Dependence of the magnetic state of polyaniline on moisture

P K Kahol† and B J McCormick‡

† Department of Physics, and National Institute for Aviation Research, The Wichita State University, Wichita, KS 67208, USA
‡ Department of Chemistry, The Wichita State University, Wichita, KS 67208, USA

Abstract. The presence of water enhances the conduction process of polyaniline in the protonated emeraldine-base form. Through magnetic susceptibility measurements on thermally aged samples it is shown that the Pauli susceptibility, which is related to the extent of conduction, and the Curie susceptibility are sensitively dependent on the presence of moisture. It is suggested that the same spin can contribute to either Curie susceptibility or Pauli susceptibility depending on its environment or temperature, and that the presence of water, even in small amounts, may determine the dynamical behaviour of the spins.

1. Introduction

The objective of this paper is to report on our magnetic susceptibility measurements, which provide new insight into the nature and origin of Pauli- and Curie-spins in polyaniline in the protonated emeraldine-based (EB) form. The present work was undertaken with the goal of determining the dependence of Curie (χ_C) and Pauli (χ_P) susceptibilities on absorbed water, which is shown here to affect significantly its conduction state.

The conductivity of emeraldine-base (EB) polyaniline has been ascribed to a 'metallic state' which was described in terms of a polaron lattice (with disorder) [1, 2]. This model was based on magnetic susceptibility data on chemically-prepared samples that showed the presence of significant Pauli susceptibility, and which varied linearly with the degree of protonation. On the other hand, the origin of Curie spins and their variation with temperature and protonation level in chemical samples of EB polyaniline has been attributed to the 'localization of polarons and bipolarons at chain ends, surfaces, and within the small granular metal particles' [1]. Recent studies of spin dynamics have, however, argued against such a metallic state and the results have been interpreted in terms of percolation between 'conducting islands' [3, 4]. The percolation threshold has been found to be at $y \approx 0.20$–0.30, where $y = [Cl]/[N_{\text{total}}]$. Through independent NMR and ESR [4, 5] investigations, these conducting islands have been described as consisting of inhomogeneously protonated, and essentially single conducting polymer chains embedded in an insulating unprotonated matrix. Simple calculations for conductivity using the equation $\sigma = ne^2 D_\perp / kT$ have also been made [4], with the assumption that the macroscopic conductivity is governed by interchain hopping (or interchain spin diffusion

rate $D_\perp$ determined from NMR and ESR experiments). These calculations show excellent agreement with the experimental dependence of σ on the protonation level around room temperature; the situation is, however, quite different at low temperatures. The charge carriers, at least at room temperature, thus seem to be the carriers of spin as well. Since $D_\parallel$ and $D_\perp$ decrease with a decrease of temperature [4, 5] and the number of Curie spins increases with a decrease of temperature [1], we believe that the Curie and Pauli susceptibilities are interrelated and that the absorbed water may influence the dynamical behaviour of the spins. While the nature of the dimensionality of the conducting islands continues to be a matter of discussion [6], ESR, magnetic susceptibility, and x-ray studies of 'recrystallized' polyaniline from N-methyl-2-pyrrolidone (NMP) show a percolation threshold in the same range (0.20–0.30) as found from previous NMR/ESR studies, but imply a picture of three-dimensional metallic-islands [7, 8].

The research presented here was stimulated by the fact that the presence of water in EB polyaniline leads to enhanced conductivity [9, 10]. This was shown by experiments performed under controlled water vapour pressure up to 15 torr [10]. Since it is very difficult to synthesize samples with no adsorbed or absorbed water, we thought it significant to remove water (rather than introduce more as in other studies) and investigate the effect on the magnetic susceptibilities, with the expectation that removing water will decrease $D_\perp$ and $D_\parallel$, hence decreasing χ_P and increasing χ_C. In order to remove absorbed water and observe detectable changes in both χ_C and χ_P without changing the oxidation state and protonation, samples were subjected to heating in vacua (thermal aging). The measurements were made as a function of temperature on thermally aged samples under a vacuum of $\approx 50 \times 10^{-3}$ torr.

2. Experimental procedure

The EB polyaniline was synthesized by the standard method of oxidative polymerization of monomeric aniline with persulfate in acidic solution. The material isolated from the synthesis was fully deprotonated by soaking it in 1 M NH_4OH for one to two days. This material, after thorough washing, was then doped into a conducting state by equilibrating small (~ 1 g) samples in 500 ml of aqueous HCl of the desired pH [11, 12] for 50–60 h. An undoped sample was prepared by equilibrating a sample at pH = 7.1 for a similar time. The pH was checked at the end of the equilibration time to ensure that the pH had remained unchanged throughout the doping procedure. The samples were then filtered and air dried before the susceptibility measurements were made. Susceptibility measurements were made with a 'Force' magnetometer in a magnetic field of 5 kG [13]. The data has been corrected for any ferromagnetic impurities after calibrating the system with Pt and Al standards.

3. Results and discussion

3.1. Experimental procedure

To determine the effects of absorbed water on the magnetic behaviour of EB-polyaniline, our preliminary experiments were concerned with making χ versus T measurements, first on as-doped samples and then on samples pumped for 24–48 h around 50×10^{-3} torr. An analysis of the results for these two samples yielded different Curie-constants at room

Table 1. Thermal aging temperature, duration and mass after aging of the four emeraldine-base polyaniline samples.

Sample	Aging temperature (°C)	Aging duration (h)	Mass after thermal aging (mg)
pH = 0.9	(a) 23	—	16.52
$y = 0.22 \pm 0.01$	(b) 50	14	15.88
	(c) 95	14	15.68
	(d) 135	19	15.19
	(e) 200	12	14.12
	(f) 235	13	13.50
pH = 1.6	(a) 23	—	27.20
$y = 0.11 \pm 0.01$	(b) 50	20	26.51
	(c) Air exposure	24	26.74
	(d) Air exposure	79	26.96
	(e) 100	19	26.16
	(f) Air exposure	20	26.30
	(g) 150	20	25.08
	(h) 200	14	23.70
	(i) 230	18	22.30
pH = 2.7	(a) 23	—	21.41
$y = 0.06 \pm 0.01$	(b) 51	14	21.12
	(c) 102	12	20.63
	(d) 135	12	19.76
	(e) 235	14	18.28
pH = 7.1	23	—	13.00
$y \approx 0$	94	16	12.91

temperature (to be discussed in section 3.3) after including corrections for buoyancy effects. Since prolonged pumping for over four days produced neither significant changes in the earlier susceptibility results, obtained on pumping for two days, not significant mass changes of the samples, it was decided to age the samples thermally at different temperatures up to ~235 °C to investigate further the dependence of both the Curie and Pauli components of the measured susceptibility on absorbed water. Although the principal purpose of thermal aging is to remove absorbed water, it may also be thought to lead to the loss of chloride ions (as HCl). However, TGA and thermal decomposition measurements reported by various authors [14] indicate that significant loss of HCl occurs only at $T \geqslant 130$ °C (depending on the protonation level) and that it is small below $T \approx 130$ °C. Thermal aging up to 100–130 °C for a duration of 10–15 h is thus believed to lead essentially to the loss only of absorbed water. This is qualitatively supported by our χ versus T measurements made on samples aged around 150 °C, 200 °C, and 230 °C which show continual decreases in Curie susceptibility beginning at ~150 °C, thus implying deprotonation of the polymer chains due to the loss of hydrogen chloride.

3.2. Experimental results

In this section we present the experimental results of susceptibility as a function of temperature for four samples of EB-polyaniline doped at four pH values, namely 0.9, 1.5, 2.7 and 7.1. These pH values have been chosen to cover the entire protonation
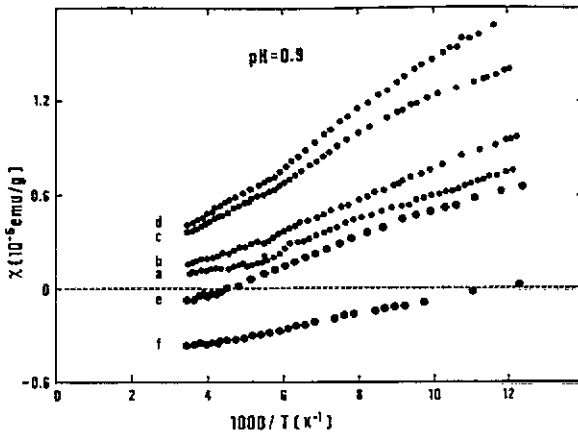
Figure 1. Dependence of the magnetic susceptibility on inverse temperature in emeraldine-based polyaniline at pH = 0.9 on (a) unaged sample; (b) aged at 50 °C for 14 h; (c) aged at 95 °C for 14 h; (d) aged at 135 °C for 19 h; (e) aged at 200 °C for 12 h; and (f) aged at 235 °C for 13 h.

region which exhibits a metal-insulator transition in the pH range 2.5–3.0 [9]. Thermal aging conditions for the various samples are summarized in table 1.

Figure 1 shows the experimental results as a function of inverse temperature for the sample equilibrated at pH = 0.9 (at various obtained thermal aging temperatures). The behaviour shown is non-linear, as reported earlier, although for temperatures in the range $220 \leqslant T \leqslant 300$ K it is nearly linear. On thermal aging at 50 °C, 95 °C, and 135 °C, for up to 15 h at each temperature, the magnitude of the measured susceptibility increases over the entire investigated temperature region. Furthermore, the slope of χ versus $1/T$ in the temperature range $220 \leqslant T \leqslant 300$ K (which is proportional to the Curie constant) also progressively increases. On further aging of the sample, at 200 °C and 235 °C, χ as well as the Curie constant decreases. The non-linearity of the χ versus $1/T$ is also found to diminish with continued thermal aging, as is evident from figure 1.

Experimental results for the measured susceptibility of the sample doped at pH = 1.6 are shown as a function of inverse temperature in figure 2. Curve a shows data on the as-doped sample, while curve b shows data obtained after thermally aging the sample at 50 °C. Exposure of the samples to air for 24 and 79 h yields materials that provide curves c and d, respectively. Analogous to the sample doped at pH = 0.9, aging up to 150 °C leads to increases in both the absolute susceptibility and the Curie constant in the temperature region of ~220–300 K (curves e, f, g). Curve f shows data obtained after exposing the sample aged at 100 °C (curve e) to air for only 20 h, whereas curve g shows data on aging at 150 °C for 20 h. Further thermal aging at 200 °C and 230 °C yields results (curves h and i) similar to that for the sample doped at pH = 0.9.

The conductivity in EB-polyaniline shows a drastic increase in the pH range 1.5–3.5, and the results for the susceptibility as a function of inverse temperature are shown in figure 3 for the sample equilibrated in HCl in the middle of this range, specifically at a pH of 2.7. The results are similar to those shown in figures 1 and 2, except that the susceptibility begins to decrease at a thermal-aging-temperature of around 135 °C, compared to ~150 °C for the samples doped at pH = 0.9 and 1.6.
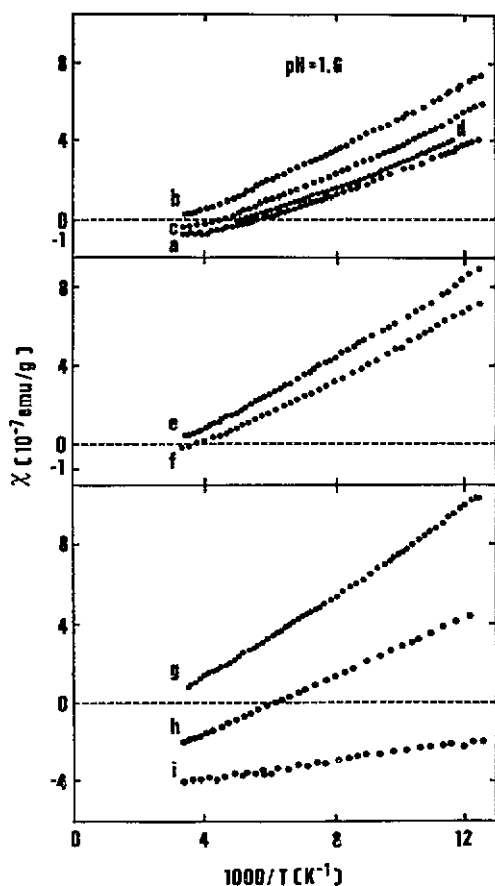
Figure 2. Dependence of the magnetic susceptibility on inverse temperature at pH = 1.6 obtained under the following conditions: (a) unaged sample; (b) aged at 50 °C for 20 h; (c) exposed (b) to air for 24 h; (d) exposed (b) for further 55 h; (e) aged the sample at 100 °C for 19 h; (f) exposed (e) to air for 20 h; (g) aged at 150 °C for 20 h; (h) aged at 200 °C for 14 h; and (i) aged at 230 °C for 18 h.
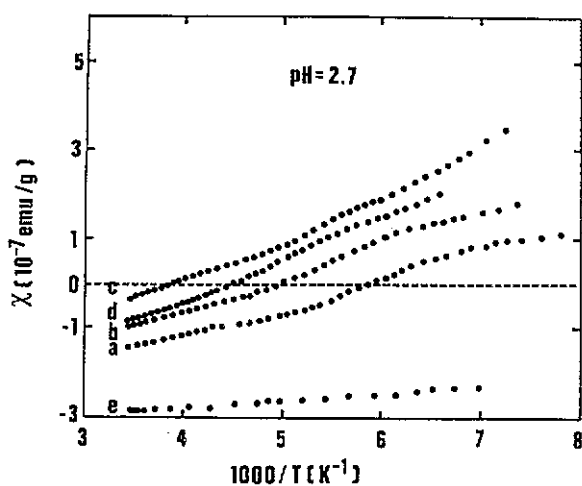

Figure 3. Dependence of the magnetic susceptibility on inverse temperature in emeraldine-base polyaniline at pH = 2.7 on: (a) unaged sample; (b) aged at 51 °C for 14 h; (c) aged at 102 °C for 12 h; (d) aged at 135 °C for 12 h; and (e) aged at 235 °C for 14 h.
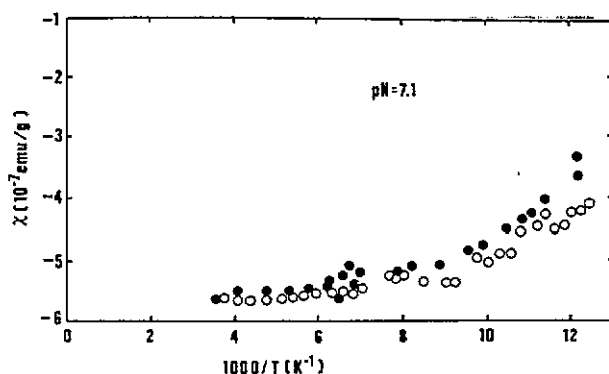
Figure 4. Dependence of the magnetic susceptibility on inverse temperature in emeraldine-base polyaniline at pH = 7.1 on unaged sample (open circles) and aged at 94 °C for 16 h (full circles).

The susceptibility versus $1/T$ behaviour of the undoped sample is shown in figure 4, where open circles denote results for the as-synthesized sample and full circles for the sample thermally aged at 94 °C respectively.

3.3. Method of analysis

The measured susceptibility can be divided and grouped as follows: (a) χ_C, χ_P and the diamagnetic core contribution of the EB backbone (χ_{BB}); (b) diamagnetic contribution due to the absorbed water (χ_W); and (c) diamagnetic contribution due to the chloride ions (χ_{Cl}). Thus,

$$\chi = (m_{BB}/m_T)(\chi_C + \chi_P + \chi_{BB}) + (m_W/m_T)\chi_W + (m_{Cl}/m_T)\chi_{Cl} \qquad (1)$$

where m_{BB}, m_W, m_{Cl} and m_T refer to the masses for the backbone of EB-polyaniline, water, chloride ions, and the total mass, respectively.

The total mass m_T is measured after pumping on the sample at room temperature at $\sim 60 \times 10^{-3}$ torr for 6–10 h. Thermal aging is then carried out at various temperatures under vacuum, typically for 12–20 h. The final thermal aging around 230 °C, after having aged the samples around 50 °C, 100 °C, 150 °C, 200 °C, is considered to lead to the removal of most of the absorbed water and the chloride ions, thus yielding the mass of the polymer backbone m_{BB}. The mass loss on aging up to ≈ 130 °C is attributable to water, m_W. The loss of any chloride ions, not explicitly taken into account, will not directly affect the analysis since the mass susceptibilities of water $(-0.72 \times 10^{-7}$ emu g$^{-1})$ and chloride ions $(-0.70 \times 10^{-7}$ emu g$^{-1})$ are the same to within 3%. That is, for the present analysis $\chi_W = \chi_{Cl} = -0.71 \times 10^{-7}$ emu g^{-1}. Furthermore, a value of -5.85×10^{-7} emu g^{-1} for χ_{BB} was obtained from our measurements on the sample (equilibrated at pH = 7.1) (figure 4) for which the doping level is believed to be zero.

For each set of χ versus T measurements, the value of the measured susceptibility at 293 K was noted and a value of χ_C was obtained from the linear data in the range 250–293 K. With this and the above described information, χ_P was then obtained from (1). The obtained values of χ_P and χ_C can also be converted to emu mol^{-1} two-ring by multiplying the emu g^{-1} values by the molecular mass of the two-ring unit.
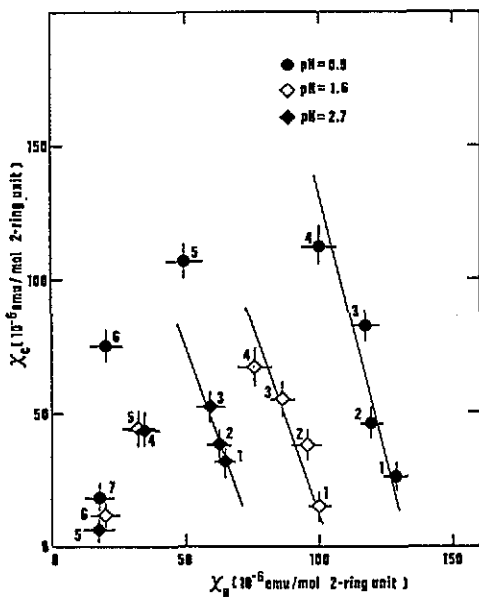
Figure 5. χ_C versus χ_P at room temperature for three samples of emeraldine-base polyaniline (pH = 0.9, 1.6 and 2.7). Numbers (1, 2, 3, ...) next to the various data points correspond to thermal aging temperatures as follows: for pH = 0.9, numbers 1–7 correspond respectively to aging at 23, 50, 95, 135, 165, 200 and 235 °C; for pH = 1.6, numbers 1–6 correspond respectively to aging at 23, 50, 100, 150, 200 and 230 °C; for pH = 2.7, numbers 1–5 correspond respectively to aging at 23, 51, 102, 135 and 235 °C.

3.4. Interdependence of χ_C and χ_P

Figure 5 show a plot of χ_C versus χ_P at room-temperature for three samples of EB polyaniline equilibrated at pH = 0.9, 1.6 and 2.7. The thermal aging temperature, its duration and the mass of the sample after aging are listed for these samples in table 1. The Curie susceptibility of all the samples increases on thermal aging as much as by a factor of 5 with an accompanying decrease of Pauli susceptibility. It is important to remember that thermal aging was carried out in a vacuum of 50×10^{-3} torr and the samples once loaded were not exposed (unless by design) to the external environment. The coupled behaviour of χ_P and χ_C is the most significant result of our measurements and our analysis of the magnetic susceptibility data. This behaviour is 70–90% reversed for samples aged up to 130–150 °C by exposing them to air for long periods. The fact that the susceptibility results can be 70–90% recovered by exposure to air clearly shows the role of absorbed water in influencing the magnetic state of these samples. The lack of complete reversibility, on the other hand, does lead us to suspect a partial loss of HCl or chloride ions. On aging the samples above 130–150 °C, χ_C, however, decreases along with a much faster decrease of χ_P. This is interpreted as being due to significant deprotonation of the chains. The behaviour below 150 °C is thus predominantly associated with the presence of absorbed water and the water molecules must thus be weakly bonded at specific sites to the polymer. Since the sample doped at pH = 7.1 showed neither a significant change in sample mass on aging nor any change in the observed small Curie susceptibility ($\approx 1.8 \times 10^{-8}$ emu g^{-1}), chloride ions seem to be playing a yet unexplained role in bonding water molecules to the chains.

3.5. Interpretation and discussion

The most likely interpretation of the observed decrease in Pauli susceptibility with the associated increase in the Curie susceptibility relates to the conversion of Pauli spins to

Curie spins. Along the lines suggested by Chiang and MacDiarmid [15], removal of water seems to lead to increased localization of the spins due to increased pinning of the charge (as well as that of spin) on the polymer backbone in the vicinity of the chloride ions. This might happen, for example, when water solvates the chloride anions, leading to reduced electrostatic interaction between the positive charge on the chain and the anions, and thereby to increased delocalization of the spins. That the above may be the correct interpretation is supported by the following results and observations.

First, the χ versus $1/T$ behaviour for all the samples investigated is non-Curie-like and is seen as the result of both the Curie-like and Pauli-like contributions. The non-Curie-like behaviour, which is more pronounced on unaged samples, becomes progressively less and less pronounced on thermal aging, to the extent that thermal aging above 150 °C yields virtually a Curie-like dependence of the susceptibility. This is interpreted as due to conversion of the Pauli spins into Curie spins. Second, the χ_C-χ_P data for aging temperatures up to $\approx$150 °C (figure 5) seems to be linear. Intercepts of the linear curves on the χ_C axis (i.e., correspondng to $\chi_P = 0$) were obtained for the three samples, and then converted to the number of spins per two-ring unit. Values of the spins obtained by this procedure are: (0.40 ± 0.07) per two-ring unit for the pH = 0.9 sample; (0.20 ± 0.06) per two-ring unit for the pH = 1.6 sample; and (0.13 ± 0.06) per two-ring unit for the pH = 2.7 sample. These values compare very favourably with those deduced from the 'pH versus doping level' curve given by Chiang and MacDiarmid [15], i.e. (0.44 ± 0.02), (0.22 ± 0.02) and (0.12 ± 0.02) per two-ring unit, respectively. Third, reversal of the magnetic susceptibility results by 70–90% on exposing the samples to air for prolonged period of time ($\sim$100 h), underlines the important role played by absorbed water on the magnetic state of polyaniline. The proposed view of spin-delocalization in terms of absorbed water thus seems to be a straightforward interpretation of the observed behaviour.

These investigations of moisture effects on the magnetic state of EB-polyaniline, provide direct confirmation of the conclusions of other experimental investigations [15–18]. EB-polyaniline exhibits a large electric loss tangent, $\tan \delta = \varepsilon''/\varepsilon'$, at microwave frequencies. For the sample at $y \sim 0.50$, $\tan \delta$ is found to be $\sim$2.3 at room temperature, and its value increases by a factor of $\sim$3.5 upon exposure to moisture. That is, the dielectric constant increases in the presence of moisture which we believe to be owing to the increased coherence length of charge carriers. The same mechanism will also explain the observed increase of microwave conductivity due to the presence of moisture [16, 17]. The role of moisture must therefore be included in the concept of 'textured metallic islands' along with local order versus long-range disorder delocalization versus incomplete localization, Coulomb correlations, and temperature [17]. It may be speculated that the removal of water introduces more disorder leading to further delocalization of the spins, and that the effects observed here should be more pronounced on samples with higher crystallinity [8]. The increase in χ_C on the removal of water also correlates well with the observation that a heavily-doped sample of EB-polyaniline showed a drastically increased ESR signal on pumping for about two days [18].

We have also investigated at 100 K the χ_C-χ_P behaviour of the samples aged thermally up to 150 °C. As at room temperature, χ_C is increased and χ_P is decreased on thermal aging. Linear regression of the data for the samples doped at pH = 0.9 and 1.6 yields 0.42 ± 0.12 and 0.25 ± 0.11 spins per two-ring unit for $\chi_P = 0$. Although large errors in the above estimates preclude our making quantitative conclusions, we can qualitatively discuss the observed behaviour as follows. At 100 K, the number of Curie spins per two-ring unit on the unaged sample equilibrated at pH = 0.9 is 0.055 ± 0.010, nearly three

times larger than that at room temperature (0.021 ± 0.002); at temperatures lower than 100 K the number of Curie spins increases still further. The maximum number of Curie spins on the same, but thermally-aged, sample is of the same order of magnitude (i.e., 0.080 ± 0.010) as at 100 K on the unaged sample. For the sample at equilibrated pH = 1.6, $n_c (100 \text{ K}) \approx 0.040 \pm 0.008$, which can be compared with the maximum number of Curie spins on the aged sample—0.053 ± 0.006. Similar results are obtained on samples equilibrated at other pH values. This leads us to the conclusion that absorbed moisture is the primary cause of the increase in the number of Curie spins with a decrease in temperature.

4. Conclusions

Via magnetic susceptibility measurements on moisture-containing samples of EB-poly-aniline, it has been shown that both the Curie and the Pauli susceptibilities are dependent on the presence of small amounts of water, and that the removal of water results in the conversion of Pauli-like spins to Curie-like spins. This has provided a direct confirmation of the conclusions of other experimental investigations [15–18]. We have also suggested that the absorbed water may play a significant role in causing an increase in the number of Curie-like spins with decreases in temperature. Further work along these lines is being planned on samples with much higher crystalinity.

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