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Abstract

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NEW POLYCONJUGATED SYSTEMS
AND THEIR ELECTROPHYSICAL PROPERTIES ==

(Presented by Academician A. P. Vinogradov, 1 VI 1963)

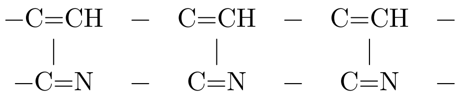
We have obtained a series of new polyconjugated systems and studied some of their electrophysical properties. Systems of this type usually possess a whole series of interesting properties: increased electrical conductivity, high thermal stability, paramagnetism, etc.

Table 1 gives the chemical formulas of the polymers obtained and the characteristic absorption bands in the infrared spectrum.

Table 1

No.	Polymers	Characteristic absorption bands in the IR spectrum, cm^{-1}
1	Polyacetylenenitrile $\left[\begin{array}{c}-C{=}CH-\\ \vert\\ -C{=}N-\end{array}\right]_n$	1420, 1630, 2250
2	Copolymer of phenylacetylene with acetylenenitrile $\left[\begin{array}{cc}-C{=}CH\ - & C{=}CH-\\ \vert & \vert\\ CN & C_6H_5\end{array}\right]_n$	760, 1100, 1475, 1620, 2210
3	Polybutoxyacetylene $\left[\begin{array}{c}-C{=}CH-\\ \vert\\ OC_4H_9\end{array}\right]_n$	1440, 1610, 3100
4	Polypropargyl alcohol $\left[\begin{array}{c}-C{=}CH-\\ \vert\\ CH_2OH\end{array}\right]_n$	1060, 1350, 1595

The polymers are powders of black and dark-brown color; they are insoluble in ordinary organic solvents and readily soluble in concentrated acids. The polymers obtained have high thermal stability; they do not melt and do not decompose up to a temperature of 450°. The greatest thermal stability is possessed by the polymer in which the formation of polyconjugation probably also occurs through the C–N bond.



$$\begin{array}{cccccc} -\mathrm{C}{=}\mathrm{CH} & - & \mathrm{C}{=}\mathrm{CH} & - & \mathrm{C}{=}\mathrm{CH} & - \\ | & & | & & | & \\ -\mathrm{C}{=}\mathrm{N} & - & \mathrm{C}{=}\mathrm{N} & - & \mathrm{C}{=}\mathrm{N} & - \end{array}$$

All the polymers are characterized by the presence of a narrow signal in the EPR spectrum, characteristic of polyconjugated systems, with a concentration of unpaired spins of 10^{18}-10^{19} per gram. The IR spectra confirm the proposed structure of the polymers and have a characteristic absorption band inherent in polyconjugation. The characteristics of the polymers obtained are given in Table 2.

Some electrophysical properties of these polymers were studied. The polymer samples investigated, in the form of pellets with copper-sputtered contacting surfaces, as was to be expected for polyconjugated structures, possess electrical conductivity and have a positive temperature coefficient of conductivity. Measurement of the temperature dependence of the conductivity $\sigma = \sigma(T)$ was carried out in vacuum at $5 \cdot 10^{-5}$ mm Hg in the temperature range 20-300° by the method described earlier (^{1}).

The effect of adsorption on the semiconductor properties of the polymers obtained was also investigated. Figure 1 shows the temperature dependence of conductivity typical of the polymers obtained. As is seen from this figure, the curves $\sigma = \sigma(T)$ have the form of a broken line, and the "activation energy" gradually increases with increasing temperature.

Each subsequent heating in vacuum leads to an increase in conductivity and a decrease in the "activation energy."

Table 2 gives some electrophysical parameters of the polymers we studied before and after heating in vacuum. As can be seen from the data

Table 2

No., item no.	Yield of theor., wt. %	Decomp. temp., °C	Before conditioning	Before conditioning	Before conditioning	After conditioning	After conditioning	After conditioning
			σ_{50}, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	E_{act}, eV	E.p.r., 1/g	σ_{50}, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	E_{act}, eV	E.p.r., 1/g
1*	87	450	$3.12 \cdot 10^{-9}$	0.87	$0.03 \cdot 10^{19}$	$8.8 \cdot 10^{-5}$	0	$0.6 \cdot 10^{19}$
1a**	82	450	$1.32 \cdot 10^{-10}$	0.72	$0.83 \cdot 10^{19}$	$2.6 \cdot 10^{-7}$	0.26	$1 \cdot 10^{19}$

Figure 1

Figure 1: Figure 1

No., item no.	Yield of theor., wt. %	Decomp. temp., °C	Before conditioning	Before conditioning	Before conditioning	After conditioning	After conditioning	After conditioning
2	79	450	$1.25 \cdot 10^{-12}$	1.14	$1.04 \cdot 10^{19}$	$1.1 \cdot 10^{-11}$	0.28	$2.4 \cdot 10^{19}$
3	85	390—400	$3.6 \cdot 10^{-18}$	2.00	$0.58 \cdot 10^{18}$	$1.5 \cdot 10^{-11}$	0.031	$1.87 \cdot 10^{18}$
4	82	370—390	$1.28 \cdot 10^{-15}$	1.34	$1.2 \cdot 10^{18}$	$2 \cdot 10^{-12}$	0.3	$1.74 \cdot 10^{18}$

* The samples are numbered in accordance with Table 1.
** Polymers 1 and 1a were obtained under different conditions.

from this table, after heating all samples significantly lowered the "activation energy" of conductivity and increased the electrical conductivity by 2-6 orders of magnitude. Figure 1 shows the curves $\sigma = \sigma(T)$ for a sample of polyacrylonitrile, the conductivity of which, having changed after heating in vacuum by 4 orders of magnitude, subsequently, in later measurements, does not depend on temperature.

In an oxygen atmosphere there occurs a gradual decrease in the conductivity of this sample by 2-3 orders of magnitude. After repeated heating in vacuum its conductivity increases. The temperature course of the conductivity corresponds to curve 3 of Fig. 1. A similar phenomenon was observed earlier on pyrolyzed polyacrylonitrile fibers (2), as well as on polymers of ferrocene. Desorption from the surface and volume of the polymers leads (Table 2) to an increase in the intensity of the narrow signal in the e.p.r. spectra. Obtaining completely desorbed samples in the form of pellets involves a number of experimental difficulties: thus, conditioning some samples in vacuum for 70 h does not lead to coincidence of the curves $\sigma = \sigma(T)$, but only a clear increase in conductivity and a decrease in activation energy are observed in subsequent measurements. Therefore, the values of σ_{50} and E given in Table 2, measured in vacuum, except for the values for polyacrylonitrile, should not be regarded as true, since they may change in the course of further desorption.

Fig. 1. Dependence of electrical conductivity on temperature for samples of polyacrylonitrile.
1, 2, 3 –sequence of measurements σ—$\sigma(T)$ in vacuum.

All these data are well explained from the standpoint of the conception of polymeric semiconductors as an aggregate of macromolecules with a system of poly-

Fig. 2. IR spectra of samples of polynitrileacetylene: a—before conditioning in vacuum, b—after conditioning in vacuum

Figure 2: Fig. 2. IR spectra of samples of polynitrileacetylene: a—before conditioning in vacuum, b—after conditioning in vacuum

conjugation, in which the transfer of an electron from one macromolecule to another occurs by a tunneling transition (2); the true activation energy of such a system can be determined from the temperature dependence of the conductivity only for completely desorbed samples.

Fig. 2. IR spectra of samples of polynitrileacetylene:
a—before conditioning in vacuum,
b—after conditioning in vacuum

The values of the activation energies of conductivity of polymeric semiconductors obtained by us and by a number of authors (3–5), from 2 to 0.01 eV, are most probably the values of the activation energies of the desorption process. It should be noted that the polymers studied were not subjected to any preliminary thermal treatment. Direct measurements have shown that many hours of heating in vacuum of the electrically conducting polymers obtained, and prolonged keeping of them under voltage, do not lead to any appreciable change in their chemical structure, as is evidenced by the data presented for the IR spectra (Fig. 2).

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