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Polymerization of Styrene under the Influence of Diazoamino Compounds and Activators

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The polymerization of unsaturated compounds in the condensed phase under the influence of initiators (peroxides, diazoamino compounds) proceeds at a considerably lower rate than in aqueous emulsions. Therefore, polymerization in the condensed phase is carried out at a higher temperature (^{1}). One of the factors determining the rate of polymerization is the rate of decomposition of the initiator (^{2}).

In the present communication, data are given on the influence of organic acids and their anhydrides on the rate of polymerization of styrene by diazoamino compounds in the condensed phase, and on the influence of these compounds on the rate of decomposition of the initiator.

The polymerization of styrene was carried out in ampoules of 10–12 ml volume, at a temperature of $70 \pm 0.2°$. Before the experiment, diazoaminobenzene (2 wt. %) and organic acids and their anhydrides in various amounts were introduced into the styrene. The polymer content in samples of the polymerizing mixture, taken at different stages of the process, was determined from the residue obtained after removal of free styrene from the sample, with a correction introduced for the content of impurities in the polystyrene. In the kinetic experiments, in addition to the polymer yield, diazoaminobenzene and nitrogen liberated in the course of polymerization and corresponding to the decomposed diazoaminobenzene were determined.

Experimental Data

The results of the investigation shown in Fig. 1 demonstrate that organic acids substantially accelerate the process of polymerization of styrene in the condensed phase under the influence of diazoaminobenzene. The ability of organic acids to accelerate the polymerization reaction in this case is a general property inherent in all acids soluble in hydrocarbons. In terms of their activity, the organic acids studied are arranged in the following order: monochloroacetic –formic –acetic –benzoic –butyric –oleic. Anhydrides of organic acids that are soluble in hydrocarbons also accelerate the polymerization process of styrene. An analogous influence of organic acids and their

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anhydrides on the rate of polymerization of styrene is observed in the presence of o, o'-dimethyldiazoaminobenzene and n, n'-dimethyldiazoaminobenzene.

The dependence of the rate of polymerization and of the decomposition of diazoaminobenzene on the reaction time is shown in Fig. 2, on which, by way of example, data obtained in the presence of monochloroacetic acid are plotted. On considering the results, attention is drawn to the fact that, under the conditions of polymerization under the influence of organic acids, transformations of diazoaminobenzene take place that are connected both with the evolution of nitrogen and ⋯

and proceeding without it. In this case, complete agreement is observed between the polymerization curves and the decomposition curves of diazoaminobenzene. By studying the kinetics of polymerization and the kinetics of decomposition of diazoaminobenzene in the

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presence of various organic acids, a dependence of the rate of polymerization and of the decomposition of diazoaminobenzene on the strength of the acid was established.

The accelerating effect of organic acids on the polymerization process of styrene in the presence of diazoaminobenzene is accompanied by their effect on the molecular weight of the polymer. We give the average molecular weights of polystyrene samples obtained by polymerization of styrene in the presence of 2% diazoaminobenzene and organic acids (at optimum concentrations):

Activator	Average molecular weight
original activator	106900
monochloroacetic	17000
formic	17800
acetic	25300
benzoic	25800

Investigation of the composition of the decomposition products of diazoaminobenzene in acid solution at a temperature of 70° under the influence of organic acids revealed the following regularities in the decomposition (see Fig. 3): 1) the rate of decomposition of diazoaminobenzene is proportional

Fig. 2. Rate of polymerization and decomposition of diazoaminobenzene: 1 —polymer yield; 2 —total decomposition; 3 —decomposition by nitrogen

Figure 2: Fig. 2. Rate of polymerization and decomposition of diazoaminobenzene: 1 —polymer yield; 2 —total decomposition; 3 —decomposition by nitrogen

to the acid concentration, 2) the rate of rearrangement of diazoaminobenzene into aminoazobenzene is proportional to the acid concentration, 3) aniline and nitrogen are formed in practically equivalent amounts, and their formation proceeds according to the cur-

Fig. 2. Rate of polymerization and decomposition of diazoaminobenzene: 1 —polymer yield; 2 —total decomposition; 3 —decomposition by nitrogen

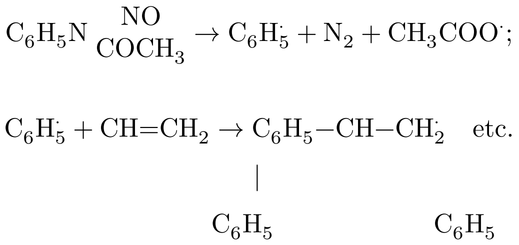
which is characterized by the presence of a maximum. If it is assumed that the process of rearrangement of diazoaminobenzene into aminoazobenzene is not related to the initiation of the polymerization process, then, apparently, the rate of polymerization is determined by the rate of decomposition of diazoaminobenzene associated with the formation of aniline and nitrogen. This, in all probability, also determines the difference in the activity of acids in the polymerization process. On the basis of the data obtained it may be noted that the discrepancy observed in the polymerization process between the total decomposition of diazoaminobenzene and its decomposition with respect to nitrogen is explained by the formation of aminoazobenzene. It was found that the compounds studied affect the rate of polymerization of styrene in the presence of diazoaminobenzene and organic acids (see Fig. 4). This effect manifests itself differently, depending on the nature of the substance studied; for example, from our data it is evident that aniline has the sharpest effect on decreasing the rate of polymerization. Determination of the molecular weight of the polystyrene samples obtained showed that aniline does not affect the length of the molecular chain, whereas aminoazobenzene has a pronounced effect in lowering the molecular weight.

Fig. 3. Composition of the decomposition products of diazoaminobenzene: *1* —total decomposition, *2* —aniline; *3* —nitrogen; *4* —aminoazobenzene

The effect of organic acids on the rate of the polymerization reaction is apparently based on acceleration of the decomposition reaction of diazoamino compounds, accompanied by the formation of intermediate compounds—nitrosoacylarylamines. For example, under the influence of acetic acid, diazoaminobenzene may decompose with formation of nitrosoacetanilide:

$$C_6H_5N{=}N{-}NH{-}C_6H_5 + CH_3COOH \rightleftarrows C_6H_5N\begin{matrix}NO\\COCH_3\end{matrix} + C_6H_5NH_2.$$

The latter, as an unstable compound, decomposes with formation of free radicals that initiate the polymerization reaction (3):



$$C_6H_5N\begin{matrix}NO\\COCH_3\end{matrix} \rightarrow C_6H_5^{\cdot} + N_2 + CH_3COO^{\cdot};$$

$$C_6H_5^{\cdot} + \underset{C_6H_5}{\underset{|}{CH}}{=}CH_2 \rightarrow C_6H_5{-}CH{-}\underset{C_6H_5}{\underset{|}{CH_2^{\cdot}}} \quad \text{etc.}$$

A study of the polymerization of styrene in the presence of nitrosoacetanilide at a temperature of 70° showed that the polymerization process proceeds

comparatively slowly and, evidently, under the influence of the isomerization and decomposition products of nitrosoacetanilide:

Time, h	Polymer yield, %	Decomposition, %
5	14.9	95.5
10	23.3	95.5
30	52.6	95.5
50	67.6	95.5
100	79.1	95.5

At the same time, nitrosoacetanilide in the course of 10-15 min of heating in fact decomposes completely. The decomposition of nitrosoacetanilide in this case was not utilized for the polymerization act. Evidently, in those cases where conditions are created for the gradual formation of nitrosoacetanilide, as, for example, in the simultaneous presence of diazoaminobenzene and acetic acid, the polymerization process is accelerated to a considerable extent under the influence of nitrosoacetanilide at the moment of its decomposition. It is known that, in the interaction of nitrosoacylarylamines with aniline, diazoamino compounds are formed. We synthesized diazoaminobenzene from nitrosoacetanilide and aniline in benzene or styrene solution at various temperatures, with a sufficiently high yield (about 90%). As a result of the reaction, acetic acid is formed simultaneously with diazoaminobenzene. It is interesting to note that, as a result of the formation of a 2% solution of diazoaminobenzene, the concentration of the acetic acid liberated in the reaction is about 0.6%. As was established, acetic acid of this concentration accelerates the polymerization process of styrene under the influence of diazoaminobenzene. By comparing the rate of styrene polymerization under the influence of synthesized diazoaminobenzene in the interaction of nitrosoacetanilide with aniline in styrene solution, followed by polymerization of the latter, it was found that the kinetics of polymerization, both with respect to the reaction rate and with respect to decomposition of the initiator, is analogous to the kinetics of styrene polymerization in experiments carried out with the corresponding concentration of diazoaminobenzene and acetic acid.

Fig. 4. Influence of decomposition products on the rate of polymerization: 1 —aniline; 2 —aminoazobenzene.

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