

Vibrational Spectroscopy of PTSA - Doped Polyaniline

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Abstract: Infrared transmittance spectra of polyaniline emeraldine base (EB) form and its different PTSA (p-toulene sulphonic acid) concentration doped samples were measured in 4000 - 400 cm^{-1} region at ambient temperature to reveal the polymeric chain oligomeric unit, interaction of sulphonate ions with these chains and effect of its concentration. The vibrational peaks of benzenoid (B) ring, quinoid (Q) ring, their combination modes and semiquinone units in PTSA doped emeraldine salts (PTSA:ES) are observed and assigned by using Oligomer Compound Approach. The para-substitution of B rings is confirmed by the appearance of B ring C-H out-of-plane deformation mode as a medium intensity band at 827 cm^{-1} in EB and at 824 cm^{-1} in ES:PTSA salts. The out-of-plane wagging mode of five adjacent hydrogen in end capped phenyl group due to conformational deformation of rings in polymeric chain is obtained as very weak bands at 712 and 682 cm^{-1} in EB and PTSA doped salts. These studies showed that B4Q1 is the basic oligomeric unit in polymer chain formation with their ends capped with phenyl rings. The strong and broad sulphonate ion stretching vibration and C-H bending of Q ring is observed at 1120 cm^{-1} due to the high degree of electron delocalization in PANI polymeric chain. On increasing PTSA concentration minor variations in intensity and position of peaks were observed.

Keywords: Polyaniline; Conducting Polymer; Doped Polymers; Vibrational Spectroscopy; Infrared spectroscopy

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INTRODUCTION

Different organic and inorganic acid doped polyaniline (PANI) conducting polymers have received considerable attention in the past decade due to their chemical, physical and environmental stability and ease of preparation with wide use in different device fabrication [1-5]. During doping, the hydrogen (H) ions form additional bonding with quinone rings to produce polarons or bipolarons as charge carriers and counter anions acquire interstitial sites which cross linked with polymeric chains through weak hydrogen bonding. These charge carriers follow hopping or tunneling conduction mechanism for charge transport. The aim of present work is to investigate basic oligomeric unit, bonding arrangements of oligomeric unit in polymeric chain, role of PTSA anion and its concentration through vibrational spectroscopy. IR transmittance spectra of EB form, 0.5M PTSA:ES and 1.0M PTSA:ES salts were recorded in 4000 - 400 cm^{-1} region at ambient temperature.

EXPERIMENTAL MEASUREMENTS

PANI semioxidized EB form was prepared by oxidative polymerization process. EB form was then protonated with 0.5M and 1M PTSA to form electrically conductive emeraldine salt of PTSA (PTSA:ES). GX 2000 Optica Perkin Elmer Fourier Transform infrared (FTIR) spectrophotometer was used for recording IR transmittance spectra at ambient temperature in 4000 - 400 cm^{-1} region. Each spectrum was recorded at 4 cm^{-1} resolution and an average of 100 scans. Samples were taken in KBr pellet form.

RESULTS AND DISCUSSION

IR transmittance spectra of EB and (0.5M and 1.0 M) PTSA doped PANI recorded for 4000 - 400 cm^{-1} region are presented in Figure 1 and Figure 2 respectively.

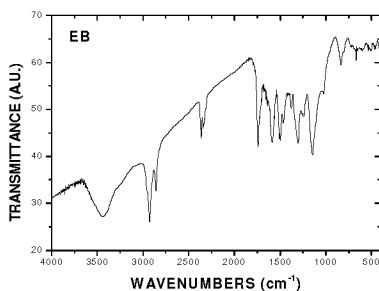


Figure 1. IR transmission spectrum of EB in 4000 - 400 cm^{-1} region

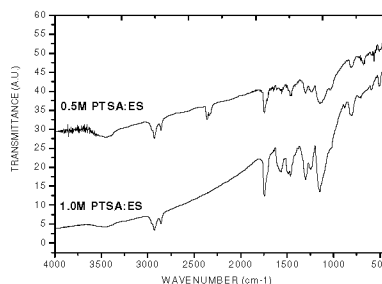


Figure 2. IR transmission spectrum of 0.5M and 1.0M PTSA:ES in 4000 - 400 cm^{-1} region

These spectra show vibrational peaks of B ring, Q ring, their combination modes and semiquinone units in PTSA:ES and their assignment is made by using Oligomer Compound Approach [6-9]. The stretching vibration of hydrogen bonded secondary amine group is observed as strong broad band at 3447 cm^{-1} in EB and with reduced intensity in PTSA doped salts. The peaks at 1560 and 1472 cm^{-1} are attributed to substituted B and Q rings respectively. The combination mode due to quadrant coupling of C=C stretching vibration of Q ring with C-H B bending vibration appeared as a strong band at 1592 cm^{-1} in EB along with weak components at 1545 and 1535 cm^{-1} . In 0.5M and 1.0M PTSA doped salt, these peaks are obtained at 1586 cm^{-1} and 1580 cm^{-1} with reduced intensity respectively. The existence of this combination mode confirms the formation of B4Q1 oligomer units. The combination vibration of C=N stretching and C-C stretching of B ring has been observed at 1498 cm^{-1} which shifts to 1486 cm^{-1} in 0.5 and 1.0M ES:PTSA with loss intensity. Tetra-amine group in doped emeraldine salts attributes this small variation in peak position and intensity to the deformation of Q ring. While the peaks at 1399 and 1297 cm^{-1} are due to aromatic C-N stretching group of B ring with secondary amine functional group. In 0.5 M and 1.0 M PTSA doped samples, the Q units were converted to B units by a proton - induced spin unpairing mechanism, which enhanced 1296.72 cm^{-1}

band intensity and reduced 1399.06 cm^{-1} peaks. The strong and broad p-toluene sulphonate ion stretching vibration and C-H bending of Q ring is observed at 1120 cm^{-1} due to the high degree of electron delocalization in PANI polymeric chain. These ions cross-link PANI chains via weak hydrogen bonding. The out-of-plane bending of C-H vibrations of isolated B ring and 1,2,4 trisubstitution are observed at 1031 and 879 cm^{-1} respectively. The para-substitution of B rings in these polymers was confirmed from the out-of-plane deformation mode of C-H group of B ring as medium intensity band at 827 cm^{-1} in EB and 824 cm^{-1} in ES: PTSA salts. The out-of-plane wagging vibration of five adjacent hydrogen in end capped phenyl group is obtained as very very weak intensity bands at 712 and 682 cm^{-1} in ES: PTSA doped salts due to conformational deformation of rings in polymeric chain.

CONCLUSION

Infrared transmittance studies of EB form and in 0.5M and 1.0M PTSA doped emeraldine salts confirmed the conformational deformations and chemical transformation of B and Q rings of polymer chains on protonation. The polymer chains are dominated by the B4Q1 oligomeric units with their ends capped by phenyl rings. p-Toluene sulphonate ions acquired interstitial sites and their strong polarizing effect caused electron delocalization in the polymeric chains. This resulted in conformational deformations and variation in intensity, position and removal of degeneracy of some peaks. On increasing doping concentration of PTSA in these salts, IR spectra showed minor variation in the intensity and position of vibrational peaks.

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