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1963

SovietRxiv

Abstract

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Chemistry

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Synthesis of *o*-Fluoro-ω-Nitrostyrene and Investigation of Its Ability to Polymerize

In connection with investigations of nitroolefins as monomers for obtaining high-molecular compounds, *o*-fluoro-ω-nitrostyrene was synthesized and its ability to polymerize was studied. *o*-Fluoro-ω-nitrostyrene was prepared by condensation of *o*-fluorobenzaldehyde with nitromethane in the presence of sodium hydroxide. The reaction proceeds through the sodium salt of the nitro derivative with a yield of 75% according to the following scheme:

$$\text{(o-fluorobenzaldehyde)} + CH_3NO_2 + NaOH \rightarrow \text{(sodium salt of the nitro derivative)}$$

$$\text{(sodium salt of the nitro derivative)} + HCl \rightarrow \text{(o-fluoro-}\omega\text{-nitrostyrene)} + NaCl + H_2O.$$

o-Fluorobenzaldehyde was prepared from *o*-fluorotoluene, which was subjected to bromination under illumination with a 500-W incandescent lamp, and the resulting dibromide was hydrolyzed in the presence of calcium carbonate (1). The yield of *o*-fluorobenzaldehyde was 57–60%. The constants of the resulting *o*-fluoro-ω-nitrostyrene differed little from the literature values.

The polymerization of *o*-fluoro-ω-nitrostyrene was carried out in the presence of sodium methylate catalyst in chloroform solution.

The influence of time, temperature, and amount of catalyst on the yield of poly-*o*-fluoro-ω-nitrostyrene was studied (Fig. 1). As is seen from the figures presented, with an increase in the amount of catalyst the polymer yield increases. However, the molecular weight of the polymer decreases. As the duration of the polymerization reaction increases, the dependence of polymer yield on time becomes insignificant.

Table 1

Characteristics of the low-molecular product of polymerization of *o*-fluoro-ω-nitrostyrene

Fig. 1. Dependence of polymer yield on the amount of catalyst (A), on temperature ( ), and on reaction duration ( )

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Formula of the elementary unit	Mol. weight*	Solubility	Softening temp., °C	Appearance
$[-CH(C_6H_4F)-CH(NO_2)-]_x$	690	In chloroform, CCl_4, lower alcohols, and other organic solvents	35-40	Brown powder

* Average, determined by the isopiestic method.

As a result of the polymerization of *o*-fluoro-ω-nitrostyrene, solid products of light-brown color were obtained; these were separated by filtration and washed with chloroform, water, dilute hydrochloric acid, and again with water to neutral reaction. Low-molecular polymerization products were precipitated with *n*-heptane in the form of a viscous brown oil. After washing with *n*-heptane, dilute hydrochloric acid, and water to neutral reaction, the product was dried at 50° for 3 hours; after cooling to room temperature

The oil solidified, and when it was ground a brown powder with a softening temperature of 35-40° was obtained.

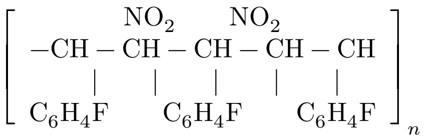
Evidently, the low-molecular-weight product under study is a tetramer of *o*-fluoro-ω-nitrostyrene.

Characteristics of the high-molecular-weight polymerization product of *o*-fluoro-ω-nitrostyrene. The highest-molecular-weight fraction of the polymer was obtained after treating the polymer with methanol. The resulting polymer, separated from the reaction mixture by filtration, was a white powder; it is soluble in ethylenediamine and in dimethylformamide on heating, and is not affected by concentrated mineral acids or alkalis even on prolonged heating.

Fig. 1. Dependence of polymer yield on the amount of catalyst (*A*), on temperature ( ), and on reaction duration ( ).

The molecular weight of the unfractionated sample, determined in dimethylformamide solution by the isopiestic method, is 7000. The polymer obtained was subjected to heat treatment. When introduced into a muffle furnace heated to 900°, the polymer did not ignite and did not change color. After calcination for 3 h at a temperature of 1200°, the polymer was converted into a white translucent enamel possessing high adhesion to porcelain and high hardness. The same white translucent enamel was formed upon calcination for 2 h in a quartz beaker in a stream of oxygen.

IR spectroscopy data confirm the proposed structure of the polymer:



$$\left[\begin{array}{ccccccccc} & & NO_2 & & NO_2 & & & & \\ -CH & - & CH & - & CH & - & CH & - & CH \\ | & & | & & | & & | & & | \\ C_6H_4F & & & & C_6H_4F & & & & C_6H_4F \end{array}\right]_n .$$

The IR spectrogram is shown in Fig. 2. The nitro group is characterized by absorption bands at 1350 cm^{-1} and 1557 cm^{-1}. Substitution of the benzene ring in positions 1-2 is represented by the band at 750 cm^{-1}.

Experimental Part

a) Bromination of *o*-fluorotoluene. The starting *o*-fluorotoluene (1 mole) was placed in a three-necked flask and irradiated with a 500 W incandescent lamp while simultaneously being heated to 105-110° in a glycerol bath; over the course of an hour, with vigorous stirring, an equimolecular amount of bromine was added dropwise. The temperature was then raised over two hours to 135°, and bromine was again added in the same amount. After addition of the bromine, the temperature of the reaction mixture was slowly raised to 250°, and the reaction mixture was kept at this temperature for 15 min. The resulting bromination product was transferred to a flask for hydrolysis.

b) **Hydrolysis of the dibromide** was carried out in the presence of calcium carbonate. The reaction mixture was heated under a reflux condenser for 16 h. After hydrolysis was complete, the contents of the flask were distilled with steam. *o*-Fluorobenzaldehyde was separated from the aqueous layer; the ether extracts obtained after treatment of the aqueous layer were added and dried over magnesium sulfate. It was then distilled, and the fraction at 98-103°/70 mm was collected. The yield of *o*-fluorobenzaldehyde was 65-66.5%. The constants of the *o*-fluorobenzaldehyde obtained did not differ from the literature data.

o-Fluoro-ω-nitrostyrene. An equimolecular mixture of *o*-fluorobenzaldehyde and nitromethane with 60 ml of methanol was cooled to $-5°$. The calculated amount of sodium hydroxide was dissolved in a minimal volume of water and added dropwise to the reaction mixture in such a way that the temperature did not exceed 10°.

After all the alkali had been added, stirring was stopped for 15 min, and an equal volume of cold water was poured into the reaction mixture. The clear

Fig. 2. IR spectrum of the polymer of *o*-fluoronitrostyrene

Figure 2: Fig. 2. IR spectrum of the polymer of *o*-fluoronitrostyrene

solution obtained was poured into a beaker containing dilute hydrochloric acid (200 ml HCl per 400 ml water), whereupon crystals of *o*-fluoro-ω-nitrostyrene immediately precipitated. The product was collected on a glass filter No. 2 and washed with distilled water until chloride ions were completely removed. To remove water, the precipitate was heated in a beaker on a water bath until it melted, forming two layers. After cooling, the water was decanted from the lower solidified layer of the nitroolefin. The crude *o*-fluoro-ω-nitrostyrene was recrystallized from methanol. The resulting *o*-fluoro-ω-nitrostyrene consisted of narrow yellow plates with a melting point of 56–57.5°. According to the literature, the melting point of *o*-fluoro-ω-nitrostyrene is 56.5–57.5°. The yield of the recrystallized product was on average 70–75%.

Fig. 2. IR spectrum of the polymer of *o*-fluoronitrostyrene

Polymerization of o-fluoro-ω-nitrostyrene in the presence of sodium methylate. The polymerization was carried out in a round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser in chloroform solution. After polymerization was complete, the solid polymer was separated by filtration on a glass filter No. 2. The polymer was washed with water, alcohol, dilute acid, again with water, and dried in a drying oven at 120°.

Moscow Institute of the Petrochemical
and Gas Industry named after Gubkin

Received
24 XI 1962

CITED LITERATURE

1. V. V. Korshak, G. S. Kolesnikov, *Syntheses of Organic Compounds*, Publishing House of the Academy of Sciences of the USSR, 1952, p. 140.

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