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STEREOREGULAR POLYMERIZATION
OF BUTADIENE

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The stereoregular polymerization of butadiene takes place in the presence of heterogeneous or homogeneous catalytic systems leading to the formation of pure stereoisomers *cis*-1,4 or *trans*-1,4 polybutadiene, respectively. The homogeneous catalytic systems are of great importance both from the practical and theoretical point of view. The best homogeneous systems for the preparation of *cis*-1,4 polybutadiene are cobalt(II) bis-acetylacetonate–diethylaluminium chloride or pyridinium complex of cobaltous chloride–diethylaluminium chloride[1,2]. A homogeneous catalytic system based on the complex rhodium compounds and diethylaluminium chloride[3,4] is suitable for preparation of sterically pure *trans*-1,4 polybutadiene. Stereoregular course of polymerization of butadiene initiated by the above mentioned catalytic system is practically not influenced by reaction conditions *i.e.* by catalyst and monomer concentrations, time and temperature[2,4]. The activity of the cobalt containing system is 4 to 5 times greater than that of the rhodium system[2,4].

The simultaneous application of two compounds of different transition metals in form of a Ziegler–Natta catalyst, each being able to govern the sterical course of polymerization in a different way, has not yet been described. The purpose of this communication is to describe the stereo-

regular polymerization of butadiene using a mixed catalytic system containing besides the aluminium component (diethylaluminium chloride) the rhodium and cobalt acetylacetonates. The technique described previously[5] was employed for the polymerization in solution; the mutual proportion of *cis*-1,4 and *trans*-1,4 structures was measured by infrared spectroscopy using calibrated standards.

The polymerization activity of a mixed catalyst depends on the ratio of rhodium and cobalt components and also upon their absolute concentration. The dependence of the polymer yield on the concentration of a rhodium component, keeping the cobalt component concentration constant, goes first through a minimum and then through a maximum. At zero concentration of a cobalt component the curve shows a maximum only (Fig. 1*a*). The highest conversion of monomer into the polymer was achieved at the [Al]/[Rh] ratio being c. 5. The decrease in the conversion at lower ratios of these components is in a good agreement with previous reports[3,4]. According to them the polymerization takes place only if the [Al]/[Rh] is higher than 2·5; a minimum seen at the concentration of the rhodium compound 2·0 mmol/l is evidently both due to the excess of rhodium over the cobalt in a mixed catalyst [Rh]/[Co] $\approx$ 50 and also due to a lower activity of the rhodium system. The ratio of stereoisomers is naturally changing with the increasing concentration of rhodium component so that the *cis*-1,4 isomers concentration increases correspondingly. This tendency is seen till [Al]/[Rh] $\approx$ 5.

When the concentration of a cobalt component is varied, keeping the concentration of rhodium and aluminium component constant, then the reaction course is similar to that observed during the polymerization without the presence of rhodium component[2]. The only difference is, that at zero concentration of the cobalt component, the conversion is determined by the concen-
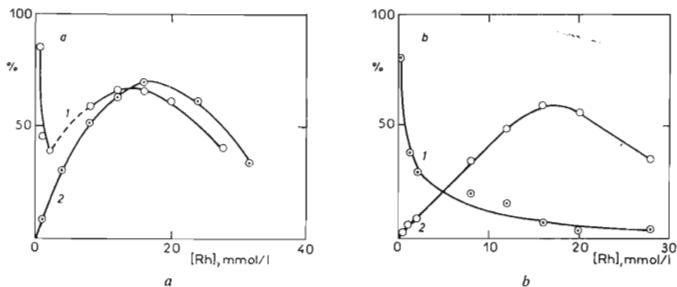

FIG. 1

The Dependence of Butadiene Conversion Into the Polymer (*a*) and Its Tactic Component (*b*) upon the Concentration of the Rhodium ([Rh]) Catalyst

Polymerization was carried out for 24 hours at 25°C. Concentration of polymerization mixture components (mmol/l): Monomer 2000, diethylaluminium chloride 80, water 4·0, *a* cobaltous acetylacetonate was either [Co] = 0·04 (○) or [Co] = 0(⊙), *b* [Co] = 0·04) ⊙ *cis*-1,4 polybutadiene ○ *trans*-1,4 polymer).

tration of the rhodium–diethylaluminium chloride catalyst[4]. Increasing the concentration of the cobalt component causes the increase of the *cis*-1,4 polybutadiene yield, whereas the conversion to *trans*-1,4 isomer remains constant (Fig. 2).
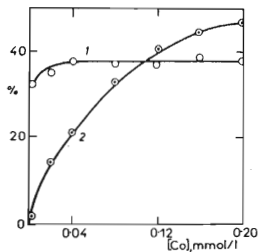

FIG. 2

The Dependence of Butadiene Conversion Into the Polymer upon the Concentration of Cobalt Component ([Co]) in the Catalytic System

20°C, reaction time 24 h. Concentration of rhodium(III) acetylacetonate 8 mmol/l; for water, butadiene and diethylaluminium chloride concentrations see Fig. 1. Polybutadiene: ⊙ *cis* −1,4, ○ *trans* 1,4.
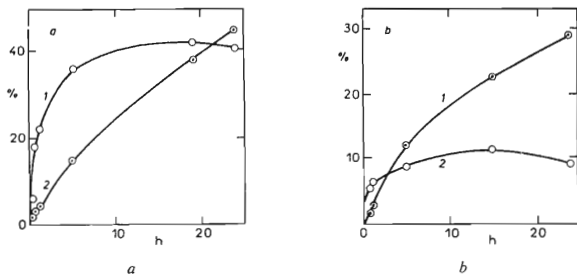

FIG. 3

Conversion of Monomer Into Polybutadiene at 25°C

Concentration of polymerization mixture components (mmol/l): Monomer 2 000, diethylaluminium chloride 80, water 4·0, cobaltous acetylacetonate Co = 0·16 at the ratio [Al]/[Rh] = 10 (*a*) and [Co] = 0·04 at the ratio [Al]/[Rh] = 40 (*b*). Polymer tacticity: ⊙ *cis*-1,4, ○ *trans*-1,4.

At the constant ratio [Rh]/[Co] = 50 the overall conversion into the polymer is dependent on the concentration of cobalt component and on the ratio [Al]/[Rh]; the polymerization reaction rate, at low concentration of the cobalt component and high [Al]/[Rh] ratio, is slower than that observed at higher concentration of this component and low [Al]/[Rh] ratio. Infrared analysis of the polymerization products has shown that initially both *cis*-1,4 and *trans*-1,4 structures are formed simultaneously. The *trans*-isomer rate of formation is, however, faster at the ratio [Al]/[Rh] being 10 (Fig. 3*a*) than that for the case [Al]/]Rh] being 40 (Fig. 3*b*). In the latter case the *cis*-1,4 isomer rate of formation is high even in spite of the fact that the cobalt component concentration is lower.

The consistence and mechanical properties of the polymer are determined by the individual stereoisomer contents. The pure *trans*-1,4 polymer is a powder, the polymer containing equal proportions of both isomeric forms is a resinous spongy matter whereas the pure *cis*-1,4 polymer has mechanical properties of rubber. Also the solubility in benzene varies with the *trans*-1,4 isomer contents; whereas the *cis*-1,4 polymer is soluble at room temperature, the polymers containing high proportions of *trans*-1,4 form dissolve at temperatures above 35°C.

Both rhodium and cobalt transition metal components show their catalytic activity even in the mixture. The ability to regulate both the initiation and propagation reaction depends on the ratio and concentration of both components. In principle there are two governing reactions: the first leads to the *cis*-1,4 isomer formation, the second leading to the *trans*-1,4 isomer. Both of them can either be parallel or they can even supersede each other during the propagation step. The above described mixed catalytic system allows to prepare a polymer of expected sterical composition.

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