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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# ON ISOTOPIC EXCHANGE BETWEEN GASEOUS HYDROGEN AND SOLID POLYMERS UNDER THE ACTION OF NUCLEAR RADIATION

*(Presented by Academician V. A. Kargin, 24 VI 1957)*

As is known ($^1$), during the irradiation of polymeric hydrocarbons there occurs the evolution of gaseous products containing chiefly hydrogen. It is of interest to clarify the question of the reversibility of the corresponding processes, i.e., the possibility of introducing hydrogen from the gas phase into polymer molecules during irradiation. We have attempted to clarify this question by means of the tracer-atom method using deuterium. Isotopic exchange between gaseous deuterium and various solid polymers was studied in the radiation field of a nuclear reactor.

The following polymers of the vinyl series were investigated: 1) Polyethylene; unplasticized; film 0.1 mm thick. 2) Polypropylene; obtained by catalytic polymerization; m.p. 110-130°; powder. 3) Polystyrene; obtained by emulsion polymerization; softening point 175°; powder. 4) Divinyl rubber; obtained by block polymerization; without addition of antioxidant; small pieces (2-3 mm). 5) Polymethyl methacrylate; obtained by emulsion polymerization; powder.

**Table 1**

| Substance | Dose, Mrad | Deuterium concentration in the polymer (mol. %) |
|---|---:|---:|
| Polyethylene | 400 | 0.18 |
| Polypropylene | 400 | 0.18 |
| Polystyrene | 800 | 0.07 |
| Divinyl rubber | 400 | 0.06 |
| Polymethyl methacrylate | 50 | 0.02 |

Samples of the polymers under investigation (~0.6 g) were placed in glass ampoules of 50-70 ml capacity, after which the ampoules were evacuated, filled with gaseous deuterium (~99.6%), and sealed, being cooled at the same time with liquid air (in order to increase the amount of deuterium in the ampoule). The sealed ampoules were placed in baskets made of thin aluminum wire and subjected to irradiation in a water-water reactor. To reduce radiational heating, the channel was filled with water to the height of the active zone. At the maximum differential dose, the temperature of the water in the channel did not exceed 60°.

The calculated equilibrium concentration of deuterium in the polymer (i.e., the concentration calculated on the assumption that isotopic exchange had reached equilibrium, and that the distribution coefficient of deuterium between C—H and H—H bonds is approximately equal to 3 (2)) under the experimental conditions is approximately 5-7 mol. %. Table 1 gives the deuterium content actually detected in each of the polymers after irradiation.

The deuterium concentration in the polymer was established by burning the substance in an oxygen atmosphere and determining, by the drop method (3), the deuterium content in the water from the combustion. For each of the substances, four combustions were carried out in parallel. The results of the parallel measurements differed by no more than 0.02%. Table 1 gives the mean values. The absolute accuracy of the drop method of isotopic analysis in the concentration range of deuterium studied (0.02-0.2 mol. %) is $±$0.01-0.02%.

For each of the polymers it was specially shown that the introduction of deuterium is not connected with adsorption of gaseous deuterium. Blind experiments carried out for this purpose showed that in the absence of radiation deuterium

is not detected in the polymer. To make certain that the action of radiation does not activate the adsorption of deuterium on the surface of the polymer, and that the incorporation of deuterium is due to isotopic exchange, separate weighed portions of each of the irradiated substances were desorbed before combustion by evacuation for 10-20 hours in a high vacuum at 100-150°. The deuterium content in the polymer was not changed as a result of this operation.

The observed effects are evidently due to chemical interaction between the polymer molecules and molecular deuterium occurring under the action of radiation, since in the absence of radiation isotopic exchange of hydrogen under the stated conditions, as is known, is not observed.

Of the polymers studied, the greatest amount of deuterium was incorporated into polyethylene and polypropylene. Exchange proceeds somewhat more slowly in the case of polybutadiene and polystyrene, whereas in polymethyl methacrylate no signs of exchange could be detected. All four polymers for which exchange was found belong to substances that undergo crosslinking under the action of radiation. At present, for polyethylene a mechanism is accepted according to which this process proceeds through free radicals, for example

$$\mathrm{R - CH_2 - R_1 \rightsquigarrow R - \dot{C}H - R_1 + \dot{H}}$$

It is quite probable that, in our case, incorporation of deuterium into the polymer occurs as a result of a reaction between the polymer radical and the deuterium molecule:

$$\mathrm{\dot{R} + D_2 \longrightarrow RD + D}, \tag{I}$$

$$\mathrm{RH + D \longrightarrow \dot{R} + HD} \tag{II}$$

and so on. The equilibrium concentration of dissolved deuterium in the polymer is of the order of $10^{-6}$ mole/g ($^4$). Therefore a mechanism in which the initial stage consists in the transformation $\mathrm{D_2 \rightarrow D + D}$ is less probable than the mechanism (I)—(II). It should be noted that the experiments were carried out under heterogeneous conditions, and therefore the amount of deuterium in the polymer cannot serve as an unambiguous characteristic of the probability that the process (I)—(II) proceeds. However, as a first approximation such a relation can nevertheless be accepted, which makes it possible to draw certain qualitative conclusions.

It is also not excluded that the observed incorporation of deuterium into polymer molecules is caused to some extent by isotopic exchange between gaseous deuterium and free radicals. Exchange of this kind in the gas phase was studied by Voevodskii and co-workers ($^5$).

Comparison of the amount of deuterium incorporated into polyethylene and into polybutadiene shows that addition of hydrogen at double bonds apparently does not occur. The comparatively weak exchange in the case of polystyrene may be explained by its high radiation stability, i.e., by a low yield of radicals.

The absence of exchange in polymethyl methacrylate may be connected with the fact that the radicals formed cannot participate in reaction (I) because of steric hindrance; however, it is not excluded that it is due to an insufficient irradiation dose.

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*Note: Figure translations are in progress. See original paper for figures.*