Communication

Synthesis of Carbon Showing Weak Antiferromagnetic Behavior at a Low Temperature

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Abstract: In this short communication, we report a new carbon material prepared from meta-linked polyaniline that exhibits weak antiferromagnetic interactions at low temperature. The synthesis of poly(meta-aniline), abbreviated as m-PANI, was conducted using the Ullmann reaction with the aid of Cu⁺ as a catalyst in the presence of K₂CO₃. After the generation of radical cations by vapor-phase doping with iodine, carbonization was performed to prepare carbon polyaniline (C-PANI), which comprises condensed benzene rings. Analysis with a superconducting quantum interference device revealed that the resultant carbon exhibits antiferromagnetism at low temperatures. The discovery of this weak antiferromagnetic carbon may contribute to the development of carbon magnets.

Keywords: polymer magnet; polyaniline; antiferromagnetism; superconducting quantum interference device

1. Introduction

Polymer magnetism has been intensively studied with the aim of obtaining polymer ferromagnets that exhibit a ferromagnetic spin alignment. For example, the magnetic coupling of triplet phenylene units was reported by Iwamura in 1989 [1]; the ferromagnetic behavior of pyrolyzed o-, m-, and p-phenylenediamine and triazine derivatives was reported by Yoshino [2]; and Nishide et al. achieved ferromagnetic spin alignment with 3,4′-bis(diphenylamino)stilbene [3]. Ferromagnetic spin interactions in polymeric aromatic amines have also been reported [4], and, in the field of high-spin polymers, ferromagnetic coupling in hexaazacyclcophenane units has been reported [5]. Moreover, carbon magnets have been widely studied by both experimental and theoretical techniques [6,7]. Finally, a combination of organic and inorganic materials has been reported to show remarkable stability and a high-spin quartet ground state [8].

Our research group has focused on the development of organic magnetic materials for a long time. Accordingly, in the present study, we synthesized poly(meta-aniline) (m-PANI) as a carbon precursor, which was subsequently carbonized in an inert atmosphere. The carbon obtained from the polymer exhibits weak low-temperature antiferromagnetism. Although the obtained carbon may exhibit spin interactions with the graphite structure, the full mechanism is currently unclear. In this short report, we present the synthetic method for the preparation of weak antiferromagnetic carbon and the superconducting quantum interference device (SQUID) analysis results as a contribution to the development of carbon magnets.
2. Materials and Methods

2.1. Synthesis

As shown in Figure 1, the Ullmann-type polycondensation between \( m \)-phenylenediamine and tribromobenzene in nitrobenzene yielded \( m \)-PANI with a highly cross-linked two-dimensional (2D) structure, according to a previously reported method [9,10]. First, equimolar amounts of \( m \)-phenylenediamine and tribromobenzene were dissolved in nitrobenzene in the presence of a copper iodide catalyst (see Table 1). The reaction was stirred for 2 days at 200 °C. The resultant black solution was filtered, and the black powder was added to ca. 200 mL of ammonia/water solution to remove the copper. The solution was then filtered again. The filtrate was then added to ca. 200 mL of water and stirred for 24 h. After filtering, the filtrate was added to ca. 200 mL of methanol and stirred for 24 h before filtering again. The black filtrate was dried under reduced pressure. During these processes, care was taken to avoid contamination by Fe and Ni. Subsequently, vapor-phase iodine doping was performed to generate radicals in the \( m \)-PANI. Then, carbonization of the resultant polymer was performed at 1,000 °C under argon. The resultant material was labeled carbon polyaniline (C-PANI).

\[
\text{NH}_2\text{NH}_2 + \text{BrBr} \xrightarrow{\text{K}_2\text{CO}_3, \text{CuI}} \text{m-PANI}
\]

\[
\text{I}_2 \xrightarrow{\text{C-PANI}} \text{m-PANI-I}
\]

\[
\text{Carbonization} \xrightarrow{\text{I}_2} \text{C-PANI}
\]

\[
\text{C-PANI-doped (tentative structure)}
\]

Figure 1. Synthesis of polymers and carbon materials in these studies. All polymer structures are representative. poly(\textit{meta}-aniline) (\( m \)-PANI): 2D poly(\textit{m}-aniline) network; \( m \)-PANI-I: iodine-doped sample containing polarons (radical cations); carbon polyaniline (C-PANI): carbonized sample; C-PANI-doped: carbonized sample with iodine doping.
Table 1. Materials and quantities used for synthesis of poly(meta-aniline) (m-PANI).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Role</th>
<th>Chemical Structure</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Phenylenediamine</td>
<td>Monomer</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.12 (g)</td>
</tr>
<tr>
<td>Tribromobenzene</td>
<td>Monomer</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.37 (g)</td>
</tr>
<tr>
<td>Copper iodide</td>
<td>Catalyst</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.019 (g)</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>Co-catalyst</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>0.47 (g)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Solvent</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>2.35 mL</td>
</tr>
</tbody>
</table>

2.2. Instruments

Magnetic susceptibility measurements of the polymer were carried out using a SQUID (Quantum Design CA, Magnetic property measurement system, MPMS). Electron Spin Resonance (ESR) measurements were conducted using a JES TE-200 spectrometer (JEOL, Tokyo, Japan) with 100 kHz modulation (X-band). Infrared (IR) absorption spectra for the polymer samples were obtained with an FT/IR-4600 spectrometer (JASCO, Tokyo, Japan) by the KBr method. Carbonization was carried out with an MIT Lincoln Lab Gold furnace (MIT, Cambridge, MA, USA). Electron Probe Micro Analyzer (EPMA) measurements for the samples were carried with a JEOL JXA-8530F Electron Probe Micro Analyzer (JEOL, Tokyo, Japan).

3. Results

3.1. IR Spectra

Figure 2a shows the IR spectra of m-PANI and C-PANI. m-PANI presents N-H stretching at 3386 cm⁻¹. The absorption band at 1591 cm⁻¹ is assigned to the C=C stretching of the one-dimensional (1D) quinonoid structures (Figure 2c) in the polymer. The absorption at 1485 cm⁻¹ is due to C=C stretching of the 1D or 2D benzenoid structures in the polymer. Three C-H out-of-plane bending absorptions for the meta-linked polymer are observed at 790, 742, and 706 cm⁻¹ (Figure 2b).

![Figure 2. Cont.](image)
As the carbon has no N-H bonds, no N-H stretching absorptions are observed. Thus, these results confirm that C-PANI, which is a condensed ring structure consisting of benzene, is formed by the complete carbonization of m-PANI-I. Figure 1 (bottom) shows a plausible structure of the carbon comprising benzene structures.

Figure 3 displays Electron probe micro analyzer (EPMA) results for m-PANI (a) and C-PANI (b). m-PANI as a sample of before carbonization consists of C, N, and O. However, C-PANI, as a carbonized sample, has no nitrogen atom, indicating that the sample after carbonization has no pyridinic structure.

Figure 2. (a) Infrared (IR) absorption spectra of m-PANI-I and C-PANI. (b) Magnification of the 1100 to 550 cm⁻¹ region of the m-PANI-I spectrum. (c) The quinonoid and benzenoid structures in m-PANI.

The carbonized sample (C-PANI) shows an absorption band at 1582 cm⁻¹ (Figure 2a). This characteristic peak implies partial graphite formation inside the bulk sample. Another prominent peak appears around 1233 cm⁻¹. These results indicate that carbonization affords a graphitic structure. As the carbon has no N-H bonds, no N-H stretching absorptions are observed. Thus, these results confirm that C-PANI, which is a condensed ring structure consisting of benzene, is formed by the complete carbonization of m-PANI-I. Figure 1 (bottom) shows a plausible structure of the carbon comprising benzene structures.

Figure 3. Electron probe micro analyzer (EPMA) results for m-PANI (a) and C-PANI (b). Scale bar = 10 m. Top: signals from atoms. Bottom: Scanning electron microscopy (SEM) images.

3.2. Magnetic Measurement

Figure 4 shows the ESR trace measured at 24 °C for m-PANI after iodine doping. Data points are 4096 in this measurement. Lorentz-type symmetric absorption is observed due to the radical cations on the N atoms. This demonstrates that the polymer has paramagnetic characteristics.

Figure 5 shows results of SQUID magnetometry measurements for C-PANI. The magnetic susceptibility (χ) of C-PANI increases as the temperature decreases. The plot of 1/χ vs. T presents
a linear decrease. This indicates that the Weiss temperature of C-PANI is $-0.3$ K due to weak antiferromagnetic behavior at a low temperature. The values of $\chi T$ in the Curie plot for C-PANI decrease at a low temperature. This result confirms that C-PANI is antiferromagnetic.

Figure 4. Electron Spin Resonance (ESR) trace for $m$-PANI after vapor-phase iodine doping.

Finally, we investigated the magnetic properties of the iodine-doped carbon prepared from $m$-PANI, labeled C-PANI-doped. C-PANI was dried in vacuo to remove oxygen before iodine doping. The $\chi$ value for C-PANI-doped increases as the temperature decreases, and the maximum is observed at ca. 43 K. In $1/\chi$ vs. $T$ plots, C-PANI-doped shows a linear decrease to 66 K upon cooling (Figure 6a). $\chi T$ increases upon cooling to 44.6 K and decreases thereafter to 0 K (Figure 6b). Figure 7 displays the occurrence of a linear regime as Ising 1D systems [11–13]. The $\chi T$ vs $T^{-1}$ plot increases linearly (dashed line). The experimental data indicate a ferromagnetic coupling.

Figure 5. Superconducting quantum interference device (SQUID) magnetometry results for C-PANI. (a) $\chi$ vs. $T$ and $1/\chi$ vs. $T$. (b) $\chi T$ vs. $T$ as Curie plots.

Figure 6. SQUID magnetometry results for C-PANI-doped. (a) $\chi$ vs. $T$ and $1/\chi$ vs. $T$. (b) $\chi T$ vs. $T$ as Curie plots.
Acknowledgments: We would like to thank the OPEN FACILITY, Research Facility Center for Science and Technology, University of Tsukuba for using EPMA and Glass Work Shop of University of Tsukuba.

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Conflicts of Interest: The authors declare no conflict of interest.

4. Discussion

m-PANI was prepared by the Ullmann polycondensation using Cu⁺ [9,10]. This reaction affords a 2D-structured polymer constructed with amine linkages. Subsequent vapor-phase iodine doping generates radicals. Radical generation in the polymer induces good carbonization activity. Carbonization under argon yields a black powder. The resultant C-PANI contains graphite structures. This carbon contains random defects in its graphite structure, which may exhibit antiferromagnetic order. In this short communication, we have reported a new carbon prepared from m-PANI, which exhibits weak antiferromagnetic interactions at low temperature. The meta-linkages in m-PANI may be related to its high-spin state [14]. The meta-form of the precursor m-PANI used in this study may endow a certain spin structure onto the resultant carbon. The structural and chemical dynamics in graphene play a central role in magnetic functionality [15]. Iodine doping may produce ferromagnetic-like interactions in the carbon sample. However, the reason for these interactions is unclear at the present time.

Author Contributions: H.G. carried out synthesis of the polymers. S.H. conducted carbonization. M.O. measured IR, EPMA, ESR and SQUID; M.O. and H.G. contributed the data analysis; M.O. and H.G. discussed the results and wrote the final version of the manuscript; All authors have read and approved the final manuscript.

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References


