

Very High-Spin Organic Polymer: π -Conjugated Hydrocarbon Network with Average Spin of $S \geq 40$

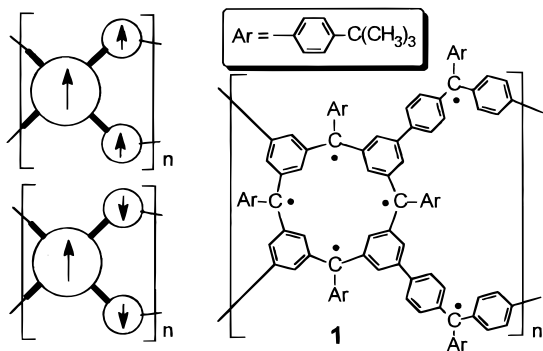
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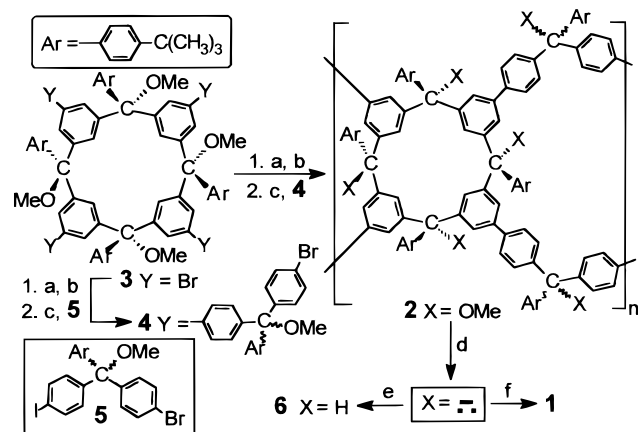
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Current interest in very-high-spin organic molecules and polymers is driven by a possibility of attaining purely organic magnetic materials based upon through-bond magnetic interactions (exchange coupling).^{1–3} The progress in this area is measured by the synthesis of molecules and polymers with increasing values of the spin quantum number (S) in the electronic ground state.^{4–8} From both synthesis and materials points of view, polymers are among the most desirable targets. However, all polymers reported to date have only $S < 5$,^{6–8} significantly below $S = 10$ obtained for a well-defined π -conjugated molecule (oligomer).⁵

We propose a novel design for a high-spin polymer as implemented in polyradical network **1**.^{9,10} Polyradical **1** consists of $S = 2$ macrocyclic modules, which are cross-linked with $S = 1/2$ connecting modules.¹¹ In **1**, high density of macrocycles should



Scheme 1. Synthesis of Polyradical **1**^a



^a (a) *t*BuLi, THF, 195 K (2 h), 253 K (15 min), (b) ZnCl₂, from 195 K to ambient temp, (c) Pd(PPh₃)₄ (3% mol per CC bond), **5** (6 equiv) or **4** (1 equiv), THF, 373 K, (d) Na/K, 283 K, (e) MeOH, (f) I₂, 170–167 K.

The synthetic route to the network polyether **2**, precursor to polyradical **1**, relies on multistep syntheses of tetrafunctionalized macrocyclic calix[4]arene modules **3** and **4**. Polymerization of **3** and **4** is expected to provide a polymer with large density of macrocyclic rings from the monomers and intramolecular macrocyclizations (annulations) (Scheme 1).

The final steps in the synthesis of **2** are implemented with two Negishi reactions:¹⁵ (1) a single 2-fold symmetric *cis/trans* isomer of tetrabromocalix[4]arene **3** and a racemic linker **5** gives a mixture of stereoisomers of **4** in 17% yield, (2) coupling of **3** and **4** (both ca. 0.015 M) provides a polyether network (Scheme 1).^{16,17} In the polymerization step, the onset of the gelation of the reaction mixture and, also, the relative amounts of the benzene-soluble and benzene-insoluble product are variable.¹⁸ The benzene-soluble product is purified by thin-layer chromatography (silica, methanol/ether, 1/3); the immobile fraction corresponds to polyether **2**.

Gel permeation chromatography (GPC) with refractive index and light-scattering detectors ($\lambda = 690$ nm at 45°, 90°, 135°) for polyether **2** in tetrahydrofuran (THF) suggests polydisperse molecular mass distributions. The weight-average (M_w) and number-average molar masses (M_n) are in the range $(8 \times 10^4) - (5 \times 10^5)$ and $(4 \times 10^4) - (3 \times 10^5)$ Da, respectively ($M_w/M_n = 2-5$). Using rigorous Schlenk techniques, **2** with $M_n \geq 1 \times 10^5$ Da is reproducibly obtained. Both ¹H NMR and IR spectra for **2** are similar to those observed for the previously reported polyarylmethyl polyethers, except that the ¹H resonances in **2** are relatively broad.¹¹

Preparation of polyradical **1** starts with treatment of polyether **2** (0.8–1.7 mg) with Na/K alloy in THF-*d*₈ (40–80 μ L) at 283 K for 4 days.¹⁹ The reaction mixture, which is partially insoluble in THF-*d*₈, is filtered (course glass frit) into 5-mm o.d. quartz tube. Iodine is added in small portions at 170–167 K until the reaction mixture turns green (Scheme 1).⁵

(15) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.

(16) For another example of cross-linked polyarylmethane, see: Urban, C.; McCord, E. F.; Webster, O. W.; Abrams, L.; Long, H. W.; Gaede, H.; Tang, P.; Pines, A. *Chem. Mater.* **1995**, *7*, 1325.

(17) Tetrabromocalix[4]arene **3** is obtained by means of methodology similar to that previously described (ref 12); the *C*_{2v}-symmetric and most soluble isomer of the four available *cis/trans* isomers is used.

(18) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953.

(19) MeOH quench of the carbopolyanion (from **2**) gives the corresponding polyarylmethane **6** (Scheme 1) (¹H NMR and IR); GPC profiles for **6** and the corresponding **2** are nearly superimposable.

address the problems with defects; the alternating connectivity of two types of radical modules with unequal spins should facilitate large net S values for either ferromagnetic or antiferromagnetic coupling between the modules.^{11–13} Although $2p_{\pi}$ -connectivity in **1** is compatible with ferromagnetic coupling,^{1–3} out-of-plane twisting within the π -conjugated system, especially about the CC bonds at the connecting biphenyl modules, may lead to reversal of spin coupling (ferromagnetic to antiferromagnetic).¹⁴ This report describes synthesis and magnetic characterization of **1** with an average spin of $S \geq 40$.

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 (14) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180. Rajca, A.; Rajca, S. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1077.

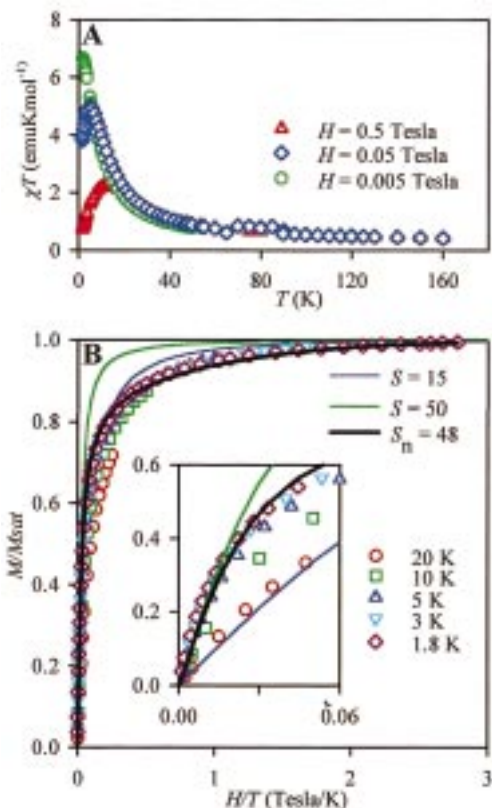


Figure 1. SQUID magnetometry for polyradical **1** in THF- d_8 . Plot A: χT vs T . Plot B: M/M_{sat} vs H/T . Representative parameters (with standard errors) for the number average, $S_n = 48 \pm 2$, ($S_s \approx 66$) at 1.8 K: $p = 0.968 \pm 0.003$ and $M_{\text{sat}}10^2 = 1.072 \pm 0.004$ emu (in the units of magnetic moment) with the parameter dependence of 0.094; S_0 , n , and w_{12} are set to 6.0, 13, and 0.2, respectively. Quantitative conversion of 1.24 mg of **2** to **1** should give $M_{\text{sat}}10^2 = 2.50$ emu; i.e., $M_{\text{sat}} = 0.43 \mu_B$ (43%). At $T = 3, 5, 10$, and 20 K, the S_n are 45, 40, 30, and 20, respectively.

X-band ESR spectra for **1** in THF- d_8 /2-methyltetrahydrofuran ($\sim 1/5$) at 80 K show an intense single-line resonance in the $\Delta m_s = 1$ region ($g \approx 2.0$) and a relatively weak $\Delta m_s = 2$ resonance. Magnetization (M) for **1** in THF- d_8 is measured as a function of magnetic field ($H = 0\text{--}5.0$ T) and temperature ($T = 1.8\text{--}160$ K), using a SQUID magnetometer.²⁰ Plots of χT vs T ($\chi = M/H$, magnetic susceptibility), show saturation (as a downward turn in the plot) at relatively small values of H/T ; at the low H (0.005 T), the χT increases even near $T = 1.8$ K (Figure 1A). Plots of M/M_{sat} vs H/T ($M_{\text{sat}} = M$ at saturation) show a steep temperature-dependent rise at low fields and slow saturation at high fields, compared to a single Brillouin function (Figure 1B). These qualitative features of the magnetic data suggest mixtures of spin

(20) Following the magnetization studies, the samples are allowed to attain room temperature for several weeks, until the paramagnetic susceptibility is $< 1\%$ of the original value, and, then, the identical sequence of measurements is repeated for point-by-point background correction. Both the negligible magnetic moment for such decomposed samples (including low H and T) and the background correction preclude interference from magnetic transition metal impurities.

systems with high S and the presence of thermally populated excited states with relatively low S .

For quantitative analysis of magnetic data, number-average (S_n) and spin-average (S_s) spin quantum numbers are defined, analogous to M_n and M_w .²¹ For a sample of **1**, $\chi T \approx 6.7$ emuK/mol at 1.8 K and $M_{\text{sat}} = 0.43 \mu_B$ are obtained (Figure 1), corresponding to the lower bound of $S_s \approx 26$ and spin concentration of 43%, respectively.²²

Average S , independent of mass balance in the generation of polyradical, is obtained from numerical fits to linear combinations of Brillouin functions (Figure 1B).³ A straightforward method for generation of Brillouin functions with a minimum of variable parameters for **1** is a simple percolation model, based on linear chains of alternating spin- $1/2$ linkers and spin- S_0 macrocyclic modules, $S_0 - 1/2 - (S_0 - 1/2)_{n-3} - S_0 - 1/2 - S_0$, where $S_0 = 2\text{--}6$ and $n = 9\text{--}13$.^{3,11,23} By assuming identical probability p for finding an unpaired electron at each triarylmethyl site (yield per site $100p\%$), the spin systems, resulting from the defects at the spin- $1/2$ sites, are explicitly enumerated. The defects at the spin- S_0 modules are approximately accounted for by pS_0 scaling and explicit addition of spin- $1/2$ systems (as fraction w_{12}). Either two (p and M_{sat}) or three (p , M_{sat} , w_{12}) variable parameters are used; only p is related to the average spin S_n .²⁴ The S_n of **1** roughly correlates with the molecular weight of the corresponding polyether **2**. Thus, **2** with $M_n \geq 10^5$ Da reproducibly give **1** with $S_n \geq 40$ (at 1.8 K); the best preparation of **1** gives $S_n = 48 \pm 2$ at 1.8 K (Figure 1B). Polyethers **2** with the lowest $M_n \approx 4 \times 10^4$ Da give **1** with $S_n \geq 17$. For all samples of **1**, the S_n sharply decrease with increasing T (Figure 1).²⁵

Polyradical network **1** possesses number average spin of $S \geq 40$, a new record spin value for polymers. The results indicate that polymer networks with cross-linked macrocyclic modules with unequal spin are promising targets for very-high-spin polymers.

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(21) Average S : number-average, $S_n = \sum_i x_i S_i / \sum_i x_i$ and spin-average, $S_s = \sum_i x_i S_i^2 / \sum_i x_i S_i$, where x_i is a fraction of spin systems with spin-value S_i .

(22) Magnetic susceptibility (χ) and magnetization at saturation ($M_{\text{sat}} = 0.2\text{--}0.5 \mu_B$) are calculated per mole of the triarylmethyl ether moiety in **2**.

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(24) All constant parameters, such as n and S_0 (and w_{12}), have little effect on the number average spin (S_n), provided that $S_n \ll nS_0 + n/2 + 1/2$.

(25) In the previously studied small-molecule polyradicals, with biphenyl-based coupling pathways, S had a constant value at low temperatures ($T \leq 5$ K) and only slowly decreased at higher temperatures. For collinear $S_1\text{--}S_0\text{--}S_1$ spin trimers ($S_1 > S_0 = 1/2$), which might be viewed as fragments of **1**, the ground states are expected to have a large net spin for either ferromagnetic or antiferromagnetic pairwise exchange coupling; the lowest excited states are low-spin in either case.¹¹ Large out-of-plane twistings of the π -conjugated system of **1** may lead to very weak ferromagnetic or antiferromagnetic intermodule exchange couplings with the resultant near degeneracy of the ground and excited states. Defects and through-space antiferromagnetic interactions between the polymer molecules or branches may also contribute to such near degeneracies.³ Defects, antiferromagnetic couplings, and an incomplete mass transfer during preparation of **1** may be responsible for the measured low spin concentration ($M_{\text{sat}} < 1.0 \mu_B$).