High-spin polymeric arylamines

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High-spin p-doped polyarylamines have been created containing small clusters (tens) of ferromagnetically coupled unpaired electrons. In these doped polymers neighbouring spins couple through a pathway analogous to that found in *meta*-quinodimethane and the spin-carriers are triarylamine radical cations. The use of polymers in which the triarylamine radical cation centres are stabilized by Ar_2N rather than RO substituents gives improved stability but much poorer spin-coupling properties. Furthermore, the much greater ease of dication (bipolaron) formation makes it difficult to dope these amine-stabilized polymers to the requisite level. Work by other groups exploiting phenoxy and triarlymethyl spin-carriers and the prospects for producing polymers with much larger clusters of ferromagnetically coupled spins are discussed.

Keywords: magnet; polymer; synthesis; radical cation

1. Polymer design

The long-term aim in creating 'polymer magnets' and 'molecular magnets' is not to replace applications of established magnetic materials but to create new materials with novel combinations of properties. 'Polymer magnets' should share many of the advantages of 'molecular magnets' in being insulating transparent light materials that are soluble and easy to process at low temperatures. However, unlike molecular magnets, polymer magnets should make it possible to exploit strong through-bond exchange interactions, and higher Curie temperatures should result. Whether we are dealing with atomic, molecular or macromolecular systems, the conditions for Hund's Rule to apply are the same (Bushby *et al.* 1996). The singly occupied orbitals need to be more-or-less degenerate (approximately of the same energy), coextensive (overlap in their spatial distributions) (Hughbanks & Yee 1990; Dougherty 1991) and orthogonal (have a zero overlap integral). These conditions are always fulfilled in those atomic systems with which we are most familiar. Hence, as shown in figure 1*a*, the degenerate singly occupied 2p atomic orbitals of atomic carbon are coextensive (they share space in common) but orthogonal. One orbital is symmetric and the other antisymmetric with respect to a vertical mirror plane so regions of positive and negative overlap exactly cancel. As is shown in figure 1*b*, exactly the same applies to the singly occupied π molecular orbitals ϕ_4 and ϕ_5 of *meta*-quinodimethane (MQDM) **1**. The singly occupied non-bonding molecular orbitals are degenerate, coextensive and orthogonal. In the case of atomic carbon the triplet state is favoured over the singlet state by 1.25 eV (Condon & Odataoi 1980) and in the case of MQDM **1** the triplet state is favoured over the singlet state by 0.43 eV. There are many other molecular π diradicals which have triplet ground states (Allinson *et al.* 1994), but this paper is almost wholly concerned with MQDM derivatives.
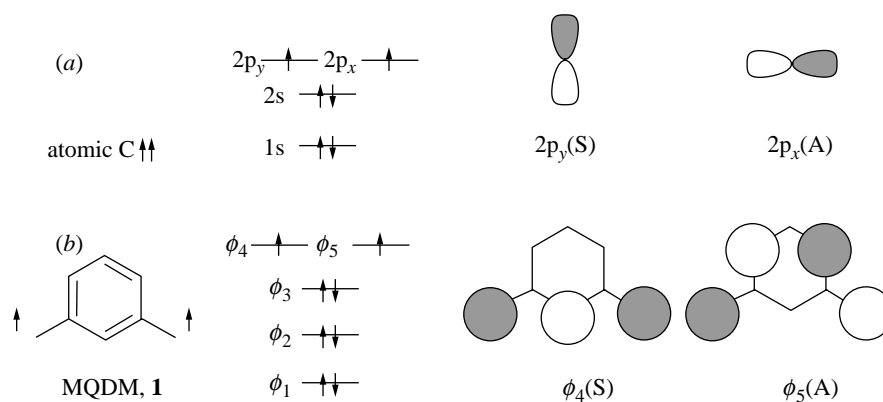
Figure 1. Basis of 'Hund's rule' ferromagnetic coupling of spins (*a*) in atomic carbon; and (*b*) in metaquinodimethane.
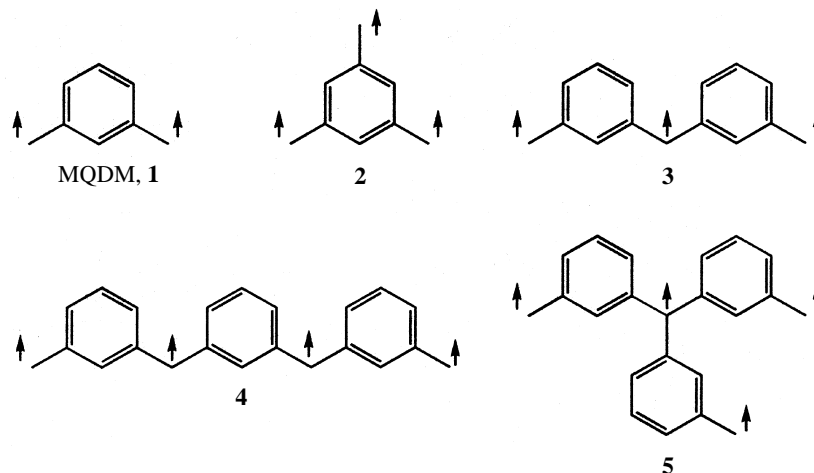

Figure 2. Oligomeric polyradicals which are extended versions of the MQDM motif.

In both MQDM and atomic carbon there are two ferromagnetically coupled spins but this number can easily be extended. Hence, in atomic nitrogen there are three degenerate singly occupied 2p orbitals and the quartet state is favoured over the doublet state by 2.37 eV (Condon & Odataoi 1980). It is predicted that the triradicals **2** and **3** (figure 2) have quartet ground states and the tetraradicals **4** and **5** have quintet ground states.

The maximum number of ferromagnetically coupled spins which can be created using cocentred atomic orbitals is small (up to three if we use three p orbitals and up to five if we use five d orbitals), but in molecular systems theory predicts that there is no limit. At least in principle, it is possible to extend the motifs shown in figure 2 to create macromolecular polyradicals containing tens, hundreds, even thousands of ferromagnetically coupled spins and perhaps even systems with bulk superparamagnetic or ferromagnetic properties (Mataga 1968; Ovchinnikov 1978). It is important to note that macromolecular polyradicals involving an extended MQDM
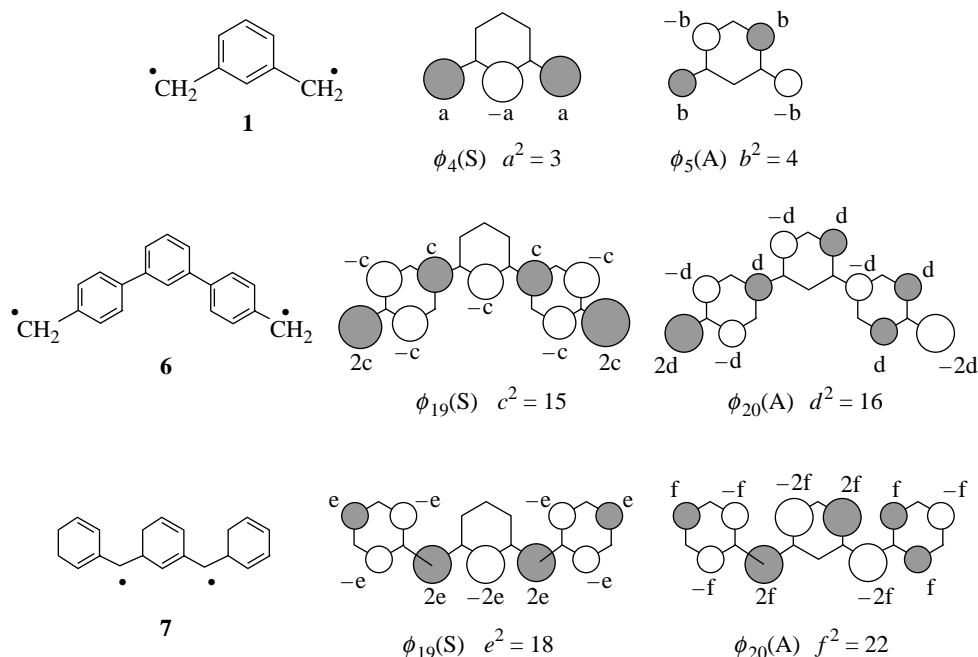
Figure 3. The effect of extending the conjugated system on the Hueckel NBMOs of MQDM.

motif are not necessarily linear (like **3** and **4**). As shown in figure 2, it is possible to create derivatives branched either through the benzene ring (as in triradical **2**) or through the α-carbon (as in tetraradical **5**). This is significant since ferromagnetic coupling always breaks down in one-dimensional systems if the chains are sufficiently long. If the ultimate aim is to make a bulk ferromagnet, the incorporation of these branched 'building blocks' is crucial since it allows the creation of two- and three-dimensional networked macromolecular structures which solve the 'dimensionality problem' (Bushby *et al.* 1996). The low thermal stability of carbon-based radicals and their poor air stability are much more challenging problems. Solutions have been found through extension of the conjugated system, by the introduction of steric hindrance (substituents like *tert*-butyl), and by the introduction of heteroatoms into the π system. Figure 3 shows two ways of extending the conjugated system. As shown, inserting a *para*-phenylene between the CH_2 and the benzene ring as in compound **6** or by introducing peripheral C_6H_5 substituents as in compound **7** does not affect the essential symmetry or the coextensive nature of the singly occupied non-bonded molecular orbitals. However, the greatest improvement in stability is seen in π-heteroatomic systems in which the atom carrying the largest part of the spin density is a nitrogen or oxygen rather than carbon.

In MQDM both of the α-carbons can be (formally) replaced by $N^{+\cdot}$. This gives an isoelectronic structure which is more stable. It leaves the symmetry of the putative singly occupied orbitals essentially unchanged but it also slightly lifts their degeneracy (Bushby 1999). Nevertheless, the spin states of amminium cation diradicals and triradicals seem to follow those of the corresponding hydrocarbons. Hence, the dication diradicals **8** (Sato *et al.* 1997), **9** (Stickley & Blackstock 1994) and **12**
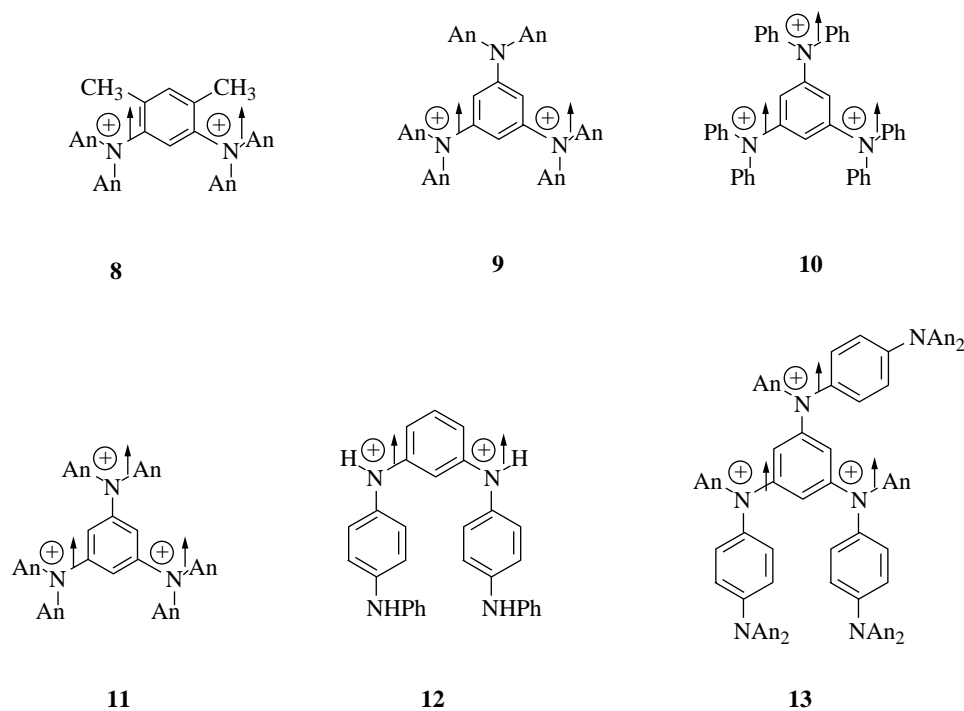
Figure 4. High-spin oligomers based on amminium radical cation spin-bearing units:
Ph, phenyl (C_6H_5); An, anisyl (p-$CH_3OC_6H_4$).

(Wienk & Janssen 1996*a, b*) (figure 4), which are analogous to the all-carbon diradical **1** (figure 2), have triplet ground states. The trication triradicals **10** (Yoshizawa *et al*. 1992*a, b*, 1996; Yoshizawa 1993), **11** (Stickley & Blackstock 1994; Yoshizawa *et al*. 1996) and **13** (Stickley *et al*. 1997) (figure 4), which are analogous to the all-carbon triradical **2** (Figure 2), give quartet spectra. The stability of aryl substituted amminium radical cations is highly structure dependent (Stickley & Blackstock 1995), but some are stable enough to be considered for use as polymer building blocks. Hence tris(o-bromophenyl)amminium pentachloroantimonate is a commercially available stable solid which is used by synthetic organic chemists as a one-electron oxidant; most of the polyradicals shown in figure 4 are stable in solution, and the quartet trication **13** is an isolable air-stable solid (Stickley *et al*. 1997). In general, triarylamminium radical cations are expected to be stabilized by extending the conjugated system or by the incorporation of *ortho-* or *para*-halogen, alkoxy, or amino substituents. The last should provide the greatest stabilization. However, for the trication **13**, the presence of the *para*-amino substituent also has an undesired effect. It results in a marked reduction in the splitting between the doublet and quartet states so that they become almost equal in energy.

2. Synthesis and characterization of the polymers

In this paper we describe the synthesis and characterization of a high-spin polymer **15**$^{\cdot+}$ (figure 5) based on the simple monomer **8** and of a high-spin polymer **22**$^{\cdot+}$
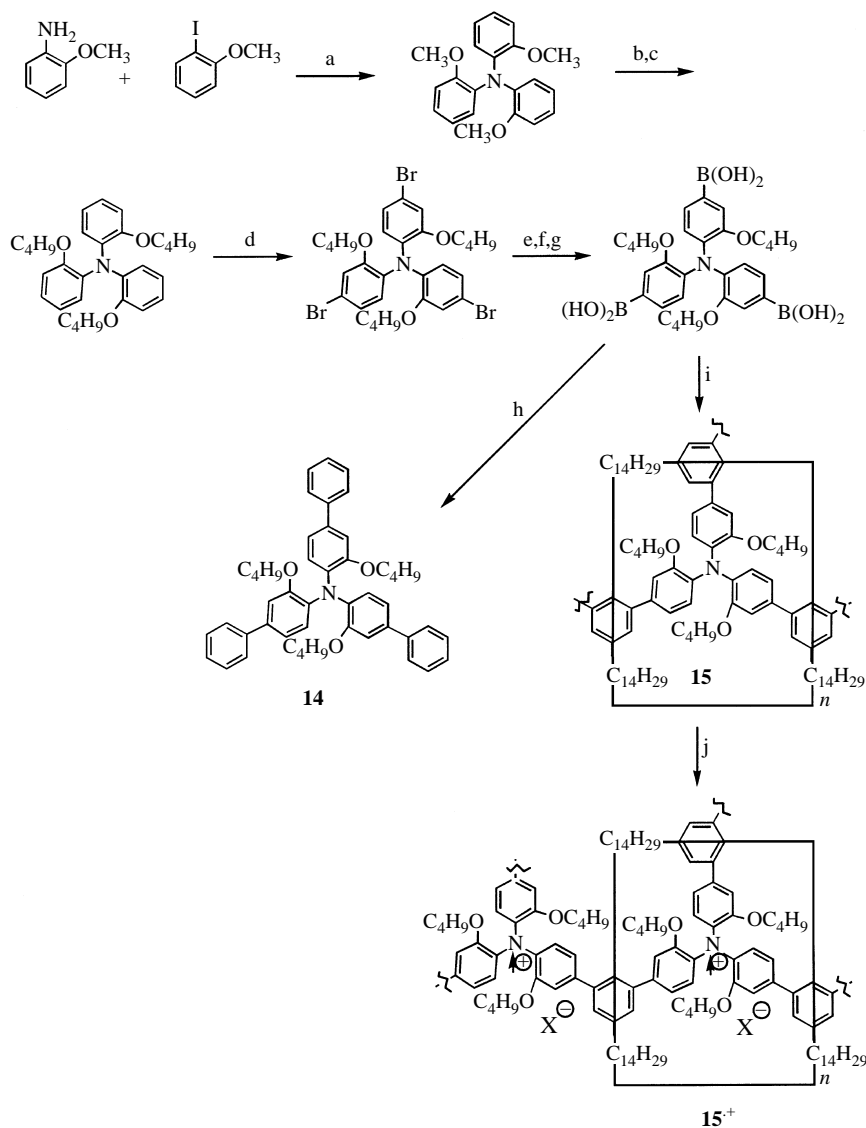
Figure 5. Synthesis of the doped polymer $15^{\cdot+}$. Reagents: (a) K_2CO_3/Cu/reflux; (b) BBr_3/$-78\,°C$; (c) C_4H_9Br/K_2CO_3/reflux; (d) Br_2/$CHCl_3$/$0\,°C$; (e) BuLi/THF/$-78\,°C$; (f) $(^iPrO)_3B$/$-78\,°C$; (g) HCl/H_2O; (h) $Pd(PPh_3)_4$/toluene/aq. Na_2CO_3/C_6H_5Br; (i) $Pd(PPh_3)_4$/toluene/aq. Na_2CO_3/3,5-dibromotetradecylbenzene; (j) $NOBF_4$/CH_2Cl_2.

(figure 6) based on the Blackstock monomer **12**. The synthetic routes employed are summarized in figures 5 and 6 together with those of model compounds **14** and **23** which contain the essential chromophores/electrophores of the undoped polymers. The synthesis of polymer **15** has been described previously (Bushby & Gooding 1998) and details for the synthesis of polymer **22** are given in the experimental section. The choice of systems **18**–**22** with *two* methoxy substituents was dictated by the fact that the synthesis of 'parent' systems (without the methoxy groups) failed because of the
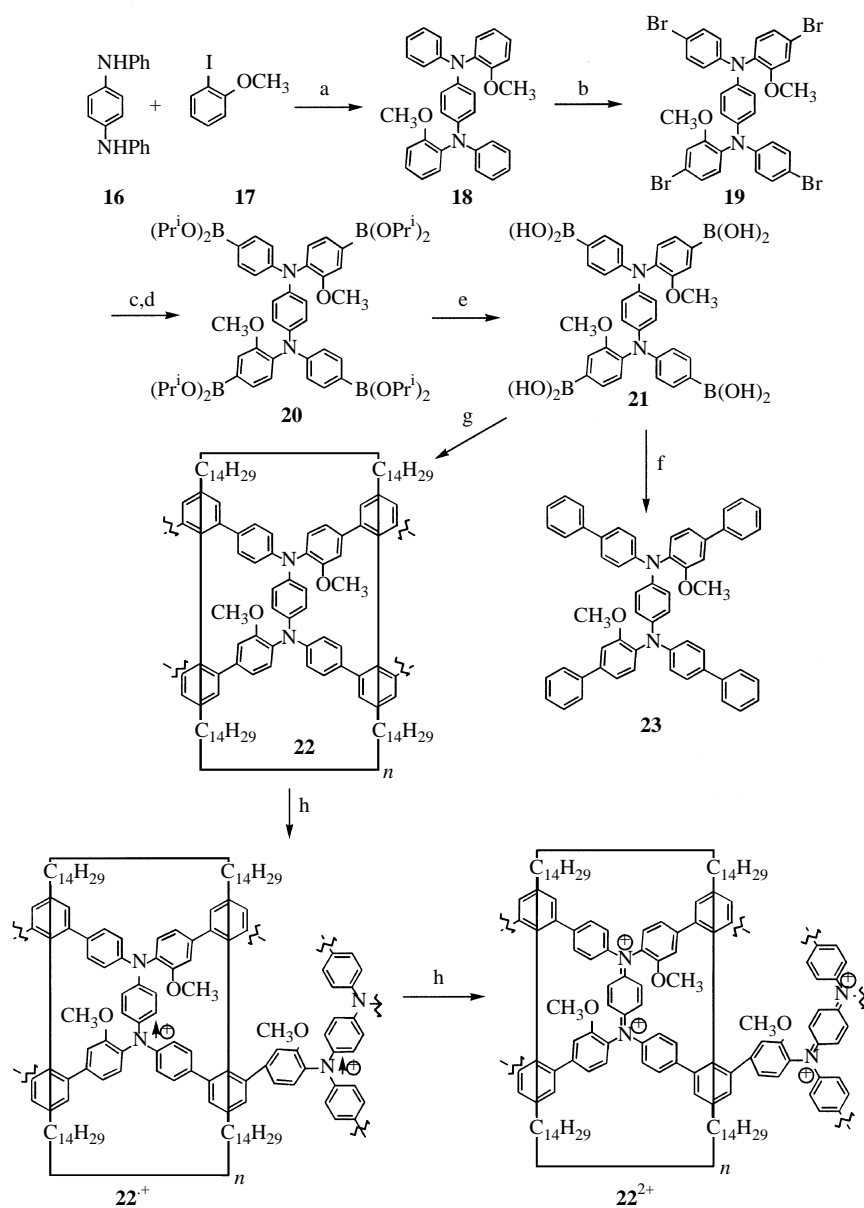
Figure 6. Synthesis of the doped polymers **22**$^{\cdot+}$ and **22**$^{2+}$. Reagents: (a) $K_2CO_3/Cu/$reflux; (b) $Br_2/CHCl_3/0\ ^\circ C$; (c) BuLi/THF/$-78\ ^\circ C$; (d) (^{i}PrO)$_3$B/$-78\ ^\circ C$: (e) HCl/H$_2$O; (f) Pd(PPh$_3$)$_4$/toluene/aq. Na$_2$CO$_3$/C$_6$H$_5$Br; (g) Pd(PPh$_3$)$_4$/toluene/aq. Na$_2$CO$_3$/3,5-dibromotetradecylbenzene; (h) NOBF$_4$/CH$_2$Cl$_2$. Pr^i = *iso*-propyl.

poor solubility of the corresponding tetrabromide and intermediates in the synthesis of systems with four methoxy substituents were found to be highly photolabile. Polymerization reactions were based on a Suzuki coupling reaction (Hoshino *et al.* 1988) and were stopped before the 'gel' point. The chloroform-soluble fraction was purified

by repeated repreciption from chloroform/methanol. Gel permiation chromatography against a polystyrene standard for two fractions of the polymer **15** gave a 'low M_{w} fraction' with $M_{\mathrm{w}} = 8500$, $M_{\mathrm{n}} = 1600$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 5.2$ and a 'high M_{w} fraction' with $M_{\mathrm{w}} = 86\,000$, $M_{\mathrm{n}} = 10\,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 8.5$. Polymer **22** had $M_{\mathrm{w}} = 36\,000$, $M_{\mathrm{n}} = 19\,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.9$. It should be noted, however, that molecular weights obtained in this way are usually underestimated for networked polymers.

A single crystal X-ray diffraction study of the model for the repeat unit **14** gave a molecular geometry with a propeller-like twist of the aryl residues about the central nitrogen (Bushby *et al.* 1999) and this is very similar to that of other triaryl amines. This is expected to change little on oxidation to the radical cation. The dihedral angles between the aryl rings in the biphenyl groups were 44, 45 and 25°. Some degree of twisting about the aryl–aryl bonds is essential to give a three-dimensional network and calculations show that, within limits, it does not affect the ferromagnetic coupling. However, near-orthogonality of the rings does reverse the ordering of the singlet and triplet states and complete orthogonality of the rings is fatal since it totally destroys the conjugated pathway on which the exchange interaction depends.

3. Doping of the polymers

Initially we experienced difficulty in obtaining quantitative or even nearly quantitative doping of these arylamine polymers (Bushby *et al.* 1996, 1997*a*; Bushby & Gooding 1998) but we have subsequently shown that these problems can be overcome (Bushby *et al.* 1999). The polymer needs to be doped with an excess of $\mathrm{NOBF_4}$ in very dilute solution otherwise it precipitates in a partly doped state. Hence, when a very dilute solution of the amine **14** in dry chloroform was titrated with a solution of $\mathrm{NOBF_4}$ in dry chloroform, the absorption $\lambda_{\max}$ at 347 nm was progressively and quantitatively (1 mole reacting with 1 mole) replaced by that for the radical cation **14**$^{\cdot+}$, $\lambda_{\max}$ at 418 nm. When the same experiment was repeated using a *ca.* 0.006 g l^{-1} solution of the polymer **15**, except that a roughly four-fold excess of $\mathrm{NOBF_4}$ had to be used and that the reaction was slower, the results were almost identical and the resultant spectra are shown in figure 7. Critically it was found that when a very large excess of $\mathrm{NOBF_4}$ was used the UV spectrum was unchanged. This system shows no tendency to overoxidize to the spinless bipolaron level.

When a *ca.* 0.006 g l^{-1} solution of the polymer **22** was doped in the same manner there was a two-stage oxidation. In the first stage the chromophore of the neutral phenylenediamine ($\lambda_{\max}$ at 349 nm) was replaced by that of the radical cation ($\lambda_{\max}$ at 422 nm, figure 8 left). In the second stage the chromophore of the radical cation was replaced by that of the dication ($\lambda_{\max}$ at 812 nm, figure 8 right). The solution of the radical cation **22**$^{\cdot+}$ was green and that of the dication **22**$^{2+}$ was blue.

The progress of the oxidation reactions was also studied by EPR spectroscopy. Integrating the signals obtained by $\mathrm{NOBF_4}$ oxidation of a *ca.* 0.006 g l^{-1} solution of compound **14** and comparison with equivalent solution of the polymer **15** treated in exactly the same gave an average doping level of 99%. In the case of polymer **22**, the spin concentration was followed in parallel to the UV experiment shown in figure 8. The integrated intensity rose to a maximum which corresponded to $92 \pm 4\%$ of the theoretical maximum at the stage we have identified as that of the radical cation/polaron ($\lambda_{\max}$ at 422 nm, figure 8 left) and fell to almost zero again once the dication/bipolaron ($\lambda_{\max}$ at 812 nm, figure 8 right) was formed.
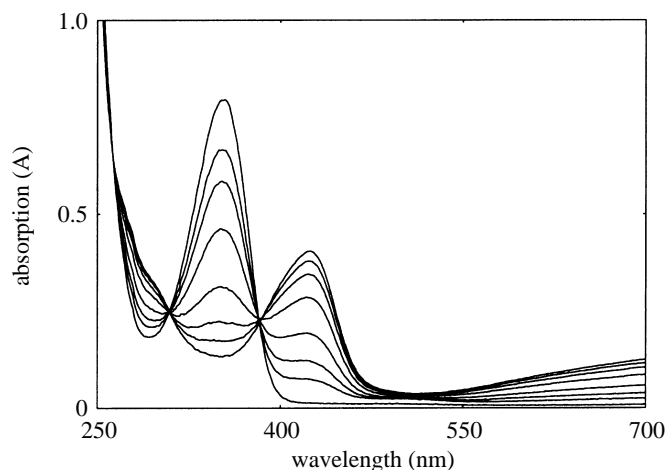
Figure 7. UV spectra showing the doping of polymer **15** in chloroform using
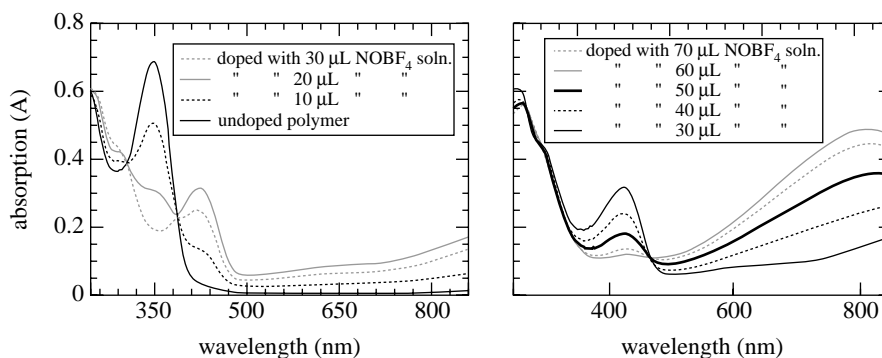aliquots of a saturated NOBF$_4$ solution in chloroform.

Figure 8. The UV spectra showing the doping of polymer **22**, firstly to the monoradical cation
level (left) **22**$^{.+}$ and subsequently to the dication level (right) **22**$^{2+}$ using a solution of NOBF$_4$.

Although, in general, all operations with the doped polymers **15**$^{.+}$ and **22**$^{.+}$ were
carried out under an inert atmosphere and using a glove-box, the doped polymer **22**$^{.+}$
was found to be air stable.

Cyclic voltammetry studies of a solution of the polymer **15** showed a first oxidation
potential of 0.22 V versus a silver–silver chloride standard electrode and a second
oxidation potential 0.75 V higher, at 0.97 V (Bushby *et al.* 1997*b*). Whereas, the first
and second oxidation potentials of polymer **15** are well separated, Blackstock has
shown that systems containing a similar electrophore to polymer **22** not only have
a lower first oxidation potential but also the first and second oxidation potentials
are closer together, typically separated by only 0.4 V (Stickley *et al.* 1997). This is
consistent with our observation that, although polymer **14** could be doped with a
large excess of reagent without bipolaron formation, the doping of polymer **22** is
much more difficult to control.

The solutions used for the UV experiments were too dilute (*ca.* 0.006 g l^{-1}) for dop-
ing on a preparative scale. For the preparative doping experiments a concentration
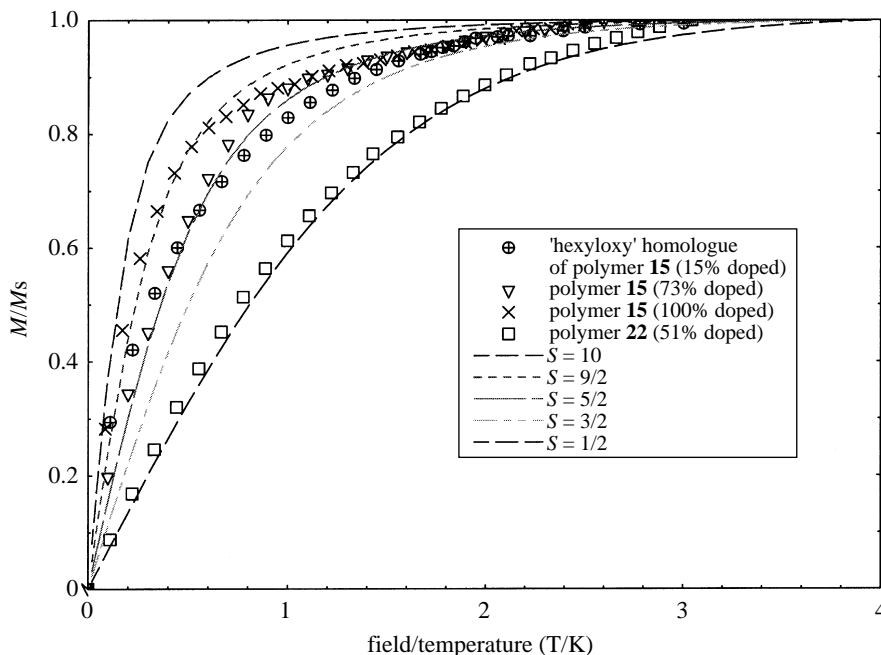
Figure 9. Field dependence of the relative magnetization of doped arlyamine polymers **15** and **22** at 2 K plotted against theoretical Brillouin functions.

of $0.6 \, \text{g} \, \text{l}^{-1}$ was employed. Under these conditions the polymer **15** with $M_{\text{w}} = 8500$ was essentially quantitatively doped but the polymer **15** with $M_{\text{w}} = 86000$ was only *ca.* 73% doped. A sample of polymer **22** with $M_{\text{w}} = 36\,000$ gave 51% radical cations.

4. Magnetic properties of the doped polymers

We have previously shown that when 15% of the available sites in the hexyloxy 'homologue' of polymer **15** were oxidized to the $N^{\cdot+}$ level, the field dependence of the bulk magnetization at 2 K fitted a Brillouin function, $S = \frac{5}{2}$ (Bushby *et al.* 1996, 1997*b*), and these data are shown in figure 9. Nutation resonance studies of this 15% doped material showed the presence of high-spin species from $S = \frac{1}{2}$ up to at least $S = 3$ (Shiomi *et al.* 1997).

Using the dilute-solution doping method for the 'high-molar-mass' ($M_{\text{w}} = 86\,000$) fraction of polymer **15** gave *ca.* 73% doping and, as shown in figure 9, 'improved' the spin-coupling behaviour. However, using the 'low-molar-mass' ($M_{\text{w}} = 8500$) fraction of polymer **15** it is possible to achieve almost 100% doping. Hence, a *ca.* $0.6 \, \text{g} \, \text{l}^{-1}$ solution of the polymer **15** in chloroform was oxidized with a 20-fold excess of powdered $NOBF_4$. The UV spectrum of the green solid obtained when this solution was evaporated, both before and after the SQUID magnetometer measurements, showed almost 100% oxidation to the $N^{\cdot+}$ level and that there had been no detectable deterioration of the sample. The absolute value of its saturation magnetization was $6.19 \, \text{emu} \, \text{g}^{-1}$, which actually corresponds to 96% doping, although, like UV, EPR spectroscopy gave a value of 100% doped. The susceptibility of the doped polymer was measured as a function of temperature (2 K to room temperature) at constant field (0.5 T)

and as a function of field (0–5 T) at constant temperature (2 K). The susceptibility measurements were corrected to allow for the diamagnetic contribution of the polymer and of the sample holder. Curie-law behaviour was observed between *ca.* 100 K and room temperature. Figure 9 shows relative magnetization as a function of field. It is clear that, as we progress from 15% to 73% to almost 100% doping, the size of the ferromagnetically coupled spin clusters increases. The behaviour is typical of a polydisperse spin system. In each case the relative magnetization rises too rapidly at low H/T (when the behaviour is dominated by the larger moments) and too slowly at high H/T (when the behaviour is dominated by the $S = \frac{1}{2}$, 1, etc., sites) as compared to Brillouin functions for monodisperse spin systems (Murray *et al.* 1994). For a disperse spin system we can write

$$M = Ng\mu_{\mathrm{B}}\Sigma_S p_S S B(S, H/T),$$

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 difficulty in interpreting the data shown in figure 9 is that the starting polymer is highly polydisperse and the distribution of spin states (the p_S terms) are unknown. Attempts to use a variety of distribution functions shows that the data cannot be fitted without assuming a wide distribution involving, at one extreme, a considerable contribution from low spin ($S = \frac{1}{2}$, 1, etc.) species and, at the other extreme, from species $S > 15$. Figure 10 shows a fit to the linear distribution function $p_S = S$ of $\frac{1}{2}$–22 shown in the inset. The data used in figures 9 and 10 were all obtained at 2 K. Figure 11 shows typical data for the temperature dependence of the moment. The moment at room temperature for a 73% doped sample is a little greater than that expected for an $S = 1$ system and this rises to that expected for an $S = \frac{5}{2}$ system just above 2 K. The Brillouin function fit for this same sample at 2 K (shown in figure 9) perhaps looks closest to $S = \frac{5}{2}$ or 3.

Characterization of the magnetic behaviour of the doped polymer $\mathbf{22}^{\cdot+}$ caused some difficulty. When a dilute solution of the polymer *ca.* 0.6 g l^{-1} was 'titrated' with $NOBF_4$ and the reaction monitored by UV spectroscopy it could be stopped at the radical cation stage $\mathbf{22}^{\cdot+}$ but this required more than one equivalent of reagent. When the resultant solution was evaporated and the solid obtained was redissolved it was found to be overoxidized and to be a mixture of $\mathbf{22}^{\cdot+}$ and $\mathbf{22}^{2+}$. On the other hand, use of just one equivalent of $NOBF_4$ gave a product which was a mixture of $\mathbf{22}$ and $\mathbf{22}^{\cdot+}$. This made it difficult to dope the polymer exactly to the radical cation level. Figure 9 shows relative magnetization data for a sample which, on the basis of its saturation magnetization and UV spectrum, was a 51:49 mixture of $\mathbf{22}^{\cdot+}$:$\mathbf{22}^{2+}$. The behaviour is essentially that of an $S = \frac{1}{2}$ material. In view of the observation that even imperfectly doped samples of polymer $\mathbf{15}$ showed some evidence of '$S > \frac{1}{2}$' behaviour, this implies that there is no significant ferromagnetic coupling of the spins in $\mathbf{22}^{\cdot+}$.

In conclusion, doped forms of the polymer $\mathbf{22}$ (based on the paraphenylenediamine motif of the Blackstock monomer) are much more stable than doped forms of polymer $\mathbf{15}$ but, because the oxidation potential is lower and the first and second oxidation potentials are closer together, the doping process is much more difficult to control. Furthermore, we have not obtained high-spin products from this polymer. In the related monomer $\mathbf{13}$, the high- and low-spin states are almost degenerate and in this less-symmetrical polymer system it appears that the low-spin state wholly dominates. However, the p-doped polymer $\mathbf{15}^{\cdot+}$ does show the desired ferromagnetic
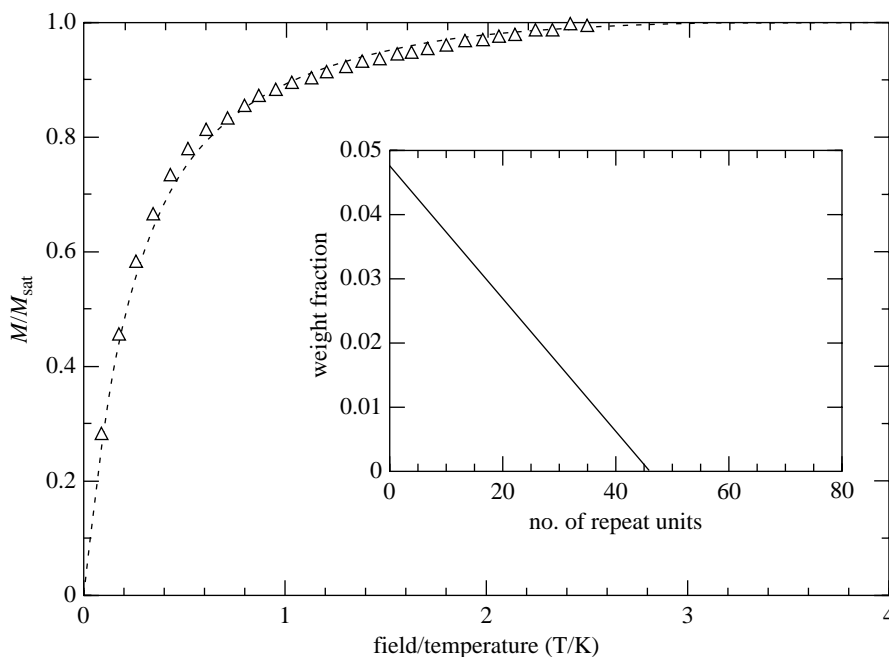
Figure 10. Field dependence at 2 K of the magnetization of polymer **15**, $M_w = 8500$, 100% doped fitted to a theoretical line calculated by summation of Brillouin functions and based on the distribution of spin states shown in the insert.
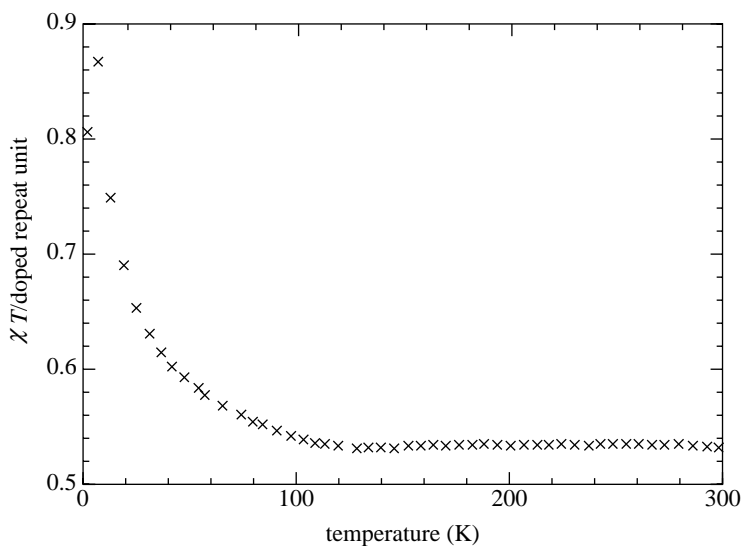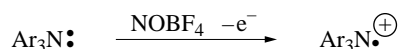

Figure 11. χT versus T plot for a sample of polymer **15**, $M_w = 86\,000$, 73% doped and measured at a field of 0.5. χ is expressed in emu per repeat unit. On this basis (for monodisperse spin systems) we expect $\chi T = 0.37$ (for $S = \frac{1}{2}$), 0.87 (for $S = \frac{5}{2}$) and 1.12 (for $S = \frac{7}{2}$). The Brillouin function 'fit' for this same sample at 2 K shown in figure 9 suggests $S \approx \frac{7}{2}$.

triaryl amminium radicals cations (Bushby *et al.*)

$$Ar_3N\!: \quad \xrightarrow{\quad NOBF_4 \;\; -e^- \quad} \quad Ar_3\overset{\oplus}{N\!\bullet}$$

triaryl methyl radicals (Rajca *et al.*)

$$Ar_3C\text{-OMe} \quad \xrightarrow{\quad \text{Li or Na/K} \quad}$$
$$Ar_3C\text{-H} \quad \xrightarrow{\quad \text{KH or NaH} \quad} \quad Ar_3\overset{\ominus}{C\!:} \quad \xrightarrow{\quad I_2 \;\; -e^- \quad} \quad Ar_3C\bullet$$
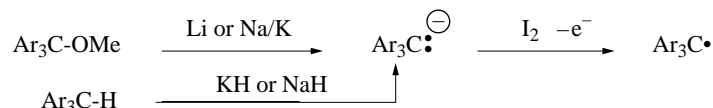
phenoxy radicals (Nishide *et al.*)

$$Ar\text{-}\overset{..}{\underset{..}{O}}\!:{}^{\ominus} \quad \xrightarrow{\quad K_3[Fe(CN)_6] \;\; -e^- \quad} \quad Ar\text{-}\overset{..}{\underset{..}{O}}\!\bullet$$
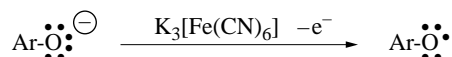
Figure 12. Methods of generating spin-carriers (p-doping methods) for
the systems discussed in this paper.

coupling. Although the spin states achieved are lower than expected on the basis of the molecular weight distribution (Bushby *et al.* 1999) and the moments are temperature dependent, even when imperfectly doped and at room temperature, it behaves like a system for which $S > 1$. In this polymer there is likely to be a range of dihedral angles between the component elements of the π system and this will lead to a range of different couplings between adjacent centres. This is the most likely explanation of the observed behaviour but it is a problem that can be overcome by modifying the structure of the polymer.

5. Related work by other groups

The idea of producing polymer magnets based on repeating non-Kekule π biradical units is simple but one which has proved difficult to translate into reality. The area of 'polymer magnets' has been poorly served by a number of overoptimistic spurious claims. However, a systematic understanding of the problem is beginning to emerge. Among systems being investigated by other groups around the world, the triarylmethyl radical systems developed by the group of A. Rajca and phenoxy radical systems by the groups of P. M. Lathi and N. Nishide seem particularly promising.

(*a*) *Triarylmethyl polyradical systems (Rajca and co-workers)*

Rajca's triarylmethyl polyradical systems use spin carriers based on the Schlenk hydrocarbon and MQDM to mediate the ferromagnetic spin coupling (Rajca 1994). The method of generating the radical sites is analogous to ours (figure 12). In Rajca's systems a one-electron oxidation of a carbanion gives a neutral carbon radical and in ours a one-electron oxidation of an amine gives the amminium radical cation. The chemistry involved in Rajca's systems appears to be more difficult since the carbanion intermediates are sensitive to moisture. One very impressive aspect of their work has been the way in which this group has produced specific (monodisperse) oligomers of well-defined structure such as the 'star-branched' decaradical **23** (Rajca *et al.* 1992) and the dendritic system **24** (Rajca & Utamapanya 1993) (figure 13). In systems of this type, spin coupling has been shown to be very sensitive to defects, particularly
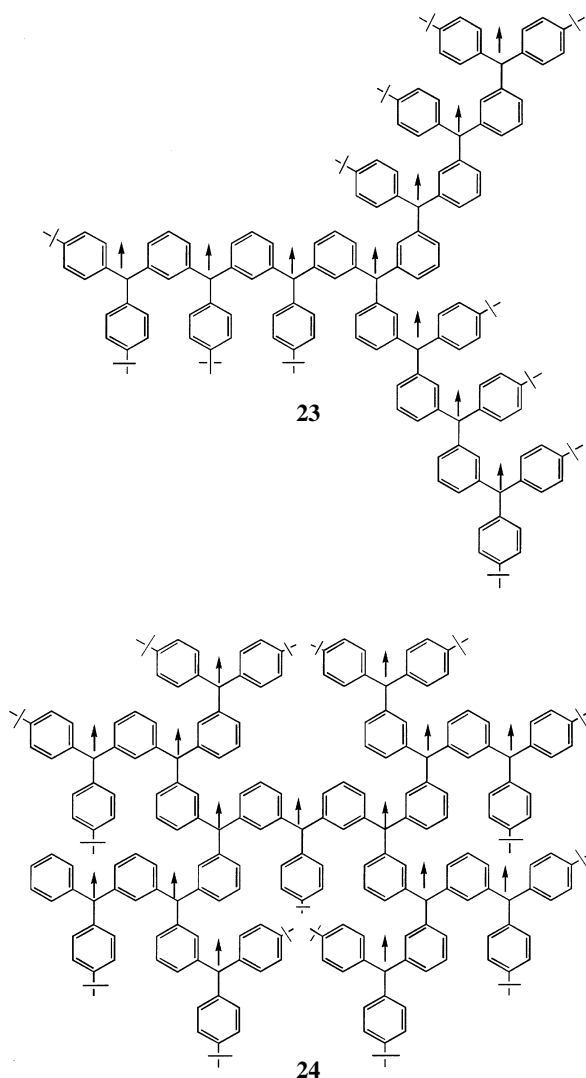
23

24

Figure 13. The 'star-branched' decaradical **23** and dendritic system **24**
of Rajca and co-workers.

defects close to the centre of the molecule. Recently, this group attempted to tackle
this problem and have produced several 'closed-loop' structures, the most interesting
of which is polyradical **25** (Rajca *et al.* 1998) (figure 14). This should have a ground
state $S = 12$. Magnetic susceptibility data give a value of $S = 10$. The authors ascribe
this discrepancy to the presence of a small density of defects, which result either from
less than 100% generation of unpaired electrons, or from synthetic impurities present
in the polyether precursor, but, as in our systems, a dispersity in the site-to-site spin
interactions may also be a significant problem and it is interesting to note that **25**
also shows evidence for a temperature-dependent moment.

The group of Rajca has also successfully synthesized and characterized a poly-
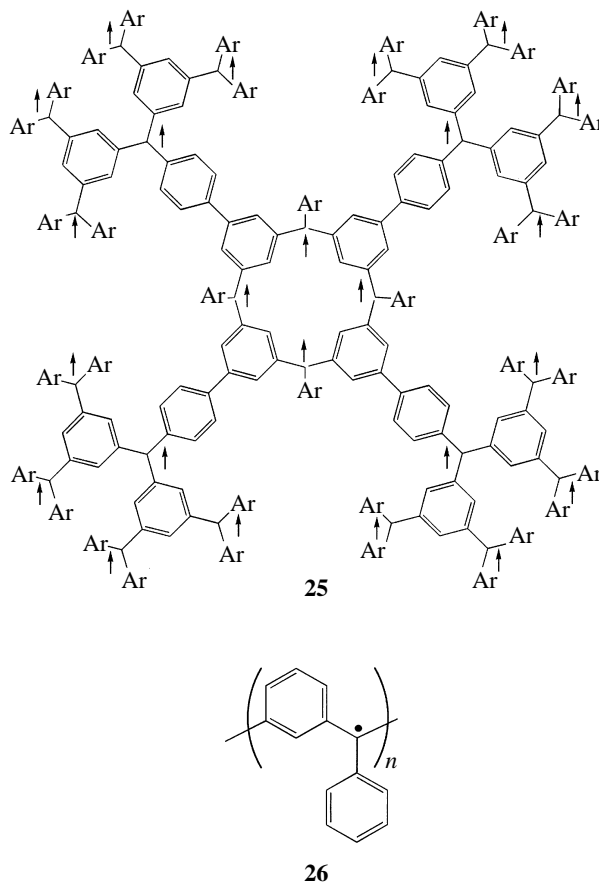
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Figure 14. The 'closed-loop' polyradical **25** (should be $S = 12$, actually $S = 10$),
Ar = $^tBuC_6H_4-$ and the 1,3-connected polyarylmethane radical 26 of Rajca and co-workers.

meric 1,3 connected arylmethane **26** (Utamapanya *et al.* 1993) (figure 14). However, incomplete generation of spin sites proved to be the limiting factor. Indeed, defects are always particularly damaging in linear/one-dimensional systems. A fit of the normalized plot of the magnetization to those of theoretical Brillouin functions gave best agreement with a system $S = 2$.

(*b*) *Phenoxy radical-based systems (Lathi, Nishide and co-workers)*

The groups of Lathi, and particularly Nishide, have developed a variety of polymers and oligomers in which the spin carriers are of the phenoxy or galvinoxyl type (figure 14). The polyradical **27** gives an average spin quantum number, $S = \frac{5}{2}$, with a spin concentration of 0.7 spins per unit (Nishide *et al.* 1996). Star-branched oligomers **28** and **29** (figure 15) were also studied. The polyradical **28** displays an average $S = 4$ (Nishide *et al.* 1998). In comparison to our systems and those of Rajca, high doping levels seem more difficult to achieve and, unlike Rajca's systems, the materials are polydisperse. However, these phenoxy radicals have the advan-
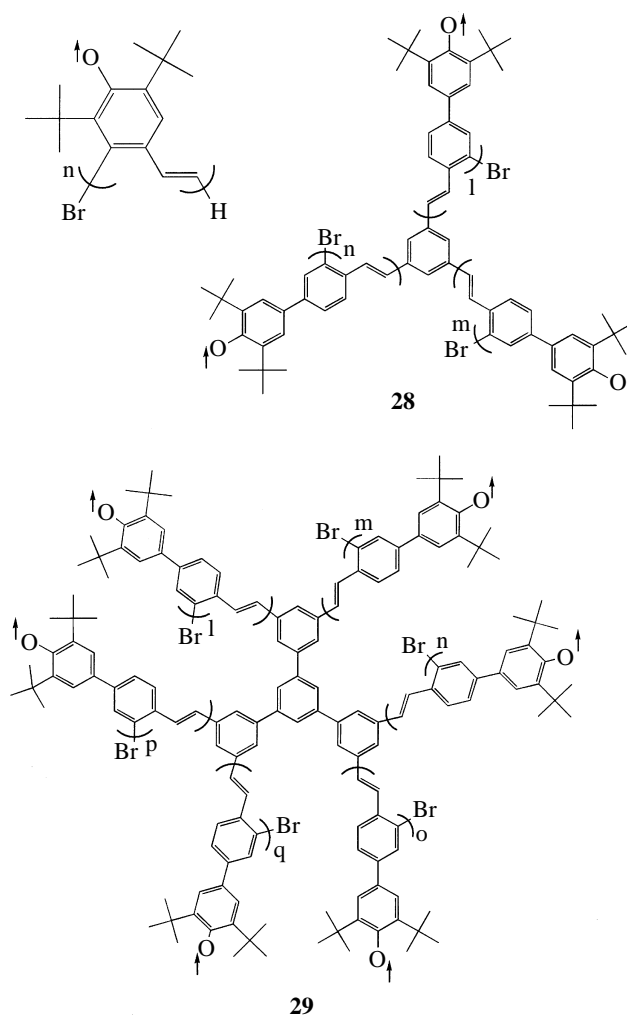
Figure 15. Phenoxy-radical based systems of Lathi and Nishide.

tage over others in that they are chemically stable and easily handled even at room temperature.

6. Conclusions and future prospects

The dream of polymer magnets has proved difficult to translate into reality and progress has been slow. The best systems made so far have involved ferromagnetic coupling of a few tens of spins at temperatures close to absolute zero. However, real progress has been made in the last few years. The feasibility of creating high-spin clusters has been established, as has the feasibility of exploiting at least three types of spin carrier. These leads will doubtless be developed and higher spin species will result. The great virtue of organic molecular materials is that the range of synthetic methods now at our disposal allows us to engineer structures almost at will at a

molecular level and to continuously refine our designs. It will become clear whether or not this will lead to materials with useful or interesting bulk properties.

7. Experimental

(*a*) *General*

The general experimental procedures and instrumentation used and those for the magnetometer studies (Bushby *et al.* 1997*a*; Bushby & Gooding 1998), for the UV studies and EPR studies (Bushby *et al.* 1999) and for the cyclic voltammetry studies (Bushby *et al.* 1997*b*) have all been described in previous publications, as have the syntheses of the polymer **14** (Bushby & Gooding 1998) and the synthesis and X-ray crystallography of compound **15** (Bushby *et al.* 1999).

(*b*) *Preparation of*
N, N′-*bis-(2-methoxyphenyl)*-N, N′-*diphenyl-paraphenylenediamine* **18**

A stirred mixture of N, N′-diphenylphenylenediamine (9.44 g, 0.04 mol), 2-iodo-anisole (25.46 g, 0.11 mol), powdered anhydrous potassium carbonate (59.62 g, 0.43 mol), copper powder (13.73 g, 0.22 mol), and degassed 1,2-dichlorobenzene (120 cm^3) was refluxed for 2 h under an argon atmosphere in the absence of light. After cooling to *ca.* 70 °C, the insoluble inorganic material was filtered off and the dark brown filtrate collected. The insoluble material was washed with dichloro-methane (2 × 100 cm^3). The combined filtrate and organic phase was washed with dilute aqueous ammonia and thoroughly with water. After drying with magnesium sulphate the mixture was cooled in ice causing precipitation of a light grey solid, which was recrystallized from hexane: CHCl$_3$ (2:1) to give the product **18** (8.3 g, 72%) as light brown crystals with m.p. (melting point) 163–164 °C. (Found: C, 79.90%; H, 5.60%; N, 5.45%. C$_{32}$H$_{28}$N$_2$O$_2$ requires: C, 80.37%; H, 5.93%; N, 5.93%.) δ_H 3.63 (6H, s, -OMe), 6.81–6.94 (10H, m, ArH), 6.93 (4H, s,p-disubstituted ArH) and 7.12–7.22 (8H, m, ArH); m/z, 472 (M$^+$, 100%), 259 (33%) and 2 (14%).

(*c*) *Preparation of* N, N′-*bis-(4-bromo-2-methoxyphenyl)*-N, N′-*bis-(4-bromophenyl)-paraphenylenediamine* **19**

A solution of bromine (9.47 g, 59.28 mmol) in dry chloroform (70 cm^3) was added to a stirred solution of amine **18** (7.00 g, 14.82 mmol) in dry chloroform (70 cm^3) at 0 °C over 60 min. After the addition, a blue–green reaction mixture formed which was allowed to warm to room temperature with stirring overnight. The reaction mixture then was washed with water (2 × 150 cm^3), dilute sodium *meta*-bisulphite solution (150 cm^3) and brine (150 cm^3), and dried with magnesium sulphate. The solvent was removed under reduced pressure to give a white solid. The product was purified by column chromatography on silica gel, eluting with 30% dichloromethane in hexane to give the product **19** as small white needles (8.31 g, 72%), m.p. 136–137 °C. (Found: C, 48.30%; H, 3.20%; N, 3.25%; Br, 40.35%. C$_{32}$H$_{24}$Br$_4$N$_2$O$_2$ requires: C, 48.53%; H, 3.03%; N, 3.54%; Br, 40.36%.) δ_H (CDCl$_3$) 3.64 (6H, s, -OMe), 6.74 (4H, d, $J = 12.0$ Hz, ArH), 6.89 (4H, s, ArH), 7.0–7.15 (6H, m, ArH) and 7.24 (4H, d, $J = 12.0$ Hz, ArH); m/z, 788 (M$^+$, 100%) and 391 (13%).

(*d*) *Preparation of* N, N′-*bis-(2-methoxyphenyl-4-boronic acid)*-N, N′-*bis-(phenyl-4-boronic acid)-paraphenylenediamine* **21**

Under rigorously dry conditions, *n*-butyl lithium in hexane (24.5 cm^3, 1.6 M, 37.9 mmol) was added to a stirred solution of the brominated amine **20** (7.46 g, 9.39 mmol) in dry tetrahydrofuran (300 cm^3) under an atmosphere of argon at $-78\,°$C over a period of 30 min. The initial development of a pale yellow solution was followed by the formation of a thick white suspension 1 h after addition. After stirring for a further 3 h at $-78\,°$C, a cold solution of tri-*iso*-propylborate (28.24 g, 150.0 mmol) in dry tetrahydrofuran (70 cm^3) at $-78\,°$C was cannulated into the reaction mixture under argon, and the entire content stirred for another 2 h before being warmed to room temperature overnight (*ca.* 12 h). The mixture was again cooled to $-78\,°$C and the intermediate ester **20** was hydrolysed by adding 2 M hydrochloric acid (42 cm^3), and slowly warming to room temperature with stirring for a further 1 h before workup. Ether (100 cm^3) was added and the organic layer separated. The aqueous layer was extracted with further ether (2×20 cm^3). The combined organic layers were washed with water and dried with magnesium sulphate. Solvents were removed under reduced pressure without heating and the green residue redissolved in tetrahydrofuran (100 cm^3). The product was precipitated by adding hexane (100 cm^3) and the pale green precipitate was collected by filtration. The solid was washed thoroughly with acetone to give the product **21** (4.08 g, 67%) as a pale green solid. The product is insoluble in ether, acetone, dichloromethane, chloroform and hexane, but is soluble in tetrahydrofuran and ethanol. (Found: C, 60.60%; H, 5.30%; N, 3.70%. $C_{32}H_{32}B_4N_2O_{10}$ requires: C, 59.95%, H, 4.94%; N, 4.33%.) In order to obtain spectroscopic data and to confirm the structure, an ester derivative was made by heating the product in the presence of ethane diol. (Found: C, 62.40%; H, 5.30%; N, 3.35%. $C_{40}H_{40}B_4N_2O_{10}$ requires: C, 62.7%; H, 5.50%; N, 3.65%.) δ_H (CDCl$_3$) 3.65 (6H, s, -OMe), 4.33 (8H, s, O—CH$_2$—CH$_2$—O), 4.38 (8H, s, O—CH$_2$—CH$_2$—O), 7.01 (4H, s, ArH of symmetrical AB system), 7.10–7.24 (2H, m, ArH), 7.25 (8H, dd $J = 12.0$ and 200 Hz, ArH of unsymmetrical AB system), 7.30–7.47 (4H, m, ArH); m/z, 752 (M$^+$, 100%).

(*e*) *Preparation of polymer* **22**

The boronic acid **21** (2.03 g, 3.13 mmol) was stirred in ethanol (20 cm^3) for 1 h and the solution degassed using a stream of argon bubbles. A mixture of 3,5-di-bromotetradecylbenzene (Murray *et al.* 1994) (2.71 g, 6.26 mmol) and palladium tetrakistriphenylphosphine (0.12 g, 0.11 mmol) was stirred for 30 min in dry degassed toluene (70 cm^3) under argon. The ethanol solution was added followed by dilute sodium carbonate (2 M, 25 cm^3), via a cannula to maintain inert conditions. The entire mixture was heated under reflux under an argon atmosphere while stirring for 4 days. When cooled, the aqueous layer was removed and extracted with chloroform (2×50 cm^3). A quantity of black 'gel' was found in the remaining organic layer, which was also extracted in the same manner. The combined organic layers were washed with dilute HCl (50 cm^3), water (2×100 cm^3) and dried with magnesium sulphate. The volume of solvent was reduced to *ca.* 15 cm^3 and the solution dropped into cold methanol, causing precipitation of a fine light-green powder which was collected at the pump and washed with acetone. The process was repeated several times to remove impurities, eventually yielding the polymer product as a green powder (2.30 g,

67%). (Found: C, 84.05%; H, 9.05%; N, 2.55%; Br, 0%. Repeat unit $C_{60}H_{84}O_2N_2$ requires: C, 85.10%; H, 8.75%; N, 2.76%; Br, 0.00%.) δ_H (CDCl$_3$) 0.83 (m, b, -CH$_3$ of C$_{14}$ alkyl chain), 1.03–1.42 (m, b, methylenes of C$_{14}$ alkyl chain), 1.70 (m, b, Ph—CH$_2$—CH$_2$), 2.64 (m, b, Ph—CH$_2$—), 3.76 (m, b, -OMe), 6.81–7.28 (m, b, ArH of phenylenediamine groups) and 7.26–7.32 (m, b, ArH of 1,3,5-trisubstituteded benzene groups). $M_w = 36\,000$ ($M_n/M_w = 1.9$) from GPC against a polystyrene standard.

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