Investigations on the electrical and structural properties of polyaniline doped with camphor sulphonic acid

S. Saravanan[a],[*],[1], C. Joseph Mathai[a], M.R. Anantharaman[a],[*],
S. Venkatachalam[b], P.V. Prabhakaran[b]

[a]*Department of Physics, Cochin University of Science and Technology, Cochin, 682 022, India*
[b]*PCM, Vikram Sarabhai Space Centre, Trivandrum, 695 022, India*

Abstract

Polyaniline is chemically synthesised and doped with camphor sulphonic acid. FTIR studies carried out on these samples indicate that the aromatic rings are retained after polymerisation. The percentage of crystallinity for polyaniline doped with camphor sulphonic acid has been estimated from the X-ray diffraction studies and is around 56% with respect to polyaniline emeraldine base. The change in dielectric permittivity with respect to temperature and frequency is explained on the basis of interfacial polarisation. AC conductivity is evaluated from the observed dielectric permittivity. The values of AC and DC conductivity and activation energy are calculated. The activation energy values suggested that the hopping conduction is the prominent conduction mechanism in this system.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Polymers; C. X-ray diffraction; D. Dielectric properties; D. Electrical conductivity

1. Introduction

Ever since the discovery of polyacetylene, the field of conducting polymers became an attractive research topic for chemists, physicists and electrical engineers alike [1]. In recent years much of the attention is devoted to the study of the semiconducting properties of these polymers. Among the various conducting polymers, polyaniline, polypyrrole and polythiophene need special mention owing to their potential applications [2–7] and interesting properties. In that polyaniline is unique because the electrical properties vary with respect to their oxidation states of the main chain and protonation.

The wide range of electrical, electrochemical and optical properties of polyaniline along with its excellent stability makes it a useful electronic material for various applications. Some of the potential devices based on polyaniline are organic light emitting diodes [8], low power rechargeable plastic batteries, gas sensors, super capacitors, photovoltaic cells [9], liquid crystal displays [10,11] and Schottky devices [12–14]. Bulk polyaniline in its pure form is an insulator, but adding dopants like camphor sulphonic acid (CSA), methane sulphonic acid and hydrochloric acid can enhance the electrical conductivity by many orders [15]. The enhancement of the conductivity in these materials is either by the generation of extended states in doped molecules or by charged defects with electronic structures [16]. Incorporation of dopants also modifies the structural properties of polyaniline. This modification plays an important role in enhancing the conductivity of the polymer. Among the various dopants, CSA doped polyaniline has got special significance because it has soluble solvents like cresol that can be cast into conducting polyaniline films [17]. Also sulphonic acid units may interact with amine/imine hydrogens, which enhances the electrical properties of polymers.

The present paper deals with the preparation as well as evaluation of structural and electrical properties of pure polyaniline (emeraldine base) and polyaniline doped with CSA.

*Corresponding authors.

E-mail addresses: shrisharavanan@yahoo.co.uk (S. Saravanan), mra@cusat.ac.in (M.R. Anantharaman).

[1]Present address: Department of Metallurgy, Indian Institute of Science, Bangalore 560 012.

2. Experimental

2.1. Sample preparation

Polyaniline is prepared by the direct oxidation of aniline using an ammonium persulphate as chemical oxidant as per the method reported elsewhere [18,19]. Monomer aniline and aqueous percholoric acid is kept at around 4 °C and to this ammonium per sulphate was added drop by drop. This mixture was stirred continuously for 2 h. Further, this product was filtered and washed with water and then with methanol. Subsequently, polyaniline doped with percholorate was converted to insulating polyaniline emeraldine base, referred to as PANIEB, using hydrazine hydrate. This PANIEB is doped with CSA by mixing CSA and emeraldine base in the molar ratio of 0.5 CSA to the polymer repeat unit in nitrogen atmosphere as per the procedure reported [18,19]. This powder is then purified and dried in vacuum oven. The final product is referred to as PANICSA.

2.2. Characterisation

XRD scans for polyaniline emeraldine base (PANIEB) and polyaniline doped with CSA (PANICSA) were recorded using a Rigaku D Max C, X-ray diffractometer with Cu Kα_1 radiation ($\lambda = 1.5415$ Å). The samples were scanned at the rate of 1° per minute in the reflection mode over a range of 2θ from 5° to 35°. Morphological studies were carried out on PANIEB and PANICSA by using a JEOL Scanning Electron Microscope. FTIR spectra of the samples in transmission mode were recorded by using Nicolet 510P FTIR spectrometer.

The powdered polyaniline doped CSA samples were pressed into the form of pellets with a diameter of ~10 mm. The dielectric permittivity studies were carried out on these samples by using a home made four probe dielectric cell and an HP 4285A LCR meter in the frequency range 100 KHz to 2 MHz and in the temperature range of 300–373 K under an dynamic vacuum (10^{-2} Torr). The dielectric measurements were fully automated with the help of LabVIEW software package. The dielectric Permittivity of samples were calculated by employing the relation [20]

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \qquad (1)$$

where A is the surface area of the sample, d the thickness of the sample, ε_r the dielectric permittivity of the sample, ε_o the dielectric permittivity of air and C is the measured capacitance of the sample. The AC conductivity was calculated by using the measured values of dielectric permittivity and the dielectric loss factor.

A four-probe electrical contact arrangement coupled with Keithley picoammeter and a homemade cell was employed for evaluating the DC conductivity of these samples.

3. Results and discussion

3.1. XRD analysis

The X-ray diffractograms obtained for PANIEB and PANICSA are shown in Fig. 1. It has been reported that the crystallinity of the polyaniline sample depends on the conditions set during the synthesis of the polymer [21]. The XRD pattern of synthesised polyaniline emeraldine base with single broad peak indicates that the synthesised PANIEB is amorphous. The reported value for this amorphous peak is at $2\theta = 19.50°$ [22]. In the case of polyaniline doped with CSA, broad and weak diffraction appeared at $2\theta \approx 13.90°$, $17.55°$ and $24.88°$. The peaks observed are an indication that doping induces a short-range ordering in the samples. However, the appearance of an appreciably sharp crystalline peak at $2\theta = 15.40°$ for CSA doped PANI and a weak crystalline peak at $2\theta = 24.88°$ may be due to the change in the crystalline form of the sample.

From the X-ray diffractogram, (intensity versus 2θ) the crystallinity index of the sample was calculated by employing a formula put forwarded by Manjunath et al. [22]. According to this, the resolution of the peak R, for X-ray spectrum with heights h_1 and h_2 and minima m_1 is given by

$$R = \frac{2m_1}{h_1 + h_2}. \qquad (2)$$

In the case of polymers, where there are more than two peaks as in polyaniline, all the peaks and the minima
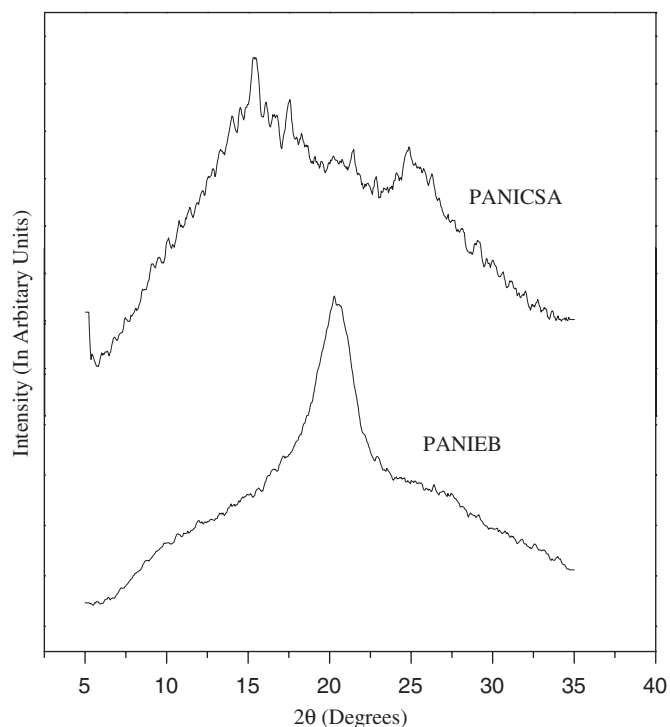

Fig. 1. XRD scans of powder PANIEB and PANICSA.

between them are measured. Thus for any polymer [22],

$$R = \frac{m_1 + 2m_2 + \cdots + m_{n-1}}{h_1 + h_2 + \cdots + h_n}, \qquad (3)$$

where m_1, m_2... are the heights of minima between two peaks and h_1, h_2... are the heights of peaks from the base line.

Fig. 1 indicates the crystalline peaks of PANICSA. Hence for calculating percentage of crystallinity appreciably sharp peaks of PANICSA at $13.90°$, $17.55°$ and $24.88°$ were considered. Hence the general formula in Eq. (3) can be reduced for three peaks as

$$R = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3}. \qquad (4)$$

Then $(1-R)$ gives the lateral order or the index of crystallinity. The percentage of crystallinity has been estimated by employing relation (4) and it has been found to be 56%.

In order to confirm the crystallinity of polyaniline doped with CSA, the SEM of polyaniline emeraldine base and polyaniline doped with CSA has been carried out and is shown in Fig. 2(a) and (b). In PANIEB, the particles are seen agglomerated without much interparticle spacing. The grain size is $\sim 0.6 \mu m$. However, in PANICSA the particles can be seen distinctively. The grain size is $\sim 0.8 \mu m$. From SEM and XRD studies, it can be concluded that polyaniline doped with CSA is more crystalline than that of polyaniline emeraldine base.

3.2. FTIR studies

Fig. 3 shows the FTIR spectrum polyaniline emeraldine base and polyaniline doped with CSA.

In the PANICSA Spectrum the peaks at 1475, 1558 cm^{-1} indicate that the aromatic ring is retained in the polymer. It also exhibits two distinct peaks at 2926 and 2960 cm^{-1}, these peaks are assigned to the C–H stretching. The peak at 3432 cm^{-1} shows the stretching of NH group. The peak at 1286 cm^{-1} corresponds to the C–H in plane of deformation [23]. Also the peaks at 792, 1042 cm^{-1} correspond to the sulphonic acid group. The existence of a peak at 1738 cm^{-1} shows that the ketone group [24] is intact. However, in the FTIR spectrum of PANIEB, there are no peaks corresponding to sulphonic acid group and ketone group. This means that the monomer aniline became polymerised and the sulphonic acid group is attached to the NH group. Based on FTIR spectra a plausible structure of PANICSA is as shown in Fig. 4.

3.3. Dielectric and AC conductivity studies

The variation of dielectric permittivity with temperature and frequency is shown in Figs. 5 and 6. The value of dielectric permittivity varies from 73 to 136 and is dependency on temperature as well as on frequency. From Figs. 5 and 6, it is seen that in the low temperature regime
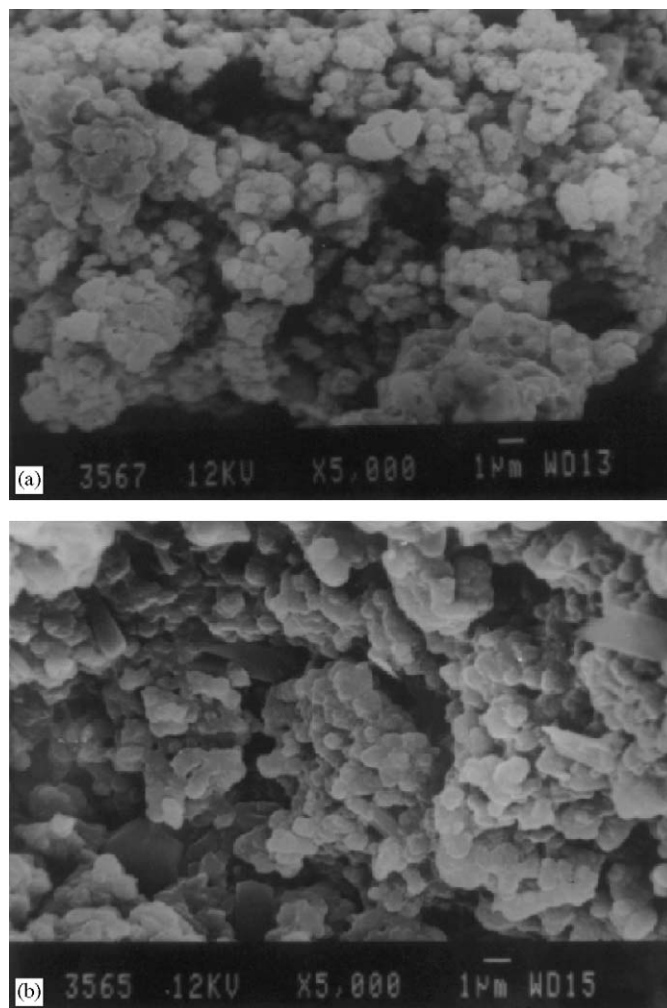

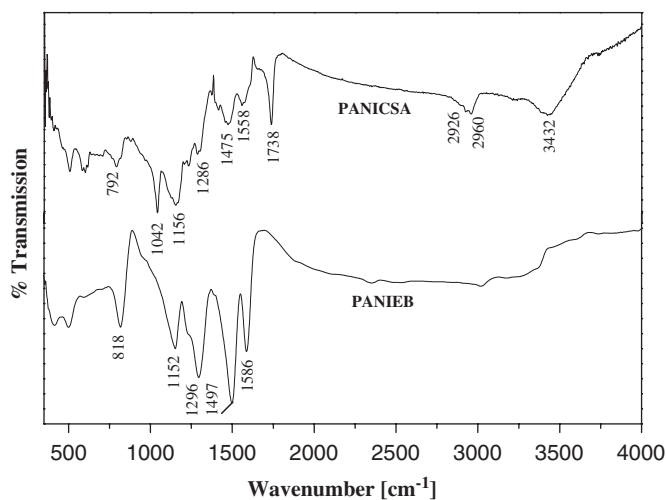Fig. 2. (a) SEM photographs of PANIEB, (b) SEM photographs of PANICSA.

Fig. 3. FTIR spectrums of PANIEB and PANICSA.

the change in dielectric permittivity is small but it rises thereafter. Also the increase is rapid at higher temperatures. The increment of dielectric permittivity is rapid
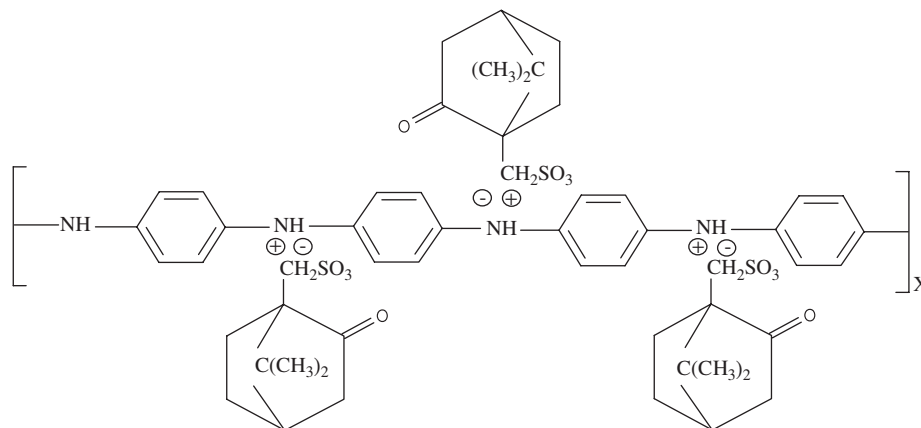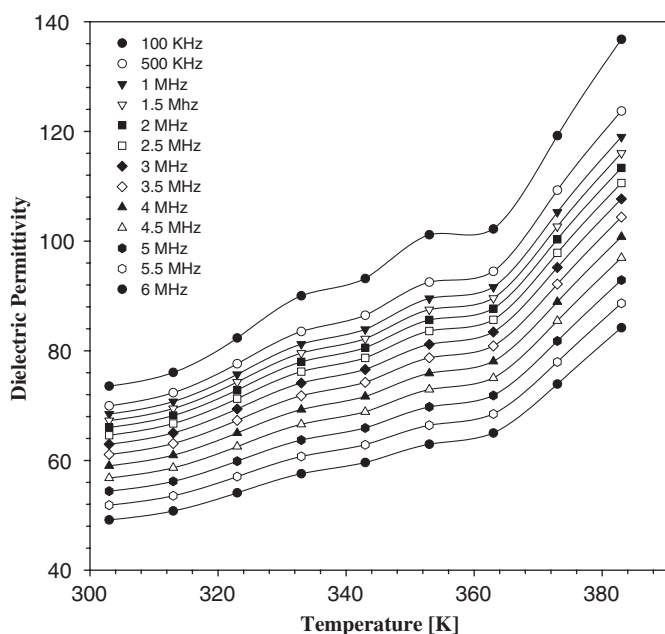
Fig. 4. Structure of PANICSA.

Fig. 5. Variation of dielectric permittivity with temperature.

Fig. 6. Variation of dielectric permittivity with frequency.

above 360 K. The increase of dielectric permittivity with temperature could be related to the well-known phenomenon that the polarisation increases with temperature, which was found to be valid in a wide range of materials [25]. This is due to the effect of interfacial polarisation caused by space charges and microscopic field distortion [26]. If the applied field is increased the probability of tunneling of electrons between molecules is also increased which cause high dielectric permittivity and dielectric loss.

The variation of AC conductivity with frequency for different temperatures is shown in Fig. 7. When frequency increases the AC conductivity also increases with temperature. The variation of σ_{AC} is small at lower temperatures and shows rapid change at higher temperatures. σ_{AC} can be interpreted with the help of the following equation [27]:
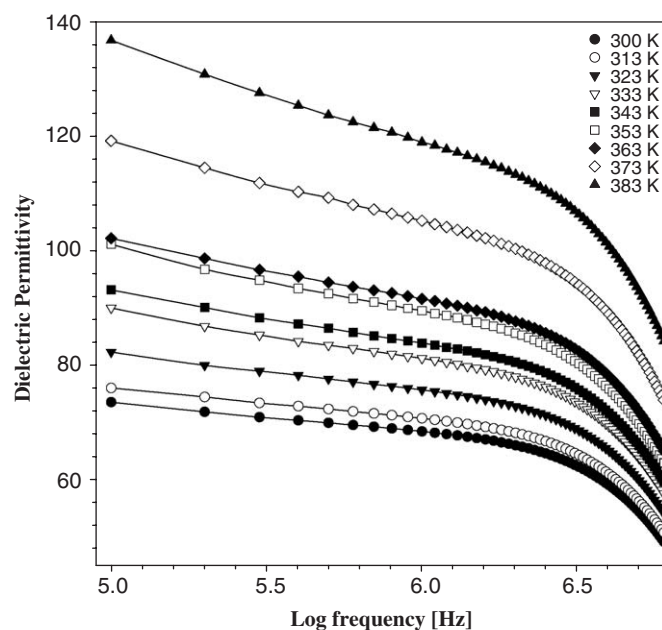
$$\sigma_{AC} \propto \omega^n, \tag{5}$$

where ω is the angular frequency and n is the index which is characteristic of the type of conduction mechanism/relaxation mechanism dominant in amorphous materials. The value of n evaluated from Fig. 7 is around 0.045 both at lower and higher temperatures. Fig. 8 shows the characteristic dependence of the ac conductivity with temperature at different frequencies. The activation energy calculated from these plots is 0.069 eV. The activation energy required for hopping process for materials with higher dielectric permittivity is assumed to be quite low. Also because of this low activation energy, a weak temperature dependence of electrical conductivity is expected to appear around room temperature [28].

3.4. DC conductivity studies

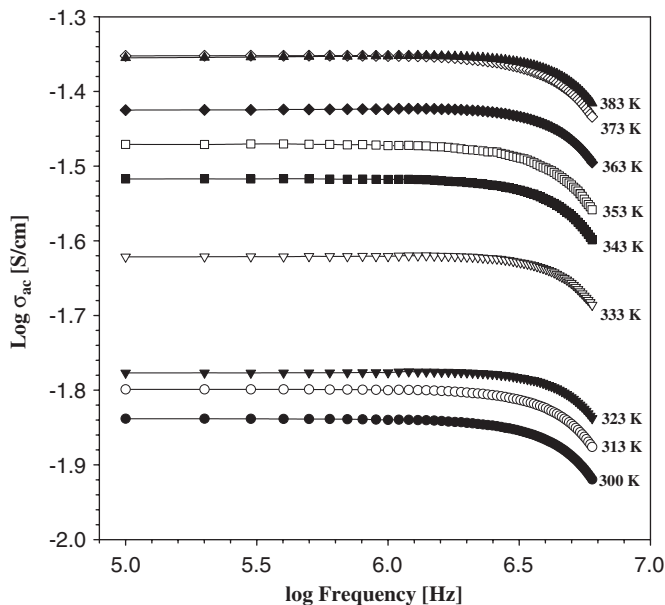The current–voltage measurements were carried out to investigate the electrical properties of these samples. These

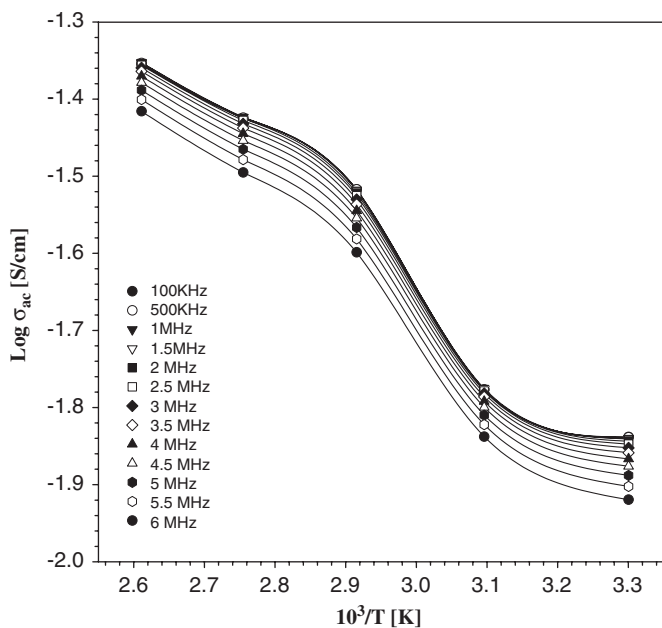Fig. 7. AC conductivity of PANICSA as a function of frequency.

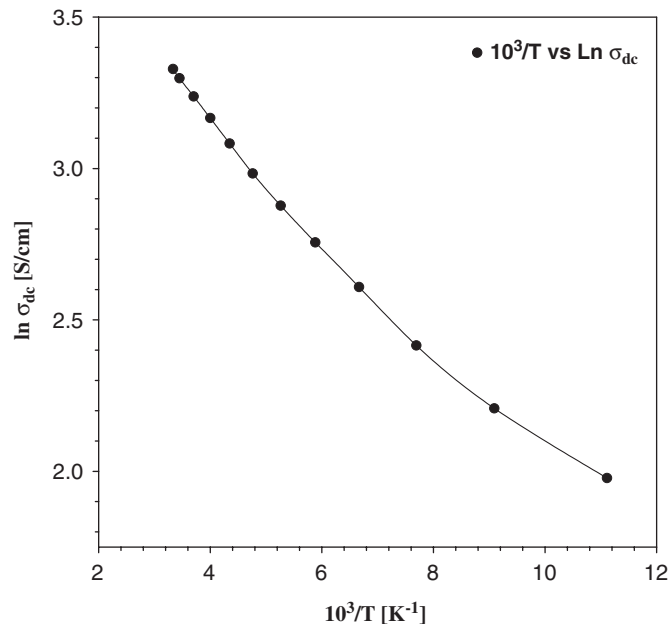Fig. 8. AC conductivity of PANICSA as a function of temperatures.

Fig. 9. DC conductivity of PANICSA as a function of temperature.

activation energy is calculated by employing the following relation:

$$\sigma_{DC} = \sigma_o \exp\left(-\frac{E_A}{K_B T}\right), \tag{6}$$

where σ_o is constant, E_A is the activation energy and K_B is the Boltzmann constant. The activation energy calculated is around 0.015 eV. The disagreement between the activation energy value of σ_{AC} and σ_{DC} suggests that the hopping conduction mechanism plays an important role for the conduction process [29].

4. Conclusion

Emeraldine base polyaniline and polyaniline doped with CSA are synthesised. These samples are characterised by FTIR and is seen that the sulphonic acid group is attached to the polyaniline chain without altering the aromatic ring. X-ray diffraction studies indicate that the doping of polyaniline with CSA modifies the structure. The percentage of crystallinity of PANICSA was calculated and found to be 56%. This is in conformity with the findings of particle size of PANICSA and PANIEB by using electron micrography studies. The dielectric properties of PANICSA are explained on the basis of interfacial polarisation. The dependence of conductivity on frequency and the low activation energies of the carriers are indicative of a hopping conduction mechanism in PANICSA.

sample shows an ohmic behaviour without any breakdown. The variation of DC conductivity with temperature is plotted and is shown in Fig. 9. The conductivity value of PANICSA calculated at room temperature is around 27 S/cm. The temperature dependence of DC conductivity indicates that the observed metallic DC conductivity is due to only a small fraction of delocalised carriers, which are primarily present in metallic islands and that the achievable conductivity for such systems when the entire charge carriers density participates is very high [6]. It has also been shown that the relaxation of the charge carrier system is attributed to the charge hopping of mobile carriers, which can lead to both short-range σ_{AC} and long-range σ_{DC}. The

References

[1] W.R. Salaneck, D.T. Clark, E.J. Samuelson (Eds.), Science and Applications of Conducting Polymers, Hilger, Bristol, 1991.

[2] A. Bohler, S. Dirr, H.H. Johannes, D. Ammermann, W. Kowalsky, Synth. Met. 91 (1997) 95.

[3] G. Yu, Synth. Met. 80 (1996) 143.

[4] R. Zhang, H. Zheng, J. Shen, Synth. Met. 106 (1999) 157.

[5] Y.O. Yakovlev, V.F. Zolin, Synth. Met. 91 (1997) 205.

[6] A.G. MacDiarmid, Synth. Met. 84 (1997) 27.

[7] F. Garten, J. Vrijmoeth, A.R. Schlatmann, R.E. Gill, T.M. Klapwijk, G. Hadziioannou, Synth. Met. 76 (1996) 85.

[8] H.L. Wang, A.G. MacDiarmid, Y.Z. Wang, D.D. Gebler, A.J. Epstein, Synth. Met. 78 (1996) 33.

[9] L. Ding, M. Jonforsen, L.S. Roman, M.R. Andersson, O. Inganas, Synth. Met. 110 (2000) 133.

[10] S.A. Jenekhe, K.J. Wynne (Eds.), Photonic and Optoelectronic Polymers, ACS Symposium Series, vol. 672, American Chemical Society, Washington, DC, 1997, p. 395.

[11] A.G. MacDiarmid, Photonic and optoelectronic polymers, Naval Research Reviews, Office of Naval research, Two/1997, vol. XLIX, pp. 6–11.

[12] S.S. Pandey, M.K. Ram, V.K. Srivastava, B.D. Malhotra, J. Appl. Polym. Sci. 65 (1997) 2745.

[13] S.S. Pandey, C.K. Misra, S. Chandra, B.D. Malhotra, J. Appl. Polym. Sci. 44 (1992) 911.

[14] H.K. Chandhari, D.S. Kelkar, J. Appl. Polym. Sci. 61 (1996) 561.

[15] M. Vijayan, D.C. Trivedi, Synth. Met. 107 (1999) 57.

[16] R.F. Bianchi, G.F. Leal Ferreira, C.M. Lepienski, R.M. Faria, J. Chem. Phys. 110 (9) (1999) 4602.

[17] B.C. Roy, M.D. Gupta, L. Bhowmick, J.K. Ray, J. Appl. Polym. Sci. 86 (11) (2002) 2662.

[18] S. Venkatachalam, P.V. Prabhakaran, Synth. Met. 97 (1998) 141.

[19] W.S. Huang, B.D. Humphery, A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 82 (1986) 2385.

[20] S. Saravanan, C. Joseph Mathai, M.R. Anatharaman, S. Venketachalam, P.V. Prabhakaran, J. Appl. Polym. Sci. 91 (2004) 2529.

[21] F.S. Wang, J.S. Tang, L. Wang, H.F. Zhang, Z. Mo, Mol. Cryst. Liq. Cryst. 160 (1988) 175.

[22] B.R. Manjunath, A. Venkataraman, T. Stephen, J. Appl. Polym. Sci. 17 (1973) 1091.

[23] X.-R. Zeng, T.-M. Ko, J. Polym. Sci. Part B, Poly. Phy. 35 (1997) 1993.

[24] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, Vogel's Text Book Of Practical Organic Chemistry, Fifth ed., Addison Wesley, London, 1998, p. 1412.

[25] A.J. Riad, M.T. Korayem, T.G. Abdul Malik, Physica B 270 (1999) 140.

[26] S. Jayalekshmi, M.G. KrishnaPillai, Thin Solid Films 122 (1984) 197.

[27] C. Joseph Mathai, S. Saravanan, M.R. Anantharaman, S. Venkatachalam, S. Jayalekshmi, J. Phys. D 35 (2002) 240.

[28] K. Morii, H. Kawano, I. Fujii, T. Matsni, Y. Nakayam, J. Appl. Phys. 78 (1995) 3.

[29] M.G. Han, S.S. Im, J. Appln. Polym. Sci. 82 (2001) 2760.