SYNTHESIS AND POLYMERIZATION OF p-NITROPHENYLACETYLENE

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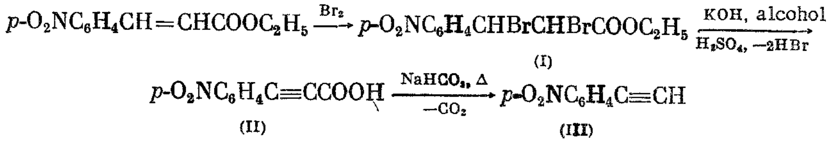
The polymers of nitrophenylacetylenes are convenient models when studying the electrophysical properties of organic semiconductors, and they are also used in the synthesis of polymeric dyes, redox polymers, etc. They are obtained by the nitration of polyphenylacetylenes [1-4] or by the polymerization of nitrophenylacetylenes [5, 6].

Some of the characteristics of the thermal bulk polymerization of p-nitrophenylacetylene (III) and the properties of the obtained polymers are discussed below.

Compound (III) was obtained by a modification of the methods given in [7-11] by the following scheme:



$$p\text{-}O_2NC_6H_4CH{=}CHCOOC_2H_5 \xrightarrow{Br_2} \underset{(I)}{p\text{-}O_2NC_6H_4CHBrCHBrCOOC_2H_5} \xrightarrow[H_2SO_4,\ -2HBr]{KOH,\ alcohol}$$

$$\underset{(II)}{p\text{-}O_2NC_6H_4C{\equiv}CCOOH} \xrightarrow[-CO_2]{NaHCO_3,\ \Delta} \underset{(III)}{p\text{-}O_2NC_6H_4C{\equiv}CH}$$

The polymerization of (III) above 150° proceeds at a fast rate and with a high monomer conversion (Fig. 1). The solubility of the polymer and the thermomechanical analysis data (Fig. 2) indicate its linear structure. The IR spectra (absorption bands at 690, 750, 860, 1015, 1110, 1180, 1450, 1590, and 3080 cm^{-1}) refer to the benzene ring, in which connection the second and third bands characterize p-substitution; the intense stretching vibrations of the nitro group at 1350 and 1520 cm^{-1}, and the elemental analysis results, are in agreement with the structure of a macromolecule that is formed via reaction of the acetylene bonds.

The mean molecular weight of the isolated poly-p-nitrophenylacetylene (PNPA) fractions, which are soluble in acetone, varied in the range from 300 to 3000. It is possible that a slight increase in the amount of carbon in some of the PNPA samples is due either to the reduction or cleavage of the nitro groups. A reduction of nitro groups to amino groups was observed in the polymerization of p- and o-nitrophenylacetylene in plasma [5]. However, under the milder conditions of our experiments the contribution of this process, if it in general occurs, is slight, as is evidenced by the absence of the absorption band of the NH_2 group in the 3300-3500 cm^{-1} region. The PNPA do not lose weight either in vacuo or in the air up to 200-250° (Fig. 3). The same as for a number of other polyconjugated systems, during thermal degradation the weight loss practically stops at a certain depth of decomposition (42% at 800°), whereas during thermo-oxidative degradation complete decomposition of the polymer occurs in the range 500-600°. The PNPA are paramagnetic, and the EPR spectra represent a single line without additional structure with an intensity of 10^{17}-10^{18} spins/g. The PNPA are reduced with comparative ease to the corresponding amino derivatives, which can be diazotized and condensed with aldehydes and ketones. The hydrochlorides of the poly-p-aminophenylacetylenes are readily soluble in methanol.

EXPERIMENTAL METHOD

The IR absorption spectra of the monomers and polymers (as KBr pellets) were taken on either a UR-10 or UR-20 instrument. The EPR spectra were recorded on an ÉPR-2 spectrometer. The molecular

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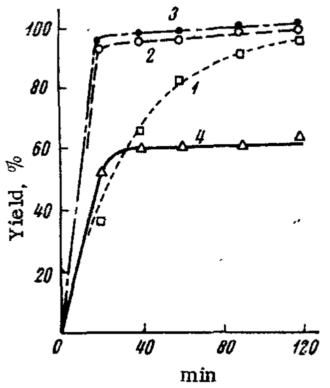

Fig. 1

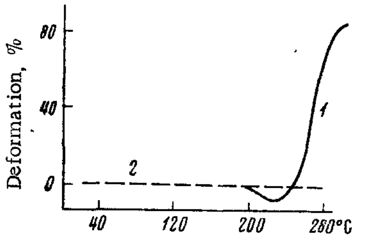

Fig. 2

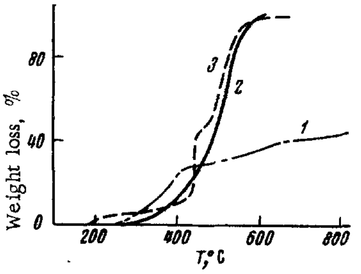

Fig. 3

Fig. 1. Effect of temperature and time of heating on yield of PNPA. Polymerization temperature, °C: 1) 170; 2) 200; 3) 250; 4) 200 (after reprecipitation).

Fig. 2. Thermomechanical curves of PNPA, obtained at 200° in 1 h: 1) soluble portion after reprecipitation; 2) insoluble portion.

Fig. 3. Heat stability of PNPA, obtained at 200° in 1 h, in vacuo (1) and in the air (2, 3): 1, 2) soluble portion after reprecipitation; 3) insoluble portion.

weight of the samples in acetone solution was determined using the thermoelectric method described in [12].

The thermogravimetric analysis of the PNPA was run on automatic balances of type ATV-2 [13] and VTV-1, designed by the Institute of Chemical Physics of the Academy of Sciences of the USSR, at a rate of temperature rise of 3 deg/min and a residual pressure (when the study was made in vacuo) of ~10^{-4} mm of Hg. The thermomechanical curves of the samples, molded as pellets with a diameter of 8 mm and a height of 2-3 mm, were taken on the apparatus described in [14] at a constant load, a specific pressure of 0.8 kg/cm^2, and a rate of temperature rise of ~100 deg/h.

Dibromide of Ethyl Ester of p-Nitrocinnamic Acid (I). With stirring and heating on the water bath, to a solution of the ethyl ester of p-nitrocinnamic acid in $CHCl_3$ (~3 liters of dry $CHCl_3$/mole of ester) was added in drops a solution of Br_2 in $CHCl_3$ (~1.3 moles of Br_2/mole of ester). After adding the Br_2 the flask contents were heated until the solution ceased to decolorize, the solvent was evaporated, and the residue was recrystallized from alcohol. The yield of (I) was 98.4%, mp 110-111°.

p-Nitrophenylpropiolic Acid (II). To a solution of (I), prepared by dissolving in boiling alcohol, was added a 25% alcoholic KOH solution [~4.5 moles of KOH/mole of (I)] at a bath temperature of 40-50°. The mixture was kept at ~20° for 3 h, the precipitate was filtered, as was the salt that was obtained after neutralizing the filtrate with several drops of conc. HCl, the filtrate was evaporated nearly to dryness, and the combined residues were dissolved in ice water (a low temperature must be maintained in order to prevent CO_2 cleavage, which lowers both the yield and purity of the desired product). With stirring, 20% H_2SO_4 solution was added to the cooled solution until strongly acid. The solution was kept for some time, after which the (II) was separated, washed on the filter with small portions of 2% H_2SO_4 solution, then with chilled water, and dried in a vacuum-desiccator.

p-Nitrophenylacetylene (III). A solution of (II) in aqueous $NaHCO_3$ solution was steam-distilled to remove the (III), which was dried and sublimed at 60° (4 mm). White crystals with mp 151-152° were obtained, which became colored in the light and are readily soluble in ether, $CHCl_3$, benzene, and hot alcohol. When based on (I), the yield was 71.2%. Found: C 64.78; H 3.54; N 10.14%. $C_8H_5NO_2$. Calculated: C 65.3; H 3.4; N 9.5%.

Polynitrophenylacetylene. The thermal bulk polymerization of (III) at 150-250° was run in sealed, evacuated (5-6 h, 10^{-3}-10^{-4} mm Hg) glass ampuls, with an inside diameter of 20 mm and a height of 135 mm. The charge was 0.5 g (the ampul bursts after heating at 200° for 15-20 min when the charge is 1 g). The unreacted monomer was extracted with ether until the ≡C−H band at 3300 cm^{-1} disappeared in the IR spectrum of a sample, and the residue was treated with benzene in a Soxhlet apparatus until the color ceased. Evaporation of the benzene gave a fraction with mol. wt. 300-400. The solid residue was dissolved in nitrobenzene (5% solution), filtered from a small amount (~3%) of insoluble product, and the polymer was precipitated by pouring into 10 volumes of methanol. The polymer was dried over P_2O_5 at 50-60° (4 mm) to constant weight. It is soluble in nitrobenzene, DMF, and partially soluble in acetone. Found: C 65.45; H 3.85; N 9.03% (PNPA, obtained at 200° in 40 min); C 66.37; H 3.44; N 9.50% (PNPA, obtained at 200° in 60 min); C 67.36; H 3.57; N 9.40% (PNPA, obtained at 200° in 6 h). $(C_8H_5NO_2)_n$. Calculated: C 65.3; H 3.4; N 9.5%.

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CONCLUSIONS

1. Starting with the ethyl ester of p-nitrocinnamic acid, the method for the synthesis of p-nitrophenylacetylene was improved.

2. The thermal polymerization of p-nitrophenylacetylene and some of the properties of the obtained polymers were studied.

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