

## Effect of Polycations Containing Aromatic Heterocyclic Compounds on the Conductivity of Their TCNQ Salts

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**ABSTRACT:** Several kinds of monomeric 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ) complex salts were prepared from aromatic cations. Polycations were obtained from the polymer reaction of poly(epichlorhydrine) (PEH) with aromatic heterocyclic amines, and their TCNQ salts were prepared. The effect of the cation structure on the electronic conductivities of the TCNQ salts is discussed, noting the interplay of steric and polarizability effects. The conductivity of the TCNQ salts increases with an increase of the longest wavelength absorption ( $\lambda_{max}$ ) of the ammonium iodides, which can be a guide in estimating the polarizability of cations. In the monomeric TCNQ complex salts, it is found from the X-ray diffraction analysis that the crystal structure is affected by the change of the cation structure. Thus, the conductivity is affected by the steric factor as well as by the polarizability. In the polycation—TCNQ salts, however, the morphological change is considered to be small, because their X-ray diffraction patterns are similar. Thus, the increase of conductivity results from the increase of polarizability of the polycations by decreasing the Coulomb repulsion between carrier electrons, since the steric factor is unchanged.

**KEY WORDS** 7, 7, 8, 8-Tetracyanoquinodimethane / Conductivity / Complex Salt / Polycation / Polarizability / Steric Factor / Aromatic Heterocyclic Compound / X-Ray Diffraction /

The organic salts of 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ) exhibit a high electric conductivity. Many studies have been made on the syntheses and physical properties of TCNQ salts.<sup>1</sup> The TCNQ salts with monomeric cations composed of aromatic heterocyclic compounds such as quinoline or acridine show very high conductivities. These compounds possess columns of TCNQ molecules with face to face stacking.<sup>2</sup> It is considered that the planer structure of the cations tends to form the TCNQ column. LeBlanc<sup>3</sup> proposed that polarizable cations increase the conductivity of the TCNQ salts by reducing the Coulomb repulsion between carrier electrons. Therefore the conductivity is influenced by two factors: the steric factor and the polarizability of the cations.

The authors have studied the effect of polycation structure on the conductivity of the TCNQ salts with polymeric cations.<sup>4</sup> In these systems,

it is found that carrier electrons move through the TCNQ moiety and the polycations play a role as the matrix for the arrangement of TCNQ molecules. However, the influence of the polarizability of the polycation on the conductivity has not been studied.

This work investigated how the structure of cations affects the conductivity of monomeric and polymeric TCNQ salts, noting the interplay of steric and polarizability effects. The polarizability effect of polycations was particularly studied. Several kinds of TCNQ complex salts were prepared with the aromatic cations from pyridine, quinoline, acridine, and their substituted compounds with methyl, amino, and cyano groups. Polycations were prepared with poly(epichlorhydrine) and amines such as trimethylamine, pyridine, 4-aminopyridine, and 4-aminoquinaldine. Their TCNQ salts were also prepared. The conductivities of the TCNQ salts thus prepared were

measured, and the effect of cation structure was studied.

## EXPERIMENTAL

### Preparation of Monomeric TCNQ Complex Salts

*N*-Methylammonium iodides were prepared by the reaction of methyl iodide and amines at 40°C. They were recrystallized from alcohol. In Table I, the reaction conditions and the yield are shown. The TCNQ complex salts were prepared by mixing the methylammonium iodide and neutral TCNQ (TCNQ<sup>0</sup>) solutions, which had been separately dissolved in hot acetonitrile. On cooling, the complex salts were crystallized from the solution. The products were recrystallized from acetonitrile and characterized on the basis of the electronic spectra and elemental analyses.

### Preparation of Polycation—TCNQ Salts

Polycations were prepared by the reaction of amines and poly(epichlorohydrine) (PEH), whose chloromethyl groups were used for quaternization. The polymer reaction of PEH with trimethylamine (TMA) proceeded according to the method reported before.<sup>5</sup> The polymeric pyridinium compound was obtained by removing the excess of pyridine (Py) after heating the bulk solution of PEH in Py. The reaction with 4-

aminopyridine (4AmPy) or 4-aminoquinaldine (4AmQna) was done in *N,N*-dimethylformamide (DMF). The obtained polycations were extracted with water to remove the unreacted amines, after evaporating the DMF solvent. The methanol solutions of the products were poured into ethylacetate or acetone for purification. The amine content introduced was determined from elemental and Volhard analyses.

Polycation—TCNQ simple salts were prepared by the reaction of polycations with LiTCNQ in methanol at 25°C. The products were precipitated from the solution. Then they were collected and washed thoroughly with methanol and ethyl ether. The complex salts were prepared by evaporating DMF under reduced pressure after dissolving the simple salt and TCNQ<sup>0</sup> in DMF. They were dried at 50°C for several days *in vacuo*.

### Measurements

The measurements of specific resistivity ( $\rho$ ) were made on pressed cylindrical compactions of the crushed TCNQ salts. An electrical contact was made with electrodes of silver paint. The  $\rho$  value was obtained using eq 1 and the method of direct current described before<sup>4</sup>

$$\rho = R(S/d) \quad (1)$$

where  $R$  is the measured resistance ( $\Omega$ ), and  $S$  and

Table I. Preparation of cations

Ammonium iodide	[Amine], mol/l	[Methyl iodide], mol/l	Solvent	Time, h	Yield, %
<i>N</i> -Methylpyridinium iodide	0.46	1.7	Bz <sup>a</sup>	137	100
<i>N</i> -Methyl-2-aminopyridinium iodide	1.0	2.0	CH <sub>3</sub> CN	30	71
<i>N</i> -Methyl-2-methylpyridinium iodide	0.032	0.18	Bulk	7	51
<i>N</i> -Methyl-2-amino-3-methyl- pyridinium iodide	0.040	0.35	Bulk	24	99
<i>N</i> -Methyl-4-aminopyridinium iodide	0.30	0.60	CH <sub>3</sub> CN	30	60
<i>N</i> -Methyl-4-methylpyridinium iodide	0.032	0.18	Bulk	7	95
<i>N</i> -Methyl-4-cyanopyridinium iodide	0.10	0.18	Bulk	72	83
<i>N</i> -Methylquinolinium iodide	0.60	1.8	Bz <sup>a</sup>	137	92
<i>N</i> -Methyl-2-aminoquinolinium iodide	0.038	0.18	Bulk	4	8.1
<i>N</i> -Methyl-2-methylquinolinium iodide	0.35	8.8	CH <sub>3</sub> CN	1	55
<i>N</i> -Methyl-4-methylquinolinium iodide	0.038	0.18	Bulk	4	80
<i>N</i> -Methyl-4-aminoquinaldinium iodide	0.20	1.0	CH <sub>3</sub> CN	3	75
<i>N</i> -Methyl-4-methylquinaldinium iodide	0.032	0.18	Bulk	24	17
<i>N</i> -Methylacridinium iodide	0.45	2.5	CH <sub>3</sub> CN	72	96
<i>N</i> -Methyl-9-aminoacridinium iodide	0.26	5.9	CH <sub>3</sub> OH—CH <sub>3</sub> CN (2 : 1)	6	75

<sup>a</sup> Benzene

$d$  are the surface area ( $\text{cm}^2$ ) and the thickness (cm) of the cylindrical compaction, respectively.

The activation energy for conduction ( $Ea$ ) was calculated from eq 2.

$$R = R_0 \exp(Ea/kT) \quad (2)$$

where  $R_0$  is a constant ( $\Omega$ ),  $k$  the Boltzmann constant (eV/K), and  $T$  the absolute temperature (K).

Electronic spectra were measured with a Union Giken SM-401 Spectrophotometer. X-Ray diffraction patterns were measured with a Rigakudenki "D-3F" X-ray Diffract Meter, using a Cu target.

## RESULTS AND DISCUSSION

### Conductivity of Monomeric TCNQ Complex Salts

The values of  $\rho$  and  $Ea$  for the monomeric TCNQ salts are listed in Table II, together with the longest wavelength absorption ( $\lambda_{\text{max}}$ ) in the region of electronic spectrum for the ammonium iodides. The values of  $\lambda_{\text{max}}$  increase from 264 nm for *N*-methylpyridinium iodide to 358 nm for *N*-methylacridinium iodide as the number of aromatic rings increases. The ammonium iodides of the substituted compounds show longer  $\lambda_{\text{max}}$  values than nonsubstituted ones. Klandermann, *et al.*,<sup>6</sup> proposed that the polarizability of molecules should be assigned in proportion to the longest-wavelength  $\pi-\pi^*$  transition. Thus, the

$\lambda_{\text{max}}$  value can be a guide for the estimation of the polarizability of the cations. The relation between  $\lambda_{\text{max}}$  and  $Ea$  is shown in Figure 1. The  $Ea$  value tends to decrease with an increase of  $\lambda_{\text{max}}$ . This shows that the conductivity of the TCNQ complex salts decreases as the polarizability of the cations increases.

In Figure 2, the X-ray diffraction patterns for (II), (III), (V), (VI), (IX), (X), and (XI) are shown. Each TCNQ complex salt shows a different pattern, which indicates that the crystal structure is different for these TCNQ salts. The change of the chemical structure of the cations is assumed to cause the

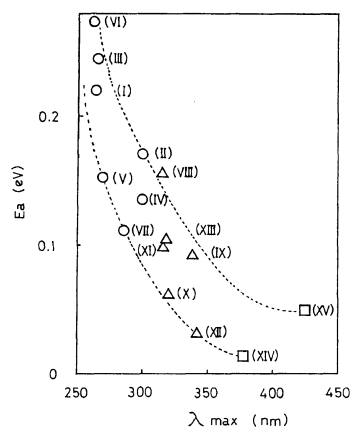


Figure 1. Relation between  $\lambda_{\text{max}}$  of cation and  $Ea$  for monomeric TCNQ complex salts.

Table II. Electronic properties of monomeric TCNQ complex salts

No.	TCNQ complex salt	$\rho$ , $\Omega\text{cm}$	$Ea$ , eV	$\lambda_{\text{max}}$ , <sup>a</sup> nm
(I)	<i>N</i> -Methylpyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$1.30 \times 10^8$	0.220	264
(II)	<i>N</i> -Methyl-2-aminopyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$8.30 \times 10^2$	0.170	300
(III)	<i>N</i> -Methyl-2-methylpyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$1.62 \times 10^8$	0.244	266
(IV)	<i>N</i> -Methyl-2-amino-3-methylpyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$5.55 \times 10^2$	0.135	300
(V)	<i>N</i> -Methyl-4-aminopyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$2.94 \times 10^2$	0.151	270
(VI)	<i>N</i> -Methyl-4-methylpyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$2.18 \times 10^8$	0.273	262
(VII)	<i>N</i> -Methyl-4-cyanopyridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$4.33 \times 10^4$	0.112	285
(VIII)	<i>N</i> -Methylquinolinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$4.12 \times 10^4$	0.156	315
(IX)	<i>N</i> -Methyl-2-aminoquinolinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$1.47 \times 10^4$	0.092	338
(X)	<i>N</i> -Methyl-2-methylquinolinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$5.39 \times 10^4$	0.061	320
(XI)	<i>N</i> -Methyl-4-methylquinolinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$3.67 \times 10^4$	0.098	315
(XII)	<i>N</i> -Methyl-4-aminoquinaldinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$1.24 \times 10^4$	0.031	342
(XIII)	<i>N</i> -Methyl-4-methylquinaldinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$3.12 \times 10^2$	0.105	318
(XIV)	<i>N</i> -Methylacridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$1.60 \times 10^0$	0.015	358
(XV)	<i>N</i> -Methyl-9-aminoacridinium—TCNQ $\frac{1}{2}$ <sup>-</sup>	$6.18 \times 10^0$	0.051	424

<sup>a</sup> Longest wavelength absorption for ammonium iodide.

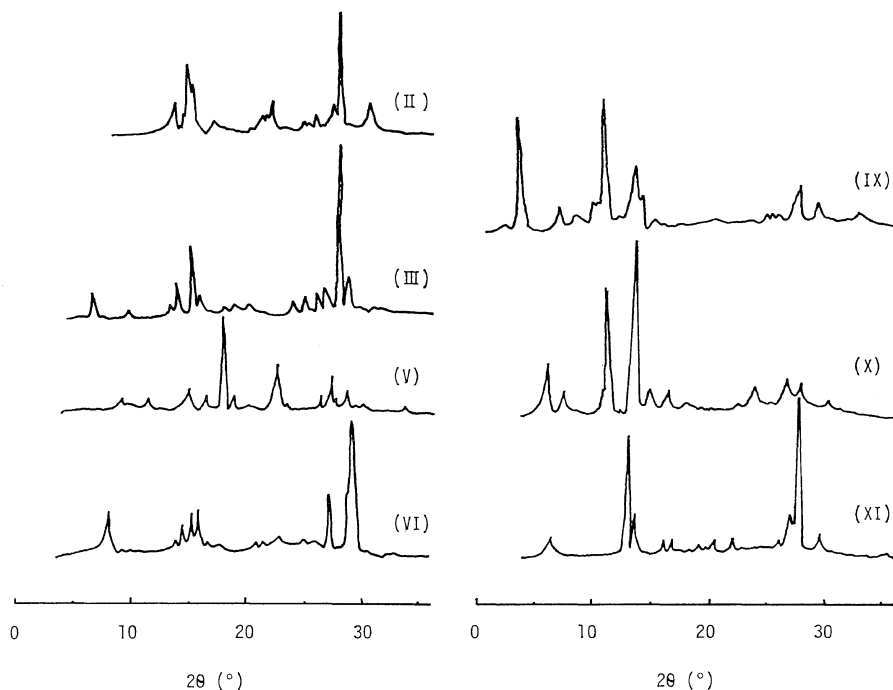


Figure 2. X-Ray diffraction patterns for monomeric TCNQ complex salts.

change of the crystal structure of the TCNQ salts. Therefore, a morphological change of the cation, which increases the cation polarizability, accompanies the change of the steric factor in the present case. This seems to cause some scatter in the relation of  $\lambda_{\max}$  and  $Ea$  shown in Figure 1. Though the conductivity of these monomeric TCNQ salts tends to decrease with the increase of the polarizability of the cations, the polarizability effect is not clear, because the steric factor cannot be neglected.

#### Conductivity of Polycation—TCNQ Salts

In Table III, the reactions with PEH and amines are summarized. Various amounts of amines were introduced into PEH by varying the reaction conditions, when TMA, Py, 4AmPy, and 4AmQna were used for amines. On the other hand, polycations were not obtained by the reaction of PEH with quinoline, acridine, and 9-aminoacridine at 100°C, for 120 h. This is attributable to the small basicity of the latter amines, or to the steric hindrance of their bulky cyclic structure. The

Table III. Preparation of polycations

Amine	Polycation abbreviation	[PEH], unit mol/l	[Amine], mol/l	Time, h	Yield, %	$Q_c^a$ , %
TMA	PEH—TMA <sub>0.87</sub> Cl	—	—	—	—	67
Py	PEH—Py <sub>0.56</sub> Cl	0.032	0.12	24	68.5	56
Py	PEH—Py <sub>0.75</sub> Cl	0.043	0.38	24	71.9	75
Py	PEH—Py <sub>0.80</sub> Cl	0.032	0.13	30	86.2	90
4AmPy	PEH—4AmPy <sub>0.22</sub> Cl	0.46	1.9	4	37.7	22
4AmPy	PEH—4AmPy <sub>0.56</sub> Cl	0.64	1.5	5	96.7	56
4AmPy	PEH—4AmPy <sub>0.85</sub> Cl	0.40	1.8	24	93.4	85
4AmQna	PEH—4AmQna <sub>0.73</sub> Cl	0.31	1.5	120	13.1	73

<sup>a</sup> Amine content.

Table IV. Preparation of polycation—TCNQ simple salts

Polycation—TCNQ simple salt	[Polycation], $\times 10^2$ unit mol/l	[LiTCNQ], $\times 10^2$ mol/l	Yield, %
PEH—TMA <sub>0.67</sub> TCNQ <sup>-</sup>	3.5	7.1	87
PEH—Py <sub>0.58</sub> TCNQ <sup>-</sup>	3.3	6.6	75
PEH—Py <sub>0.75</sub> TCNQ <sup>-</sup>	2.7	5.3	100
PEH—Py <sub>0.80</sub> TCNQ <sup>-</sup>	3.0	6.1	73
PEH—4AmPy <sub>0.22</sub> TCNQ <sup>-</sup>	1.2	2.6	72
PEH—4AmPy <sub>0.58</sub> TCNQ <sup>-</sup>	3.6	7.3	70
PEH—4AmPy <sub>0.85</sub> TCNQ <sup>-</sup>	3.3	6.7	95
PEH—4AmQna <sub>0.73</sub> TCNQ <sup>-</sup>	1.2	2.6	72

decomposition of PEH occurred by raising the reaction temperature or prolonging the reaction time. Thus, the useful amine for the reaction with PEH is limited.

In Table IV, the preparation results of the polycation—TCNQ simple salts are shown. It was found that the counter chloride ions were completely exchanged to TCNQ<sup>-</sup> on the basis of visible spectra. The relation between the values of  $\rho$  and the doping ratio of TCNQ<sup>o</sup> ( $[\text{TCNQ}^o]/[\text{TCNQ}^-]$ ) is shown in Figure 3, for PEH—Py<sub>0.75</sub> and PEH—4AmQna<sub>0.73</sub> TCNQ salts. The values of  $\rho$  decrease by doping TCNQ<sup>o</sup>, and the complex salts show their minimum  $\rho$  value ( $\rho_{\text{min}}$ ) at  $[\text{TCNQ}^o]/[\text{TCNQ}^-]=0.6-0.8$ . A similar tendency was also observed for the present polycation—TCNQ salts. In monomeric TCNQ complex salts, TCNQ<sup>o</sup> and TCNQ<sup>-</sup> are generally columnar stacked one by one to form the charge—transfer complex. It is expected that the maximum conductivity of polycation—TCNQ complex salts should be observed at the doping ratio of TCNQ<sup>o</sup> of 1.0, where doped TCNQ<sup>o</sup> molecules are packed one by one with TCNQ<sup>-</sup>. However, in polycation—TCNQ complex salts,  $\rho_{\text{min}}$  is sometimes observed at smaller amounts of  $[\text{TCNQ}^o]/[\text{TCNQ}^-]$  than 1.0.<sup>4,7</sup> Quarternized nitrogen atoms (N<sup>+</sup>) in polycations are covalently bonded on the main chain, so the regularity of the cation sites is dependent on the polycation structure. Thus, the

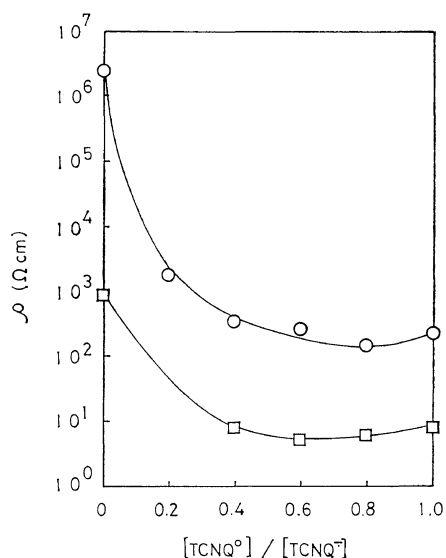


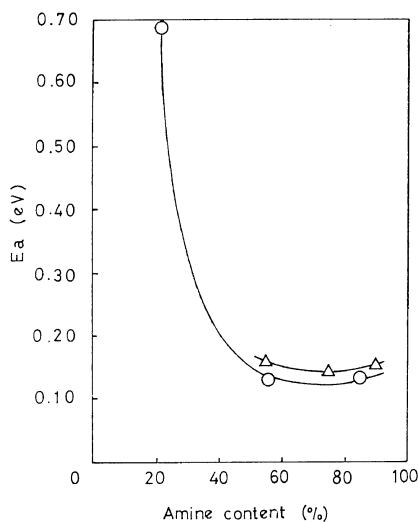
Figure 3. Relation between  $[\text{TCNQ}^o]/[\text{TCNQ}^-]$  and resistivity ( $\rho$ ) for polycation—TCNQ salts: O, PEH—Py<sub>0.75</sub> TCNQ salt; □, PEH—4AmQna<sub>0.73</sub> TCNQ salt.

arrangement of TCNQ molecules is affected by the polycation chain. In the present system, the main chain is composed of a flexible polyether chain and N<sup>+</sup> atoms exist apart from the main chain. It is considered that the TCNQ<sup>-</sup> molecules are arranged randomly along the flexible polycation chain, because the regularity of the N<sup>+</sup> sites is low. Therefore, sufficient space around TCNQ<sup>-</sup> for the doped TCNQ<sup>o</sup> to fit is not available. The doped TCNQ<sup>o</sup> molecules do not form a favorable complex with TCNQ<sup>-</sup> because there are hindrances by the TCNQ<sup>-</sup> and the main chain at high doping ratios of TCNQ<sup>o</sup>.

The conductivities ( $\rho$  and  $Ea$ ) of the polycation—TCNQ salts are listed in Table V, with  $\lambda_{\text{max}}$  of the polycation chlorides. In Figure 4, the relation between the amine content and  $Ea$  is shown for the PEH—Py and PEH—4AmPy TCNQ complex salts. The conductivity is affected by the amine content. The highest conductivity is observed at the amine content of 60–80%. In studying the conductivity of the TCNQ salts of polycations prepared with PEH and amines, the amine content for the polycations should be the same. Bruce, *et al.*,<sup>8</sup> proposed that all the chloromethyl groups of PEH should react in order to prepare a high con-

Table V. Electronic properties of polycation—TCNQ salts

Sample	Simple salt		Complex salt		$\lambda_{\max}^b$ , nm
	$\rho_s^a$ , $\Omega$ cm	$Ea$ , eV	$\rho_s^a$ , $\Omega$ cm	$Ea$ , eV	
PEH—TMA <sub>0.67</sub> TCNQ salt	—	—	$6.84 \times 10^2$	0.185	250
PEH—Py <sub>0.58</sub> TCNQ salt	$2.64 \times 10^3$	0.302	$2.32 \times 10^2$	0.157	270
PEH—Py <sub>0.75</sub> TCNQ salt	$3.44 \times 10^3$	0.181	$4.64 \times 10^2$	0.142	266
PEH—Py <sub>0.90</sub> TCNQ salt	$3.51 \times 10^3$	0.326	$1.66 \times 10^2$	0.150	266
PEH—4AmPy <sub>0.22</sub> TCNQ salt	—	—	$6.54 \times 10^3$	0.695	275
PEH—4AmPy <sub>0.58</sub> TCNQ salt	$6.46 \times 10^3$	0.210	$5.70 \times 10^2$	0.130	275
PEH—4AmPy <sub>0.85</sub> TCNQ salt	$2.46 \times 10^3$	0.439	$5.38 \times 10^2$	0.134	272
PEH—4AmQna <sub>0.73</sub> TCNQ salt	$9.74 \times 10^2$	0.093	$8.15 \times 10^0$	0.061	330

<sup>a</sup> Measured at 25°C.<sup>b</sup> Longest wavelength absorption for polycation.Figure 4. Relation between the amine content and  $Ea$  for polycation—TCNQ salts:  $\Delta$ , PEH—Py TCNQ complex salt;  $\circ$ , PEH—4AmPy TCNQ complex salt.

ducting polymer in the PEH—Py system. However as mentioned above, it is necessary to maintain sufficient space around  $\text{TCNQ}^-$ , namely the sufficiently large distances between the  $\text{N}^+$  atoms. The lower amine content (60—80%) seems more favorable.

The relation between  $\lambda_{\max}$  and  $Ea$  is shown in Figure 5. The  $Ea$  value decreases as the  $\lambda_{\max}$  value increases. In Figure 6, the X-ray diffraction patterns are shown for PEH—Py<sub>0.75</sub> and PEH—4AmPy<sub>0.85</sub> TCNQ salts. These salts show the similar patterns. The polycations are prepared from PEH, and the regularity of the  $\text{N}^+$  sites is

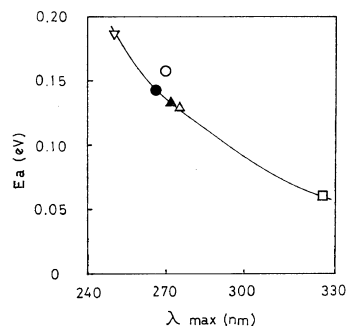
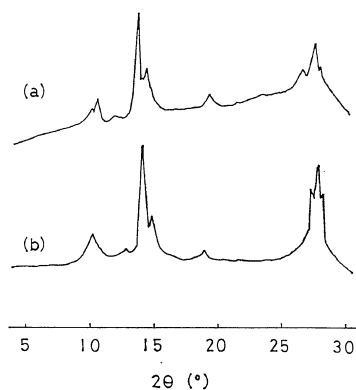
Figure 5. Relation between  $\lambda_{\max}$  of polycation and  $Ea$  for polycation—TCNQ complex salts:  $\nabla$ , PEH—TMA<sub>0.67</sub> TCNQ;  $\circ$ , PEH—Py<sub>0.58</sub> TCNQ;  $\bullet$ , PEH—Py<sub>0.75</sub> TCNQ;  $\Delta$ , PEH—4AmPy<sub>0.85</sub> TCNQ;  $\blacktriangle$ , PEH—4AmPy<sub>0.58</sub> TCNQ;  $\square$ , PEH—4AmQna<sub>0.73</sub> TCNQ.

Figure 6. X-Ray diffraction patterns for (a) PEH—4AmPy TCNQ complex salt and (b) PEH—Py TCNQ complex salt.

considered to be similar in the present system. The arrangement of TCNQ, which is affected by the polycations, is also similar. This shows that the steric factor for these TCNQ salts is constant.

LeBlanc<sup>3</sup> suggested that  $Ea$  for TCNQ salts can be shown as eq 3.

$$2 Ea = C - A \quad (3)$$

where  $C$  is the electrostatic energy and  $A$  is a bandwidth. He used a Heitler—London model for the conductivity and Mott's criterion for the metal—semiconductor transition, based on Hubbard's many-body treatment. Garito and Heeger<sup>9</sup> proposed that the bandwidth could be described in terms of the intermolecular transfer integral  $t$ . The magnitude of  $t$  is related to the nearest neighbor intermolecular overlap  $S$ , which is estimated to be  $S \sim \exp(-a/a_0)$  where  $a$  is the intermolecular spacing and  $a_0$  is a radius of the  $2p_z$  carbon wave function. Thus the bandwidth is expected to be affected by the spacing of the TCNQ molecules.

Applying these arguments to polycation—TCNQ salts, the bandwidth is dependent on the steric factor, which is affected by the polycation structure. The decrease of  $Ea$  with the increase of  $\lambda_{\max}$  is regarded as depending on the decrease of  $C$ , because the steric factor is constant in the present system. Of course the polycation—TCNQ salts are intrinsically amorphous, so the conduction mechanisms for crystalline monomeric TCNQ salts cannot be simply applied. However, it is plausible that the influence of amines on the conductivity of the present polycation—TCNQ salts is independent of the steric factor. Thus, it is concluded that the polarizability of the polycations increases the conductivity of the polycation—TCNQ salts.

#### Stability of Polycation—TCNQ Salts

The decomposition of PEH occurred in the preparation of polycations by heating. Some compactations of the polycation—TCNQ salts were observed to dilate by the heating involved in measuring the activation energy. This shows that the TCNQ salts of polycations prepared from PEH are thermally unstable. It has also been suggested that the TCNQ salts of the polycations composed of polyether chain are chemically unstable by Bruce, *et al.*,<sup>8</sup> and the authors.<sup>10</sup>

The chemical stability of the polycation—TCNQ

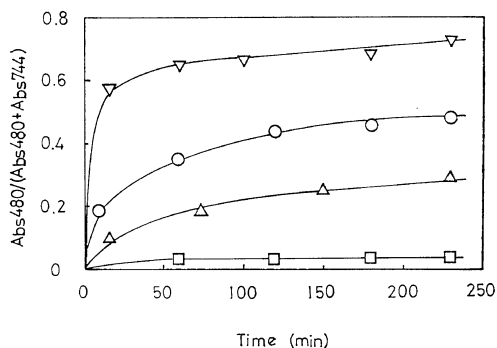
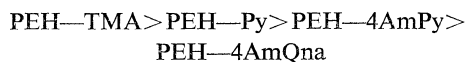


Figure 7. Change of  $Abs_{480}/(Abs_{380}+Abs_{744})$  with time in polycation—TCNQ simple salts in DMF: ▽, PEH—TMA; ○, PEH—Py; △, PEH—4AmPy; □, PEH—4AmQna.

simple salts was studied using visible spectra. The TCNQ salts were dissolved in DMF, and the change with time of the absorption at 480 nm attributable to  $\alpha, \alpha'$ -dicyano-*p*-toluoylcyamide, which is the decomposition product of  $TCNQ^{\cdot-}$ ,<sup>10</sup> was measured. As shown in Figure 7, the rates of the decomposition are in the following order.



The complex salts were more stable than the simple salts, and the salts of the polycations of high amine content were more stable than those of lower amine content. Thus, high conducting polycation—TCNQ salts are stable. Though the effect of polycation structure on the stability of the TCNQ salts is not clear, it is plausible that the tight binding TCNQ column gives stable TCNQ salts because of the large intermolecular interaction.

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