Magnetic properties of pyrolyzed poly-ε-caproamide

W. KAPPEL*, S. JIPAa,b, R. SETNESCUa,b, T. ZAHARESCU*, T. SETNESCUa,b, E. BURZOA

*ICDIE, ICPE-CA Bucharest, 313, Splaiul Unirii, Bucharest, Romania
b Valeaia University of Targoviste, Faculty of Sciences, Department of Chemistry, 18-22 Unirii Bd., Targoviste, Romania
a Babes-Bolyai University of Cluj Napoca, Faculty of Physics, 1, Mihail Kogalniceanu Bd., Cluj-Napoca, Romania

A new molecular ferromagnetic substance was prepared and its magnetic properties were examined. The product obtained by the pyrolysis of poly-ε-caproamide (PCA) at 700-1000 °C has exhibited a ferromagnetic behaviour. Especially the pyrolysis at 900 and 1000 °C has been most effective. The larger values of magnetic susceptibility and spontaneous magnetization at 80 K as well as Curie temperature have been evaluated for the studied pyro-PCA samples. The spin concentration was also presented. The results are tentatively discussed in terms of parallel spin orientation of the nitrogen radicals.

(Received January 18, 2006; accepted March 23, 2006)

Keywords: Molecular ferromagnetism, Pyrolysis, Poly-ε-caproamide

1. Introduction

The magnetic properties of organic materials have attracted considerable interest in the last decade. The idea is to create the macroscopic spins of long-range order in molecular systems. The spin density should be enough high to ensure substantial magnetization, high Curie temperature, and dipole interaction required to develop a domain magnetic structure.

Several organic ferromagnets have been obtained by chemical synthesis or pyrolysis [1-10]. However, the pyrolyzed materials only present critical temperatures of practical use.

Ovchinnikov et al. have proposed ferromagnetic polyradicals based on the graphite-net motif in which some carbon atoms are substituted by nitrogen [11].

Dixon et al. [12] have also suggested that the organic materials containing N atoms can be candidates for the ferromagnets.

The pyrolysis of the mixture of phenylenediamine and triazine derivatives, which contain N atoms exhibits a ferromagnetic behaviour [13].

However, the experimental studies of the preparation of such organic ferromagnets containing N atoms are very few.

This paper describes the results of our investigation on ferromagnetic compound obtained by the pyrolysis of poly-ε-caproamide.

2. Experimental

Poly-ε-caproamide (PCA) results by ε-caprolactamide polycondensation and have the structure shown below:

\[
\text{NH} \rightarrow (\text{CH}_2)_{5} \rightarrow \text{CO} \]

Poly-ε-caproamide sample (M = 35400) was supplied as a powder form by Relon-Fibrex SA, Romania.

The samples (3 g) were placed in quartz crucibles and pyrolyzed in the temperature range of 700-1000 °C under argon atmosphere for 2 h at each temperature. Black powder obtained after pounding of the pyrolysis product in porcelain mortar was nearly 50 % of the total weight of the starting material. Some part of the pyrolyzed material was found to be attracted by a magnet. Content of this magnetically active part was around 10% (W/W) from product amount.

It should be mentioned that any magnetic impurity such as a transition metal element was not detected by atomic absorption spectrochemical analysis (less than 0.5 ppm).

The magnetic susceptibility data were obtained in the temperature range 80-300 K with a Faraday balance. The magnetic resonance spectra were recorded in the same temperature range using a ART-5 spectrometer.

3. Results and discussion

Table 1 presents the magnetic susceptibility (\(\chi\)) and spontaneous magnetization (\(M_s\)) at 80 K as well as Curie temperature (\(T_c\)) of the pyro-PCA as a function of the pyrolysis temperature.

<table>
<thead>
<tr>
<th>Pyrolysis temperature (°C)</th>
<th>(\chi) (10^3) (emu.cm(^3)/g)</th>
<th>(4\pi M_s) (Gs)</th>
<th>(T_c) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>2.52</td>
<td>6.28</td>
<td>700</td>
</tr>
<tr>
<td>800</td>
<td>3.82</td>
<td>18.00</td>
<td>830</td>
</tr>
<tr>
<td>900</td>
<td>6.22</td>
<td>29.54</td>
<td>950</td>
</tr>
<tr>
<td>1000</td>
<td>6.42</td>
<td>30.14</td>
<td>960</td>
</tr>
</tbody>
</table>

Table 1. The values \(\chi\) and \(M_s\) (80K) as well as \(T_c\) of the pyro-PCA as a function of the pyrolysis temperature.
The largest values both for magnetic susceptibility and the magnetization were obtained at 900 and 1000 °C. On this basis taking also into account that the ferromagnetic behaviour is due to exchange coupling between uncompensated spins of the nitrogen atoms, it can be estimate that spin density \((4 \pi M/\mu_B)\) for pyro-PCA is around of \(3.3 \times 10^{21} \text{ cm}^{-3}\).

Fig. 1 presents the temperature dependences of the gram magnetic susceptibility for pyro-PCA pyrolyzed at 1000 °C.

![Fig. 1. The temperature dependence of the magnetization susceptibility for pyro-PCA obtained at 1000 °C.](image)

The non-linear graphs similar to that shown in Fig. 1 (obeying the Curie-Weiss law) were obtained for all pyrolysis temperatures. It means that the magnetic susceptibility of the pyro-PCA is independent on temperature. The ferromagnetic properties are due to the uncompensated spin moments of the valence electrons from the nitrogen atoms. Between these species, strong exchange interactions take place explaining the very high values of the Curie temperatures.

The gram magnetic susceptibility and Curie temperature as a function of the pyrolysis temperature are shown in Fig. 2.

![Fig. 2. The gram magnetic susceptibility and Curie temperature of pyro-PCA as a function of the pyrolysis temperature.](image)

Fig. 3 illustrates the spontaneous magnetization as a function of the pyrolysis temperature.

![Fig. 3. The spontaneous magnetization of pyro-PCA as a function of the pyrolysis temperature.](image)

As it can be remarked, all of pyro-PCA samples show a ferromagnetic behaviour. The measured susceptibilities follow the Curie-Weiss law over the whole range of temperature. The Curie temperatures are very high as is reported for organic ferromagnets.

The product pyrolyzed at 900 °C exhibits a value for spin concentration of \(2.9 \times 10^{20} \text{ spins/cm}^2\). According to Buchachenko [14] at spin densities of about 1 spin per \(10^3 \text{ Å}^2\) the magnetization is of the order of 10 Gs.

In comparison to the pure iron, the magnetization of the pyro-PCA (1000 °C) lies in ratio of 1:727.

It would be pointed out that the molecular structure of the obtained pyro-PCA is complex and it can not be simply interpreted. However, we tentatively interpreted the results as follows. The pyrolyzed PCA are expected to show two phases: one moiety is highly ordered (ferromagnetic) and the other part is strongly disordered (paramagnetic) material. The cluster formation of radicals having the higher spin multiplet states (s>1/2) for PCA samples pyrolyzed to high temperature (>80 °C) could be supposed.

4. Conclusions

- All of the pyrolyzed PCA samples show ferromagnetic behaviour;
- The magnetic susceptibility, magnetization, spontaneous magnetization and Curie temperature are strongly dependent on the pyrolysing temperature;
- The product pyrolysed at 900 °C exhibits the largest value for spin concentration \(2.9 \times 10^{20} \text{ spins/ cm}^2\) measured at room temperature;
- By increasing the pyrolysis temperature the spin sites (at the nitrogen atom) are formed mainly due to the elimination of hydrogen. The spatially correlated spins are considered to be distributed as spin-island in the pyrolyzed
material. The fraction of spins contributing to ferromagnetic ordering is small and randomly distributed over the pyro-PCA volume;

- The pyrolyzed materials (PCA) are expected to show two phases: one is highly ordered (ferromagnetic) and the other is strongly disordered (paramagnetic);
- The cluster formation of organic radicals coupled with positive effective exchange and having the higher spin multiplet states (s>1/2) for the PCA samples pyrolyzed to high temperature (>800 °C) could be also supposed;
- The molecular ferromagnets can hardly compete with classical metallic ferromagnets as far as the static magnetization is concerned. More detailed studies are now in progress.

References


*Corresponding author: Jipasilviu@yahoo.com