Reports of the Academy of Sciences of the USSR

CHEMISTRY

1962

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR
1962, Volume 143, No. 6

CHEMISTRY

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ON THE SIGNIFICANCE OF CONJUGATION AND ORDERING FOR THE SEMICONDUCTOR PROPERTIES OF POLYMERS

(Presented by Academician B. A. Kazanskii, January 5, 1962)

In recent years the number of works devoted to the study of the distinctive physical properties of polymers with a system of conjugated bonds has been increasing ([1]). In most works the main attention is given to the degree of conjugation (delocalization of π-electrons) along the molecular chain of the polymer as the principal factor determining the special properties of such substances ([2]). There is an indication in the literature that the electrical properties of polymers may depend not only on the degree of conjugation in the polymer molecule, but also, to a certain extent, on the structure of the polymer specimen as a whole ([3]). In work ([4]) a decrease in the activation energy of conductivity upon the appearance of crystallinity in polyacetylene was found.

In order to clarify the role of the degree of conjugation in the molecule and of the polymer structure in the emergence of semiconductor properties, we studied the electrical, magnetic, and crystallographic properties of polyazophenylenes and aromatic polymers containing between the benzene rings $-\dot{C}H_2-$and $-CH_2-CH_2-$groupings. The electrical conductivity of the polymers, pelletized at 5000 kG/cm^2, was determined in vacuum of $5 \cdot 10^{-3}$ mm Hg under direct current; the temperature dependence of the electrical conductivity corresponded to the exponential relation $\sigma = \sigma_0 e^{-E_\sigma/kT}$. EPR spectra were recorded on an RE-1301-type spectrometer, and X-ray diffraction patterns were obtained on a URS-55 installation with Cu K_α radiation and a Ni filter in RKD cameras.

The values of the activation energy of electrical conductivity (E_σ) in the interval 120-250° for polymers 1-3 (see Table 1) show that introduction into the macromolecular chain of methylene groups, which decrease conjugation along the chain,** does not lead to disappearance of the semiconductor character of the electrical conductivity. Moreover, introduction of methylene groups into the conjugation chain (polymer 2) is even accompanied by a decrease in E_σ in the temperature interval studied, which is wholly inexplicable from the standpoint of ideas about a direct interrelation between conjugation in the chain and the

electrical properties of the polymer.

The data obtained are readily understood if it is taken into account that the electrical characteristics depend not only on the degree of conjugation along the chain, but also on the structure of the polymer specimen as a whole, which determines the ease of electronic transitions between macromolecules. From this point of view, methylene bridges, increasing the flexibility of the polymer chain, should promote denser packing of macromolecules and, consequently, facilitate electronic interaction between individual chains. Indeed, comparison of X-ray diffraction patterns *a*, *b*, and *c* in Fig. 1 shows that the degree of crystallinity of the initial polymers increases with lengthening of the methylene bridges between the benzene rings. Such a difference in the packing density of polymers 1, 2, and 3 is also indicated by the character of the irreversible change in their electrical conductivity as a result of heating (see Table 1 and Fig. 2).

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* A. A. Berlin took part in the work.
** A study of the EPR spectra ([5]) shows that the $-CH_2CH_2-$group between benzene rings still does not interrupt conjugation.

Table 1

Structural formula of the polymer	Mol. wt.	Activation energy of electronic conduction E_σ (at 250°), eV	σ, $ohm^{-1} \cdot cm^{-1}$	Irreversible change after heating	Number of unpaired spins per 1 g (by EPR)
1. $Cl-[C_6H_4-C_6H_4]_m-[N=N-C_6H_4]_n-Cl$	1700	1.64	$1 \cdot 10^8$	Increases strongly	$2.6 \cdot 10^{19}$
2. $Cl-[C_6H_4-CH_2-C_6H_4]_m-[N=N-C_6H_4-CH_2-C_6H_4]_n-Cl$	1250	1.24	$1.3 \cdot 10^3$	Increases weakly	$4.3 \cdot 10^{18}$

Structural formula of the polymer	Mol. wt.	Activation energy of electronic conduction E_σ (at 250°), eV	σ, $ohm^{-1} \cdot cm^{-1}$	Irreversible change after heating	Number of unpaired spins per 1 g (by EPR)
3. Cl — $[C_6H_4 - CH_2 - CH_2 - C_6H_4]_m$ — $[N{=}N - C_6H_4 - CH_2 - CH_2 - C_6H_4]_n$ — Cl	2600	1.92	$2.1 \cdot 10^{13}$	Decreases weakly	$8.0 \cdot 10^{17}$
4. Iodinated polyazophenylene*	~ 1800	1.00	$1.8 \cdot 10^{2}$	Does not change	$8.4 \cdot 10^{18}$

* Iodinated polyazophenylene contains, on average, one iodine atom per two benzene rings.

Heating polymer 1, which contains no methylene bridges and therefore is packed most loosely, is accompanied by a strong irreversible decrease in resistance, which indicates ordering of the structure during the heating process (this conclusion is also confirmed by comparison of Fig. 1, *a* (the initial specimen) with the X-ray diffraction pattern in Fig. 1, *g*, of the same polymer after heating). In the case of polymer 2, which has more flexible chains and, consequently, denser packing in the initial state, heating leads to a considerably smaller irreversible drop in resistance; while polymer 3, with the most flexible chains, is packed rather densely already at lower temperatures and, upon heating in the temperature range studied, changes its properties hardly at all.

Replacement in the phenyl rings of some hydrogen atoms by the much larger iodine atoms (polymer 4) not only leads to loose packing of the initial polymer (X-ray diffraction pattern *d*), but also hinders change in its structure during heating (absence of an irreversible change in electrical conductivity).

Proceeding from the ideas considered about the structure of the polymers, the decrease in E_σ of polymer 2 in comparison with polymer 1 can be explained by the fact that the introduction of methylene bridges, despite lowering conjugation

Fig. 1. X-ray diffraction patterns of polymers of the polyazophenylene series: a—polymer 1, b—polymer 2, c—polymer 3, d—polymer 1 after heating at 250° in vacuum, e—polymer 4

Figure 1: Fig. 1. X-ray diffraction patterns of polymers of the polyazophenylene series: a—polymer 1, b—polymer 2, c—polymer 3, d—polymer 1 after heating at 250° in vacuum, e—polymer 4

Fig. 2. Dependence of electrical conductivity σ on temperature: a —polymer 1, b —polymer 2, c —polymer 3; I —up to 200°, II —up to 250°, III —after heating at 250° (4 hours). The polarization region is indicated by a dashed line (maximum values of electrical conductivity are plotted).

Figure 2: Fig. 2. Dependence of electrical conductivity σ on temperature: a —polymer 1, b —polymer 2, c —polymer 3; I —up to 200°, II —up to 250°, III —after heating at 250° (4 hours). The polarization region is indicated by a dashed line (maximum values of electrical conductivity are plotted).

along the macromolecule, facilitates electron transfer between individual chains owing to their denser packing. The bridges, however, of ···

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Fig. 1. X-ray diffraction patterns of polymers of the polyazophenylene series: *a* —polymer 1, *b* —polymer 2, *c* —polymer 3, *d* —polymer 1 after heating at 250° in vacuum, *e* —polymer 4.

groups $-CH_2—CH_2-$(polymer 3) reduce the conjugation so much that this is no longer compensated by a further increase in the packing density, and E_σ increases. The decrease in the degree of conjugation is also manifested in a decrease in the intensity of the EPR signal.

An extremely interesting phenomenon is the effect of relaxation polarization found for all the polymers studied (i.e., a reversible decrease in electrical conductivity during the passage of a direct current through the polymer). Leaving aside the question of the causes of the appearance of charges in the polymer molecules, one may consider that the polarization is due to displacement of charged segments of the polymer chain in an electrostatic field. The temperature at which polarization appears in polymer 3 (200°) is 30-50° lower than in the other polymers, which confirms the conclusion that the chains of the macromolecules of this polymer have the greatest flexibility.

Fig. 2. Dependence of electrical conductivity σ on temperature: *a* —polymer 1, *b* —polymer 2, *c* —polymer 3; *I* —up to 200°, *II* —up to 250°, *III* —after heating at 250° (4 hours). The polarization region is indicated by a dashed line (maximum values of electrical conductivity are plotted).

Thus, the work has shown that the semiconductor properties of polymers con-

taining conjugated bonds are created by two competing factors: 1) the properties of the individual macromolecules (degree of delocalization of π-electrons, chain flexibility) and 2) the properties of the solid as a whole (packing density, character of the electronic interaction between molecules*). In this case, if the degree of conjugation is not too small, the electrical characteristics are determined by the second factor.

Similar conclusions were also drawn on the basis of electrical data for polyferrocenes ([7]).

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Received
2 I 1962

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* The question of the various types of electronic interaction in polymers with conjugated bonds is discussed specially in article ([6]).

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