理學碩士學位論文

ELECTRICAL TRANSPORT OF POLYMER TCNQ COMPLEX SALTS AND ITS MONOMERIC MODEL COMPOUNDS

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AND ITS MONOMERIC MODEL COMPOUNDS

UNDER THE SUPERVISION OF

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ABSTRACT

Electrical conductivity and thermoelectric power (TEP) of polymer TCNQ complex salts are measured as a function of temperature, and corresponding monomeric model compounds are also measured and compared. The room temperature conductivity of the polymers and its monomeric model compounds show three or four order of magnitude increase as the $[TCNQ^O]/[TCNQ^-]$ ratio increases to 1. The sign of TEP for for all the samples is negative indicating that electrons are the major carriers in these complex salts. Both polymers and monomers show the thermally activated type conductivity but the temperature dependence of conductivity and TEP show large differences. The differences are discussed using the localized band model and hopping model.

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SCHEME CAPTION

Scheme I.   Synthetic procedure of monomeric complex salts

Scheme II.   Synthetic procedure of polymer complex salts

Scheme III. Redox process of TCNQ molecule

FIGURE CAPTION

I. INTRODUCTION

The organic conducting materials have been studied long. Early in this century it was found that a lot of simple organic materials such as benzene, naphthalene, and anthracene showed detectable conductivity. Later it was assumed that the π−electrons in organic double bonds played the important role in electrical conduction. In 1960, TCNQ (7,7,8,8−tetracyanoquinodimethan) was synthesized in DuPont company, which was a very strong electron acceptor.[1] Thereafter a lot of one−dimensional single crystallic charge transfer complex salts were synthesized using TCNQ and other organic molecules and studied widely. TTF−TCNQ, NMP−TCNQ, and $\beta-(BEDT-TTF)_2I_3$ are some examples.[2~11] These organic molecules have 2−dimensional planar structure with large molecular weight and the resulting donor−acceptor charge transfer complex salts have quasi−one−dimensional structure.[2,3,5] This system gave the incentive for the further study of one−dimensional system. Recently active researches are succeeded in the field of organic superconductor.[9,10,11]

On the other hand, a great deal of studies have been devoted to the conjugated conducting polymers. In 1971,

Shirakawa found that acetylene could be polymerized to thin film form with good mechanical properties.[12] Later MacDiarmid and Heeger found that I_2 or AsF_6- doped polyacetylene showed large conductivity.[13] Recently $FeCl_4-$ doped stretched oriented polyacetylene showed highest conductivity 30000 $(\Omega cm)^{-1}$ in our laboratory. Another conducting polymers such as PAn, PP, PPP, and PT were also studied extensively.[14~17]

In the meanwhile, it was found that organic molecule TCNQ could be substituted into the polymer chain in the form of radical—anion salt, and that conductivity increased drastically doping by neutral TCNQ.[18~20] The polymer chain should contain the effective cations mainly N^+ in pyridine ring which interact coulombically with TCNQ radical—anion ($TCNQ^-$). It was difficult that the polymer chain contained both N^+ cations and proper conjugated structure. Until now, a series of experiments were performed in this structure by varying the intercation distance, modifying the chain structure, and varying the doping ratio.[20~25] In this experiment, polymer TCNQ complex salts and its monomeric model compounds with the molar ratio $y=[TCNQ^o]/[TCNQ^-]$ 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5 were prepared, whose polymer backbone unit was

composed of one benzene, two vinylene, two pyridine ring, and some methyl chain.[26,27] For each sample the D.C conductivity and TEP were measured as a function of temperature from 300 K to 10 K.

Chemically, the purpose of this experiment is to study the effect of the intercation distance and the conjugated structure in chain to conductivity. Physically, it is to find the possible conduction mechanism and to determine what is the important variable.

In section II, I will give a simple description of sample preparation. Experimental techniques are followed in section III. And the results and discussions are given in section IV. Finally in section V, I will give a brief summary.

II. SAMPLE PREPARATION

The scheme I shows the synthetic procedure of mono—meric complex salts.[26,27] Benzene, vinylene, pyridine, and butane were combined to the monomer backbone (III) (N,N'—di—n—butyl— 1,4—bis[β—pyridyl—4—vinyl] benzene bro—mide). Reacting with LiTCNQ, Br$^-$ in compound (III) was displaced by TCNQ$^-$ forming the monomeric TCNQ simple salt. Now by adding neutral TCNQ to compound (IV), monomeric TCNQ complex salts were formed. The molar ratio $y=$ [TCNQ^o]/[TCNQ$^-$] were prepared to 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5. Each compound in the synthetic procedure was identified by IR, and NMR spectrum, and the composion y were confirmed by UV-visible spectroscopy.

Polymer complex salts were synthesized similarly along the scheme II.[26,27] Benzene, vinylene, pyridine, and hexamethylene were combined to the polymer backbone (VI) (poly [hexamethylene-1,4-bis (β-pyridyl-4-vinyl) benzene bromide]). Reacting with LiTCNQ polymer TCNQ simple salt was formed, and then adding the neutral TCNQ polymer TCNQ complex salts were formed. The molar ratio y were the same as the monomer. Structure and composions were confirmed by the same method.

III. EXPERIMENTAL TECHNIQUES

1. D.C conductivity

General 4-probe conductivity measurements were per-
formed as a function of temperature from 300 K to 10 K.
Our samples are power form and must be pressed into pallet
to perform the measurements. We make the pallet with the
diameter 1 cm and 1 mm thickness under pressure 400
Kgf/cm^2, then cut the sample to the desired size. Simple
block diagram of the conductivity measurement system is in
Fig.1. Displex system is used to lower the temperature
to liquid helium temperature and 3700 APDE digital tempe-
rature indicator/controller maintain the given temperature.
Conductivity holder is very simple. Thin quartz plate is
attached to the Cu holder by the G.E.7031 varnish which
gives good thermal contact and also good electrical insu-
lation. Samples are laid on the quartz plate and Electro-
dag-502 paint contact or silver paint contact is used to
contact the platinum electrode on the sample. Keithley
220 programmable current source supplies the constant
current to sample under the allowed impedance range which
can also change the current polarity. Keithley 181 Nano-
voltmeter is used to measure the voltage drop. Keithley

642 Electrometer is used for high impedance sample.

2.   Thermoelectric power

TEP measurements were also carried out in the same temperature range.   The block diagram of TEP measurement system is illustrated in Fig.2, and Fig.3 shows the TEP holder.   Cold OFHC plate is glued to the Cu holder by G.E. 7031 varnish and hot OFHC plate is supported by plexiglass rod on the Cu holder.   270 Ω carbon resister is glued underneath the hot OFHC plate with G.E. 7031 varnish which acts as a heater.   Cu—constantan thermocouple junctions are glued to each OFHC plate with G.E. 7031 varnish to obtain the electrical insulation and optimal temperature reading.   Constantan wire must be thin and long enough to prevent the direct heat transfer through the constantan wire.   The copper wires for the voltage measurement are soldered on each plates.   The whole setting is surrounded by Cu cap to obtain the isothermal condition.   For the TEP measurement sample is mounted on the top of the two plates by silver paint contact.   At each measurement the temperature of the holder is fixed using the temperature controller and heating the carbon resister the temperature gradient ΔT is set up across the sample.   Typical tempera—

ture gradient is about 1~2 K. By measuring ΔV and ΔT simultaneously, we can determine the TEP of the sample by

$$\frac{\Delta V}{\Delta T} = \frac{S_{sample} - S_{Cu}}{S_{DTC}}$$

where S_{DTC} is the TEP of the differential thermocouple for the temperature gradient reading.

I will mention the calibration process briefly. We measure $\Delta V/\Delta T$ and we need S_{DTC} and S_{Cu} to obtain S_{sample}. To determine S_{DTC} and S_{Cu} of the holder we use two reported results, $S_{constantan-Cu}$ and S_{Pb}. First we use the constantan wire as a sample. The configuration is fully symmetric but $\Delta V/\Delta T$ is larger than 1 due to the incomplete thermal contact between the thermocouple junction and the OFHC plate. Therefore

$$S_{DTC} = \frac{S_{constantan-Cu}}{(\Delta V/\Delta T)}$$

Secondly we use Pb as a sample which is good to calibrate S_{Cu}, because S_{Pb} is small enough and comparable to S_{Cu}. Then using the known result S_{Pb}

$$S_{Cu} = S_{Pb} - \frac{\Delta V}{\Delta T} S_{DTC}$$

Using the calibrated S_{DTC} and S_{Pb}, the TEP of the sample is given by

$$S_{sample} = \frac{\Delta V}{\Delta T} S_{DTC} + S_{Cu}$$

IV. RESULTS AND DISCUSSIONS

Figure 4 shows the room temperature conductivity of all the samples. Both polymers and monomers show the 3 or 4 order of magnitude increase of conductivity as the molar ratio $y=[TCNQ^0]/[TCNQ^-]$ increases to 1 which indicates that TCNQ molecular stack is more important for the electrical conduction than the polymer backbone itself. Maximum conductivity of polymer is 6.1×10^{-3} $(\Omega cm)^{-1}$ and that of monomer is 6.2×10^{-2} $(\Omega cm)^{-1}$.

For $y \geq 0.5$ conductivities are more or less the same and do not vary as much as y varies. This indicates that electrical transport is not stoichiometric to y.

It is worth noting that for $y \geq 0.5$ monomers have higher conductivity than polymers and for $y \leq 0.3$ polymers have higher conductivity than monomers. Generally, monomeric model compounds show higher conductivity than polymer. This is inferred from the fact that polymer chain gives to the TCNQ molecule the periodic condition to be satisfied which interrupts the more compact stack of TCNQ molecule and gives lower conductivity. This is consistent to the previously reported results.[20] But for $y \leq 0.3$ TCNQ density is low, so the polymer chain conduction due

to the conjugated π-electron is more important. So polymers have higher conductivity due to the long range periodicity.

Our results show that conductivity maximum is at y=1.0 and decrease a little for y=1.5. This must be compared with the previously reported results which show maximum conductivity at various y.[20,21,24,25] Maximum conductivity depends on the intercation (N^+) distance and the chain structure. If there exists other molecular structure perpendicular to the chain, $TCNQ^o$ doping will be difficult. Also, if the intercation (N^+) distance is too small, $TCNQ^o$ doping will be difficult. Our data show maximum conductivity at y=1.0 without any other perpendicular molecular structure. From this we can see that the optimal spacing between TCNQ molecules is about 7~8 Å. But we can also see that the absolute maximum conductivity decrease if the intercation distance is too long.

Scheme III shows the TCNQ molecule and its ionization process. Neutral TCNQ is the fully oxidized form and one electron addition gives semireduced radical—anion, and one more electron addition gives the fully reduced dianion. The redox potential is $E_1 = 0.127$ V and $E_2 = -0.219$ V respectively, i.e, $TCNQ^o$ and $TCNQ^{\bar{\cdot}}$ are more stable form

than $TCNQ^{2-}$. This relation explains simply the conducti-
vity enhancement by the $TCNQ^{o}$ addition. TCNQ simple salt
has only $TCNQ^{-}$ and one electron in $TCNQ^{-}$ hop to the neigh-
boring $TCNQ^{-}$ forming ($TCNQ^{o}-TCNQ^{2-}$) pairs, which requires
large energy. However, TCNQ complex salts have both $TCNQ^{-}$
and $TCNQ^{o}$ and one electron in $TCNQ^{-}$ can hop to the neigh-
boring $TCNQ^{o}$ without making $TCNQ^{2-}$, which requires no
energy. So complex salts have higher conductivity.

Figure 5 and 6 show the temperature dependence of
conductivity $Ln(\sigma/\sigma_{RT})$ vs. $1/T$ for monomers and polymers
respectively, and Figure 7 shows the corresponding activa-
tion energy. Both of them show the semiconductor type
thermally activated behavior, but we can see the large
differences. Monomers have two different temperature
regions. Slope of $Ln(\sigma/\sigma_{RT})$ vs. $1/T$ for T>200 K is
smaller than that for T<200 K, and the slopes are more or
less the same for all the samples except y=0.1 sample. At
T>200 K the activation energy is about 70 meV, and at
T<200 K it is about 90 meV. However, all the polymer
samples have consistent slope through the whole tempera-
ture range and the activation energy is about 100 meV.
This will be discussed later.

The activation energy data also show the nonstoichio-

metric behavior. y=0.1 sample shows high activation energy with small conductivity. We can see that the activation energy is reduced largely with the complex formation.

Figure 8 shows the room temperature TEP for all the samples except y=0.1 sample. y=0.1 sample is so resistive that thermal fluctuations are too large w.r.t. the small TEP signal. So, TEP measurement is difficult. All the samples show the negative TEP indicating that electrons are the major carriers which come from the radical-anion of TCNQ (TCNQ$^-$). Polymer complex salts have larger TEP about -60 μV/K and show large variation as y varies. On the other hand, monomeric complex salts have a rather constant TEP about -30 μV/K. Monomers have higher conductivity and lower TEP.

Figure 9 and 10 show the temperature dependence of TEP for monomers and polymers respectively. These also show large differences. Monomers have two different temperature regions. For T > (200~240) K TEP increase as T increase and for T < (200~240) K TEP increase rapidly as T decrease which is best fitted to 1/T plot. On the other hand, polymers have a rather constant TEP w.r.t. temperature. This result is somewhat consistent with the conductivity data.

To analyze these results more systematically, we begin with the general theory of conductivity and TEP. Boltzmann equation approach reduces to the following electric current under the electric field and temperature gradient,[31]

$$J = e^2 \mathcal{K}_0 \cdot E + \frac{e}{T} \mathcal{K}_1 \cdot (-\nabla T) \tag{1}$$

where the transport coefficients are defined by

$$\mathcal{K}_n = \frac{\tau}{4\pi^3 \hbar} \int\int vv (\epsilon - \zeta)^n \left(-\frac{\partial f^0}{\partial \epsilon} \right) \frac{ds}{v} d\epsilon \tag{2}$$

Under the isothermal condition, $\nabla T = 0$, the electrical conductivity is

$$\sigma = e^2 \mathcal{K}_0 \tag{3}$$

Temperature gradient in a sample with an open circuit, $J=0$, give rise to an electric field, which defines TEP S.

$$E = \frac{1}{eT} \frac{\mathcal{K}_1}{\mathcal{K}_0} \nabla T = S \nabla T \tag{4}$$

$$S = \frac{1}{eT} \frac{\mathcal{K}_1}{\mathcal{K}_0} \tag{5}$$

In dilute limit simple kinetic consideration gives an intuitive interpretation of conductivity,

$$\sigma = \frac{ne^2 \tau}{m} = n|e|\mu \tag{6}$$

where n is the carrier concentration and μ is the carrier mobility. This states that carrier concentration and mobility determine the conductivity.

Diffusion concepts give another interpretation of TEP.[30,32,33]

$$J = -\sigma \nabla\Phi + eD \nabla n \qquad (7)$$

Using the generalized Einstein relation

$$\sigma = \frac{e^2 D}{(\partial\zeta/\partial n)_T} \qquad (8)$$

equation (7) becomes,

$$J = -\sigma \nabla\Phi + \frac{\sigma}{e}(\partial\zeta/\partial T)_n + \frac{\sigma}{e} \nabla\zeta$$

$$= -\sigma \nabla (\Phi - \frac{\zeta}{e}) + \frac{\sigma}{e} (\partial\zeta/\partial T)_n \nabla T \qquad (9)$$

where $-\nabla (\Phi - \frac{\zeta}{e})$ is the thermal EMF at J=0. So

$$S = \frac{1}{e} (\partial\zeta/\partial T)_n = \frac{1}{e} [\frac{\partial}{\partial T}(\frac{\partial F}{\partial n})_T]_n$$

$$= \frac{1}{e}(\frac{\partial S}{\partial n})_T \qquad (10)$$

where S is an entropy of the system. From this results, we can see that TEP is a zero current transport coefficient, and is a measure of the entropy per carrier.

For a direct band calculation, the following form is more convenient.[34~37]

$$\sigma = -e \int N(E) \ \mu(E) \ KT \ \frac{\partial f(E)}{\partial E} \ dE \qquad (11)$$

where $f(E) = \dfrac{1}{1 + \exp[(E-E_F)/KT]}$

and

$$S = -\frac{K}{e} \int \frac{E - E_F}{KT} \ \frac{\sigma(E)}{\sigma} \ dE$$

$$= -\frac{K}{e} \ \frac{\displaystyle\int \mu(E) \ N(E) \ \frac{E - E_F}{KT} \ f(1-f) \ dE}{\displaystyle\int \mu(E) \ N(E) \ f(1-f) \ dE} \qquad (12)$$

This shows that TEP contains the integration by energy over the occupied energy band both in numerator and denominator. So energy independent terms are cancelled.

Now consider these in our case. We find that the optimum distance between TCNQ molecules is about 7~8 Å. In monomer, we think that TCNQ molecules can stack more closely than this. Macroscopically monomers are largely disordered but each monomer unit gives good short range order in the range of 30 Å. In this case, localized band can be formed above the Fermi level, and has low mobility

in nature. The addition of neutral TCNQ which is n-type doping gives donor level in the middle of the energy gab. Carriers are activated from the donor level to the local—ized state band and its mobility is also activated giving the hopping conduction. In this band structure, eq. (11) becomes

$$\sigma = eN(E_A)KT\mu_{hop}\exp[-(E_A - E_F)/KT] \tag{13}$$

assumming the constant density of states, where μ_{hop} is the hopping mobility and E_A is the localized band edge. Thermally activated hopping gives the mobility of the form

$$\mu_{hop} = \frac{1}{6} \nu_{ph}\frac{eR^2}{KT} \exp[-W/KT] \tag{14}$$

So the conductivity of the hopping conduction in localized band has the form

$$\sigma_{hop} = \sigma_{o.hop} \exp[-(E_A-E_F+W)/KT] \tag{15}$$

where

$$\sigma_{o.hop} = \frac{1}{6} \nu_{ph} e^2R^2N(E_A) \tag{16}$$

This is the low temperature case of monomers. At high temperature, the carrier density is saturated exhaust—ing all the donor levels. In this case only mobility is

activated and the conductivity becomes

$$\sigma_{hop} = \sigma_{o.hop} \exp[-W/KT] \qquad (17)$$

On the other hand, the TEP equation (12) yields

$$S = -\frac{k_B}{e} \left(\frac{E_A - E_F}{k_B T} + A \right) \qquad (18)$$

where A is the kinetic term which depends on the scatter-
ing process. If the carrier density is saturated, eq.
(18) becomes constant. The experimental results are
fitted well to this model.

In polymer complex salts, TCNQ molecules can not
stack more closely than 7~8 $\overset{o}{A}$ due to the periodicity.
Although the long range order is possible, localized bands
are not formed because of the long intermolecular distance.
Simply narrow donor bands are formed at Fermi level. In
this case charges are transported by the thermally acti-
vated hopping between the localized states. Carrier
density is not activated and only mobility is activated.
Conductivity eq. (11) becomes

$$\sigma_{hop} = \sigma_{o.hop} \exp[-w/kT] \qquad (19)$$

Conductivity data of polymers are fitted well to this

form. However, TEP analysis of polymers needs more consi-
derations.

For the narrow band materials with large manybody
interactions, the Boltzmann equation approach does not
work well.[38,39] Instead, the Kubo formalism of an
interacting system can be used.[38,40] The TEP is given by

$$S = - \frac{S^{(2)}/S^{(1)} - \mu/e}{T} \tag{20}$$

where $S^{(1)}$, $S^{(2)}$ are the transport coefficients and μ is
the chemical potential. The first term represents the
energy transport which we assume negligible and the second
term is the entropy term. From the definitions of the
chemical potential μ and entropy σ of the system with the
degeneracy g.

$$\frac{\mu}{T} = - (\partial\sigma/\partial N)_{E.V} \tag{21}$$

$$\sigma = K \ Ln \ (g) \tag{22}$$

TEP in the high temperature limit becomes

$$S(T \to \infty) = \frac{\mu}{eT} = - \frac{k}{e} \frac{\partial \ Ln(g)}{\partial N} \tag{23}$$

This eq. (23) also indicates that TEP is a measure of the
entropy per carrier.

For spinless fermion, Heikes first calculated TEP in this way [30,32,41]

$$S(T \to \infty) = -\frac{k}{e} \, Ln \, [(1-\rho)/\rho] \qquad (24)$$

where ρ is the ratio of particles to sites.

Later Chaikin generalized this Heikes formula to the interacting system with spin.[38] For strong on-site repulsion, TEP becomes

$$S(T \to \infty) = -\frac{k}{e} \, Ln \, [2(1-\rho)/\rho] \qquad (25)$$

Our data satisfy this formula well, which shows the temperature independent behavior. $S=-60$ µV/K of polymers needs $\rho=0.5$ and $S=-34$ µV/K for y=0.3 of polymer needs $\rho=0.57$.

Now compare our results to these models. The activation energy of mobility W can be considered as the intermolecular potential height.[39,42~45] For monomer potential height is of the order of 70 meV whereas it is 100 meV for polymer. We can see that monomers have lower potential height, which indicates the smaller distance between TCNQ molecules. The carrier activation energy of monomer at low temperature is about 10~20 meV from the conductivity data and is about 3.5 meV from TEP data. I think that this results from the fact that TEP is an intrinsic

property of the polymer and monomer itself while conduc-
tivity is the composite of interchain and intrachain
conduction. From this point of view we can see that the
intrachain conduction is more conductive and have smaller
activation energy. From the monomer data, the carrier
saturation temperature is about 200~240 K which corres-
ponds to 17~20 meV.

We note that almost all conductivity data of monomer
and polymer show the slope change at very low temperature.
I think this is the range where electrons are transported
by the variable range hopping between the localized states
at Fermi level which is best fitted to $T^{(-1/4)}$ plot. [34~36]

Summarizing our results, monomers and polymers show
different behavior. Monomers have localized band above
the Fermi level and both the carrier density and the
mobility are activated depending on the temperature range,
while polymers have only narrow donor band at Fermi level
and only mobility is activated. But the main feature of
conduction mechanism is the thermally activated hopping
between the localized states both for polymer and monomer.
Conductivity and TEP data show good consistence to this
model.

V. CONCLUSIONS

It is found that the TCNQ molecular stack is more important to charge conduction than the polymer backbone itself. Monomers and polymers show different conduction mechanism which results from the different intermolecular distance. Monomers have localized state band above the Fermi level and both band type and hopping type conduction exist, while polymers have only narrow donor band at Fermi level and hopping type conduction is dominent. The main feature of conduction is the thermally activated hopping between localized TCNQ molecules. The important variable to determine the conduction mechanism is the intermolecular distance.
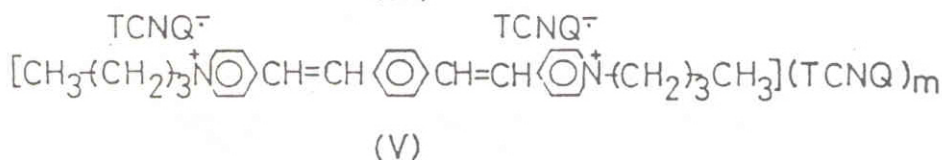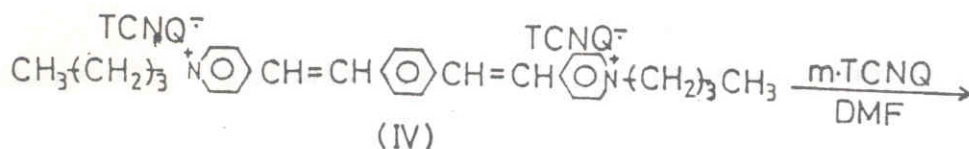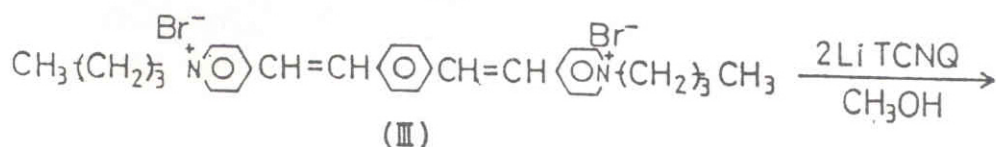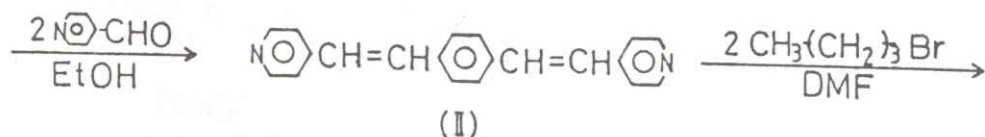
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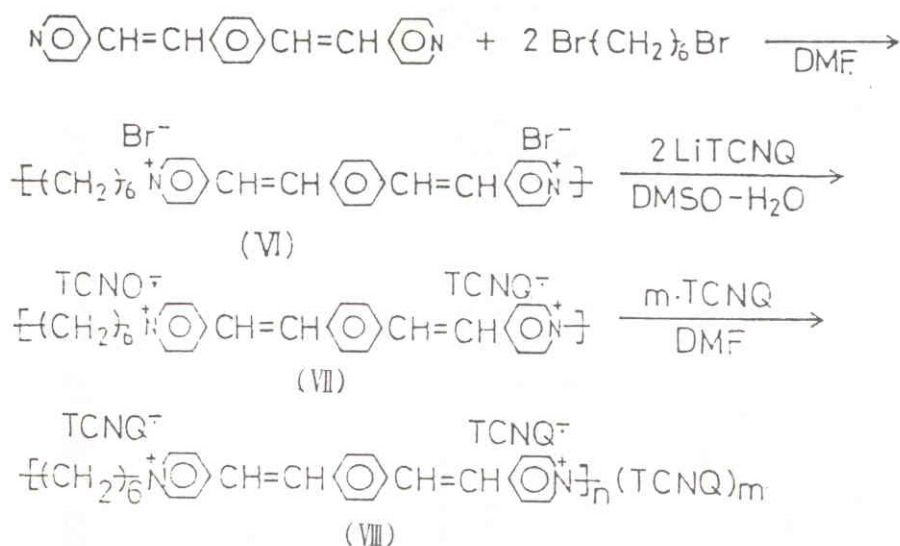   J. Polym. Sci. Polym. Chem. Ed. <u>17</u>, 561 (1979).

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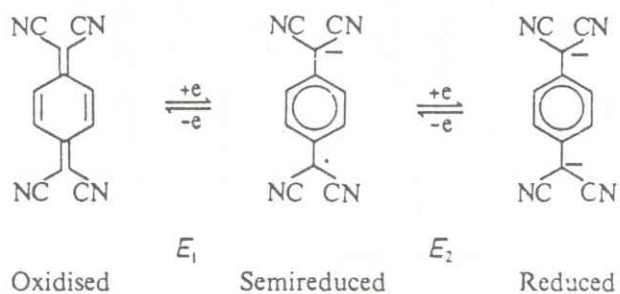   Cambridge Univ.press (1979).

$$ClCH_2\langle O \rangle CH_2Cl \ + \ \emptyset_3P \ \xrightarrow[DMF]{} \ Cl^-\emptyset_3\overset{+}{P}CH_2\langle O \rangle CH_2\overset{+}{P}\emptyset_3Cl^-$$

(I)

$$\xrightarrow[EtOH]{2\,N\langle O \rangle\text{-}CHO} \ N\langle O \rangle CH=CH\langle O \rangle CH=CH\langle O\,N \ \xrightarrow[DMF]{2\,CH_3\langle CH_2\rangle_3\,Br}$$

(II)

$$CH_3\langle CH_2\rangle_3 \overset{Br^-}{\underset{+}{N}}\langle O \rangle CH=CH\langle O \rangle CH=CH\langle O\overset{Br^-}{\underset{+}{N}}\langle CH_2\rangle_3\,CH_3 \ \xrightarrow[CH_3OH]{2\,Li\,TCNQ}$$

(III)

$$CH_3\langle CH_2\rangle_3 \overset{TCNQ^{\overline{\cdot}}}{\underset{+}{N}}\langle O \rangle CH=CH\langle O \rangle CH=CH\langle O\overset{TCNQ^{\overline{\cdot}}}{\underset{+}{N}}\langle CH_2\rangle_3\,CH_3 \ \xrightarrow[DMF]{m\cdot TCNQ}$$

(IV)

$$[CH_3\langle CH_2\rangle_3 \overset{TCNQ^{\overline{\cdot}}}{\underset{+}{N}}\langle O \rangle CH=CH\langle O \rangle CH=CH\langle O\overset{TCNQ^{\overline{\cdot}}}{\underset{+}{N}}\langle CH_2\rangle_3\,CH_3](TCNQ)_m$$

(V)

$$m = 0.6 \quad 1.0 \quad 1.4 \quad 2.0 \quad 3.0$$

Scheme I. Synthetic procedure of Monomeric complex salts.

$$N\bigcirc CH=CH\bigcirc CH=CH\bigcirc N \ + \ 2\,Br\{CH_2\}_6\,Br \ \xrightarrow{DMF}$$

$$\overset{Br^-}{\underset{}{}}\ \overset{Br^-}{\underset{}{}}$$

$$\left[(CH_2)_6\ \overset{+}{N}\bigcirc CH=CH\bigcirc CH=CH\bigcirc \overset{+}{N} \right] \ \xrightarrow{\ 2\,LiTCNQ\ }_{DMSO-H_2O}$$

(VI)

$$\overset{TCNQ^{\bar{\ }}}{\underset{}{}}\ \overset{TCNQ^{\bar{\ }}}{\underset{}{}}$$

$$\left[(CH_2)_6\ \overset{+}{N}\bigcirc CH=CH\bigcirc CH=CH\bigcirc \overset{+}{N} \right] \ \xrightarrow{\ m\cdot TCNQ\ }_{DMF}$$

(VII)

$$\overset{TCNQ^{\bar{\ }}}{\underset{}{}}\ \overset{TCNQ^{\bar{\ }}}{\underset{}{}}$$

$$\left[(CH_2)_6\ \overset{+}{N}\bigcirc CH=CH\bigcirc CH=CH\bigcirc \overset{+}{N} \right]_n (TCNQ)_m$$

(VIII)

Scheme II.   Synthetic procedure of polymer complex salts.

| Oxidised | E_1 | Semireduced | E_2 | Reduced |

Scheme III.   Redox process of TCNQ molecule,

$$E_1 = 0.127\ V, \quad E_2 = -0.219\ V.$$
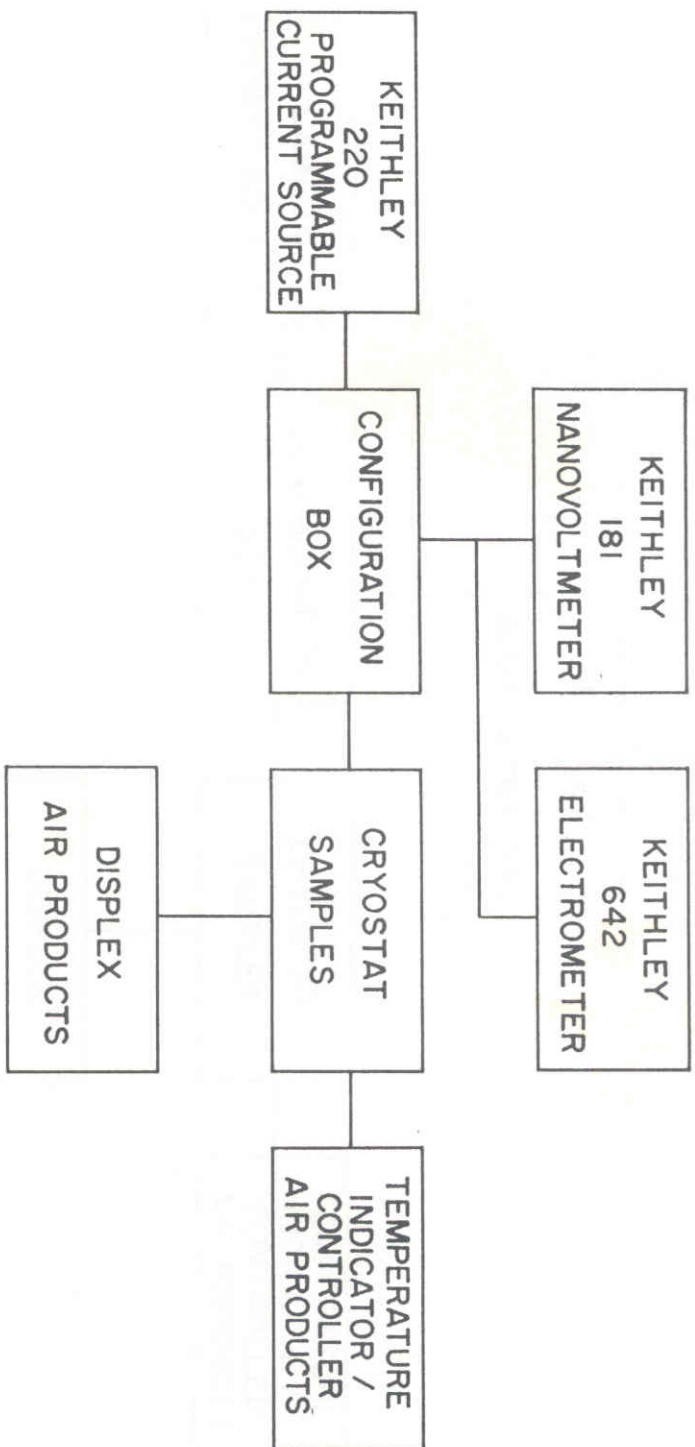
Fig. 1 Schematic diagram of the conductivity measurement system
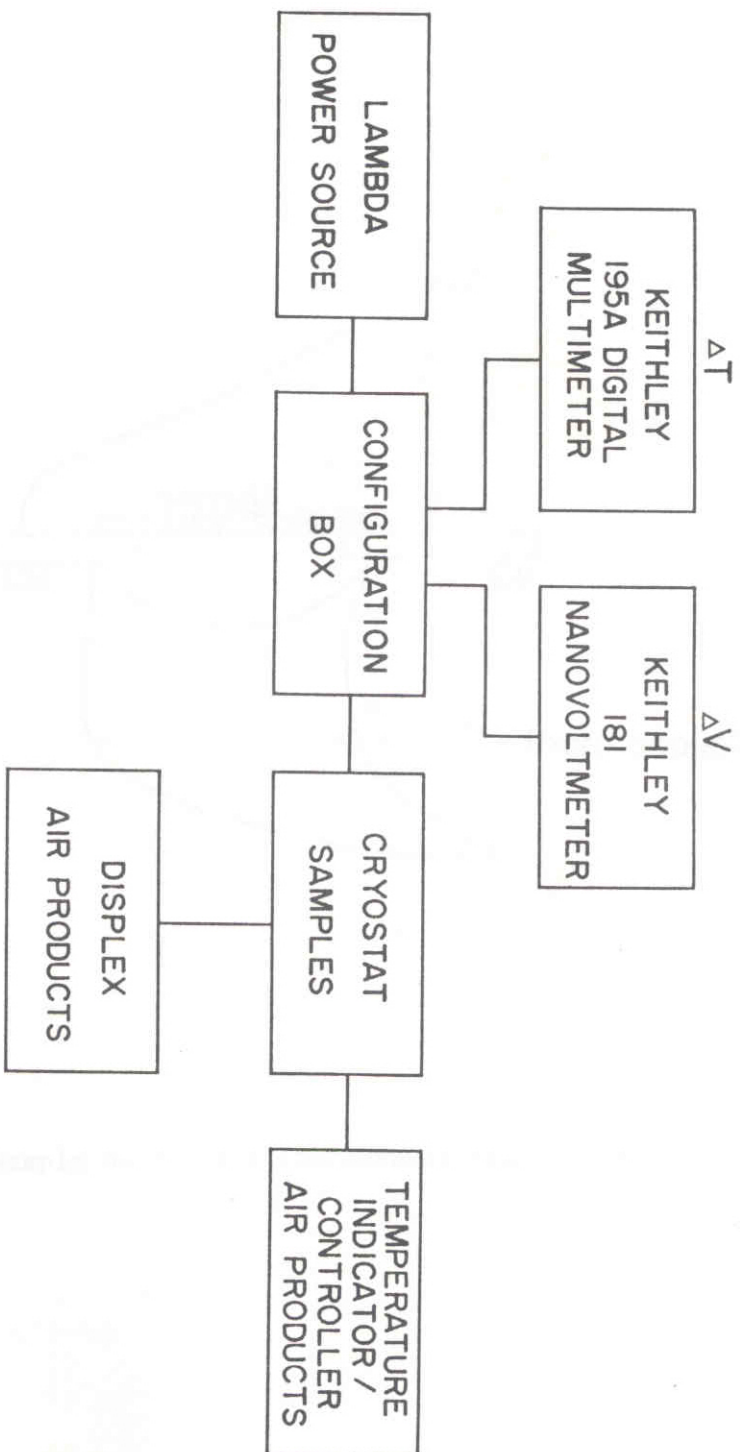
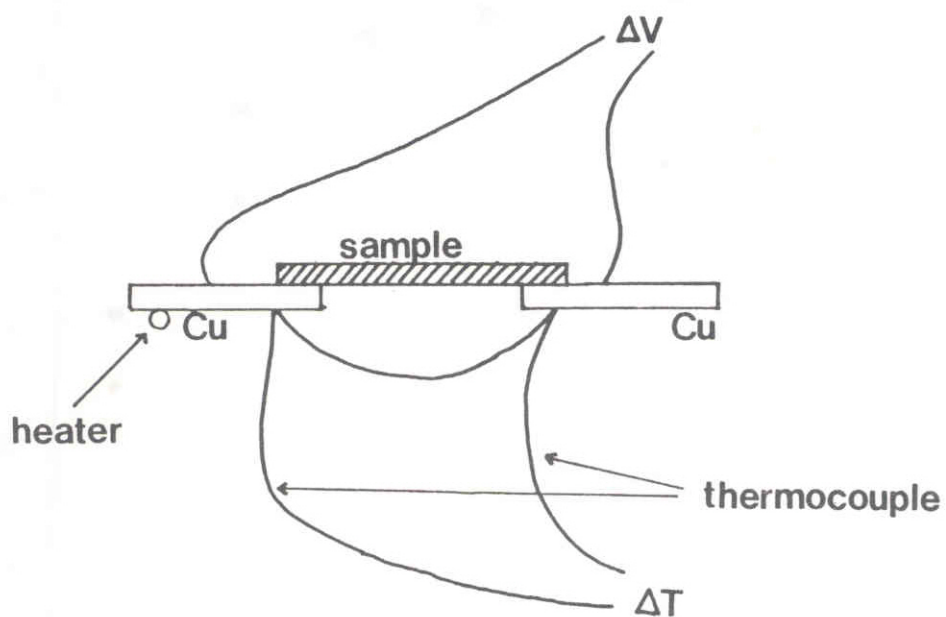Fig. 2 Schematic diagram of the thermoelectric power measurement system

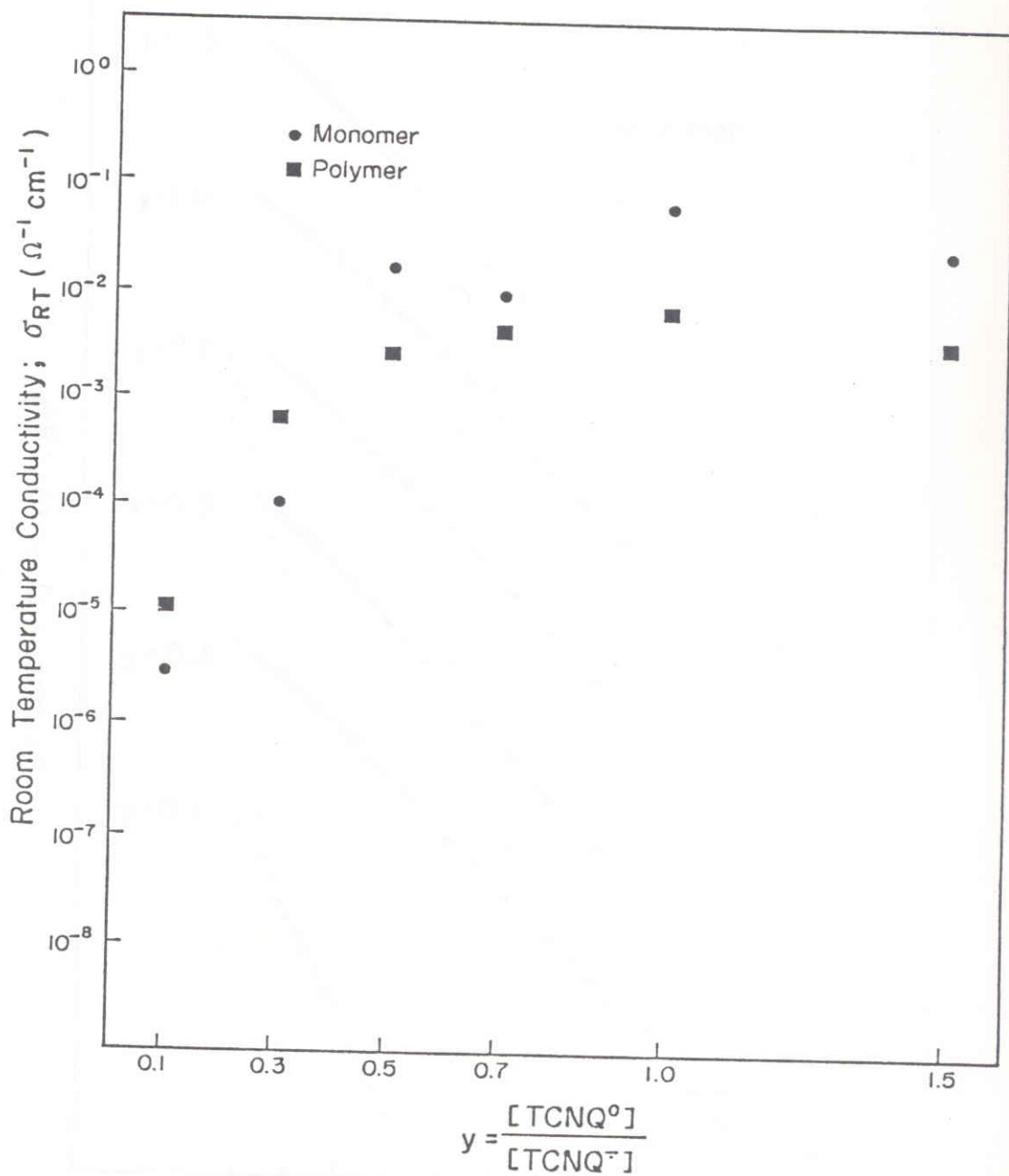Fig. 3 Sample holder for thermopower measurement

Fig. 4 Room temperature conductivity of polymer TCNQ complex salts and its monomeric model compounds
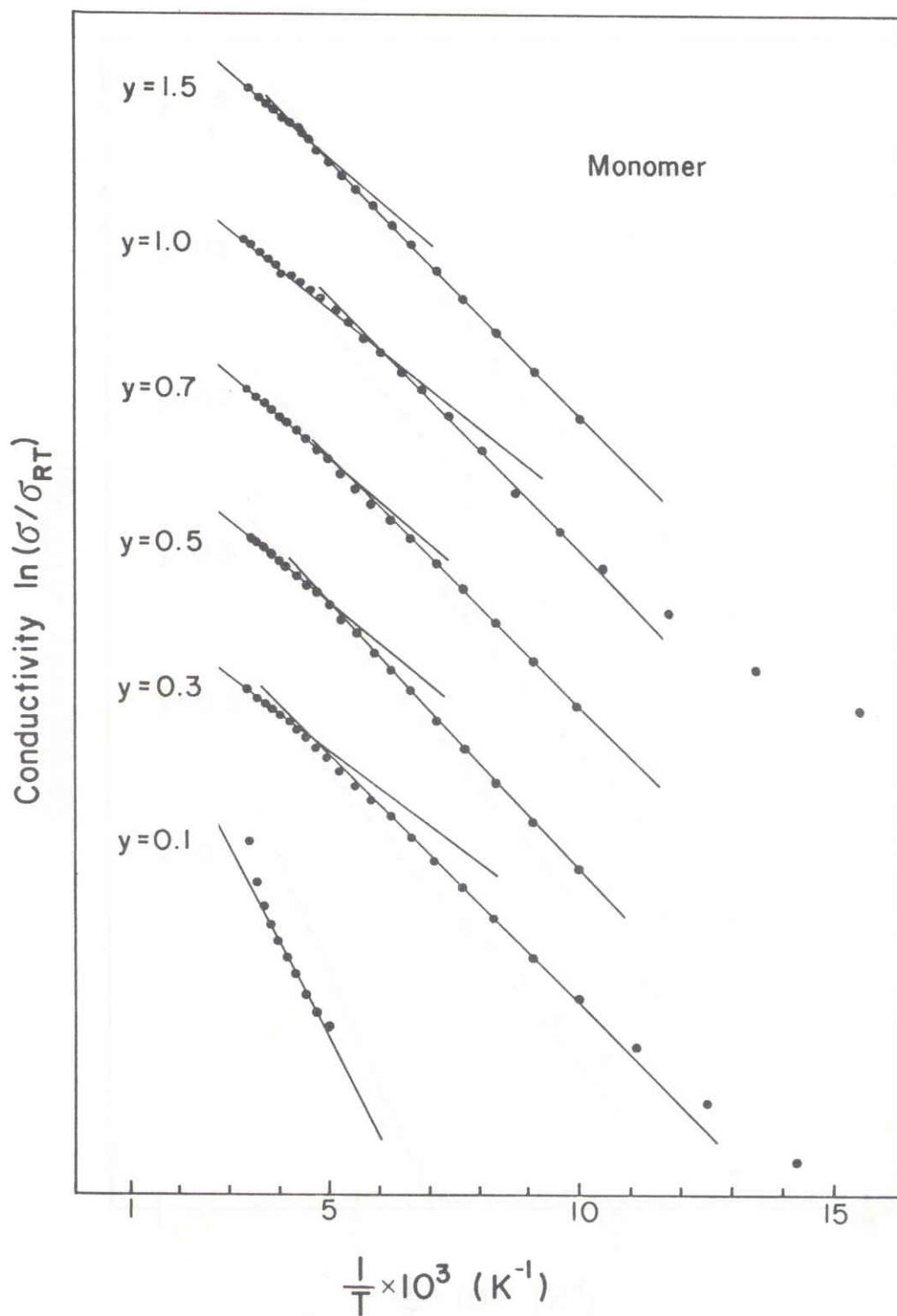
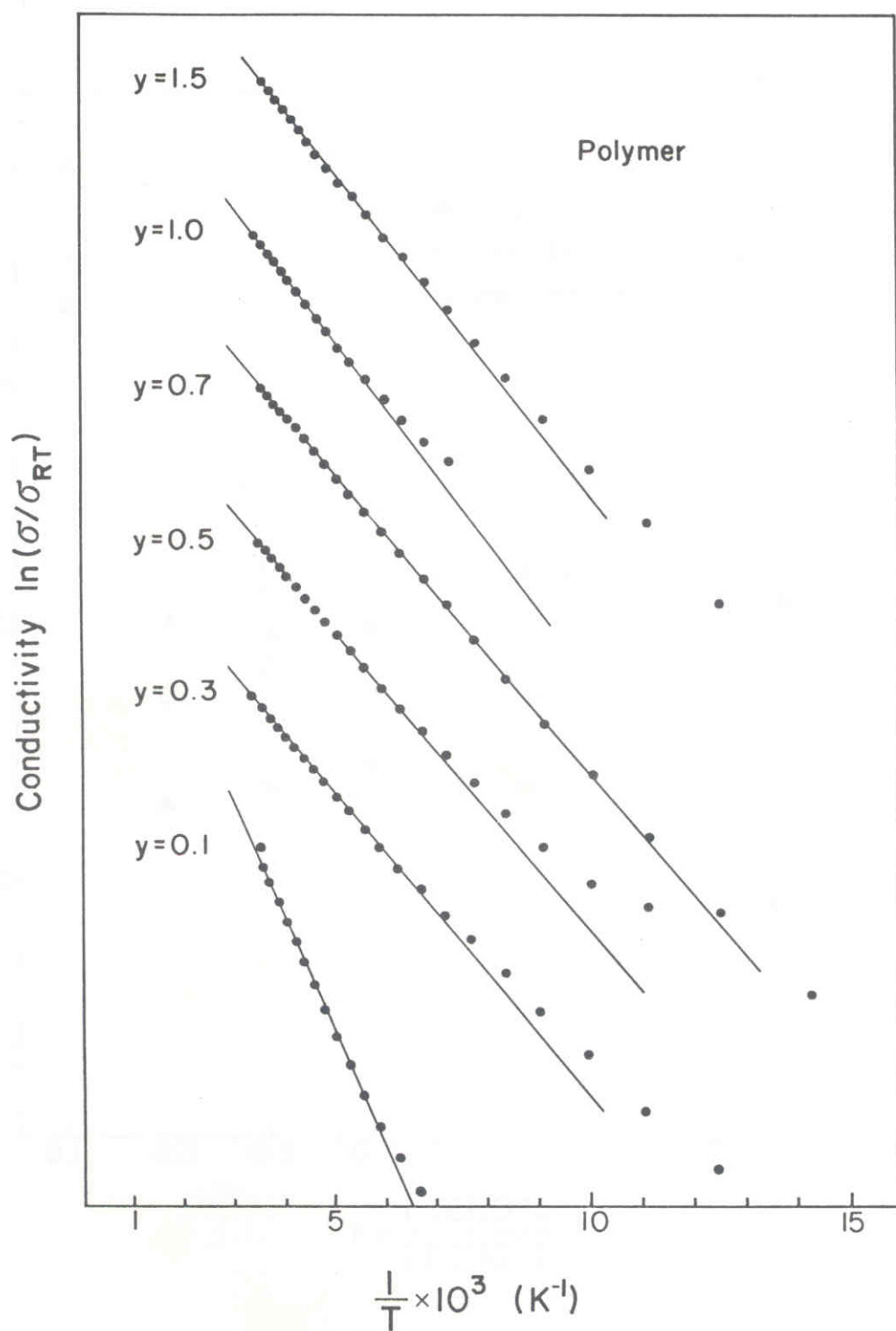Fig. 5 Temperature dependence of conductivity of monomers

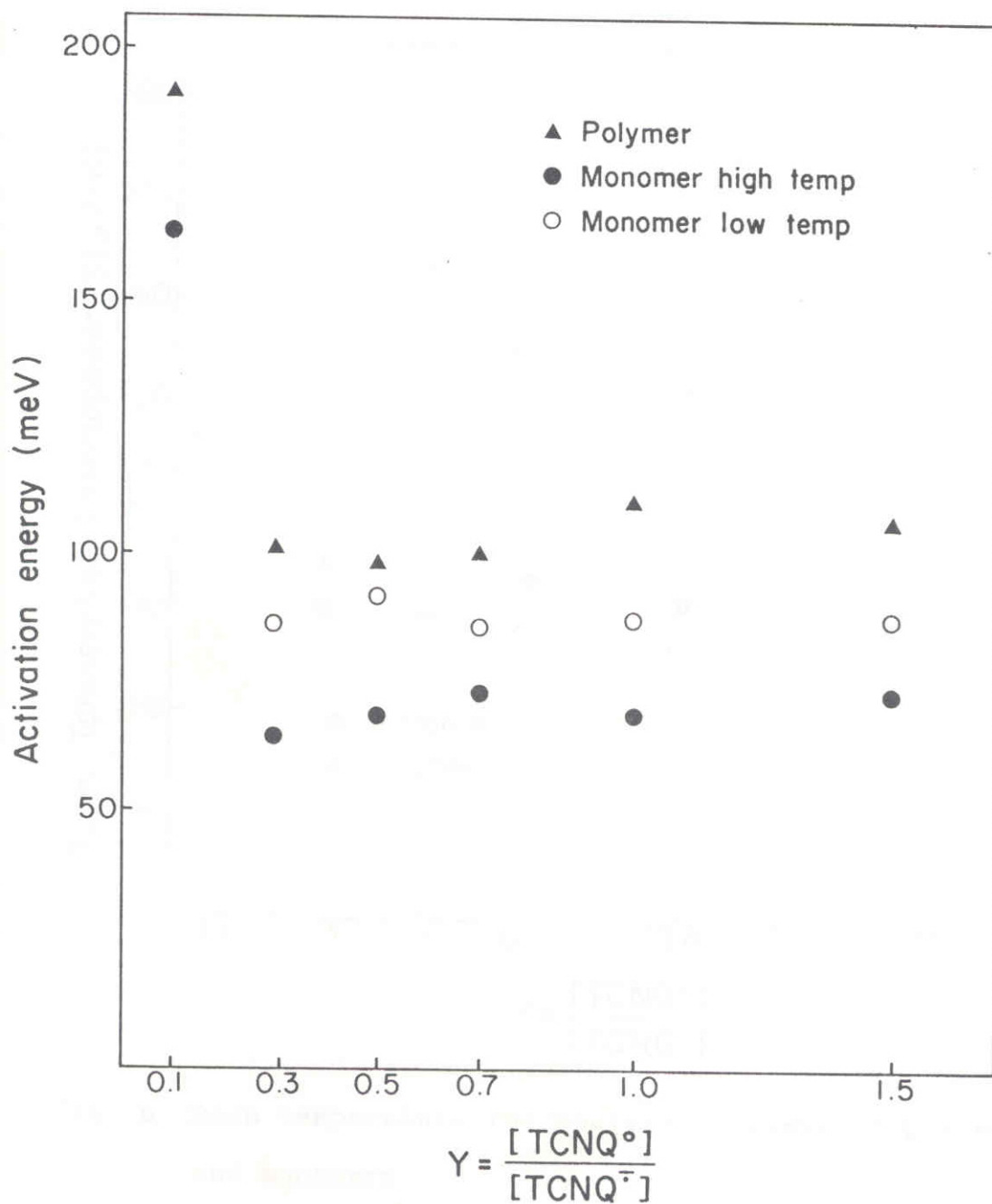Fig. 6 Temperature dependence of conductivity of polymers
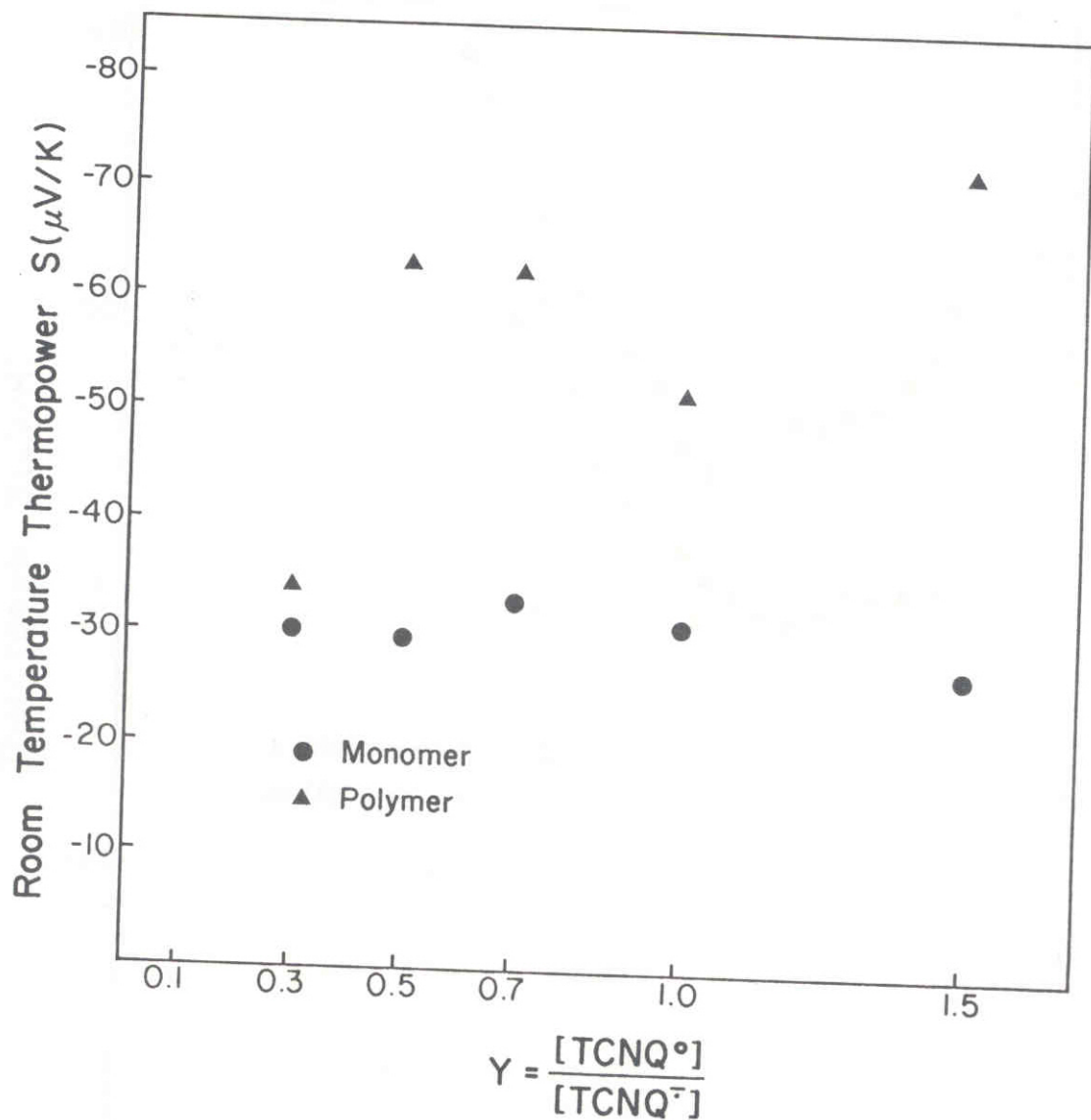
Fig. 7 Activation energy of polymers and monomers

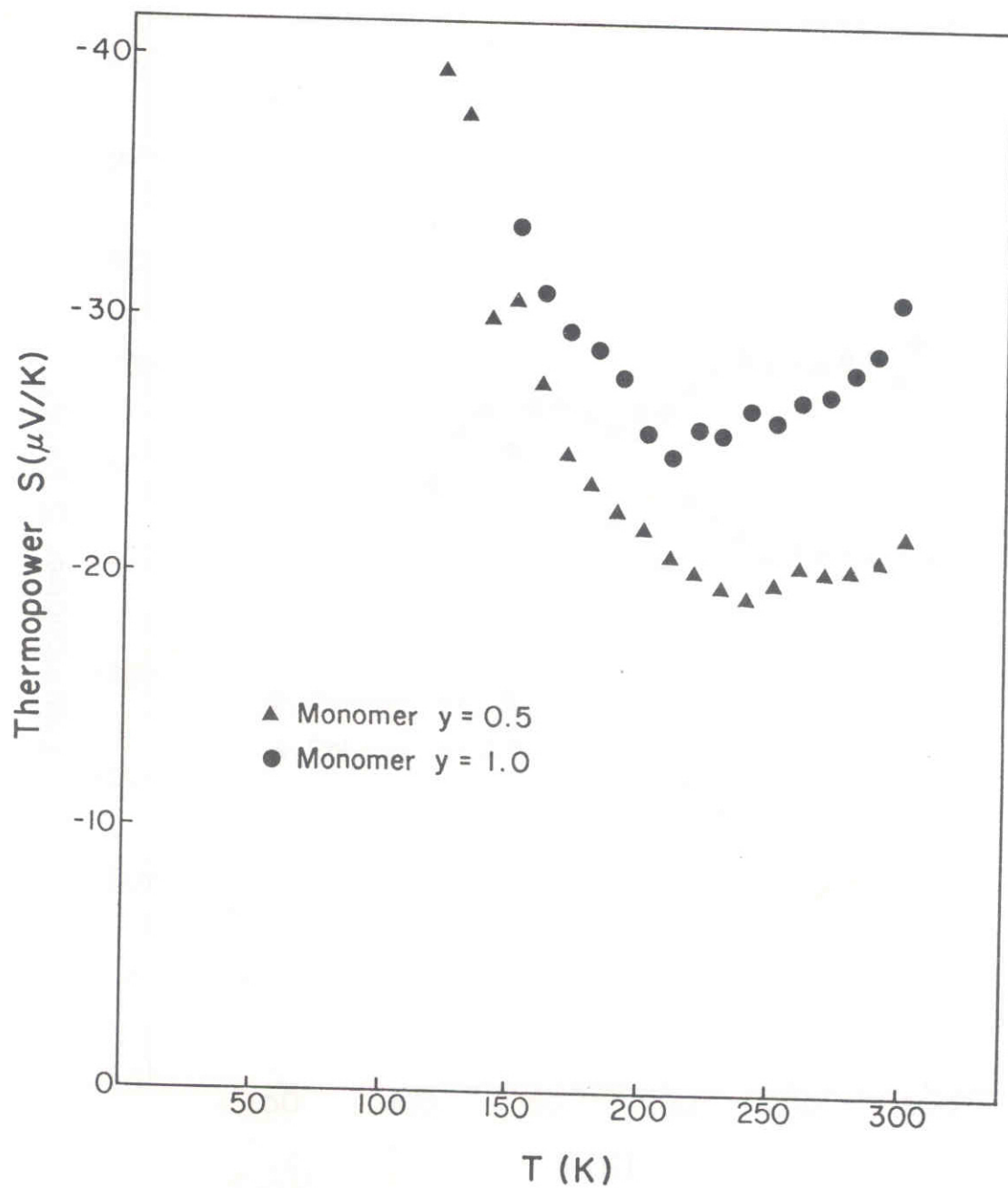Fig. 8   Room temperature thermoelectric power of polymers
and monomers

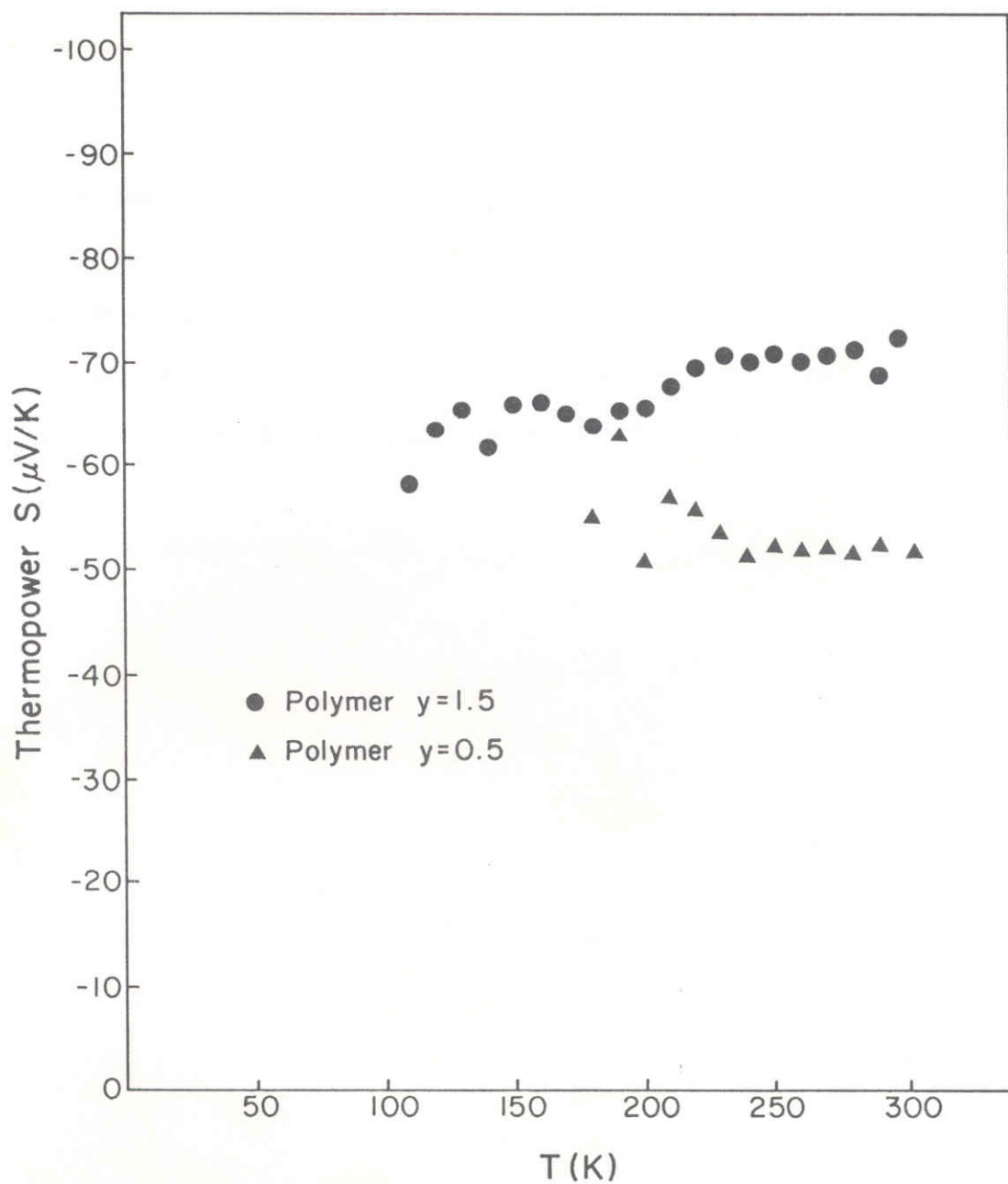Fig. 9 Temperature dependence of thermopower of monomers

Fig. 10   Temperature dependence of thermopower of polymers

감사의 글

이 논문을 마치기까지 충고와 지도를 아끼지 않으신 박영우 교수님께 진심으로 감사를 드립니다. 또한 박 철, 이윤석 선배와, 실험에 많은 도움을 주고 유용한 토론을 해준 실험실 동료 문정선, 김주진, 윤철오에게도 감사를 드립니다. 그리고 시료를 준비하고 화학적인 이해에 많은 도움을 주신 고려대학교 화학과의 민경선 선배와 진정일 교수님께도 감사를 드립니다.

끝으로 격려와 지원을 아끼지 않으신 부모님과 가족들에게 이 논문을 드립니다.