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Abstract

Full Text

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ON THE QUESTION OF THE POLYMERIZATION OF NITROOLEFINS

In connection with our studies on the polymerization of nitroolefins, nitroisobutylene and cyclohexylidenenitromethane were synthesized and their capacity for polymerization was investigated.

Investigation of the capacity of nitroisobutylene for polymerization. The starting material for obtaining nitroisobutylene—nitroisobutanol—was obtained by condensation of acetone with nitromethane ([1]). In the course of the experiments, the starting material and additives (sodium methylate, alkali, piperidine) were varied. The best yield of nitroisobutanol, 53.3%, was achieved in the presence of sodium methylate at a temperature of 20° and a stirring time of 30 hours. Nitroisobutylene was obtained by dehydration of nitroisobutanol. As a result of a series of experiments, the most effective method was found to be dehydration in the presence of phthalic anhydride. The yield of nitroisobutylene was 65%.

In the present work the capacity of nitroisobutylene for polymerization was studied in the presence of the following catalysts: benzoyl chloride, benzoyl peroxide, ammonium persulfate, sodium methylate, boron fluoride and phosphoric acid saturated with boron fluoride. The polymerization experiments with nitroisobutylene were carried out in a three-necked flask equipped with a stirrer and a reflux condenser. The different experimental temperatures were regulated by means of baths (oil, water, ice-salt).

Fig. 1. Dependence of polymer yield on catalyst (a) and on reaction temperature (b). 1 —catalyst —benzoyl chloride, 2 —catalyst —benzoyl peroxide.

In the experiments, the temperature, amount of catalyst, and time were varied. The polymer obtained as a result of the reaction dissolved in benzene and was precipitated with methyl alcohol. After filtration the polymer was dried under

Fig. 2. IR spectrogram of polycyclohexylidenenitromethane

Figure 2: Fig. 2. IR spectrogram of polycyclohexylidenenitromethane

vacuum.

After distillation of the solvent, the filtrate was distilled under vacuum. The investigations carried out showed the following results. In the presence of the catalysts boron fluoride, molecular compounds of boron fluoride with phosphoric acid, and ammonium persulfate, polymerization of nitroisobutylene was not observed. Sodium methylate, used as a catalyst and having shown itself to be the best catalyst in the polymerization of nitropropylene, α-furylnitroethylene ([2]), and ω-nitrostyrene ([3]), likewise did not promote the polymerization of nitroisobutylene.

Benzoyl chloride and benzoyl peroxide may be used as catalysts for nitroisobutylene. In the presence of these two catalysts, various conditions for the polymerization of nitroisobutylene were studied.

The polymerization of nitroisobutylene in the presence of benzoyl chloride was studied with different amounts of catalyst, at different times and different temperatures. The maximum polymer yield of 80% is observed when the amount of catalyst is 10% of the starting material taken (Fig. 1a).

The effect of temperature was studied in the range from -10 to $+150°$. The optimum temperature proved to be 150°; with a decrease in temperature the polymer yield fell sharply (Fig. 1b). Polymerization time: 14 h.

The polymerization of nitroisobutylene in the presence of benzoyl peroxide. The amount of benzoyl peroxide in the polymerization reaction of nitroisobutylene was varied from 1 to 10%. As the results of the study showed, the catalyst in an amount from 1 to 10% has little effect on the polymer yield (Fig. 1). Polymerization of nitroisobutylene in the presence of benzoyl peroxide, with a polymer yield of 20–21%, proceeds in the temperature range 120–140°. Below these temperatures polymerization practically does not take place (Fig. 2). Liquid polymerization products are absent.

Fig. 2. IR spectrogram of polycyclohexylidenenitromethane

The polymer of nitroisobutylene is a dark (almost black) powder, insoluble in water, alcohols, and ether, and readily soluble in benzene and acetone.

Characteristics of polynitroisobutylene: m.p. 98°; molecular weight by Rast 1700; η_{rel} 1.14; η_{sp} 0.14; ash content 0.16%.

Found, %: C 47.7; H 6.82; N 13.14
Calculated, %: C 47.6; H 6.92; N 13.90

The polynitroisobutylene obtained showed paramagnetic properties.

Study of the ability of cyclohexylidenenitromethane to polymerize. The monomer was obtained by dehydration of 1-(nitromethyl)cyclohexanol, which, in turn, was synthesized by condensation of cyclohexanone with nitromethane in the presence of basic catalysts (4,5).

A disadvantage of almost all the catalysts used is their poor selectivity, which leads to the formation of contaminated nitro alcohol. In the present work, in order to obtain the purest product, a series of basic catalysts was studied. The condensation reaction of cyclohexanone with nitromethane was carried out in the presence of sodium methylate, caustic soda, and also in the presence of ion-exchange resins. The condensation reaction of cyclohexanone with nitromethane proceeds according to the scheme:

$$\underset{\text{cyclohexanone}}{\text{(CH2)5CO}} + CH_3NO_2 \xrightarrow{\text{CH3ONa}} \underset{\text{1-(nitromethyl)cyclohexanol}}{\text{(CH2)5C(OH)(CH2NO2)}}$$

1-(Nitromethyl)cyclohexanol was obtained by condensation of cyclohexanone with nitromethane in the presence of sodium methylate in 41–45% yield, and also in the presence of the anion exchangers AV-17 and Amberlite IRA-401 in 22–24% yield. In condensation in the presence of anion-exchange resins, a purer nitro alcohol is formed, and the method for obtaining it is considerably simplified.

Cyclohexylidenenitromethane was obtained by dehydration of 1-(nitromethyl)cyclohexanol over phthalic anhydride. In this process a mixture of two isomers is formed: 1-cyclohexenylnitromethane (b.p. 98–102°/12 mm) and cyclohexylidenenitromethane (b.p. 108–110°/12 mm).

$$\text{1-(Nitromethyl)cyclohexanol} \xrightarrow[CH_2NO_2]{\text{phthalic anhydride}} \begin{cases} \text{1-cyclohexenylnitromethane} & (I), \\ \text{cyclohexylidenenitromethane} & (II). \end{cases}$$

The yield of the fraction with b.p. 108–110°/12 mm was 33–36%. The cyclohexylidenenitromethane obtained was investigated as a monomer. In studying the polymerization reaction of cyclohexylidenenitromethane it was found that its polymerization in the presence of sodium methylate can proceed in methyl ethyl ketone at a temperature of 20° with a yield of up to 57%.

The polymer obtained was a yellow amorphous powder, soluble in water and lower organic acids. It is insoluble in ether, benzene, dimethylformamide, and other organic solvents. The molecular weight of the polymer, determined by the isopiestic method, was 900.

Table 1

Polymer charge, mg	Temp., °C	Time, h	Amount of unburned residue, %	Appearance
11.390	1000	2	23.88	White, translucent, hard enamel possessing high adhesion to quartz and porcelain
17.550	1000	2	24.22	White, translucent, hard enamel possessing high adhesion to quartz and porcelain

Table 1 gives the results of heat treatment in a stream of oxygen of the polymer of cyclohexylidenenitromethane obtained.

The proposed structure of the polymer

$$[-C(C_6H_{10}) - CH(NO_2) - C(C_6H_{10}) - CH(NO_2) - C(C_6H_{10}) - CH(NO_2)-]_x$$

is confirmed by IR spectroscopy data (Fig. 2). In the IR spectrum of polycyclohexylidenenitromethane, the nitro groups are represented by bands at 1384 cm^{-1} and 1568 cm^{-1}. Substitution of the cyclohexane ring in the 1,1-position is confirmed by bands at 962 cm^{-1}, 390 cm^{-1}, 1152 cm^{-1}, 1176 cm^{-1}, and 1264 cm^{-1}.

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