Electrical Transport of a New Conducting Polymer Salted with TCNQ

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The electrical conductivity and thermoelectric power of a new conducting polymer and its mono-meric model compound converted to salts with the different ratios of the $[TCNQ^\circ]/[TCNQ^{\bar{\cdot}}]$ complex are measured as a function of temperature. The room temperature conductivity of the polymer and its monomeric model compound are of the same order of magnitude and their TCNQ complex salts show a three to four order of magnitude increase in conductivity as the $[TCNQ^\circ]/[TCNQ^{\bar{\cdot}}]$ ratio increases to 1. The sign of the room temperature thermoelectric power data is negative for all samples indicating that electrons are the major carriers in these complex salts. The results are discussed in terms of $[TCNQ^\circ]-[TCNQ^{\bar{\cdot}}]$ stack formation.

I. INTRODUCTION

Organic charge transfer salts have received considerable attention over many years[1]. This interest has arisen from the fact that the flat planar molecules involved lead to anisotropic structures and therefore to quasi one-dimensional electronic properties. One of the known real physical systems of organic charge transfer salts is the ion-radical salt of 7,7,8,8— tetracyano-quinodimethane (TCNQ) and its compounds.

More recently, studies on linear chain conduct-ing polymers have been carried out extensively because of the exciting possibilities associated with a one-dimensional electron gas[2]. Poly-acetylene, $(CH)_x$, which involves the solitonic charge transfer mechanism, is the simplest carbon based linear chain compound.

Efforts to combine charge transfer salts with conducting polymers have also been made and various polymeric salts of the TNCQ anion radical, mainly of the quaternary ammonium type, have

been produced[3,4].

In this paper, the electrical transport properties of a new conducting polymer complexed with TCNQ salts are studied. The electrical conduc-tivity and thermoelectric power (TEP) of the corresponding monomeric model compound TC-NQ salts are also studied for comparison.

II. EXPERIMENTAL

A new conducting polymer was prepared from 1, 4-bis (β-pyridyl-(4)-vinyl) benzene (PVB) and 1, 6-dibromohexance. This polymer was treated with LiTCNQ solution and then mixed with the desired amount of $[TCNQ^\circ]/[TCNQ^{\bar{\cdot}}]$ solution to form TCNQ complex salts. The final $[TCNQ^\circ]/[TCNQ^{\bar{\cdot}}]$ concentration ratios of the samples used in the measurements are 0.1, 0.3, 0.5, 0.7, 1.0 and 1.5. Monomeric model com-pound TCNQ salts were obtained by similar pro-cedures as above except that 1-bromobutane was used instead of 1, 6-dibromohexane. The

chemical structures of the obtained product TCNQ complex salts were confirmed by elemental analysis as well as by IR and UV-visible spectra. Details of the chemical synthesis and analysis of these compounds are presented in reference 5.

The final products of these compounds are in powder form. For the conductivity and TEP measurements, these powders were pressed under 1200 PSI pressure into compaction pallets and

Electrodag 502 paint contacts were used for both four-probe conductivity and TEP measurements. Techniques for the conductivity and TEP measurements are the same as published elsewhere[6].

III. RESULTS

The chemical structure of the polymer TCNQ complex salt is as follows.

$$\{[+CH_2)_6 - N^+ \text{\textcircled{O}} - CH=CH-\text{\textcircled{O}}-CH=CH-\text{\textcircled{O}}N^+]_{\overline{n}} (TCNQ)_m\} \quad (1)$$
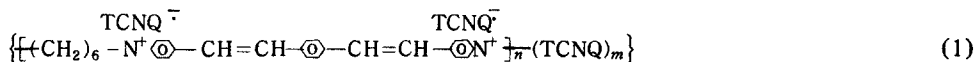
The corresponding monomeric model compound TCNQ salt has the following structure.

$$\{[(CH_3 - (CH_2)_3 -N^+\text{\textcircled{O}}- CH=CH-\text{\textcircled{O}}-CH=CH-\text{\textcircled{O}}N^+ - (CH_2)_3 -CH_3](TCNQ)_m\} \quad (2)$$
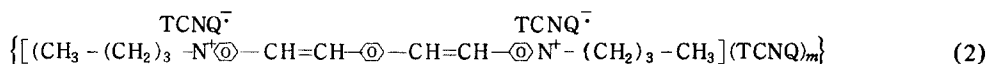
Figure 1 shows the room temperature conductivity vs $y=[TCNQ^{\circ}]/[TCNQ^{\overline{\cdot}}]$ of the complex salts. Both polymeric and monomeric complex salts show an increase in conductivity of three to four orders of magnitude upon the addition of

$[TCNQ^{\circ}]$. The maximum conductivity occurs at the 1:1 ratio of $[TCNQ^{\circ}]:[TCNQ^{\overline{\cdot}}]$ and then starts to decrease for higher $[TCNQ^{\circ}]$ concentration. The maximum room temperature conductivity is $\sigma_{RT} \cong 6.2 \times 10^{-2} \Omega^{-1} cm^{-1}$ for the monomeric complex salt and $\sigma_{RT} \cong 6.1 \times 10^{-3} \Omega^{-1} cm^{-1}$ for the polymer complex salt, respectively.

The temperature dependencies of the selected samples are shown in figure 2. For the $y \geq 0.5$ samples, the temperature dependencies are more or less the same as for the $y=1.0$ samples and therefore the data was eliminated in figure 2
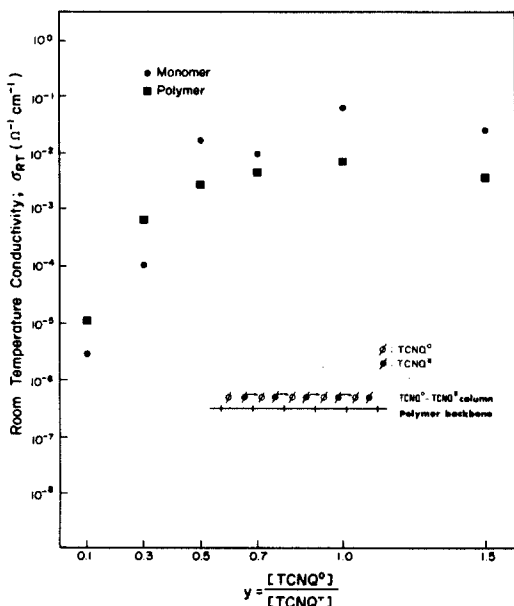

Fig. 1. Room temperature conductivity vs. $y=[TCNQ^{\circ}]/[TCNQ^{\overline{\cdot}}]$ concentration. The insert shows the y=1 case.
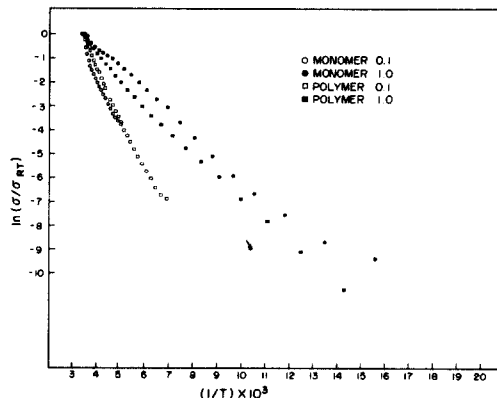
Fig. 2. Temperature dependence of conductivity.

Fig. 3. Activation energy vs. y.

Fig. 4. Room temperature themoelectric power vs. y.
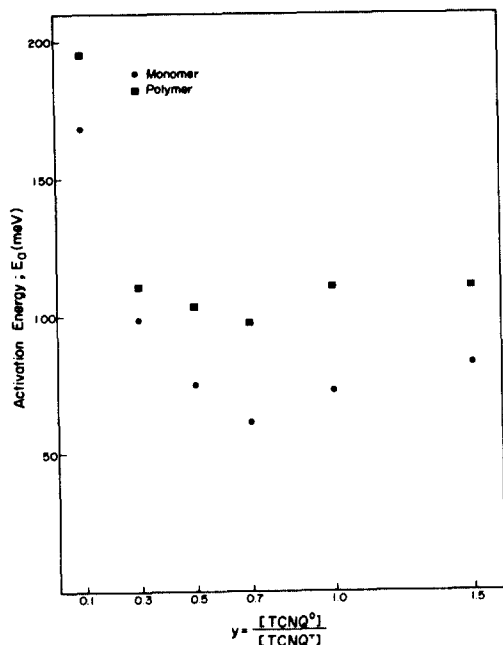
to avoid confusion. The slope of the log σ/σ_{RT} vs 1/T plot gives the activation energy and these are plotted for all samples in figure3. For the $y \geq 0.5$ samples, the data are in the 100 meV range for the polymer complex salts and in the 70 meV range for the monomer complex salts. The polymer complex salts show a lower conductivity and thus a higher activation energy than the monomer complex salts. However, the temperature dependence curves for the polymer complex salts are smoother. Fitting of the conductivity data to $(T_0/T)^n$ with n=1/4 or 1/2 shows more straight line behavior over a wider temperature range than the 1/T plot. Such behavior is expected when phase separation into conductive and nonconductive regions occurs and is also broadly characteristic of pressed powder samples.

Figure 4 shows the room temperature TEP vs y=[TCNQ°]/[TCNQ⁻]. The sign of the TEP data for all samples is negative indicating that electrons are the major carriers. This confirms that the electrons in the TCNQ ⁻ anion radicals
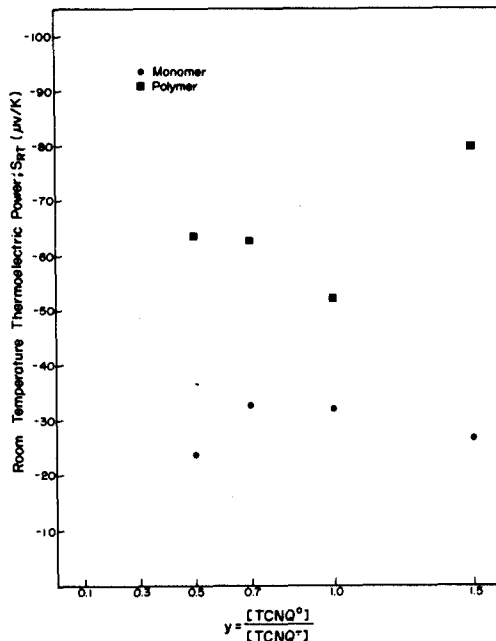
are the source of the charge transport in these complex salts. The magnitude of the TEP of the polymer complex salts decreases as y increases to 1 and start to increase for the y > 1 sample. On the other hand, the magnitude of the TEP of the monomeric complex salts increases until $y \simeq 1$ and then decreases for y > 1. Unlike the conductivity which increases for both polymeric and monomeric complex salts, the change in the magnitude of the TEP is opposite. The temperature dependencies of TEP for these samples are difficult to measure because of the high resistance of these materials but our preliminary results over a very narrow temperature range just below room temperature show a weak temperature dependence, which suggests that the carriers are only weakly activated. This is consistent with the Hall effect measurement results[5] which showed that the mobility, rather than the carrier, is activated in these complex salts.

IV. DISCUSSION

In figure 1, it is observed that the room temperature conductivity for the polymeric complex salts is initially higher than that of the monomeric complex salts. But, as y increases, the conductivity of the monomeric complex salts increases more rapidly than the polymeric complex salts, becoming higher at room temperature for $y > 0.5$. However, as shown in figure 3, the activation energies of the polymeric complex salts are larger than those of the monomeric complex salts for all concentrations of $[TCNQ^{\circ}]/[TCNQ^{-}]$. The maximum room temperature conductivity occurs at y=1, i.e., $[TCNQ^{\circ}]:[TCNQ^{-}]=1:1$, for both polymeric and monomeric samples. Also, it should be noted that this drastic increase in conductivity does not require stoichiometric proportions; thus increasing the ratio of $[TCNQ^{\circ}]:[TCNQ^{-}]$ from 0.5 to 1 changes the conductivity values only slightly and has little effect on the activation energy. A similar drastic increase in conductivity by addition of neutral TCNQ to a paramagnetic TCNQ salt has been previously reported.[2,4] In our case, however, the structure of the conducting polymer and its monomeric compound is different. The distance between N^{+} cations as shown in equations (1) and (2) is lengthened by inserting CH–ⓞ–CH in the middle of the previously reported[3] conducting polymer complex; Du^{+} $TCNQ^{-}$. The effect of this elongation of the N^{+} cation distance seems not to be significant. The polymer complexes are slightly less conductive than those of the monomer, which is the same as observed in conducting polymers with shorter distance between N cations. This observation together with the fact that the maximum room temperature conductivity occurs for y=1 samples suggests that a column of TCNQ molecules is formed in which $[TCNQ^{\circ}]$ and $[TCNQ^{-}]$ are packed one upon another. The distance between the N^{+} cations in polymeric

and monomeric compounds is important for the short distance compound such as the BP, n-TCNQ complex,[4] but once the distance reaches a certain length, the conductivity increment behavior saturates more or less. Therefore, as the distance between N^{+} cations in the Du^{+} $TCNQ^{-}$ compound studied in reference 3 is already in the conductivity saturation range, the insertion of a CH-ⓞ-CH unit as in our measurements does not enhance the conductivity significantly.

Peculiar behavior is observed in the TEP data shown in figure 4. The magnitudes of the TEP data at room temperature for the polymeric and monomeric complex salts are quite different. Moreover, the magnitude of the TEP for the polymeric complex salts decreases as the conductivity of the corresponding samples increase to a maximum and then the TEP starts to increase as conductivity decreases for $y > 1$. Contrary to this behavior, the magnitude of the TEP for the monomeric complex salts increases as conductivity increases until it reaches a maximum and then the TEP decreases as conductivity decreases for $y > 1$. Since the TEP is a measure of the entropy per carrier,[6] it can indicate the number of carriers contributing to the conductivity. Therefore, the magnitude change observed for the polymeric complex salts can be understood in relation to a change in conductivity, i.e., the higher conductivity corresponds to larger carrier concentrations contributing to the charge transport, so that the configuration entropy decreases resulting in the smaller TEP magnitude. However, the change in TEP magnitude observed for the monomeric complex salts can not be understood as above. It is opposite. The slightly higher room temperature conductivity of the monomeric complex salts than that of the polymeric complex salts for $y > 0.4$ also unexpected because the polymeric complex salts have a longer range

periodicity for charge transport.

Perhaps this conductivity and TEP behavior is due to the fact that the actual charge transport mechanism is dominated by the $[TCNQ^{\circ}]$–$[TCNQ^{-}]$ column like stack formation rather than the polymer or monomer back bone. Then the higher conductivity in the complex salts results from the creation of hole-electron pairs without placing two electrons on the same TCNQ site, there being "neutral" molecules available to take the extra electron. However, this TCNQ column formation in polymeric complex salts seems to be limited by the regularity of the repeated unit of its monomer. The TCNQ column formation in monomeric complex salts does not have such a boundary condition limit. Consequently, the monomeric TCNQ complex salts has higher conductivity and smaller magnitude TEP for $y > 0.4$, even though the conductivity of the polymeric complex salts are higher at low concentrations because of the longer range periodicity in the polymeric salts. The TEP magnitude increase of the monomeric complex salts might be related to the greater disorderliness induced by the $[TCNQ^{\circ}]$ addition, hence higher entropy.

In summary, we have studied conducting polymer TCNQ complex salts which have a longer distance between N cations and the corresponding monomeric TCNQ complex salts as a function of the $[TCNQ^{\circ}]/[TCNQ^{-}]$ concentration. A drastic conductivity enhancement is observed similar to that in other conducting polymer TCNQ complex salts and the effect of the elongation of the distance between N^{+} cations turns out to be not significant compared to the effect in Du^{+} $TCNQ^{-}$. The polymer complexes are slightly less conductive than the monomer complexes. The negative sign of the TEP data indicates that electrons are the major carriers in these complex salts. These results are consistent with the idea of the $[TCNQ^{\circ}]$–$[TCNQ^{-}]$ stack formation when $[TCNQ^{\circ}]$ is added and the charge transport occurs mainly along the TCNQ molecule column.

ACKNOWLEDGEMENT

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새로운 전도성고분자 및 그단분자와의 TCNQ 복합체들이 갖는 전기적특성

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새로운 전도성 고분자 및 그 단분자를 $[TCNQ^\circ]/[TCNQ^-]$의 비를 변화시켜가며 화합시킨 복합체들의 전기 전도도 및 열전기력을 온도의 함수로 측정하였다. 이 고분자 및 단분자의 상온에서의 전기 전도도는 같은 정도의 크기를 보였으며 TCNQ 복합체를 만들었을때 $[TCNQ^\circ]$와 $[TCNQ^-]$의 비가 1:1에 이를때까지 1000배 – 10000배 정도의 전기 전도도 증가를 보였다. 상온에서의 열전기력 값의 부호가 모든 시료들이 모두 음으로 나타나고 있는데 이는 이들 시료내의 주된 전하가 전자들임을 말해주고 있다. 이 결과들을 $[TNCQ^\circ]-[TCNQ^-]$이 교대로 원주형 모형으로 쌓여 있는 것으로 설명하였다.