ISSN 0973-3450 (Print)
JUC Vol. 22(3), 40-48 (2026). Periodicity 2-Monthly
ISSN 2319-8036 (Online)

JOURNAL OF ULTRA CHEMISTRY
An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering
website:- www.journalofchemistry.org
Estd. 2005

Photophysical, Electrical and Structural Properties of Poly(3-Hexylthiophene-2,5-dyil)/Poly Methyl Methacrylate Films

SNEHA ANKOLEKAR[1], TANISHA REVANKAR[1], SHRESHTHA NAIK[1], ULLAS N SHETTI[2], G. RAJESHA SHETTY[3], SHREEDATTA HEGDE[4] and ISHWAR NAIK[5]*

[1]Post Graduate Department of Industrial Chemistry, Government Arts and Science College (Autonomous) Karwar-581301 (INDIA)
[2]Department of Chemistry , Government First Grade College Hulkoti - 582205 (INDIA)
[3]Department of Physics, Maharani's Science College for Women (Autonomous), Mysuru - 570005 (INDIA)
[4]Department of Physics, Government First Grade College for Women, Balmatta, Mangaluru - 575001 (INDIA)
[5*]Department of Physics, Government First Grade College Kumta - 581343 (INDIA)
Corresponding Author: Ishwar Naik iknaik@rediffmail.com.
DOI : http://dx.doi.org/10.22147/juc/220302

Acceptance Date 31st August 2026 **Online Publication Date 1st September 2026**

Abstract

Poly(3-hexylthiophene-2,5-dyil) (P3HT) doped Polymethyl methacrylate (PMMA) free standing films are prepared by solution cast method. Weight ratios are maintained at very low concentrations of the dopant in the range 0.001wt% to a maximum of 0.7wt%. UV-Visible ,Fluorescence, AC conductivities and Xray diffraction studies are carried out. A multi band gap material with band gaps in the ranges of 4.5 to 5eV, 4 to 4.5 eV, 3 to 3.5eV and 1.5 to 2eV have been noticed. PMMA being an insulating matrix turns out to be a conducting material with the insertion of highly conjugate P3HT polymer. Fluorescence excited by 375nm at room temperature affirmed no drastic changes in the emission property of P3HT inside PMMA environment. There is increase in ac electrical conductivity, dielectric constant as expected. XRD diffractograms revealed diffused diffraction bands indicating the polycrystalline nature of the new material. Transparent polymer films can be used in the construction of solar cells, LEDs, display systems and even as a transparent electrode.

Key words : P3HT, PMMA, ICP, Band gap, chain conformations.

This is an open access article under the CC BY-NC-SA license (https://creativecommons.org/licenses/by-nc-sa/4.0/)

Introduction :

Intrinsically conductive polymer (ICP) are of much research importance due to their wide band absorption and also emission of high quqntum yield in the visible region of electromagnetic spectrum. Because of high conjugacy, polymer chain is more rigid and brittle, due to which they cannot be easily processed in the form of freestanding films. However film forming ability is enhanced by blending intrinsic conducting polymers with good film forming insulating matrixes like PMMA or polystyrene. Moreover, the photophysical properties also get altered in the inert-polymer environment.[1]. Incorporating conjugate polymers into easily available insulating polymers also reduce cost and hence an economic process [2,3]. Among conjugate polymers the polythiophenes ie poly(3-hexylthiophene-2,5-dyil) (P3HT) is widely investigated in organic electronics because of Efficient hole mobility, tunable energy gap, strong absorption and emission in the visible light range[4]. P3HT with the chemical versatility of its thiophene ring exhibits tailored physical and electronic properties. On blending this light emitting polymer with PMMA, better mechanical properties environmental and thermal stability can be incorporated for electronic applications[5]. PMMA has good tensile strength, highly transparent, enough thermal stability and long term weather resistance. The unique properties of PMMA make it the most commercially important acrylic available till date [6,7]. Sihui et al prepared organic thin film transistors (OTFTs) using PMMA/P3HT blends which worked as nitrogen dioxide (NO_2) sensors and the sensitivity was dependent on P3HT and PMMA ratio[8]. Nassir et al studied the electrical properties of spin coated PMMA/P3HT films and reported the increased electrical conductivity with the increased concentration of P3HT caused by enhanced charge carriers[9]. M.E.nicho *et al* reported Polysterene doped with P3HT and also PMMA doped with P3HT and noticed bipolaron bands in the PS/P3HT and PMMA/P3HT blends [5]. Present experiment is carried out expecting some changes in the spectroscopic or photophysical behavior of P3HT/PMMA polymer films.

Experimental

Materials used :

P3HT is purchased from Sigma Aldrich Corporation. The molecular weight is 15000 with HOMO and LUMO positions at 5eV and 3eV respectively. Polymethyl methacrylate (PMMA) (molecular weight, M_w~15000g/mol)is procured from Himedia Laboratories PVT Limited, Mumbai, India. The common solvent, Chlorobenzene (molecular weight. M_w=112.56g/mol) is purchased from RFCL (Rankem Chemicals) limited, India.

Sample preparation :

Simple solution cast method is used to prepare the samples. 2gm of PMMA is dissolved in 90cc of chlorobenzene and kept for magnetic stirring for about 48hrs at room temperature. This gives a solution of PMMA of concentration 29.41mg/cc. Similarly 75mg of P3HT dissolved in 0.132mg/cc of chlorobenzene and kept for magnetic stirring for about 48hrs at room temperature. Dopant and host solutions are mixed at different weight percentages as shown in table 1. The doped solutions are again magnetically stirred at room temperature for about 48 hours to ensure complete blending. Blended solutions are transferred to petri plates and dried in oven at a temperature of about 50^{o}C, for about 24 hours and the films are peeled off from petri plates and subjected to characterization.

Characterizations :

JASCO UV-Vis NIR 670 (Karnatak University Dharwad) is used for UV-Visible Characterization. Fluorescence spectroscopic studies are accomplished with HITACHI(Japan) model F7000 Spectrophotometer (Department of Physics Karnatak University Dharwad). Agilent 4294A Precision Impedance Analyzer (Microtron Centre, Mangalore University) is utilized for impedance spectroscopy & Rigaku Miniflex-II X-ray diffractometer (MIT Manipal, Karnataka)is opted for X ray characterization.

Table 1. Sample compositions

SET NO.	PMMA	P3HT	PERCEN-TAGE
1.	285.7mg	–	PURE
2.	285.7mg	0.0028mg	0.001%
3.	285.7mg	0.014mg	0.005%
4.	285.7mg	0.028mg	0.01%
5.	285.7mg	0.1142mg	0.04%
6.	285.7mg	0.249mg	0.08%
7.	285.7mg	0.499mg	0.17%
8.	285.7mg	0.999mg	0.35%
9.	285.7mg	1.999mg	0.07%

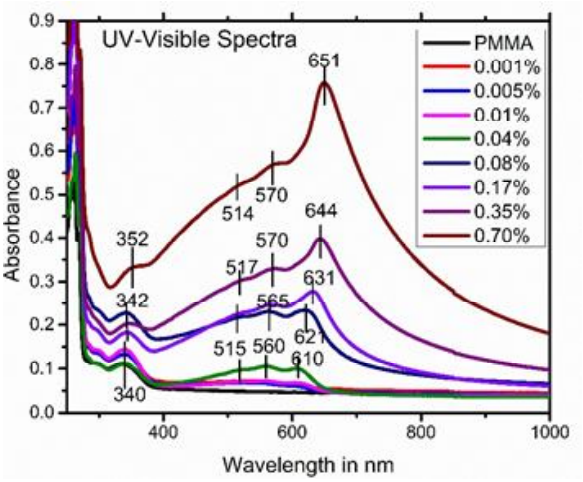

Figure 1. Overlay of absorption spectra

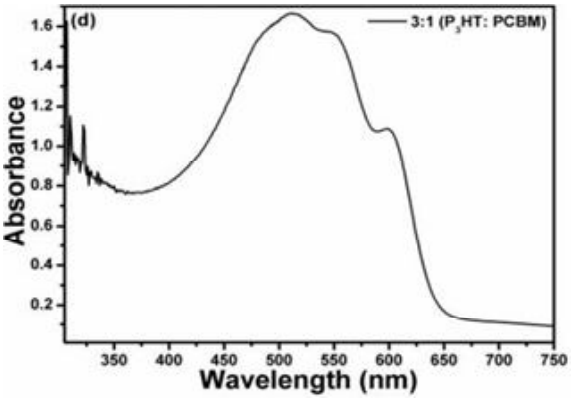

Figure 2. Absorption spectra of pure P3HT film

Result and Discussion

UV-Visible Spectroscopy:

JASCO UV -Vis NIR V 670 Spectrometer is used to take absorption spectra of the samples (USIC Karnatak University Dharwad). The composite films of the size 1 cm × 2 cm were placed in the path of the excitation light (absorption maximum of 335 nm) with a 500 W Xenon lamp at 400 V. The overlay of UV visible spectra is shown infigure 1. Figure 2 represents the absorption spectra of pure P3HT film. The sharp increase of light absorption in PMMA below 220 nm corresponds to $\pi \rightarrow \pi^*$ transitions of –carbonyl group of COOCH3 and weak absorption peak near to260 nm corresponds to $n \rightarrow \pi^*$ transition of carbonyl group. However, the pure P3HT film has absorption extending from 300 nm to 640 nm. The spectrum has two peaks at 520 nm and 560 nm with one shoulder around 620nm, having on set of absorption (the absorption edge) at about 640nm, matching well with the strongest solar spectrum . The first two peaks arise from $\pi - \pi^*$ transition and the shoulder is due to inter chain interactions [10,11]. On doping the P3HT on to PMMA, the absorption is extended into the visible region.The respective peaks of pure P3HTcan be

seen in the P3HT/doped PMMA.With the increase in doping concentration the intensities of the respective emission peaks are altered such that the peak intensity is increased for the shoulder indicating the enhanced interchain interaction. The peak of the shoulder also gets red shifted from 610nm to 651nm. A shift in the onset wavelength is also observed towards the higher wavelength of upto 700nm, indicating the reduction in the energy gap. The Tauc's plot s for determination ofenergy gaps(Direct and Indirect) are depicted in fig 4 and Fig 5. The plot of lnα with hν affirmed the existence of multi bandgap structure as shown in fig 3. The Highest band gap values and also Urbach energies are indicated in table 2. Table 3 indicates the lowest possible energy gaps of the films based on onset wavelength concept.

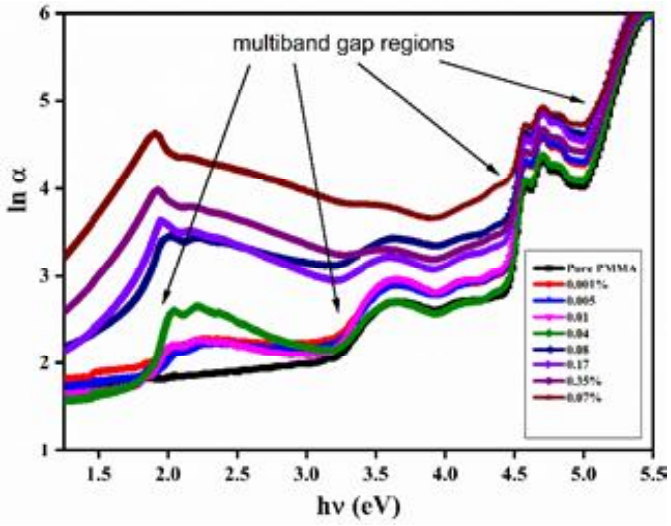

Figure 3. Plot of lnα with hν

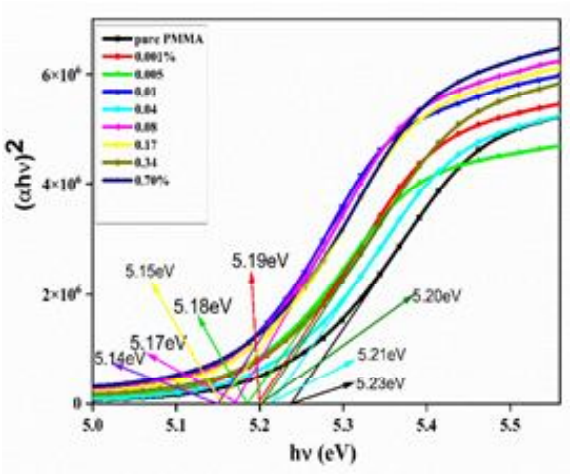

Figure 4. Tauc's plot for direct band gap

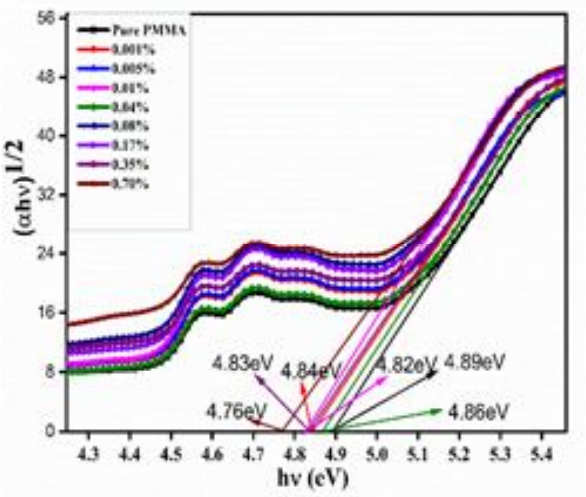

Figure 5. Tauc's plot for indirect band gap

Table 2. Absorption parameters

Sample	Direct band gap	Indirect band gap	Urbach energy
Pure PMMA	5.23	4.89	0.1745
0.001%	5.19	4.84	0.1781
0.005%	5.18	4.82	0.1810
0.01%	5.14	4.82	0.1821
0.04%	5.21	4.86	0.1744
0.08%	5.17	4.75	0.1934
0.17%	5.15	4.77	0.1910
0.35%	5.20	4.83	0.1968
0.70%	5.12	4.76	0.2149

Table 3. Lowest Band gap values calculated from onset wavelength

Samples	Absorption peaks	Onset wavelength	Energy Gap
PMMA	260nm	270nm	4.59eV
P3HT	510nm	650nm	1.90eV
0.001%	560nm	650nm	1.90eV
0.005%	560nm	650nm	1.90eV
0.01%	560nm	650nm	1.90eV
0.04%	560nm	650nm	1.90eV
0.08%	565nm	660nm	1.88eV
0.17%	631nm	670nm	1.85eV
0.35%	644nm	685nm	1.81eV
0.70%	651nm	700nm	1.77eV

Fluorescence spectroscopy

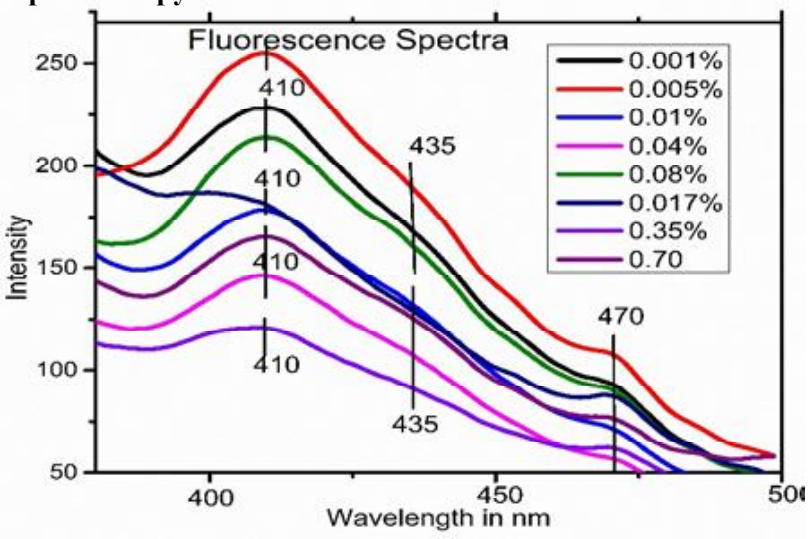

Figure 6. Overlay of emission spectra

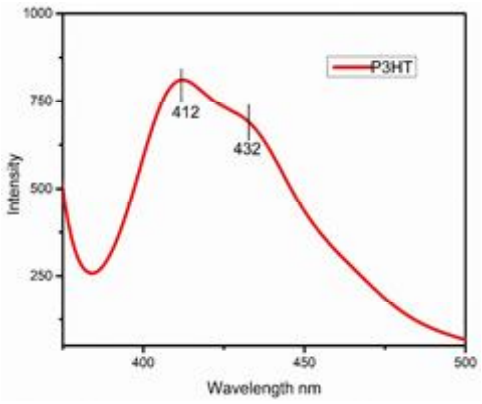

Figure 7. Emission spectra of P3HT

HITACHI (Japan) model F-7000 spectrophotometer characterizes emission spectra (Department of Physics, Karnatak University Dharwad) at room temperature. Overlay of emission spectra of the samples is as depicted in fiure 6. Figure 7 represents the fluorescence by pure P3HT film. In the present work the samples are excited by the UV radiation of wavelength around 345nm and the emission is observed with a peak around 410nm followed by the shoulder at 435 nm. There is no chang in the emission wavelength with the doping concentrations. Only change in quantum efficiency of the emission is observed with the increased doping level of P3HT. The effect of the aggregation of P3HT is not observed in the fluorescence spectra. The fluorescence involves the excitation of the ground state electrons to the higher energy states by the incident photons and then de-excitation to the ground state. Photons of less energy than that of the exciting photons will be emitted because of the energy loss before the de-excitation process. The amount of the energy lost determines the Stokes shift. Fluorescence spectra reveals that the quantum efficiency is continuously decreasing with the increased doping level of P3HT. This indicates that fluorescence quenching might have dominate than emission with the increased doping level[12,13]

AC Impedance spectroscopy :

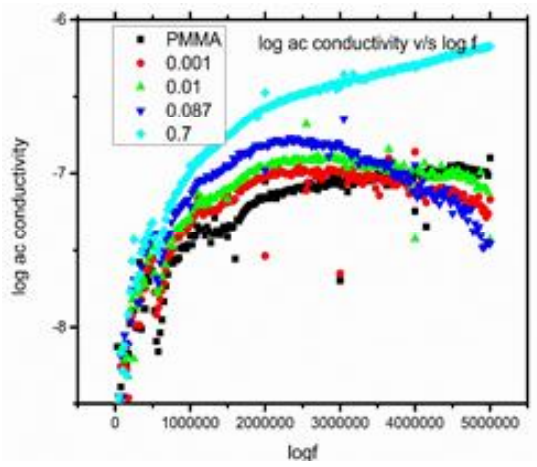

Figure 8.Variation of log ac conductivity with logf

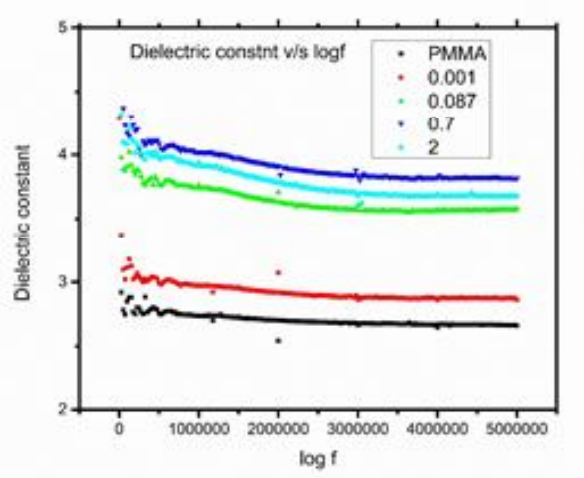

Figure 9. Variation of dielectric constant with frequency

The dielectric properties and AC conductivity of these films were measured using the Agilent 4294A precision impedance analyzer at room temperature in the frequency range from 40 Hz to 5 MHz (MICROTRON center Mangalore University Karnataka). Figure 8, figure 9, and figure 10are the overlay plots of ac conductivity, dielectric constant and the dielectric loss with the frequency. Ac conductivity is enhanced at higher

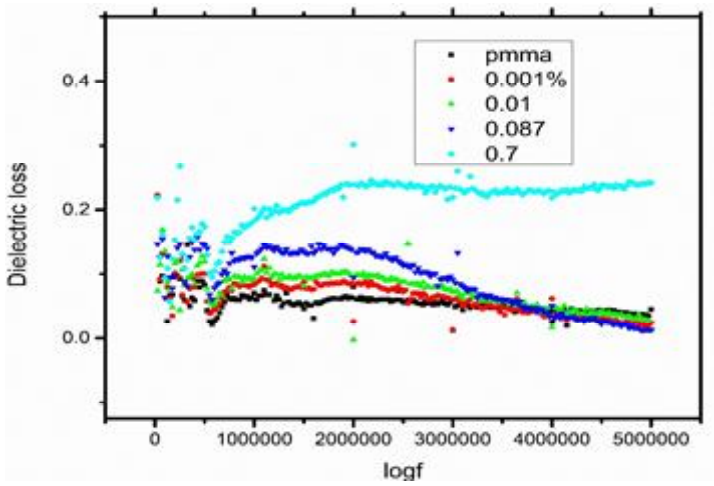

Fig. 10. Variation of dielectric loss with frequency

frequencies and also increases with doping level of P3HT. Increased conductivity is due to delocalized pi electrons induced by the conjugate polymer to the inert polymer matrix .The dielectric constant of the doped samples is more than the neat film. With the increase in the dopant level the dielectric constant as well as the dielectric loss increase [14,15]

X-Ray Diffraction study :

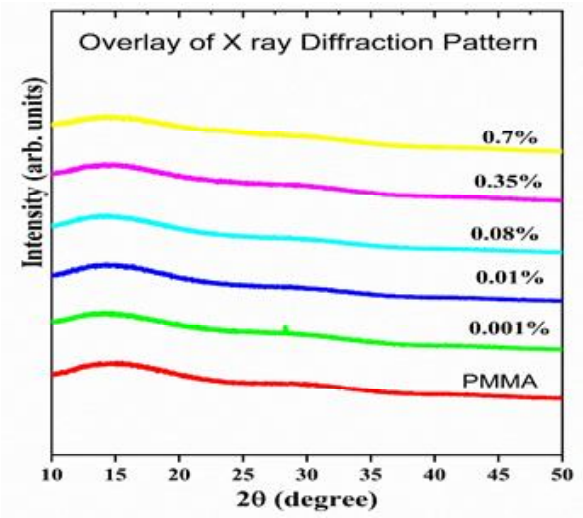

Figure 11. X Ray Diffractograms overlay

X ray diffraction studies were carried out with RIGAKU MINIFLEX-600 (MIT Manipal, Karnataka) benchtop X-ray diffractometer with Cu-Kα radiation of wavelength 1.5406 A^0 in the 2θ range 5–60° with a scan rate of 1° per min and step size 0.02°. The diffraction bands are observed for pure PMMA at 14.8 and 30.02 degree. The broad band is the indication of amorphous nature of PMMA. The dopant P3HT is also amorphous with diffracting angle at23.87^0 and d spacing of 4A^0. Considerable changes in the XRD pattern of the P3HT doped PMMA films are not observed. There is slight decrease in the second order diffracting angle in the composite film compared to pure PMMA. Polymers are amorphous or polycrystalline in nature. Because of this semicrystalline nature, the X-ray diffraction pattern of polymer contains defused bands [16,17].

Conclusion

The dopant's (P3HT) absorption property undergoes fascinating changes indicating the effect of PMMA environment on the behavior of the dopant. Highly transparent PMMA is made

absorptive in the visible region. Band gap of the new material is drastically reduced from 4.59 eV to about 1.77eV. The films are more conductive than pure PMMA as revealed by the ac conductivity graphs. P3HT/PMMA films are semi transparent so that they can be used in the construction of transparent electrodes. There is no such drastic changes observed in the fluorescence behavior of P3HT inside PMMA matrix. Material can be used in the construction of LED and other display devices. Increased dielectric constant of PMMA on doping with P3HT can open a way for the construction of good dielectric films.

Scope for future work :

UV Visible spectra of P3HT doped PMMA films can be further tailored by addition dyes of or other metal oxide nanoparticles. Since P3HT is highly absorbent in most of the visible region of electromagnetic spectrum, Plasmon resonance of metal oxide nanoparticles can be exploited to harvest huge amount of solar energy. The experiment can be repeated for higher doping concentrations of P3HT. At higher impregnation of p3H, one can expect the effect of chain conformation effect on fluorescence property of the material. Experiment can be done with different host matrix like a binary or ternary blends of insulating polymers like PMMA, PVAC, PS etc. Effect of different common solvents can also be investigated. One can increase the electrical conductivity of the films by doping with suitable ionic liquids. The P3HT/PMMA films can be tested for construction of photovoltaic cells or as LED material.

References

1. Abd-El Kader FH, Osman WH. and Hafez RS Effect of blend ratio on thermal and optical properties of pmma/pvac films International Journal of Current Research, Vol. 4, Issue, 01, pp.149-156, January, 2012.
2. Ahmed, R. M., Optical Study on Poly (methyl methacrylate)/Poly (vinyl acetate) Blends, International Journal of Photoenergy, 2009, 150389, 7 pages, 2009. https://doi.org/10.1155/2009/150389
3. Gumyusenge, Aristide, Tran, Dung T.; Luo, Xuyi; Pitch, Gregory M.; Zhao, Yan; Jenkins, Kaelon A.; Dunn, Tim J.; Ayzner, Alexander L.; Savoie, Brett M.; Mei, Jianguo Semiconducting polymer blends that exhibit stable charge transport at high temperatures Science, Volume 362, Issue 6419, pp. 1131-1134 (2018).
4. Shinohara, H., Nishide, H. Molecularly doped polythiophene film as an efficient photocathode for oxygen reduction to hydrogen peroxide. MRS Communications 14, 281–286 (2024). https://doi.org/10.1557/s43579-024-00523-w
5. M.E. Nicho, C.H. García-Escobar, M.C. Arenas, P. Altuzar-Coello, R. Cruz-Silva, M. Güizado-Rodríguez, Influence of P3HT concentration on morphological, optical and electrical properties of P3HT/PS and P3HT/PMMA binary blends, Materials Science and Engineering: B,Volume 176, Issue 17,2011, Pages 1393-1400, https://doi.org/10.1016/j.mseb.2011.05.008
6. Tudor DA, David S, Gheorghiu M, Gáspár S. The Impact of Physical Form on the Biocompatibility of Poly(3-hexylthiophene-2,5-diyl). Materials (Basel). 2025 Oct 11; 18(20):4671. doi: 10.3390/ma18204671. PMID: 41156903; PMCID: PMC12565759.
7. Nahyeon Gu, Yeong Don Park; Improvement of the chemical and physical gas adsorption ability of poly(3-hexylthiophene) thin films by ultraviolet-ozone exposure. J. Mater. Chem. C 2025; 13 (22): 11077–11083. https://doi.org/10.1039/d5tc00053j
8. Sihui Hou, Junsheng Yu, Xinming Zhuang, Dengfeng Li, Yiming Liu, Zhan Gao, Tianying Sun, Feng Wang, Xinge Yu; Phase Separation

of P3HT/PMMA Blend Film for Forming Semiconducting and Dielectric Layers in Organic Thin-Film Transistors for High-Sensitivity NO_2 Detection. *ACS Appl. Mater. Interfaces 27* November 2019; 11 (47): 44521–44527. https://doi.org/10.1021/acsami.9b15651

9. Nassir Lamis Faaz, Mohammed Hadi Shinen, Study of Electrical Properties of PMMA/P3HT Films Neuro Quantology; Bornova Izmir Vol. 20, Iss. 3, (2022): 47-50. DOI: 10.14704/nq.2022.20.3. NQ22039
10. Kaushlendra Agrahari, Ming Han Chi, S. Lakshmi Priya, Yu Han Cheng, Yu Wu Wang, Low voltage driven P3HT/PS phototransistor for ultra-high power efficiency UV sensing, Organic Electronics,Volume 128,2024,107033, https://doi.org/10.1016/j.orgel.2024.107033.
11. Roy, Santanu: Aguirre, Alica; Higgins Daniel A; Chickan Victor Investigation of charge transfer interactions in CdSe Nanorod P3HT/PMMA Blends by optical Microscopy, ACS publications https://doi.org/10.1021/jp20792v
12. S. Srivastava, A. K. Rai, M. Shrivastava, and P. C. Ramamurthy, " Ultra-Thin P3HT Film Processing with Precise Thickness Control for Next-Generation OFET Devices." Adv. Funct. Mater. 36, no. 21 (2026): e17865. https://doi.org/10.1002/adfm.202517865
13. Kai Zhang, Wenchao Zhao, Biao Xiao, Long Ye; Beyond organic photovoltaics: unlocking the potential of P3HT and its derivatives in perovskite and quantum dot solar cells. EES Sol. 2026; 2 (1): 108–117. https://doi.org/10.1039/d5el00154d
14. N. Sharma, U. R. Bagal and G. D. Jindal, "High-Dimensional Impedance Spectroscopy Analysis of Homeopathic Medicines: A Machine Learning Approach*," 2025 International Conference on Biomedical Engineering and Sustainable Healthcare (ICBMESH),* Manipal, India, 2025, pp. 1-5, doi: 10.1109/ICBMESH66209.2025.11182244.
15. Yuhao Zhang, Jiayuan Xu, Xinyi Xie, Qiu-An Huang, Shijie Cheng, Jia Xie; Measurement, interpretation, and application of electrochemical impedance spectroscopy to lithium-ion batteries. EES Batteries 2026; 2 (1): 80–102. https://doi.org/10.1039/d5eb00153f
16. Tatsuya Arai, Masahiro Kuramochi, Kazuhiro Mio, Hiroshi Sekiguchi, Sakae Tsuda, Daisuke Sasaki, Tomoyasu Aizawa, Yuji C. Sasaki; Fluctuation of Time-Resolved X ray Diffraction Reveals the Rotational Dynamics of Nanoparticles in Polymer Materials. Nano Lett. 24 September 2025; 25 (38): 14156–14165. https://doi.org/10.1021/acs.nanolett.5c03840
17. Ganghoon Jeong, Divya Rajan Panikar, Zhang Dianqi, Gaeun Jeong, Hyonseok Yoon, Vinh Van Tran, Byoungnam Park, Jong Hun Han, Nayan Ranjan Singha, Mincheol Chang; Enhanced NO_2 sensing performance in organic field-effect transistors via regio-regularity-controlled P3HT blend films. J. Mater. Chem. A 2025; 13 (39): 33646–33660. https://doi.org/10.1039/d5ta05576h