The Effect of Trace Iron in the Magnetic Property of the Fine Particle Prepared by ArF Laser-Induced Ablative Photodecomposition of Solid Perylenetetracarboxylic Dianhydride

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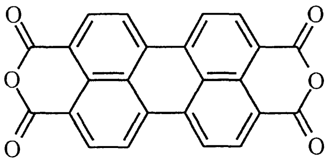
Organic fine particles were prepared by ArF laser-induced ablative photodecomposition of 3,4,9,10-perylenetetracarboxylic dianhydride containing trace amount of iron (3.5 ~ 2200 ppm). Sudden change in the magnetic property of the particles, from diamagnetic to paramagnetic, was observed between the iron content of 2000 and 2100 ppm.

Among organic ferromagnetic compounds, polymeric systems[1] have been studied extensively because of their preparative simplicity. In the preparation of such compounds, much cares have been taken to avoid contamination of the products by inorganic ferromagnets, particularly iron. However, contamination with iron is often unavoidable so that it is significant to know the effect of trace iron in the magnetic property of such compounds. To the best of our knowledge, such effect has not been thoroughly studied so far. We report here a considerable effect of trace iron in the magnetic property of organic fine particles which were prepared by the polymerization of solid 3,4,9,10-perylenetetracarboxylic dianhydride (**PDA**)[2] by ArF (193 nm) excimer laser-induced ablative photodecomposition .[2a]



PDA

All equipments used in the experiments were washed successively with 2N HCl aq. and ion free water, and then dried prior to use. The particle was prepared in vacuo (ca. 10^{-3} Pa) by irradiation of focused ArF excimer laser (180 mJ·pulse^{-1}, ca. 1 x 2 mm^2, 30 Hz) to the pellets of **PDA**, which were prepared by the application of pressure in vacuo (400 kg·cm^{-2}, < 100 Pa).[2a] The initial content of Fe in **PDA** was varied from 3.5 to 2220 ppm. **PDA 3.5-295** were prepared by the treatment of **PDA 2220** (Fe was included as oxides and sulfides) with 2N HCl and successive drying in a vacuum oven. Other **PDA**s were prepared by mixing appropriate amount of **PDA 66.7** and **PDA 2220.**

Quantitative analyses of Fe, Co, Ni, Cr, and Mn in **PDA** and the products (**PRO**s) were conducted by X-ray fluorometry (XRF) and partly by inductive coupled plasma atomic emission spectrometry (ICP-AES). The content of Co, Ni, Cr, and Mn was below the detection limit, *i.e.* < 1 ppm, and that of Fe in each run is shown in Table 1.

Quantitative magnetic measurements of **PDA** and **PRO** were conducted with a vibrating sample magnetometer (VSM), part of whose results are shown in Figure 1. The spectra of **PDA 3.5 - 2100** were same as that of **PDA 2220** (Figure 1a), which clearly showed diamagnetic property. The spectra of **PRO 3.5 - 1833** were similar to that of **PRO 2000** (Figure 1d) except for the increasing magnitude of the ferromagnetic property, which was superimposed on the diamagnetic property. A sudden change in the magnetic property, diamagnetic to paramagnetic, was observed at the initial Fe content between 2000 and 2100 ppm (Figures 1d *versus* 1e). Ferromagnetic property was also superimposed on the paramagnetic property for **PRO 2100 -**

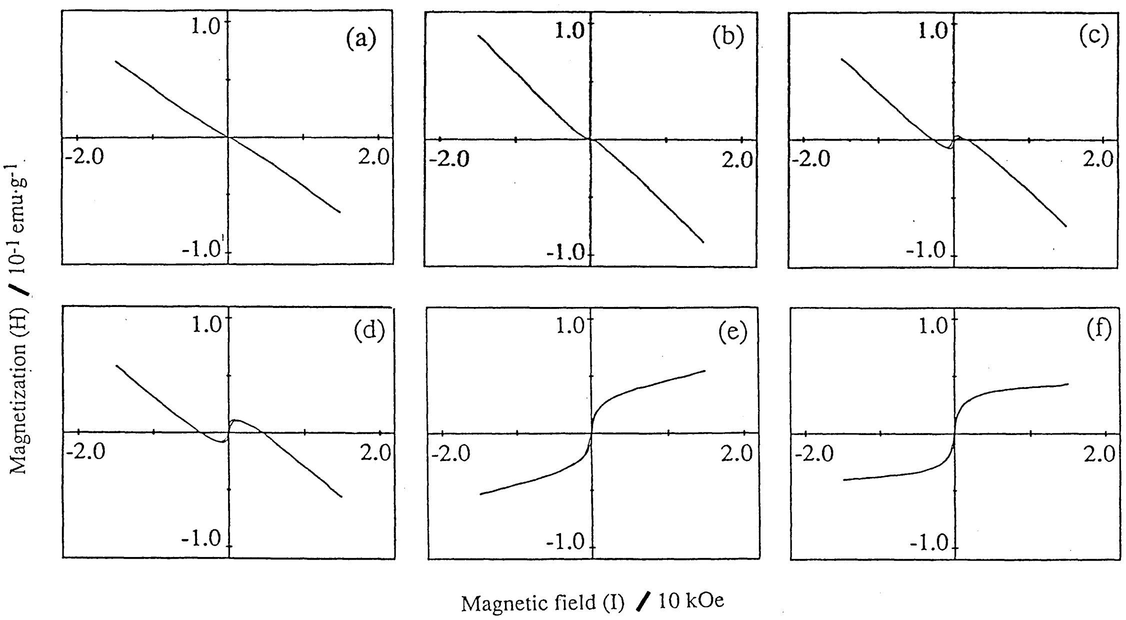


Figure 1. VSM spectra of **PDA**s and **PRO**s. (a) **PDA 2220**, (b) **PRO 295**, (c) **PRO 900**, (d) **PRO 2000**, (e) **PRO 2100**, (f) **PRO 2220**. The measurements were conducted at room temperature.

Table 1. Amount of iron in **PDA** and **PRO**

Run	Starting material	Amount of Fe (ppm)[a]	Product	Amount of Fe (ppm)[a]
1	**PDA 3.5**	3.5	**PRO 3.5**	15.6
2	**PDA 66.7**	66.7[b]	**PRO 66.7**	97.9
3	**PDA 295**	295[b]	**PRO 295**	417
4	**PDA 900**	900	**PRO 900**	1534
5	**PDA 1499**	1499	**PRO 1499**	1757
6	**PDA 1833**	1833	**PRO 1833**	3144
7	**PDA 2000**	2000	**PRO 2000**	2591
8	**PDA 2100**	2100	**PRO 2100**	3697
9	**PDA 2220**	2220[b]	**PRO 2220**	3746

[a] Measured by XRF.

[b] Also measured by ICP-AES, which gave the same result.

2220. The magnetic property of **PRO 2220** did not show considerable change even after the storage of 15 months in the air at room temperature.

Figure 2 shows the relation between the saturation magnetization (I_{max}) of the products and the Fe content. The irregular change of I_{max} at Fe content of 2000 ppm indicates that the ferromagnetic property is not simply originated from the amount of Fe compounds. Such irregular change was also observed in the residual magnetization at the same Fe content. Coercive force (H_c) of the product showed two maxima at the Fe content of 900 and 1900 ppm, which indicates the presence of two different magnetic domains. The role of iron for the formation of the two domains and the sudden change in the magnetic property is still not clear. However, it is less likely that the two magnetic domains are solely due to iron compounds because it was reported that ferromagnetic property was not observed in the iron-impregnated active carbon when the Fe content was below 8%,[3] which is much higher in the concentration of Fe than that of **PRO 2220**.

In order to know the origin of the ferromagnetic property, ESR measurements were conducted (Figure 3). In contrast to **PDA**s, which showed *no* absorption in ESR, strong absorptions were observed in the products. The products with low Fe content only showed a sharp signal at 334.95 mT (Figure 3a), which can be attributed to π radical spins;[4] however, additional broad absorption gradually appeared over the range 100 ~ 600 mT with increasing Fe content (Figure 3b); the band is often observed in organic ferromagnetic compounds.[5]

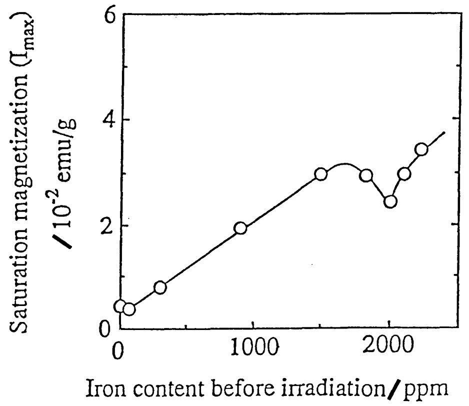


Figure 2. Saturation magnetization (I_{max}) of **PRO**s as a function of Fe content before irradiation. The measurements were conducted at room temperature.

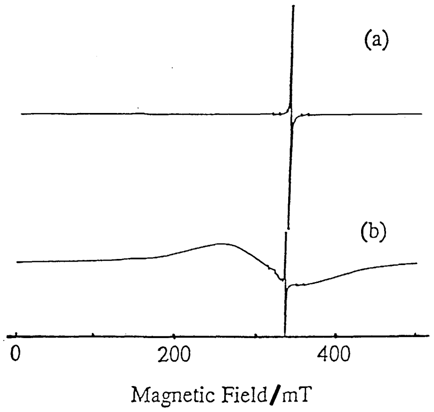


Figure 3. ESR spectrum of (a) **PRO 3.5** and (b) **PRO 2220**. Microwave frequency: 9.23 MHz. Internal standard: MnO. The intensity of the spectra was normalized to the unit weight sample.

These results indicate the existence of stable carbon radicals such as triarylmethyl radicals, which was evidenced by IR and ^{13}C-NMR spectroscopies. The IR measurements showed formation of aliphatic ν C-H at 2900 cm^{-1} and extended aromatic ν C=C at 1650 cm^{-1} (broad) with the decrease of aromatic ν C-H at 3050 cm^{-1} and carbonyl ν C=O. ^{13}C-NMR spectra of **PRO** showed formation of a new broad absorption at δ 0 - 80 ppm. The chemical shift of alkanes and monoaryl-substituted aliphatic carbons appears usually at δ 10 ~ 50 ppm[6] so that the low field shift of the observed carbon is attributed to diaryl- and triaryl-substituted aliphatic carbons.

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References and Notes

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