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LETTER TO THE EDITOR

Preparation, molecular structures and novel magnetic properties of organic ferromagnetic compounds by pyrolysis of triphenoxy-triazine and benzoguanamine

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Abstract. The product obtained by the pyrolysis of a mixture of triphenoxy-triazine (TPTA) and benzoguanamine (BG) at 400–1000 °C has exhibited novel ferromagnetic behaviour. The product with the highest spin concentration (1.4×10^{20} spins g^{-1}) was obtained when a TPTA/BG mixture of molar ratio 1.1 : 0.9 was pyrolysed at 700 °C. The possible compound structures of the products prepared at 350 °C and 600 °C are proposed from the results of elemental analysis. The ferromagnetic behaviour is considered to be caused by parallel spins of the nitrogen and/or oxygen radicals in those structures.

Since the observation of novel ferromagnetic behaviour in a pyrolysed organic compound, the pyrolysing method has often been utilized for the preparation of organic ferromagnets [1–4].

The origin of the novel ferromagnetic behaviour, however, has not been clarified, because it has been difficult in most cases to determine the molecular structure of the pyrolysed compound. The reproducibility of obtaining an organic compound exhibiting ferromagnetic behaviour by this method was also relatively low.

On the other hand, we have found that ferromagnetic products can be obtained with a high reproducibility by the pyrolysis of the mixture of 2,4,6-triphenoxy-1,3,5-triazine (TPTA) and phenylenediamine (PDA) [5–7]. Magnetically active parts, however, constituted just a fraction of 10^{-4} – 10^{-2} of the batch prepared by the pyrolysis: this is expected to increase if products with a high spin concentration can be prepared.

In the present study, we attempt to determine the pyrolysing conditions necessary for preparing the products with the highest spin concentration from a mixture of TPTA and benzoguanamine (BG). The spin concentration of the products is examined as a function of either the mixture ratio of TPTA/BG or the pyrolysing temperature. In this letter, we discuss mainly the most appropriate preparation conditions. In addition, using the results of elemental analysis for the products prepared at various pyrolysing temperatures, their possible molecular structures are proposed. The magnetic properties of the pyrolysed material are examined using measurements of ESR and magnetization.

Sample preparation and experimental procedures were as follows. Pyrolysis of the mixture of TPTA and BG was carried out in an infrared image furnace (ULVAC E-45P) equipped with a quartz glass tube (25 mm \times 500 mm). Heating was performed under Ar gas flow with the two steps in series, i.e. firstly for 0.5 h at 233 °C (the melting point of

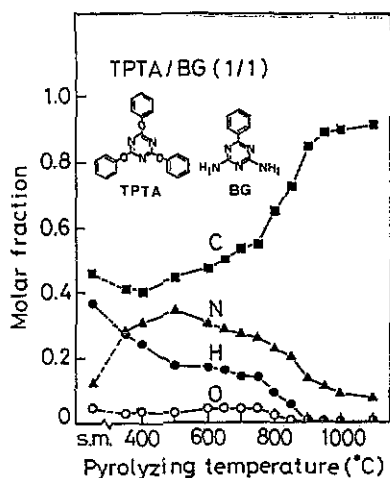


Figure 1. The change in molar fraction in the products prepared by the pyrolysis of the mixture of TPTA and BG (molar ratio 1:1) as a function of the pyrolyzing temperature.

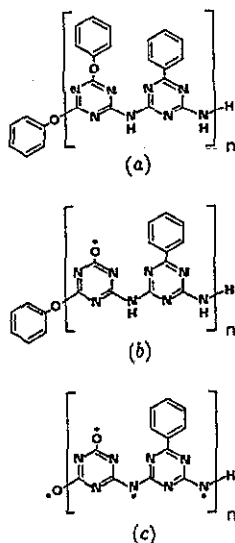


Figure 2. The possible molecular structures of the products prepared at (a) 233–300 °C, (b) 350 °C and (c) 600 °C.

TPTA) and secondly for 1.5 h at various temperatures between 350 and 1100 °C. The heating rate to each temperature (233 °C or 350–1100 °C) was 40 °C min⁻¹.

A small fraction of the batch prepared in the temperature range 400–1000 °C was found to be attracted by a magnet. In the preliminary experiment, we found that the fraction of magnetically active parts depended on the pyrolyzing temperature and the mixture ratio of TPTA and BG, and increased with the increase in the unpaired spin concentration (estimated from the ESR measurements).

ESR measurements were performed at room temperature with a Bruker ESP 300 spectrometer. The sample was first cracked into minute pieces, put into a quartz tube with a diameter of 2 mm, heated at 300 °C in a high vacuum and then sealed. A 1,1-diphenyl-2-picrylhydrazyl (DPPH) film diluted in polystyrene was used as a reference sample for the determination of the spin concentration (N_s) and the g value. Magnetization (M)–magnetic field (H) curve tracing was carried out with an alternating force magnetometer (PM-2900) at room temperature. Atomic absorption spectrochemical analysis of magnetic impurities in the pyrolysed material was performed: no transition metal elements were detected with a concentration above 0.5 ppm. It should be mentioned that the influence of the magnetic impurities upon the ferromagnetic behaviour observed in the present experiments was negligible.

The dependence on pyrolyzing temperature of the molar fraction (determined from the elemental analysis of the sample prepared from TPTA/BG) is shown in figure 1. Below 500 °C, a remarkable elimination of hydrogen and oxygen was observed: the elimination of hydrogen was enhanced with increasing temperature, while the elimination of nitrogen was negligible. In the range 500–750 °C, the molar fraction of hydrogen and nitrogen decreased only slightly with increasing temperature. In the range 750–950 °C, the elimination of hydrogen and nitrogen was accelerated with increasing temperature. The elimination of oxygen was furthermore enhanced above 750 °C.

We can tentatively speculate on the molecular structures of the products pyrolysed at some selected temperatures from the elemental analysis data. Molecular structure 1 (shown in figure 2) is considered to be produced from the thermal reaction between TPTA and BG at a temperature below 300 °C. The molar fractions of hydrogen and nitrogen in the sample prepared at 350 °C were 0.27 and 0.29, respectively, while the molar fraction of hydrogen is larger than that of nitrogen for all n in structure 1. For example, the molar fractions of hydrogen and nitrogen for $n = 1-12$ in structure 1 are estimated to be 0.35-0.31 and 0.15-0.20, respectively, which are too large (hydrogen) and too small (oxygen), compared with the experimental values referred to above. For the compound pyrolysed at 350 °C structure 2 is proposed and suggests that an oxygen radical is produced from phenoxy by the slight heat treatment. The molar fraction values of elements C, H, N and O in structure 2 for $n = 7-12$ are estimated to be 0.431-0.429, 0.263-0.258, 0.268-0.275 and 0.038-0.037, respectively. These values are comparable with the molar fractions (C/0.414, H/0.272, N/0.285 and O/0.029) in the sample prepared at 350 °C.

The decrease in the molar fraction of hydrogen with increasing pyrolysing temperature in the range 400-600 °C was not followed by the increase in the elimination of carbon. From these results, the molecular structure 3, in which the elimination of hydrogen yields a nitrogen radical, is suggested for the compound pyrolysed at 600 °C. The molar fraction values (C/(0.450-0.458), H/(0.200-0.194), N/(0.300-0.306) and O/(0.052-0.041)) of elements in structure 3 for $n = 3-12$ exhibit a good coincidence with the molar fractions (C/0.474, H/0.172, N/0.309 and O/0.045) in the sample prepared at 600 °C.

The structure of the products prepared above 750 °C is considered to be complicated, because, surprisingly, nitrogen and oxygen, as well as hydrogen, are eliminated.

The dependence on pyrolysing temperature of the spin concentrations, N_s , the peak-to-peak linewidth, ΔH_{pp} , and the g value in the samples prepared from TPTA/BG (molar ratio 1:1) shown in figure 3 were obtained from the ESR measurements. A weak ESR signal detected at the pyrolysing temperature of 350 °C is considered to arise from the oxygen radical shown in structure 1. An intensive increase in the concentration of unpaired spins was observed at the pyrolysing temperatures of 500-600 °C and 700 °C. Most of those spin concentrations should be provided by the nitrogen radical in structure 3 and/or by the oxygen radical as mentioned above. The rapid decrease in the spin concentration observed above 750 °C can be caused by the elimination of those radicals.

As the spin concentration increased with increasing pyrolysing temperature, the linewidth decreased continuously. The minimum linewidth occurred when the spin concentration reached a maximum value. When the concentration began to drop, the line started to broaden again.

The g value was generally independent of the pyrolysing temperature and was slightly larger than that of a free electron.

TPTA/BG mixtures of varying molar ratio were pyrolysed at 700 °C: the results of ESR measurements are shown in figure 4 in which the mixture ratio is indicated in terms of the molar fraction of TPTA in the mixture of TPTA and BG. The maximum value of spin concentration, which was attained under the most appropriate pyrolysing conditions, was 1.4×10^{20} spins g^{-1} for a molar fraction of 0.55. The linewidth was minimized at the point of maximal spin concentration, and the g value was independent of the molar fraction of TPTA.

For the pyrolysed samples, the variations of the molar fraction of elements with the TPTA molar fraction were examined. Those variations, however, were small (see figure 5), in contrast with the intensive variation of the spin concentration. For instance, when

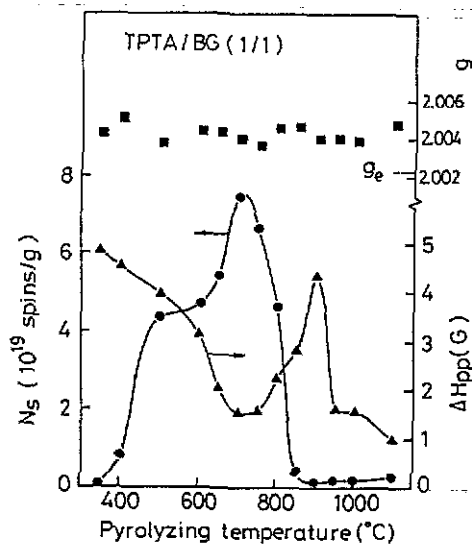


Figure 3. The dependence on pyrolyzing temperature of the spin concentration N_s for the products prepared by the pyrolysis of the mixture of TPTA and BG (molar ratio 1:1).

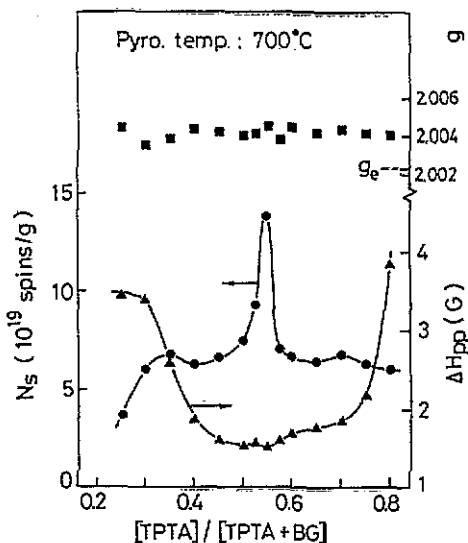


Figure 4. The change of the spin concentration, N_s , for the products prepared by pyrolysis at 700°C, as a function of the molar fraction of TPTA in the mixture of TPTA and BG.

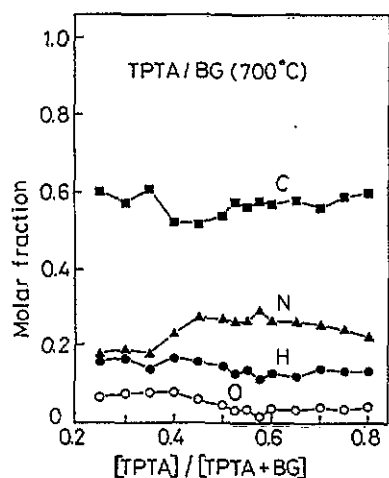


Figure 5. The change in molar fraction in the products prepared by pyrolysis at 700°C, as a function of the molar fraction of TPTA in the mixture of TPTA and BG.

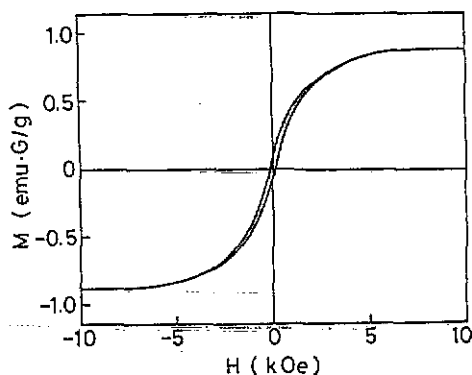


Figure 6. The magnetization curve of TPTA/BG (molar ratio 1:1) pyrolysed at 600°C, measured at room temperature.

the molar fraction of TPTA was less than 0.45, a slight decrease in the molar fraction of nitrogen and a slight increase in the molar fraction of oxygen occurred.

We succeeded in observing hysteresis in the magnetization at room temperature for the magnetically active parts separated by a magnet. The M - H curve of the product prepared from TPTA/BG (molar ratio 1:1) by pyrolysis at 600°C is shown in figure 6: the

saturation magnetization (M_s) is $0.88 \text{ emu G g}^{-1}$, the residual magnetization (M_r) is $0.07 \text{ emu G g}^{-1}$, and the coercive force (H_c) is 124 Oe .

In molecular structure 3, realization of parallel spin orientation among those nitrogen radicals or between the oxygen radical and the nitrogen radical is expected by a spin polarization effect [8] of triazine derivatives in the present conjugated system.

In conclusion in the present study, we have determined the pyrolysing temperature and the mixture ratio necessary for preparing an organic compound with maximum spin concentration by the pyrolysis of TPTA and BG. The main results are summarized as follows.

(i) The products with spin concentration of $1.4 \times 10^{20} \text{ spins g}^{-1}$ were obtained when the mixture of TPTA and BG of molar ratio 1.1:0.9 was pyrolysed at 700°C under Ar gas flow.

(ii) From the elemental analysis of the pyrolysed products, the possible compound structures of the products prepared at 350°C and 600°C were determined. The ferromagnetic behaviour observed in those products is considered to be caused by parallel spins of the nitrogen and/or oxygen radicals in those structures.

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