Pyrolysis of Di-*n*-Propylamine: Chromatographic Characterization of Hexane-Soluble Product and XPS Analysis of Insoluble Carbons

Kazuhisa MURATA,* Hirobumi USHIJIMA, Yoshikazu SUGIMOTO, Hiromichi SHIMADA, Motoyasu IMAMURA,
and Akio NISHIJIMA
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

(Received September 16, 1992)

Synopsis. Characterizations of soluble and insoluble products prepared from di-*n*-propylamine by CVD method were carried out using GC-MS and XPS methods in addition to magnetic measurements. GC-MS analysis of hexane-soluble product showed the presence of a series of aromatics with aromatic nitrile and/or heterocyclic compounds. XPS spectra of insoluble carbon product exhibited little difference in the C1s binding energy between plasma-treated and -untreated samples. However, it is found that the amorphous-like carbon content, calculated from the C1 energy loss spectra, is dependent on the plasma power and attains a maximum at 120 W, in good accordance with a plasma dependence of the apparent saturation magnetization of the carbons.

Recently, there has been a growing interest in the magnetic properties of carbonaceous materials prepared by pyrolysis of organic monomers such as hydrocarbons, aliphatic amines.[1)] However, characterizations of soluble- and insoluble- products are still not completely done. In this study, first, we briefly report our results of chromatographic characterization of these products by using column chromatography, gas-chromatograph mass spectrometry (GC-MS) and gas-chromatograph infrared analysis (GC-IR). And, second, we report XPS spectra of insoluble carbons, the purpose of which is to examine a correlation between an amorphous-like structure[1)] of the insoluble carbons and their magnetic nature. Since it is known that, possibly, the plasma treatment could cause a slight change in an amorphous structure[2)], XPS measurements of plasma-treated and -untreated carbons are performed and compared with the results of magnetic measurements.

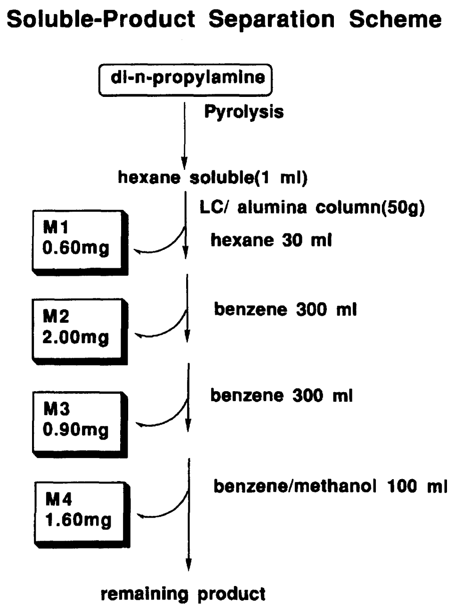

Fig. 1. Separation scheme showing the sequence of extraction.

Experimental

Pyrolysis was carried out in a furnace equipped with a quartz tube. Commercially available di-*n*-propylamine (DPA) as starting material was separately placed in the quartz tube and heated to 950°C under vacuum. Then, the DPA was introduced and rapidly pyrolyzed: The deposition time was 45 min. After the subsequent evacuation at 950°C, the quartz tube was cooled. For soluble product analysis, resulting carbon product was removed in hexane solution and a fraction of the soluble product (ca. 1 ml) was subjected to alumina column chromatography and other measurements. The GC-MS analyses were carried out with HP 5970 and HP 5890 GC-atomic emission detector (GC-AED). And the GC-IR was recorded on a HP 5965B system.

Prior to XPS and magnetic measurements, after cooling the quartz tube, the same tube was subjected to the radio-frequeny (R. F.) plasma treatment. Treatment conditions were as follows; air pressure: ca. 66 Pa, plasma power: 30—195 W (13. 56 MHz), reaction time: 5—60 min. After the treatment, the resulting carbon was removed. The XPS spectra was recorded on a PHI-5500 using monochromatized Al *K* α radiation (1486. 6 eV).

Results and Discussion

Characterization of Hexane-Soluble Product. As shown in Fig. 1, four fractions were obtained by col-

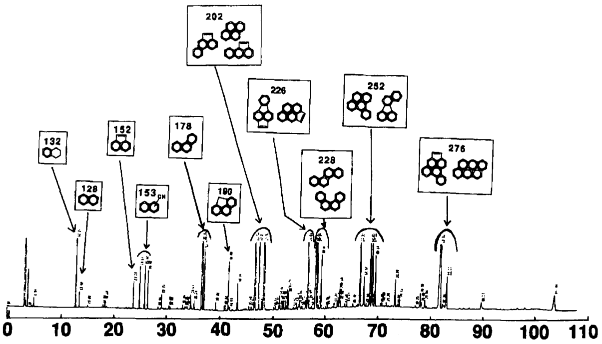

Fig. 2. GC-MS analysis of M2 sample separated by column chromatography (alumina column).

umn chromatography: of these, M1 fraction contained mixtures of low boiling hydrocarbons and N-containing compounds. The M2 fraction mainly consists of aromatic compounds. Fig. 2 shows the results of GC-MS analysis of M2 fraction showing that an aromatization occurs to form a series of aromatics with cyanonaphtalene. The M3 and M4 fractions seems mainly to consist of not only higher boiling aromatics than those of M2 sample but also aromatic nitrile and/or heterocyclic compounds such as mass number=179, 203, and 227, the mass chromatograms of which were shown in Fig. 3. The N-containing aromatics in the M3 fraction mainly contains aromatic nitrile, confirmed by GC-IR and GC-AED analyses, while that in the M4 fraction mainly heterocycles, confirmed by an extraction by acid. Therefore, possibly, the nitrile can be converted into the heterocycles, as the reaction proceeds (A). Thus, it seems likely that pyrolysis of di-*n*-propylamine could proceed via aromatization and/or heterocyclization and, finally, lead to the formation of insoluble carbons (Chart 1).

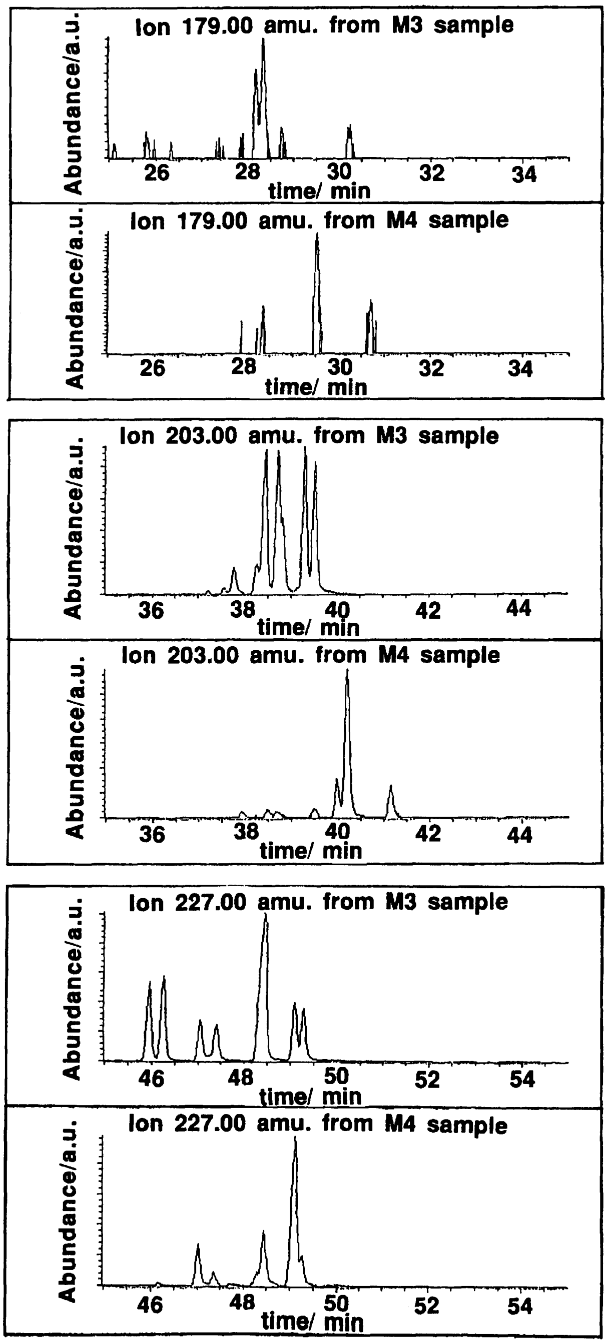

Fig. 3. Mass chromatograms of mass number=179, 203 and 227, detected from GC-MS spectra of M3 and M4 samples.

XPS Analysis of Carbons. XPS spectra of insoluble carbon product showed carbon 1s (284.6 eV) and nitrogen 1s (400.1 eV) absorptions. When the carbon surface was plasma-treated, there was little difference in the C1s binding energy between plasma-treated (PLC) and -untreated (NPLC) samples[3] (Table 1). However, there were some differences in the carbon 1s energy loss region at 295 to 335 eV, which was divided into respective spectra of three kinds of carbons by background subtraction followed by curve fitting[4] (Fig. 4, inset), according to the literature.[5,6] As shown in Table 1 and Fig. 4 (●), it is found that the amorphous-like carbon content could be changed by the plasma treatment and attains a maximum at 120 W. The XPS valence band spectra were also influenced by the plasma power and exhibited integrated bands consisting of signals from

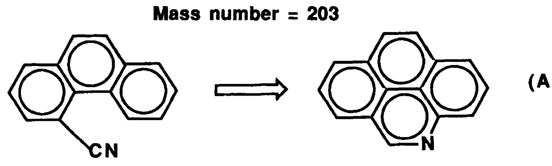

Chart 1.

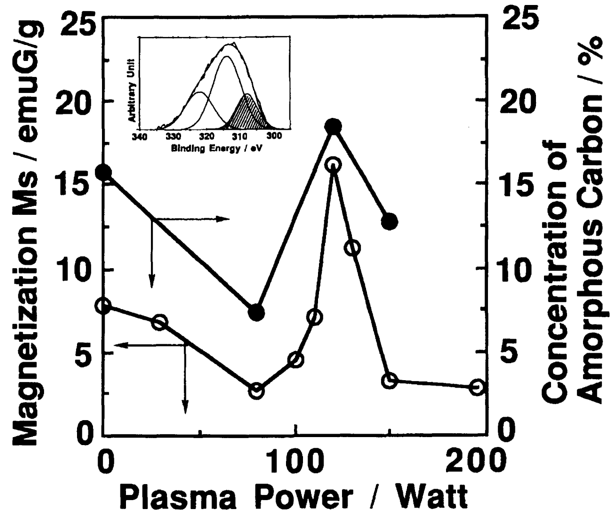

Fig. 4. Plasma power dependences of 1) amorphous carbon content (●) and 2) the M_s value at room temp. (○) of the carbon material. Inset: An example of analysis of C1s energy loss spectra of the carbon.

Table 1. XPS Analysis for Plasma-Treated Carbon Films

	Binding energies and concentrations					
Plasma power	C1s	C1s energy loss/eV			Valence band	
W	eV	Amorphous	Graphite	Diamond	sp/s[a]	C–H/s[b]
0	284.6	307.8	313.8	322.1	0.74	0.43
		15.8%	63.7%	20.5%		
80	284.6	307.4	313.1	322.1	0.85	0.44
		7.3%	68.7%	24.0%		
120	284.7	307.3	313.7	321.6	0.79	0.50
		18.5%	64.6%	16.9%		
150	284.6	306.9	313.3	322.0	0.72	0.42
		12.7%	65.2%	22.1%		

a) The ratio of the intensity of sp-like to that of s-like. b) The ratio of the intensity of C–H -like to that of s-like.

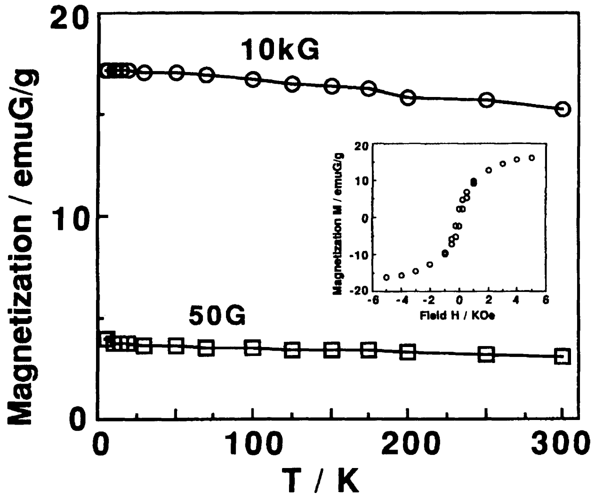

Fig. 5. Temperature dependence of magnetization at 10 kG (○) and 50 G (□) of the carbon material plasma-treated at 120 W. Inset: Field dependence of magnetization of the carbon material at room temperature.

C–H (ca. 9.0 eV), sp-like (13.9 eV) and s-like (17.9 eV).[6] The ratio of the intensity of sp-like band to that of s-like was between graphite (ca. 0.70) and diamond (ca. 0.98)[7] and the ratio of C–H to s-like, associated with an amorphous structure, was the greatest for the plasma treatment at 120 W (see Table 1). There has been observed an increase in the intensity of C–H band of plasma-treated carbon film.[8] The slight increase in amorphous phase by the plasma treatment is supported by the decreased electrical conductivity (330 S cm^{-1} → 243 S cm^{-1}).

Magnetic Measurements. In general, the magnetic natures of PLC sample were analogous to those of the NPLC (Fig. 5),[1b] except that the intensity of a broad, poorly resolved ESR signal over the range from 1000 to 6000 was much stronger than that of NPLC. An apparent saturation magnetization (Ms) of the PLC[9] was dependent on both plasma power and treatment time; A maximum Ms value was obtained when the plasma power was 120 W (Fig. 4, ○) and the time was 10 min. As can be seen from Fig. 4, the Ms values thus obtained seems to be closely related to the amorphous carbon content[1].

In conclusion, the insoluble carbon product was formed via aromatization and/or heterocyclization from di-*n*-propylamine and it seems likely that amorphous-like structure could be associated with the observed magnetic properties.

References

1) a) K. Murata, H. Ushijima, H. Ueda, and K. Kawaguchi, *Synth. Met.*, **44**, 357 (1991); K. Murata, H. Ushijima, H. Ueda, and K. Kawaguchi, *J. Chem. Soc., Chem. Commun.*, **1991**, 1265; b) K. Murata, H. Ushijima, H. Ueda, and K. Kawaguchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 567.

2) F. K. McTaggart, "Plasma Chemistry in Electrical Discharges," Elsevier, Amsterdam (1967); T. Miyasato, Y. Kawakami, T. Kawano, and A. Hiraki, *Jpn. J. Appl. Phys.*, **23**, L234 (1984); A. Hiraki, Y. Kawakami, T. Kawano, M. Hayashi, and T. Miyasato, *Solid State Commun.*, **45**, 34 (1984).

3) The FT-IR-ATR spectra of the PLC film, deposited on the quartz substrate using the amine followed by plasma treatment, exhibited spectra rather similar to those of the NPLC sample,[1b] although their intensities were a little weaker: These include intergrated bands at from 2850 to 3000 cm^{-1} and a number of bands from 1350 to 1750 cm^{-1}, and the bands at from 850 to 1100 cm^{-1}.

4) Background subtraction was performed by matching the Gaussian–Lorentzian function to the data. If relative sensitivities are 0.07 for diamond-like carbon, 0.045 for graphite, and 0.064 for amorphous, respectively, then each carbon concentrations can be calculated from their integrated intensities.

5) F. Bechstedt, R. Enderlein, R. Fellenberg, P. Streubel, and A. Meisel, *J. Electron Spectrosc. Relat. Phenom.*, **31**, 131 (1983).

6) F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Cavell, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B*, **9**, 5268 (1974); R. G. Cavell, S. P. Kowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, *Phys. Rev. B*, **7**, 5313 (1973).

7) A. Zunger, *Phys. Rev. B*, **17**, 626 (1978); A. Zunger

and R. Englaman, *Phys. Rev. B*, **17**, 642 (1978).

8) O. Matsumoto and T. Katagiri, *Thin Solid Films*, **146**, 283 (1987).

9) When the effect of plasma treatment on the M_s was examined using other some amines, the M_s values of the carbon samples treated at 120 W were in the order: di-*n*-propylamine (16.2) > diethylamine (13.1)>*n*-butylamine (12.7) >*n*-propylamine (11.8) > di-*n*-butylamine (10.3) > 1,2-diaminopropane (5.86). Also, the plasma treatment was found to be effective for the increase in the Ms values of carbons prepared form hydrocarbon monomers such as pyrene, 1-hexane, *p*-cyclophane, although their M_s values were much smaller than those from amines.