Volume 7, Number 6
1004-423X/98/07060458-06

ACTA PHYSICA SINICA
(Overseas Edition)

June, 1998
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MAGNETIC AND ELECTRICAL PROPERTIES OF TWO POLYANILINE FAMILIES: PANI-H_3PO_4 and PANI-$C_4H_6O_6$ *

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(Received 13 October 1997)

We report a comparative study between two kinds of polyaniline, PANI-H_3PO_4 and PANI-$C_4H_6O_6$. We have measured the temperature dependence of the dc-conductivity $\sigma_{dc}(T)$ and magnetic susceptibility $\chi_T(T)$. The structure of polyaniline was characterized by Fourier transform infrared technique, electron-spin-resonance and X-ray diffraction. Polyaniline synthesized with phosphoric and tartaric acids leads to high magnetic susceptibility χ_T(at $T = 295\,K$) $\approx 10^{-4}$ emu/mol. 2rings. The dc-conductivity of both kinds of PANI shows a semiconductor behavior and follows the quasi-one-dimensional variable-range-hopping model. A comparison of the magnetic susceptibility shows greater electron localization in PANI-$C_4H_6O_6$, which is in agreement with the lower conductivity at room temperature for PANI-$C_4H_6O_6$.

PACC: 7280L; 7550

I. INTRODUCTION

Polyaniline (PANI) is an interesting material, because of its potential applications in a variety of areas, e.g., batteries, sensors, optical and electronic devices[1], and its excellent stability under ambient conditions. Polyaniline with conductivity $\sigma_{dc} = 10^{-19} - 10^{-12}$ S/cm is an insulator, from $\sigma_{dc} = 10^{-11} - 10^{-1}$ S/cm a semiconductor and $\sigma > 1$ S/cm is a metal. Wang *et al*.[2] reported that the dc-conductivity of PANI depends on the sample conditions (doping level, moisture, sample age). The chemical synthesis conditions of PANI include the polymerization media, the type and concentration of protonic acids, the oxidizing agents, the washing agents and the drying temperature.[3] Electrical conductivity can be varied by as much as 18 order of magnitude by varying dopant concentration, so that the electronic property control is feasible over the whole range from insulator to semiconductor and then to metal.[4] The emeraldine base (EB) form of polyaniline with σ(at $T = 295\,K$)$\approx 10^{-10}$ S/cm can be transformed to the emeraldine salt (ES) form with σ = (at $T = 295\,K$) = 5 S/cm if protons are added to the—N═sites while the number of electrons in the chain is held constant.[5,6] The purpose of this paper is to compare two kinds of acids (phosphoric-and tartric acid) used to synthesize polyaniline, which give to the material good magnetic and electrical properties.

* Project supported by the National Natural Science Foundation of China.

II. EXPERIMENTAL

The polyaniline was synthesized by the method of oxidative polymerization of monomeric aniline with ammonium persulfate in acidic solution. Two families of reaction were considered. They differed only on the acid used throughout the whole procedure: H_3PO_4 and $C_4H_6O_6$. The quantity of aniline used was 0.15 mole for all samples here reported. The synthesis procedure was the same for the two samples: first, 0.15 mole of aniline was dissolved in 800 ml of 2.0 M acid, under continuous stirring inside the reactor. The solution was kept at temperature 4 ℃ by putting in a water-ice bath. Then a solution of 0.25 mole of $(NH_4)_2S_2O_8$ in 200 ml of 2.0 M acid was added under vigorous stirring. The reaction mixture was agitated continuously for another 5 h. Finally the polyaniline was recovered by filtration, washed several times with a 0.1 M acid in solution and dried in air for approximately 24 h.

III. RESULTS AND DISCUSSION

A. Fourier transform infrared technique (FTIR)

The FTIR of PANI-H_3PO_4 are similar to that of PANI-$C_4H_6O_6$ except for bands 3425 and 2926 cm^{-1}, which are difficult to observe for PANI-$C_4H_6O_6$ as shown in Fig.1.

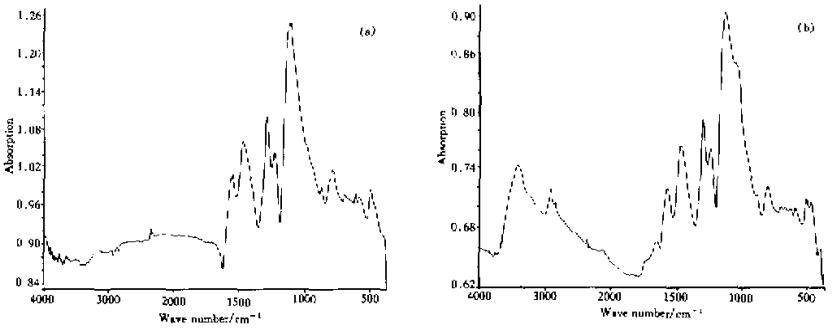

Fig.1. FTIR spectrum of polyaniline. (a)PANI-$C_4H_6O_6$; (b)PANI-H_3PO_4.

B. X-ray diffraction

Powder X-ray diffraction (XRD) observations were made using a computer-controlled XRD system, RINT 2000 wide angle goniometer at an operating rate of 40 kV and 140 mA Cu$K\alpha$ radiation, $\lambda = 0.1540$ nm in the 2θ range of 5 − 80 degree; the step-scanning rate was 0.02 degree for a scan speed 10 deg/min. The XRD patterns of the two PANI-samples are similar, as shown in Fig.2. According to Pouget *et al.*[7]

classification, our two PANI-samples have a semicrystalline structure.

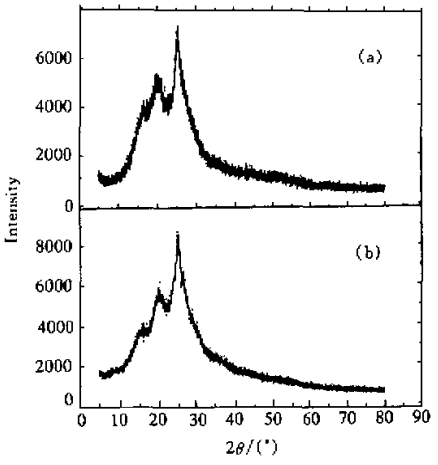

Fig.2. XRD Patterns of polyaniline. (a)PANI-H_3PO_4; (b)PANI-$C_4H_6O_6$.

C. DC-conductivity

Figure 3 shows our conductivity data, which show that the conductivity of PANI-H_3PO_4 is greater than that of PANI-$C_4H_6O_6$. The σ_{dc} of both kinds of polyaniline shows a semiconductor behavior, so σ_{dc} starts to increase from low temperature until $T \approx 270$ K, after that starts again to decrease. We interpret our results using quasi-one-dimensional variable-range-hopping(VRH)model between nearest neighbor chains[8],

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}], \tag{1}$$

$$T_0 = 8\alpha/N(E_F)k_B Z, \tag{2}$$

where α^{-1} is the localization length, $(N(E_F)$ is the density of states at the Fermi-level, k_B is Boltzmann constant, T_0 is the characteristic temperature and Z is the number of nearest neighbor chains (in our calculation $Z = 4$). From the plot of $\ln \sigma_{dc}(T)$ versus $T^{-1/2}$ (Fig.4) the slopes of the lines give the values of T_0, which are equal to 915 and

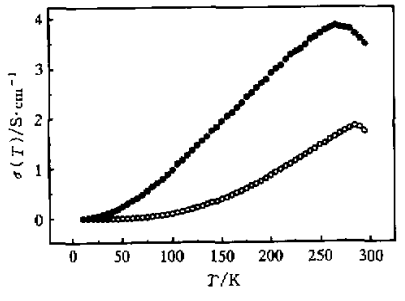

Fig. 3. Temperature dependence of dc-conductivity, for PANI-H_3PO_4 (filled circles) and PANI-$C_4H_6O_6$ (open circles).

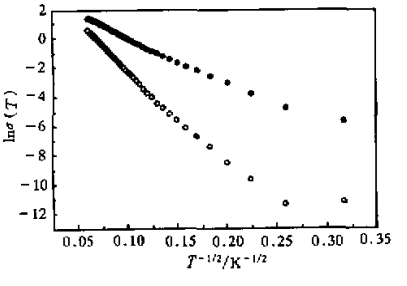

Fig. 4. VRH-plot, $\ln\sigma_{dc}(T)$ versus $T^{-1/2}$, for PANI-H_3PO_4 (filled circles) and PANI-$C_4H_6O_6$ (open circles).

3242 K for PANI-H_3PO_4 and PANI-$C_4H_6O_6$, respectively.

D. Magnetic susceptibility

The temperature dependence of magnetic susceptibility of both PANI-samples was measured in the range between 1.4 and 300 K (Fig.5).

Figure 6 shows the experimental results for the total magnetic susceptibility multiplied by the temperature, $(\chi_C + \chi_P)T$, as a function of temperature T. The slope of $(\chi_C + \chi_P)T$ versus T yields Pauli-susceptibility χ_P (temperature independent). The total electronic paramagnetic susceptibility can be written as

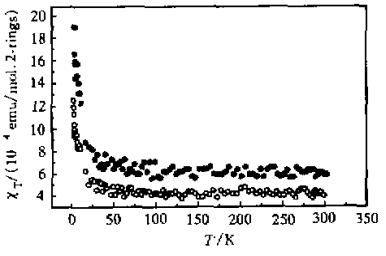

Fig. 5. Temperature dependence on the magnetic susceptibility for PANI-H_3PO_4 (open circles) and PANI-$C_4H_6O_6$ (filled circles).

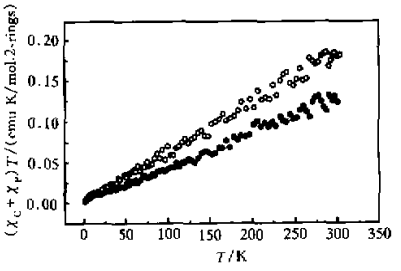

Fig. 6. The total magnetic susceptibility multiplied by the temperature $(\chi_C + \chi_P)T$ as a function of temperature T for PANI-H_3PO_4 (filled circles circles) and PANI-$C_4H_6O_6$ (open circles).

$$\chi_T = \chi_P + \chi_C = \chi_P + C/T, \tag{3}$$

where χ_C is the temperature-dependent $(\sim 1/T)$ Curie susceptibility and C is the Curie-constant. The values of $N(E_F)$ and α^{-1} obtained from the equation

$$\chi_P = \mu_B^2 N(E_F) \tag{4}$$

and Eq. (2), respectively, are also given in Table 1, where μ_B is the Bohr-magneton. From the Curie law

$$\chi_C(T) = \mu_B^2 N_c / k_B T, \tag{5}$$

Table 1. Magnetic and electrical properties of PANI-H_3PO_4 and PANI-$C_4H_6O_6$ compared with PANI-HCl and PANI-POT (Refs. [5] and [2]), all data being room-temperature values.

PANI-	T_0/K	$\chi_P/10^{-5}$ emu per mol.2rings	$\chi_C/10^{-5}$ emu per mol.2rings	$N(E_F)$/states per eV 2rings	N_c/per 2rings	α^{-1}/nm	Ref.
H_3PO_4	915	43	0.48	1.33	0.0038	1.9	This work
$C_4H_6O_6$	3242	61	1.29	1.88	0.01	0.38	This work
HCl	*3000*	*11*	3.0	3.4	0.023	4.5	[5]
POT	15000	5.4	8.5	1.7	0.065	0.9	[2]

the number of singly occupied states (per unit volume) N_c with spin 1/2 can be calculated.

In our calculation N_c was calculated in units (per mole two rings), and converted from 1/mol.2-rings value to 1/2-rings by dividing over the Avogadro's number N_A. A comparison of the magnetic and electrical properties of PANI-$C_4H_6O_6$ and PANI-H_3PO_4 with those of PANI-HCl and PANI-poly(o-toluidine) (Refs. [5] and [2]) are summarized in Table 1.

E. Electron spin resonance(ESR)

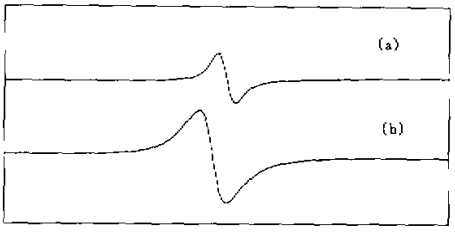

Fig.7. ESR spectra of polyaniline. (a)PANI-H_3PO_4; (b)PANI-$C_4H_6O_6$.

The ESR signals of PANI-H_3PO_4 and PANI-$C_4H_6O_6$ have been observed. However, the g- value of both samples are almost equal (g = 2.0037 for PANI-H_3PO_4 and g = 2.0038 for PANI-$C_4H_6O_6$). The linewidth (LW) of PANI-$C_4H_6O_6$ is larger ($LW = 3.45 \times 10^{-4}$ T) than that of PANI-H_3PO_4 ($LW = 1.93 \times 10^{-4}$ T) as shown in Fig.7. This may be related to the high degree of localization of electrons in PANI-$C_4H_6O_6$, which is consistent with its lower conductivity at room temperature.

Table 2. The g -factor and linewidth of different polyaniline families.

PANI-	*g-factor*	$LW/10^{-4}$ T	Ref.
H_3PO_4	2.0037	1.93	This work
$C_4H_6O_6$	2.0038	3.45	This work
H_3PO_4	2.0035	1.7	[9]
HCl	2.0038	0.3	[5]
H_2SO_4	2.0038	1.8	[9]
HCOOH	2.0039	2.3	[9]
POT	2.0034	0.7	[2]

IV. CONCLUSION

To our knowledge, we report for the first time the low-temperature dc-conductivity and magnetic susceptibility of polyaniline synthesized with tartaric acid. Polyaniline synthesized with phosphoric-and tartaric acids leads to high room-temperature magnetic susceptibilities, in which the values of χ_T (at T = 295 K) = 4.35×10^{-4} and 6.23×10^{-4}emu/mol.2rings, are found, respectively. They are one or two order of magnitude higher than those reported earlier for PANI-HCl[5], PANI-POT[2], PANI-H_2SO_4[10] and PANI-CSA[11], in which the values of 14×10^{-5}, 13.9×10^{-5}, $2.1 \times 10^{-6}$and 3.0×10^{-5}emu/mol.2rings, have been found, respectively. A comparison of the magnetic properties of both PANI-samples is given in Table 1. Though the total room-temperature

χ_T is almost the same, the PANI-$C_4H_6O_6$ has larger χ_C. This implies a greater electron localization in PANI-$C_4H_6O_6$. Also PANI-$C_4H_6O_6$ has a larger ESR linewidth than PANI-H_3PO_4. This suggests there is less motional narrowing in PANI-$C_4H_6O_6$ and hence electrons are more localized. In contrast, the g-factors of PANI-H_3PO_4 and PANI-$C_4H_6O_6$ are similar. The conductivity of both kinds of polyaniline shows a semiconductor behavior and follows the quasi-one-dimensional VRH-model. X-ray studies of PANI-H_3PO_4 and PANI-$C_4H_6O_6$ show similar crystallinity.

REFERENCES

[1] J. Lippe and R. Holze, *Mol. Cryst. Liq. Cryst.*, **208**(1991), 99.

[2] Z. H. Wang, A. Ray, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev.*, **B43**(1991), 4373.

[3] K. L. Tan, B. T. G. Tan, S. H. Khor, K. G. Neoh and E. T. Kang, *J. Phys. Chem. Solids*, **52**(1991), 673.

[4] R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer and L. W. Shacklette, *Chem. Rev.*, **82**(1982), 209.

[5] J. M. Ginder, A. F. Richter, A. G. MacDiarmid and A. J. Epstein, *Solid State Commun.*, **63**(1987), 97.

[6] F. Zuo, M. Angelopoulos, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev.*, **B39**(1989), 3570.

[7] J. P. Pouget, M. E. Jozefowicz, A. J. Epstein, X. Tang and A. G. MacDiarmid, *Macromolecules*, **24**(1991), 779.

[8] N. F. Mott and E. Davis, Electron Processes in Non-crystalline Materials (Clarendon, Oxford, 1979).

[9] S. Palaniappan and B. H. Narayana, *J. Polymer Science*, **A32**(1994), 2431.

[10] C. Fite, Y. Cao and A. J. Heeger, *Solid State Commun.*, **73**(1990), 607.

[11] Y. Cao and A. J. Heeger, *Synth. Met.*, **52**(1992), 193.