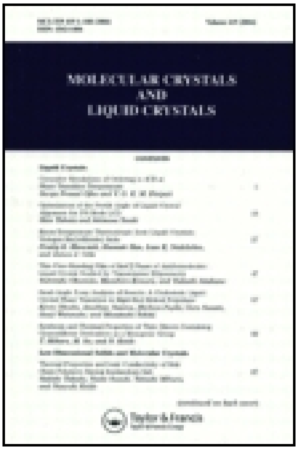

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Richard J. Bushby [a], Daniel Gooding [a], Mark Thornton-pett [a] & Matthew E. Vale [a]

[a] School of Chemistry, University of Leeds, Leeds, LS2 9JT, U.K.

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High-Spin p-Doped Arylamine Polymers

RICHARD J. BUSHBY, DANIEL GOODING,
MARK THORNTON-PETT and MATTHEW E. VALE

School of Chemistry, University of Leeds, Leeds, LS2 9JT, U.K.

A method has been developed for quantitatively p-doping conjugated polymers based on an expanded *m*-phenylenediamine motif. This produces a disperse population of high-spin species. However, these clusters of ferromagnetically coupled spins are not quite as large as would be expected on the basis of the molar mass/molar mass distribution of the polymers.

Keywords: High-spin; polymers; p-doping; Brillouin function

INTRODUCTION

In our attempts to produce high-spin polymers[1-4] we have used triarylamminium ions (Ar_3N^{+}) as stable S=1/2 spin-bearing units,[5] *meta*quinodimethane as the ferromagnetic coupling unit[6] and a networked polymer architecture to mediate spin-coupling in three dimensions. The amminium ion centres were generated by oxidative doping the corresponding neutral polyarylamine (Fig. 1). In our first experiments[1] doping involved treating a ca 1% w/v solution of the polymer in dichloromethane with a large excess of $NOBF_4$. Under these conditions up to 20% of the available sites were oxidised to the N^{+} level. Nutation resonance showed the presence of species from S = 1/2 up to at least S = 3[4] and field dependence of the bulk magnetisation at 2K fitted most closely a Brillouin function S = 5/2.[1] By oxidising a thin (ca 1μm) film of the polymer with gaseous antimony pentachloride, doping levels were increased to 60%. The field dependence of the magnetisation at 2K then fitted most closely a Brillouin function S = 4.[3] In this paper we report the results of almost quantitative doping which was achieved by treating a ca 0.06% w/v solution of the polymer with an excess of $NOBF_4$. At this level of doping one would expect the size and distribution of the high-spin species to be limited only by the molar mass/ molar mass distribution characteristics of the polymer.[1]

RESULTS AND DISCUSSION

Synthesis of the Polymers and Single Crystal X-Ray Diffraction Characterisation of a Model for the Repeat Unit.

The polymers **1-3** and a model for the repeat unit (**4**) were synthesised as shown in Fig. 1.[1,3] The polymerisation was interrupted before the point at which the polymer became wholly insoluble and the products were purified by repeated reprecipitation from chloroform/methanol. As can be seen from the GPC data for polymer **2** (Fig. 3) it is a highly disperse material containing between 2 and 62 repeat units. A single crystal X-Ray diffraction study of the model for the repeat unit **4** gave the molecular geometry shown in Fig. 1.[7] The propeller-like twisting of the aryl residues about the central nitrogen is very similar to that found in other triaryl amines[8] This is expected to change little on oxidation to the radical cation.[9] Most significant from the standpoint of our study is the dihedral angles between the aryl rings in the biphenyl groups (44°, 45°, 25°) Orthogonality of these rings would be fatal to our strategy since it would destroy the conjugated pathway on which the exchange interaction depends.[1]

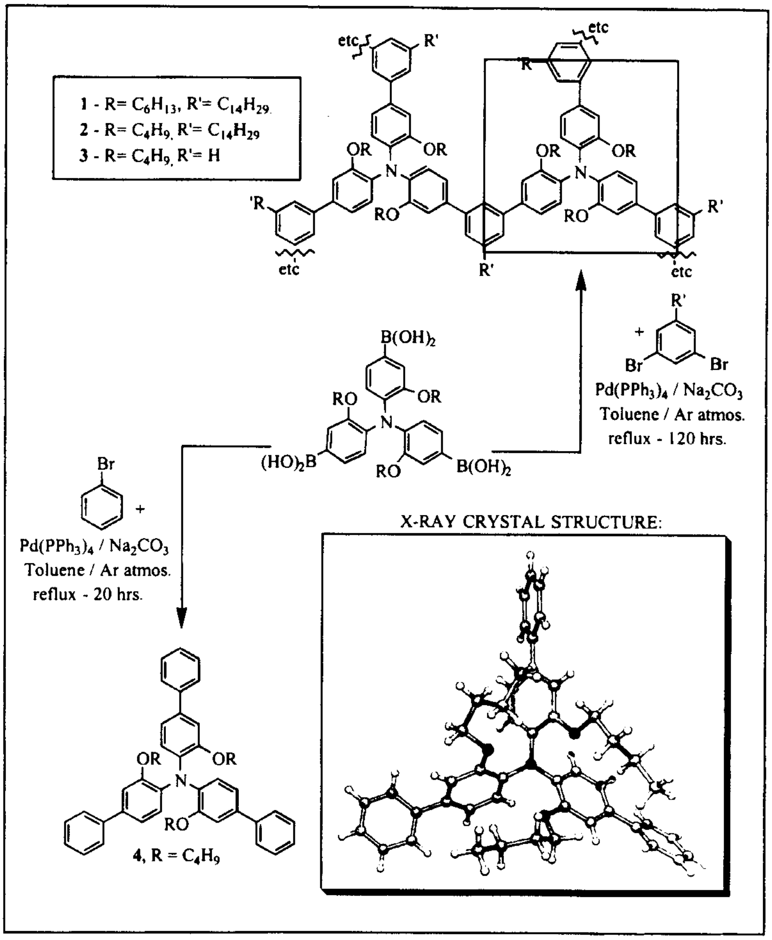

FIGURE 1. Synthesis of the polymers **1-3** and of the model 'repeat unit' **4**. (See Color Plate at the back of this issue)

Studies of Doping of the Model for the Repeat Unit and of the Polymers by UV and EPR Spectroscopy.

When a dilute solution of the amine **4** in dry chloroform was titrated with a solution of $NOBF_4$ in dry chloroform, the absorption $\lambda_{max.}$ at 347 nm was progressively and quantitatively replaced by that for the radical cation $\mathbf{4}^{\cdot+}$ at $\lambda_{max.}$ 418 nm (Fig. 2, left). When the same experiment was repeated using one of the polymers **1-3**, except that a roughly four-fold excess of $NOBF_4$ had to be used, the results were almost identical. (Fig 2, right) This shows (i) that, as expected, the chromophore of compound **4** and of the polymers are the same and (ii) that, in these very dilute solutions, the polymers can be quantitatively doped. The limited levels of doping obtained in our previous attempts to use $NOBF_4$[1] were the result of using solutions that were too concentrated and, almost certainly, the polymer was precipitating from solution before oxidation was complete. These experiments also establish UV spectroscopy as a sensitive method of monitoring doping levels in these systems.

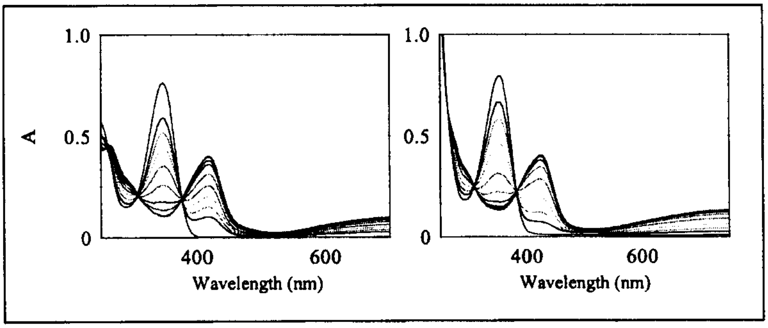

FIGURE 2. UV spectra showing the progress of oxidation of compound **4** (left) and polymer **1** (right) in $CHCl_3$ on adding aliquotes of $NOBF_4$ solution.

The oxidations were also studied by EPR spectroscopy. Integrating the signals obtained by $NOBF_4$ oxidation of a 10^{-5}M solution of compound **4** and comparison with equivalent solution of the polymers treated in exactly the same way suggests average doping levels (based on the concentration of spins) of 94(standard deviation 5), 99(4), and 97(2)% for **1**, **2** and **3** respectively.

Characterisation of the Magnetic Properties of the Doped Polymers.

A ca 20-fold excess of powdered $NOBF_4$ was used to oxidise a ca 0.06% w/v solution of the polymer in chloroform. The UV spectrum of the reaction mixture showed that the oxidation was complete. Whilst maintaining an inert atmosphere the solvent was removed under reduced pressure. The UV spectrum of the residue showed no depletion in oxidation level. Following SQUID magnetometer measurements the UV spectrum was checked again and this showed that there had been no detectable deterioration of the sample. The susceptibility of each doped polymer was measured as a function of temperature (2K to room temperature) at constant field (5T) and as a function of field (0 to 5T) at constant temperature (2K). The susceptibility measurements were corrected to allow for the diamagnetic contribution of the polymer and of the sample holder.[1] Curie Law behavior was observed between ca 10K and room temperature. The value of XT was independent of T in this temperature range but was higher than previously obtained (6.41 X 10^{-4} deg.emu/g for polymer **2**). A downturn in XT was observed at <ca 10K (as in previously published plots[1]). This was a consequence of the high field used (5T) and certainly most of this downturn could be quantitatively accounted for in terms of saturation of the moment.[10] Fig. 3 shows relative magnetization as a function of field for the doped polymer **2**. The absolute value of the saturation magnetization for this polymer was 6.19 emu/g which corresponds to 96% doping. The data shown in Fig. 3 is typical of a polydisperse spin system rising too rapidly at low H/T and too slowly at high H/T relative to a Brillouin function for a monodisperse spin system.[11] For a polydisperse spin system we can write:

$$M = N.g.\mu_B.\Sigma_S.p_S.S.B(S, H/T)$$

where B(S, H/T) is the Brillouin function and p_S is the fractional contribution to the magnetization from species of spin S. The factors p_S are not known but if we estimate p_S values from the GPC data by assuming that the absolute value and distribution of molecular weights this gave are reliable[12] and further that, within each macromolecule there is 'perfect' doping and 'perfect' ferromagnetic spin-coupling, we obtain the theoretical line (continuous curve labeled 100%) shown in Fig. 3. Clearly the experimental points fall below this line and the degree of ferromagnetic coupling is less than this predicts. However, if we make the alternative assumption that the spin state distribution is of the same general form as the molecular weight distribution but spans only 70% of the range (between 2 and 43 rather than 2 and 62 ferromagnetically coupled spins) a reasonably good fit to the magnetization data is obtained (dashed curve labeled 70%).

CONCLUSIONS

Since polymer ferromagnets can exploit strong through-bond exchange interactions it should be easier to attain high Curie temperatures than in true molecular systems. However, genuine polymer magnets have proved elusive. The highly disperse nature of the polymers used in the present study leads to some difficulties in interpreting the results but the 'doping' problem has been overcome and degree of ferromagnetic spin-coupling obtained is higher than in any previous studies.[1,3,4] It is now important to repeat these measurements on less polydisperse samples, to improve the modelling of the polymer systems and to obtain a realistic picture of the spin-coupling pathways. At present the most plausible explanation of the fact that the spin-clusters are smaller than 'expected' is that UV spectroscopy gives an overestimate of the level of doping, that the value obtained from the magnetometer measurement is more realistic and that there are significant gaps in the spin-coupling pathways.

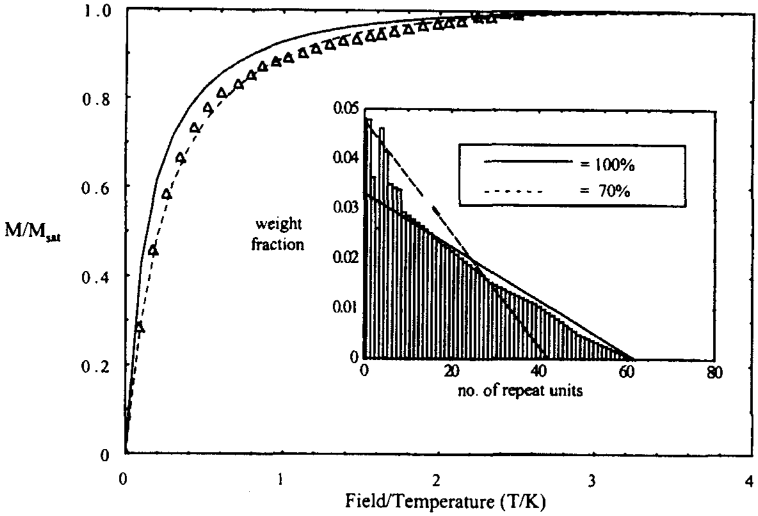

FIGURE 3. Field dependence of the magnetization of polymer **2** at 2K. The theoretical 100% and 70% lines were calculated by summation of Brillouin functions based on the polymers (GPC) molecular mass/ mass distribution which is shown in the insert.

EXPERIMENTAL

Synthesis

Compounds **1-4** were produced using the methods described in our previous publications, or simple variants on these.[1,3] Polymer **1**; Found: C, 81.75%; H, 9.9%; N, 1.50; Br, 0.0%. Requires C, 83.3%; H, 10.2; N, 1.5; Br, 0.0%. Polymer **2**; M_w (GPC polystyrene standard), 10,900; Found: C, 81.3%; H, 10.0%; N, 1.70; Br, 0.65%. Requires C, 83.1%; H, 9.7; N, 1.6; Br, 0.0%. Polymer **3**; M_w , 26,600; Found: C, 80.35%; H, 7.5%; N, 2.1; Br, 0.0%. Requires C, 81.8%; H, 7.4%; N, 2.5; Br, 0.0%.Compound **4**; mp (from chloroform/hexane) 249°C; Found: C, 82.95%; H, 7.8%; N, 1.95%.

$C_{48}H_{51}NO_3$ requires C, 83.2%; H, 7.5%; N, 2.0%. All compounds **1-4** gave clean ^{1}H-NMR spectra with the expected integration values.

Oxidative Doping: UV Studies

The UV spectrum of a dilute (ca. 1.0 x 10^{-5}molL^{-1}) solution of a known weight of the compound in dry chloroform in a 1cm path length cell was recorded. Under inert conditions, the spectrum was re-recorded after successive 250μL additions of a solution of $NOBF_4$ in dry chloroform (1.0x10^{-3}molL^{-1}) until no further change was observed. Software corrections to make allowance for the volume of oxidant solution added were applied to the spectra shown in Fig. 2. Compound **4**, $\lambda_{max.}$ 347nm ($\log_{10}\varepsilon$ 4.71); **4**$^{\cdot+}$, 418(4.48); Polymers: **1**, 352(4.71, per repeat unit), doped-**1**, 423(4.45); **2**, 347(4.62); doped-**2**, 422(4.38); **3**, 351(4.67); doped-**3**, 417(4.42).

Oxidative doping: EPR Studies

An EPR tube was filled with a solution of compound **4** (1.0 x 10^{-5} molL^{-1}) in chloroform which had been treated with sufficient $NOBF_4$ (according to the UV studies) to bring about complete oxidation to the imminium ion level, and of sufficient depth of the solution to span the microwave cavity. The EPR spectrum (a singlet) was recorded at room temperature on a Bruker ER 200 spectrometer with a Bruker ESP 1600 data acquisition system which was used for the double integration. Under identical conditions measurements were then taken for solutions of polymers **1-3** (1.0 x 10^{-5}molL^{-1}) in chloroform also doped to 100% using $NOBF_4$ according to their UV spectra. Hence, by a comparison of values for the double integral of EPR signals, the number of spins relative to the **4**$^{\cdot+}$ imminium ion solution could be calculated.

Magnetic properties of the doped polymers

Typical procedure: Powdered $NOBF_4$ (1.022g) was added with stirring to a thoroughly dried and deoxygenated solution of polymer **2**, (115 mg, 0.2mmol of repeat unit) in chloroform (200ml) (purified by passage through active alumina) at 0°C under a dry argon atmosphere. After 30min. UV analysis of the reaction mixture showed the polymer to be 100% oxidised. Whilst maintaining an inert atmosphere at all times, all traces of solvent were removed under reduced pressure. UV spectroscopy showed no depletion in oxidation levels. Using non-metallic instruments, a portion of the doped polymer/excess $NOBF_4$ mixture (98.0mg, containing 9.99mg of polymer) was transferred in a glove box to a sealed sample holder, and immediately placed into the Quantum-Design SQUID magnetometer, in which it was maintained under an atmosphere of helium. The saturation magnetisation at 2K and 5T of 6.19 emu/g or 5360 emu/repeat unit corresponds to a level of doping of 96%. Once measurements were complete[1,3] the sample was removed from the SQUID. The UV spectrum of the polymer was rerecorded and was shown to be unchanged.

Acknowledgements

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References

[1] R.J. Bushby, D.R. McGill and K.M. Ng, in *Magnetism: a Supramolecular Function.* edited by. O. Kahn (Kluwer, Dordrecht, 1996) p. 181; R. J. Bushby and K.M. Ng, *J. Chem. Soc., Chem. Commun,* 659 (1996); R.J. Bushby, D.R. McGill, K.M. Ng and N. Taylor, *J. Mater. Chem,* **7,** 2343 (1997).

[2] R.J. Bushby, D.R. McGill, K.M. Ng and N. Taylor, *J. Chem. Soc., Chem. Commun.,* 2641 (1996); R.J. Bushby, D.R. McGill, K.M. Ng and N. Taylor, *J. Chem. Soc., Perkin Trans.* **2,** 1405 (1997).

[3] R.J. Bushby and D. Gooding, *J. Chem. Soc., Perkin Trans.* **2,** 1069 (1998).

[4] D. Shiomi, K. Sato, T. Takui, K. Itoh, D.R. McGill, K.M. Ng and R.J. Bushby, *Synthetic Metals*, **85,** 1721 (1997); D. Shiomi, K. Sato, T.Takui, K. Itoh, D.R. McGill, K.M. Ng, and R.J. Bushby, *Mol. Cryst. Liq. Cryst.*, **306,** 513 (1997).

[5] K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi and M. Shiro, *J. Amer. Chem. Soc.*, **114,**5994 (1992); K.R. Stickley, and S.C. Blackstock, *J. Amer. Chem. Soc.*, **116,** 11576 (1994).

[6] M.S. Platz, in *Diradicals* edited by W.T. Borden (Wiley, New York, 1982) p195; J.A. Berson, in *The Chemistry of the Quinonoid Compounds, Vol. 2, Part 2'* edited by S. Patai and Z. Rappoport (Wiley, New York, 1988) p455.

[7] R.J. Bushby, D. Gooding and M. Thornton-Pett to be published.

[8] E.R. Howells, F.M. Lovell, D. Rogers and A.J.C. Wilson, *Acta Cryst.*, **7,** 298 (1955); E. Schlemper and J. Hausemann, *Acta Cryst.*, **16,** 1069 (1963).

[9] R.I. Walter, *J. Amer. Chem. Soc.*, **77,** 5999 (1955).

[10] Ref. 1 ascribed the low temperature downturn of the XT versus T plot to long-range antiferromagnetic interactions but it is now clear that it is (wholly or almost wholly) the result of saturation of the moment and a consequence of the excessively high fields used.

[11] M.A. Murray, P. Kaszynski, D.A. Kasisaki, W.-H. Chang and D.A. Dougherty, *J Amer Chem Soc* **116,** 8152 (1994).

[12] In fact this method substantially underestimates the molecular weight of networked polymers. K.E. Uhrich, C.J. Hawker, S.R. Turner and J.M.J. Freschet, *Macromolecules*, **25,** 4583 (1992).