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Magnetic Ordering in an Organic Polymer

Andrzej Rajca,* Jirawat Wongsriratanakul, Suchada Rajca

We describe preparation and magnetic properties of an organic π -conjugated polymer with very large magnetic moment and magnetic order at low temperatures. The polymer is designed with a large density of cross-links and alternating connectivity of radical modules with unequal spin quantum numbers (S), macrocyclic $S = 2$ and, cross-linking $S = 1/2$ modules, which permits large net S values for either ferromagnetic or antiferromagnetic exchange couplings between the modules. In the highly cross-linked polymer, an effective magnetic moment corresponding to an average S of about 5000 and slow reorientation of the magnetization by a small magnetic field (less than or equal to 1 oersted) below a temperature of about 10 kelvin are found. Qualitatively, this magnetic behavior is comparable to that of insulating spin glasses and blocked superparamagnets.

Recent investigations into the properties of organic magnets have generally concentrated on materials, such as crystalline solids of small molecule radicals or charge transfer salts, in which the exchange interaction involves s- and p-orbitals (1–5). An alternative approach to organic magnets may be based on π -conjugated polymers, as envisioned by Mataga in 1968 (6). Because exchange interactions between electron spin through the π -conjugated system can be made relatively strong, compared to the through-space interactions in molecular solids of organic radicals, this macromolecular approach has a potential for obtaining interesting magnetic properties at relatively high temperatures, even room temperature (7). Although significant progress has been made in the prepara-

tion of π -conjugated oligomers and polymers with large values of spin quantum number S , organic polymer magnets have remained elusive (8–15). We report the observation of magnetic properties comparable to that of insulating spin glasses and blocked superparamagnets in an organic π -conjugated polymer.

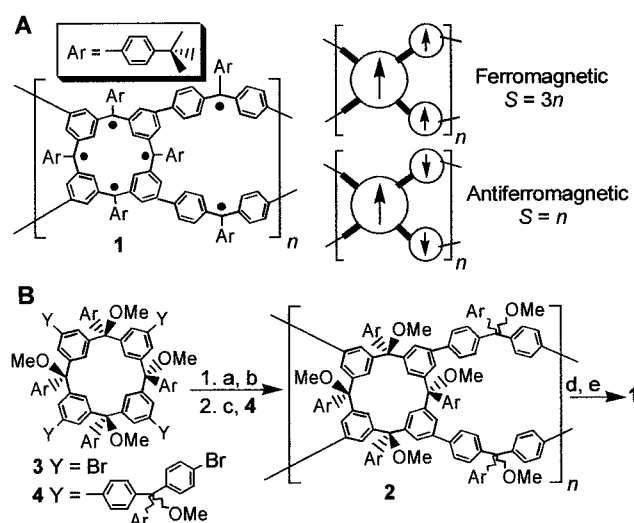
Our magnetic polymer, polymer **1**, is designed with a large density of cross-links and alternating connectivity of radical modules with unequal spin quantum numbers, i.e., macrocyclic $S = 2$ and cross-linking $S = 1/2$ modules (13). This connectivity permits large net S values for either ferromagnetic or antiferromagnetic exchange couplings between the modules (Fig. 1A). The cross-linking and connectivity is set in the synthesis of network polyether **2**, precursor to polymer **1**, based upon Pd-catalyzed Negishi coupling of two tetrafunctionalized macrocyclic monomers **3** and **4** (Fig. 1B) (13, 16).

Representative data for condensations

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Fig. 1. (A) Polymer **1** with ferromagnetic or antiferromagnetic coupling between the macrocyclic $S = 2$ and cross-linking $S = 1/2$ modules. **(B)** Synthesis of polyether **2** and polymer **1**. Reagents: (a) *t*-BuLi, THF, 198 K (2 hours), 253 K (15 min); (b) ZnCl₂, from 198 K to ambient temperature; (c) Pd(PPh₃)₄ (3 mol % per CC bond), THF, 373 K (10 min to 5 hours); (d) Na/K, 15-crown-5, THF-d₈, 283 K (several days); and (e) I₂, 167 to 170 K.



leading to organic insoluble polyether **2** are shown in Table 1 (17, 18). Dissolved metal (Na/K/15-crown-5) reduction of polyether **2**, as a gel with perdeuterated tetrahydrofuran (THF-d₈), followed by the iodine oxidation of the corresponding carbopolyanion, gave polymer **1** (Fig. 1 and Table 1) (19).

The samples of polymer **1** obtained from polyethers **2** after long polymerization times (Table 1, run 3) have the most interesting magnetic behavior. Magnetic data of the thermally decomposed polymer **1** (essentially diamagnetic) and metal analyses both preclude any significant interference from magnetic metals on the reported magnetic behavior for polymer **1** (19). The magnetic field ($H = 0$ to 50 kOe) dependence of magnetization (M), measured at several temperatures ($T = 1.8$ to 20 K), shows an extraordinarily fast rise at low H ; however, complete saturation is not attained even at $H = 50$ kOe (Fig. 2A) (20). Numerical fits of the M versus H/T data ($T = 1.8, 2.5, 3.5$ K) to a linear combination of one Langevin and three Brillouin functions give average spin quantum numbers (S) and magnetizations at saturation (M_{sat}) that are temperature-dependent (19, 21). Again, because ideal paramagnet (Curie-like) behavior is not found, the maximum value of average $S \approx 5000$ at 3.5 K, obtained

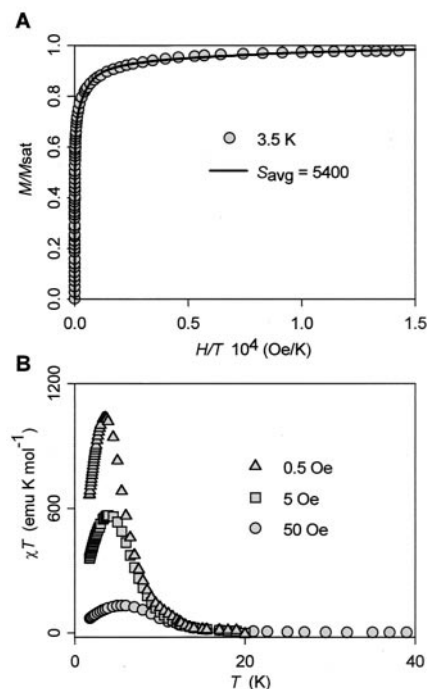


Fig. 2. (A) Magnetic field (H) dependence of the magnetization (M) of polymer **1** at $T = 3.5$ K, plotted as M/M_{sat} versus H/T , where $M_{\text{sat}} = 0.54 \mu_B$ is M at saturation. The solid line corresponds to the least-squares fit using linear combination of Langevin and Brillouin functions corresponding to average $S = 5400$ (19). **(B)** Plot of χT versus T (dc susceptibility, $\chi = M/H$).

from the M versus H/T plot, provides only a very approximate estimate for an effective ferro- or ferrimagnetic correlation of 10^4 electron spin. Values of $M_{\text{sat}} = 0.5$ to $0.6 \mu_{\text{B}}$ and their increase with increasing temperature are both compatible with the presence of weak antiferromagnetic and ferromagnetic interactions between the $S = 2$ and $S = 1/2$ modules in polymer **1** (Fig. 1).

The plots of χT versus T (dc susceptibility, $\chi = M/H$) show a rapid rise below about 10 K. The values of χT are highly field-dependent, as expected for very large magnetic moments (or values of S). For the smallest applied field, $H \approx 0.5$ Oe, χT reaches maximum of about 1000 electromagnetic units (emu) K mol $^{-1}$ at 3.6 K (Fig. 2B). Very approximately, this corresponds to an effective magnetic moment $\mu_{\text{eff}} \approx 8000 \mu_{\text{B}}$ or an average $S \approx 4000$, comparable to that found in the M versus H/T plots. These values may be viewed as lower bound estimates, because polymer **1** does not follow the Curie law and quantitative conversion of polyether **2** to polymer **1** is assumed.

More detailed studies of the temperature dependence of M at low applied magnetic fields ($H = 0.5$ to 1.0 Oe) reveal that the zero field-cooled (ZFC) and the field-cooled (FC) magnetizations diverge below ~ 10 K, indicating the slow relaxation (blocking) of the magnetization (Fig. 3). This behavior is highly sensitive to the applied magnetic fields (H); in larger magnetic fields, e.g., $H = 5$ Oe, the difference between the ZFC and FC magnetizations is undetectable. Even at a relatively low magnetic field, $H = 0.5$ Oe, the large values of $\mu_{\text{eff}} \approx 8000$ give $\mu_{\text{eff}} H/k_{\text{B}} \approx 2.7$

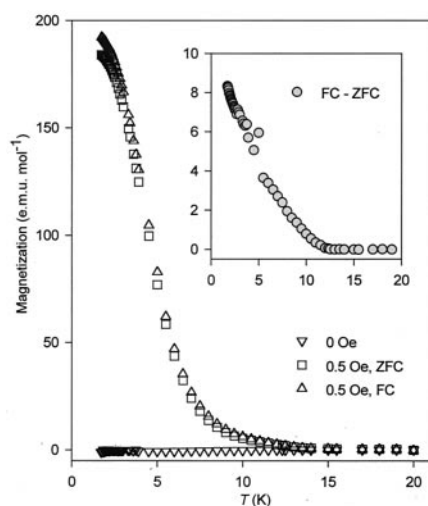


Fig. 3. Temperature dependence of the magnetization of polymer **1** measured by increasing the temperature in the indicated field. For $H = 0.5$ Oe measurements, the sample was cooled either in the zero-field (ZFC) or in the 0.5 Oe field (FC) prior to the measurement. (Inset) Difference between the FC and ZFC magnetization.

K, which is within the range of blocking temperatures.

The relaxation of the magnetization for polymer **1** at low temperatures is best observed in the temperature and frequency dependence of the ac susceptibility. The temperature dependence of χ' (in-phase component) shows a steep rise around 10 K, with a broad peak in the 1.9 to 3 K region (Fig. 4A) (19). The peak maximum in χ' at T_m' shifts to lower temperatures, and it gains intensity with decreasing frequency. The out-of-phase component, χ'' , is detectable at about 10 K and shows a frequency-dependent maximum in the 1.8 to 2.0 K region (Fig. 4B). The peak maximum in χ'' at T_m'' shifts to lower temperatures and becomes less intense with decreasing frequency; at lower frequencies, e.g., $\nu_{\text{ac}} < 250$ Hz, only continuous increase of χ'' is found down to 1.7 K, the lower limit for the temperature control in our supercon-

ducting quantum interference device (SQUID) magnetometer. This behavior is consistent with blocking of the magnetic moments in polymer **1** at low temperatures on the time scale of the ac experiment (22). The value of $\Delta T_m'/[T_m' \Delta(\log \omega)] \approx 0.09$ to 0.08 , indicating the change in T_m' per decade of angular frequency, $\omega = 2\pi\nu_{\text{ac}}$, suggests that the relaxation behavior falls between that in typical superparamagnets $\{\Delta T_m'/[T_m' \Delta(\log \omega)] \approx 0.2\}$ and insulating spin glasses $\{\Delta T_m'/[T_m' \Delta(\log \omega)] \approx 0.06\}$ (23). The smaller frequency shifts, compared to superparamagnets, may indicate some interaction between the moments (24). For a superparamagnet, the maxima T_m'' , in the out-of-phase component of the susceptibility, allow for derivation of the activation barrier E_A associated with moment blocking, according to the Arrhenius law, $\tau = \tau_0 \exp(E_A/k_{\text{B}}T)$. In this equation, $\tau = 1/2\pi\nu_{\text{ac}}$ is the relaxation

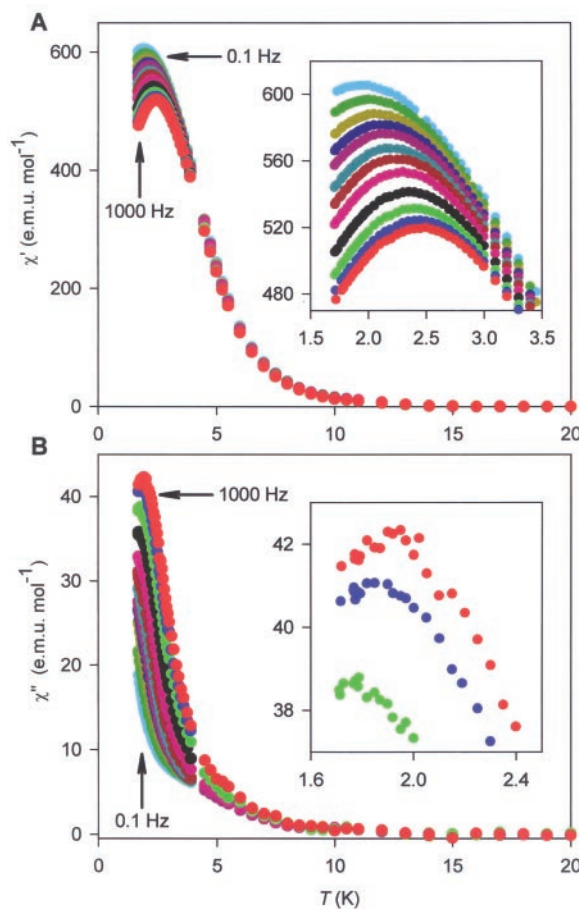


Fig. 4. Temperature dependence of the ac susceptibility χ' (A) and χ'' (B) of polymer **1** measured in the zero applied field. The ac driving field is 0.1 Oe and the frequencies are 1000, 800, 500, 250, 100, 50, 25, 10, 5, 2, 0.5, and 0.1 Hz. [Diameter of the symbols for χ'' in the inset of (B) represents approximately one standard deviation for three measurements.]

Table 1. Synthesis of polyether **2** and generation of polymer **1**.

Run	Gelation point (min)	Polymerization time (hours)	Yield of 2 (%)	Average S in 1
1	<10	0.2	71	600 to 1300*
2	<15	0.5	53	700 to 1500†
3	<10	5	73	3000 to 7000*

*Four samples. †Three samples.

time of the magnetization. With the very few T_m'' data points and narrow frequency range, the plot of $\ln(\tau)$ versus $1/T$ gives a straight line ($R = 0.996$) with an order of magnitude estimates for the barrier $E_A/k_B = 15$ K and the microscopic limiting relaxation time $\tau_0 = 9 \times 10^{-8}$ s. Both E_A/k_B and τ_0 are comparable to those found in slowly relaxing molecular cluster-based superparamagnets (e.g., in Fe_8 , $E_A/k_B = 22.2$ K and $\tau_0 = 1.9 \times 10^{-7}$ s) (25).

Analogous to ZFC/FC magnetizations, both χ' and χ'' , as measured at the frequency of 1000 Hz and the ac driving field of 0.1 Oe, are highly sensitive to the applied H . For $H \approx 0.5$ and 1 Oe, T_m' shifts from 2.50 K (at zero-field) to 2.10 and 1.75 K, respectively; the intensity is significantly lowered (at 1 Oe, 60% of the zero-field value). The T_m'' shifts to ≤ 1.7 K even at 0.5 Oe and the intensity decrease of χ'' is even more pronounced than for χ' (at 1 Oe, 25% of the zero-field value at 1.7 K).

Polyethers **2** obtained after short polymerization times (Table 1, runs 1 and 2) give polymers **1** with relatively lower values of average $S = 600$ to 1500 (seven samples). No peaks in ac susceptibility are detected; however, a small and frequency-dependent $\chi'' < 1$ emu mol⁻¹ is observed at low temperatures, suggesting an onset of magnetic blocking.

In conclusion, our experimental data show that organic polymer magnets can be prepared. In polymer **1**, both blocking of magnetization and very large magnetic moments are found below a temperature of about 10 K. Overall, the magnetic behavior falls between insulating spin glasses and blocked superparamagnets, but closer to spin glasses.

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17. The ¹H NMR (500 MHz, 348 K) spectra of polyether **2** gelled with benzene-d₆ are identical for different polymerization times. The three broad peaks (7.5, 3,

- and 1 ppm) have the chemical shifts as expected for the aromatic, methoxy, and *tert*-butyl protons of polyether **2**. Analogously, ¹³C NMR (125 MHz) spectrum has four broad resonances at 88, 53, 34, and 32 ppm, corresponding to the triarylmethyl, methoxy, quaternary *tert*-butyl, and methyl *tert*-butyl carbons; the aromatic region is obstructed by the benzene-d₆ peak.
18. The minor, organic soluble polyether **2** ($M_w = 3 - 5 \times 10^5$ Da) gave paramagnetic polymers with an average $S \approx 40$ (13). These values of M_w may be considered as the lower ends of the molecular weight distributions for entries in Table 1.
19. Experimental procedures involving generation of polymer **1**, magnetic measurements, numerical fitting of magnetic data, determination of magnetic impurities are available on Science Online (www.sciencemag.org/cgi/content/full/294/5546/1503/DC1).

20. All magnetic measurements were carried out using Quantum Design DC/AC SQUID MPMS55 magnetometer.
21. The values of average S [or $S(S + 1)$] follow qualitatively the χT versus T plot (Fig. 2B).
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Confinement Effect on Dipole-Dipole Interactions in Nanofluids

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Intermolecular dipole-dipole interactions were once thought to average to zero in gases and liquids as a result of rapid molecular motion that leads to sharp nuclear magnetic resonance lines. Recent papers have shown that small residual couplings survive the motional averaging if the magnetization is nonuniform or nonspherical. Here, we show that a much larger, qualitatively different intermolecular dipolar interaction remains in nanogases and nanoliquids as an effect of confinement. The dipolar coupling that characterizes such interactions is identical for all spin pairs and depends on the shape, orientation (with respect to the external magnetic field), and volume of the gas/liquid container. This nanoscale effect is useful in the determination of nanostructures and could have unique applications in the exploration of quantum space.

The dipole-dipole interaction is ubiquitous in nature and is responsible for many physical phenomena. For nuclear spin systems, it plays an important role in most solid-state NMR experiments (1), as well as in studies of complex molecules (2) and of liquid crystals (3). Dipolar couplings are widely used in NMR to extract structural information, as well as dynamics. Although these microscopic interactions average to zero in bulk gases and liquids, liquid-state dipolar field effects have been predicted and observed (4, 5), leading to applications such as new imaging techniques (6, 7). Here, we report both theoretically and experimentally on microscopic dipolar interactions that do not average to zero in gases and liquids confined to nanoscale volumes. This effect is quite different from the dipolar field effects observed

in macroscopic samples. In the effect we observed, restricted diffusion leads to a non-zero intermolecular, dipolar Hamiltonian characterized by a single universal dipolar coupling constant. This coupling constant can be tuned by the shape and size of the nanovolume, which leads to sensitive dependence of the NMR linewidth on the nanostructure at a constant gas/liquid density. This residual intermolecular dipolar coupling could have a wide range of applications, such as structural determination of nanostructures and nanoporous media, as well as the study of quantum dynamics of high-order quantum coherences made accessible by the unique Hamiltonian.

Consider a gas or liquid system of N molecules, each bearing a nuclear spin I , contained in an axially symmetric ellipsoidal container with principal axes a , b , and $c = b$. The Hamiltonian of dipole-dipole interactions of N spins in an external magnetic field is given by (8)

$$H = \gamma^2 \hbar^2 \sum_{j < k} P_2(\cos\theta_{jk}) (1/r_{jk}^3) (\vec{I}_j \cdot \vec{I}_k - 3I_{jz}I_{kz}) \quad (1)$$

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