Chemistry

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1965

SovietRxiv

Abstract

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INVESTIGATION OF THE PROCESS OF STEREOSPECIFIC POLYMERIZATION OF BUTADIENE IN AN AQUEOUS MEDIUM IN THE PRESENCE OF RHODIUM CHLORIDE BY THE METHOD OF LABELED ATOMS

(Presented by Academician B. A. Dolgoplosk on 30 XI 1964)

It is known that rhodium compounds initiate the polymerization of butadiene in an aqueous medium with the formation of stereoregular polybutadiene containing up to 99% trans-1,4 units ([1,2]). The mechanism of this process remains unclear at present. However, thanks to the work of a number of authors, it can be stated with certainty that the reaction is ionic rather than free-radical ([1–4]). The available data still do not permit a final choice in favor of a cationic or anionic mechanism, although Natta, on the basis of a study of the polymerization of cyclobutene with rhodium chloride, proposes a coordination–anionic mechanism ([5]).

It is known that polymerization of butadiene under the influence of rhodium chloride proceeds only in an aqueous medium; in alcohol, dimerization and hydrogenation of butadiene take place ([1]). According to our data, in hydrocarbon solvents rhodium chloride does not cause polymerization of butadiene.

In order to study the specific role of water in the polymerization of butadiene, we carried out the process in tritiated water with an activity of 1 mCi/ml, with a ratio of aqueous to hydrocarbon media of 2 : 1 and a molar ratio $RhCl_3 \cdot 3H_2O$: butadiene = 1 : 500.

Sodium dodecylbenzenesulfonate was used as the emulsifier; the polymerization temperature was 50°. The method for measuring radioactivity was analogous to that described previously ([6]).

All the activity values given below refer to our counting geometry, without corrections for efficiency.

The polymers obtained when the process was carried out in tritiated water possessed appreciable radioactivity.

Special experiments established that this radioactivity was not caused by isotopic exchange of tritiated water with the polymer chain.

Repeated reprecipitation of the radioactive polymer (scheme) from benzene solution with substances having no labile hydrogen atoms and incapable of isotopic exchange (heptane, isopentane) did not lead to a decrease in the activity of the polybutadiene, whereas even a single reprecipitation with alcohol or treatment of the polymer with ordinary water in an extractor led to a decrease in the initial activity by 50–70%, and no further treatments reduced this activity. It should be noted that reprecipitation of the polymer labeled in hydroxyl alcohol $C_2H_5OH^3$, with a molar activity equal to the molar activity of tritiated water, did not lead to a decrease in the activity of the polybutadiene.

These data allow us to state that the total radioactivity of polybutadiene obtained under the influence of rhodium chloride in tritiated water consists of two components:

Scheme for processing the polymer (activity of polymers in pulses/100 sec)

trans-1,4-Polybutadiene obtained by polymerization of butadiene in tritiated water in the presence of rhodium chloride

- **Precipitation from benzene with heptane**
  - Polymer 1400
  - Twofold precipitation from benzene with heptane
  - Polymer 1400
  - Precipitation from benzene with alcohol
  - Polymer 300
  - Threefold precipitation from benzene with alcohol
  - Polymer 300
- **Treatment with tritiated water in an extractor**
  - Threefold precipitation from benzene with heptane
  - Polymer 1400
    - Precipitation from benzene with radioactive alcohol
      - Polymer 1300
      - Precipitation from benzene with alcohol
      - Polymer 300
    - Precipitation from benzene with alcohol
      - Polymer 340
- **Treatment with water in an extractor**
  - Polymer 300
  - Threefold precipitation from benzene with alcohol
  - Polymer 300

a) radioactivity removed from the polymer upon interaction with substances having labile hydrogen atoms; b) radioactivity which, as a result of such treatments, remains.

It may be assumed that radioactivity of the first type is due to the presence in the polymer of groups

$$C{-}OH^3,$$

whereas radioactivity of the second type is due to groups

$$C{-}H^3.$$

From these positions the rapid loss of radioactivity of the first type upon treatment of the polymer with alcohol or water is readily explained:

$$\sim COH^3 \xrightarrow[\text{excess}]{ROH} \sim COH + ROH^3. \qquad \text{(I)}$$

The validity of the proposition that hydroxyl groups are present in polymers obtained in the presence of $RhCl_3$ is confirmed by the fact, established by us, that the reaction reverse to (I) takes place:

$$\sim COH \xrightarrow[\text{excess}]{H^3O} \sim COH^3. \qquad \text{(II)}$$

trans-1,4-Polybutadiene obtained by emulsion polymerization in the presence of rhodium chloride in ordinary water, and carefully purified from emulsifier and catalyst by a large number of reprecipitations with alcohol and washing with ordinary water, was treated in an extractor with tritiated water or with solutions of tritiated water in benzene. In both cases the polymer acquired radioactivity that was easily removed by treatment with ordinary water or alcohol.

Nonreactive polybutadiene obtained in the presence of other catalysts, when treated with tritiated water under analogous conditions, did not acquire radioactivity.

The appearance of radioactivity in the polymer can evidently occur both in the course of the polymerization process and as a result of secondary reactions taking place in the polymer chain under the influence of the catalyst. To clarify the role of each of these reactions, a benzene solution of inactive polybutadiene, obtained in the presence of other catalysts, was treated with tritiated water containing an emulsifier and $RhCl_3$ at 50°, i.e., under the conditions in which the polymerization process was carried out.

This treatment led to the appearance in the polymer of radioactivity that did not change under the action of either pentane or compounds with labile hydrogen atoms (active and inactive alcohol, water), i.e., to the appearance of groups

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$C—H^3$.
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However, this radioactivity is an order of magnitude lower than the radioactivity detected in polybutadiene obtained in tritiated water in the presence of rhodium chloride.

From the data presented it may be concluded that, in the stereospecific polymerization of butadiene under the influence of rhodium chloride in an aqueous emulsion, water participates in the polymerization process.

Although it can be stated unequivocally that hydroxyl groups of water appear in the polymer as a result of elementary acts of initiation or termination, water protons can add to the polymer both during the course of the polymerization process and in secondary reactions of the polymer chain under the influence of the catalyst.

All-Union Scientific Research Institute
of Synthetic Rubber
named after S. V. Lebedev

Received
24 XI 1964

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