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# ELECTRICAL AND STRUCTURAL PROPERTIES OF A NEW CONDUCTING POLYMER : PYROLYTIC POLY(*p*-PHENYLENE-1,3,4-OXADIAZOLE)

M. Murakami, H. Yasujima, Y. Yumoto, S. Mizogami and S. Yoshimura

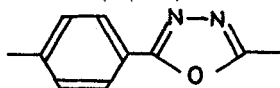
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**Résumé** - Des films de poly (*p*-phénylène-1,3,4-oxadiazole) ont été pyrolysés à diverses températures et leurs propriétés électriques et structurales étudiées. Les films pyrolysés présentaient des états électroniques étendus contribuant à une conductivité métallique indépendante de la température (jusqu'à 510 S/cm) et des états localisés entraînant un mouvement des électrons par sauts. La structure est supposée du type graphite ayant des couches condensées d'aromatiques avec des noyaux hétérocycliques contenant des azotes.

**Abstract** - Poly(*p*-phenylene-1,3,4-oxadiazole) films were pyrolyzed at various temperatures and their electrical and structural properties were investigated. The pyrolyzed films were composed of both extended electronic states which contribute to a temperature-independent metallic conductivity (up to 510 S/cm) and localized states giving rise to a variable range hopping motion of electrons. The structure was thought to be a graphite-like crystal having condensed aromatic layers with nitrogen-containing heterocyclic rings.

Although polymer pyrolysis is a simple procedure which presents planar conjugated polymers of relatively high electrical conductivity /1/, the pyrolytic polymers have not been well appreciated as a synthetic metal, partly because their chemical and electronic structures cannot be accessed very easily. However, the fact that there have been quite a few number of highly conducting pyrolytic polymers /2-5/ may arouse interest in designing a molecular structure of the starting polymers in favor of unique physical properties. Such an interest seems to be growing with recent studies on pyrolytic polyimide and polyacrylonitrile in connection with their pyrolysis mechanisms /2,5/ and the nature of the conduction process /3-5/.

In this paper we will report on a new highly conducting pyrolytic polymer based on poly(*p*-phenylene-1,3,4-oxadiazole) (POD):



We will report the realization of electrical conductivity as high as 510 S/cm at room temperature, showing the structural aspects of the new conductor as a function of the pyrolysis temperature,  $T_p$ .

## I - ELECTRICAL PROPERTIES

Figure 1 shows the dependence of the room temperature conductivity,  $\sigma_{RT}$ , on  $T_p$ , where each POD film was kept at  $T_p$  for 60 min after being heated at a rate of 10°C/min. The figure also includes data for polyimide film pyrolyzed under the same condition, indicating that the pyrolyzed POD has  $\sigma_{RT}$  more than twice as high as that of polyimide /3/. The pyrolyzed POD exhibits  $\sigma_{RT}$  of 68, 350, 410 and 510 S/cm for  $T_p$  =

800, 1000, 1200 and 1400°C, respectively. Figure 2 shows the temperature dependence of the electrical conductivity of the POD pyrolyzed at 800, 1000 and 1200°C. The  $\sigma$  vs.  $T$  curves are expressed with an equation:  $\sigma(T) = \sigma(0) + \sigma_1(T)$ , where  $\sigma(0)$  is a zero-temperature limit conductivity. This dependence differs markedly from that of pyrolyzed polyimide /4/ for which metallic behavior of the conductivity has not been observed over a wide temperature range.

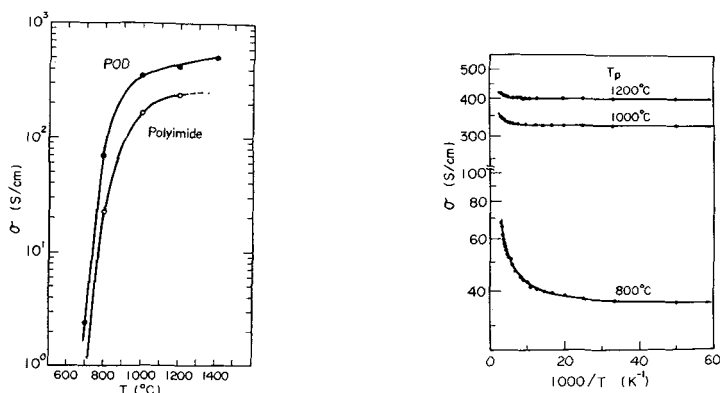


Fig. 1 - Electrical conductivity at room temperature vs. pyrolysis temperature for POD (●) and polyimide, Kapton H (○) films.

Fig. 2 - Temperature dependence of conductivity of pyrolyzed POD.

The existence of  $\sigma(0)$  has been observed with inorganic metals, such as Nb-Cu /6/ and Si-Au /7/, which has attracted much attention in connection with a metal-insulator transition in a disordered system. In such disordered metals,  $\sigma_1(T)$  is given by  $T^n$  ( $n = 1/2$  or  $1/3$ ) or  $\log T$ . If we want to fit the  $\sigma$  vs.  $T$  curves (Fig. 2) to the  $T^n$  form, a value of  $n$  between 1.6 and 1.8 is obtained, which we cannot rationalize with an ordinary theory. After all, the best fit was obtained to a function of the form  $\sigma(T) = \sigma(0) + \sigma(\infty)\exp\{-(T_0/T)^{1/4}\}$  as shown in Fig. 3.

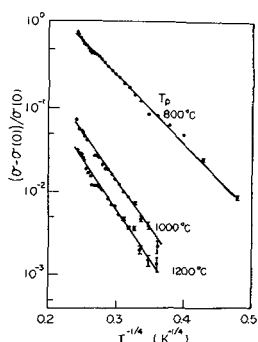


Fig.3 - Temperature-dependent part of the conductivity vs.  $T^{-1/4}$  for pyrolyzed POD. Zero-temperature conductivity,  $\sigma(0)$ , was obtained from extrapolation of  $\sigma(T)$  vs.  $T$  curves to  $T = 0$  K. Solid lines indicate the best fit lines.

The  $T^{-1/4}$ -dependence can be interpreted on the basis of a three dimensional variable range hopping model /8/. The slope  $T_0$  is obtained from the figure as  $1.21 \times 10^5$ ,

$4.96 \times 10^5$ , and  $5.86 \times 10^5$  K for  $T_p = 800, 1000$  and  $1200^\circ\text{C}$ , respectively. These  $T_0$  values are much smaller than that observed with ordinary amorphous carbon films /9/, indicating that the density of the localized state is much higher for the pyrolyzed POD. In the variable range hopping model, the  $T_0$  is expressed as:  $T_0 = 16 \alpha^3 / kN(E_F)$ , where  $k$  is Boltzmann's constant,  $1/\alpha$  is the radius of the localized state wave function and  $N(E_F)$  is the density of the localized state at the Fermi level. The change in  $T_0$  going from  $T_p = 800$  to  $1200^\circ\text{C}$  is thus understood if we assume a decrease in  $N(E_F)$  for higher  $T_p$ . The temperature-independent conductivity,  $\sigma(0)$ , offers evidence of a metallic conduction path with extended electronic states. A simple explanation to the increase in  $\sigma(0)$  with increasing  $T_p$  is that there are two parallel conduction paths in the pyrolyzed POD with extended states contributing to  $\sigma(0)$  and localized states to  $\sigma_1(T)$ , and the latter is converted to the former at higher  $T_p$ . This idea is qualitatively supported by the increase in  $\sigma(0)/\sigma(\infty)$  with increasing  $T_p$  as 0.015, 0.027 and 0.043 for 800, 1000 and  $1200^\circ\text{C}$ , respectively.

## II - STRUCTURAL PROPERTIES

Powder X-ray patterns (with Cu-K $\alpha$  radiation) of the pyrolyzed POD films are illustrated in Fig. 4. The lattice spacings are 3.62, 3.57 and 3.49 Å for  $T_p = 800, 1000$  and  $1200^\circ\text{C}$ , respectively, and the peak width becomes narrower for higher  $T_p$ . These results indicate that the pyrolyzed POD has an increased ordering in the (002) direction of the graphite structure at higher  $T_p$ , but it has not completely been converted to graphite ( $d(002) = 3.34$  Å). The narrower line width of the X-ray patterns as compared with that of ordinary carbons implies that POD is a polymer in which a graphite-like structure can easily be formed at relatively low pyrolysis temperature. The crystalline character of the starting polymer /10/ with a sharp diffraction line from a plane of  $d = 3.4$  Å may account for the result.

The elemental and XPS analyses of the pyrolyzed POD confirmed that complete conversion did not occur even for  $T_p$  as high as  $1400^\circ\text{C}$ . The relative amount of nitrogen in the pyrolyzed products (for example, N/C = 1/19 by weight for  $T_p = 1000^\circ\text{C}$ ) is much higher than that of pyrolyzed polyimide (N/C = 1/44 for  $T_p = 1000^\circ\text{C}$ ) /11/. Figure 5 shows XPS spectra in the  $N_{1s}$  region for POD pyrolyzed at various temperatures, which

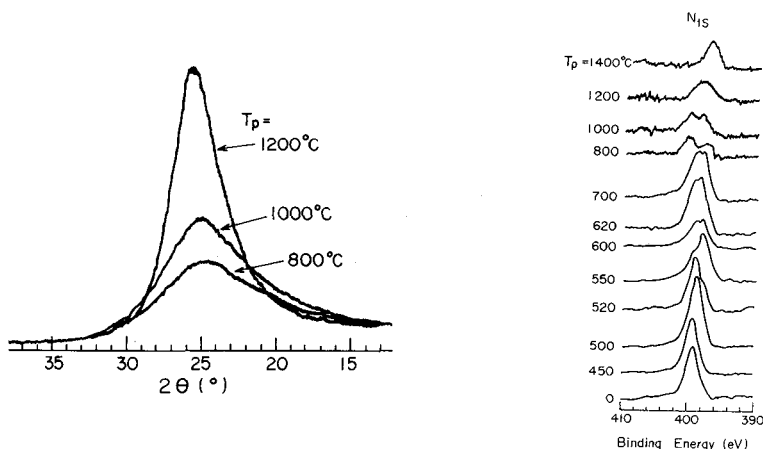


Fig. 4 - Powder X-ray diffraction patterns for pyrolyzed POD.

Fig. 5 - X-ray photoelectron spectroscopy peaks in the  $N_{1s}$  region for POD pyrolyzed at various temperatures.

were measured with samples etched with argon ion. For  $T_p < 500^\circ\text{C}$ , only one type of nitrogen exists with a change in the binding energy starting at  $450^\circ\text{C}$  (nearly equal to the decomposition temperature). For  $T_p$  higher than  $520^\circ\text{C}$ , however, two peaks are clearly observed at about 398.0 and 399.0 eV, the latter shifting to 400.0 eV as  $T_p$  goes up to  $1000^\circ\text{C}$ . And again only one peak which corresponds to the former remains to exist for  $T_p > 1200^\circ\text{C}$ . The nitrogen with higher binding energy in the range  $T_p = 520 - 1000^\circ\text{C}$  may be that in intermediate products of the pyrolysis. The most probable is a product with a -CN end group, because the N-N bond in the oxadiazole ring has the lowest energy (160.7 kJ/mol) and in fact Fourier-transform infrared spectroscopy data indicated a strong -CN absorption at  $2225\text{ cm}^{-1}$ . The peak at the lower binding energy (ca. 398.0 eV), on the other hand, is likely come from nitrogen in a final product of polycondensation. Since the lower binding energy suggests a conjugated nitrogen, the final product may contain heterocyclic rings like pyridine, pyrazine, triazine or fused rings of them, which can possibly be formed with the -CN group /12/ produced in the intermediate products. The enhancement of the X-ray diffraction peak for higher pyrolysis temperatures (Fig.4) is thus interpreted on the basis of the formation of condensed aromatic layers with nitrogen-containing heterocyclic rings.

### III - CONCLUSIONS

We have shown that the POD films were converted to a high electrical conductor on pyrolysis. The pyrolyzed POD has two conducting channels: one is a metallic channel with extended electronic states, with which the conductivity has no temperature dependence, and the other is a channel with localized states where the electronic motion is described by the three dimensional variable range hopping model. It was suggested by X-ray diffraction and XPS analyses that the pyrolyzed product has a graphite-like planar structure in which nitrogen-containing heterocyclic rings are included. The relation between the high conductivity and the crystal structure has not fully been explained, but further studies on reaction mechanism and physical properties will bring forth more information. Chemical aspects of the pyrolysis and chemical doping made with pyrolysis are being investigated and results will be published in the near future.

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