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SYNTHESIS AND CHARACTERIZATION STUDIES OF ORGANICALLY SOLUBLE ACRYLIC ACID DOPED POLYDIPHENYLAMINE

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Abstract. Polydiphenylamine (PDPA) doped with acrylic acid was synthesized by oxidative chemical polymerization. This is a new chemical polymerization method developed for the direct synthesis of emeraldine salt form of polydiphenylamine which exhibits remarkably improved solubility in a common organic solvent. These polymers have been characterized by the physical techniques such as UV-visible, FTIR, XRD and conductivity measurement. The results are discussed with reference to the H₂SO₄ doped polydiphenylamine. The use of functionalized acrylic acid (AA) made it possible to obtain the polymer in doped state with enhanced solubility in organic solvent such as N-methyl pyrrolidinone (NMP) and *m*-cresol directly without converting to emeraldine base form. The UV-visible spectra of acrylic acid doped PDPA in *m*-cresol showed a free carrier tail commencing at 950 nm, which may be attributed to secondary doping due to extended coil conformation. Whereas in NMP spectra excitonic peak at ~ 320 nm and 610 nm typical for emeraldine base form indicates that NMP dose hinders the doping ability of dopant. The FTIR spectra shows a broad and intense band at ~ 3400 cm⁻¹ and 1150–1050 cm⁻¹ in acrylic acid doped PDPA account for the higher doping level than H₂SO₄ doped polydiphenylamine polymers. This is further manifested by the X-ray studies and conductivity measurement. The X-ray diffractograms of acrylic acid doped polymer show an enhancement in the crystallinity indicating better ordered chain alignment. These results are well supported by the conductivity measurements, where the conductivity of acrylic acid doped polymers is greater than that of H₂SO₄ doped polymers.

Key words: polydiphenylamine, functionalized dopant, solubility, crystallinity, conductivity.

1. Introduction

The field of conducting polymers has been flourishing rapidly day by day and these materials are

becoming indispensable for next century. Many industries are already basing market of their products on conducting polymers [1-3]. Polyaniline and its substituted derivatives have attracted much attention in the recent years because of their electronic, electrochemical, and optical properties and especially because of their proper environment and thermal stability [2, 3]. These materials have a considerable potential for commercial application in electronics, batteries, solar energy conversion, chemical sensors, corrosion resistance, *etc.* However, major problems relating to the successful utilization of conducting polymers lies in its poor mechanical properties and processibility due to its insolubility in a common organic solvent. Recently much effort has been made to improve both these aspects [4-7] of route of chemical synthesis method and the use of functional dopant is made more attractive, as it eliminates the use of volatile dopant. More recently, synthetic routes have been developed for polymers by introducing substituents [7, 8] or using a functional dopant [9-12]. The incorporation of a functional dopant in electronically conducting polymer is found to enhance its solubility processibility and conductivity that can be attributed to the conformational changes to the polymer chains. Another important chemical modification has been the addition of alkyl, alkoxy or aromatic substituents to the polymer backbone [4, 5]. This approach has been successfully applied to solubilize the intractable conducting polymer with substituents. These polymers exhibit interesting thermal and morphological properties in the solid state. From the viewpoint of this aspect we have synthesized conducting acrylic acid doped polydiphenylamine, which provides improved electrical and optical as well as solubility and solid state properties. In this paper, the chemical synthesis of novel acrylic acid and H₂SO₄ doped polydiphenylamine is described. This reaction is unique, since the polymer obtained has maximum solubility in a common organic solvent directly without the need for a post doping process step, which involves:

i) neutralization of emeraldine salt to form emeraldine base and ii) secondary doping of the base with a secondary protonic acid. However research has been carried out on structural feature of the acrylic acid doped PDPA in comparison with the doped PDPA.

2. Experimental

All chemical used were of analytical reagent grade. The monomer diphenylamine (Qualigens), ammonium persulphate (Qualigens), and H_2SO_4 reagent grade (Qualigens) were used as received. Water used in this investigation was double distilled water. General method of synthesis of these conducting polymers involves the chemical oxidation reaction of monomer diphenylamine. The acrylic acid doped polymer was synthesized as *in situ* oxidative polymerization after addition of 0.4 ml of acrylic acid to the reaction mixture maintained at 273 to 278 K. The H_2SO_4 was used as a protonic acid. The monomer to oxidizing agent ratio was kept as 1:1. Ammonium peroxide sulphate solution prepared in double distilled water was added dropwise to the reaction mixture over a period of one hour under constant stirring. After complete addition of the oxidant the reaction was kept under stirring for 24 h. The precipitated polymer salt was recovered from the reaction vessel by filtration and washing followed by drying at 333–343 K for 24 h. A similar procedure was employed for synthesis of polydiphenylamine without acrylic acid media. The synthesized polymers were characterized by using various analytical techniques. UV-visible absorption spectra of these polymers solution in H_2SO_4 , *m*-cresol and NMP were recorded on a UV-vis double beam spectrophotometer (λ -20) in the range of 300–1000 nm. Fourier-transform infrared spectra (FTIR) of the polymer samples in the range of 400–4000 cm^{-1} were recorded on a Perking-Elmer 1600 spectrometer. Measurements of wide-angle X-ray diffraction were taken on a Philips X-ray diffractometer using $CuK\alpha$ radiation source ($\lambda = 1.542$ nm). The scan range (2θ) was 5–50° and the scanning was performed at the rate of 2°·min⁻¹. Conductivity measurements were made on compressed pellets of the powder of the polymer sample using two-probe method at room temperature.

3. Results and Discussion

3.1. Optical Properties of Polymer

Optical properties have played a key role in the elucidation of the basic electronic structure and solution properties of the conducting polymers. The UV-vis spectra of the polymer doped with acrylic acid and that

doped with H_2SO_4 were recorded by dissolving these polymers (5 % w/v) in 50% H_2SO_4 , *m*-cresol and NMP and are represented in Fig. 1. The spectral features reveal the enhanced solubility of the acrylic acid doped polymer in comparison with the H_2SO_4 doped polymer in each solvent. This can be attributed to the presence of greater number of charges on the polymer chain in the acrylic acid doped polydiphenylamine leading to a higher degree of solvation of the polymer due to hydrogen bonding between the solvent and the polymer chains [13–15]. Consequently, the compact coil structure of the polymer would undergo transition to an expanded coil or linear structure [14]. Also, in the presence of a large number of charged centers the electrostatic repulsion between the similar charged units over the polymer chain would be greater in the polymer and it would increase as the distance between the charged units on the polymer chain and its counter ion increases.

Furthermore, one can note that the optical spectra of the polymer show appreciable changes in 50% H_2SO_4 , *m*-cresol and NMP. In H_2SO_4 solvent (Fig.1a) acrylic acid doped polymer exhibits a sharp

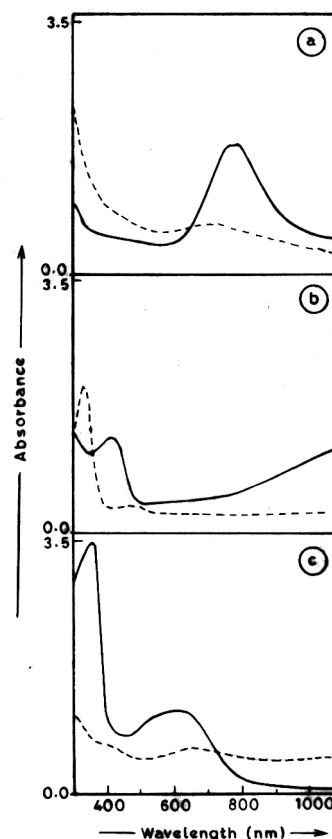


Fig. 1. UV-visible spectra of polydiphenylamine doped in acrylic acid (—) and H_2SO_4 (---): H_2SO_4 media (a); *m*-cresol media (b) and NMP media (c)

peak ~ 700 nm representing the conducting emeraldine salt phase of the polymer. The shoulder at ~ 320 and 420 nm corresponds to the electronic transition within the benzenoid segment and the protonation of polydiphenylamine polymer chains respectively [15-17]. The overall peak intensity of the H_2SO_4 doped polymer is less than acrylic acid doped PDPA, which accounts for the presence of greater fraction of quinoid phase form indicating the presence of mixed phases. The spectral nature is found to differ when spectra was compared in different organic solvent implying the influence of solvent on the polymer properties as seen in Fig. 1b.

In *m*-cresol solvent, the acrylic acid doped polymer exhibits a shoulder ~ 320 nm and a broad intense peak ~ 415 nm with an extended free carrier tail characteristic of an extended coil conformation with increasing absorbance ~ 800 - 1000 nm [14-17]. The shoulder ~ 320 nm is typical for the transition of the benzene ring, while the sharp intense peak ~ 415 nm corresponds to the localized polarons which are characteristic of the protonated emeraldine salt form. The presence of free carrier tail absorption indicates that the polymer backbone adopts an expanded conformation allowing increased conjugation. It is observed that doping of acrylic acid doped PDPA is more efficient in *m*-cresol than H_2SO_4 doped PDPA. Further, the extended tail at higher wavelength depicts that *m*-cresol not only serves as a solvent but also as an efficient secondary dopant [15, 16]. In comparison with the absorption spectra of acrylic acid doped PDPA, the intensity of the peak at ~ 313 and ~ 800 nm of H_2SO_4 doped PDPA are significantly lower. This can probably be attributed to the lower doping level and the lower electron density in the polymer backbone. The optical absorptions of these polymers are also varied by the change of the solvent system. Fig. 1c shows the UV-visible spectra of acrylic acid and H_2SO_4 doped PDPA in NMP solvent. In the presence of NMP solvent the absorption maximum at ~ 850 nm along with free carrier tail absorption and ~ 420 nm (polaron peak) is seen to disappear while a sharp peak is observed: ~ 620 nm and ~ 320 nm. The absorption at ~ 322 nm is ascribed to the transition of the benzenoid rings at ~ 600 nm, which is assigned to exciton absorption of the quinoid rings. This reflects the solvent effect on the polymer properties. NMP is a highly polar solvent ($\epsilon = 32$), so the solvent-solute interaction would be stronger than that in *m*-cresol medium. The C=O group present in NMP molecule would try to form a hydrogen bond with the H of the COOH group of dopant or those present the N atoms of the polymer chain. This, in turn, would bring about deprotonation of the polymer chain resulting in the conversion of conducting salt phase into insulating emeraldine base form of the polymer in

addition to the coiling up of the polymer chain. Therefore, one observes a sharp peak at ~ 600 nm, while the peak representing the polarons is weaker along with the weak absorbance at higher wavelength [12-15].

3.2. FTIR Spectra

The infrared spectra of H_2SO_4 and acrylic acid doped polymers are shown in Fig. 2 and the peak locations related to corresponding chemical bonds are summarized in Table 1. However, a remarkable difference is observed in the spectra in terms of specific bonds and shifts in the two polymers. The key bands in salt form match well with those reported in the literature [15-20]. The broad and intense band at ~ 3400 - 3300 cm^{-1} with a shoulder around 2920 cm^{-1} and ~ 1170 , 1000 cm^{-1} in acrylic acid doped polymer accounts for the higher degree of doping and protonation of amine and imine nitrogens [16-18]. Interestingly, the peak intensities at ~ 1025 cm^{-1} and ~ 630 cm^{-1} increase in the acrylic acid doped polymer, which confirms that acrylic acid doped polymer were effectively doped by dopant than H_2SO_4 doped PDPA. These bands appearing in H_2SO_4 doped PDPA become relatively sharp and narrow indicating lower degree of protonation and doping [19-20]. However, both of the polymers exist in conductive form. This can be attributed to breaking up of a large number of inter-chain hydrogen bonds that arise due to the addition of acrylic acid since it acts as pseudo-protonic acid dopant and coordinates with the imine N-atom of the polymer chain [17-20]. Stronger mutual interaction between the functional dopant and polymer may allow the two polymer chains to have their positions in space closer to each other and to result in more efficient doping of the PDPA. This leads to disaggregation of the polymer chains and hence the expanded coil structure and crystallinity. Moreover, the absorption band clearly observed in acrylic acid doped PDPA ranging at ~ 2500 cm^{-1} are assigned to the vibration associated with stretching vibration of protonated amine and imine N atoms [19-20]. These are relatively weak in doped PDPA polymer. In addition to this, the acrylic acid doped polymer shows a peak ~ 1620 cm^{-1} in which there could be convolution of a bending vibration of the water molecule and the asymmetrical stretching of the carboxylate group ($-\text{COO}$) resulting from the acid base reaction between acrylic acid and polymer. The interaction bands at 1238 and 1415 cm^{-1} for C-O stretching and C-OH in plane bending reveal the presence of free acrylic acid in the polymer matrix. Strong bands due to different stretching modes of benzene rings are located at 1595 and 1500 cm^{-1} in H_2SO_4 doped PDPA polymer. Furthermore, in acrylic acid doped PDPA these bands are seen to be broadened and shifted to lower wave number: ~ 1558 and 1492 cm^{-1} . The bands at ~ 1300

and $\sim 1250\text{ cm}^{-1}$ are attributed to the C–N stretching and deformation modes of the aromatic amine respectively [18–20]. The symmetric stretching vibrations of S=O groups appear between $1170\text{--}1028\text{ cm}^{-1}$. The asymmetric stretching of S=O group ($\sim 1300, 1320\text{ cm}^{-1}$) may overlap with the characteristic –N stretching vibration. In acrylic acid doped PDPA the intensity of these bands is high and the

presence of these bands is ascribed to the higher doping level because of the strong electrostatic interaction between dopant and polymer. The presence of strong absorption peaks at $\sim 810\text{ cm}^{-1}$ is assigned to a 4-substituted phenyl group compared to the low intensity of the peak at 743 and $\sim 692\text{ cm}^{-1}$ due to the terminal phenyl groups. This indicates that polymers were obtained through the 4, 4 C–C phenyl coupling of monomer unit [21].

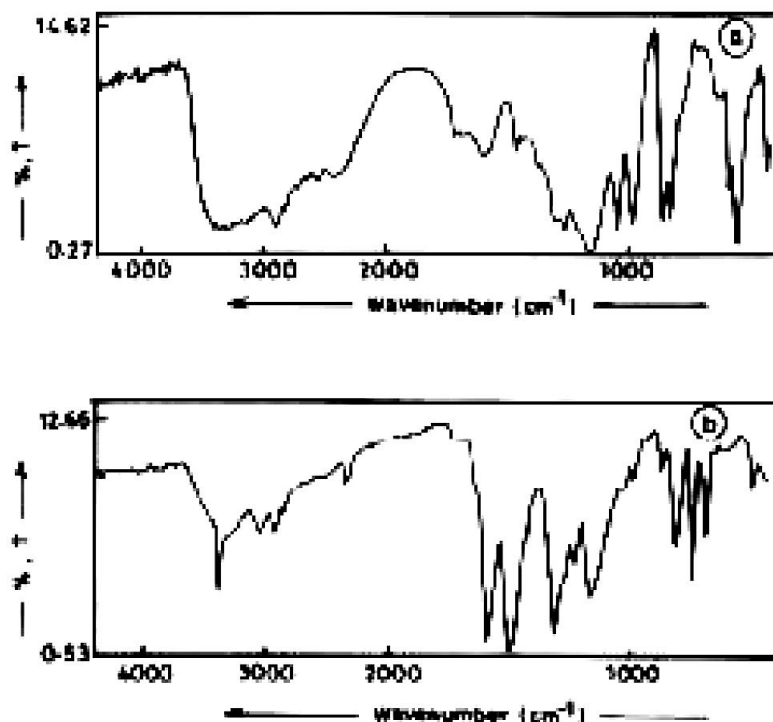


Fig. 2. FTIR absorption spectra of acrylic acid (a) and H_2SO_4 doped PDPA (b)

Table 1

FTIR spectral data of polydiphenylamine doped in acrylic acid and H_2SO_4 media

PDPA/AA	PDPA/H ₂ SO ₄	Peak Assignment
710-743	627-748	Out of plane C–H bending vibration
850	821	<i>Para</i> -disubstituted benzene ring
1008,1060	1028,1037	Vibration band of dopand anion
1173	1173	B N H B stretching vibration
1285	-	(–COO) stretching band
1322	1317	Aromatic (C–N) stretching band
1493	1504	Benzenoid ring stretching band
1590	1595	Quinoid ring stretching band
Broad 1620	-	–v(–COO) asymmetrical stretching band
1743	-	Carbonyl (–C=O) stretching band
2920	2921	C–H stretching band
3404	3386	N–H stretching band

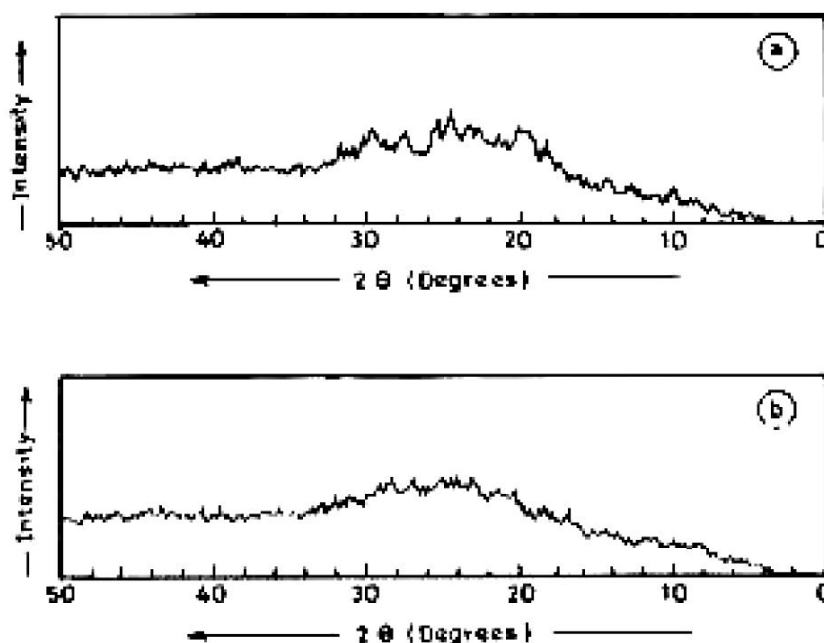


Fig. 3. X-ray diffraction patterns of acrylic acid (a) and H_2SO_4 doped PDPA (b)

3.3. X-ray Diffraction Studies

Fig. 3 shows the X-ray diffraction pattern of the acrylic acid and H_2SO_4 doped PDPA. As seen from Fig.3, H_2SO_4 doped PDPA sample showed broadening pattern indicating the amorphous nature of polymer, due to short range order [19–22]. However several sharp peaks are observed in acrylic acid doped PDPA polymer at 2θ of 14, 18, 19.8, 21, 22, 23, 24, 25, 27, 29, 30, 38 indicating the presence of a rigid chain and ordered structure resulting in partial crystallinity [16-21]. It is interesting to note that the degree of crystallinity in acrylic acid doped polymer is greater than the H_2SO_4 doped polymer as observed from the intensity of the peaks which is consistent with the conformational changes of the polymer chain in acrylic acid doped polymer together with the increased sharpness in the amorphous scattering at 2θ of 20 [19, 22-24].

3.4. Electrical Conductivity

These results are well supported by the conductivity data obtained for the both polymers. Acrylic acid doped PDPA polymer exhibits higher conductivity ($4.5 \cdot 10^{-2} S \cdot cm^{-1}$) compared to H_2SO_4 doped PDPA polymer ($7.6 \cdot 10^{-3} S \cdot cm^{-1}$). This can be attributed to the presence of large concentration of COO ions serving as a functional dopant along with few H_2SO_4 doped sites and trapped COOH molecules present in the polymer matrix. In addition, it has been suggested that the functional dopant counter anion is capable of enhancing conductivity [22-25]. Chen and Lee have reported the

results on the polyacrylic acid doped polyaniline blend having a conductivity of $\sim 2.9 \cdot 10^4 S \cdot cm^{-1}$. The polymer synthesized in the present case exhibits a conductivity higher than that reported by them [26-27].

4. Conclusions

Acrylic acid and H_2SO_4 doped polydiphenylamine PDPA were synthesized by chemical oxidative polymerization. The reaction is unique which yields a truly soluble conducting emeraldine salt directly without the need for a postdoping process step. This was an easy and scalable one-step method to produce PDPA in its conductive state. In addition to the solubilizing effect, this dopant gives better crystallinity and conductivity. The conductivity differences between acrylic acid doped and H_2SO_4 doped PDPA may occur due to stronger mutual interaction between the functional acid dopant and the polymer, which may allow the two polymer chains to have their position in space closer to each other and result in more efficient doping of the polymer. These observations imply that there is a correlation between the functionality of dopant counter anion and the solid state polymer properties.

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СИНТЕЗ І ХАРАКТЕРИСТИКА ОРГАНІЧНО РОЗЧИННОГО ПОЛІДИФЕНІЛАМІНУ З ДОДАТКОМ АКРИЛОВОЇ КИСЛОТИ

Анотація. Окислювальною хімічною полімеризацією з використанням невеликої кількості акрилової кислоти синтезовано полідифеніламін (ПДФА). Запропонований новий метод хімічної полімеризації може бути використаний для керованого синтезу солевих форм ПДФА, які здатні розчинятися у звичайних органічних розчинниках. Отримані полімери охарактеризовані фізичними методами, зокрема УФ-, Фур'є-спектроскопією, рентген-дослідженнями, а також вимірюванням провідності. Використання функційної акрилової кислоти дозволило отримувати полімер з підвищеною розчинністю в таких органічних розчинниках, як *N*-метил піролідон і *m*-крезол без перетворення в основну форму емеральдину.

Ключові слова: полідифеніламін, функційний додток, розчинність, кристалічність, електропровідність.