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Soviet-era science, translated into English

# Chemistry

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1958

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**Abstract****Full Text***Chemistry*

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**APPLICATION OF THE POLYRECOMBINATION REACTION TO THE PREPARATION OF POLYMERS**

Many investigators, under the action of free radicals formed as a result of the decomposition of peroxides, have observed the formation of compounds that are dimers of those radicals which are obtained from the solvent after abstraction of a hydrogen atom from it <sup>(1)</sup>.

The investigation carried out by us showed that, under certain conditions, the reaction may proceed in such a way that its products are not dimers formed from the solvent, but high-molecular compounds <sup>(2)</sup>. The formation of these compounds occurs as a result of a polyrecombination reaction. We have subsequently obtained new experimental data, the presentation of which constitutes the content of this article.

The principal experimental material was obtained in reactions in which the starting substance was *n*-diisopropylbenzene. Various peroxides served as the source of free radicals; of these, the main attention was devoted to tert-butyl peroxide.

The reaction was carried out in such a way that tert-butyl peroxide was gradually added, beneath a layer of hydrocarbon, to the hydrocarbon heated to a temperature of 170–200°. As a result, a polymer is formed which, depending on the reaction conditions, contains a greater or lesser amount of an insoluble three-dimensional fraction. The soluble fraction was isolated by extraction with benzene and precipitated with methanol. The polymer obtained was a white powder with a melting temperature of 210–230°.

**Fig. 1.** Change in the composition of the reaction products and in the molecular weight of the soluble polymer as a function of the peroxide:hydrocarbon ratio. *I*—unchanged hydrocarbon; *II*—low-molecular products; *III*—high-molecular products (soluble and insoluble in benzene); *IV*—molecular weight of the benzene-soluble polymer.

X-ray diffraction investigation of this polymer showed that it is practically amorphous, since its degree of crystallinity does not exceed 10%. The insoluble

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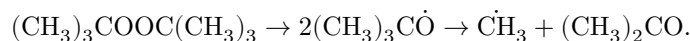
polymer decomposes at a temperature of about 300°, and, according to X-ray diffraction data, its degree of crystallinity reaches 60%.

We investigated the dependence of the yield and molecular weight of the polymer formed on the amount of tert-butyl peroxide taken. The results obtained are shown in Fig. 1; as is evident from it, with an increase in the quantity

peroxide, an increase is observed in the molecular weight of the polymer formed. At a molar ratio of tert-butyl peroxide to hydrocarbon equal to 1, practically all of the initial hydrocarbon is converted into various reaction products. However, at this ratio the amount of high-molecular-weight products is still small; it continues to increase as the amount of peroxide is increased and, at a peroxide-to-hydrocarbon ratio equal to 3, reaches 100%. At the same time, the amount of low-molecular-weight reaction products, containing chiefly dimer and trimer, reaches a maximum at a peroxide-to-hydrocarbon ratio equal to 1, and then decreases to zero when the ratio reaches 3. Thus, only the first mole of peroxide reacts with the initial hydrocarbon. The second and third moles of peroxide react not with the initial hydrocarbon, but with the conversion products, which, as we have already indicated, consist of a mixture of dimer and trimer.

The reaction that proceeds in the formation of these polymers is divided into the following stages:

The first stage is the decomposition of the peroxide with formation of free radicals:

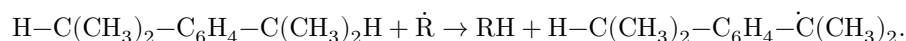


In this process, both tert-butoxy and methyl radicals are usually formed, in a ratio that depends on the temperature and on the properties of the solvent <sup>(3)</sup>.

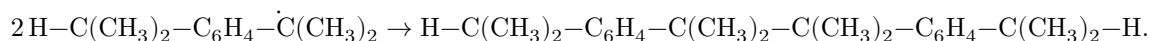
Raley, Rust, and Vaughan <sup>(4)</sup>, as a result of studying the kinetics of the decomposition of tert-butyl peroxide in the liquid phase, found that this decomposition is a monomolecular reaction, and came to the conclusion that, as the temperature rises, the stability of the butoxy radical decreases and its decomposition

reaction with formation of a methyl radical becomes increasingly noticeable.

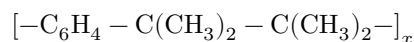
On the basis of the amount of tert-butyl alcohol trapped by us, it may be concluded that approximately half of the peroxide taken decomposes with formation of butoxy radicals. The free radical formed as a result of peroxide decomposition acts on *n*-diisopropylbenzene, abstracting from it a tertiary hydrogen atom in the isopropyl group:



The diisopropyl radical formed as a result of this reacts with an analogous radical, forming a dimer according to the equation:



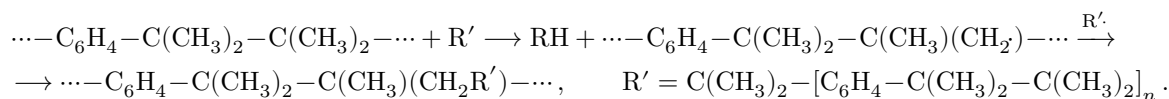
This dimer, in turn, can be subjected to the action of free radicals and, thus, through separate stages, growth of the polymer chain occurs, leading to the formation of a polymer of the general formula:



Thus, the polymer is formed as a result of multiply repeated acts of recombination of radicals that have arisen from solvent molecules. Therefore, this reaction has been called by us the polyrecombination reaction.

As a method for synthesizing high-molecular-weight compounds, the polyrecombination reaction differs fundamentally from the polymerization reaction in that the starting products are saturated compounds; and although the reaction proceeds by a radical mechanism, it has a stepwise rather than a chain character. The polyrecombination reaction has certain features that make it akin to polycondensation, including the stepwise character of the increase in molecular weight and the presence of low-molecular-weight products—tert-butyl alcohol and methane; however, unlike polycondensation, it is an irreversible process, and there is no reverse reaction involving destruction of the polymer chain (5).

The formation of insoluble three-dimensional polymers apparently occurs as a result of interaction between radicals formed during peroxide decomposition and the hydrogen atoms of the methyl groups of the polymer.



As the reaction proceeds further, the number of tertiary hydrogen atoms continually decreases, and therefore the reaction involving methyl groups, which leads to branching of the polymer chain, becomes more probable. In connection with this, an insoluble polymer is formed in increasingly large amounts, as is seen in Fig. 2.

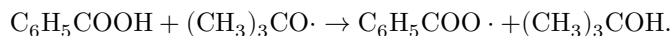
We observed that, when benzoyl peroxide was used, even when large amounts of it were employed, insoluble products were not formed. This can evidently be attributed to the fact that benzoate radicals, being less active, do not react with the hydrogen atoms of the methyl group.

This observation was used by us in order to reduce the amount of insoluble products; for this purpose benzoic acid was added to *n*-diisopropylbenzene, and only after this was tert-butyl peroxide added. It turned out that, upon addition of 0.5 mole of benzoic acid per 1 mole of hydrocarbon, only soluble linear polymers are formed, although with lower molecular weight. The ratio of linear and three-dimensional polymers obtained in the presence of benzoic acid and without it is shown in Fig. 2; from this it is evident that the presence of benzoic acid practically eliminates the formation of insoluble three-dimensional products. Evidently, benzoic acid is a modifier of the process and serves as a source of benzoate radicals, which pri-

**Fig. 2.** Yield of soluble and benzene-insoluble polymers obtained in the presence of benzoic acid and without it.

*I*—insoluble polymers without benzoic acid; *II*—soluble polymers without benzoic acid; *III*—soluble polymers in the presence of benzoic acid; *IV*—insoluble polymers in the presence of benzoic acid.

lead to the formation only of linear polymers. The formation of benzoate radicals may be represented by the following equation:



Some confirmation of such a mechanism is provided by the fact that, when benzoic acid is replaced by methyl benzoate, an insoluble polymer is again formed.

**Table 1**

Starting compound	Molecular weight of polymer	Melting point of polymer, °C
Diphenyl	1500	136–166
<i>p</i> -Xylene	1600	108–130
Diisopropyl ketone	800	130–172
Diisopropylferrocene	8200	155–180
<i>p</i> -Dichlorobenzene	4500	230–280

The preparation of polymers by means of the polyrecombination reaction was also carried out by us starting from other substances. Table 1 presents the results obtained.

The results obtained show that the polyrecombination reaction can be applied to a broad range of starting substances as a method for the synthesis of high-molecular-weight compounds.

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Received  
28 III 1958

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

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