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One Pot Synthesis and Characterization of Copolymer Poly [(Thiophene-2, 5-Diyl)-Co-4-Hydroxy Benzylidene] Using Polycondensation

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Abstract: **A one pot copolymerization technique was used to synthesize copolymer Poly [(Thiophene-2, 5-diyl)-co-4-hydroxy benzylidene]. In this technique we used catalyst phosphorous oxy chloride and 1, 4 dioxane solvent for copolymerization of 4-hydroxy benzaldehyde with thiophene. Synthesis was carried out at 70ºC and took 28 hours for completion. Reaction was monitored by thin layer chromatography. Catalyst was removed using ammonia. Product was obtained using menthol. Chemical structure was confirmed by using spectral analysis like ultraviolet, infrared, nuclear magnetic resonance as well as ^{13}C nuclear magnetic spectroscopy. The amorphous phase was confirmed using structural analysis. Regular clusters with spherical shapes with approximately 0.5 µm sizes were indicated by surface morphology. Copolymer is thermally stable up to 363ºC which was confirmed by thermo gravimetric analysis. Optical absorption study proved band gap value 2.50 eV and conductivity value is 5.54 x 10^{-7} S/cm measured by two probe methods. Such copolymer can be used like semiconducting material and energy storage in the field of conducting polymers.**

Index Terms: **Amorphous, Conjugated copolymer, Physical properties, Polycondensation, Surface morphology.**

I. Introduction

In recent years organic conjugated polymers have attracted more attention due to their excellent electrical and optical properties (Bura T., et al., 2016) Homopolymers like polypyrrole, poly thiophene previously prepared by electrochemical method are also now being synthesized by chemical polymerization process which is low cost and product obtained in bulk amount powdered form. All results showed the success in refining the mechanical and physical properties of polypyrrole. However, these synthetic methods contained many steps and firm condition, leading to limited application of these copolymers (Borole, D. et al.,2006). Oxidative polymerization is one of the cleanest and low-cost methods in polycondensation. Polycondensation between two different monomers offers copolymerization which modifies the properties of a homopolymer by the introduction of appropriately selected second repeating unit (Larbi B. et al.,2013). Several studies have been acceptable on conducting copolymers on their applications over homopolymer for conductivity, solubility and stability (Zerza G., et al.,2001; Pei, J., et al.,2000). The extended conjugation of the polymer chain backbone is also a major factor in creating new optical properties (Patil, A., et al., 2002). Donor–acceptor polymers with donor and acceptor moieties have extended particular attention during current years as active components of organic electronics. By submission of suitable subunits inside the conjugated backbone, these polymers can be made either electron deficient or rich. It is expected that in polymers with charge carrier motilities the ordered domains are consistent by loose polymer chains that ensure a charge transfer (Patil, A., et al., 2016; Noriega R.,2013). Synthesis of polymers for a particular application may go for selective polymerization method. Suzuki/Stile polycondensation technique is mostly chosen for optoelectronic device applications (Alessandro S.,2020; Murugesan V.,2012). Conjugated polymers have been attracting more and more attention because they acquire various electrical, magnetic and optical properties. In the balanced state, conjugated polymers are utilized in electronic devices such as photovoltaic cells, solar cells; light emitting diodes (Burroughes J.et al.,1990) field effect transistors, nonlinear optical devices, chemical, biochemical and thermal sensors (Garnier, F., 1990). Conjugated polymers are light-weight as they

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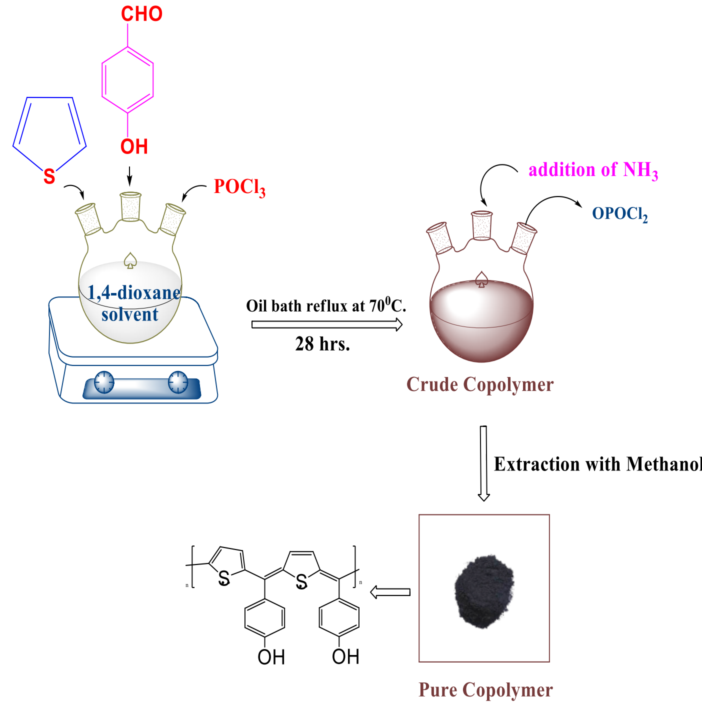
are organic in nature and can be made-up into flexible, bendable appliances. Due to the property of electrical conductivity of these polymers; they are called as conducting polymers. Conjugated polymers contain π electrons responsible for electrical conductivity (Abdelkarim R., et al.,2011; Liao L., et al., 2007). There are a lot of possibilities to modify the chemical structures of conjugated polymers to change their physical properties. The technique of copolymerization has been widely used as a way to obtain materials with properties intermediate between those of the individual homopolymers (Oliver R.., et al.,2006; Bundgaard E.,2006). Thus, physical and chemical properties of the final material can be controlled through the appropriate choice of monomers that form the polymer chain. There is basic need to search for new precursors which are easily available in the laboratory to form polymers with new physical properties using simple chemical route and to study the effect of electron withdrawing and electron donating para substituent on the electronic and optical properties of the conjugated polymers ([Innami Y., et al., 2012). Alternations of single and double bonds resulted conjugation in the organic compounds which is useful to change the electronic and physical properties as well as applications of the organic polymers. In this paper we used substituted aldehyde 4-hydroxy benzaldehyde having electron donating group. Copolymer of thiophene and para choro (Mahashabde J., et al., 2018) para methyl (Mahashabde J., et al., 2018) showed variations in their material properties due to different substituent present at para position of benzaldehyde. A similar approach was taken to synthesize copolymer of Thiophene with 4-hydroxy benzaldehyde by polycondensation and characterization studied to look at material and its application in various fields like semiconducting material and energy storage. Copolymerization could be a necessary way because the chemical linkage between the insulating matrix and the conjugated polymer can improve the chemical stability of the polymer (Baik D., et al., 1999). The resulting copolymers with new functional groups showed different properties from Polythiophene homopolymer, which probably widen the application of conducting polymer (Rajasekhar M., et al., 2009). The objective of this chemical synthesis was to study unique characteristics of copolymers synthesized by chemical polymerization having applications in the various fields of conducting polymers (Jadoun S., et al., 2019).

In this paper brief synthesis of Copolymer Poly [(Thiophene-2,5-diyl)-co-4-hydroxy benzylidene] derived from thiophene with 4-hydroxy benzaldehyde, characterization of copolymer and studied physical properties conjugated copolymer as semiconducting material.

II. MATERIALS AND METHODS

The authors have presented the one step synthesis of conjugated polymer of thiophene with 4- hydroxy benzaldehyde. The same method of polycondensation was used to synthesize conjugated copolymer of thiophene and 4-methoxy benzaldehyde. Here substituted aldehyde 4- hydroxy benzaldehyde is used for investigation which is different from previous work.

Thiophene, 4-hydroxy benzaldehyde were used as received obtained from Aldrich Chemical Co. Dehydrating agent $POCl_3$ used as catalyst and reaction was carried out in 1, 4-dioxane. Ammonia and methanol are used to obtain the product from reaction mixture.



A. Scheme for copolymer synthesis.

III. INSTRUMENTATION

The UV-Visible spectrum of samples in CH_2Cl_2 was taken using UV-Vis SHIMADZU 2450 unit in the wavelength range of 200-800 nm to investigate conjugation. The UV-Vis spectroscopy is also used to know the optical properties of the material as well as for estimation of optical band gap. The FTIR spectrum of samples was taken using FTIR, IR Affinity 1 SHIMADZU unit with DRS sampling technique in the range of 4000-400 cm^{-1}. X-ray diffraction (XRD) measurements were carried out by using BrukerD8 Advance diffractometer having CuKα incident beam with λ = 1.5406 Å in 2θ range from 20 to 80 degrees. The surface morphology of the samples was characterized by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, and 15 kV) unit. The thermo gravimetric analysis was carried out using thermal analyzer (TGA 50) under the stream of nitrogen gas (flow rate 50ml/min) was monitored around the sample chamber to minimize heat dissipation during measurements. The % weight loss is plotted as function of temperature to get thermogram.

IV. RESULTS AND DISCUSSION

A. Optical Absorption and Conductivity Measurement

An optical property of the copolymer prepared was investigated by using UV visible spectroscopy. From optical study, it is found that the polymer material prepared by using polycondensation method has conducting properties. Variation in optical absorbance of copolymer solutions in dichloromethane as a function of wavelength was studied and results are showed in figure 2. Optical absorption spectra showed two major absorptions bands. The band in range of 280 - 300 nm is assigned to the π - π* transition of the aromatic heterocyclic since it corresponds to the same band as its precursor, and the band in the range of 490 to 510 nm is assigned to the π - π* band gap transition.

Band gap is calculated by equation Band gap = 1240/λ where λ is wavelength in nanometers. From optical absorption spectra maximum wavelength responsible for band gap 495 nm. Which confirmed band gap value 2.50 eV. Conductivity of copolymer was measured at room temperature using two probe method value obtained 5.54 x 10-^{7}S/cm.

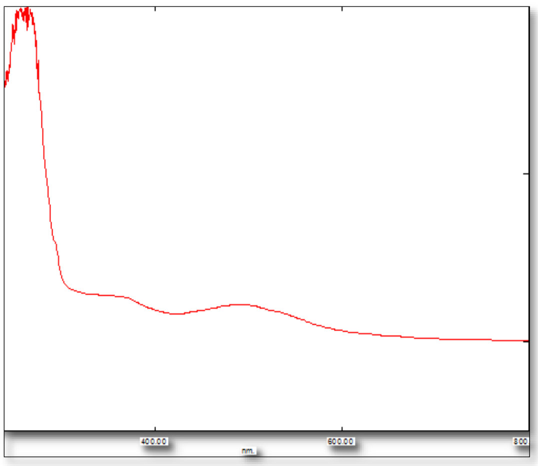


Fig. 1: Optical absorption spectra of copolymer

B. Functional Group Determination by Infrared Spectroscopy

FTIR is a powerful technique to determine changes in the functional groups that occur during synthesis. Figure 2 showed functional group changes during the synthesis. In Table 1 I R values for corresponding functional groups are observed. During polycondensation process a small molecule like water eliminated and C=C double bond is formed with disappearing C=O frequency of 4-methoxy benzaldehyde.

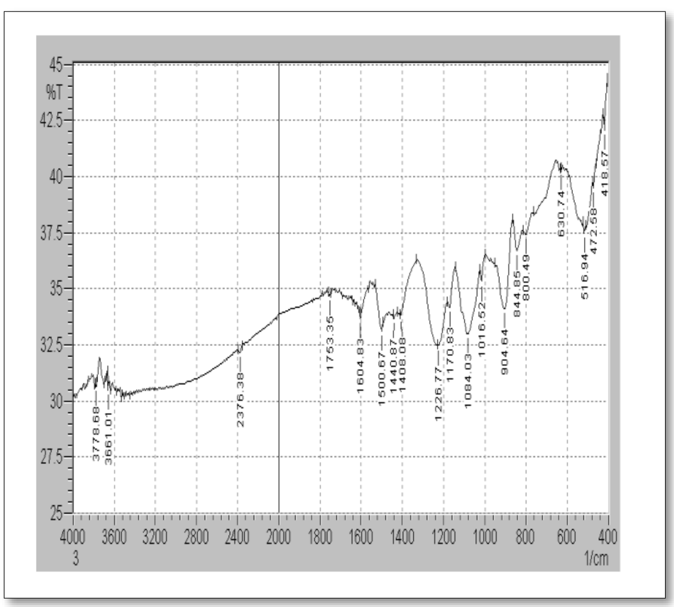


Fig. 2: FTIR spectra of copolymer

Table 1: I.R. functional groups wave numbers observed in copolymer

Functional Groups	Standard IR frequencies	Observed IR frequencies
Ar (C=C)	1500-1600 cm^{-1}	1604 cm^{-1}
C-S Thiophene	1010-1100 cm^{-1}	1084 cm^{-1}
Ar (C-H)	2900-3000 cm^{-1}	3092 cm^{-1}
C-OH	3200-3600 cm^{-1}	3500 cm^{-1}

C. *NMR data*

^{1}HNuclear Magnetic Resonance (BRUKER ADVANCE) ($CDCl_3$):

8.6δ(3H,s),6.97δ(2H,m)dd,7.29δ(2H,m)dd,7.33δ(1H,d),7.17δ (1H,m)dd,7.33δ(d,1H),6.22δ(1H,d),4.44δ(1H,m)dd,5.20δ(1H,q).

^{13}CNuclear Magnetic Resonance: (BRUKER ADVANCE) ($CDCl_3$):

24.33, 36.52, 42.74, 55.23, 113.78, 123.03, 126.50, 129.38,131.57,147.6,157.7.

D. Structural Studies

A structural property of copolymer was determined by X-ray diffraction. Figure 3 indicated the XRD pattern of the copolymer sample. The XRD specified that copolymer was amorphous.

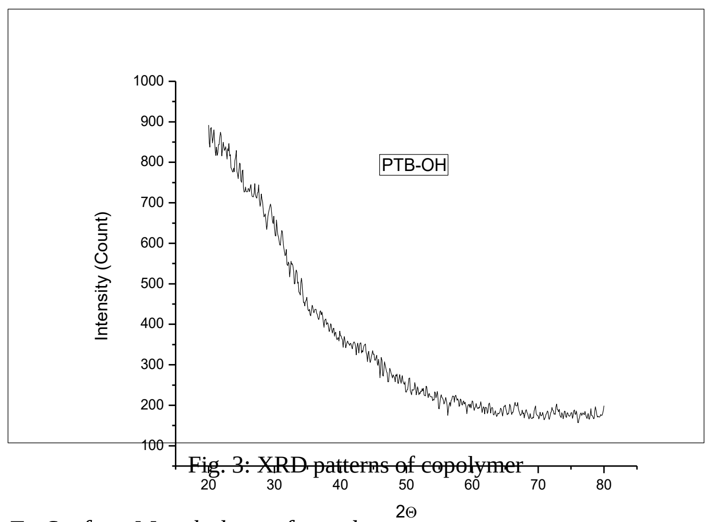


Fig. 3: XRD patterns of copolymer

E. Surface Morphology of copolymers

Figure 4 showed field emission scanning electron microscopy of copolymer. Surface morphology copolymer is shown in figure 5 at lower magnification. Surface morphology shown by the copolymer is smooth regular interconnected cluster with spherical shapes with approximately 0.5 µm sizes.

F. Thermo gravimetric Analysis

In order the check the thermal stability, copolymer sample was also characterized by thermo gravimetric analysis as shown in figure 5. The curves did not show the sharp peak in the range 90 to 100 ºC confirmed the absence of moisture. The melting started at 363.45 ºC (onset) and finished at 427.92ºC (end set). From

TGA it is confirmed that the sample is thermally stable at high temperature.

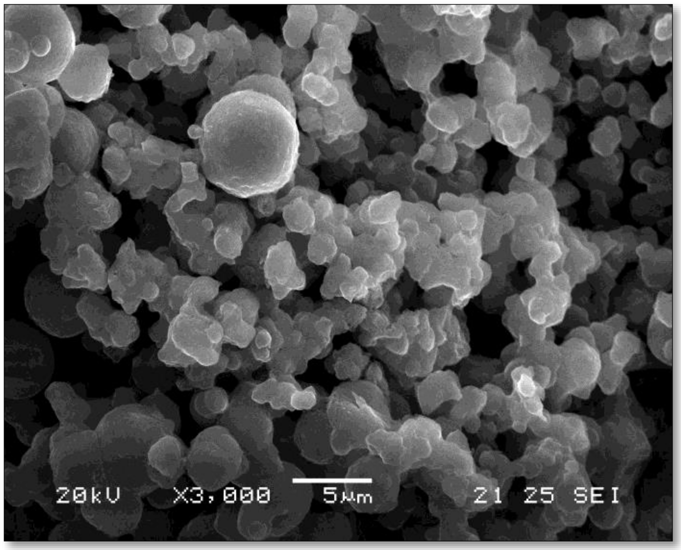


Fig. 4: Surface morphology of copolymer

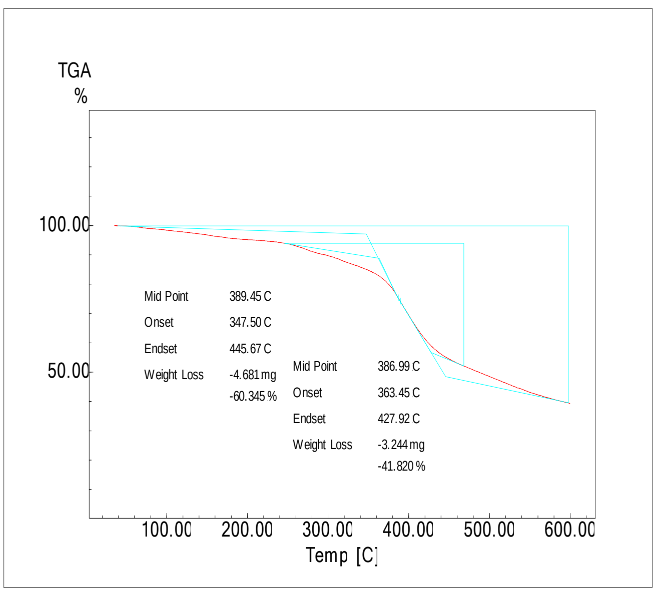


Fig. 5: TGA of copolymer

CONCLUSION

Copolymer synthesis by polycondensation of thiophene with 4-hydroxy benzaldehyde in presence of phosphorous oxychloride is cost effective and possible under normal laboratory condition. Resultant copolymer having intermediate properties between those of the individual homo polymers. Copolymer obtained is in the powder form and can allows easy processing. This conjugated copolymer is amorphous, interconnected regular clusters with spherical shapes approximately 0.5 µm sizes even more stable up to 363ºC temperature having band gap 2.50 eV. In the field of conducting polymers, the surface morphology, thermal stability, and structural characteristics are notably unique and can be applied as semiconducting materials.

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