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The Role of Molecular Recognition in Charge Transport Properties of Doped Polyaniline

A. K. MUKHERJEE AND REGHU MENON*

Department of Physics, Indian Institute of Science,
Bangalore-560 012, India,
E-mail: rmenon@physics.iisc.ernet.in

Abstract

Molecular recognition plays a significant role in the counterion-induced processibility, morphological features, and physical properties of doped polyaniline (PANI). The interaction of the counterion and solvent controls the chain conformation and, as a result, the formation of extended and localized electronic states; hence, it holds the key for tuning a wide range of electrical and optical properties of doped PANI. The combined effects of counterion, solvent, and processing conditions tune the metal-insulator transition, temperature dependence of conductivity, magnetoresistance, and so forth in doped PANI. The typical examples are shown in the case of PANI doped by camphor sulfonic acid, 2-acrylamido-2-methyl-1-propane sulfonic acid, and dodecylbenzoyl sulfonic acid.

Index Entries: Molecular recognition; polyaniline; electrical conductivity; magnetoresistance.

Introduction

Although the phenomenon called molecular recognition is well known in several biological systems, in conducting polymers it was observed in polyaniline (PANI) doped by sulfonic acids consisting of surfactant-counterions. The typical example of molecular recognition can be described in a hydrogen-bonded system in which the strength of interactions between the hydrogen-bonding donors and acceptors depends crucially on the alignment of the interacting entities. The bonding strength could be drastically reduced by the slightest misalignment from their optimal orientation. When such a molecular matching is present between the interactive moieties, several hydrogen bonds can form in a constructive manner. This concept of

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*Author to whom all correspondence and reprint requests should be addressed.

molecular matching is called molecular recognition. For example, in the case of DNA, three hydrogen bonds can form simultaneously between the monomer units of cytosine and guanine. Another example is when uracil and 2,6-diacylaminopyridine is modified by nonmesogenic alkyl groups. Then it forms a mesogenic molecular complex linked by three sterically fitting hydrogen bonds *(1)*.

Among various conducting polymers, PANI is quite well known for several commercial applications *(2)*. PANI can be prepared by either chemical polymerization or electropolymerization. The emeraldine salt was obtained by oxidative polymerization of aniline at –26°C, and it is converted into the insulating emeraldine base. Then, it is protonated with acid to obtain the conducting PANI. Cao et al. *(3)* showed that the surfactant-counterions can induce solubility of doped PANI in various solvents. Later, Ikkala et al. *(4,5)* investigated the role of molecular recognition in the formation of supramolecular structures based on hydrogen bonding and phenyl ring stacking. In this process, the molecular recognition of the counterion and the solvent plays a crucial role in determining the morphology and the physical properties of doped PANI.

Molecular Recognition in PANI-Camphor Sulfonic Acid

In the context of counterion-processed PANI, the concept of molecular recognition can be stated as follows. Phenolic solvents have relatively large interactions with sulfonate anions of the counterions, and the amines of PANI as well as a properly functionalized counterion may form cyclic associations provided that there is a steric match between the molecules concerned *(4,5)*.

In general, a functionalized protonic acid can be denoted by $H^+(M^- - R)$, in which the counterion anion is $(M^- - R)$, and it contains the functional group (R) that is chosen to be compatible with the corresponding organic solvents. For example, in the case of dodecylbenzenesulfonic acid (DBSA), as shown in Fig. 1A, the long alkyl chain induces the solubility in common solvents such as toluene, xylene, decaline, and chloroform. Similarly, PANI doped by sulfonic acid containing polar counterions such as 10-camphor sulfonic acid (CSA), as shown in Fig. 1B, is soluble in polar solvents such as *m*-cresol. The chemical structures of emeraldine base and protonated PANI are shown in Fig. 2. This counterion-solvent interaction can induce conformational changes in the structure of the PANI chain. For example, when PANI-CSA is solvated in chloroform (*m*-cresol), the chains are coiled (extended). Xia et al. *(6)* have shown that by exposing a PANI-CSA film prepared in chloroform to *m*-cresol vapor, its chain conformation changes from coiled to extended form. Moreover, the absorption spectrum shows the corresponding transformation of some of the localized states to extended states. This type of counterion-solvent interaction can also induce a liquid-crystalline state in doped PANI.

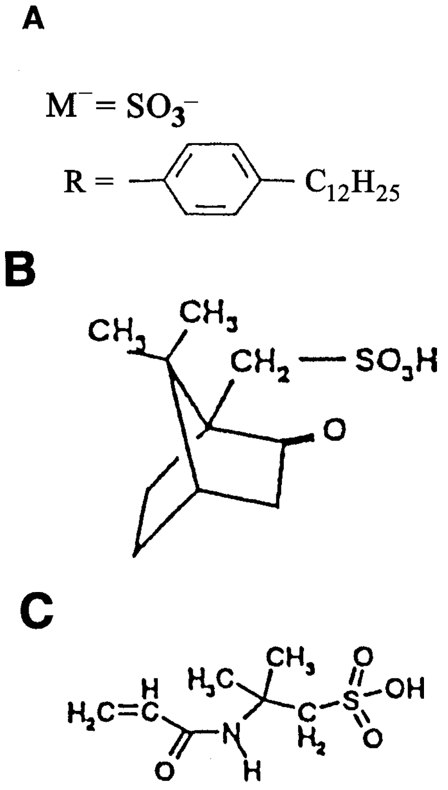

Fig. 1. Typical functionalized protonic acids: **(A)** DBSA; **(B)** CSA; **(C)** AMPSA.

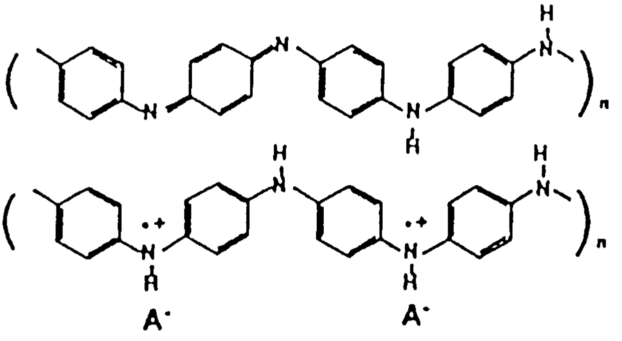

Fig. 2. Emeraldine base (**top**) and emeraldine salt (**bottom**) forms of PANI.

The solution of PANI-CSA in *m*-cresol is of special interest for the following reasons:

1. It has the highest reported electrical conductivity of nonoriented films obtained by evaporating *m*-cresol on silicon substrate, 200–400 S/cm *(3)*.

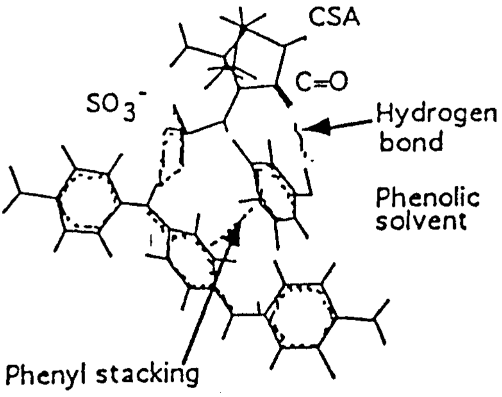

Fig. 3. Molecular recognition of PANI-CSA in *m*-cresol solvent. Adapted from ref. *4*.

2. It has a positive temperature coefficient of resistivity (metallic) above 150 K *(7)*.
3. It has a temperature-independent Pauli susceptibility above 10 K *(8)*.
4. It has a large negative dielectric constant at microwave frequencies *(9)*.
5. It exhibits lyotropic liquid crystalline behavior at volume fractions exceeding ~14.5% vol of PANI complex *(10)*.

In the case of PANI-CSA in *m*-cresol, the restricted Hartree Fock calculations have shown that steric matching can lead to supramolecular structures owing to the combination of three simultaneous interactions *(4,5)*:

1. The sulfonic acid is bonded to PANI owing to proton transfer.
2. The hydroxyl group of phenol is hydrogen bonded to the carbonyl group of the CSA molecule.
3. The phenyl groups of phenol and PANI are stacked, thus yielding enhanced mutual dispersion forces.

These interactions are possible because the molecular dimensions and the steric details simultaneously allow a charge transfer, phenyl stacking, and a hydrogen bond, as shown in Fig. 3 *(4,5)*. The steric combination of the bonding thus satisfies the requirements of molecular recognition. Following similar guidelines, Adams et al. *(11)* reported a new processing route for PANI by the combination of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and dichloroacetic acid (DCA).

The counterion-solvent interaction in the case of CSA/*m*-cresol combination is rather strong with respect to that in AMPSA-DCA and DBSA-xylene/toluene, since both CSA and *m*-cresol are highly polar in nature. The chains of PANI are relatively more extended in the highly polar environment owing to the counterion-solvent interaction, as in the case of CSA/*m*-cresol. Hence, the role of molecular recognition in the chain extension of PANI, in the presence of CSA/*m*-cresol, is quite significant compared with that in AMPSA-DCA and DBSA-xylene/toluene. Nevertheless,

Table 1
Protonic Acids of PANI in Different Solvents
with Corresponding Room Temperature Conductivities in Film Form

Protonic acid	Solvent	Conductivity (S/cm)
CSA	*m*-Cresol *(3)*	200–500
	Hexafluoro-2-propanol *(15)*	220
	DCA *(16)*	80
	Chloroform *(3)*	≈0.1
Amidopropane sulfonic acid	Triflouroethanol *(17)*	100
AMPSA	Dichloroacetic acid *(11)*	10–100
Poly(sodium-4-styrene sulfonate) *(18)*	Dioxane mixture	10^{-3}–10^{-7}
Methyl sulfonic acid	Chloroform *(19)*	≈0.1
DBSA	Chloroform *(19)*	≈0.1
Dinonylnaphthalene sulfonic acid *(20)*	Methanol	2.3
	Methlethylketone	0.9
	2-Propanol	8.1×10^{-3}
	Ethanol	2.4×10^{-2}
	m-Cresol	2.9×10^{-3}
	Xylene	6.5×10^{-6}–63×10^{-6}

the three-dimensional molecular level interactions in the case of PANI-DBSA/xylene and PANI-AMPSA/DCA are yet to be studied in detail. These typical examples show that a judicious choice of the combination of functionalized protonic acid and solvent can take advantage of the molecular recognition features in the processing of PANI.

Conductivity and Magnetoresistance

One of the immediate effects of molecular recognition in PANI-CSA dissolved in *m*-cresol is the increase in conductivity. Prior to this, when PANI dissolved in *N*-methyl pyrrolidonone (NMP) was protonated by HCl or H_2SO_4, the maximum achievable conductivity was about 20 S/cm *(12)*, whereas in PANI-CSA, values as high as 500 S/cm were observed *(3,13)*. The conductivity of doped PANI prepared by various combinations of acids and solvents is given in Table 1.

The temperature dependence of conductivity of PANI-CSA/*m*-cresol and PANI-Cl/NMP is shown Fig. 4 *(3,12)*. Since the room temperature conductivity of PANI-Cl is rather low, its temperature dependence is rather strong, and it becomes an insulator at low temperatures. By contrast, a finite value of conductivity was observed for PANI-CSA even at millikelvin temperatures *(14)*. The temperature dependence of conductivity of PANI-CSA and PANI-AMPSA samples is nearly similar in both systems, with a positive temperature coefficient of resistivity above 150 K, as shown in Fig. 5. Moreover, a finite value of conductivity was observed down to 1 K

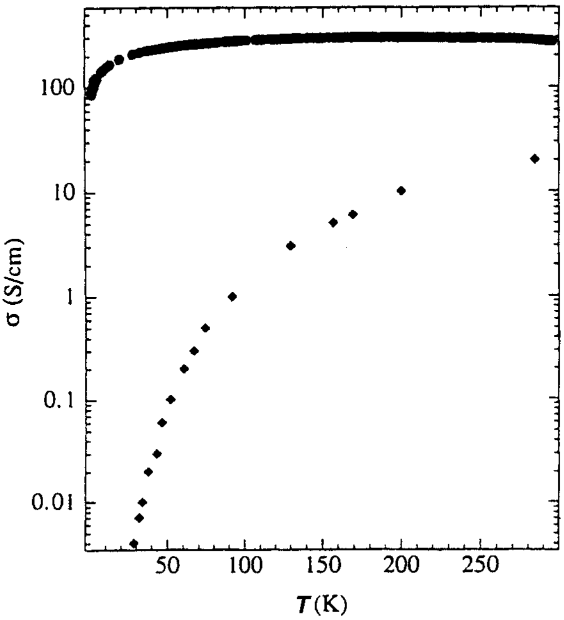

Fig. 4. Conductivity vs temperature for PANI-CSA (**upper**) and PANI-Cl (**lower**).

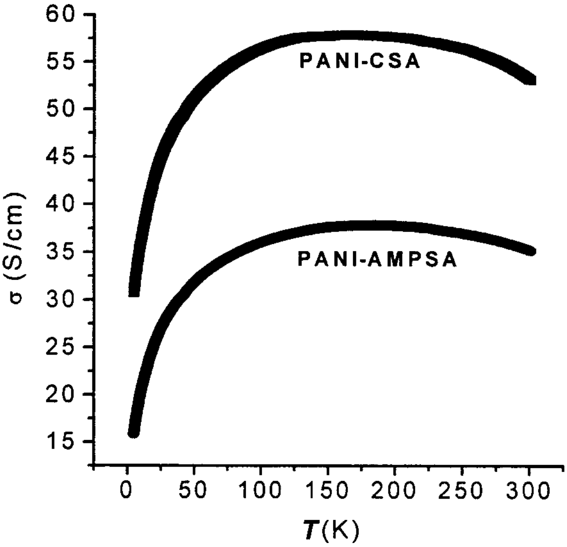

Fig. 5. Conductivity vs temperature for PANI-CSA (**upper**) and PANI-AMPSA (**lower**).

in both systems. These results suggest that in PANI-CSA/AMPSA, the counterion-solvent interaction via molecular recognition assists the formation of extended chains and extended electronic states, whereas in PANI-Cl the coiled chains lead to the formation of localized states.

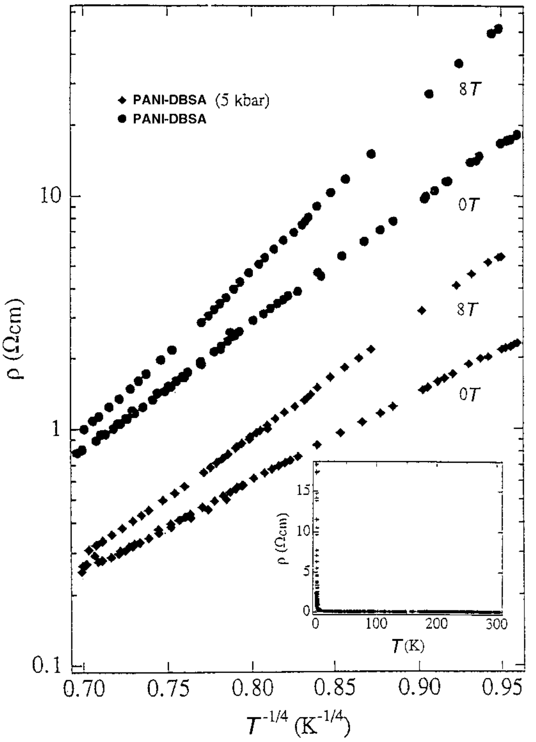

Fig. 6. Resistivity vs temperature for PANI-DBSA.

The low-temperature conductivity of PANI-DBSA, as a function of pressure and magnetic field, is shown in Fig. 6. Although the room temperature conductivity of PANI-DBSA (nearly 50 S/cm) is nearly the same as that of PANI-CSA/AMPSA, its temperature dependence is rather different. First, the positive temperature coefficient of resistivity was not observed in the case of PANI-DBSA. Second, the Mott's $T^{-1/4}$ fit [$\sigma(T) \propto \exp(-T_0/T)^{1/4}$] shows that the low-temperature conduction mechanism is owing to variable range hopping, as observed in insulators. The value of T_0 in $T^{-1/4}$ fit yields the activation energy for hopping transport. The pressure (magnetic field) increases (decreases) the overlap of the wave functions of the localized states. Hence, the wave functions of the electronic states in PANI-DBSA are highly susceptible to external perturbations by pressure and magnetic field.

The transverse magnetoresistance of PANI-CSA and PANI-AMPSA is shown in Fig. 7. Since the conductivity and its temperature dependence are nearly identical in both systems, it is hard to expect any variation in the behavior of magnetoresistance in both systems. Moreover, both systems are three dimensional (thickness of about 30 μ) and isotropic (chains are randomly oriented). However, the data show that the sign of magnetoresistance is negative for PANI-AMPSA, and it is positive for PANI-CSA. Since the magnetoresistance probes the microscopic transport mechanism, this

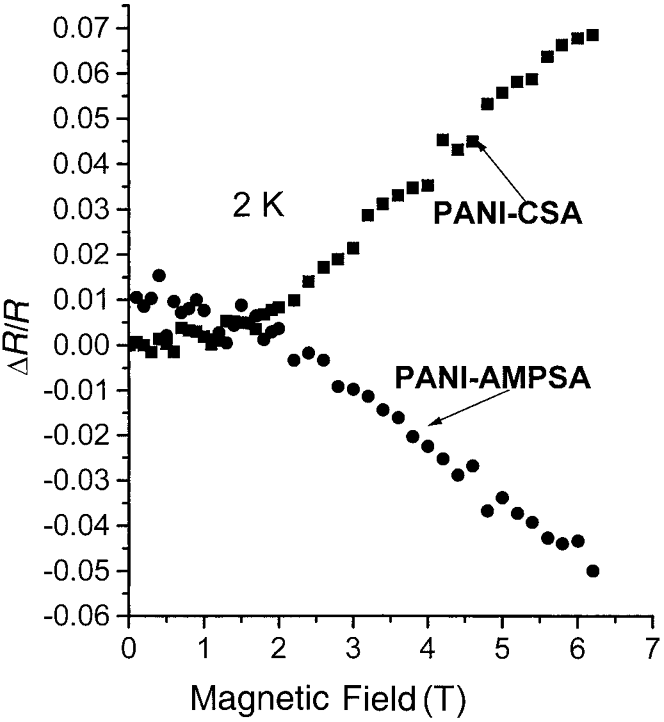

Fig. 7. Magnetoresistance ($\Delta R/R$) vs field of PANI-CSA and PANI-AMPSA.

suggests that the mechanism for charge transport in both systems shows some variations owing to subtle morphologic differences in these systems. Usually, in barely metallic three-dimensional systems, the sign of magnetoresistance is positive at all temperatures and fields *(13)*. Hence, the positive magnetoresistance in PANI-CSA is as expected. However, the negative magnetoresistance in PANI-AMPSA is quite unusual, and this suggests the presence of some two-dimensional mesoscopic structure in this system. This shows that the supramolecular assembly in both systems is different owing to the subtle variations in the molecular recognition process in the PANI-CSA and PANI-AMPSA systems.

Conclusion

The importance of the role of molecular recognition via the counterion-solvent-polymer interactions was observed in the conductivity, temperature dependence of conductivity, and magnetoresistance measurements in PANI-CSA, PANI-AMPSA, and PANI-DBSA samples. A positive temperature coefficient of resistivity, above 150 K, was observed in PANI-CSA and PANI-AMPSA, but not in PANI-DBSA. Among these systems, PANI-CSA showed the most metallic features, since the CSA—*m*-cresol interaction favors the formation of extended chains and delocalized electronic states. In insulating PANI-DBSA samples, pressure (magnetic field) decreases (increases) the activation energy. The sign of the transverse magnetoresistance is negative (positive) for PANI-AMPSA (PANI-CSA). The negative magnetoresistance suggests the possibility of two-dimensional mesoscopic regions in PANI-AMPSA.

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