

Synthesis and Characterization of Electroactive Poly (*N*-Methylaniline-Co-*O*-toluidine)

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Abstract: Chemically oxidative polymerisation of *N*-methylaniline and *o*-toluidine with 5 molar ratios was performed using potassium persulfate as an oxidant in a H₂SO₄ medium at 0-5 °C. The resulting copolymers were characterized by using UV-Visible and Fourier Transform IR spectroscopy. Two probe techniques were used to measure the electrical conductivity of the copolymer. The structural characteristics and particle size were determined through XRD experiments. The results showed that the conductivity of the copolymer (60% PNMA 40%POT) was found to be 5.932x10⁻³ s/cm.

Keywords: Oxidative polymerization, Copolymer, Poly (N-Methylaniline-Co-O-toluidine)

Introduction

Conducting polymers are novel plastics that conduct electricity. Electrically conducting polymers described as a new class of “synthetic metals” reached a high interest in the last years, confirmed by the 2000-Nobel Prize in chemistry for the discovery and development of conductive polymers¹.

Polyaniline occupies the most important place in the very promising class of ICPs. It is unique and has been in the forefront of the global search because of its low cost, ease of preparation, chemical stability, variable electrical conductivity, well behaved electrochemistry, electrochromic effects as well as excellent environmental stability^{2,3-6}. Flexibility, density and chemical inertness, non-linear optical behaviour and exceptional mechanical properties⁷⁻⁹ such as tensile strength and resistance to harsh environments are other important advantages of the conducting polymers.

Conducting polymers have been applied in a really impressive application range in different fields such as in batteries¹⁰⁻¹², electromagnetic shielding^{13,14}, energy storage systems¹⁵, corrosion protection¹⁶, electrochemical chromatography¹⁷, electrochromic devices¹⁸⁻²⁰, optical and electronic devices^{21,22}, sensors²³⁻²⁵ including biosensors²⁶, gas sensors²⁷, light emitting devices²⁸ photovoltaic applications²⁹, neural probes, controlled drug delivery and tissue engineering applications^{30,31}.

The derivatives of PANI have also attracted considerable attention especially due to their higher solubility in common solvents than PANI³²⁻³⁴. The chemical properties of PNMA essentially differ from those of PANI since in PNMA the proton exchange sites are irreversibly blocked by methyl substituent. As a consequence, the deprotonation of the imino groups and proton expulsion during the second oxidation step of PANI is not observed in PNMA. The absence of the second oxidation process in PNMA reduces a risk of the oxidative deterioration by hydrolysis during the electrochemical oxidation and this fact is an advantage of PNMA over PANI³⁵.

Poly(*o*-toluidine) is one of substituted derivative of polyaniline in which -CH₃ group is introduced at ortho position of benzenoid ring of polyaniline. MacDiarmid and co-workers suggested that substitution of methyl group at ortho position, increases steric interactions between benzenoid rings along the polymer chains, resulting decrease in the extent of conjugation³⁶ poly(*o*-toluidine) shows faster reversibility between oxidized and reduced form therefore chosen as an active conductive polymer along with polyaniline^{37,38}.

Chemical polymerization³⁹ is the versatile technique for preparing large amounts of conducting polymers. Oxidative chemical polymerizations result in the formation of the polymers in their doped and conducting state. One of the criteria, governing the quality of the material, is its molecular mass.

In the present work poly (*N*-methylaniline-co-*o*-toluidine) is synthesized and doped with H₂SO₄ by the chemical oxidative polymerization method. The physicochemical properties of the polymers were investigated by spectroscopic techniques, XRD analysis and conductivity measurements.

Experimental

Ortho toluidine (AR), *N*-methylaniline (AR), K₂S₂O₈ (AR), H₂SO₄ (LR) and ethanol (LR) were used. Aqueous solutions were prepared using the double distilled water.

Synthesis of poly (N-methylaniline-CO-o-toluidine)

The copolymerization of *N*-methylaniline with *o*-toluidine was carried out by free radical chemical oxidative polymerization method using K₂S₂O₈ as an oxidant/initiator in H₂SO₄ solution (0.1 M).

N-Methylaniline (0.1 M) and *o*-toluidine (0.1 M) were mixed to precooled 0.1 M H₂SO₄ solution at 0-5 °C. An aqueous solution of K₂S₂O₈ (0.1 M) was added drop wise to the reaction mixture with constant stirring for 4-5 hour to ensure completion of the reaction mixture indicated the formation of polymer. This green precipitate so obtained was filtered and then washed repeatedly with distilled water and ethanol until the green colour of filtrate disappears. Now this precipitate was dried under dynamic vacuum at 60-80 °C for 8 hours. The five polymer samples were synthesized by using different feed ratio of the monomers *N*-methylaniline (100%, 80%, 60% and 40%) and *o*-toluidine (100%, 20%, 40% and 60%).

Results and Discussion

UV- Visible behaviour of copolymer

The UV-Visible analytical data were obtained using SYSTRONICS 2203 double beam spectrophotometer. The absorption bands of homo polymers and their corresponding copolymers are recorded in DMF solvents.

The visible absorption spectra of samples A-E are as shown in Figures 1-5. The absorption in the range 550-620 nm (Table 1) is due to the molecular exciton associated with

the quinine-dimine structure⁴⁰. The exciton band produced by the inter/intra chain charge transfer is due to an absorption from the HOMO band centered on the benzenoid units to the LUMO band centered on the quinonoid units⁴¹.

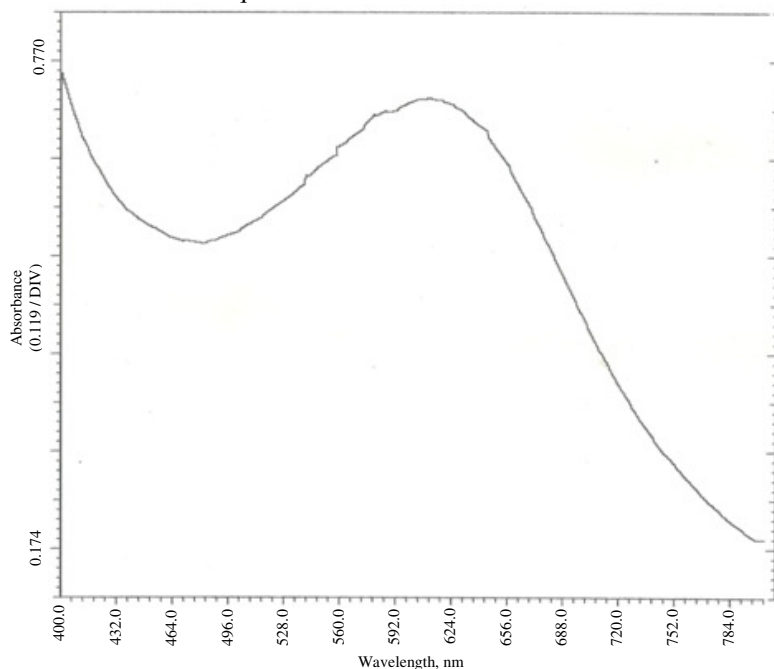


Figure 1. Visible spectrum of 100% PNMA (Sample A)

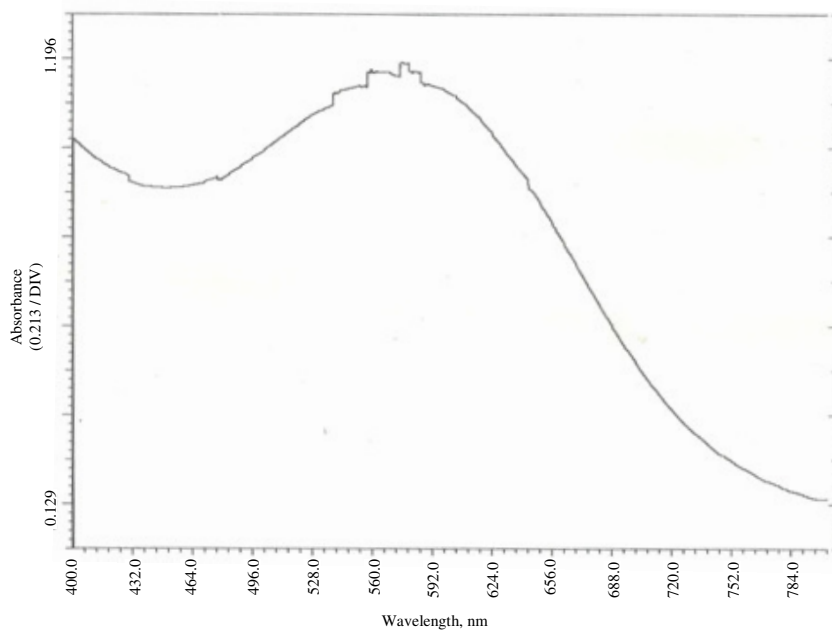


Figure 2. Visible spectrum of 100% POT (Sample B)

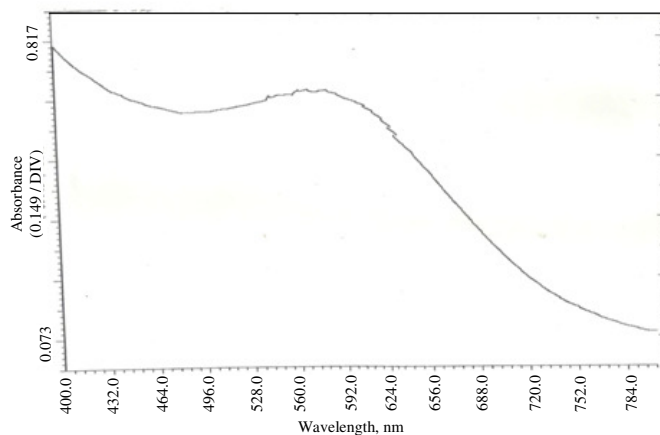


Figure 3. Visible spectrum of 80% PNMA 20% POT (Sample C)

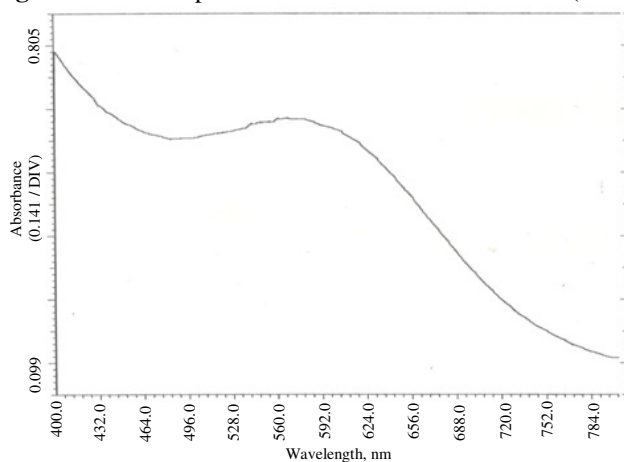


Figure 4. Visible spectrum of 60% PNMA 40% POT (Sample D)

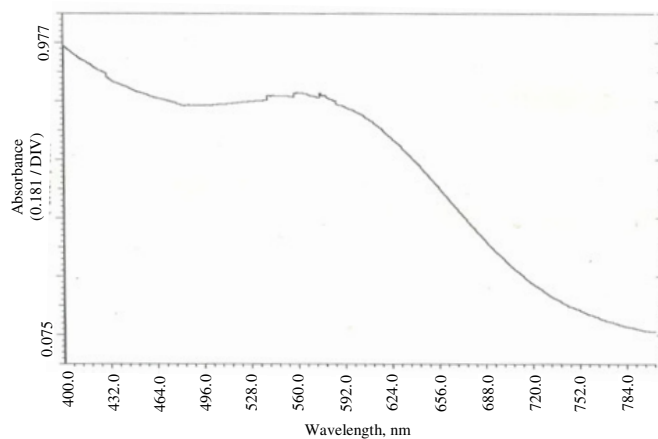


Figure 5. Visible spectrum of 40% PNMA 60% POT (Sample E)

Table 1. Absorption bands of copolymer in DMF

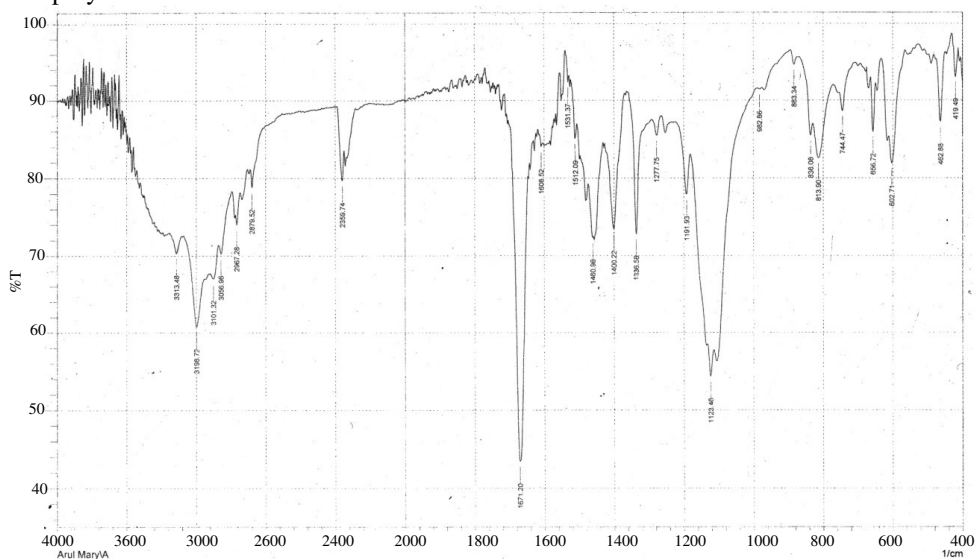
Polymer	λ_{max} , nm
100% PNMA (A)	612
100% POT (B)	580
80% PNMA and 20% POT (C)	573
60% PNMA and 40% POT (D)	565
40% PNMA and 60% P OT (E)	560

The absorption bands in copolymer samples shift to the lower wavelength (hypsochromic shift), which is attributed due to the increase in number of side groups, which alter the torsion angle and leading to decrease in conjugation length. The peaks gradually blue shifted as the *o*-toluidine ratio increased.

FTIR behaviour of copolymer

The FTIR spectra of poly (NMA-CO-OT) were recorded on SHIMADZU FTIR spectrophotometer in KBr pellets. The peak at 3300 cm^{-1} is due to the N-H stretching vibration of the imino groups from *N*-methylaniline and *o*-toluidine⁴². The peak observed at 2950 cm^{-1} is attributed to the aromatic C-H stretching. The characteristic peak at 2880 cm^{-1} represents the aliphatic C-H stretching vibration of CH_3 group. The peak observed at 1670 cm^{-1} is assigned for the bending vibration of the N-H bond. The 1590 cm^{-1} and 1485 cm^{-1} absorptions are characteristic of stretching bands of nitrogen quinonoid ($\text{N}=\text{Q}=\text{N}$) and benzenoid ($\text{N}-\text{B}-\text{N}$) respectively, the conducting state of the polymer.

Another characteristic band in the FTIR spectra for the acids doped PANI- derivatives is the $\text{C}=\text{N}^+$ stretching absorption of the QBQ (1400 cm^{-1}) which arises due to protonation of PANI-derivatives by dopant^{43,44}. The peak at 1325 cm^{-1} indicates the aromatic C-N stretching frequency⁴⁵. The absorption at 1120 cm^{-1} is due to the charge delocalization over the polymeric backbone. The band appearing at 815 cm^{-1} is characteristic of C-H-out of plane bending vibrations of the para substituted benzene ring and confirms the formation of the polymer⁴⁶.

**Figure 6.** FTIR Spectrum of 100% PNMA (A)

Even though many of the absorption peaks of homopolymers remain unchanged in copolymer, stark variations are noticed in quinanoid ring stretching, benzenoid ring stretching, aromatic C-N stretching, vibration band of dopant anion and the intensity which confirm unequivocally the formation of copolymers (Figures 6-10). The FTIR spectral data of poly (NMA-CO-OT) are summarized in Table 2.

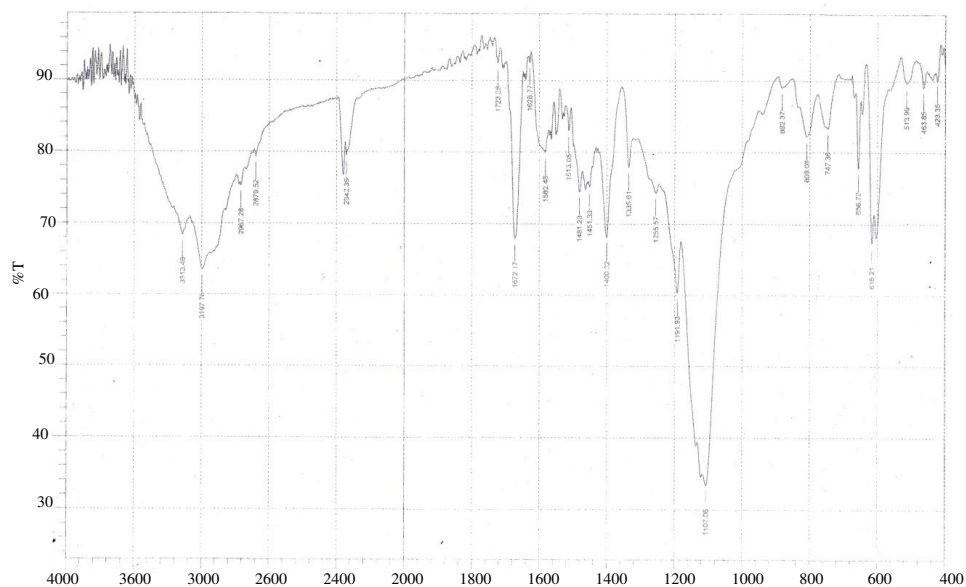


Figure 7. FTIR Spectrum of 100% POT (B)

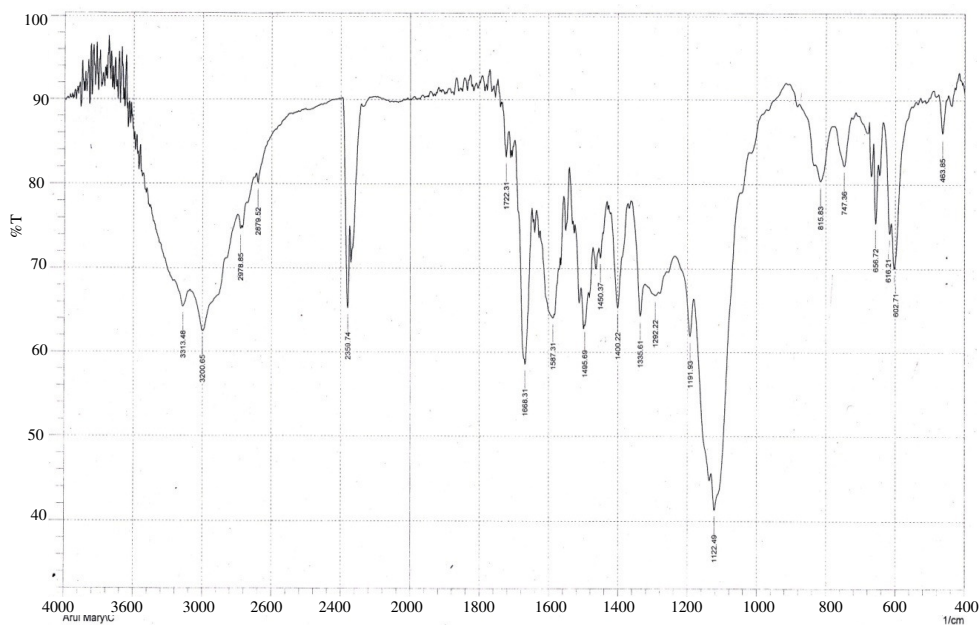


Figure 8. FTIR Spectrum of 80% PNMA 20% POT (C)

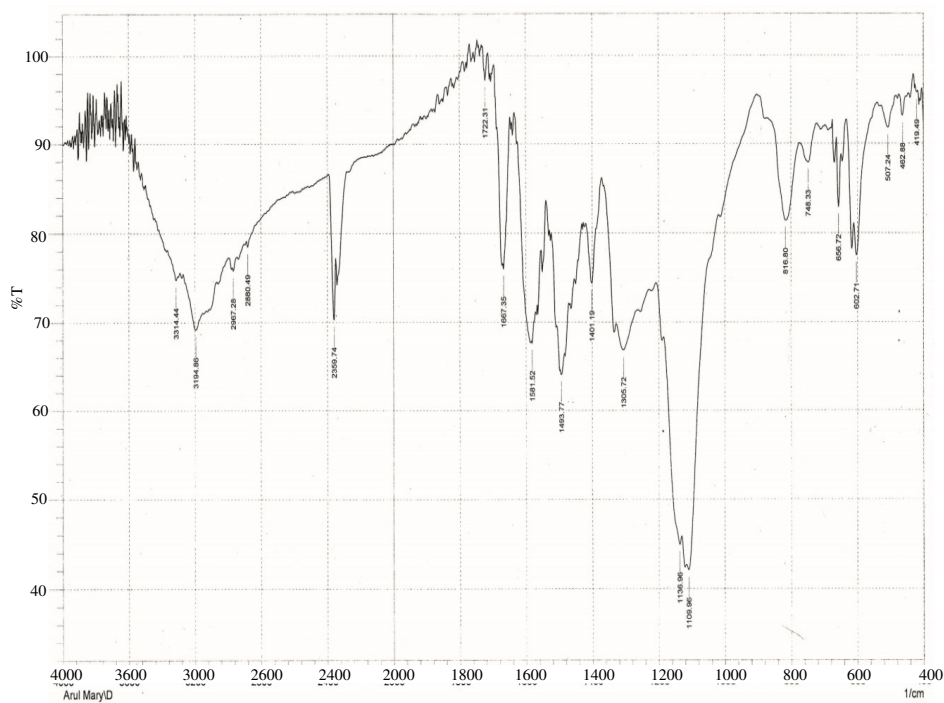


Figure 9. FTIR Spectrum of 60% PNMA 40% POT (D)

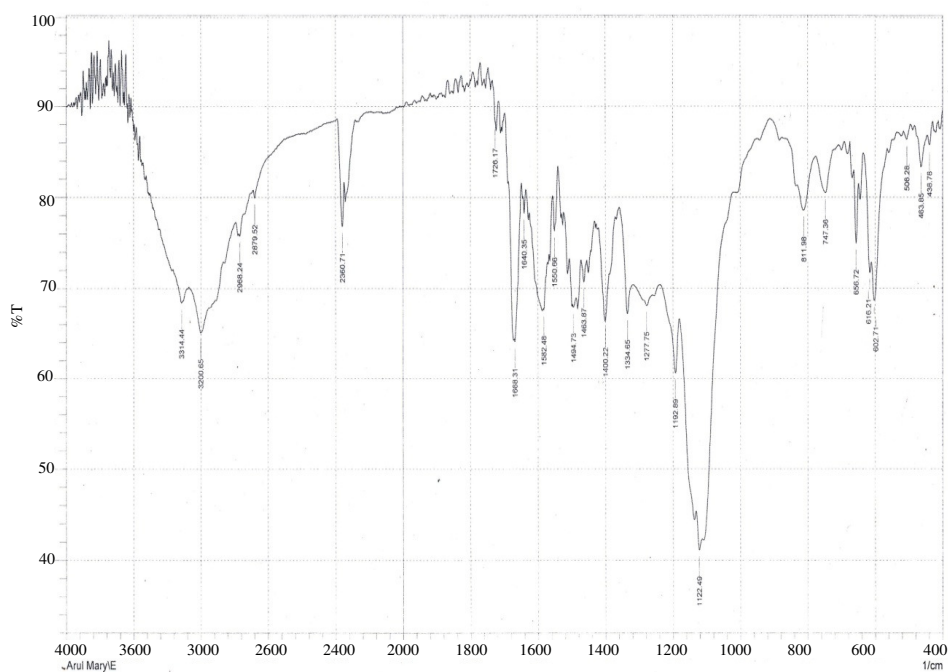


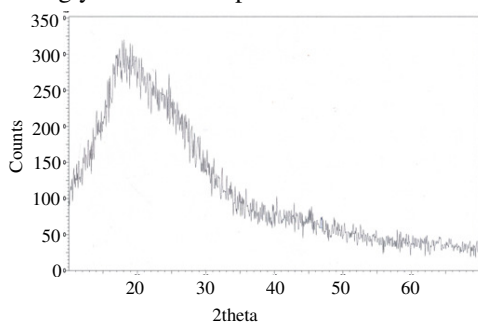
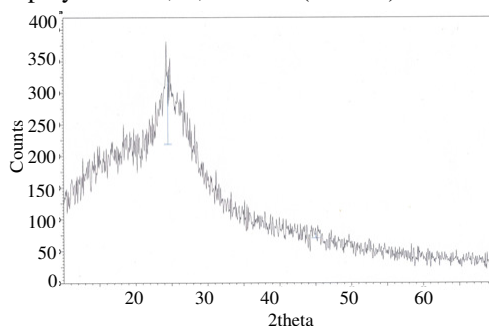
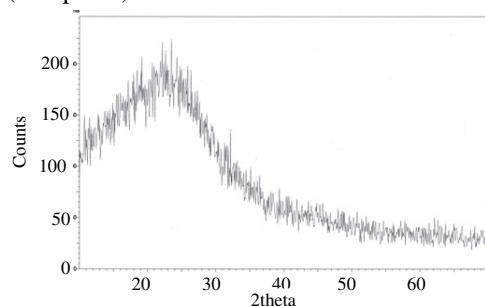
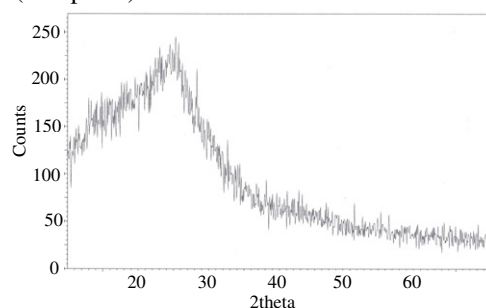
Figure 10. FTIR Spectrum of 40% PNMA 60% POT (E)

Table 2. FTIR data of copolymer

Vibrations	Wave number cm^{-1}				
	Sample A	Sample B	Sample C	Sample D	Sample E
N-H Stretching	3313	3313	3313	3314	3314
Aromatic C-H Stretching	2967	2967	2978	2967	2968
Aliphatic C-H Stretching	2879	2879	2879	2880	2879
Quinonoid ring stretching (N=Q=N)	1608	1582	1587	1581	1582
Benzenoid ring stretching (N-B-N)	1460	1481	1495	1493	1494
C=N ⁺ stretching (Protonation by dopant)	1400	1400	1400	1401	1400
Aromatic C-N Stretching	1336	1335	1335	1305	1334
Vibration band of dopant anion	1123	1107	1122	1109	1122
C-H out of plane bending (Para substituted benzene ring)	813	809	815	816	811

XRD behaviour of copolymer

X-ray diffraction studies were carried out using a PANalytical's X'pert PRO x-ray diffractometer with Cu $\text{k}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The x-ray diffraction pattern for the copolymer (Figures 11-15) is obtained from using various percentage of NMA and OT. The XRD behaviour of A, B, C and E samples exhibit less crystalline nature. XRD pattern of D sample does not show sharp peak characteristic of crystalline material and suggest generally an amorphous nature. The particle size calculated from XRD studies using Scherrer's formula strongly indicates the presence of nano structured polymer in A, B, C and E (Table 3).

**Figure 11.** XRD behaviour of 100% PNMA (Sample A)**Figure 12.** XRD behaviour of 100% POT (Sample B)**Figure 13.** XRD behavior of 80% PNMA 20% POT (Sample C)**Figure 14.** XRD behaviour of 60% PNMA 40% POT (Sample D)

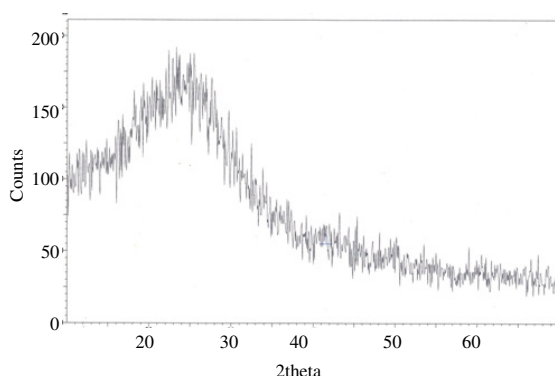


Figure 15. XRD behaviour of 40% PNMA 60% POT (Sample E)

Table 3. XRD data and particle size

Polymer/ Copolymer	Angle (2θ)	Height (counts)	FWHM (2θ)	d-spacing Å ^o	Particle size nm
A	46.8389	14.65	0.4010	1.9380	22.60
B	24.5246	108.10	1.0695	3.6267	7.94
C	44.1560	8.17	0.4010	2.0493	22.34
D	-	-	-	-	-
E	41.5395	7.03	1.6042	2.1721	5.53

In the sample D, the intermolecular chain spacing and amorphous nature increase due to steric hindrance of methyl group. The characteristic distance between the planes of benzene rings in adjacent planes⁴⁷ (d-space), and is also said to be the interchain distance are affected by the size and shape of the interlying dopants which result in an increase in electron delocalization length and conductivity on higher d-space^{48,49}.

Conductivity studies of copolymer

The electrical conductivity is measured, using two probe method and the results are summarized in Table 4. Conductivity calculated is based on the average of five pairs of consistent readings taken at different points on the pressed pellets.

Table 4. Conductivity of copolymer

Polymers	Conductivity Scm ⁻¹
Sample A	6.968x10 ⁻⁵
Sample B	1.273x10 ⁻³
Sample C	1.158x10 ⁻⁴
Sample D	5.932x10 ⁻³
Sample E	5.467x10 ⁻⁴

Length of conjugation, doping level and d-space play a vital role in increase of conductivity⁵⁰. Conductivity is high in the amorphous D sample. The increase in hole mobility for the amorphous conducting polymers^{51,52}. The conductivity is high in B when the d-space is high, but less than that of D. The observed order of conductivity is D>B>E>C>A.

Conclusion

The copolymerization of *N*-methylaniline and *o*-toluidine have been carried out by chemical polymerization method in sulphuric acid medium. The UV visible and FTIR spectroscopical

studies confirm the formation of copolymers. XRD analysis of 100% PNMA, 100% POT, 80% PNMA 20% POT and 40% PNMA 60% POT reveal their less crystalline nature and the particle size in the order of nanometer. 60% PNMA 40% POT exhibits amorphous nature and intermolecular chain spacing increases due to steric hindrance of methyl group. The copolymer 60% PNMA 40% POT has the highest conductivity. Copolymerization could lead to innovation in synthetic method for better conducting polymers.

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