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Synthesis and Characterization of Polyaniline / [BMIM][BF₄] Polyionic Liquid by Interfacial Polymerization

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Abstract

Polyaniline (PANI) was prepared by polymerization via the chemical oxidation of aniline monomer with ammonium persulfate as the initiator. The interfacial polymerization method was used to prepare PANI/1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] polyionic liquid (PIL). The obtained PANI/[BMIM][BF₄] PIL was investigated by the XRD, EDX, SEM, FTIR, and UV-Visible characterizations. X-ray diffractogram of PANI showed five prominent characteristic peaks at 27.1°, 24°, 21.8°, 19.8°, and 18.2°. This demonstrates the semi-crystalline character of the polyaniline produced through the interfacial polymerization process. Incorporation of [BMIM][BF₄] into PANI reduced the crystalline phase and enhanced amorphicity. From the EDX pattern, several elements appeared in this test; oxygen had of the highest weight percentage of 54.2%. The SEM image showed a clear hierarchal porous structure with nano-sticks particles and forms a cross-linked framework between PANI and [BMIM][BF₄]. From FTIR spectra of PIL, a prominent absorption peak at 3163.26 cm⁻¹ was noted because of the N-H stretching vibrations present in the polymer. The UV-Vis spectra for PANI/[BMIM][BF₄] polyionic liquid showed three peaks between 200 and 1060 nm. These bands result from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, which are related to the excitement absorption of benzenoid and quinoid groups.

Keywords: Polyaniline, [BMIM][BF₄] ionic liquid, interfacial polymerization, polyionic liquid.

تحضير و تشخيص البوليمر انيلين / السائل متعدد الأيونات بواسطة البلمرة البينية

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الخلاصة

تم تحضير البوليمر انيلين بواسطة البلمرة عن طريق الأكسدة الكيميائية لجزيئات الانيلين مع كبريتات الأمونيوم كبادئ. بعد ذلك تم استخدام طريقة البلمرة السطحية لتحضير البوليمر انيلين / السائل متعدد الأيونات.

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تم فحص البولي انيلين/ السائل متعدد الأيونات الذي تم الحصول عليه بواسطة خصائص حيود الأشعة السينية، مطيافية تشتت الطاقة بالأشعة السينية، المجهر الإلكتروني الماسح، مطيافية الأشعة تحت الحمراء باستخدام تحويل فورييه ومطياف الأشعة فوق البنفسجية-المرئية. يظهر مخطط حيود الأشعة السينية للبولي التوالي. على 18.2° , 19.8° , 21.8° , 24° , 27.1° انيلين القمم المميزة الخمس الرئيسية يوضح هذا الطابع شبه البلوري للبولي انيلين الناتج من خلال عملية البلمرة البينية، اندماج السائل متعدد الأيونات في البولي انيلين يقلل الطور البلوري و يعزز الطور غير المتبلور. من نمط الأشعة السينية المشتتة للطاقة، هنالك عدة عناصر ظهرت في هذا الاختبار، كان اعلاها عنصر الأوكسجين بمعدل 54.2%. اظهرت صورة المجهر الإلكتروني الماسح بنية مسامية هرمية واضحة مع جزيئات العصي النانوية و تشكل ايضا هيكل مترابط بين البولي انيلين و السائل متعدد الأيونات. من طيف الأشعة تحت الحمراء للسائل متعدد الأيونات، من الممكن رؤية قمة امتصاص كبيرة عند 3163.26 cm^{-1} للرابطة N-H الموجودة في البوليمر بسبب الاهتزازات التمديدية. يظهر طيف الأشعة فوق البنفسجية للبولي انيلين/ السائل متعدد الأيونات ثلاث قمم تتراوح بين (200 to 1060)nm , تنتج هذه النطاقات من الانتقالات

$n \rightarrow \pi^*$ و $\pi \rightarrow \pi^*$, و التي ترتبط بامتصاص الاثارة لمجموعات البنزينويد و الكينويد.

Introduction

One of the most technologically promising organic polymers is polyaniline (PANI) [1-3]. High flexibility, simplicity in synthesis, affordability, environmental stability, excellent optical and magnetic properties, the ability to control electrical conductivity by altering either the oxidation or protonation state and the affordability of the aniline monomer are a few of the many key factors that made PANI unavoidable in almost every aspect of daily life [4-6]. PANI is an organic semiconductor and conducting polymer that belongs to the family of semirigid and flexible rod polymers [7,8]. It has a significant potential for use in conductive, smart materials in optical and electrical research. It is the second most commonly used electrically conductive polymer after polypyrrole (PPy). PANI is regarded as an appropriate microwave-absorbing material for use in antistatic fabric, sensors, stealth materials, etc., [9-12]. The most popular process for producing PANI is oxidant polymerization [4]. Aniline, an oxidant, and an acidic media are necessary to synthesize PANI in chemical methods [13,14]. However, interfacial polymerization is the most common technique for preparing polyionic liquid [15].

Unlike conventional polymers, polyionic liquids (PILs) are repeating units that resemble the structure of a typical ionic liquid and contain at least one ion center in a polymer chain [16-18]. The key benefits of PILs over Ionic Liquids (ILs) and polymers are their higher thermal stability, flexibility, improved processability, durability, and nontoxicity [19-21]. A specific class of polyelectrolytes known as polymeric/polymerized ionic liquids, or polyionic liquids (PILs), contains an IL species in the cationic or anionic centers [22,23]. PILs have generated a lot of attention in polymer chemistry and materials science, not only due to how they combine the special qualities of ILs with the structure of macromolecules but also because they have the potential to add new qualities and functions [24,25]. The earliest studies on PILs can be traced back to the 1970s when cationic vinyl monomer free radical polymerization became increasingly popular [26].

PIL preparation can be done in one of two ways. The easiest and most popular method is the direct radical polymerization of IL monomers [27]; The other method involves using IL monomers to modify the polymer after polymerization [28,29]. To introduce an environmentally friendly effect into the reaction system, Gao et al. chose ionic liquid (IL) as

the organic phase. They succeeded in producing PANI nanoparticles with sizes of 30-80 nm from the interfacial polymerization of aqueous/IL [30].

In this study, a new polyionic liquid was synthesized by polymerizing polyaniline in an ionic liquid. Adding ionic liquid improves the ionic transport characteristics of conducting polymers while maintaining their high electrical mobility.

Fourier transform infrared spectrometer (FTIR) and ultraviolet-visible spectrometer (UV-Vis) were used to determine the chemical structure of PANI. SEM and X-ray diffraction (XRD) were used to confirm the morphology of the synthesized PANI fibers. The findings demonstrated that the PANI and ionic liquid's ion and electron mixing properties enhance the processability of the nanoporous PANI film with good performances.

Experimental Materials

Aniline, $C_6H_5NH_2$, and ammonium persulfate (APS), $(NH_4)_2 S_2O_8$, which were used to prepare PANI, were purchased from Thomas Baker (Chemicals) Pvt. Ltd, India. Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were purchased from CDH, India. Ionic Liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] (purity > 98.0%) ($M_w = 226.02$ g/mol) was purchased from Sigma-Aldrich (USA). All the solutions were prepared and rinsed with deionized water.

Preparation method

The chemical process of oxidative polymerization was used to synthesize PANI. 50 ml of 1.5 M hydrochloric acid (HCl) and 4.3 ml of aniline monomer were combined to prepare a monomer solution. A second solution was prepared by mixing 8.4 g of ammonium persulfate (APS) powder with 50 ml of 1.5 M HCl. The two solutions were then mixed in a glass beaker. The combination was agitated for two hours at 50 °C before adding 5 ml of 2 M H_2SO_4 to the finished product. PANI polymer was formed when the solution changed from a clear color to one that was blackish-green. The interfacial polymerization method was used to prepare PANI polyionic liquid by adding 5 ml of [BMIM][BF₄] ionic liquid to the prepared PANI solution with continuous stirring for 1 hour at 25 °C. The preparation and structure of the polymerization of PANI polyionic liquid are shown in Figure 1 and Figure 2, respectively.

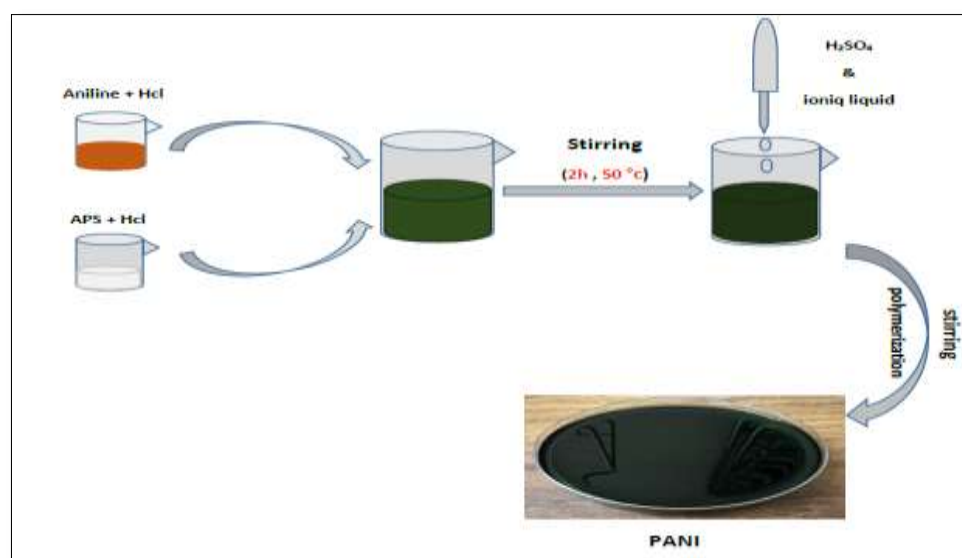


Figure 1: Schematic diagram of the preparation of PANI/[BMIM][BF₄] polyionic liquid.

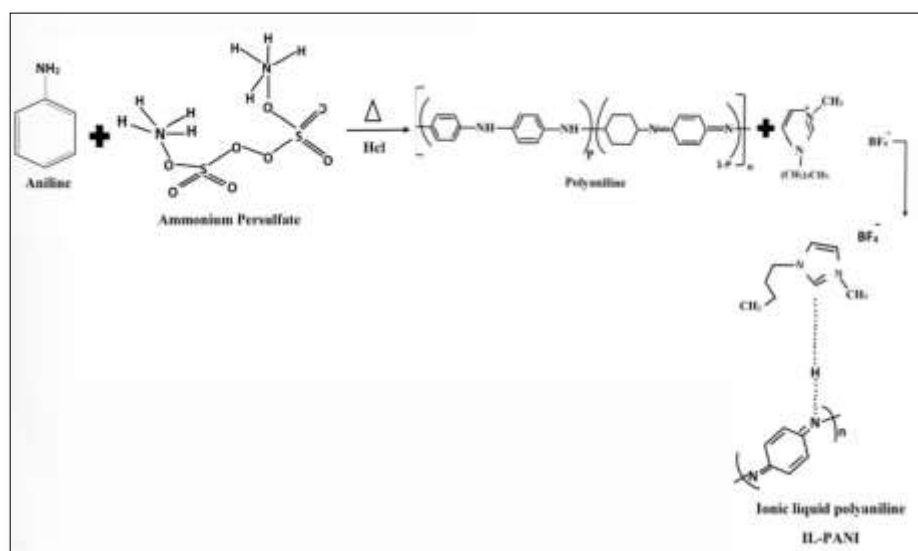


Figure 2: Schematic structure of the polymerization of PANI and PANI/[BMIM][BF₄] polyionic liquid.

Characterization techniques

The X-ray diffraction spectra of PANI and PANI/[BMIM][BF₄] polyionic liquid were obtained with an X-ray diffractometer (Aeris Research – Benchtop XRD) with Cu-K α monochromatic radiation ($\lambda = 1.5406 \text{ \AA}$) at ambient temperature and 2θ between 10° and 80° . Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) (Axia ChemiSEM) was used to observe the morphology of the sample, as well as to analyze the elemental composition in the prepared polyionic liquid. The formation of PANI-[BMIM][BF₄] PIL and interaction between PANI and [BMIM][BF₄] were determined by FTIR using Shimadzu FT-IR spectrometer (Made in Japan) in the region $4000\text{-}400 \text{ cm}^{-1}$ at a resolution of 1 cm^{-1} . The UV-Vis (ultraviolet-visible) spectra of PANI-[BMIM][BF₄] PIL measurements were made at room temperature in the wavelength range of $190 - 1100 \text{ nm}$ with a Lambda 35 UV-Vis spectrometer (Perkin Elmer, United States).

Results and Discussion

XRD analysis

The XRD pattern of the prepared PANI polymer is shown in Figure 3. The primary distinctive peaks of PANI polymer were observed at 27.1° , 24° , 21.8° , 19.8° , and 18.2° related to the emeraldine salt of PANI indicative of the (200), (002), (020), (001), and (011) crystal planes, respectively. The strong peaks in the pattern indicate that polyaniline is a semi-crystalline polymer because it contains benzenoid and quinonoid groups [31]. This finding suggests that the semi-crystalline character of the polyaniline polymer was produced by the interfacial polymerization pathway [32].

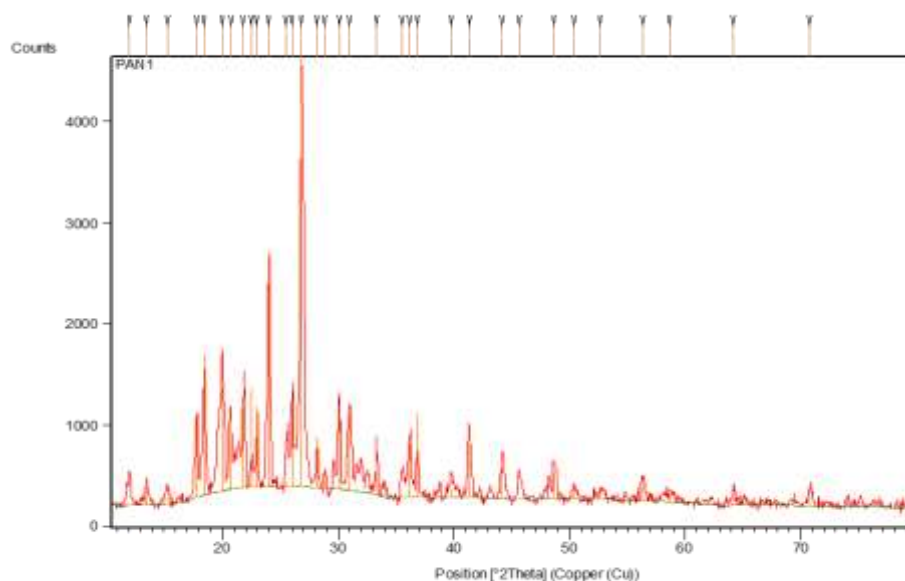


Figure 3: XRD pattern of PANI.

The XRD pattern of the polyionic liquid PANI/[BMIM][BF₄] is shown in Figure 4. From the figure, one can note that the PANI/[BMIM][BF₄] polyionic liquid XRD pattern contains a broad hump, which attributes to the addition of [BMIM][BF₄] ionic liquid, which acted as the plasticizer and therefore reduced the crystalline phase due to the molar amount of imidazolium ion. The PANI chain's electrons were rearranged as a result of the imidazole heterocycle's existence [33]. In addition to delivering mobile ions, ionic liquid has been discovered to also increase amorphicity. Hence, its addition is likely to change the degree of crystallinity [34]. The degree of crystallinity is impacted by the structural changes in the polymer, which is caused by the complexation of the ionic liquid cations with the polymer backbone [35].

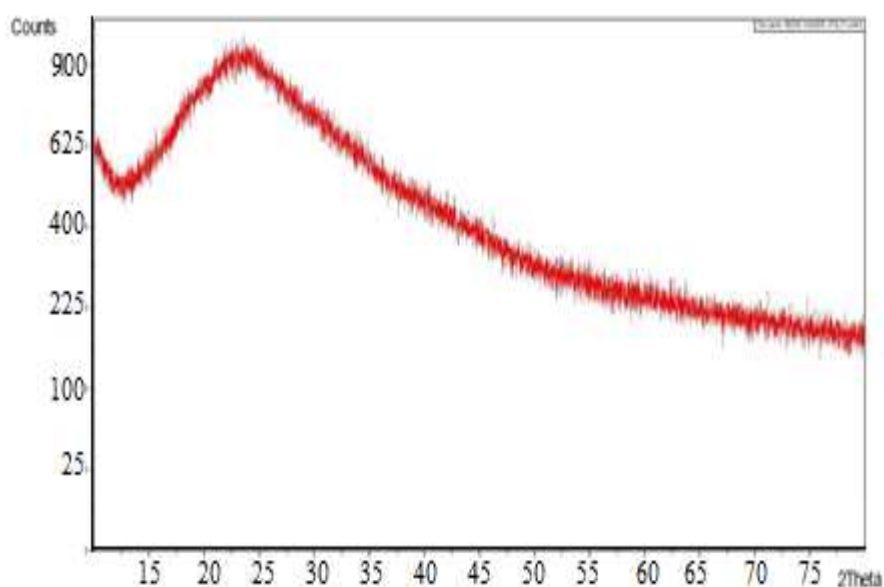


Figure 4: XRD pattern of PANI/[BMIM][BF₄] polyionic liquid.

EDX studies

EDX spectroscopy was used to evaluate the chemical composition of PANI/[BMIM][BF₄] polyionic liquid, as depicted in Figure 5. Table 1 shows the elemental composition of

PANI/[BMIM][BF₄] polyionic liquid with their percentage distribution by weight. According to Table 1, oxygen comprised most of the polyaniline, accounting for 54.2% of the total weight. The presence of oxygen and sulfur is assumed to derive from ammonium peroxydisulfate ((NH₄)₂S₂O₈), which is produced when sulfuric acid oxidizes polyaniline [35,36]. Carbon (the second abundant element with an average weight of about 22%) was formed by the molecular formula C₆H₅NH₂ of aniline [36].

The effective bonding of the ionic liquid to the polymer backbone is demonstrated by the elevated sulfur (S) and oxygen (O) contents in the EDX spectra. The peaks for the elements sulfur (S), oxygen (O), and carbon (C) could be seen at three different energies: 2.5, 0.68, and 0.34 keV. These peaks could each be attributed to SK_α, OK_α, and CK_α, respectively. A significant increase was seen for each absorbing element when the input photon's energy was equivalent to the binding energy of an electron shell in the absorber, such as K, L, or M, etc. [36]. This required the least energy to create a void in that specific shell. According to reports, the characteristics of the mesoporous PANI/[BMIM][BF₄] polyionic liquid were improved by the addition of the S components [37].

Table 1: The elemental composition of PANI/[BMIM][BF₄] polyionic liquid.

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	30.7	0.4	22.0	0.3
O	56.8	0.4	54.2	0.4
Si	0.1	0.0	0.2	0.0
S	12.3	0.1	23.5	0.1

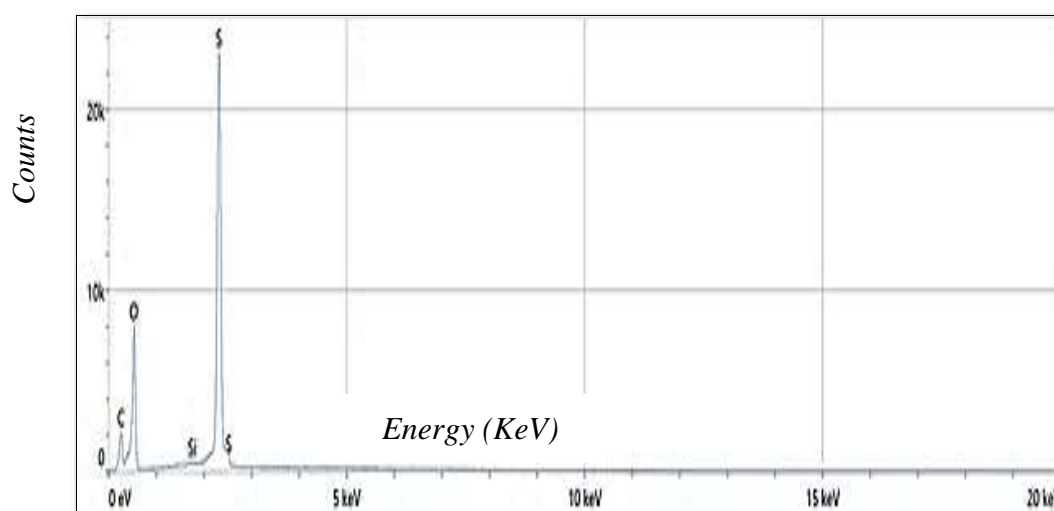


Figure 5: EDX analysis of PANI/[BMIM][BF₄] polyionic liquid.

SEM analysis

The surface morphology of the synthesized PANI/[BMIM][BF₄] polyionic liquid was investigated by SEM, as shown in Figure 6. It represents a clear hierarchical porous structure with nano-sticky particles, which may result from the various degrees of polymerization. From Figure 6, it can be observed that the PANI/[BMIM][BF₄] polyionic liquid particles are entangled with each other to form a cross-linked framework and corresponding meso and macroporous structures [33,37]. The surface morphology of the prepared PANI/[BMIM][BF₄] polyionic liquid is comprised of tiny, equally distributed crystalline grains with a lamellar structure [34, 35]. These grains' tiny sizes were impacted by the incorporation of the [BMIM][BF₄] ionic liquid during polymeric polymerization. The resultant membrane

exhibited an increasing degree of amorphicity when the [BMIM][BF₄] ionic liquid was introduced during polymerization [36,38]. The XRD results stated above were also used to support the claim that increased IL content enhances amorphicity [34,39].

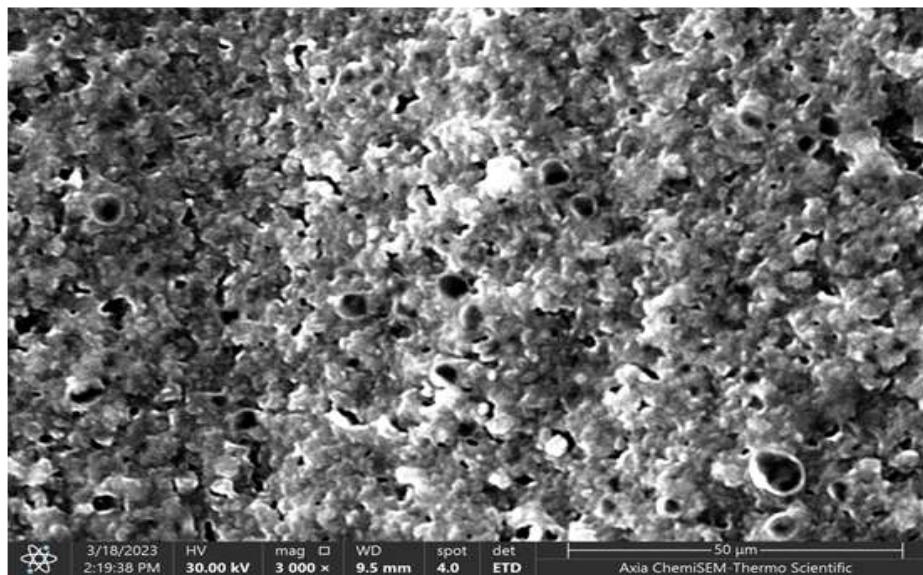


Figure 6: SEM micrographs of PANI/[BMIM][BF₄] polyionic liquid.

FT-IR Studies

The FT-IR spectrum is shown in Figure 7 for the polyionic liquid PANI/[BMIM][BF₄]. It exhibited a broad absorption band at 3163.26 cm⁻¹ due to the polymer backbone's N-H stretching vibrations [40].

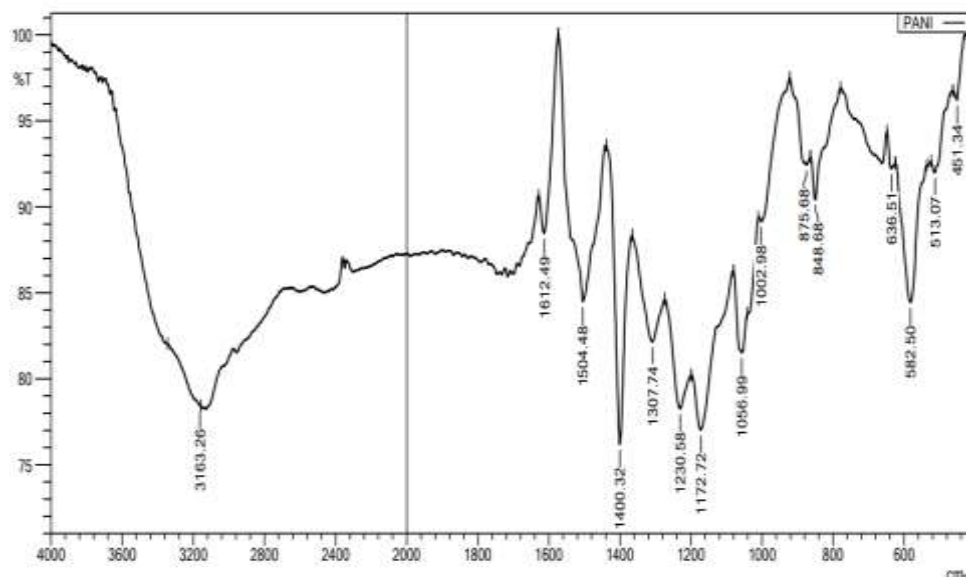


Figure 7: FTIR spectrum of PANI/[BMIM][BF₄] polyionic liquid.

The typical transmittance bands of pure PANI are detected at 1504 cm⁻¹, corresponding to the C=C stretching of the quinoid ring; at 1400.32 cm⁻¹ corresponding to the C=C stretching of the benzenoid ring; at 1230.58 and 1307.74 cm⁻¹ related to the C-N stretching; and at 848.68 and 1172.72 cm⁻¹ corresponding to the C-H stretching. Para-substituted imidazole rings are responsible for the transmittance bands at 884.68 cm⁻¹ [33,41]. The peaks obtained

at 1056.99 and 582.5 cm^{-1} are due to the dopant surfactant's sulfonate (S=O) group stretching; this indicates a high degree of electronic delocalization [42-44].

UV-Vis studies

The UV-Vis spectrum of PANI/[BMIM][BF₄] polyionic liquid is shown in Figure 8. It shows three peaks between the wavelengths (200 and 1060) nm. These bands resulted from transitions called $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, which are related to the excitation absorption of benzenoid and quinoid, respectively [19,20]. The benzenoid units of the linear polyaniline chain's $\pi \rightarrow \pi^*$ electronic transitions are responsible for the HCl and H₂SO₄ doped polyaniline derivative's prominent absorption bands at 1058 nm [45-47]. The weak absorption band between 292 and 426 nm is due to the $n\text{-}\pi^*$ exciton transition between the HOMO of the benzenoid ring and the LUMO of the quinoid ring [21,22]. The UV-Vis study demonstrated that the presence of [BMIM][BF₄] ionic liquid in the polymer backbone affected the position of the absorption bands caused by $\pi \rightarrow \pi^*$ electronic transitions and the extent of the $n \rightarrow \pi^*$ exciton transitions [48-50].

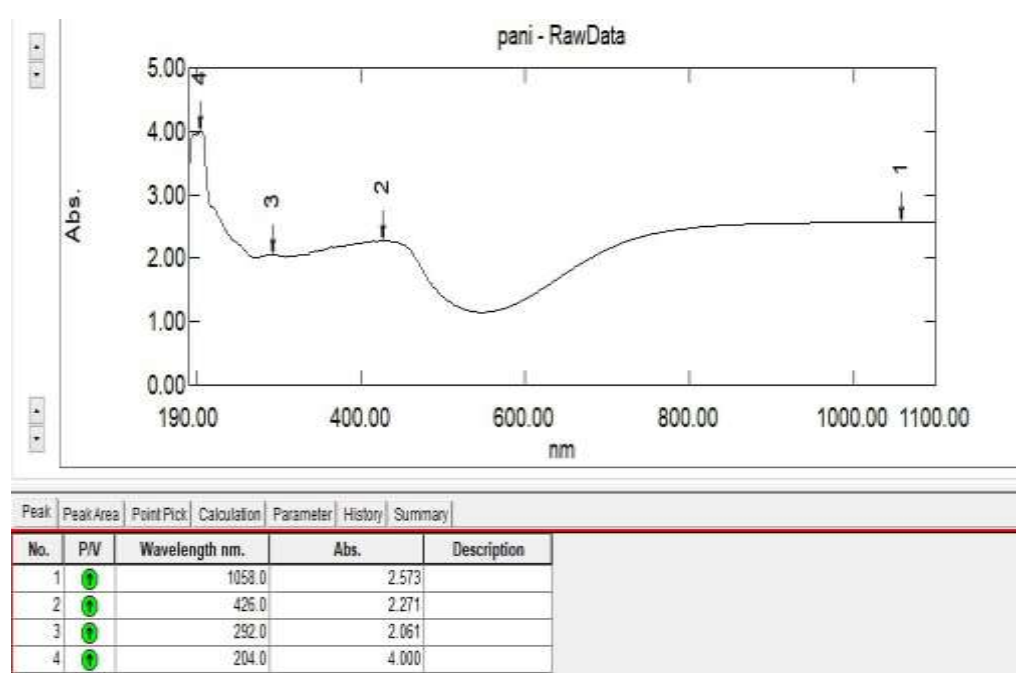


Figure 8: UV-Vis spectrum of PANI/[BMIM][BF₄] polyionic liquid.

Conclusion

In this work, PANI/[BMIM][BF₄] polyionic liquid was successfully synthesized by interfacial polymerization. In addition to offering mobile ions, ionic liquid was proved to increase amorphicity according to the XRD tests. The degree of crystallinity was impacted by the complexation of the ionic liquid cations with the polymer backbone during the structural alteration of the polymer. The surface morphology of the prepared PANI polyionic liquid was made up of tiny, uniformly distributed lamellar-shaped crystals with a crystalline structure. As the [BMIM][BF₄] ionic liquid was incorporated during polymerization, the resulting membrane became increasingly amorphous. The complex formation and interaction between PANI and [BMIM][BF₄] ionic liquid was confirmed by FT-IR and XRD analysis. The position of the absorption bands as a result of the number of $n \rightarrow \pi^*$ exciton transitions and the $\pi \rightarrow \pi^*$ electronic transitions were demonstrated by the UV-Vis studies.

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