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Reactions Between AlRCl_2 and $\text{Ti}(\text{OR}')_4$ and Activity in Diolefin Polymerization*

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SUMMARY

Through the use of a $\text{Ti}(\text{OR}')_4$ – AlRCl_2 catalyst system, high 1,4-cis isoprene polymers and crystalline 1,4-trans polybutadiene are obtained. Neither monomer is polymerized at a Al/Ti mole ratio of less than 4. The maximum activity and stereospecificity for isoprene is observed at Al/Ti = 4. For 1,4-trans butadiene polymers the activity increases progressively with increasing Al/Ti ratio. The investigations carried out on this catalyst system show that at a Al/Ti mole ratio of 4 the formation of crystalline β - TiCl_3 takes place, while at lower ratios insoluble chloroalkoxide derivatives of Ti^{III} with different compositions separate. Soluble complexes containing aluminium and titanium are initially formed before precipitation occurs. Chemical data and investigations by IR and NMR spectroscopy indicate exchange reactions between Al–Cl, Al–R, and Ti–OR groups, together with reduction of the transition metal. A reaction mechanism and a hypothesis on the nature of the active catalyst are given.

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INTRODUCTION

The preparation of polymers of butadiene and isoprene having predominantly 1,2 and 3,4 structures, respectively, by means of Ziegler-Natta catalyst prepared from titanium alkoxides and aluminum trialkyls is well known [1]. It has been reported that aluminum alkyl dichloride is not a stereospecific catalyst for the polymerization of diolefins with either TiCl_4 or $\beta\text{-TiCl}_3$ [2].

$\text{AlRCl}_2\text{-Ti(OR')}_4$ catalyst was employed [3] in the polymerization of olefins and in their copolymerization with vinyl monomers. The catalytic activity of this system is related to soluble, uncharacterized complexes. The insoluble part, which formed on aging, was completely inactive.

In view of this, it is rather surprising that we obtained completely different results when employing $\text{AlRCl}_2\text{-Ti(OR')}_4$ systems in the polymerization of diolefins. Thus, polymerization of the aforementioned diolefins with $\text{AlC}_2\text{H}_5\text{Cl}_2$ and $\text{Ti(O-nC}_4\text{H}_9)_4$ yields high 1,4-cis (up to 96%) polyisoprene and crystalline 1,4-trans polybutadiene.

EXPERIMENTAL

Materials

Aluminum alkyl dichloride was synthesized by reaction of AlR_3 with AlCl_3 and purified by distillation. Pure commercially available titanium alkoxides were purified by distillation. Phillips "polymerization grade" butadiene was dehydrated by standing on Al_2O_3 and bubbling through an $\text{Al(C}_2\text{H}_5)_3$ solution. Pure Phillips isoprene was dehydrated by distillation on Na. Solvents were purified and dehydrated according to the usual accepted methods. All operations were carried out under a dry, inert atmosphere.

Polymerization

The polymerizations were carried out in screw-cap bottles of about 200 ml capacity as previously described [4]. The catalysts were preformed in the absence of the monomer and aged 30 min at room temperature. During the course of polymerization the bottles were left in a rotating thermostatic bath, then the content of the bottles was poured into methyl alcohol containing an antioxidant. IR determinations on the polymer were carried out in CS_2 solutions by the Binder method [5].

Catalyst Investigations

The catalysts were prepared by adding a AlRCl_2 solution in 50 ml of n-heptane dropwise to a stirred solution of 10 mmoles of $\text{Ti}(\text{OR}')_4$ in 250 ml of n-heptane. The reactions were carried out at room temperature for 20 hr. The mixture was filtered through a porous glass filter G4 and washed five times with 50 ml of heptane each time. The solid part was dried in vacuum and analyzed. The liquid phase and the washing solvent were concentrated and analyzed.

The reactions were carried out at higher concentrations ($\text{Ti} = \sim 0.25 \text{ M}$) and performed under UV light when AlCH_3Cl_2 was used.

Analyses and Physicochemical Measurements

Both aluminum and titanium were determined colorimetrically [6]. Chlorine was determined by the Vohlard method. Low valency titanium halides were determined using the Martin and Stedefeder method [7]. Deuterobenzene solutions were employed for NMR measurements (Varian A 60) 15 min after the mixing of reactants. Heptane solutions were used for infrared (Perkin Elmer 125) and EPR (Varian 45021) investigations.

RESULTS

The influence of Al/Ti molar ratio on the polymerization of isoprene is shown in Table 1. The best yield, together with the higher 1,4-cis content, corresponds to a Al/Ti molar ratio of 4. At lower ratios the system was inactive; at higher ratios the yield, and then the stereospecificity, decrease gradually.

Further investigations is necessary in order to clarify whether the polymers obtained at $\text{Al/Ti} > 7$ are mixtures of high 1,4-cis and 1,4-trans polymers or copolymers.

In the case of the butadiene polymerization (Table 2), 1,4-cis polymers prevailed for initial Al/Ti ratios of 4–6. On the basis of the similarity of composition for soluble and insoluble fractions, it is possible to conclude that the polymers do not consist of a mechanical mixture of all 1,4-cis and 1,4-trans chains. Furthermore, a weak 1,4-trans crystallinity present in the raw polymer suggests the existence of block copolymers. By further increasing of the Al/Ti ratio the polymer structure changed to a prevailing 1,4-trans enchainment. As shown in Table 3, the amount of these polymers extracted by different boiling solvents was more than 80%. According to IR

Table 1. Polymerization of Isoprene by $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2 - \text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$ System^a

Test No.	Al/Ti mole ratio	Yield (g)	$[\eta]^b$ (dl/g)	Infrared analysis		
				1,4 cis (%)	1,4 trans (%)	3,4 (%)
1	4	9.8	1.77	96	0	4
2	5	8.8	2.77	96	0	4
3	6	6.2	3.86	96	0	4
4	7	2.6	2.75	88	8	4
5	8	1.5	n.d.	75.5	20	4.5
6	9	1.4	n.d.	63.5	31.5	4
7	10	1.1	n.d.	58	38	3

^aConditions: n-heptane, 50 ml; isoprene, 15 ml; $\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$, 1 mmole; temperature, 30°C; polymerization time, 17 hr; catalyst aged 30 min at room temperature.

^b $[\eta]$ at 30°C in toluene.

Table 2. Polymerization of Butadiene by $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2 - \text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$ System^a

Test No.	Butadiene (g)	Al/Ti mole ratio	Yield (g)	X-ray crystallinity (%)	Soluble fraction in CS_2	Infrared analysis		1,2 (%)
						1,4 cis (%)	1,4 trans (%)	
1	12.3	3	—	—	—	—	—	—
2	8.2	4	6.9	—	30	63.5	34.5	2b
3	12.0	5	3.8	5	40	65.5	33	1.5c
4	10.0	6	5.0	5	60	66.0	31.0	3b
5	9.0	8	2.9	25	80	72	36.0	2c
6	11.0	10	6.7	30	80	58.0	39.0	3b
7	11.0	12	8.3	50	80	73.0	26	1c
8	10.0	14	8.0	50	80	17.0	79.0	4b
						4.0	94.0	2b
						5.0	93.0	2b
						5.0	93.0	2b

^aConditions: *n*-heptane, 50 ml; $\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$, 1 mmole; temperature, 30°C; polymerization time, 17 hr; catalyst aged 30 min at room temperature.

^bInfrared determinations on soluble fraction.

^cInfrared determinations on insoluble fraction.

Table 3. Fractionation Results with Different Boiling Solvents for Butadiene Polymers Obtained by $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2 - \text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$ System at High Al/Ti Ratios

Al/Ti	Diethyl ether ^a extract (%)	Hexane ^b extract (%)	Benzene extract (%)	Residue ^c (%)
8	46.3	33.6	0.3	19.4
10	45	36.4	2.1	12.1
12	49	42.5	0.9	11.8
14	50	44.3	0.2	5.5

^aInfrared analysis: 1,4 cis, % = 17.5–9; 1,4 trans, % = 81.5–90; 1,2 % = 1–2. Total found = 93–85.

^bInfrared analysis: 1,4 cis, % = 6–5.5; 1,4 trans, % = 93.5–94; 1,2 % = 0–1. Total found = ~105. X-ray crystallinity, % = 50–70.

^cX-ray crystallinity, % < 5.

and X-ray determinations, the soluble fractions consist of prevailing 1,4-trans chains. The residue, which was difficult to characterize, shows a low degree of crystallinity (< 5%) and probably contains cyclized polymers.

An investigation of the reaction between the components of the catalyst was necessary in order to explain the polymerization data.

By adding n-heptane (or benzene) solutions of AlRCl_2 to solutions of $\text{Ti}(\text{OR}')_4$ ($\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5$; $\text{R}' = -\text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$), a reaction takes place which brings about the final separation of different insoluble chloro-alkoxides of Ti^{+3} , depending on the initial Al/Ti ratio.

Our investigations have been carried out by taking in account both the chemical analyses and EPR measurements on the final insoluble products, and NMR and IR measurements on the reaction mixture before precipitation.

Chemical Analyses

Chemical analyses of the reaction products between $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ and $\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$ are reported in Table 4. At a Al/Ti mole ratio of 4, where the higher catalytic activity in the isoprene polymerization is observed, the solid part of the catalyst consists exclusively of crystalline $\beta\text{-TiCl}_3$. At lower Al/Ti

Table 4. Chemical Analyses of Reaction Products between $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ and $\text{Ti}(\text{O}-\text{nC}_4\text{H}_9)_4$

Test No.	Initial Al/Ti mole ratio	Insoluble phase						Soluble phase		
		Ti (%)	Cl (%)	Al (%)	Cl/Ti	Al/Ti	TiII/TiIII	X-ray examination	Ti	Cl/Al
1	2	23.7	32.92	0.76	1.87	0.067	n.d.	n.d.	Traces	1.09
2	3	23.51	41.03	0	2.36	0	0.03	n.d.	Absent	1.33
3	4	27.18	61.20	0	3.03	0	0	Crystalline $\beta\text{-TiCl}_3$	Absent	1.34
4	10	27.57	58.97	2.28	2.9	0.14	0	Crystalline $\beta\text{-TiCl}_3$	Absent	1.72

mole ratios different chloro-alkoxides of Ti^{III} separate. At $\text{Al/Ti} = 1$ the reaction is very slow, ethane and ethylene are evolved, and insoluble Ti^{III} derivatives whose composition is $\text{Ti}(\text{OR}')_{2-x}\text{Cl}_{1-x}$ ($x = 0.2-0.5$) precipitate. For Al/Ti ratios higher than 4, the $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ excess does not further reduce $\beta\text{-TiCl}_3$.

In an attempt to follow the different steps of the reaction, we have extended our investigations to a similar system based on AlCH_3Cl_2 , whose reaction with titanium alkoxides is slower. This behavior agrees with the higher stability of titanium compounds containing Ti-CH_3 bonds with respect to the other alkyl derivatives [8]. Furthermore, a more simple interpretation of the spectroscopic data (NMR) is available by employing AlCH_3Cl_2 .

The analytical data for the reaction products of AlCH_3Cl_2 and $\text{Ti}(\text{O-nC}_4\text{H}_9)_4$ are in good agreement with the data reported in Table 4.

Spectroscopical Investigations

The course of the reactions was followed by NMR, IR, and EPR measurements at different initial Al/Ti mole ratios.

EPR spectra of the reaction mixtures in which insoluble compounds were already formed show a broad signal with a g -value of 1.959, attributed to the trivalent titanium species, in agreement with other authors [9]. No EPR signal is present before separation of the insoluble compounds.

NMR investigations were carried out in deuterio-benzene solutions using tetramethylsilane as the internal standard. Three kinds of NMR signals can be observed for the reaction between AlCH_3Cl_2 and $\text{Ti}(\text{O-nC}_4\text{H}_9)_4$ at $\text{Al/Ti} = 1$: a signal at -19 Hz attributed to the Al-CH_3 resonance [10]; a complex pattern of signals at about 90 Hz due to protons on the β -, γ -, and δ -carbon atoms of alkoxy groups; and a triplet not resolved at 280 Hz with a broader signal at 255 Hz. The 280 Hz signal is correlated to the protons on the α -carbon atoms of alkoxy radicals. The signal centered at 255 Hz has been assigned to the presence of $\text{Ti-O}(\text{CH}_2\text{R})\text{-Al}$ bridges. The presence of bridged methyl protons, AlCH_3Ti , should correspond to a signal at ~ 90 Hz (i.e., an average value between 137 and -24 Hz observed for TiCl_3CH_3 and AlCH_3Cl_2 , respectively). In any event, we have not been able to observe such a signal, owing to the complexity of the alkyl signal in that area.

At higher Al/Ti mole ratios a large number of signals appear in the range -19 to -25 Hz for the presence of different methyl-aluminum species, depending on the formation of methyl-alkoxy-aluminum derivatives. A progressive shift to higher fields of the signal centered at 255 Hz could be

justified by the increasing chlorination of the titanium atom. At the same time the increase in intensity of this signal is correlated with the decrease of Ti-OR terminal (not bridged) alkoxy groups and the increase of alkoxy aluminum-titanium bridge derivatives. For $\text{Al/Ti} \geq 3$ the signals at 270–280 Hz, due to the protons of terminal alkoxy radicals on titanium atoms, are completely absent, while a new triplet appears at 220 Hz attributed to a new Ti-O(CH₂R)-Al species. Again, at $\text{Al/Ti} \geq 3$ a signal for TiCH₃ methyl appears at 137 Hz. This interpretation is consistent with the presence of a signal at the same field for TiCH₃Cl₃.

IR data on heptane solutions generally agree with NMR data. At increasing Al/Ti mole ratios a decrease of the intensity of absorption bands at 1115 and 1080 cm^{-1} is observed. These bands are assigned to Ti-OCH₂R groups, in good agreement with other authors [11].

At the same time the intensities of the absorptions both of Al-OCH₂R groups at 1060 and 1025 cm^{-1} and of TiCl at 490 cm^{-1} increase. In addition, absorption bands at 450 and 535 cm^{-1} , due to the Ti-C bond [12], distinctly appear at $\text{Al/Ti} = 4$.

DISCUSSION

On the basis of the above results, the mechanism scheme reported in Fig. 1 is proposed. The principal steps can be summarized as follows:

- 1). Soluble complexes between AlRCl_2 and $\text{Ti}(\text{OR}')_{4-x}\text{Cl}_x$ are formed, in which the chlorine content on the titanium atoms increase with increasing initial Al/Ti ratio.
- 2). An internal exchange reaction $\text{AlCl} + \text{TiOR}' \rightarrow \text{AlOR}' + \text{TiCl}$ takes place in these complexes.
- 3). The stability of the complexes decreases with an increase in the number of chlorine ligands on the titanium atom.

No attention was given to the exact coordination of titanium; thus, an addition aluminum species (e.g., alkoxy derivative) could complex on the titanium without influencing the general trend of the reactions.

In order to verify the general mechanism of the reaction, we have reacted the chloro-alkoxy-titanium^{IV} derivatives [viz., $\text{Ti}(\text{OR})_3\text{Cl}$, $\text{Ti}(\text{OR})_2\text{Cl}_2$, $\text{Ti}(\text{OR})\text{Cl}_3$] with stoichiometric amounts of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, and we have compared the chemical analyses of the insoluble products obtained with the values obtained for the corresponding products at the different reaction steps. Good agreement was observed (Table 5).

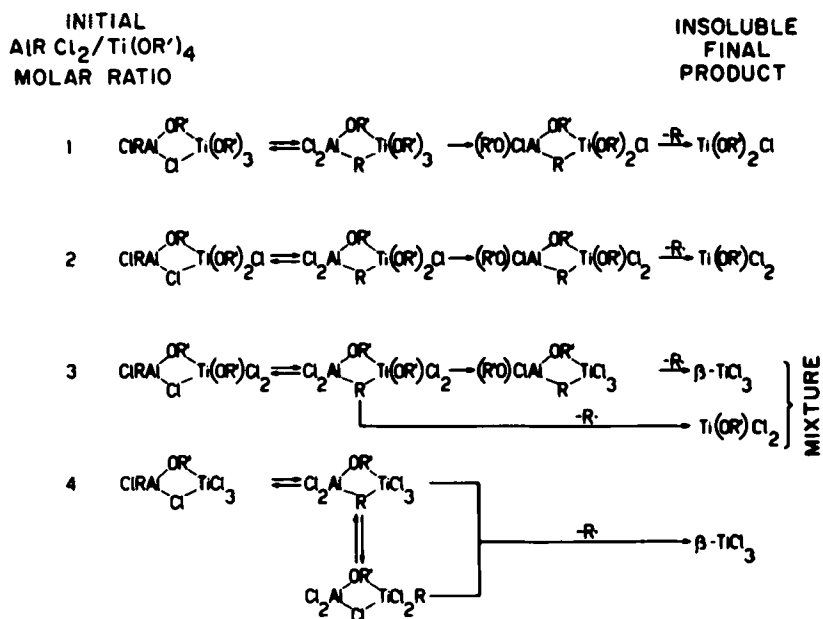


Figure 1.

In addition, we have observed an almost complete correlation between the NMR spectra of deuterio-pyridine solutions of the soluble intermediates from the reactions of $\text{Ti}(\text{OR})_4$ and AlCH_3Cl_2 at Al/Ti mole ratios of 1, 2, 3, and 4 and the NMR spectra of deuterio-pyridine solutions of $\text{Ti}(\text{OR})_4$, $\text{Ti}(\text{OR})_3\text{Cl}$, $\text{Ti}(\text{OR})_2\text{Cl}_2$, and $\text{Ti}(\text{OR})\text{Cl}_3$, respectively (Table 6). This could confirm that the $\text{TiOR} \rightarrow \text{TiCl}$ exchange takes place almost completely in the homogeneous phase before the reduction of the titanium.

The formation of $\beta\text{-TiCl}_3$ (which we find enhanced by UV radiation) explains the activity of these systems in the isoprene polymerization. The initiator is certainly originated by the absorption of some aluminum alkyl species (derived from the reactions of AlRCl_2) on the $\beta\text{-TiCl}_3$ surface; in fact, we obtained up to 96% 1,4-cis polyisoprene by employing, e.g., the catalytic system $\beta\text{-TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)(\text{OR})\text{Cl}$.

The different chloro-alkoxides of Ti^{3+} separated from the reaction mixtures at $\text{Al/Ti} < 4$ have no catalytic activity under our experimental conditions.

At $\text{Al/Ti} \geq 6$ some cationic character appears (due to the large excess of AlRCl_2) and was evidenced by the progressive activity in the polymerization of isobutylene at -78°C . However, the polymerization of butadiene

Table 5. Chemical Analyses of Insoluble Products Obtained from Reaction between Stoichiometric Amounts of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ and Different Chloro-alkoxy-titanium Derivatives

Titanium derivatives	Ti (%)	Cl (%)	Al (%)	Cl/Ti	Al/Ti	X-ray test
$\text{Ti}(\text{O}-n\text{C}_3\text{H}_7)_3\text{Cl}$	24.15	32.99	0.67	1.84	0.05	Amorphous
$\text{Ti}(\text{O}-n\text{C}_3\text{H}_7)_2\text{Cl}_2$	26.8	44.38	1.17	2.27	0.09	Amorphous
$\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)\text{Cl}_3$	27.75	57.3	1.39	2.85	0.088	Crystalline β - TiCl_3

Table 6. NMR Signals for Protons on α -Carbon Atoms of Ti-O-CH₂-R Groups

AlCl ₃ Cl ₂ Ti(O-nC ₄ H ₉) ₄ initial mole ratio	NMR Signals (Hz)		Titanium alkoxides ^a	NMR signals (Hz)	
	Without D-pyridine	With D-pyridine		Without D-pyridine	With D-pyridine
1	280; 255	282	Ti(O-nC ₄ H ₉) ₄	280	280
2	270; 250	290	Ti(O-nC ₄ H ₉) ₃ Cl	280	280
3	250; 220	287	Ti(O-nC ₄ H ₉) ₂ Cl ₂	280	286
4	220	298	Ti(O-nC ₄ H ₉)Cl ₃	249	300

^aPurified commercial products.

is not related merely to the cationic activity of AlRCl_2 . In fact $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ itself, under the same experimental conditions, gives completely amorphous products in low yield; on the contrary, crystalline 1,4-trans polybutadienes were obtained by using $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ together to $\beta\text{-TiCl}_3$ at a $\text{Al/Ti} \geq 2$ ratio.

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