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ORIGINAL ARTICLE

Two-dimensionally extended organic high-spin poly(aminium cationic radical)s and their magnetic force microscopic images

Tsuyoshi Michinobu[1,2], Jun Inui[1] and Hiroyuki Nishide[1]

Purely organic high-spin poly(aminium cationic radical)s of two-dimensionally extended soluble aromatic polyamines P1 and P2 were prepared by the palladium-catalyzed polycondensation of two multifunctional monomers, followed by chemical or electrochemical oxidations. The chemical structures of the precursor polyamines were fully characterized by [1]H- and ^{13}C nuclear magnetic resonance (NMR), infrared and MALDI-TOF mass spectra (MS). The aminium radical sites of N,N,N',N'-tetraaryl-p-phenylenediamines were connected through the m-phenylene ferromagnetic coupler, which satisfies the non-Kekulé-type molecular design. Oxidation of radical sites was facilitated by electron-donating methoxy substituents. The first oxidation potential ($E^{o'}(1)$) of P2 with methoxy substituents, evaluated from the cyclic voltammograms in CH_2Cl_2, was 0.69 V (vs Ag/Ag$^+$), whereas the $E^{o'}(1)$ of P1 without electron-donating substituents was 0.78 V. This result was further verified by spectroelectrochemistry measurements. The electrochemically oxidized P2 displayed a more intense low-energy band at ca. 800 nm ascribed to aminium cationic radicals and bications. Chemical oxidation of P1 and P2 with NOPF$_6$ solubilized with 18-crown-6 in CH_2Cl_2 gave the corresponding poly(aminium cationic radical)s. The high-spin ground states were confirmed by the temperature dependence of forbidden electron spin resonance (ESR) transition peak intensities, and the average spin quantum number (S) determined by the magnetic curves reached 8.4/2 at low temperatures. Remarkably, when a small amount of trifluoroacetic acid was added, the half-life of polyradicals reached ca. 1 week at room temperature (RT). This result prompted us to observe the single polymer-based molecular and magnetic images by atomic force microscopy and magnetic force microscopy, respectively. The precursor polyamine P1 showed globular-shaped polymer particles with an average vertical distance of 1.43 nm. After chemical oxidation, the vertical distance of P1 definitely decreased, reflecting the improved p-type character of the nitrogen atoms. Moreover, the detection of weak MFM images supported the presence of magnetic spins in the single polymers.
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INTRODUCTION

In the last two decades, considerable synthetic efforts have been devoted toward purely organic high-spin polyradicals that show magnetic behavior.[1–3] Previous studies demonstrated the importance of molecular design on the basis of the non-Kekulé and nondisjoint rule, as well as the selection of radical sources. π-Conjugated polyradicals precisely prepared according to the non-Kekulé and nondisjoint rule show a very high spin quantum number (S) in proportion to the degree of polymerization.[4–6] Two- or three-dimensionally extended polymer structures, such as hyperbranched polymers or dendrimers, are generally superior to the corresponding linear ones, because of the increasing number of unpaired electrons and multidimensional magnetic interactions.[7] In particular, it is straightforward to introduce networked or macrocyclic structures in hyperbranched polymers for multiple pathways of spin exchange interactions using

the self-polycondensation of AB2-type monomers or polycondensation between two multifunctional monomers.[8] This molecular design could excellently solve the radical defect problem. Rajca et al.[9,10] reported the most successful result of this approach by using highly crosslinked triarylmethine-based neutral polyradicals that displayed an S-value of > 40 for the soluble fraction and an S-value of ∼5000 for the higher-molecular-weight insoluble gel. However, one significant disadvantage of these remarkable polyradicals is that triarylmethine radicals are stable only below 200 K and rapidly decompose at room temperature (RT). To apply organic polyradicals to practical uses, more chemical stable radical sources are desired.

Along with others, we have been pursuing the possibilities of aromatic amine-based cationic radicals (aminium cationic radicals) as a persistent radical source.[11–35] Our recent examples include triarylamine-based high-spin oligo- and poly(cationic radical)s,[36–41]

[1]Department of Applied Chemistry, Waseda University, Tokyo, Japan and [2]Global Edge Institute, Tokyo Institute of Technology, Tokyo, Japan
Correspondence: Professor H Nishide, Department of Applied Chemistry, Waseda University, Shinjuku, Tokyo 169-8555, Japan.
E-mail: nishide@waseda.jp

polymer gels of *p*-phenylenediamine-based cationic radicals,[42] as well as their applications to organic devices.[43,44] During the course of this series of studies, we have shown an RT ground state multiplet polyradical using a poly[1,2,(4)-phenylenevinyleneanisylaminium] hyperbranched structure, prepared by a tedious multistep synthesis of the AB2-type monomer, followed by self-polycondensation and terminal protection.[45] This triarylamine-based cationic polyradical displayed a remarkable thermal stability even at 70 °C. Because it is generally known that *p*-phenylenediamine-based cationic radicals are more stable than triarylamine-based cationic radicals, we became interested in designing new soluble but networked *p*-phenylenediamine-based poly(cationic radical)s. In this paper, we report the efficient synthesis of two-dimensionally extended aromatic polyamines containing partial network structures by polycondensation between bi- and trifunctional monomers, and the magnetic properties of the corresponding poly(aminium cationic radical)s.[46] Compared with previous triarylamine-based poly(cationic radical)s, the synthetic route is simple and enhanced chemical stability is expected. To reveal the remarkable stability of the generated poly(cationic radical)s under ambient conditions, we used magnetic force microscopy (MFM) as a relatively new technique for detecting nm- to µm-sized weak paramagnetism.

EXPERIMENTAL PROCEDURE
Materials
All reagents were obtained from Kanto (Tokyo, Japan), Wako (Osaka, Japan), Tokyo Kasei (Tokyo, Japan) and Aldrich (St Louis, MO, USA), and used without further purification. Solvents for the reactions were distilled before use. *N,N'*-Bis(4-methoxyphenyl)-1,4-phenylenediamine (2) was prepared according to the method described in literature.[47]

Measurements
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of monomers were measured on a JEOL 500 spectrometer (JEOL, Tokyo, Japan) at 20 °C. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer (JASCO, Tokyo, Japan). Gel permeation chromatography was measured on a Tosoh LS-8000 instrument (Tosoh, Tokyo, Japan) using tetrahydrofuran as an eluent. MALDI-TOF mass spectra (MS) were measured with a Shimadzu/Karatos AXIMA-CFR (Shimadzu, Kyoto, Japan) using dithranol as a matrix. Thermogravimetric analysis was carried out under N_2 flow on a Rigaku Thermoplus TG8120 (Rigaku, Tokyo, Japan), at the heating rate of 10 °C min^{-1} between 20 and 1000 °C. Differential scanning calorimetry measurements were carried out on a Rigaku Thermoplus DSC8230 equipped with a liquid N_2 controller. Ultraviolet-visible spectra were recorded on a JASCO V-550 spectrophotometer at 20 °C. For the electrolytic oxidation of polymers, an optically transparent thin-layer platinum working electrode, a commercial Ag/AgCl electrode as the reference and a platinum wire as the counter were placed in a special cell with a 2 mm light-path length. Polymer solutions in CH_2Cl_2 (83 µM per radical unit) with 0.1 M $(nC_4H_9)_4NBF_4$ were placed in the cell and the solution was kept under N_2. A potentiogalvanostat Nikko Keisoku NPGS-301 (Nikko Keisoku, Atsugi, Japan) was then used for potential application. Cyclic voltammetry measurements were carried out with a glassy carbon electrode as a working electrode using a function generator Nikko Keisoku NPG-3 and potentiogalvanostat NPGS-301 under flowing Ar at the scanning rate of 0.1 V s^{-1}. All measurements were determined in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$ as the supporting electrolyte. Electron spin resonance (ESR) spectra were taken using a JEOL JES-2XG ESR spectrometer with 100 kHz field modulation.

Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer (Quantum Design Inc., San Diego, CA, USA). After chemical oxidation, the solution samples of poly(aminium cationic radical)s were transferred to a quartz tube in a glove box. The tube was sealed off and then subjected to magnetic measurements. Magnetization was measured from 0.5 to 7 T at 2.5, 3 and 5 K. Static magnetic susceptibility was measured from 2 to 200 K at a field of 0.5 T. Ferromagnetic

magnetization ascribed to the impurities was determined by Honda–Owen plots. Although the quantity was very low, it was subtracted from the overall magnetization. Diamagnetic susceptibility of the sample solution and of a part of the tube was estimated by the Curie plots of magnetic susceptibility, which almost agreed with the value calculated from the Pascal constant of the solvent.

Atomic force microscopy (AFM) and MFM measurements were determined using a Nanoscope IIIa multimode AFM/MFM microscope (Digital Instruments Inc., Santa Barbara, CA, USA). A drop of dilute CH_2Cl_2 solution of polyradicals (0.2 mg l^{-1}) was transferred onto a mica surface, and the solvent was carefully blotted off by air drying. Approximately 200 samples were collected for the statistical analysis of each polymer. Tapping-mode AFM using a Si probe (type TESP) was applied to estimate the horizontal and vertical distances of the polymers. MFM images were presented as an amplitude or phase shift acquired with the Lift Mode technique. The scan lift height was controlled by the scanning parameters, assuming that the sensitivity of the cantilever was 0.03 V nm^{-1}. A commercially available MFM probe (type MESP) coated with a ferromagnetic CoCr alloy possessing a magnetic moment of 10^{-13} EMU was used, which was magnetized in the direction perpendicular to the sample surface.

Monomer synthesis
N,N'-*Bis(3-bromophenyl)-N,N'-diphenyl-1,4-phenylenediamine (3)*. *N,N'*-Diphenyl-1,4-phenylenediamine (1) (1.0 g, 3.8 mmol) and 1,3-dibromobenzene (9.1 g, 38 mmol) were dissolved in 38 ml of toluene. Sodium *t*-butoxide (NaO*t*Bu) (1.1 g, 12 mmol), Pd(OAc)$_2$ (35 mg, 0.16 mmol) and 1,1'-bis(diphenylphosphino)-ferrocene (DPPF) (0.17 g, 0.31 mmol) were added to the solution, and the reaction mixture was stirred at 110 °C for 24 h under N_2. After cooling to RT, the mixture was treated with saturated aqueous NH_4Cl (300 ml) and extracted with CH_2Cl_2. After washing the organic phase with brine, the crude product was purified by flash column chromatography (SiO$_2$, hexane/EtOAc 20:1) to yield the desired compound as a white solid (1.2 g, 53%).

^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 6.66 (t, *J*=8 Hz, 2 H), 6.80 (s, 4 H), 6.80–7.01 (m, 14 H), 7.36 (t, *J*=2 Hz, 2 H); ^{13}C NMR (125 MHz, C_6D_6, 298 K) δ 121.72, 123.34, 123.82, 124.97, 125.26, 125.87, 126.00, 129.74, 130.71, 143.00, 147.39, 149.71 p.p.m.; EI-MS: *m/z* 568, 570, 572 ([M–2]$^+$, M$^+$, [M+2]$^+$); elemental analysis calculated (%) for $C_{30}H_{22}Br_2N_2$ (570.01): C 63.2, H 3.9, N 4.9; found: C 64.0, H 3.9, N 4.6.

N,N'-*Bis(3-bromophenyl)-N,N'-bis(4-methoxyphenyl)-1,4-phenylenediamine (4)*. A solution of 2 (0.37 g, 1.2 mmol) and 1,3-dibromobenzene (2.8 g, 12 mmol) in toluene (12 ml) was reacted at 110 °C for 37 h in the presence of NaO*t*Bu (0.34 g, 3.5 mmol), Pd(OAc)$_2$ (11 mg, 0.049 mmol) and DPPF (52 mg, 0.093 mmol). Column chromatography (SiO$_2$, hexane/EtOAc) yielded the desired compound (66%).

Melting point 156 °C ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 3.25 (s, 6 H), 6.63 (dd, *J*=3, 9 Hz, 4 H), 6.69 (t, *J*=8 Hz, 2 H), 6.87 (dd, *J*=2, 8 Hz, 2 H), 6.89 (s, 4 H), 6.91–6.96 (m, 6 H), 7.39 p.p.m. (t, *J*=2 Hz, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ 54.93, 115.38, 120.06, 123.43, 124.20, 124.37, 125.26, 127.96, 130.65, 140.12, 143.00, 150.32, 157.30 p.p.m.; EI-MS: *m/z* 628, 630, 632 ([M–2]$^+$, M$^+$, [M+2]$^+$); elemental analysis calculated (%) for $C_{32}H_{26}Br_2N_2O_2$ (630.37): C 61.0, H 4.2, N 4.4; found: C 61.8, H 3.8, N 4.0.

N,N',N''-*Tris(4-(phenylamino)phenyl)-N,N',N''-triphenyl-1,3,5-benzenetriamine (6)*. 1,3,5-Tribromobenzene (0.74 g, 2.3 mmol) and 1 (5.5 g, 21 mmol) were dissolved in 23 ml of toluene. NaO*t*Bu (1.0 g, 11 mmol), Pd(OAc)$_2$ (16 mg, 0.073 mmol) and P(*t*Bu)$_3$ (57 mg, 0.28 mmol) were added to the solution, and the reaction mixture was stirred at 100 °C for 22 h under N_2. After cooling to RT, the mixture was quenched by aqueous ammonia (20 ml) and taken up in ether. The organic phase was evaporated, and the crude product was washed with methanol (1000 ml) and was then purified by flash column chromatography (SiO$_2$, hexane/EtOAc 3:1) to yield the desired compound as a milky white solid (0.32 g, 16%).

Melting point 88 °C ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 4.92 (br s, 3 H), 6.67–7.20 p.p.m. (m, 45 H); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ 111.86, 117.31, 119.95, 120.61, 122.33, 123.62, 127.05, 129.31, 129.52, 139.17, 141.28, 144.11, 148.11, 149.97 p.p.m.; EI-MS: *m/z* 853 (M$^+$); elemental analysis calculated (%) for $C_{60}H_{48}N_6$ (852.39): C 84.5, H 5.7, N 9.8; found: C 84.9, H 6.1, N 9.0.

Polymerization

P1. In a 10 ml ampule tube, **6** (0.149 g, 0.175 mmol) and **3** (0.298 g, 0.523 mmol), NaOtBu (76.9 mg, 0.800 mmol), Pd$_2$(dba)$_3$ (3.4 mg, 3.7 μmol) and P(tBu)$_3$ (4.3 mg, 21 μmol) were placed. After addition of toluene (0.88 ml), the tube was attached to a vacuum line, sealed off and then heated to 100 °C in an oil bath for 24 h. After cooling to RT, the crude product was treated with aqueous ammonia (5 ml) and extracted with CH$_2$Cl$_2$ (50 ml). The organic phase was concentrated and precipitated into methanol (50 ml) to yield the desired polymer as a yellow solid (0.156 g). Reprecipitation from CH$_2$Cl$_2$ or tetrahydrofuran into methanol was repeated until the oligomers were completely removed.

^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K) δ 6.67–7.38 p.p.m. (m); ^{13}C NMR (125 MHz, C$_6$D$_6$, 298 K) δ 112.17, 117.74, 117.92, 117.97, 118.88, 119.13, 121.53, 122.91, 122.98, 123.17, 123.40, 123.66, 124.30 (overlapped), 124.59, 124.78, 125.08, 125.58, 125.75, 125.96, 126.05, 126.22, 126.30, 129.43, 129.53, 129.78, 130.36, 130.78, 142.27, 142.54 (weak (w)), 142.91, 142.98, 143.09 (w), 143.16, 143.26, 143.51 (w), 143.93, 147.60, 147.72, 147.88, 148.01, 148.14 (w), 148.31 (w), 148.41 (w), 149.06, 149.15, 149.19, 149.36 (w), 149.47 (w), 149.78, 149.94, 150.03 (w) p.p.m.; MALDI-TOF MS: m/z 2932.5 (2 cyclic (c)), 3502.8 (1 c), 4073.5, 4683.6 (2 c), 5253.9 (1 c), 5824.5, 6433.9 (2 c), 7004.2 (1 c), 7574.3, 8183.4 (2 c), 8751.6 (1 c).

P2. In a 10 ml ampule tube, **6** (0.150 g, 0.176 mmol) and **4** (0.330 g, 0.524 mmol), NaOtBu (76.9 mg, 0.800 mmol), Pd$_2$(dba)$_3$ (3.4 mg, 3.7 μmol) and P(tBu)$_3$ (4.3 mg, 21 μmol) were placed. After addition of toluene (0.88 ml), the tube was attached to a vacuum line, sealed off and then heated to 100 °C in an oil bath for 24 h. After cooling to RT, the crude product was treated with aqueous ammonia (5 ml) and extracted with CH$_2$Cl$_2$ (50 ml). The organic phase was concentrated and precipitated into methanol (50 ml) to yield the desired polymer as a yellow solid (0.0824 g). Reprecipitation from CH$_2$Cl$_2$ or tetrahydrofuran into methanol was repeated until the oligomers were completely removed.

^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K) δ 3.27, 3.29, 3.31 (s, 12 H), 6.64–7.37 p.p.m. (m, 85 H); IR (KBr) $\nu_{(C-O-C)}$ 1241, 1036 cm^{-1}; MALDI-TOF MS: m/z 3193.4 (1c), 3825.8, 3967.1 (1c), 4595.6, 5146.7, 5694.8, 5838.3 (1c), 6467.4 (1c), 6936.6 (1c).

Chemical oxidation

A CH$_2$Cl$_2$ solution of NOPF$_6$ (22.9 mM) solubilized with a minimum amount (ca. 6 equivalent to NOPF$_6$) of 18-crown-6 was added to a CH$_2$Cl$_2$/CF$_3$COOH/(CF$_3$CO)$_2$O solution of polyamines under N$_2$ at 20 °C. The solution rapidly turned dark green but it was stirred for 5–10 min to complete the reaction. The final polymer concentration was adjusted to 10 mM per radical unit. A small amount of CF$_3$COOH (9 volume %) was added to stabilize the generated poly(cationic radical)s, and a much smaller amount of (CF$_3$CO)$_2$O (0.4 vol%) was used for dehydration.

RESULTS AND DISCUSSION

Polymer synthesis and characterization

p-Phenylenediamine-based multifunctional monomers **3**, **4** and **6** were prepared by a palladium-catalyzed amination reaction.[48–53] The suitable combination of catalyst and ligand was examined, and the use of P(tBu)$_3$ as a ligand was found to most effectively improve the reaction yields.[54] However, a part of the products was decomposed during column chromatography on silica gel because of the shallow HOMO levels. This effect became more pronounced when the number of nitrogen atoms increased. Thus, the yield of hexamine **6** was disappointingly low (16%).

The networked aromatic polyamines were also prepared by polycondensation between bifunctional monomer **3** or **4** and trifunctional monomer **6** using palladium-catalyzed amination reaction (Scheme 1). In a typical polymerization procedure, a mixture of the monomers in toluene was heated to 100 °C for 22–24 h in the presence of Pd$_2$(dba)$_3$, P(tBu)$_3$ and NaOtBu. The reaction time was determined by saturation of the molecular weight increase. The monomer feed ratio was maintained at [NH]/[Br]=1:2 so as not to include any NH
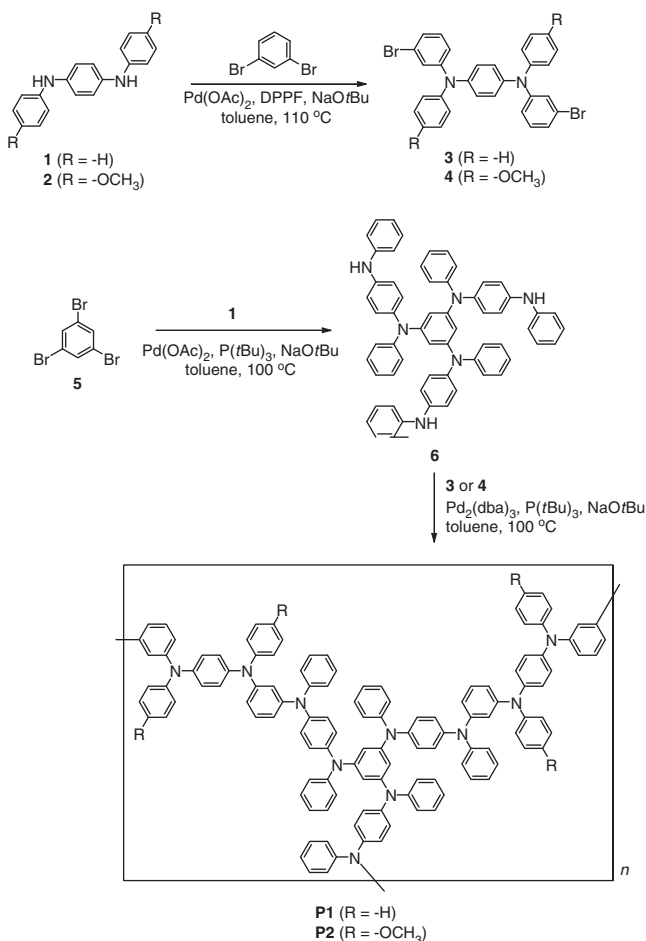
Scheme 1 Polymer synthesis by palladium-catalyzed polycondensation.

Table 1 Polymerization results and thermal properties

Polymer	Yield (%)	M$_w$[a]	M$_n$[a]	M$_w$/M$_n$[a]	T$_d$ (°C)[b]	T$_g$ (°C)[c]
P1	43	76800	16000	4.8	508	180
P2	22	10000	6500	1.5	383	160

Abbreviations: DSC, differential scanning calorimetry; GPC, gel permeation chromatography; TGA, thermogravimetric analysis; THF, tetrahydrofuran.
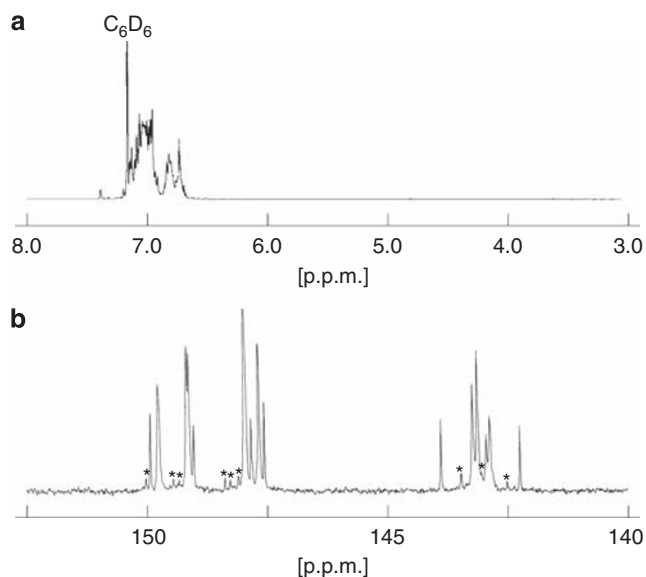[a]Determined by GPC (polystyrene standard, THF eluent).
[b]Temperature at which 5% decomposition occurred on heating, determined by TGA.
[c]Glass transition temperature determined by DSC.

terminals in the polymers, the corresponding radicals of which are unstable, but to yield a polymer with a preferably higher molecular weight. According to Flory's theory, this monomer feed ratio would provide very high-molecular-weight polymers with all bromine terminal groups.[55] The reaction of **3** and **6** yielded the soluble polyamine **P1** with a high molecular weight (M$_w$=76800, M$_n$=16000) (Table 1). A monomer combination of **4** and **6** also afforded the corresponding polyamine **P2**, but the molecular weight was lower than that of **P1** (M$_w$=10000, M$_n$=6500). The difference in molecular weight is assumed to reflect the different reactivity of aryl bromide in the palladium-catalyzed coupling reaction caused by the different electron density of the aryl groups.

The chemical structures of polyamines were characterized by ^{1}H- and ^{13}C-NMR, IR and MALDI-TOF MS. Figure 1a displays the ^{1}H-NMR spectrum of **P1** in C$_6$D$_6$ at 20 °C. Only aromatic proton peaks were observed, indicating the absence of NH groups as a
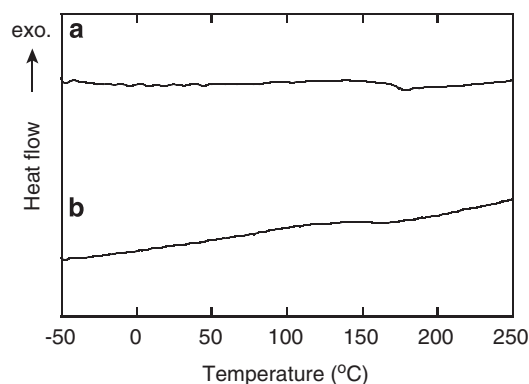
polymer terminal. IR spectra also supported this result. In the ^{13}C-NMR spectrum of **P1**, 15 well-defined peaks plus 9 very weak peaks appeared in the region of the quaternary carbons adjacent to a nitrogen atom (Figure 1b). The nine weak peaks are assumed to be ascribed to the terminal triarylamine moieties, suggesting three chemically different terminal structures enforced by the rigid network

structures. MALDI-TOF MS of **P1** and **P2** provided further evidence of macrocyclic structures (Figure 2). The intended molecular ion peaks of the polymer structures with all-bromide terminal groups were observed, and many of them contained macrocyclic structures, implying the formation of networked two-dimensional polymers.

The thermal properties of the polyamines were investigated by thermogravimetric analysis and differential scanning calorimetry measurements (Table 1). Both polymers showed high thermal stability with 5% weight loss temperatures (T_d) of 508 °C for **P1** and 383 °C for **P2**. The methoxy substituents tended to lower the thermal stability. These T_d values are slightly lower than those of the corresponding aromatic polyamine gels.[42] Thus, the networked structures most likely contributed to the enhancement of thermal stability. In contrast to aromatic polyamine gels, soluble polyamines exhibited a glass transition at 180 °C for **P1** and 160 °C for **P2** (Figure 3).

Figure 1 (a) ^{1}H NMR of **P1** and (b) ^{13}C NMR of **P1** in the region of the quaternary carbon atoms adjacent to nitrogen atoms in C_6D_6 at 20 °C. Marked peaks correspond to the terminal triarylamine moieties.

Figure 3 Differential scanning calorimetry thermograms (second heating scan) of (a) **P1** and (b) **P2** at the scanning rate of 10 °C min^{-1}.
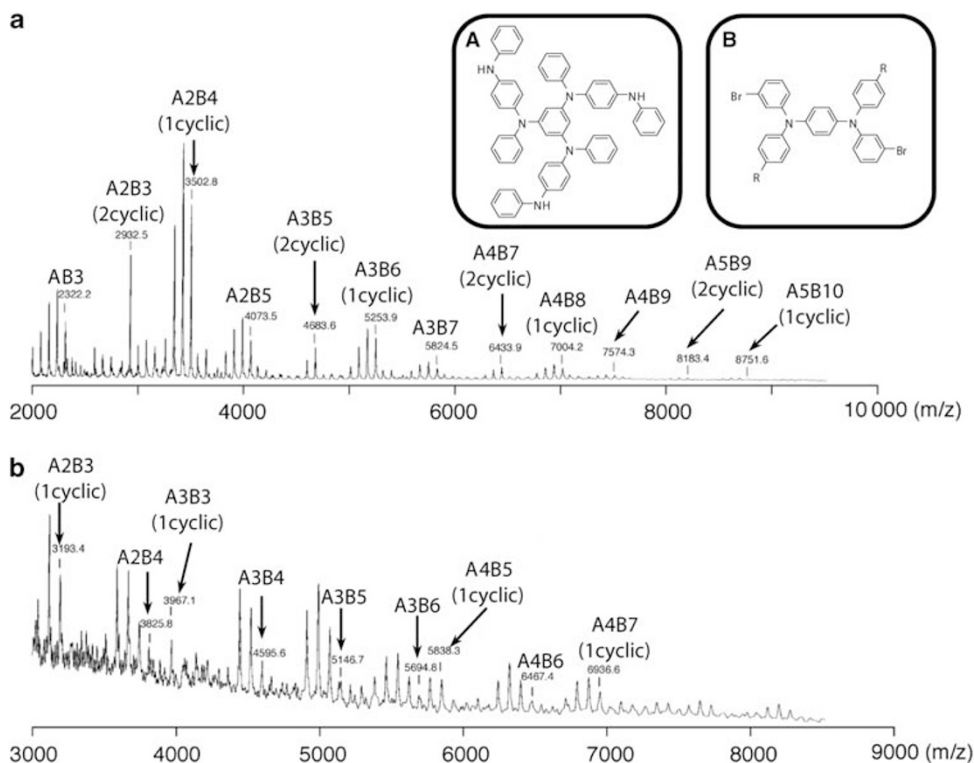
Figure 2 MALDI-TOF mass spectra of (a) **P1** and (b) **P2** (matrix: dithranol). A*m*B*n* represents polymer structures, in which A and B are **6** and **3/4**, respectively.
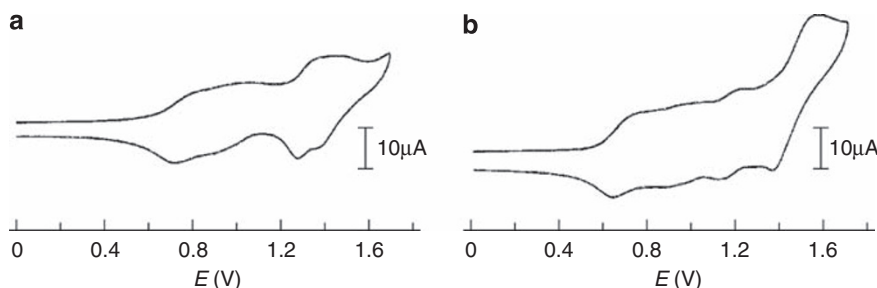
Figure 4 Cyclic voltammograms of (a) P1 and (b) P2 in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$ at the concentration of 1 mM per radical unit, measured at 20 °C and at a scanning rate of 0.1 V s^{-1}. Potentials vs Ag/AgCl.

Table 2 Cyclic voltammetry data of P1 and P2 in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$[a]

Polymer	$E^{o\prime}(1)$	$E^{o\prime}(2)$	$E^{o\prime}(3)$	$E^{o\prime}(4)$	$E^{o\prime}(5)$
P1	0.78	0.93	1.03	1.33	1.42
P2	0.69	0.92	1.01	1.16	1.45

[a]Potentials vs Ag/Ag$^+$. Fc/Fc$^+$=0.65 V. $E^{o\prime}(1)$–$E^{o\prime}(3)$ correspond to one-electron removal from neutral amine to cationic radical, whereas $E^{o\prime}(4)$ and $E^{o\prime}(5)$ represent the subsequent oxidation from the cationic radical to bication.
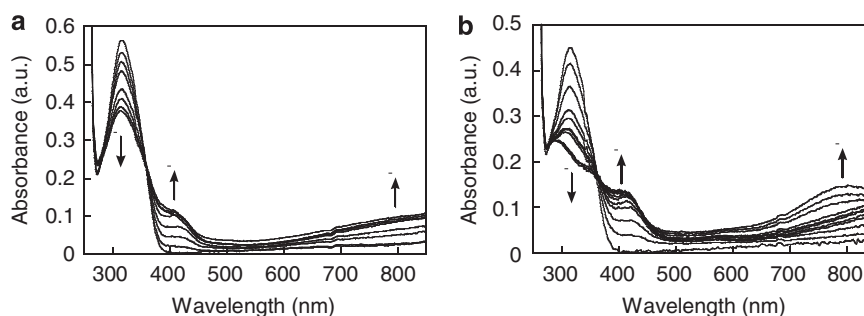
Figure 5 Ultraviolet-visible-NIR spectral change of (a) P1 and (b) P2 during the electrolytic oxidation of polymers at 83 μM per radical unit in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$ at 20 °C.

Radical generation

Generation of aminium cationic radicals was investigated by electrochemical and chemical methods. First, cyclic voltammetry was applied to estimate the oxidation potentials of the polyamines. Both polyamines displayed completely reversible oxidation waves in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$ at 20 °C (Figure 4). The stepwise oxidation implies electrostatic repulsion between the generated cationic radicals or strong spin exchange interactions within polyamines. The redox potentials are summarized in Table 2. The first oxidation potential $E^{o\prime}(1)$ of P2 was slightly lower than that of P1. The same behavior was observed for $E^{o\prime}(4)$. These results suggest that the first oxidations are derived from the one-electron removal from the neutral amine to the aminium cationic radical of the monomer unit 3 or 4, and the fourth ones are the further one-electron oxidation from the aminium cationic radical to the corresponding bication. Accordingly, $E^{o\prime}(2)$ and $E^{o\prime}(3)$ originate from the stepwise oxidation of monomer unit 6 to aminium cationic radicals, and $E^{o\prime}(5)$ corresponds to the overoxidation.

Spectroelectrochemistry of the polyamines was monitored at the given potentials in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NBF_4$ at 20 °C. Application of 1.0 V led to a gradual decrease in the initial absorption intensity at 316 nm for P1 and 317 nm for P2, and a new low-energy band appeared (Figure 5).[56,57] The presence of an isosbestic point at 358 nm for P1 and 364 nm for P2 indicates the generation of

poly(aminium cationic radical)s without any side reactions and any deposition during oxidation. When the applied voltage was increased to 1.4 V, the solution of P2 displayed a further spectral change accompanying a new peak at 792 nm. This peak maximum is ascribed to the generation of partial bications. In contrast, P1 could not be overoxidized under the same conditions, because of either higher molecular weight or the absence of methoxy substituents.
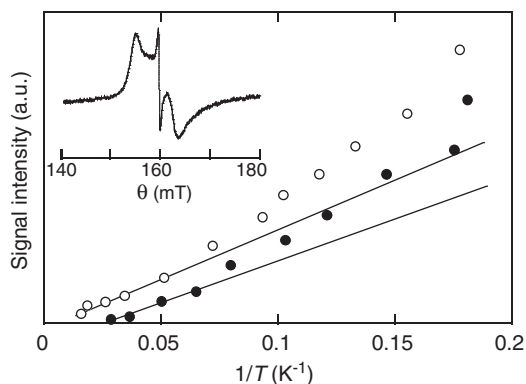
With these electrochemical results in mind, we optimized the chemical oxidation conditions. In this study, we selected NOPF$_6$ as the oxidant because it possesses a sufficiently high oxidation potential and the NO radicals generated through electron transfer from the amine center can readily be removed during chemical oxidation.[58] Although the solubility of NO salts in organic solvents is generally low, we fortunately found that they can be solubilized in chlorinated solvents such as CH_2Cl_2 in the presence of 18-crown-6, which ensures a homogeneous chemical oxidation. The amount and half-life of the generated radicals were estimated from the ESR intensities at g=2. Chemical oxidation of the polyamines afforded green-colored corresponding poly(aminium cationic radical)s. The ESR spectra were composed of a broad singlet line, which is characteristic of organic polyradicals. The g value of 2.003 suggests an amine-centered radical species. A small amount of trifluoroacetic acid was also found to stabilize the aminium cationic radicals.[59] Chemical oxidation of the

polyamines in CH_2Cl_2 sometimes resulted in the production of a dark gel with a short half-life (ca. 3 h). The positions protonated by trifluoroacetic acid are thought to be overlapped with the spin density distribution of the aminium cationic radicals, which successfully prevents the intra- or intermolecular dimerization of the radicals. Thus, the half-life of the polyradical of **P1** reached ca. 1 week at 20 °C in CH_2Cl_2/CF_3COOH (95/5 vol%).
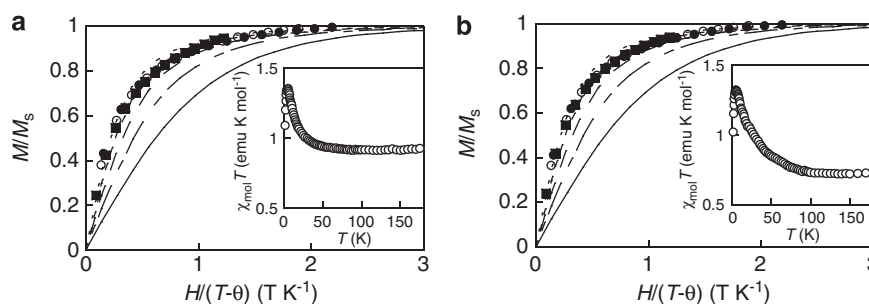
Magnetic measurements

The ESR forbidden transition at $g=4$ is ascribed to the triplet species. The ESR of polyradicals clearly showed such forbidden transition peaks at <50 K (Figure 6). The peak possesses a fine structure, indicating the presence of multiplet states higher than a triplet. The temperature dependence of these signal intensities was plotted as a function of inverse temperature in Figure 6. The upward deviation of plots from the linear Curie line with the decreasing temperature reveals the intramolecular ferromagnetic interactions between adjacent cationic radicals and the multiplet ground state for the polyradicals.

The magnetization and static magnetic susceptibility of the polyradicals were measured with a SQUID magnetometer. To reduce the intermolecular antiferromagnetic interaction, a frozen solvent was used as a matrix. A small amount of trifluoroacetic acid and anhydride was added to improve the radical stability and remove trace water, respectively. The magnetization normalized with saturated magnetization, M/M_s, plots for the polyradicals are shown in Figure 7. The plots of both polyradicals were located between the theoretical Brillouin

Figure 6 Temperature dependence of the $\Delta M_s = \pm 2$ signal intensities for the polyradicals of **P1** (○) and **P2** (●) in CH_2Cl_2/CF_3COOH/$(CF_3CO)_2O=$91:8.5:0.5 vol%. Inset: ESR $\Delta M_s = \pm 2$ spectrum for the polyradical of **P2** at 5.6 K.

curve for $S=10/2$ at low fields and $S=7/2$ at high fields (Figure 7). The radical amount or spin concentration was determined by the saturated magnetization of the weighted polyradicals as 0.66 for the polyradical of **P1** and 0.75 for the polyradical of **P2**. Plots of the product of the unit molar magnetic susceptibility (χ_{mol}) and temperature (T) vs T for the polyradicals are included in the inset of Figure 7. The $\chi_{mol}T$ values below 180 K were much higher than the theoretical single paramagnetic spin of 0.375, suggesting the presence of ferromagnetic interactions even at a relatively high temperature of 180 K. As temperature decreases, the values started to increase at 50 K for the polyradical of **P1** and at 100 K for the polyradical of **P2**, finally reaching 1.30 corresponding to $S=8.4/2$ at 5 K. The slight decrease in $\chi_{mol}T$ values below 5 K is ascribed to the weak intermolecular antiferromagnetic interactions, suggesting efficient minimization of intermolecular interactions by the solvent matrix. The average spin alignment number of 8–9 spins for poly(aminium cationic radical)s is comparable to those reported by Bushby and Gooding.[60]

Scanning probe microscopy measurements

Because the molecular weight of **P1** is sufficiently high, we studied the difference in molecular shape and magnetism before and after chemical oxidation at RT using AFM and MFM techniques, respectively.[61–66]

The dilute dichloromethane solutions of **P1** and the corresponding poly(aminium cationic radical) were transferred onto a mica surface and subjected to AFM measurements (Figure 8). A globular-shaped image was detected for both polymers. The average horizontal (diameter) and vertical (height) distances of the globular images were statistically analyzed for approximately 200 samples. Figure 8a reveals the broad distribution of both horizontal and vertical distances for the neutral polyamine **P1**. This result would probably be attributable to the large polydispersity of the polymer, as well as to its partial aggregation. On the other hand, a single peak with a narrow distribution was observed for the poly(aminium cationic radical) of **P1** (Figure 8b). The average horizontal and vertical distances were 17.4 and 0.83 nm, respectively, indicating that the aggregated polymers were excellently dispersed into single polymers in terms of the electrostatic repulsion between the positive charges of the poly(cationic radical). It should be noted that the average vertical distance of the neutral polyamine **P1** in the anticipated single molecular size range (15–20 nm) was 1.43 nm (Figure 8a). The decrease in vertical distance after the chemical oxidation is most likely caused by conversion of sp^3 nitrogen atoms into sp^2 ones, accordingly leading to enhanced coplanarity of the aromatic polymer. This enhanced coplanarity is essential for efficient intramolecular ferromagnetic interactions.
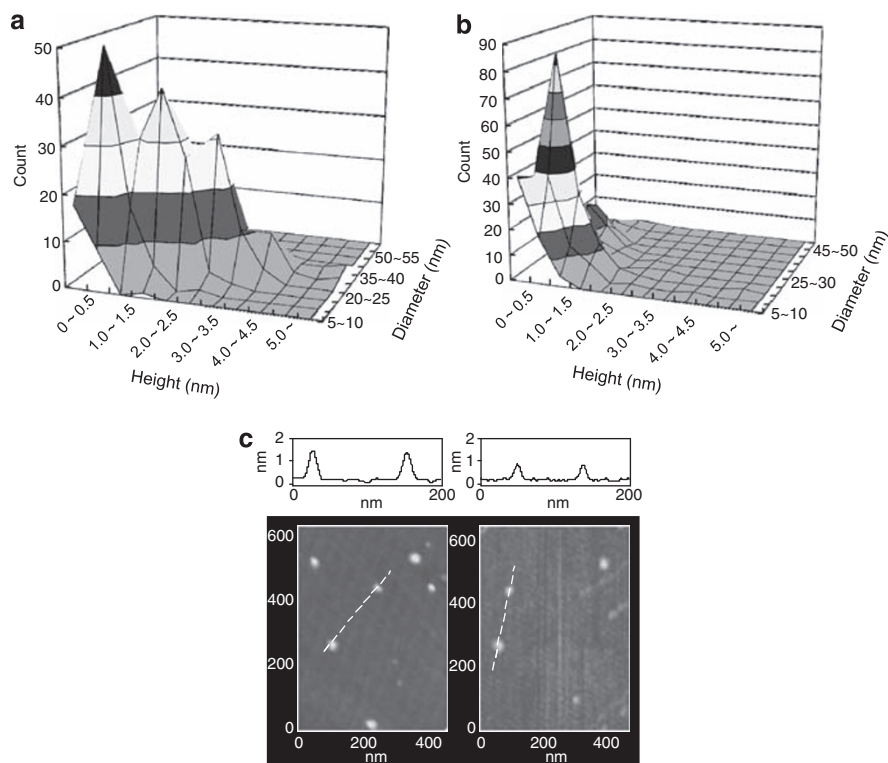
Figure 7 Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and temperature ($H/(T-\theta)$) for the polyradicals of (**a**) **P1** with the spin concentration of 0.66 and (**b**) **P2** with the spin concentration of 0.75 in CH_2Cl_2/CF_3COOH/$(CF_3CO)_2O=$91:8.5:0.5 vol% at $T=2.5$ (●), 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: $\chi_{mol}T$ vs T plots of the polyradicals.

Figure 8 Statistical summary of the globular shape sizes of (**a**) **P1** with the molecular weight of $M_n=16000$ and (**b**) the corresponding polyradicals, detected by AFM imaging on a mica substrate at 20 °C. (**c**) Representative AFM images of (left) **P1** and (right) polyradicals.
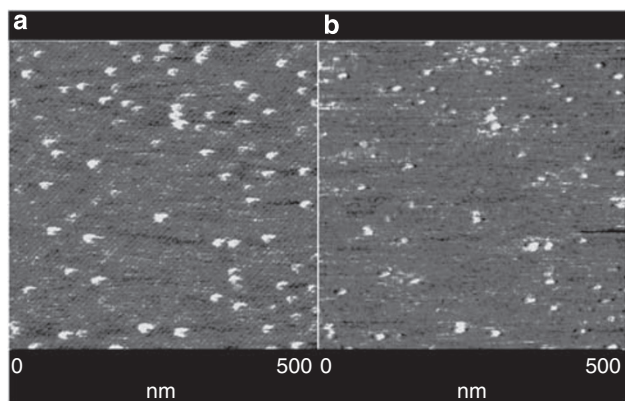
Figure 9 (**a**) AFM (tapping mode) and (**b**) MFM (noncontact mode) images of the polyradical of **P1** dispersed on a mica substrate at 20 °C.

CONCLUSION

p-Phenylenediamine-based poly(aminium cationic radical)s that extended two-dimensionally in a non-Kekulé manner were reported. The magnetic behavior elucidated by ESR and SQUID measurements revealed a ground state multiplet and an average spin alignment number of 8–9 spins at low temperatures. The high chemical stability of poly(aminium cationic radical)s at RT allowed us to apply the AFM and MFM techniques, which showed a clear change in the visualized size distribution after chemical oxidation and 10 nm-sized magnetic dot images, respectively. Poly(aminium cationic radical)s are promising single molecule-based magnetic materials for future information technology.

Taking into account the sufficient chemical stability of the polyradical of **P1** at RT, MFM detection of the dispersed polyradicals was attempted. Previously, we succeeded in MFM imaging of the RT high-spin poly(aminium cationic radical).[45] By using the same measurement conditions, the polyradical of **P1** was subjected to MFM measurements in the noncontact mode after AFM imaging. MFM successfully visualized the magnetic gradient responses exactly on the AFM imaging positions (Figure 9). Some small globular images detected by AFM did not provide well-defined magnetic images, probably because of the detection limit of a low radical amount or small molecular size. These MFM responses gradually became weaker, and they completely disappeared after 1 week.

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