JOURNAL OF MATERIALS SCIENCE 24 (1989) 3091–3095

Electrical, optical and ESR study of thin films of plasma polymerized acrylonitrile

A. H. BHUIYAN*, S. V. BHORASKAR
Department of Physics, University of Poona, Pune 411 007, India

Thin films of plasma-polymerized acrylonitrile (PPAN) were deposited by glow discharge polymerization and were made semiconducting by the process of pyrolysis. Electrical and optical measurements along with electron spin resonance (ESR) measurements were used to study the extent of conjugation in the pyrolysed system. The onset and building up of conjugation due to the structural remodifications was investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infrared (IR) spectroscopy. A major structural transition was observed at around 550 K which is responsible for the drastic reduction in the electrical resistivity and optical band gap. ESR studies revealed that pyrolysis causes conjugation and generation of free radicals in PPAN, thereby enhancing the electrical conductivity. The mechanism of conduction was observed to be dominated by the variable-range hopping.

1. Introduction

Recently, material preparation, processing and surface modification has become one of the most prominent areas of research in the development of science and technology. In this respect, plasma prepared polymers [1–3] and plasma modified surfaces [4–6] have gained considerable interest. Plasma prepared polymers have additional advantages over conventionally synthesized polymers, like excellent adhesion to the substrate, ease of preparation in a completely dry atmosphere, and the possibility of preparing extremely thin, uniform and pin-hole free films [7].

However, before getting full credit, a polymer needs complete characterization. The work reported in this paper consists of synthesis and characterization of thin films of semiconducting plasma-polymerized acrylonitrile (PPAN). Plasma deposition was chosen for obtaining device quality thin films of PPAN and post pyrolysis was used for tailoring the semiconducting properties in it. Although, there is no dearth of literature [8, 9] on chemically synthesized polyacrylonitrile (PAN); plasma deposited and pyrolysed semiconducting films of acrylonitrile (AN) have not been extensively studied.

PAN, an organic vinyl polymer, consists of a carbon backbone with a nitrile group on alternate carbon atoms [8]. It becomes semiconducting on pyrolysis (controlled heat treatment) and exhibits photoconductivity in this state. Although, the semiconducting behaviour of pyrolysed PAN is correlated to the structural changes and conjugated ladder structure [8, 9], there is little experimental evidence in literature on PPAN.

2. Experimental details

The plasma polymerization system and deposition parameters used in this experiment are the same as reported earlier [7]. Samples were pyrolysed in vacuum (at about 1.33×10^{-3} Pa) from 473 to 773 K for 3 h under dynamic condition. The temperature dependence of conductivity was measured for three different samples from 300 to 770 K in vacuum (at about 1.33×10^{-1} Pa). Vacuum deposited aluminium was used as an electrode for electrical measurements.

UV–visible and infrared (IR) spectra were taken at room temperature using Hitachi model-330 and Perkin Elmer-783 spectrometer respectively.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were obtained by Derivatograph-MOM, Hungary. Platinum crucibles were used and "Deadburned" Al_2O_3 was taken as a suitable reference material.

Electron spin resonance (ESR) spectra were recorded on ESR spectrometer E112, Varian Associates, USA with a magnetic field modulation of 100 kHz.

3. Results and discussion

3.1. DTA and TGA

The DTA and TGA traces taken at 2.5 K min^{-1} for PPAN sample are shown in Fig. 1. The DTA thermogram shows an exotherm which reaches a maximum at 550 K. The corresponding TGA trace from 300 to 773 K shows a gradual weight loss and can be divided in three broad regions (A, B and C), each associated with a different rate of weight loss. The weight losses at the extremities of these regions are about 5%, 42% and 62.5% respectively. The weight loss in region A may be due to the loss of adsorbed water and gaseous species. This is not necessarily associated with any change in the structure. However, in region B, the gases evolving could be responsible for the major change in the PPAN structure because the DTA curve exhibits a peak in this region. The possible species evolving at this stage are most probably hydrogen,

---

* *Permanent address:* Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

0022–2461/89 $03.00 + .12

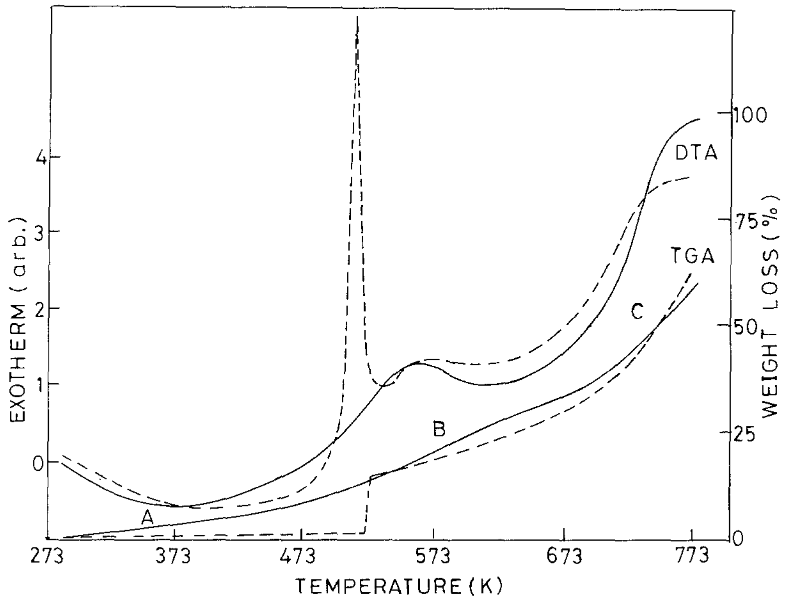

Figure 1 DTA and TGA traces of PPAN (full curves) and commercial PAN (broken curves) heated at 2.5 K min^{-1}.

NH_3, and HCN. A weight loss of 42%, in region B, can not be accounted for from the loss of hydrogen only but evolution of NH_3 or HCN or both may appropriately balance the weight loss. The third region seems to be a further extension of the same pattern in a slightly modified background structure of the polymer. Thus, the true degradation may be represented by the regions B and C starting from 50 K.

If the DTA and TGA traces for PPAN are compared with those for the commercial PAN (Fig. 1, broken curves), the marked difference is only in a step loss in the TGA curve at 533 K, associated with 13% weight loss and a sharp peak in the DTA trace at the same temperature. Except for this remarkably sharp transition, the rest of the TGA trace represents a similar pattern. The broad peak around 550 K in the DTA of PPAN is also reflected around the same temperature region in the DTA of commercial PAN. The overall behaviour of PPAN, thus, looks similar to the commercial PAN except for some structural differences. These differences can be further clarified from IR analysis.

3.2. IR analysis

IR spectra of as-deposited PPAN and PPAN pyrolysed at two different temperatures are presented in Fig. 2 which shows the structural changes accompanying the process of pyrolysis. The IR spectrum of as-deposited PPAN shown in Fig. 2, curve A, indicates the presence of the following structures: CH_2(2940, 1450 cm^{-1}); C≡N (2240 to 2200 cm^{-1}); CH stretching (1400 cm^{-1}); C≡C (2020 cm^{-1}); C=N and C=O (weak and small broad band at 1700 to 1500 cm^{-1}) and NH vibration (broad band at 3600 to 3300 cm^{-1}). The first three structures are of interest as far as acrylonitrile (AN) is concerned. The appearance of the remaining structures in the spectrum is probably caused by the change in the monomer structure as a result of the impact of energetic particles within the plasma during deposition. In fact, there is evidence for such structural changes in AN during its plasma polymerization [10, 11]. As shown in Fig. 2, curves B and C, the IR spectra of PPAN films pyrolysed at about 523 and 723 K, respectively, indicate the structural modifications at two pyrolysis temperatures. In particular, the slow disappearance of the 2240 to 2200 cm^{-1} band

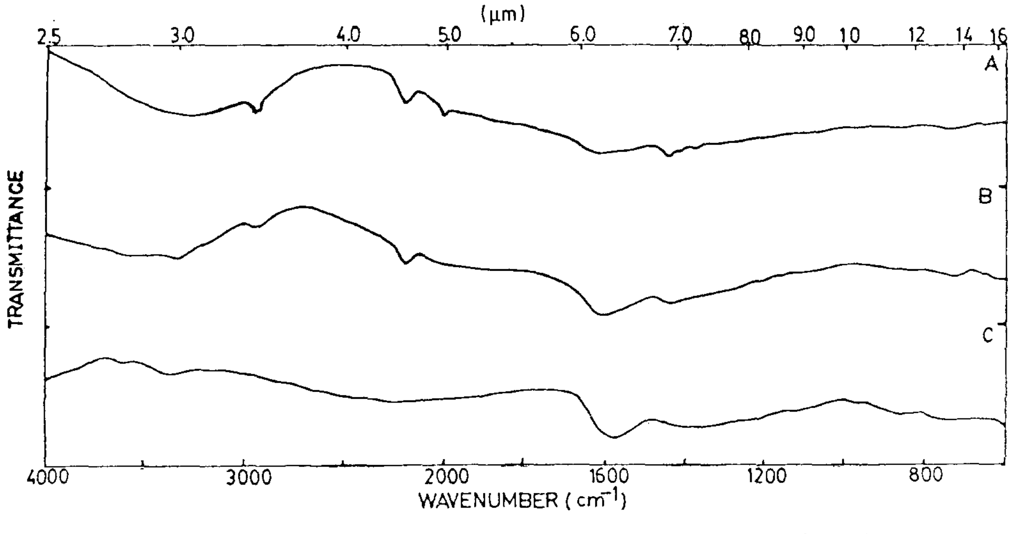

Figure 2 IR spectra of PPAN; (a) as-deposited, (b) pyrolysed at about 523 K and (c) pyrolysed at about 723 K.

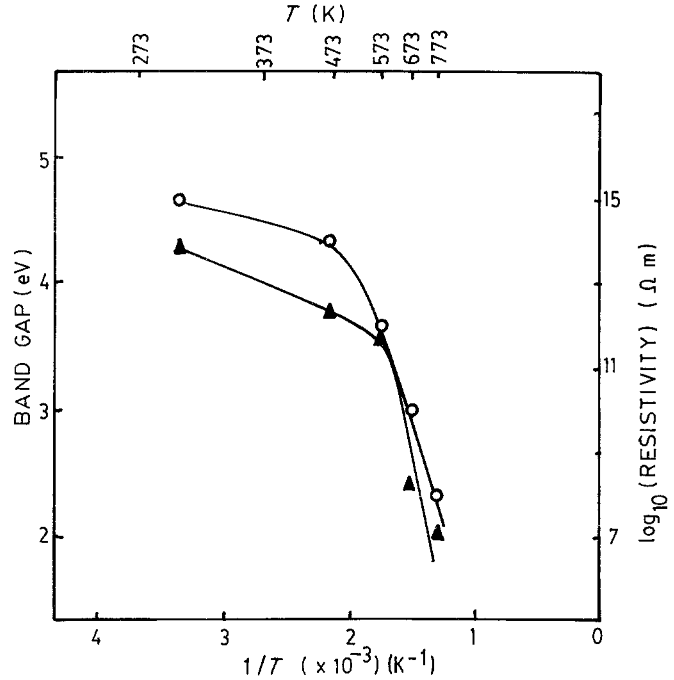

Figure 3 Room temperature electrical resistivity (○) and optical band gap (▲) of PPAN as a function of pyrolysis temperature.

indicate the loss of C≡N. At the same time, the weak broad band at 1700 to 1500 cm^{-1} in Fig. 2, curve A, becomes most intense for sample pyrolysed at 723 K (Fig. 2, curve C) indicating more conjugation (C=N and C=C) in the structure as pyrolization temperature increases [12]. It is apparent from Fig. 2 that the IR absorptions for CH_2 and C≡N disappear simultaneously in the intermediate temperature range (about 523 K) which is not the case for PAN prepared by conventional methods [12, 13] where absorption for C≡N disappears and that for CH_2 remains to some extent. Further, on annealing at about 723 K, both the absorption disappeared and a broad absorption appears at 1700 to 1500 cm^{-1} which has been discussed earlier. This implies that the structural changes in PPAN occurring due to pyrolysis may be different from those reported. Crosslinking may also occur between different carbon of the chains due to the loss of hydrogen/nitrogen, particularly, in the plasma polymerized films.

3.3. Electrical and optical measurements

Room temperature electrical resistivity and optical band gap for PPAN samples pyrolysed at different temperatures are shown in Fig 3. This reveals a drastic change in both electrical resistivity and optical band

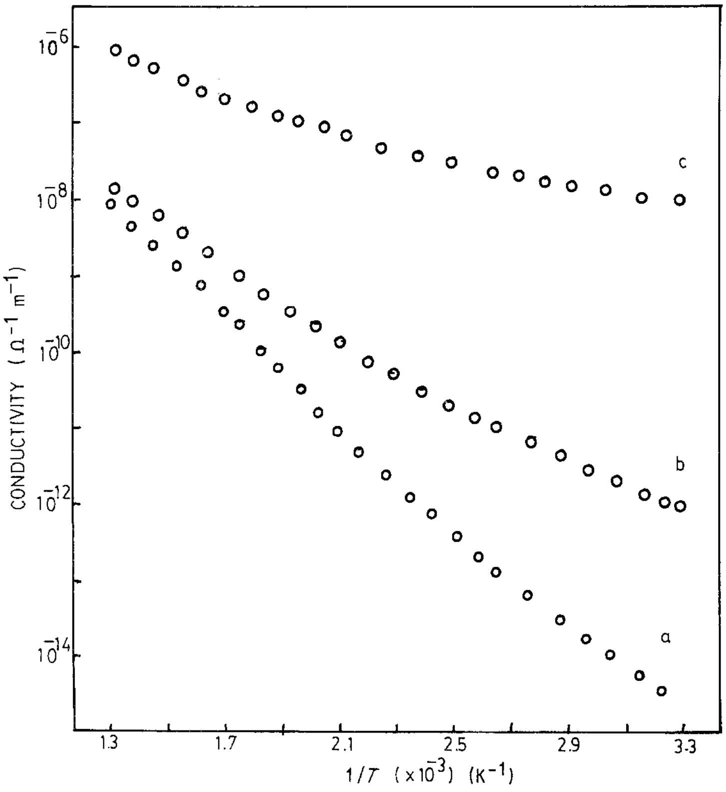

Figure 4 Electrical conductivity plotted against absolute temperature curves for PPAN; (a) as-deposited, (b) pyrolysed at about 573 K and (c) pyrolysed at about 773 K.

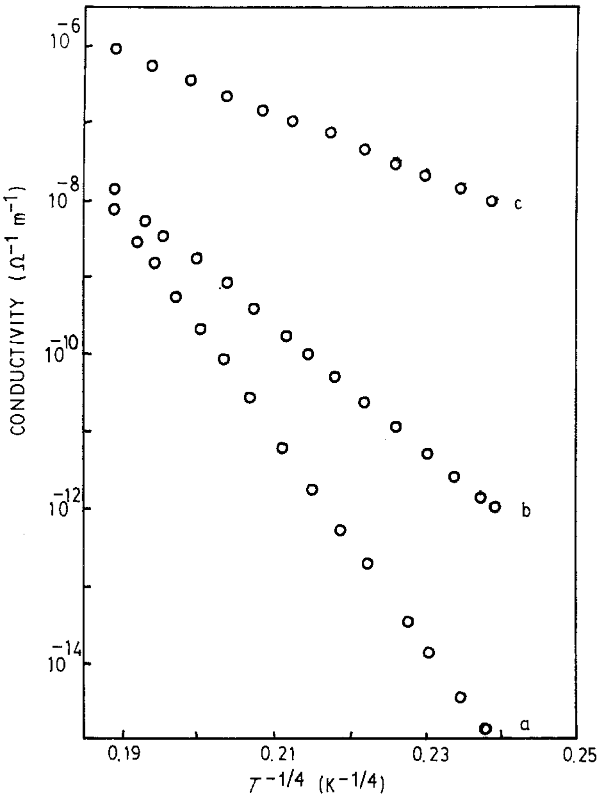

Figure 5 Electrical conductivity plotted against absolute temperature curves for PPAN. Sample specifications are same as in Fig. 4.

gap which occurs for PPAN pyrolysed at around 573 K. This is nearly the same temperature where TGA indicated major weight loss. Corresponding IR spectra indicated the loss of C≡N and appearance of conjugation around the same temperature.

Figs 4 and 5 describe the temperature dependence of electrical conductivity, σ, for three different PPAN samples. Log σ plotted against $1/T$ for as-deposited and samples pyrolysed at two different temperatures are illustrated in Fig. 4. The activation energy deduced from σ–T curves varies from 0.70 to 0.19 eV from as-deposited to pyrolysed samples (at about 773 K). The curves did not exhibit simple straight line relationship. The same data are presented in Fig. 5 as log σ plotted against $T^{-1/4}$ which shows almost straight line behaviour. These results are typical of transport in disordered and amorphous materials [14]. Here, the variable-range hopping [15] between localized states leads to a temperature dependence of the form σ exp $[-(T_0/T)^{1/(d+1)}]$, where d is the dimensionality of transport (e.g., $d = 3$ for three-dimensional motion etc.). This behaviour is quite acceptable because of the presence of conjugation, free radicals and free carriers in PPAN which are further enhanced by pyrolysis. Thermoelectric measurements, carried out on PPAN and pyrolysed PPAN, did not show appreciable variation with temperature. This corroborated the fact that the charge carriers may undergo hopping conduction [16, 17]. The activation energies found from thermoelectric measurements are much smaller than those from electrical conductivity measurements quoted above. Therefore, the electrical conductivity in PPAN could be considered due to the thermally activated hopping of charge carriers having a low mobility [17].

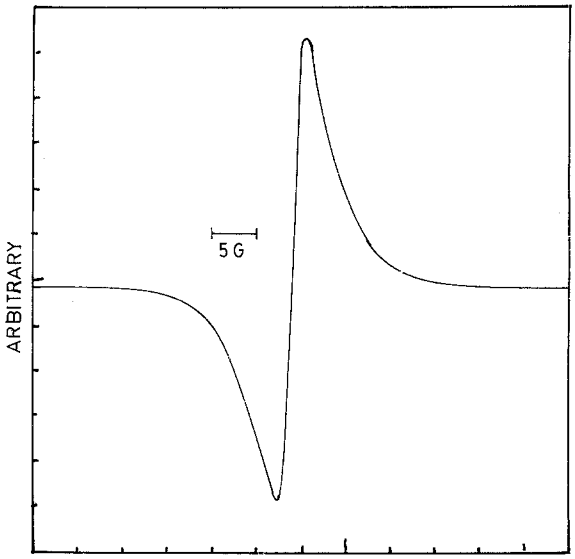

Figure 6 A typical ESR spectrum recorded for PPAN.

3.4. ESR measurements

The ESR spectra were recorded at four recording temperatures (above room temperature) at an interval of 50 K for three different PPAN samples. A typical ESR spectrum for PPAN is shown in Fig. 6 which is a single component, narrow and symmetric one. It is interesting to note (as expected) that as-deposited PPAN shows a very intense ESR peak due to the large amount of free spins produced during plasma deposition.

Figs 7, 8 and 9 show the variation of the g factor, linewidth (ΔH_{pp}) and relative peak–peak height of ESR signal respectively. It is seen in Fig. 7 that g factor has increased from 2.0026 to 2.0037 with pyrolysis temperature. This change could be due to the formation of more single and multiple carbon and/or nitrile dangling bonds owing to the loss of hydrogen or nitrogen from the PPAN structure during pyrolysis. The g values for the pyrolysed (at about 773 K) sample, around 2.0035, are consistent with these reported by Wnek *et al.* [18] for a delocalized π-electron system in pyrolysed PAN. The variation in g factor with respect to the recording temperature within the experimental accuracy is not significant.

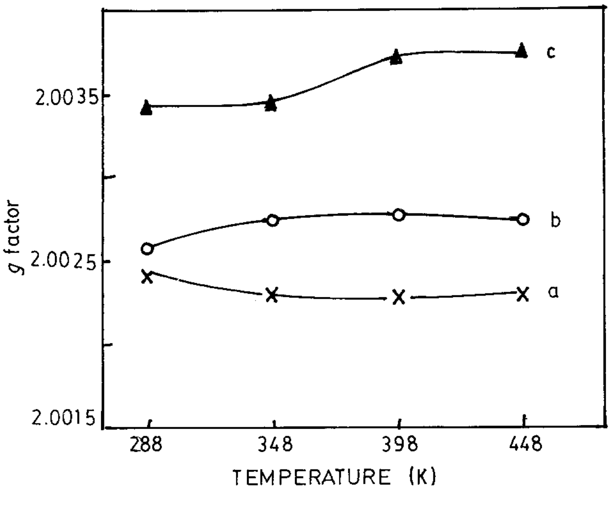

Figure 7 Variation of g factor with recording temperature. Sample specifications are as in Fig. 4.

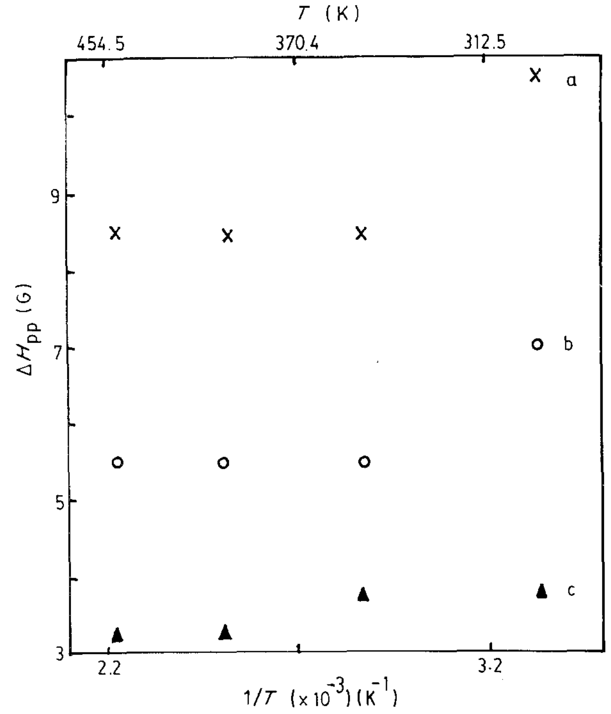

Figure 8 Variation of ΔH_{pp} with recording temperature. Sample specifications are as in Fig. 4.

ΔH_{pp} decreased with the increase of pyrolysis temperature, as is evidenced from Fig. 8. The variation in the ΔH_{pp} value for every sample has the same trend on going from room temperature towards 448 K. The narrowing of ΔH_{pp} with the increase of pyrolysis temperature could be due to the formation of more free radicals or unpaired electron and hence possibly increased interaction between dangling bonds. This is also indicative of delocalization of the carriers and suggests the formation of the conjugated double bonds [19, 20], such as, C=C and/or C=N within the PPAN structure. The IR analysis also confirms the fact.

The relative ESR peak-peak height was measured for individual samples. This reflects the nature of the variation of spin density with the recording temperature for each sample. In fact, all the samples showed a similar trend. This nature of change could be due to thermally released carriers from traps. Thus, these carriers take part in the hopping conduction in PPAN.

4. Conclusions

It is observed that different analytical methods used for identifying the changes taking place in PPAN reveal some common features. From DTA and TGA it was found that major structural change occur around 550 K. IR spectra recorded for PPAN, pyrolysed above that temperature, indicate the presence of a conjugated structure. The electrical resistivity and optical band gap show a drastic decrease as a result of these structural changes. The formation of conjugated bonds in PPAN due to pyrolysis is evidenced by the decrease in the linewidth of ESR signal and increase in its *g* factor. It is interesting to note that the electrical conduction in PPAN and pyrolysed PPAN is dominated by the hopping mechanism resulting from the thermally activated charge carriers having low mobility. The spin density variation in the ESR measurements may also be correlated to the same effect. The thermoelectric data agrees wth the above fact.

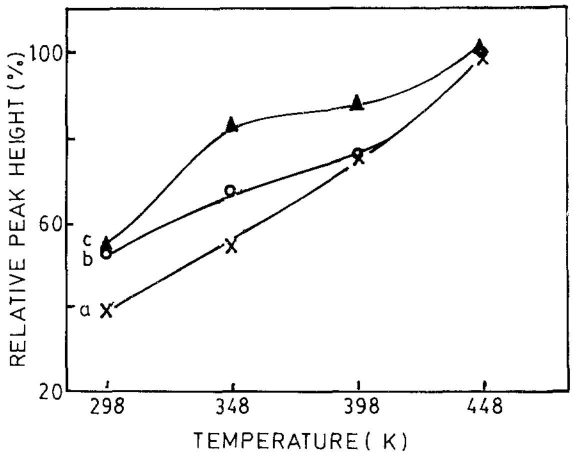

Figure 9 Relative peak-peak height of ESR signal as a function of recording temperature. Sample specifications are as in Fig. 4.

References

1. R. WATANABE, T. NAKANO, T. SATOH, H. HATOH and Y. OHKI, *Jpn J. Appl. Phys.* **26** (1987) 373.
2. K. HARADA, *J. Appl. Polym. Sci.* **26** (1981) 3707.
3. H. YASUDA, *J. Polym. Sci., Polym. Chem. Edn* **19** (1981) 199.
4. P. W. ROSE and E. M. LISTON, *Plast. Engng* **41** (1985) 41.
5. H. YASUDA, H. C. MARSH, E. S. BRANDT and C. N. REILLEY, *J. Polym. Sci., Polym. Chem. Edn* **15** (1977) 991.
6. T. J. HOOK, J. A. GARDELLA Jr. and L. SALVATI Jr., *J. Mater. Res.* **2** (1987) 117.
7. A. H. BHUIYAN and S. V. BHORASKAR, *Thin Solid Films* **162** (1988) 333.
8. W. D. BRENNAN, J. J. BROPHY and H. SCHONHORN in "Organic semiconductors" edited by J. J. Brophy and J. J. Buttrey (Macmillan, New York, 1962) p. 159.
9. T.-C. CHUNG, Y. SCHLESINGER, S. ETEMAD, A. G. MACDIARMID and A. J. HEEGER, *J. Polym. Sci., Polym. Phys. Edn* **22** (1984) 1239.
10. A. BRADLEY, *J. Electrochem. Soc.* **119** (1972) 1153.
11. S. I. IVANOV, *Eur. Polym. J.* **20** (1984) 415.
12. A. J. CLARK and J. E. BAILEY, *Nature* **243** (1973) 146.
13. A. V. TOPCHIEV, *J. Polym. Sci.* **A-1** (1963) 591.
14. A. K. JONSCHER, *J. Vac. Sci. Technol.* **8** (1971) 135.
15. N. F. MOTT, *Phil. Mag.* **19** (1969) 835.
16. I. WATANABE and T. SEKIYA, *Jpn J. Appl. Phys.* **26** (1987) 633.
17. M. S. PATIL, *J. Macromol. Sci., Phys.* **B26** (1987) 97.
18. G. E. WNEK, B. WARSENMAN, I.-H. LOH, in the Proceedings of the Symposium on "Ion implantation and ion beam processing of materials", Boston, 1983, p. 435.
19. S. ONISHI, Y. IKEDA, S. SUGIMOTO and I. NITTA, *J. Polym. Sci.* **47** (1960) 503.
20. M. S. DRESSELHAUS, B. WASSERMAN and G. E. WNEK, in the Proceedings of the Symposium" Ion implantation and ion beam processing of materials", Boston, 1983, p. 430.

Received 26 May
and accepted 11 October 1988