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FLUORESCENCE AND SPECTROSCOPIC CHARACTERIZATION OF NOVEL TERPOLYMERS BASED ON PHENOLPHTHALEIN, ERIOCHROME BLACK T AND THYMOL BLUE FOR SENSOR APPLICATIONS

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Abstract. In this study, two novel terpolymers were synthesized via condensation copolymerization using phenolphthalein, Eriochrome Black T (EBT) and Thymol Blue with terephthaloyl chloride in the presence of titanium dioxide (TiO_2). The aim was to develop functional materials with enhanced fluorescence and structural properties. The synthesized terpolymers, (phenolphthalein-co-Eriochrome T) and (phenolphthalein-co-Thymol Blue), were characterized using FTIR, SEM, EDX, UV-Vis and fluorescence spectroscopy. FTIR confirmed successful polymerization through the disappearance of hydroxyl groups and the appearance of ester carbonyl bands. SEM images revealed porous, fibrous surfaces, while EDX verified the elemental composition and incorporation of TiO_2. Optical analysis showed emission peaks at 590 nm and 530 nm for the Ph-EBT and Ph-ThB terpolymer, respectively, highlighting their fluorescence potential. These findings suggest that the prepared terpolymers possess promising properties for applications in sensing, imaging and smart materials.

Keywords: *Eriochrome T, fluorescence, phenolphthalein, Thymol Blue.*

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1. Introduction

Polymers have been extensively studied for their versatile applications in various scientific and industrial fields, including materials science, biomedical engineering and environmental sciences. In recent years, functionalized polymers with specific optical, electronic and biological properties have gained significant attention. Among these, terpolymer - macromolecules formed by the copolymerization of three different monomers - have emerged as promising materials due to their enhanced structural and functional diversity (Carraher, 2017). The synthesis and characterization of new terpolymer incorporating dye molecules have been of particular interest due to their potential applications in fluorescence sensing, drug delivery and optoelectronic devices (Santos *et al*., 2019).

Fluorescence spectroscopy is a powerful tool for investigating the photo-physical properties of organic and polymeric materials. By analyzing the fluorescence emission and excitation spectra of polymeric compounds, researchers can gain insights into molecular interactions, conformational changes and photo-stability. This technique has been widely used in polymer science to study the behavior of functionalized materials in various environments, particularly those containing chromophores or fluorophores (Lakowicz, 2006).

This study delves into the synthesis and comprehensive spectroscopic analysis of two novel terpolymers: (Phenolphthalein-co-Eriochrome T) and (Phenolphthalein-co-Thymol blue). These terpolymers are strategically designed by incorporating phenolphthalein, a well-known pH indicator exhibiting fluorescence properties in its alkaline form, with two other structurally distinct chromogenic indicators, Eriochrome T and thymol blue. The rationale behind this copolymerization approach lies in the potential to create materials with enhanced or novel functionalities arising from the synergistic interplay of the individual monomer units (Bouriche *et al*., 2021; Elmas *et al*., 2021).

Phenolphthalein, a widely recognized synthetic organic compound, is renowned for its pH-dependent color change, transitioning from colorless in acidic and neutral solutions to pink in alkaline media. This property has made it an indispensable indicator in acid-base titrations and a valuable component in various chemical sensors (Pipil & Saini, 2023; Zhang & Liu, 2023). The incorporation of phenolphthalein units into a polymer chain can impart pH-responsive optical properties to the resulting material, opening avenues for the development of pH-sensitive fluorescent probes and smart coatings (Gayathri *et al*., 2022; Alshareef *et al*., 2024). Eriochrome T (EBT), another prominent azo dye, is extensively employed as a metallochromic indicator in complex metric titrations, particularly for the determination of water hardness (Baig *et al*., 2022; Shi *et al*., 2023). Integrating EBT units into a polymer backbone could lead to materials with dual functionalities: pH-responsiveness derived from the polymer matrix and metal ion sensitivity originating from the EBT moieties, potentially paving the way for multi-analyte sensing platforms (Wilhelm, 2014). Thymol blue, a sulfonephthalein indicator, shares the pH-dependent color-changing properties with phenolphthalein but exhibits a more complex behavior with two distinct transition ranges: one in the acidic region (red to yellow) and another in the alkaline region (yellow to blue) (Shimada *et al*., 2019; Tang *et al*., 2019). Incorporating thymol blue into a copolymer could generate materials with a broader pH response range and potentially more intricate optical modulation capabilities compared to those containing only phenolphthalein (Kowalczyk *et al*., 2024).

The aims of this research to provide a detailed understanding of fluorescence and spectroscopic analysis of these novel (Phenolphthalein-co-Eriochrome T) and (phenolphthalein-co-thymol blue) terpolymer. By systematically investigating their absorption and fluorescence characteristics under varying conditions, this study seeks to highlight their potential as advanced functional materials for applications in sensing, imaging and beyond.

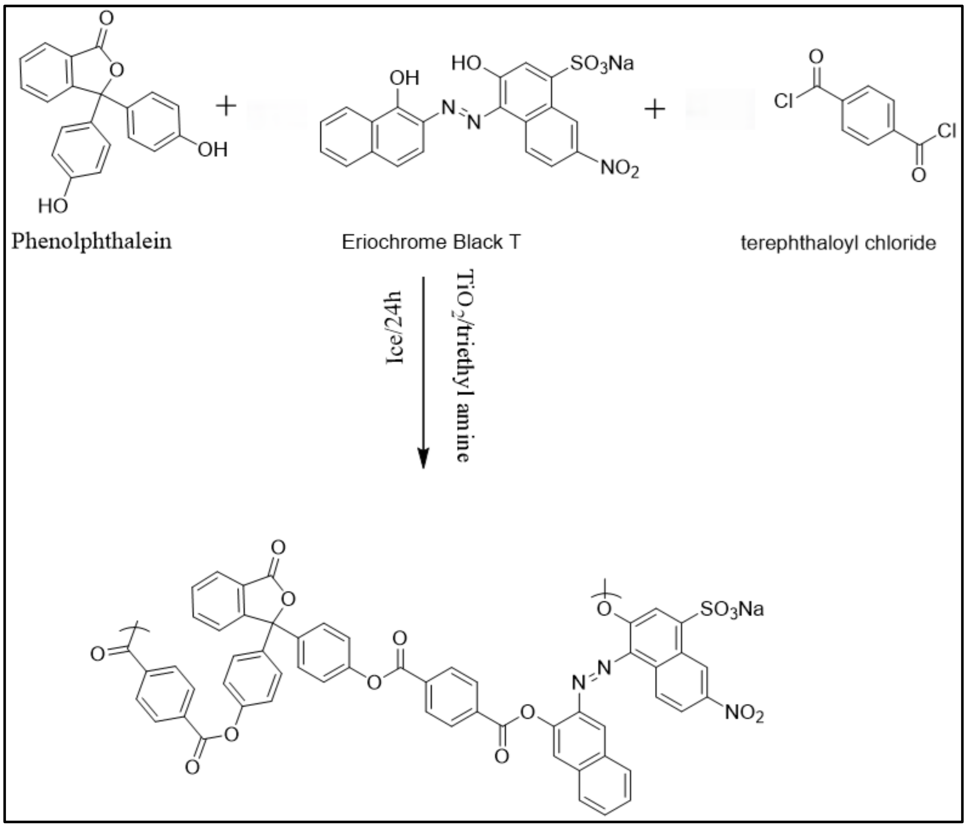
2. Materials and methods

Chemicals

All reactions were performed utilizing clean, oven-dried glassware in a nitrogen atmosphere. All compounds utilized were obtained from commercial suppliers and employed without additional purification. Phenolphthalein, Eriochrome Black T (EBT), titanium oxide, tri-ethyl amine (TEA, Assay 99.9 %), terephthaloyl chloride, Thymol blue, methanol, dichloromethane (DCM) (Assay 99.5 %), acetone and hydrochloric acid were acquired from Sigma Aldrich. A range of analytical techniques was utilized to identify the copolymer, including FT-IR, XRD, SEM and fluorescence.

Synthesis of Phenolphthalein- Eriochrome Black T (Ph-EBT) Terpolymer (Huang *et al*., 2019)

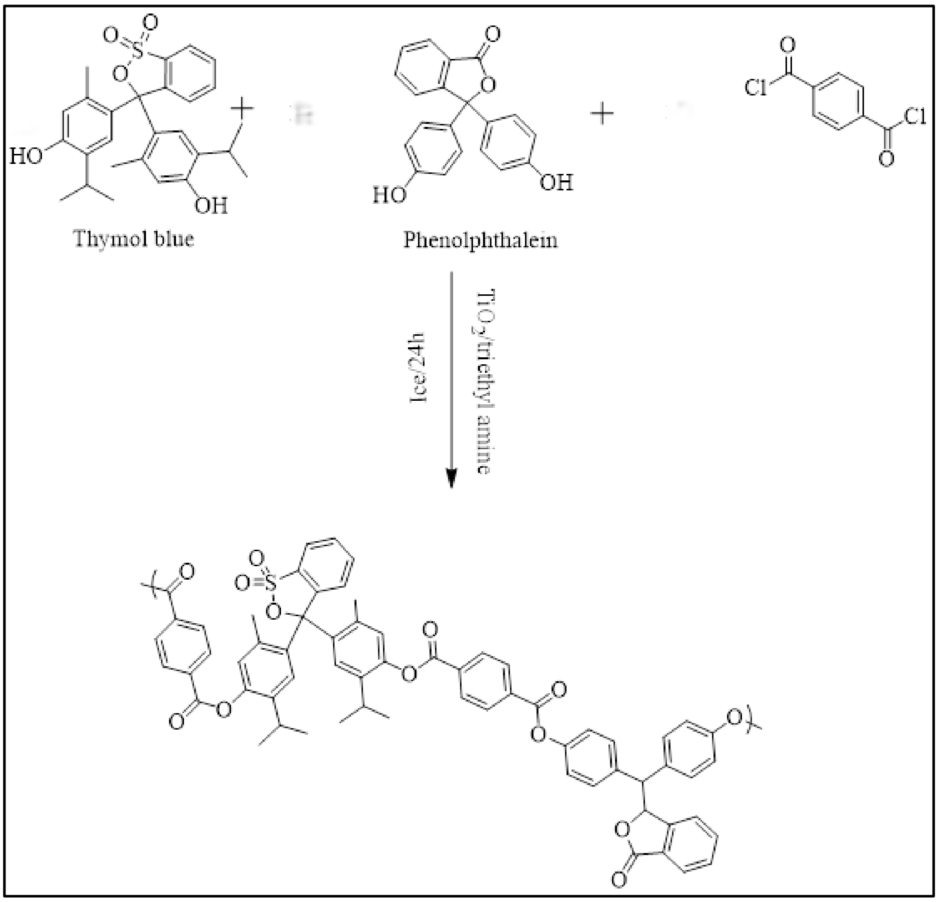
To make the mixture, dissolve equal amounts of phenolphthalein (0.636 g) and Eriochrome black T (0.920 g) in 50 ml of dichloromethane (DCM) in a 250 ml round flask at 10°C using condensation polymerization. Dissolve (0.1 g) TiO_2 in 25 ml of dichloromethane, place it in the ultrasound for 20 min and then add drop by drop to the above mixture. After stirring for 30 min in nitrogen, trimethylamine (TEA) (1 mL, 0.008 mmol) was added dropwise and the reaction mixture was constantly stirred for 1:30 hours. Then, 0.812 g (0.004 mole) of terephthaloyl chloride dissolved in 25 ml of dichloromethane was slowly added drop by drop to the mixture; the color changed from black to maroon red. The polymerization process lasted for 24 hours in a nitrogen and an ice bath, during which a red solid formed by using n-hexane to help it separate. The terpolymer was purified by washing it in methanol and water, the yield of the finished product was 65 %.



Scheme 1. The chemical equation for the synthesis Ph-EBT Terpolymer

Synthesis of Phenolphthalein - Thymol blue (Ph-ThB) Terpolymer (Huang *et al*., 2019)

To prepare the mixture, dissolve equal amounts of phenolphthalein (0.636 g) and Thymol blue (0.933 g) in 50 ml of dichloromethane (DCM) in a 250 ml round flask at 10 °C using condensation polymerization. Dissolve (0.1 g) TiO_2 in 25 ml of dichloromethane, place it in the ultrasound for 20 min and then add drop by drop to the above mixture. After stirring for 30 min in nitrogen, trimethylamine (TEA) (1 mL, 0.008 mmol) was added dropwise and the reaction mixture was constantly stirred for 1:30 hours. Then, 0.812 g (0.004 mole) of terephthaloyl chloride dissolved in 25 ml of dichloromethane was slowly added drop by drop to the mixture. The polymerization process lasted for 24 hours in a nitrogen and an ice bath, during which a pomegranate color formed by using n-hexane to help it separate. The terpolymer was purified by washing it in methanol and water, followed by filtration. The yield of the finished product was 62 %.



Scheme 2. The chemical equation for the synthesis Ph-ThB Terpolymer

3. Results and discussions

3.1. Characterization of terpolymer by Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infrared Spectroscopy (FTIR) is a critical technique for identifying chemical functionalities and monitoring structural changes during polymerization. This method allows for the detection of functional groups and molecular interactions within the synthesized copolymers.

Terpolymer (Ph-EBT) and (Ph-ThB) demonstrate significant spectral changes, which are indicative of successful polymerization. One of the most noticeable changes is that the hydroxyl (-OH) stretching bands, which were seen in the monomers around 3300-3500 cm^{-1}, are no longer present, showing that the condensation reactions are finished. At the same time, the strong absorption bands for ester carbonyl (C=O) between 1725-1741 cm^{-1} show clear proof that ester bonds have formed. The C-O-C stretching vibrations appearing in the range of 1150-1250 cm^{-1} further support the formation of ester linkages, which are characteristic of these condensation polymers.

A noticeable TiO_2 stretching band in the region of 635-680 cm^{-1} further confirms the integration of TiO_2 nanoparticles into the matrix for terpolymer (Ph-EBT) and (Ph-ThB), which incorporate TiO_2. This structural modification is expected to enhance UV resistance and thermal stability, contributing to improved material performance in industrial applications.

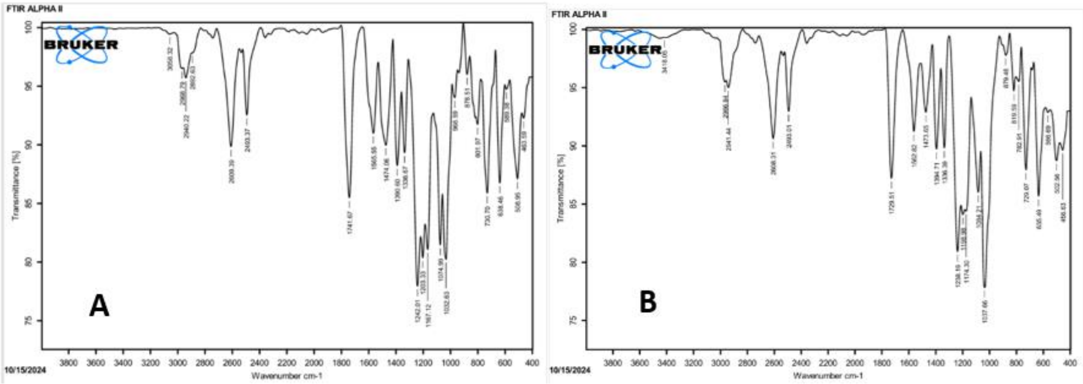


Figure 1. FT-IR spectra: (A) Terpolymer (Ph-EBT), (B) Terpolymer (Ph-ThB)

3.2. Characterization of Terpolymers by Energy Dispersive X-ray Spectroscopy (EDX) Analysis

Energy Dispersive X-ray Spectroscopy (EDX) is a widely utilized technique for determining the elemental composition of synthesized copolymers. By detecting characteristic X-ray emissions from different elements, EDX provides a quantitative assessment of the presence and distribution of essential components such as carbon (C), nitrogen (N), oxygen (O), chlorine (Cl) and titanium (Ti). This method is especially helpful for checking if reinforcing agents like Ag and TiO_2 have been added successfully and for understanding how the makeup of elements affects the properties of polymers.

For the terpolymer (Ph-EBT) and (Ph-ThB), as shown in Figure 2, changes in chlorine and oxygen levels show that their chemical makeup is different. Chlorine content ranged from 2.19% to 4.8%. The oxygen content in the (Ph-ThB) co-polymer is 26.57%, which is related to its phenolphthalein and thymol blue changes, indicating that it has a lot of oxygen-containing groups. Additionally, titanium levels ranged from 0.81% to 1.52%, signifying variations in TiO_2 distribution across these polymers. Table 1 illustrates these variations.

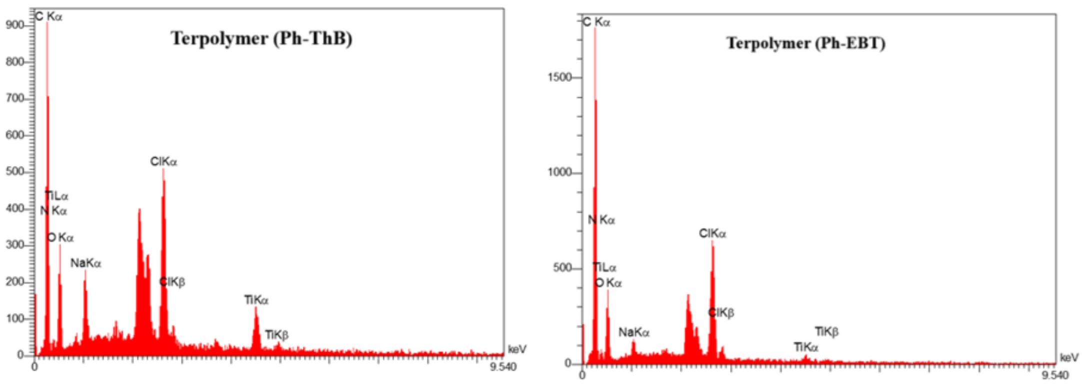


Figure 2. XRD spectra for Ter-polymers (Ph-EBT) and Ter-polymers (Ph-ThB)

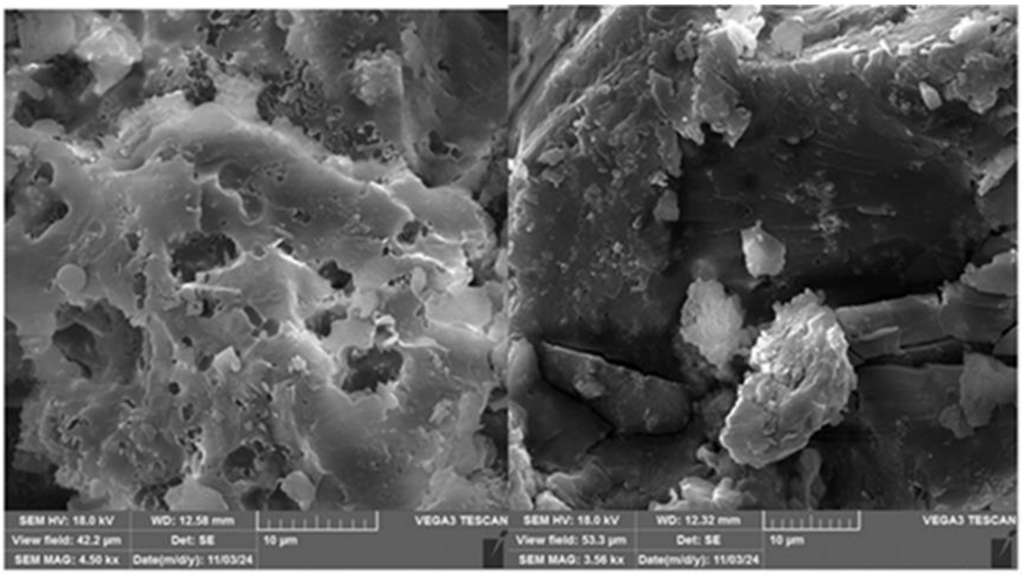
Table 1. Summarizes the elemental composition obtained from EDX analysis

Terpolymer	Carbon (%)	Nitrogen (%)	Oxygen (%)	Titanium (%)	Chlorine (%)	Sodium (%)
Ph-EBT	55.94	13.73	25.43	0.81	2.19	1.90
Ph-ThB	50.84	15.69	26.57	1.52	2.87	2.51

3.3. Characterization of Terpolymer by Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) is a key imaging method used to study the surface features, particle arrangement and small-scale structures of polymer materials. Using a focused electron beam, SEM takes clear images that show important details like smoothness, tiny holes, evenness and clumps of nanoparticles. The SEM analysis of the made copolymers provides important information about their strength, consistency and possible uses in areas like filtration, coatings and sensors.

The SEM images of the terpolymer (Ph-EBT and Ph-ThB), as shown in Figure 3, demonstrate porous and fibrous surface textures. The tiny holes and connected pathways in these copolymers indicate they could be useful for filtering membranes and systems that release substances in a controlled way. The fibrous nature observed in these polymers may also contribute to improved mechanical flexibility, making them suitable for sensor applications and flexible coatings.



FE-SEM for terpolymer Ph-EBT **FE-SEM for terpolymer Ph-ThB**

Figure 3. FE-SEM for Terpolymer (Ph-EBT and Ph-ThB)

3.4. Characterization of Terpolymer by Fluorescence and UV-Vis Spectroscopy Analysis

The UV-Vis absorption spectrum of the terpolymer (Ph-EBT) in Figure 4 shows a distinct peak at 520 nm, which is linked to electronic transitions in the conjugated backbone. Its fluorescence emission at 590 nm, which is of moderate strength, suggests a slight decrease in fluorescence, likely due to interactions between molecules or aggregation effects. Its fluorescence emission at 590 nm with moderate intensity indicates some reduction in fluorescence, possibly caused by interactions between molecules or aggregation effects. Its fluorescence emission at 590 nm with moderate intensity suggests the presence of partial fluorescence quenching, which may be due to intermolecular interactions or aggregation effects (Swaminathan, 2021). The IR spectrum supports the presence of functional groups such as hydroxyl or carbonyl, which might contribute to the observed fluorescence properties through hydrogen bonding or excited-state stabilization (Hoffmann, 2023).

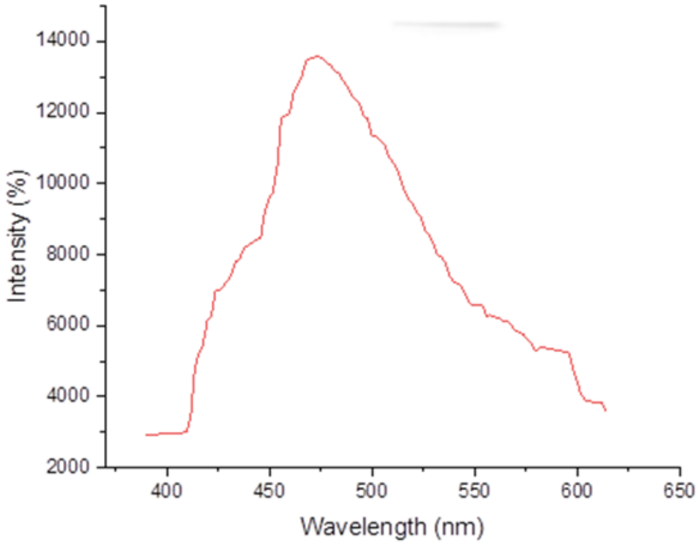


Figure 4. Fluorescence spectroscopy for terpolymer (Ph-EBT)

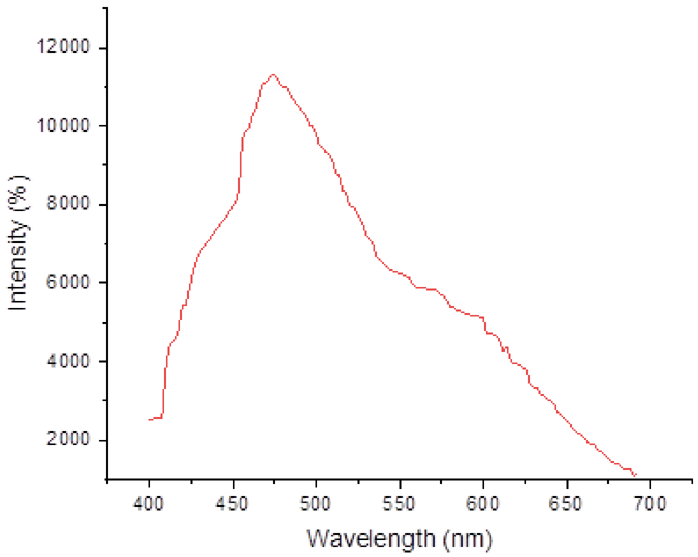


Figure 5. Fluorescence spectroscopy for terpolymer (Ph-ThB)

The UV-Vis spectrum of the terpolymer (Ph-ThB), shown in Figure 5, shows an absorption band at 450 nm, which suggests it has a strong conjugated structure (Chanu *et* *al*., 2024). Its fluorescence emission at 530 nm is very bright, meaning there are few energy losses and good ways for energy to relax. Its fluorescence emission at 530 nm exhibits high intensity, implying minimal non-radiative losses and effective energy relaxation pathways (Huang *et al*., 2019). The presence of electron-donating or electron-withdrawing groups identified in the IR spectrum might enhance fluorescence efficiency by stabilizing the excited-state energy levels and reducing intersystem crossing to non-radiative states (Wang *el at*., 2013).

4. Conclusion

The synthesis and comprehensive characterization of novel terpolymers incorporating phenolphthalein (PP), Eriochrome Black T (EBT) and thymol blue (TB) demonstrate their significant potential as advanced materials for optical and chemical sensor applications. The terpolymer was synthesized via a condensation polymerization strategy, leveraging the distinct chromophoric and ionophoric properties of each monomer to engineer a multifunctional material. Structural analysis using FTIR and FE-SEM-EDX spectroscopy confirmed the successful integration of all three monomers into the polymer backbone.

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