

## Magnetic state of poly(*m*-toluidine): Dependence on absorbed water

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Magnetic-susceptibility results as a function of temperature are reported on unaged and thermally aged samples of poly(*meta*-toluidine) equilibrated at  $pH=0.90$ . Analysis of the results at low temperatures provides possible confirmation of the existence of metallic "regions" in such systems. Interrelationship of the Curie and Pauli susceptibilities, investigated through their dependence on absorbed water, is also shown to be similar to that observed for polyaniline.

This paper describes our magnetic-susceptibility results and their analysis on a derivative of polyaniline—poly(*meta*-toluidine) (PMT), shown schematically in Fig. 1—from the following four perspectives. First, possible evidence for the proposed existence of metallic or conducting regions<sup>1</sup> is presented from analysis of the low-temperature susceptibility measurements. Second, the methodology developed earlier<sup>2</sup> on polyaniline for studying the role of absorbed water in determining the system's magnetic state is extended to PMT, thus emphasizing a close relationship between the Curie susceptibility ( $\chi_C$ ) and the Pauli susceptibility ( $\chi_P$ ). Third, the methodology is used to show the interdependence of  $\chi_C$  and  $\chi_P$  not only at room temperature as done earlier<sup>2</sup> but also at temperatures below room temperature. Fourth, it is observed that, on the average, approximately one water

molecule is bound to each counterion relatively strongly.

PMT samples for present investigations were prepared as described elsewhere by MacDiarmid and co-workers.<sup>3</sup> Susceptibility measurements were made with a force magnetometer at a magnetic field of 0.5 T. Magnetization vs magnetic-field behavior was found to be linear up to a field of 0.8 T.

Figure 2 shows the experimental results for  $(\chi_C + \chi_P)T$  as a function of temperature for the sample of PMT equilibrated at  $pH = 0.9$  under the following conditions: (a) unaged sample, (b) aged at 30 °C for 13 h, (c) aged at 50 °C for 15 h, (d) aged at 67 °C for 17 h, and (e) aged at 96 °C for 16 h. Susceptibility measurements were also made on the sample aged at 137 °C for 15 h and at 176 °C for 15 h.  $(\chi_C + \chi_P)$  has been obtained from the measured susceptibility  $\chi_{\text{expt}}$ ;

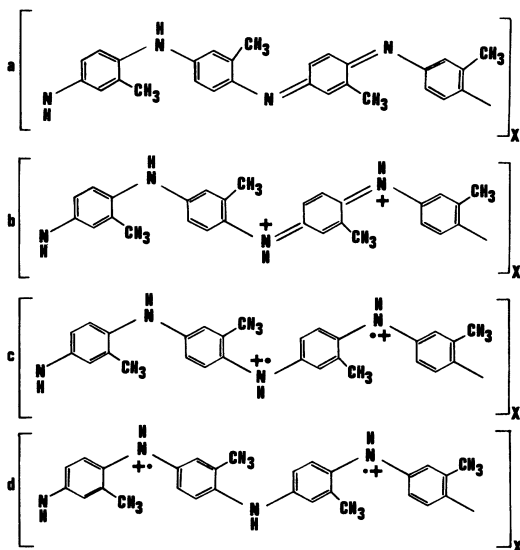


FIG. 1. Schematic structure of (a) undoped poly(*m*-toluidine) and (b) poly(*m*-toluidine) doped with 1 M HCl solution showing the generation of a bipolaron. The bipolaron disassociates into two polarons (c), which eventually rearrange themselves to form a polaron "lattice" (d).

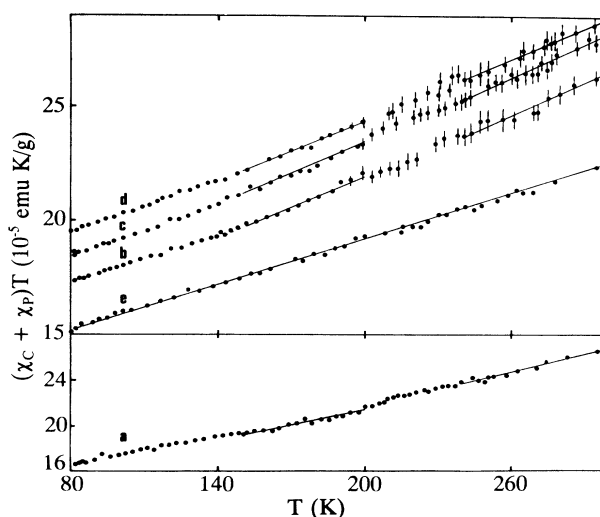


FIG. 2. Temperature dependence of the magnetic susceptibility of poly(*m*-toluidine) at  $pH = 0.90$ , plotted as  $(\chi_C + \chi_P)T$  vs  $T$ , on (a) unaged sample; (b) aged at 30 °C for 13 h; (c) aged at 50 °C for 15 h; (d) aged at 67 °C for 17 h; and (e) aged at 96 °C for 16 h.

$$\chi_{\text{expt}} = (m_{\text{BB}}/m_T)(\chi_C + \chi_P + \chi_{\text{BB}}) \\ + (m_W/m_T)\chi_W + (m_{\text{Cl}}/m_T)\chi_{\text{Cl}};$$

as discussed earlier;<sup>2</sup>  $m_{\text{BB}}$ ,  $m_W$ ,  $m_{\text{Cl}}$  and  $m_T$  refer to the masses for the backbone of PMT, water, chloride ions, and the total mass, respectively. The value for  $m_T$ , as measured after pumping on the sample at room temperature at around  $80 \times 10^{-3}$  Torr for  $\approx 10$  h, was 37.66 mg. On the other hand, the value for  $m_{\text{BB}}$  (= 32.21 mg) was taken as the mass of the sample, which had already been aged at 30, 50, 67, 96, 137, and 176 °C, measured after aging it again at 230 °C for 8 h. The mass lost ( $m_W + m_{\text{Cl}}$ ) on aging relative to  $m_T$  was measured to be 0.20 mg on heating at 30 °C, 0.68 mg on heating at 50 °C, 1.20 mg on heating at 67 °C, 2.35 mg on heating at 96 °C, 4.13 mg on heating at 137 °C, 4.47 mg on heating at 176 °C, and 5.45 mg on heating at 230 °C. The slope of  $(\chi_C + \chi_P)T$  vs  $T$  yields  $\chi_P$ , whereas its intercept yields the Curie constant (and hence  $\chi_C$ ). The behavior shown is nonlinear, and is believed to be due to a gradual change of some of the Pauli-like spins to Curie-like spins with decrease in temperature. We have therefore calculated the Curie constants from the intercepts of the fitted data in the temperature ranges 250–300 K and 150–200 K, and hence the Curie susceptibility  $\chi_C$  at 300 and 200 K.  $\chi_P$  can be obtained either from the slope of the plotted data or by subtracting  $\chi_C$  from  $(\chi_C + \chi_P)$  at 300 and 200 K; both procedures yield estimates to within about 3%. Figure 3 shows the  $\chi_C$  vs  $\chi_P$  behavior at 300 K. The behavior at 200 K is similar to that at 300 K, and parallels that observed for emeraldine-base polyaniline.<sup>2</sup> However,  $\chi_C$  in PMT begins to decrease on aging in the range 70–90 °C compared to around 150 °C in polyaniline, suggesting weaker binding of water molecules to the counterions. Simple calculations based upon the observed water loss on aging show approximately one water molecule per

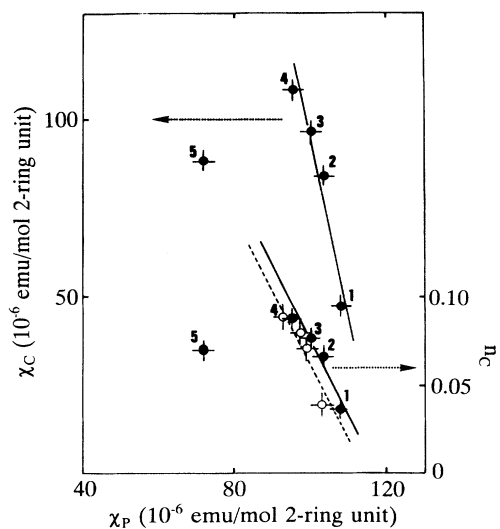


FIG. 3.  $\chi_C$  vs  $\chi_P$  at 300 K (left-hand scale), and  $n_C$  vs  $\chi_P$  at 300 and 200 K (right-hand scale) for poly(*m*-toluidine) at pH = 0.90. Numbers 1–5 correspond to the conditions (a)–(e) of Fig. 1 as discussed in the text.

counterion at the maximum in the  $\chi_C$ - $\chi_P$  plot. On further aging at higher temperature, both  $\chi_C$  and  $\chi_P$  decrease. The same behavior is also observed in polyaniline, suggesting thereby that one water molecule is rather strongly bound to each counterion. The dependence of the number of Curie spins per 2-ring unit  $n_C$  (deduced from  $\chi_C$ ) as a function of  $\chi_P$  is also shown at 300 and 200 K in Fig. 3. Extrapolated values of  $n_C$  for zero Pauli susceptibility are  $0.44 \pm 0.05$  and  $0.42 \pm 0.05$  at 300 and 200 K, respectively, which compare very favorably with that for polyaniline at the same doping level.<sup>2</sup> It is thus apparent that, as in the case for polyaniline, the Curie and the Pauli susceptibilities in PMT are also dependent on the presence of small amounts of water whose removal through aging results in the conversion of Pauli spins to Curie spins.

While a detailed analysis of electrical conductivity measurements as a function of temperature on aged samples of PMT, polyaniline, and its substituents will be reported elsewhere, we have observed a gradual reduction of conductivity in PMT on aging up to  $\approx 70$  °C. Aging at higher temperatures leads to a much faster decrease of conductivity. This correlates well with the behavior shown in Fig. 3 where  $\chi_P$  is seen to exhibit a similar variation.

The possible presence of antiferromagnetic interactions between adjacent Curie-like spins has recently been shown in poly(*o*-toluidine) (POT) by Epstein and co-workers.<sup>4</sup> The behavior exhibited by PMT is very similar to that for POT, i.e., nearly linear behavior of  $(\chi_C + \chi_P)T$  vs  $T$  from 300 down to 50 K (slope here determines  $\chi_P$ ) with continuous deviations from linearity toward smaller values at lower temperatures. If it is argued that  $\chi_P$ , as determined from the slope of the data in the temperature range 50–100 K, is appropriate for the range 6–50 K as well, values of  $\chi_C$  can be obtained as a function of temperature. A plot of  $\chi_C^{-1}$  vs  $T$  may then yield Curie-Weiss behavior ( $\chi_C = C/T + \Theta$ ) with a particular value for  $\Theta$  which in the mean-field approximation is proportional to the number of nearest-neighbor spins ( $z$ ) and the

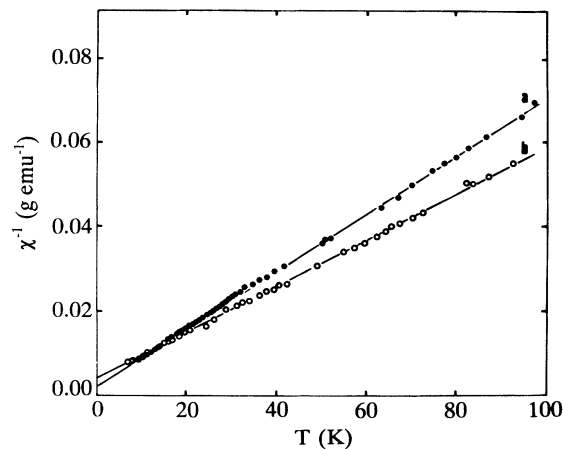


FIG. 4. Temperature dependence of the Curie susceptibility of the (a) unaged sample and (b) the aged sample (at 50 °C for 48 h) in the temperature range 6–100 K.

exchange-interaction coupling constant ( $J$ ). Figure 4(a) shows our results for  $\chi_C^{-1}$  as a function of  $T$  for the sample equilibrated at  $pH = 0.90$ , which yields  $\Theta = 3.5 \pm 1$  K. Since thermal aging leads to enhanced  $\chi_C$  at the expense of  $\chi_P$ , experiments on the same sample as above but aged at  $50^\circ\text{C}$  for 48 h were performed to find whether reduced overlap of wave functions on neighboring sites, caused by removal of water, leads to a smaller value of  $J$  (and hence  $\Theta$ ) or not. As in the case of unaged sample, a reasonable Curie-Weiss behavior but, however, with a larger value of  $\Theta = 6.5 \pm 1.2$  K is obtained [Fig. 4(b)]. A rather qualitative interpretation of this behavior is given as follows. The magnetic state in PMT is ascribed to the existence of conducting or "metallic" regions (like that proposed in polyaniline) which are comprised of sufficiently localized (Curie-type) and sufficiently delocalized (Pauli-type) spins—or polarons. Small "metallic" regions/particles

are believed to be formed upon protonation due to a transition from doubly charged spinless bipolarons to energetically stabilized polarons.<sup>1</sup> This sequence of disproportionation is shown in Fig. 1, and was discussed in detail by Epstein and co-workers.<sup>1</sup> Removal of absorbed water leads to reduced overlap between the neighboring spins, enough for some of the Pauli spins to behave like Curie spins and hence increase the number of nearest Curie neighbors to a particular Curie spin. This behavior is not expected in the model in which conducting regions consist essentially of single conducting polymer chains embedded in an insulated matrix.<sup>5</sup>

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<sup>1</sup>J. M. Ginder, A. J. Epstein, and A. G. MacDiarmid, *Solid State Commun.* **72**, 697 (1989); J. M. Ginder and A. J. Epstein, *Phys. Rev. B* **41**, 10 674 (1990); A. J. Epstein, A. G. MacDiarmid, and J. P. Pouget, *Phys. Rev. Lett.* **65**, 664 (1990).

<sup>2</sup>P. K. Kahol, H. Guan, and B. J. McCormick, *Phys. Rev. B* **44**, 10 393 (1991); P. K. Kahol and B. J. McCormick, *J. Phys.: Condens. Matter* **3**, 7963 (1991).

<sup>3</sup>Y. Wei, W. W. Focke, G. E. Wnek, A. Ray, and A. G. MacDiarmid, *J. Phys. Chem.* **93**, 495 (1989); A. Ray, A. G. MacDi-

armid, J. M. Ginder, and A. J. Epstein, in *Advanced Organic Solid State Materials*, edited by L. Y. Chiang, P. Chaikin, and D. O. Cowan, MRS Symposia Proceedings No. 173 (Materials Research Society, Pittsburgh, 1990), p. 353.

<sup>4</sup>Z. H. Wang, A. Ray, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B* **43**, 4373 (1991).

<sup>5</sup>K. Mizoguchi, M. Nechtschein, J.-P. Travers, and C. Menardo, *Phys. Rev. Lett.* **63**, 66 (1989); J.-P. Travers, F. Genoud, C. Menardo, and M. Nechtschein, *Synth. Met.* **35**, 159 (1990).