

Study of Chemically Synthesized Nanocomposite Copolymer of N-Methyl Pyrrole and 2,5-Dimethoxy Aniline

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Copolymer nanocomposite of N-Methyl pyrrole (NMPy) and 2,5-dimethoxy aniline (DMOA) doped with HCl was synthesized using chemical oxidative polymerization. Ammonium persulfate (APS) was used as an oxidant. The nanocomposite samples were characterized for structural configurations by UV-Vis, FTIR, TGA and XRD. Four probe method was adopted for the measurement of electrical conductivity. Spectroscopy confirms the π - π^* transition in nanocomposite copolymer. FTIR confirms the formation of copolymer and its structure. XRD analysis shows the amorphous nature of polymer nanocomposite. The electrical conductivity of sample was comparable to the intrinsic conductive polymers used. Size and surface morphology was demonstrated by SEM.

Key words: Nanocomposite, copolymer, XRD, TGA, SEM, four probe method.

1. INTRODUCTION

Intrinsically conducting polymers (ICP) are the organic polymers capable of electric conduction having high metallic conductivity to semiconductor [1]. ICPs are highly advantageous in terms of their processability, mainly by dispersion [2]. Nanocomposites of conducting polymers polyaniline and polypyrrole have gathered special attention due to the excellent redox recyclability [3] and their derivatives are deliberated to be one of the most promising classes of organic conducting polymers [4] owning good environmental stability [5], ease of doping [6]. Polypyrrole, because of good environmental stability and ease of synthesis is another important and most studied conducting polymer [7,8]. It's an integral biocompatible polymer [9]. Due to their exceptional properties, they can be used in various applications such as biosensors [10,11], gas sensors [12], anti-electrostatic coating [13], solid electrolytic capacitors [14,15], light weight batteries and anticorrosive devices [16] etc. Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential [17]. Nanocomposite copolymer of N-Methyl pyrrole (NMPy) and Aniline-2-Sulphonic acid (ASA) exhibits fair thermal stability [18].

In this study we reported the synthesis of nanocomposite of copolymer of N-Methyl pyrrole (NMPy) and 2,5-dimethoxy aniline (DMOA) by chemical oxidative polymerization. Synthesized nanocomposite is evaluated for various physical properties like optical, thermal stability, surface morphology, electrical conductivity, crystallinity and solubility. Results obtain are compared and discussed based on previous reported findings.

2. MATERIALS AND METHODS

Analytical grade chemical N-methyl pyrrole (NMPy) and 2,5-Dimethoxy aniline (DMOA) were obtained from Acros Organics, USA while ammonium persulphate (APS) and hydrochloric acid (HCl) were obtained from Qualigens, India. All the solutions were prepared in double distilled water. Among various prominent polymerization techniques, chemical oxidative method [19-21] is a very versatile and easy route-to-synthesize even in scale up arrangement for obtaining the conducting polymers, hence been adopted to synthesize the nanocomposite of the copolymer of N-Methyl pyrrole and 2,5-Dimethoxy aniline. Chemical oxidative polymerization [22] is followed by oxidation of comonomer to cation radical and their coupling to form di-cation and repetition of this process generates a polymer.

2.1. Synthesis of nanocomposite of copolymer of N-Methyl pyrrole and 2,5-Dimethoxy aniline

1.521 g (0.01875 moles) of N-methyl pyrrole and 2.872 g (0.01875 moles) of 2, 5-Dimethoxy aniline were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared by using 17.115 g (0.075 moles) with 50ml of 1M HCl. Then APS solution was dropped over a period of 30 minutes into a continuously stirred reactor which contained aniline and pyrrole solution maintained at melting ice temperature. Obtained solution was further agitated for 12 hours after dropping process yielding a dark violet compound.

2.2. Characterization

Absorption spectra is obtained using UV-VIS (Shimadzu 1900) double beam spectrometer to characterize the structures of intrinsically conducting polymers (ICPs) and to determine the conjugation in polymer backbone. The Fourier transform infrared spectrophotometer (Perkin Elmer) was used to determine the chemical structure of the nanocomposite. Surface morphology of the prepared nanocomposite was characterized by scanning electron microscopy (SEM.LEO 435 VP). The ordered structure and crystallinity of the composites were obtained by X-ray diffraction method (XRD). Thermal analysis was done by using Thermogravimetric analyzer. Electrical conductivity was measured by Four Probe method.

3. RESULTS AND DISCUSSIONS

3.1. UV-VIS Spectrum

UV-VIS absorption spectral analysis of the synthesized copolymer nanocomposite of N-Methyl pyrrole and 2,5-Dimethoxy aniline is shown in Figure 1.

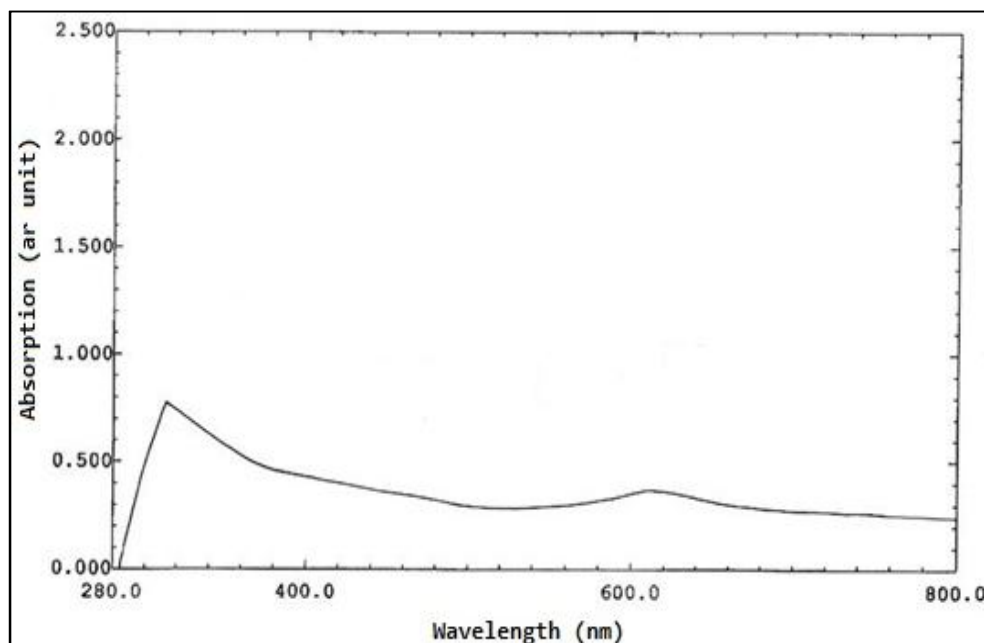


Fig. 1: UV-Vis absorption spectra of copolymer nanocomposite of N-Methyl pyrrole and 2,5-Dimethoxy aniline.

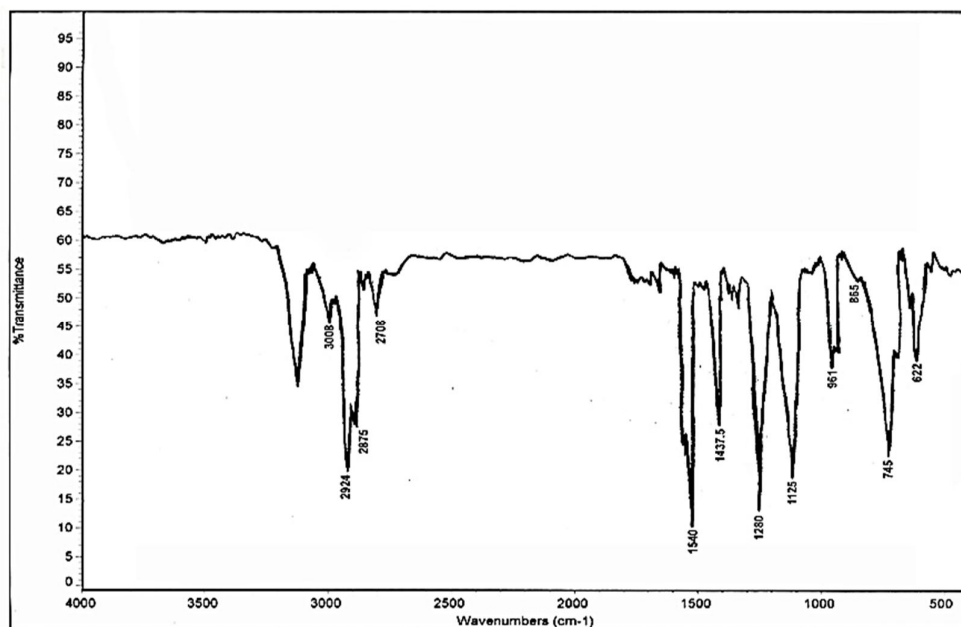
Absorption peaks are observed at around 310 nm and 601 nm. First peak around 310 nm is due to the π - π^* transition (band gap) and is directly related to the extent of conjugation. The other peak near 601 nm is due to molecular exciton associated with the quinone-diamine structure [23] i.e. transition between HOMO orbital of benzenoid rings and LUMO of the quinoid rings.

3.2. FTIR Spectrum

The FTIR spectra of doped form of N-Methyl pyrrole (NMPy), 2,5-dimethoxy aniline (DMOA) and nanocomposite material respectively in the range 400-4000 cm^{-1} is shown in Figure 2, Figure 3 and Figure 4. Respectively. The band at 1524 cm^{-1} and 1467 cm^{-1} in the spectrum of nanocomposite shows C=C stretching frequencies of quinoid and benzenoid ring respectively. The spectrum of DMOA shows these peaks at 1610 cm^{-1} and 1475 cm^{-1} [24-26]. The band characteristic of the conducting protonated form is observed at about 1280 cm^{-1} , 1300 cm^{-1} and 1300 cm^{-1} in the protonated NMPy, DMOA and nanocomposite respectively and it is interpreted as C-N stretching vibration in the polaron structure. The N-H stretching is at 3413.26 cm^{-1} and 3430 cm^{-1} in DMOA and nanocomposite respectively. This peak is absent in NMPy. The band at 1740 cm^{-1} and 1713 cm^{-1} in the spectrum of DMOA and nanocomposite corresponds to the presence of a carbonyl group. The spectrum of nanocomposite reveals all characteristic peaks of homopolymers. It is observed that the peaks shifted towards lower wave number and it confirms the presence of copolymer unit in composite material.

Table 1: FTIR data of homopolymers and copolymer nanocomposite of NMPy and DMOA.

	N – H stretch	- CH ₃ stretch	C – N stretch	C – H in plane	C – H out of plane
NMPy homopolymer	---	2875, 2924, 3008	1280	1125	868
DMOA homopolymer	3431.26	---	1300	1100	815
Copolymer nanocomposite	3430.37	2916, 2840	1300	1113	721

**Fig. 2:** FTIR of homopolymer of poly-N-methyl pyrrole (NMPy).

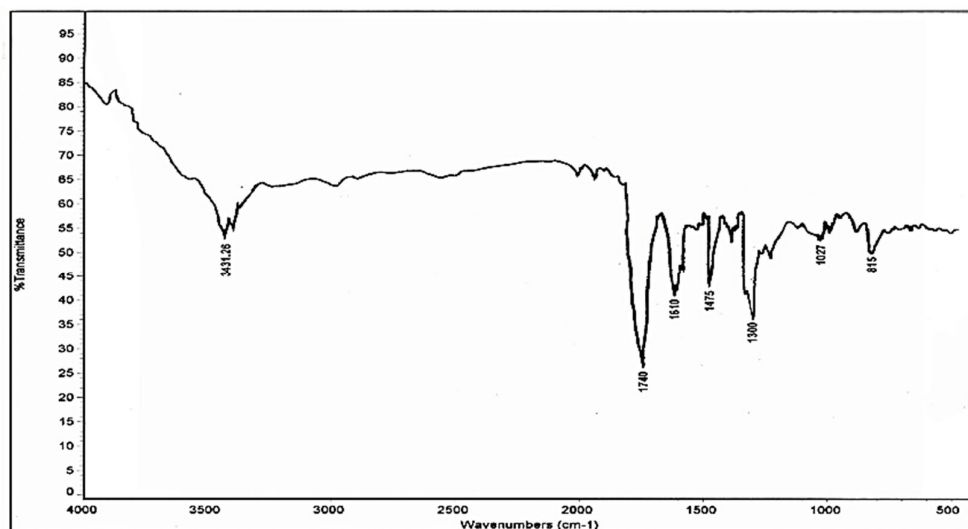


Fig. 3: FTIR of homopolymer of poly-2, 5-dimethoxy aniline (DMOA).

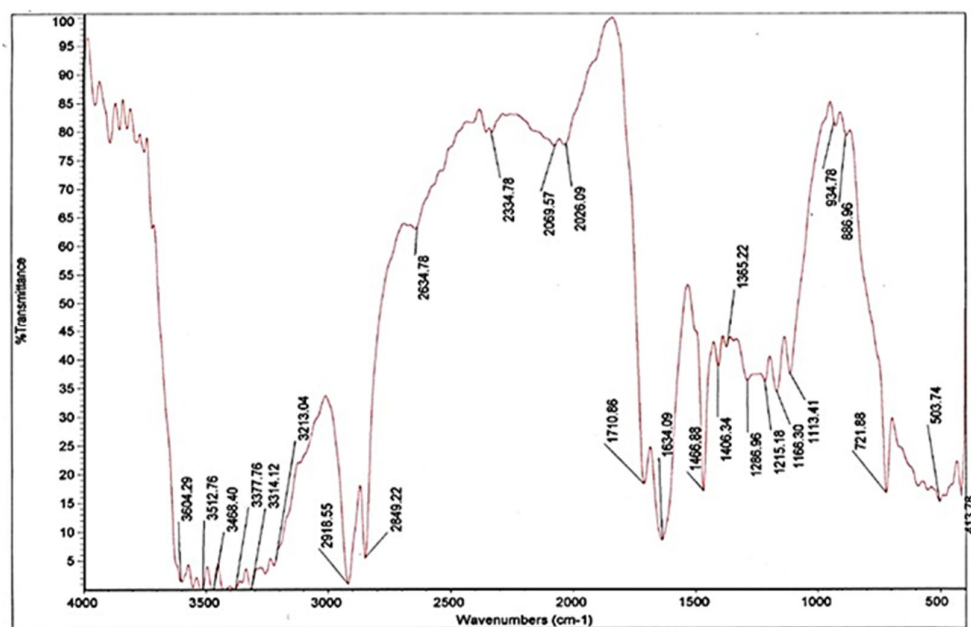


Fig. 4: FTIR of copolymer of poly-N-Methyl Pyrrole (NMPy) and poly-2, 5-dimethoxy aniline (DMOA).

3.3. Thermal Analysis

Thermogravimetric analysis measurements were carried out from room temperature to 800° C at a heating rate of 10° per minute under nitrogen atmosphere. The comparative TGA curves of homopolymers of ICP and the copolymer nanocomposite (CP - 4) of poly-N-Methyl Pyrrole (NMPy) and poly-2, 5-dimethoxy aniline (DMOA) is shown in Figure 5. Thermogram of nanocomposite shows three distinct regions of weight loss.

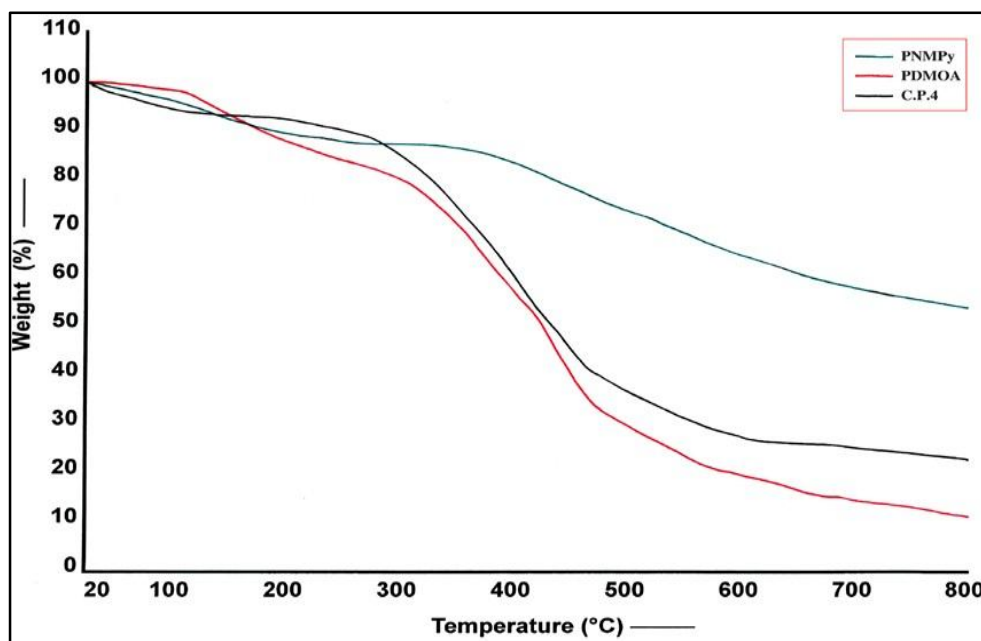


Fig. 5: TGA curves of NMPy, DMOA and nanocomposite of copolymer of NMPy and DMOA.

The TGA curves shows loss of moisture in the first step of decomposition after 100° C. Second weight loss occurs at around 250° C due the removal of dopant. The highest percentage weight loss is observed at decomposition temperature between 250° C to 600° C.

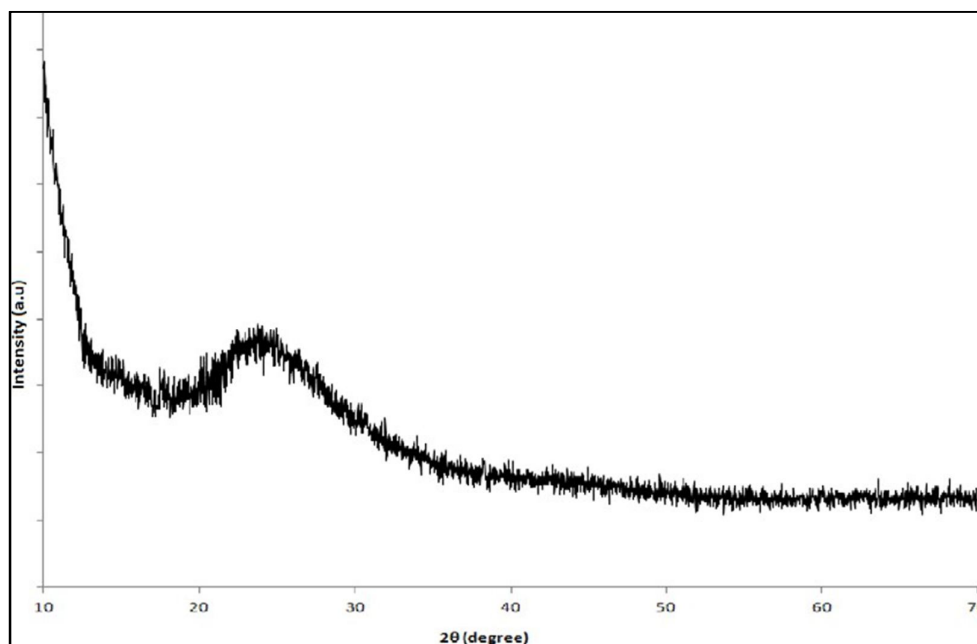
Nanocomposite shows 7.5% weight loss at 120° C due to the elimination of water molecule and second weight loss of about 2.5% at 260° C is attributed to removal of dopant. The polymer backbone degradation starts above 450° C and it is maximum for DMOA and lowest for NMPy. Thus, synthesized copolymer nanocomposite exhibits significant thermal stability at normal room temperature to 250° C. All results were tabulated in Table 2.

Table 2: TGA weight loss in NMPy, DMOA and nanocomposite of copolymer of NMPy and DMOA.

	1 st weight loss		2 nd weight loss		3 rd weight loss	
NMPy	6%	120° C	7.75%	280° C	23.75%	608° C
DMOA	9%	163° C	7.5%	262.5° C	49.75%	465° C
Nanocomposite	7.5%	130° C	2.5%	232° C	46.5%	451° C

3.4. X-Ray Diffraction

XRD pattern shown in Figure 6 for the nanocomposite exhibits broad peak at $2\theta = 20^\circ$ to 30° and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at $2\theta = 24^\circ$ [24] and it is due to the scattering from PPy chains at the interplanar spacing [25]. The copolymer of poly-2, 5-dimethoxy aniline and polypyrrole has shown broad characteristic peaks for their amorphous nature [26-28]. Thus, on the behalf of earlier reported XRD graphs of poly aniline, polypyrrole and copolymer of aniline and pyrrole we can predict the formation of nanocomposites of substituted aniline and pyrrole and broadness of peak in the range of 20° to 30° is due to their amorphous nature.

**Fig. 6:** XRD spectrum of nanocomposite of copolymer of NMPy and DMOA.

3.5. Surface Morphology

Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Figure 7a and 7b shows the SEM micrographs at 500X and 1000X magnifications. It shows two different types of structure. One is cylindrical fiber type and other granular forms. Micrograph indicates formation of granular particles of 325 nm size distributed over cylindrical fibers for the nanocomposite copolymer of NMPy and PNDMA.

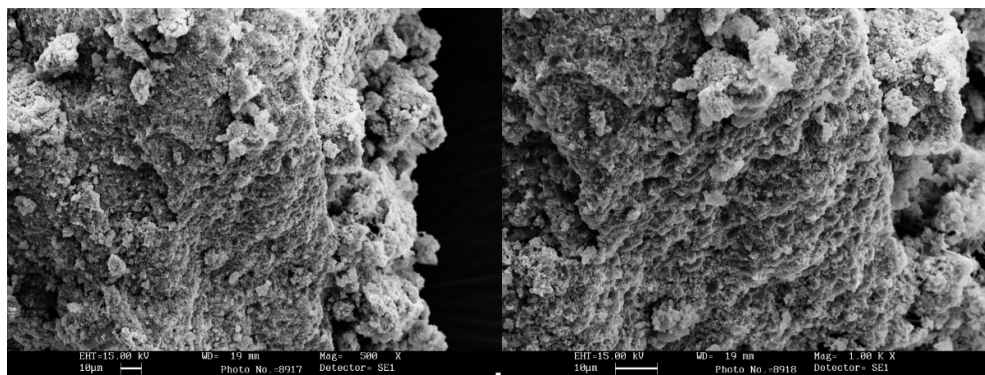


Fig. 7: SEM images of nanocomposite copolymer of NMPy and PNDMA at (a) 500X and (b) 1000X magnification.

3.6. Electrical Conductivity Measurement

Electrical conductivity of prepared nanocomposite was measured by 'Four Probe Method'. It is observed that the conductivity decreases from 10^{-2} to 10^{-5} s/cm when aniline was polymerized with pyrrole. The conductivity of prepared NMPy and PNDMA nanocomposite was 2.5×10^{-5} s/cm. The lowering of conductivity for copolymer than Polyaniline is expected to arise from the steric effect of the bulky substituent ($-\text{OCH}_3$, $-\text{C}_2\text{H}_5$ etc.) may provide torsional twist in the polymer backbone, reducing the coplanarity and average electron delocalization length. Such type of observation has been noted for substituted polyaniline and copolymers of aniline with substituted aniline. The results indicate that when polymerizing aniline with pyrrole. The conductivity decreases for polyaniline and improve for polypyrrole. This means copolymerization can increase the conductivity of polypyrrole. This is evidence that the copolymer formed is not just the combination of polypyrrole and polyaniline but completely new material with new properties. The presence of longer alkyl chain would reduce the conjugation length in copolymer backbone which in turn lower the concentration of charge carrier/conductivity.

3.7. Solubility Test

The nanocomposite of NMPy and PNDMA copolymer of substituted aniline and pyrrole was tested for solubility in preferred solvents for ICPs such as DMSO, NMP, H_2O_2 , CCl_4 , and H_2O . Solubility for the synthesized nanocomposite was found to be insoluble in H_2O_2 , CCl_4 , and H_2O solvents except for DMSO and NMP which showed sparingly solubility.

forming a dark green colour solution similar to DMPy and DMSO nanocomposite copolymer [29].

4. CONCLUSIONS

The nanocomposite of copolymer of poly-N-Methyl Pyrrole (NMPy) and poly-2, 5-dimethoxy aniline (DMOA) was successfully synthesized via chemical oxidative polymerization using APS as dopant. The particle size of nanocomposite was 325 nm. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble, except in DMSO and NMP.

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