



Synthesis and characterization of pyromellitic dianhydride based sulfonated polyimide: Survey of structure properties with DFT and QTAIM

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Abstract

Pyromellitic dianhydride (PMDA) and 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) were polymerized by polycondensation in 1:1 Sulfonated Polyimide (SPI) m-Cresol. The SPI was characterized by spectroscopic analyses (Fourier transform infrared (FT-IR), proton nuclear magnetic resonance (¹H-NMR), carbon nuclear magnetic resonance (¹³C-NMR), ultraviolet–visible spectroscopy (UV–Vis), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA)/ differential thermal analysis (DTA), solubility tests and elemental analysis (EA) techniques. Furthermore, quantum chemical calculations of the synthesized SPI were analyzed by density-functional theory (DFT) with Becke-3-Parameter-Lee–Yang–Parr (B3LYP)/6–311-G basis set to understand electrical and optic features of SPI. Natural Bond Orbital (NBO) analysis and molecular electrostatic potential (MEP) surfaces were calculated. Quantum theory analysis of atoms in molecules (QTAIM) was made using the AIMAll program to find H-bonding, proton interaction, proton transfer and water uptake script. The second degradation stage was observed at a temperature higher than 450 °C in TGA/DTA curve. The variation of the heat flow in reverse heat flow was based on the T_g of SPI occurring around 353.11 °C.

Keywords Pyromellitic dianhydride · Sulfonated polyimide · Fuel cells · QTAIM, DFT

Introduction

Polyimides are high-performance materials and widely used in industrial applications due to their high thermal, mechanical chemical stability and variable machinability properties [1]. Fuel cell (FC) technology is a solution to the global problems of the energy crisis and environmental pollution [2, 3]. FC membranes have become an excellent separation technology in recent years as it operates without needing additional chemicals with very low energy usage [4]. Polymer electrolyte membranes (PEMs) should have the potential to chemically and electronically separate chemical reactions that exist (to the anode from the cathode) [2]. Facilitating free movement of the proton is the main feature

of the fuel cell membrane. The key component PEM in polymer electrolyte membrane fuel cells (PEMFC) should have better properties such as higher proton conductivity, higher chemical and physical stability and lower gas permeability to increase the performance and durability of PEMFCs [5–9]. State-of-the-art for technology PEMs are perfluorosulfonic acid (PFSA) polymers consisting of a perfluorocarbon polymer main chain with hanged perfluorosulfonic acid groups. PFSA's are used as the most common electrolyte for PEMFCs due to their high proton conductivity as well as chemical and thermal stability [9–12]. However, high production costs and environmental incompatibility continue to be a problem for such perfluorinated materials. Today, nafion, aciplex, and flemion are typical perfluoro polymer membranes that are practically used in fuel cells [13–15]. Although perfluorinated sulfonic acid (PFSA) aliphatic polymers such as nafion are widely used for PEMs due to their excellent proton conductivity and durability, their membranes have critical problems such as low thermal stability, high gas permeability environmental incompatibility and high production cost [15–18]. Alternative fluorinated proton conductive membranes are desired. Therefore, the

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development of a low-cost and stable membrane that can operate at high temperatures is a priority. Functionalization of sulfonic acid by linking groups is now generally preferred. Looking for low-cost and high-performance polymers as an alternative material is the main goal in this field. For this purpose, a large number of sulfonated hydrocarbon polymers and sulfonated polyimide (SPI) have been identified as the most promising membrane material, especially for PEMFC application [19]. SPIs have high mechanical, thermal, and chemical resistance for similarity with polyimide [20, 21].

According to literature, only a few molecular dynamics (MD) simulations have been attempted about SPI materials. In this article, MD simulations of the oligomeric forms of this polymer were performed. The cohesive energy density (CED) of the polymers was estimated to calculate the solubility parameter (δ) as a function of the composition. The interaction parameter electronegativity (χ) was calculated to understand the energy indicating negative interactions that occurred in polymers. Besides the calculated results, our simulation findings are in agreement with the reported literature data [22, 23]. The formation of sulfonated polyimides synthesized using pyromellitic dianhydride (PMDA) and diamine-bearing sulfonic acid groups was well confirmed by spectroscopic methods. The polyamide structure was calculated with a 6–311 G basis set of the DFT/B3LYP method. The results were interpreted by the small molecule approach method for the polymer through one structural unit, three structural units and five structural units of SPI. Besides, quantum theory analysis of atoms in molecules (QTAIM) was performed for one structural unit.

Experimental

Materials

Pyromellitic dianhydride (PMDA, 97%) Alpha Aesar product, benzoic acid and dimethyl sulfoxide (DMSO) Merck product, 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD, 85%), triethylamine (used without further purification.), *m*-Cresol (99%), acetone (99.5%), ethyl acetate (99.5%), dimethylacetamide (DMac, $\geq 99.0\%$), *N*-methyl-2-pyrrolidone (NMP), *N,N* dimethylformamide (DMF), chloroform (CHCl_3), toluene (99.8%), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and acetone Sigma Aldrich product were purchased and used as.

Polymer characterization

^1H -NMR Bruker Avance III HD 600 MHz model device (Germany) was operated in structure lighting of organic compounds etc. NMR spectroscopic data were recorded in DMSO using as internal standards the residual non-deuterated signal for ^1H NMR. The IR spectrum was obtained by a Perkin-Elmer spectrum one FTIR spectrophotometer. UV–Visible analysis was

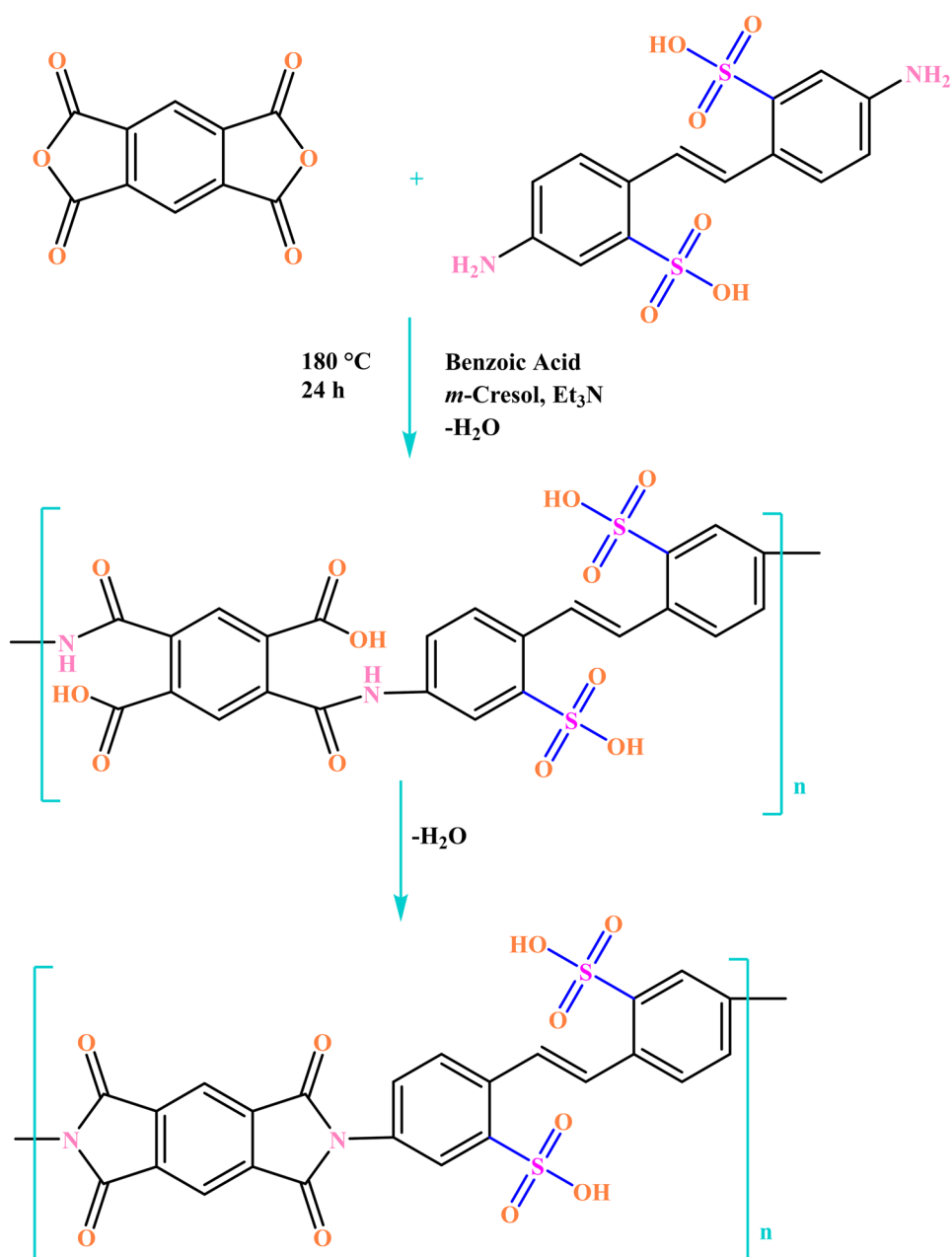
practiced by a Multiskan Sky microplate spectrophotometer without a screen (model with bathtub reader) skanlt software and computer. The DSC analysis was carried out by DSC-60 SHIMADZU (Japan) 100 ml/min with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen gas to specify the glass transition temperatures and melting temperatures of the polymers. Thermal analysis measurements of the polymers were practiced under nitrogen using a Setaram Labsys Evo (TGA/DTA 1600) to determine thermal degradation. Elemental analysis was determined by EA / IRMS using a Delta V Advantage (Thermo Fisher Scientific, Bremen, Germany) interfaced with Flash 2000 (Thermo Fisher Scientific, Bremen, Germany).

The analysis of theoretical simulations

^1H -NMR j values were calculated in the MestRaNova (Mnova) program [24]. One structural unit and three structural units of SPI were drawn in ChemDraw. The molecules drawn in the same way were converted into a 3D MOL2 file in Chem3D and transferred to GaussView 6.0. DFT study was calculated on a 6-311G basis set in the B3LYP method and images of each calculation were saved. The gaussian formatted checkpoint file with one structural unit of SPI was transferred to the AIMAll program in the same way. The QTAIM study was calculated using the parameters by increasing the number of water molecules each time and their images were also saved.

Synthesis of polyimide

0.44 g (1.2 mmol) of 4,4'-diamino stilbene-2,2'-disulfonic acid, 6 mL of *m*-cresol and 0.4 mL of triethylamine were added sequentially under a stream of nitrogen to a 250 mL fully dried flask. After the 4,4'-diamino stilbene-2,2'-disulfonic acid was completely dissolved, and then 0.222 g (1.0 mmol) PMDA and 0.173 g benzoic acid were added. The mixture was stirred at room temperature for a couple of minutes and then heated at $80\text{ }^\circ\text{C}$ for 4 h to obtain polyamic acid (PAA). The resulting PAA was then heated at $180\text{ }^\circ\text{C}$ for 24 h. Before cooling the mixture, for dilution event was added 10 mL *m*-cresol was procured high-viscous solution. Then the solution was poured into ethyl acetate. The precipitated polyimide was collected by filtration, washed with acetone, and dried in a vacuum at $60\text{ }^\circ\text{C}$ for 15 h. Thus, from the condensation reaction with PMDA, a polyimide containing the sulfonic acid group was synthesized (Fig. 1). FT-IR spectrum (ν , cm^{-1}): 1780 (C=O), 1720 (C=O), 1537 (aromatic C-H), 1483 (C–C), 1228 (C=C), 1366 (C–N), 1019 (S–O). ^1H -NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.21 (s, 1H), 8.85 (s, 2H), 8.40 (d, $J=2.2\text{ Hz}$, 1H), 8.28 (s, 1H), 8.03 (s, 1H), 7.84 (s, 1H), 7.52 (s, 1H), 7.07–6.96 (m, 1H), 6.61–6.51 (m, 2H), 3.09 (qd, $J=7.3, 4.7\text{ Hz}$, 7H), 2.55 (s, 0H), 2.21 (s, 2H), 1.16 (t, $J=7.3\text{ Hz}$, 13H). ^{13}C -NMR (101 MHz, $\text{DMSO}-d_6$) δ 157.22, 138.63, 129.07, 119.54, 115.80, 112.28, 45.77, 21.03, 8.59.

Fig. 1 Synthesis mechanism of SPI

Results and discussion

Characterization of polyimide SPI synthesized by PMDA

¹H-NMR spectrum of SPI

¹H-NMR chemical shifts (δ) are calculated through nuclear magnetic shielding tensors of protons in tested molecules. Analysis of ¹H-NMR spectra, DFT calculations for the chemical shift of molecules, the atomic orbital method at DFT/B3LYP/6–311-G levels. Isotropic protection values were used to calculate the chemical shifts associated

with DMSO. The experimentally observed and theoretically calculated chemical shifts for H atoms are in a very low range for a structural unit PI. It can be seen that the theoretical chemical shift values are in good agreement with the experimental values for the polymer [25–27]. NMR analysis confirms the formation of [28, 29] the imide polymer chain. ¹H-NMR spectra of SPI shows characteristic signals (Fig. 2). Resonance peaks in the region of 0.85–3.77 ppm corresponds to protons of ethylene, SO₃H, as well as SPI. Aromatic protons demonstrate signals between 6.51–6.61 ppm. Peaks of CH–N protons appear in the region of 8.25–8.40 ppm. Finally, –OH proton signals are observed at δ value of 8.50 ppm.

^{13}C -NMR spectrum of SPI

^{13}C -NMR spectroscopic analysis is performed for various isotopic verification of the carbon contained in the SPI [30]. Figure 3 shows ^{13}C -NMR spectroscopy of SPI. The peak at 157.22 ppm belongs to the amine-bonded carbon. The peaks at 138.63, 129.07, and 129.07 ppm are related to the carbon attached to the sulphonic SO_3H group. The carbon peaks of DMSO are in the range of 40.11–38.85 ppm. Stilbene carbon peaks appeared in the range of 112.28–119.54 ppm.

FT-IR spectrum of SPI

Further functionality in polymer chains can be verified with FT-IR analysis. Common FT-IR absorbances of the SPI polymeric compound are shown in Fig. 4. The change in functionality during certain reactions or processes may be followed by the disappearance or appearance of peaks in

the FT-IR. The complete imidization of SPIs is difficult to analyze due to their chemical stability, i.e. SPIs are insoluble in most solvents. Therefore, completion of the imidization process was verified using FT-IR [31, 32]. Besides, a small peak at 1780 cm^{-1} ($\text{C}=\text{O}$ asymmetric stretching) and a large peak at 1720 cm^{-1} ($\text{C}=\text{O}$ symmetric stretching) have appeared. Other peaks at 1537 (aromatic C-H overtone aromatic), 1483 cm^{-1} ($\text{C}-\text{C}$ stretching of aromatic), 1228 cm^{-1} ($\text{C}=\text{C}$ stretching of p-substituted benzene), 1366 cm^{-1} ($\text{C}-\text{N}$ stretching of imide) and 1175 cm^{-1} are a complete Imide ring deformation appeared indicating imidization. The peak of 1019 cm^{-1} ($\text{S}-\text{O}$ groups) showed sulfonated groups of SPI (Fig. 4).

UV-VIS spectrum of SPI

UV-VIS provides information about the polymer structure. The obtained data are important in Polyimide formation and

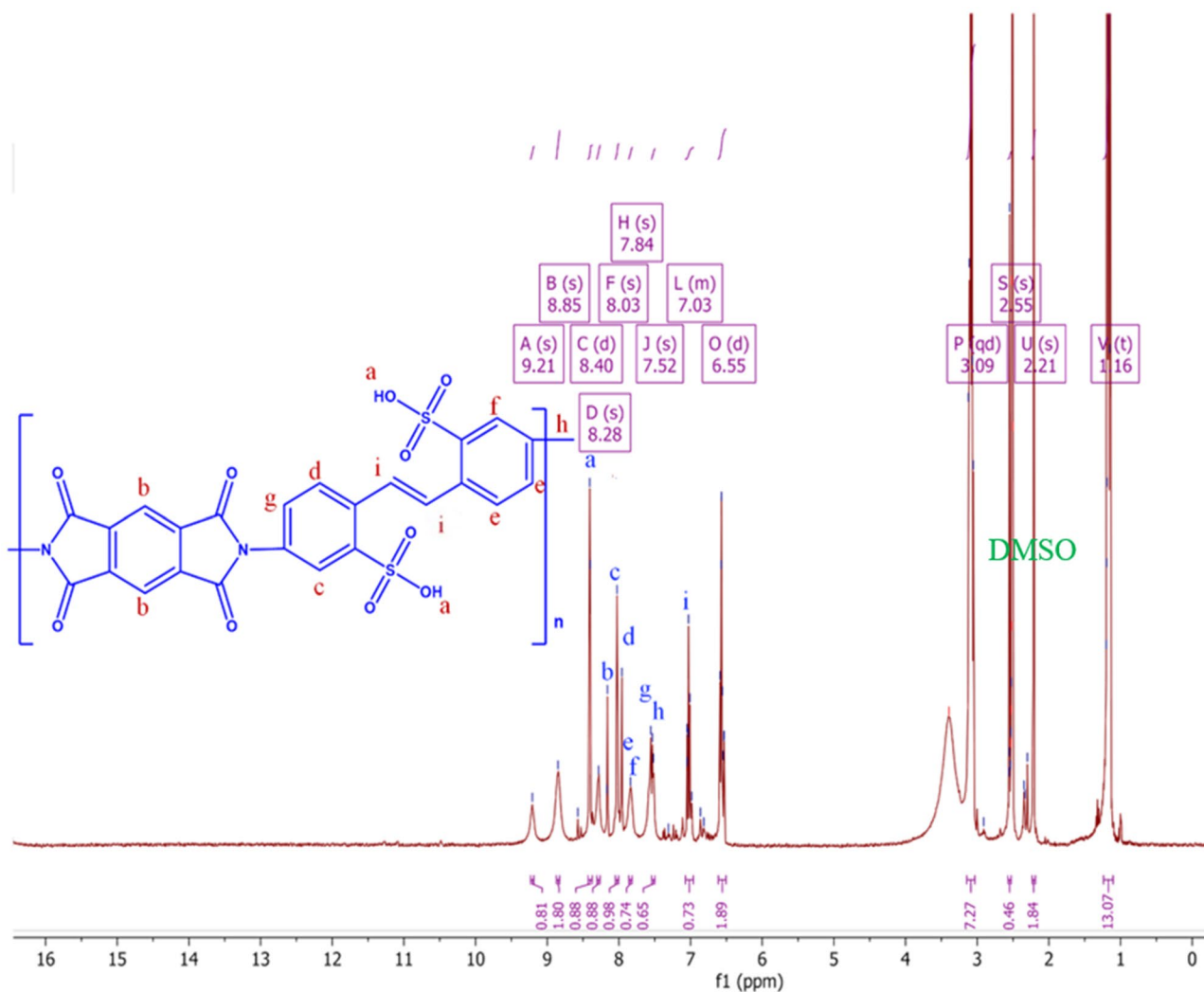


Fig. 2 ^1H -NMR Spectrum of SPI

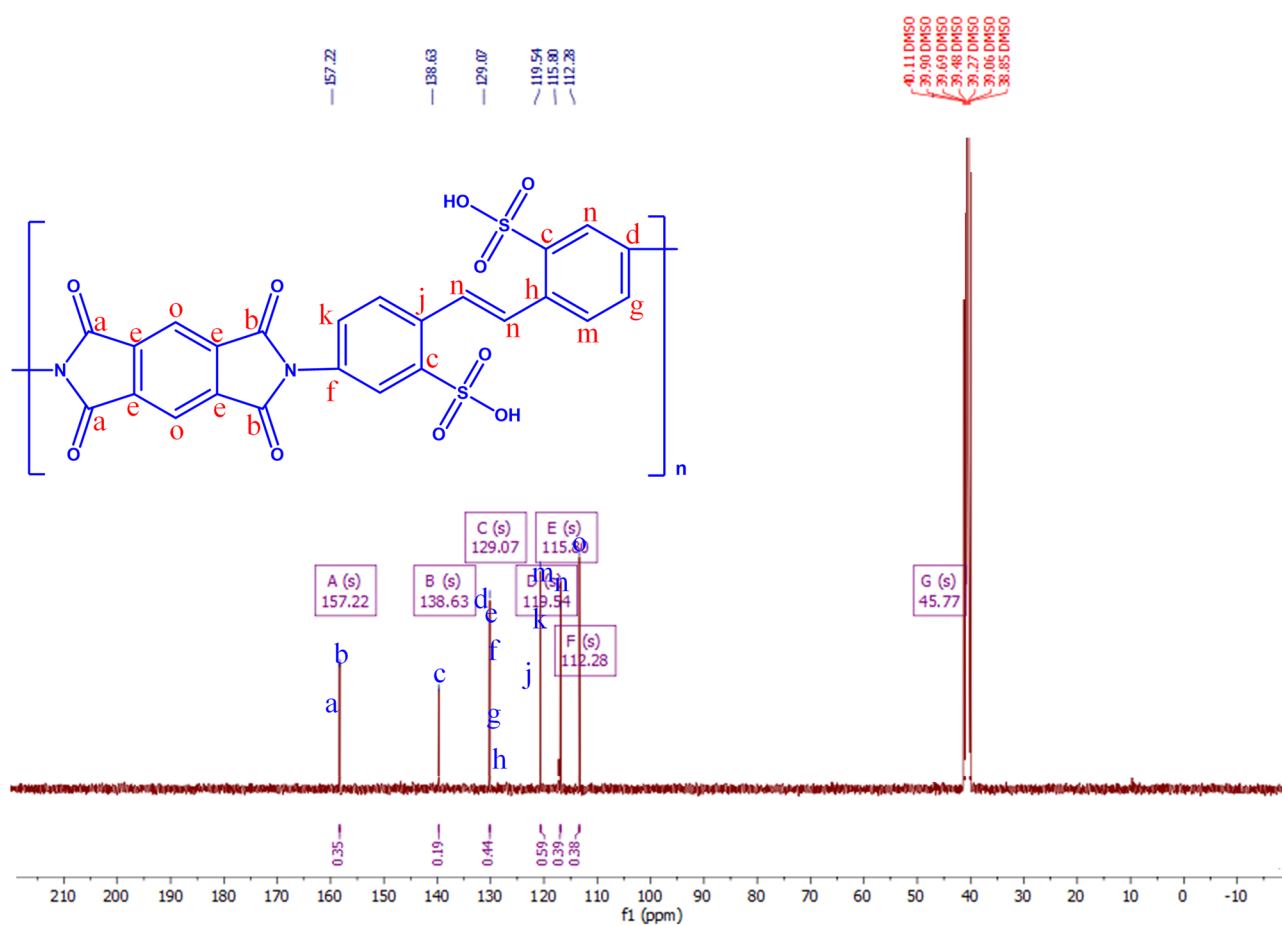
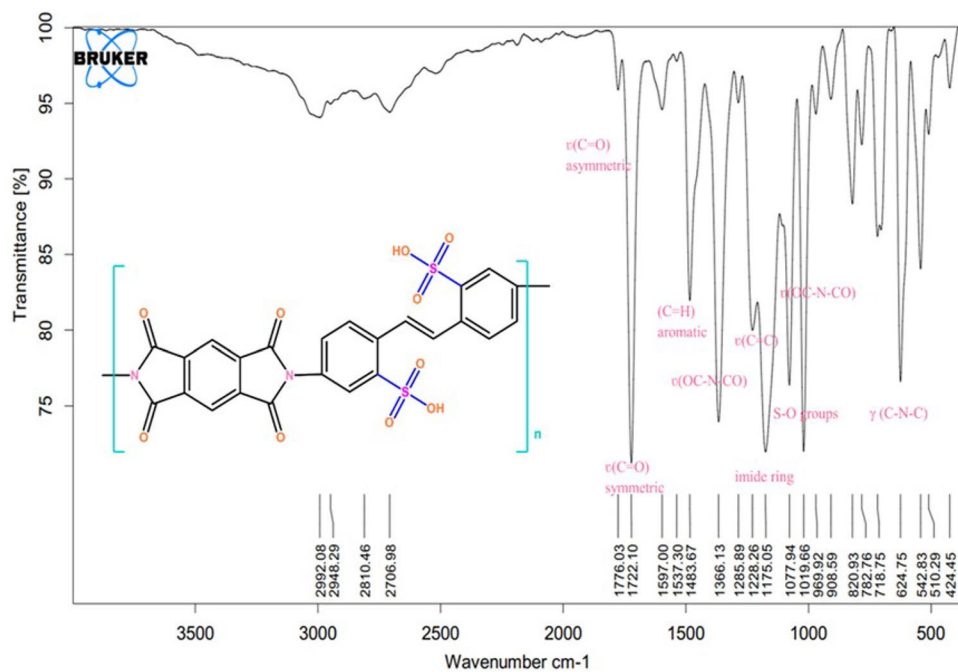
Fig. 3 ^{13}C -NMR Spectrum of SPI

Fig. 4 FT-IR Spectrum of SPI



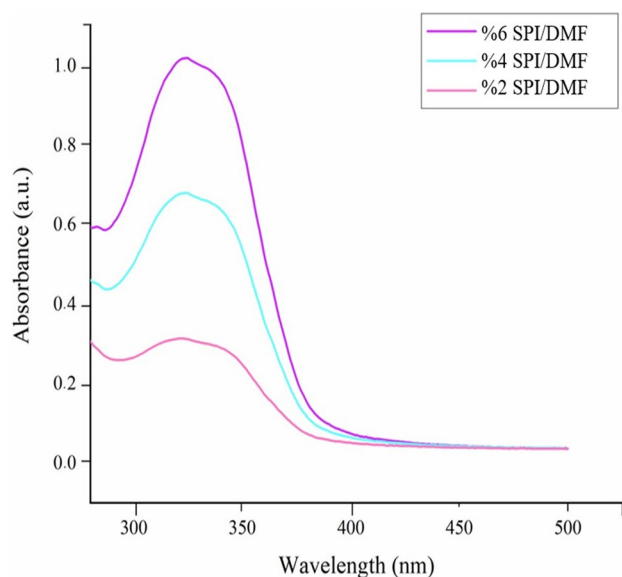


Fig. 5 UV–VIS absorption spectra

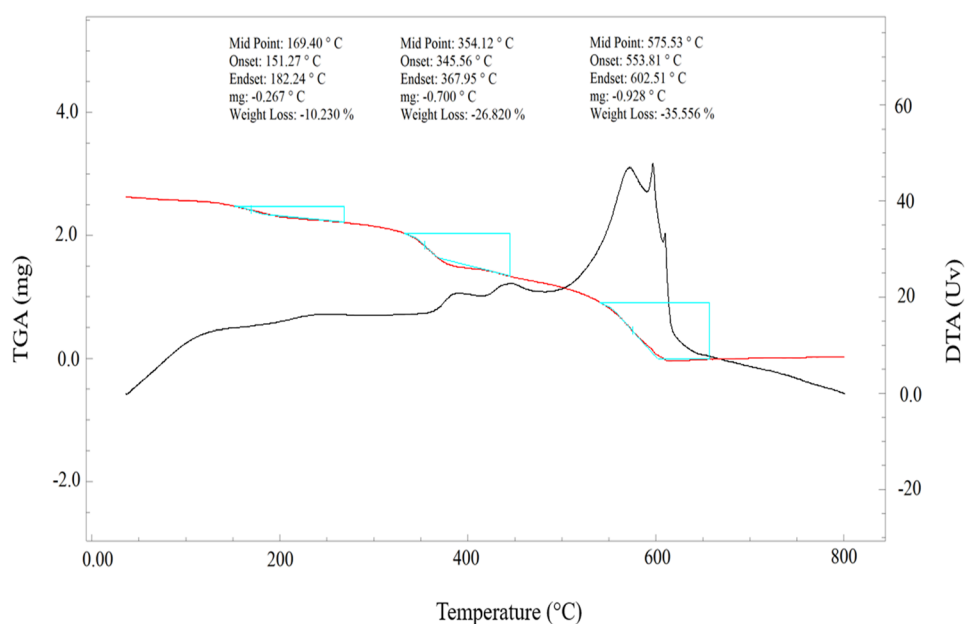
provide clarity in building block [33]. SPI was dissolved in N, N-dimethylformamide. The measurement was carried out in solution medium. Thus, optical properties of SPI were examined by UV–Vis spectrometer. The UV–vis absorption of this polymer exhibited strong absorption at 290–400 nm in DMF solutions that could be assigned to a $\pi-\pi^*$ transition resulting from conjugation between aromatic rings and nitrogen atoms [34, 35]. The UV–Vis absorption of SPI also showed triple absorbance at 300–380 nm in the solution state. Figure 5 shows the UV–Vis absorption of different SPI concentrations in DMF. The aromatic polyimide can be

effectively attributed to the charge transfer complex formation by the aromatic with the electron receiving dianhydride moiety compared to the strong electron-donating aromatic diacids.

TGA / DTA analysis of SPI

Concerning polymer stability, TGA is often used to find the temperature of the initial mass loss visible during the onset of degradation [36, 37]. Here, thermal analysis of the sample was performed by using the analysis of the obtained curves and TGA / DTA. The thermal stability of SPI was obtained using TGA up to 1000 °C in N₂ purge. Also, Fig. 6 presents interesting features that demonstrate that mass loss has been defined. Above 200 °C, a two-step degradation profile for SPI was observed. SPI's TGA thermogram presents two major degradations at approximately 300 and 650 °C [38, 39]. The initial weight loss between 25 and 140 °C consists of hydrated water loss due to the sulfonic acid group number. The second weight loss before 140–200 °C corresponds that the residual m-Cresol solvent is removal [40, 41]. At temperatures higher than 200 °C, desulfonation occurs up to 400 °C. The first degradation step observed around 350 °C corresponds to the degradation of aromatic sulfonyl groups. The second degradation stage is observed at a temperature higher than 450 °C and dependent on the degradation of the polymer backbone. The synthesized polymer shows thermal stability until 350 °C. So, the thermal stability of the synthesized polymer should be taken into account for any potential application in the future. DTA curve has three different peaks in the gas environment. There are peaks in the DTA curve of

Fig. 6 TGA and DTA curve of Polyimide SPI



SPI from polyimide. SPI has the individual decomposition temperatures as shown in Fig. 6 (Roundabout $\sim 370^{\circ}\text{C}$, $\sim 420^{\circ}\text{C}$, $\sim 500^{\circ}\text{C}$, and 590°C respectively). The first decomposition observed at about $\sim 300^{\circ}\text{C}$ may have been caused by the solvent traces.

DSC analysis of SPI

As it is known DSC, irreversible heat flux, enthalpy relaxation, crystallization, thermal degradation, thermal curing, solvent evaporation, etc. should contain information. Above the glass transition temperature (T_g) of PAA, it is in the rubbery state but has been successfully converted to PI in the glassy state. This re-vitrification should produce the change in heat capacity that will occur as an exothermic shift of heat flow during the transition. Here, although the glass transition temperature appeared as a gradual change in heat capacity, it was observed as an endothermic increase curve in this study. Figure 7 demonstrates the results of the DSC thermogram of SPI. Also, the variation of the heat flow in reverse heat flow is based on the T_g of SPI occurring around 353.11°C . The T_g value is very close to the thermal stability values in the TGA/DTA graph.

Solubility test of SPI

Solubility performance of the synthesized polyimide was carried out on 10 different solvents. Solubility behavior was determined by taking the solvent/solute ratio at a concentration of 3% by weight. Detailed resolution of SPI are summarized in Table 1. The samples were analyzed at room temperature. The SPI was difficult to dissolve in these solvents at room temperature. Even a small amount of SPI did not dissolve in DMF, CHCl_3 , toluene, THF, and CH_2Cl_2 and acetone. However, it was observed that the sample taken from SPI dissolved very easily in DMSO, DMac and NMP. Besides, since m-cresol was already used in the synthesis phase and solved the SPI sample very easily.

Elemental analysis of SPI

As seen in the elemental analysis (EA) results, the percentage of sulfur (S) in the structure shows that it is sufficient to turn the structure into a strong proton-conducting membrane. EA results show up at the oligomer level. By EA, it is aimed to determine the mass percentage of the elements in the molecule [42]. According to the results of EA of the

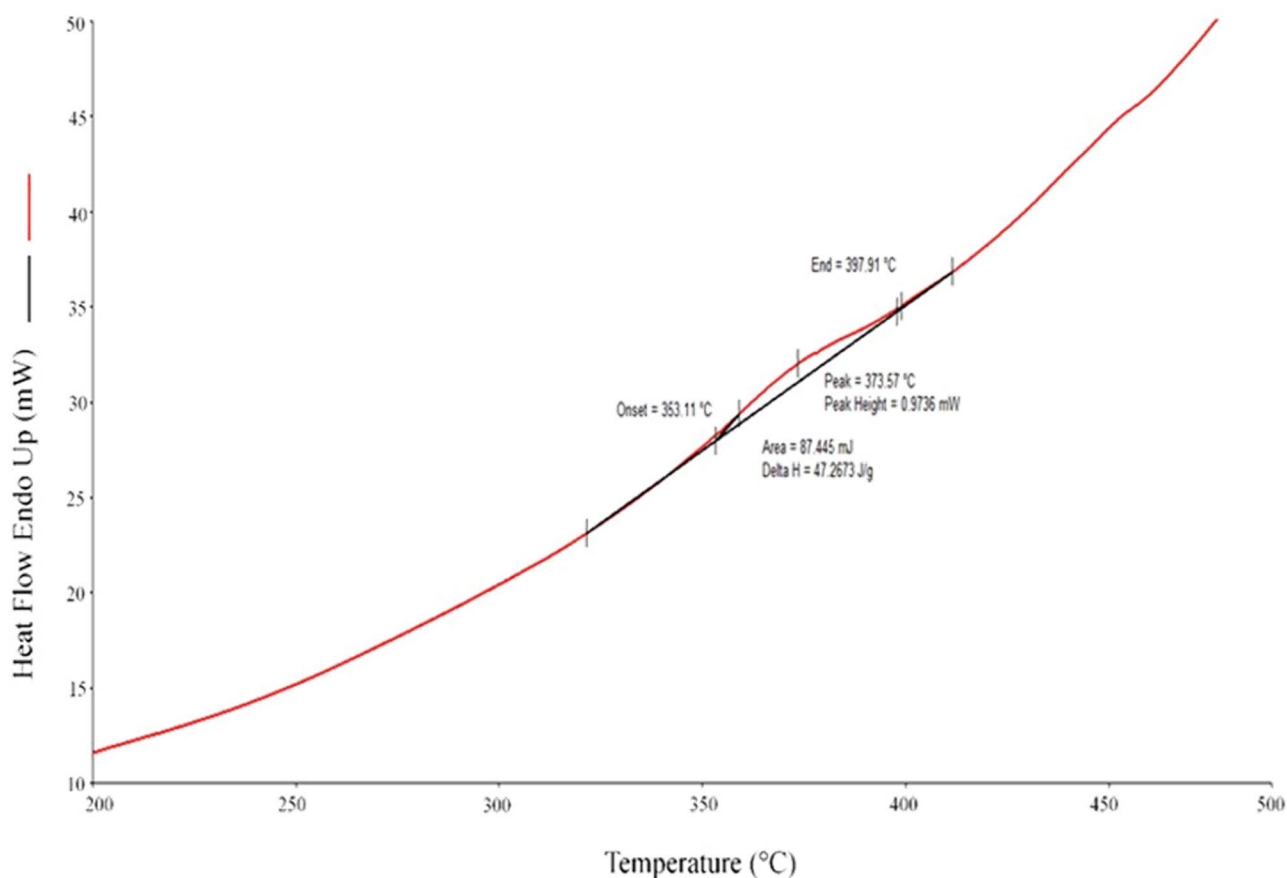


Fig. 7 DSC curve of SPI

Table 1 Solubility summaries of SPI in common organic solvents at room temperature

SPI	m-Cresol	DMSO	DMac	NMP	DMF
	++	++	++	+	+
	CHCl ₃	Toluene	THF	CH ₂ Cl ₂	Acetone
	-	-	-	-	-

++: Very solved, +: Solved, -: Not solved

sample; carbon response ratio, weight [mg] and weight [%], those determined when comparing by available elements and time; 14.62% and 0.120 mg of the weight of the nitrogen element with the carbon response ratio 0.198 in 2 min 32 s, 56.60% and 0.464 mg of the weight of the carbon element with a carbon response ratio 1.000 in 3 min 18 s, 10.63% and 0.087 mg of the mass of the hydrogen element with a carbon response ratio 2.365 in 8 min 42 s, 0.09% and 0.001 mg of the mass of the sulfur element with a carbon response ratio 0.001 in 24 min and 2 s. As a result of the analysis, the peaks were normal and the total weight of the sample was 81.93% and 0.820 mg (Table 2).

Studies of DFT

Geometry optimization

B3LYP is known efficient and permanent works in quantum chemical calculations. This method has been used in many analyses of metallic-organic compounds. This method accepts the linearity of the kernel and the planarity of the periphery, together with the optimized structures. It is significant to perceive the dense phases of the complexes [43–45]. Optimized basic state structure and total energy conversion of one, three, and five structural units of SPI owing to their condensation polymerization are given in Fig. 8. Optimized bond length parameters calculated with B3LPY / 6-311G are listed in Table 3. The comparison was made by giving all the experimentally obtained values calculated from the optimized geometry of the one, three, and five structural units of SPI. This means that the structure has minimum potential

energy. The bond lengths of the sulfonic acid compound were found to be 1.797–1.799 Å for the one structural unit of SPI, 1.885–1.885 Å for the three structural units of SPI and 1.890–1.890 Å for the five structural units of SPI respectively. All other values were presented in Table 3. As seen in Table 3 below, although the molecular structures of the one, three, and five structural units of SPI have grown, there is not much difference between their values.

HOMO and LUMO analysis

The main electrical parameters associated with orbitals in a molecule are the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) and energy gaps. HOMO is the outermost (highest energy) orbital electron that can function as an electron donor. LUMO is the innermost (lowest energy) orbit that has enough space to accept electrons and can function as an electron receiver. HOMO and LUMO orbitals determine the interaction of the molecule with other species. Determination of HOMO–LUMO energies also helps to understand the chemical stability of a molecule for a parameter known as chemical hardness (η). Molecules with large HOMO–LUMO energy gaps, hard molecules and molecules with small HOMO–LUMO energy gaps are considered soft molecules [46–48]. The volume orbit of HOMO and LUMO for molecules is shown in Fig. 9. Besides, the LUMO + 1 and HOMO - 1 graphics of the compound were taken. From Table 4, HOMO -6.68 eV–LUMO -3.66 eV value for one structural unit of SPI, HOMO -6.96 eV–LUMO -4.3049 eV value for three structural units of SPI, and HOMO -6.94 eV–LUMO -4.33 eV value for five structural units of SPI were calculated. For other orbitals; HOMO -1 -7.80 eV-LUMO + 1 -2.71 eV value for one structural unit of SPI, HOMO -1 -7.02 eV-LUMO + 1 -4.29 eV value for three structural units of SPI, HOMO -1 -6.96 eV-LUMO + 1 -4.32 eV value was calculated for the five structural units of SPI. Energy Gap (Δ) | $E_{\text{HOMO}} - E_{\text{LUMO}}$ | values for 3.02 eV for one structural unit of SPI, 2.65 eV for three structural units of SPI, and 2.61 eV for five structural units of SPI were found.

Table 2 Result of elemental analysis for SPI

Result Table (ESTD-Colibrick-1) Sample Weight [mg]: 0.8200							
	Reten Time [min.]	Response	Weight [mg]	Weight [%]	Peak Type	Element Name	Carbon Response Ratio
1	2.320	2928.077	0.120	14.62	Ordnr	Nitrogen	0.198
2	3.180	14,813.608	0.464	56.60	Ordnr	Carbon	1.000
3	8.420	35,036.967	0.087	10.63	Ordnr	Hydrogen	2.365
4	24.027	8.152	0.001	0.09	Ordnr	Sulfur	0.001
Total	-	-	0.820	81.93	-	-	-

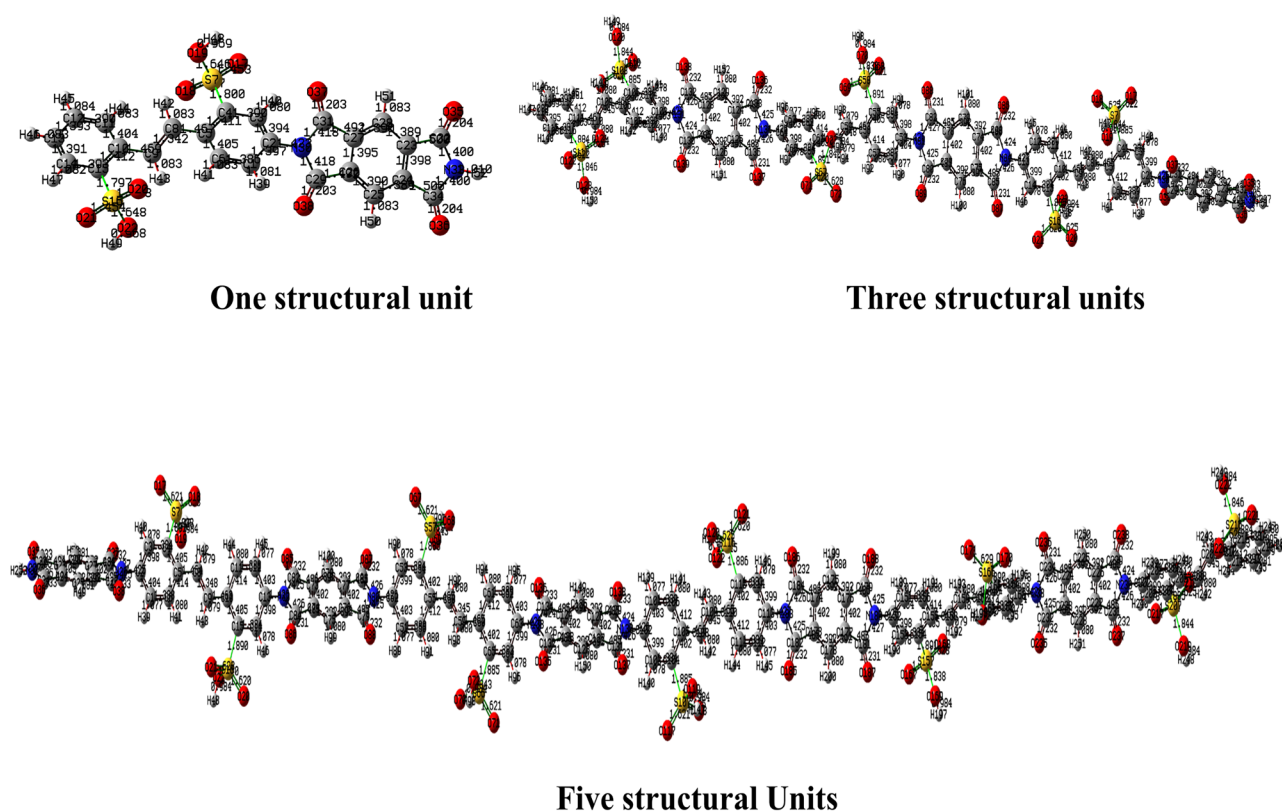


Fig. 8 The optimized structure of the compound using the B3LPY / 6-311G basis set

Table 3 Theoretically obtained bond lengths (Å) and bond angles (°) of the one structural unit, three structural units, and five structural units of SPI

Bond lengths (Å)				Bond lengths (Å)			
Atom Groups	One structural unit	Three structural units	Five structural units	Atom Groups	One structural unit	Three structural units	Five structural units
C2-N30	1.423	1.425	1.425	C2-N30-C31	124.2	124.6	124.5
C29-N30	1.418	1.425	1.425	C32-N33-C34	113.7	113.2	113.2
C32-N33	1.399	1.404	1.404	C15-S16-O21	108.5	109.3	113.7
C4-C5	1.410	1.401	1.404	O18-S7-C4	110.0	113.0	113.4
C8-C9	1.341	1.345	1.348	C23-C28-C27	114.9	115.2	115.2
C31-O37	1.203	1.231	1.231	C26-C29-O38	128.1	128.1	128.1
C4-S7	1.799	1.885	1.890	C24-C34-O36	128.8	128.7	128.7
C15-S16	1.797	1.885	1.890	C10-C15-S16	121.5	120.8	121.5
C29-O38	1.203	1.232	1.232	C1-C2-C3	119.5	119.4	119.2
S7-O17	1.453	1.621	1.621	C13-C14-C15	119.6	117.9	118.0
C32-O35	1.203	1.232	1.232	S7-C4-C3	115.6	113.7	112.8
C14-C15	1.393	1.383	1.383	O37-C31-C27	128.2	128.2	128.3
C23-C24	1.398	1.405	1.405	C5-C8-C9	123.9	124.1	124.7
C1-H39	1.080	1.077	1.077	C2-N30-C29-C26	179.8	179.8	179.7
C3-H40	1.079	1.078	1.078	O35-C32-N33-C34	179.9	179.9	179.9
O19-H48	0.968	0.984	0.984	O18-S7-C4-C3	135.1	143.1	142.2
O22-H49	0.968	0.984	0.984	C13-C14-C15-S16	177.8	179.5	178.7
C9-H43	1.082	1.079	1.079	C5-C8-C9-C10	179.9	179.4	178.3

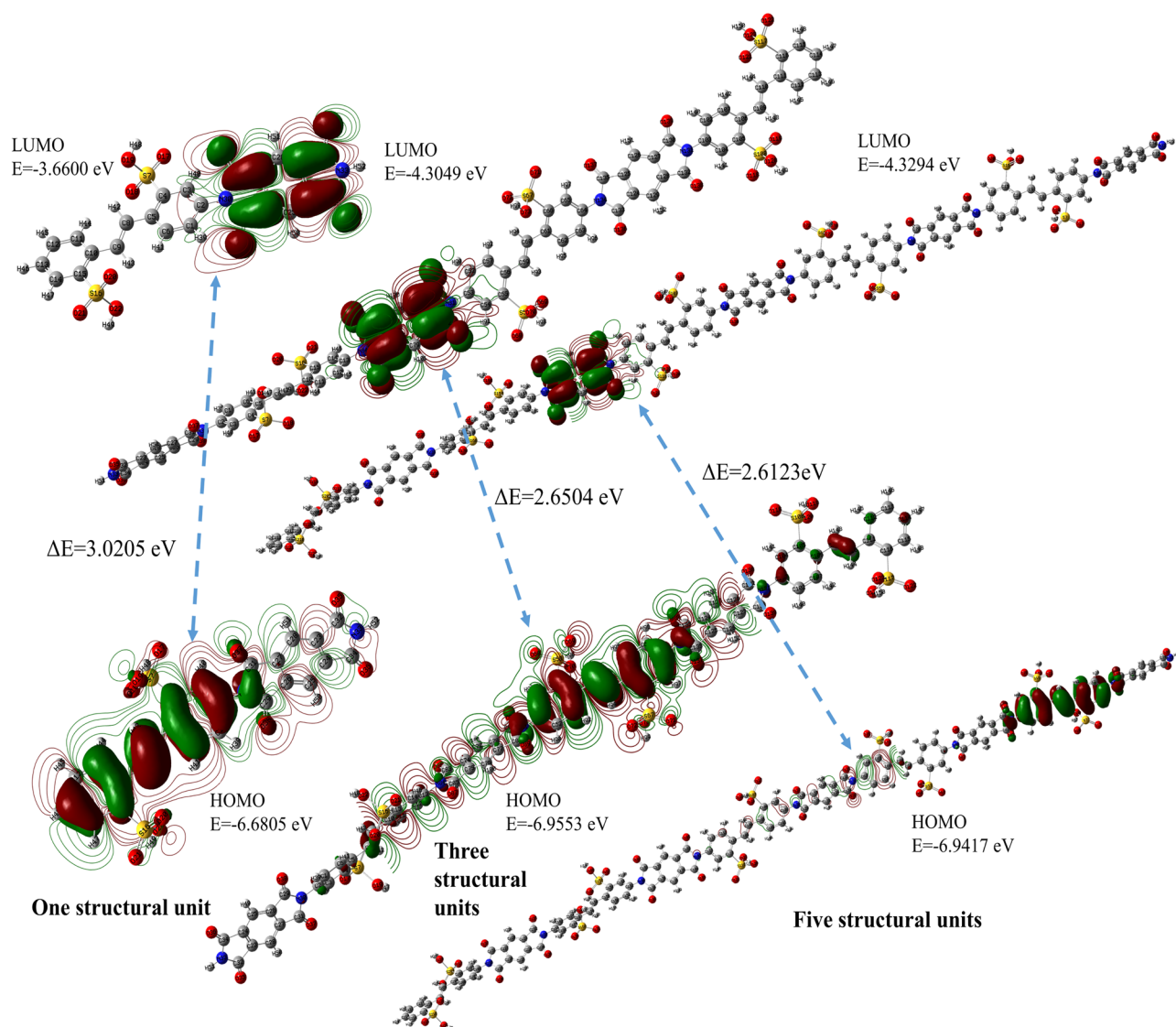


Fig. 9 DFT_{HOMO} and DFT_{LUMO} of Atomic orbital composition of SPI one structural unit, three structural units, and five structural units molecules

Table 4 The comparison HOMO, LUMO, energy gaps (HOMO–LUMO), and properties of related one structural unit, three structural units, and five structural units of SPI

Molecules Energy	One structural unit	Three structural units	Five structural units
E_{LUMO}	-3.66	-4.31	-4.31
E_{HOMO}	-6.68	-6.96	-6.94
$E_{\text{LUMO}+1}$	-2.71	-4.29	-4.32
$E_{\text{HOMO}-1}$	-7.80	-7.02	-6.965
Energy Gap (Δ) $ E_{\text{HOMO}} - E_{\text{LUMO}} $	3.02	2.65	2.61
Ionization Potential ($I = -E_{\text{HOMO}}$)	6.68	6.96	6.94
Electron Affinity ($A = -E_{\text{LUMO}}$)	3.66	4.31	4.33
Chemical hardness ($\eta = (I - A)/2$)	1.51	1.36	1.31
Chemical softness ($s = 1/2 \eta$)	0.76	0.66	0.65
Chemical Potential ($\mu = -(I + A)/2$)	-5.17	-5.65	-5.64
Electronegativity ($\chi = (I + A)/2$)	2.33	2.65	2.66
Electrophilicity index ($\omega = \mu^2/2 \eta$)	8.85	12.04	12.16

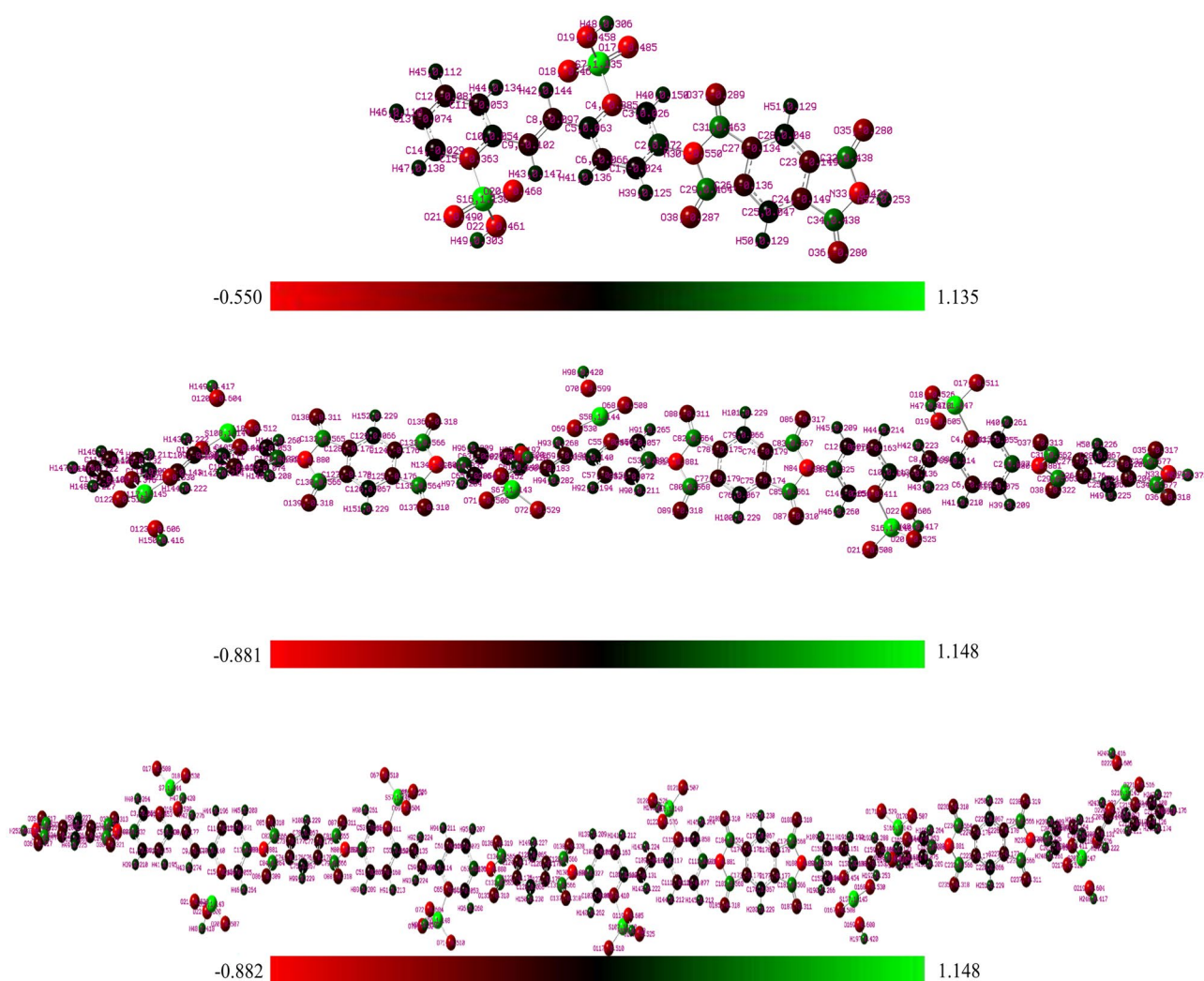


Fig. 10 Mulliken atomic charges for the one structural unit, three structural units, and five structural units of SPI

Table 4 also shows the chemical reactivity indices. Quantum chemistry calculations are for single-phase gas molecules. However, there may be a deviation from the experimental values recorded in the presence of intermolecular interactions. As a result of DFT studies, with this small molecule group approach, it was observed that although the molecular structures of the one, three, and five structural units of SPI have grown, there is not much difference between the calculated values. This is because the increase in polymer chains contributes to the same electronic region, so HOMO–LUMO energy values are very close to each other. The electronic properties of polymers can be determined with the small group approximation.

Mulliken atomic charges, dipole moment, and molecular electrostatic potential (MEP)

The calculation of the Mulliken atomic charge has an important role in the application of quantum chemical calculation on the molecular system. Because atomic charges affect the dipole moment, molecular polarization, electronic structure and many properties of molecular systems. The charge distribution on the atom indicates the formation of the donor and acceptor pair, which includes the charge transfer in the molecule [49, 50]. The Mulliken atom, one, three, and five structural units of SPI were calculated on the set of B3LYP / 6-311G. The Mulliken charge distribution for sulfur (S) atom; one structural unit (1.14), three structural units (1.15)

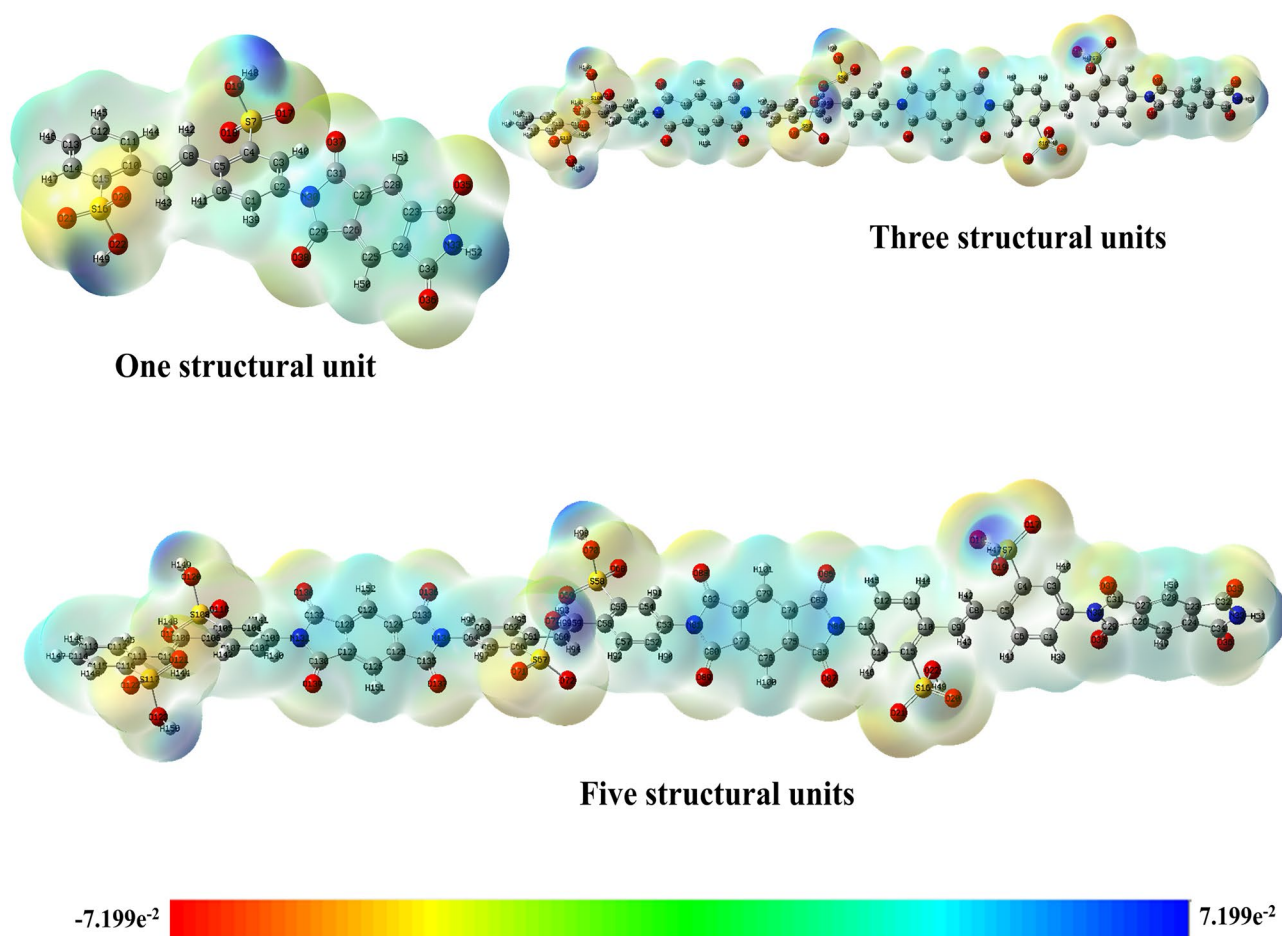


Fig. 11 Molecular electrostatic potential mapped of molecules

and five structural units (1.14) for S7, and then for the oxygen (O) atom; one structural unit O17-O20-O35 (-0.49)—(-0.47)—(-0.28), three structural units O17-O20-O35 (-0.51)—(-0.525)—(-0.32) and five structural units O17-O20-O35 (-0.51)—(-0.51)—(-0.32). The charge value

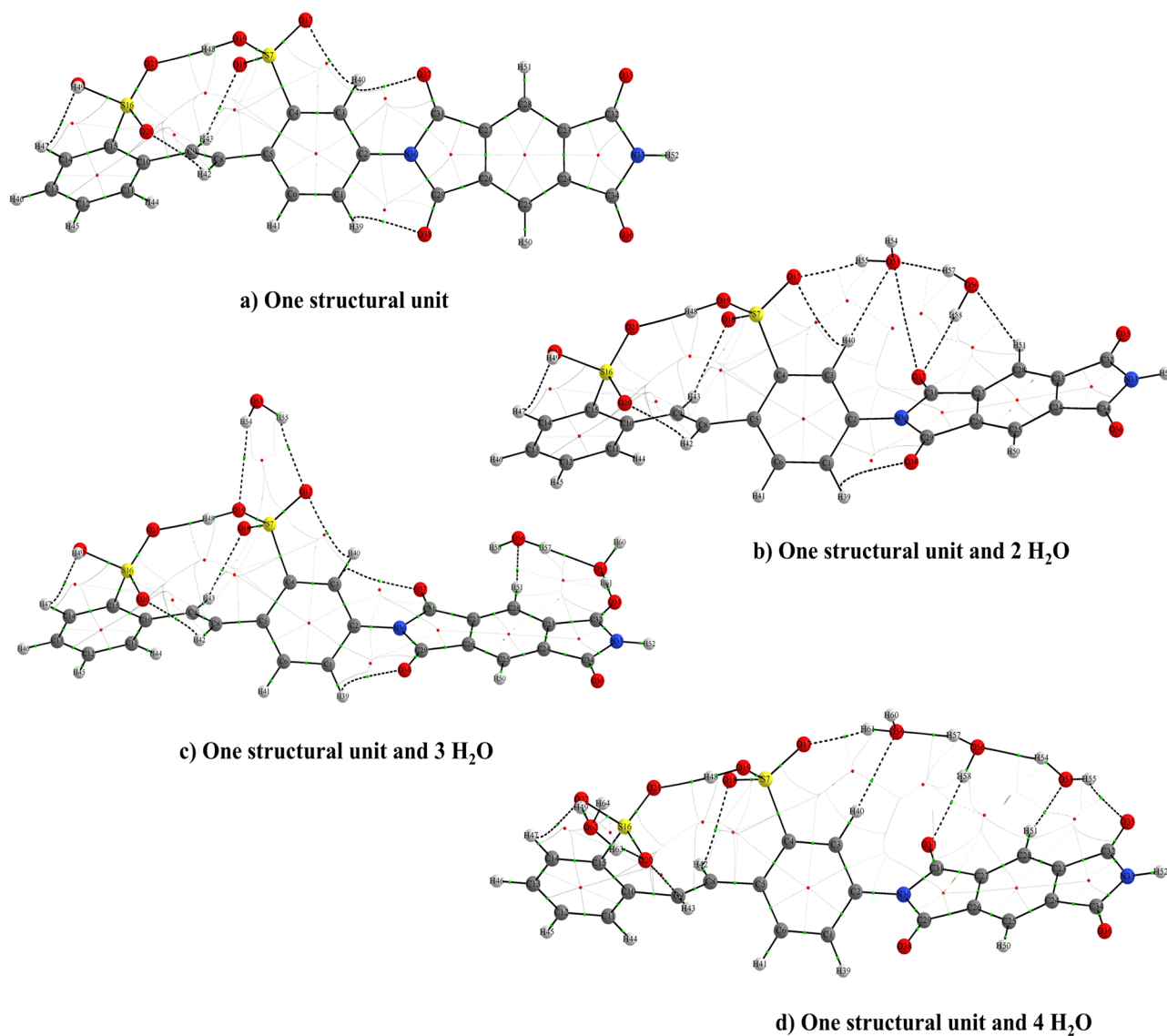
of the C atom attached to both oxygen and nitrogen has a positive charge for the C32 atom; one structural unit (0.44), three structural units (0.58), and five structural units (0.58) (Fig. 10). Some C atoms were positively charged, other were negatively charged.

Table 5 In DFT study of one structural unit, three structural units, and five structural units of SPI with the B3LYP/ 6-311G basis set, dipole moments (Debye), (au) polarizability, β components, and β total value

Parameters	One structural unit	Three structural units	Five structural units	Parameters	One structural unit	Three structural units	Five structural units
μ_x	-0.05	-0.4320	-0.47	β_{XXX}	-223.04	670.30	-292.50
μ_y	0.04	0.1764	1.75	β_{XXY}	58.45	-898.75	1837.4
μ_z	-0.10	1.8380	1.57	β_{XYY}	-43.12	-445.71	1593.5
$\mu(D)$	0.12	1.8963	2.40	β_{YYY}	11.65	24.341	36.948
α_{xx}	-192.68	-546.24	-913.14	β_{XXZ}	-122.21	-534.51	5704.9
α_{yy}	-254.74	-775.94	-1277.20	β_{XYZ}	-131.80	-372.81	-367.79
α_{zz}	-236.14	-754.49	-1261.70	β_{YYZ}	23.33	31.95	-42.64
α_{XY}	-14.48	-54.46	21.54	β_{XZZ}	-6.88	436.25	-1161.0
α_{XZ}	13.07	29.68	3.18	β_{YZZ}	0.23	-43.98	119.82
α_{YZ}	12.31	7.94	-19.65	β_{ZZZ}	0.27	48.65	37.71
$\alpha(\text{au})$	448.67	367.49	1605	$\beta(\text{esu})$	3.3×10^{-30}	8.2×10^{-29}	1.6×10^{-29}

Table 6 σ - σ^* and π - π^* transitions in the natural bond analysis

Donor NBO (i)		Acceptor NBO (j)		E (2) kcal mol ⁻¹	E(j)-E(i) a. u	F(i,j) a. u
C 116- S 117	σ	S 117- O 121	σ^*	16.17	0.01	0.029
C 66- S 67	σ	S 67- O 72	σ^*	12.74	0.01	0.029
C 15- S 16	σ	S 16- O 20	σ^*	12.24	0.01	0.029
C 132- O 138	π	C 127- C 128	π^*	76.59	0.03	0.070
C 82- O 88	π	C 77- C 78	π^*	75.54	0.03	0.070
C 29- O 38	π	C 26- C 27	π^*	69.79	0.03	0.070
N 33	LP (1)	C 34- O 36	LP*(3)	53.05	0.26	0.107

**Fig. 12** Optimized (B3LYP/6-311G(d,p)) structure of isolated one structural unit of SPI containing PMDA; **(a)** dry one structural unit of SPI containing PMDA; **(b)** hydrated one structural unit of SPI at thelevel of 2 water molecule; **(c)** hydrated one structural unit of SPI at the level of 3 water molecule; **(d)** hydrated one structural unit of SPI at the level of 4 water molecule

As shown in Fig. 11, the B3LPY / 6-311G basis set shows the molecular electrostatic potential (MEP) map. The MEP map shows that the region characterized by blue color around the central atom has a positive charge. Besides, the hydrogen atom in the ligand carries the maximum power of the positive charge in dark blue color. Most of the aromatic ring zone means green color and is almost neutral [51]. One, three, and five structural units of SPI parameters for the gas phase compound; μ (D)=0.12, 1.90 and 2.40, α (au)=448.67, 367.49 and 1605, β (esu)= 3.3×10^{-30} , 8.2×10^{-29} , 1.65×10^{-29} found as. These values indicate that they can be considered as NLO materials for the one, three, and five structural units of SPI examined (Table 5). Because polarity α (au) and static high degree polarity β (esu) parameters were determined from the calculations of molecules. From the data obtained for these molecules, theoretically high polarity values are considered to be a good candidate for nonlinear optical materials [52].

NBO analysis of three units of SPI

Investigation of intramolecular and intermolecular binding analysis can be carried out effectively by Natural Bond

Orbital (NBO) analysis and provides a supportive method for the study of charge transfer or hyper conjugative interactions. The energies of hyperconjugation interaction are subtracted from the second-degree perturbation approach. Adhesion and anti-bonding interactions owing to second-degree perturbation are quantitatively analyzed by the NBO approach, which expresses perturbation energies E (2). The larger value of E (2), the more intense the interaction between electron donors and electron acceptors, i.e. the greater the tendency to donate from electron donors to electron acceptors and the more conjugation of the whole system [53]. In this analysis, neutral band orbital energies were calculated using the second-order perturbation theory of the Fock matrix method under the basic sets of DFT / B3LYP / LANL2DZ and 6-31G. The natural bond analysis for the molecule was presented in Table 6.

QTAIM analysis of one structural unit of SPI

QTAIM was done using the AIMAll program. A powerful tool, QTAIM of atoms in molecules characterizes chemical bonds. Always a critical point (BCP) and bond path (BP) among bound atoms accompany chemical bonds in this theory. Each BCP involves well-to-do chemical information that

Table 7 QTAIM parameters: electron density (ρ_{BCP}), Laplacian of electron density ($\nabla^2 \rho_{BCP}$); Energetic parameters: electron kinetic energy density (G_{BCP}), electron potential energy density (V_{BCP}), total electron energy density (H_{BCP}); Ellipticity (δ) (all in a.u.)

n H ₂ O	Contact	ρ_{BCP}	$\nabla^2 \rho_{BCP}$	G_{BCP}	V_{BCP}	H_{BCP}	$\delta(O,H)$
0	O17-H40	0.016	0.068	0.014	-0.012	-0.002	2.849
	O19-H48	0.332	-2.338	0.062	-0.710	0.647	0.017
	O20-H42	0.010	0.034	0.007	-0.006	-0.001	0.350
	O22-H49	0.353	-2.475	0.066	-0.752	0.685	0.021
	O37-H40	0.010	0.040	0.008	-0.007	-0.001	0.748
2	O17-H55	0.019	0.080	0.017	-0.014	-0.002	0.061
	O37-H58	0.016	0.059	0.013	-0.011	-0.001	0.063
	O53-O37	0.004	0.016	0.003	-0.002	-0.000	0.475
	O53-H57	0.022	0.085	0.019	-0.016	-0.002	0.089
	O53-H40	0.009	0.030	0.006	-0.005	-0.001	0.347
3	O56-H51	0.013	0.040	0.008	-0.007	-0.001	0.055
	O17-H55	0.014	0.051	0.011	-0.010	-0.001	0.005
	O19-H54	0.008	0.030	0.006	-0.006	-0.000	0.143
	O35-H61	0.022	0.092	0.020	-0.017	-0.003	0.032
	O56-H51	0.023	0.076	0.017	-0.015	-0.001	0.053
4	O59-H57	0.032	0.115	0.028	-0.027	-0.000	0.020
	O17-H61	0.022	0.092	0.020	-0.017	-0.002	0.021
	O20-H63	0.018	0.069	0.015	-0.014	-0.001	0.124
	O35-H55	0.363	-2.456	0.008	-0.007	0.689	0.022
	O37-H58	0.016	0.060	0.013	-0.011	-0.001	0.034
	O53-H51	0.018	0.058	0.013	-0.011	-0.001	0.011
	O56-H54	0.025	0.099	0.022	-0.020	-0.002	0.111
	O59-H40	0.010	0.032	0.006	-0.005	-0.001	0.269
	O59-H57	0.025	0.099	0.022	-0.020	-0.002	0.084
	O62-H49	0.056	0.145	0.046	-0.056	0.010	0.042

fully identifies the form of the chemical bond. Parameters such as electronic energy density (H_{BCP}), kinetic energy density (G_{BCP}), potential energy density (V_{BCP}), electron density (ρ_{BCP}) and Laplacian of electron density ($\nabla^2 \rho_{BCP}$) yield to qualify a chemical bond in BCP [54, 55]. The molecular graph of the polyimide one structural unit containing different functionalized PMDA is shown in Fig. 12. Parameters in the BCP of the acidic proton of the OH group were analyzed for sulfonated monomer in diversified hydration states and reported in Table 7. As regards these conclusions, as the water, molecule is added, the covalent character of acidic O–H bond protected the hydrogen atom and hydrogen atom did not separate from the oxygen of the sulfonate group. However, when 2, 3 and 4 water molecules were added, the separation of acidic hydrogen occurred in all three cases. V_{BCP} , H_{BCP} , and $\nabla^2 \rho_{BCP}$ values exhibited that the HB energy and covalent character of O–H be reduced via a rise in the numeral of water molecules. With rising the water molecules, the H_{BCP} value was reduced from 0.685 to 0.002 a.u., and also the $\nabla^2 \rho_{BCP}$ value was decreased from 0.068 to 2.456 a.u. As long as the numeral of water molecules rises, hydrogen bond energy (E_{HB}) decreased. As a result, proton transfer was easier in superior hydration states. Extra, the above-mentioned coactions, nitrogen atoms stabilized the hydronium ion and facilitate hydrogen transfer properly the creation of hydrogen bond (HB) by water molecules. Besides, the hydrogen bonds among the oxygen atom of the sulfonate group and the water molecules with the hydrogen atom were examined. Actions have clarified that their energy is over the range 1.0–28.0 kcal/mol in distinct hydration states and weak and strongly interactive water molecules are absorbed around the sulfonate group.

Conclusion

Sulfonated hydrocarbon polymers have been investigated and sulfonated polyimides (SPI) have been identified as the most promising membrane materials especially for PEMFC application. Moreover, quantum chemical calculations of the synthesized SPI were examined. HOMO -6.68 eV—LUMO -3.66 eV values for one structural unit of SPI, HOMO -6.96 eV—LUMO -4.31 eV values for three structural units of SPI and HOMO -6.94 eV—LUMO -4.33 eV values for five structural units of SPI were calculated. In the results, one, three, and five structural units were focused on the small molecule approach method for the polymer. The quantum theory of atoms in molecules (analysis of hydrogen bonds and proton decomposition) (QTAIM analysis) was made using the AIMAll program. In the results, with an increase in the number of water molecules, it was observed that V_{BCP} , $\nabla^2 \rho_{BCP}$, and H_{BCP} values

plus HB energy and covalent character of O–H decreased. According to the report, the formation of sulfonated polyimide was well confirmed and this SPI was a good alternative to be used as a membrane and FC technology.

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Declarations

Conflicts of interests/Competing interests We declare that there is no a conflict of interest with any person, institute, company, etc.

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