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Abstract

Full Text

Physical Chemistry

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ELECTRICAL CONDUCTIVITY AND ACTIVATION ENERGY OF CERTAIN DITHIOOXAMIDE, N-SUBSTITUTED DITHIOCARBAMATE, AND THIOCYANATE (Cu, Co, Ni) POLYMERS

(Presented by Academician V. A. Kargin, December 2, 1961)

In the preceding communication it was indicated that metal polychelates containing the groups $S = C'$—NH—possess semiconducting properties (^{1}). In the present work, a number of new data have been obtained on the electrical conductivity and activation energy of dithiooxamide, N-substituted dithiocarbamate, and thiocyanate (Cu, Co, Ni) polymers. These data are given in Table 1. Investigation of the temperature dependence of the electrical conductivity of polymers (M = Cu, Ni, Co) of structure I showed that the magnitude of the electrical conductivity depends substantially on the nature of the metal and decreases in the order Cu, Ni, Co. The value of the activation energy changes little with variation in the nature of the metals and is equal for the Cu-, Ni-, and Co-polymers studied to $E = 0.6$–0.7 eV (Fig. 1). It should be noted that good reproducibility of the values of σ and E was obtained for different preparations of the polymers. There are indications in the literature that measurements of the magnetic susceptibility confirm the coplanarity of the chelate units of the Ni-polymer (^{2}).

Fig. 1. Temperature dependence of electrical conductivity for polymers of structure I: 1—Cu-polymer, $E = 0.6$ eV; 2—Ni-polymer, $E = 0.6$ eV; 3—Co-polymer, $E = 0.7$ eV

For Cu-polymers of structure II it was found that the magnitude of the electrical conductivity depends on the nature of the radicals and decreases in the series: phenylene, diphenylene, and hexamethylene. In the structure of the diphenyl molecule, the angle between the planes of the phenyl rings is 41.6° (^{3}). This is an obstacle to π-interaction between the phenyl rings. For polymers with $-C_6H_4-$and $-(C_6H_4)_2-$radicals, the activation-energy values differ little and are, respectively: $E_1 = 0.42$, $E_2 = 0.62$ eV and $E_1 = 0.36$, $E_2 = 0.60$ eV. The activation energy for the Cu-polymer with $-(CH_2)_6-$radicals, $E = 0.72$ eV, is twice as high as for the polymer with $-(C_6H_4)_2-$radicals ($E_1 = 0.36$ eV) (Fig. 2a). The investigation of new samples of Cu-polymers confirmed the conclusions of work (^{1}), namely that incorporation into the polymer of phenylene rings containing π-bonds lowers the activation energy and raises the electrical conductivity in comparison with methylene groups having σ-bonds. The Cu-polymer with R-$-(CH_2)_6-$is less stable, and therefore measurements of the temperature dependence of electrical conductivity were carried out up to the beginning of thermal destruction of the polymer (up to $T \approx 360°$ K). The absence of destruction of the polymers was checked by repeated measurement of the electrical conductivity, and also by X-ray and chemical analyses. For all the polymers studied, the dependence of $\lg \sigma$ on $1/T$ was measured several times for each specimen (both on raising and on lowering the temperature). The experimental values fit sufficiently well ···

Table 1

Electrical conductivity σ and activation energy E of dithiooxamide and N-substituted dithiocarbamate Cu-, Ni-, and Co-polymers

Structure no.	Polymer	M, R	Temperature interval, °K	$\sigma_{290°K}$, $\Omega^{-1} \cdot cm^{-1}$	σ_0, $\Omega^{-1} \cdot cm^{-1}$	E, eV
I	Dithiooxamide polymer, structural unit shown schematically as a chelate chain $[\cdots S{=}C{-}NH{-}M{-}NH{-}C{=}S\cdots]_n$	Cu	290—350	$4 \cdot 10^{-8}$	$1 \cdot 10^4$	0.6

Structure no.	Polymer	M, R	Temperature interval, °K	$\sigma_{290°K}$, $\Omega^{-1} \cdot$ cm^{-1}	σ_0, $\Omega^{-1} \cdot$ cm^{-1}	E, eV
I	Dithiooxamide polymer, structural unit shown schematically as a chelate chain $[\cdots \mathrm{S{=}C{-}NH{-}}M\mathrm{{-}NH{-}C{=}S} \cdots]_n$	Ni	290–500	$2 \cdot 10^{-11}$	$7 \cdot 10^{-1}$	0.6
I	Dithiooxamide polymer, structural unit shown schematically as a chelate chain $[\cdots \mathrm{S{=}C{-}NH{-}}M\mathrm{{-}NH{-}C{=}S} \cdots]_n$	Cu	400–500	$7 \cdot 10^{-16}$ *	$1 \cdot 10^{-3}$	0.7

Structure no.	Polymer	M, R	Temperature interval, °K	$\sigma_{290°K}$, $\Omega^{-1} \cdot$ cm^{-1}	σ_0, $\Omega^{-1} \cdot$ cm^{-1}	E, eV
II	Cu polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $-NH-C(=S)-S \cdots Cu-S-C(=S)-NH-R-NH-C(=S) \cdots Cu-$	n-C_6H_4-	290–425	$7 \cdot 10^{-11}$	1	0.42; 0.62
II	Cu polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $-NH-C(=S)-S \cdots Cu-S-C(=S)-NH-R-NH-C(=S) \cdots Cu-$	n,n'-$(C_6H_4)_2-$	290–450	$5 \cdot 10^{-13}$	$1 \cdot 10^{-3}$	0.36; 0.60

Structure no.	Polymer	M, R	Temperature interval, °K	$\sigma_{290^\circ\mathrm{K}}$, $\Omega^{-1} \cdot$ cm^{-1}	σ_0, $\Omega^{-1} \cdot$ cm^{-1}	E, eV
II	Cu polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $-\mathrm{NH}-\mathrm{C}(=\mathrm{S})-\mathrm{S}\cdots\mathrm{Cu}-\mathrm{S}-\mathrm{C}(=\mathrm{S})-\mathrm{NH}-R-\mathrm{NH}-\mathrm{C}(=\mathrm{S})\cdots\mathrm{Cu}-$	$(CH_2)_6$	310–380	$1 \cdot 10^{-13}$	$2 \cdot 10^{-1}$	0.72
III	Co polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $\cdots\mathrm{Co}\,[\mathrm{S}-\mathrm{C}(=\mathrm{S})-\mathrm{NH}-R-\mathrm{NH}-\mathrm{C}(=\mathrm{S})-\mathrm{S}\cdots\mathrm{Co}]_n$	n-C_6H_4−	370–460	$9 \cdot 10^{-12}$ **	$1 \cdot 10^{-3}$	0.58

Structure no.	Polymer	M, R	Temperature interval, °K	$\sigma_{290^\circ\mathrm{K}}$, $\Omega^{-1} \cdot$ cm^{-1}	σ_0, $\Omega^{-1} \cdot$ cm^{-1}	E, eV
III	Co polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $\cdots \mathrm{Co}\,[\mathrm{S{-}C(=S){-}NH{-}}R\mathrm{{-}NH{-}C(=S){-}S} \cdots \mathrm{Co}]_n$	n, n'-$(C_6H_4)_2$—	380—460	$3.5 \cdot 10^{-12}$ **	$3 \cdot 10^{-3}$	0.62
III	Co polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $\cdots \mathrm{Co}\,[\mathrm{S{-}C(=S){-}NH{-}}R\mathrm{{-}NH{-}C(=S){-}S} \cdots \mathrm{Co}]_n$	$(CH_2)_6$	400—460	$1.7 \cdot 10^{-12}$ **	$5 \cdot 10^{-3}$	0.76

Figure 2: Temperature dependence plots of electrical conductivity for Cu polymers and Co polymers

Figure 2: Figure 2: Temperature dependence plots of electrical conductivity for Cu polymers and Co polymers

III	Co polymer with N-substituted dithiocarbamate bridges, schematic chain fragment: $\cdots\mathrm{Co}\,[\mathrm{S{-}C(=S){-}NH{-}}R\mathrm{{-}NH{-}C(=S){-}S}\cdots\mathrm{Co}]_n$	$(CH_2)_2$	400—460	$8 \cdot 10^{-13}$ **	$1 \cdot 10^{-3}$	0.74

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* The value of $\sigma_{290^\circ\mathrm{K}}$ was found by extrapolation.

** $\sigma_{400^\circ\mathrm{K}}$. The molecular weight of the Co polymer lies within the range 50,000 –70,000, with degree of polymerization $n \approx 180$.

into a rectilinear dependence between $\lg \sigma$ and $1/T$. As an example, the results of the measurement (Fig. 3) are given for a Cu polymer with $R =$ —$(CH_2)_6$—. The electrical conductivity of some samples of Cu polymers from different syntheses has different values. It is possible that this is due to the presence of impurities, since changes occur in the intensity curve measured on an X-ray diffractometer.

Fig. 2. Temperature dependence of the electrical conductivity for Cu polymers of structure II (left) and Co polymers of structure III (right):

1—$R =$ — phenylene,
2— biphenylene,
3—$(CH_2)_6$,
4—$(CH_2)_2$

For Co polymers of structure III, analogous data were obtained as for Cu polymers. The electrical conductivity also decreases in the series of radicals: phenylene, diphenylene, hexamethylene, and dimethylene. The activation energy changes little depending on the nature of the radical and is, for —(C_6H_4)— and —$(C_6H_4)_2$, $E = 0.58$—0.62 eV, and for —$(CH_2)_2$— and —$(CH_2)_6$, $E =$ 0.74—0.76 eV at temperatures $T > 370^\circ$ (Fig. 2b). In the previous work (^{1}) it

Figure 3: Temperature dependence plot of electrical conductivity for a Cu polymer

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Fig. 4. Temperature dependence of the electrical conductivity of copper thiocyanate

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was shown that there is a correlation between the values of electrical conductivity and magnetic susceptibility of Co polymers. For Co polymers, the magnitude of the electrical conductivity depends on the electronic state of the cobalt atom, which changes easily during synthesis or thermal treatment. Therefore, for the investigated samples of Co polymers, measurements of magnetic susceptibility were carried out (μ_{eff} value equal to $3.5\,\mu_B$). For all the above-mentioned polymers, an interesting feature is observed with respect to the activation energy. In the presence of phenylene or diphenylene radicals in Cu polymers, the activation energy at a temperature of approximately $T < 360°$ is 0.36—0.42 eV, while at $T > 360°$ the activation energy increases to 0.60—0.62 eV. In the presence of hexamethylene radicals, the activation energy has an increased value,

Fig. 3. Temperature dependence of the electrical conductivity of a Cu polymer of structure II; $R =$ —$(\mathrm{CH_2})_6$ during the first heating (1), during cooling (2), during the second heating (3)

equal to 0.72 eV, already at $T < 360°$ (Fig. 2a). The activation energy of Co polymers, measured at $T > 370°$, has an elevated value of 0.58-0.76 eV for all radicals (phenylene, diphenylene, hexamethylene, and dimethylene) (Fig. 2b). For Cu-, Ni-, and Co-polydithiooxamides into which no radicals were introduced, the activation energy has the same elevated value, equal to 0.6-0.7 eV in the temperature range $T = 290°–500°$. From the data presented it is evident that, for all polymers having identical groups

$$\mathrm{S}=\overset{|}{\mathrm{C}}-\mathrm{NH}-,$$

similar values of the activation energy were obtained, equal to 0.58-0.76 eV, whereas when phenylene rings were included in the polymer chain, reduced values of the activation energy, equal to 0.36-0.42 eV, were obtained at $T < 360°$.

Fig. 4. Temperature dependence of the electrical conductivity of copper thiocyanate

According to crystal-chemistry data (4), it has been established that the greatest conjugation of the p_π-electron bonds of nitrogen and sulfur atoms, due to the participation of free electron pairs in σ-chemical bonds, is found in the groups

$$\mathrm{S = \overset{|}{C} - N <} \quad \text{and} \quad \mathrm{S = C = N -} \, .$$

On the basis of structural data it may be assumed that polymeric metal thiocyanates containing bridging groups

$$\mathrm{S - C = N -}$$

possess semiconductor properties. Determination of the structure of silver thiocyanate (^{5}) showed that the crystals contain polymeric chains

$$\mathrm{-Ag - SCN - Ag - SCN - Ag -} \, .$$

However, this compound is stable only up to 120°C. Copper thiocyanate is a more stable compound and decomposes at 1084°C. The electrical conductivities of three CuSCN specimens were measured (two factory specimens and one specimen obtained by a laboratory method). For these specimens the electrical conductivities are of the order 10^{-6}–10^{-8} $\Omega^{-1} \cdot \mathrm{cm}^{-1}$. In the plots of the dependence of $\lg \sigma$ on $1/T$ there are two straight-line segments ($E_1 = 0.4$, $E_2 = 0.1$ eV), shown for one of the specimens in Fig. 4. After heat treatment of CuSCN, carried out at 400°C for 1-2 h, the small value of the activation energy $E = 0.1$ eV is reproduced. Polymeric metal thiocyanates $M\mathrm{Hg(SCN)_4}$, containing tetrahedral groups $\mathrm{Hg(SCN)_4}$ (^{6}), are also semiconductors.

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