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Low-temperature heat capacities of polyaniline and polyaniline polymethylmethacrylate blends

Anasuya Raghunathan, P. K. Kahol, and J. C. Ho
Department of Physics, Wichita State University, Wichita, Kansas 67260-0032

Y. Y. Chen, Y. D. Yao, and Y. S. Lin
Institute of Physics, Academia Sinica, Taipei, Taiwan

B. Wessling
Ormecon Chemie Gmbh & Co., KG, Ferdinand-Harten-Straße 7, D-22949 Ammersbek, Germany

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Heat-capacity measurements between 0.4 and 10 K have been made on doped polyaniline and its blends with polymethylmethacrylate. At lower temperatures, a finite electronic term (γ) prevails in all samples. The value of γ for polyaniline is 14 mJ/mol K^2, but higher by a factor of about 6 for the blends. Using the free-electron model, the corresponding density of states at the Fermi level $[N(E_F)]$ are calculated and compared with that obtained from magnetic susceptibility measurements on the same samples. It is shown that caution must be used in determining $N(E_F)$ from magnetic susceptibility measurements in polyaniline and other less conducting polymeric materials. [S0163-1829(98)51448-8]

The objective of this paper is to present our heat-capacity results on polyaniline (PANI) and its blends with polymethylmethacrylate (PMMA) for the following reasons. First, polyaniline has not been studied so far for its thermal behavior at low temperatures although a wide variety of other techniques have been employed for understanding its electronic properties.[1] Second, analysis of the dc transport data requires a good estimate of $N(E_F)$, the density of states at the Fermi level, which has been obtained from magnetic susceptibility measurements for polyaniline based materials. In the free-electron model, $N(E_F)=\chi_P/\mu_B^2$, where χ_P is the Pauli susceptibility and μ_B is the Bohr magneton. The observed values for χ_P and hence the magnetically derived $N(E_F)$ are relatively large for a number of polyaniline derivatives which have rather small conductivity.[2] Third, applicability of the free-electron model to polyaniline and other conjugated conducting systems has been recently questioned, especially when the systems are less conducting and show no ''metallic'' behavior. Alternative models to account for magnetic susceptibility, dc conductivity, dielectric constant, and thermoelectric power have thus been proposed.[3–5] Some of these models do not require the existence of Pauli susceptibility or free-electron spins. It thus becomes all the more important to obtain $N(E_F)$ from heat-capacity measurements to help theoretical developments.

Calorimetric measurements in the temperature range ~0.4–10 K were made on PANI, PANI(40%)-PMMA(60%) (to be abbreviated as PP4060) and PANI(33%)-PMMA(67%) (to be abbreviated as PP3367) (Ref. 6) using a thermal-relaxation type microcalorimeter in a He^3 cryostat. A mg size specimen was thermally anchored with a minute amount of grease to a sapphire holder on which thin films of ruthenium oxide and nickel-chromium alloy were deposited to serve as a temperature sensor and a joule-heating element, respectively. The holder was thermally linked by four Au-Cu alloy wires to a temperature regulated copper block. Following each heat pulse, the specimen temperature relaxation rate was monitored to yield a time constant τ. Heat capacity was then calculated from the expression, $c=k\tau$, where k is the thermal conductance of the Au-Cu wires. The heat capacity of the sample holder was measured separately for addenda correction. Judging from the measurements on a copper standard, overall uncertainties in the final results are within a few percent. The specific heat (C) of the sample was then obtained from $C=c/(m/M)$ with m and M being the sample mass and the molecular mass, respectively. Each mole is defined here as a mole of two-ring units of the polymeric sample. Values of M for the polymeric samples are listed in Table I.

The measured specific heat of polyaniline (PANI) as a function of temperature is shown in Fig. 1 in the form of a C vs T plot. The surprisingly weak temperature dependence at the lower temperature end suggests additional contributions to specific heat than the expected electronic (γT) and lattice (βT^3) terms. Indeed the data in the temperature range 0.4–2 K can be well represented by the following expression:

$$C=A+\gamma T+\beta T^3, \tag{1}$$

with the constants A, γ, and β; γ and β are listed in Table I. This is illustrated by the linear nature of the $(C-A)/T$ versus T^2 data in Fig. 2. The origin of the constant term, A, is not clear at present. This term reflects the presence of classical oscillator-type modes interacting weakly with the surroundings. For N such oscillators, one would expect a thermal excitation energy Nk_BT and consequently a temperature-independent specific heat Nk_B $(=A)$, where k_B is Boltzmann's constant. From the experimental value of 15 mJ/(mol of 2 rings K) for A, we obtain $N=1.1\times10^{21}$ modes/(mol of 2 rings) or 0.002 modes/2 rings. Similar observations have been made for magnetic clusters in paramagnetic alloys.[7,8] For PANI, this term may arise from the presence of Curie-type electronic spins localized in amorphous regions.

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TABLE I. Values of γ, β, θ_D (from β for $T<2$ K) and $N(E_F)$ (from heat capacity and magnetic susceptibility) for polyaniline and its blends.

		γ (mJ/mol K^2)		β (mJ/mol K^4)			$N(E_F)$ (states/eV 2 rings)	
Sample	M (g/ mol 2 rings)	$T<2$ K	$T>2$ K	$T<2$ K	$T>2$ K	θ_D (K)	Heat capacity	Magnetic susceptibility
PANI	373	14	0	6.5	11.6	87	3	21
PP4060	933	80	86	20.3	52.2	45	17	16
PP3367	1126	80	81	31	66	40	17	12

A linear variation of specific heat with respect to temperature can arise due to disorder as well as linear bonding in one-dimensional polymeric systems and free electrons in the metallic state. However, a much smaller value for ''γ'' equal to 0.29 mJ/mol K^2, arising due to disorder, was reported for undoped trans-polyacetylene,[9] which may be considered as typical of polymeric materials of the kind considered here. The value of γ determined here is therefore considered predominantly due to ''free'' electrons in the ''metallic'' state of PANI. Facing highly anisotropic and multidimensional lattice dynamics, only an effective Debye temperature θ_D (in K) can be calculated from β (in mJ/mol K^4) $(=1944/\theta_D^3)$. It is listed in Table I along with the density of states at the Fermi level, $N(E_F)$ (in states/eV mol)$=0.212$ γ (in mJ/mol K^2).

We now look into $N(E_F)$ as determined from magnetic susceptibility measurements.[10] A plot of χT vs T behavior is shown in Fig. 3 for PANI and its PMMA blends (to be discussed later), where χ is the experimental spin susceptibility. In the free-electron model, slope and intercept of the χT vs T plot yield Pauli susceptibility and Curie constant, respectively. $N(E_F)$ calculated from χ_P, using $\chi_P=\mu_B^2 N(E_F)$, is found to be 20.7 states/eV 2 rings for PANI which is larger by a factor of 7 compared to the value from heat-capacity measurements.

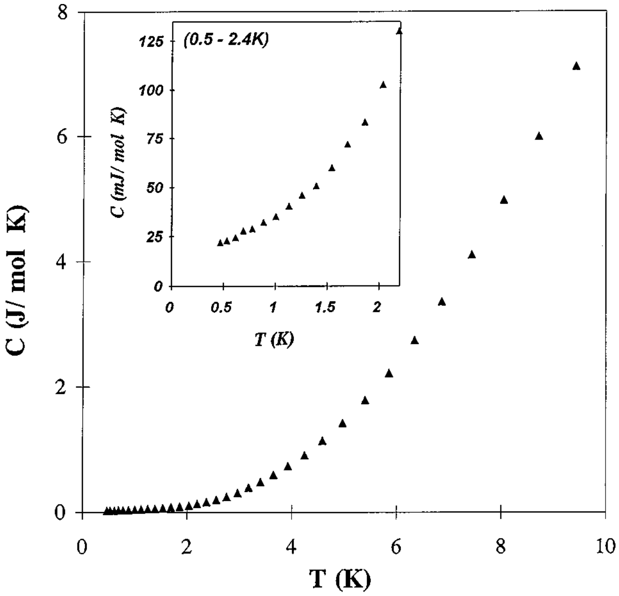

FIG. 1. Heat capacity as a function of temperature for polyaniline. Inset: Low-temperature heat-capacity data on an expanded scale.

To investigate further into the nature of the above discrepancy, heat-capacity measurements were done on PP4060 and PP3367 blends (Fig. 4). These blends were chosen because they show much smaller decrease of conductivity with decrease in temperature compared to polyaniline.[6] Since this can be interpreted as a signature of better ''metallic'' character, increased electron delocalization is expected to lead to a larger value for the number of states at the Fermi level. A plot of C/T versus T^2 for these blends is shown in Fig. 5. It can be seen from the figure that both blends, PP4060 and PP3367, show an anomaly near 2 K; in this respect, PANI also shows a change of slope near 2 K in Fig. 2. However, in either case, same γ values are obtained whether the data are analyzed in the temperature range 3–7 K or 0.4–2 K implying little change in the nature of free electrons through this anomalous region. This indicates that the observed anomaly around 2 K is likely not associated with electrons, but may rather be due to stiffening of the lattice in these polymers. This anomaly may be related to temperature-independent elastic tunneling conduction observed around this temperature.[11] Fitted γ and β values for both polymeric blends are also given in Table I along with the calculated θ_D and $N(E_F)$ values. A few other observations are in order at this point. An increase in specific heat is observed for blends with respect to PANI (Fig. 4). Changes in lattice dynamics due to the incorporation of the relatively high mass of the

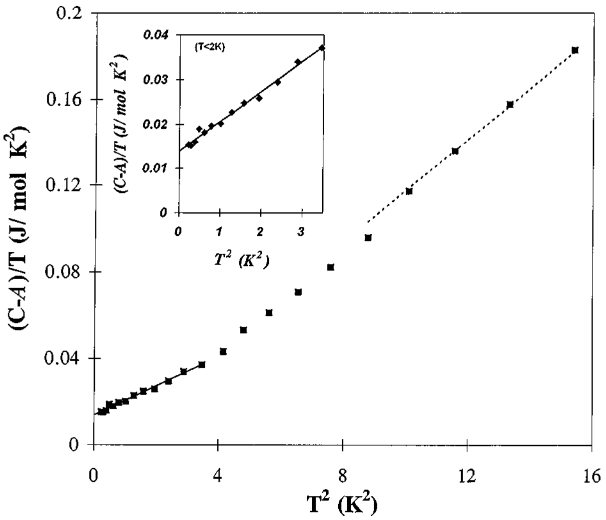

FIG. 2. $(C-A)/T$ vs T^2 for polyaniline below ~4 K. Inset: $(C-A)/T$ versus T^2 for polyaniline for temperatures below ~2 K. Linear fits to the low ($T<2$ K) and high (7 K$>T>$3 K) temperature data are shown by continuous and broken lines, respectively.

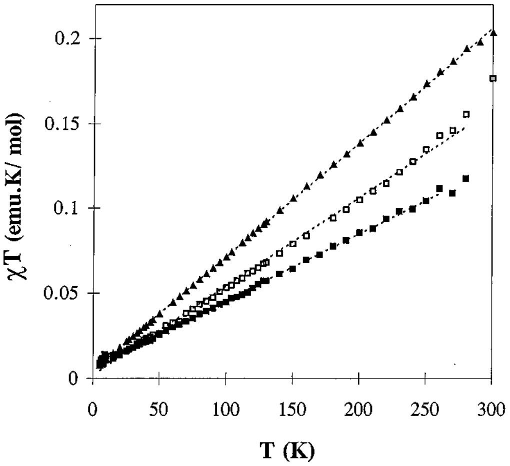

FIG. 3. χT vs T for polyaniline and its blends: PANI (▲), PP4060 (☐), PP3367 (■). Least-square fits of the data to Eq. (3) are shown by broken lines.

insulating PMMA polymer between PANI chains are believed to be responsible for this increase. The absence of a constant specific heat contribution (i.e., A term) for these blends compared to PANI shows that Curie-like electron spins are relatively more delocalized and strongly coupled to the lattice.

The calorimetrically determined γ values correspond to $N(E_F)=17$ states/eV 2 rings for both PP4060 and PP3367. Compared to PANI, these values are higher by a factor of 6 or so. The magnetic susceptibility data shown in Fig. 3 for the blends can also be used to obtain $N(E_F)$ as described earlier. This analysis gives $N(E_F)=16$ states/eV 2 rings for PP4060 and $N(E_F)=12$ states/eV 2 rings for PP3367; these values are also listed in Table I. In spite of different sensitivities of the two techniques, the above values for PP4060 and PP3367 are smaller from their heat capacity counterparts by only about 6% and 30%, respectively. The above values therefore suggest that the free-electron model is applicable to both the heat-capacity and magnetic-susceptibility data for the blends. Since the γ term in the measured heat capacity arises predominantly from the presence of free electrons in the sample (see discussion above), we assert that the calorimetrically determined $N(E_F)$ of 3 states/eV 2 rings has its origin in the presence of free electrons in the present sample of polyaniline; this sample also exhibits a metallic behavior[6] above 250 K. Recalling that the magnetic susceptibility measurements on the present PANI sample lead to a much larger value for $N(E_F)$ (=21 states/eV 2 rings) than from heat-capacity measurements, we must conclude that the simple interpretation of the so-called ''linear'' part of the χT vs T curve in terms of Pauli susceptibility (in a free-electron model) may not be correct for polyaniline. We propose below a possible model for a Pauli-like term in the χT vs T behavior of these polymers.

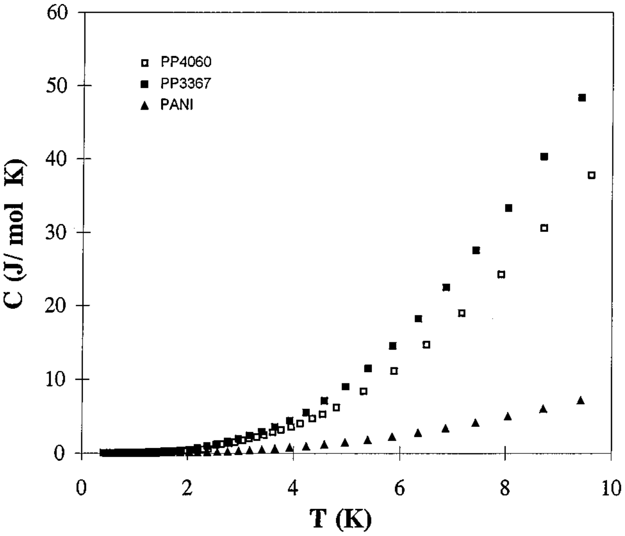

FIG. 4. Temperature dependence (0.4–10 K) of heat capacity of PP4060 and PP3367. Heat capacity of PANI is also shown for comparison.

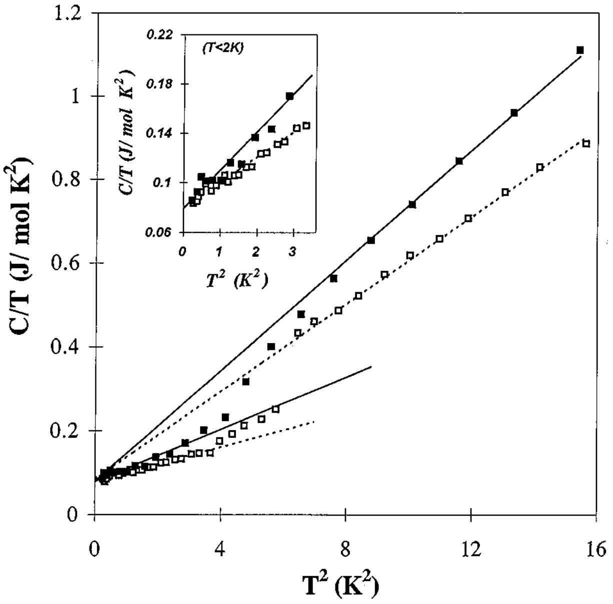

FIG. 5. C/T versus T^2 for PP4060 (☐) and PP3367 (■). Linear fits to the low ($T<2$ K) and high (7 K$>T>$3 K) temperature data are shown by continuous lines for PP3367 and broken lines for PP4060. Inset shows the behavior at low temperature.

For an ensemble of $N/2$ independent pairs with a random distribution of exchange couplings according to the distribution function $P(J)$, the magnetic susceptibility can be written as[12]

$$\chi T=(Ng^2\mu_B^2/k_BT)\int[3+\exp(-2J/k_BT)]^{-1}P(J)dJ. \tag{2}$$

Assuming $P(J)=$constant, and integrating the above expression from 0 to J_0, we get

$$\chi T=A_1-(A_1\ \ln|4|T)/2A_2+(A_1/2A_2)T$$
$$\times\ln|3+\exp(-2A_2/T)|+A_3, \tag{3}$$

where A_1 (in emu K/mol) $=Ng^2\mu_B^2/3k_B$, A_2 (in K) $=J_0/k_B$, and a constant A_3 (in emu K/mol) has been added to Eq. (3) to account for Curie spins in the sample. The presence of a random distribution of exchange couplings (from 0 to J_0/k_B) in polyaniline suggests that its magnetic state, which only requires the condition $J\lesssim k_BT$, will be obtained down to very low temperatures. The number of thermally excited triplet bipolarons will therefore naturally increase as a function of temperature. In a way, this situation is akin to the one with Pauli spins where only the fraction (T/T_F) of the total number of spins contributes to magnetic susceptibility at a given temperature T and makes χT to increase linearly as a function of temperature; T_F here is the Fermi temperature. Values of A_1 (in emu K/mol), A_2 (in K) and A_3 (in emu K/mol) obtained from best fits to Eq. (3), as shown by broken lines in Fig. 5, are 0.773, -793, and 0.00405 for PANI, 1.099, -1461, and 0.00207 for PP4060, and 0.795, -1407, and 0.006 for PP3367. The quantity of practical interest here is A_2 or J_0/k_B, which for blends is larger compared to that for PANI, indicating more electron delocalization in the case of blends.

In conclusion, calorimetric measurements at low temperatures characterize conducting polyaniline as a metal with a finite density of states at the Fermi level $[N(E_F)]$. Although magnetic susceptibility measurements on polyaniline (and many polyaniline-based materials[2]) yield a *Pauli-like* susceptibility, great caution must be exercised in obtaining $N(E_F)$ from such measurements.

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