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Electronic Spectra and Electric Properties of Poly(1-methyl-4-vinylpyridinium)–TCNQ Salt

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Electronic spectra and conductivities of poly(1-methyl-4-vinylpyridinium)–TCNQ anion radical salts and complex salts which contain additional neutral TCNQ were studied. By addition of neutral TCNQ, a new electronic absorption band appears at 3500 cm^{-1} and the charge-transfer band between TCNQ anion radicals disappears. It was concluded that this new absorption band is the charge-resonance band between a TCNQ anion radical and neutral TCNQ molecule from the dependence of its absorption intensity on the amount of added neutral TCNQ. The conductivity of the salt changed from 7×10^{-8} to 8×10^{-3} Ω^{-1} cm^{-1} by inclusion of the neutral TCNQ. This change of conductivity was explained in relation with the change of the absorption spectra of these polymer salts.

The salts of tetracyanoquinodimethane(TCNQ) anion radical have high electrical conductivity which depends on the properties of the counter cations and the whole crystal structure.1,2) There are many kinds of crystals of the type M$^+$(TCNQ)$_n^-$(n>1).3,4) The relation between the crystal structure5) and anisotropy of the electrical conductivity6) shows that the conduction arises from the transfer of unpaired electrons through the TCNQ molecules which are stacked face-to-face.3,4) The optical properties of TCNQ salts were discussed in connection with the motion of unpaired electrons.7) Iida obtained electronic spectra of various TCNQ salts from diffuse reflectance spectra and found that some salts have intense bands in the infrared region besides the charge-transfer bands.8,9) Kondow and Sakata found that the infrared absorption spectra show a remarkable temperature dependence and explained it by employing a singlet-triplet model and a band model.10)

Poly-4-vinylpyridinium TCNQ salt is a film-forming polymer salt,11,12) suitable for the measurement of electronic spectra. Lupinski *et al.* reported that the conductivity of poly-2-vinylpyridinium TCNQ salt increases remarkably by addition of neutral TCNQ.11) Recently, Mizoguchi *et al.* proposed the conduction mechanism of TCNQ salts of ionene polymers.13)

In this paper we report the electronic spectra and electrical conductivity at various temperatures of poly-4-vinyl-pyridinium TCNQ salt (P4VP$^+$TCNQ$^{\overline{\cdot}}$) and complex salts (P4VP$^+$TCNQ$^{\overline{\cdot}}$TCNQ$_x$) ($0\leqq x<1.5$).

Experimental

Synthesis. Poly(1-methyl)-4-vinylpyridinium TCNQ salt and the complex salts including neutral TCNQ were synthesized according to the method in the literature.11)

Electronic Spectra. The polymer salt was dissolved in dimethylformamide under nitrogen atmosphere. By evaporation on a quartz plate, a coherent film was deposited. The electronic absorption spectra of films were measured with a Shimadzu: SL-50L spectrometer.

Infrared Absorption Spectra. A coherent film was deposited on a thin aluminum mirror, which was prepared by evaporating aluminum on a glass surface. The infrared absorption spectra were measured with a Hitachi-Perkin Elmer infrared spectrometer, and a reflectrance apparatus we made, shown in Fig. 1.

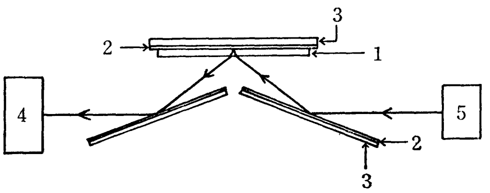


Fig. 1. Infrared reflectance apparatus.
1: Sample film, 2: Evaporated Al mirror, 3: Glass plate, 4: Detector, 5: Monochromator.

Electrical Conductivity. The electrical conductivity was measured with a compaction sample prepared by pressing at 50 kg/cm^2, with a Yokogawa-Hewlett Packard Model 4305 A Volt-Ohm meter. The temperature dependence of the electrical resistance was measured *in vacuo* by use of a surface-type cell, consisting of a sample film and vacuum-evaporated Au electrodes.

Results

Electronic Spectra. Both P4VP$^+$TCNQ$^{\overline{\cdot}}$ and P4VP$^+$TCNQ$^{\overline{\cdot}}$TCNQ$_x$ form homogeneous green films.11) As Fig. 2 shows, the spectrum of P4VP$^+$-TCNQ$^{\overline{\cdot}}$ changes by inclusion of neutral TCNQ so that the charge-transfer band between TCNQ$^{\overline{\cdot}}$s at around 9000 cm^{-1} disappears and a new band appears in the near infrared region below 7000 cm^{-1}. As shown

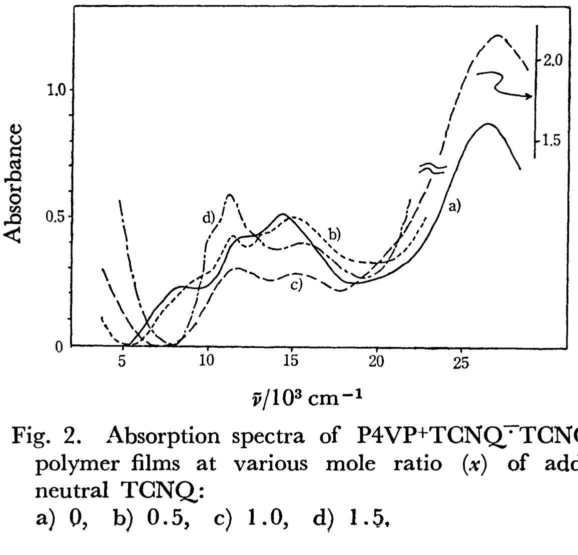


Fig. 2. Absorption spectra of P4VP$^+$TCNQ$^{\overline{\cdot}}$TCNQ$_x$ polymer films at various mole ratio (x) of added neutral TCNQ:
a) 0, b) 0.5, c) 1.0, d) 1.5.

in Fig. 3, by increasing the amount of neutral TCNQ, the intensity of the new infrared band increases to a mole ratio of about 1.0 and levels constantly. Figure 4 shows the infrared spectrum measured by the mirror reflection method. The new infrared absorption band is seen to have a maximum near 3500 cm^{-1}.

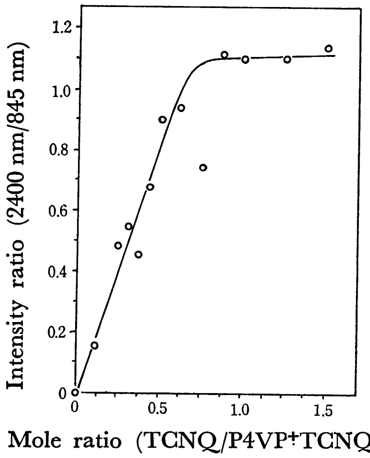


Fig. 3. The dependence of intensity of the new IR band (at 2400 nm) on the neutral TCNQ content.

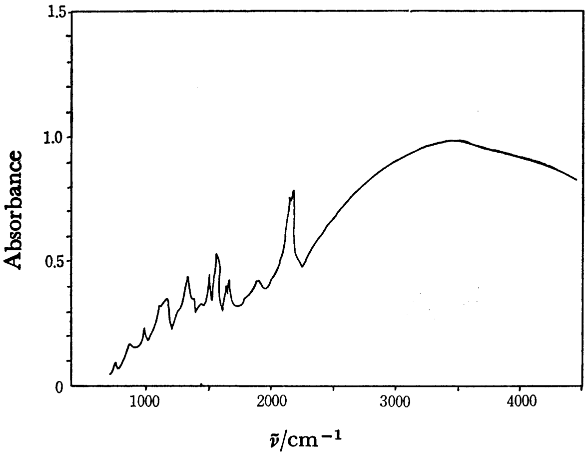


Fig. 4. Infrared spectrum of P4VP$^+$TCNQ$^{\cdot -}$TCNQ

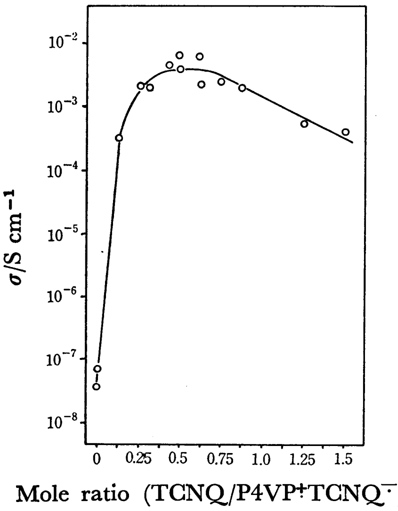


Fig. 5. The dependence of electric conductivity on the neutral TCNQ content.

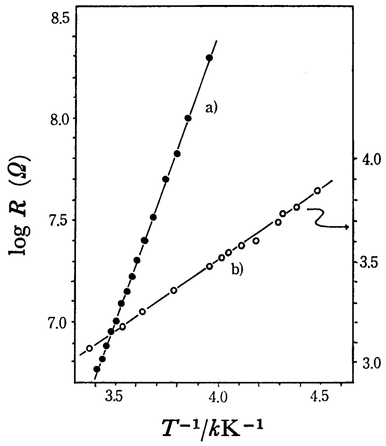


Fig. 6. The temperature dependence of electric resistance. a) P4VP$^+$TCNQ$^{\cdot -}$ b) P4VP$^+$TCNQ$^{\cdot -}$TCNQ$_{1/2}$

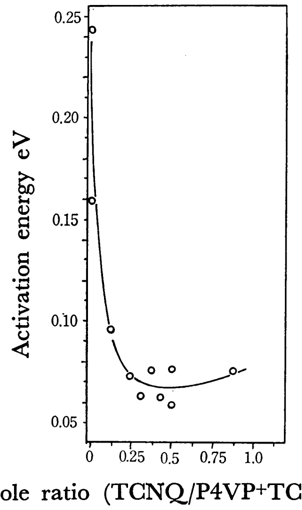


Fig. 7. The dependence of activation energy (E_a) on the neutral TCNQ content.

Electrical Properties. The electrical conductivities of powdered samples are shown in Fig. 5 at various mole ratios of neutral TCNQ *vs.* polymer TCNQ salt. With increasing neutral TCNQ, the conductivity changes from 7×10^{-8} to 8×10^{-3} Ω^{-1} cm^{-1} and has a maximum at about a mole ratio of 0.5. The conductivity decreases with the addition of more neutral TCNQ. Log R(electrical resistance) *vs.* T^{-1} (Fig. 6) gives good straight lines for both P4VP$^+$TCNQ$^{\cdot -}$ and P4VP$^+$TCNQ$^{\cdot -}$TCNQ$_{1/2}$.

As shown in Fig. 7, the activation energy(E_a) calculated from $R_{(\Omega)}\propto\exp(E_a/KT)$ changed from 0.24 eV for the sample containing no neutral TCNQ to 0.07 eV for the sample containing neutral TCNQ. The variation of activation energy with the TCNQ content has a relationship similar to that of the electrical conductivities (see Figs. 5 and 7) and has a minimum near the mole ratio of 0.5.

Discussion

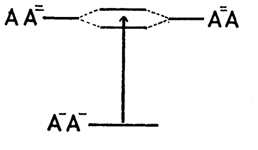
Absorption Spectra. Poly-4-vinylpyridine is an atactic polymer[11] but the structures of the polymer

TCNQ salts are not known. The absorption spectra of the films are similar to those of other TCNQ salts. It can therefore be presumed that in these polymer salts the TCNQ molecules are packed face-to-face forming somewhat irregular columns as in other TCNQ salts whose crystal structures[5] are known.

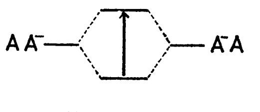
The band of P4VP$^+$TCNQ$^{\dot{-}}$ at *ca.* 9000 cm^{-1} (Fig. 2) can be assigned to a charge transfer band arising from the charge transfer between the highest half occupied orbitals of TCNQ$^{\dot{-}}$ molecules.[8,9] The CT energy has been calculated by use of the SCF-MO method.[14] We measured the absorption spectra of films at various temperatures, from 150 K to room temperature. It was found that the intensity of the CT band increases by lowering the temperature. This suggests that an antiferromagnetic interaction arises between odd electrons of TCNQ$^{\dot{-}}$ molecules.[15] The band at *ca.* 11000 cm^{-1} is assigned to the TCNQ$^{\dot{-}}$ monomer since the band resembles that of TCNQ$^{\dot{-}}$ in EtOH.[16] The band at *ca.* 15000 cm^{-1} (Fig. 2) is attributable to aggregated TCNQ$^{\dot{-}}$s since the band resembles that of the TCNQ$^{\dot{-}}$ dimer in an aqueous solution[16] and of solid TCNQ$^{\dot{-}}$ salts.[8,9]

In the absorption spectra of complex salts with growing amount of neutral TCNQ, the intensity of the CT band at 9000 cm^{-1} decreases and a new absorption band in the IR region below 7000 cm^{-1} arises (Figs. 2 and 3). The intensity of the TCNQ$^{\dot{-}}$ monomer band at 11000 cm^{-1} increases relative to that of the TCNQ$^{\dot{-}}$ aggregation band at 15000 cm^{-1}. These results can be explained by taking into consideration the fact that added neutral TCNQ is introduced into the TCNQ column as shown by $\langle \cdots A^{\circ}A^{\dot{-}}A^{\circ}A^{\dot{-}}A^{\circ}\cdots \rangle$ so that the anion radicals are separated from each other by it. From the two results described above, it seems probable that the new IR absorption band is a charge-resonance band between TCNQ$^{\dot{-}}$ and neutral TCNQ. This charge-resonance band is shown to have a peak at 3500 cm^{-1}. Figure 8 illustrates the transitions corresponding to the CT absorption between TCNQ$^{\dot{-}}$s and the charge-resonance absorption between TCNQ$^{\dot{-}}$ and neutral TCNQ by adopting dimer models.

We have estimated the resonance integral $\langle \phi(A^-A^{\circ})|H|\phi(A^{\circ}A^-)\rangle$ to be *ca.* 0.2 eV from the maximum position of the charge resonance band at ~0.4 eV. This value agrees in the order of magnitude with values obtained by other methods.[7,17] The intensity of this charge-resonance band saturated at about the mole ratio of one neutral TCNQ molecule to one TCNQ$^{\dot{-}}$ ion (Fig. 3). This shows that the number of neutral TCNQ molecules which can be inserted into the TCNQ$^{\dot{-}}$ column is *ca.* one per one TCNQ$^{\dot{-}}$. The CT absorption between TCNQ$^{\dot{-}}$ molecules disappeared at a mole ratio of 1.0, suggesting that the neutral TCNQ molecule is evenly distributed and TCNQ$^{\dot{-}}$ is isolated (Fig. 2).



CHARGE TRANSFER



CHARGE RESONANCE

Fig. 8. Schematic illustration of the charge transfer and charge resonance absorptions.

Electrical Properties. According to Onodera's measurements of compressed powder samples, the electrical resistances of both P4VP$^+$TCNQ$^{\dot{-}}$ and P4VP$^+$-TCNQ$^{\dot{-}}$TCNQ drop rapidly by applying pressure up to *ca.* 100 kbar.[18] This shows that the conduction is due to electron motions[19,20] along the TCNQ column as seen in other TCNQ salts.[21]

The electrical conduction in the solid P4VP$^+$TCNQ$^{\dot{-}}$ can be attributed to an electron transfer from a TCNQ$^{\dot{-}}$ anion to another, forming TCNQ$^0\cdots$TCNQ^{2-}.[22] The charge-transfer spectrum, on the other hand, corresponds to an electron transfer from one TCNQ$^{\dot{-}}$ to an adjacent TCNQ$^{\dot{-}}$. For the usual solid, this corresponds to an excited state, its energy being still much lower than the conduction state. However, in the present case, the two states lie close to each other, because of the lack of coulombic attraction between the hole, TCNQ^0, and electron, TCNQ^{2-}. In the case of the complex salt containing neutral TCNQ, the conduction state corresponds to the charge resonance between TCNQ and TCNQ$^{\dot{-}}$, and, hence, corresponds in energy to the charge-resonance band we observed. The absorption spectra of P4VP$^+$TCNQ$^{\dot{-}}$ polymer films show that the CT band between TCNQ ions is rather intense and the local excitation bands shift largely as compared with those of monomer ion in solution. This suggests that the interaction between TCNQ$^{\dot{-}}$s is not weak in this polymer matrix. The mobility of a carrier is related to the resonance integral expressed as $\beta=\langle\phi_n|H|\phi_{n+1}\rangle$, where ϕ is the lowest vacant molecular orbital of TCNQ, and the suffix n represents the site number.[17] Oohashi and Sakata reported that the resonance integral between the half-occupied orbitals of TCNQ$^{\dot{-}}$ is 0.15~0.4 eV, depending on the kind of salt investigated, from the intensity of CT band of reflection spectra.[17] From our preliminary ESR measurement for P4VP$^+$TCNQ$^{\dot{-}}$, exchange energy (J) was obtained to be about 0.06 eV and the resonance integral was was calculated as ~0.12 eV by means of the equation $J=4\beta^2/E_{\text{CT}}$(E_{CT}=CT energy) which holds for the linear chain radical crystal.[23] This value is slightly smaller than the resonance integral 0.2 eV for the complex salt estimated from the peak position of the charge-resonance band.

Since the difference in resonance integral is small, it can be concluded that the mobility of the simple salt does not differ so much from that of the complex salt.

The variation of conductivity with the mole ratio is parallel to that of activation energy obtained from temperature dependence of resistance (Figs. 5 and 7).

The band gap from the lowest wavelength absorption edge can be roughly estimated as $\Delta E_1=0.74$ eV for P4VP$^+$TCNQ$^{\cdot-}$ and $\Delta E_2=0.18$ eV for P4VP$^+$TCNQ$^{\cdot-}$-TCNQ, if the CT band and the charge-resonance band are assumed to correspond to transitions from the valence band to the conduction band. The number of carriers per unit cell is assumed to be N for P4VP$^+$-TCNQ$^{\cdot-}$ and 1/2 N for P4VP$^+$TCNQ$^{\cdot-}$TCNQ. Then, the ratio of conductivity σ_c(P4VP$^+$TCNQ$^{\cdot-}$TCNQ)/σ_s(P4VP$^+$TCNQ$^{\cdot-}$) can be represented by the equation

$$\sigma_c/\sigma_s=e\mu 2^{-1}N\exp(-\Delta E_1/2kT)/e\mu N\exp(-\Delta E_2/2kT),$$

which leads to 2.5×10^4 with use of the above values of of ΔE_1 and ΔE_2. This value is in good agreement with the experimental result of the variation of conductivity. Thus, contrary to the explanation given by Mizoguchi *et al.*,[13] the remarkable difference in conductivity might be attributed to the difference in the band gaps. The band gap estimated from the temperature dependence of resistance is about 0.14 eV for P4VP$^+$TCNQ$^{\cdot-}$TCNQ, which is also in good agreement with $\Delta E_2=0.18$ eV obtained from the absorption spectrum. For P4VP$^+$-TCNQ$^{\cdot-}$, the band gap estimated from the activation energy is *ca.* 0.48 eV and smaller than the value, 0.74 eV, obtained from the absorption spectrum, which can be interpreted as giving the lower limit for the band gap. The discrepancy seems to arise from the presence of a trace of neutral TCNQ in P4VP$^+$TCNQ$^{\cdot-}$. Most samples of P4VP$^+$TCNQ$^{\cdot-}$ contain neutral TCNQ. By extracting with benzene, the electrical conductivity of the sample decreases. However, it seems impossible to exclude all the neutral TCNQ which behaves as electron-accepting impurities from the polymer salt.

The intensity of charge-resonance band saturates at over 1.0 mole ratio of neutral TCNQ (Fig. 3). This suggests that the column can include neutral TCNQ molecules as long as the mole ratio becomes 1.0 with TCNQ$^{\cdot-}$ and TCNQ packed one by one, and the TCNQ molecules further added are present at the interstices. The present view also explained the results of conductivities (Fig. 5). The decrease in conductivity at the higher TCNQ content can be attributed to the increasing amount of neutral TCNQ present in the interstices which hinders the electron transfer. The results show that the conductivity shows a maximum at the TCNQ content much lower than unity. This might suggest that, at an increasing TCNQ content, there grows a chance for two TCNQ molecules being packed between two TCNQ$^{\cdot-}$ ions.

In conclusion, the polymer TCNQ salts can be classified into four types according to the neutral TCNQ content.

(1) P4VP$^+$TCNQ$^{\cdot-}$, which does not contain neutral TCNQ and whose conduction state arises from the charge transfer between TCNQ$^{\cdot-}$s.

(2) A salt containing a small amount of neutral TCNQ which acts as an electron-accepting impurity. The situation seems to be analogous to the impurity-doped semiconductor.

(3) P4VP$^+$TCNQ$^{\cdot-}$TCNQ $(0.25<x<1.0)$. The conducting state arises from the charge-resonance interaction between TCNQ$^{\cdot-}$ and TCNQ, acquiring quite a different electronic structure from that of P4VP$^+$-TCNQ$^{\cdot-}$. (4) P4VP$^+$TCNQ$^{\cdot-}$TCNQ $(x>1.0)$, containing a large amount of neutral TCNQ. The presence of excess neutral TCNQ diminishes the electronic conduction.

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