

Conducting Behaviour of Polyphenyl Amines Copolymer

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Abstract

Aniline has been copolymerized in the presence of substituted aniline as comonomer to prepare conducting copolymer of poly(aniline-co-o-methoxyaniline) type via the chemical oxidation polymerization route. The chemical structure and conducting behaviour are studied by means of Fourier transform infra-red (FTIR) spectroscopy and two-probe conductivity method. The conductivity of emeraldine salt form of poly(aniline-co-o-methoxyaniline) is $2.23 \times 10^{-4} \text{ S cm}^{-1}$ and energy band gap is 0.2185 eV.

Keywords: Polyaniline, Copolymer, Conductivity and FTIR

Introduction

In the recent years, conductive polymers have received considerable attention worldwide due to their novel electronic and electrical properties. These polymers have diverse applications ranging from energy storage, sensors, anticorrosive materials, electromagnetic interference shielding, electrostatics charge dissipation, organic light emitting diodes, plastic solar cells¹ and supporting material for catalysis². However, among other conducting polymers, polyaniline (PANI) has been extensively studied not only because its electronics conductivity can easily be tuned by adjusting the oxidation state and degree of doping of the backbone as but also due to its environmental stability as well as economic feasibility. Polyaniline is a promising material for various techno-commercial applications and hence the electrical properties, thermal and environmental stability of PANI is highly dependent on the nature and the size of its dopant.

The basic chain structure in PANI exists in three insulating states, Leucoemeraldine base (LB) Emeraldine base (EB) and Pernigraniline base. The general formula of PANI is $[(-\text{B}-\text{NH}-\text{B}-\text{NH}-)_Y (\text{B}-\text{N}=\text{Q}=\text{N})_{1-Y}]_X$ in which B and Q denote the C_6H_4 rings in the benzenoid and quinoid form respectively. The main issue with PANI is the processing difficulties due to its infusibility and relative insolubility in common solvent. It can be made processable/soluble either by polymerizing functionalised anilines³ or by copolymerizing aniline with substituted monomers⁴⁻⁵.

In the present study, the copolymerization of aniline in presence of o-methoxyaniline as comonomer to prepare conducting copolymer of poly(aniline-co-o-methoxyaniline) type via the chemical oxidative polymerization route has been reported. The copolymer was characterized by the FTIR and their

electronic conductivity has been measured by two- probe technique, where resistivity and conductivity varies with temperature.

Polymerization

The doped polyaniline substituted polyaniline and their processable copolymer was chemically prepared by free radical oxidative polymerization route⁶⁻⁹. The concentration of both of aniline and substituted aniline was 0.1M and that of HCl was 1.0 M for the copolymer, aniline and substituted aniline were mixed in the mole ratio 90 : 10 polymerization was initiated by the drop wise addition of ammonium peroxydisulphate 0.1M (NH₄)₂S₂O₈ in 100 ml H₂O). The polymerization was carried out at a temperature of 0-4⁰C and over a period of 4-6 hrs. Then the doped polymer powder was obtained by the process of precipitation, filtration, rinsing and drying, successively. The above synthesized powder was treated with 0.1M aqueous ammonia and stirred for 2 hrs to obtain their base (undoped) forms.

Measurements

FTIR spectra were recorded on Shimadzu FTIR-8101A spectrophotometer. Temperature dependent DC conductivity measurements were carried out with the samples in the temperature range from 30 to 140⁰C. The resistance was measured on DC resistance bridge LCR meter 923. The conductivity value was calculated from the measured resistance and sample dimensions.

Results and Discussion

Polymerization mechanism

The Polymerization of aniline and copolymer proceeds via a typical free radical oxidative polymerization route. The main steps are involved in the process are:

Initiation

Initiation was effected by (NH₄)₂S₂O₈ (APS), which generates the free radicals. These under the proper pH conditions react with aniline monomer to form radical cations. However, the radical cations are resonance stabilized and can be represented by various canonical forms¹⁰.

Propagation

Propagation step involves the addition of radical cations to oligomeric species to form polymeric chains. Each radical cation has two active sites that may be attributed to the increased electron density at ortho and para positions of benzene ring. However, coupling of radicals depends upon several factors including reaction medium, temperature, pH and presence of bulky substituents. Therefore, due to the steric hindrance offered by the - NH₂ group, ortho coupling has almost been excluded leading to the formation

of para product. However some ortho coupling¹¹ also occurs leading to the formation of corrupted polymer. Chain growth continued till it is arrested either by chain transfer or by coupling of radicals. Low temperature favours the formation of long chains (high molecular weights) due to the retardation of the rate of termination and chain transfer reactions.

Termination

Termination occurs due to the exclusion of radicals either due to coupling or by disproportionation reaction. The copolymerization is a powerful method to improve processability of conducting polymers. In general solubility of substituted polyanilines in organic solvents is significantly higher than pure polyaniline. However, their thermal stability and electronic conductivities are substantially lower than doped polyaniline. In order to maintain balance between conductivity, stability and processability copolymerization has been done. However, the relative proportions of aniline and substituted aniline in the copolymers determine exact properties.

FTIR Spectra

The FTIR spectra of copolymer was obtained. The vibrational peak at 1587 cm^{-1} assigned to the stretch of the quinoid ring and a peak at 1499 cm^{-1} assigned to the stretch of the benzenoid ring. The stretching peak of N-H appeared in the range $3500\text{--}3100\text{ cm}^{-1}$. In the spectra of the salt form copolymer, absorption peak at 1120 cm^{-1} and 1260 cm^{-1} , indicates the existence of the methoxy group on the benzene ring.

UV- Visible absorption spectra

The absorption bands of copolymer was recorded in NMP DMF and DMSO solvents. There are two peaks in the Visible range one around 328 nm is due to $\pi\text{--}\pi^*$ transition (band gap) and is directly related to the extent of conjugation. The other peak 616 nm is due to the molecular excitation associated with the quinone-diimine structure¹², i.e transition between HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoid rings. The UV - visible data reveals that $\pi\text{--}\pi^*$ band in copolymer shifts to the lower wavelength (hypsochromic shift) which can be attributed to the addition of more side groups which alters the torsional angle and leads to the lower conjugation lengths. The degree of hypsochromic shift is directly related to the size of the substituent.

Conductivity

PANI-co-PoMANI acts as an electrically conductive material only in the protonated form of emeraldine salt. Arrhenius relation gives the relationship between the activation energy E_a and the conductivity:

$$\sigma_T = A \exp^{-E_a/kT} \text{-----(1)}$$

where A is pre-exponential constant, k is Boltzman constant and E_a is activation energy (eV). Transport properties¹³ (DC electrical conductivity) was measured using the eq. (2)

$$\rho = \frac{1}{AT^{3/2} \exp^{-E_g/2kT} \cdot e (\mu_h + \mu_e)} \text{----- (2)}$$

Where ρ is resistivity (ohm cm), E_g is energy gap (eV), e is the charge on electron (esu)

μ_h is hole mobility ($\text{m}^2\text{v}^{-1}\text{s}^{-1}$) μ_e is electron mobility ($\text{m}^2\text{v}^{-1}\text{s}^{-1}$) and A is pre-exponential factor.

The measurement of conductivity was performed over a wide range of temperature above room temperature as:

$$\ln \rho = \ln \frac{1}{A \cdot e (\mu_h + \mu_e)} - \frac{3}{2} \ln T + \frac{E_g}{2kT} \text{----- (3)}$$

If the carrier, conductivity does not vary much with the temperature, then the second term in eq. (3) is negligible. Then it becomes:

$$\ln \rho = \ln K + \frac{E_g}{2kT} \text{----- (4)}$$

$$\text{Where } K = \frac{1}{Ae (\mu_h + \mu_e)}$$

$$\log_{10} \rho = \frac{1000 E_g}{2.303 \times 10^3 \times 2kT} + \log_{10} K \text{-----(5)}$$

If graph is plotted between $\log_{10} \rho$ and $1000/T$, (Fig.1) then the slope on form eq. (5) is

$$m = \frac{E_g}{2.303 \times 2k \times 10^3} \text{ and}$$

band gap $E_g = 2k \times m \times 2.303 \times 10^3$ Joule,

$$\text{Where } k = \frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV} = 8.6 \times 10^{-5} \text{ eV}.$$

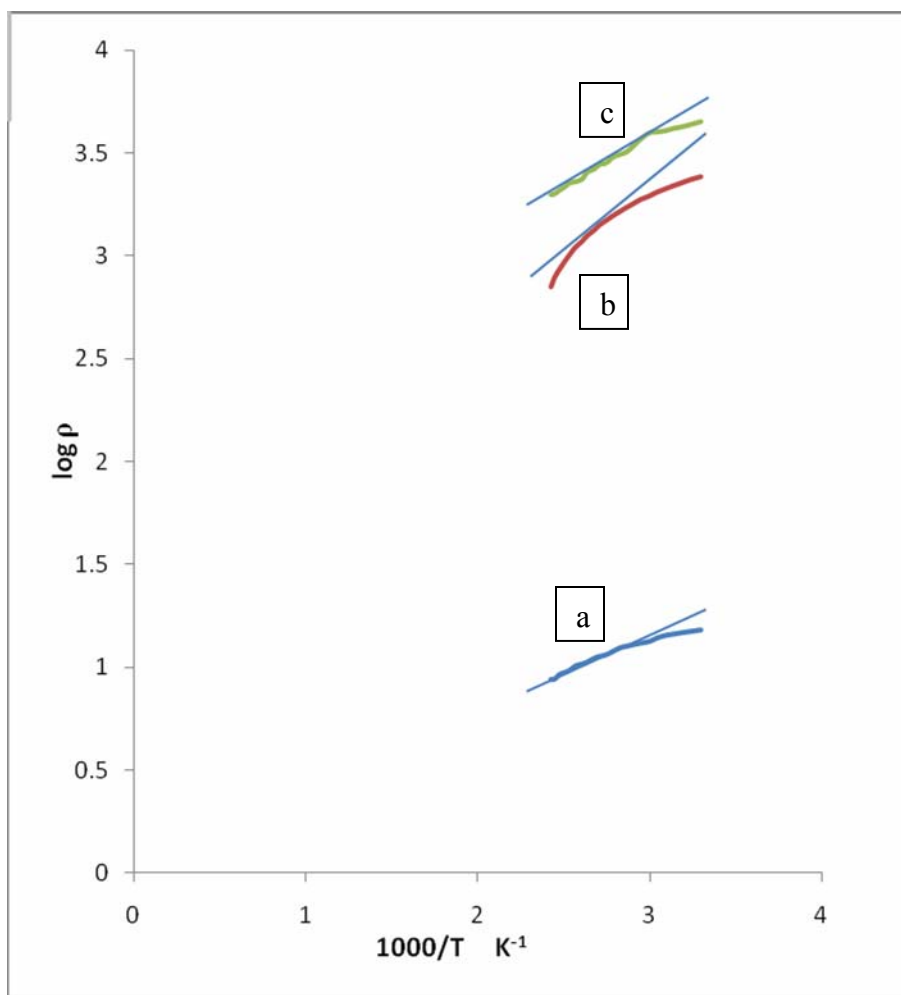


Fig. 1 Plot between $\log \rho$ and $1000/T$ (a) PANI (b) PoMANI (c) PANI-co- PoMANI

The conductivity of copolymer increased with increase in temperature. The conductivity, activation energy, band gap and slope of PANI, PoMANI and PANI-co-PoMANI are reported in Table 1.

Table 1. Conductivity, activation energy, band gap and slope for PANI, PoMANI and PANI-co-PoMANI

Polymer/Copolymer	Conductivity σ (S cm ⁻¹) (303K)	Activation energy E_a (eV)	Band gap E_g (eV)	Slope m
PANI	6.55×10^{-2}	0.047	0.1017	0.2562
PoMANI	4.10×10^{-4}	0.120	0.2073	0.5218
PANI-co-PoMANI	2.23×10^{-2}	0.130	0.2185	0.5500

Conclusions

Conducting copolymer of poly(aniline-co-o-methoxyaniline) type have been prepared. The electrical conductivity of copolymer increases with decreasing reaction temperature and is optimum almost at stoichiometric ratio of oxidant, dopant and monomer. The conductivity of copolymer does not depend on the temperature of surroundings, which indicates a small energy gap.

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