High-spin organic polymers

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New high-spin organic polymers are obtained by oxidative doping of networked polyarylamines and show ferromagnetic coupling between radical cation sites and bulk behaviour which, in the best case, corresponds to spin (*S*) = *ca.* 2.5.

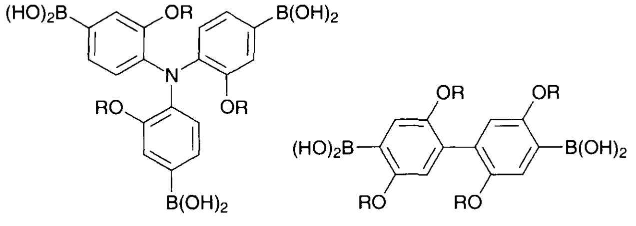
Almost thirty years ago, Mataga[1] suggested that organic ferromagnets could be created by bonding together spin-bearing centres creating a conjugated polymer in which the local topology mimicked that of a triplet ground state pi-biradical.[2] So far experimentalists have failed to produce a genuine *ferromagnetic* polymer by this route but the use of this approach has resulted in the preparation of some interesting *high-spin* polymers. These include polyphenoxy systems,[3] doped poly*meta*phenylenediamines (which behave as an S = *ca.* 1 system),[4] polymer derivatives of phenylenebis*tert*butylnitroxide (also maximum S = *ca.* 1),[5] polymers of the poly*meta*quinodimethane type (maximum S = *ca.* 2)[6] and most particularly varieties of 'polaronic' magnet[7] developed by the Dougherty group. The best of these, based on a doped repeating *meta*phenylenevinylenethienyl moiety, shows a maximum S = *ca.* 9/2.[8] The polymers we have made show a maximum S of *ca.* 5/2. Like Dougherty's polymers ours are based on radical-ion spin-bearing units and the spin is introduced by doping with an oxidizing agent. The rationale behind the doping–radical-ion strategy is that, whereas stable neutral carbon-centred radicals are rare, stable organic radical-ions abound providing a wide choice of building-blocks. Studies of model oligomers[9] lead us to concentrate on doped polyarylamine systems[4,10] and those in which aryl radical-cations are *meta* coupled through a benzene ring.[11]

Many of the original proposals by Mataga[1] and Ovchinnikov[12] were for 'one-dimensional ferromagnets' and most experimental work has been directed towards the creation of one-dimensional systems. However, each defect site (undoped or 'bipolaron' site) in a one-dimensional system would cause a fatal break in the spin-propagation mechanism. Furthermore fundamental theory shows that even if a one-dimensional system were perfectly doped there could be no transition to a ferromagnetic state.[13] Hence, unlike Dougherty's polymers, which were one-dimensional, ours are networked–crosslinked and were made from the monomers **1–6** using the palladium mediated coupling of aryl boronic acids and aryl bromides. The monomers used to make each polymer and the 'best' doping agents are given in Table 1. Each polymer was based on a network in which each spin-bearing centre should be ferromagnetically coupled to up to three others. The percolation limit for such systems (the point at which 'all the spins should link up') is probably reached about the 70% doping level.[14] In the case of polymers **7** and **10** the networking–crosslinking is provided through spin-bearing ($N^{\cdot +}$) centres. In the case of polymers **11**, **12** and **13** it is provided through the 1,3,5-trisubstituted benzene residues and in the case of polymers **8** and **9** through both of these. Polymers **7**, **8** and **9** contain extended versions of the *meta*diaminobenzene motif (after oxidation, having $N^{\cdot +}$ centres 1,3 coupled through a benzene ring).[10] Oxidation of polymer **10** should generate $N^{\cdot +}$ centres coupled 3,4′ through a biphenyl moiety[15] whereas, oxidation of polymers **11**, **12** and **13** should produce systems in which biphenyl radical cations are *meta* coupled through a benzene ring.[11] Investigation of the bulk magnetic properties of the doped polymers **7**, **8**, **9** and **12** showed evidence of the desired

Table 1

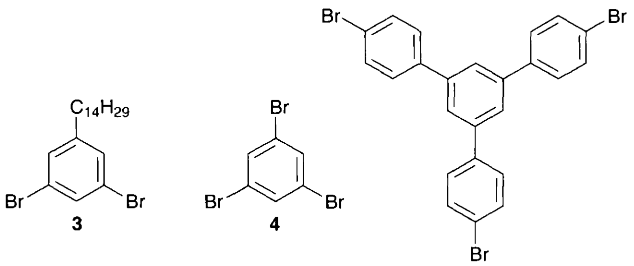
Polymers (starting monomers)	M_w[a]/10^3	Doping agent	% of sites doped[b]	*ca.* spin system S[b]
7 (**1a** + **3**)	80	$NOBF_4$	15	5/2
8 (**1b** + **4**)	42	$NOBF_4$	9.6	3/2
9 (**1b** + **5**)	84	$NOBF_4$	9.9	1
9 (**1b** + **5**)	84	$SbCl_5$[c]	8.7	1
10 (**1b** + **6**)	104	$NOBF_4$	3.9	1/2
11 (**2a** + **4**)	5.5	DDQ	5.8[d]	—
12 (**2a** + **5**)	115	$NOBF_4$	16[e]	1
13 (**2b** + **3** + **4**)[f]	18	$SbCl_5$	15	1/2

[a] GPC against polystyrene standards. [b] SQUID measurements at *ca.* 2 K. [c] Vapour phase doping of a thin film. [d] Based on ESR measurements at room temp. [e] Film sample rather than powder. [f] Equal parts of **3** and **4**.

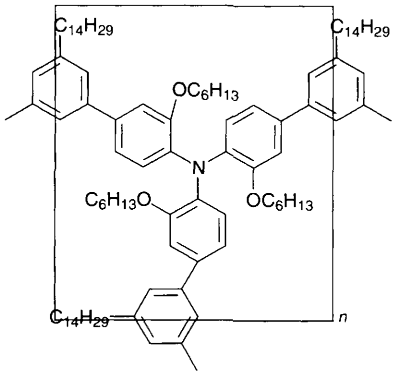


1a R = C_6H_{13}
b R = $C_{10}H_{21}$

2a R = C_6H_{13}
b R = Me



3 **4** **5**



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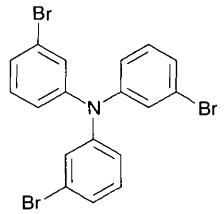

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ferromagnetic spin coupling. The results for the 'best' polymer, polymer **7**, will be discussed in detail.

Polymer **7** was prepared in 31% yield by the $Pd(PPh_3)_4$ catalysed reaction of a 2:3 mixture of the trisboronic acid **1a** and the dibromide **3** in refluxing toluene for three weeks in the presence of sodium carbonate and was purified by repeated reprecipitation from dichloromethane–methanol. The elemental analysis of the purified polymer (C: 83.2, H: 10.4, N: 1.3, Br: 1%. Polymer **7** requires C: 82.6, H: 9.8, N: 1.7, Br: 0%) showed that it contained about 5% unreacted 'end' groups. The molecular weight was determined by gel permeation chromatography against polystyrene standards. For such networked polymers this gives useful relative values but is known to underestimate substantially the absolute values.[16] The measured average of 80000 with a long tail into the several hundred thousand regime suggests that, at least for a fraction of the polymer, we may be approaching a molecular weight in the region of 10^6. In the longer term, the aim is to produce a ferromagnet rather than a superparamagnetic material and 10^3–10^4 coupled spins are needed to sustain a ferromagnetic domain structure.[17] Susceptibility studies on the purified, undoped polymer between 2 K and room temperature showed straightforward diamagnetic behaviour and that it was free from significant magnetic impurities. A solution of the polymer in chloroform was treated with 1 equiv. of $NO^+ BF_4^-$ and the solvent removed under vacuum. After drying for 15 h under high vacuum the doped polymer was transferred to a sample holder under an atmosphere of dry nitrogen (although this particular doped polymer is moderately air stable). Using a SQUID magnetometer the susceptibility of the doped polymer was measured as a function of temperature and field. There is paramagnetic behaviour and the Curie Law is obeyed with the intercept of the $1/\chi$ plot being quite close to zero. The χT *vs.* T plot shows the expected downturn at very low temperatures associated with the onset of long-range antiferromagnetic coupling. The interesting behaviour is that in which magnetization was studied as a function of Field (Fig. 1). As can be seen, comparison with theoretical Brillouin functions indicates behaviour 'better' than $S = 1/2$. In systems such as this, where the coupled spin systems are disperse in nature, an 'average' Brillouin Function is never followed in a strict manner and typically the magnetisation increases 'too rapidly' at low fields and 'too slowly' at high fields.[8] Overall, the behaviour for polymer **7** is perhaps closest to that for a spin 5/2 system.

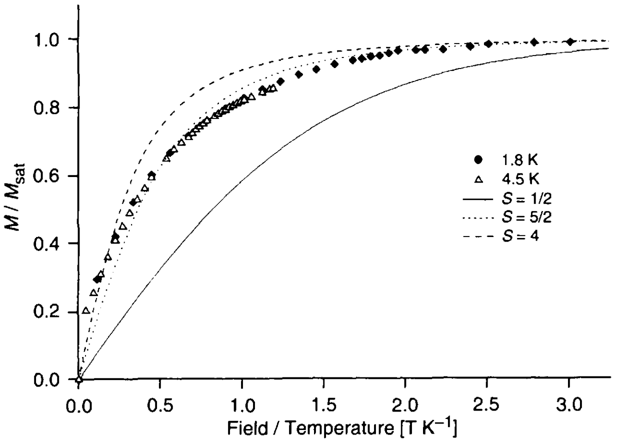

Fig. 1 Field dependence of the magnetisation of polymer **7** doped with $NOBF_4$, measured at 1.8 and 4.5 K and compared to theoretical Brillouin functions for spin systems $S = 1/2$, 5/2 and 4. M = magnetisation, M_{sat} = saturation magnetisation.

In terms of the 'extent of ferromagnetic spin coupling observed', the results for these new doped polymers are somewhat better than those reported for most high spin polymers but are short of the best results reported by Dougherty.[8] However, unlike Dougherty's polymers, which are linear, these new polymers are networked and so should display an attainable percolation limit. A problem with both our polymers and those studied by Dougherty is that the doping levels achieved are disappointingly low. Until this problem is solved we will not know whether this approach to 'molecular' magnets is a feasible alternative to those already explored.

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