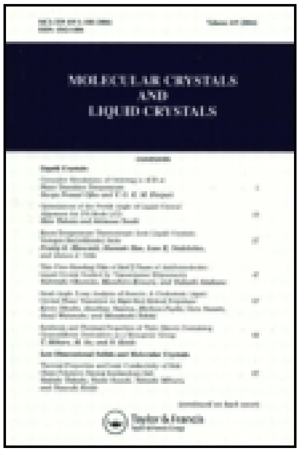

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Daisuke Shiomi, Kazunobu Sato, Takeji Takui, Koichi Itoh, D. R. McGill, Kai M. Ng & Richard J. Bushby (1997): High-Spin States of Hyperbranched Polycationic Organic Polymers as Studied by Ft Pulsed-Esr/Electron Spin Transient Nutation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 513-520

To link to this article: http://dx.doi.org/10.1080/10587259708044608

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 513–520
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HIGH-SPIN STATES OF HYPERBRANCHED POLYCATIONIC ORGANIC POLYMERS AS STUDIED BY FT PULSED-ESR/ELECTRON SPIN TRANSIENT NUTATION

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Abstract As a novel electron magnetic resonance technique for the characterization of organic molecule-based magnetic materials, an electron spin transient nutation method based on Fourier-transformed pulsed ESR spectroscopy was applied to polycationic organic polymers of π-topology-mediated molecular design. The polymers are triphenylamine-based in the hyperbranched three-dimensional network with the unpaired electrons at the nitrogen cation sites. The FID-detected nutation spectrum from one of the polymers exhibited several nutation-frequency components corresponding to high-spin species containing S=1 to S=3. The static magnetic susceptibility of the polymer supported the high-spin ground state in the system under study. The present results demonstrate the potentialities of the pluri-charged high-spin polymeric systems as well as the methodological advantage of nutation spectroscopy in identifying the spin multiplets of the molecule-based magnetic materials in the frequency domain.

INTRODUCTION

Polycationic Polymers as Novel Organic High-Spin Systems

Organic molecule-based magnetism has attracted increasing interest in recent years.[1] The conceptual proposals of the organic magnetism based on intramolecular through-bond approach has been made as early as in 1960's.[2] The approach exploits the topological symmetry of *meta*-connectivity in π-conjugated electronic network which gives rise to the unlimited degrees of orbital degeneracy of π-non-bonding molecular orbitals (π-NBMO's) in organic polymers with *meta*-connected phenyl rings. Figure 1(a) shows the π-band (π-crystal orbital) structure of a hypothetical one-dimensional high-spin polymer which is calculated in terms of a simple tight-binding method, or the Hückel method. Incompletely filled π-electron spins are parallel in the degenerate NBMO's of the neutral polymer to give a high-spin or ferromagnetic ground state.

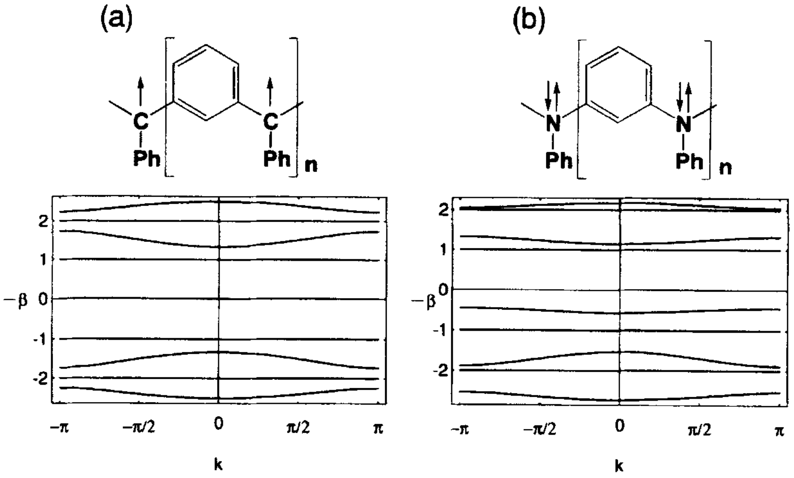

FIGURE 1 π-Orbital band structures of homoatomic neutral (a) and heteroatomic cationic (b) π-conjugation of model polymers obtained from the simple tight-binding method. The upper parts of the figure show the *meta*-connectivity of the neutral high-spin polymer (a) and the neutral precursor of the cationic high-spin polymer (b).

On the other hand, charged (cationic or anionic) organic high-spin systems with heteroatomic perturbation have recently attracted attention as models for novel organic molecule-based magnetic materials with electronic multifunctionality.[3-6] One of the targets of such systems is synthetic and organic magnetic metals. In Figure 1(b) is shown the π-band structure of a heteroatomic neutral precursor of the pluri-cationic high-spin polymers. The highest doubly-occupied band of the polymer exhibits small energy dispersion or small band width. Thus, after one-electron oxidation per repeating unit, the electronic ground state of the polymer is dominated by competition of kinetic energy in the wave-vector k space and exchange energy between the π-electrons in the band. The polycationic polymer in Figure 1(b), after oxidized, has a possibility of exhibiting high-spin, or ferromagnetic ground state. Some oligo-cationic model compounds have been synthesized and examined in terms of ESR spectroscopy.[3] Recently a quartet (S=3/2) ground state has been identified unequivocally for the trication of a 1,3,5-triaminobenzene derivative by an ESTN (Electron Spin Transient Nutation) method,[4-6] which is a novel spectroscopic technique based on FT pulsed ESR spectroscopy as described below.

In this paper we report the magnetic properties of two kinds of polycationic organic polymers as an example of pluri-charged polymeric organic magnets.[7] The polymers under study, A and B, are triphenylamine-based in the hyperbranched three-dimensional network as shown in Figure 2.[8,9] A 3,4'-substituted biphenyl unit is incorporated in the polymer networks. Although the biphenyl unit is not taken into account in the band calculation of the hypothetical polymer, a dicationic biradical molecule with the unit has been shown to possess a triplet ($S=1$) ground state.[8] This is expected in terms of the π-topology-mediated molecular design in which the *m*- and *p*- (3- and 4'-) positions of the biphenyl unit are linking modes. Therefore, an oxidative doping of the polymers A and B can yield the highest band which is incompletely filled with parallel spins, giving rise to high-spin states.

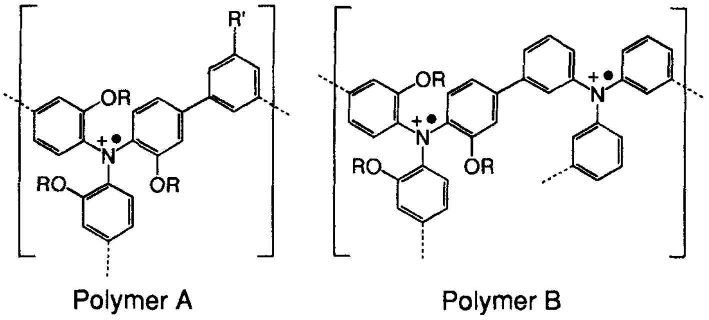

FIGURE 2 Polymer A and Polymer B. (A: $R=C_6H_{13}$, $R'=C_{14}H_{29}$; B: $R=C_{10}H_{21}$).

Electron Spin Transient Nutation (ESTN) Spectroscopy

We have been examining the potentialities of the ESTN method as a novel spectroscopic technique for the characterization of molecule-based magnetic materials.[10-12] The detailed methodology for non-oriented systems has been published elsewhere.[12] In the presence of a static field $\boldsymbol{B}_0$ as well as an oscillating microwave (MW) field $\boldsymbol{B}_1$, the macroscopic magnetization precesses around the effective field vector $\boldsymbol{B}_{\rm eff}$ which is the summation of $\boldsymbol{B}_0-\omega_{\rm MW}/\gamma$ and $\boldsymbol{B}_1$ (γ: electron gyromagnetic ratio) in the frame rotating at the MW frequency ω_{MW}. The precession around $\boldsymbol{B}_{eff}$ in the rotating frame is called a transient nutation of the magnetization. The nutation frequency ω_N for $S>1/2$ is dependent on the magnitude of the $\boldsymbol{B}_1 \cdot \boldsymbol{g} \cdot \boldsymbol{S}$ term relative to that of the fine structure term, $\boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}$, in the spin Hamiltonian. In the extreme limit of $\boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S} >> \boldsymbol{B}_1 \cdot \boldsymbol{g} \cdot \boldsymbol{S}$, the nutation frequency is given by,

$$\omega_N = \gamma B_1 \sqrt{S(S+1) - M_S(M_S - 1)}, \tag{1}$$

for the allowed ESR transitions between the spin sublevels $|M_S\text{-}1>$ and $|M_S>$ under the on-resonance condition.[10-12] The quantum numbers S and M_S of the transition can be determined in terms of the relation in Equation (1), leading to unequivocal identification of spin multiplicity of the system under study. The pluri-charged polymers such as A and B are almost certainly mixtures of components with various spin multiplets, bringing about spectral overlap of conventional cw ESR spectroscopy. For such complicated spin systems the ESTN method has advantage in discriminating between the spin multiplets in the frequency domain as shown in Equation (1).

The spin states of the polymers A and B are elucidated in the following by using the ESTN method. The bulk magnetic properties of the polymers are also examined by means of magnetic susceptibility (χ) measurements. The potentialities of the charged polymers as novel high-spin systems are clarified from the experimental results.

EXPERIMENTAL

The polymers were synthesized and oxidized according to the reported method[8,9] and then sealed into glass tubes under vacuum. The whole procedure of preparing the tubes was made under a nitrogen atmosphere in a grove box. The bulk magnetic susceptibilities of the polymers were measured on a Quantum Design SQUID magnetometer MPMS2. Owing to the uncertainty of the amount of reacted and unreacted oxidizing reagent ($NOBF_4$) remaining in the powder solid of the polymers, the diamagnetic susceptibility has not been subtracted from the measured susceptibility. The susceptibilities are discussed only in a qualitative way; the dominant interaction is ferromagnetic or antiferromagnetic. The nutation spectra and conventional cw ESR spectra of the powder samples of the polymers were measured at temperature T=4.2 K on a Bruker X-band FT-ESR spectrometer ESP380 equipped with a Q-tunable dielectric cavity and a traveling-wave-tube microwave amplifier. The nutation spectra were recorded in two-dimension (2D) (magnetic field vs. nutation frequency) by monitoring the FID intensity with sweeping the static field in the range where a cw ESR signal appeared.

RESULTS AND DISCUSSION

Polymer A

The temperature T dependence of χT for Polymer A is shown in Figure 3. From the χT value extrapolated to zero K, the paramagnetic portion in the oxidized polymer is found to be 17 % by assuming the high-temperature χ values (T > 70 K) to obey Curie's law. The χT value deviates upward from Curie's law at lower temperatures, indicating the high-spin ground state in the polymer network. This is consistent with the

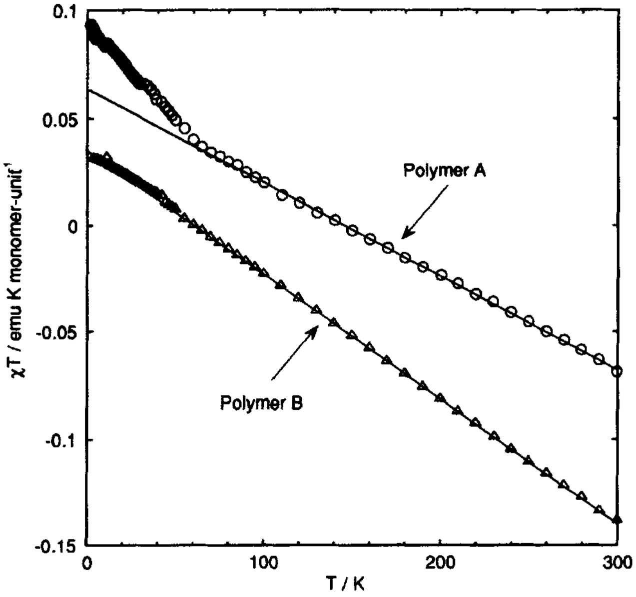

FIGURE 3 Temperature dependence of χT (the circles: Polymer A, the triangles: Polymer B). The solid lines represent simple Curie's law calculations.

reported result of magnetization curve measured up to the saturation field which has suggested the averaged spin quantum number, S=5/2.[8,9]

The 2D nutation spectrum of A exhibited several nutation-frequency components. A slice of the 2D spectrum at the central field of the cw signal is depicted in Figure 4. The most intense peak with the frequency of ω_N=9.1 MHz is assignable to S=1/2 since the ω_N value is equal to the γB_1 value (ω_N for S=1/2) measured for DPPH radical (an S=1/2 frequency-reference). The stick spectrum in Figure 4 is calculated by using Equation (1) and γB_1=9.1 MHz. By comparing the calculation with the observed spectrum, it is concluded that the observed higher-frequency components correspond to high-spin species ranging to S=3. From the nutation experiment, Polymer A is identified as a mixture of "high-spin oligomers" with dominant spin quantum numbers S≦3. The result is consistent with the magnetization measurement[8,9] as mentioned above. The 17 % of the nitrogen sites are oxidized and some of the unpaired electrons on the oxidized sites adjacent to each other are ferromagnetically coupled to afford the high-spin oligomers.

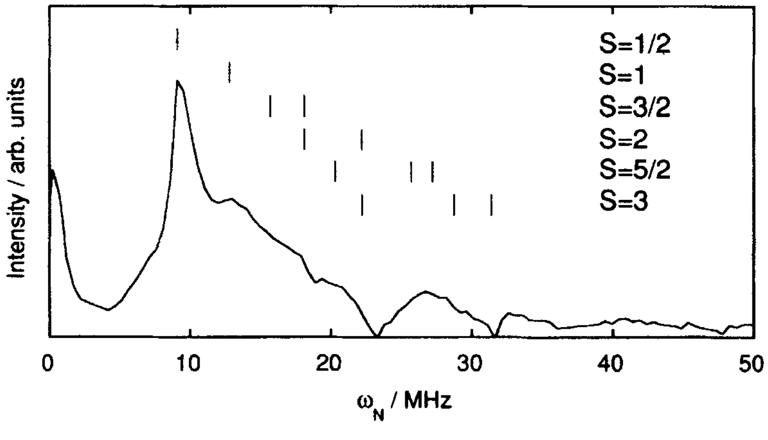

FIGURE 4 Slice nutation spectrum of Polymer A with the static field applied at the center of the cw-ESR signal (348.4 mT). The sticks indicate the nutation frequencies calculated for S=1/2 to S=3.

Polymer B

The extrapolation of χT to zero K revealed the paramagnetic portion of 5.1 % in Polymer B when Curie's law of S=1/2 is assumed. The Curie behavior of χT

appearing in the whole temperature range examined, i.e., a straight line as a function of temperature, as shown in Figure 1 indicates that the temperature-dependent Boltzmann distribution over the spin states with different S values is negligible. The averaged S value is independent of temperature. However, the S values of such states are not clear in the χ measurement.

In the 2D nutation spectrum of B, only one frequency component of $S=1/2$ was detected. This result together with the χ data described above shows that an assembly of magnetically independent $S=1/2$ radicals dominates in Polymer B. The magnetic interaction in the polymer network is negligibly small. This is presumably ascribed to the insufficient concentration of doped sites compared with that of A.

CONCLUSION

ESTN spectroscopy has revealed the polycationic polymer A is a mixture of high-spin components containing $S=1$ to $S=3$. The result indicates the effectiveness of the strategy of pluri-charged polymers as novel high-spin systems of the π-topology-mediated molecular design with heteroatomic perturbation. Furthermore, from the methodological viewpoint, the present results illustrates that ESTN spectroscopy enables us to characterize unequivocally a mixture of paramagnetic components, particularly in amorphous solids, with different molecular spin multiplets larger than doublet in the frequency domain.

ACKNOWLEDGMENTS

This work has been supported by Grants-in-Aid for Scientific Research on Priority Area “Molecular Magnetism” (Area No. 228/04 242 103 and 04 242 105) from the Ministry of Education, Science and Culture, Japan. The authors (D. S. and K. S.) acknowledge the Ministry of Education, Science and Culture, Japan for Grants-in-Aid for Encouragement of Young Scientists (No. 07740553 and 07740468). The financial support from the Ministry of International Trade and Industries, Japan (NEDO Project "Organic Magnets") is also acknowledged. The authors thank Professor Kiyoshi Isobe and Professor Isamu Kinoshita at Osaka City University for our use of the grove box.

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