Preparation of Elastomeric Ionene Polymers Containing 4,4'-Bipyridinium or 1,2-Bis(4-pyridinium)ethylene Ring and the Conductivity of Their TCNQ Salts

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ABSTRACT: Elastomeric ionene polymers containing 4,4'-bipyridinium (BP) or 1,2-bis(4-pyridinium)ethylene (BPE) ring were prepared by the Menshutkin reaction of 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene with an alkyl iodide-terminated prepolymer derived from poly(propylene glycol) (PPG). Resistivity (ρ) and activation energy for conduction (E_a) were measured for the 7,7,8,8-tetracyanoquinodimethane (TCNQ) salts of these elastomeric ionenes. The values of ρ were 26.7 Ωcm and 24.8 Ωcm , and the values of E_a were 0.077 eV and 0.079 eV for (BP-PPG)-TCNQ complex salt and (BPE-PPG)-TCNQ complex salt, respectively. The complex salts were processible from solutions in the form of flexible films. A microheterogeneous structure of continuous conduction columns composed of TCNQ^- and TCNQ° and the poly(oxypropylene) chain brought about a high conductivity and favourable mechanical properties. These TCNQ salts were stable in an ambient condition, and the values of ρ at the storage time of about 300 days were nearly twice as large as the initial values.

KEY WORDS 7,7,8,8-Tetracyanoquinodimethane (TCNQ) / Elastomeric Ionene / 4,4'-Bipyridinium / 1,2-Bis(4-pyridinium)ethylene / Poly(propylene glycol) / Conductivity / Complex Salt / Flexible Film /

The complex composed of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and polycation is known as an organic semiconducting polymer, soluble in organic solvents and processible in film form.¹ Electronic conductivity of polycation-TCNQ salts is affected by polycation structure. Complex salts, obtained by doping TCNQ° into simple salts, show higher conductivity than simple salts. The authors have shown that ionene polymers containing N^+ atoms in the main chain, especially, whose intervals between N^+ atoms are fixed to 6—8 Å by rigid ring structure, allowed the complex formation of $[\text{TCNQ}^\circ]/[\text{TCNQ}^-]=1.0$.^{2,3} This brings about simultaneously a lowering of the Coulomb repulsion between carrier electrons and an increase in the overlap of π -electrons of TCNQ molecules.³ Consequently, the complex salt of these polycations shows high conductivity. It was also found that the polycations containing highly polarizable aromatic heterocyclic amines reduced the Coulomb repulsion between carrier electrons and contributed to the

high conductivity of their complex salts.⁴ The ionene polymers containing 4,4'-bipyridinium (BP) or 1,2-bis(4-pyridinium)ethylene (BPE) rings satisfy the above-mentioned conditions, and the conductivity of these TCNQ salts was highest among the polycation-TCNQ complex salts obtained.^{5,6} However, the films obtained are generally brittle and lack mechanical strength as polymeric materials. In order to be suitable for industrial application, an electrically conductive polymer should be flexible and capable of being shaped by a normal process.

In this study, elastomeric ionene polymers containing BP or BPE rings were prepared in order to obtain high conductive and good processible polycation-TCNQ salts. The complex salts of these elastomeric ionenes were found to show resistivity (ρ) of about 25 Ωcm and activation energy for conduction of 0.07—0.08 eV, and to be processable into flexible films from the solution. The change in ρ with time was also investigated.

EXPERIMENTAL

Purification of Reagents and Solvents

4,4'-Bipyridine and 1,2-bis(4-pyridyl)ethylene were recrystallized from methanol. Poly(propylene glycol) was obtained from Wako Pure Chemical Industry Co., Ltd. and used as obtained. The molecular weight determined from viscosity measurement was found to be 1290. 2,4-Toluylenediisocyanate (TDI) and 2-dimethylaminoethanol (DMAE) were purified by distillation under reduced pressure of 87°C/4 mmHg and 53°C/56 mmHg, respectively. 1,5-Diiodopentane was obtained from Eastman Kodak Co., Ltd. and used without further purification. TCNQ^o was recrystallized twice from purified acetonitrile. LiTCNQ was synthesized according to the previously established procedure.⁷

Methanol was purified by distillation over calcium oxide. *N,N*-Dimethylformamide was treated with 4 Å molecular sieves and then distilled (60°C/30 mmHg). Acetonitrile was refluxed over phosphorus pentoxide for 2 h and distilled twice.

Preparation of Elastomeric Ionene Polymers

The elastomeric ionene polymers (BP-PPG, BPE-PPG) were prepared according to the procedure shown in Figure 1.

PPG was allowed to react with TDI at 60°C for 18 h in a bulk system with stirring, at a molar ratio of [TDI]/[PPG]=2.0. Proceeding of the reaction was observed by infrared spectra, and completion of the reaction was confirmed by titration of the isocyanate groups. The product (I) was cooled to room temperature and a stoichiometric amount of DMAE was added. The contents were heated to 60°C again, and the reaction was allowed to continue for 2.5 h with stirring. The completion of the reaction was confirmed by the disappearance of the characteristic absorption of isocyanate groups in the infrared spectra. Unreacted DMAE was completely removed by a vacuum evaporator to yield a dimethylamino-terminated prepolymer (II). Molecular weight of the prepolymer (II) was determined by titration of the amino groups. Afterwards, the prepolymer (II) (0.1 mol l⁻¹) was allowed to

Figure 1. Procedure for preparation of elastomeric ionene polymers.

react with 1,5-diiodopentane (0.2 mol l^{-1}) in methanol at 60°C for 24 h, in a flask equipped with a condenser and a stirrer. Successively, the stoichiometric amount of 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene was added to the methanol solution of the prepolymer (III) as a chain extender, and the polymerization proceeded by the Menshutkin reaction for 150 h. The reaction solution was diluted by methanol and poured into a large excess of diethyl ether. Precipitates were collected and dried *in vacuo* at 80°C for 48 h. Yield: BP-PPG, 76.3%; BPE-PPG, 77.9%.

Preparation of TCNQ Salts

Simple salts were obtained by a counter ion exchange reaction between the elastomeric ionenes and LiTCNQ. A methanol solution of LiTCNQ was dropped into a methanol solution of the elastomeric ionene. The mixed solution (elastomeric ionene: $1.1 \times 10^{-2} \text{ unit mol l}^{-1}$, LiTCNQ: $4.8 \times 10^{-2} \text{ mol l}^{-1}$) was stirred for 30 min at room temperature under a nitrogen atmosphere. The simple salts precipitated from the solution were filtered off, thoroughly washed with methanol and diethylether, and dried *in vacuo*. It was apparent from electronic spectra that the iodine ion of the elastomeric ionene was completely exchanged by TCNQ^- of LiTCNQ.⁸ Yield: (BP-PPG)-TCNQ simple salt, 69.9%; (BPE-PPG)-TCNQ simple salt, 66.3%.

Complex salts were obtained by evaporating DMF under reduced pressure after dissolving the simple salt and TCNQ^- in DMF. They were dried *in vacuo* at 70°C for 72 h.

Electrical Measurement

A DMF solution of TCNQ salts was concentrated to about 0.2 g ml^{-1} by evaporating DMF and casted on clean glass plates. The solvent was completely removed under reduced pressure at 50°C for 24 h at first and at 70°C for 48 h at the last. Electrodes were made with the silver paste on the sample films of the glass substrates. Resistance was measured by the four probe method with direct current, using a Keithley 616 digital electrometer.

Activation energy for conduction (E_a) was calculated from the temperature dependence of the resistance, ranging from 25°C to 100°C , using the equation,

$$R = R_0 \exp(E_a/kT), \quad (1)$$

where k is the Boltzmann constant (eV K^{-1}), T is the absolute temperature (K), and R_0 is a constant (Ω).

X-ray Diffraction Patterns

X-ray diffraction patterns were measured with a Rigaku-Denki D-3F X-ray diffractometer using a Cu target.

Spectral Measurements

Infrared spectra were obtained with a JASCO IRA-1 diffraction grating infrared spectrophotometer, using NaCl plates. Electronic spectra was obtained with a Union Giken SM-401 spectrometer in acetonitrile.

RESULTS AND DISCUSSION

Preparation of Elastomeric Ionene Polymers

Figure 2 shows the infrared spectra of PPG, prepolymer (I) and prepolymer (II). As PPG reacted with TDI, the absorption at 3470 cm^{-1} , being assignable to terminal hydroxy groups of PPG, gradually faded out. Instead, absorption appeared at 3300 cm^{-1} and 1720 cm^{-1} as shown in Figure 2(a), (b) and these bands are assignable⁹ to hydrogen bonded N-H groups and carbonyl groups of urethane bonds respectively. After 18 h following the onset of the reaction, the absorption at 3470 cm^{-1} completely disappeared. The functionality of the isocyanate end-capped prepolymer (I) was found to be 1.99. When DMAE was added to the prepolymer (I), the absorption at 2280 cm^{-1} , due to the iso-

Figure 2. Infrared spectra of PPG, prepolymer (I) and prepolymer (II): (a), PPG; (b), prepolymer (I); (c), prepolymer (II).

Table I. Elemental analyses and intrinsic viscosities of elastomeric ionenes

Sample	Elemental analyses/%				$[\eta]^b$ dl g ⁻¹
	C	H	N	I ^{-a}	
BP-PPG	Found 50.6	7.27	4.50	19.7	0.270
	Calcd (51.7)	(7.51)	(4.28)	(19.3)	
BPE-PPG	Found 50.4	7.42	4.26	19.9	0.245
	Calcd (51.3)	(7.48)	(4.20)	(19.1)	

^a Determined by Volhard analyses.^b In CH₃OH at 25°C.

cyanate groups of TDI, rapidly decreased and completely disappeared after 2.5 h, as shown in Figure 2(c). The molecular weight of the prepolymer (II) was found to be 1830 (Calcd 1820). Preparation of the prepolymer (III) was confirmed by the disappearance of dimethylamino groups using amino group titration. The prepolymer (III) was allowed to react with 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene. With the proceeding of the reaction, the reaction solution turned from colorless to red, indicating that nitrogen atoms of the aromatic amines were quarternized by the prepolymer (III). Furthermore, the viscosity of the reaction solution increased. Elemental analyses and intrinsic viscosities $[\eta]$ of the elastomeric ionenes are shown in Table I. The experimental results from the elemental analyses are consistent with the calculated values. These results verify that the elastomeric ionenes can be prepared by the procedure shown in Figure 1.

The polymers obtained were red, transparent and elastic rubbery materials. The chemical structure of the elastomeric ionenes is characterized by alternating rigid polycation and flexible poly(oxypropylene) segments, and is analogous to segmented polyurethanes containing polycation segments as a hard segment.

Conductivity of TCNQ Salts

Figure 3 shows current-voltage characteristics of the TCNQ salts. In all samples, the response of current to the applied voltage was rapid and absorption current was hardly observed. This indicates that continuous conduction paths are formed in the TCNQ salts, despite the introduction of insulative poly(oxypropylene) chain in the elastomer-

Figure 3. Current-voltage characteristics of TCNQ salts at 25°C: ○, (BP-PPG)-TCNQ simple salt; △, (BP-PPG)-TCNQ complex salt 0.5; □, (BP-PPG)-TCNQ complex salt 1.0; ●, (BPE-PPG)-TCNQ simple salt; ▲, (BPE-PPG)-TCNQ complex salt 0.75; ■, (BPE-PPG)-TCNQ complex salt 1.0.

Figure 4. Relation between $\log \rho$ and inverse of absolute temperature for TCNQ salts: ○, (BP-PPG)-TCNQ simple salt; △, (BP-PPG)-TCNQ complex salt 0.5; □, (BP-PPG)-TCNQ complex salt 1.0; ●, (BPE-PPG)-TCNQ simple salt; ▲, (BPE-PPG)-TCNQ complex salt 0.75; ■, (BPE-PPG)-TCNQ complex salt 1.0.

ic ionenes. In the simple salts, ohmic behavior was observed up to a current density at least of 2 mA cm⁻², whereas in the complex salts, up to at least 10 mA cm⁻². The values of resistivity (ρ) were calculated from the slopes of the current-voltage characteristics.

Table II. Electronic properties of elastomeric ionene-TCNQ salts

Sample	$\frac{[\text{TCNQ}^\circ]}{[\text{TCNQ}^\cdot]}$	$\rho_{25^\circ\text{C}}$	E_a
		Ωcm	eV
(BP-PPG)-TCNQ	0	1.28×10^3	0.091
	0.5	4.12×10^4	0.070
	1.0	2.67×10^4	0.077
(BPE-PPG)-TCNQ	0	1.41×10^3	0.123
	0.75	3.46×10^4	0.103
	1.0	2.48×10^4	0.079

The relation between $\log \rho$ and inverse absolute temperature is shown in Figure 4. Since this relation was linear in the temperature range from 25°C to 100°C, the values of E_a were calculated from the slopes. The values of ρ at 25°C and those of E_a for the TCNQ salts are summarized in Table II. The reproducibility of the electrical data was excellent. For the simple salt, the values ρ and E_a were $\sim 10^3 \Omega\text{cm}$ and 0.09–0.12 eV, respectively. They are fairly small, compared with the values of ρ and E_a for other ionene-TCNQ simple salts.^{3,10,11} BP or BPE in the elastomeric ionenes has high electron affinity and can be easily reduced to form colored species.¹² The small ρ and E_a values of the simple salts may be explained by an electron-transfer reaction from $\text{TCNQ}^\cdot$ to BP or BPE which leaves TCNQ° in the resulting structure. Similar results have been reported on the TCNQ salts from 4,4'-bipyridine.^{13,14}

The values of ρ decreased by doping TCNQ° in the simple salts, and took the minimum value at $[\text{TCNQ}^\circ]/[\text{TCNQ}^\cdot] = 1.0$. Consequently, the values of ρ for the complex salts were $\sim 25 \Omega\text{cm}$, which were relatively low among the polycation-TCNQ salts ever obtained. The values of E_a were 0.07–0.08 eV. These results indicate the following facts. In complex salts, the TCNQ° molecules are incorporated into the polymer matrix and the conductive moiety composed of $\text{TCNQ}^\cdot$ and TCNQ° is formed. Since the polarizable polycation segments in the elastomeric ionene are rigid and have the optimum intervals between N^+ atoms for the packing of the TCNQ molecules, an effective arrangement of the TCNQ molecules on conduction is formed under the influence of the structure of polycation segments. Since the polycation segment is separated by the poly(oxypropylene) segment, the

Figure 5. X-ray diffraction patterns of TCNQ salts: (a), (BP-PPG)-TCNQ simple salt; (b), (BP-PPG)-TCNQ complex salt 1.0; (c), (BPE-PPG)-TCNQ simple salt; (d), (BPE-PPG)-TCNQ complex salt 1.0.

TCNQ moiety of a polycation segment is connected to the TCNQ moiety of a polycation segment of inter and/or intra polymer chain by strong interaction between $\text{TCNQ}^\cdot$ and TCNQ° . As a result, a continuous conduction path is formed.

Figure 5 shows the X-ray diffraction patterns of the TCNQ salts. For the simple salts, only haloes characterizing amorphous materials were observed. On the contrary, for the complex salts, diffraction peaks were observed at $2\theta = 14^\circ$ (Bragg spacing of 6.33 Å) and $2\theta = 27^\circ$ (Bragg spacing of 3.30 Å).

In TCNQ salts of monomeric cations, segregated columns of TCNQ molecules and cations are generally formed.¹⁵ Ashwell *et al.*¹⁶ investigated the crystal structures of the complex salts of many biscations containing aromatic amines, and found that TCNQ molecules are stacked along the biscations and form a column structure. Murakami *et al.*¹⁷ pointed out that in the X-ray diffraction patterns of TCNQ salts the diffraction peaks around 14° were attributable mainly to planes parallel to the axes of the TCNQ columns and those around 27° mainly to planes intersecting the column axes and nearly parallel to the molecular plane of TCNQ.

Applying these arguments the complex salts of the elastomeric ionenes, we can ascribe the diffraction peaks of the complex salts to the regularity in the arrangement of the TCNQ molecules. The TCNQ moiety composed of $\text{TCNQ}^\cdot$ and TCNQ°

forms a stacking structure about the polycation segments. Continuous conduction columns, which are of course less regular than crystalline TCNQ salts of low molecular weight cations, are made by a sequence of these stackings. A microheterogeneous structure of these continuous conduction columns and the poly(oxypropylene) chain makes the complex salts of the elastomeric ionenes high conductive.

The TCNQ salts are soluble in organic solvents such as DMF and processible from solution as flexible films. The simple salts are dark purple and very flexible. The complex salts are black. Though the complex salts are stiffer than the simple salts, they are still flexible. The increase in stiffness can be attributed to the crystallinity of the complex salts. A microheterogeneous structure of the rigid TCNQ moiety and the flexible poly(oxypropylene) chain, which has a low glass transition temperature ($\sim -70^\circ\text{C}$), gives rise to these favorable mechanical properties.

Change in Resistivity with Time

Figure 6 shows the change in ρ with time for the TCNQ salts in an ambient condition. The change in ρ with time does not depend on the structure of the elastomeric ionenes and the simple and the complex salts, but ρ increases slightly with time. The values of ρ after a storage time of about 300 days were nearly twice as large as the initial values. For example, the values of ρ for the (BPE-PPG)-TCNQ

Figure 6. Change in resistivity (ρ) with time for TCNQ salts in an ambient condition: $\square$, (BP-PPG)-TCNQ simple salt; $\triangle$, (BP-PPG)-TCNQ complex salt 0.5; $\square$, (BP-PPG)-TCNQ complex salt 1.0; $\bullet$, (BPE-PPG)-TCNQ simple salt; $\blacktriangle$, (BPE-PPG)-TCNQ complex salt 0.75; $\blacksquare$, (BPE-PPG)-TCNQ complex salt 1.0.

complex salt ($[\text{TCNQ}^-]/[\text{TCNQ}^0]=1.0$) went from $24.8\ \Omega\text{cm}$ to $45.0\ \Omega\text{cm}$ during this period of time, indicating the stability of these TCNQ salts.

CONCLUSION

In this paper, we have put forth to a method for obtaining highly conductive and very processible polycation-TCNQ salts. The method is outlined with synthesis of the complex salts of the elastomeric ionenes characterized by alternating rigid polycation and flexible poly(oxypropylene) segments. The polycation segments contribute to generating the high conductivity of the TCNQ salts, making a polarizable structure with an optimum intervals between N^+ atoms. The complex salts were obtained as flexible films with a high conductivity of $\sim 25\ \Omega\text{cm}$ in ρ and $\sim 0.07\ \text{eV}$ in E_a . A microheterogeneous structure of continuous conduction columns composed of TCNQ^- and TCNQ^0 and the poly(oxypropylene) chain brought about high conductivity and favorable mechanical properties.

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