Ferromagnetic Spins Interaction in Randomly Networked Polyarylamines

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The search of purely organic magnetic materials is a great challenge nowadays. Although spectacular progress in the design and the synthesis of conjugated oligomers and polymers for electronics and optoelectronics have been achieved, the advancement in the synthesis of stable magnetic organic compounds are rather limited up to now. These types of materials should fulfill the following requirements: i) they should show a very large S value, ii) radicals or radical cations should exhibit sufficient chemical stability, iii) organic molecules should be insensitive to spin defects.

In 1968 Mataga proposed a 2D model of organic polyradicals in which spins can be ferromagnetically coupled which can lead to the formation of "organic pseudo-magnet". In such a network the magnetic interactions can be realized on multiple paths and the spins interaction is possible even in the presence of spin defects.

In this report we present a new attempt to create a Mataga-like structure. To form entangled polymer network we have used a star-shaped arylamine with prolonged conjugation linked with 1,3-benzene (the polymer 1) or 1,3,5-benzene unit (the polymer 2). In this type of structures arylamine unit can be considered as "spin bearing unit" whereas 1,3- or 1,3,5benzene can be considered as "ferromagnetic coupling units". Spins were created by the oxidation of both polymers to radical cations. This process was accomplished on chemical and electrochemical ways. The magnetic properties of both polymers were studied by the use of SQUID measurements.

Magnetization of both polymers was measured as a function of magnetic field (up to 7 T) and temperature (2-400 K) using a SQUID magnetometer. The polymers showed dominant



Fig.1 The product of the susceptibility and temperature vs. temperature $(T\chi \text{ vs. T})$ of *Polymer 2* at B=1T.

paramagnetic (PM) behavior. However, the close inspection of the magnetization data indicate that they depend on the polymer structure. Magnetization of *Polymer* 2 saturates faster with increasing magnetic field than magnetization of *Polymer 1* and the both saturates faster than Brillouin-type saturation for S=1/2. Such behavior suggests FM interaction between spins of radicals, most probably between three unpaired electrons of three neighboring radical cations. This is exemplified in Fig.1 as low temperature increase of M*T vs. T (we recall that M*T vs. T of noninteracting magnetic centers should be a constant value, independent of temperature). Moreover, at lowest temperatures manifestation of a week antiferromagnetic (AFM) coupling between the 'triple spins' was also

observed. Similar behavior *i.e.*, the presence of both FM and AFM interactions in the alternating branched polyarylamines were reported previously [1]. The model calculation considering FM spin interaction returned an exchange coupling constant of J=1 meV.

[1] J. Gosk, V. Maurel, S. Gambarelli, D. Djurado, R. Szymczak⁻, A. Twardowski and I. Kulszewicz-Bajer, *J. Appl. Phys.* **109**, 074911 (2011).