Coulombic effects in radical-cation-based high-spin polymers

Richard J. Bushby, David R. McGill, Kai M. Ng and Norman Taylor

School of Chemistry, The University of Leeds, Leeds, UK LS2 9JT

A comparison of the cyclic voltammetric behaviour of a high-spin polymer precursor having the local topology of a 3,4′-diaminobiphenyl with that of related oligomers shows that the hole–hole repulsion associated with the coextensive spin–spin distribution is < 0.2 V, a noticeable effect but not one large enough to explain the difficulty of doping these polymers.

Several groups are involved in the production of high-spin polymers in which the spin-bearing units are radical cations and the spin is introduced by doping with an oxidizing agent.[1–3] We have concentrated on doped polyarylamines in which each spin-bearing centre is linked to three others in a randomly cross-linked polymer network.[1] Application of percolation theory shows that > *ca.* 70% of the sites in such a polymer need to be doped before there is ferromagnetic coupling throughout the whole covalently linked framework. Depending on the molecular mass of the polymer, this should result in a material with either superparamagnetic or ferromagnetic properties. Unfortunately, both in our polymers and the corresponding linear polymers made by the group of Dougherty,[2] the maximum doping levels that have been attained so far are < *ca.* 35%, sufficient to demonstrate their high-spin character but well below the percolation limit. *A priori* it can be argued that these difficulties are the result of coulombic effects. To ensure local ferromagnetic spin coupling the local topology of these polymers has to mimic that of a coextensive diradical diion.[1,4] There has to be spatial overlap of the unpaired spin distributions and hence of the charges (Fig. 1). Furthermore, the stronger the ferromagnetic coupling, the bigger this overlap, the bigger the charge–charge repulsive effect and the more difficult the polymer will be to dope; a self-defeating and potentially fatal flaw in the whole strategy. The present study shows that these coulombic effects are significant and measurable but not the limiting factor.

In the case of oxidation of two isolated equivalent sites in the same molecule which are 'non-conjugated' like the metal-ion centres in a bimetallic complex[5] or 'cross-conjugated' like the triarylamino centres of compound **1**, a disjoint[4] diion is produced; one in which the charge distributions do not overlap. The coulombic part of ΔE, the difference between the first and second oxidation potentials in such systems, measures the difference in the coulombic field acting on the second centre as a result of oxidation of the first, and provided the charge distributions are radially symmetric, it can be treated as a point charge–point charge repulsion. Compared to these disjoint systems [Fig. 1(*a*)] the situation in coextensive[4] systems [Fig. 1(*b*)] is more complex but the hole–hole repulsion should undoubtedly be greater. To obtain an estimate of the magnitude of the difference between disjoint and coextensive systems we have studied the electrooxidation of two structurally similar model oligomers; the diamine **1**, which on oxidation gives a disjoint diradical diion, and the diamine **2**, which gives a coextensive diradical diion. We have determined the coulombic contribution to ΔE for these amines by measuring ΔE as a function of solvent polarity in benzonitrile–chloroform mixtures with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.[5,6] A three-electrode system was employed with platinum working and counter electrodes and a silver-saturated lithium chloride–chloroform reference electrode. Since these cyclic voltammetry studies required accurate measurement of small values of ΔE, convolution/deconvolution voltammetry had to be used to aid determination of the half-wave potentials using the semi-integral I_1 of the voltametric current and time.[7] Fig. 2 (inset) shows deconvolution cyclic voltammetry results for both diamino compounds. In these deconvolution traces the splitting between the first and second half-wave potentials is clear, as is the greater splitting for compound **2**. Since the splittings are small they could not be accurately measured, directly, and were determined from the half-widths of the overall dI_1/dE response by direct comparison with simulated values for fast electron transfer obtained using

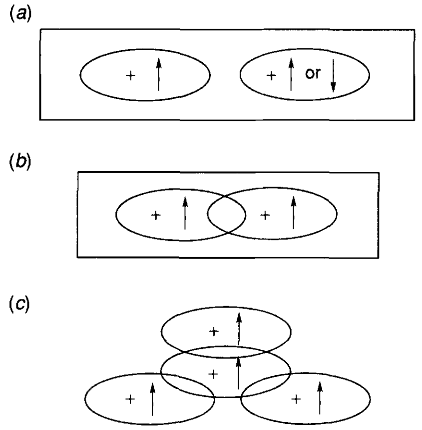
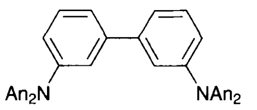
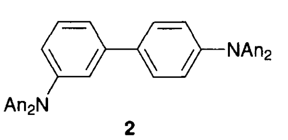


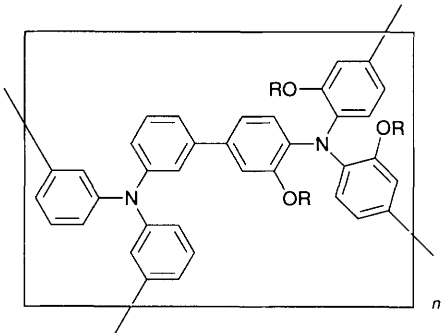
Fig. 1 Schematic representation of the spin–hole interactions (*a*) in a disjoint diradical diion, (*b*) in a coextensive diradical diion and (*c*) in a segment of a doped high-spin polymer



1, An = *p*-methoxyphenyl



2



3, R = $OC_{10}H_{21}$

the CONDESIM package (EG&G Instruments). Using this approach a reproducibility in the measured splittings of about 1 mV was achieved. A plot of the dependence of the splittings for diamines **1** and **2** as a function of relative permittivity for mixtures of benzonitrile and chloroform was similar in general form to that which we previously reported for bimetallic complexes.[5] Above $\varepsilon_u \approx 15$ the splitting decreases with increasing relative permittivity as the solvent increasingly shields the hole–hole repulsion and, in this region, there are no complications arising from ion-pair formation.[5,6] As expected, a plot of ΔE *vs.* $1/\varepsilon_u$ is linear (Fig. 2) and the slope of this plot is larger (by about five times) for the coextensive diradical diion than for the disjoint system. This difference is the result of the disjoint/coextensive divide and is not simply the result of differences in geometry which are quite minor. Using hypothetical planar geometries and standard bond lengths, the N···N distances are a minimum of 6.98 Å and a maximum of 8.43 Å for $\mathbf{1}^{2+}$ (depending on whether the amino groups are *syn* or *anti*) and 8.65 Å for $\mathbf{2}^{2+}$. If there was no 'leakage' of charge density across the central bond at all and the change in positive charge was localised on the nitrogen (or had a radially symmetric non-overlapping distributions about each nitrogen) the maximum difference in hole–hole repulsion arising purely from these geometric factors can be calculated as $<25\%$ as compared to the observed difference of *ca.* 500%.

The high-spin polymers we have made[1] are based on a repeating metaphenylenediamine[8] or 3,4′-diaminobiphenyl[9] motif in which each centre is coextensively linked to three neighbouring centres as shown schematically in Fig. 1(*c*). The extra repulsion energy associated with the coextensive hole distribution for three nearest-neighbour sites in polymer **3** should be about three times that in the structurally related dimer **2** and so the magnitude of this factor in the polymers can now be estimated. Based on the data in Fig. 2 ($\varepsilon_u > 15$) it has a minimum value of 3×0.039 V = 0.117 V and a maximum value of 3×0.054 V = 0.162 V. Data (not shown) for compounds **2** and **3** in the region $5 < \varepsilon_u < 15$ leads to values <162 mV. We have also addressed the problem directly. A cyclic voltammetry study of a solution of the polymer **3** in dichloromethane shows two oxidation steps at 0.29 and 0.55 V (with respect to ferrocene–ferrocenium under these conditions). This polymer has two distinct types of site and the observed oxidation potentials are those expected for triarylamines of the type $N\{[C_6H_3(OR)]Ph\}_3$ and NPh_3, respectively.[10] The width of each peak at half height is *ca.* 250 mV as compared to a width of $90/n$ mV expected for reversible transfer of n electrons from each site. The other arylamine polymers we have made[1] show similar or slightly smaller peak-broadening effects. The broadening apparent for the peaks undoubtedly arises in part from inhomogeneities frozen into the structure and unavoidable in a randomly cross-linked polymer, but it is also of the order estimated for coulombic factors. Hence it seems that the need for coextensive charge and spin distributions in these radical-ion-based high-spin polymers produces a coulombic effect that can be detected but that doping of the arylamine precursors is not coulombically limited. Particularly for the cross-linked polymers, a more likely explanation of the low doping levels is the steric difficulty of incorporating counter ions into a relatively rigid polymer network. However, this is unlikely to be an insuperable problem.

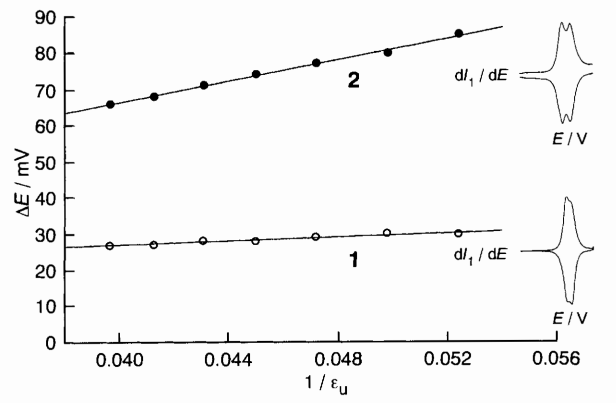


Fig. 2 Splittings ΔE (the difference between first and second oxidation potentials) in the region ($\varepsilon_u > 15$) plotted against the inverse of the effective relative permittivity in chloroform–benzonitrile mixtures. The effective relative permittivity ε_u was taken as the weighted average of the values for the two solvents based on the volume fraction of each component and was uncorrected for supporting electrolyte.

We thank the EPSRC for the award of a Research Studentship to D. R. M. and of a Post-Doctoral Fellowship to K. M. N., and Dr R. Luo for assistance and advice in the cyclic voltammetry studies.

References

1 R. J. Bushby, D. R. McGill and K. M. Ng, in *Magnetism; A Supramolecular Function*, NATO ARW, Carcans-Maubisson, Kluwer, Dordrecht, 1995, pp. 181–204; R. J. Bushby and K. M. Ng, *Chem. Commun.*, 1996, 659.

2 M. A. Murray, P. Kaszynski, D. A. Kaisaki, W.-H. Chang and D. A. Dougherty, *J. Am. Chem. Soc.*, 1994, **116**, 8152.

3 K. Yoshizawa, K. Tanaka, T. Yamabe and J. Yamauchi, *J. Chem. Phys.*, 1992, **96**, 5516; A. Ito, K. Ota, K. Tanaka, T. Yamabe and K. Yoshizawa, *Macromolecules*, 1995, **28**, 5618.

4 D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88; W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1977, **99**, 4587.

5 N. Taylor, T. Boddington, I. Dobson, B. Gill, R. Luo and B. Shaw, in *Molecular Electrochemistry of Inorganic, Bioorganic and Organometallic Compounds*, ed. A. J. L. Pombeiro and J. A. M. McCleverty, Kluwer Academic Publ., Dordrecht, 1993, p. 467.

6 A. Blagg, S. W. Carr, G. R. Cooper, I. D. Dobson, J. B. Gill, D. C. Goodall, B. L. Shaw, N. Taylor and T. Boddington, *J. Chem. Soc., Dalton Trans.*, 1985, 1213.

7 K. B. Oldham and J. Spanier, *J. Electroanal. Chem.*, 1970, **26**, 331; K. B. Oldham, *Anal. Chem.*, 1972, **44**, 196; M. Grenness and K. Oldham, *Anal. Chem.*, 1972, **44**, 1121.

8 K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi and M. Shiro, *J. Am. Chem. Soc.*, 1992, **114**, 5994; K. R. Stickley and S. C. Blackstock, *J. Am. Chem. Soc.*, 1994, **116**, 11576; P. M. Lathi, C. Ling, N. Yoshioka, F. C. Rossitto and H. van Willigen, *Mol. Cryst. Liq. Cryst.*, 1993, **233**, 17.

9 G. Allinson, R. J.Bushby and J.-L. Paillaud, *J. Mater. Sci., Mater. Electronics*, 1994, **5**, 67; Y. Teki, I. Fujita, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 11499; M. Minato, P. M. Lathi and H. van Willigen, *J. Am. Chem. Soc.*, 1993, **115**, 4532.

10 E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498; R. J. Bushby, D. R. McGill and N. Taylor unpublished work.

Received, 12th July 1996; Com. 6/04895A