JOURNAL OF MATERIALS SCIENCE 24 (1989) 3113–3117

Carbon film from polyphenylene prepared by electrochemical polymerization

YOSHIO YAMADA, TAKESHI FURUTA, MINORU SHIRAISHI
National Research Institute for Pollution and Resources, 16-3 Onogawa, Tsukuba-shi, Ibaraki 305, Japan

MASA-AKI SATO, KYOJI KAERIYAMA
Research Institute for Polymers and Textiles, Yatabe-higashi, Ibaraki 305, Japan

A carbon film was produced from polyphenylene (PP) film prepared by electrochemical polymerization of benzene to obtain a uniform and thin film. The PP film (~10 μm thick) was transformed into the carbon or graphite film without drastic changes of shape or size. The electrical conductivity of the film was remarkably enhanced by heat-treatment between 600 and 800° C, but further increase in the conductivity was not observed by treating at higher temperatures. This behaviour is considered to correlate with a poor degree of graphitization of the PP film. The carbonization and graphitization mechanisms of the film are discussed in connection with the structure of polyphenylene in the film.

1. Introduction

Carbon film is an attractive material from fundamental and practical aspects. It has been prepared chiefly by moulding powder carbon at high pressure or by vapour-phase deposition of carbon. In recent years it has been reported that commercially available polymer films [1, 2] or cast films of soluble precursor polymers [3, 4] are pyrolysed to give characteristic carbon films. However, it is generally difficult to produce thin carbon films from polymers because most of these carbon precursor polymers are insoluble in solvent.

The present authors have attempted to obtain thin carbon films via aromatic polymer films which are easily formed by electrochemical polymerization of aromatic compounds such as benzene. Because these precursor films with a high carbon yield are nonfusible in the heat-treatment process, their film forms are maintained while being carbonized and then graphitized. Therefore, it is expected that the characteristics of the precursor polymers will be reflected upon the carbon film obtained. Also, the thickness of the film can be controlled by changing the polymerization conditions. This paper presents the results on the structural changes of a polyphenylene film formed from benzene during heat-treatment and on the electrical property and graphitizability of the carbon film obtained.

2. Experimental procedure

PP film was electrochemically prepared according to the procedure given by Satoh *et al.* [5]: 1.2 mol l^{-1} solution of benzene in nitrobenzene was electrolysed using a composite electrolyte of 0.1 mol l^{-1} copper(II) chloride and 0.1 mol l^{-1} lithium pentafluoroarsenate or tetraethylammonium tetrafluoroborate. By applying a constant current of 2 mA cm^{-2} for 1 h without stirring, between platinum (as a working electrode) and nickel (as a counter electrode) a uniform and black film ~ 10 μm thick with a size of 20 × 20 mm^2 was deposited on the platinum anode plate. After anions doped in the film had been removed with aqueous ammonium solution, the film was dried at 110° C *in vacuo*. The film was then treated at various temperatures between 200 and 1000° C for 1 h at a heating rate of 3° C min^{-1} in an argon atmosphere. In order to graphitize the film, the precursor PP film pyrolysed at 800° C for 1 h was retreated for 30 min in the temperature range up to 2800° C in an argon atmosphere.

Thermogravimetric measurement and gas analysis were carried out on a Rigaku Corporation model TG-8066 thermobalance equipped with a Yanaco Gas chromatograph G-180. Fourier transform–infrared (FT–IR) spectra of heat-treated PP films were obtained using a Digilab FTS-20 IR spectrometer. Raman spectra were recorded on a Spex Ramalog 1403 spectrophotometer using the 514.5 nm argon line with 500 mW.

3. Results and discussion

Scanning electron micrographs of the as-grown PP film are shown in Fig. 1; it is seen that the surface on the electrode side is smooth whereas the growth side has a fairly rough surface, characteristic of electrochemical polymerization [6, 7]. As shown in Fig. 1, the features of both surfaces still remained after treatment at 1000° C, except for a slight shrinkage and the formation of some holes on the growth side. Fig. 2 represents the weight loss of the film with heat-treatment temperature (HTT). It is well known that PP has a high carbon yield [8]. In this case the curve indicates that the loss up to 1000° C is very low (~ 15%). This may be one reason why the film shape is maintained in these temperature ranges.

0022–2461/89 $03.00 + .12

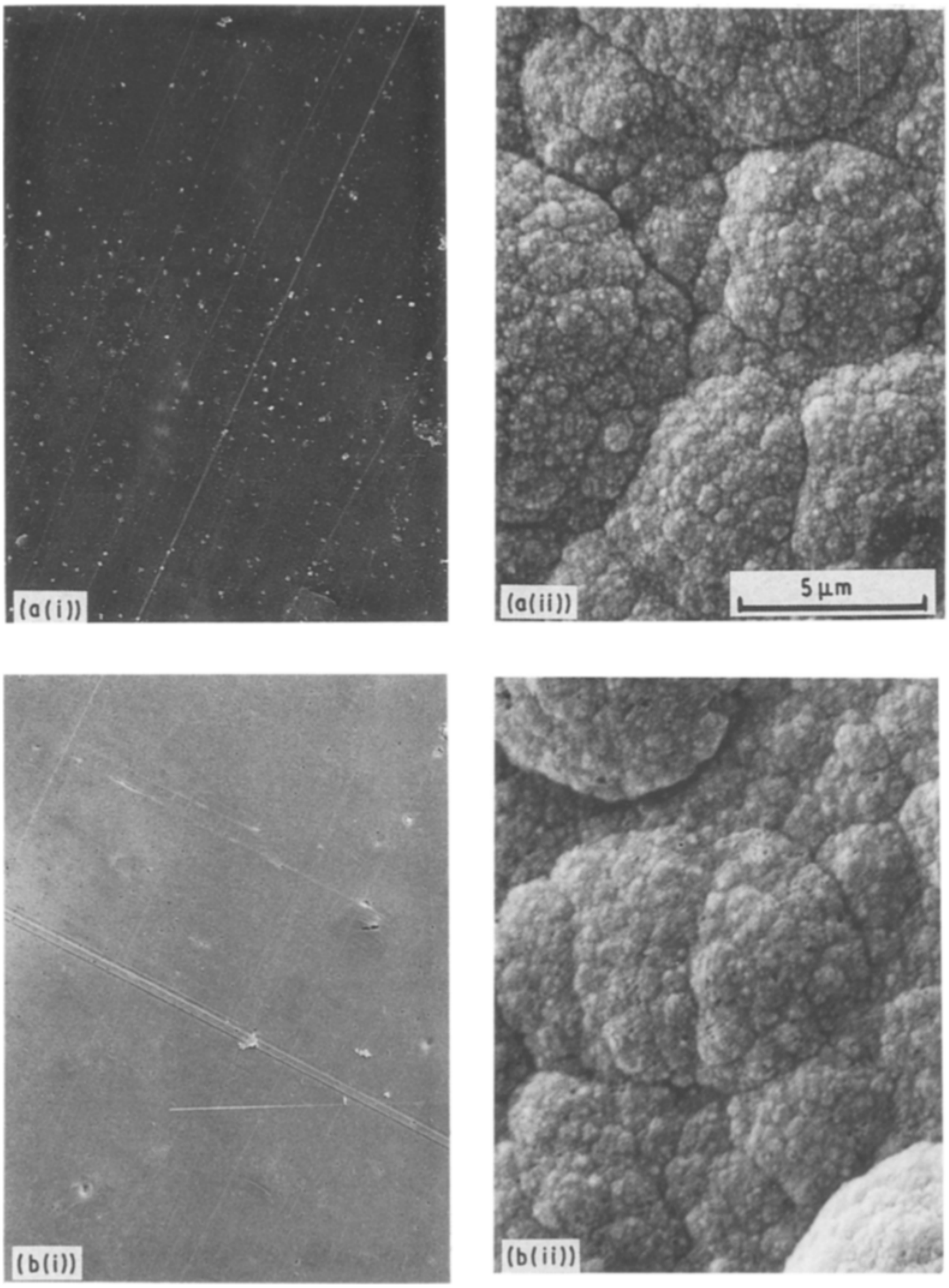

Figure 1 Scanning electron micrographs of as-grown and heat-treated films. (a) As-grown, (b) heat treated at 1000° C; (i) electrode side, (ii) growth side.

The amounts of hydrogen and methane gases evolved from the film were measured to estimate the structural changes during the treatment. The results are shown in Fig. 3. Hydrogen gas begins to generate around 500° C, reaches a maximum at 750° C and then decreases. Table I shows that the carbon to hydrogen atomic ratio calculated from elemental analysis data of the treated film increased rapidly between 600 and 800° C. These results imply that dehydrogenation of the film occurs mainly in these temperature ranges.

TABLE I Elemental analysis and C/H atomic ratio of heat-treated PP films

Film	C (%)	H (%)	N (%)	$O_{dif.}$* (%)	$O_{meas.}$† (%)	C/H (atomic ratio)
As-grown	89.4	4.2	0.9	5.5	2.8	1.80
400° C, 1 h	91.2	3.9	0.7	4.2	–	1.96
600° C, 1 h	93.1	3.6	0.6	2.7	–	2.15
800° C, 1 h	91.3	1.4	0.6	6.7	5.0	5.32
1000° C, 1 h	92.3	1.1	0.3	6.3	4.8	7.12

*$O_{dif.}$: 100 − C(%) − H(%) − N(%).
† $O_{meas.}$:directly measured.

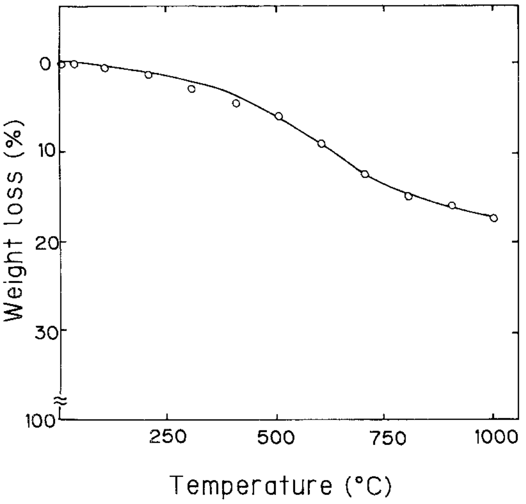

Figure 2 Weight loss of PP film with HTT.

The evolution of methane gas can also be seen in Fig. 3, although the amount of the gas is very low, compared with that of hydrogen. The formation of methane gas suggests that the partial cleavage of phenyl rings takes place probably at the polymer terminals [8]. A considerable amount of oxygen was detected in the as-grown and heat-treated films as can be seen in Table I. In addition, carbon monoxide and carbon dioxide gases are generated in the early stages of the heat treatment (Fig. 3). Contamination with oxygen in the as-grown film seems to arise from oxidation during the formation of PP and/or the cleaning process of the film, described in Section 2. In order to avoid oxidation of the film during polymerization, the reaction was carried out in a closed system in which oxygen in the reaction cell was thoroughly displaced by argon gas in a vacuum line. The evolution of carbon monoxide and carbon dioxide gases became much lower, but some formation of these gases was observed, as plotted by the dotted line in Fig. 3. Therefore, the surface of the as-grown film is considered to be easily oxidized even after electrochemical polymerization.

Fig. 4 shows the FT–IR spectra of the heat-treated PP films, together with that of the as-grown film. The as-grown film was found to have a structure in which phenyl rings are linearly linked at para-positions from the following assignments [5, 9]; a peak at 3035 cm^{-1} in the spectrum of the as-grown film is identified as the C–H stretching vibration of aromatic rings; three peaks at 1480, 1395 and 1000 cm^{-1} are due to C–C stretching, and the peak at 805 cm^{-1} is due to C–H out-of-plane vibration of para-positioned phenyl groups. In addition, there are peaks at 765 and 690 cm^{-1} due to C–H out-of-plane vibration at terminal phenyl groups. An absorption band near 870 cm^{-1} due to an out-of-plane vibration of isolated C-H bond rarely appears in the as-grown film. However, its intensity gradually increases with HTT, as indicated by an arrow in Fig. 4. This suggests that dehydrogenation proceeds between adjacent linear chains of phenyl groups toward the development of a two-dimensional layer structure. Because the peaks identified as poly(*p*-phenylene) are weak in the spectrum of the film treated at 700° C, very broad bands around 1700 and 1300 cm^{-1} indicating the presence of oxygen-containing functional groups (carbonyl and ether groups) are unequivocally observed. These groups are considered to be concerned with the surface oxidation of the as-grown films mentioned above.

The carbonization mechanism of the PP film was presumed from the results, as shown in Fig. 5; linear polyphenylene polymers grow perpendicular to the anode plate. Therefore, partial dehydrogenation

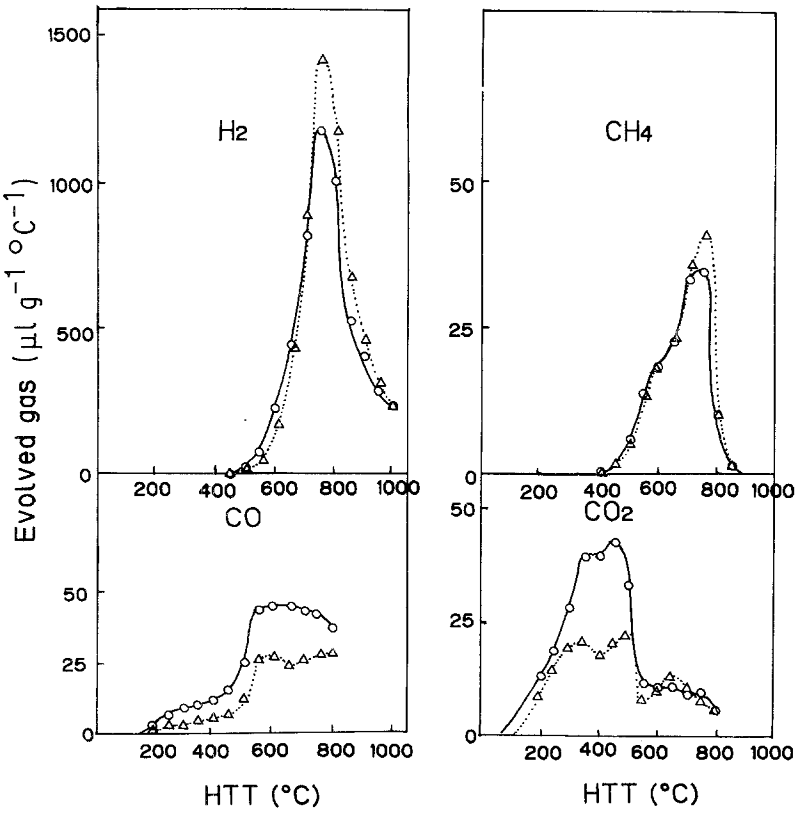

Figure 3 Amounts of H_2, CH_4, CO and CO_2 gases evolved from heat-treated PP film. Films prepared (○) in air, (△) in argon.

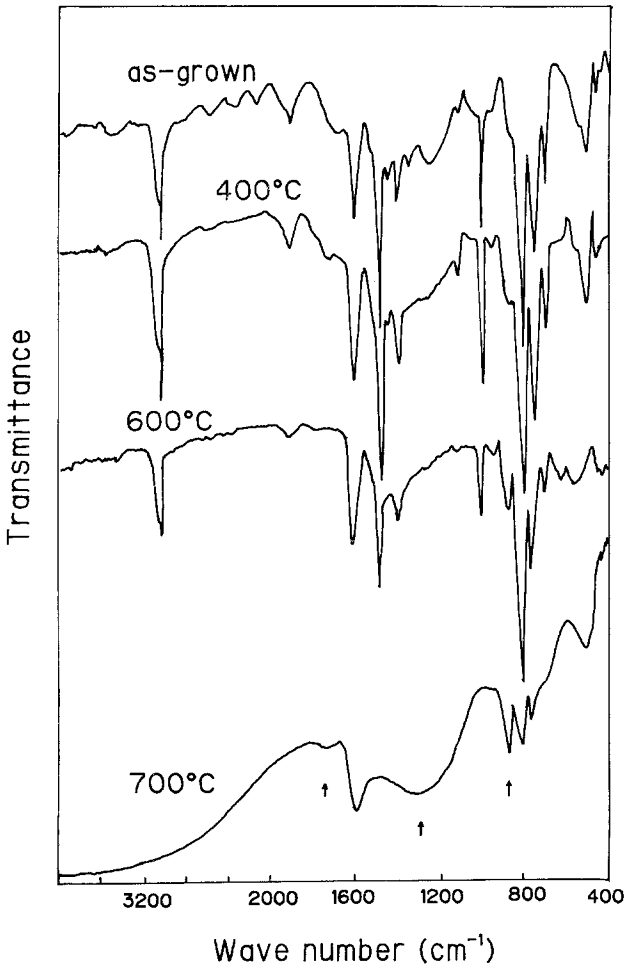

Figure 4 FT–IR spectra of heat-treated PP films.

occurs between the adjacent chains around 600° C and a two-dimensional layer structure is formed with increase in treatment temperature (600 to 800° C) [8]. However, the development of the layer structure might be limited within a short range, because two successive benzene rings are twisted with respect to each other by about 23° [10, 11].

Fig. 6 shows the electrical conductivity of the films treated up to 2800° C. The film behaves as an insulator up to 600° C, but a remarkable increase in the conductivity was observed between 600 and 800° C. This temperature range corresponds to the structural changes described above. That is, it suggests that the development of the two-dimensional layers enhances the electrical conductivity. The conductivity of the graphitized film (2.7×10^2 s cm^{-1}) is almost the same as that of a film heat-treated at 800° C. The *d*-spacing and L_c of the X-ray parameters were obtained from the 0 0 2 diffraction pattern of a powder sample of the film graphitized at 2800° C. The values of 0.3421 and 5.49 nm are very close to those obtained from graphitized samples of biphenyl and *p*-terphenyl, being low molecular analogues of poly(*p*-phenylene) [12]. This result indicates that the PP film may be classified as non-graphitizable carbon.

The graphitizability was also investigated from Raman spectra of PP film heat-treated between 2000 and 2800° C (Fig. 7). Two scattering peaks at 1580 and 1360 cm^{-1} were observed in the graphitized films. The peak at 1580 cm^{-1} was assigned to graphite carbon and that at 1360 cm^{-1} to disordered carbon [13]. The

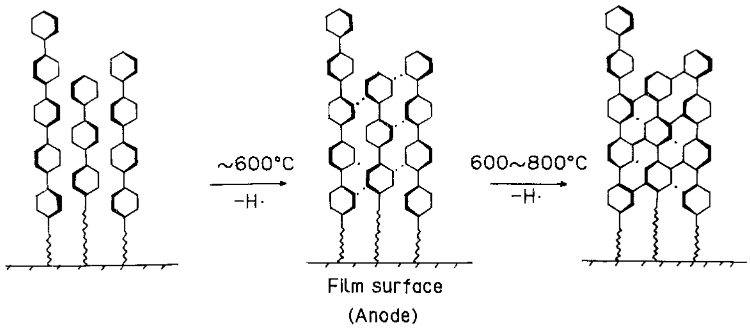

Figure 5 Carbonization scheme of polyphenylene polymer.

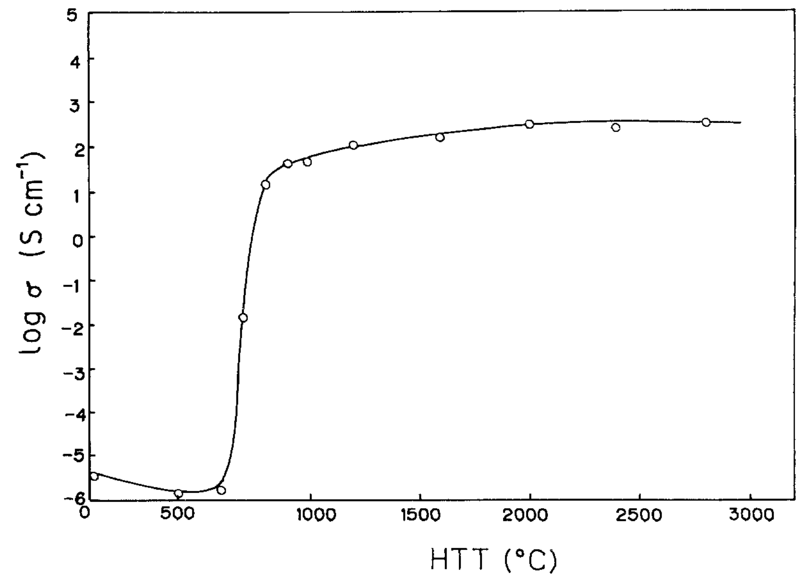

Figure 6 Change of electrical conductivity of PP film with HTT.

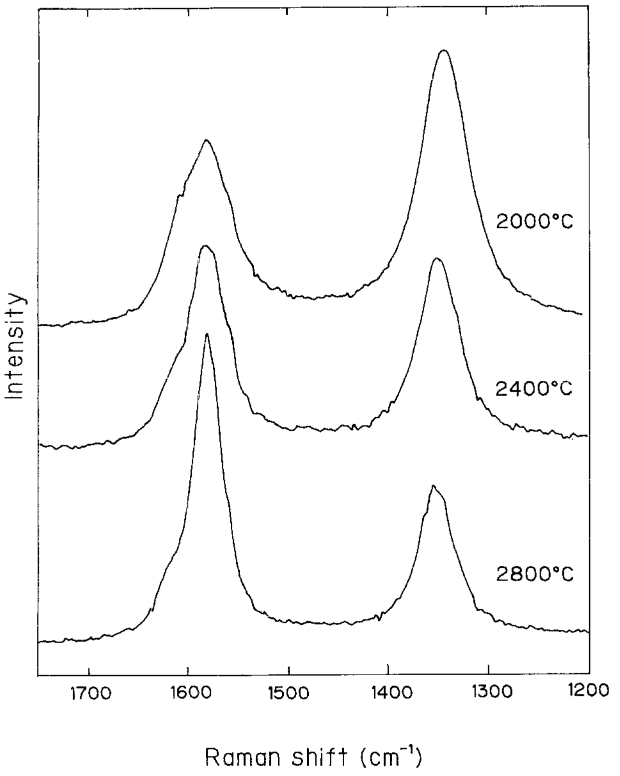

Figure 7 Raman spectra of PP films heat-treated at 2000, 2400 and 2800° C.

intensity ratio of the higher wave number peak to the lower one gradually increases with HTT, but the peak at 1360 cm^{-1} still remains above 2800° C. Such a poor degree of the graphitizability of the film may be responsible for the insufficient development of the layer structure at low temperatures, as previously described. Recently it was reported that some carbon films obtained from polymers have a high electrical conductivity of 10^3 to 10^4 S cm^{-1} [2, 4]. These polymers show a high orientation of crystallites on graphitization. Thus, in this case, a poor growth of graphite crystallites may be one cause of the non-enhancement of the conductivity of the PP film treated at higher temperatures. However, the low conductivity may be improved to some extent by doping with electron-accepting agents such as I_2 or AsF_5 [14].

Acknowledgement

The authors thank Dr M. Nakamizo, Government Industrial Research Institute, Kyushu for help with the observation of FT–IR spectra.

References

1. A. BURGER, E. FITZER, M. HEYM and B. TERWIESCH, *Carbon* **13** (1975) 149.
2. M. MURAKAMI, H. YASUJIMA, Y. YUMOTO, S. MIZOGAMI and S. YOSHIMURA, *Solid State Commun.* **45** (1983) 1085.
3. M. KINOSHITA, K. OKUNO, T. HASHIMOTO and A. TAKAKU, *Tanso* **127** (1986) 157.
4. T. OHNISHI, I. MURASE, T. NOGUCHI and M. HIROOKA, *Synthetic Metals* **14** (1986) 207.
5. M. SATOH, K. KANETO and K. YOSHINO, *J. Chem. Soc. Commun.* **1985** 1629.
6. R. J. WALTMAN and A. F. DIAZ, *J. Electrochem. Soc.* **132** (1985) 631.
7. G. TOURILLON and F. GARNIER, *J. Polym. Sci. Polym. Phys. Edn* **22** (1984) 33.
8. E. FITZER and J. KALBE, *High Temp. High Press.* **3** (1971) 53.
9. M. SATO and K. KAERIYAMA, *Makromol. Chem.* **184** (1983) 2241.
10. A. WEINTRAUB and P. L. WALKER Jr, in Proceedings of 3rd International Carbon and Graphite Conference, London, Vol. 9, edited by J. G. Gregory (Society of Chemical Industry, London, 1971) p. 159.
11. J. L. BREDAS, B. THEMANS, J. G. FRIPIAT and J. M. ANDRE, R. R. CHANCE, *Phys. Rev. B* **29** (1984) 6761.
12. E. FITZER, K. MUELLER and W. SCHAEFER, in "Chemistry and Physics of Carbon", Vol. 7, edited by P. L. Walker Jr (Dekker, New York, 1971) p. 349.
13. F. TUINSTRA and J. K. KOENING, *J. Chem. Phys.* **53** (1970) 1126.
14. L. W. SHACKLETTE, R. R. CHANCE, D. M. IVORY, G. G. MILLER and R. H. BAUGHMAN, *Synthetic Metals* **1** (1979) 307.

Received 5 July
and accepted 23 November 1988