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Preparation of semiconducting carbon fibre by pyrolysis of polyacrylonitrile precursor

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Semiconducting carbon fibres were prepared from polyacrylonitrile precursor by pyrolysis in an inert atmosphere in temperature range 550–800 °C. The obtained fibres have an electrical resistivity between 10^4 and $10^{-2}\ \Omega\,\mathrm{cm}^{-1}$ and showed negative temperature coefficients. Electrical resistivity was mainly governed by the pyrolysis temperature and both electrical resistivity, ρ, and thermistor constant, B, decreased with increasing pyrolysis temperature and duration. A linear relation between log ρ and thermistor constant B was observed. Chemical analysis and infrared spectra indicated that the concentration of nitrogen and hydrogen decreased and basal plane structure developed accompanying an increase in carbon content as the pyrolysis temperature increased.

1. Introduction

The preparation of semiconducting materials from organic precursor has been the object of scientific inquiry for many years. The interests in this subject have increased recently owing to its advantages over other preparation processes. Among the organic precursors, polyacrylonitrile has been widely studied as a precursor for carbon fibre [1–4]. One of the research interest is its electrical properties. Semiconducting properties have been observed in polyacrylonitrile pyrolysed in temperature ranges of 500 to 800 °C [5]. A more recent study has shown that the pitch-based and rayon-based carbon fibres demonstrate rapid responses to infrared incidence due to their very small heat capacity and negative temperature coefficients of electrical resistivity [6]. This suggests the importance of semiconducting carbon fibres as a promising material for applications, utilizing semiconductance and fibrous shape, such as thermal-type infrared sensors.

There have been several studies on the electrical behaviour of pyrolysed polyacrylonitrile [7–8]. It is known that the resistivity of pyrolysed polyacrylonitrile depends greatly on its preparation conditions and the composition of precursor. Generally, pyrolysed polyacrylonitrile has a resistivity covering the whole range, 10^1–$10^{10}\ \Omega\,\mathrm{cm}^{-1}$, depending on the pyrolysis conditions, which corresponds to an activation energy of 0.06–0.33 eV [10]. The preparation of carbon fibre from polyacrylonitrile precursor usually consists of two steps, i.e. a low temperature pre-oxidation or stabilization in air or oxygen atmosphere, followed by a high temperature pyrolysis, namely carbonization, in an inert atmosphere such as nitrogen or argon [11, 12]. The temperature for pre-oxidation depends on the composition of precursors, usually, the pre-oxidation is carried out at 200 to 300 °C for sufficient duration to render it infusible and flameproof. Temperatures above 300 °C cause violent exothermic reactions resulting in significant weight loss and formation of tarry substances. The pyrolysis of pre-oxidized precursor in temperatures ranging from 500 to 800 °C is accompanied by a rapid drop in electrical resistivity, i.e. conversion from an insulator to a semiconductor. Therefore, careful control of conditions in both pre-oxidization and subsequent pyrolysis is required for the preparation of semiconducting carbon fibres.

In the present work, electrical resistivity was measured for carbon fibres prepared by various pyrolysis conditions and the pyrolysis passway are also discussed.

2. Experimental procedure

Polyacrylonitrile precursors for carbon fibre with an average diameter of 10 µm supplied by Nippon Carbon Company were employed in this work. For determination of the temperature profile of heat treatment, thermogravimetric–differential thermal analysis (TG–DTA) measurements were conducted using a Rigaku Thermoflex in air and nitrogen up to 700 °C. The precursor was pre-oxidized in air for 3 h at a heating rate of $5\ ^\circ\mathrm{C\,min}^{-1}$ and subsequently heated at temperatures ranging from 500 to 800 °C in nitrogen for various durations. During heat treatment, both ends of precursor fibres were fixed on an alumina holder so that it was subjected to a tensile stress by the shrinkage of itself. After pyrolysis was finished, the fibres were cooled at a rate of $-5^\circ\mathrm{C\,min}^{-1}$ to ambient temperature.

Electrical resistivity of prepared carbon fibres was measured in a temperature range from room temperature to 120 °C by direct current four-probe method and the thermistor constant was calculated from temperature dependence of electrical resistivity by using the general equation.

$$B = \{T_1T_2/(T_2 - T_1)\} \ln R_2/R_1 \qquad (1)$$

where, R_1 and R_2 are the electrical resistances at temperatures of T_1 and T_2, respectively.

The infrared absorption was measured with a Shimane infrared spectrometer using powdered samples diluted in anhydrous KBr pellets. Gas chromatography was employed to determine the gaseous carbon, nitrogen and hydrogen contents, in which the powdered specimen were burned out in oxygen. The surface and cross-section of fibres was examined by scanning electron microscope (SEM) after coating with a thin layer of gold.

3. Results and discussion

Fig. 1 presents the results of TG–DTA runs of polyacrylonitrile precursor used in this work. In Fig. 1a, a very sharp exothermic peak at 298 °C followed by a weaker exothermic peak at 400 °C and a broad exothermic peak between 570 and 700 °C were observed. The weight loss corresponding to the first peak is about 18%. The violent exothermic reaction with onset at 260 °C is reported to be associated with the cyclization of chain polyacrylonitrile molecules which resulted in the formation of ladder structure [11]. In regard to the second peak, it may be attributed to the cross-linking of adjacent cyclized molecules. The third peak is obviously caused by the gradual degradation of molecules because it is absent in the DTA curve obtained in nitrogen atmosphere. As shown in Fig. 1b, the temperature and weight loss corresponding to the first exothermic peak for the TG–DTA curves in nitrogen are essentially similar to those in air, but the second peak shifts to a higher temperature. To prevent the fibre from damage during the release of volatiles and to ensure the sufficient pre-oxidation, the pre-oxidation temperature was determined to be 270 °C, a temperature somewhat higher than the on-set of exothermic reaction.

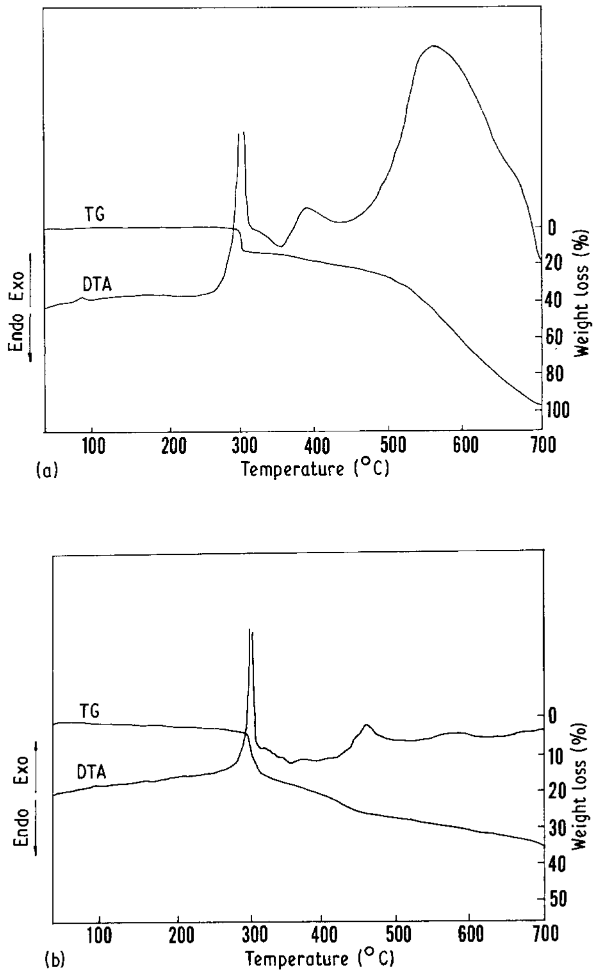

Figure 1 TG–DTA curves of polyacrylonitrile precursor (a) in air; (b) in nitrogen.

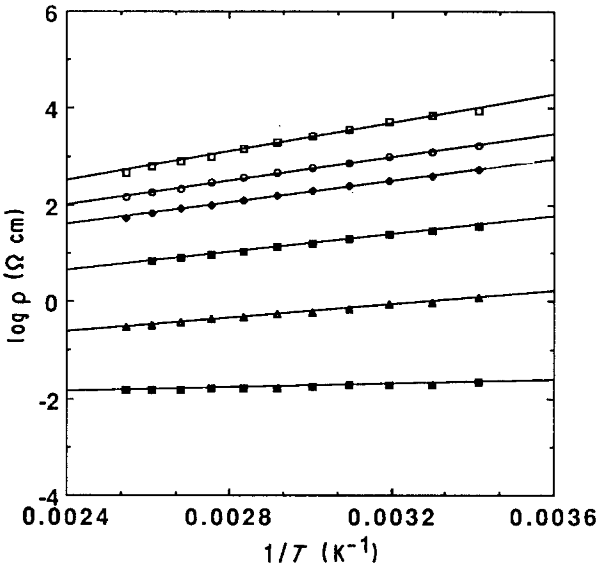

Figure 2 Temperature dependence of electrical resistivity of fibres pyrolysed at various temperatures for 30 min: (□) 550; (○) 590; (◆) 610; (▣) 650; (△) 700 and (■) 800 °C.

The temperature dependence of resistivity of the fibres pyrolysed at various temperature are illustrated in Fig. 2. All of the fibres showed a negative temperature coefficient of resistivity. Both electrical resistivity at 25 °C and thermistor constant decreased with increasing pyrolysis temperature as represented in Fig. 3. The effect of pyrolysis temperature on resistivity of fibres was remarkable. In the investigated temperature range, the resistivity decreases as many as six orders of magnitude. Fig. 4 illustrates the temperature dependence of electrical resistivity for fibres pyrolysed at 610 °C for various durations. Fig. 5 shows the influence of pyrolysis duration on electrical resistivity and thermistor constant. It is noted that the trend of resistivity change is quite different from that in Fig. 3. The curve can be roughly divided into two parts, in which each has a different slope, i.e. a rapid drop in electrical resistivity during the first 30 min of pyrolysis, followed by a slow change at longer durations. An acceptable interpretation would be that at lower temperatures the pyrolysis reaction is controlled by the diffusion rate of gases such as N_2, HCN, NH_3 etc. which were evolved during the pyrolysis process. However, further analysis will be required for a satisfying explanation.

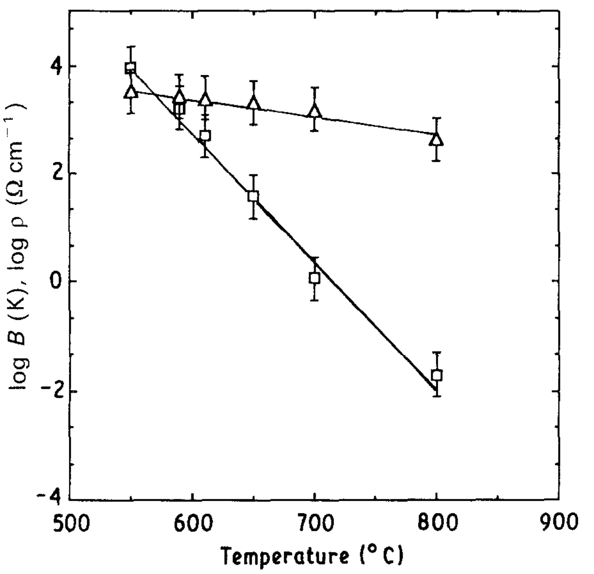

Figure 3 Electrical resistivity (□) at 25 °C and thermistor constant (△) of fibres as a function of pyrolysis temperature.

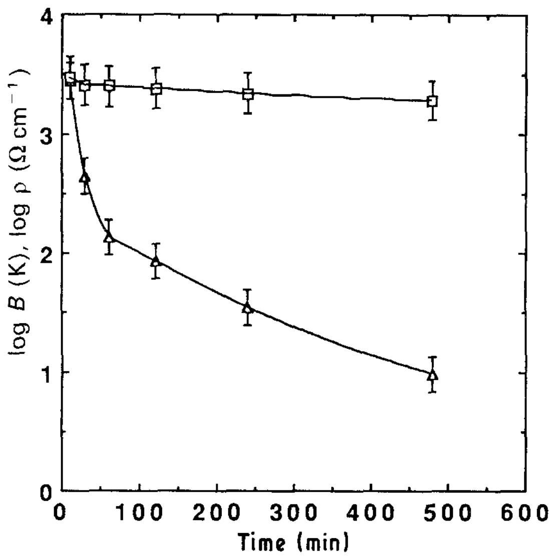

Figure 5 Electrical resistivity (△) at 25 °C and thermistor constant (□) of fibres as a function of pyrolysis duration.

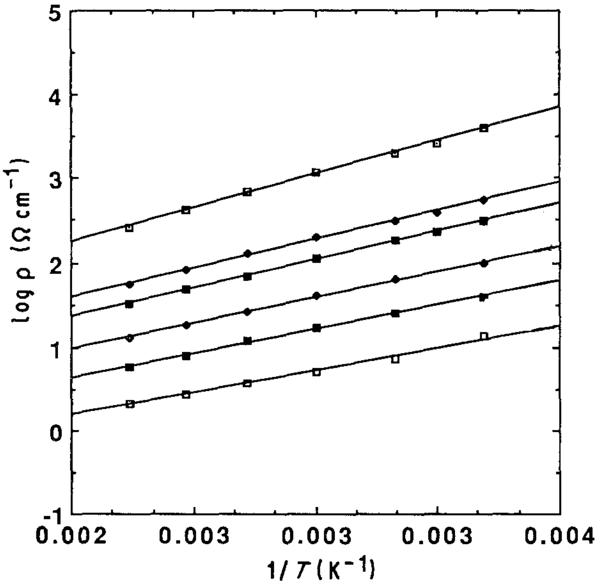

Figure 4 Temperature dependence of electrical resistivity of fibres pyrolysed at 610 °C for various durations: (⊡) 10; (◆) 30; (◘) 60; (◇) 120; (■) 240 and (□) 480 min.

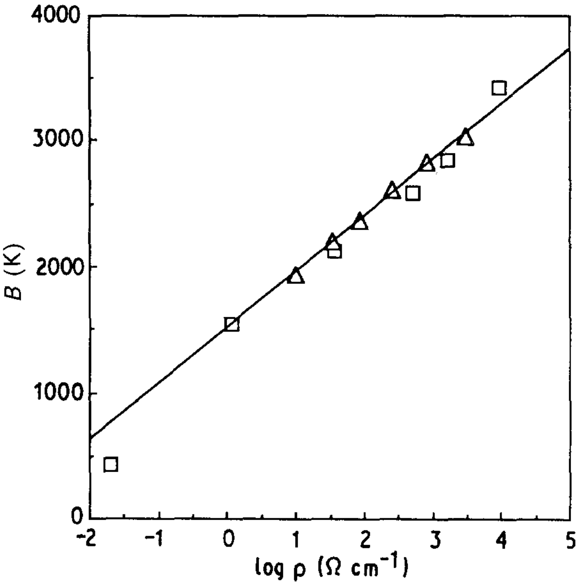

Figure 6 Relation between thermistor constant and log ρ; (□) pyrolysing at different temperatures; (△) pyrolysing at different durations.

Fig. 6 represents the relation between resistivity at 25 °C and thermistor constant. A linear relation between log ρ and thermistor constant was observed. In general, resistivity of semiconductors obeys an equation of the form

$$\rho = \rho_0 \exp(E/kT) = \rho_0 \exp(B/T) \qquad (2)$$

where ρ is the resistivity at absolute temperature, T, ρ_0 is a constant referred to as the resistivity at infinite temperature, E is the activation energy for conduction and k is the Boltzmann constant. Changes in both ρ_0 and E should contribute to the variation of resistivity. Figs 7 and 8 show the variation of ρ_0 and E calculated from the results in Figs 2 and 4, respectively. As can be seen in Fig. 7, E decreased linearly with increasing pyrolysis temperature but the change in ρ_0 was not so evident compared to that of E. In Fig. 8, the curve of E is also similar to that in log ρ as known in Fig. 5. Accordingly, it can be inferred that the decrease in resistivity of fibres with an increase in pyrolysis temperature and duration is mainly attributed to the decrease in activation energy. Fig. 9 illustrates the results of SEM observations. The fibre pyrolysed at 800 °C, (a), exhibits a porous surface, however, the fibre pyrolysed at 610 °C, (b), has a fairly smooth surface.

Table I lists the chemical composition of the fibres pyrolysed at different temperatures and durations.

To estimate the structure modification in the pyrolysis process, namely the degree of basal plane development, the atom ratios of hydrogen, nitrogen and carbon were calculated from Table I and presented in Fig. 10 as a function of pyrolysis temperature. It was found that the changes in atom ratios were similar to

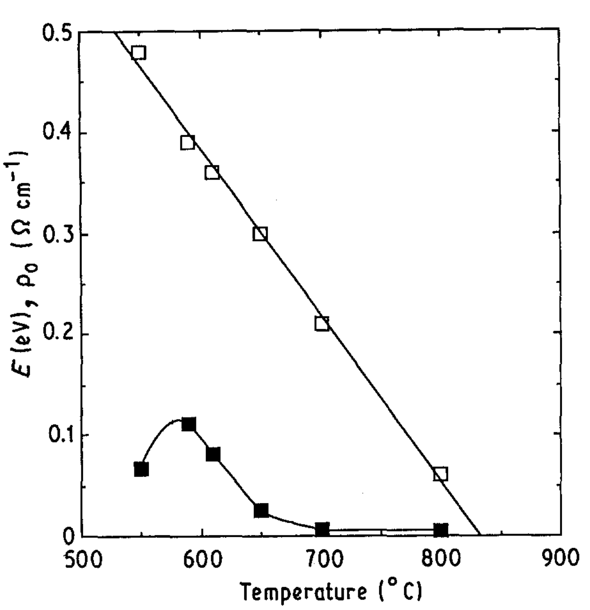

Figure 7 Variation of E (□) and ρ_0 (■) with pyrolysis temperature.

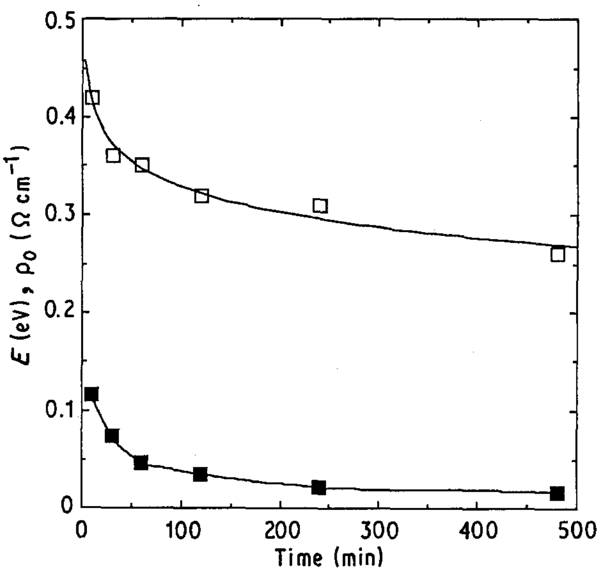

Figure 8 Variation of E (□) and ρ_0 (■) with pyrolysis duration.

those in electrical resistivity as shown as Figs 3 and 5.

Infrared absorption of precursors pyrolysed at various temperatures are presented in Fig. 11 which indicated the structure modification accompanying the progress of pyrolysis. Three absorption peaks were observed between 4000 and 400 cm^{-1}. The absorption at 1570 cm^{-1} may be assigned to C=C and C=N groups. In addition, no absorption associated with –CH$_2$ and C≡N at 2940 cm^{-1} and 2240 cm^{-1} were found. It implies that the chain polyacrylonitrile molecules have completely cyclized to form a ladder structure after pre-oxidation in air. The absorption peak in the region from 1298 to 1233 cm^{-1} is probably a consequence of overlap of several groups since the in-plane vibration of =C–H and the stretching vibration of C–C and C–O would be expected to absorb in this region. The out-plane = C–H vibration might be responsible for the absorption at 800 cm^{-1}.

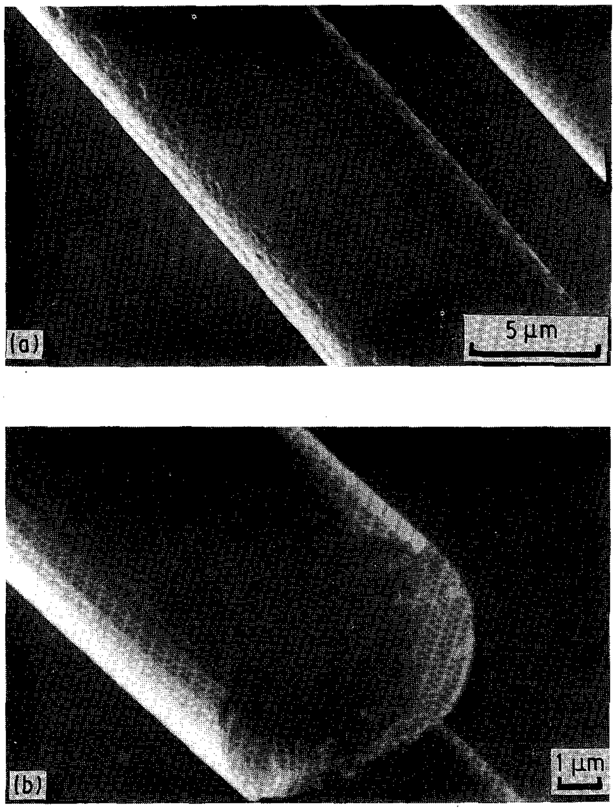

Figure 9 SEM micrograph of fibre pyrolysed at: (a) 800 °C for 30 min showing pores on the surface; (b) 610 °C for 30 min.

TABLE I Chemical compositions of the fibres pyrolysed at different conditions

Temp. (°C)	Duration (min)	C (wt %)	N (wt %)	H (wt %)
550	30	62.82	20.78	1.85
610	30	65.17	20.18	1.64
800	30	66.03	15.74	1.10
610	10	63.79	21.03	1.62
610	60	65.24	20.20	1.59
610	480	66.51	19.39	1.46

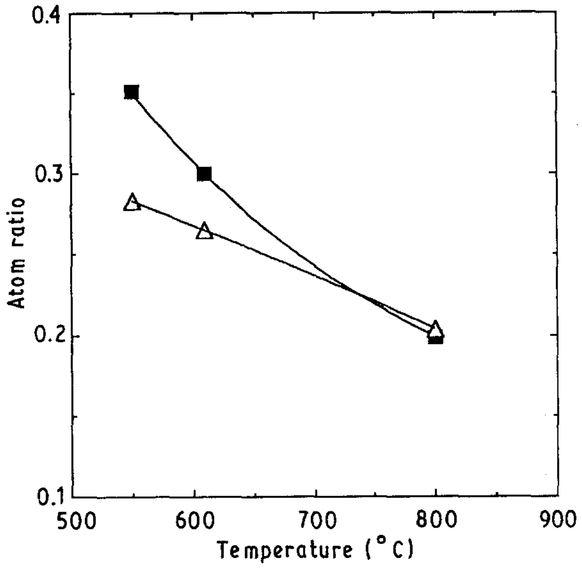

Figure 10 Composition change in atom ratio as a function of pyrolysis temperature: (△) N/C; (■) H/C.

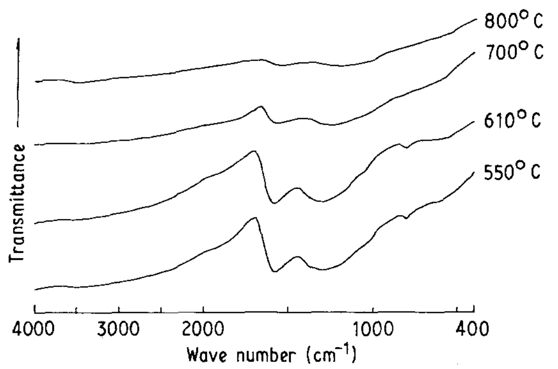

Figure 11 I.r. spectra of fibres pyrolysed at different temperatures for 30 min.

Furthermore the intensities of observed absorption decreased with increasing temperature. This suggests that the basal plane structure develops into a larger section due to the intermolecular polymerization of ladder-type structure into a larger section. It is assumed that the development of basal plane structure brings about a decrease in activation energy for conduction and a following decrease in electrical resistivity.

4. Conclusions

1. Semiconducting fibres were prepared by pyrolysis of polyacrylonitrile precursor and resistivities of 10^4–10^{-2} Ωcm^{-1} were obtained when the pyrolysis temperature varies from 550 to 800 °C. The electrical resistivity of fibres is mainly controlled by the pyrolysis temperature.

2. All of the obtained fibres showed negative temperature coefficient of electrical resistivity. The thermistor constant of fibres was found to reduce linearly with a decrease in electrical resistivity.

3. Concentrations of hydrogen and nitrogen decreased with increasing pyrolysis temperature and duration.

4. It is possible to prepare semiconducting fibres with proper electrical resistivity and thermistor constant by controlling the pyrolysis conditions.

References

1. A. SHINDO, *Carbon* **1** (1964) 391.
2. W. WATT, *ibid.* **10** (1972) 121.
3. P. W. McKEE and V. J. MIMEAULT, in "Chemistry and Physics of Carbon", Vol. 8, edited by P. A. Thrower and P. L. Walker (Dekker, New York, 1973) p. 151.
4. P. J. GOODHEW, A. J. CLARKE and J. E. BAILEY, *Mater. Sci. Eng.* **17** (1975) 3.
5. M. A. GEIDERKH, B. E. DAVYDOV, B. A. KRENTSEL, M. KUZANOVICH, L. S. POLAK, A. V. TOPCHIEV and R. M. VOITENKO, *J. Polym. Sci.* **54** (1961) 621.
6. M. MUTO, M. MIYAYAMA, H. YANAGIDA, T. KAJIWARA, N. MORI, H. ICHIKAWA and H. HARADA, *J. Mater. Sci. Lett.* **9** (1990) 1269.
7. J. J. BROPHY, *J. Appl. Phys.* **33** (1962) 114.
8. A. BRADLEY and J. P. HAMMES, *J. Electrochem. Soc.* **110** (1963) 543.
9. W. D. BRENNER, J. J. BROPHY and H. SCHONHORN, "Organic Semiconductors, Proceedings", edited by J. J. Brophy and J. W. Buttrey, (Macmillan, New York, 1962) p. 159.
10. F. GUTMANN and L. E. LYONS, "Organic Semiconductors" (Wiley and Sons, New York) p. 472.
11. M. K. JAIN and A. S. ABHIRAMAN, *J. Mater. Sci.* **22** (1987) 278.
12. M. BARASUBRAMANIAN, M. K. JAIN and S. K. BHATTACHARYA, *ibid.* **22** (1987) 3864.

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