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ELECTRICAL CONDUCTIVITY OF POLYMERS WITH CONJUGATED BONDS

By Ye. I. Balabanov, et al.

- USSR -

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ELECTRICAL CONDUCTIVITY OF POLYMERS WITH CONJUGATED BONDS

- USSR -

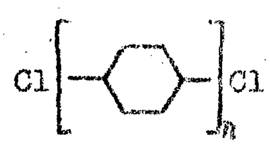
/Following is a translation of the article by Ye. I. Balabanov, A. A. Berlin, V. P. Parini, V. L. Tal'roze, Ye. L. Frankevich, and M. I. Cherkashin entitled "Elektroprovodnost' polimerov s sopryazhennymi svyazyami" (English version above) in Doklady Akademii Nauk SSSR (Reports of the Academy of Sciences USSR), Vol 134, No 5, Moscow, 1960, pages 1123-1126./

(Presented by Academician V. N. Kondrat'yev 14 June 1960)

In connection with the problem of obtaining organic polymeric substances with different electro-physical properties, including the problem of organic semiconductors, the extensive study (1) of electrical properties of different types of polymeric substances with systems of conjugated bonds and heterocyclic atoms in the conjugating chain is of interest. The authors have synthesized the class of polymers enumerated below and have made a study of their electrical conductivity and of its dependence on temperature.

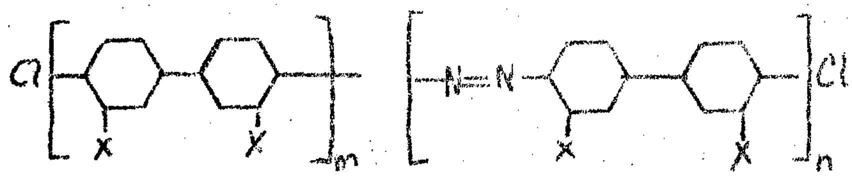
1. Polymers with acyclic conjugating chains (2,3): polyphenylacetylene (1) and copolymers of polyphenylacetylene with hexyne (2) and with paradiethinylbenzene (3).

2. Polymers with benzene rings in the conjugating chain: polyphenylene

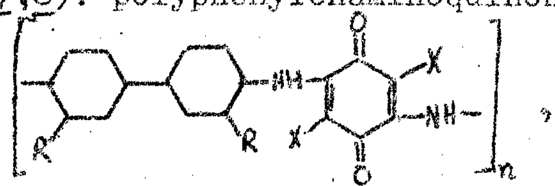


(4),

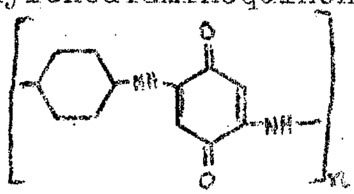
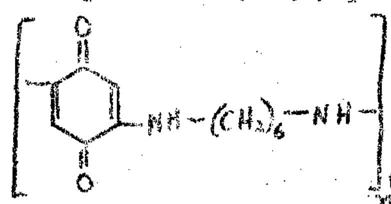
polyphenylenazo compounds (4-6) of the type



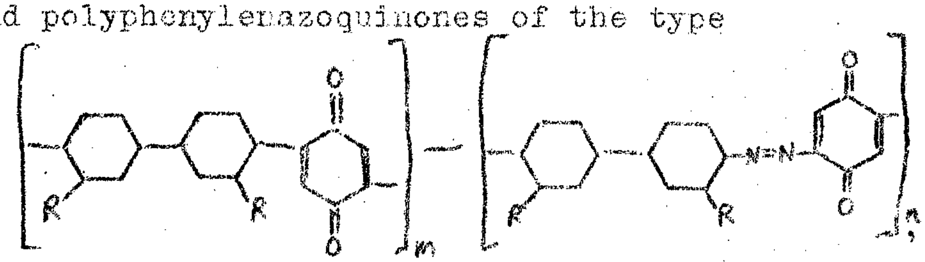
where X = H (5), CH_3 (6), COOH (7); polymeric aromatic and aliphatic-aromatic compounds containing quinoid and amino groups (7,8): polyphenylenaminoquinones of the type



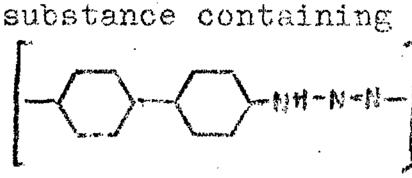
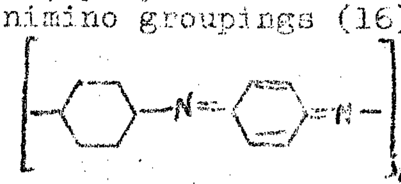
where X = H (8), Cl (9), with R = H and X = H (10) with R = COOH; poly-n-phenylendiaminoquinone (11), polyhexamethylenediaminoquinone (12)


(11)

(12),

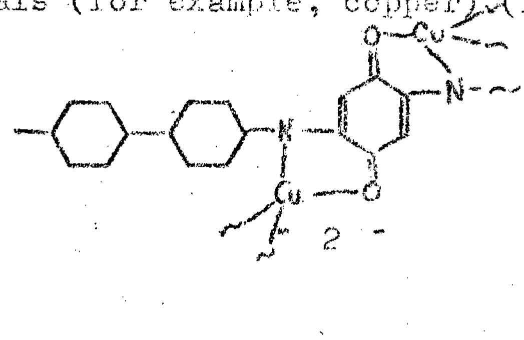
and polyphenylenazoquinones of the type



where R = H (13) and COOH (14); polymeric triazene (15), a substance containing quinonimino groupings (16)

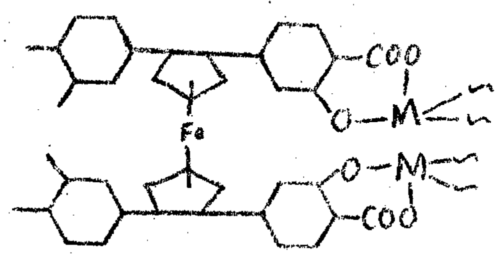

(15);

(16);

polymeric chelate compounds (9) of polydiphenylaminoquinone with metals (for example, copper) (17)



Molecular complexes of acenaphthene with chloranil (18) and with the pyridone derivative of polyphenylenaminoquinone (19) were also synthesized.

3. Compounds with nonbenzoid rings in the conjugating chains: tetrasalicylferrocene (20) and polymeric chelate complexes of it (10) with Fe^{++} and with Be^{++} (21,22)



Polymeric chelate groups of percyanethylene with Cu^{++} (23) and with Fe^{++} (11,12).

The synthesis and properties of some of the above-enumerated compounds (for example, 8, 10, 11, 13, and 14) have up till now not been illuminated in publications. In the near future special publications will be devoted to them.

Polymers containing quinoid nuclei (10,14) in the conjugating chain, and particularly compounds in which the quinoid structure is connected to the chain by a hetero-atom of nitrogen (16), are of considerable interest. In such substances a sharp decrease in the energy excitation of the triplet state can be expected and, in some cases, also the formation of radical ionic structures.

The specimens investigated were, for the most part, tablets 10-12 mm in diameter.

In the present report we will limit ourselves to general characterization of the derived regularities. In all cases with temperature increase the electrical conductivity rose in accordance with the law, $\sigma = \sigma_o \cdot \exp(-E/kt)$ where σ_o and E are constants in the given example.

Deviations from this law occurred only close to the disintegration temperature level of the substance. The values of E obtained from 4.6 kilocal/mole (0.2 ev) for substance 16 to 49.5 kilocal/mole (2.1 ev) for polyphenylacetylene, and even up to 92 kilocal/mole for the complexes of acenaphthene with chloranil.

The manner of processing the specimens has a great effect on these parameters. Thus, for example, the size of the pre-exponent for polyphenylacetylene decreases 22 orders of magnitude in the transition from the film that was obtained from the solvent, to the tablet compressed at 200° C.

There occurs, however, at this time a decrease in the "activation energy" E, so that the electrical conductivity of both specimens at room temperature appears to be approximately equal. A similar phenomenon in the symbatic change of the pre-exponent and the activation energy is often called a compensating effect, and there exist a series of analogies in chemical kinetics and catalysis, but for electrical conductivity observed on metal oxides (13). The nature of the compensating effect is still not clear; one of the theoretical approaches to the solution of the problem was examined recently (14).

It seemed that in our cases the compensating effect appeared to be the rule covering all, or almost all, derived substances. This is especially graphically evident from figure 1, where the given table 1 is broken down into coordinates $\lg \sigma_0$ -- E.

TABLE 1

Spec Nr	σ_0, $ohm^{-1} \cdot cm^{-1}$	E, $\frac{kcal}{mole}$	$\sigma_{300^\circ K}$	Remarks
1a	$4 \cdot 10^{18}$	49.5	10^{-17}	Polymer film formed at 150° C
1b	$5 \cdot 10^{17}$	47.6	$2 \cdot 10^{-17}$	Polymerization conducted at 400°C
1c	$2 \cdot 10^{11}$	37	$3 \cdot 10^{-19}$	Film from mixture of polymers 1a and 16
1d	$3 \cdot 10^{6}$	32.2	10^{-15}	
1e	10^{2}	22	10^{-14}	Fraction of specimen 16 dissolved in benzene
1f	$2 \cdot 10^{-2}$	8.5	10^{-3}	Fraction of specimen 16 dissolved in pyridine
1g	$2 \cdot 10^{-4}$	15.4	$2 \cdot 10^{-15}$	Polymerization conducted at 150° C, tablets compressed at 200° C
2'	10^{10}	49	10^{-15}	Temperature range 20-50°C*
2"	$5 \cdot 10^{7}$	29	---	Temperature range 50-100°C
3	$6.4 \cdot 10^{-6}$	17.5	10^{-16}	
4	10^{-12}	3.1	$2 \cdot 10^{-16}$	
5a	40	25	$4 \cdot 10^{-17}$	Specimen heated at 200° C
5b	1	21	10^{-15}	Without heating
6	1-0.1	20-22	$10^{-14}-10^{-15}$	
7	1	18.4	$4 \cdot 10^{-14}$	
8	30	24	10^{-16}	
9	$2 \cdot 10^{3}$	23.7	10^{-15}	

T A B L E 1 (continued)

Spec. Nr.	σ_0 $ohm^{-1} \cdot cm^{-1}$	E, $\frac{kcal}{mole}$	$\sigma_{300°K}$	Remarks
10a	10^{8}	29	10^{-13}	Derived under the same conditions
10b	10^{-3}	9.2	$2 \cdot 10^{-10}$	
11	10	20.2	$2 \cdot 10^{-14}$	
12	10^{-4}	15.6	$5 \cdot 10^{-16}$	
13a	10^{-7}	13	$2 \cdot 10^{-16}$	Derived under the same conditions
13b	10^{-8}	39	10^{-20}	
14	$5 \cdot 10^{4}$	20.2	10^{-10}	
15a	50	23	10^{-15}	
15b	$6 \cdot 10^{6}$	30.2	10^{-15}	
16'	10^{3}	10.3	$3 \cdot 10^{-9}$	Temperature range 20-40°C
16"	30	4.6	---	Temperature range 40-80°C
17	10^{4}	25.4	$4 \cdot 10^{-15}$	
18a'	$3 \cdot 10^{24}$	67.5	$3 \cdot 10^{-15}$	Ratio of acenaphthene: chloranil 1:1; temperature range 20-50°C
18a"	$5 \cdot 10^{25}$	48.5	---	Temperature range 50-80°C
18b	$6.4 \cdot 10^{41}$	92	$2 \cdot 10^{-15}$	Ratio of acenaphthene: chloranil 1:2; temperature range 20-45°C
19	$3 \cdot 10^{4}$	24.8	$3 \cdot 10^{-3}$	
20a	10^{-1}	12.6	10^{-10}	
20b	$5 \cdot 10^{-3}$	12	10^{-11}	Substance 20a heated at 200°C
21	1	10.6	10^{-5}	
22	5	11.7	10^{-9}	
23	2	15.3	10^{-11}	

* Specimens whose straight line lgσ---1/T underwent fissure. Numbers with one and two strokes refer to the same specimen before and after fissure.

/Some of the small numbers representing powers of ten appeared blurred in the original and so have not been typed with certainty./

Here we have an absolutely remarkable occurrence of the compensating effect in the range of sixty (!) orders of magnitude of change in the pre-exponent and a twenty-fold change in the activation energy for substances of different structure.

A series of specimens studied possesses electrical conductivity surpassing the electrical conductivity of the common organic non-conductors by several orders of magnitude. This refers, first of all, to specimens 16, 21, and 22, which, in terms of their electrical conductivity, approach some of the organic semiconductors, known from publications (13-17).

/Caption to Figure 1 on page 1125 of original, not reproduced here./:

Figure 1. Relation between the pre-exponent multiplier and the activation energy of electrical conductivity.

The strong dependence of σ to T, which is correlated with the high value of E, in cases of polyphenylacetylene (which are typical insulators at room temperature) is of great interest. In conjunction with a large σ_0 this leads to the result that, with an increase in temperature the σ of polyphenylacetylene "attains" the σ of a whole series of polymers which show high electrical conductivity at room temperature.

One can expect that further investigations will permit us to establish the connection between electrophysical properties and the structure of single polymer molecules and the materials derived from them.

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11 June 1960

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