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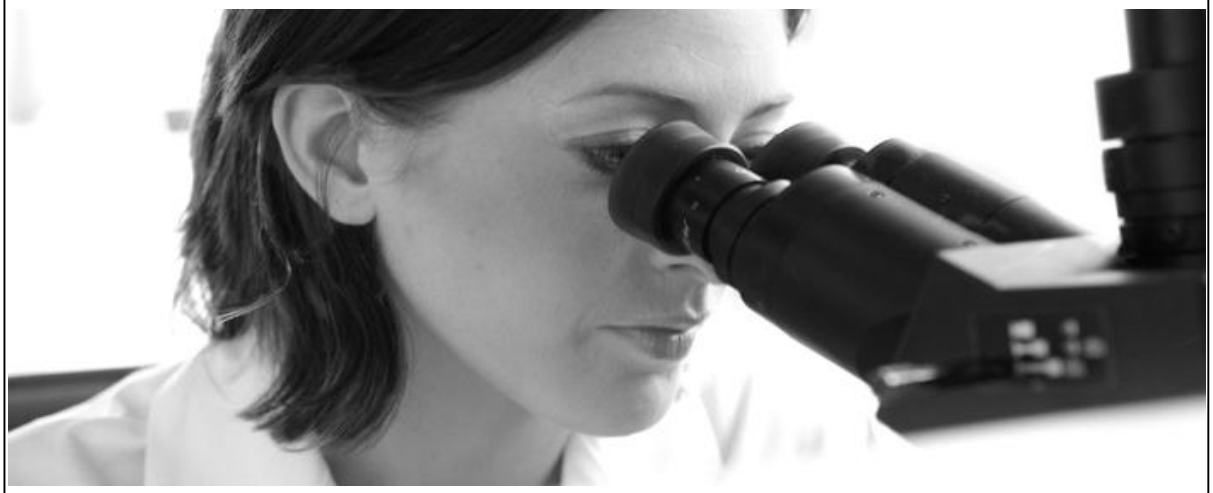

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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF POLY [(THIOPHENE-2, 5-DIYL)-CO-BENZYLIDENE] USING $POCL_3$ CATALYST

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ABSTRACT

Conjugated Poly Thiophene Benzylidene complex (PTB) has been synthesized by a simple condensation method. Condensation of thiophene with benzaldehyde catalyzed by $POCl_3$ in 1,4 dioxane was carried out for 24 hours and characterized by UV-Vis, FTIR,NMR,XRD,SEM and DSC. The result reveals that the yield of PTB is quite good using $POCl_3$in single step polymerization. The results obtained with optical measurements and analyzed by different models. The surface morphology clearly shows the petal like structure of the material (PTB) with porous network consisting of nano sheets which are interconnected with each other. XRD pattern confirms that the synthesized material is in nano form. From optical absorption, the band gap is calculated and observed to be around 2.78 eV and hence it can be used in optoelectronic applications as a good semi-conducting material with conductivity 1.34×10^{-4} S/cm

INTRODUCTION

Conjugated polymers have an increasing interest because of the broad range of their probable applications, which contain organic light emitting diodes, photovoltaic cells, due to their unique optical, electrical and mechanical properties[1].In this field, polythiophene and thiophene-based functional polymers have been extensively investigated and synthetic interest has been focused on new low band gap materials[2,3].A previous inspection of the acid –catalyzed polycondensation of several derivatives of *2-hydroxymethylthiophene*was focused on their kinetics and mechanistic features and on the structure of the ensuring oligomers and polymers[4,5].Synthesis and Properties of Poly Thiophene Benzylidene was carried out in presence of catalyst Maghnite-H^+ by Abdelkarim and his coworkers in 2011 for Photovoltaic Applications[6]. He also synthesized a new poly [2, 5 diyl thiophene (2-Thiophenenyl Methine)] from acid catalyzed polycondensation of thiophene which showed average band gap around 5eV[7].Several approaches have been taken to improve processibility of conducting polymers[8,9]. One effective method is to introduce insulating polymeric material into them due to the excellent processibility of classical insulating polymers[10,11].It can be achieved by copolymerization. Copolymerization could be a desirable way to increase the chemical stability of polymer[11, 12].The resulting polymer showed different properties than homopolymer which has wide application of conducting polymer[13]. In the present work, wede signed Poly [(Thiophene-2, 5-diyl)-co-Benzylidene] (PTB) in one step namely by the polycondensation of thiophene and benzaldehyde catalyzed by $POCl_3$.

Experimental

Polycondensation between benzaldehyde and thiophene was carried out to obtained methine type conjugated polymer. Benzaldehyde reacts with phosphorous oxychloride to form electrophile which sequentially reacts with active sites (α, α'-position) of thiophene.

MATERIALS

Thiophene was purchased from Aldrich Chemical Co. and distilled under reduced pressure. 1, 4 dioxane and benzaldehyde was used as received. Phosphorous oxychloride used as mild dehydrating agent.

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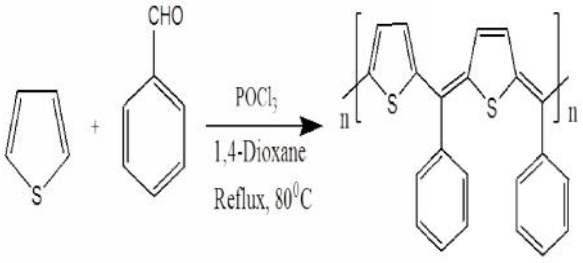
Synthesis of poly [(Thiophene-2, 5-diyl)-co-Benzylidene] (PTB)

Experimental of reported work was carried for chemical polymerization. The synthesis of conjugated polymer derived from thiophene and benzaldehyde to Polythiophene benzylidine (PTB) obtained in a single step polymerization through a simple condensation of thiophene and benzaldehyde in the presence of 5/6 drops $POCl_3$ as a catalyst which is mild dehydrating agent and 1, 4 dioxan was used as a solvent. Benzaldehyde (0.002 mmoles) and Thiophene (0.002 mmoles) were mixed and 15 ml 1, 4 dioxan was added as a solvent and of $POCl_3$. Then reaction mixture was refluxed using heating mental at 80°C constant temperature for 24 hours. The condensation was carried out for 24 hours at 80°C. Reaction mixture was added in methanol, then near about 2 ml of ammonia was added and fine dark brown powder obtained was washed several times by methanol and finally dried at room temperature for 24 hours. After drying the fine product was purified using column chromatography. Benzaldehyde reacts with $POCl_3$ in 1,4 dioxan as solvent which reacts with thiophene to form dehydrative polycondensation product called poly [(thiophene-2, 5-diyl)-co-benzylidene] which is amorphous and dark brown in color.



Scheme Synthesis of Methine bridge polymer-

Instrumentation

The UV-Visible spectrum of sample was taken using UV-visible SHIMADZU 2450 instrument in CH_2Cl_2 in the range 200-800 nm to investigate conjugation and optical property. 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 sample was taken using FTIR, IR Affinity 1 SHIMADZU instrument with DRS sampling technique in the range of 4000-400cm^{-1}. ^{1}H-nuclear magnetic resonance (NMR) measurements were carried out on a 500 MHz BRUKER NMR spectrometer equipped with a probe BB05 mm, in $CDCl_3$.

Tetramethylsilane (TMS) was used as the internal standard in these cases. X-ray diffraction (XRD) measurements were carried out by using BrukerD8 Advance diffract to meter having CuK_α incident beam with λ = 1.5406 Å in 2θ range from 20 to 80 degrees. The surface morphology of the films was characterized by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, and 15 kV) unit. Thermal analysis of the synthesized polymer was done by using differential scanning colorimeter unit (DSC 60 Shimadzu).

RESULT AND DISCUSSIONS

Optical absorption studies

Figure 1 shows the UV-Vis absorption spectra of the synthesized polymer as a function of wavelength. UV-Vis absorption showed strong absorption bands at 280-300 nmassigned to the π-π* transition of aromatic character since it corresponds to the same band assign starting material and broad absorption band in the range 445-468 nm responsible for π-π* band gap transition[6].In present case, PTB is having direct band gap with the exponent n=1/2 and is measured by plotting $(\alpha h\upsilon)^2$ versus hυ. The extrapolation of the straight line in the graph to

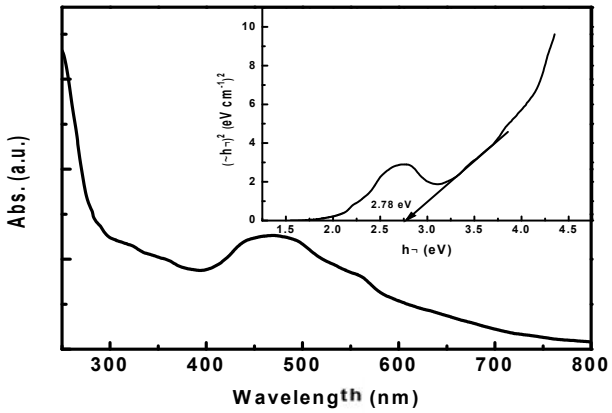


Figure 1 Optical absorbance of PTB sample. Inset shows the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$.

$(\alpha h\upsilon)^2$= 0 gives the value of the energy band gap (Figure 1 inset). The value of band gap was obtained as 2.78 eV for PTB material. Kawashima *et al.*[14] reported the value of optical band gap as 2.8 eV with electrical conducting of 1.34 X 10^{-4} S/cm measured by four probes and suggesting the material is considered to be a semiconducting organic material[14].

Fourier Transform Infrared (FTIR) spectroscopy and NMR studies

Figure 2 shows the FTIR spectrum of the synthesized polymer sample.

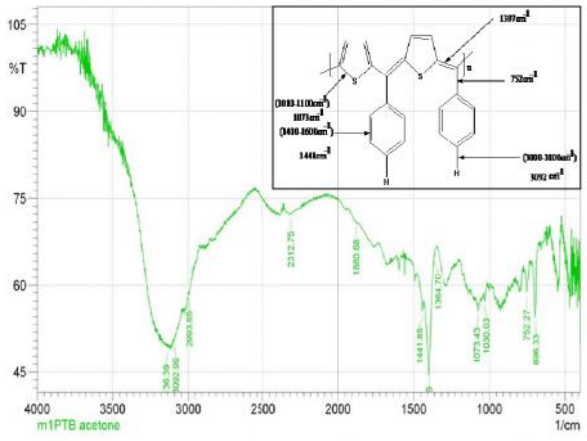


Figure 2 Fourier Transform Infrared (FTIR) spectroscopy of PTB sample.

IR spectroscopy concludes that there was no absorption band at 1700 cm^{-1}frequency for C=O group. Characteristics bands for aldehyde at 2750$cm^{-1}$and 2850 $cm^{-1}$are totally absent which confirmed that aldehyde was consumed. Appearance of strong absorption band at 1598 cm^{-1} confirmed formation of C=C[15]. Thus condensation product of thiophene and aldehyde was obtained.

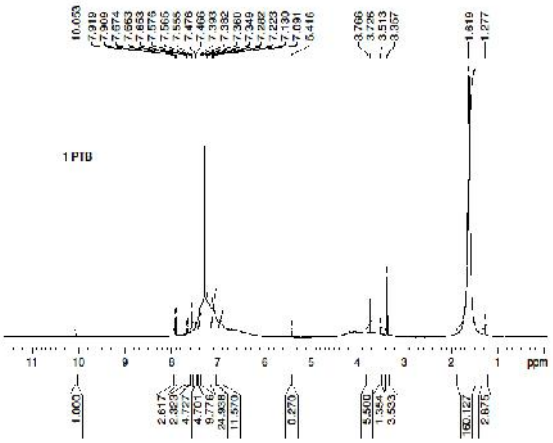


Figure 3 NMR spectra of PTB sample

NMR Data

^{1}HNMR (500MHz, δ from TMS (ppm), CDCl3-7.33, (m), 1H,7.21, (m), 2H, J= 8 Hz,7.30, (dd=m), 2H, J= 8 Hz, 7.0, (d), 1H and 7.0, (s), 1H, 7.2, (d), 1H, 7.09, 1H.
IR (KBr, thin film, cm–1):-1598 (C=C)cm^{-1},1033cm^{-1},1440cm^{-1},3092cm^{-1}, 752cm^{-1}.
UV–vis(CH_2Cl_2) λmax, nm (ε):280 nm for conjugation, 468 nm for band gap.

Structural studies

X-ray diffraction (XRD) measurements were carried out by using Bruker D8 Advance diffractometer having CuK_{α} incident beam with λ = 1.5406 Å in 2θ range from 20 to 80 degrees. X-ray diffraction (XRD) patterns of PTB were depicted in Figure 3. The diffraction graph does not reflect any strong peak confirm the amorphous nature of the prepared sample[16].

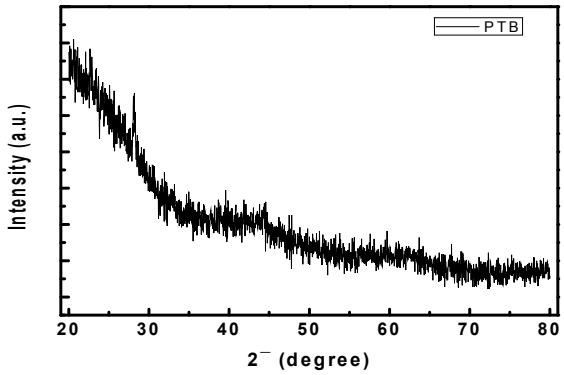


Figure 4 XRD of PTB sample

Surface morphological studies

The surface morphology of the polymer was characterized by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, and 15 kV) unit. The FE-SEM images of powder sample of PTB where taken on the carbon tap mounted on sample holder. Figure 4(a) shows the porous surface morphology of PTB sample showing petal like structure at lower magnification (10 µm scale bar). Figure 4(b) shows FE-SEM images at higher magnification (1 µm scale bar) showing formation of nanosheets of PTB providing high surface area and these nanosheets are found to be interconnected with each other which are beneficial for creating unidirectional path for the electrons transport and hence it can be useful in optoelectronic applications.[14]

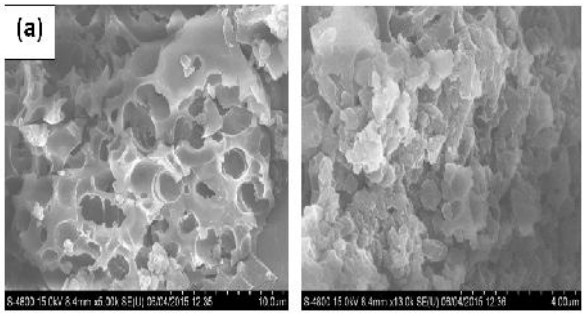


Figure 5 (a) Surface morphology of PTB sample showing porous petal like structure at lower magnification and (b) at higher magnification.

Differential scanning colorimeter

Synthesized sample was also characterized by Differential Scanning Colorimeter to check the thermal stability. The curve does not show the sharp peak in the range 90^{o} to100 ^{o} confirms the absence of moisture. The melting started at 111.3^{o}C (onset) and finished at 147.1^{o}C (endset) but sharp peak at 140.1^{o}C may be the melting point of the polymer. Above 189^{o}C, degradation of the polymer starts confirms the thermal stability of the complex.

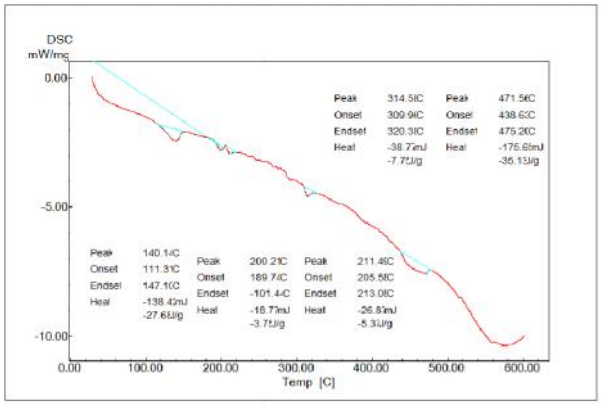


Figure 6 Differential scanning colorimeter curve of PTB material

CONCLUSIONS

In conclusion, synthesized polymer poly (thiophene-2,5diyl)co-benzylidene which has a π conjugated chain was synthesized by polycondensation of benzaldehyde and thiophene catalyzed by $POCl_3$ as a mild dehydrating agent. The resultant polymer showed good solubility in common organic solvent. PTB is amorphous, SEM shows porous surface morphology of the PTB and interconnected nanosheets and band gap of the polymer is estimated to be 2.78 eV evaluated from optical absorption spectroscopy. From optical and surface

morphological studies, we conclude that the synthesized polymer can be useful in optoelectronic applications.PTB is thermally stable.

Acknowledgments

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References

1. MacDiarmidA. G.,2001.Synthetic Metals: A Novel Role for Organic Polymers (Nobel Lecture) Angew. Chem. Int. 40, 2581- 2590.
2. HasiahS., Ibrahim K., Senin , H.B., Halim K.B.K., 2008. *Journal of Physical Science*, Electrical Conductivity of Chlorophyll with Polythiophene Thin Filmon Indium Tin Oxide asP-NHeterojunction Solar Cell Vol. 19(2), 77–92.
3. Stagnaro P., Panizza M., Gandini A. , Prevosto D., Lucchesi M.,2011.Unraveling the Detailed Microstructure of a Semiconducting(Quasi-Metal) Soluble Polymer Incorporating Conjugated Thienylene Methine Sequences, *Journal of polymer science part a: Polymer Chemistry*, 49, 5227–5238.
4. Stagnaro P, Costa G and Gandini A.,2001. Acid-catalyzed polycondensation of 2-hydroxymethylthiophene and some of its homologues, Macromolecules, 34, 26-32.
5. Stagnaro P, Costa G, Pioli F and Gandini A.,2003. The acid catalyzed polycondensation of 2-acetoxymethylthiophenes, Kinetics and Mechanisms, Polymer, 44, 1359-1365.
6. Abdelkarim R.B., Yahiaoui A., Hachemaoui A., Belbachir M., Khelil A.,2011. Synthesis and properties of Polythiophene Benzylidene and Their Photovoltaic Applications, Material Sciences and Applications, 2, 1014-1021.
7. BelmokhtarA., YahiaouiA., HachemaouiA., SahliN., BenyoucefA., BelfedalA.,BelbachirM.,2012. A Novel poly {(2,5-diyl thiophene) (2-Thiophenyl Methine)} from the Acid-Catalyzed Polycondensation of thiophene and thiophene-2-carbanaldehyde,IOP Conf. Series: Materials Science and Engineering 28 - 012033doi:10.1088/1757-899X/28/1/012033
8. De Paoli M. A., Gazotti W. A., 2002. Conductive polymer blends: Preparation, properties and applications. Macromolecular Symposia, 189, 83–103.
9. Balci N., Toppare L., Akbulut U., Stanke D., Hallensleben M. L.,1998.Polypyrrole grafts synthesized via electrochemical polymerization. Journal of Macromolecular Science: Pure and Applied Chemistry, 35, 1727–1739.
10. Lee Y, Shin D, Cho J, Park Y. H, Son Y, and Baik D. H.,1998. Ionic Interactions in Polyacrylonitrile/Polypyrrole Conducting Polymer Composite J. Appl. Polym. Sci. 69, 2641-2648.
11. Stanke D., Hallensleben M., Toppare L.,1995. Graftcopolymers and composites of poly(methyl methacrylate) and polypyrrole. Synthetic Metals, 73, 261–266.
12. Park Y. H., Shin H. C., Lee Y., Son Y., Baik D. H.,1999. Formation of polypyrrole copolymer in PSPMS precursor film by electrochemical polymerization. Molecular Crystals and Liquid Crystals Science and Technology: Section A, Molecular Crystals and Liquid Crystals, 327, 221–224.
13. S. Richard Prabhu Gnanakan, M. Rajasekhar and A. Subramania., 2009. Synthesis of Polythiophene Nanoparticles by Surfactant -Assisted Dilute Polymerization Method for High PerformancRedox SupercapacitorsInt. J. Electrochem. Sci., 4,1289 – 1301.
14. Kerileng M. Molapo, Peter M. Ndangili, Rachel F. AjayiInt., 2012. Electronics of Conjugated Polymers (I): Polyaniline, *J. Electrochem. Sci*., 7, 11859 – 11875.
15. Innami Y , Kawashima H , Kiebooms R, Aizawa H, Matsuishi K, Goto H.,2012. Synthesis and Properties of Poly(Isothianaphthene Methine)swith Chiral Alkyl Chain, Materials, 5, 317-326.
16. Mouchaal Y,Toumi A.L, Bendoukha A. R, Khehl A, Bernede J.C., 2013. Structural & Optical characteristics of spin coated Poly [(Thiophene-2,5-diyl)-co—(benzylidene)] PTB thin films & their photovoltaic applications, ICERN-01/2013 February 16-17,, Constantine, Algeria, First international conference on Renewable Energies and Nanotechnology impact on Medicine and Ecology.

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