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Transport studies of emeraldine salts protonated by phosphoric acids

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Abstract

Electrical transport properties of polyaniline prepared by chemical oxidative polymerization in the presence of phosphoric acid were investigated by low temperature conductivity and thermoelectric power measurements. As the ratio of acid to aniline is optimized ($Z=6$) at the stage of polymerization, the freshly prepared emeraldine salt form of the polyaniline shows (i) relatively high electrical conductivity, $\sigma \sim 40$ S/cm at room temperature, (ii) temperature dependence of the conductivity characteristic of the variable range hopping (VRH), $\ln \sigma \propto -(T_0/T)^x$, with exponent $x=1/3$, and (iii) linear temperature dependence of the thermoelectric power. As the molar ratio Z decreases from 6 to 1, the VRH exponent x systematically changes from $1/3$ to $1/2$ and the thermoelectric power decreases from $+7.6$ to $+0.2$ $\mu\text{V/K}$. The systematic variation of the transport parameters obtained from the temperature dependence was attributed to combined contributions from the metallic transport and VRH process in the disordered polymeric system.

Keywords: Polyaniline; Phosphoric acid; Transport

1. Introduction

Doped polyaniline [1–10] is one of the most attractive materials for the potential use of conducting polymers in the area of electrical or electrochemical application. Although the electrical conductivity of the pristine emeraldine salt form of polyaniline prepared via the conventional synthetic route [1,2] is relatively low ($\sigma \sim 10$ S/cm), recent progress in the fabrication of processible polyaniline [3–8] has shown that the electrical properties of the polymer could be remarkably improved by various processing methods. The uniaxially stretched films of polyaniline cast from the solution of emeraldine base in *N*-methyl-pyrrolidone (NMP) show enhanced electrical conductivity ($\sigma \sim 200$ S/cm before pumping) in the direction of stretch orientation after doping in strong acids [3]. The functional surfactant counterion induces the processibility of polyaniline in common organic solvents, in the doped form, leading to the conductivity $\sigma \sim 300$ S/cm [4,5]. Transport studies on polyblends of polyaniline with insulating polymers have shown that the level of the electrical conductivity could be controlled for many orders of magnitude from 10^2 to 10^{-5} S/cm by the variation of the polyaniline content in the blends [6,7].

In parallel to the development of new processing technology, an approach to improve the quality of polyaniline at the stage of chemical synthesis was recently reported by Boara

and Sparpaglione [9]. As a result of the optimization of synthetic conditions and compulsory quenching of the exothermic polymer reaction, the conductivity of polyaniline in pellet form increases up to $\sigma \sim 50$ S/cm when protonated by phosphoric acids. The optimization procedure provides high molecular weight of polyaniline as observed by gel permeation chromatography and possibly reduces overoxidized or decomposed contents in polyaniline. The existence of the longer mean free path of charge carriers was also suggested, based on the results of the solid-state proton NMR experiment [10]. To date, however, few results on the quantitative analysis of electrical transport properties of the material have been reported.

The electrical quality of the material can be more rigorously characterized by the temperature (T) dependence of the electrical conductivity and the thermoelectric power (S). The temperature dependence of conductivity for polyaniline prepared by a conventional procedure [2] follows the variable range hopping (VRH) transport model of the form:

$$\ln \sigma \propto -(T_0/T)^x \quad (1)$$

where $x=1/2$ and $T_0=10^4$ – 10^5 K. The U-shaped temperature dependence of the thermoelectric power is typical in this material [2,3]. The stretched films of polyaniline show a similar temperature dependence of conductivity with the reduction of T_0 to about 10^3 K and quasi-linear temperature

dependence of the thermoelectric power in the direction parallel to the stretching [3]. The solution-processed polyaniline–camphorsulfonic acid (PANI–CSA) shows critical behaviors of $\sigma(T)$ near the boundary of the metal–insulator (M–I) transition [4]: the power-law temperature dependence of the conductivity was observed in the critical regime, where the conductivity follows VRH temperature dependence with $x=1/4$ in the insulating regime of the M–I transition. The linear temperature dependence of the thermoelectric power indicates that the intrinsic transport nature is metallic [8]. As the content of PANI–CSA is diluted by the formation of polyblends with insulating polymer, the $\sigma(T)$ shows peculiar transport phenomena: the VRH exponent continuously increases from $x=1/4$ to $x=1$ until the system reaches the percolation threshold and becomes $x=1/2$ below the percolation threshold [6,7]. The inherent metallic temperature dependence of the thermoelectric power was observed in the polyblend with a trace of U-shaped dependence only at low temperature below 50 K [6].

In this paper, we report the temperature dependence of the electrical conductivity and thermoelectric power for a series of phosphoric-acid-doped polyaniline samples prepared by following the procedure proposed by Boara and Sparpaglione [9]. The electrical properties substantially change, depending upon the ratio of phosphoric acid to aniline monomer (Z) controlled at the stage of polymerization. The molar ratio Z was optimized by analyzing various transport parameters such as the room temperature conductivity and thermoelectric power, the resistivity ratio defined as $\rho_r \equiv \rho(10\text{ K})/\rho(290\text{ K})$, the VRH exponent (x) and slope (T_0) in Eq. (1). For the sample prepared at $Z=6$, the temperature dependence of the conductivity characteristic of VRH conduction with the exponent $x=1/3$ and the linear temperature dependence of the thermoelectric power were observed for the first time in the pellet form of as-prepared polyaniline. The systematic variation of the transport parameters obtained from the temperature dependence was observed upon change of Z ratio and attributed to combined contributions from the metallic transport and VRH process in a disordered polymeric system.

2. Experimental

Polyaniline samples were synthesized by the oxidative polymerization of aniline monomers in acidic media by following the procedure developed by Boara and Sparpaglione [9]. Distilled aniline (0.5 mol) was added dropwise to a solution containing 0.5 ml of phosphoric acid (25 wt.% in water) with continuous stirring. An additional phosphoric acid was added to the solution in such a way that the molar ratio of total acid to aniline (Z) varied from $Z=1$ to $Z=7$, whereas the total volume of the polymerization solution was maintained at 450 ml by adding water. After 1 h of stirring, 0.25 mol of ammonium peroxydisulfate solution (45 wt.%) was continuously dropped into the reactor containing the solution of acid and aniline. The temperature of reaction

mixture reached 50–70 °C within 12–15 min, and the reaction was rapidly quenched by applying an ice–water bath. After stirring for 30 min, the polyaniline was collected by filtration and washed several times with 1 M H_3PO_4 solution. The resulting powder was dried under dynamic vacuum for 2 days. Pellets of the samples with thickness 200–500 μm were made for electrical measurements under a pressure of about 10^3 kg/cm^2 for 3 s.

The four-probe technique was used for the d.c. conductivity measurement. Electrical contacts were made with 25 mm diameter gold wires by using conducting graphite adhesive. The electrical resistances of up to six samples were continuously measured by using automated data taking software during the slow cooling (less than 2 K/min) of the sample chamber in an Oxford Variox liquid helium cryostat from room temperature down to 1.5 K. A differential technique was used for the thermoelectric power measurements. The samples were mounted across two thermally isolated copper blocks. The temperature difference between the two copper blocks was measured by a Chromel–constantan thermocouple ($T > 50\text{ K}$) or a gold (7% iron)–Chromel thermocouple at low temperature ($T < 50\text{ K}$). The thermometry was calibrated for the entire temperature range ($5 < T < 300\text{ K}$). The absolute thermoelectric power of the sample was obtained using the absolute scale for lead [11].

3. Results and discussion

Fig. 1 shows the electrical d.c. conductivity at 290 K for polyaniline samples prepared in emeraldine salt form at various ratios of acid to aniline (Z) ranging from 1 to 7. The conductivity of the samples prepared at low acid concentration is $\sigma(290\text{ K}) < 10\text{ S/cm}$, and it increases with higher Z value. The maximum value of the conductivity $\sigma(290\text{ K}) = 40\text{ S/cm}$ is observed at $Z=6$ and the conductivity decreases as the ratio increases further. Shown also in Fig. 1 is the variation of the resistivity ratio, defined as $\rho_r \equiv \rho(10\text{ K})/\rho(290\text{ K})$. The resistivity ratio is about a 10^5 order of magnitude at $Z=1$ and rapidly decreases until it reaches the minimum value 45 at $Z=6$. Compared with previous results [1–3] in which the conductivity of the samples

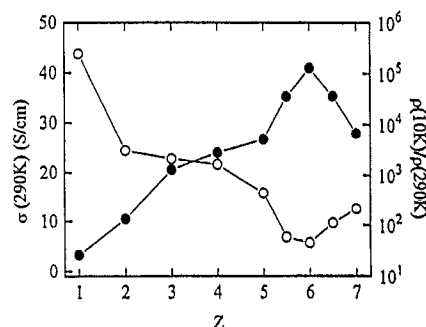


Fig. 1. Variation of electrical conductivity at $T=290\text{ K}$ (●) and the resistivity ratio (○) for phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z).

prepared by the conventional method changes by several orders of magnitude upon cooling down to temperatures below 10 K, the remarkably low resistivity ratio of phosphoric-acid-doped polyaniline indicates the improved electrical quality.

Fig. 2 shows the temperature dependence of the conductivity normalized to $\sigma(290\text{ K})$ for phosphoric-acid-doped polyaniline samples on a linear scale. As the acid concentration increases from $Z=1$ to 6, the curvature of data changes from downward to upward, suggesting that the mechanism related to the hopping transport at high temperature is undergoing a transition. Similar behaviors have been reported in other conjugated systems on variation of doping level [12].

The temperature dependence of the conductivity at low temperature follows the variable range hopping conduction of Eq. (1) as shown in Fig. 3. Data for the samples of $\sigma(290\text{ K}) > 20\text{ S/cm}$ ($Z > 3$) fit well to the VRH exponent $x=1/3$. The characteristic VRH temperature in Eq. (1) obtained from the linear fit in Fig. 3 ranges between $T_0 = 1600\text{ K}$ (for the sample of $Z=6$) and $T_0 = 21\,000\text{ K}$ (for the sample of $Z=3$) when calculated at the assumed value of $x=1/3$.

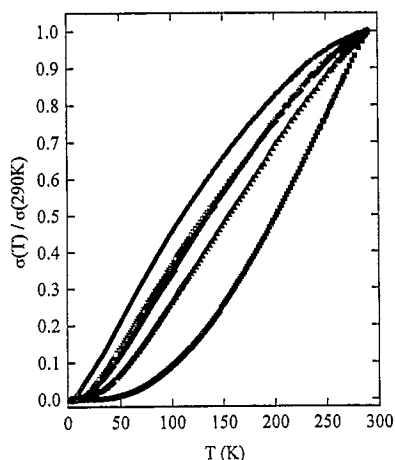


Fig. 2. Temperature dependence of electrical conductivity normalized to $\sigma(290\text{ K})$ for phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z): (■) $Z=1$; (▲) $Z=3$; (◆) $Z=5$; (●) $Z=6$; (+) $Z=7$.

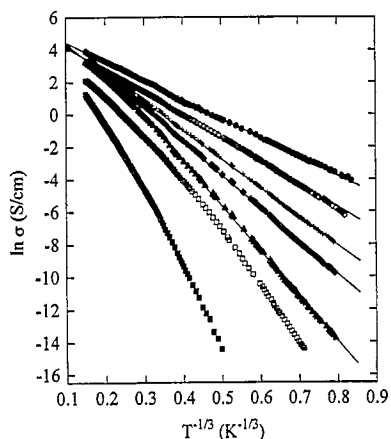


Fig. 3. Correlation of $\ln \sigma(T)$ with $T^{-1/3}$ for phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z): (■) $Z=1$; (□) $Z=2$; (▲) $Z=3$; (◆) $Z=5$; (◇) $Z=5.5$; (●) $Z=6$; (+) $Z=7$. The solid lines are linear fits for the data.

To determine explicitly the VRH exponent x and temperature T_0 , we calculated the reduced activation energy defined as $W \equiv d(\ln \sigma)/d(\ln T)$ [13,14]. By using Eq. (1) the reduced activation energy becomes:

$$\log_{10} W(T) = A - x \log_{10} T \quad (2)$$

where $A = x \log_{10} T_0 + \log_{10} x$. One can determine both x and T_0 from the slope and Y cut in a plot of $\log_{10} W$ versus $\log_{10} T_0$, as shown in Fig. 4. Sets of data with 50–100 data points are extracted from the raw conductivity data with the interval of $\Delta(\ln T) = 0.05$ – 0.1 , and successive differences are taken to calculate the logarithmic derivatives after the data-smoothing procedure. The solid lines in Fig. 4 represent the linear fits of data. The obtained x and T_0 values for the samples prepared at various acid concentrations are listed in Table 1.

Careful analysis on VRH parameters shows that the VRH exponent systematically varies from $x=0.44$ to $x=0.33$ as the $\sigma(290\text{ K})$ increases from 4 to 40 S/cm, or as the resistivity ratio decreases from $\rho_r = 2.4 \times 10^5$ to $\rho_r = 46$. The VRH temperature ($T_0 = 1500$ – 4500 K) is relatively insensitive to the variation of sample quality. The results are partly consistent with the results observed in the PANI-CSA polyblend system where the VRH exponent continuously varies from $x=1/4$ to $x=1$ upon dilution of PANI-CSA content in the blend [6]. The remarkable resemblance of the gradual change in VRH exponent suggests the percolation nature of electrical transport in pristine-doped polyaniline. According to the theory of VRH transport in Fermi glass [15,16], the average hopping distance is determined by the carrier tunneling probability between localized wavefunctions and the relative energy difference between localized states. The fractional VRH exponent $x=1/n$ depends upon the system dimension d ($n=d+1$), and the non-integer value of n could arise from the energy dependence of the state distribution [16,17]. However, the systematic variation of the VRH exponent is a new class of phenomenon, particularly observed in the system of a percolative network consisting of quasi one-dimensional fibrillar elements. The fractal characteristics resulting from the random geometrical distribution of polymeric chains

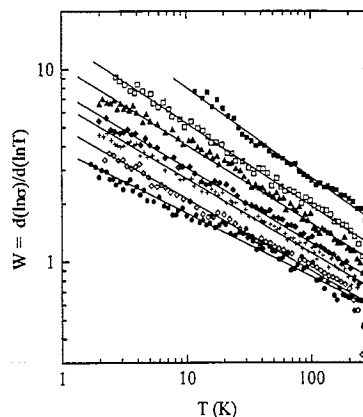


Fig. 4. Log-log plots of the reduced activation energy $W \equiv d(\ln \sigma)/d(\ln T)$ vs. T for phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z): (■) $Z=1$; (□) $Z=2$; (▲) $Z=3$; (◆) $Z=5$; (◇) $Z=5.5$; (●) $Z=6$; (+) $Z=7$. The solid lines are linear fits for the data.

Table 1

Electrical properties of phosphoric-acid-doped polyaniline samples prepared at various acid-to-aniline molar ratios (Z)

Z	$\sigma(290\text{ K})$ (S/cm)	ρ_t	x	T_0 (K)	$S(290\text{ K})$ ($\mu\text{V/K}$)	A^a ($\mu\text{V/K}^2$)	B^a ($\mu\text{V/K}^2$)
1	3.34	2.44×10^5	0.466	4500	+0.2	8.01×10^{-3}	-4.78×10^{-4}
2	10.5	3.08×10^3	0.431	3320	+1.3	1.02×10^{-2}	-5.59×10^{-4}
3	20.6	2.11×10^3	0.409	2730	+2.9	1.31×10^{-2}	-3.40×10^{-4}
4	23.9	1.66×10^3	0.394	2780			
5	26.6	439	0.392	1930	+5.6	2.45×10^{-2}	-5.02×10^{-4}
5.5	35.2	59.2	0.374	1040			
6	40.9	46.1	0.328	1510	+7.6	2.95×10^{-2}	-6.08×10^{-4}
6.5	35.3	111	0.363	2060			
7	27.8	212	0.387	1760			

^a For coefficients A and B , refer to Eq. (5). See text.

could render the non-integer system dimension [7,18]. In the pristine-doped polyaniline case, it is suggested that the non-fractional VRH exponent could be determined from the particular geometry of the conduction path optimized by the intrachain transport and interchain hopping contribution with the activation energy required for hopping conduction around 0.1–0.4 eV.

Fig. 5 shows the temperature dependence of the thermoelectric power of phosphoric-acid-doped polyaniline samples. As the acid concentration increases from $Z=1$ to $Z=6$ the thermoelectric power increases from $S(290\text{ K}) = +0.2$ to $+7.6\text{ }\mu\text{V/K}$. The $S(T)$ for the sample prepared at $Z=6$ is linear, indicating that diffusive metallic carrier transport is dominant. The thermoelectric power for samples with Z values lower than 3 shows U-shaped temperature dependence around 50 K, similar to results for the samples prepared by the conventional method [3,19], with a tendency of being flat near room temperature. This peculiar transport behavior arises from the combination of large-scaled inhomogeneity (metallic island) or microscopic disorder (localization), and the intrinsic metallic nature of polymer chains. Wang et al. [3] considered coupled metallic chains in an inhomogeneously disordered system. Li et al. [20] suggested that the U-shaped $S(T)$ could result from temperature-dependent tunneling between granular metallic islands. However, our data

show a gradual change of $S(T)$ from the positive linear temperature dependence to the negative U-shaped $S(T)$, suggesting additional negative hopping contributions (S_h) to the metallic diffusion thermoelectric power (S_m).

For the VRH transport, the temperature dependence of the thermoelectric power is related to the temperature dependence of the activation energy W as

$$S_h(T) \propto (k_B/e)(W^2/k_B T) \quad (3)$$

where $W^2/k_B T \propto k_B(T_0 T)^{1/2}$ for the three-dimensional Mott VRH ($x=1/4$) and $W^2/k_B T \propto k_B T_0$ for the VRH conduction with the Coulomb interaction ($x=1/2$) [21]. Using the reduced activation energy for the hopping transport, $W=x(T_0/T)^*$, a generalized expression for the hopping thermoelectric power can be written as [22]

$$S_h(T) \propto (k_B/e)(k_B T_0)(T/T_0)^{1-2x} \quad (4)$$

where x is the generalized VRH exponent. Considering the additive contribution of hopping thermoelectric power to the linearly temperature-dependent metallic thermopower, we have an expression for the total thermoelectric power as

$$S/T = A + B(T/T_0)^{-2x} \quad (5)$$

where A and B are coefficients indicating relative contributions to the total thermoelectric power.

Fig. 6 shows the plots of S/T versus temperature for data shown in Fig. 5. The solid lines are the least-squares error fits to Eq. (5) by using VRH exponents obtained from the temperature dependence of the conductivity (see Table 1). As Z increases from 1 to 6 the contribution of linear thermoelectric power (coefficient A) increases, while the variation of coefficient B is relatively small. The systematic variation of hopping contribution to the thermoelectric power is mainly related to the change of energy barrier between disordered states characterized by T_0 .

The series of measurements clearly show critical effects of the ratio of acid to aniline monomer on transport properties of resultant polymers. The effective oxidative polymerization of aniline and facile protonation doping of polyaniline at a moderately increasing concentration of acid competes with the decomposition process in highly acidic reaction media, as suggested by Boara and Sparglione [9]. Difficulties in

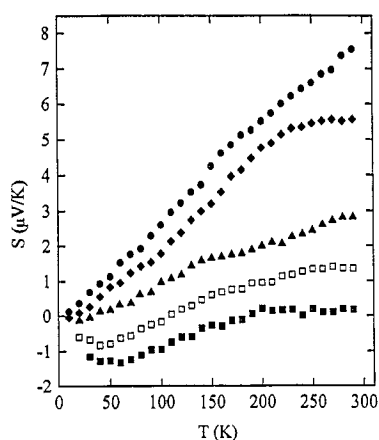


Fig. 5. Temperature dependence of the thermoelectric power of phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z): (■) $Z=1$; (□) $Z=2$; (▲) $Z=3$; (◆) $Z=5$; (●) $Z=6$.

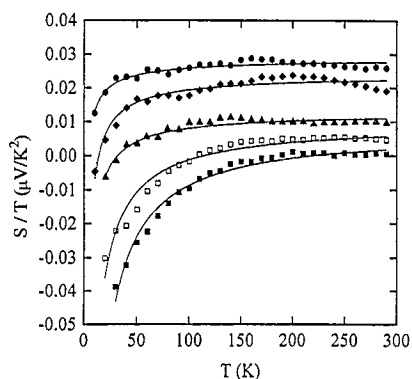


Fig. 6. Plots of S/T vs. T for phosphoric-acid-doped polyaniline prepared at various acid-to-aniline ratios (Z): (■) $Z=1$; (□) $Z=2$; (▲) $Z=3$; (◆) $Z=5$; (●) $Z=6$. The solid curves are the results of fitting using Eq. (5) (see text).

the deprotonation process during polymerization are also expected in highly acidic media. Elementary analysis of the samples shows no variation of relative content of phosphorous atoms, implying that there is no significant change in protonation level [23]. Meanwhile, the improved thermal stability of phosphoric-acid-doped polyaniline [24] and similar effects observed in polyaniline modified by the interposing phosphoric matrix group [25] suggest the possible coupling between the nitrogen atom of the aniline and dopant anion, which may suppress the bonding between the carbon atom in the benzene ring and dopant anion. The effect of phosphoric acid counterions is also detected in ongoing studies on the microscopic structure of phosphoric-acid-doped polyaniline, which show a clear difference in the X-ray diffraction pattern compared with that of polyaniline protonated by conventional strong acids such as hydrochloric acid [26].

The transport data of phosphoric-acid-doped polyaniline suggest that inhomogeneity of the material is in such a degree that the charge transport can occur both through hopping between partially disordered states and through diffusion between partially metallic states. From the similarity of transport data to those of polyaniline conductive blends [7,8], we conclude that the percolation nature can be observed even in pristine polyaniline samples by considering the inhomogeneous distribution of partially metallic states in the partially disordered matrix. The generalized VRH conduction with VRH exponent less than 1/2 observed in the temperature dependence of conductivity implies transport through the network of fibrillar geometry consisting of less disordered conductive objects. The observation of intrinsic metallic transport in thermoelectric power indicates the existence of the connected structure of conducting polyaniline well above the percolation threshold analog. However, the serial combination of quasi-one-dimensional polymer chains with finite size renders the resistive interchain or interboundary conduction dominant in bulk electrical conductivity [27]. In such an inhomogeneous system the quality of the material, in a sense of the electrical property, critically varies depending upon the extent of disorder determined at the stage of synthesis.

4. Summary

The electrical properties of a series of emeraldine salt forms of polyaniline, protonated by phosphoric acid, systematically change as the ratio of phosphoric acid to aniline ratio is varied at the stage of synthesis. The electrical properties of the sample were optimized at $Z=6$: (i) relatively high electrical conductivity at room temperature ($\sigma \sim 40$ S/cm), (ii) reduction of the resistivity ratio $\rho_r \equiv \rho(10\text{ K})/\rho(290\text{ K}) = 46$, (iii) $\ln \sigma \propto -(T_0/T)^x$ ($x=1/3$) temperature dependence of the conductivity, and (iv) linear temperature dependence of the thermoelectric power were observed for the first time in the pellet form of polyaniline. The VRH exponent x continuously varies from 1/3 to 1/2, implying the percolative nature of transport through the connected network with peculiar geometry. The temperature dependence of the thermoelectric power was analyzed by considering contributions from the diffusive carrier transport and VRH conduction.

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