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Abstract

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On the Synthesis and Properties of Polyacetylene

It is known that oxidation of acetylides leads to the formation of bis-acetylenes (^{1}). It was also noted (^{2}) that, in the oxidation of acetylides of bis-acetylenes of the type $HC \equiv C - (CH_2)_n - C \equiv CH$, along with the formation of cyclic diynes, a small amount of polymeric products is formed; these products were not investigated.

It may be assumed that, in obtaining copper acetylide from acetylene and salts of divalent copper, the following reactions occur:

$$4HC \equiv CH + 2Cu^{2+} \longrightarrow HC \equiv C - C \equiv CH + 2HC \equiv CCu + 4H^+;$$

$$4HC \equiv C - C \equiv CH + 2Cu^{2+} \longrightarrow HC \equiv C - C \equiv C - C \equiv C - C \equiv CH + 2HC \equiv C - C \equiv CCu + 4H^+, \text{ etc.}$$

With an excess of copper ions, the reaction will give a mixture of polyynes and copper acetylides. Oxidation of the reaction mixture will evidently lead to the formation of polyynes having the structure $H - (C \equiv C)_n - H$.

Proof of the proposed mechanism of polyacetylene formation is provided by our earlier (^{3}) oxidation of n-diethynylbenzene acetylide, as a result of which the dimerization product n, n'-diethynyl-(diphenyl)-butadiyne was isolated and identified,

$$HC \equiv C - C_6H_4 - C \equiv C - C \equiv C - C_6H_4 - C \equiv CH.$$

We prepared the acetylide by passing acetylene into an ammoniacal solution of a divalent copper salt. Oxidation was carried out with an aqueous solution of red prussiate at the boiling temperature of the mixture. As a result of the reaction, a black insoluble powder was obtained which, on the basis of elemental-analysis data, contained 98% C. The product obtained is probably a mixture of polymer homologues of polyacetylene. Indeed, when the product was heated in a high vacuum, a certain amount of a crystalline substance soluble in benzene was isolated; with an ammoniacal solution of monovalent copper it gave a derivative characteristic of acetylenes.

Fig. 2. X-ray patterns of polyacetylene and the products of its thermal treatment.

Figure 1: Fig. 2. X-ray patterns of polyacetylene and the products of its thermal treatment.

Fig. 1. Weight-loss curve of polyacetylene as a function of temperature

Figure 2: Fig. 1. Weight-loss curve of polyacetylene as a function of temperature

The weight-loss curve shown in Fig. 1 for one of the polyacetylene samples as a function of treatment temperature (heating rate 8° per 1 min) on a dynamometer with a quartz spring in a stream of purified nitrogen also confirms the presence of relatively low-molecular volatile products. The EPR spectrum of the substance obtained showed a narrow intense band characteristic of conjugated systems (the concentration of unpaired electrons per 1 gram of substance was about 10^{19}), and the presence of chemically bound copper. These data permit the conclusion that the product obtained is a polymer of cumulenic structure, apparently having the structure $\mathrm{H-(C=C=C=C)_n-H}$ and containing a certain amount of copper.

The X-ray pattern of polyacetylene obtained by oxidation of the acetylide

Fig. 2. X-ray patterns of polyacetylene and the products of its thermal treatment: **a** –initial–after prolonged treatment with HCl; **b** –obtained with a strong oxidizing agent; **c** –calcined at 1800°; **d** –calcined at 1300°, treated with HCl; **e** –at 1500°, treated with HCl; **f** –at 1800°, treated with HCl; **g** –at 2000°, treated with HCl; **h** –at 2300°; **i** –at 2500°; **k** –at 2800°; **l** –calcined at 3000°. The isothermal holding time at the given temperature was 15 min.

copper formate and demineralized by short-term treatment with hydrochloric acid, in addition to the halo it contains a relatively strong interference band corresponding to the period $d = 3.85$ Å, which may be assigned to the intermolecular distance in an ordered system of parallel linear molecules $(=\mathrm{C}=\mathrm{C}=)_n$.

Evidence of the copper content in polyacetylene obtained by oxidation with copper formate is the formation of crystalline copper upon high-temperature treatment, which is clearly recorded on the X-ray diffraction patterns (Fig. 2,).

High-temperature treatment at different temperatures was carried out under isothermal conditions (±25°) in a resistance furnace with a graphite heater in a nitrogen stream. The samples were placed in a closed graphite crucible. During high-temperature treatment, the carbon remains in the form of polyacetylene, and carbonization or graphitization is not observed. Only treatment at 2300° leads to the formation of graphite (Fig. 2,), which indicates the high thermal stability of polyacetylene.

Fig. 1. Weight-loss curve of polyacetylene as a function of temperature

After demineralization of the initial polymer with concentrated hydrochloric acid, only an intense halo is observed on the X-ray diffraction pattern (Fig. 2,), characteristic of a liquid type of molecular ordering. An X-ray diffraction pattern of the same type, in the form of a halo, is obtained for samples of polyacetylene synthesized with the use of a stronger oxidizing agent (Fig. 2,).

On the X-ray diffraction patterns, a very interesting phenomenon is noted: the formation of graphite during prolonged boiling in concentrated hydrochloric acid of calcined polyacetylene samples (Fig. 2, , , ,). In contrast to polyacetylene, with molecules in the form of straight chains of carbon atoms, the basic structural element of coals and graphite is a monolayer of atoms in a trigonal valence modification. The surprising ease of rearrangement of the atomic chains of carbon into graphite monolayers, with the corresponding transformation of valence forms during treatment with hydrochloric acid, is striking.

Figure 3 presents the results of measuring the specific electrical resistivity ρ of a polyacetylene sample obtained by oxidation with copper formate, as a function of the treatment temperature (in a nitrogen stream). The measurements were carried out by the zero method using an MTB-type bridge. All the indicated values of the electrical resistivity of the powders were determined under a pressure of 50 $\mathrm{kg/cm^2}$. For the initial sample $\rho \sim 10^6\ \Omega \cdot \mathrm{cm}$. The decrease in ρ with increasing temperature should be attributed to the accumulation of crystalline copper, owing to thermal dissociation and the liberation of terminal copper atoms from polyacetylene. The specific electrical resistivity, however, continues to decrease also at a higher temperature (above 2000°), when the copper has evaporated from the polymer, while graphite formation has not occurred. This fact indicates an increase in the length of the polyacetylene chains in the process of pyrogenetic synthesis, owing to thermal dissociation and the liberation of copper with subsequent recombination of the free polymer radicals that are formed.

In the same Fig. 3 are given the results of measuring the thermoelectromotive force (relative to copper) of the same products of thermal treatment.

The thermoelectromotive force was measured by the compensation method using a high-resistance PPTV potentiometer. A mirror galvanometer with internal resistance $R_{\text{int}} = 50\ \Omega$ was used as the null instrument. The temperature of the specimen-electrode contacts was measured by means of two chromel-alumel thermocouples. For the initial specimen a very large thermoelectromotive force of negative sign is observed ($\alpha = 1.38 \cdot 10^4\ \mu\mathrm{V/deg}$). At temperatures of 1300 and 1500°, α proves to be close to zero. With an increase in temperature above 1500°, α has a positive sign and varies with temperature along a characteristic curve with a maximum at 2300°, which corresponds to the temperature of the transition of polyacetylene into graphite.

Fig. 3. Specific electrical resistivity ρ and thermoelectromotive force α of products of thermal treatment of polyacetylene

The results of studies of ρ and α of polyacetylene obtained by oxidation with red

Fig. 3. Specific electrical resistivity ρ and thermoelectromotive force α of products of thermal treatment of polyacetylene

Figure 3: Fig. 3. Specific electrical resistivity ρ and thermoelectromotive force α of products of thermal treatment of polyacetylene

blood salt make it possible to suggest that the initial specimen studied belongs to n-type semiconductors, in which the role of electron donors is played by copper atoms incorporated into the carbon molecular chain with double bonds of the polyallene structure. For polyacetylene specimens obtained using stronger oxidizing agents—nitrate ion or hydrogen peroxide—and not containing copper, the value of the thermoelectromotive force proves to be equal to zero. This confirms the donor role of residual copper atoms. The observed change in the sign of the thermoelectromotive force upon thermal treatment corresponds to the transition of the polyacetylene specimen studied into a p-type semiconductor with positive hole current carriers. Such a transition, as can be seen, is associated with thermal dissociation and the elimination of copper and hydrogen atoms from the carbon chain and, apparently, is connected with the acceptor properties of the terminal carbon atoms.

The general character of the change in ρ and α with increasing temperature at a constant holding time is associated with the temperature dependence of the rates of thermal dissociation and recombination in the process of pyrolytic synthesis. As a result, copper and also hydrogen are eliminated and the length of the carbon chains of polyacetylene increases.

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