

Electrical Conductivities of Polyazophenylene Based Amorphous Carbon

BARBRO LÖFGREN,^a JORMA RAUTAVUORI^b
and PERTTI TÖRMÄLÄ^b

^a Department of Wood and Polymer Chemistry, University of Helsinki, Malminkatu 20, SF-00100 Helsinki 10, Finland and ^b Institute of Materials Science, Tampere University of Technology, SF-33101 Tampere 10, Finland

It has been known for many years that certain thermosetting polymers pyrolyze to form disordered nongraphitizing carbons with glass-like properties. However, because of the large volume of gaseous decomposition products which were evolved during the reaction, these carbons were generally quite porous. About fifteen years ago it was found that carbon with very low gas permeability, glass-like isotropic properties, high temperature stability, and chemical inertness can be achieved by slow carbonization of the precursor polymer under carefully controlled conditions in the solid state.¹⁻⁵ Amorphous and ordered carbons (e.g. carbon fibers) are bringing about a revolution in the field of materials and composites because of their unique chemical, thermal or mechanical properties.⁶

In an earlier study we found that polyazophenylenes can be pyrolyzed to amorphous carbon by heating to 1000 °C in an inert atmosphere.⁷ Polyazophenylenes are semiconducting polymers.⁸ Therefore we have studied the effect of carbonization on the conductivity of these polymers.

Experimental. The studied polymers, poly(2,4-diaminotoluene), I, ($M_n = 62\,800$) and poly(2,5-diaminotoluene), II, ($M_n = 36\,800$) were prepared by oxidative coupling.⁹ The molecular weights were determined by titration of the residual amine groups with perchloric acid in glacial acetic acid. The polymers were thermally stable up to 400 °C, measured by DSC (Differential Scanning Calorimetry).

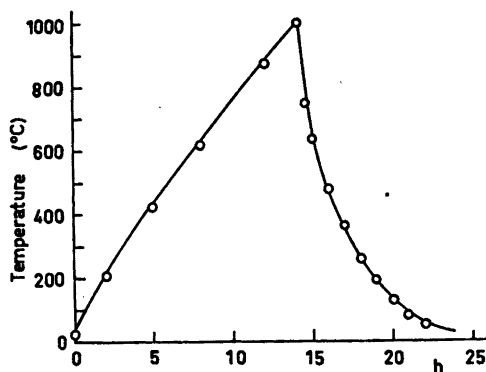
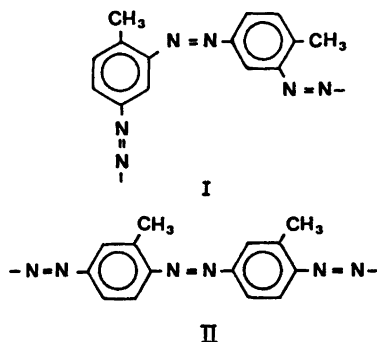


Fig. 1. The heat-treatment diagram.

The polymers were powdered and examined as molded pellets. Pellets (13 mm diameter and 1–2 mm thick) were molded at pressures up to 30 MPa. The pellets were carbonized in a tube furnace by heating to 1000 °C in nitrogen atmosphere. The heat treatment diagram is given in Fig. 1. The yield of carbon was $56 \pm 0.1\%$ in each case.

The pellets were equipped with silver paint electrodes for conductivity measurements. The conductivity measurements were performed in vacuum using an electrometer, and the conductivity was studied as a function of temperature.

X-Ray diagrams were taken of carbon samples to detect any traces of graphite. The

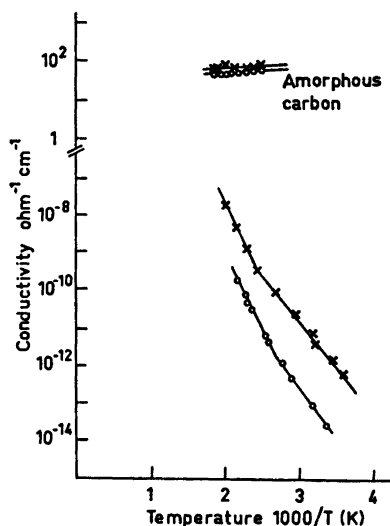


Fig. 2. Conductivity as a function of temperature. \times , poly(2,4-diaminotoluene); O , poly(2,5-diaminotoluene).

reflections of graphite were totally absent. Therefore it was concluded that the samples were amorphous by nature.

Results and discussion. The conductivity σ as a function of temperature is shown in Fig. 2 for polyazophenylenes⁸ and corresponding amorphous carbon. Fig. 2 shows that the heat-treatment of polyazophenylenes significantly enhanced the electrical conductivity, and also changed the conductivity behaviour. Before the heat-treatment the conductivity increased with increasing test temperature as for conventional semiconductors. The conduction mechanism in polyazophenylenes have been described^{8,10} in terms of a thermally activated rotational movement of polymer molecules or parts of polymer molecules and a non-activated tunnelling process, according to the theory originally presented by Gutmann.¹¹

The electrical conductivity of polyazophenylenes after being heat-treated at 1000 °C shows a similar behaviour to that of graphite,¹² as the conductivity decreases with increasing test temperature, indicating that the scattering process mainly is thermal. In the resistivity map,¹³ shown in Fig. 3, the electrical resistivity of amorphous carbon is compared with the resistivity of various types of graphite in direction parallel to layer planes on grain. That the amorphous carbon has a resistivity several orders of magnitude higher than the various types of graphite is due to the turbostratic structure of amorphous carbon.

It is known that the turbostratic structure of phenolic resin carbon consists of small graphite-like lamellae (diameter 15–50 Å) which are strongly disturbed by structural de-

fects (such as vacancies, dislocations, kinks and jogs). These lamellae are strongly twisted and distorted in relation to each other.⁸ Fig. 3 indicates that the degree of order and the resistivity of carbon are inversely proportional to each other. Because the resistivities of poly-(diaminotoluene) carbons are somewhat higher than the resistivity of phenolic resin carbon it can be concluded that poly(diaminotoluene) carbons have a still more distorted structure than phenolic resin carbons.

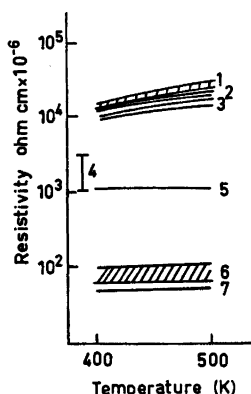


Fig. 3. Resistivity of polyazophenylenes based amorphous carbon, phenolic resin carbon,⁷ and various types of graphite. 1, poly(2,4-diaminotoluene) carbon; 2, poly(2,5-diaminotoluene) carbon; 3, phenolic resin carbon; 4, amorphous carbon; 5, manufactured graphite; 6, pyrolytic filaments annealed to 3000–3200 °C; 7, single crystal graphite.

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