

POLYMERIZATION OF 1,3-PENTADIENE BY COBALT  
CATALYSTS. INFLUENCE OF THE ALKYL ALUMINUM  
COMPOUND ON THE STRUCTURE OF THE POLYMER

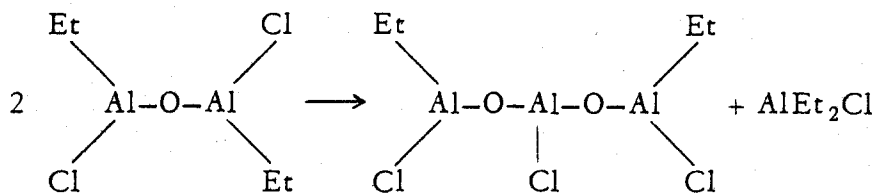
In a previous communication (1) it was reported that the catalyst system  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Co}(\text{acac})_3^*$  yields, in n-heptane or other aliphatic solvents, polymers of 1,3-pentadiene having a 1,2-syndiotactic structure.

Continuing our work in this field, we now have noticed that if, instead of  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ , the product of reaction between  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and  $\text{H}_2\text{O}$  ( $\text{Al}/\text{H}_2\text{O}$  molar ratio = 1:0.5) is used for the preparation of the catalyst, cis-1,4-polypentadiene, instead of 1,2, is obtained. X-ray investigation shows that the cis-1,4 polymer so obtained is crystalline, with a syndiotactic structure.

The reaction between  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and  $\text{H}_2\text{O}$ , in the molar ratio indicated, has already been described (2). In our experiments we have carried out the reaction in a manner slightly different than reported in the literature, i.e., by adding slowly benzene, previously saturated with  $\text{H}_2\text{O}$ , to the calculated amount of  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ , under vigorous stirring. After the addition was complete, the solution was heated at about  $50^\circ\text{C}$ . for 1/2 hr., then the benzene was distilled off under vacuum (0.1-0.2 mm. Hg). A dense liquid was obtained as a residue. The product has

been reported (2) to have the formula  $\left( \begin{array}{c} \text{Et} \\ \diagdown \\ \text{Al} \\ \diagup \\ \text{Cl} \end{array} \right)_2\text{O}$  ( $\text{Et} = -\text{C}_2\text{H}_5$ ) with an

oxygen bridge between two aluminum atoms. We think that the reaction product has a more complex structure than reported. In effect, due to the possibility of exchanges between the groups bonded to Al, for example, as indicated by the equation



molecules can be formed having more than two Al atoms, bonded through oxygen bridges.

For the sake of brevity, we shall use in the following the name chloro-

\* $\text{Co}(\text{acac})_3$  = cobalt triacetylacetonate.

ethylaluminumoxane to indicate the reaction product between  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and  $\text{H}_2\text{O}$ , in the given molar ratio.

A typical polymerization run with the system chloroethylaluminumoxane- $\text{Co}(\text{acac})_3$  in n-heptane is the following. To 50 ml. of anhydrous n-heptane are added  $5.7 \times 10^{-3}$  mmoles of  $\text{Co}(\text{acac})_3$ , 0.50 ml. of chloroethylaluminumoxane, and 7.5 ml. of 1,3-pentadiene (trans isomer, 99% pure), respectively. After a polymerization time of 6 hr. at room temperature, 5 g. of solid polymer ( $[\eta] = 1.1$  dl./g., determined in toluene at  $30^\circ\text{C}$ .) were obtained, which exhibits at room temperature the crystallinity typical of cis-1,4 syndiotactic polypentadiene. IR and NMR examinations indicate the following microstructure: cis-1,4, about 83%; 1,2 about 17%.

We may recall that polymerizations carried out under the above conditions, but using  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  instead of chloroethylaluminumoxane, give polypentadiene having up to 97% 1,2 units (1).

The two systems based on  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and on aluminumoxane, respectively, also show significantly different rates of polymerization. The curves of Figure 1 indicate that the chloroethylaluminumoxane system is faster than the  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  system, other conditions being constant.

It is interesting that the nature of the aluminum compound has much less influence on the type of polymer obtained when benzene is used as the solvent, instead of n-heptane. In benzene, in fact, the system  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Co}(\text{acac})_3$  and the system chloroethylaluminumoxane- $\text{Co}(\text{acac})_3$  both give polymers having a predominantly cis-1,4 structure (3). However, the percentage of cis-1,4 units is slightly higher for the polymers obtained with the catalyst based on chloroethylaluminumoxane.

It is difficult to give an explanation for the different behavior, in n-heptane, of the catalysts based on  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and chloroethylaluminumoxane, respectively.

It seems plausible that the formation of a cis-1,4 unit is determined by a coordination of the monomer to the catalyst through the two double bonds, in the cis conformation. On the other hand, 1,2 units are most probably derived from a coordination of the monomer through only the vinyl group.

The different mode of coordination of the monomer to the catalyst presumably depends on the different type of coordination existing around cobalt in the systems from chloroethylaluminumoxane and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ , respectively. It could be, for example, that the Co of the system chloroethylaluminumoxane- $\text{Co}(\text{acac})_3$  has an octahedral coordination, while the Co of the system  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Co}(\text{acac})_3$  has a tetrahedral or planar coordination. This fact could influence, in a way which is still to be clarified, the different mode of coordination of the monomer to Co and, hence, the different structure of the monomeric unit.

Independently of their interpretation, it seems that the results of this communication contribute to clarifying an aspect of the Co catalyst.

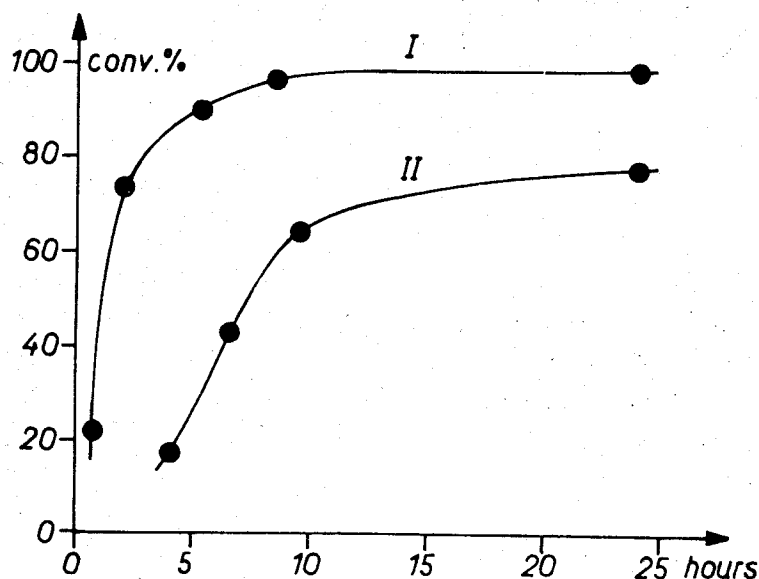


Fig. 1. Conversion vs. time curves for the polymerization of 1,3-pentadiene (trans isomer) by Co catalysts. Experimental conditions: solvent (n-heptane) cc 50;  $\text{Co}(\text{acac})_3$   $5.7 \times 10^{-6}$  moles; aluminum compound: curve I aluminoxane cc 0.5, curve II  $\text{AlEt}_2\text{Cl}$  cc 0.5; monomer cc 7.5; polymerization temperature  $20^\circ\text{C}$ .

Some authors, who have worked on the polymerization of butadiene by these catalysts, affirm that the system  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ -cobalt compound is inactive in anhydrous medium, while the addition of  $\text{H}_2\text{O}$  activates the system (4). Considering that  $\text{H}_2\text{O}$  leads to the formation of aluminoxane, this is equivalent to saying that only the catalyst based on aluminoxane is active.

The results of this work on the polymerization of pentadiene indicate that the system  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ -Co compound is also active as a catalyst for polymerization, although it differs from the catalyst based on aluminoxane both from the kinetic point of view and with respect to the type of polymer obtained.

#### References

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