

# *m*-Phenylene-Linked Aromatic Poly(aminium cationic radical)s: Persistent High-Spin Organic Polyradicals

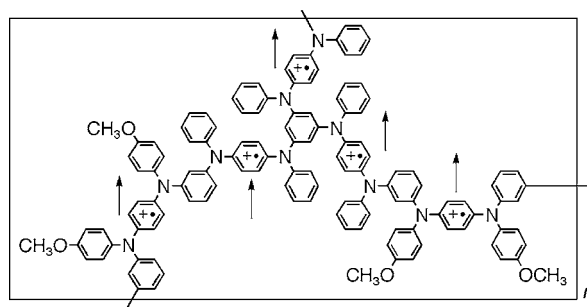
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Received April 11, 2003

## ABSTRACT



High molecular weight and networked aromatic polyamines prepared by palladium-catalyzed polycondensation were oxidized to yield the corresponding poly(aminium cationic radical)s, which displayed a substantial stability and an intramolecular ferromagnetic interaction of eight or nine spins.

High-spin polyradicals have been extensively investigated as possible candidates for organic ferromagnetic materials.<sup>1</sup> The design of such molecules is based on the precise connectivity of robust spin sources and non-disjointed couplers in a  $\pi$ -conjugated polymer. It was recently reported that the highly cross-linked polyradical with a triarylmethine radical as a spin source showed a very large magnetic moment and magnetic ordering at low temperature.<sup>2</sup> However, the triarylmethine radical can survive only below 200 K, so chemically stable radical species are desired in such a networked polyradical to raise the magnetic ordering temperature and provide feasibility as a material. Aromatic polyamines are an attractive material for this purpose because the aromatic amines are expected to be a prominent spin carrying site with both a substantial chemical stability even

at room temperature and large spin polarization after a one-electron removal.<sup>3</sup> A series of oligoradicals have been synthesized to evaluate the radicals,<sup>4,5</sup> and *p*-phenylenediamine-based cationic radicals were found to be more stable than the triarylammonium cationic radicals.<sup>6</sup> The attempted integration of the *p*-phenylenediamine-based cationic radical into linear and two-dimensional polyradicals was tried;<sup>7</sup> however, there has been no report on a successful radical generation to yield the chemically stable and high-spin poly(aminium cationic radical)s. By adjusting the monomer geometry and the feed ratio during the polycondensation and utilizing the effect of trifluoroacetic acid (TFA) on aromatic polyamines, we now prepared, for the first time, two-dimensional networked and persistent polyradicals, in which *p*-phenylenediamine-based cationic radicals effectively interacted through 1,3-phenylene or 1,3,5-benzenetriyl couplers

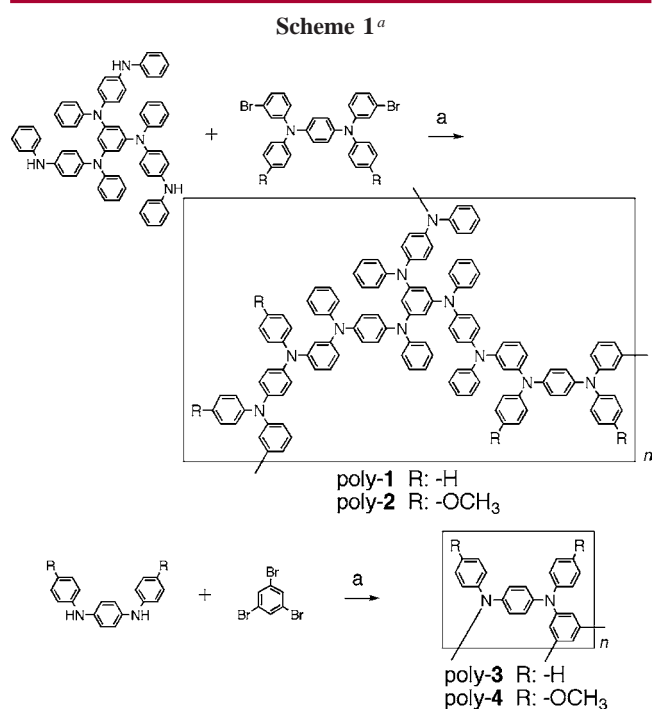
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to bring about their innate high-spin character with an average spin quantum number ( $S$ ) of 8/2 to 9/2.

The networked aromatic polyamines were prepared by using the palladium-catalyzed amination of two multifunctionalized monomers (Scheme 1). The bifunctionalized



<sup>a</sup> Reagents and conditions: (a) Pd<sub>2</sub>(dba)<sub>3</sub>, P(*t*-Bu)<sub>3</sub>, NaOtBu, toluene, 100 °C, 24 h.

monomer and the trifunctionalized monomer were reacted in toluene at 100 °C for 24 h with Pd<sub>2</sub>(dba)<sub>3</sub> and P(*t*-Bu)<sub>3</sub> as the catalyst and ligand, respectively. The monomer feed ratio was maintained at [sec-amine]/[bromide] = 1/2 so as not to include any *sec*-amines as a terminal group whose corresponding radicals are known to be unstable, but to yield a

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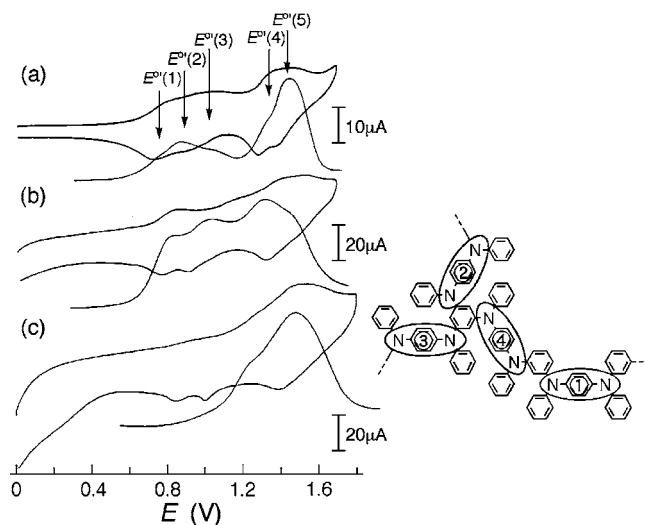
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polymer with a preferably higher molecular weight and bearing all the terminal bromide groups.<sup>8</sup> Although the reaction of *N,N'*-diaryl-*p*-phenylenediamine and 1,3,5-tribromobenzene gave a yellow gel and trace amounts of a soluble fraction with the number average molecular weight ( $M_n$ ) of  $<3.0 \times 10^3$  measured by GPC (THF eluent, calibrated by polystyrene standards), that of the trifunctionalized *sec*-amine monomer and the aryl dibromide yielded solvent-soluble but high molecular weight polymers, poly-1 and poly-2, with  $M_n$  (degree of dispersion) values of  $1.6 \times 10^4$  (4.8) and  $6.5 \times 10^3$  (1.5), respectively. This result suggests that the monomer geometry is also one of the most important factors in producing a soluble polymer.

The IR and NMR spectra of these soluble polymers substantiated their structures. In the <sup>13</sup>C NMR spectrum of poly-1, 9 very weak absorptions ascribed to the terminal triarylamine moieties appeared beside the 15 well-defined ones in the region of the quaternary carbon adjacent to a nitrogen atom, which indicated the presence of three kinds of terminal structures under chemically different environments (see Supporting Information). The MALDI-TOF mass spectrum provided further evidence. All observed signals corresponded to the proton adduct of the polymer with all bromide terminal groups but not *sec*-amines, and some of them were consistent with the formation of cyclic products, which would lead to the restricted conformation of the polymer chain. This result supported the idea of three kinds of terminal structures for this polymer and the formation of the anticipated networked polymer.

Cyclic voltammetry of the polymers in CH<sub>2</sub>Cl<sub>2</sub> showed completely reversible oxidation and reduction waves at room temperature (Figure 1). The generated cationic radicals were stable enough even in the polymer framework to be further one-electron oxidized from each *p*-phenylenediamine site.



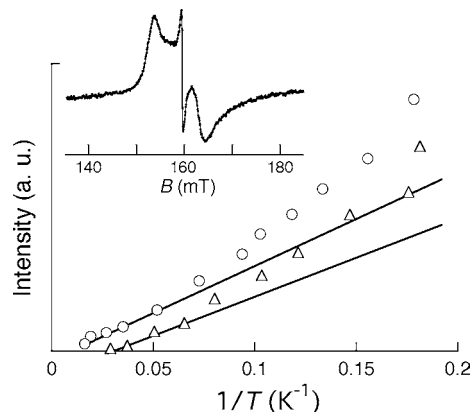
**Figure 1.** Cyclic voltammograms and differential pulse voltammograms of poly-1 (1 mM/radical unit) in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub> at room temperature, at 100 mV s<sup>-1</sup> scan rate: (a) without TFA, (b) with 1 vol % of TFA, and (c) with 5 vol % of TFA. Potential vs Ag/AgCl.

Differential pulse voltammetry of the polymers displayed unequivocal waves step by step. For poly-1, the oxidation–reduction potentials  $E^{\circ}(1) - E^{\circ}(3)$  at 0.78, 0.93, and 1.03 V (vs Ag/AgCl) are attributed to the redox between the amine and the aminium cationic radical, and their potential difference reflects a strong spin-exchange interaction between adjacent radicals. The potentials  $E^{\circ}(4)$  and  $E^{\circ}(5)$  at 1.33 and 1.42 V, respectively, represent the subsequent oxidation from the aminium cationic radical to the bication (Figure 1a). The UV/vis spectra of the electrolytic solution indicated the generation of the poly(aminium cationic radical) without any side reaction for all polymers and any deposition of the poly(bication) for poly-2 (see Supporting Information). The  $E^{\circ}(4)$  of poly-2 (1.16 V) was so low that it was easy to produce the soluble poly-2 containing aminium cationic radical and some bication moieties, which enabled us to examine the magnetic property of the polyradical with various electronic states as will be discussed below.

The exact assignment of the potentials to the polymer structures in  $\text{CH}_2\text{Cl}_2$  was ascertained by the addition of TFA to the electrolyte solution. TFA is known to undergo protonation at the aromatic ring of non-Kekulé type arylamines.<sup>5,9</sup> For poly-1 and poly-2, the addition of 1 vol % of TFA resulted in the anodic shift of  $E^{\circ}(2)$  and  $E^{\circ}(3)$ , while  $E^{\circ}(1)$  did not shift (Figure 1b). The 1,3,5-benzenetriamine is supposed to be protonated prior to the 1,3-benzenediamine moiety because it has more tautomeric intermediates in the protonated form and has an essentially high nucleophilicity. The oxidation potential of an amine group adjacent to the protonated moiety would anodically shift due to an electrostatic repulsion. The addition of 5 vol % of TFA brought about the anodic shift of the  $E^{\circ}(1)$  potential besides  $E^{\circ}(2)$  and  $E^{\circ}(3)$  to yield a fused unimodal oxidation wave: This also supports the protonation of the 1,3-benzenediamine moiety (Figure 1c). Thus the redox at  $E^{\circ}(1)$  in  $\text{CH}_2\text{Cl}_2$  results from the *p*-phenylenediamine residue (①) interposed between two *m*-phenylene couplers, and  $E^{\circ}(2)$  and  $E^{\circ}(3)$  in  $\text{CH}_2\text{Cl}_2$  are attributable to the stepwise redoxes of the *p*-phenylenediamines (②–④) connected to 1,3,5-benzenetriamine. This was also supported by the fact that the overall potentials of poly-3 and poly-4, which have only 1,3,5-benzenetriyl couplers, anodically shifted with the addition of only 1 vol % of TFA.

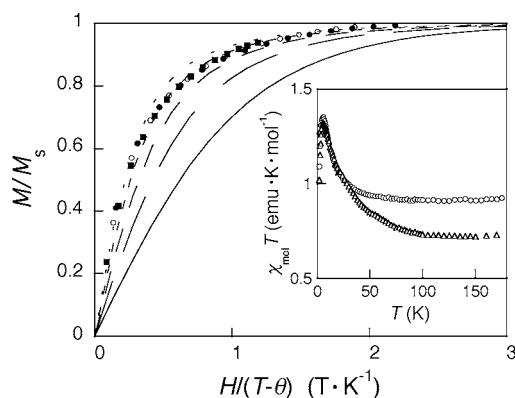
The chemical oxidation of poly-1 and poly-2 with  $\text{NOPF}_6$  solubilized in  $\text{CH}_2\text{Cl}_2$  with a minimum amount of 18-crown-6 also gave the corresponding poly(aminium cationic radical)s. The ESR spectra at room temperature were composed of a broad singlet line at  $g = 2.003$ , which is characteristic of aminium cationic radicals. The addition of a small amount of TFA to the  $\text{CH}_2\text{Cl}_2$  solution dramatically improved the spin concentration and chemical stability of the polyradicals.<sup>10</sup> The half-life of the polyradical of poly-1 estimated by ESR at room temperature was 1 week in a  $\text{CH}_2\text{Cl}_2/\text{TFA}$  (95/5 vol %) solution under nitrogen, which is extremely persistent among the  $\pi$ -conjugated organic polyradicals re-

ported up to now. ESR of the polyradicals at low temperature clearly showed a  $\Delta M_s = \pm 2$  forbidden transition with a fine structure, indicating multiplet states at least higher than a triplet. The temperature dependence of these signals revealed the ferromagnetic interaction between adjacent radicals and the multiplet ground state for the polyradicals (Figure 2).



**Figure 2.** Temperature dependence of the  $\Delta M_s = \pm 2$  signal intensity for the polyradicals of poly-1 (○) and poly-2 (Δ) in  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{COOH}/(\text{CF}_3\text{CO})_2\text{O}$  (91/8.5/0.5 vol %). Inset: ESR  $\Delta M_s = \pm 2$  spectrum for the polyradical of poly-2 at 5.6 K.

The magnetization and static magnetic susceptibility of the polyradicals in the frozen media including TFA were measured with a SQUID magnetometer. The magnetization normalized with saturated magnetization,  $M/M_s$ , plots for the polyradicals of poly-1 and poly-2 with a spin concentration of 0.66 and 0.75, respectively, were very close to the theoretical Brillouin curve for  $S = 10/2$  at low fields and lay on the curve for  $S = 7/2$  at high fields (Figure 3).<sup>11</sup> The



**Figure 3.** Normalized plots of magnetization ( $M/M_s$ ) vs the ratio of magnetic field and temperature ( $H/(T - \theta)$ ) for the polyradical of poly-2 with a spin concentration of 0.75 in  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{COOH}/(\text{CF}_3\text{CO})_2\text{O}$  (91/8.5/0.5 vol %) at  $T = 2.5$  (●), 3 (○), and 5 (■) K and theoretical curves corresponding to the  $S = 2/2, 4/2, 6/2, 8/2,$  and  $10/2$  Brillouin functions. Inset:  $\chi_{\text{mol}}T$  vs  $T$  plots for the polyradicals of poly-1 (○) and poly-2 (Δ) with a spin concentration of 0.66 and 0.75, respectively.

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spin concentration was determined by the saturated magnetization of the weighed polyradical. Plots of the product of the unit molar magnetic susceptibility ( $\chi_{\text{mol}}$ ) and temperature ( $T$ ) vs  $T$  for these polyradicals are shown in the inset of Figure 3. The  $\chi_{\text{mol}}T$  values were much higher than the theoretical value of 0.375 for  $S = 1/2$  below 180 K and increased below 50 and 100 K for the polyradicals of poly-1 and poly-2, respectively, reaching 1.30 for  $S = 8.4/2$  at 5 K. This indicates a ferromagnetic coupling, on average, between eight or nine unpaired electrons in these polymers at low temperature. The values at higher temperature are supposed to reflect the effective extension of a  $\pi$ -conjugated system in each polyradical framework.<sup>12</sup>

However, the  $S$  value seems to be overestimated, taking into account the cross-conjugated structure of the polyradicals and the spin concentration. Janssen et al. reported the specific change in the intervalence band during the oxidation of  $N,N',N''$ -tris[4-(diphenylamino)phenyl]- $N,N',N''$ -triphenyl-1,3,5-benzenetriamine or the constituent of the present polymers,<sup>5</sup> from which we can find the possibility that the corresponding mono- or bis(aminiium cationic radical) tends to disproportionate into the corresponding triradical. If this is also the case for the 1,3,5-benzenetriamine moiety in poly-1 and poly-2, the generated radicals will assemble together to form local spin clusters in the polyradicals. The electrochemical measurement of the polymers in the presence

(10) The chemical oxidation of the polymers in  $\text{CH}_2\text{Cl}_2$  often resulted in the production of a dark gel with a short half-life (e.g., 3 h for the polyradical of poly-1) even if  $<1.0$  equiv of the oxidant was added. The position protonated by TFA seems to be overlapped with the spin density distribution of the aminiium cationic radical, which prevents the intra- or intermolecular dimerization of the radicals.

(11) For a dispersed spin system, the  $M/M_s$  plots tend to decrease at high fields due to low  $S$  fractions.

of 5 vol % of TFA definitely supported the polyradical generation via multielectron oxidation in one step. Furthermore, the cyclic structure in the networked polymers would effectively act to compensate the radical defects with multiple pathways. To verify these assumptions, 0.4 equiv of  $\text{NOPF}_6$  was used in the oxidation of poly-2 under the same conditions. The resulting polyradical showed as high an  $S$  value of 8/2 to 9/2 even with a spin concentration of 0.33 as the same sample with a spin concentration of 0.75.<sup>13</sup> This result strongly supports the idea of radical assembly to provide the observed high  $S$  value for the polyradicals.

**Acknowledgment.** This work was partially supported by Grants-in-Aid for COE Research “Practical Nano-Chemistry” and “Molecular Nano-Engineering” from MEXT, Japan. T.M. acknowledges the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

**Supporting Information Available:** Synthesis and characterization for the monomers and the polymers, UV/vis spectra during electrolytic oxidation of the polymers, and corrections of the magnetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Atomic force microscopy measurement of poly-1 on mica at room temperature clearly revealed that an average vertical distance of the single polymer (about 500 samples) decreased from 1.43 to 0.83 nm after the chemical oxidation, indicating the higher  $\pi$ -coplanarity for the polyradical.

(13) The  $S$  value of the polyradical oxidized with 2.0 equiv of  $\text{NOPF}_6$  in the presence of 9 vol % of TFA reasonably decreased to 3/2 with a spin concentration of 0.38. The addition of TFA is essential for the present results and discussion, because the polyradical with a low spin concentration oxidized in the absence of TFA only displayed  $S = 1/2 - 2/2$ , consistent with the electrochemical measurements. However, the possibility of the magnetic impurities in TFA was ruled out from the magnetic measurement of the background media including TFA.