Influence of Diphenyl Ether and Water on the Polymerization of Isoprene with Triisobutylaluminium and Titanium Tetrachloride

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Synopsis

In the polymerization of isoprene with the i-Bu$_3$Al/TiCl$_4$ catalyst at the mole ratio of 1.0 the diphenyl ether adduct of the i-Bu$_3$Al showed no effect on the catalyst efficiency. The ether did not improve the low efficiency of the catalyst at ratios slightly above 1.0, but below 1.0 it brought the catalyst activity up to optimum. The ether compensated for the deleterious effects upon the catalyst of low amounts of water present in the isoprene solution in hexane. At the Al/Ti mole ratio slightly above 1.0, water and diphenyl ether were found to act synergistically in raising catalyst efficiency. In addition, at or close to optimal operating Al/Ti mole ratios the diphenyl ether had a very marked effect in improving the polymerization rate. Polymer properties were generally unaffected by use of the ether-coordinated catalyst.

INTRODUCTION

It is known[1,2] that the efficiency of the R$_3$Al–TiCl$_4$ catalyst in polymerizing isoprene to a high *cis*-1,4 polymer is critically dependent upon the mole ratio of the R$_3$Al and TiCl$_4$. This has been confirmed in the work described here. The term "catalyst efficiency" as used in this report denotes the conversion of isoprene to polymer recoverable by the alcohol coagulation of the polymerizate. For maximum conversion power, the mole ratio of these components was experimentally found to be 1.0. At this ratio the reaction between i-Bu$_3$Al and TiCl$_4$ at room temperature, and with the given period of aging, is generally believed to lead mainly to i-Bu$_2$AlCl and β-TiCl$_3$, assuming that no interfering impurity is present which could act upon the reactants and products to alter these species. These products then function by a mechanism as yet not fully understood in the polymerization of isoprene.

Because of the high degree of specificity of the i-Bu$_2$AlCl and β-TiCl$_3$ so produced toward the efficient polymerization of isoprene, it follows that the presence of altered forms of these specific components will result in a departure from the maximum catalyst efficiency and also the characteristic properties of the polymer product. The catalyst so altered would depend upon the extent to which reactions can take place between the catalyst and

extraneous substances in the system, particularly water, and also on the initial mole ratio of the reacting catalyst components.

Early reports on the polymerizations of isoprene with the alkylaluminum–titanium tetrachloride catalyst indicated a polymer product of moderate conversion and considerable gel.[3-7] Later work described better catalyst efficiency and also the reduction of the polymer gel content to from tolerable to negligible amounts. At the same time studies were reported of additives to the catalyst which improved polymerization rates and polymer molecular weight and reduced the gel content. The important modifications consisted of the addition to the catalyst of electron donors such as ethers,[8,9] amines,[1] and oxygen.[4] Attributed to the ether were increased rates and also improved properties of the compounded and cured polyisoprene rubber.[10] The ether and the amine additives were said to act synergistically[1] to increase the polymerization rate and molecular weight and to suppress gel formation.

We have made a study of the interrelationship between the critical Al/Ti mole ratio, the presence of low levels of the common impurity water in the isoprene–solvent solution, and the mole ratio of the diphenyl ether adduct of the triisobutylaluminum component.

The study of the effects of diphenyl ether and water in the catalysis process was carried out at a constant level of 3.0 mmoles of TiCl₄ per 100 g of monomer at the various Al/Ti mole ratios investigated. Studies made above and below this constant level of TiCl₄ were not carried out, although the introduction of another parameter, such as the variation in total catalyst, could conceivably have led to other trends. It was felt, however, that the subsequently suggested mechanism of interaction between the catalyst components would be independent of the total amount of catalyst used, and that more or less total catalyst would produce the horizontal changes which are known to result from changes in catalyst level.

EXPERIMENTAL

The following materials were used in carrying out the polymerizations: isoprene (Shell); commercial hexane (Aycock); triisobutylaluminum, commercial, used without further purification; titanium tetrachloride, 99.5% pure, used without further purification, and diphenyl ether, mp 26–28°C, dried over CaH₂.

Hexane was washed with concentrated H_2SO_4 until colorless, then with water, followed by a wash with 10% NaOH, and lastly with water until neutral. The hexane was distilled, a 10% by volume forerun was discarded, and about two-thirds of the remainder were distilled directly into a silica gel column. The purified hexane was collected in bake-dried 28-oz. beverage bottles and stored over CaH₂ until used.

For a polymerization run, the required amount of hexane, less added solvents, was transferred to a bake-dried bottle and about 20 g of CaH₂ was added, followed by the required amount of purified isoprene. Isoprene

was purified by refluxing with sodium for 1 hr, distilled, the first 10% by volume were discarded, and the two-thirds of the remainder were collected in the hexane. The isoprene solution over CaH_2 was allowed to stand overnight, then transferred to a fresh bake-dried 28-oz. bottle and charged with the catalyst.

Titration of the hexane–isoprene blend with sodium triphenylmethyl showed the presence of 4 ppm water. The amount of added water plus residual water was made to equal the amounts required for the H_2O/Al mole ratios shown.

The catalyst was prepared in a 7-oz. baked beverage bottle by adding to a volume of hexane an approximate molar solution of i-Bu_3Al in hexane, followed by the rapid injection of the $TiCl_4$ solution of a similar concentration, so that the final volume was 30.0 ml and contained 3.0 mmoles of titanium at the required Al/Ti mole ratio. The bottle contents became warm and the bottle was gently swirled for 1 min, then allowed to age on the desk top for 1 hr before use. Where diphenyl ether was used, the ether and the i-Bu_3Al were mixed and aged for 10 min before mixing with $TiCl_4$.

Polymers were coagulated with isopropanol containing phenyl-2-naphthylamine and dried under vacuum at 50°C.

Infrared measurements were made on polymer samples purified by solution in toluene and re-precipitation with alcohol. The method of Binder and Ransaw[11] developed in this laboratory was used to measure the percent cis, trans, 1,2, and 3,4 structures.

The Critical Al/Ti Mole Ratio

It is generally accepted that the final predominant catalytic products formed by the reaction between R_3Al and $TiCl_4$ at room temperature over the range of useful Al/Ti mole ratios are as given in Table I. The actual products at the several ratios shown are not as strictly stoichiometric as indicated, but rather tend to diffuse to some extent across the stoichiometric limits. This may be because the complex reactions are not instantaneous.

The ratio of 1.0 leads mainly to R_2AlCl and the dark-brown hydrocarbon-insoluble β-$TiCl_3$. This has been found, under the experimental conditions

TABLE I
Reactions of R_3Al and $TiCl_4$ at Different Al/Ti Mole Ratios

Al/Ti mole ratio	Reactions
3	$3 R_3Al + TiCl_4 \rightarrow 3 R_2AlCl + R_2TiCl + R \cdot$
2	$2 R_3Al + TiCl_4 \rightarrow 2 R_2AlCl + RTiCl_2 + R \cdot$
1	$R_3Al + TiCl_4 \rightarrow R_2AlCl + TiCl_3 + R \cdot$
0.5	$R_3Al + 2 TiCl_4 \rightarrow RAlCl_2 + TiCl_3 + 2R \cdot$
0.33	$R_3Al + 3 TiCl_4 \rightarrow AlCl_3 + TiCl_3 + 3R \cdot$

described here, to be the optimum ratio for isoprene polymerization to a maximum yield of high cis-1,4-polyisoprene. Under these conditions, i-Bu₂AlCl and β-TiCl₃ are presumed to be the specific catalyst for isoprene. Above the ratio of 1.0, the products are alkylated titanium halides and R₂AlCl. Below 1.0, the products are β-TiCl₃ and progressively dealkylated aluminum chlorides which are essentially higher in Lewis acidity as the ratio approaches 0.33.

The ratios above and below 1.0, while not yielding optimum catalysts for isoprene, are nevertheless optimal in olefin polymerization. With isoprene, catalysts prepared from i-Bu₃Al/TiCl₄ mole ratios between about 1.1 or 1.2 and up to about 2.0 have been reported to produce low yields of alcohol-insoluble polymer and a considerable amount of very low molecular weight polymers, cyclic compounds of the vinylcyclohexene type, dimers, trimers, etc.[2]

The catalyst prepared from ratios of less than 1.0 will polymerize isoprene at a very rapid rate to a low conversion polymer containing gel in amounts proportional to the decrease in the Al/Ti mole ratio. This is not unexpected, for the nature of the catalyst at the low ratios becomes more of the Friedel-Crafts type, or cationic, in character. The deviation from maximum catalyst efficiency at the ratios above and below 1.0 will be noted in the data to be given and in Figure 1, which is a plot of polymer conversion versus Al/Ti mole ratio. The Gaussian-type distribution demonstrates the sensitivity of polymer conversion to small changes in the ratio. Polymer conversion in excess of 80% occurred between the 0.95 and 1.05 ratios.

Diphenyl Ether at Different Al/Ti Mole Ratios

Polymers were prepared at 5°C in a dry solution of isoprene in hexane, using i-Bu₃Al–TiCl₄ catalysts at mole ratios of 0.8, 0.9, 1.0, and 1.1. Each of these four types of catalysts were made with i-Bu₃Al which was previously reacted with 0, 1.0, 2.0, 4.0, and 6.0 moles of diphenyl ether per mole of i-Bu₃Al before being combined with the TiCl₄.

The results of the polymerizations are given in Table II. At the ratio of 1.0, the optimum for isoprene, where the specific catalyst consists essentially of i-Bu₂AlCl and β-TiCl₃, the diphenyl ether adduct of i-Bu₃Al had no effect on the catalyst efficiency compared with the uncomplexed i-Bu₃Al. Nor did it make much difference, if at all, whether the φ₂O/Al ratio was 1.0 or 6.0.

At the 1.1 ratio, the diphenyl ether adduct had no discernible effect on the low polymer conversions usually obtained at this ratio with uncomplexed i-Bu₃Al.

At the Al/Ti ratios below 1.0, the diphenyl ether showed considerable effect. Catalyst efficiency was brought up to the maximum with at least one φ₂O per i-Bu₃Al at Al/Ti = 0.9, and two φ₂O per i-Bu₃Al at Al/Ti = 0.8. Further addition of the ether had no effect.

The polymer dilute solution viscosity (DSV) was generally unaffected, and showed only small decreases in value which rather reflected the changes

noted in the gel content of these polymers. In the absence of diphenyl ether, the polymer DSV showed a minimum at the Al/Ti ratio of 1.0.

The introduction of diphenyl ether at the Al/Ti ratios of 1.0 and 1.1 resulted in small amounts of gelled polymer, particularly with the higher amounts of the base used. But at the 0.8 and 0.9 ratios, diphenyl ether caused gel formation with at least one ϕ_2O per i-Bu$_3$Al. Contrary to the large amounts of gel so often associated with the polymerization of isoprene

TABLE II
Interaction Study.[a] Relationship Between Diphenyl Ether and Al/Ti Ratio

	Al/Ti = 0.8	0.9	1.0	1.1
	Conversion, %			
ϕ_2O/Al = 0	22.1	55.2	98.3	55.0
1	64.9	97.7	89.5	54.9
2	93.7	98.9	95.5	56.5
4	96.0	97.9	98.2	55.4
6	97.3	97.2	99.0	52.8
	cis-1,4 Content, %			
ϕ_2O/Al = 0	95.8	96.1	96.6	96.4
1	96.0	94.3	97.1	96.1
2	96.6	96.9	96.1	96.3
4	96.5	96.8	96.4	91.9
6	96.8	96.8	95.2	96.4
	Dilute solution viscosity (DSV)			
ϕ_2O/Al = 0	4.5	3.8	2.9	4.1
1	3.6	2.7	3.1	3.6
2	3.0	2.8	3.0	3.5
4	3.1	2.7	2.7	3.9
6	2.8	3.1	2.7	3.8
	Gel, %			
ϕ_2O/Al = 0	5.0	0	0	0
1	25.0	20.0	10.0	0
2	20.0	17.5	1.5	0
4	17.5	17.5	10.0	12.5
6	20.0	25.0	5.0	5.0

[a] 3.0 mmoles TiCl$_4$ phg, 20% isoprene in hexane, polymerization temperature 5°C.

with the i-Bu$_3$Al–TiCl$_4$ catalyst, as observed in much of the published work, no gel formation was noted in all the polymerizations carried out with the two-component catalyst alone.

The polymer microstructure remained entirely unaffected by the changes in the Al/Ti and ϕ_2O/Al mole ratios. The resistance of these polyisoprenes to appreciable changes in their microstructure as the result of the modifications introduced into the catalyst is an important characteristic of the system.

Water at Different Al/Ti Mole Ratios

As stated above, the data obtained in the study of the influence of diphenyl ether on the catalysis of isoprene at the several Al/Ti ratios given were based upon polymerizations carried out under dry conditions. The results of the influence of water on the catalyst, and the interrelation between water and diphenyl ether to be described below, were based upon polymerizations carried out under conditions of isoprene–solvent blend wetness produced by the addition to the blend of measured amounts of a benzene solution of water. The wetness is expressed as the mole ratio of H_2O to Al, or mole percent of H_2O based on the i-Bu$_3$Al.

TABLE III

Solvent	Conv., %	cis, %	trans, %	1%,2%	3%,4%	DSV	Gel, %
Hexane	97.6	95.7	1.4	0.0	2.9	3.4	5.0
Benzene	88.5	96.0	0.0	0.0	4.0	3.5	5.0

TABLE IV
Interaction Study.   Relationship Between Water and Al/Ti Ratio

	Al/Ti = 0.8	0.9	1.0	1.1
		Conversion, %		
$H_2O/Al = 0$[a]	22.1	55.2	98.3	55.0
0.2	49.8	92.4	79.9	42.3
0.5	43.8	67.1	69.5	42.9
0.8	30.6	38.2	57.8	50.1
1.0	28.9	42.1	52.7	52.2
		cis-1,4 Content, %		
$H_2O/Al = 0$[a]	95.8	96.1	96.6	96.4
0.2	95.9	96.4	96.4	96.1
0.5	93.9	94.2	93.7	95.9
0.8	84.1	87.3	92.7	94.0
1.0	83.6	88.1	85.0	86.1
		Dilute solution viscosity (DSV)		
$H_2O/Al = 0$[a]	4.5	3.8	2.9	4.1
0.2	4.3	3.0	3.1	3.2
0.5	3.7	2.7	3.5	3.5
0.8	2.7	3.1	2.6	2.9
1.0	1.9	3.1	2.1	2.3
		Gel, %		
$H_2O/Al = 0$[a]	5.0	0	0	0
0.2	27.5	20.0	7.5	20.0
0.5	32.5	27.5	27.5	25.0
0.8	32.5	32.5	27.5	30.0
1.0	30.0	35.0	32.5	35.0

[a] Ratio actually 0.046 due to residual H_2O in monomer–solvent blend.

The inertness of the benzene so introduced was shown by the preliminary test reported in Table III.

Table IV gives polymer conversions, DSV, percent gel and percent cis-1,4 for the polymers made in solutions of isoprene and hexane containing different known degrees of wetness at the four Al/Ti ratios, but in the absence of diphenyl ether in the catalyst.

The normal Al/Ti = 1.0 catalyst, which yielded a maximum conversion polymer in a dry system, showed a regular decline in efficiency with increased H_2O/Al ratios. The 1.1 Al/Ti catalyst was as unaffected by the presence of water, as it was by the presence of diphenyl ether, in its constancy of low-conversion capacity. The 0.9 and 0.8 Al/Ti catalysts seemed to show a low degree of peaking at 20 mole-% of water based on the Al. This may perhaps be attributed to the appearance of some of the higher Lewis acids at these ratios and the requirement for trace water with these cationic forms.

Polymer DSV declined with added water at all Al/Ti ratios, and this might be expected to parallel the high gel formation. Gel was not much of a factor at the 1.0 Al/Ti ratio up to 20 mole-% of water.

The data in Table IV showed no effect upon the high cis-1,4 content of the polymers at all the Al/Ti ratios studied, again up to 20 mole-% of water. With more than 50 mole-% of water in the isoprene–hexane solution the microstructure becomes significantly affected. Although the cis-1,4 content of the polymers made at this level of water were still high, they do nevertheless lie below what is believed to be the critical 95% or 96% cis-1,4 content, and would therefore lie outside the boundary of excellence in synthetic polyisoprene.

Relationship Between Conversion and Diphenyl Ether–Water Variables

In Table V the polymer conversion data were arranged to show the results of given diphenyl ether and water combinations at fixed Al/Ti mole
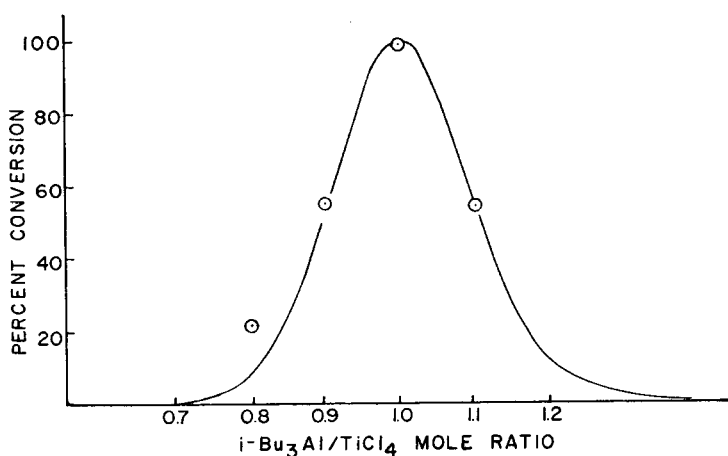

Fig. 1. Sensitivity of the catalyst efficiency to the Al/Ti mole ratio.

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TABLE V

Interaction Study.   Relationship Between Al/Ti Ratio, Diphenyl Ether, and Water
Toward Per Cent Polymer Conversion

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	Polymer conversion, %				
	$H_2O/Al = 0^a$	0.2	0.5	0.8	1.0
Al/Ti = 1.1					
$\phi_2O/Al = 0$	55.0	42.3	42.9	50.1	52.2
1	54.9	64.5	78.6	76.8	80.6
2	56.5	97.2	96.7	84.7	74.8
4	55.4	98.8	98.0	79.2	29.3
6	52.8	97.1	95.9	98.3	89.2
Al/Ti = 1.0					
$\phi_2O/Al = 0$	98.3	79.9	69.5	57.8	52.7
1	89.5	97.3	97.8	89.5	88.8
2	95.5	95.6	95.6	54.0	39.7
4	98.2	92.7	97.9	44.5	37.5
6	99.0	96.9	96.9	98.2	66.3
Al/Ti = 0.9					
$\phi_2O/Al = 0$	55.2	92.4	67.1	38.2	42.1
1	97.7	97.0	72.5	68.1	38.6
2	98.9	91.4	76.6	33.4	8.8
4	97.9	97.2	94.1	25.3	16.4
6	97.2	97.5	94.6	62.1	25.7
Al/Ti = 0.8					
$\phi_2O/Al = 0$	22.1	49.8	43.8	30.6	28.9
1	64.9	56.0	49.9	40.5	38.4
2	93.7	45.0	41.9	18.0	14.9
4	96.0	79.2	49.5	13.2	0
6	97.3	90.7	59.6	35.4	25.7

[a] Ratio actually 0.046 due to residual H_2O in monomer–solvent blend.

ratios.   Beginning with the zero water polymer at Al/Ti = 1.0, it was
observed that increased amounts of water in the isoprene–hexane solution
caused the polymer conversion to fall off regularly, which has been pointed
out above.   With a 1:1 complex of ϕ_2O and i-Bu₃Al instead of the uncom-
plexed i-Bu₃Al, the system could tolerate as much as 50 mole-% of water
based on the i-Bu₃Al without reduction in catalyst efficiency.   These data
demonstrate that the low polymer conversions caused by the presence of
water in the isoprene solution can be restored to the high conversions
obtained in the absence of water by using the diphenyl ether complex of
i-Bu₃Al in the catalyst.

At the 80 mole-% level of water in the isoprene-hexane solution (or 86
ppm H_2O in a 20 wt-% solution of isoprene in hexane), the data indicated
that ϕ_2O/i-Bu₃Al = 6.0 restores full catalyst efficiency.   In the presence
of a molar equivalent of water to the Al, the response to ϕ_2O-complexed
i-Bu₃Al was considerably reduced.
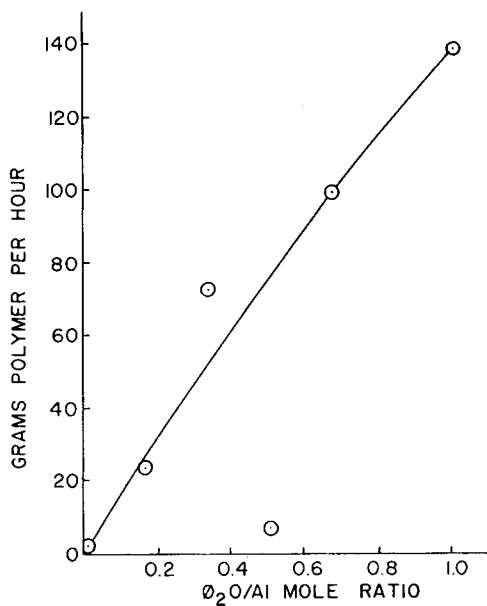
Fig. 2. Dependence of rate of polymer conversion on ϕ_2O/Al mole ratio.

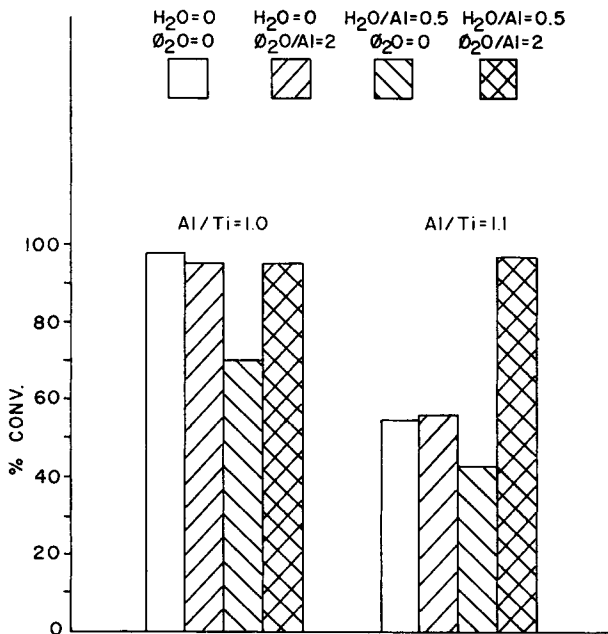
Fig. 3. Illustration of synergistic behavior of water and diphenyl ether on catalyst efficiency at the Al/Ti = 1.1 mole ratio.

The limited ability of the 1.1 Al/Ti catalyst to polymerize isoprene to high-conversion polymer has already been shown to be unchanged in the presence of increased amounts of water or diphenyl ether. But in the presence of both water and diphenyl ether, the response of the catalyst was unexpected. Despite some scatter in the data, the 1.1 Al/Ti catalyst approached the 1.0 Al/Ti catalyst in performance when there were present about 20 to 80 mole-% water based on the i-Bu$_3$Al and at least two moles of diphenyl ether per mole of i-Bu$_3$Al. This compensating effect was observed even in the drastic case of 100 mole-% water in the system. A graphic representation of an example of this synergistic effect of water and diphenyl ether at the Al/Ti ratio of 1.1, as compared with the ratio of 1.0, is shown in Figure 3.

At Al/Ti ratios below 1.0, the diphenyl ether effect was less noticeable, and was present only with low levels of water. At the 0.8 Al/Ti ratio,

TABLE VI

Interaction Study. Relationship Between Al/Ti Ratio, Diphenyl Ether, and Water Toward Polymer DSV

	Dilute solution viscosity (DSV)				
	H$_2$O/Al = 0[a]	0.2	0.5	0.8	1.0
Al/Ti = 1.1					
ϕ_2O/Al = 0	4.1	3.2	3.5	2.9	2.3
1	3.6	3.5	3.2	2.5	2.3
2	3.5	2.7	2.5	2.0	1.4
4	3.9	2.9	2.7	1.6	2.5
6	3.8	2.5	2.7	2.5	1.6
Al/Ti = 1.0					
ϕ_2O/Al = 0	2.9	3.1	3.5	2.6	2.1
1	3.1	3.1	2.7	2.3	1.9
2	3.0	2.5	2.8	2.2	2.5
4	2.7	3.0	2.7	2.2	2.4
6	2.7	2.5	2.5	2.4	1.3
Al/Ti = 0.9					
ϕ_2O/Al = 0	3.8	3.0	2.7	3.1	3.1
1	2.7	2.6	2.6	2.5	2.5
2	2.8	2.7	2.8	2.6	0.3
4	2.7	2.9	2.8	2.3	1.2
6	3.1	3.0	2.6	2.3	2.5
Al/Ti = 0.8					
ϕ_2O/Al = 0	4.5	4.3	3.7	2.7	1.9
1	3.6	3.6	3.3	3.1	2.7
2	3.0	3.5	3.3	2.1	1.2
4	3.1	3.4	3.6	1.1	—
6	2.8	3.0	3.0	2.9	2.6

[a] Ratio actually 0.046 due to residual H$_2$O in monomer–solvent blend.

TABLE VII

Interaction Study.   Relationship Between Al/Ti Ratio, Diphenyl Ether, and Water
Toward Polymer Gel

	Gel, %				
	$H_2O/Al = 0^a$	0.2	0.5	0.8	1.0
Al/Ti = 1.1					
$\phi_2O/Al = 0$	0	20.0	25.5	30.0	35.0
1	0	5.0	17.5	17.5	24.0
2	0	10.0	13.5	50.0	62.5
4	12.5	12.5	20.0	50.0	37.5
6	5.0	0	18.0	16.5	43.5
Al/Ti = 1.0					
$\phi_2O/Al = 0$	0	0	27.5	27.5	32.5
1	10.0	15.0	22.5	27.5	35.0
2	1.5	22.5	27.0	50.0	50.0
4	10.0	26.5	25.0	47.5	35.0
6	5.0	2.5	27.5	23.0	56.5
Al/Ti = 0.9					
$\phi_2O/Al = 0$	0	20.0	27.5	32.5	35.0
1	20.0	17.5	30.0	37.5	50.0
2	17.5	22.5	27.5	40.0	7.5
4	17.5	27.5	30.0	36.0	37.0
6	25.0	22.5	25.0	34.0	36.5
Al/Ti = 0.8					
$\phi_2O/Al = 0$	5.0	27.5	32.5	32.5	30.0
1	25.0	27.5	27.5	45.0	45.0
2	20.0	22.5	33.5	35.0	37.0
4	17.5	27.5	37.5	35.0	—
6	20.0	14.0	27.5	32.5	33.0

a Ratio actually 0.046 due to residual H_2O in monomer–solvent blend.

more diphenyl ether was required, especially in the presence of water, to bring the catalyst efficiency up to maximum.

It is therefore possible to extend the sensitivity of the Al/Ti mole ratio beyond 1.0 to include the 0.8 Al/Ti ratio, and even the 1.1 ratio, with the correct amount of water present in the isoprene solution in the latter case.

The data obtained for the DSV and gel contents of polymers made with catalysts modified by both diphenyl ether and water are also included (Tables VI and VII).   That diphenyl ether had little or no effect upon the molecular weight of the polymer, as reflected in the DSV, was shown by the constant DSV values found for constant conversion polymers containing from zero to negligible amounts of gel in the case of the separate groups of polymers made in dry systems with either the 1.0 or 1.1 Al/Ti catalysts.

Another point of interest was the tendency of diphenyl ether in the dry systems to cause a low degree of polymer gel with the 1.0 and 1.1 Al/Ti catalysts, and very pronounced gel at the Al/Ti ratios below 1.0.   But

such gel which can be attributed to the action of water on the catalysts at these ratios was neither increased nor decreased by the diphenyl ether.

Effect of Diphenyl Ether on Polymerization Rates

It has been reported in the patent literature that diphenyl ether in this catalyst system increases the rate of polymerization[9] and also that it tends to decrease the rate.[1] We have found that the rate of polymerization was very markedly increased by using the ether-complexed i-Bu$_3$Al with dry solutions of isoprene in hexane.

A number of polymerization runs were carried out in the pilot plant with thoroughly dried hexane solutions of isoprene. The mole ratios of diphenyl ether to i-Bu$_3$Al were varied from zero to 1.0 in a series of replicate runs at each ratio. The polymer conversions ranged from 75% to 99%. The data from those runs which gave the fastest rate at each ϕ_2O/Al ratio are shown in Table VIII and Figure 2. The increase in the rate of polymerization appears to be linear, or approximately so, with increased diphenyl ether.

TABLE VIII
Polymerization Rate Data at 5°C of Diphenyl Ether-Complexed Triisobutylaluminum–
TiCl$_4$ Catalyst[a]

ϕ_2O/Al ratio	Conv., %	Pzn time, Hours	Polymer yield, g/hr
0	63.0	23.0	2.7
0.16	95.3	4.0	23.8
0.33	94.0	1.3	72.3
0.50	96.0	13.5	7.1
0.67	99.0	1.0	99.0
1.0	97.0	0.7	138.5

[a] Al/Ti = 0.95, 3.0 mmoles TiCl$_4$ phg, 10% isoprene in hexane, polymerization temperature 5°C.

The behavior of the polymerization rate can be related to the ether-enhanced dissociation of the i-Bu$_2$AlCl from the dimeric form in which it exists. Bushick and Stearns[12] have shown that Et$_3$Al, its mono- and di-chloroderivatives, and i-Bu$_3$Al have a higher conductance in benzene than i-Bu$_2$AlCl, and this was found to parallel the increased tendency, in the order given, for these aluminum alkyls to coordinate as ion aggregates which must further dissociate. Jacober and Kraus[13] showed that the increase in conductivity of (CH$_3$)$_2$AlBr and CH$_3$AlBr$_2$ in MeBr was due to the dissociation of the bimolecular forms of the solutes when complexed with ether. It is of interest, in connection with the enhanced polymerization rates caused by the diphenyl ether-complexed triisobutylaluminum, to note that Bushick and Stearns[12] also found that the rate of propylene polymerization was linearly proportional to the equivalent conductance of several alkylaluminum species and hence to their ionic nature.

Effect of Diphenyl Ether on Compounded and Cured Polymer Properties

Two polyisoprene polymers were made from isoprene solutions which were rigorously dried before adding the catalysts, one of which contained uncomplexed i-Bu$_3$Al and another contained i-Bu$_3$Al·ϕ_2O. The polymers were compounded and cured in a tread stock recipe and their physical properties given in Table IX.

Generally, there were no large differences in the properties of the polymers made with either type of catalyst. The diphenyl ether-containing catalyst resulted in a low-level improvement in stress–strain properties. The uncomplexed i-Bu$_3$Al catalyst gave a polymer of greater tack, but even here the values of 15.2 and 11.6 are not considered wide enough apart to be very significant. The same may be true of the green stress–strain properties and the remaining physical properties examined.

DISCUSSION

Diphenyl ether did not modify the catalyst in the water-free system with respect to changes in maximum polymer conversion, polymer dilute solution viscosity, appreciable changes in the gel content, and polymer microstructure. Further, it may be inferred from the practically identical physical properties of the polymers made with and without diphenyl ether that the polymers did not possess any significant macrostructural differences. The one positive modifying effect of the diphenyl ether was, as shown above, to markedly increase the rate of polymerization.

The complex formed from diphenyl ether and i-BuAlCl$_2$ or AlCl$_3$, both of which are present to a greater or lesser extent as the Al/Ti ratio is decreased to values below 1.0, is the result of the donation of a free electron pair from the ether oxygen to the acidic aluminum. It is believed that in so doing the diphenyl ether serves to reduce the Lewis acidity of the higher alkylaluminum acids in the direction of the optimum i-Bu$_2$AlCl. The data substantiated such an empirical interpretation, as in the case of the Al/Ti = 0.9 catalyst which increased its polymer conversion efficiency from 55.2% to 97.7% when the ϕ_2O/Al ratio equaled at least 1.0 (Table II). Since at the Al/Ti ratio of 0.9 most of the Al component is in the form of i-Bu$_2$AlCl, somewhat less than one molecule of the ether per molecule of i-Bu$_3$Al might be required.

The reduction in the acidity of i-BuAlCl$_2$ and AlCl$_3$ by complex formation with an electron donor is supported by the observed reduction in the electronegativity of the Al in these Lewis acids. Brownstein and co-workers[14] have shown by means of proton magnetic resonance measurements that the electronegativity, and hence the electron-acceptor ability of Al in Et$_3$Al decreased by coordination with diethyl ether. In an analogous reaction between EtAlCl$_2$ and hexamethylenephosphoric triamine (HPT), Zambelli et al.[15] postulated the occurrence of a dismutation reaction according to

$$2EtAlCl_2 + HPT \rightarrow Et_2AlCl + AlCl_3 \cdot HPT,$$

TABLE IX
Physical Properties Data on Laboratory-Prepared Ziegler Polyisoprene[a]

	Al–Ti Polymer	Al·ϕ_2O–Ti Polymer
Conv., %	97.6	98.9
cis-1,4 content, %	96.8	97.2
DSV	3.0	2.7
Gel, %	0.0	0.0
Instron Windup Tack		
Aver., lb/in.	15.2	11.6
Green Stress–Strain		
Peak, lb	4.7	3.8
Break, lb	4.7	3.8
Elong., %	1175	975
Normal Stress–Strain		
300% Mod., psi 30 min	1000	1200
45 min	1375	1675
60 min	1500	1750
90 min	1500	1675
Tensile, psi 30 min	3050	3200
45 min	3575	3900
60 min	3625	3850
90 min	3400	3500
Elong., % 30 min	560	540
45 min	540	520
60 min	480	500
90 min	510	480
Stress–Strain at 212°F, 60 min Cure		
200% Mod., psi	670	730
300% Mod., psi	1200	1170
Tensile, psi	2530	2490
Elong., %	570	560
Stress–Strain at 275°F, 60 min Cure		
200% Mod., psi	590	630
300% Mod., psi	900	1010
Elong., %	540	550
Tensile, psi	1650	1730
Stress–Strain after 2 Days at 212°F		
300% Mod., psi 30 min	1100	1200
45 min	1025	1175
60 min	1175	1100
90 min	—	—
Tensile, psi 30 min	1800	2050
45 min	1225	1225
60 min	1175	1100
90 min	1200	1250
Elong., % 30 min	440	440
45 min	350	300
60 min	300	300
90 min	260	260
Ring Tear, 60 min Cure		
at 212°F	459	372
at 275°F	342	355

TABLE IX (continued)

	Al–Ti Polymer	Al·ϕ_2O–Ti Polymer
Forced Vibrator at 212°F, 60 min Cure		
Dynam. Mod., psi	177	187
Static Mod., psi	150	177
Internal Frict., kps	3.03	3.19
Steel-Ball Rebound, 60 min Cure		
at 73°F, %	47.5	46.0
at 212°F, %	70.5	71.0
Firestone Flexometer Test, 60 min Cure		
Shore A at 73°F	63.0	64.0
Shore A, Hot	60.0	61.0
Deflection, %	17.3	17.3
Running Temp., °F	250	244

[a] Al/Ti = 0.95, 3.0 mmoles TiCl$_4$ phg, 10% isoprene in heptane, polymerization temperature 5°C. Compounding recipe: polymer 100; stearic acid 2.6; Ajone DDX 0.4; Ajone DD 2.2; HAF black 50.0; ZnO 3.0; Dutrex 726 3.0; Vultrol 0.5; sulfur 2.6; Santocure NS 0.35; cured at 280°F.

and the Et$_2$AlCl so formed was responsible for the catalyst formation with TiCl$_3$ in the polymerization of alpha-olefins. It also illustrates the preferential reactivity of a Lewis base to complex with the more acidic of two Lewis acids. This is also borne out by the general ability of a Lewis acid to accept an electron pair with greater affinity the greater the number and electronegativities of the attached atoms to the Al.[16] Boor[17] objected to the dismutation of EtAlCl$_2$ with HPT and showed that the reaction between AlCl$_3$·HPT and R$_2$AlCl led to RAlCl$_2$·$^1/_2$ HPT. The distinction between Zambelli's and Boor's products may well be the same as that between R$_3$Al$_2$Cl$_3$ and R$_2$AlCl + RAlCl$_2$ in solution, and may well be equivalent.

Whether 1-BuAlCl$_2$·ϕ_2O exists as i-Bu$_2$AlCl and AlCl$_3$·ϕ_2O in which the cationic activity of this form of AlCl$_3$ makes a minimal contribution to the polymerization, and the main contribution is from re-formed i-Bu$_2$AlCl; or whether we are dealing with i-BuAlCl$_2$·$^1/_2$ ϕ_2O in which the electron receptivity, and hence the Lewis acidity, is reduced from what it is for i-BuAlCl$_2$ does not detract from the fact that diphenyl ether restored to maximum efficiency the catalyst which contains some alkylaluminum chloride higher in Lewis acidity than the normal and most efficient i-Bu$_2$AlCl.

It should be noted, however, that while the catalyst efficiency was maximized with diphenyl ether at the Al/Ti = 0.9 mole ratio and less, the formation of gel was a concomitant result. This may perhaps be due to the existence of the diphenyl ether-complexed higher Lewis acid in the form of ionic species, which possesses a gel-forming property comparable to the uncomplexed acid acting as a Friedel-Crafts catalyst.

Cunningham and Dove[18] compared the n-Pr$_3$Al–TiCl$_4$ and n-Pr$_3$Al·O-(CH$_3$)ϕ–TiCl$_4$ catalysts on the basis of the nature of the products found in

the solid and liquid portions of these catalysts formed at Al/Ti mole ratios of 0.2–1.1. They reported that, at the higher ratio, the solid had a lower Cl/Ti ratio in the etherate catalyst, indicating a greater degree of reduction or alkylation or both of the Ti species. At the higher ratio, more anisole was found in the solid, as well as some phenol. The latter formation was attributed to cleavage of the anisole during catalyst formation. The effects of the more basic diphenyl ether were not investigated.

Hamilton et al.[19] studied the action of various ethers on TiCl$_4$. They observed that anisole formed a solid addition compound with TiCl$_4$, but which gradually decomposed at room temperature. Certain other ethers formed simple addition compounds of varying stability.

The action of diphenyl ether in the presence of water is not easily rationalized. In the course of the experimental work carried out, it was observed that when diphenyl ether was added to the wet isoprene–hexane blend following the addition of the i-Bu$_3$Al–TiCl$_4$ catalyst, considerable gel formation occurred.

In the absence of diphenyl ether, an amount of i-Bu$_2$AlCl equivalent to the molar amount of water present is converted to i-BuAl(OH)Cl. As such, or as in the form of the more preferred i-BuAl(Cl)–O–Al(Cl)i-Bu, this higher Lewis acid now reduces the catalyst efficiency. It should also be responsible for gel formation, and perhaps cyclization, by the recognized polymerization route attributed to cationic catalysts of the Lewis acid types, to the extent it is present.

In view of this, it cannot be considered that the function of the diphenyl ether is too complex and thereby eliminate, in this case, the higher (oxygenated) Lewis acid. If the diphenyl ether must be reacted with the i-Bu$_2$AlCl before the latter contacts water, then the assumption must be made of a complex between the i-Bu$_2$AlCl and diphenyl ether which is more resistant to the action of water in increasing its degree of Lewis acidity through dealkylation.

Cryogenic measurements of the associative stability of a number of alkylaluminum compounds and certain ethers have shown that i-Bu$_2$AlCl and diphenyl ether are entirely dissociated.[20] However, since freezing point depression measurements merely lead to information about the number of moles of nonsolvent particles in solution, but not about the nature of the particles themselves, the data cited would not distinguish between the free existence of i-Bu$_2$AlCl and ϕ_2O and the possibility of an unstable polarized complex which dissociated into ionized species, since a donor–acceptor complex usually involves a polarization.

At Al/Ti ratios above 1.0, it was observed that water and diphenyl ether behaved synergistically. At the Al/Ti ratio of 1.1, i-Bu$_2$AlCl is the only Al product of the reaction between i-Bu$_2$AlCl and TiCl$_4$. Although the major amount of the titanium is present as TiCl$_3$, there is also present some alkylated titanium chloride originating from the small excess of initial i-Bu$_3$Al. This would be the relatively less stable i-BuTiCl$_2$ (compared to the TiCl$_3$), particularly against hydrolysis. RTiCl$_2$ is the co-catalyst

component which causes the polymerization of isoprene to dimers, trimers, low molecular weight oils, etc., and which contributes therefore to low conversions of alcohol-insoluble polymer. Diphenyl ether alone, in a dry system, causes no change in the catalysis activity of the components present. Water alone, in the absence of diphenyl ether, not only dealkylates the i-Bu$_2$AlCl to higher Lewis acids and thereby causes typical low polymer conversions, but also hydrolyzes the i-BuTiCl$_2$ (and TiCl$_3$ if excessive water is present). By removing the low-conversion polymer co-catalyst i-BuTiCl$_2$ with water and preventing the formation by water of higher Lewis acids from the i-Bu$_2$AlCl by the addition of diphenyl ether, the Al/Ti = 1.1 catalyst can thus be made as fully efficient as the Al/Ti = 1.0 catalyst by adjusting the water and ether content in the catalyst. The synergism in the action of water and diphenyl ether is shown graphically in Figure 3.

It is proposed that the specific catalyst consists of i-Bu$_2$AlCl and β-TiCl$_3$, that these need not necessarily be present in 1:1 molar amounts, and that the significance of the narrowly limited initial mole ratio of Al/Ti = 1.0 with respect to high catalyst efficiency lies in minimizing the formation of such alkylaluminum halides and alkylated titanium compounds which arise from the reaction between i-Bu$_3$Al and TiCl$_4$ at molar ratios slightly above and below 1.0. The suppression of these compounds within the narrow Al/Ti range is made possible by the use of optimum amounts of diphenyl ether with and without water, depending on the ratio of the initial reactants.

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