

M. NAVEEN KUMAR, M. NAGABHOOSHANAM, M. ANAND RAO*,
M. BHAGVANTH RAO

College of technology, Osmania University, Hyderabad, India.

*Department of Chemistry, Osmania University, Hyderabad, India.

Preparation and Characterization of Doped Polybenzidine

The polybenzidine has been synthesized by thermal method and characterized by X-ray diffraction and infrared absorption studies. Further, polybenzidine has been doped with nitrate, sulfate and acetate ions. The electrical conductivity behavior of doped and undoped polybenzidine has been studied for various concentrations of dopants between room temperature and 200°C. All these polymers were found to behave like semiconductors. The activation energies of all the samples within the semiconducting region are estimated and analysed with the variation in dopant concentration. The results are explained with the effective charge formation due to ion pair association.

Keywords: Polybenzidine, dopants, semiconductors

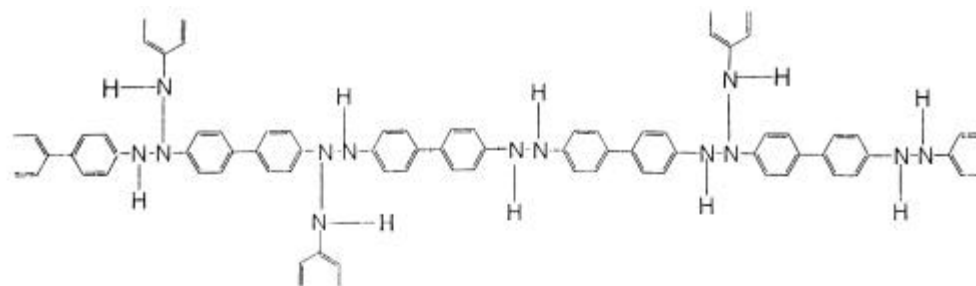
(Received October 23, 2000; Accepted February 28, 2001)

1. Introduction

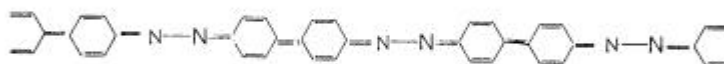
Most of the electronic devices made out of conventional semiconductors suffer with mechanical limitations i.e., due to brittleness of the material used for their fabrication. As a result devices like solar cells, with their optimum shape and size, cannot be arranged effectively on typical curved roofs. Though the semiconducting thin films are developed as an alternate to these materials, they to are governed by the elastic properties of the substrates. Subsequently, few semiconducting polymers like polypyrrole, polythiophene and polyaniline (FROMMER, KANAZAWA) have been discovered. Semiconducting polymers may also have other properties such as electroactivity and non linear optical properties (PRASAD). But when such a polymer is put into application the stability becomes an important parameter. It has been observed that most of the conducting polymers are unstable except those containing hetero atoms like N or S atoms in polymer backbone such as polypyrrole, polythiophene and polyaniline. Polyaniline has attracted considerable attention because of its unique electrical and optical properties, structural transformation by oxidation and protonation and good stability in atmosphere. Extensive studies have been carried out on chemically and electrochemically synthesized polyaniline, owing to the potential significance of the technological applications (MAC DIARMID, CHIANG, SALANECK, HUANG, FENIES, GUPTA, NEOH). In polyaniline it has been shown that electrical conductivity is a strong function of doping (MAC DIARMID) and very less carrier mobility when compared to conventional semiconductors. Therefore, search is continued to find out various aromatic amines other than aniline as monomers whose electrical behaviour is very sensitive to temperature, pressure and solvent used during the synthesis.

So far the synthesis of most of the polyanilines and aromatic amines were carried out in the acid medium and the protonated polymers were then neutralized (BHARADWAJ). In out

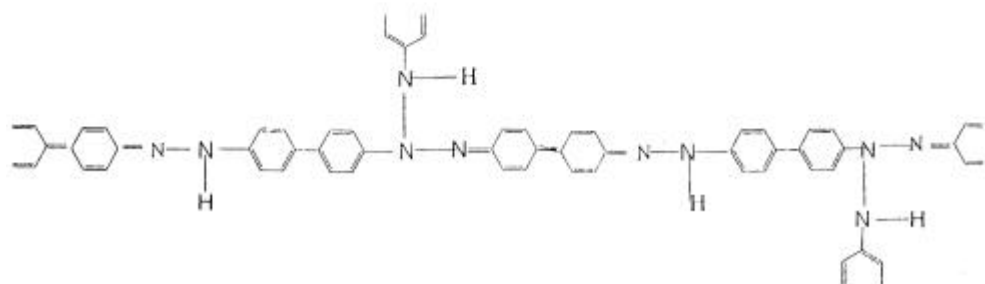
present study, unlike the conventional methods (synthesizing aromatic amines in acid medium and neutralizing the protonated polymers), the polybenzidine has been synthesized in an organic medium. The neutral polymer, thus obtained, is then doped using various mineral acids to see the effect of doping on the electrical conductivity. The effect of dopant concentration on the semiconducting behavior of polybenzidine is also carried out in order to optimize the concentration level by estimating the energy gap.



Amine - amine linkage



Imine - imine linkage



Amine - imine linkage

Chart 1

2. Experimental

2.1 Synthesis and doping

In 100ml of acetonitrile (E. MERCK, India), 1.84 gms(0.1M) of high pure benzidine (LANCASTER, England) and 0.46gms (0.02M) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (SIGMA, USA) in 3ml of

water are added with constant stirring at 5°C. Within few minutes, a blue colored precipitate is obtained and the stirring is continued for another 12 hours. Then the solution is filtered, and the precipitate is washed with acetonitrile and soxhletted with acetonitrile for 24 hours. The neutral form of polybenzidine obtained is dried at room temperature.

Polybenzidine is doped with 1M HNO₃ by adding 1gm of polybenzidine in 100ml of 1M HNO₃ and stirred overnight at room temperature. Doped polymer was filtered under suction and washed with 100ml of 1M HNO₃, and then with 100ml of water. The final polymer product is dried at room temperature. A similar procedure was adopted to dope polybenzidine with different acids (H₂SO₄ and CH₃COOH) of different concentrations ranging from 0.1 to 1M.

2.2 Characterization

An XD-610 Shimadzu diffractometer was used to obtain the X-ray diffractogram of benzidine and polynbenzidine powders in order to test the polymerization of benzidine. Infrared spectrum of polybenzidine was also taken using Perkin-Elmer Infracord 337 spectrophotometer so as to confirm the polymerization.

Doped polybenzidine is powdered and then it is cold pressed under a die into pellets of 15mm diameter and 1mm thickness (approximately) by applying a load of 5 tones.

Conductivity of all the undoped and doped polymers was measured by two-robe technique at various temperatures ranging from room temperature to 200°C. A constant current of 100mA was passed through the sample and the voltage was measured with 182-Keithley nano voltmeter.

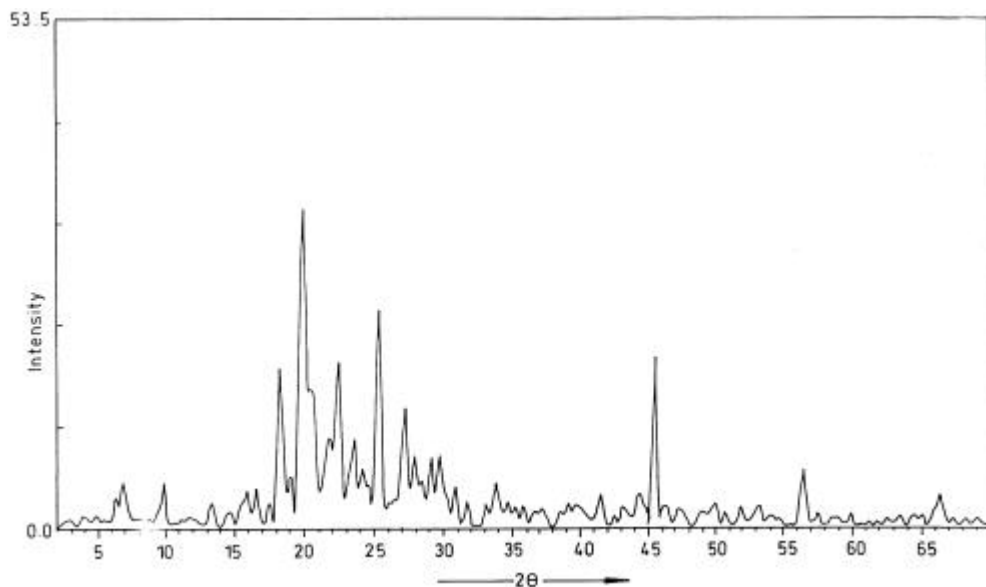


Fig. 1: X-ray diffractogram of benzidine.

3. Results & Discussion

To understand the crystallinity of benzidine and polybenzidine, X-ray diffractograms of these compounds are taken and are presented in Figs.1,2. These figures show clearly that

both benzidine and polybenzidine are polycrystalline in nature. The peak positions are indexed using the ASTM data of benzidine. The difference in the intensity of some peaks between benzidine and polybenzidine may be due to the difference in the alignment of hydrogen atoms to the nitrogen in the crystal lattice.

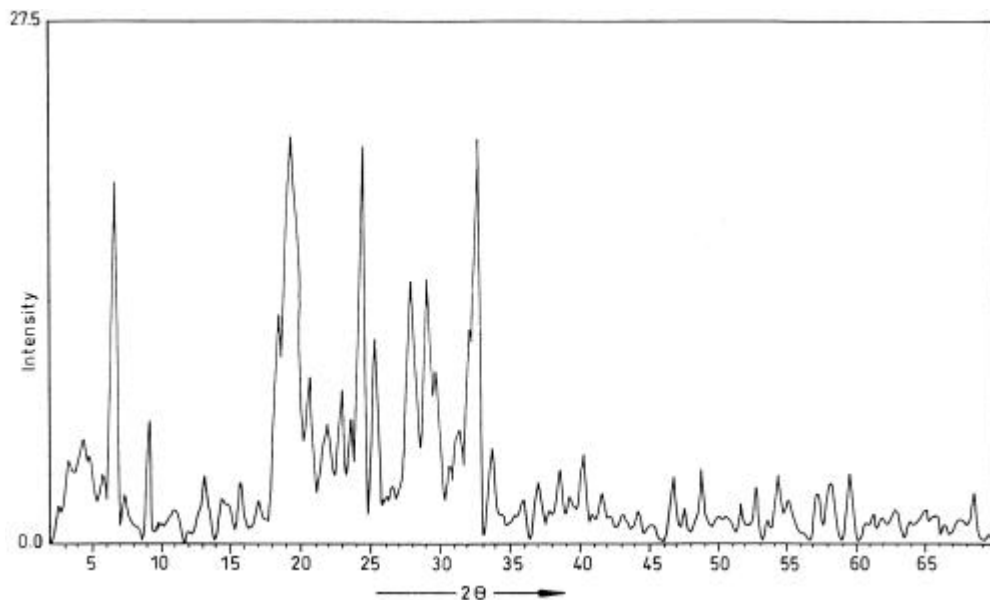


Fig. 2: X-ray diffractogram of polybenzidine.

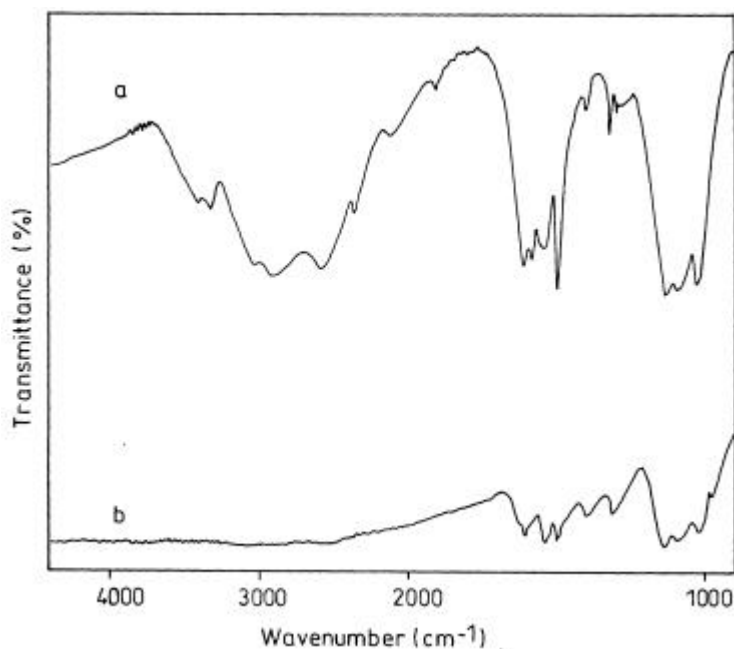


Fig. 3: IR spectra of benzidine and polybenzidine.

On polymerization, the monomers may be linked through nitrogen linkage. The nitrogen may be in amine (reduced), imine (oxidised) or combined amino-imine forms as shown in the chart-1. To understand this, a IR spectrum has been taken using Perkin-Elmer infracord 337 Spectrophotometer and the same is shown in Fig.3. From the figure we understand that N-H bending vibrations ($1613, 1531 \text{ cm}^{-1}$) are present whereas, H-H stretching are not observed. This indicates that the polymerization might have been taken place by forming branches in three dimensional network and the polymer contains nitrogen linkage in the form of either amino-amine or amino-imine. We could not examine the nitrogen linkages further by U.V.Spectrophotometer as the compound remained insoluble in the common organic solvents.

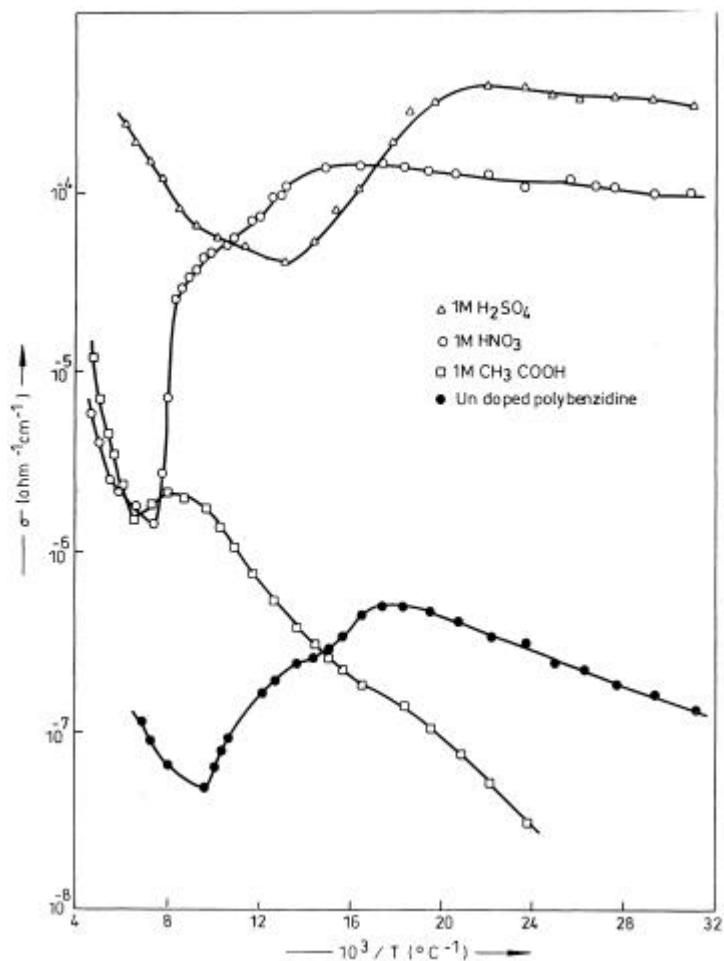


Fig. 4: Variation of electrical conductivity of undoped and doped polybenzidine with temperature ($\log \sigma$ vs $1/T$) with H_2SO_4 and HNO_3 and CH_3COOH of 1M concentration.

The polybenzidine is then protonated with H_2SO_4 , HNO_3 and CH_3COOH . After the protonation its color changed to deep brownish black. An XRD taken on doped polymer was found similar to the one obtained on undoped polybenzidine showing that the polycrystalline nature of polybenzidine is not affected with doping.

The electrical conductivity studies on undoped and doped polybenzidine with different acids of different concentrations have shown that the conductivity variation with temperature

of all doped and undoped polybenzidine has been similar in the sense that the conductivity increased initially with the temperature (a semiconducting behavior), then decreased (a metallic behavior) and later on it again increased (switching to semiconducting behavior). For the sake of graphical clarity, the electrical conductivity variation with temperature in undoped and doped polybenzidine with different acids of 1M concentration is only shown in Fig.4. It is also seen from Fig.4 that the conductivity in undoped polybenzidine is low and it is more by 10^3 times in polybenzidine doped with H_2SO_4 and HNO_3 . Further, the conductivity in polybenzidine doped with CH_3COOH is more only for 10^2 times that of undoped polybenzidine at higher temperature where as it is slightly less than that of undoped polybenzidine in the lower temperature.

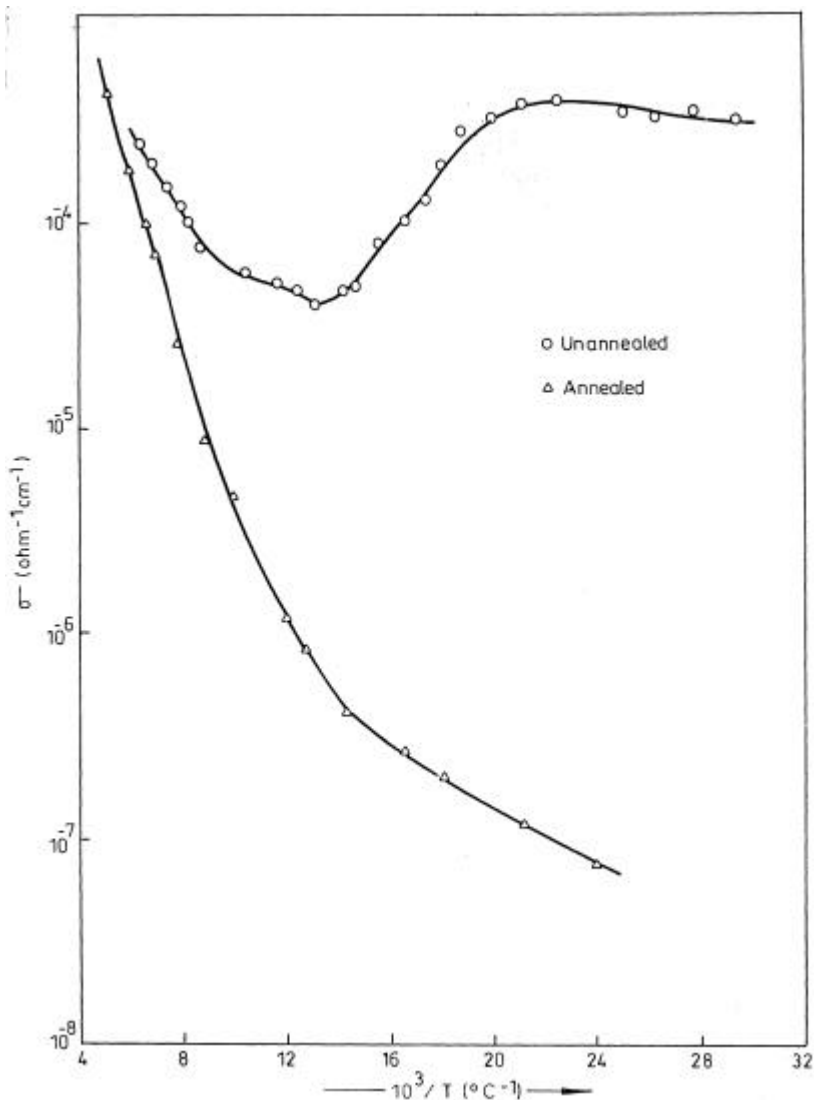


Fig. 5: Variation of electrical conductivity with temperature (log σ vs $1/T$) Of unannealed and annealed polybenzidine doped with H_2SO_4 of 1M concentration.

The polarons that are formed due to the dominant electrical carriers may be responsible for the electrical conductivity. Doping polybenzidine with H_2SO_4 and HNO_3 acids increases the concentration of polarons resulting in a widening of the bonding and antibonding levels into the band gap and hence it increases conductivity with doping. Whereas doing with CH_3COOH acid does not increase the gap as that of H_2SO_4 and HNO_3 . This may be because of its weak acidic nature. Instead CH_3COOH may require a minimum temperature beyond which it produces ion pairs in the matrix of polybenzidine and the gap becomes significant.

A similar behavior was also reported earlier in polybenzidine doped with 1M concentration of H_2SO_4 (RAWAT, KANSAYA, RAMA). A metallic behavior in the intermediate range of temperature may be due to the moisture content in the sample. This is confirmed by repeating the conductivity studies on sample annealed at an elevated temperature of 100°C for 5 hours in an inert atmosphere and then cooled slowly to room temperature. These studies on all the samples have clearly indicated a sign of elimination of moisture content by showing a gradual variation of conductivity with temperature (Fig.5). The studies made before and after annealing are referred as I and II cycles respectively. The activation energies of the charge carries in the semiconducting region for all the samples are calculated (for both the cycles) from the graphs and are given in Table.1. The variation of activation energy with the dopant concentration in unannealed samples doped with different acids is given in Fig.6. This figure shows that the activation energies in polybenzidine doped with strong acids H_2SO_4 and HNO_3 are almost same at the end concentration. Also the activation energy for both these samples is found to obtain a maximum at 0.5M concentration. Unlike the polybenzidine doped with H_2SO_4 and HNO_3 , the polybenzidine doped with weak acid (CH_3COOH) shows a large difference in activation energy at 0.1M and 1M concentrations and a minimum at 0.5M concentration.

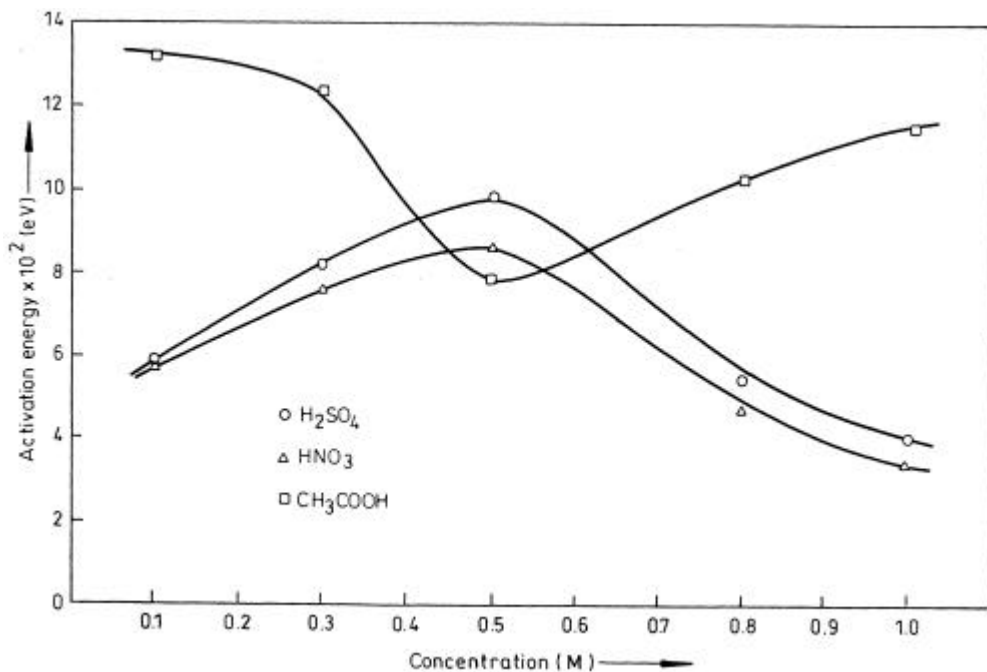


Fig. 6: The variation of activation energy with the concentration in unannealed samples doped with H_2SO_4 , HNO_3 , and CH_3COOH .

Table 1: The observed activation energies of the charge carriers in I and II cycle

| Concentration | Acitivation Energy [$\times 10^{-2}$ (eV)] | | | | | |
|---------------|---|----------|---------|----------|------------|----------|
| | H_2SO_4 | | HNO_3 | | CH_3COOH | |
| | Cycle I | Cycle II | Cycle I | Cycle II | Cycle I | Cycle II |
| 0.1M | 5.89 | 11.22 | 6.44 | 9.00 | 13.08 | 13.21 |
| 0.3M | 8.22 | 11.75 | 7.64 | 9.52 | 10.39 | 17.89 |
| 0.5M | 9.91 | 12.15 | 8.70 | 10.06 | 7.93 | 19.83 |
| 0.8M | 3.96 | 7.93 | 4.10 | 9.52 | 10.31 | 16.26 |
| 1.0M | 4.16 | 9.02 | 3.39 | 12.89 | 11.50 | 12.71 |

The variation of activation energy with the concentration in annealed sample (taken from cycle-II) for different dopants is shown in Fig.7. This figure shows that the difference in activation energy between samples doped with 0.1M concentration of CH_3COOH and other acids is remarkable, and more at 0.5M concentration and later the difference decreases while the concentration approaches to 1M. This may be explained interms of the nature of the strong mineral acids (H_2SO_4 and HNO_3) and weak organic acid (CH_3COOH) taken as dopants in the present study. Strong acids may develop higher activation energies at optimum concentration (0.5M) because of more effective charge formation due to ion-pair association. Whereas, weak acid may create low activation energy due to less effective charge formation at limiting concentration(i.e., 0.5M) of the dopant.

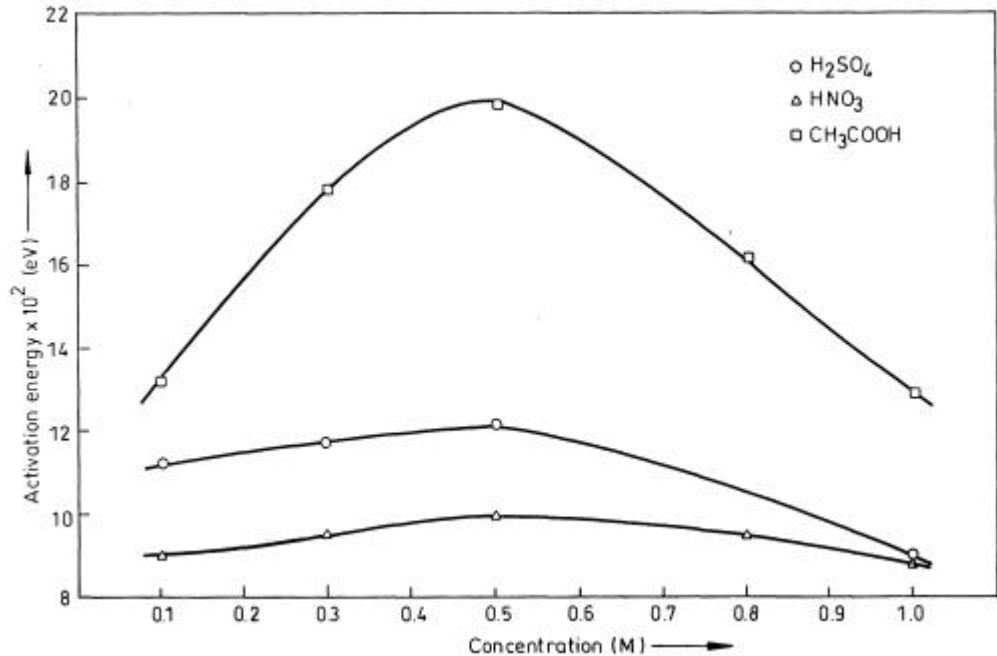


Fig. 7: The variation of activation energy with the concentration in doped and annealed samples.

Acknowledgment

Authors thank the University Grants Commission for granting funds to conduct the research work. One of the authors, M Naveenkumar is thankful to U.G.C, New Delhi for extending financial assistance during the work.

References

- BHARADWAJ, I S: Polymer science Resent advance, Vol.No.1., Allied publishers Lt., India. P 497-502(1994)
- CHIANG, J C, MAC DIARMID, A G: synth. Met. 13, 193 (1986)
- DIAZ, A F, RUGINSOON, J F, MARK, A B Jr.: In Olive G H, Olive S (eds) Springurlag Berlin (Advances in Polymer Science, pp 114)
- FROMMER, J E. CHANCE, R R: Encyclopedia of polymer science and Engineering 5,462 91986)
- FENIES, E M, SAYED, A F, TSINTAVIS, C: Mol. Cryst. Liq. Cryst. 121, 181 (1985)
- GUPTA, M C, UMARE, S: S Macromolecules 25,138 (1992)
- HUANG, W S, HUMPHREY, B C, MAC DIARMID, A G: J.Chem. Soc. Faraday Trans. 82.2385 (1986)
- KANAZAWA, K K, DIAZ, A F, GARDINI, G P, GILL, W D, GRANT, P M, KWAK, J F and STREET, G B: Synth.Met. 1,329 (1980)
- MAC DIARMID, A G, CHIANG, J C, RITCHER, A F, EPSTEIN, A: J Synth. Met. 18,285 (1987)
- MAC DIARMID, A G, RAY, A, ANGELOPOULOS, M : Synth. Met. 21,21 (1987)
- MACINNES, D Jr., FUNT, B L : Synth.Met. 25,235 (1988)
- NEOH, K G, TAN, K L, TAN, T C, KANG, E T: J. Macromol. Sci. 27(3), 347 (1990)
- PRASADA, P N, ULRICH, D R :Nonlinear Optical and Electroactive Polymers, Plenum Press, New York (1988)
- RAWAT, B, KANSARA, S S, RAMA, H S : Poly. International 26,233 (1991)
- SALANECK, W R, WU, C R, NILSSON, J : O Synth. Met. 21,57(1987)

Contact information:

Dr. M. ANAND RAO
Professor of Chemistry
Osmania University
Hyderabad - 500 007
India

e-mail : msj1952@yahoo.com