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# Ferromagnetic spins interaction in alternating branched polyarylamines

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The chemical oxidation of alternating branched polyarylamines leads to the formation of radical cations, the presence of which was manifested by the appearance of new bands in the UV–visible–near infrared spectra. Spins of radical cations can be magnetically coupled. The nutation pulsed-EPR technique was used to determine the multiplicity of spin systems for different oxidant:polymer unit ratios. It was found that spins of polymers oxidized to a radical cation in each conjugated amine segment interact magnetically to form dominant quartet state ( $S = 3/2$ ). Magnetization measurements confirmed the ferromagnetic interaction of spins, returning an exchange integral  $J = +0.75$  meV. © 2011 American Institute of Physics. [doi:10.1063/1.3553882]

## I. INTRODUCTION

There is great interest in ferromagnetic materials that could be used for spin electronics, for which organic materials are one option. Therefore, the task of synthesizing stable, purely organic ferromagnetic materials is an important challenge. These types of materials should contain alternating spin carrying and ferromagnetic coupling units. It is well accepted that a meta-substituted benzene ring (more precisely, a 1,3-benzenediyl core) can be successfully used as a ferromagnetic coupling unit. On the other hand, oligoanilines, which can form stable radical cations with unpaired electrons, are promising compounds as spin-carrying units. However, the presence of radical cations in the chemical structure of magnetic materials creates the problem of competition between overlapping spin distributions and hole/hole repulsion, as was pointed out by Bushby *et al.*<sup>1</sup> For stability reasons, most attempts have been devoted to alternating oligo- and polyanilines containing conjugated arylamine segments altered with meta-substituted ferromagnetic coupling units. Applying this method, linear oligoanilines containing *p*-phenylenediamine altered with meta-benzene<sup>2–4</sup> or 2,7-naphthalene<sup>5</sup> have been prepared, which after partial oxidation to radical cations showed a triplet ground state. On the other hand, the use of 1,3,5-benzene as a core unit in star-shaped arylamines should lead to magnetic interaction of up to three spins after oxidation to the triradical tricationic state. Tanaka's group has carefully studied the multiplicity of this system.<sup>6,7</sup> In the case of star-shaped arylamine containing methyl substituents the presence of  $S = 1/2$  and  $S = 3/2$  was detected,<sup>6</sup> whereas in the case of similar compounds with prolonged conjugation lengths, the generation of an almost pure quartet state was observed.<sup>7</sup> Star-shaped arylamines can

be considered as model compounds for branched polymeric systems containing 1,3,5-benzenetriyl units.

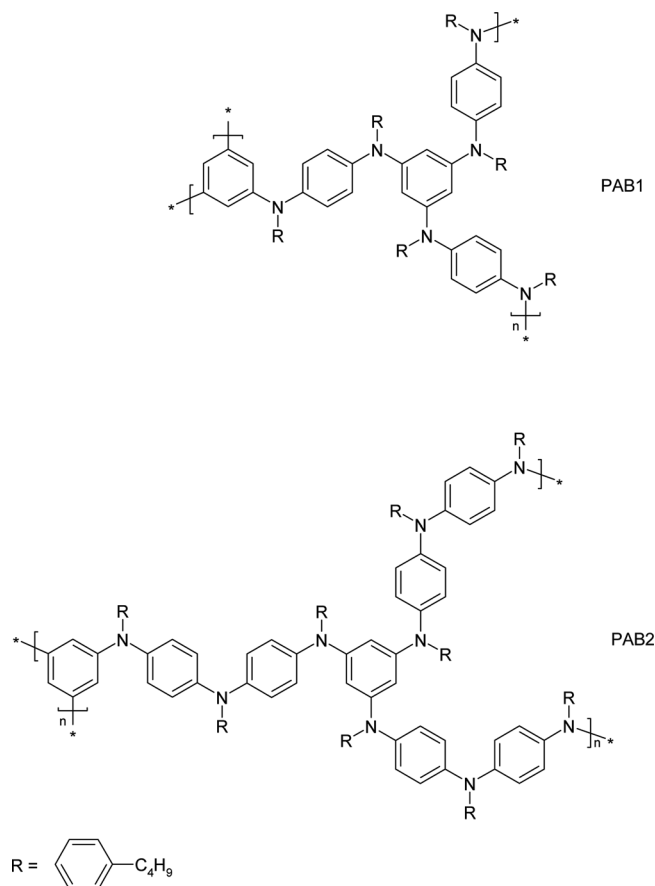
We have prepared this type of branched polymer with amine units of different conjugation, i.e., PAB1 with *p*-phenylenediamine segment (alternating *m-p*-bonding) and PAB2 with *p*-aminophenyl-*p*-phenylenediamine segment (alternating *m-p-p*-bonding) (see Scheme 1). Both polymers contain 1,3,5-benzene cores, which serve as bridging units connected by conjugated arylamine segments. Thus, each 1,3,5-benzene core is linked to three amine segments and each amine segment is connected to two 1,3,5-benzene cores. Taking into account the role of a meta-substituted benzene ring as a ferromagnetic coupler and regarding the chemical structures of both polymers, we can consider the interaction of spins created in arylamine segments that surround a 1,3,5-benzene core. However, in the case of polymers, ferromagnetic spin interactions can be interrupted by local conformation of conjugated amine segments. Thus it seems to be important to answer the question of whether spin interactions can be preserved in a polymer network.

In this paper, we report a study of the multiplicity of partially oxidized branched polymers, PAB1 and PAB2, by the use of pulsed EPR spectroscopy and magnetization measurements [using the superconducting quantum interference device (SQUID) technique].

## II. EXPERIMENTAL

Branched polymers PAB1 and PAB2 have been prepared according to a method reported previously.<sup>8</sup> The polymers were oxidized chemically using tris(4-bromophenyl)aminium hexachloroantimonate (TBA SbCl<sub>6</sub>) as an oxidant. The oxidation reaction was carried out in an argon atmosphere. In a typical procedure 0.01 mmol of polymer was dissolved in 0.5 ml of dry CHCl<sub>3</sub> and oxidized with corresponding amounts of TBA SbCl<sub>6</sub> in 0.5 ml of dry acetonitrile. The

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SCHEME 1. Chemical structures of polymers PAB1 and PAB2.

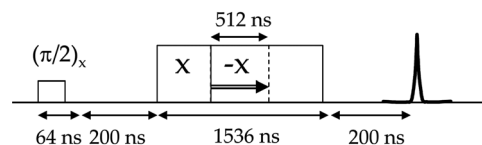
oxidant:polymer unit molar ratios were equal to 2.4:1, 3:1, and 3.6:1. The solutions of oxidized polymers were used directly for EPR.

For magnetization measurements the solution of oxidized polymer with oxidant:polymer unit ratio 3:1 was evaporated and pumped under vacuum for 1 h. The obtained solid-state sample was placed under a protective argon atmosphere in a gelatin capsule (exhibiting a controlled diamagnetic signal). In all measurements polymer samples were exposed to air for 5–15 min during mounting in the apparatus. Magnetization of the samples was measured as a function of magnetic field (up to 6T) and temperature ( $2\text{ K} < T < 300\text{ K}$ ) using superconducting quantum interference device (SQUID) magnetometer. The magnetization data were corrected for diamagnetism of the gelatin capsule and the samples themselves (extrapolated from high-temperature magnetization).

### A. Pulsed EPR nutation measurements by PEANUT experiment

Nutation pulsed EPR experiments were performed using a Bruker Elexsys 580 EPR spectrometer in pulsed mode at  $T = 7\text{ K}$ . The PEANUT experiment (phase-inverted echo amplitude detected nutation) introduced by Stoll *et al.*<sup>9</sup> was used in order to achieve an optimal resolution of nutation frequencies in the recorded spectra.

The PEANUT experiment is described in Scheme 2. In a typical experiment the first pulse used was a selective low-



SCHEME 2. Pulse sequence used for the PEANUT experiments.

power pulse ( $B_1 \sim 0.7\text{ G}$ ). This pulse was set up to be a true  $\pi/2$  pulse for species having nutation frequencies twice as high as  $S = 1/2$  species, in order to better detect signals of the  $S = 3/2$  and  $S = 2$  species. Two-step phase cycling ( $+x, -x$ ) was performed on this first pulse. The high-turning-angle pulses ( $B_1 \sim 7\text{ G}$ ) had a constant length of 1536 ns and the  $x$  pulse ( $-x$  pulse) was incremented (decremented) by 256 steps of 2 ns, respectively. At every step, the spin rotary echo was integrated using a 76 ns gate centered at its maximum.

The obtained time-domain oscillating signal was treated with second-order polynomial baseline correction, sine bell transformation, and symmetrical zero-filling (256 zeros added). Then it was Fourier transformed using numerical FFT software to yield the corresponding nutation spectrum. Two-dimensional maps (magnetic field versus nutation spectra) were obtained by successively performing PEANUT experiments at 200 magnetic field values spaced by steps of 1 Gauss.

The spin multiplicities of detected species were obtained by comparing the measured nutation frequency ( $\nu_{\text{nut}}$ ) to the nutation frequency previously measured for a known  $S = 1/2$  system ( $\nu_{S=1/2}$ ) and using the following relationship:

$$\nu_{\text{nut}} = \sqrt{S(S+1) - m_S(m_S+1)} \cdot \nu_{S=1/2}. \quad (1)$$

This relationship is given for an EPR  $|S, m_S\rangle \longleftrightarrow |S, m_S+1\rangle$  transition and is valid for low-magnetic field excitation ( $B_1 < D$ ;  $D$  being the axial zero field splitting parameter of the considered species).<sup>10</sup>

## III. RESULTS AND DISCUSSION

Conjugated arylamine segments of branched polymers show multiredox properties. The chemical oxidation of polymers PAB1 and PAB2 led to the formation of radical cations with unpaired electrons, the presence of which can be spectroscopically detected. The UV–visible–near infrared (NIR) spectra of partially oxidized PAB1 dissolved in  $\text{CHCl}_3$  show new bands at 420 and 870 nm, which can be attributed to radical cations.<sup>8</sup> The evaporation of solvents led to a bathochromic shift of the NIR band to 940 nm in the spectrum of thin polymeric film. In the case of polymer PAB2 with prolonged conjugated arylamine segments, weak oxidation caused the formation of radical cations. In the UV–visible–NIR spectra the appearance of three new bands located at 430, 770, and ca. 1250 nm can be observed. The presence of two visible–NIR bands in this case can be related to nonequivalent structures of radical cations, which have localized and delocalized charge/spin distributions within conjugated amine segments.

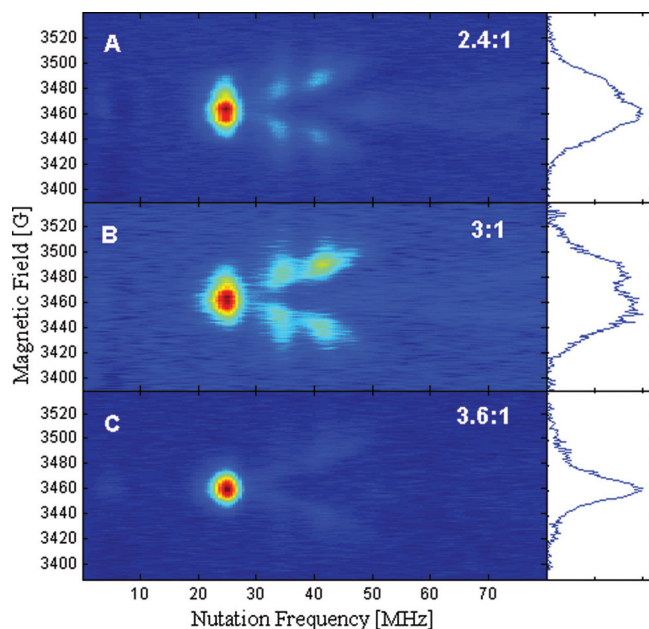


FIG. 1. (Color online) Field-swept pulsed EPR nutation spectra of samples of oxidized PAB1 in frozen solution ( $T = 7$  K) with various oxidant:polymer unit ratios: 2.4:1 (spectrum A), 3:1 (spectrum B), 3.6:1 (spectrum C).

### A. Spin multiplicity versus oxidation state

The field-swept PEANUT spectra of the polymer PAB1 were recorded for several samples prepared with oxidant:polymer unit molar ratios from 1.5:1 to 4.5:1 in steps of 0.3 and also for ratios 6:1 and 9:1. Figure 1 shows the spectra obtained for oxidant:polymer unit ratios 2.4:1, 3:1, and 3.6:1. Under the experimental conditions used, the nutation frequency of the  $S = 1/2$  species ( $\nu_{S=1/2}$ ) is 24 MHz. At a 2.4:1 oxidant:polymer unit ratio (spectrum A) a dominant signal at 24 MHz nutation frequency is observed, with a broad hyperfine structure. We attribute this signal to the  $S = 1/2$  species. Only weak signals with higher nutation frequencies are detected. For an oxidant:polymer unit ratio of 3:1 (which corresponds to the oxidation of each of the three amine segments constituting one polymer unit to one radical cation; spectrum B) several spectral features appear clearly at higher nutation frequencies, indicating high spin species (*vide infra*). At an oxidant:polymer unit ratio of 3.6:1 (spectrum C), the signal at 24 MHz nutation frequency is again dominant, but it is clearly different from the signal observed at a 2.4:1 ratio since it is less broad and exhibits no hyperfine structure. Such a sharpening of  $S = 1/2$  signals in EPR spectra of over-oxidized samples compared to  $S = 1/2$  in low oxidation states is also observed for a linear para-para-meta polymer analogous to PAB2 but based on 1,3-benzene cores.<sup>11</sup> This result contrasts with EPR spectra of oxidized oligoarylamines with 1,3-benzene cores<sup>12</sup> and 1,3,5-benzene cores<sup>6,7</sup> reported in the literature, where  $S = 1/2$  spectra of low oxidation states and over-oxidized states have both hyperfine structure and comparable broadness. The sharpening observed for the  $S = 1/2$  signals of over-oxidized PAB1 suggests that in these paramagnetic states, spin density is delocalized over more than one amine segment (also for PAB2, data not shown). At higher oxidant:polymer unit

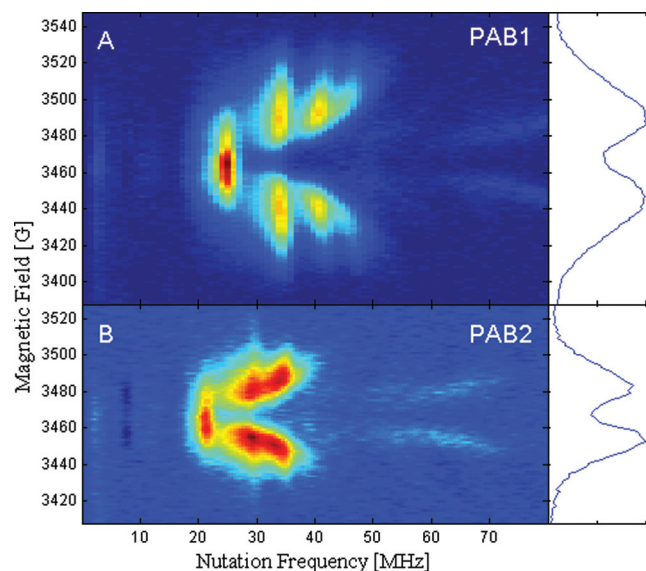


FIG. 2. (Color online) Field-swept pulsed EPR nutation spectra of oxidized PAB1 (spectrum A) in frozen solution ( $T = 7$  K) and PAB2 (spectrum B), for oxidant:polymer unit ratio 3:1.

ratios this signal weakens and no new signal appears (data not shown).

From these results we can conclude that an oxidant:polymer unit ratio of 3:1 is required to produce high-spin multiplicity states. The same trend was observed with the polymer PAB2 (data not shown), and so we focused our study on samples of these two polymers prepared with a 3:1 oxidant:polymer unit ratio.

### B. High-spin states obtained for 3:1 oxidant:polymer unit molar ratio

Spectra shown in Fig. 2 were recorded for PAB1 (spectrum A) and PAB2 (spectrum B) for an oxidant:polymer unit molar ratio of 3:1. The presence of spectral features at distinct nutation frequencies indicates that several spin multiplicities coexist in both samples. Due to slight differences in ESR cavity tuning, the nutation frequency of the  $S = 1/2$  species ( $\nu_{S=1/2}$ ) is 24 MHz in spectrum A and 21 MHz in spectrum B. In spectrum A, two other sets of spectral features are observed at 33 MHz ( $= 1.37\nu_{S=1/2}$ ) and 40 MHz ( $= 1.67\nu_{S=1/2}$ ). They can be attributed unequivocally to  $S = 1$  and  $S = 3/2$  states, since Eq. (1) predicts  $\nu_{\text{nut}} = 1.41\nu_{S=1/2}$  for  $S = 1$  and  $\nu_{\text{nut}} = 1.73\nu_{S=1/2}$  for  $|3/2, +3/2\rangle \longleftrightarrow |3/2, +1/2\rangle$  and  $|3/2, -3/2\rangle \longleftrightarrow |3/2, -1/2\rangle$  transitions in a  $S = 3/2$  state. In the case of PAB2 (spectrum B, Fig. 2) the same conclusions can be drawn for spectral features observed at 29 MHz ( $= 1.38\nu_{S=1/2}$ ) and 34 MHz ( $= 1.62\nu_{S=1/2}$ ).

On both spectra another slight signal can be observed at a higher nutation frequency: 46 MHz ( $= 1.92\nu_{S=1/2}$ ) for PAB1 and 39 MHz ( $= 1.86\nu_{S=1/2}$ ) for PAB2. According to Eq. (1),  $\omega_n = 2\nu_{S=1/2}$  is expected for the  $|3/2, +1/2\rangle \longleftrightarrow |3/2, -1/2\rangle$  transition for  $S = 3/2$  multiplicity and/or for  $|2, +2\rangle \longleftrightarrow |2, +1\rangle$  and  $|2, -2\rangle \longleftrightarrow |2, -1\rangle$  transitions in  $S = 2$  multiplicity.

For choosing between these two possibilities, it is helpful to compare spectra shown in Fig. 2 with pulsed EPR



nutaton spectra<sup>4,6,13</sup> and continuous wave EPR spectra<sup>13,14</sup> of  $S = 3/2$  spin states already reported in the literature for oligoarylamines with 1,3,5-benzenetriyl core as a spin coupling unit (see Ref. 14 for a detailed description of energy levels and transitions in such  $S = 3/2$  systems). In all these studies it appears that, at the first-order approximation level,  $|3/2, +1/2\rangle \longleftrightarrow |3/2, -1/2\rangle$  transitions are not affected by zero field splitting anisotropy and are detected only at magnetic fields close to the center ( $g = 2$ ) of the EPR spectrum (3465 G in our experimental conditions), while  $|3/2, +3/2\rangle \longleftrightarrow |3/2, +1/2\rangle$  and  $|3/2, -3/2\rangle \longleftrightarrow |3/2, -1/2\rangle$  transitions are affected by zero field splitting anisotropy and are detected at magnetic fields up to  $2D \sim 90$  G distance from the center of the EPR spectrum.<sup>15</sup> The signals observed at nutation frequencies 46 MHz ( $= 1.92\nu_{S=1/2}$ ) in spectrum A and 39 MHz ( $= 1.86\nu_{S=1/2}$ ) in spectrum B have their maximal intensity at magnetic field values shifted by 30 G (resp. 25 G) from the center of the spectrum. This is not consistent with the expected nutation spectrum of  $|3/2, +1/2\rangle \longleftrightarrow |3/2, -1/2\rangle$  transitions in this kind of paramagnetic systems. This possibility is then ruled out and these signals should be attributed to  $|2, \pm 2\rangle \longleftrightarrow |2, \pm 1\rangle$  transitions of states with  $S = 2$  multiplicity, which are expected to be affected by zero field splitting anisotropy.

From spectra reported in Fig. 2, we can conclude that PAB1 and PAB2 samples doped with a 3:1 molar oxidant:polymer unit ratio contain high-spin states, including  $S = 1$ ,  $S = 3/2$ , and  $S = 2$ . However,  $S = 1/2$ ,  $S = 1$ ,  $S = 3/2$ , and  $S = 2$  have different relaxation times and the sensitivity of a pulsed EPR nutation experiment depends strongly on the frequency of nutation, so it is not possible to deduce the relative quantities of the various spin states in the sample from this technique. The branched polymers PAB1 and PAB2 were then investigated by SQUID magnetometry.

### C. Magnetic properties

Representative magnetization results are shown in Fig. 3(a) for PAB1 (doped with oxidant:polymer unit ratio 3:1). Magnetization reveals typical Brillouin behavior: at low temperatures it tends to saturate with magnetic field, while at higher temperatures it is almost linear with magnetic field and decreases with increasing temperature.

Noninteracting unpaired electrons of radical cations should be the source of magnetic moments with  $S = 1/2$ , and their magnetization  $M$  should be described by a standard Brillouin function (BF)  $M = B_S(B, T)$  with  $S = 1/2$ , where:  $B$  and  $T$  are magnetic field and temperature, respectively. If there is coupling between spins, magnetization should deviate from the Brillouin function. Figure 3(b) shows the BF fit to the low temperature data of PAB2 with  $S = 1/2$ , where the only adjustable parameter was concentration of radical cations. It is clearly visible that no reasonable matching was obtained for  $S = 1/2$ , as the experimental data saturate faster than the Brillouin function for  $S = 1/2$ . For this reason we should consider the interaction of spins surrounding the 1,3,5-benzene core. We focused on meta-substituted benzene which can have 1, 2 or 3 spins in its vicinity, thus forming magnetic centers with different multiplicity. The use of spin values larger than  $S = 1/2$  yields much bet-

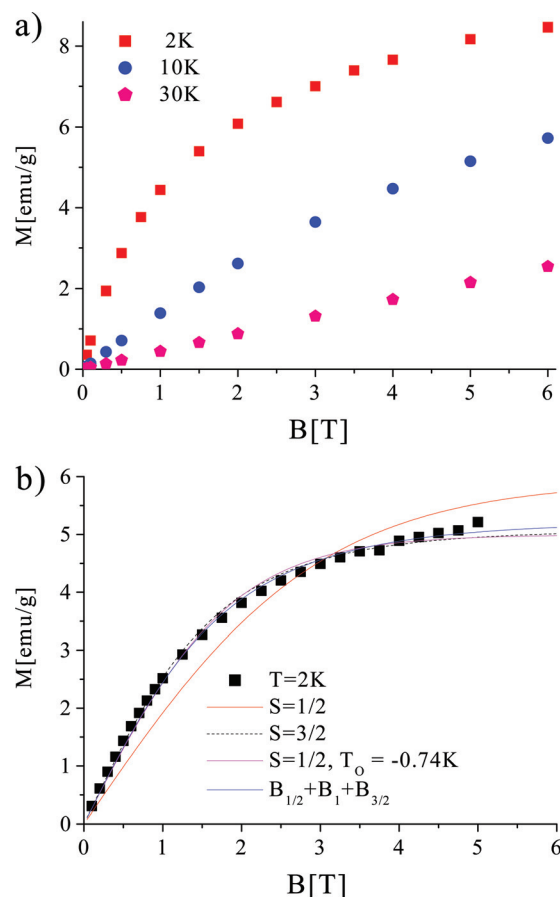


FIG. 3. (Color online) (a) Magnetization of PAB1 versus magnetic field at different temperatures. Magnetization was corrected for diamagnetic contribution, as described in the text. (b) Magnetization of PAB2 measured as a function of magnetic field at  $T = 2$  K. The solid and dashed lines represent Brillouin function fits to experimental data for  $S = 1/2$  and  $S = 3/2$ , effective Brillouin function fit with  $S = 1/2$ , and the sum of the three Brillouin functions with  $S = 1/2$ ,  $S = 1$ , and  $S = 3/2$ , respectively.

ter matching, as exemplified for  $S = 3/2$  [Fig. 3(b)]. This observation suggests ferromagnetic coupling between the  $S = 1/2$  spins of unpaired electrons of radical cations and strongly supports the EPR observation of spin quartet and triplet states. Following these results one should regard magnetization as resulting from magnetic centers with spins  $S = 1/2$  (one unpaired electron surrounding a 1,3,5-benzene core),  $S = 1$  (two ferromagnetically coupled electrons surrounding a 1,3,5-benzene core) and  $S = 3/2$  (3 interacting electrons). Consequently, magnetization should be composed of Brillouin functions with  $S = 1/2$ ,  $S = 1$  and  $S = 3/2$ , weighted by the concentration of particular magnetic centers  $x_S$ :  $M \sim x_{1/2} B_{1/2}(B, T) + x_1 B_1(B, T) + x_{3/2} B_{3/2}(B, T)$ . The result of such a fit is depicted in Fig. 3(b). Although one should not rely too much on estimated relative concentrations of spins with different multiplicity, definitively, the majority of the centers was found to be in the  $S = 3/2$  configuration.

An alternative way to describe low-temperature magnetization of an interacting spin system is to use the effective Brillouin function  $B_{1/2}(B, T_{\text{eff}})$ ,<sup>16</sup> where instead of the real experimental temperature  $T$  one can use effective temperature  $T_{\text{eff}} = T + T_0$ , with  $T_0$  being an adjustable parameter. In the case of ferromagnetic interaction (FMI) between spins,

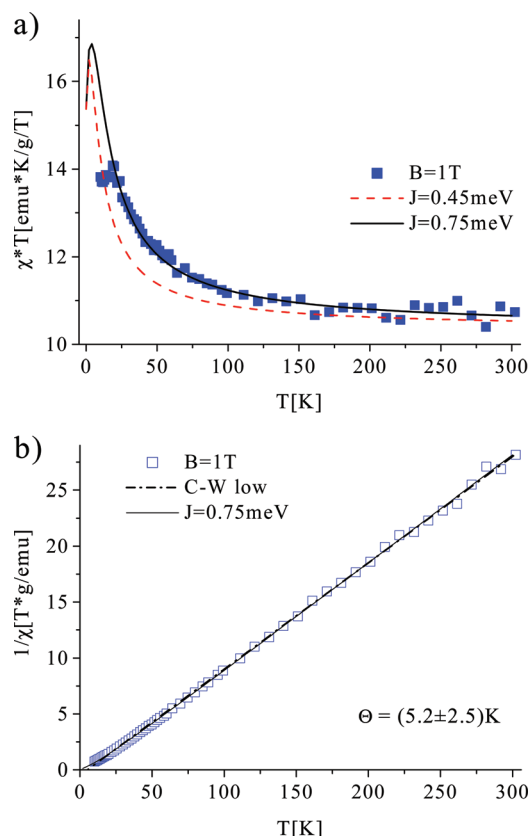


FIG. 4. (Color online) (a) The product of susceptibility and temperature  $T \times \chi$  versus temperature  $T$  of PAB1. Susceptibility was evaluated at  $B=1$  T and corrected for diamagnetic contribution. The dashed and solid lines represent calculations based on Hamiltonian Eq. (2) with  $J=+0.45$  meV and  $x=1.16$ , and  $J=+0.75$  meV and  $x=1.16$ , respectively. (b) Inverse susceptibility of PAB1 as a function of temperature. Susceptibility was evaluated at  $B=1$  T and corrected for diamagnetic contribution. The dashed line represents the Curie–Weiss law with  $\Theta=+5.2$  K. The solid line represents a calculation based on Hamiltonian Eq. (2) with  $J=+0.75$  meV and  $x=1.16$ .

magnetization saturates faster than the simple Brillouin function indicates, which corresponds to an effective temperature lower than experimental  $T$ , thus  $T_0 < 0$ . On the other hand, for antiferromagnetically coupled spins the situation is reversed (i.e.,  $T_0 > 0$ ). Fitting magnetization data of PAB1 and PAB2 with the effective Brillouin function returned  $T_0 = -0.74$  K [Fig. 3(b)], suggesting ferromagnetic interactions in our spin systems.

Another way to demonstrate coupling between spins is to plot the product of the temperature and susceptibility versus temperature [ $T \times \chi$  vs.  $T$ , Fig. 4(a)]. For a noninteracting spin system,  $T \times \chi$  should remain independent of temperature. In our case the observed upward deviation of  $T \times \chi$  with decreasing temperature indicates ferromagnetic coupling between magnetic moments.

The value of interactions between spins (exchange integral) can be estimated from a traditional  $1/\chi$  versus  $T$  plot, assuming the data follow the Curie–Weiss law. Figure 4(b) shows that reversed magnetization/susceptibility of PAB1 is indeed linear with temperature, at least for  $T > 30$  K. This proves that the Curie–Weiss law can be applied for high-temperature data. The extrapolated Curie–Weiss temperature

is positive  $(5.2 \pm 2.5)$  K, which again points for ferromagnetic coupling. The estimated Curie–Weiss temperature corresponds to an exchange integral  $J = +0.45$  meV. A similar exchange interaction was found for another polymer (with diradical-containing meta-terphenyl coupling unit<sup>1,17</sup>), where a ferromagnetic Curie–Weiss temperature of 3 K was found, which corresponds to  $J = +0.52$  meV. Since the Curie–Weiss constant (measuring the slope of  $1/\chi$  versus  $T$ ) is proportional to the single spin value (i.e.,  $S = 1/2$ ) and the total spin concentration  $x$ , the latter can be estimated from the experimental data. In our case we obtained  $x = 1.16$ , while  $x = 1.00$  is expected for the oxidation of each amine segment to one radical cation. This higher than expected  $x$  value can suggest either a slight deviation from stoichiometry of the sample or that there are some amine segments which possess more than 1 spin.<sup>18</sup> At present we are not able to discriminate between the two possibilities.

The magnetization of our system can be calculated exactly, taking into account a polymer unit composed of two 1,3,5-benzene cores and three amine segments and basing the calculation on the following assumptions: there is no inter-polymer unit interaction, intra-polymer unit interactions can be described by a Heisenberg exchange, each unit contains 3 spins  $S = 1/2$  (as suggested by results presented above), and the Hamiltonian for a single unit can be written in the form:

$$H = (-2J_{12}S_1S_2 - 2J_{23}S_2S_3 - 2J_{31}S_3S_1) + \mu_B(2S_1 + 2S_2 + 2S_3)B, \quad (2)$$

where the first term corresponds to a Heisenberg exchange and the second is the Zeeman term. Since we have no information about possible differences between exchange integrals we assumed that they are all equal:  $J_{12} = J_{32} = J_{13} = J$ . Numerical solution of the Hamiltonian allows one to determine eigenstates and then calculate magnetization:

$$M = -\frac{\mu_B N_{Av}}{m_{mole}} x \frac{\sum_{i=1}^N 2\langle \phi_i | \hat{S}_1 + \hat{S}_2 + \hat{S}_3 | \phi_i \rangle \exp(-E_i^n/k_B T)}{\sum_{i=1}^N \exp(-E_i^n/k_B T)}, \quad (3)$$

where  $E_i^n$  and  $\phi_i$  are eigenenergies and eigenstates of Hamiltonian Eq. (2), respectively,  $\mu_B$  is the Bohr magneton,  $m_{mole}$  is the molar mass of the polymer unit,  $N_{Av}$  is the Avogadro number and  $x$  is the concentration of polymer units.

The result of such a calculation is shown in Fig. 4(a), where  $J = +0.45$  meV and  $x = 1.16$  were used, as estimated from the Curie–Weiss law. No parameters were adjusted. We note that variation of  $x$  scales the value of  $T \times \chi$  at high temperatures. Using  $x = 1.00$  would result in too low  $T \times \chi$  values at high temperatures.

A better matching with the experimental was obtained if  $J$  was adjusted. The best fit was obtained for  $J = +0.75$  meV [see Fig. 4(a)]. We believe that the latter exchange constant is more reliable than the one resulting from the Curie–Weiss law, which is based on averaging over many neighbors. In our case every spin has only 2 neighbors (assuming no

inter-unit interactions), thus the “triple” model described above that takes into account exchange interaction in an exact way is more appropriate.<sup>19</sup> A similar situation was encountered for the above mentioned diradical linked by meta-terphenyl (only 2 electrons per unit), where the exchange integral evaluated from the pair model was found to be  $J = +1.8$  meV, as compared to  $J = +0.52$  meV resulting from the Curie–Weiss law.<sup>17</sup>

Despite the simplicity of the model we used, the matching with experimental data is quite reasonable, although not perfect. The major discrepancy is found at low temperatures ( $T \leq 20$  K), where measured  $T \times \chi$  increases much slower than is predicted by the model. This indicates the appearance of antiferromagnetic interactions (AFI) in the system. The observation is supported by magnetization measurements at low temperatures, i.e.,  $T = 2$  K, 10 K, 30 K. The fit of the calculated curves from Eq. (3) to experimental data return  $x < 1$  which is equivalent to the freezing out of some spins by antiferromagnetic coupling. Such behavior could be explained by at least two possible mechanisms. First, one of the exchange integrals would become negative, i.e., antiferromagnetic (see also Ref. 7). In principle this is not excluded if the geometry of the amine segments surrounding the 1,3,5-benzene core changes slightly at low temperatures.<sup>20</sup> Theoretical calculations suggest that both AFI and FMI could be present in the system and that their strengths are strongly structure dependent. We note that similar behavior, i.e., the presence of both FMI and AFI in one system, was reported for other organic materials.<sup>7,17</sup> We believe that at this stage, the application of a more complicated model (in particular spin clusters other than triples and different exchange integrals) is irrelevant. Second, one should take into account the presence of a small intermolecular AFI between polymer chains which may manifest itself at  $T \leq 20$  K. To gain full understanding of the microscopic mechanism of spin interactions in this kind of alternating oligo- and polyanilines, these interactions should be the subject of more extensive theoretical and experimental investigations.

Finally, magnetization of PAB1 and PAB2 is compared in Fig. 5, where scaled magnetization  $M(B)/M(B = 6$  T) is plotted. Apparently magnetization of PAB1 saturates faster with magnetic field than that of PAB2, which indicates that

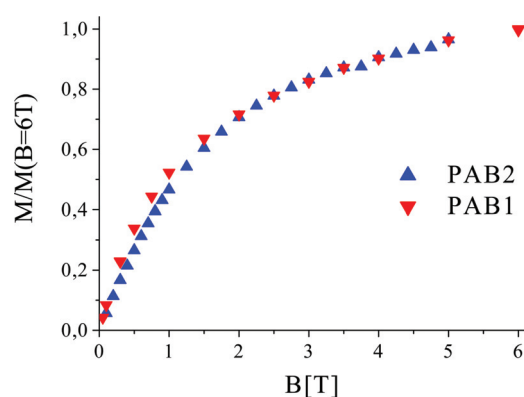


FIG. 5. (Color online) Reduced magnetization  $M(B)/M(B = 6$  T) of PAB1 and PAB2 versus magnetic field at  $T = 2$  K.

ferromagnetic coupling in the latter case is weaker. This may be understood by taking into account the fact that magnetic electrons in PAB1 are localized in shorter conjugated segments than that of PAB2 (as indicated by UV–visible–NIR spectroscopy). Therefore, effectively, the spins of PAB1 are better localized near the meta-benzene coupler than in the case of PAB2, which leads to stronger interactions. The rather slight difference between PAB1 and PAB2 suggests that the effect of the length of conjugated segments is not very strong.

#### IV. CONCLUSIONS

Branched polyarylamines containing conjugated amine segments surrounding meta-substituted benzene cores can be oxidized to relatively stable radical cations. Unpaired electrons of radical cations serve as the source of magnetic moment via spins  $S = 1/2$ . The meta-benzene core can act as a magnetic coupler, thus spins of radical cations can form high-spin states. It turned out that oxidation of each conjugated amine segment to one radical cation leads to the generation of a dominant quartet state ( $S = 3/2$ ) in both of the studied polymers, as was evidenced by pulsed-EPR spectroscopy. Magnetization measurements confirmed ferromagnetic spin interactions and returned an exchange coupling constant of  $J = +0.75$  meV.

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- <sup>18</sup>In other words, there could be some amine segments that are occupied by at least 2 spins, which could be the source of  $S = 2$  observed in the EPR experiment (PEANUT) discussed above, or it could be related to different stoichiometries of polymer chain ends in which the amine segments:1,3,5-benzene core ratio is higher than that shown in Scheme 1.
- <sup>19</sup>In particular, the Curie–Weiss temperature extrapolated from high-temperature susceptibility calculated within the model is about 50% larger in value than that estimated from the plot  $1/\chi$  versus  $T$ .
- <sup>20</sup>Jean-Marie Mouesca, to be published.