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Abstract

Full Text

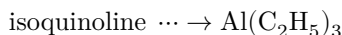
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ON THE POLYMERIZATION OF ISOPRENE IN THE PRESENCE OF COMPLEXES OF TITANIUM TETRACHLORIDE, TRIETHY- LALUMINUM, AND AMINES

(Presented by Academician B. A. Kazanskii, June 12, 1963)

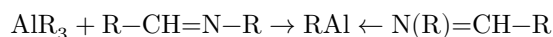
The reactivity of trialkylaluminum is a consequence of a certain electron deficiency⁽¹⁾, responsible for the initiation of other reactions. Usually trialkylaluminum is in an associated state, but as a result of its reactions with compounds that are electron donors, complex compounds are formed in which alkylaluminum is in a monomolecular state. These complexes have a distinctly reduced reactivity. Thus, compounds of trialkylaluminum with amines are less reactive than trialkylaluminum.

The complex of trialkylaluminum with isoquinoline according to Bonitz⁽²⁾



was isolated by us and proved to be stable in an inert atmosphere.

Azomethine compounds also form complexes with trialkylaluminum⁽³⁾:



In one of Gudrich's patents⁽⁴⁾ it is stated that deactivation of organometallic catalysts, especially of the type $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$, in systems for the polymerization of olefins or dienes, can be carried out by treatment with a compound containing basic nitrogen (ammonia, aliphatic amines, or aromatic primary, secondary, tertiary hydroxyamines, aminophenols, etc.). Adams⁽⁵⁾ showed that polymerization of isoprene in the presence of the catalytic system $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ does not proceed in basic solvents (aniline, dimethylaniline, pyridine), probably because of the formation of a complex between the solvent and TiCl_4 .

In order to investigate the stability of the catalytic complex $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ during isotactic polymerization, we undertook a study of the polymerization of isoprene in the presence of a mixture of the complex $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ and nitrogen-containing substances. The first experiments were carried out with the

commonly used antioxidant phenyl- β -naphthylamine and with ammonia, the addition of which was performed at various stages of polymerization.

In the experiments carried out we used isoprene, triethylaluminum and titanium tetrachloride, phenyl- β -naphthylamine (PBN) with m.p. 106-107°, pure heptane, pure nitrogen, and gaseous anhydrous ammonia.

The general conditions of all experiments (see Table 1) were as follows: the ratio isoprene : heptane = 1 : 7, molar ratios

$$\frac{\text{Al}(\text{C}_2\text{H}_5)_3}{\text{TiCl}_4} \simeq 0.97, \quad \frac{\text{Al}(\text{C}_2\text{H}_5)_3}{\text{PBN}} \simeq 0.76;$$

room temperature; the reaction proceeds with evolution of heat.

In order to investigate the effect of PBN on the characteristics of the polymers obtained, the reagents were added in different orders. In the final stage, after the end of the reaction, 96% ethyl alcohol was added and the product was then analyzed.

Polymerization initiated normally (experiments Nos. 1 and 2) proceeds after the addition of PBN without significant differences in the rate of polymerization. As is evident from the data of experiment No. 3, when PBN is added immediately after introduction of the last component of the reaction mixture (TiCl_4),

Table 1

Polymerization of isoprene with $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ in the presence of phenyl- β -naphthylamine

Experiment Nos.	Reaction		Intrinsic		1,4-cis	1,4-trans	3,4-trans	1,2-trans
	time, h	Concentration, %	viscosity	Gel, %				
1	2.5	49	1.9	Tr.	96.81	—	2.87	0.32
2	2.5	53	2.44	Absent	95.85	—	3.51	0.66
3	20	42.8	2.66	»	95.50	—	3.81	0.68
4	20	25.3	1.58	»	—	—	—	—
5	20	30.0	1.85	Tr.	87.44	5.19	5.34	2.00
6	20	22.6	1.95	Absent	—	—	—	—
7	20	18.2	3.2	»	—	—	—	—

the rate of polymerization decreases considerably, the exothermicity of the reaction is insignificant, the temperature rises no higher than 25°C, and, at a conversion equal to that in experiments Nos. 1 and 2, the duration of the reaction is 8 times greater. In the case of initiation in the presence of PBN, polymerization proceeds at lower rates. Thus, in experiment No. 4, when $\text{Al}(\text{C}_2\text{H}_5)_3$ was

added to the heptane–isoprene mixture and then PBN was added simultaneously with TiCl_4 , the conversion proved to be approximately 2 times lower in comparison with the conversion obtained in experiment No. 3. In experiments Nos. 5 and 6, in which the complex was formed in heptane, PBN was added after 10 min, and then the heptane–isoprene mixture was added, very little heat was evolved, while the conversion nevertheless remained comparable with the conversion obtained in experiment No. 4.

The lowest conversion (18.2%), with a temperature rise of only 1°C and with the same polymerization duration as in experiments Nos. 3, 4, 5, and 6, was achieved in experiment No. 7, in which PBN was dissolved in heptane directly in the polymerization vessel; then $\text{Al}(\text{C}_2\text{H}_5)_3$, TiCl_4 , and, finally, the heptane–isoprene mixture were added.

As for the intrinsic viscosity, the latter was maintained within the range 1.58–2.5, on average about 2; the highest value, 3.2, was obtained in experiment No. 7, where the complex was formed in the presence of PBN and the monomer was then added.

In studying the structure by the IR method of polymers obtained under the conditions of experiments Nos. 1, 2, 3, and 5, it may be concluded that, practically speaking, their structure does not differ from that of polymers obtained in the presence of the catalytic system $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ in the absence of PBN. In addition to these conditions, it is also important to note that, unlike the polymers obtained only in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ and TiCl_4 , where the gel content varies over wide limits, in these experiments the gel content was practically zero or amounted to barely perceptible traces, as, for example, in the case of experiments Nos. 1 and 5.

From the experiments we conducted it follows that phenyl- β -naphthylamine is not a complete inhibitor of the catalytic system $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$, and that the polymers obtained have properties comparable with those of polymers obtained in the absence of PBN, with the exception of the gel, which in the case of these polymers is practically absent.

From several experiments carried out in the presence of gaseous anhydrous ammonia (under conditions of preliminary formation of the complex, addition of ammonia, then isoprene; or bubbling ammonia through heptane, formation of the complex, and then addition of isoprene), it may be concluded that ammonia completely inhibits the polymerization reaction.

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Note: Figure translations are in progress. See original paper for figures.

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