Synthesis and magnetic behaviour of polyradical: poly(1,3-phenyleneethynylene) with π-toporegulated pendant stable aminoxyl and imine *N*-oxide–aminoxyl radicals

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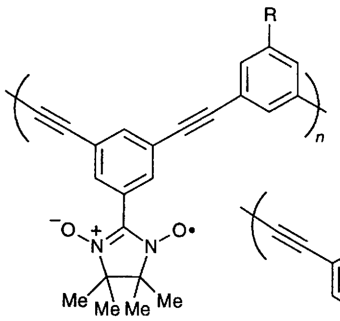
The palladium-catalysed polycondensation of *N*-*tert*-butyl-*N*-(3,5-diethynylphenyl)aminoxyl with 2-(3,5-diiodophenyl)-4,4,5,5-tetramethyl-3-oxido-2-imidazolin-3-ium-1-yloxyl in pyridine–triethylamine at room temperature afforded poly(1,3-phenyleneethynylene) with pendant aminoxyl and imine *N*-oxide–aminoxyl radicals as a light blue powder in 78–83% yields. The number-average molecular weights ($\bar{M}_n$) of the polyradical determined by GPC were 2670–3030 and the spin concentrations determined by EPR were $1.91–2.02 \times 10^{21}$ spins g^{-1}. Both solution (CH_2Cl_2) and powder EPR measurements of the polyradicals gave a hyperfine-smeared single line spectrum, suggesting that spin-exchange narrowing took place due to the high spin concentrations of the polyradicals. The magnetic susceptibility (χ) measurements of the polyradicals were carried out on a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 1.8–300 K. The χT *vs.* T plots showed that the polyradicals were a paramegnetic species yielding a weak antiferromagnetic coupling ($\theta = -1.5$ K) below 30 K. The absence of the through-bond ferromagnetic interaction is accounted for by masking of the interaction by the stronger through-space antiferromagnetic interactions.

Of the many models proposed for the design of new, molecule-based magnetic materials, polyradical magnets have proved to be one of the most interesting.[1] Our approach to polyradical ferromagnets has developed along two paths: one is poly(ethynylbenzenes) with π-toporegulated pendant stable free radicals[2–5] and the other is poly(1,3-phenyleneethynylenes) with π-toporegulated pendant stable free radicals.[6–9] One of the most important requirements in the magnetic studies of polyradicals is the synthesis of structurally well-defined polyradicals with high spin concentrations. We have therefore prepared polyradicals by the polymerization of monomers bearing a stable free radical moiety under mild conditions such that the radical sites are not decomposed.

In a previous paper we reported the synthesis and magnetic characterization of poly(1,3-phenyleneethynylene) with pendant imine *N*-oxide–aminoxyl groups **1**.[7] Although the spin concentrations of the polyradicals were very high [$1.12–1.33 \times 10^{21}$ spins g^{-1} (0.82–0.91 spin per repeating unit)], their magnetic susceptibility measurements showed no significant magnetic interactions among the spins. This was ascribed to a lack of sufficient polarization of the unpaired electron spins in the 1,3-phenylenediethynylene coupling units. Based on this result we decided to synthesize poly(1,3-phenyleneethynylene) bearing aminoxyl radicals **2** because these have a more extensively delocalized unpaired electron spin. Since aminoxyl radicals are less stable than imine *N*-oxide–aminoxyl radicals, some difficulties were anticipated in the synthesis of **2**. We therefore investigated the palladium-catalysed polycondensation of aminoxyl monomer **4** with 1,3-diiodo-5-*tert*-butylbenzene giving **2** as a preliminary study.[8] When the polycondensation was carried out in pyridine–triethylamine (1 : 1), the resulting polyradicals showed a low spin concentration of 0.49 spins per repeating unit, suggesting that significant decomposition of the aminoxyl radical sites took place during the polycondensation. However, when polycondensation was carried out in 1 : 4 triethylamine–pyridine, the resulting polyradical showed a high spin concentration of 0.86 spins per repeating unit. After this preliminary study, we investigated the synthesis of poly(1,3-phenyleneethynylene) with π-toporegulated pendant aminoxyl and imine *N*-oxide–aminoxyl stable radicals **3** by the palladium-catalysed polycondensation of aminoxyl monomer **4** with imine *N*-oxide–ami-



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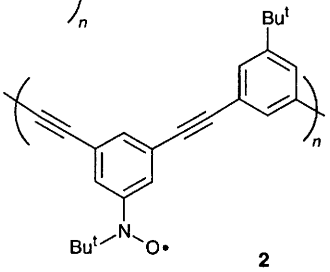
R = Bu^t, C_6H_{11}



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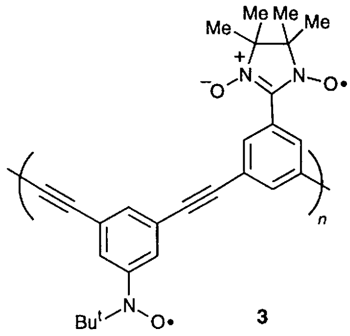

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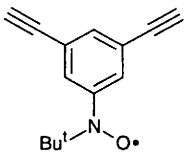

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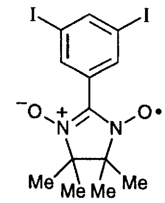

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noxyl monomer **5** in triethylamine–pyridine (1:4). This polyradical has delocalized electron spins at the aminoxyl sites and the unpaired electron spin centres are closer to each other than in **1** and **2**. Herein we report the synthesis and magnetic characterization of **3**.

Results and Discussion

Design of polyradicals

According to the valence bond theory of topological symmetry of alternant hydrocarbon π-systems,[10] the ground spin states (S) are predicted by eqn. (1), where n^* is the number of starred atoms and n is the number of unstarred atoms (where adjacent atoms are respectively starred and unstarred, and identically denoted

$$S=(n^*-n)/2 \qquad (1)$$

atoms are not adjacent to each other). In Fig. 1, all the atoms in the π-system of the corresponding repeating unit **6** are either starred or unstarred according to this rule. As seen from Fig. 1, n^* is 10 and n is 8, predicting that the ground state of **6** is a triplet ($S=1$). On the basis of this consideration it is expected that the intramolecular (through-bond) interactions between the π-unpaired electron spins in **3** are ferromagnetic.

It is also important to ascertain for **4** and **5** that the unpaired electron spin is delocalized to the benzene ring; it is particularly important to evaluate the spin density at the *meta* positions because the connection of the radical units is made at the *meta* positions of the phenyl group. To date, extensive EPR studies on *N*-aryl-*N*-*tert*-butylaminoxyls have been undertaken,[11] and for *N*-*tert*-butyl-*N*-phenylaminoxyl **7**[12] the hyperfine coupling constants have been determined as follows: $a_{o\text{-H}}=a_{p\text{-H}}=0.19$, $a_{m\text{-H}}=0.08$ mT. On the other hand, for 2-phenyl-3-oxido-2-imidazolin-3-ium-1-yloxyl **8** the spin density distribution on the benzene ring has been determined by an ^{1}H ENDOR/TRIPLE resonance study,[13] a ^{1}H NMR study,[14] and the polarized neutron diffraction method.[15] For example, the ^{1}H ENDOR/TRIPLE resonance method gave the following hyperfine coupling constants: $a_{o\text{-H}}=0.0518$, $a_{m\text{-H}}=-0.0292$, $a_{p\text{-H}}=0.0466$ mT. When eqn. (2) is applied, the spin densities on the *meta* positions are estimated to be 0.033 (**7**) and 0.012 (**8**), respectively, from the hyperfine coupling constants. Therefore, it is obvious that there are some spin densities at the *meta* positions of both monomers.

$$a_{\mathrm{H}}=-2.4\rho_{\mathrm{c}} \qquad (2)$$

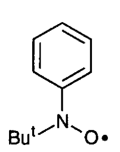
Synthesis of monomers 4 and 5

N-*tert*-Butyl-*N*-(3,5-diethynylphenyl)aminoxyl **4** was obtained by our previously reported method and purified by sublimation prior to use. The radical purity determined by EPR was 87%.

2-(3,5-Diiodophenyl)-4,4,5,5-tetramethyl-3-oxido-2-imidazolin-3-ium-1-yloxyl **5** was prepared according to Scheme 1. Thus, treatment of *p*-toluidine with benzyltrimethylammonium dichloroiodate (BTMA ICl_2) in CH_2Cl_2 in the presence of $CaCO_3$ gave 2,6-diiodo-*p*-toluidine in 78% yield.[16] Deamination of this compound was accomplished by treating the corresponding toluidine sulfate with $NaNO_2$ in EtOH–benzene, giving 3,5-diiodotoluene in 50% yield. 3,5-Diiodotoluene was then treated with *N*-bromosuccinimide (NBS) in 1,2-dichloroethane in the presence of catalytic amounts of benzoyl peroxide, affording 3,5-diiodobenzyl bromide in *ca.* 100 yield. This benzyl bromide was then treated with hexamethylenetetraamine in $CHCl_3$ and the subsequent hydrolysis in aqueous HCl–AcOH gave 3,5-diiodobenzaldehyde in 47% yield. 3,5-Diiodobezaldehyde was then allowed to react with 2,3-bis(hydroxyamino)-2,3-dimethylbutane in MeOH–THF to give 1,3-dihydroxy-2-(3,5-diiodophenyl)-4,4,5,5-tetramethyl-2-imidazoline in 55% yield.[17] The resulting imidazoline compound was oxidized with PbO_2 in benzene–ethanol. Crystallization from hexane–benzene gave **5** as dark blue needles in 62% yield. The radical purity determined by EPR was *ca.* 100%.

Polycondensation

Based on previous results showing that the palladium-catalysed polycondensation of **4** with 1,3-diiodo-5-*tert*-butylbenzene in 1:4 triethylamine–pyridine gave polyradical **2** with a high spin concentration of 0.86 spins per repeating unit, the polycondensation of **4** with **5** was also carried out in the same triethylamine–pyridine (1:4) solvent (Scheme 2). The procedure for the polycondensation was as follows: a mixture of 1 equiv. of **4** and **5**, 0.05 equiv. of $(PPh_3)_2PdCl_2$, and 0.02 equiv. of CuI in



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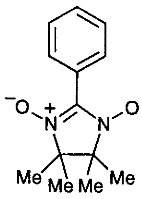

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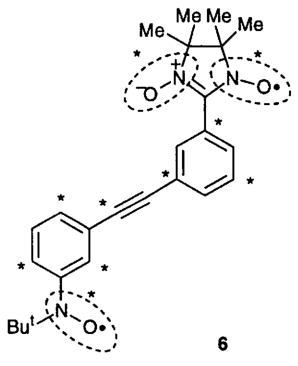

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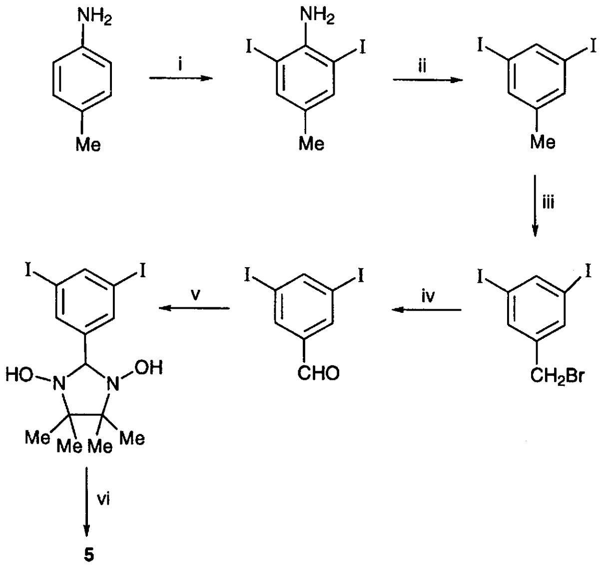
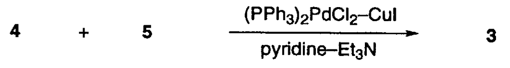
Fig. 1 Prediction of the ground spin state of **6** by the starred and unstarred valence bond theory



Scheme 1 *Reagents and conditions*: i, BTMA ICl_2, $CaCO_3$, CH_2Cl_2–MeOH, reflux; ii, H_2SO_4, $NaNO_2$, EtOH-benzene, reflux; iii, NBS, CH_2ClCH_2Cl, reflux; iv, $(CH_2)_6N_4$, $CHCl_3$, reflux, then HCl, AcOH–H_2O, reflux; v, $HONHCMe_2CMe_2NHOH$, MeOH–THF, room temp.; vi, PbO_2, benzene–ethanol, room temp.



Scheme 2

triethylamine–pyridine (1:4) was stirred at 20 °C under nitrogen. After 2–6 h, the mixture was poured into a large amount of methanol, and the light green–blue powder deposited was collected by filtration and dried *in vacuo*. The results are summarized in Table 1.

Table 1 shows that the yields of the polyradical are in the range 78–83% and the number-average molecular weights ($\bar{M}_n$) of the polyradicals determined by GPC using polystyrene standards are 2670–3030, which correspond to a degree of polymerization of 5.5–6.9. It is also shown that the increases in the yields and $\bar{M}_n$ are small after 2 h of polycondensation, indicating that the polycondensation is almost finished. We therefore did not attempt further prolonged polycondensation, since a gradual decrease in the radical concentration of the polyradicals obtained was observed with prolonged polycondensation (see Table 1).

The IR spectra of the polyradical showed the complete disappearance of the absorption due to the stretching vibration of the C≡CH bond (3250 cm^{-1}) characteristic of monomer **4** and the appearance of the absorption (weak) due to the stretching vibration of the C≡C bond (2200 cm^{-1}). It is therefore suggested that the polyradicals are terminated by iodines. To confirm this IR result, iodine content was determined by combustion analysis of the polyradicals. The iodine percentages of 9.2–9.3 suggest that structure **9** ($n=5$) has iodine atoms at both ends, in good agreement with the results from the GPC analyses ($n=5.5$–6.9). The observed C, H and N analyses for the polyradicals [C, 66.2; H, 5.6; N, 8.0; I, 9.2% (run 2 of Table 1) and C, 66.0; H, 5.7; N, 8.2; I, 9.3% (run 3 of Table 1)] also agree with the theoretical values calculated for **9** (C, 66.02; H, 5.61; N, 8.84; I, 9.43%). This good agreement of $\bar{M}_n$ is somewhat surprising since the GPC calibration is based on polystyrene, whose molecular size is different from that of the polyradical.

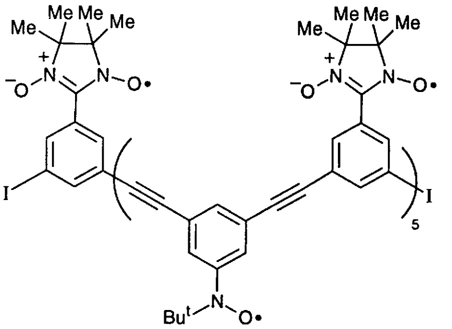


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Table 1 The results of the palladium-catalysed polycondensation of **4** with **5**[a]

run	t/h	yield (%)	$\bar{M}$[b,c]	spin conc./spins g^{-1}[d] (number of spins per repeating unit)
1	2	83	2670 (5.5)	2.02×10^{21} (1.48, 1.64[f])
2[e]	4	83	2900 (6.6)	1.99×10^{21} (1.46, 1.62[f])[g]
3[e]	6	78	3030 (6.9)	1.91×10^{21} (1.40, 1.55[f])

[a] **4**, 80 mg (0.38 mmol); **5**, 183 mg (0.38 mmol); $(PPh_3)_2PdCl_2$, 13.3 mg (0.018 mmol); CuI, 1.5 mg (0.0078 mmol); solvent, Et_3N (2.3 cm^3)–pyridine (9.2 cm^3). [b] Determined by GPC. [c] The value in parentheses refers to the degree of polymerization. [d] Determined by EPR. [e] Elemental analyses: C, 66.2; H, 5.6; N, 8.0; I, 9.2% (run 2); C, 66.0; H, 5.7; N, 8.2; I, 9.3% (run 3). [f] The number of spins per repeating unit calculated as the structure of **9**. [g] The spin concentration derived from the magnetic susceptibility measurements is 2.07×10^{21} spins g^{-1} (1.52 spins per repeating unit).

Polyradicals **3** are soluble in dimethylformamide (DMF), dichloromethane and chloroform, and partially soluble in benzene and toluene to give a green–blue solution. However, they are insoluble in methanol and hexane.

The spin concentrations of **3** were determined by EPR using dichloromethane as solvent and using 1,3,5-triphenylverdazyl as the reference radical. As shown by Table 1, the spin concentrations of **3** are in the range 1.91–2.02×10^{21} spins g^{-1}, which corresponds to 1.40–1.48 spins per repeating unit. If the structure of polyradical **9** has two heavy iodine atoms, this increases to 1.55–1.64. The spin concentrations of the polyradical were also determined by magnetic susceptibility measurements of the polyradical to be 2.07×10^{21} spins g^{-1}, as mentioned below. Although it is obvious that some decomposition of the radical moieties occurs during the polycondensation, their spin concentrations are satisfactorily high. Although we do not know what kinds of decomposition reactions occur for the radical moieties during the polycondensation, the good agreement between the experimental and calculated elemental analyses suggests that serious decomposition of the polyradical moieties does not occur.

The UV–visible spectra of **3**, **4** and **5** were measured using dichloromethane as the solvent, and the results are shown in Fig. 2. The concentration of the polyradical **3** is calculated as the unit mole concentration, and ε values are corrected based on the spin concentration determined by EPR spectroscopy. Monomer **4** shows absorption maxima at 500 (ε 121), 416 (280) and 302 nm (12000), and monomer **5** at 633 (ε 300), 592 (340), 371 nm (14600) and 357 nm (7750). The orange colour characteristic of the aminoxyl group is attributable to λ_{max} at 500 nm, and the blue colour characteristic of the imine *N*-oxide–aminoxyl group is attributable to λ_{max} at 633 and 592 nm. On the other hand, the polyradical **3** shows absorption maxima at 622 (ε 450), 585 (500) and 370 nm (16200). These absorption maxima are found in the spectra of **4** and **5**, and no bathochromic shifts in the visible region are observed. Since the polyradical is based on a cross-conjugated poly(1,3-phenyleneethynylene) structure, the spectrum of the polyradical **3** can be interpreted as a superposition of the spectra of **4** and **5**.

The solution EPR spectra of **3**, **4** and **5** were measured at 20 °C using benzene or dichloromethane as the solvent. Their spectra are shown in Fig. 3. The spectrum of **4** consists of three sets of a 1:3:3:1 quartet [$a_N = 1.210$, $a_{o\text{-H}}$ and $a_{p\text{-H}} = 0.198$ mT, $g = 2.0061$ (in benzene)], and that of **5** consists of a 1:2:3:2:1 quintet [$a_N = 0.747$ mT, $g = 2.0067$ (in benzene)]. In contrast, the polyradical **3** in dichloromethane gives a hyperfine-smeared single line with a peak-to-peak width of 0.65 mT ($g = 2.0063$) (in dichloromethane), suggesting the occurrence of spin—

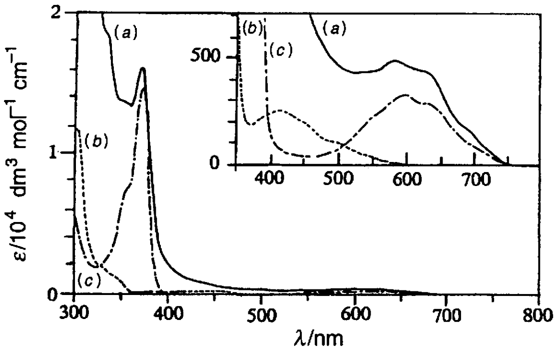

Fig. 2 UV–VIS spectra of (*a*) **3** (run 2 in Table 1), (*b*) **4** and (*c*) **5** in dichloromethane. The inset shows an expansion of the visible region. Absorptions ε is corrected for the spin concentration determined by EPR spectroscopy.

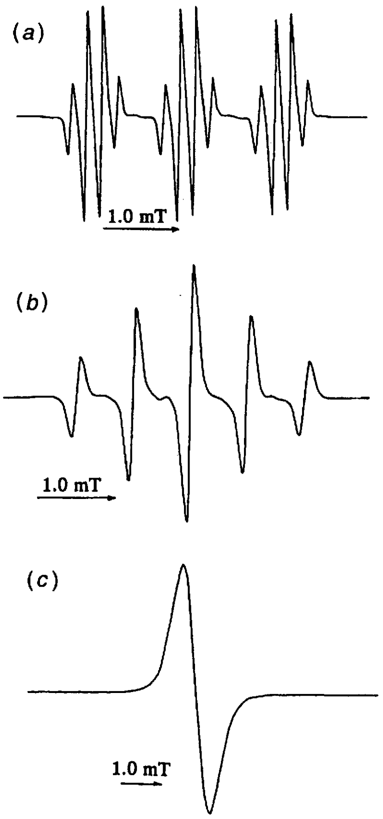

Fig. 3 Solution EPR spectra of 3, 4 and 5 at 20 °C: (*a*) 4 in benzene; (*b*) 5 in benzene; (*c*) 3 (run 2 in Table 1) in dichloromethane

exchange narrowing due to the high spin concentration of the polyradical.

Magnetic susceptibility measurements

The magnetic susceptibility (χ) measurements of polyradical 3 having the spin concentration of 1.99×10^{21} spins g^{-1} (run 2 of Table 1) was carried out in the temperature range 1.8–300 K with a superconducting quantum interference device (SQUID) magnetometer. The molar susceptibility is calculated as the unit molar susceptibility. The diamagnetic contribution from the sample was estimated from Pascal's constants.

When the magnetic interactions among the unpaired electron spins are smaller than the energy of the thermal fluctuation kT, and the orbit angular momentum is neglected, the magnetic susceptibility χ is expressed by eqn. (3), where N is Avogadro's number, μ_B is the Bohr magneton, g is the Landé factor, and θ is the Weiss temperature; $N\mu_B{}^2g^2S(S+1)/3k$ is called the Curie constant, C.

$$\chi = \frac{N\mu_B{}^2g^2S(S+1)}{3k} \frac{1}{T-\theta} \quad (3)$$

$$\frac{1}{\chi} = \frac{T-\theta}{C} \quad (4)$$

According to eqn. (4), $1/\chi$ was plotted against T in the temperature range 1.8–300 K, and an almost linear curve with a Weiss temperature (θ) of -1.5 K was obtained. Fig. 4 shows the χT *vs.* T plots of the polyradical 3. The curve is flat in the high temperature region (300–30 K), showing that the polyradical is paramagnetic in this temperature region. From the χT value of 0.570 emu K (repeating unit)$^{-1}$ in this temperature region the spin concentration of the polyradical can be determined to be 1.52 spins per repeating unit [theoretical 0.752 emu K (repeating unit)$^{-1}$], provided that S is 1/2, and this value corresponds to 2.07×10^{21} spins g^{-1}. If the structure of polyradical is 9, the number of spins per repeating unit becomes 1.69. Accordingly, the spin concentration determined by the magnetic susceptibility measurements is in good agreement with that determined by EPR though the SQUID magnetic measurements give a somewhat higher value. In the temperature region below 30 K, on the other hand, the χT *vs.* T plot shows a downward turn, indicating that unpaired electron spins interact antiferromagnetically. This antiferromagnetic interaction is most probably due to intramolecular and intermolecular through-space interactions between the unpaired electron spins. In most cases through-space interactions are antiferromagnetic. If the expected through-bond ferromagnetic interactions are sufficiently strong, an upward turn of the χT *vs.* T plots showing ferromagnetic interactions will be observed. However, if the ferromagnetic interaction between the spins is very or negligibly weak, they will be masked by through-space antiferromagnetic interactions. This is assumed to be this case in the present example. Recently, Nishide *et al.* observed ferromagnetic interactions for poly(phenylenevinylene)-based polyphenoxyl and polyaminoxyl.[18] In that case the ferromagnetic through-bond interactions seem to be strong. Consequently, only when there are strong through-bond ferromagnetic interactions between the electron spins will polyradicals show ferromagnetic behaviour. Magnetic measurements of polyradicals diluted with diamagnetic materials are in progress.

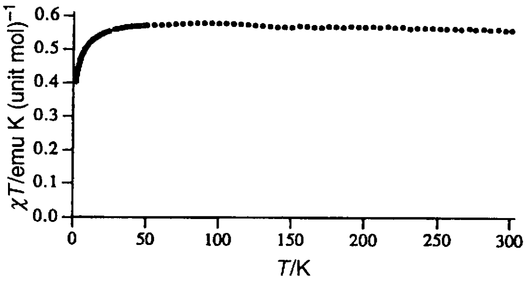

Fig. 4 Plot of χT *vs.* T for 3

Experimental

All mps were measured on a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer. UV–VIS spectra were measured with a Shimadzu UV-2200 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL α-400 spectrometer (400 MHz) with Me_4Si as internal reference; J values are given in Hz. GPC was run on a Tosoh GPC 8000 series using Shodex G5000HHR, GMHHR-L, and GMHHR-L columns calibrated with polystyrene standards, eluting with THF and with monitoring of the refractive index.

EPR spectra were recorded on a JEOL ME-3X spectrometer operated at the X-band. Hyperfine splitting constants (*a*) and *g* values were determined by simultaneous measurements with a dilute Fremy's salt in aqueous K_2CO_3 solution ($a_N = 1.309$ mT, $g = 2.0055$). The spin concentrations of monomers and polyradicals were determined by the double integrated EPR spectra of the samples in CH_2Cl_2 recorded on a Bruker ESP 300 spectrometer. Calibration curves were drawn with 1,3,5-triphenylverdazyl solutions using the same EPR cell and solvent and the same instrument settings as for the sample measurements.

The magnetic susceptibility measurements were carried out on a Quantum Design SQUID MPMS2 system in the temperature range 1.8–300 K. The diamagnetic contribution of the samples was estimated from Pascal's diamagnetic constants.

Materials

N-*tert*-Butyl-*N*-(3,5-diethynylphenyl)aminoxyl was prepared by our previously reported method and purified by sublimation.[8] This monomer was again purified by sublimation prior to use. Pyridine and triethylamine used in the polycondensation was purified by distillation. CuI was of commercial grade.

2,6-Diiodo-4-toluidine

This compound was obtained by treating *p*-toluidine (13.5 g, 0.126 mol) with benzyltrimethylammonium dichloroiodate (BTMA ICl_2) (117.5 g, 0.338 mol) in the presence of $CaCO_3$ (40 g) in CH_2Cl_2 (1170 cm^3)–MeOH (473 cm^3) at reflux temperature for 1 day.[16] After the usual workup, the product was refluxed in 100 cm^3 of methanol for 10 min to remove polar byproducts, giving almost pure 2,4-diiodo-4-toluidine in 78% yield (35.5 g, 0.099 mol). Recrystallization from hexane–benzene gave light brown needles, mp 122–123 °C (lit.,[16] 123.5–125 °C).

3,5-Diiodotoluene

To a stirred solution of 2,6-diiodotoluidine (12.58 g, 0.035 mol) in EtOH (600 cm^3)–benzene (230 cm^3) was added a solution of $NaNO_2$ (4.44 g) in water (31 cm^3) and conc. sulfuric acid (8.3 cm^3). After stirring for 30 min at room temperature, the mixture was refluxed for 1 day and the solvent removed *in vacuo*. After the residue had been neutralized with NaOH (2 mol dm^{-3}), the organic products were extracted with CH_2Cl_2, dried ($MgSO_4$), evaporated and chromatographed on silica gel (Wako gel C200) with benzene–hexane (1 : 9) to give pure 3,5-diiodotoluene in 50% yield (6.06 g, 17.6 mmol). Recrystallization from MeOH gave colourless needles, mp 40–41 °C (lit.,[19] 44.5–45.5 °C).

3,5-Diiodobenzyl bromide

A solution of 3,5-diiodotoluene (6.0 g, 17.4 mmol), *N*-bromosuccinimide (NBS) (6.0 g, 33.7 mmol) and benzoyl peroxide (20 mg) in 1,2-dichloroethane (60 cm^3) was gently refluxed for 6 h. The reaction mixture was then washed with 10% $NaHSO_3$ and brine, dried ($MgSO_4$), and solvent was evaporated. The resultant crude product (7.36 g, 100%) was used in the following step without purification. Recrystallization from hexane–benzene gave colourless needles, mp 79–80 °C; $\delta_H(CDCl_3)$ 4.31 (2 H, s, CH_2Br), 7.69 (2 H, d, *J* 1.5, ArH) and 7.98 (1 H, t, *J* 1.5, ArH).

3,5-Diiodobenzaldehyde

To a solution of hexamethylenetetraamine (3.0 g, 21.4 mmol) in $CHCl_3$ (150 cm^3) was added 3,5-diiodobenzyl bromide (7.36 g, 17.4 mmol), and the resulting mixture was gently refluxed for 15 h. After the solvent had been removed by evaporation, acetic acid (36 cm^3), water (36 cm^3) and conc. HCl (5.7 cm^3) were added, and the mixture was refluxed for 30 min. The resultant reaction mixture was then neutralized with 10% Na_2CO_3, extracted with CH_2Cl_2, dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica gel with benzene–hexane (1 : 1) as the eluent to give 3,5-diiodobenzaldehyde in 47% yield (2.94 g, 8.21 mmol). Recrystallization from hexane gave colourless needles, mp 131–132 °C; δ_H ($CDCl_3$) 8.15 (2 H, d, *J* 1.5, ArH), 8.30 (1 H, t, *J* 1.5, ArH) and 9.83 (1 H, s, CHO).

1,3-Dihydroxy-2-(3,5-diiodophenyl)-4,4,5,5-tetramethyl-2-imidazoline

A solution of 3,5-diiodobenzaldehyde (2.94 g, 8.21 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane (1.80 g, 12.1 mmol)[20] and 2,3-bis(hydroxyamino)-2,3-dimethylbutane monosulfate salt (20 mg)[20] in MeOH (40 cm^3)–THF (20 cm^3) was stirred at room temperature for 3 days. The solvent was then evaporated, and addition of methanol (30 cm^3) and water (15 cm^3) gave crystals of the desired imidazoline in 93% yield (3.74 g, 7.66 mmol) as a crude product. The imidazoline was used in the following reaction without purification. Recrystallization of the crude product from benzene gave colourless plates in 55% yield (2.21 g, 4.52 mmol), mp 226–227 °C; $\delta_H(CDCl_3)$ 1.09 (6 H, s, Me), 1.15 (6 H, s, Me), 4.54 (1 H, s, NCHN), 7.90 (2 H, d, *J* 1.4, ArH) and 7.97 (1 H, t, *J* 1.4, ArH) (Found: C, 32.0; H, 3.8; N, 5.7. $C_{13}H_{18}I_2N_2O_2$ requires C, 31.99; H, 3.72; N, 5.74%).

2-(3,5-Diiodophenyl)-4,4,5,5-tetramethyl-3-oxido-2-imidazolin-3-ium-1-yloxyl 5

The imidazoline (0.60 g, 1.23 mmol) was dissolved in benzene (50 cm^3)–EtOH (10 cm^3) with stirring. To this stirred solution, K_2CO_3 (6.0 g) and PbO_2 (6.0 g) were added. After stirring for 30 min, the resulting dark blue reaction mixture was filtered and the filtrate was evaporated under reduced pressure to give dark blue powder or needles containing a small amount of white by-products. This dark blue solid was then refluxed for 5 min in hexane (20 cm^3) and the hexane was discarded by decantation. Recrystallization of the residue from hexane–benzene gave **5** as dark blue needles in 45% yield (0.268 g, 0.552 mmol). The use of the pure imidazoline also gave **5** in 62% yield, mp 205–207 °C; a_N (benzene)/mT 0.747 (*g* 2.0067); $\lambda_{max}(CH_2Cl_2)$/nm 633 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 300sh), 592 (340), 371 (14600) and 357 (7750) (Found: C, 32.4; H, 3.3; N, 5.7. $C_{13}H_{15}I_2N_2O_2$ requires C, 32.19; H, 3.12; N, 5.78%).

Polycondensation of 4 with 5

In a two-necked flask was placed **4** (80 mg, 0.38 mmol), **5** (183 mg, 0.38 mmol), $(PPh_3)_2PdCl_2$ (13.3 mg, 0.018 mmol), CuI (1.5 mg, 0.0078 mmol), Et_3N (2.3 cm^3) and pyridine (9.2 cm^3). After the flask had been charged with nitrogen, the mixture was stirred at room temperature (*ca.* 20 °C) for 2–6 h under nitrogen. The reaction mixture was then poured into a large amount of methanol, and the light blue powder deposited was collected by filtration and dried *in vacuo*. The results of the polycondensation are summarized in Table 1.

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