DC and AC Conductions in Sodium 7,7,8,8-Tetracyanoquino-dimethanide–Polymer Composites

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ABSTRACT: DC and AC conductions in NaTCNQ–polymer composites of high NaTCNQ content composed of sodium 7,7,8,8-tetracyanoquinodimethanide (NaTCNQ) grains dispersed in poly(vinyl chloride)(PVC)–polyurethane(PU) blend polymer have been studied. In the composites, NaTCNQ is mainly dispersed granularly and a slight proportion of NaTCNQ is molecularly. The DC conduction has nonohmic characteristics and shows straight lines in log $\sigma_{dc} - E^{1/2}$ plots. On the other hand, its temperature dependence shows a linear relation in log $\sigma_{dc} - 1/T^{1/4}$ plots. The DC conduction is interpreted in terms of the variable range hopping (VRH) conduction with the Poole–Frenkel-like field dependence. It is deduced that the Poole–Frenkel (PF) mechanism mainly contributes to the generation of carriers and the carriers are transported due to the VRH mechanism; that is, the VRH carriers will generate under PF field dependence. The frequency dependence of AC conductivity shows that the VRH is a multiple process and the multiplicity increases with temperature and NaTCNQ content.

KEY WORDS   Electrical   Conduction   /   7,7,8,8-Tetracyanoquinodi-methanide Salt / 7,7,8,8-Tetracyanoquinodimethanide Salt–Polymer Composite / DC Conductivity / AC Conductivity / Poole–Frenkel Conduction / Variable Range Hopping

In recent years, studies on conducting polymers have been carried out extensively, and development of conductive polymers with good mechanical properties such as flexibility, film-forming ability, and normal moldability, have been desired for electronics industry. Composite materials consisting of an ion-radical salt dispersed in a polymer matrix can retain the desirable mechanical properties due to the ease of making blends. The author reported in the previous paper[1] that the electrical conduction behavior of composite of a thermally stable anion-radical salt NaTCNQ (sodium 7,7,8,8-tetracyanoquino-dimethanide) in polyvinyl chloride (PVC) plasticized by polyurethane (PU) is characterized by molecular and granular dispersion of the TCNQ salt in the polar polymer. The conduction mode changes from the con-

duction due to molecularly dispersed sites (CMDS) to the conduction due to granularly dispersed sites (CGDS) with increasing NaTCNQ content. In this paper, DC and AC conduction behavior of NaTCNQ–polymer composite in the CGDS region which includes much NaTCNQ (mainly 40%) is mainly reported.

EXPERIMENTAL

Samples were prepared by the same method as reported in the previous paper.[1] NaTCNQ used here was a crystalline powder of mean grain size 2–3 μm having a resistivity of 10^5 $\Omega \cdot$ cm at room temperature (RT).[1] Polymer matrix (PVC + PU) composed of PVC and PU (1 : 1) has the resistivity of the order of 10^{12} $\Omega \cdot$ cm at RT, as shown in Figures 1 and 5 in

the previous paper,[1] where PVC and PU were molecularly compatible with each other. In the NaTCNQ–polymer composite including 40% NaTCNQ, most of NaTCNQ is granularly dispersed, and a part of it is molecularly dispersed because of the low solubility of NaTCNQ to PVC + PU. The molecularly dispersed NaTCNQ causes the decrease of resistivity of one order of magnitude from 10^{12} $\Omega \cdot$ cm at RT within a NaTCNQ content of less than about 1%, while the granularly dispersed NaTCNQ causes a great decrease of resistivity from the value 10^{11} to 10^9 $\Omega \cdot$ cm.[1] In this study, only sheet samples prepared by the solution method (S-sample)[1] were used for electrical measurements. Colloidal graphite (Aquadag) was coated to both surfaces of the sheets as electrodes. Electrical properties of the sheet samples were measured in the direction of the thickness. These properties were confirmed to be due to bulk properties from the thickness dependence of the current in the previous paper.[1] The DC conductivity was measured by potential-fall method in a wide temperature range from -72 to $120°C$. The AC conductivity was calculated from a complex dielectric constant ($\varepsilon^* = \varepsilon' - j\varepsilon''$) measured under application of a voltage of 5V at temperatures of 26 and 98°C by using a dielectric loss meter TRS-10C (Ando Electric Co., Ltd.).

RESULTS AND DISCUSSION

The conduction mode of the NaTCNQ–polymer composite which includes 40% NaTCNQ is CGDS mode. In this region, the carriers are mainly transported through grain-channels. Therefore, the conduction properties are greatly affected by the boundary conditions between the grains, i.e., the intergranular potential barrier. The electrical properties in the composite show dielectric properties in the well-known Maxwell–Wagner type heterogeneous dielectrics and are approximately represented as an equivalent circuit constituted

of series and/or parallel connections of many resistors and capacitors.[2] The intergranular potential barrier in the composite will correspond to an intergranular micro-capacitor or a micro-resistor. However, since NaTCNQ used here is semiconducting crystalline particles and dispersed both in molecular and granular states in the polymer matrix, many localized states of the molecularly dispersed NaTCNQ are formed in the grain boundary region between the semiconducting grains. Such a NaTCNQ–polymer system has very interesting electrical properties. The DC and AC conduction characteristics are hereinafter represented in connection with the intergranular conditions.

DC Conduction

It was shown in the previous paper[1] that the current-voltage characteristics of the NaTCNQ–polymer composite of high NaTCNQ content are nonohmic and the $\log \sigma_{dc} - E^{1/2}$ plots have linearity. From these results, we concluded in the previous paper that the Poole–Frenkel type conduction is most probable. Figure 1 shows the $\log \sigma_{dc} - E^{1/2}$ characteristics in the range of low temperature from -72 to $12°C$. Each characteristic shows a straight line with similar slope. Each slope shows nearly the same value and slightly increases with the increase of temperature. The Poole–Frenkel coefficient β_{PF} (10^{-24} $C \cdot V^{1/2} \cdot m^{1/2}$) is determined to be 4.54 ($-72°C$), 6.28 ($-50°C$), 6.70 ($-23°C$), and
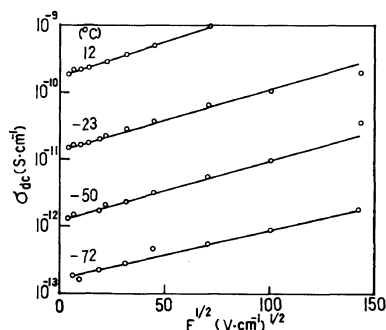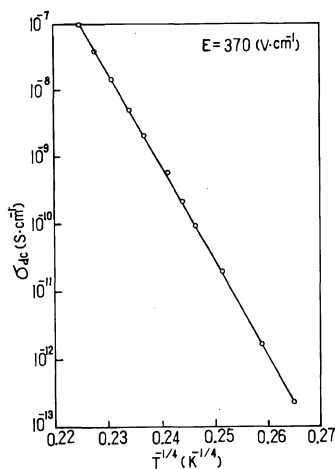

Figure 1. $\log \sigma_{dc} - E^{1/2}$ plots.

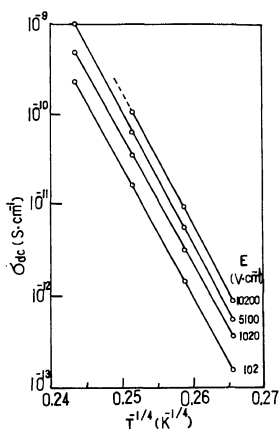**Figure 2.** $\text{Log}\,\sigma_{dc} - 1/T^{1/4}$ plots.

Figure 3. $\text{Log}\,\sigma_{dc} - 1/T^{1/4}$ plots at each electric field strength.

9.38 (12°C) from the slope $\beta_{PF}/\gamma kT$ based on the Poole–Frenkel's equation $\sigma_{dc} = \sigma_0 \cdot \exp(\beta_{PF}E^{1/2}/\beta kT)$, where σ_0 is the low-field conductivity, k is the Boltzmann constant, T is the absolute temperature, and γ is the compensation factor.[1] β_{PF} is also related to the dielectric constant as represented by the equation $\beta_{PF} = (e^3/\pi\varepsilon_h\varepsilon_0)^{1/2}$, where e is the unit of electronic charge, ε_0 is the permittivity of free space, and ε_h is the high-frequency relative dielectric constant. However, because the value of ε_h determined thereby has a higher value with decreasing temperature, the

slope in Figure 1 does not seem to reflect simply the dielectric constant of the material.

On the other hand, the temperature dependence of DC conductivity plotted in the form of $\text{log}\,\sigma_{dc}$ vs. $1/T^{1/4}$ plots shows a straight line in the wide temperature range from -72 to 120°C, as shown in Figure 2, where σ_{dc} is measured at the electric field strength E of $370\,\text{V cm}^{-1}$. The $\text{log}\,\sigma_{dc} - 1/T^{1/4}$ plots at each electric field strength similarly have linearity as shown in Figure 3. Since in the NaTCNQ–polymer composite, the carriers are mainly transported through the grain-channels, these characteristics mainly reflect a conduction mechanism based on the intergranular electron transport of the dispersed NaTCNQ grains. The linearity of $\text{log}\,\sigma_{dc} - 1/T^{1/4}$ plots are characteristics observed in disordered inorganic solids.[3] From analogy with the electronic states in the non-crystalline inorganic solids, it is considered that the three dimensional VRH conduction is probable in the NaTCNQ–polymer composite. This NaTCNQ–polymer composite has also linearity in the $\text{log}\,\sigma_{dc} - E^{1/2}$ plots. Considering these results, it can be deduced that the conduction mechanism will be due to thermally and field-assisted hopping from one localized state to another, that is, the VRH conduction with the Poole–Frenkel-like field dependence. The Poole–Frenkel effect is caused by a lowering of a Coulombic potential barrier in the bulk of an insulator having a conduction band when it interacts with an electric field. The field dependence in these materials is interpreted in terms of carrier generation from isolated or localized NaTCNQ grains to the conduction channels through the potential barrier lowered by the Poole–Frenkel-like effect. The $E^{1/2}$ term is related to the carrier generation leading to VRH conduction; the carriers will be transported due to the VRH mechanism. The $\text{log}\,\sigma_{dc} - 1/T^{1/4}$ characteristics is similar to the $1/T^{1/4}$ behavior ascribed to the thermally-assisted hopping which is observed in disordered system having an extensive band tail
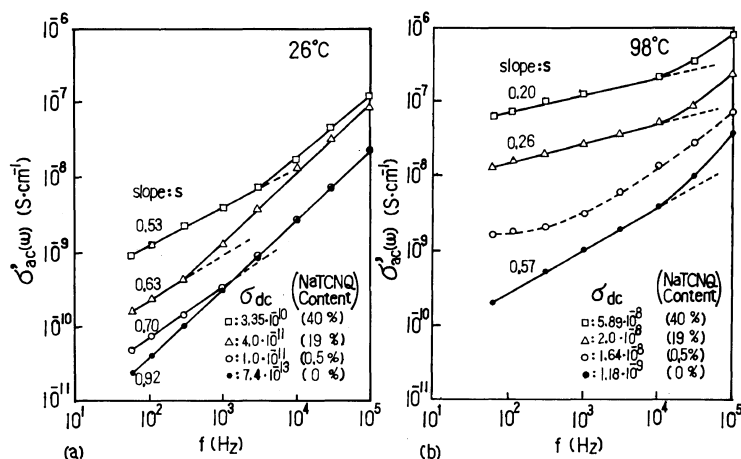
Figure 4. Frequency dependence of AC conductivity in NaTCNQ–polymer composites.

together with the absence of a sharp mobility edge.[4] The extensive band tail states are related to the intergranular potential barriers and the molecular sites due to the molecularly dispersed NaTCNQ. In such a system, the Coulombic barrier of intergrains will be lowered by the field to enable thermally-assisted field emission of electron from the NaTCNQ grain.

AC Conduction

The electrical properties of the composite under AC field are affected by various types of dielectric polarizations and AC conductivity etc. These dielectric polarizations, that is, electronic, atomic, orientational, intergranular, and ionic polarizations will correspond to each material segment in the composite as shown in Table I. Ionic and electronic conductions have also an intimate relation with the behavior of such material segment shown in the table. In this composite, NaTCNQ grains mainly contribute to the intergranular polarizability (χ_g) and the electronic conductivity (σ_e). Molecularly dispersed NaTCNQ and the dissociated ions of NaTCNQ contribute to the ionic polarizability (χ_i) and the ionic conductivity (σ_i), but in the composite of high NaTCNQ content, the

Table I. The degree of contribution of material segments to the dielectric polarization in NaTCNQ(40%)–polymer composites

Material segment	ε'			ε''	
	(χ_e, χ_a, χ_o) χ_g χ_i			σ_e σ_i	
Polymer matrix (PVC+PU)	○	×	△	×	△
NaTCNQ grain	○	◎	×	◎	×
Molecularly-dispersed NaTCNQ	○	×	△	△	△
Dissociated ion-radical of NaTCNQ	○	×	○	×	○

[a] χ_e, χ_a, χ_o, χ_g, and χ_i are electronic, atomic, orientation, intergranular, and ionic polarizability, respectively. σ_e and σ_i are electronic and ionic conductivity, respectively.

[b] Degree of contribution: (large)-◎-○-△-×-(none).

contribution of them to the total electrical properties is scarce in comparison with that of the NaTCNQ-grains. The behavior described below reflects the conduction behaviors due to the NaTCNQ grain channels. The frequency dependence of AC conductivity $\sigma'_{ac}(\omega)$ at 26 and 98°C are shown in Figure 4, where $\sigma'_{ac}(\omega)$ were calculated from the equations $\sigma'_{ac} = \omega\varepsilon_0\varepsilon''$ and $\sigma'_{ac}(\omega) = \sigma'_{ac} - \sigma_{dc}$ where ω is the angular frequency. The DC conductivity for the same is also shown in Fig-

ure 4. The figure shows that the frequency dependence of $\sigma'_{ac}(\omega)$ has linearity following the equation $\sigma'_{ac}(\omega) = A \cdot \omega^s$. The values of s determined from the slope are also shown in the figure. It has been reported that the value of s is related to the multiplicity of hopping in electronic conduction and the low values of s suggest that multiple hops are dominant.[5,6] In such NaTCNQ–polymer composites, conduction is determined by the hopping process through the intergrain state, and it is considered that the many localized states formed in the grain boundary region dominate the conductivity. Therefore, from analogy with the electronic state in the inorganic disordered system, an application of the above theory[5] to this system will be possible.[7] When applying the above theory to this material, Figure 4 shows that the electron hopping varies to high multiplicity with increase of temperature and NaTCNQ content, and single hops become more significant at high frequencies. In such a composite of high NaTCNQ content, conduction carriers are mainly composed of the intergranular hopping electron, intragranular mobile electron, and molecularly dispersed NaTCNQ. In the 40% NaTCNQ sample, the intergranular hopping electron mainly dominates the conductivity at low frequency and its conduction is considered to be multiple hops, considering the slope shown in the figure. With increasing frequency, the hopping electron response is delayed, and the hopping becomes gradually difficult. At a high frequency region, the contribution of the intragranular mobile electron and molecularly dispersed NaTCNQ to AC conductivity is considered to become dominant. Therefore, such a transition will appear as bending points in Figure 4. In support of this consideration, the position of this bending point shifts toward high frequency with increase of temperature (26→98°C), and also shifts with increase of NaTCNQ content (19→40%) as shown in Figure 4(a). The characteristics of 0.5% NaTCNQ composite

at 26°C, due to the contribution of the molecularly dispersed NaTCNQ, has a higher value of $\sigma'_{ac}(\omega)$ at low frequency than that of 0% sample, and its value is nearly the same at high frequency as that of 0% sample. However, its $\sigma'_{ac}(\omega)$ at 98°C shows a higher value in the range of whole frequency than that of the 0% sample. This behavior may reflect change of the molecularly dispersed NaTCNQ to the mobile dissociated ion and its molecular motion.

The composite material studied here is the Maxwell–Wagner type heterogeneous dielectrics. These observed frequency dependences of the AC conductivity $\sigma'_{ac}(\omega)$ at low frequency region can be explained in terms of intergranular potential barriers due to the Maxwell–Wagner polarization mechanism as shown by Bahl et al.[5] $\sigma'_{ac}(\omega)$ will be indicative of the AC field-assisted carrier hopping between localized states, i.e., NaTCNQ sites. In general, the DC conductivity is due to the continuing percolation of carriers between electrodes and reflects the most probable hops. The AC conduction reflects all short-range hops which become shorter in terms of the numbers of consecutive hops as the frequency increases, and represents all possible hops of the entire set of transition regardless of whether they give rise to percolation or not, as shown by Jonscher et al.[8] and Saha et al.[9] Therefore, the AC conductivity in such a composite will reflect all possible hopping behavior through the intergranular potential barriers and the molecular sites due to the molecularly dispersed NaTCNQ formed therein.

In conclusion, from such DC and AC conduction behavior, it is deduced that in this NaTCNQ–polymer composites, VRH conduction occurs in multiple processes with the Poole–Fenkel-type field dependent carrier generation. In order to relate in detail these characteristics to the molecular behavior, the effects of the CMDS or the effects of the elastomeric deformation by electric field must

be also considered in detail, but they are not clear now. Such a conduction mechanism of organic semiconductor particles dispersed molecularly and granularly in polymer matrix should be studied in detail in the future.

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