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Electron localization length in polyaniline

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Abstract

Electrical DC conductivity, magnetic susceptibility, and EPR measurements are used to investigate the electron localization behavior of polyaniline as a function of the dopant type using seven sulfonic acid based doping acids. In spite of differences in the magnitude and the temperature dependences of DC conductivity and magnetic susceptibility data, the experiments reveal a localization length of approximately 30 Å for all the samples. We conclude that this result is essentially due to disorder in the basic morphological structure of a polymer that seems to be determined, among other factors, by the nature of the monomeric units comprising the polymer chains.

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1. Introduction

Polyaniline's technological significance arises due to its processability into films and fibers, which is achieved by synthesizing soluble conducting polyaniline either by using functionalized protonic acids or by including substituent groups in the ring giving polymers such as alkyl polyanilines, alkoxy polyanilines, sulfonic acid ring-substituted polyanilines, and highly sulfonated polyanilines [1–11]. The quality of the synthesized material depends on a combination of factors during the synthesis and doping processes [1–11].

An electrical DC conductivity study on polyaniline films doped with benzene sulfonic acid (BSA), toluene sulfonic acid (TSA), camphor sulfonic acid (CSA) and naphthalene sulfonic acid (NSA), but cast in chloroform, benzyl alcohol (BeOH) and *m*-resol, was recently reported [12]. Using the result $T_0 = 16/[k_B N(E_F)\alpha^{-1}]$, where T_0 is determined from the slope of a $\ln(\sigma)$ versus $T^{-1/2}$ plot and $N(E_F)$ is the density of states at the Fermi level, a localization length (α^{-1}) was determined [13]. The localization length in *m*-cresol cast films of polyaniline was obtained to be 80, 51, 38 and 25 Å for the dopants BSA, CSA, TSA and NSA, respectively. In the case of films cast in chloroform, the localization length was 34, 32, 29 and 27 Å for the dopants BSA, CSA, TSA and NSA, respectively. For the third solvent benzyl alcohol, the localization length was 25, 25, 28 and 49 Å for the dopants BSA, CSA, TSA and NSA, respectively. A few observations are in order from the above measurements and analysis. First, α^{-1} exhibits a large range of values for the four dopants in the solvent *m*-cresol. Second, α^{-1} in the benzyl alcohol cast films does not change for the dopants BSA, TSA and CSA, but surprisingly shows an increase by a factor of 2 in the case of the dopant NSA. The four dopants in the case of chloroform cast films also do not show any significant change in α^{-1}.

Before determining the role of solvent-induced secondary doping on the electronic properties such as the

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localization length, it is, however, important to quantitatively know the magnitude of the localization length before introducing solvent-effected changes in the chain structure. In this paper, we report results of our investigations on the electronic behavior of polyaniline that is doped with a number of dopants belonging to the same family. This study was also prompted by our earlier magnetic, optical, and EPR studies of polyaniline that showed some differences when it was doped with paratoluenesulfonic acid (PTSA) and sulfosalicylic acid (SSA) [14].

Since a detailed study of the electron localization behavior of polyaniline as a function of only the dopant type, 'with all other factors influencing the synthesis remaining the same', has not been reported, we have chosen the following seven dopants for the present study: (1) 2,5-dimethylbenzenesulfonic acid (PXSA), (2) 3,4-dimethylbenzenesulfonic acid (OXSA), (3) 4-hydroxybenzenesulfonic acid (PSA), (4) 4-hydroxy-*m*-benzenedisulfonic acid (PDSA), (5) 4,6-dihydroxy-*m*-benzenedisulfonic acid (RDSA), (6) 2-hydroxy-4-methylbenzenesulfonic acid (MCSA), and (7) 3-chloro-4-hydroxybenzenesulfonic acid (OCPSA). It is to be noted that the size is not too drastically changed from one dopant to the other in this series.

2. Experimental

The fine powder of blue emeraldine base, obtained from standard synthesis procedures, is dispersed in 1 M aqueous solution of functionalized aromatic sulfonic acids like 2,5-dimethylbenzenesulfonic acid, 3,4-dimethylbenzenesulfonic acid, 4-hydroxybenzene sulfonic acid, 4-hydroxy-*m*-benzenedisulfonic acid, 4,6-dihydroxy-*m*-benzenedisulfonic acid, 2-hydroxy-4-methylbenzene sulfonic acid and 3-chloro-4-hydroxybenzenesulfonic acid under vigorous stirring for 24 h. After doping reaction, solution is filtered under suction and collected material is given washing with 1 M aqueous solution of aromatic sulfonic acid. A doping level of approximately 50 mol% is achieved this way. The polymer is then dried at 60–80 °C under dynamic vacuum for 12 h [15].

Powders pressed into the shape of a parallelpiped were mounted on the cold finger of a Janis closed cycle refrigerator for conductivity measurements. A Keithley Model No. 220 constant current source was used to pass a constant current through the sample and the voltage was measured using a Keithley Model No. 614 electrometer. The conductivity σ was measured in the ohmic region from room temperature down to about 30 K. A small quantity of the powdered sample was placed in an EPR tube of a computer-controlled X-band Bruker EMX 6/1 spectrometer for the EPR magnetic susceptibility and hence the density of state at the Fermi level, $N(E_F)$.

3. Results and discussion

Fig. 1 shows the results of DC conductivity $\sigma(T)$, plotted as $\ln \sigma$ versus $T^{-1/2}$, on pressed pellets of the seven samples. It is found that σ for all the samples, except OCPSA whose value is 1×10^{-1} S/cm, lies in the range 1.0 ± 0.6 S/cm. The room temperature conductivity is 0.9, 0.6, 1.4, 1.6, 1.0, 0.5 and 0.1 S/cm for PXSA-PANI, OXSA-PANI, PSA-PANI, PDSA-PANI, RDSA-PANI, MCSA-PANI and OCPSA-PANI, respectively. The values of T_0 obtained from the above plots are 7200, 9600, 8500, 7400, 4600, 6200 and 11,000 K for PXSA-PANI, OXSA-PANI, PSA-PANI, PDSA-PANI, RDSA-PANI, MCSA-PANI and OCPSA-PANI, respectively. Except for OCPSA-PANI, which exhibits the smallest conductivity and the largest T_0 compared to the six other samples, we do not see in our results any correlation between T_0 and the room temperature conductivity.

As far as the DC electrical conductivity is concerned, all the seven samples are found to obey the relation

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

$$T_0 = 16/[\alpha^{-1} N(E_F) z k_B], \tag{2}$$

where α^{-1} is the decay length of the localized electron state, $N(E_F)$ the density of states at the Fermi level, z the number of nearest neighbor chains (which is 4 for polyaniline [13]), and k_B the Boltzmann constant. The form (1) of the conductivity is characteristic of quasi-one-dimensional variable range hopping between nearest neighbors [13]. A fit of the experimental data to Eq. (1) yields T_0. Determination of α^{-1} also requires $N(E_F)$ which is obtained from magnetic susceptibility measurements as presented next.

The EPR magnetic susceptibility was measured as a function of temperature for the seven samples. The data were calibrated with the standard K_3CrO_8. The data thus obtained can be fitted to an equation of the type

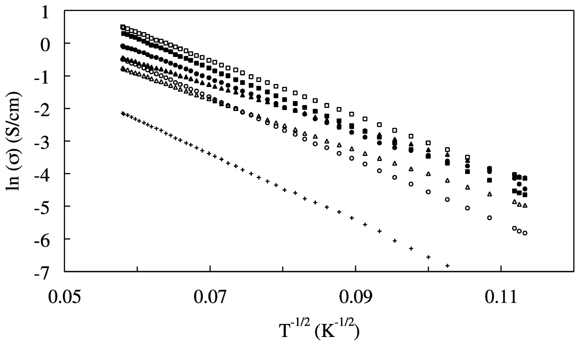

Fig. 1. Dependence of DC conductivity on temperature for the seven samples: PXSA-PANI (solid circles); OXSA-PANI (open circles); PSA-PANI (solid squares); PDSA-PANI (open squares); RDSA-PANI (solid triangles); MCSA-PANI (open triangles); OCPSA-PANI (plusses).

$\chi = \chi_P + C/T$, which leads to the values of the Pauli and Curie susceptibilities. The slope of the χT versus T plots yields χ_P, which can be used to obtain $N(E_F)$ using $\chi_P = [\mu_B^2 N(E_F)]$. The values of χ_P, arising from fits of the data for PXSA-PANI, OXSA-PANI, PSA-PANI, PDSA-PANI, RDSA-PANI, MCSA-PANI and OCPSA-PANI are 65×10^{-6}, 55×10^{-6}, 60×10^{-6}, 67×10^{-6}, 95×10^{-6}, 75×10^{-6} and 70×10^{-6} emu/(mole 2-rings), respectively. Using the result $\chi_P = \mu_B^2 N(E_F)$, the following respective values of $N(E_F)$ are obtained for the above seven samples: 0.030, 0.039, 0.035, 0.028, 0.011, 0.022, and 0.026 states/eV 2-rings.

We are now in a position to determine the localization length (σ^{-1}) using Eq. (1). The values of σ^{-1} obtained this way for PXSA-PANI, OXSA-PANI, PSA-PANI, PDSA-PANI, RDSA-PANI, MCSA-PANI and OCPSA-PANI are 32, 28, 29, 30, 32, 32 and 27 Å, respectively. The value of σ^{-1} is seen to be nearly the same for all the samples. This is a rather surprising result especially because no correlation was observed between σ (at room temperature) and T_0.

The DC conductivity is a bulk quantity and provides an overall picture for the nature of the inhomogeneities in a material. The EPR lineshape and linewidth, on the other hand, can provide useful information about the presence of mesoscopic disorder through a study of local magnetic interactions in the polymer. In all the samples studied here, the lineshape is close to a Lorentzian for a magnetic field up to approximately six times the full width at half maximum ($\Delta H_{1/2}$). Fig. 2 shows the data for the temperature dependence of the peak-to-peak linewidth (ΔH_{pp}) for the seven samples. The temperature-dependent linewidth is seen to fall into three distinct categories. The room-temperature linewidth is around 5.8 G in the case of PSA-PANI, PDSA-PANI and RDSA-PANI (samples 3, 4 and 5, respectively), around 3 G in the case of PXSA-PANI, OXSA-PANI and MCSA-PANI (samples 1, 2 and 6, respectively), and 1.3 G in the case of OCPSA-PANI (sample 7). While the dopants in samples 3, 4 and 5 have only OH and SO_3H (single or double) substituent groups and give rise to the top set of linewidth curves, the dopants in samples 1 and 2 contain two CH_3 units and one SO_3H unit and yield the middle set of curves. Since the dopant in sample 6 contains one OH group in addition to the CH_3 and SO_3H groups, the magnitude of Δ_{pp} is larger than that for samples 1 and 2 at all temperatures. Finally, for the dopant OCPSA that contains the substituent Cl in addition to OH and SO_3H, Δ_{pp} is the lowest and it increases very slowly with a decrease in temperature. Unlike DC conductivity, the EPR linewidth as a function of temperature is thus sensitively dependent on the dopant type.

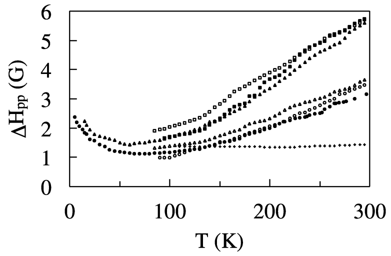

Fig. 2. Dependence of the peak-to-peak linewidth on temperature for the seven samples: PXSA-PANI (solid circles); OXSA-PANI (open circles); PSA-PANI (solid squares); PDSA-PANI (open squares); RDSA-PANI (solid triangles); MCSA-PANI (open triangles); OCPSA-PANI (plusses).

Although the localization length in the case of the seven samples turns out to be approximately the same, the EPR linewidth shows a distinct dependence on the nature of the dopant. This difference is due to the fact that EPR probes local magnetic interactions. The local structural order in the polyaniline family is a function of various synthesis parameters of a particular chemical procedure [8–11], but the formation of an inhomogeneous structure—comprised of relatively ordered semi-crystalline regions separated by disordered regions—seems like a common occurrence in the polyaniline system [16,17]. The chains in the amorphous regions show a coil-like morphology and improved synthesis techniques can instead introduce rod-like chain morphology in these regions. The localization length depends on the morphology of the disordered regions, and it is larger for the rod-like morphologies compared with the coil-like morphologies. Although most of the charge is stored as localized spinless bipolarons in the disordered regions, conduction between two ordered regions occurs via diffusion along quasi-one-dimensional chains, which connect these ordered regions through the disordered regions. The fact that σ^{-1} (≈ 30 Å) is nearly the same in polyaniline doped with different dopants, chain morphology in the disordered regions must therefore be of the same type. This result implies that the disorder due to the presence of coil-like morphologies in the disordered regions basically dominates the electron localization behavior of polymers.

4. Conclusions

A localization length in the range 27–32 Å is obtained on polyaniline doped with various organic acids belonging to the same family. A nearly constant localization length is concluded to imply that the disorder present in the as-synthesized, but doped, samples of polyaniline dominates over the disorder created locally by a dopant molecule. The localization length is an on-chain property and its magnitude is a measure of chain disorder between the ordered regions. Much larger localization length obtained on samples subjected to secondary doping is believed to be due to significantly reduced disorder especially in the coil-like disordered morphologies.

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