Chemistry

1965

SovietRxiv

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Chemistry

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Hydrogenation of cis-1,4-polybutadiene in the presence of soluble catalysts

(Presented by Academician B. A. Dolgoplosk, 15 X 1964)

Recently, considerable attention has been devoted to the study of the process of hydrogenation of polymers, both in our country and abroad ([1−5]). Products of polymer hydrogenation have found practical application ([6,7]).

Most often the process has been carried out on heterogeneous catalysts (metals, metals on supports, etc.), which had a number of substantial disadvantages. To achieve a considerable depth of hydrogenation it was necessary to use large amounts of catalyst, which sometimes exceeded the amount of polymer; on the nickel-kieselguhr catalyst, widely used in industry as a hydrogenation catalyst, the temperature had to be raised to 150—200°; the concentration of polymer solutions usually did not exceed 1%, since the rate and depth of the reaction decreased substantially with increasing solution concentration. There was also difficulty in purifying the hydrogenation products from the catalyst, and the hydrogenated polymers usually contained significant amounts of ash. In addition, the products of heterogeneous hydrogenation of polymers are chemically nonuniform. In work ([8]), the possibility is indicated of hydrogenating olefins on soluble catalysts of the Ziegler-catalyst type under comparatively mild conditions.

The use of soluble catalysts for the hydrogenation of polymers is of particular interest, since under these conditions the stage of adsorption of the polymers on the heterogeneous surface of the catalyst is eliminated. Adsorption of the polymer may be partially irreversible, which complicates the reaction. In addition, an improvement may be expected in the conditions for transport of the catalyst to the rubber molecules.

In the present work, hydrocarbon-soluble catalysts of the Ziegler-catalyst type, consisting of an organometallic compound and a transition-metal compound, were used for the hydrogenation of cis-1,4-polybutadiene. The use of soluble catalysts made it possible sharply to reduce the amount of catalyst in the system in comparison with the heterogeneous process. At the same time, hydrogenation of polymers with a viscosity-average molecular weight of 300,000 can be successfully carried out in solutions with concentrations up to 4%. The process of homogeneous hydrogenation of cis-1,4-polybutadiene proceeds at a high rate,

Fig. 1. Rate curves for hydrogenation of polybutadienes: 1—on the triisobutylaluminum—cobalt(III) acetylacetonate catalyst, 2—on the palladium-on-calcium carbonate catalyst

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and the hydrogenation products can be readily purified from the catalyst by reprecipitation of the polymers.

Experimental part

For the work, cis-1,4-polybutadiene with a viscosity-average molecular weight of 300,000, obtained with a Ziegler-type catalyst, was taken. The polymer was purified by the method described previously ([9]). The unsaturation of the rubber, determined with a solution of iodine bromide ([10]), was 92%. Decalin was used as the solvent.

Hydrogenation at atmospheric pressure was carried out in a special apparatus ([9], [11]) in a one-percent polymer solution at a temperature of 80°, because products of deep hydrogenation of cis-1,4-polybutadiene dissolve poorly at lower temperatures. In addition, hydrogenation was carried out at the same temperature under elevated hydrogen pressure in a rotating autoclave. Under these conditions the concentration of the cis-1,4-polybutadiene solution was increased to 4%, and in the case of lower-molecular-weight polymers—to 8%. The residual unsaturation of the hydrogenation products was determined with bromine vapor by the method developed for hydropolybutadienes insoluble at room temperature ([2]).

Fig. 1. Rate curves for hydrogenation of polybutadienes:
1—on the triisobutylaluminum—cobalt(III) acetylacetonate catalyst, 2—on the palladium-on-calcium carbonate catalyst

For hydrogenation, catalysts were used consisting of triisobutylaluminum and acetylacetonates of cobalt(III), chromium(III), or tetraisopropoxytitanium. The catalysts were prepared by mixing the components in decalin before hydrogenation. All work was carried out with careful removal from the reaction volume of traces of moisture and oxygen. For each catalytic system, definite component ratios must be strictly observed. Changing the ratio can lead to a decrease or complete loss of catalyst activity.

Hydrogenation curves were recorded for the polymer on the triisobutylaluminum—cobalt(III) acetylacetonate catalyst at an aluminum/cobalt ratio of 3 : 1 in a 0.5% polymer solution at atmospheric pressure and a temperature of 80°. The rubber/catalyst ratio was 25 : 1.

Table 1

Hydrogenation of cis-1,4-polybutadiene in the presence of soluble organometallic catalysts at 80° and a rubber/catalyst ratio of 50/1

No.	Catalyst	Molar ratios Al/Me	Concentration of rubber solution, %	Pressure, atm	Time, h	Unsaturation, %
1	$Al(iso\text{-}C_4H_9)_3 - Co(C_5H_7O_2)_3$	3/1	1	1	1	11
2	$Al(iso\text{-}C_4H_9)_3 - Cr(C_5H_7O_2)_3$	10/1	1	1	12	14
3	$Al(iso\text{-}C_4H_9)_3 - Cr(C_5H_7O_2)_3$	10/1	2	55	2	4
4	$Al(iso\text{-}C_4H_9)_3 - Ti(O\text{-}iso\text{-}C_3H_7)_4$	10/1	4	60	1.5	6
5	$Al(iso\text{-}C_4H_9)_3 - Ti(O\text{-}iso\text{-}C_3H_7)_4$	10/1	8*	100	2	11

* Molecular weight of the polymer 60,000.

The rate of polymer hydrogenation was followed by hydrogen absorption in the system. Fig. 1 shows the reaction-rate curve in coordinates of the logarithm of the concentration of saturated groups versus time, which shows that in the case studied the process is a first-order reaction. For comparison, the hydrogenation curve of divinyl rubber on a palladium-on-calcium carbonate catalyst is given.

As a result of the study performed, the possibility has been shown of effective hydrogenation of cis-1,4-polybutadiene in the presence of soluble complex organometallic catalysts both at atmospheric and at elevated hydrogen pressure. It has been established that at atmo-

at atmospheric pressure, hydrogenation is a first-order reaction with respect to the unsaturated substance.

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Received
8 IX 1964

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