http://www.e-journals.in
DOI:10.7598/cst2015.1008

Chemical Science Transactions
2015, **4(2),** 620-628

RESEARCH ARTICLE

Chemical Synthesis and Characterization of Poly(phenylhydrazine-*co*-4,4′-diaminodiphenyl Sulphone)

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Received 15 December 2014 / Accepted 29 December 2014

Abstract: A new copolymer with nanostructure was chemically synthesized using an oxidizing agent between phenyl hydrazine hydrochloride (PH.HCl) and biologically active 4,4′-diaminodiphenyl sulfone (DADPS). The copolymer showed considerable solubility in common organic solvents such as chloroform, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF). The copolymer showed electrical conductivity of 2.14×10^{-2} S cm^{-1}. The copolymer formation between these two monomers was confirmed by Fourier Transformation IR, ^{1}H NMR spectral studies, X-ray diffraction studies and scanning electron microscopic (SEM) data. The UV-Visible spectrum also showed the presence of benzene and NH units in the copolymer.

Keywords: Copolymer, Phenyl hydrazine, FTIR, NMR, XRD, SEM

Introduction

Copolymerization is a simple way of preparation for new polymers which greatly increases the scope of tailor-making materials with specifically desired properties[1]. Polyaniline is widely used as materials in electrochemical devices such as lightweight batteries, light-emitting diodes (LEDs)[2], optical and electronic devices[3], capacitors[4], electrochromic devices[5,6], *etc*. Polyaniline has high conductivity[7] at ambient temperatures. The insolubility of polyaniline in common solvents is its great disadvantage. Introduction of alkyl substituents in the benzene ring increased its solubility[8]. The addition of anions as dopant and copolymerization with other monomers improved the solubility. Recently great attention has been paid to synthesize aniline based copolymers. The conductivity of self-doped polyaniline synthesized by chemical copolymerization of aniline with *o*-amino benzenesulfonic acid was reported to depend on pH 0 to pH 3[9].

The self-doped sulfonated polyaniline was prepared chemically through the copolymerization of *p*-aminodiphenylamine with *o*-aminobenzenesulfonic acid[10]. The chemical copolymerization of aniline with *N*-methylaniline, *N*-butylaniline and 2-(4-aminophenyl)-6-methylbenzothiozole have also been reported[11, 12]. Lukachova *et al.* reported the chemical copolymerization of aniline with *m*-aminobenzenesulfonic acid using ammonium persulfate as the oxidant[13]. The copolymer prepared in this manner showed improvements in solubility, conductivity and stability in organic solvents[14]. Copolymers of aniline and 3-aminophenol derivatives with oligo(oxyethylene) side chains as novel water soluble conducting polymers were reported[15]. The phenyl-substituted and *N*-substituted copolymers of polyaniline with disordered structure exhibited better solubility and decreased conductivity[16-18].

Usage of materials with biological importance for the preparation of newer polymeric compounds assumes importance in the present environment[19]. Aligned or ordered, otherwise called poled polyurea sulfone thin films having excellent transparency from near UV to visible region were prepared by carrying out additional polymerization of 1,4-phenylene diisocyanate and 4,4′-diaminodiphenyl sulfone simultaneously. Electrochemically synthesized copolymer of aniline (ANI) and 4,4′-diaminodiphenyl sulfone (DADPS)[20] exhibited novel electrochromic properties. Copolymers of diphenylamine (DPA) and 4-aminodiphenylamine (ADPA) with 4,4′-diaminodiphenyl sulfone (DADPS) were prepared[21,22] characterized and their electrochromic properties also evaluated.

In this article, the chemical copolymerization of phenyl hydrazine (PH) with 4,4′-diaminodiphenyl sulfone (DADPS) using an oxidizing agent is presented. Solubility of the copolymers in various organic solvents and conductivities were studied. The copolymer formation was supported by FTIR, ^{1}H NMR, UV-visible spectra, XRD and SEM studies and the results are discussed.

Experimental

Reagent grade phenyl hydrazine hydrochloride (E-Merck) and potassium persulphate (E-Merck) were used as received. The other monomer 4,4′-diaminodiphenyl sulfone (DADPS) was synthesized[23] by reacting thionyl chloride (reagent grade obtained from Zigma-Aldrich) with acetanilide (reagent grade obtained from Zigma-Aldrich), followed by oxidation to the sulfone with CrO_3 (reagent grade obtained from Zigma-Aldrich). DADPS was then recrystallized to white crystals (m.p. 178 – 179 °C) using ethanol. All solutions were prepared using ultra pure double distilled water.

Chemical polymerization

Phenyl hydrazine hydrochloride (PH.HCl) with 4,4′-diaminodiphenyl sulfone (DADPS) was polymerized by chemical oxidative method, using potassium persulphate as oxidizing agent in 1 M HCl medium. DADPS of 0.05 M with 0.05 M of PH.HCl in 250 mL of 1 M HCl having 15 g of potassium persulphate were stirred for 30 min in an ice bath by controlling the temperature between 0±5 °C. After stirring for 10 h at room temperature, the polymer was precipitated with ammonia, centrifuged repeatedly, washed with ultrapure water followed by methanol and dried in vacuum at about 45 °C for more than 12 h.

Characterization of chemically synthesized copolymer

The solubility of copolymer, poly(phenyl hydrazine-*co*-4,4′-diaminodiphenyl sulfone) was tested in various organic solvents. The conductivity of this poly(PH-*co*-DADPS) was observed using four probe conductivity meter on pressed polymer pellets. UV-visible spectral studies were performed in a quartz cuvette with a path length of 1 cm utilizing a computer controlled JASCO V-530 UV-Visible spectrophotometer. The synthesized copolymer was characterized by FTIR spectral data recorded using KBr-copolymer pellets on a SHIMADZU 8400S spectrophotometer. The polymers also characterized by ^{1}H NMR data obtained using BRUKER 300 MHz NMR spectrometer. The surface morphology of the polymer films was studied utilizing SEM images obtained from a Hitachi S3000 H SEM instrument. The grain size of the copolymer was measured using XRD data obtained from an XRERT PRO PANALYTICAL instrument using Cu K_α radiation with $\lambda = 1.5418$ Å.

Results and Discussion

Solubility of copolymers

The solubility of the copolymer was tested with various organic solvents. The copolymer, poly(PH-*co*-DADPS) showed considerable solubility in dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), tetrahydro furan (THF) and chloroform. The presence of amino groups as a side chain in the back bone of polymer may render the solubility in most of organic solvents.

Conductivity studies of copolymers

The electrical conductivity of pressed pellets of copolymer was measured, through four probe conductivity meter and it showed the conductivity of 2.14×10^{-2} S cm^{-1}. Compared to the conductivity of poly(4,4′-diaminodiphenyl sulfone)[19] slightly higher values are found for this copolymer.

FTIR spectral behavior of copolymers

FTIR spectral studies of the copolymers and homopolymers were carried out. The FTIR spectrum of poly4,4′-diaminodiphenyl sulfone (PDADPS) was already discussed[21]. In Figure 1, (A) and (B) represented the FTIR spectra of polyphenylhydrazine (PPH) and poly(PH-*co*-DADPS) respectively. The vibrational frequencies observed for PDAPS and PPH along with that of copolymer, P(PH-*co*-DADPS) were presented in Table 1.

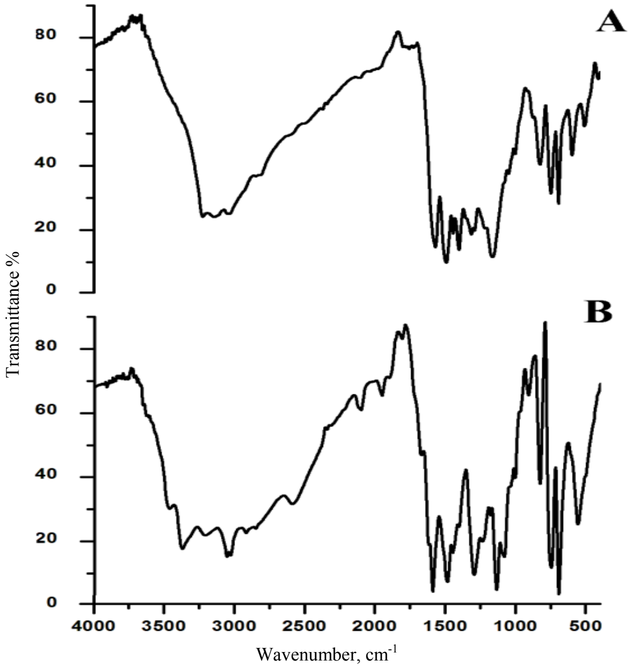
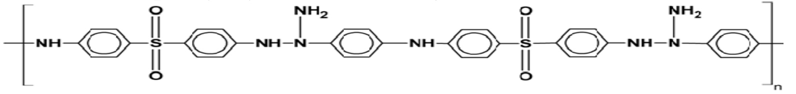


Figure 1. FTIR spectrum of (A) PPH and (B) P(PH-*co*-DADPS)

Table 1. FTIR Spectral data of PDADS, PPH and P(PH-*co*-DADPS)

Modes of vibrations	Expected wave number, cm^{-1}	Observed wave number, cm^{-1}		
		Homopolymers		Copolymer
		PDAPS	PPH	P(PH-*co*-DADPS)
Secondary $(N\text{-}H)_s$	3300-3400	3369	3225	3373
Secondary $(N\text{-}H)_b$	1550-1650	1627	-	-
$(N\text{-}H)_s$ of NH_2 group	3400-3500	3464	-	3464
$(N\text{-}N)_s$	1050	1015	1001	1084
$(N\text{-}N)_b$	660	648	597	696
$(N{=}N)_s$	1575-1630	1591	1570	1593
$(C{=}C)_s$	1400-1600	1427	1402	1448
$(C\text{-}N)_s$	1000-1250	1149	1163	1138
(C-H) in plane bending	1000-1300	1103	1049	1138
(C-H) out of plane bending	690-900	686	694	748
(C-H) out of plane bending of 1,4-disubstituted benzene ring	800-850	837	823	829
$(S{=}O)_s$	~1300	1302	-	1298

The presence of secondary N-H stretching frequency of PDADPS, PPH and P(PH-*co*-DADPS) at 3369, 3225 and 3373 cm^{-1} respectively confirmed the -NH- units in the polymer chain. The frequency of 3464 cm^{-1} corresponding to the N-H stretching of NH_2 group was observed for P(PH-*co*-DADPS) showed that this copolymer contain $-NH_2$ units in its back bone. The N-N stretching frequencies[24] are clearly observed at 1015, 1001 and 1084 cm^{-1} for PDADPS, PPH and P(PH-*co*-DADPS) respectively. Therefore it was supported that during homo and copolymerization processes the aromatic benzene rings of DADPS and PH are inter connected by -N-N- linkages. Further the presence of sulfone group in the copolymer was evidenced by a sharp peak at 1298 cm^{-1} due to S=O stretching vibration. The presence of free $-NH_2$ group and -N-N- linkages in the copolymer, P(PH-*co*-DADPS) by the IR spectra claimed that the phenyl hydrazine must be joined to DADPS as shown in Scheme 1.



Scheme 1. Proposed Structure of poly(PH-*co*-DADPS)

^1H *NMR spectral studies of copolymers*

The proton NMR spectra for PPH and P(PH-*co*-DADPS) dissolved in $CDCl_3$ are presented in Figures 2 and 3 respectively. The ^1H NMR spectrum of PDADPS was already reported and discussed[21]. A broad peak at 4.8 ppm was noticed in the ^1H NMR spectrum of PPH given in Figure 2 and this correspond to the NH protons that might seen in the intermediate positions between various benzene units of polymer chain. The signals of aromatic (benzene/quinone) protons of PPH were observed as a multiplet between 7.030 to 7.947 ppm[25]. A small peak seen at 8.7 ppm was due to $N{=}NH^+$ protons of PPH in its polaronic / bipolaronic forms as given in Scheme 2.

The proton NMR spectrum of copolymer, P(PH-*co*-DPA) given in Figure 3 showed a group of three multiplet peaks between 7.221 to 7.758 ppm. These peaks were due to three different types of benzenoid/quinoid protons as seen in the Scheme 3 belong to both PH and DADPS monomer units in the polymer back bone.

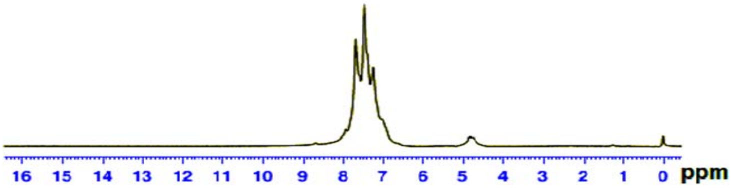


Figure 2. ^1H NMR spectrum of polyphenyl hydrazine in $CDCl_3$

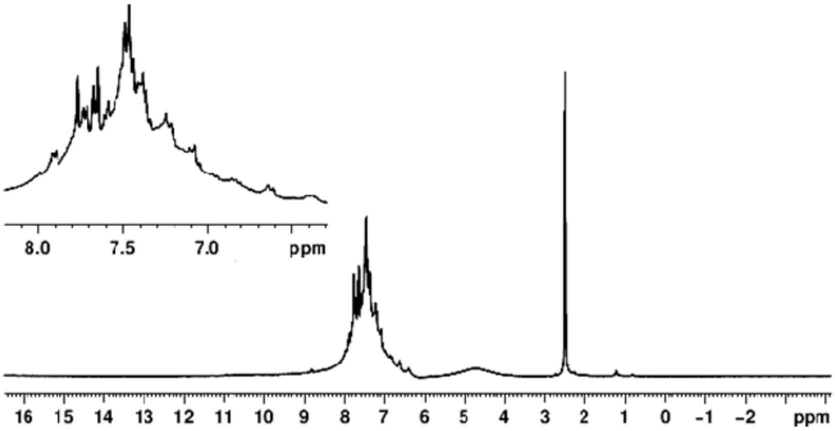
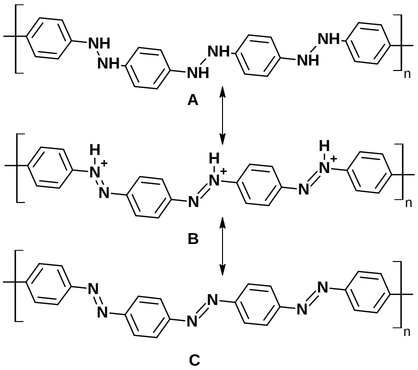
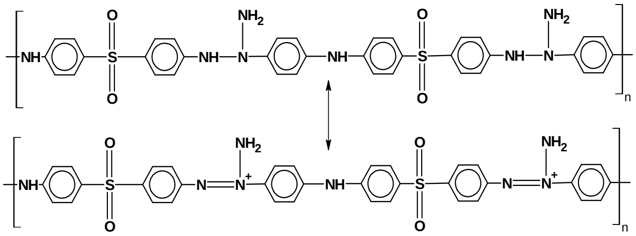


Figure 3. ^1H NMR spectrum of poly(phenylhydrazine-*co*-4,4’-diaminodiphenyl sulfone) in $CDCl_3$.



Scheme 2. (A) Reduced PPH, (B) polaronic/bipolaronic PPH and (C) Oxidized PPH

The signals for two types of NH protons as seen in the Scheme 3 were appearing at 7.155 and 7.081 ppm. The $–NH_2$ protons present as a side chain on the polymer gave its signal at 4.8 ppm as a broad peak. Most of the coupling constants measured for these proton signals existing between 6 and 10 Hz and this fact confirmed the coupling between ortho protons of benzene ring. This is possible only in the case of para disubstituted benzene rings. Thus most of the benzene units present in the polymer chain were 1,4-disubstituted and the structure for poly(PH-*co*-DADPS) as proposed in the above Scheme 3 was supported. The signals for $–NH_2$ protons attached to $-N=N^+-$ unit of the copolymer as shown in one of the resonance form of Scheme 3 were appeared at 8.9 ppm.



Scheme 3. Proposed structure for poly(PH-*co*-DADPS)

XRD studies of copolymers

The crystalline regions in the copolymers are shown by the presence of relatively sharp peaks. The amorphous regions are visible by the broad low intensity peaks. X-ray diffraction profile of the PPH and P(PH-*co*-DADPS) are shown as A and B in Figure 4. The XRD profile of PDAPPS was already discussed[21]. The homopolymer PPH showed lesser amorphous and more crystalline nature obviously due to the presence of sharp peaks. The XRD pattern of P(PH-*co*-DADPS) indicated substantial increase in degree of amorphous nature evidenced the formation of copolymer. The particle size[26-28] of homopolymer and copolymer were calculated from XRD studies using the Scherrer's formula as follows.

$$\text{Grain size} = \frac{K\lambda}{FW\cos\theta}$$

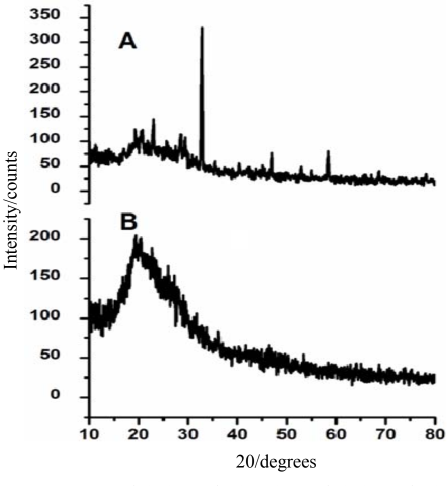


Figure 4. XRD pattern of (A) Poly(PH) and (B) Poly(PH-*co*-DADPS)

Where K is the shape factor of the average particle (expected to be 0.94), λ is the wave length (usually 1.5418 A°), θ is the peak position and FW is the full width at half maximum. Using this formula the grain sizes of PPH and P(PH-*co*-DADPS) were found to be 97 and 98 nm respectively. These facts evidenced the presence of nano structured copolymers.

SEM Behaviour of copolymers

Chemically copolymerized materials were characterized by scanning electron microscopic (SEM) analysis. SEM photographs of chemically synthesized homopolymers, PDADPS and PPH are presented in Figures 5 and 6 respectively. The SEM image of PDADPS appeared like a gathering of dried leaves while that of PPH showed spongy buds like structure in the micro meter scales respectively. The copolymer formed given in Figure 7 showed different structures in the form of scaled tiles like arrangement. This fact provides concrete evidence that newer polymeric materials are formed between the monomers and PH and DADPS.

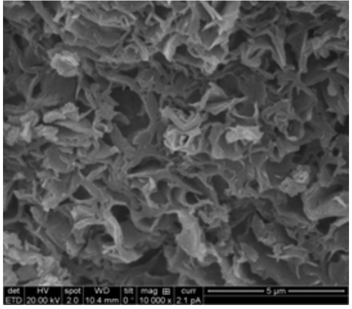


Figure 5. Scanning electron microscope photograph of PDADPS surface

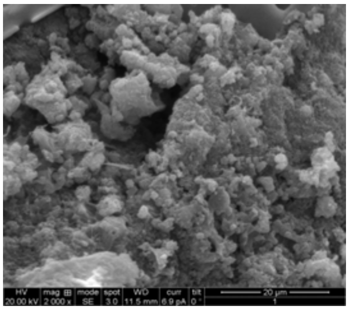


Figure 6. Scanning electron microscope photograph of PPH surface

UV-VIS spectra of copolymers

The UV-Visible spectral studies were carried out for copolymer, poly(PH-*co*-DADPS) in DMF and the spectrum was shown in Figure 8. Peaks with wavelength maximum at 280 and 350 nm were observed for the copolymer in DMF. These peaks may be associated with $\pi-\pi^*$ transition and conjugated benzenoid rings. This confirmed the presence of benzene rings in poly(PH-*co*-DADPS) as in phenylhydrazine and 4,4′-diaminodiphenyl sulfone. Another absorption band observed at 550 nm in copolymer was due to the polaron/bipolaron band transition. This band may be responsible for the dark brown color of the copolymer.

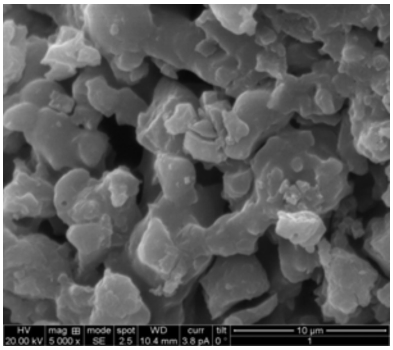


Figure 7. Scanning electron microscope photograph of P(PH-*co*-DADPS) surface

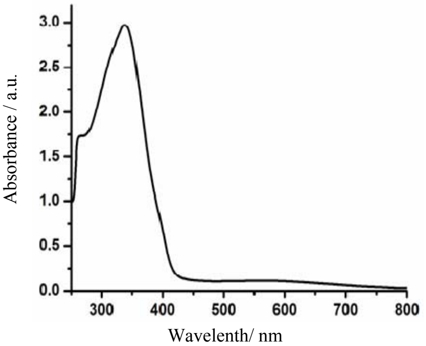


Figure 8. The UV-visible spectrum of poly(DPA-*co*-PH) in DMF

Conclusion

The various methods of characterization on the copolymers of phenyl hydrazine (PH) and 4,4′-diaminodiphenyl sulfone synthesized using an oxidizing agent have been explained. Characterization of the copolymers by this host of techniques supports their copolymerization. These copolymers exhibited conductivity as well as solubility in common organic solvents. The copolymer formation and characteristics of functional groups were confirmed through FTIR and proton NMR spectral studies. The surface morphology and grain size were understood from SEM experiments. The XRD studies also evidenced the formation of micro sized copolymers.

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