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POLYMORPHISM AND PHASE TRANSITIONS IN A FAMILY OF ORGANIC CONDUCTORS

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We found that the substituted pyridinium-TCNQ complex salts exhibited a variety of polymorphs and first-order phase transitions. The irreversible transition was correlated to the appearance of polymorphism and nonstoichiometry. The reversible transition manifested itself for specific cations; N-n-propylpyridinium$(TCNQ)_X$ and N-n-butylpyridinium$(TCNQ)_X$.

Phase transitions of the highly conductive quasi-one-dimensional organic system based on TCNQ ion radical salts have been the subject of recent investigations.1),2) Various kinds of reversible and irreversible phase transitions with anomalous changes in electrical conductivity have been reported.3) In this paper, we deal with a variety of phase transitions in substituted pyridinium TCNQ complex salts and discuss factors governing the nature of the transitions.4)

After the salt was synthesized from onium iodide and TCNQ, recrystallization was made at 5°C from an acetonitrile or acetone solution of concentration of about 50 mmol/l. Crystallized salts were separated from the solution by at least four times (after one hour, four hours, one day and five days) and the crystal form, conductivity and composition were examined for each deposit.

The various properties of N-substituted pyridinium (Py) and picolinium (Pi) TCNQ complex salts are summarized in Table 1. The first typical feature of the result is that the stoichiometry was not assigned to an integral ratio such as 1:2 or 2:3, for example. The stoichiometry was determined by a spectral analysis,5) and the obtained values are correct within an experimental error of ± 0.04. So that these results indicate that the completely stoichiometric salts are rather difficult to obtain, being contrary to previous observations in which the experimental accuracy may have obscured the result. There are, however, some good reasons for the nonstoichiometry of the TCNQ complex salts: 1) Missing TCNQ molecules from the normal lattice site does not affect the charge neutrality, the TCNQ molecule itself being multivalent. 2) As the one dimensional system is believed to be unstable toward a structual distortion, there is a possibility that the growing crystal in solution is subjected to such an instability and TCNQ molecules stack with distortions.

In case where some specific cations were used, two forms of crystals were obtained from the same solution, which was another typical feature of Table 1. The crystals marked (I) were those deposited at an early stage of crystallization from a concentrated solution and (II) were those obtained by slow crystallization from the dilute solution after the crystal (I) was removed. According to Ostwald's law of stages, multiple phases of different stabilities can appear in order of their relative stabilities from a solution left in a metastable state; so that at least the salts (I) may be a metastable crystal.$^{5)}$

Figure 1 shows the resistivity and stoichiometry of the synthesized salts plotted against the total number of carbon atoms in N-n-alkyl substituents. The appearance of polymorphs was governed by the cation size or length, for the size of n-C_3H_7Py and n-C_4H_9Py is very similar to that of $C_2H_5\gamma$-Pi and n-$C_3H_7\gamma$-Pi, respectively, and substituted α- or β-Pi salt had no polymorphs. And, while the CH_3Py or C_2H_5Py$(TCNQ)_x$ salt was almost of a 1:2 stoichiometry, those salts with polymorphic modifications had a large deviation from 1:2 stoichiometry. So that the nonstoichiometry is presumably caused by the possibility of the specific salts of assuming polymorphic modifications. From the relation between the resistivities and the kind of cation, the salts were divided sharply into two groups. The salts in the first group consisted of metastable crystals (I) and the

Table 1. Characteristic properties of substituted pyridinium TCNQ complex salts.

Cation		Composition (TCNQ/cation)	Before transition Resistivity ρ_{20} (Ωcm)	Before transition Activation energy (eV)	After transition Resistivity ρ_{20} (Ωcm)	After transition Activation energy (eV)	Remark
Py	(I)	1.65	0.16	0.07			unstable
	(II)	2.09	14	0.10			
CH_3Py		1.96	2600	0.28			
C_2H_5Py		1.92	2900	0.33			
n-C_3H_7Py	(I)	2.45	1.4	0.08	300	0.46	I,$^{1)}$ R$^{2)}$
	(II)	1.88	2000	0.34	500	0.45	I, R
i-C_3H_7Py		1.97	60	0.11	5000	0.44	I
n-C_4H_9Py	(I)	1.86	7.0	0.05	45	0.11	I, R
	(II)	1.67	50	0.14	45	0.11	I, R
s-C_4H_9Py		1.96	7.0	0.14			
i-C_4H_9Py		1.86	200	0.14	30	0.13	I
n-C_5H_{11}Py		1.96	230	0.15	2400	——$^{3)}$	I
n-C_6H_{13}Py		2.11	7.5	0.08	35	0.17	I
$C_2H_5\gamma$-Pi	(I)	2.51	2.0	0.14			
	(II)	1.46	120	0.29			
n-$C_3H_7\alpha$-Pi		2.00	1200	0.26	600	——	I
n-$C_3H_7\beta$-Pi		2.00	950	0.28	14	0.07	I
n-$C_3H_7\gamma$-Pi	(I)	2.91	14	0.15			
	(II)	1.50	1200	0.36	5000	——	I

1) Irreversible transition 2) Reversible transition 3) Not measured

conductivity of each salt was always higher than that of the corresponding polymorph. Especially, a new metastable form of Py(TCNQ)$_X$ (I) had a conductivity of about 10 mho·cm^{-1} (powder sample) which is comparable to that of organic metals of highest conductivity.$^{6)}$ X-Ray and IR measurements suggest that the TCNQ column structure of the salts (I) had almost a monomeric stack but those of the salts (II) had a tetramer stack, so that the difference in the stacking speed of the columns between TCNQ and cation at the growing surface in solution is thought to be one of the essential factor of the appearance of polymorphs.

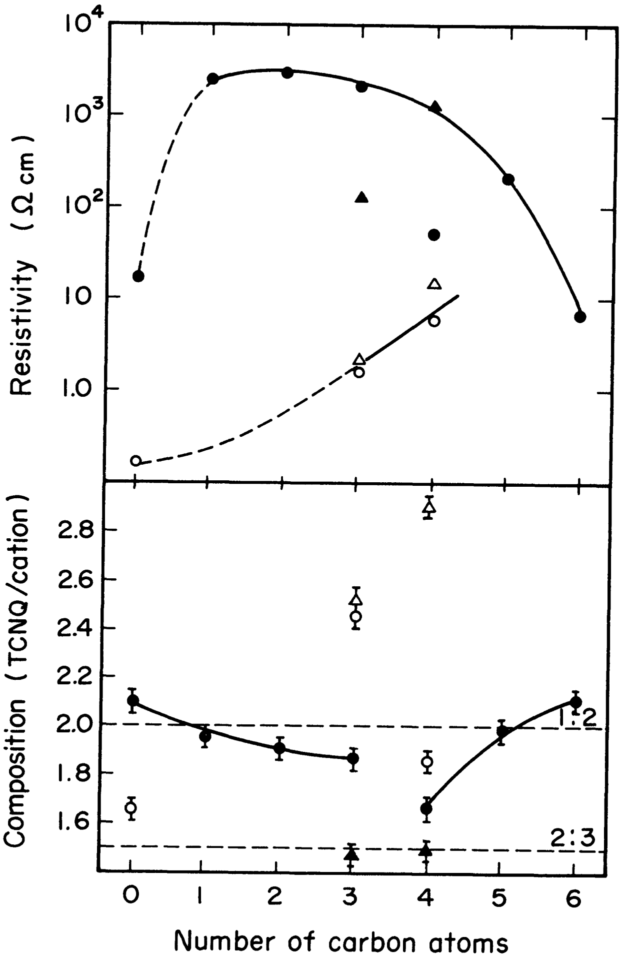

Fig. 1 Resistivity and stoichiometry of n-alkyl·Py (●○) and ·Pi(▲△)-TCNQ against the total number of C atoms. (open: metastable, filled: stable crystals)

The temperature dependence of the electrical resistivity of powder sample of n-C_3H_7Py(TCNQ)$_X$ (I) and (II) were shown in Fig. 2. At the first sweep of temperature, the resistivity of (II) sharply decreased irreversibly at 383 K by a factor of about 50. After the transition, the salt had a reversible transition which is characterized by both an abrupt change in resistivity at 376 K by a factor of about 8, and a temperature hysteresis of about 10 K. The activation energy for the resistivity of higher-temperature modification was 0 eV. In case of salt (I), an irreversible transition appeared in a broad temperature range starting at 390 K, where the resistivity increased by a factor of about 5. Since the transition temperature was varied by temperature rising rate or crystal perfection, the transition may be a polymorphic transition from a metastable to a stable form. After the irreversible transition, the salt became to have the same reversible transition as the salt (II). The result suggests that the initial irreversible transition was controlled by the crystallization process and/or composition of the salt, but the reversible transition was only affected by the kinds of cations and was insensitive to the composition.

Temperature dependence of resistivities of n-C_4H_9Py(TCNQ)$_X$ (I) and i-C_3H_7Py(TCNQ)$_X$ salts are shown in Fig. 3. After two steps of irreversible transition, the n-C_4H_9Py(TCNQ)$_X$ (I) salt exhibited a reversible transition in which the resistivity increased toward the high temperatures by a factor of about 2. This may be the first finding of the phase transition with a positive temperature

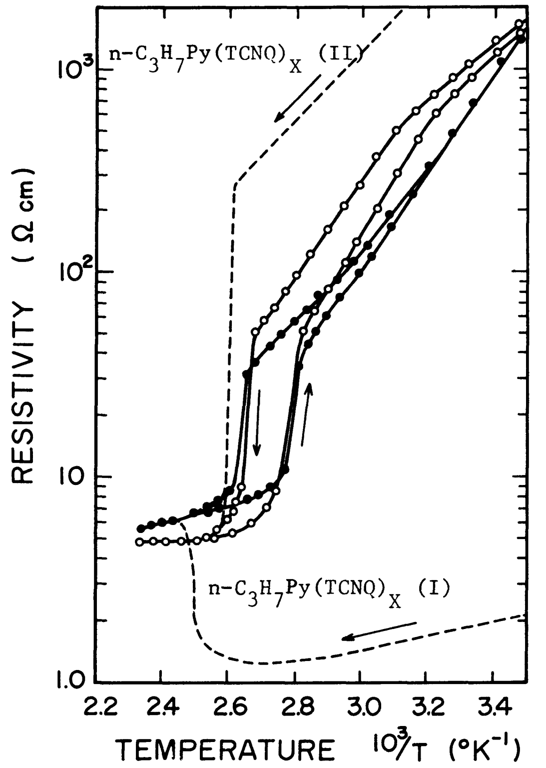

Fig. 2 The specific resistivity vs T^{-1} for $n\text{-}C_3H_7Py(TCNQ)_X$ (I) and (II).

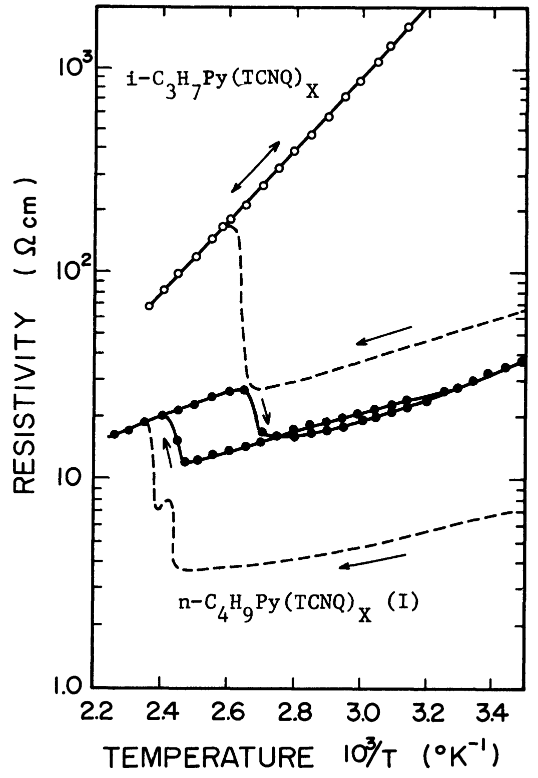

Fig. 3 The specific resistivity vs T^{-1} for $n\text{-}C_4H_9Py(TCNQ)_X$ (I) and $i\text{-}C_3H_7Py(TCNQ)_X$.

coefficient of resistance in the TCNQ system. The results for the $n\text{-}C_3H_7Py$ or $n\text{-}C_4H_9Py(TCNQ)_X$ salts suggest the important role of the alkyl substituent on the nature of transition; rotation or folding of the alkyl substituents may change the interplanar spacing of the TCNQ molecules. The fact that the reversible transition was not observed with the $n\text{-}C_3H_7\gamma\text{-}Pi$ or $C_2H_5\gamma\text{-}Pi(TCNQ)_X$ salts implies the importance of pyridinium ring rotation; the methyl group may obstacle the motion of the cation molecules. In case of the $i\text{-}C_3H_7Py(TCNQ)_X$ salt, only irreversible transition appeared at 383 K. The transition had a definite transition temperature and was not affected by the temperature rise rate or crystal perfection, which contrasts with the irreversible transition of the $n\text{-}C_3H_7Py(TCNQ)_X$ (I). The irreversible transitions can be divided into two groups; a gradual transition from metastable to stable crystal structure and a sharp transition characterized by a difinite transition temperature.

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