

A facile synthesis of DBSA doped poly (aniline-co-3-bromoaniline) nanostructured copolymer: Its electro active properties

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Abstract

A new copolymer, aniline-co-m-bromoaniline has been synthesized using DBSA with different molar ratio of monomers by chemical oxidative in-situ polymerization method. These polymers possess unique electrical and magnetic properties leading to wide range of industrial applications such as sensors, rechargeable batteries, electromagnetic shielding and solar cells etc. The synthesized polymer composites were subjected to various characterization techniques such as UV-visible spectroscopy, FT-IR spectroscopy, X-ray diffraction, Scanning electron microscopy. The copolymer samples were found to be soluble in common organic solvents like DMSO, NMP, THF and DMF. The UV-visible spectra show two major peaks at 342 nm attributing the $\pi - \pi^*$ transition and 600 nm indicating the $n - \pi^*$ transition. FT-IR spectra confirmed the formation of the benzenoid ring and quinoid ring of the copolymer system.

X-ray diffraction pattern confirms the amorphous nature of the polymer. SEM image reveals a large number smooth surfaced and agglomerated granular structure. Thermal analysis shows that the copolymer composite is highly decomposition temperature, thermal stability than that of its homopolymer possessing higher thermal stability. The electrical conductivity study indicates that the increase in 3-bromoaniline monomer feed ratio causes decreased in conductivity.

Keywords: Aniline, 3-bromoaniline, in-situ polymerization, surfactant, conductivity.

Introduction

Syntheses of nanosized conducting polymers have gained more interest because of their captivating properties. Among the various electro active polymer, polyanilines (PANI) have grabbed a great attention due to ease of synthesis, high conductivity, environmental stability and low cost. PANI is found to have electrifying applications in light emitting devices (LEDs), schottky diodes, solar cells, light weight batteries, sensors and electro chromic devices^{8,28}. Conversely the applications of PANI are limited due to its

poor solubility in common organic solvents and processability. The poor solubility produces some complexity in the film formation, which is the main requirement for device fabrication²⁶.

Therefore, copolymerization reaction of aniline with different monomers was found to improve the processability. Several research works were done to improve the solubility of PANI, substitution in alkyl chain, derivatives of PANI and copolymers have been synthesized¹⁹. The lateral substituent present in the polymer chain reduces the stiffness of the polymer chain and improves the solubility characteristics.

Also, it decreases the overlap of p-electron, nitrogen lone pairs and leads to decreases in the conductivity²⁴. Substituted PANI can be prepared by chemical or electrochemical polymerization of aniline with ring substituted derivatives²⁰. Also doping of PANI with suitable dopant like protonic acid, sulfonic acid is another way to improve the processability^{5,17,18}. Recently, nanostructured conducting polymer was synthesized by template assisted method and self assembly processes to obtain ordered nanoscaled dimensions.

Several studies has been reported to prepare PANI dispersion; polymerization of aniline in micelle^{3,13}, emulsion^{15,16} and reversed microemulsion⁷ as a polymerization medium. Halogen substituted aniline copolymers such as fluorine², chlorine¹, iodine³² and bromine¹⁰ groups in polymer chain have been examined well. It has been reported that the presence of electronegative group such as fluorine and chlorine decreases the electrical conductivity¹².

The halogen substituted aniline copolymers depict significant electrical conductivity and superior solubility⁹. The electrical properties of the copolymer also depend on the electron withdrawing and electron donating group present in the polymer chain because of the variation in electron charge density in the polymer matrix, forces, bonding nature and therefore a research attempt was made to synthesize a novel polyaniline copolymer in nanoscaled features with improved electrical conductivity for industrial applications^{6,11}.

Roy et al²² reported on the chemical synthesis of homopolymer and a copolymer based on o-bromoaniline and

aniline in the presence of methane sulfonic acid in an aqueous solution. However, only a few reports on copolymerization of aniline and bromine substituted aniline at meta position were studied. The novelty of our work is to find the role of monomer concentration in absorption, crystallinity, endothermic phase transition, morphological characteristics and electrical conductivity. Here, we report the synthesis of oxidative copolymers of aniline and m-bromoaniline monomers at various concentrations in presence of DBSA and ammonium persulphate as oxidant. The resulting nanocomposites are characterized by UV-Visible and FT-IR techniques. The crystallinity, morphology and electrical conductivity nature of these nanocomposites are investigated using XRD, SEM and four probe techniques.

Material and Methods:

Materials: Aniline (Rankem, India) and 3-bromo aniline (Sigma-Aldrich, USA) were distilled under reduced pressure and stored at low temperature. DBSA (Merck, India), Ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and concentrated Hydrochloric acid were purchased from E-MERCK, India. All other supplementary chemicals were of analytical grade and double distilled water was also used for the synthesis.

Instrumentation: The UV-absorbance spectra of samples were recorded from 200 to 900 nm using ELICO SL-218 UV-Visible double beam spectrophotometer. FT-IR spectra of DBSA doped poly(An-co-m-TFMA) nanocomposites were monitored by ABB BOMEM B3000 FTIR in the region of $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets. The surface morphology of the nanocomposites was analysed by Scanning electron microscope (HR-SEM) HITACHI-SU6600L operating at 25 KV. The phase identification of the fine powdered sample was performed by Philips X'Pert Pro X-Ray diffractometer, with Nickel filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5402\text{ \AA}$) with the operation of 40 KV. The analysis was performed in the diffraction angle 2θ from 5 to 80° at a speed of $2^\circ/\text{min}$. The room temperature conductivity was measured using a Keithley 6517B electrometer.

In-Situ Chemical synthesis of DBSA doped poly(An-co-3-BA) copolymers: The DBSA doped poly(An-co-3-BA) nanocomposites were prepared as follows: Aqueous micellar dispersion was prepared first by introducing DBSA in distilled water (90 ml) under slow stirring. Then 0.05 M each of aniline monomer and 3-bromoaniline were added to the solution. Then 10 ml 1M HCl aqueous solution was slowly

added into the reaction mixture and continuously stirred to form a homogeneous solution.

Finally, 0.1M of APS solution was added drop wise to initiate the polymerization. The reaction mixture was stirred continuously for 12 hr in an ice-cold water bath. As the polymerization proceeded, the colour of the solution changed from colourless to yellow, brown and finally to green, confirming the formation of DBSA doped poly(aniline-co-3-bromoaniline) salt. The dark greenish precipitate of DBSA doped poly(aniline-co-3-bromoaniline) formed was centrifuged and washed with double distilled water, acetone and methanol. The product was dried in a vacuum oven at 50° C for 24 hr. The synthesis route of DBSA doped poly(aniline-co-3-bromoaniline) copolymer composite is shown in the reaction fig. 1.

Result and Discussion

UV- Visible Spectroscopy: The UV-Visible spectra DBSA doped poly(An-co-3-BA) copolymer is shown in fig. 2. It shows two major absorption bands at 342 and 600 nm. The first band is ascribed to the $\pi\text{-}\pi^*$ electronic transition³⁰ and is related to extent of conjugation between the phenyl rings along the polymer chain. The second band is assigned to $n\text{-}\pi^*$ electronic transition^{14,21}.

This is attributed to the charge transfer process of the HOMO of benzenoid to LUMO of quinoid segments²⁷. A blue shift is observed due to higher torsional angle increase in the size of substituent in the benzene ring²⁵. Thus, the lower shift indicates that the DBSA molecules are doped well into the copolymer matrix and confirms the formation of nanostructured copolymers.

XRD analysis: Figure 3 shows the powdered XRD spectrum of DBSA doped poly (An-co-3-BA) copolymer. The amorphous phase of the copolymer evidenced from the peak at $2\theta = 22\text{--}25^\circ$ and is due to irregular arrangement of the polymer chains. The existence of surfactant molecule as side group in the polymer chain increases the distance between the polymer chains and the steric hindrance caused by the bromo group in the polymer chain does not allow to crystallize easily³³.

The sharpness of peaks decreased as the increasing bromoaniline concentration in the feed. The higher concentration of comonomer modifies the chain growth resulting amorphous nature.

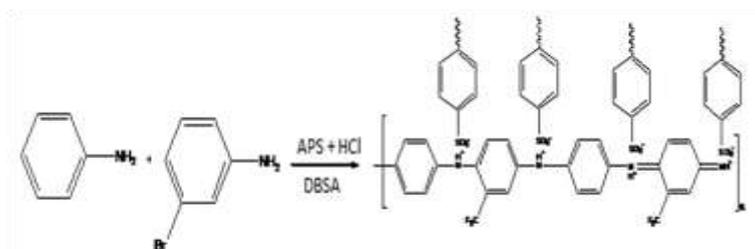


Fig. 1: Synthesis route of poly(Aniline-co-3-bromoaniline) copolymer

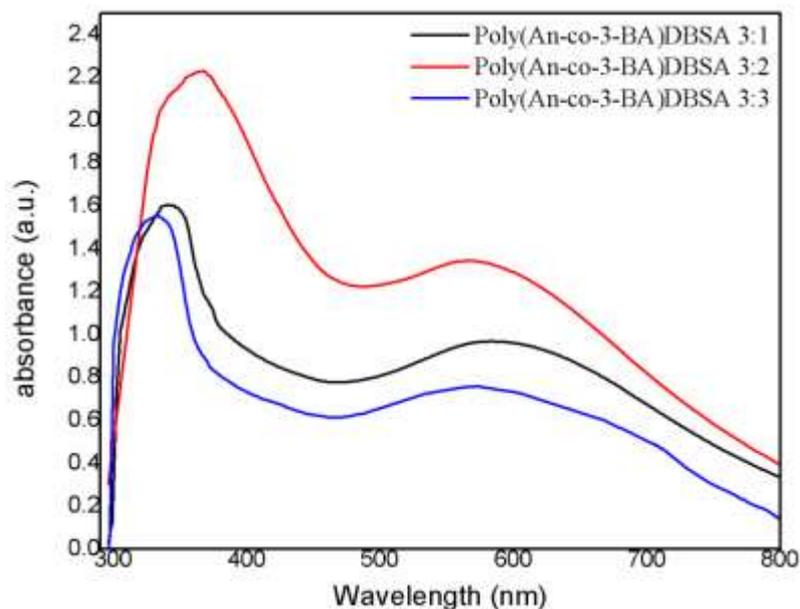


Fig. 2: UV-Vis spectra of DBSA doped poly(An-co-3-BA) copolymer

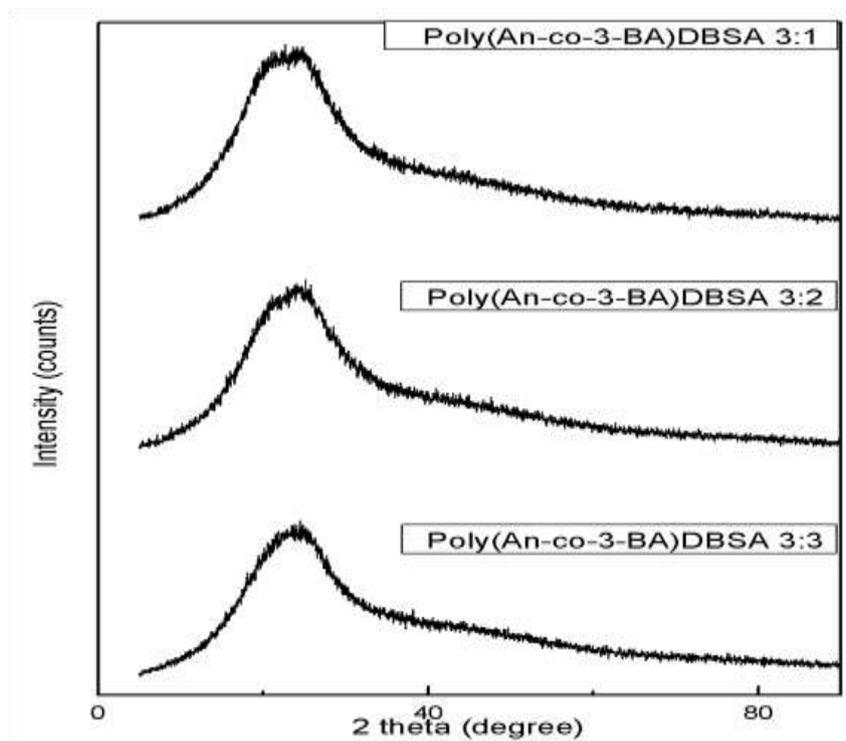


Fig. 3: XRD spectrum of Ag DBSA doped poly(An-co-3-BA)

The surfactant molecule size, atoms or molecules attached in the side chain influence structure of the polymer.

FTIR analysis: The FTIR spectrum of DBSA doped poly(An-co-3-BA) copolymer is shown in fig. 4 and the spectral values are listed in the table 1. It shows the characteristic bands at 3224, 3053, 1567, 1498, 1294, 1136, 1034, 819 and 660 cm^{-1} . The characteristic peak at 3224 cm^{-1} is assigned to C-H aromatic stretching of DBSA molecule and the band at 2871 cm^{-1} is attributed to NH stretching. The peaks at 1567 cm^{-1} and 1498 cm^{-1} are C=C stretching of quinoid (Q) ring

and benzenoid (B) ring respectively. These two peak values confirm the formation of benzenoid and quinoid in the copolymer. The C-N stretching in quinoid and benzenoid sequences was ensured from the peak at 1294 cm^{-1} . The electrical conducting nature of the copolymer is confirmed from the peak at 1136 cm^{-1} due to the electron delocalization. The peak observed at 1034 cm^{-1} is assigned to bromo groups in the polymer backbone.

The formation of para coupling in the phenyl ring ensured from the peak at 819 cm^{-1} has been assigned to C-H out plane

pending. The nitrogen atom connects two benzene rings and is confirmed from the peak at 660 cm^{-1} showing the C-N-C bending vibration of amine group²⁹.

Surface Morphology: The surface morphology of DBSA doped poly (An-co-3-BA) copolymer is shown in fig. 5. It shows that the polymer is made of aggregates of large number of nanoparticles and smooth flat like surfaces and layered like globular particles of size 150-300 nm. These globular particles assist the rapid diffusion of polymer chain in the micelle, which are coiled together to give a spherical morphology. However, the spherical morphology can be obtained by doping of DBSA surfactant molecules which acts as soft template. Moreover it acts as soft template for the growth of polymer with uniform granular morphology. The morphology and structure are determined by the concentration of surfactant molecules³¹.

Thermal analysis: Figure 6 exhibits the differential scanning calorimetric analysis of surfactant aided poly (An-co-3-BA) 3:3 copolymer. It was performed between ambient temperature and 220°C . The DSC graph showing an endothermic peak at 73°C is due to the elimination of volatile matter from the polymer sample. The peak between 100°C and 125°C is attributed to the second endothermic and is due to the vaporization of water molecules. The other endothermic peak around 210°C is related to the elimination of dopant molecules, polymer backbone.

The copolymer shows a slight variation in the slope around 99°C which is due to the small change in the enthalpy values. The peak at 30°C reveals the glass transition temperature of the copolymer which is found to be higher than homopolymer⁴. A small curve at 96°C is found on cooling due to the enthalpy change of the copolymer.

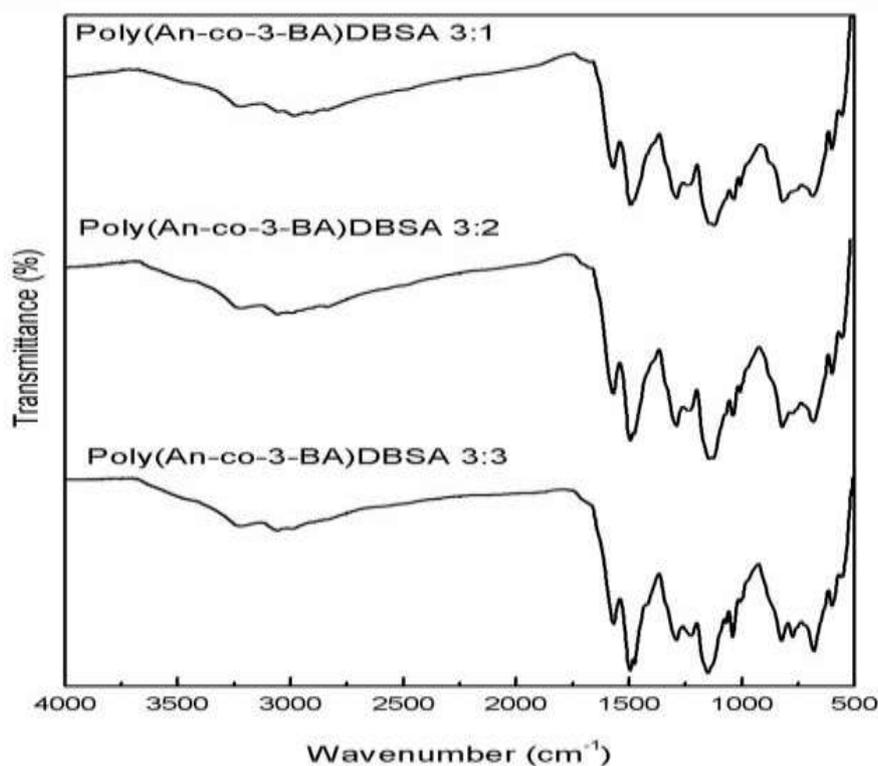


Fig. 4: FTIR spectrum of DBSA doped Poly(An-co-3-BA) copolymer

Table 1
Band assignments of DBSA doped P(AN-co-3-BA) copolymer

Stretching Vibrations	Poly(An-co-3-BA) DBSA		
	3:1	3:2	3:3
N-H stretching	3224	3226	3225
C-H stretching DBSA	3053	3055	3042
C=C double bond associated with the Quinoind ring	1567	1580	1578
C=C double bond associated with the benzenoid ring	1498	1500	1495
C-H stretching	1294	1295	1298
Presence of a halogen (bromo) group	1034	1036	1048
C-H out plane bending	819	822	810

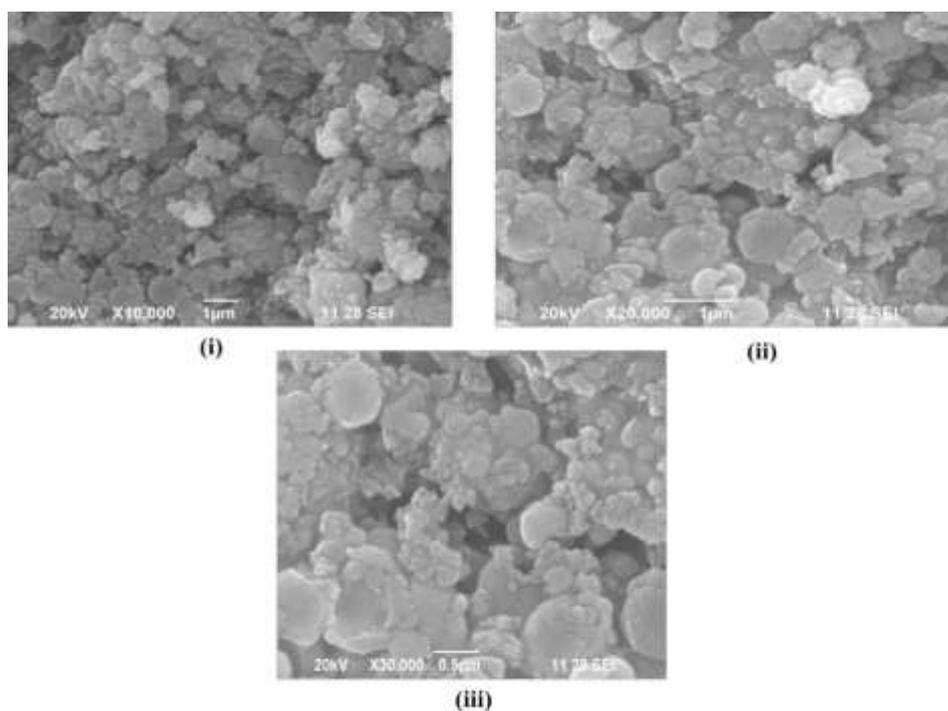


Fig. 5: SEM images of DBSA doped Poly(An-co-3-BA) copolymer

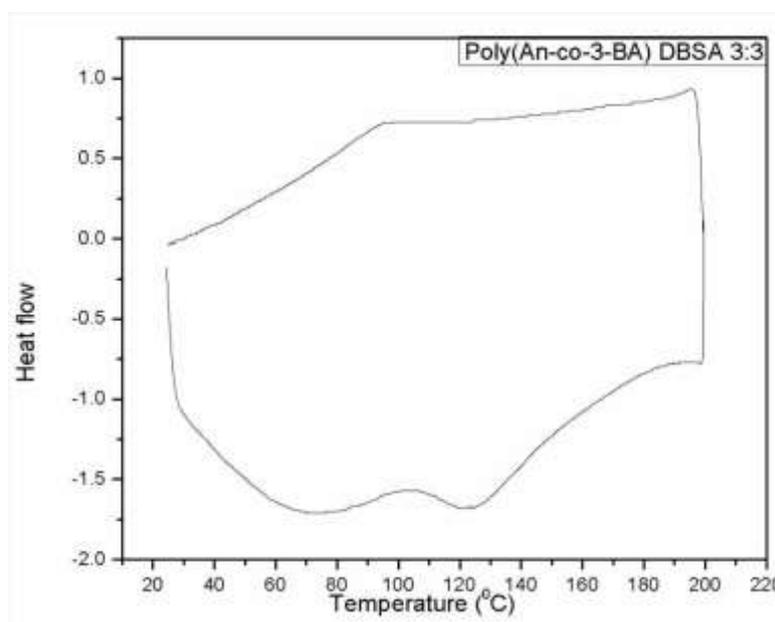


Figure 6: DSC of DBSA doped Poly (An-co-3-BA)

Table 2
Electrical Conductivity Values of DBSA doped Poly (An-co-3-BA) copolymer

Copolymer composition	Conductivity (S/cm)
Polyaniline	1.98×10^{-2}
Poly (An-co-3-BA) DBSA 3:1	4.19×10^{-7}
Poly (An-co-3-BA) DBSA 3:2	1.10×10^{-7}
Poly (An-co-3-BA) DBSA 3:3	1.98×10^{-9}

Electrical conductivity: The electrical conductivity values of surfactant aided poly (An-co-3-BA) copolymer are shown in table 2. The electrical conductivity in the copolymer chain may be due to the electron charge transfer through the

hydrogen bonding between the polymer chains. The DBSA doped poly (An-co-3-BA) copolymer illustrates the lower conductivity than the pure polyaniline and is due to decreases in the delocalization and π bond conjugation in the

polymer chain caused by steric effect of bulky DBSA dopant molecules. It hinders the movement of charge carriers and weakens the electrical conductivity²³. The substitution decreases the intermolecular distances.

Conclusion

A new series of DBSA doped poly (aniline-co-3-bromoaniline) copolymer nanostructures was synthesized using chemical oxidative polymerization method. The UV-Visible spectrum shows the π - π^* and n - π^* electronic transition between the energy levels. The XRD spectrum confirms the amorphous nature of the synthesized copolymer. DSC curve depicts the endothermic and exothermic peaks and glass transition temperature of the polymer.

SEM microscopic study reveals that the polymer is made of aggregates of large number of nanoparticles and smooth flat like surfaces and layered like globular particles of size 150-300 nm. Since the copolymer is highly soluble, this copolymer can be used in the fabrication of flexible electronic devices.

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