucture, though their amounts are not equal to each other depending upon the relative stability of the trivalent state.

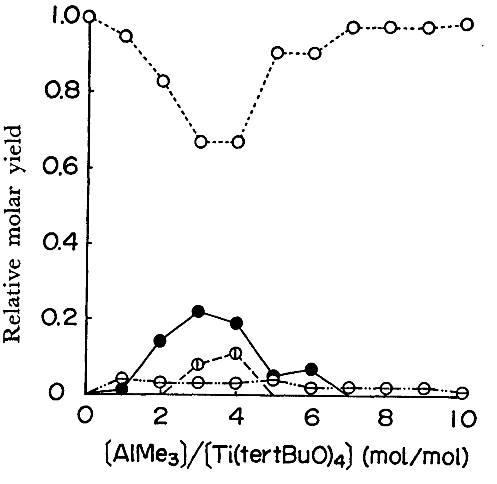


Fig. 1. Yield of the reaction products of isoprene in the catalytic system prepared by trimethylaluminum and titanium(IV) *t*-butoxide. Reaction was performed in benzene at 100 °C for 20 h after aging the catalyst at 140 °C for 30 min. ○, ⏀, ⊖, and ● show isoprene, 2,6-dimethyl-1,3,6,-octatriene, 1-methyl-4-isopropenyl-1-cyclohexene, and 1,4-polyisoprene, respectively.

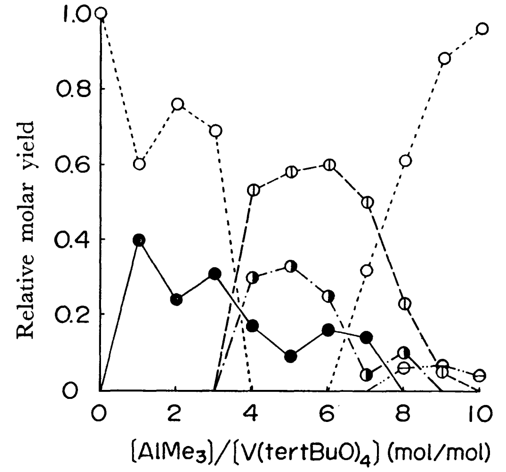


Fig. 2. Yield of the reaction products of isoprene in the catalytic system prepared by trimethylaluminum and vanadium(IV) *t*-butoxide. Reaction was performed in benzene at 100 °C for 20 h after aging the catalyst at 100 °C for 30 min. ◑ show 3,4-polyisoprene, and other circles are the same as in Fig. 1.

When the reaction of isoprene was performed at 100 °C, 1,4-polyisoprene showed the maximum yield at *A*=2—4 and 1—3 with the catalysts containing titanium and vanadium, respectively, and the highest selectivity at *A*=1—2. Both 3,4-polyisoprene and 2,6-dimethyl-1,3,6-octatriene were produced at *A*=3—5 and 4—7 with the catalysts containing titanium and vanadium, respectively. 1-Methyl-4-isopropenyl-1-cyclohexene was observed in the whole region of *A*, and its yield decreased when the catalytic system was aged at relatively low temperature. A similar result was obtained by using triethyl- or triisobutylaluminum instead of trimethylaluminum. However, the catalytic system prepared from triisobutylaluminum caused formation of 2-methyl-4-isopropenyl-1-cyclohexene, the yield of which increased with increase in the *A* value. Thermal reactions of isoprene[9] took place above 140 °C to produce 1- and 2-methyl-4-isopropenyl-1-cyclohexenes.

^{1}H-NMR Spectra. Trivalent aluminum complexes are diamagnetic, their valence state being stable. Trimethylaluminum reacts with aluminum isopropoxide to form three kinds of tetranuclear and two kinds of binuclear complexes, structures of which were determined by means of ^{1}H-NMR in benzene.[10] Similar complexes were observed with the ^{1}H-NMR spectra when aluminum *t*-butoxide was used instead of isopropoxide. Titanium(IV) is also diamagnetic, while the complexes of titanium(III) or vanadium(IV) are paramagnetic because of the electronic configuration of 3d^1. The diamagnetic complexes showed ^{1}H-NMR signals with high resolution even when a considerable amount of paramagnetic complexes coexisted, though the latter displayed either broad or no signals.

^{1}H-NMR spectra (Fig. 3) were measured with a mixture of trimethylaluminum and titanium(IV) *t*-butoxide at 30 °C after being heated in benzene at 140 °C for 30 min. Bradley *et al.*[11] measured volatility

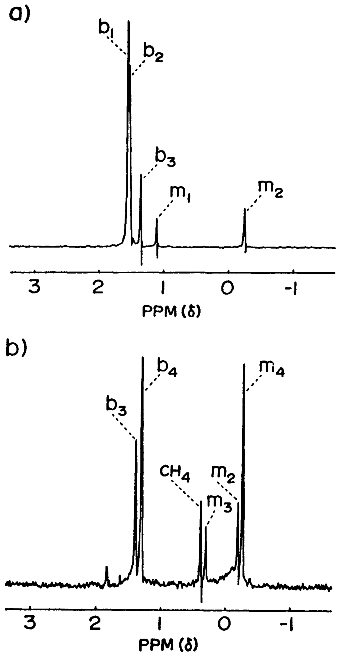
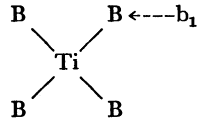
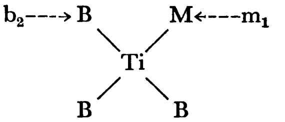


Fig. 3. ^{1}H NMR spectra of the mixture of trimethylaluminum and titanium(IV) *t*-butoxide in benzene at 30 °C after heating at 140 °C for 30 min. The prepared molar ratio of trimethylaluminum and titanium(IV) *t*-butoxide is a) 0.40 : 0.60, and b) 0.90 : 0.10.



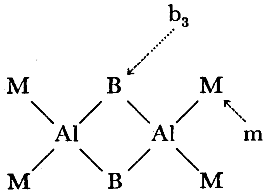
T^1



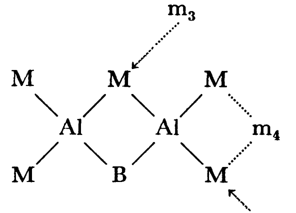
T^2

B=$(CH_3)_3CO$- M=CH_3-

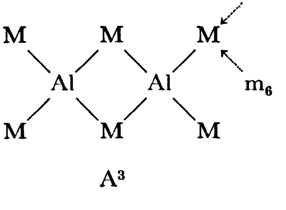
of titanium(IV) *t*-butoxide in order to determine a monomeric stucture of T^1. The monomeric structure was reconfirmed by the fact that titanium(IV) *t*-butoxide shows a ^{1}H-NMR signal, b_1, alone, which represents no splitting attributable to two or more kinds of coordination states of the ligands in toluene even below −50 °C. A pair of signals, b_2 and m_1, with a molar ratio of 3 : 1 are assigned to the *t*-butoxyl and the methyl groups, respectively, of methyl-tri-*t*-butoxotitanium(IV), T^2. Signals of b_3, b_4, m_2, m_3, and m_4, which increased in intensity with increase in the amount of added trimethylaluminum, are assigned to the ligands of binuclear aluminum complexes, A^1 and A^2, from the result of the ^{1}H-NMR measurements of the reaction mixture of trimethylaluminum and aluminum *t*-butoxide.



A_1



A_2



A^3

Hoffmann,[12] and Haaland *et al.*[13] determined the structure of A^1 by use of ^{1}H-NMR and electron diffraction, respectively. A dimeric stucture of trimethylaluminum, A^3, is well-known. The NMR assignment was performed by Muller *et al.*[14]

Vanadium(IV) *t*-butoxide displayed a ^{1}H-NMR signal with a half-height width of 147 Hz at $\tau=6.82$ in benzene at 30 °C, though the line broadening caused by the paramagnetic effect of vanadium(IV) prevented structural examination. On addition of trimethylaluminum to the solution, NMR signals of the binuclear aluminum complexes appeared but none of vanadium(III) and vanadium(II) complexes.

ESR Spectra of Vanadium Complexes. On the basis of volatility measurements, Bradley *et al.*[8] found that vanadium(IV) *t*-butoxide as well as other tertiary alkoxides are monomeric so that the question is the coordination symmetry of the complex. If vanadium(IV) *t*-butoxide takes Td symmetry, the 3d orbitals split into two levels, lower and upper ones of which are degenerate 2-fold with E symmetry and 3-fold with T_2 symmetry, respectively. Taking the spin-orbit interaction as a first-order perturbation to the ligand field splitting, principal values of the *g*-tensor of the tetrahedral complex are represented by

$$\begin{aligned} g_x &= g_e - 2\rho^2\zeta\varepsilon[\sin(\theta/2) - 3\cos(\theta/2)]^2 \\ g_y &= g_e - 2\rho^2\zeta\varepsilon[\sin(\theta/2) + 3\cos(\theta/2)]^2 \qquad (1) \\ g_z &= g_e - 2\rho^2\zeta\varepsilon[2\sin(\theta/2)]^2 \end{aligned}$$

where g_e, ρ, and ζ are the *g*-factor for a free electron, an orbital reduction factor, and a spin-orbit coupling constant, respectively. θ is a tortion angle of the ligand about a coordination bond caused by the Jahn-Teller effect.[15] ε denotes the reciprocal of the energy difference between the orbitals with E and T_2 symmetries.

As shown in Fig. 4 the ESR spectrum of vanadium(IV) *t*-butoxide, which was measured in toluene at −196 °C, represents a double octet pattern with an axial symmetry. Anisotropic *g*-values obtained are $g_{//}=1.9395\pm0.0005$ and $g_{\perp}=1.9870\pm0.0005$, and anisotropic hyperfine coupling constants $A_{//}=1.46\times10^{-2}$ cm^{-1} and $A_{\perp}=2.13\times10^{-3}$ cm^{-1}. When θ is π in Eq. 1, g_x and g_y become equivalent resulting in the axial symmetry of the complex, *i.e.* $g_{//}=g_z$ and $g_{\perp}=g_x=g_y$. Thus the axial symmetry of the experimental *g*-values can be interpreted to support the view that vanadium(IV) *t*-butoxide takes the tetrahedral structure. The condition, $\theta=\pi$, indicates that the tetrahedral structure is compressed along one of the 3-fold improper axes.[15]

The magnitude of the spin-orbit coupling constant is estimated from the atomic spectrum as $\zeta=248$ cm^{-1} for the vanadium(IV) ion.[16] The ligand field splitting of the 3d orbitals of vanadium(IV) *t*-butoxide was determined from the near-infrared absorption

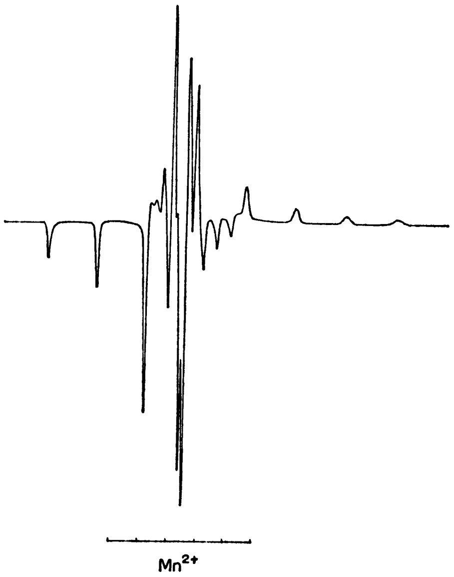


Fig. 4. ESR spectrum of vanadium(IV) *t*-butoxide in toluene at −196 °C.

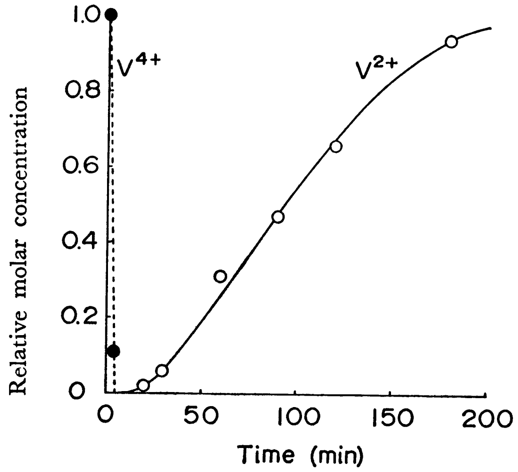


Fig. 5. Concentration of the paramagnetic species measured by the ESR spectrum of the mixture of trimethylaluminum and vanadium(IV) *t*-butoxide in toluene at 25 °C. The prepared molar ratio of trimethylaluminum and vanadium(IV) *t*-butoxide is 0.90 : 0.10.

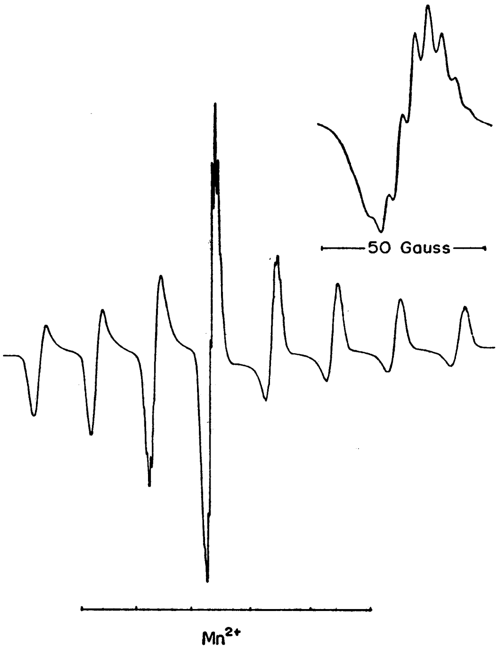


Fig. 6. ESR spectrum of the mixture of trimethylaluminum and vanadium(IV) *t*-butoxide in toluene at −196 °C. The prepared molar ratio of trimethylaluminum and vanadium(IV) *t*-butoxide is 0.90 : 0.10.

spectrum in benzene as $\varepsilon^{-1}=1.45\times10^4\ \mathrm{cm}^{-1}$, a little larger than that obtained by Kokoszka *et al.*[17] The orbital reduction factor of the complex was determined to be $\rho=0.67$ by comparing the calculated values of $g_{//}$ and $g_{\perp}$ with observed values. The anisortopic g-values are averaged to be $\bar{g}=1.9712$, which agrees closely with the observed value at 25 °C.

A mixture of trimethylaluminum and vanadium(IV) *t*-butoxide exhibited ESR signals from two kinds of vanadium(IV) complexes besides the signal of vanadium(IV) *t*-butoxide at −196 °C immediately after mixing in toluene at 25 °C. However, partial overlapping of the signals made it difficult to determine both the values of the g-factor and the hyperfine coupling constant of the complexes. After the mixture of trimethylaluminum and vanadium(IV) *t*-butoxide was allowed to stand for 1 h at 25 °C ,the signal of vanadium(IV) *t*-butoxide vanished, and the remaining signals varied with the A value as follows: signals of the two kinds of vanadium(IV) complexes were observed at $A<6$, a singlet signal with a maximum slope width of 280—300 Gauss at $6\leq A<8$, an octet signal with a super hyperfine structure, which displayed a coupling with two aluminum nuclei, at $A\geq9$, and the latter two signals at $8\leq A<9$. Since the broad signal observed at $6\leq A<9$ become wider and disappeared with increasing A value, it is suggested that the 3d electron of the complex moves between the nuclei of vanadium(IV) and vanadium(III) in the stationary state.

After the disappearance of the signals of vanadium(IV) complexes at $A=9$ (Fig. 5), the octet signal (Fig. 6) became large in intensity, attaining maximum intensity in 3 h. The signal is, therefore, attributed to a vanadium(II) complex, which takes an electron configuration of $3d^3$. Each peak of the octet signal is composed of eleven consitituent lines to represent the super hyperfine coupling with the spins of a pair of aluminum nuclei. ESR measurements were carried on 21 combinations of alkylaluminums and vanadium(IV) alkoxides in toluene at −196 °C, the values of the ESR parameters being almost invariant with changes in the alkyl groups, *i.e.* methyl, ethyl and isobutyl, or the alkoxyl groups, *i.e.* methyl, ethyl and isobutyl, or the alkoxyl groups, *i.e.* methoxyl, ethoxyl, propxyl, isopropoxyl, butoxyl, isobutoxyl, and *t*-butoxyl. Each combination resulted in an almost isotropic g-value, 1.9835 ± 0.0004, and almost isotropic values of hyperfine and super hyperfine coupling constants,

Table 1. Observed values of $\bar{g}$-factor, hyperfine coupling constant, $\bar{A}$, and super hyperfine coupling constant, $\bar{B}$, of vanadium(II) complexes[a)]

Alkyl group[b)]	Alkoxyl group[c)]	$\bar{g}$-Value	$\bar{A}$ (10^{-3} cm^{-1})	$\bar{B}$ (10^{-4} cm^{-1})
CH_3-	CH_3O-	1.9836	8.23	3.8
	CH_3CH_2O-	1.9336	8.18	3.7
	$CH_3(CH_2)_2O$-	1.9839	8.22	3.7
	$(CH_3)_2CHO$-	1.9833	8.21	3.7
	$CH_3(CH_2)_3O$-	1.9833	8.21	3.8
	$(CH_2)CHCH_2O$-	1.9835	8.26	3.7
	$(CH_3)_3CO$-	1.9835	8.25	3.7
CH_3CH_2-	CH_3O-	1.9835	8.18	3.7
	CH_3CH_2O-	1.9831	8.22	3.7
	$CH_3(CH_2)_2O$-	1.9833	8.26	3.6
	$(CH_3)_2CHO$-	1.9834	8.16	3.7
	$CH_3(CH)_3O$-	1.9836	8.26	3.6
	$(CH_3)_2CHCH_2O$-	1.9833	8.21	3.6
	$(CH_3)_3CO$-	1.9833	8.20	3.6
$(CH_3)_2CHCH_2$-	CH_3O-	1.9835	8.17	3.7
	CH_3CH_2O-	1.9836	8.16	3.7
	$CH_3(CH_2)_2O$-	1.9833	8.25	3.7
	$(CH_3)_2CHO$-	1.9836	8.23	3.7
	$CH_3(CH_2)_3O$-	1.9835	8.22	3.8
	$(CH_3)_2CHCH_2O$-	1.9835	8.25	3.7
	$(CH_3)_3CO$-	1.9835	8.26	3.8

a) The complex was obtained by the reaction of alkylaluminum with vanadium(IV) alkoxide in toluene at 25 °C, and the ESR spectrum was measured at −196 °C. b) Alkyl group of alkylaluminum. c) Alkoxyl group of vanadium(IV) alkoxide.

$(8.21\pm0.05)\times10^{-3}$ and $(3.7\pm0.1)\times10^{-4}$ cm^{-1}, respectively, as listed in Table 1.

It is difficult to determine the structure of the vanadium(II) complexes from the g-value and the hyperfine and the super hyperfine coupling constants. However, the dependence of the signal intensity upon the A value indicates that they are possibly bis(di-μ-alkyldialkylaluminum)vanadium(II), which is regarded as the final product of a series of reductions of the vanadium(IV) alkoxides with the alkylaluminums as follows. The reactions are summarized as

$$\begin{aligned}&(A/2)(AlR_3)_2 + V(R'O)_4 \rightarrow\\&\quad V(R_2AlR_2)_2 + (A-6)R_2Al(R'O)_2AlR_2\\&\quad + (1/2)(10-A)R_2AlR(R'O)AlR_2 + R_2 \qquad (2)\end{aligned}$$

where R and R'O denote the alkyl and the alkoxyl groups, respectively. The condition $6\leq A\leq10$, which is required in Eq. 2, agrees with the result of ESR measurements. The vanadium(II) complexes and the vanadium(IV) alkoxides caused none of the reactions of isoprene.

ESR Spectra of Titanium Complexes. The catalytic reactions of isoprene took place in the region of A in which the transition element assumed a trivalent state. The structures of the catalytic complexes were studied from the ESR spectra of titanium(III) complexes. The ESR spectra of the catalytic system prepared from trimethylaluminum and titanium(IV) t-butoxide are shown in Fig. 7. They were measured in benzene at 25 °C after aging at 140 °C for 30 min, and showed little change through the reactions of isoprene at 100 °C for 20 h.

The ESR signal with $\bar{g}=1.963$ observed at $A=2$—4

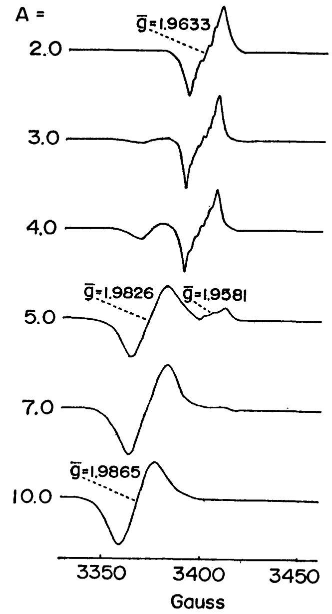


Fig. 7. ESR spectra of titanium(III) complexes of the catalytic system at 25 °C after aging at 140 °C for 30 min. Trimethylaluminum and titanium(IV) t-butoxide were mixed in benzene at the molar ratio, A.

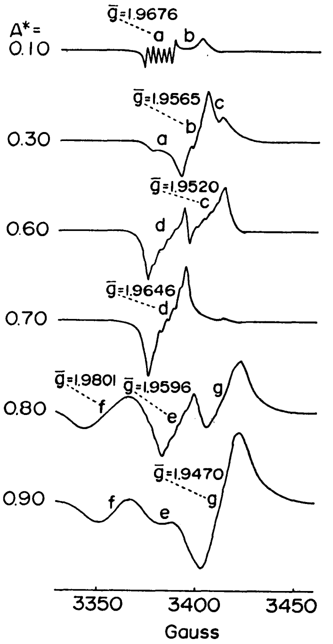


Fig. 8. ESR spectra of titanium(III) complexes at 25 °C immediately after mixing trimethylaluminum and titanium(IV) *t*-butoxide in benzene.
A* designates the prepared molar fraction of trimethylaluminum.

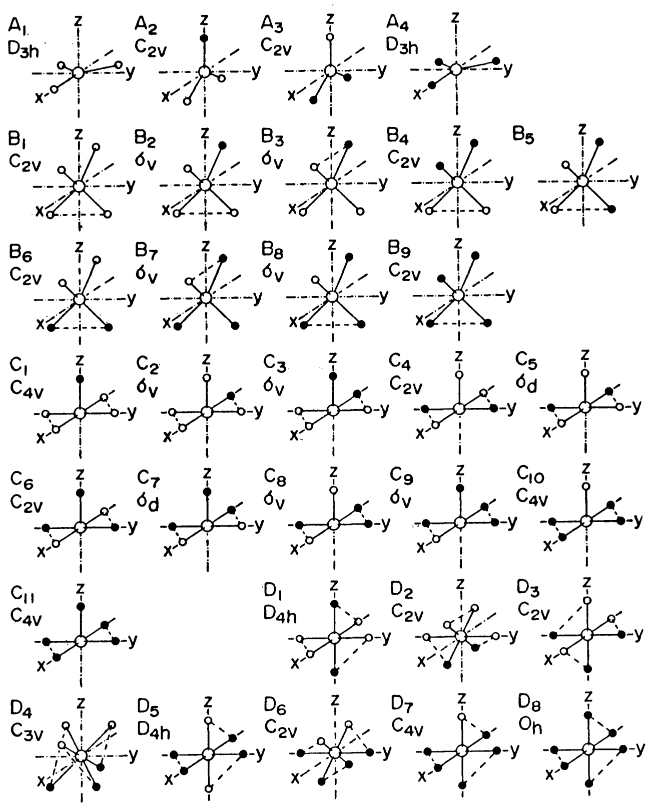


Fig. 9. Model structures of titanium(III) complexes. The titanium(III) nucleus is located at the origin. Dashed line shows chelation formed by a pair of ligands between aluminum and titanium(III) nuclei. The alkoxy and the alkyl groups are shown by ○ and ●, respectively.

is attributed to the catalyst which caused 1,4-polymerization of isoprene. The signal exhibited a super hyperfine structure bearing six constituent lines to show coupling with an aluminum nucleus, and was affected little by the reactions of isoprene. Some of the other signals might correspond to the titanium(III) complexes, which caused reactions of isoprene other than 1,4-polymerization. Similar results were obtained by using triethylaluminum instead of trimethylaluminum. However, when triisobutylaluminum was used, the signal with $\bar{g}=1.963$ virtually disappeared during the course of reaction of isoprene and turned into signals of other titanium(III) complexes. Before aging the catalyst, seven kinds of signals, denoted by a, b, c, d, e, f, and g in order of appearance with increase in the amount of trimethylaluminum, were observed in the mixed solution of trimethylaluminum and titanium(IV) *t*-butoxide at 25 °C as shown in Fig. 8. The signals a, b, c, d, and g displayed a super hyperfine structure owing to coupling with an aluminum nucleus, and the signal e showed coupling with two aluminum nuclei. When trimethylaluminum was added at the molar fraction of 0.10—0.70 in the solution, only the signal d with $\bar{g}=1.965$ remained after aging at 140 °C for 30 min. The signal is attributed to the catalyst for 1,4-polymerization of isoprene.

The molecular structures of the titanium(III) complexes were determined by caluclating the *g*-values with use of models of the coordination structures. The model structures are shown in Fig. 9, where the titanium(III) nucleus is situated in the origin of the Cartesian coordinates. The dashed line designates chelation formed by a pair of ligands between titanium(III) and aluminum nuclei. The structures are classified into four groups, A, B, C, and D, in accordance with the number of aluminum nuclei combined with a titanium(III) nucleus, zero, unity, two and three, respectively, which have four, nine, eleven an eight kinds of stuctures, respectively. The structural symmetry of each is designated by the ordinary symbols except the structure, B_5, which has no center of symmetry.

The wave function of the 3d orbital of the titanium(III) complexes, φ_i, is given by a linear combination of d functions, d_0, $d_{\pm1}$ and $d_{\pm2}$, which are classified into six groups (Table 2). In groups 1, 2, 3, and 4 the Jahn-Teller distortion resolves orbital degeneracy of the ground level changing φ_i to φ_i' or φ_i'', while the ground level takes none of the degenerate orbitals in groups 5 and 6. On the basis of the ligand field theory, energy of the orbital, φ_i, is expressed as

$$E_i = Ze^2 \sum_j (\alpha \overline{r^2} \gamma_j R_j^{-3} + \beta \overline{r^4} \delta_j R_j^{-5}) \qquad (3)$$

where the subscript j denotes the coordination electron of the ligand, e the charge of an electron, and *Ze* the effective nuclear charge of the transition element. The charge of a coordination electron is estimated to be *e* and *e*/2 at the terminal and the bridging ligands, respectively, and *r* and *R* designate the radius of the 3d electron and the distance between the coordination

TABLE 2. WAVE FUNCTIONS OF 3d ORBITALS OF TITANIUM(III) COMPLEXES[a)]

Structures A_1 and A_4.[b)] (E_3, $E_4 \neq E_{\min}$)

i	$\varphi_i(E_5=E_{\min})$	$\varphi_i'\ (E_1=E_2=E_{\min})$
1	$(1/\sqrt{2})(d_1-d_{-1})$	$\varphi_1\cos(\theta/2)-\varphi_2\sin(\theta/2)$
2	$(1/\sqrt{2})(d_1+d_{-1})$	$\varphi_1\sin(\theta/2)+\varphi_2\cos(\theta/2)$
3	$(1/\sqrt{2})(d_2-d_{-2})$	φ_3
4	$(1/\sqrt{2})(d_2+d_{-2})$	φ_4
5	d_0	φ_5

Structures C_1, C_5, C_7, C_{10}, C_{11}, D_1, D_5, and D_7. ($E_4 \neq E_{\min}$)

i	$\varphi_i(E_3$ or $E_5=E_{\min})$	$\varphi_i'(E_1=E_2=E_{\min})$	$\varphi_i''(E_1=E_2=E_{\min})$
1	$(1/\sqrt{2})(d_1-d_{-1})$	φ_1	$(1/\sqrt{2})(\varphi_1+\varphi_2)$
2	$(1/\sqrt{2})(d_1+d_{-1})$	φ_2	$(1/\sqrt{2})(\varphi_1-\varphi_2)$
3	$(1/\sqrt{2})(d_2-d_{-2})$	φ_3	φ_3
4	$(1/\sqrt{2})(d_2+d_{-2})$	φ_4	φ_4
5	d_0	φ_5	φ_5

Structure D_8. (E_4, $E_5 \neq E_{\min}$)

i	φ_i	$\varphi_i'(E_1=E_2=E_3=E_{\min})$	$\varphi_i''(E_1=E_2=E_3=E_{\min})$
1	$(1/\sqrt{2})(d_1-d_{-1})$	φ_1	$(1/\sqrt{3})(\varphi_1+\varphi_2+\varphi_3)$
2	$(1/\sqrt{2})(d_1+d_{-1})$	φ_2	$(1/\sqrt{6})(\varphi_1+\varphi_2-2\varphi_3)$
3	$(1/\sqrt{2})(d_2-d_{-2})$	φ_3	$(1/\sqrt{2})(\varphi_1-\varphi_2)$
4	$(1/\sqrt{2})(d_2+d_{-2})$	φ_4	φ_4
5	d_0	φ_5	φ_5

Structure D_4. (E_2, $E_4 \neq \mathrm{E}_{\min}$)

i	φ_i	$\varphi_i'(E_1=E_3=E_5=E_{\min})$
1	$(1/\sqrt{6})[\sqrt{2}(d_1-d_{-1})-(d_2+d_{-2})]$	$(1/\sqrt{10})(\varphi_1\sqrt{5+\sqrt{5}}+\varphi_5\sqrt{5-\sqrt{5}})$
2	$(1/\sqrt{6})[d_1-d_{-1}+\sqrt{2}(d_2+d_{-2})]$	$(1/\sqrt{10})(\varphi_1\sqrt{5-\sqrt{5}}-\varphi_5\sqrt{5+\sqrt{5}})$
3	$(1/\sqrt{6})[\sqrt{2}(d_1+d_{-1})+d_2-d_{-2}]$	φ_3
4	$(1/\sqrt{6})[-(d_1+d_{-1})+\sqrt{2}(d_2-d_{-2})]$	φ_2
5	d_0	φ_4

Structures A_2, A_3, B_1, B_4, B_6, B_9, C_2, C_3, C_4, C_6, C_8, C_9, D_2, D_3, and D_6.[c)] ($E_4 \neq E_{\min}$)

i	$\varphi_i(E_1$, E_2, E_3 or $E_5=E_{\min})$
1	$(1/\sqrt{2})(d_1-d_{-1})$
2	$(1/\sqrt{2})(d_1+d_{-1})$
3	$(1/\sqrt{2})(d_2-d_{-2})$
4	$(1/\sqrt{2})C_{44}(d_2+d_{-2})+C_{45}d_0$
5	$(1/\sqrt{2})C_{55}(d_2+d_{-2})+C_{55}d_0$

Structures B_2, B_3, B_7, and B_8.[c)] ($E_1 \neq E_{\min}$)

i	φ_i (E_2, E_3, E_4 or $E_5=E_{\min}$)
1	$(1/\sqrt{2})[C_{11}(d_1+d_{-1})+C_{12}(d_2-d_{-2})]$
2	$(1/\sqrt{2})[C_{21}(d_1+d_{-1})+C_{22}(d_2-d_{-2})]$
3	$(1/\sqrt{2})[C_{33}(d_1-d_{-1})+C_{34}(d_2+d_{-2})]+C_{35}d_0$
4	$(1/\sqrt{2})[C_{43}(d_1-d_{-1})+C_{44}(d_2+d_{-2})]+C_{45}d_0$
5	$(1/\sqrt{2})[C_{53}(d_1-d_{-1})+C_{54}(d_2+d_{-2})]+C_{55}d_0$

a) Wave function is designated by φ_i when the ground level is not degenerate, and by φ_i' or φ_i'' when the ground level is degenerate. b) θ shows magnitude of the Jahn-Teller distortion. c) C_{ij} is a constant characteristic of the coordination structure.

electron and the center of the transition elements, respectively. α, β, γ_j, and δ_j are variables characteristic of the symmetry of the coordination stucture about the transition element.

If we assume that the 3d electron is distributed spherically around the transition element, $\bar{r}^2$ and $\bar{r}^4$ are substituted by r^2 and r^4, respectively, and r is supposed to be equivalent to the ionic radius, the magnitude of which is known to be 0.76 and 0.60 Å for titanium(III) and vanadium(IV), respectively.[18)] Crystallographic data suggest that the length of the coordination bond, L_j, is little affected by the species of the metal atom as well as the saturated alkyl group of the ligand as far as the present compounds are concerned.[19-23)] Magnitude of L_j is 1.78 and 2.01 Å for the terminal and the bridging alkoxyl groups, respectively which were determined from the results of studies on titamium(IV) methoxide,[19)] titanium(IV) ethoxide,[20)] bis[2-methylpentane-2,4-dioxydimethyltitanium(IV)],[21)] and oxyvanadium(V) methoxide,[22)] and 2.15 and 2.34 Å for the terminal and the bridging methyl groups, respectively, from the data of trimethylaluminum.[23] A symbol, f_j, is employed to define an attraction rate of the coordination electron toward the transition element on the coordination bond. Then R_j is replaced by $L_j(1-f_j)$. For the sake of simplicity f_j's of the alkyl and the alkoxyl groups are denoted by f_R and f_{RO}, respectively. The value of $G=Ze^2(\rho^2\zeta)^{-1}$ (g_e-g) is then calculated by means of the model structures except B_5 of the titanium(III) complexes, as a function of f_R and f_{RO}.

Numerical calculation was performed with the model structures of group B to obtain a set of values of f_R and f_{RO} so that a linear relation holds between the value of $\bar{G}=(1/3)(G_x+G_y+G_z)$ and the observed value of $g_e-\bar{g}$. The condition $f_R>f_{RO}$ was assumed based on the empirical fact that the alkyl group is stronger in reducing power than the alkoxyl group. The molar ratio of the methyl and the *t*-butoxyl groups of the titanium(III) complexes was assumed to increase with increase in the amount of trimethylalumiunm. Under the conditions that $f_R/f_{RO}=1.4$ and $f_{RO}=0.14$, a linear relation was ontained by choosing pairs of the model structures and the ESR signals as B_1 and a, B_2 and b, B_3 and c, B_4 and d, and B_7 and g as shown in Fig. 10. No other values of f_R and f_{RO} gave such a linear relation. The numerical calculation was also carried out with groups A, C and D to find the linear relation for the pairs of C_6 and e, and D_5 and f. The values of $\bar{G}$ and $g_e-\bar{g}$ are plotted in Fig. 11, where the slope of the straight line yields $\rho^2\zeta(Ze^2)^{-1}=5.0\times10^{-3}$. The $\bar{g}$-values of the model structures thus calculated are given in Table 3. The structures having the degenerate ground level would not exhibit the ESR signal because of molecular vibration.

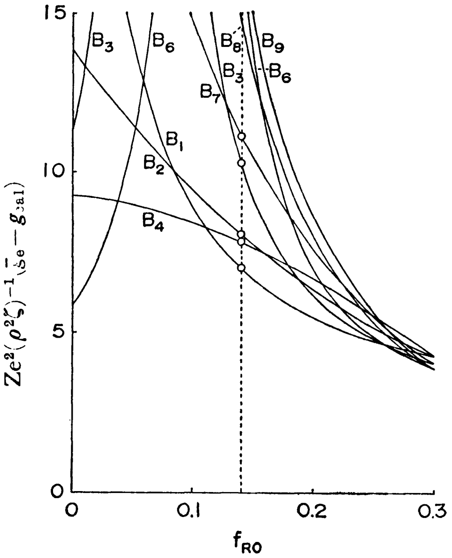


Fig. 10. Variation of calculated $\bar{g}$-value with attraction rate of the coordination electron toward the titanium(III) nucleus at $f_R/f_{RO}=1.4$.

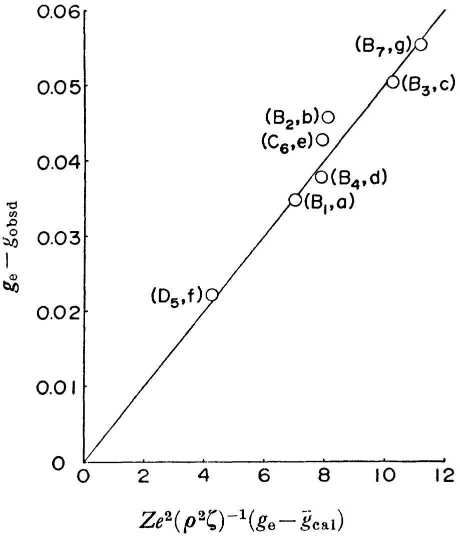


Fig. 11. Calculated and observed $\bar{g}$-values of titanium(III) complexes prepared by trimethylaluminum and titanium(IV) *t*-butoxide.

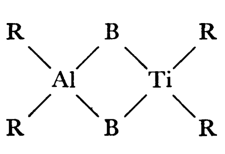
It is known that the magnitude of ζ of the titanium(III) ion is 154 cm^{-1},[16] and that the ratio of the effective nuclear charge of titanium(III) and that of vanadium(IV) is 3 : 4.[24] Hence the orbital reduction factor of the titanium(III) complex is estimated to be $\rho=0.59$ by using the experimental value of the orbital splitting energy of vanadium(IV) *t*-butoxide. The ρ value suggests that the titanium(III) complexes are larger in covalency of the coordination bond than vanadium(IV) *t*-butoxide. It can be seen from the coordination structure and the electronic state of the titanium(III) complex of B_4 that one of three molecular structures designated by AT^1, AT^2, and AT^3 is

TABLE 3. $\bar{g}$-VALES OF TITANIUM(III) COMPLEXES

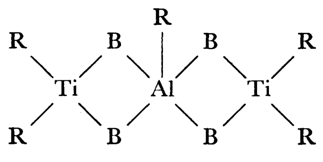
Structure	$\bar{g}$-Value		Structure	$\bar{g}$-Value	
	Calcd[a]	Obsd[b]		Calcd[a]	Obsd[b]
A_1	1.985		C_4	1.987	
A_2	1.978		C_5	1.989	
A_3	1.977		C_6	1.963	1.960
A_4	1.984		C_7	1.975	
			C_8	1.987	
B_1	1.967	1.968	C_9	1.978	
B_2	1.962	1.957	C_{10}	1.986	
B_3	1.951	1.952	C_{11}	1.981	
B_4	1.963	1.965			
B_6	1.917		D_1	(1.986)	
B_7	1.946	1.947	D_2	1.970	
B_8	1.928		D_3	1.965	
B_9	1.916		D_4	(1.994)	
			D_5	1.981	1.980
C_1	(1.994)		D_6	1.958	
C_2	1.989		D_7	1.972	
C_3	1.939		D_8	(1.989)	

a) $\bar{g}$-values given in parentheses indicate that the complex will not show the ESR signal as a result of degeneracy of the ground level. b) The complex was obtained by the reaction of trimethylaluminum with titanium(IV) *t*-butoxide in toluene, and ESR spectrum was measured at 25 °C.

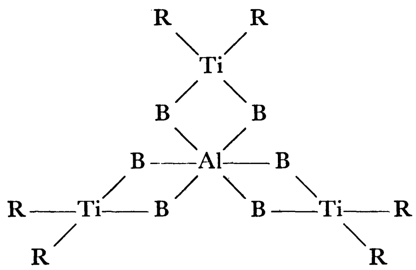
possible as the catalyst for 1,4-polymerization of isoprene.



AT^1



AT^2



AT^3

R = CH_3-, CH_3CH_2-, or $(CH_3)_2CHCH_2$-

Chemical Ionization Mass Spectra. Measurement of molecular weight is useful for determination of the molecular structure of the catalyst for 1,4-polymerization of isoprene. However, the titanium(III) complex is unstable in the air and its isolation is very difficult, so that ordinary techniques for molecular weight measurements are not available. Chemical ionization mass spectrometry is a useful means for the determination of the molecular weight of such a compound since ions are produced under mild conditions as compared with electron impact mass spectrometry.

The chemical ionization mass spectrum of the reaction mixture of trimethylaluminum and titanium(IV) *t*-butoxide at the molar ratio of 0.60 : 0.40, prepared in benzene followed by aging at 140 °C for 30 min to exhibit the ESR signal of d alone, is shown in Fig. 12. M and B denote the methyl and the *t*-butoxyl groups, respectively. None of the mass peaks observed are from a tetranuclear ion bearing an aluminum nucleus and three titanium nuclei. Peaks at *m/e* 550, 506 and 477 are assigned to ions containing an aluminum nucleus and two tiatnium(III) nuclei, $[AlTi_2M_4B_5H]^+$, $[AlTi_2M_6B_4]^+$ and $[AlTi_2M_4B_4H_2]^+$, respectively, and peaks at *m/e* 492 and 434 to ions having the nuclei of an aluminum, a titanium(III) and a titanium(IV), $[AlTi_2M_5B_4H_2]^+$ and $[AlTi_2M_6B_3H_2]^+$, respectively. On the other hand, the ESR spectrum of this sample showed a single species of the titanium(III) complex, and therefore AT^1 can not exist. If the catalyst is AT^2, the peak at *m/e* 506 should not be observed. An adequate explanation of the mass pattern is that fragments from a tatranuclear complex displayed the mass peaks of the trinuclear ions. Hence AT^3 is the molecular structure of the catalyst for 1,4-polymerization of isoprene.

The catalytic complex, AT^3, is named tris[di-μ-*t*-butoxo-dialkyltitanium(III)]aluminum. The aluminum nucleus is located at the center of the tetranuclear complex with the coordination number of six, while the titanium(III) nuclei occupy the outer three positions at a distance suitable for bidentate coordination of isoprene. Three pairs of the *t*-butoxyl groups combine three titanium(III) nuclei with an aluminum nucleus to support the tetranuclear structure. The alkyl group takes the terminal positions of the titanium(III) nuclei, and may participate directly in the reaction of isoprene.

A proposal is made to interpret the mechanism of 1,4-polymerization of isoprene as follows. Three molecules of isoprene can form bidentate coordi-

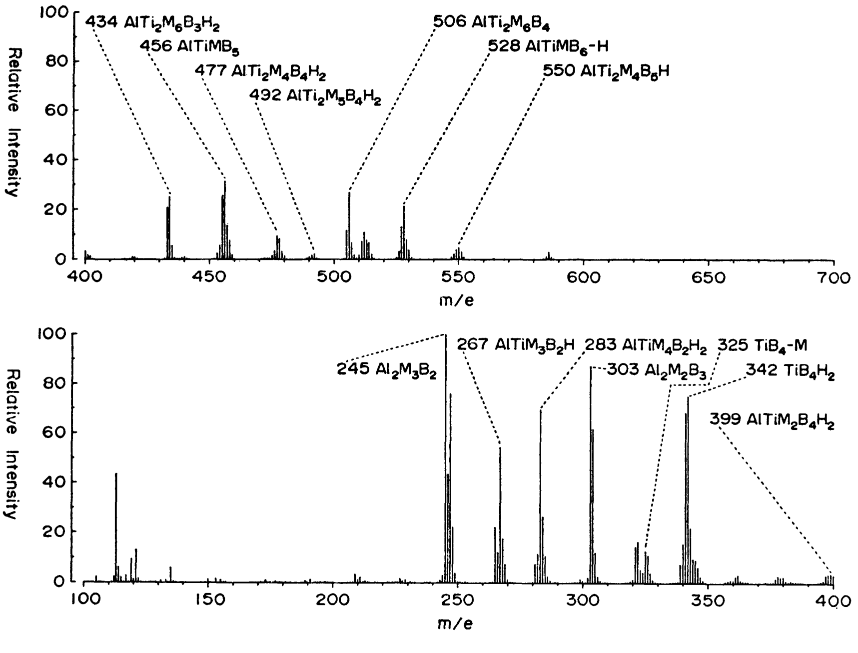


Fig. 12. Chemical ionization mass spectrum of the mixture of trimethylaluminum and titanium(IV) *t*-butoxide at the molar ratio of 0.60 : 0.40 after heating in benzene 140 °C for 30 min.

nation to a catalyst molecule at the same time. As soon as an alkyl group of the catalyst activates one of the terminal carbons of isoprene on the catalyst, another terminal carbon attacks the end of the neighboring isoprene releasing the coordination bond. A new isoprene molecule then takes the unoccupied sites of the catalyst. Thus, 1,4-polyisoprene is produced through the successive coordination of isoprene followed by formation of new carbon-carbon bonds, although the mechanism can not explain regular head to tail polymerization of isoprene and its *cis-trans* selectivity.

Conclusion

Structures of the Ziegler-Natta catalysts for the polymerization of isoprene were studied by means of ^{1}H-NMR, ESR and chemical ionization mass spectrometry. The catalyst was prepared in benzene or toluene by the reaction of alkylaluminum with titanium(IV)- or vanadium(IV) *t*-butoxide. The experiment of polymerization was carried out at 80—140 °C for 20 h after heating the catalyst.

The alkoxide was monomeric in the solution, and reduced by the alkylaluminum to produce a bivalant complex *via* trivalent complexes. The final product of the reduction of vanadium(IV) *t*-butoxide was bis(di-μ-alkyl-dialkylaluminum)vanadium(II). When the transition element took the trivalent state, the catalytic system caused five kinds of polymerization of isoprene.

Coordination structure of seven kinds of titanium(III) complexes was determined by comparing the observed *g*-values with the calculated ones, three kinds of molecular structures remaining as the catalyst for 1,4-polymerization of isoprene. As a result of molecular weight determination it was found that the catalytic complex was tris[di-μ-*t*-butoxo-dialkyltitanium(III)]aluminum.

The catalyst has a tetranuclear stucture suitable for bidentate coordination of isoprene. A proposal was made to interpret the reaction mechanism: the 1,4-polymerization takes place through succssive coordination of isoprene to the catalyst followed by bond formation between a terminal carbon of isoprene and a propagating chain end of polyisoprene, both of which occupy adjacent positions on the catalyst.

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