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High-Spin Polymers. Synthesis of 1,3-Connected Polyarylmethane and Its Carbopolyanion and Polyradical

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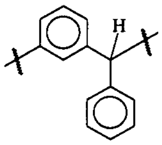
Synthesis and studies of very high-spin polymers may contribute to the recent topic of organic magnetism.[1–5] One of the problems encountered in approaches to high-spin organic polymers is weakness of intramolecular coupling between unpaired electrons.[5] Our previous studies suggest that in the series of 1,3-connected polyarylmethyls, extension of conjugation does not significantly affect their electronic structure;[6] that is, the strong ferromagnetic coupling between two unpaired electrons in 1,3-connected diradicals does translate into a significant stabilization of a high spin ground state in the $S = 1$–5 polyradicals with 2–10 unpaired electrons.[6b,d,7,8]

Now we report an exploratory approach to a polymeric structure of 1,3-connected polyarylmethyl polyradical with ca. 30 sites for unpaired electrons. We describe the synthesis and characterization of 1,3-connected polyarylmethane **1** (poly[*m*-phenylene(phenylmethylene)], ca. 30 triarylmethane centers), and the corresponding π-conjugated carbopolyanion **2** and polyradical **3**.



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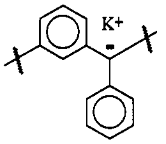

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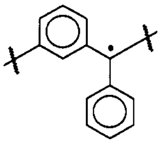

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3,3′-Dibromotriphenylmethane is dilithiated via the Br/Li exchange with *n*-BuLi and then quenched by addition of methyl benzoate. Subsequent removal of the OH groups using red phosphorus and hydrogen iodide gives polyaryl-

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methane polymer 1.[9] After each of the above two synthetic steps, polymers are isolated following aqueous workup and precipitation with either cyclohexane or hexane. Polymer 1 is obtained as a white solid, soluble in organic solvents, e.g., chloroform and tetrahydrofuran (THF). The average number of triarylmethane centers in 1 is about 30 according to GPC and VPO measurements.[9] Because of one spectral overlap in the CH aromatic region, the ^{13}C NMR spectrum consists of only eight resonances. The ^{13}C chemical shifts are as expected for a polyarylmethane.[10,15] In the ^{1}H NMR spectrum, the aromatic and the triarylmethane protons are assigned to multiplets in the 6.71–7.60 and 5.25–5.60 ppm regions, respectively; the 10:1 integration for the two regions should be compared to the theoretical 9:1 ratio for the polymer with infinite number of triarylmethane centers.[15]

Vigorous stirring of 1 in THF-d_8 with multifold excess of KH under vacuum (vapor pressure of solvent and evolved hydrogen gas) for 10 days produces a red solution of the corresponding carbopolyanion 2 (eq 1).[11] The ^{1}H NMR spectrum possesses three groups of multiplets (6.8–7.4, 6.2–6.7, and 5.6–6.0 ppm) with the integrations of 3:5:1; a similar spectral pattern is observed in the related carbotetraanion.[6c,15] The UV–vis spectrum shows a broad band at λ_{max} 488 nm, which is similar to analogous carbopolyanions.[6c]

Treatment of 2 in THF or 2-methyltetrahydrofuran (2-MeTHF) with approximately 0.5 equiv of I_2/triarylmethane center at 180 K for 30 min produces a yellow/brown solution of polyradical 3 (eq 1).[11a] The $\Delta m_s = 1$

$$\mathbf{1} \xrightarrow{\text{KH}} \mathbf{2} \xrightarrow[\text{180 K}]{I_2} \mathbf{3} \qquad (1)$$

region of the EPR spectrum at 4 K for 3 in 2-MeTHF/THF consists of a single peak; a weak half-field $\Delta m_s = 2$ resonance is observed that suggests presence of a high spin species ($S \geq 1$). The intensity of the EPR signal decreases several times after the solution of 3 is kept at ambient temperature for 10 min.

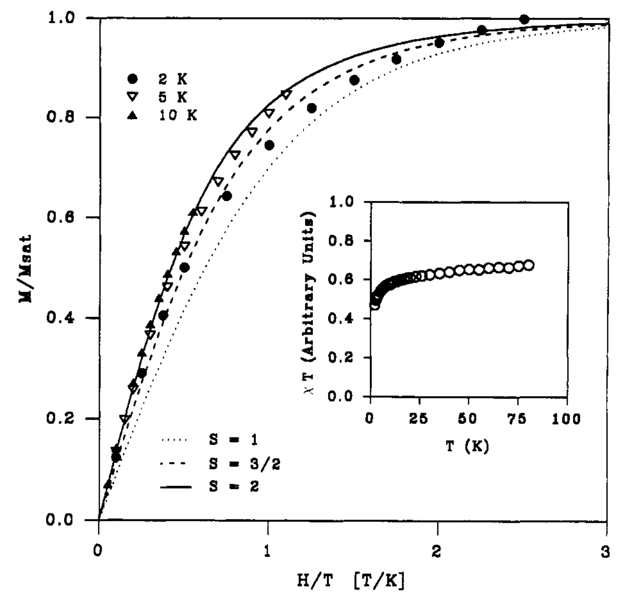

Figure 1. Polyradical 3 in THF. Normalized plots of magnetization (M/M_{sat} vs H/T); experimental points at T = 2, 5, and 10 K and the theoretical curves corresponding to the S = 1, $^3/_2$, and 2 Brillouin functions. Insert: plot of the product of magnetic susceptibility (χ) and T versus T (χT vs T); external magnetic field, H = 0.5 T.

SQUID measurements of 3 in frozen solution (THF and 2-MeTHF) are carried out as described previously.[6d] The magnetization (M) is measured at T = 2, 5, and 10 K in the magnetic field (H) range of 0–5.5 T. Two-parameter fitting of the magnetization to the Brillouin function gives "effective" spin (S) and saturation magnetization (M_{sat}) at each temperature. M_{sat} at T = 2 K is used to compare the data as normalized plots of magnetization (M/M_{sat}) vs H/T to the Brillouin curves (Figure 1). The M/M_{sat} experimental points do not closely follow the Brillouin curves and appear in the vicinity of the S = 2 curve at 10 K and S < 2 curves at T = 5, 2 K. Furthermore, the downward slope in the plots of the product of magnetic susceptibility (χ) and T versus T (2–80 K, χT vs T) is observed (Figure 1). This suggests antiferromagnetic (AFM) interactions, presumably, between the polymer chains.[13]

In the presence of AFM interactions, the "effective" $S \approx 2$ would mean that the average length for the spin-coupled segments of the polyradical corresponds to at least four ferromagnetically coupled electrons (four triarylmethane centers). An average polymer chain of 30 triarylmethane centers can accommodate a few such segments of various length. Such interruptions of spin coupling in the chain may occur when certain centers are defective, e.g., those without an unpaired electron. Pos-

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[9] (a) Polymer 1. Step I: 3,3′-dibromomotriphenylmethane (12.0 mmol) in ether (100 mL) was added to n-BuLi (24.0 mmol, 1.56 M in hexane) at 0 °C under inert atmosphere. After 90 min, methyl benzoate (12.0 mmol) in toluene (100 mL) was added over 4 h. After an additional 12 h at 0 °C, the reaction mixture was quenched with 50% aqueous MeOH (100 mL). After the aqueous workup, the dried organic layer was poured into cyclohexane (volume ca. 20 times that of solution); the resultant precipitate collected by filtration and then vacuum oven-dried (1.51 g, 36%). Anal. Calcd for $C_{26}H_{20}C$: C, 89.7; H, 5.7. Found: C, 89.0; H, 5.5. ^{1}H NMR ($CDCl_3$) 6.55–8.12 (m, 18 H), 5.25–5.68 (br m, 1 H), 2.3–3.0 (br, 1 H). ^{13}C NMR ($CDCl_3$) 146.6, 143.8, 143.4, 133.4, 130.2, 129.3, 129.2, 129.0, 128.5, 128.2, 127.8, 127.1, 126.2, 126.0, 81.9, 56.7. IR (KBr, cm^{-1}) 3510, 3050, 2890, 1605, 1489, 700. Step II: The polymer from step I (1.0 g) in benzene (50 mL) was refluxed with excess of HI (55%) and red phosphorus (5.9 g) for 72 h under N_2 flow. After the aqueous workup, filtering off the phosphorus, the dried organic layer was poured into hexane (volume ca. 20 times that of solution); the resultant precipitate collected by filtration and then vacuum oven-dried (0.60 g, 63%). Anal. Calcd for $C_{13}H_{10}$: C, 94.0; H, 6.0. Found: C, 92.1; H, 6.0. GPC (THF, 40 °C, polystyrene standard): $M_n = 3248$, $M_w = 4585$, M_n(VPO) 4870. ^{1}H NMR ($CDCl_3$) 6.71–7.60 (m, 10 H), 5.25–5.60 (br 1 H). ^{13}C NMR ($CDCl_3$) 144.0, 143.7, 130.7, 129.3, 128.1, 127.2, 126.1, 56.5. IR (KBr, cm^{-1}) 3050, 2890, 1605, 1489, 700. Inductively coupled plasma (ICP) atomic emission spectroscopy (ppm) Fe (5.0), Si (26.0), Al (29.0), Zn (2.1), Co (<1.1), Ni (<1.3), Cr (<1.1). (b) 3,3′-Dibromotriphenylmethane was prepared by reduction of 3,3′-dibromtriphenylmethanol, using excess red P/55% HI and heated under reflux for 48 h. See: Vingiello, F.; Buese, G. J.; Newallis, P. E. *J. Org. Chem.* **1958**, *23*, 1139. (c) 3,3′-Dibromotriphenylmethanol was prepared by the addition of 3-bromophenylmagnesium bromide (2 equiv) to methyl benzoate (1 equiv) in ether.

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[11] (a) Rajca, A.; Utamapanya, S. *J. Org. Chem.* **1992**, *57*, 1760. (b) Polymer 1 is isolated after proton quenching (MeOH) of 2 in THF-d_8.

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[13] (a) The AFM interactions are observed for frozen solutions of various 1,3-connected polyarylmethyl polyradicals; e.g., ref 6d and references therein. (b) Using Brillouin functions for determination of an "effective" spin for a mixture of different spin species which interact antiferromagnetically is very approximate; that is, Brillouin functions are applicable to isolated paramagnetics and, in general case, they are not additive. Rajca, A. *Chem. Rev.*, manuscript in preparation. (c) Disruption of ferromagnetic coupling by extension of conjugation or ring twisting is plausible but it is not found in the lower analogous of polyradical 3 (see refs 6d and 14).

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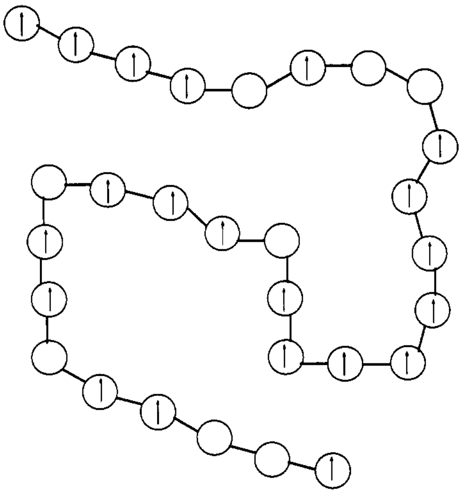
[15] Supplementary material.



sible sources of the defects are: partial protonation of **2**, incomplete or overcomplete oxidation of **2** (also, CI bond formation), inter- or intramolecular cross-linking (CC bond formation) for **3**, etc.[13c] The last type of the defects may be curtailed by sterically hindering radical centers using bulky alkyl substituents.[14] The important point is that even small number of defects may drastically lower tha "average" S for linear polymer such as **3**.

A rationally designed high spin polymer **3** was synthesized. The "average" spin value, $S \approx 2$, is among the highest achieved so far for high-spin polymers.[1,4,5] Further progress in this field may require development of the ultraefficient methods for generation of radicals and design of the structures with strong spin coupling but less sensitivity to defects; that is, the number of defects and their impact on the spin coupling should be minimized.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for polymer **1** and ^{1}H NMR spectrum of carbopolyanion **2** (3 pages). Ordering information is given on any current masthead page.

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