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1960

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ELECTRICAL CONDUCTIVITY OF POLYMERS WITH CONJUGATED BONDS

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

In connection with the problem of obtaining organic polymeric substances with various electrophysical properties, including the question of organic semiconductors, a broad study of the electrical properties of various types of polymeric substances with systems of conjugated bonds and heteroatoms in the conjugation chain is of interest ([1]). The authors synthesized the classes of polymers listed below, studied their electrical conductivity σ, and its dependence on temperature.

1. Polymers with an acyclic conjugation chain ([2,3]): polyphenylacetylene (1), copolymers of polyphenylacetylene with hexine (2) and with paradiethynylbenzene (3).
2. Polymers with benzene nuclei in the conjugation chain: polyphenylene

$$\left[\mathrm{Cl}-\text{phenylene ring}-\mathrm{Cl}\right]_n \qquad (4)$$

polyphenylene azo compounds ([4–6]) of the type

$$\left[\mathrm{Cl}-\underset{X}{\text{phenylene ring}}-\underset{X}{\text{phenylene ring}}\right]_m-\left[-\mathrm{N}=\mathrm{N}-\underset{X}{\text{phenylene ring}}-\underset{X}{\text{phenylene ring}}-\mathrm{Cl}\right]_n,$$

where $X = H$ (5), CH_3 (6), COOH (7), polymeric aromatic and fatty-aromatic compounds containing quinoid and amino groups ([7,8]): polyphenyleneaminoquinones of the type

$$\left[-\underset{R}{\text{phenylene ring}}-\underset{R}{\text{phenylene ring}}-\mathrm{NH}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\text{quinone ring}}}-\mathrm{NH}-\right]_n,$$

where $X = H$ (8), Cl (9) at $R = H$, and $X = H$ (10) at $R = COOH$; poly-*p*-phenylenediaminoquinone (11), polyhexamethylenediaminoquinone (12)

$$\left[-\text{phenylene ring}-\text{NH}-\underset{\text{O}}{\overset{\text{O}}{\text{quinone ring}}}-\text{NH}-\right]_n \qquad (11)$$

$$\left[\underset{\text{O}}{\overset{\text{O}}{\text{quinone ring}}}-\text{NH}-(\text{CH}_2)_6-\text{NH}-\right]_n \qquad (12)$$

polyphenyleneazoquinones of the type

$$\left[-\underset{R}{\text{phenylene ring}}-\underset{R}{\text{phenylene ring}}-\underset{\text{O}}{\overset{\text{O}}{\text{quinone ring}}}-\right]_m-\left[-\underset{R}{\text{phenylene ring}}-\underset{R}{\text{phenylene ring}}-\text{N=N}-\underset{\text{O}}{\overset{\text{O}}{\text{quinone}}}\right.$$

where R = H (13) and COOH (14); polymeric triazene (15), a substance containing quinone-imine groups (16)

$$[-\text{cyclohexyl}-\text{cyclohexyl}-\text{NH}-\text{N=N}-]_n \qquad (15);$$

$$[-\text{cyclohexyl}-\text{N=phenylene=N}-]_n \qquad (16);$$

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

[structural formula of a copper chelate of polydiphenylaminoquinone]

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

3. Compounds with nonbenzenoid rings in the conjugation chain: tetrasalicylferrocene (20) and its polymeric chelate complexes [10] with Fe^{2+} and Be^{2+} (21, 22)

[structural formula of a polymeric chelate complex of a ferrocene derivative with metal M]

Polymeric chelate complexes of perianthene with Cu^{2+} (23) and Fe^{2+} [11,12].

The synthesis and properties of some of the compounds listed above (for example, 8, 10, 11, 13, 14) have not yet been covered in the literature. Special publications will be devoted to them in the near future.

Of considerable interest are polymers containing quinoid nuclei in the conjugation chain (10, 14), and especially compounds in which the quinoid structure is incorporated into the chain through a nitrogen heteroatom (16). In such substances one may expect a sharp decrease in the excitation energy to the triplet state and, in some cases, the formation of ion-radical structures.

The samples studied were, for the most part, tablets 10–12 mm in diameter.

In the present communication we shall confine ourselves to a general characterization of the regularities obtained. In all cases, with increasing temperature the electrical conductivity increased according to the law

$$\sigma = \sigma_0 \cdot e^{-E/kT},$$

where σ_0 and E are constants for the given sample.

Deviations from this law occurred only near the decomposition temperature of the substance. The obtained values of E vary from 4.6 kcal/mol (0.2 eV) for substance 16 to 49.5 kcal/mol (2.1 eV) for polyphenylacetylene, and even up to 92 kcal/mol for the acenaphthene complex with chloranil. The values of σ_0 vary from 10^{-12} $\Omega^{-1} \cdot \text{cm}^{-1}$ for polyphenylene to $6 \cdot 10^{51}$ $\Omega^{-1} \cdot \text{cm}^{-1}$ for the acenaphthene complex with chloranil.

The nature of the treatment of the sample has a great influence on these parameters. Thus, for example, the pre-exponential factor for polyphenylacetylene decreases by 22 orders of magnitude on going from a film obtained from solution to a tablet pressed at 200°C.

At the same time, however, there is also a decrease in the "activation energy" E, so that the electrical conductivity of both samples at room temperature

turns out to be approximately the same. Such a phenomenon of symbatic change of the pre-exponent and the activation energy is often called the compensation effect (c. e.) and has a number of analogies in chemical kinetics and catalysis, and for electrical conductivity it has been observed in metal oxides ([13]). The nature of the c. e. is still not clear; one of the theoretical approaches to solving this question was considered recently ([14]).

It turned out that in our case the c. e. is a regularity that encompasses all, or almost all, of the substances obtained. This is especially clearly seen from Fig. 1, where the data of Table 1 are plotted in the coordinates $\lg \sigma_0 - E$.

Table 1

Sample No.	σ_0, ohm^{-1}·cm^{-1}	E, kcal/mol	$\sigma_{300^\circ\mathrm{K}}$	Note
1a	$4 \cdot 10^{18}$	49.5	10^{-17}	Polymer film obtained at 150°C
1b	$5 \cdot 10^{17}$	47.6	$2 \cdot 10^{-17}$	Polymerization was carried out at 400°C
1v	$2 \cdot 10^{11}$	37	$3 \cdot 10^{-16}$	Films from mixtures of polymers 1a and 1b
1g	$3 \cdot 10^{8}$	32.2	10^{-15}	
1d	10^{2}	22	10^{-14}	Fraction of sample No. 1b soluble in benzene
1e	$2 \cdot 10^{-2}$	8.5	10^{-8}	Fraction of sample No. 1b soluble in pyridine
1zh	$2 \cdot 10^{-4}$	15.4	$2 \cdot 10^{-15}$	Polymerization was carried out at 150°C; the pellet was pressed at 200°C
2′	10^{20}	49	10^{-15}	Temperature range 20–50°C*
2″	$5 \cdot 10^{7}$	29	–	Temperature range 50–100°C
3	$6.4 \cdot 10^{-4}$	17.5	10^{-16}	
4	10^{-12}	5.1	$2 \cdot 10^{-16}$	
5a	40	25	$4 \cdot 10^{-17}$	Sample heated at 200°C
5b	1	21	10^{-15}	Without heating

Sample No.	σ_0, ohm^{-1}·cm^{-1}	E, kcal/mol	$\sigma_{300^\circ\mathrm{K}}$	Note
6	1–0.1	20–22	10^{-14}–10^{-16}	
7	1	18.4	$4 \cdot 10^{-14}$	
8	30	24	10^{-16}	
9	$2 \cdot 10^2$	23.7	10^{-15}	
10a	10^8	29	10^{-13}	Obtained according to one and the same procedure
10b	10^{-3}	9.2	$2 \cdot 10^{-10}$	Obtained according to one and the same procedure
11	10	20.2	$2 \cdot 10^{-14}$	
12	10^{-4}	15.6	$5 \cdot 10^{-16}$	
13a	10^{-7}	13	$2 \cdot 10^{-16}$	Obtained according to one and the same procedure
13b	10^{-8}	39	10^{-20}	Obtained according to one and the same procedure
14	$5 \cdot 10^4$	20.2	10^{-10}	
15a	50	23	10^{-15}	
15b	$6 \cdot 10^6$	30.2	10^{-15}	
16′	10^2	10.3	$3 \cdot 10^{-6}$	Temperature range 20–40°C
16″	30	4.6	–	Temperature range 40–80°C
17	10^4	25.4	$4 \cdot 10^{-15}$	
18a′	$3 \cdot 10^{34}$	67.5	$3 \cdot 10^{-15}$	Acenaphthene:chloranil ratio 1:1; range 20–50°C
18a″	$5 \cdot 10^{20}$	48.5	–	Range 50–80°C

Fig. 1. Relationship between the pre-exponential factor and the activation energy of electrical conductivity

Figure 1: Fig. 1. Relationship between the pre-exponential factor and the activation energy of electrical conductivity

Sample No.	σ_0, $\text{ohm}^{-1}\cdot\text{cm}^{-1}$	E, kcal/mol	$\sigma_{300^\circ\text{K}}$	Note
18b	$6.4 \cdot 10^{51}$	92	$2 \cdot 10^{-15}$	Acenaphthene:chloranil ratio 1:2; range 20–45°C
19	$3 \cdot 10^{5}$	24.8	$3 \cdot 10^{-13}$	
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^{-8}	
22	5	11.7	10^{-8}	
23	2	15.3	10^{-11}	

* Samples for which the straight line $\lg\sigma$—$1/T$ underwent a break. Numbers with one and two primes refer to the same sample before and after the break.

We have here an entirely exceptional manifestation of the c. e.: over a range of sixty (!) orders of magnitude of change in the pre-exponent and a twentyfold change in the activation energy for substances differing in structure.

A number of the samples studied possess electrical conductivity several orders of magnitude greater than the conductivity of ordinary organic dielectrics. This applies above all to samples 16, 21, and 22, which in electrical conductivity approach certain organic semiconductors known from the literature ([15–17]).

Fig. 1. Relationship between the pre-exponential factor and the activation energy of electrical conductivity

Of great interest is the very strong dependence of σ on T, corresponding to high values of E, in the case of polyphenylacetylenes (which at room temperature are typical insulators). In combination with a large σ_0, this leads, as the temperature is raised, to the fact that the σ of polyphenylacetylene "catches up" with the σ of a whole series of polymers that exhibit high electrical conductivity at room temperature.

It may be expected that further investigations will make it possible to establish a relationship between the electrophysical properties and the structure of individual polymer molecules and of the materials obtained from them.

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Received
11 VI 1960

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

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