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Poly(4-diphenylaminium-1,2-phenylenevinylene): A High-Spin and Durable Polyradical

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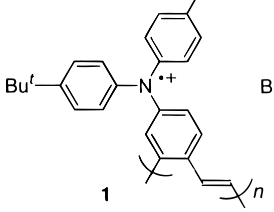
Much effort has been expended in synthesizing purely organic high-spin polyradicals which are predicted to display molecular-based magnetism.[1,2] One of the approaches to ferromagnetically align the spins on the radical groups is focused on a π-conjugated linear polymer that has multiple pendant radical groups;[1d,e] the pendant radicals are attached to one π-conjugated backbone that satisfies a non-Kekulé and nondisjoint structure of nonbonding molecular orbitals. We have succeeded in designing an intramacromolecular high-spin alignment between the pendant unpaired electrons, by synthesizing poly(1,2-phenylenevinylene)s that are 4-substituted with the 3,5-di-*tert*-butyl-4-oxyphenyl,[3a,b] *N*-*tert*-butyloxyamino,[3c] galvinoxyl,[3d] or nitronylnitroxide group.[3d] The poly(1,2-phenylenevinylene) backbone was characterized as being relatively coplanar with extended π-conjugation even after the introduction of the pendant radical groups.

Besides the backbone structure, a spin source, which is to be pendantly introduced to the π-conjugated backbone, should be carefully selected from the list of radical species in order to provide both a sufficient ferromagnetic interaction and chemical stability. It is known that aminium radicals derived from the para-substituted triarylamines, e.g. **2**, are quite stable.[4] In addition, the spin density of the aminium radicals delocalized into the aryl groups. The aminium cationic radical is a favorable candidate for the spin source to be utilized in a chemically durable and high-spin organic macromolecule. Recently, Bushby et al. reported a series of poly(aminium cationic radical)s which are derived from *m*-phenylene-connected and cross-linked polyarylamines; the cationic radicals cross-conjugatively formed in the backbone displayed nonet multiplicity.[5] We have recently reported the cationic diradical of 3,4′-bis[di(4-*tert*-butylphenyl)amino)stilbene] as a durable triplet molecule.[6] In this communication, we have, for the first time, synthesized the pendant-type poly(aminium cationic radical) based on poly(1,2-phenylenevinylene) (**1**) with a definite chemical structure and report its intramolecular high-spin algnment.



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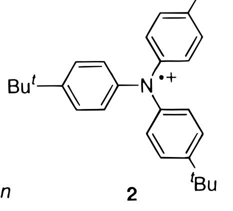

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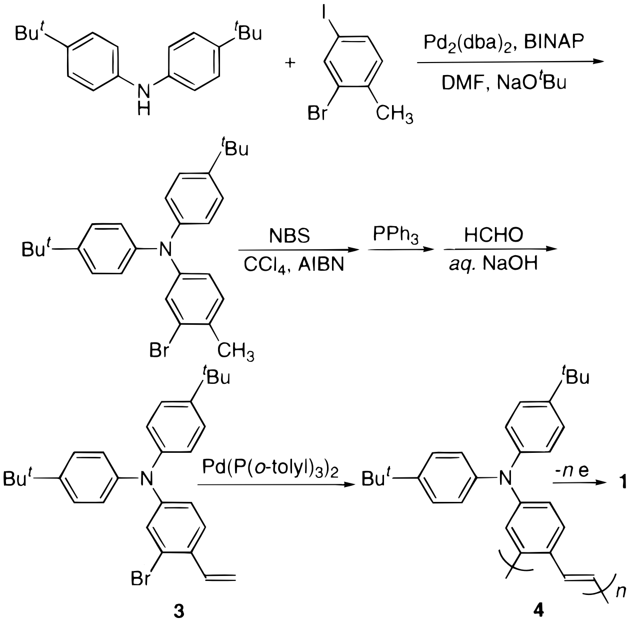
2-Bromo-4-[di(4′-*tert*-butylphenyl)amino]styrene (**3**) was synthesized as a monomer to be linked with head-to-tail bonds via the Heck reaction using a palladium/phosphine catalyst. Each para position of the triphenylamine is protected with the *tert*-butyl or the vinylene group in order to suppress dimerization and/or disproportionation of the formed aminium cationic radical. *N*,*N*-Di(4-*tert*-butylphenyl)amine was introduced onto the 2-bromo-4-iodotoluene by selective coupling at the iodo position using a catalyst of bis(diphenylbenzylideneacetonato)palladium and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl to afford 2-bromo-4-(*N*,*N*-di(4-*tert*-butylphenyl)amino)toluene. The methyl group was brominated and converted to a vinyl group via the Wittig reaction to yield **3**.[7] **3** was polymerized using the catalyst of palladium acetate and tri(*o*-tolyl)phosphine in the presence of triethylamine as a base in DMF solution at 100 °C for 12 h. The product was purified by reprecipitation from chlorofom into methanol to obtain the yellow-green powder of **4**.[8] The polymer was soluble in common solvents such as dichloromethane, benzene, THF, and cyclohexane. The degree of polymerization (DP) of the polymer **4** measured by GPC with a polystyrene standard, the terminal bromine content, and the terminal vinyl proton were 13, 13, and 12, respectively. The NMR data and this result supported the head-to-tail linked primary structure of **4**.



The chloroform solution of **4** showed two UV absorption maxima at 306 and 365 nm ($\epsilon = 2.2 \times 10^4$ and 1.2×10^4 M^{-1} cm^{-1}), which were ascribed to the triarylamine moiety and the $\pi-\pi^*$ transition of the backbone and were bathochromically shifted in comparison with **2** ($\lambda_{max} = 304$ nm) and poly(1,2-phenylenevinylene) ($\lambda_{max} = 292$ nm). The solution exhibited a photoluminescence ($\lambda_{em} = 512$ nm) which was also bathochromically shifted in comparison with that of poly(1,2-phenylenevinylene) ($\lambda_{em} = 456$ nm).

Cyclic voltammetry of **4** in dichloromethane showed complete reversibility but unimodal oxidation and reduction waves. The redox potential (vs Ag/AgCl) was 0.91 V, which almost agrees with that of **2** (0.93 V) for the redox to and from the corresponding aminium cationic radical. The cyclic valtammogram was revers-

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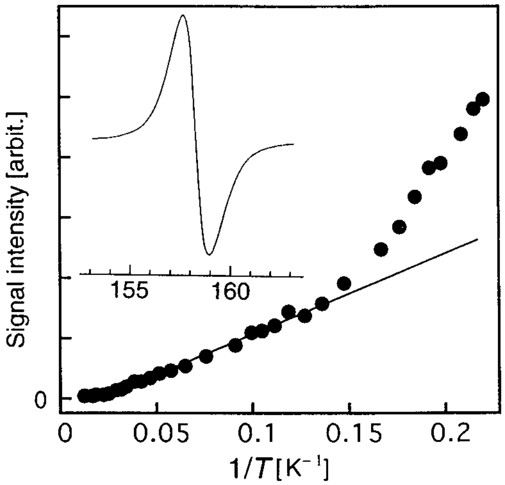

Figure 1. Curie plots for the peak in the $\Delta M_s = \pm 2$ regions for the poly(aminium cationic radical) **1** with spin concentration = 0.41 spin/unit in dichloromethane glass. Inset: $\Delta M_s = \pm 2$ spectrum for **1**.

ibly recorded in the repeated potential sweeps (e.g., 100 times) at room temperature. This denotes chemical stability of the poly(aminium cationic radical) even at room temperature.

The oxidation of **3** using antimony pentachloride gave a deep blue solution of the poly(aminium cationic radical) **1**. The spin concentration of **1** in a dichloromethane solution was estimated to be 0.41 spin/monomer unit using the ESR signal intensity. The half-life of the radical was 1.5 days for **1** in the solution at room temperature, which was much longer than those previously reported for the *m*-phenylene-coupled oligo(triarylamine)s. (These radicals could be handled only under 200 K.)

The ESR of **1** with a low spin concentration gave a three-line spectrum ($a_N = 0.90$ mT) at $g = 2.0028$. With increasing spin concentration, the ESR spectrum changed to a broadened signal without zero-field splitting, indicating a local high spin concentration along the polymer backbone. The frozen glass of **1** gave a $\Delta M_s = \pm 2$ (half-field and forbidden) transition at 158 mT (inset of Figure 1) which is assigned to a triplet species. The signal intensity of the $\Delta M_s = \pm 2$ transition of **1** was proportional to the reciprocal of the temperature and followed Curie's law at higher temperature (>6 K), indicating a triplet ground state with a large triplet−singlet gap. This triplet state is most likely caused by an exchange interaction between the neighboring radical sites. On the other hand, the signal intensity deviated upward in the lower temperature range, which could be ascribed to a weak ferromagnetic interaction (lower than 6 K) caused by a long-distance interaction between remote radical sites.

The static magnetic susceptibility (χ) and magnetization (M) of **1** were measured using a SQUID magnetometer. The inset of Figure 2 shows $\chi_{mol}T$ vs T plots. The plots are flat in the higher temperature region although they decrease at lower temperatures (<50 K); the latter indicates a strong antiferromagnetic (probably through-space) interaction under these conditions. The flat $\chi_{mol}T$ plots mean that the triplet−singlet gap for the triplet species caused by the neighboring radical sites is significantly large ($\sim k_BT$) in the poly(aminium cationic radical) **1**. (However, it does not rule out the possibility of a degenerate singlet−triplet state for **1**.)

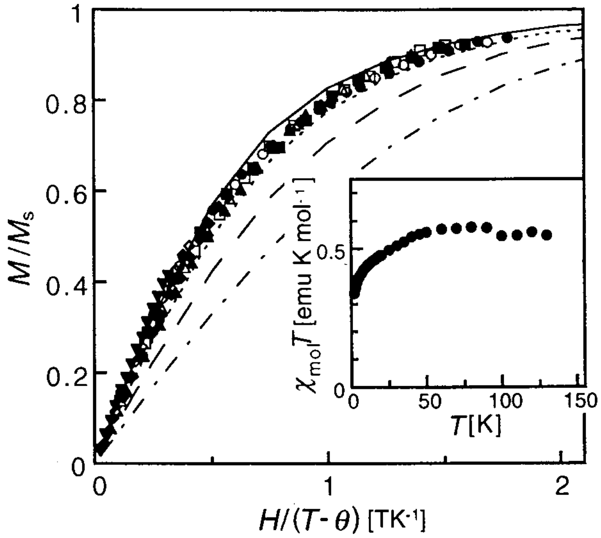

Figure 2. M/M_s vs $H/(T - \theta)$ plots for the poly(aminium cationic radical) **1** with spin concentration = 0.37 spin/unit in dichloromethane glass at 1.8 (●), 2.0 (○), 2.25 (■), 2.5 (□), 3 (▲), 5 (△), 10 (◆), 15 (◇), and 20 K (▼) ($\theta = -1.8$ K) and the theoretical Brillouin curves for $S = {}^1/_2$ (− • −), ${}^2/_2$ (− −), ${}^3/_2$ (- - -), and ${}^4/_2$ (—). Inset: $\chi_{mol}T$ vs T plots of **1**.

The normalized plots of magnetization (M/M_{sat}) (Figure 2) are close to the Brillouin curves for ${}^3/_2$ and ${}^4/_2$, indicating a high-spin ground state for **1**. The average S value of (3.5)/2 is reasonable by taking into account both a DP of 12 and a spin concentration of 0.37 for the present polyradical. After optimizing the radical generation step, S is expected to proportionally increase with the DP of the poly(aminium cationic radical).

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(7) Selected data of **3**: MS (m/e) 462.47 (calcd), 461 (M^+), 463 ($M^+ + 2$); δ_H(500 MHz, $CDCl_3$) 7.63−6.92 (m, 12H, phenyl), 5.56 (d, J = 18.4 Hz, 1H, vinyl), 5.21 (d, J = 12.1 Hz, 1H, vinyl), 1.30 (s, 18H, *tert*-butyl); δ_C(125 MHz, $CDCl_3$) 148.77, 146.57, 144.24, 135.24, 129.95, 126.66, 126.24, 125.11, 124.51, 123.99, 121.08, 114.14, 34.35, 31.42. IR (KBr pellet, cm^{-1}) 3033 (ν_{C-H}), 2954 (ν_{C-H}), 1622 ($\nu_{C=C}$), 1267 (ν_{C-N}). Anal. Calcd for $C_{28}H_{32}BrN$: C, 72.7; H, 7.0; Br, 17.3; N, 3.0. Found: C, 72.4; H, 6.8; Br, 17.5; N, 2.9.

(8) Selected data of **4**: GPC (THF eluent, polystyrene standard) $M_W = 5.1 \times 10^3$. δ_H(500 MHz, $CDCl_3$) 7.5−6.6 (m, phenyl), 5.55 (d, J = 18.4 Hz, terminal vinyl), 5.20 (d, J = 12.1 Hz, terminal vinyl), 1.30 (s, *tert*-butyl). IR (KBr pellet, cm^{-1}) 3033 (ν_{C-H}), 2962 (ν_{C-H}), 959 ($\delta_{C=C}$). UV/vis (in dichloromethane) $\lambda_{max} = 306$ ($\epsilon = 2.2 \times 10^4$ M^{-1} cm^{-1}), 365 nm (1.2×10^4). Fluorescence (in dichloromethane) 512 nm (λ_{ex} = 350 nm). Anal. Calcd for $Br(C_{28}H_{31}N)_nH$ (n = 12.9): C, 86.7; H, 8.0; Br, 1.6; N, 3.6. Found: C, 86.4; H, 8.3; Br, 1.6; N, 3.6.

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