

## M. Novel magnetic behavior of multidimensional organic polymer synthesized by cycloaddition reaction

Kiyoshi Takagi<sup>a</sup>, Sadamu Takeda<sup>b</sup>, Wasuke Mori<sup>b,\*</sup>, and Nobuo Nakamura<sup>b</sup><sup>a</sup> Department of General Education, Kochi National College of Technology, Monobe, Nangoku-shi, Kochi 783, Japan<sup>b</sup> Department of Chemistry, Faculty of Science, Osaka University, Toyonaka Osaka 560, Japan**Abstract**

We report the magnetic properties of a novel organic polymer. The material gives the large saturation magnetization (0.15 G/g) at room temperature. Electron spin resonance (ESR) revealed a ferrimagnetic character, i.e., the existence of "exchange resonance branch" with extremely large  $g$ -value. The new organic polymer with large saturation magnetization can be stoichiometrically and reproducibly synthesized under ambient conditions and expected to be useful for practical applications.

Magnetic properties in organic substances have extensively examined recently [1-3]. One of the present authors (K. T.) synthesized a new polymer (named as poly-BAZA because of bis-aza structure of the main frame) which shows strong magnetism at room temperature. This paper presents characterizations and a microscopic nature of its magnetism.

The poly-BAZA was synthesized by direct catalyst-free 1,3-dipolar cycloaddition reaction between one part of *p*-phenylenebis-(3-sydnone) and twice of *N,N'*-(1,4-phenylene)-bis-maleimide in boiling concentrated dimethylsulfoxide solution in almost 100% yield. The product polymer particles with dark brown or black color can crudely be divided into three fractions, I, II, and III. The particles I stick fast to a bar magnet, while particles III remain unmoved by a bar magnet. Magnetic properties of II is in between I and III. The maximum fraction of I was about 1% of the total amount of the product (I + II is about 16% on average). Rapid polymerization in the highly concentrated solution led to the maximum fraction of polymers I and II. The field dependence of the magnetization of I was measured and the ferromagnetic behavior was evidenced between 4.2 and 300 K. Significant hysteresis of the magnetization curve was observed (Fig. 1). The magnetization at 300 K reaches a saturated value, 0.15 G/g (0.16 G/g at 4.2 K).

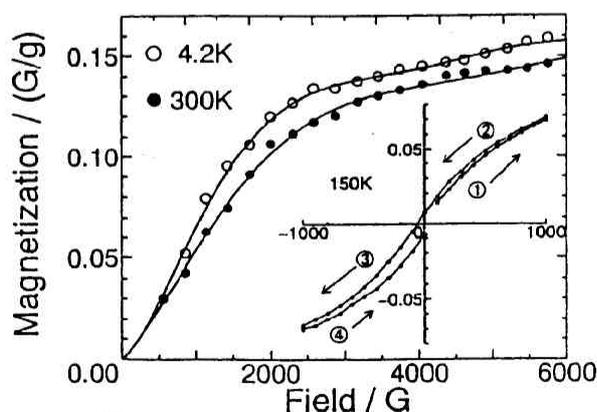


Figure 1. Field dependence of magnetization of poly-BAZA-I. The measurement was performed with magnetic balance on polymer particles (1.93 mg) with nujol (12.5 mg) to restrain the mobility of polymer particles in a quartz cell. The back ground magnetization due to the quartz cell as well as nujol was subtracted. Copper sulfate was used as a reference sample.

Separate measurement with SQUID magnetometer (QUANTUM Design, MPMS-5) in the region of  $\pm 1$  T almost reproduced the result and evidenced a significant hysteresis (figure inserted). Corrections were made to the data for the diamagnetic contribution. Solid curves are guide to the eye.

Monotonous increase in the magnetization on cooling from 300 to 4.2 K was also observed at constant fields, 100, 1733, 3467, and 5749 G. The amounts of magnetic metal impurities were analyzed to be negligibly small by induction-coupled argon plasma atomic emission spectra; Fe: 20 ppm, Co: none, Ni: none (detection limit : 10 ppm). The origin of the impurity of Fe is not clear and a possible impurity is  $\text{Fe}_3\text{O}_4$  which exhibits a large saturation magnetization, about 100 G/g, among the ferrous compounds. Supposing that a small amount (20 ppm) of  $\text{Fe}_3\text{O}_4$  is included in the organic polymer, the estimated magnetization due to such impurity is the order of  $10^{-3}$  G/g, which is negligibly small compared with the observed value, 0.15 G/g, for the poly-BAZA I. Thus the observed saturation magnetization is intrinsic of the organic polymer. It should be noted that the strong magnetism in poly-BAZA is well preserved under atmosphere for at least a few years.  $^{13}\text{C}$ -CP/MAS nuclear magnetic resonance of poly-BAZA-I (8 mg) gave almost the same spectrum ( $\delta$  (TMS reference) = 51.6 with a shoulder at 38.6, 69.6, 131.9, and 173.9 ppm by Bruker MSL-200; resonance frequency = 50.323 MHz) as that of a well characterized monomer compound [4] except the large line width in poly-BAZA-I ( $\Delta = 10, 10, 15,$  and  $7$  ppm, respectively), suggesting that the local skeletal structure of poly-BAZA is the same as that of the monomer. The elemental analyses of poly-BAZA-I, II, and III led to very similar compositions of H, C, and N to each other and are almost in agreement with the proposed structure of the polymer enclathrating one molecule of dimethylsulfoxide per unit structure (Fig. 2) [5]. The shoulder signal of  $^{13}\text{C}$ -NMR at 38.8 ppm can therefore be assigned to dimethylsulfoxide enclathrated in the polymer.

Microscopic nature of the magnetism of poly-BAZA was examined by ESR. A remarkably broad resonances superimposed by a sharp line was observed at 9.259 GHz in poly-BAZA-I (insert in Fig. 3). The intensity of the broad component was diminished to 1/25 in poly-BAZA-II and lost in poly-BAZA-III. This trend is parallel to the response ability of the respective fractions, I, II, and III, to a bar magnet. Thus the broad ESR

\* Present address: Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-1293.

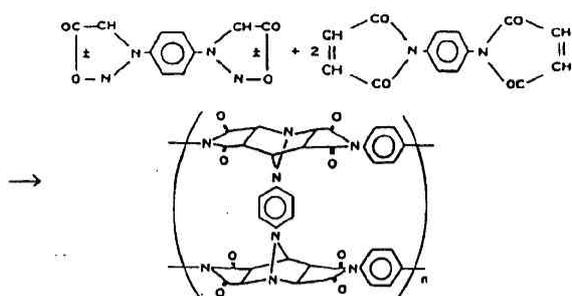


Figure 2. Polymerization reaction and estimated structure of the poly-BAZA. Two and three dimensional networks are realized by cross linkage between the chains. An assembly of unstable dangling bonds and radicals produced during the rapid polymerization may be maintained in the polymer matrix.

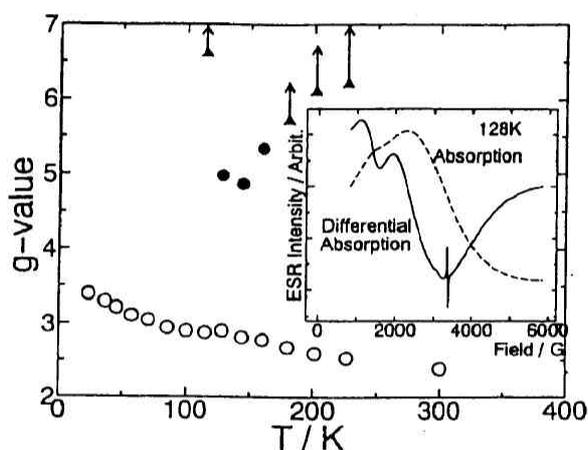


Figure 3. Apparent  $g$ -value of two branches of ESR spectra of poly-BAZA as a function of temperature. The field position of a broad peak at lower field in an inserted figure was determined from the middle point of a pair of peaks of full differential line at 128, 144, and 160 K (●), while at other temperatures the upper limit of the field position (minimum  $g$ -value, ▲) was estimated from a half of differential absorption because of lack of another half data at lower field. Insert shows typical differential absorption and absorption spectra of ESR at 128 K. The differential absorption line was recorded at 9.259 GHz with the field modulation at 100 kHz with the modulation amplitude of 20 G. Then the absorption was obtained by numerical integration of the differential line. The peak-to-peak width of the broad component at higher field was 1300 G which was independent of the temperature between 23 and 300 K, while the peak-to-peak width of broad component at lower field was 500 G between 128 and 160 K. The  $g$ -value of a sharp component of poly-BAZA-I is 2.0015 and peak-to-peak width was determined to be 8.5 G with the modulation amplitude of 0.8 G. The sharp component with the same  $g$ -value was also observed for poly-BAZA-II and -III with 7 times larger intensity and with smaller width (6.5 G) compared with poly-BAZA-I.

absorption can be ascribed to the strong magnetic property. Apparent  $g$ -value was calculated for the broad absorption by the formula  $h\nu = g\beta H$ , where  $H$  is the magnitude of the applied magnetic field at the position of the maximum absorption. The  $g$ -value (○) is plotted in Fig. 3 as a function of temperature. In

addition to the main strong absorption, a noticeable peak at a lower field appears and vanishes on heating. Although it overlaps with the main peak, its location (●, ▲) was successfully determined from the differential absorption line (Fig. 3). This lower-field peak gives the maximum intensity at 128 K. Here we emphasize that the novel temperature dependence of  $g$ -values of two branches and of the intensity of the upper branch (corresponding to the lower field peak) in Fig. 3 is similar to that of a famous ferrite,  $\text{Li}_{0.5}\text{Cr}_{1.25}\text{Fe}_{1.25}\text{O}_4$ , which shows a typical "ferrimagnetism" [6]. Eventually the upper branch with an extremely large  $g$ -value in Fig. 3 was assigned to "exchange resonance" which is controlled by strong molecular field [7]. Since Wangness showed theoretically that the exchange resonance of ferrimagnet can be observed at ordinary frequency near the angular momentum compensation point, at which total angular momentum approaches zero [7], its observation is an evidence of ferrimagnetism in the material [8]. It is obvious from Fig. 3 that the compensation of the angular momentum in poly-BAZA-I occurs over very wide temperature region (more than 100 K) contrary to the case of  $\text{Li}_{0.5}\text{Cr}_{1.25}\text{Fe}_{1.25}\text{O}_4$ , ferrite for which the compensation occurs within 10 K [6]. It is expected that the compensation leads to a reduction of the magnetization. This is true in the above ferrite but reduction of magnetization is not obvious in poly-BAZA-I. This fact may be related to the wide range compensation in this material. Thus apparent magnetism of poly-BAZA-I seems to be caused by an intrinsic organic ferrimagnetism. Further work is in progress.

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5. The elemental analysis in wt%, H:3.60; C:58.69; N:14.33 for poly BAZA-I, H:3.79; C:59.51; N:14.49 for II, H:3.65, C:59.39, N:14.18 for III. These data for poly BAZA-I, II and III agree fairly well with the structure,  $[-(\text{C}_{36}\text{N}_8\text{O}_8\text{H}_{22})-(\text{CH}_3)_2\text{SO}]_n$ , calculated H:3.65; C:59.06; N:14.50; O:18.63; S:4.15. The polymer is slightly hygroscopic. The water was removed by heating up to 200 °C *in vacuo* for six hours before the analysis.
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