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THE INFLUENCE OF TCNQ⁰ CONTENT IN TCNQ SALTS ON POLYCATIONS WITH SULFONIUM GROUPS IN THE MAIN CHAIN

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ABSTRACT

The influence of the TCNQ⁰ content defined as $x = [\text{TCNQ}^0]/[\text{TCNQ}^-]$ on the properties of TCNQ complex salts containing S⁺ in the main chains are presented and discussed. Both the specific resistivity and the thermal activation energy of the conductivity had a minimum for x close to 0.9. The decrease of resistivity with an increase in the x ratio is explained by a decrease in the dimer concentration. The increase of resistivity for x increasing above 0.9 is explained by the formation of crystalline TCNQ⁰ domains. The discussion is based on ESR, optic absorption, and crystallinity data.

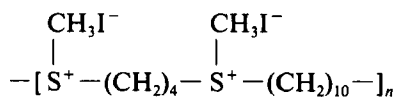
INTRODUCTION

The complex salts of TCNQ with polycations containing S⁺ or N⁺ are known to be organic semiconductors [1–4]. A replacement of N⁺ with S⁺ in polycations of the same type results in a dramatic change of properties of TCNQ salts. Salts containing S⁺ show a lower specific resistivity (ρ), a lower activation energy (E_a) [5, 6], a higher crystallinity [7], and a better solubility.

These differences in properties of salts can be explained if the properties of S^+ and N^+ cations are taken into consideration. The higher polarizability of the S^+ cation determines a decrease of coulombic interactions in the complex and a decrease of the activation energy of the charge transfer [8]. Consequently, different crystalline structures of TCNQ complexes with S^+ - and N^+ -containing polycations result from the different configuration of the sulfonium cation as compared with that of the ammonium one.

The properties of complex salts can be varied by choices other than the heteroatom in the polycation. The influence of the content of $TCNQ^0$ on the properties of the complex salt, expressed mainly through ρ and E_a , has been reported in numerous papers [5, 6, 9-25]. In many cases, ρ and E_a had minimum values for a $[TCNQ^0]/[TCNQ^-]$ molar ratio close to 1 [5, 6, 9-12]. The decrease of resistivity for $[TCNQ^0]/[TCNQ^-]$ ratios higher than 0.2-0.5 has also been reported [13, 16, 17]. A minimum resistivity has also been found at a ratio of $[TCNQ^0]/[TCNQ^-] = 0.5$ for salts of the type $M^{2+}(TCNQ^-)_2TCNQ^0$ [1, 16, 17-20]. For complex salts of TCNQ with elastomeric polycations, the minimum resistivity has been recorded at $[TCNQ^0]/[TCNQ^-] = 0.4$ [21]. However, in some cases no dependence has been observed between the minimum resistivity and the content of $[TCNQ^0]$ of salts [22-25], perhaps since the values of the $[TCNQ^0]/[TCNQ^-]$ ratio for the investigated salts were not large enough.

Although there are many publications in this field (not all of them are cited above), the role of TCNQ in complex TCNQ salts with polycations has not been explained. It is the aim of this paper to discuss the influence of the content of $TCNQ^0$ on electric and magnetic properties of the complex salt of the following polycation (abbreviated $P_3[4,10]$)



as well as the influence of the $TCNQ^0$ content on the crystallinity of salts of different $[TCNQ^0]/[TCNQ^-]$ ratios.

EXPERIMENTAL

Synthesis of TCNQ Salts

Details on the synthesis of the investigated TCNQ salts, abbreviated $K_3[4,10]_x$, where $x = [TCNQ^0]/[TCNQ^-]$, were given previously [4, 5]. Polymeric TCNQ simple salts ($x = 0$) were obtained via a reaction of

$P_3[4,10]$ polycation with LiTCNQ in water/methanol mixture at room temperature. Complex salts ($x = 0$) were prepared by a one-stage method described earlier [5].

Electronic Absorption Spectra

UV-visible light absorption spectra of solutions in acetonitrile and of powdered TCNQ salts were recorded by using Unicam SP-1700 and Specord M-40 spectrophotometers. The molar ratio $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ in complex salts was determined according to the following relations [27]:

$$[\text{TCNQ}^-] = A_{744}/\epsilon_{744}[\text{TCNQ}^-] \quad (1)$$

$$[\text{TCNQ}^0] = \{\epsilon_{744}[\text{TCNQ}^-]A_{394} - \epsilon_{394}[\text{TCNQ}^-]A_{744}\} / \epsilon_{394}[\text{TCNQ}^0]\epsilon_{744}[\text{TCNQ}^-] \quad (2)$$

where $\epsilon_{394}(\text{TCNQ}^-)$ and $\epsilon_{744}(\text{TCNQ}^-)$ are the molar absorption coefficients of TCNQ^- at $\lambda = 394$ and 744 nm, respectively, and $\epsilon_{394}(\text{TCNQ}^0)$ is the molar absorption coefficient of TCNQ^0 at $\lambda = 394$ nm. The values of these coefficients were taken from the work of Mizoguchi et al. [26].

Measurement of Electric Properties

The measurements of electric properties of TCNQ salts were performed on 1-mm thick pellets of polycrystalline samples prepared under pressure (1000 kg/cm) in vacuum. The electrodes were made by vacuum deposition of gold.

Measurement of Magnetic Properties

The electron spin resonance (ESR) spectra were recorded by using a Polish SE/X-20 ESR spectrometer [27].

Crystallinity

The studies on crystallinity of TCNQ complex salts with polycations, abbreviated as $K_3[4,10]_x$, were performed by the X-ray diffraction method [7] by using a DRON-2(USSR) diffractometer with Cu anode and Ni filter. A voltage of 30 kV was applied. The impulse counting rate

was 2000 imp/s and the angular rate of the counter was $2^\circ/\text{min}$. The total scattering power I was estimated according to the method described in Ref. 29.

RESULTS AND DISCUSSION

Both the dependence of the specific resistivity ρ and of the thermal activation energy of conductivity E_a on the content of $K_3[4,10]_x$ are shown in Fig. 1. As seen in Fig. 1, the value of x has a strong influence on the electric properties. This influence was also observed in the case of TCNQ salts with other polycations [1-20]. The minimum values for E_a and ρ were recorded for $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratios as equal to 0.8-0.9. By changing the x ratio in the range 0.0-0.1, the conductivities of the compounds may be varied from 10^{-4} to 10^{-1} S/cm.

The conductivities of organic TCNQ salts are strongly dependent on the structure of the TCNQ column, which determines the delocalization of electrons along it, and the crystallinity. The results presented in Fig. 1 suggest that the amount of TCNQ also has an influence on these factors. Therefore, complex studies of magnetic and optic properties as well as

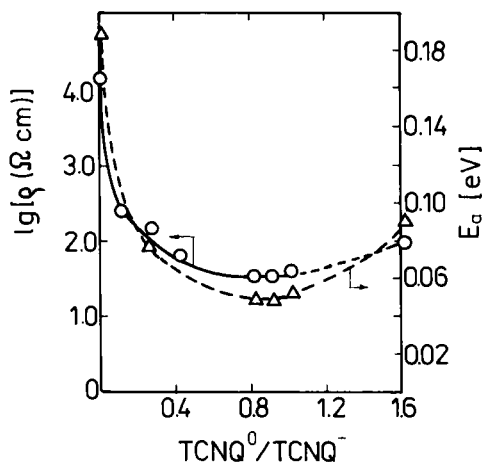


FIG. 1. The dependence at room temperature of specific resistivity ρ and of thermal activation energy E_a for $K_3[4,10]_x\text{TCNQ}$ complex salts on the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio.

of crystallinity of $K_5[4,10]_x$ salts were performed. The optical absorption spectra of solid salts with different $[TCNQ^0]/[TCNQ^-]$ ratios are shown in Fig. 2. A decrease of absorption around 630 nm can be observed for increasing $[TCNQ^0]/[TCNQ^-]$ ratios. Since the absorption at 630 nm is attributed to dimers [29], this decrease indicates that the increase of the TCNQ concentration in the complex salt brought about a diminishing of the dimer concentration. The change of dimer concentration should have an influence on the electron distribution along the TCNQ column since the presence of dimers determines a decrease of electron delocalization. Because the decrease of dimer concentration should cause a continuous decrease of resistivity, a correlation between the dependence of resistivity on the $[TCNQ^0]/[TCNQ^-]$ ratio and the dependence of absorption on the same ratio should be expected. However, as seen in Fig. 3, the dependence of the absorption ratio $A_{630}/(A_{630} + A_{385})$, which can be taken as a measure of the dimer concentration, does not show any peculiarity in the range of x for which a minimum of resistivity is observed, i.e., 0.8–0.9 (compare with Fig. 1). This fact indicates that conductivity is not only related to dimer concentration. Therefore, in order to explain the

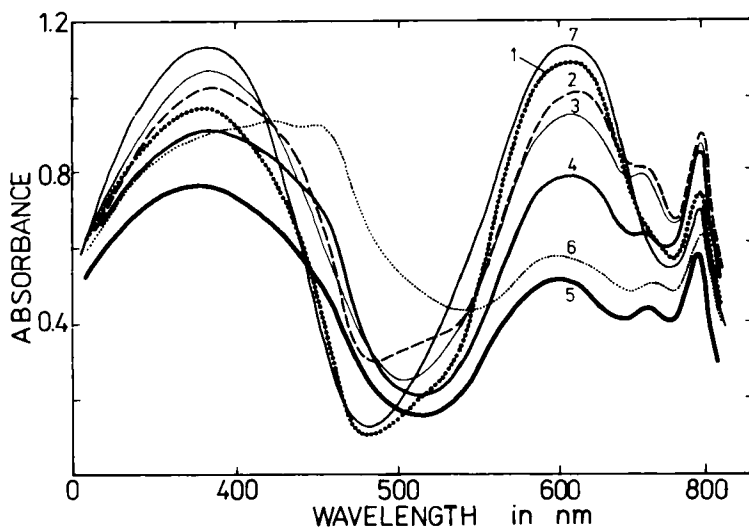


FIG. 2. Electronic absorption spectra of TCNQ salts. Numbers 1–6, $K_5[4,10]_x$ -TCNQ salts of different $[TCNQ^0]/[TCNQ^-]$ ratios: (1) 0.00; (2) 0.10; (3) 0.25; (4) 0.40; (5) 0.90; and (6) 1.60. No. 7, LiTCNQ (simple salt).

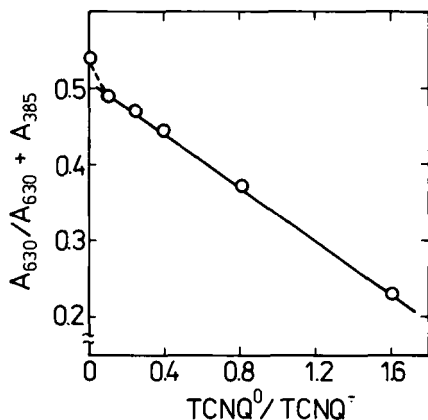


FIG. 3. The dependence of optical absorption ratio $A_{630}/(A_{630} + A_{385})$ of $K_s[4,10]_x\text{TCNQ}$ complex salts on the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio (compare with Fig. 1).

observed minimum of resistivity, the interactions between molecules in the TCNQ column and the crystallinity of salts with different $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratios have been considered.

The increase of exchange interactions between molecules in the TCNQ column is reflected by the diminished width of the spectral lines $\Delta H_{1/2}$ (i.e., width of symmetrical ESR line at half height of the integral line). In the case of $K_s[4,10]_x$ complex salts, the dependence of $\Delta H_{1/2}$ on the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio exhibits a minimum for x in the range 0.8–0.9 (Fig. 4), corresponding to minimum resistivity (compare with Fig. 1). The increase of $\Delta H_{1/2}$ for values of x higher than 0.9 can be explained by the increase of the disorder in the crystalline structure.

A total scattering factor ΣI was taken as the measure of crystallinity of the salts investigated [7]. As seen in Fig. 5, ΣI increases with the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio. For values of x less than 0.8, an increase of ΣI is accompanied by an increase of intensity of diffraction patterns at angles 2θ equal to 27.4 and 14° . The diffraction at these angles is attributed to the formation of $\dots \text{TCNQ}^0 \dots \text{TCNQ}^- \dots$ columns. For x higher than 0.9, a stronger increase of ΣI might be observed. However, a new diffraction pattern appears, which corresponds to the formation of a new crystalline phase of TCNQ^0 [7].

The presence of crystalline TCNQ^0 domains is also manifested by an

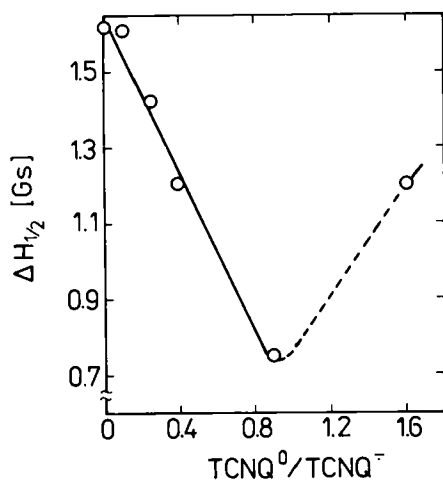


FIG. 4. The dependence of the line width of symmetrical ESR lines at half of the integral line height ($\Delta H_{1/2}$) for $K_s[4,10]_xTCNQ$ complex salts on the $[TCNQ^0]/[TCNQ^-]$ ratio.

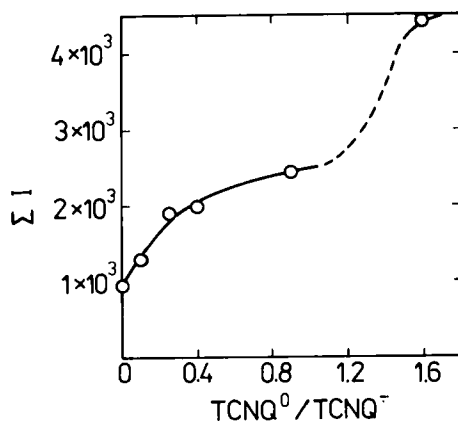


FIG. 5. The dependence of the total scattering factor I for $K_s[4,10]_xTCNQ$ complex salts on the $[TCNQ^0]/[TCNQ^-]$ ratio.

increase of the molar concentration of unpaired spins if the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio is higher than 0.9 [27]. The formation of crystalline domains of TCNQ may explain the decrease of conductivity and the increase of activation energy. It seems that the excess of TCNQ^0 (above the content corresponding to x close to 1) cannot be incorporated in the TCNQ column, thus forming a poorly conductive phase in the crystallites. Further detailed investigations are necessary to determine how large these domains are and how they build up in salt crystallites.

CONCLUSIONS

The content of TCNQ in complex salts of TCNQ with $P_s[4,10]$ polycations strongly influences the electric properties of salts and their crystallinity. This fact can be considered as an advantageous characteristic from the point of view of tailoring organic materials exhibiting different conductivities from the same compounds.

The increase of TCNQ^0 content in salts up to a $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio close to 0.9 leads to more ordered structures (i.e., increased crystallinity) and to a better delocalization of electrons along the acceptor chain (the increase of the exchange interaction between TCNQ molecules was registered as a decrease of the half-width of ESR lines). Consequently, the electrical conductivity increased and the thermal activation energy of conduction decreased. A further increase of the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio (above 0.9) resulted in the formation of crystalline TCNQ^0 domains which brought about the decrease of conductivity and a corresponding increase of its thermal activation energy. The results obtained show that the value of the $[\text{TCNQ}^0]/[\text{TCNQ}^-]$ ratio in complex salts of TCNQ with polycations has a versatile influence on their electric and magnetic properties.

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