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Figure 1

Figure 1: Figure 1

Abstract

Full Text

CHEMISTRY

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POLYMERIZATION OF DIENES UNDER THE INFLUENCE OF HOMOGENEOUS CATALYTIC SYSTEMS CONTAINING COBALT AND NICKEL SALTS

For the synthesis of regularly structured diene polymers, insoluble Ziegler–Natta complex catalysts are usually used, formed by the interaction of organoaluminum compounds with titanium halides (1–4), or certain oxide catalysts (5,6). Natta was the first to point out the possibility of using, for the polymerization of butadiene, a catalytic system soluble in hydrocarbons and consisting of diethylaluminum chloride and cobalt dinitrosyl chloride (7).

In the present study, the possibility is shown of obtaining cis-polybutadiene through the use of homogeneous catalysts formed by the interaction of dialkylaluminum chlorides with various cobalt and nickel compounds. In studying the polymerization of butadiene in benzene solution it was established that catalytic systems consisting of hydrocarbon-soluble complexes of cobalt chloride with pyridine or with ethyl alcohol, in combination with dialkylaluminum chlorides, are very effective catalysts. They make it possible to carry out the polymerization process at a cobalt chloride concentration of 0.005 wt.% relative to the monomer at a temperature of about 0°, and the structure of the polymer does not depend on the polymerization temperature. The polymers thus formed contain 90–97% cis-1,4 units. Figures 1 and 2 present experimental data illustrating the dependence of the polymerization rate and of the molecular weight of the polymers on the concentration of cobalt chloride. The polymerization rate reaches a limiting value when the concentration of cobalt salts is increased to 0.01 wt.% relative to the monomer, while at the same time the molecular weight of the polymer decreases continuously over the entire range of concentrations studied.

Fig. 1. Polymer yield as a function of the concentration of cobalt chloride.

Fig. 2. Molecular weight of the polymer as a function of the concentration of

Figure 2

Figure 2: Figure 2

cobalt chloride.
1 –for diethylaluminum chloride; 2 –for diisobutylaluminum chloride

Raising the polymerization temperature leads to a substantial decrease in the molecular weight of the polymer. For the temperature interval from 5 to 30°C, the molecular weight of the polymer decreases by a factor of 2–3. The role of displacement reactions increases strongly in the presence of lower olefins. β-Butene, already in an amount of about 1% relative to the monomer, noticeably lowers the polymerization rate.

and molecular weight of the polymer (from 150,000 to 90,000). Table 1 gives data on the microstructure of polybutadiene obtained with "cobalt" catalysts as a function of the polymerization conditions.

Table 1

Polymerization of divinyl under the influence of catalytic systems containing derivatives of cobalt, nickel, and iron

Catalytic system	Molecular weight of polymer	Number of units, %	Number of units, %	Number of units, %
		1,2	1,4-trans	1,4-cis
$CoCl_2 \cdot 4C_2H_5OH + (C_2H_5)AlCl$	600 000	4	3	93
$CoCl_2 \cdot C_5H_5N + (C_2H_5)_2AlCl$	250 000	6	5	89
$CoCl_2 \cdot 4C_2H_5OH + (iso\text{-}C_4H_9)_2AlCl$	1 000 000	1	2	97
$CoCl_2 \cdot C_5H_5N + (iso\text{-}C_4H_9)_2AlCl$	500 000	4	6	90
$CoCl_2 \cdot 4C_2H_5OH + (iso\text{-}C_4H_9)_3Al$	–	40	0	60

Catalytic system	Molecular weight of polymer	Number of units, %	Number of units, %	Number of units, %
Co-stearate + (iso-$C_4H_9)_3Al$	–	70	22	8
Co-stearate (1%) + $(C_2H_5)_2AlCl$	–	12	15	73
Co-stearate (0.05%) + $(C_2H_5)_2AlCl$	316 000	5	8	87
Co-benzoate (0.05%) + $(C_2H_5)_2AlCl$	–	17	12	71
Co-naphthenate (0.05%) + $(C_2H_5)_2AlCl$	338 000	3	5	92
Ni stearate (0.05%) + $(C_2H_5)_2AlCl$	25 000	3	3	94
Fe stearate (1%) + $(C_2H_5)_2AlCl$	–	22	31	47

The maximum amount of cis-1,4 units was obtained in systems with diethylaluminum chloride and diisobutylaluminum chloride. In the latter case the amount of 1,4 units in the cis configuration reaches 97%. It is interesting to note that, when triisobutylaluminum is used, the amount of 1,2 units increases sharply (up to 70%). When cobalt salts of carboxylic acids are used in concentrations ensuring homogeneity of the system, the chain structure does not differ substantially from that given above for complex cobalt salts. However, an increase in the concentration of cobalt stearate above the solubility limit (transition to heterogeneous systems), as is seen from Table 1, leads to a substantial deterioration of the chain structure. In the case of cobalt benzoate, which has very limited solubility in hydrocarbons, the content of 1,4-cis units does not exceed 70%.

For the polymerization of butadiene we also used complexes formed by the interaction of diethylaluminum chloride with nickel stearate, and also with iron stearate and benzoate. Polybutadiene obtained in the presence of nickel stearate is characterized by a lower molecular weight, and in chain structure does not differ from the polymer obtained under analogous conditions in the presence of cobalt stearate. Iron stearate and benzoate, on interaction with diethylaluminum chloride, also form complexes effective for the polymerization of butadiene. But the rate of the polymerization process in the presence of iron salts is considerably lower than under analogous conditions in the presence of cobalt and nickel salts. "Cobalt" systems are also effective for the polymerization of other diene hydrocarbons, in particular isoprene.

The polymerization process was carried out under conditions customary for work using organometallic compounds, i.e., in an atmosphere of inert gas, with careful removal of traces of oxygen and moisture both from the reaction vessel and from all components of the reaction mixture.

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