Chapter 4

Section 1: New metallophthalocyanines posturing pyridine and quinoline pendants via 1,3,4-oxadiazole bridge: Synthesis, Optical and Electrical studies

Section 2: Poly(1,3,4-oxadiazole-aryl ether) embedded tetra carboxy metalphthalocyanines: Synthesis, Characterization and Electrical studies
4.1.1. Introduction

High-performance electroactive, high dielectric constant polymers are used in electromechanical fields such as high performance sensors, actuators [1–3], artificial muscles [4], as well as bypass capacitors in microelectronics and energy-storage devices [5–8], that demand service at enhanced temperatures and easy processability. Recently, preeminent processes in the incorporation of various heterocyclic units into a poly(aryl ether) has been made. The introduction of 1,3,4-oxadiazole rings into the polymer backbone improves their properties, which is known to be highly thermoresistant [9–13]. Poly(1,3,4-oxadiazole-aryl ether) have the common problem of being difficult to process owing to their infusibility and poor solubility in organic solvents. The reasons are strong interchain forces, inherent macromolecular rigidity or semicrystallinity. Therefore, much effort has been made to develop structurally modified polymers with improved solubility, for easy processability. Furthermore, solubility of the polymers are often increased when flexible bonds, large pendent groups or polar substituents are incorporated into the polymer chain [14].

In the past several decades, there has been a great deal of effort to build up polymers with enhanced functional properties. One of the focuses of these research and development efforts is to raise the dielectric constant of polymers significantly. Usually the polymers suffer from a low dielectric constant 2.98–3.5 reported by C. Hamciuc, et.al., [15, 16]. The dielectric constant of the polymer was embellished by the incorporation of polar pendants such as nitriles, sulfonic, carboxylic acid. The present study demonstrates the synthesized poly(1,3,4-oxadiazole-aryl ether) (POAE) exhibit high dielectric constant (~340 at 50 Hz) because of the presence of polar carboxylic
acid pendants, and a high concentration of $H^+$ ions exchange rapidly in the polymer matrix by the application of electric field.

The present energized trends in polymer chemistry will be the wide-scale employment of elements of the periodic table for the synthesis of metal containing high-performance polymers [17] and enhancement of dielectric constant. In this regard, phthalocyanines (Pcs) are very attractive molecules to show high dielectric constant, unusual physical properties and accommodate a great variety of metals in their central cavity [18]. These properties can be achieved by incorporating Pc macrocycle in to polymer chain. Moreover, metalphthalocyanines (MPc) are molecules that can produce other beneficial effects such as improved processability due to separation of the polymer chains induced by the bulky group. These high dielectric constant metal-containing polymers have raised as a new generation materials in the development of polymer electronic devices. The researchers Eva M. Maya et al., and Wiener et al., reported earlier by taking much effort for the incorporation of Pc in to polymer containing carboxylic acid pendants by a simple $N,N'$-dicyclohexylcarbodiimide (DCC) assisted reaction [19, 20].

Polymeric materials have various characteristics, they can be configured into almost any conceivable shape and their properties can be tailored to suitable for electrical applications. These results inspired us to work on this, and we report, the inclusion of tetra amino metalphthalocyanines (TAMPs) into a POAE containing carboxylic acid by a simple DCC mediated synthetic route. The addition of TAMP is varied stochiometrically (10, 20, 30 mass %) to yield high dielectric constant polymer embedded MPc (PEMP 1–9). The resulting polymers were characterized with FTIR, NMR spectroscopic techniques, optical and dielectric properties. A significant advantage of this approach is that a great variety of metals can be introduced into
polymer through the inclusion of MPc as side groups. These high dielectric constant polymers have emerged as new candidates to show their potential in aforesaid applications.

4.1.2. Experimental

4.1.2.1. Materials

4-nitrophthalic anhydride, 3-(3,4-dihydroxyphenyl)propanoic acid, p-fluoro benzoic acid and DCC were purchased from Sigma Aldrich and used without further purification, N,N-dimethylformamide (DMF) procured from Sigma Aldrich was dried over 5 Å molecular sieves for at least 48 h before use, polyphosphoric acid (PPA) and hydrazine sulphate were obtained from Spectrochem Chemicals and used as received. Other reagents and solvents were research grade and used as received.

The POAE containing the carboxylic acid groups were synthesized by a conventional polymerization method [16, 21–25]. TAMP were prepared according to the described procedure [26].

4.1.2.2. Instrumentation

The number and weight average molecular weight (Mn and Mw) of POAE was estimated by gel permeation chromatography (HP/GPC, Waters). Moisture free tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 ml/min, monodisperse polystyrene standard samples in the range of 10³–10⁷ was used for the calibration of molecular weight. Infrared (IR) spectra were recorded on a FT-IR 8400s Shimadzu spectrometer in KBr pellets. Solid state electronic absorption spectra were recorded on a Perkin-Elmer UV-Vis spectrometer, model UV/VIS-35. ¹H and ¹³C-NMR spectra were recorded on a Bruker SFO1- 400 MHz (internal standard was TMS). Thermal analysis was carried out in SHIMADAZU TA-60WS thermal analyzer in air at a
heating rate of 5 °C min⁻¹. Powdered XRD measurements were carried out on a Bruker D8 Advance X-ray diffractrometer. The dielectric and AC conductivity measurements were carried out using impedance analyzer model HIOKI 3352-50 HiTESTER Version 2.3. Making of pellets and the procedure used for electrical measurements to be similar as presented in Chapter 2.

4.1.2.3. Preparation

4.1.2.3.1. 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole

To a mixture of 4-fluorobenzoic acid (14.05g, 10 mmol) and hydrazine sulphate (6.57g, 5 mmol), 125g of polyphosphoric acid was added under nitrogen atmosphere, in to a round-bottom flask equipped with a magnetic stirrer and a condenser. The solution was heated to 150 °C and then the reaction temperature was slowly increased to 180 °C over 3 h for effective ring closure. The solution was allowed to further react for an additional 1 h at this temperature. The reaction mass was then poured into 500 ml of ice cold distilled water with stirring. The white precipitate so obtained was collected by filtration and finally washed several times with hot water until the filtrate was neutral. The purification of dried crude product was done by recrystallization from a 95% Ethanol/THF (90/10) mixture twice, producing 10.8 g of the pure white crystals with a yield of 85% [27].

Yield: 85%, Calc: C (65.12), H (3.12), N (10.85), O (6.20). Found: C (65.6), H (3.9), N (11.26), Co (6.96) %.¹H–NMR (DMSO-d6) (δ, ppm): 8.18–7.43 (d, 4H, Ar–H).

4.1.2.3.2. Poly(1,3,4-oxadiazole aryl ether)s (POAE) [Scheme1].

POAE with pendant carboxyl groups was executed (Scheme 1) by the similar nucleophilic aromatic substitution reaction previously described [16, 21–25]. The polycondensation procedure described was carried out as follows.
In a 250 ml three-necked flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap and condenser. 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (3.45g, 0.015 mol), 3-(3,4-dihydroxyphenyl)propanoic acid (1.65g, 0.015 mol), K₂CO₃ (5.52g, 0.04 mol), N-methyl pyrrolidone (NMP) (37 ml) and toluene (15 ml) were placed. The mixture was allowed to reflux for 6 h and the toluene was removed. The reaction temperature was raised up to 180 °C and kept for 16 h before the polymerization was completed; the viscous solution was poured into a 200 ml of 30% hydrochloric acid solution. Finally, the polymer powder was washed several times thoroughly with hot water, a little with methanol and dried at 100 °C for 24 h.

Yield: 90%. IR [(KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3432 (COO-H), 2929 (C-H), 1724 (-C=O), 1609 (C=N), 1489 (C=C), 1227 (-C-O-C-), 1165 (-C-O), 1010, 961 (=C-O-C=). UV-Vis (solid state) \(\lambda_{\text{max}}/\text{nm}\): 432. \(^1\)H-NMR (DMSO-d6) (\(\delta, \text{ppm}\)): 2.57 (t, 2H, -CH₂), 2.84 (t, 2H, -CH₂-), 8.19–6.94 (m, 11H, Ar-H), 12.14 (s, 1H, -COOH). \(^{13}\)C-NMR (DMSO-d6), (\(\delta, \text{ppm}\)): 173.64 (COOH), 163.60, 163.19 (oxadiazole C₄), 159.81, 159.68 (ArC_b,c-0), 145.50 (ArC_d - O), 139.84 (ArC_e - CH₂), 129.43, 129.17 (ArC_fg - Oxadiazole), 126.35, 122.68, 117.67, 117.00, 116.73, 116.51 (ArC_h,l,m,j,k,l) respectively, 36.17 (-C₈H₂), 29.23(-C₈H₂). GPC: Mn: 2513, Mw: 12150.

4.1.2.3.3. General procedure for the synthesis of 2,9,16,23-tetra amino metalphthalocyanines (TAMPs (M = Co, Ni & Cu) [Scheme-2].

Tetra nitro metalphthalocyanines (TNMPs): The mixture of 4-nitrophthalic anhydride (10g, 0.05 mol), urea (30g, 0.5 mol), ammonium chloride (1.24g, 0.023 mol), ammonium molybdate (1g, 0.8 mmol) and the required metal salt (0.06 mol): (i.e. cobalt (II) chloride for cobalt tetra nitro phthalocyanine (CoTNP), nickel (II) chloride for nickel tetra nitro phthalocyanine (NiTNP) and copper (II) chloride for copper nitro
amine phthalocyanine (CuTNP)) were finely ground and added to nitrobenzene (150 ml). The mixture was stirred by using mechanical stirrer for 6 hours at 180–190 °C. A dark-green solid resulted which was filtered off and washed with methanol under Soxhlet extraction until the smell of nitrobenzene could no longer be detected, which was filtered, washed three times with water and then with dilute HCl and NaOH followed by water and methanol until the filtrate to be colourless, dried in oven at 60 °C for 24 hours [26].

4.1.2.3.3a. Tetra nitro cobalt phthalocyanine (CoTNP).

Yield: 89%, Calc: C (51.1), H (1.6), N (22.3), Co (7.84). Found: C (51.6), H (1.9), N (22.6), Co (7.96) %. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3092 (ArC–H), 1532 (N=O), 1336, 1090, 1052, 945, 846, 760. UV-Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 301, 432, 569.

4.1.2.3.3b. Tetra nitro nickel phthalocyanine (NiTNP).

Yield: 88%, Calc: C (51.1), H (1.6), N (22.3), Ni (7.82). Found: C (51.56), H (1.93), N (22.63), Ni (7.97) %. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3097 (ArC–H), 1520 (N=O), 1338, 1090, 1057, 938, 855, 763. UV-Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 303, 432, 583.

4.1.2.3.3c. Tetra nitro copper phthalocyanine (CuTNP).

Yield: 90%, Calc: C (50.83), H (1.59), N (22.33), Cu (8.40). Found: C (51.26), H (1.88), N (22.73), Cu (8.87) %. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3098 (ArC–H), 1512 (N=O), 1338, 1090, 1058, 938, 856, 763. UV-Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 302, 432, 586.

Tetra amino metalphthalocyanines (TAMPs): Tetra amino-metal-phthalocyanine was prepared according to published procedures [26]. Sodium sulfide nonahydrate (7.4g, 30.9 mmol) was added to a solution of tetra nitro-nickel-phthalocyanine (1.94g, 2.5 mmol) in DMF (50 ml). The reaction mixture was stirred under N₂ and heated at 60 °C.
After 1.5 h, the mixture was cooled to room temperature, diluted with ice water (150 ml) and the resulting precipitate collected by centrifugation. The precipitate was repeatedly washed with MeOH/ether (1:9), EtOAc and dried to afford a dark green solid of nickel tetra amine phthalocyanine (NiTAP) (1.2g, 75%). The same procedure was repeated for cobalt and copper tetra amino phthalocyanines.

4.1.2.3.3d. Tetra amino cobalt phthalocyanine (CoTAP).

Yield: 79%, Calc: C (60.88), H (3.19), N (26.62), Co (9.33). Found: C (61.2), H (3.56), N (26.96), Co (9.96) %. IR [(KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3280 (-N-H), 3092 (ArC-H), 1420 (C=N), 1345, 1309, 1132, 1098, 1058, 950, 825, 782. UV-Vis (solid state) \(\lambda_{\text{max}}/\text{nm}\): 432, 579.

4.1.2.3.3e. Tetra amino nickel phthalocyanine (NiTAP).

Yield: 75%, Calc: C (60.88), H (3.19), N (26.62), Ni (9.34). Found: C (61.23), H (3.51), N (26.91), Ni (9.91) %. IR [(KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3278 (-N-H), 3095 (ArC-H), 1412 (C=N), 1345, 1305, 1136, 1095, 1052, 951, 822, 752. UV-Vis (solid state) \(\lambda_{\text{max}}/\text{nm}\): 432, 593. \(^1\)H-NMR (400 MHz, d6-DMSO) \(\delta\) 8.93–7.38 (m, 12Ar-H), \(\delta\) 6.26 (br. s, 8(NH)).

4.1.2.3.3f. Tetra amino copper phthalocyanine (CuTAP).

Yield: 77%, Calc: C (60.42), H (3.17), N (26.42), Cu (9.99). Found: C (60.76), H (3.57), N (26.86), Cu (10.26) %. IR [(KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3283 (-N-H), 3094 (ArC-H), 1409 (C=N), 1340, 1339, 1133, 1096, 1052, 949, 832, 746. UV-Vis (solid state) \(\lambda_{\text{max}}/\text{nm}\): 432, 593.
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4.1.2.3.4. General procedure for POAE embedded TAMP ((M = Co, Ni & Cu) [PEMPl–9] [Scheme-3].

The modification of POAE was carried out using DCC as dehydrating agent at room temperature for 22 h. In a typical reaction, 500mg of POAE was dissolved in 10 ml of anhydrous DMF under dinitrogen. After complete dissolution, 10mg (0.48 mmol) of DCC was added followed by the addition of 50mg (10 wt %) of TAMP. The mixture was maintained at room temperature for 22 h. The fibrous green PEMP polymer was filtered after pouring in to excess of water and washed with boiling hexane in a soxhlet unit and dried in a vacuum oven at 100 °C overnight. The same procedure was repeated for 20% TAMP and 30% TAMP to afford PEMPl–9 shown in scheme 3.

4.1.2.3.4a. POAE embedded CoTAP (10, 20 & 30 wt%) (PEMP1–3).

Yield: 98–99%, IR [(KBr) v_max/cm⁻¹]: 3328 (COO-H), 2929 (C-H), 2852 (-N-H of amide), 1699 (-C=O of amide), 1611 (C=N), 1489 (C=C), 1166 (-C-O). UV-Vis (solid state λ_max/nm) 432, 680–684.

4.1.2.3.4b. POAE embedded NiTAP (10, 20 & 30 wt %) (PEMP4–6).

Yield: 97–99%, IR [(KBr) v_max/cm⁻¹]: 3327 (COO-H), 2928 (C-H), 2851 (N-H of amide), 1697 (-C=O of amide), 1611 (C=N), 1489 (C=C), 1165 (-C-O). UV-Vis (solid state λ_max/nm) 432, 661–664. ¹H-NMR (DMSO-d6) (δ, ppm): 1.19 (t, 2H, -CH₂), 1.72 (t, 2H, -CH₂–), 7.96–6.85 (m, 23H, Ar-H), 5.53 (s, 1H, -NH).

4.1.2.3.4c. POAE embedded CuTAP (10, 20 & 30 wt %) (PEMP7–9).

Yield: 97–98%, IR [(KBr) v_max/cm⁻¹]: 3327 (COO-H), 2928 (C-H), 2851 (N-H of amide), 1697 (-C=O of amide), 1610 (C=N), 1489 (C=C), 1166 (-C-O). UV-Vis (solid state λ_max/nm) 432, 696–699.
4.1.3. Result and Discussion

4.1.3.1. Synthesis

The POAE was synthesized containing carboxylic acid groups via a nucleophilic aromatic substitution reaction [16, 21–25]. TAMP was synthesized by the cyclotetramerization method described elsewhere [26] and the spectral data confirms the synthesized TAMPs were desired. Later, the POAE containing COOH side groups were tailored with peripheral amino groups of TAMP via –CONH– (amide) link using DCC as a dehydrating mediator to acquire PEMPl–9 (Scheme 3). The incorporation of the TAMP into the POAE via amide linkage was carried out by using a simple, efficient and mild reaction conditions. Similar methodologies were reported earlier by Eva M. Maya et al., and Wiener et al., for ester linkages [19, 20].

Our first aim is to incorporate TAMP in POAE with utmost possible percentage to make high dielectric constant materials and we also consider the properties such as thermal stability, visible region absorption and solubility. Based on this by varying the stoichiometric % of TAMP (M = Co, Ni & Cu) to POAE results PEMPl–9 were synthesized. Here, the main challenge is the complete incorporation of TAMP to POAE matrix, for this additional two equivalents of DCC was used by activating the more carboxylic acids groups of POAE and making them to react with four amino groups of TAMP. This way complete incorporation of TAMP is possible and the inclusion percentage limit to 30 wt %. At higher ratios, aggregation of Pc compounds occurs by association of the macrocyclic rings [19] and insoluble materials results. So, 10, 20 % PEMP shows solubility in DMF, N,N-dimethylacetamide (DMAc) & dimethyl sulphoxide (DMSO) and 30% PEMP was soluble in only hot DMSO. Above 30 wt % even in the presence of free acid groups, there was no considerable increase in thermal stability was noticed and solubility decreases. Further, the successive amide linkage
formation between the Pc units and the polymer was confirmed by FTIR and NMR techniques.

**Monomer Synthesis:**

![Monomer Synthesis Diagram](image)

Synthesis of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole monomer.

**Scheme 1.** Synthesis of poly(1,3,4-oxadiazole aryl ether)s (POAE).

![Scheme 1](image)

**Scheme 2.** Synthesis of tetra amino metal phthalocyanines (TAMPS).

4.1.3.2. $^1$H-NMR & $^{13}$C-NMR spectra

The POAE structure was confirmed by both $^1$H-NMR and $^{13}$C-NMR spectra presented in figures 1–4. In the $^1$H-NMR spectra, the peaks at 2.57 and 2.84 ppm were assigned to the hydrogen atoms of aliphatic side chain. The hydrogen atom of the COOH was observed at 12.14 ppm and the aromatic protons are overlapped in the region of 8.19 to 6.94 ppm. However, in the $^{13}$C-NMR spectra, the peak at 173 ppm was attributed to the carbon atom of COOH group. The carbon atoms of 1,3,4-oxadiazole rings $C_a$ appeared at 163 ppm, the aromatic $C_{b,c}$ attached to ether linkage (–O–) appeared at 159 ppm, aromatic $C_e$ attached to aliphatic side chain show peak at 139 ppm, the aromatic $C_{f,g}$ attached to oxadiazole ring appears at 129 ppm, the remaining aromatic carbons appears in the range from 126 to 116 ppm and finally the aliphatic
carbons show absorption peak at 36 and 29 ppm. From the $^1$H–NMR and $^{13}$C–NMR of the polymer it was found that the composition of the polymer is similar to the composition of the reactants used for the synthesis.

The NiTAP inclusion into the POAE to get polymer embedded MPc (PEMP4–6). The structure were confirmed by $^1$H–NMR presented in figure 5, the peaks at 1.72 and 1.19 ppm were assigned to aliphatic side chain, here one interesting observation was made that, the electron donating nature of Pc attached to the polymer through amide linkage, the electron density around aliphatic side chain increase causes shielding of carbons and appears at high field compared to that of bare POAE. The amide connection confirmed by the existence of $-\text{NH}$ peak shows absorption at 5.53 ppm and finally the aromatic protons of Pc and polymer overlapped appears in the range 7.96 to 6.85 ppm, it also somewhat shielded due to inclusion of Pc. As a result, $^1$H–NMR spectra indicated that PEMP5 was synthesized as desired. Unluckily, $^1$H–NMR spectroscopy is uninformative because the paramagnetic character of the cobalt and copper centre prevents the resolution of the signals [19].

![Figure 1. $^1$H-NMR spectra for the POAE.](image-url)
Figure 2. Aromatic region enlarged $^1$H-NMR spectra for the POAE.

Figure 3. $^{13}$C-NMR spectra for the POAE.
Figure 4. Aromatic region enlarged $^{13}$C-NMR spectra for the POAE.

Figure 5. $^1$H-NMR spectra for the PEMP4.
4.1.3.3. Gel permeation Chromatography (GPC)

Figure 6. Gel permeation chromatogram for the POAE.

The weight and number average molecular weights of polymer POAE was determined by gel permeation chromatography (GPC). The value of weight-average molecular weight (Mw) is 12150 and number-average molecular weight (Mn) is 2513 with polydispersity ratio 4.83. The GPC curves showed narrow molecular weight distribution and low quantity of oligomers (see figure 6). Further accomplishment of PEMPl-9 from POAE under mild condition does not affect the polymer main chain.

4.1.3.4. Solubility Data

The solubility data of POAE polymer and polymer embedded MPC materials (PEMP1–9) presented in table 1. The solubility was determined at 10% solid content; +, soluble at room temperature, the solid polymer was completely dissolved in the solvent.
to afford a clean, homogeneous solution; ++, soluble upon heating; −, insoluble; the solid polymer did not dissolve in the solvent.

<table>
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<th>NMP</th>
<th>DMAC</th>
<th>DMF</th>
<th>DMSO</th>
<th>DCE</th>
<th>Acetone</th>
<th>THF</th>
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<tr>
<td>POAE</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>+</td>
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<tr>
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<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
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Table 1. Solubility data for the POAE and PEMPl-9.

4.1.3.5. Electronic absorption spectra

The UV-vis spectrum of POAE and after inclusion of TAMP is depicted in figure 7. The POAE shows transition at 432 nm and TAMP shows B-band transition at 432 nm and Q-band transition varied depending on metal centre, CoTAP shows Q-band transitions at 579 nm, NiTAP and CuTAP shows Q-band transitions at 593 nm. After inclusion of TAMP into POAE ensuing polymers shows two absorption bands, one is B-band transition at 432 nm and other is Q-band transition varies from different metal centre. The CoTAP, NiTAP and CuTAP incorporated POAE (PEMPl-9) shows Q-band transitions in the range of 680–684 nm, 661–664 nm and 696–699 nm, presented in figure 7. A large shift in Q-band and broad range of absorption was observed as compared to TAMP after TAMP incorporation. By this we can conclude that after Pc inclusion into the polymer extension of π-electrons and more delocalization of π-electrons leads large Q-band shift and broad visible window absorption. Here both B
and Q-band transition is attributed by $\pi-\pi^*$ transition of PEMP1–9. Figure 7, shows some interesting observation, as the percentage of TAMP increases its extinction coefficient also increases, but PEMP3 shows less extinction coefficient compare to PEMP1 & 2 due to certain amount of Pc aggregation in PEMP3, it reduces extinction coefficient of the Q band of the Pc to some extent [19] and similar results are observed for PEMP6. This can be further confirmed by solubility data, the 30% TAMP (PEMP3 & 6) incorporated POAE shows less solubility due to some extent of aggregation as compare to 10 & 20% TAMP. The solubility data’s are depicted in table 1.

Optical band gaps of POAE and PEMP1–9 were determined by the absorption lower edge of the absorption spectrum of each sample in the solid state and the data are summarized in table 2. Since interactions of TAMP macromolecules with the polymer chain causes movement of electrons alter the energy band gap between valence and conduction bands.

![Figure 7. Solid-state electronic absorption spectra for the POAE and PEMP1–9.](image)
### Table 2. Optical band gap data for the POAE and PEMP1-9.

<table>
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<th>Samples</th>
<th>Peaks $\lambda_{\text{max}}$(nm)</th>
<th>Band gap(eV)</th>
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<tr>
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<td>432</td>
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#### 4.1.3.6. FT-IR Spectra

The IR spectrum of POAE displayed the characteristic stretching bands at 2929 (C–H), 1609 (C=N), 1489 (C=C), 1227 (-C-O-C-) and 1165 cm$^{-1}$ (-C-O). The spectrum showed a broad band at 3432 cm$^{-1}$ due to the COO–H stretching vibrations, the carbonyl stretching of the pendant carboxylic group at around 1724 cm$^{-1}$ and the bands appeared at 1010 and 961 cm$^{-1}$ were characteristic of (=C-O-C=) stretching in 1,3,4-oxadiazole rings [15]. After TAMP inclusion into POAE, the IR spectrum of PEMP1–9 shows some new stretching bands in addition to the above mentioned bands. The PEMP1–9 display band at 2851 cm$^{-1}$ due to -N–H stretching of amide linkage and the electron donating nature of Pc increases the electron density after its incorporation to polymer and even after 30 % TAMP inclusion presence of free acid functionality was
confirmed by IR but at low concentration as compare to bare POAE. Its absorption region shift from 3432 cm\(^{-1}\) to low frequency at around 3327 cm\(^{-1}\) (COO–H) and finally the amide formation was confirmed by the -C=O stretching frequency at 1697 cm\(^{-1}\) of amide. The IR spectra confirm that PEMPl–9 was synthesized as desired and for comparison the IR spectra of POAE and PEMP5 presented in figure 8.

![IR spectra comparison](image)

Figure 8. Comparison of IR-spectra for the POAE and PEMP5.

4.1.3.7. Thermal Analysis

The thermal behaviour of POAE and PEMPl–9 was studied by thermogravimetric analysis (TGA) (figure 9). All polymers exhibited two-step degradation pattern, the first one was observed around 110 °C, which was attributed due to the loss of absorbed moisture in the polymers and all showed only 10% weight loss. The second weight loss of bare POAE from 350 to 596 °C, a large decomposition range was observed. It starts with the loss of side chain carboxylic acids (around 350 to 400 °C) [19], after complete decarboxylation the main chain degradation start and it was seen up to 596 °C. This high thermal stability of POAE was due to the presence of thermal inertness shown by 1,3,4-oxadiazoles in the polymer chain. The second step degradation of PEMPl–9 shows variation in decomposition temperature range.
depending on metal centre and percentage of TAMP. PEMP1's decomposition start at 390 °C and varied upto 540 °C results some appreciable improved thermal stability compare to bare POAE, this was attributed by the inclusion of high thermally stable MPcs. As the percentage of TAMP increases further in PEMP2 & 3, the stability also increase slightly in the range of 395 to 575 °C and 415 to 540 °C respectively. These steep slopes suggest the decomposition of polymer matrix and Pc ring. The thermal degradation of PEMP4–9 shows an almost similar pattern as mentioned above, the decomposition ranges of PEMP4–9 was clearly mentioned in table 3.

Kinetic and thermodynamic parameters study is to know the thermal oxidative stability (TOS) of the materials via accelerated thermal techniques. Different methods are there to explore the kinetic parameters, among them most probable kinetic method to be employed. In particular, we have used TGA to characterize the degradation pathways of the POAE and PEMP1–9 and kinetic parameters were computed using Broido’s method [28]. Because in Broido's method, the thermal degradation process was considered to be of first-order and the analysis was done easily using standard equations. Plots of -\ln(\ln(-1/y)) versus 1/T (Figure 10) (where ‘y’ is the fraction of the compound undecomposed) were developed for the decomposition segment. The slopes of the plots are determined and used to evaluate the activation energies of the POAE and PEMP1–9. The activation energy and other kinetic parameters are influenced by the variation of the central metal atom. The pre-exponential factor (A) is related to collision number, i.e. number of collisions dm⁻³s⁻¹. The high value of A indicates that the thermal degradation reaction is very fast [29]. The activation properties like change in enthalpy (ΔH), entropy (ΔS), free energy (ΔG) and pre-exponential factor (A) are calculated using Broido’s method and the values are summarized in table 3.
Figure 9. TGA graphs for the POAE and PEMP1-9.

Figure 10. Plots of -Ln(ln(-1/y)) vs 1/T x 10^3 for the second step decomposition for the POAE and PEMP1-9.
Table 3. Kinetic and thermodynamic parameters for the POAE and PEMPl-9.

4.1.3.8. XRD studies

The powdered XRD pattern of POAE, PEMPl-9 shown in figure 11, the d-spacing and 2θ values are presented in table 4. The XRD pattern of POAE exhibited characteristic sharp peaks at 15.2°, 17.9° and 25.9° (2θ) corresponding to an interplanar space of 5.80, 4.93 and 3.42 Å respectively. The characteristic XRD patterns of the TAMP can invariably be seen in the 2θ=13°–16° range and the consequent d-spacing is 6.1–5.4 Å. The XRD interplanar spacing’s for the broad peaks of Co, Ni and CuTAP are found to be 13.52, 13.44 and 15.29 respectively indicates that these tetra-amines are amorphous in nature [30, 31]. These TAMPs can be included into POAE, and the resulting PEMPl-9 resembles the same peak, but it shift considerably to right and overlap with the POAE absorbance at 5.8 Å (2θ = 15.26°) are close to 6.1–5.4 Å. The observed sharpness of the peak suggests that POAE are crystalline form and after inclusion of TAMP broadness of the peaks were observed in PEMPl-9 XRD suggest
that they are in semi-crystalline form [32]. Apart from the TAMP and POAE peaks at \(2\theta = 15^\circ - 25^\circ\), the XRD pattern of PEMP1–9 hybrid materials shows new peaks appeared at 20.24°, 21.41°, 21.92° and 22.41°. It was suggested that PEMP1–9 are a new materials, peak shifts and reduction in peak intensities relative to the peak intensities in pure POAE could indirectly confirm the formation of an linkage between POAE and TAMP [32, 33].

Figure 11. XRD graphs for the POAE and PEMP1-9.
Chapter 4

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Table 4. Powdered XRD data for the POAE and PEMP1-9.

4.1.3.9. AC electrical measurements

The electrical properties were executed for POAE and PEMP1–9 in the form of compressed pellet Ag/Polymer/Ag in the frequency range of 50 Hz to 5 MHz using an oscillating voltage with amplitude 1V peak-to-peak. Results have been reported for pellets of polymeric materials maintained under vacuum.
4.1.3.9.1. Frequency dependence of dielectric constant ($e'$)

Figure 12 shows variation of $e'$ with frequency for the POAE and PEMP1–9 at room temperature. Initially, $e'$ decreases with increase in frequency and finally at higher frequencies reaching a constant value for POAE and PEMP1–9. The observed large values of $e'$ at lower frequencies are attributed to the charge carriers present in the polymeric material, which migrate upon the application of the field. The decrease in $e'$ may be due to the decrease in space charge carries or interfacial polarization in the polymeric material [34, 35]. That is at low frequencies; the dipoles align themselves along the field and contribute fully to the total polarization. At higher frequencies, variation in the field is too rapid for the dipoles to align themselves. So $e'$ variation is small, becomes nearly frequency independent and approaches a constant value as can be seen clearly in figure 12. This can be attributed to rapid polarization process [36].

The raise of dielectric constant of a polymer is a main challenge. The POAE shows high value of $e'$ (340 at 50 Hz) was attributed by the presence of polar carboxylic acid group possess high concentration of electronic, atomic and dipolar polarizable units ($H^+ & -COO^-$), its exchange rapidly in the polymer matrix. As expected, the $e'$ of POAE embedded MPc are enhanced compared with that of the pure POAE (340 at 50 Hz) by increase in the weight percentage of TAMP inclusion. The variation of $e'$ with different weight fractions of TAMP as a function of frequency 1 kHz, 10 kHz and 1 MHz are measured at room temperature (Figures 13, 14 & 15). The PEMP1–9 shows enhanced dielectric constant values in comparison with bare POAE. These high dielectric constant polymers look like to be better than the early reported polymers by C. K. Chiang et.al, [37, 38] and can emerge as promising candidates in electromechanical fields such as high performance sensors, actuators, artificial muscles, as well as bypass capacitors in microelectronics and energy-storage devices.
Figure 12. Variation of dielectric constant with frequency for the POAE and PEMP1-9.

Figure 13. Variation of dielectric constant with composition (wt %) for PEMP1–9 at constant frequency 1 kHz.
Figure 14. Variation of dielectric constant with composition (wt %) for PEMP1–9 at constant frequency 10 kHz.

Figure 15. Variation of dielectric constant with composition (wt %) for PEMP1–9 at constant frequency 1 MHz.
4.1.3.9.2. Frequency dependence of dielectric loss (\(\tan\delta\))

Figure 16 show that dielectric loss (\(\tan\delta\)) decreases initially with increasing frequency. The dielectric loss curves also show the same trend as the dielectric constant curves and can be explained on lines similar to those advanced for explaining the dielectric constant. The values of dielectric loss observed at room temperature for POAE is 0.0039 and for PEMP1–9 are in the range of 0.0031 to 0.0099 was observe at 5 MHz. The low dielectric losses obtained for the present POAE and PEMP1–9 polymeric materials make them suitable for in microelectronics [39, 15]

![Figure 16. Variation of dielectric loss with frequency for the POAE and PEMP1-9.](image)

4.1.3.9.3. Frequency dependence of AC conductivity (\(\sigma_{ac}\))

Figure 17 displays the frequency dependence of AC conductivity for POAE and PEMP1–9 at room temperature revealing an increasing trend in the conductivity with the change of frequency, which was due to an increased density of charge carriers for conduction. The AC conductivity of all the polymeric materials shows the same trend
and resemble as remain constant for increase in the frequency from 50 Hz to 1 MHz and found to increase suddenly for further increase in the frequency up to 5 MHz [40]. As the TAMP content (10, 20 & 30 wt%) incorporation increases in the polymer, increase in the AC conductivity (Figures 18, 19 & 20) results by plotting composition (wt %) against AC conductivity at a fixed frequency 1kHz, 10kHz & 1MHz respectively. The observed trends in frequency dependence of AC conductivity can be explained on the basis of electron hopping model and the values are in the range of 3.2x10^{-5} to 4.8x10^{-5} (S/m) at 5 MHz frequency measured at 20 °C [41, 42].

**Figure.17.** Variation of AC conductivity with frequency for the POAE and PEMP1-9.
Figure 18. Variation of AC conductivity with composition (wt %) for PEMPl-9 at constant frequency 1 kHz.

Figure 19. Variation of AC conductivity with composition (wt %) for PEMPl-9 at constant frequency 10 kHz.
Conclusion

By an effective approach, the hybrid PEMP1–9 materials was successfully synthesized, characterized and subjected for AC electrical studies. The incorporation of Pc makes the ensuing polymeric materials as visible light absorbers from 400–800 nm and remarkable drop off in optical band gap with admirable thermal stability. As the percentage of MPc increases in the polymer matrix, it enhances the dielectric constant of the polymer and shows low dielectric loss in the interval of measured frequency and composes these polymers as potential candidates in applications such as sensors, actuators, artificial muscles, bypass capacitors in microelectronics, energy-storage devices. The AC conductivity for the polymeric materials was explained by electron hopping model and values are in the range of $3.2 \times 10^{-5}$ to $4.8 \times 10^{-5}$ (S/m) at 5 MHz frequency measured at 20 °C.
References


4.2.1. Introduction

High-performance electroactive polymers with high dielectric constant finds the applications in electrochemical fields such as high performance sensors, actuators [1–3], artificial muscles [4], as well as bypass capacitors in microelectronics and energy-storage devices [5–8]. The poly(arylene-ether) containing 1,3,4-oxadiazole rings are important class of high performance electroactive polymers, which are of special interest for the production of advanced materials due to their high thermal oxidative stability and from the electronic and spectral points of view, the oxadiazole ring is similar to a p-phenylene structure, which is known to be a strong electron-withdrawing character. Also, it does not contain any hydrogen atoms, not any possibilities for rearrangement, it has structural symmetry and it is thermally unreactive [9]. The following features motivated the introduction of 1,3,4-oxadiazole rings in the macromolecular chain. Poly(arylene-ether) containing 1,3,4-oxadiazole is of great interest due to electron-withdrawing character can facilitate the injection and transport of electrons [10, 11] possessing high thermal resistance, tough mechanical properties [9] and the polymers generally suffer from a low dielectric constant 2.98–3.5 reported by C. Hamciuc, et.al.,[12, 13] and poor solubility in organic solvents. Therefore, solubility and dielectric constant of the polymers is often increased when flexible bonds, large pendent groups or polar substituents (nitriles, sulfonic, carboxylic acid) are incorporated into the polymer chain for easy processability and for the enhancement of dielectric constant [14]. In this regard poly(1,3,4-oxadiazole-aryl ether) (POAE) containing carboxylic acid groups derived from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and 3-(3,4-dihydroxyphenyl)propanoic acid have been synthesized from
typical aromatic nucleophilic substitution reaction exhibit good solubility and high
dielectric constant ~340 at 50 Hz reported by us [15].

As suggested in section-1, here we describe other way to enhancement the
dielectric constant of the POAE was achieved effectively by inserting high dielectric
constant metalphthalocyanine (MPC) [16–23]. In this study, we synthesize high-
performance electroactive, photoactive and high dielectric constant metal containing
polymer to place in latter thought purpose will be demonstrated. The POAE is
functionally active because of the presence of carboxylic acid pendants; it is much
needful to make POAE into photoactive, high dielectric constant polymer by the
inclusion of tetra carboxy metalphthalocyanines (TCMPc, M = Co, Ni & Cu) via 1,3,4-
oxadiazole bridge and is achieved by polyphosphoric acid (PPA) assisted condensation
followed by cyclization reaction with hydrazine sulphate [24–27] affording polymer
embedded metalphthalocyanines (PETCP 1–9) (Scheme 1). The oxadiazole
characteristics can be enhanced by incorporating MPC into the polymer by side groups
via 1,3,4-oxadiazole bridge and they are well recognized as a class of high performance
polymers. TCMPc inclusion into POAE to be varied stochiometrically as 10, 20 and 30
weight% results in high dielectric constant polymeric materials PETCP 1–9 and possess
low dielectric loss in the measure frequency range (50 Hz to 5 MHz). The variation of
weight fractions of TCMPc limits to 30% because at this percentage results insolvability
of the polymer and difficult in processing for further studies. The tailor-made polymers
enjoy a number of advantages such as improved thermal properties and become
photoactive materials by catching maximum visible light compare to bare POAE. All
polymers were characterized with FTIR, NMR spectroscopic techniques, optical and
electrical properties have been performed. A significant advantage of this approach is
that a great variety of metals can be introduced into polymer through the inclusion of
TCMPc as side groups. These metal-containing high performance electroactive dielectric polymeric systems are addressable to show their potential in above mentioned fields.

4.2.2. Experimental

4.2.2.1. Materials and Instrumentation

The materials used for synthetic part and instruments used for characterization to be similar as described in section 1. The POAE containing the carboxylic acid groups was synthesized by a conventional polymerization method reported by us in section-1[15]. TCMPc [M = Co, Ni & Cu] were prepared according to the described procedure [28] and making of pellets and the procedure used for electrical measurements to be similar as presented in chapter 2.

4.2.2.2. Preparation

4.2.2.2.1. General procedure for POAE embedded TCMPc (M = Co, Ni & Cu) [PETCP 1-9].

To achieve advanced materials the POAE is modified with TCMPc; it was carried out using PPA as dehydrating followed by cyclization agent with hydrazine sulphate at 150 °C for 24h. In a typical reaction, 500mg of POAE, 50mg (10 wt %) of NiTCPc and 26.13mg of hydrazine sulphate (0.2 mmol) was mixed well in a quartz mortar, then transfer into a 250 ml round bottom flask. Add preheated 50g PPA containing 5g of P2O5 and the reaction mixture was maintained at 150 °C for 24 h. The fibrous green PETCP polymers were filtered after pouring in to 300 ml water. The product obtained was treated with 0.1 M sodium bicarbonate solution followed by water to remove unreacted NiTCPc and dried in a vacuum oven at 100 °C overnight.
The same procedure was repeated for 20%, 30% NiTCPc and also for CoTCP and CuTCP to afford PETCP 1–9 as show in Scheme 1.

### 4.2.2.2.1a. *POAE embedded CoTCPc (10, 20 & 30 wt %) (PETCP1–3)*

Yield: 88%. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3401–3417 (COO–H), 2923 (C–H), 1705–1715 (–C=O of acid), 1606–1608 (C=N), 1490 (C=C), 1273, 1216–1218 (C–O–C), 1168 (–C–O), 1072, 1011 (–C–O–C=), 844, 745 (Pc skeleton). UV–Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 434, 688–691.

### 4.2.2.2.1b. *POAE embedded NiTCPc (10, 20 & 30 wt %) (PETCP4–6)*

Yield: 89%. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3404–3421 (COO–H), 2925 (C–H), 1705–1713 (–C=O of acid), 1608 (C=N), 1489 (C=C), 1272, 1217 (C–O–C), 1167 (–C–O), 1072–1087, 1011 (–C–O–C=), 842–844, 742–744 (Pc skeleton). UV–Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 434, 656–659. \(^1\text{H NMR (DMSO-d6)}\) (δ, ppm): 0.85 (t, 2H, –CH₂), 1.25 (t, 2H, –CH₂–), 8.45–6.80 (m, 23H, Ar–H).

### 4.2.2.2.1c. *POAE embedded CuTCPc (10, 20 & 30 wt %) (PETCP7–9)*

Yield: 90%. IR [(KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3398–3424 (COO–H), 2928 (C–H), 1701–1707 (–C=O of acid), 1608 (C=N), 1489 (C=C), 1272, 1218–1218 (C–O–C), 1166–1168 (–C–O), 1073–1086, 1011 (–C–O–C=), 844, 738–744 (Pc skeleton). UV–Vis (solid state) \( \lambda_{\text{max}}/\text{nm} \): 434, 655–672.

### 4.2.3. Result and Discussion

#### 4.2.3.1. Synthesis

In section-1 we report the synthesis of POAE was achieved via a nucleophilic aromatic substitution reaction and was confirmed by \(^1\text{H-NMR}\) and gel permeation chromatography (GPC). The TCMPc was synthesized by the cyclotetramerization
method described in Chapter-2 [28]. In the next step, the POAE containing COOH groups are tailored with MPc containing peripheral COOH groups via 1,3,4-oxadiazole bridge with hydrazine sulphate using PPA [24–27] as a catalyzing reagent at 150 °C for 24 h to acquire PETCP 1–9 (Scheme 1).

Our first intention was to generate high dielectric constant polymeric materials for advanced studies by the inclusion of TCMPc in POAE with highest possible percentage and we also think about the properties such as visible region absorption, thermal stability and solubility. Based on this thought stoichiometric % of TCMPc (M = Co, Ni & Cu) to POAE was varied and POAE set in TCMPc ((M = Co, Ni & Cu) [PETCP 1–9] were synthesized. Here, the whole assimilation of TCMPc to POAE is not easy and we are try to maximum MPc inclusion and stop it to 30%, because at this stage polymers reveal insolubility and hard to process for further studies. Here the dilemma of this method for the total incorporation of TCMPc in to the polymer matrix by adding up two equivalent excess of hydrazine sulphate, there is a possibility of self oxadiazole creation between two carboxylic acid groups of polymer or in between two TCMPc. But the maximum proportion of TCMPc inclusion into the polymer was confrirmed by yields of the product and the electronic spectra show strong absorption band in the region of 600–800 nm. This way utmost incorporation of TCMPc was achieved, with inclusion percentage limit to 30 wt%. At higher ratios, aggregation of phthalocyanine (Pc) compounds occurs by association of the macrocyclic rings [29] and insoluble materials results. So, 10, 20% PETCP shows solubility in DMF, DMAc and DMSO and 30% PETCP were insoluble. The insertion of MPc% increases in POAE, there is a considerable improvement of thermal stability was noticed, because of its high thermal inertness nature. Further, the successive oxadiazole creation between
the TCMPc and the polymer has been confirmed through FTIR and $^1$H-NMR techniques.

![Scheme.1. Synthesis of polymer embedded tetra carboxy metalphthalocyanine (PETCP 1-9) (M = Co, Ni & Cu).](image)

4.2.3.2. $^1$H-NMR spectra

The $^1$H-NMR spectra of PETCP 5 presented in figure 1, confirms the inclusion of NiTCPc into POAE. The two triplets at 0.85 and 1.25 ppm were assigned to the hydrogen atoms of aliphatic side chain, here one interesting observation can be seen, the electron donating nature of MPc attached to the polymer via 1,3,4-oxadiazole bridge, the electron density around aliphatic side chain increase causes shielding of protons and appears at strong field as contrast to bare POAE [15]. The $^1$H–NMR spectra of POAE polymer confirms the composition of the polymer is similar to the composition of the reactants used for the synthesis presented in section-1. By compare
to POAE, the peak at 12.14 ppm due to hydrogen atom of –COOH utmost disappeared was confirmed the carboxylic acid group of the polymer involved in the construction of 1,3,4-oxadiazole bridge with MPc. And finally the aromatic protons of Pc and polymer overlap resonances at 8.45–6.80 ppm as a multiplet, it also fairly shielded due to inclusion of MPc. As a result, $^1$H–NMR investigations of PETCP 5 provided the characteristic chemical shifts for the expected structures. Unfortunately, $^1$H–NMR spectroscopy is uninformative for cobalt and copper containing polymers because the paramagnetic character of the cobalt and copper centre prevents the resolution of the signals [29].

![Figure 1. $^1$H-NMR spectra for the PETCP 5.](image)

### 4.2.3.3. Solubility

The POAE was soluble in polar solvents like NMP, DMAc, DMF, DMSO and in less polar solvents like dichloroethane (DCE), pyridine, tetrahydrofuran (THF). After MPc inclusion the resulting polymers solubility decreases to some extent. The PETCP 1, 2 & 4–8 are soluble in DMF, DMAc and DMSO, except PETCP 3 & 9, because in
these two polymers certain amount of aggregation of Pc occurs in the polymer matrix and the solubility data’s are depicted in table 1.

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<tr>
<td>PETCP2</td>
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<tr>
<td>PETCP3</td>
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<td>PETCP4</td>
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<tr>
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<td>+</td>
<td>+</td>
<td>-</td>
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<tr>
<td>PETCP6</td>
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<td>PETCP7</td>
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</tbody>
</table>

**Table 1. Solubility data for the POAE and PETCP 1-9.**

The solubility was determined at 10% solid content; +, soluble at room temperature, the solid polymer was completely dissolved in the solvent to afford a clean, homogeneous solution; ++, soluble upon heating; -, insoluble; the solid polymer did not dissolve in the solvent.

**4.2.3.4. Electronic absorption spectra**

Solid state electronic spectra are especially useful to establish the structures of POAE and PETCP 1–9 is presented in figure 2. The UV–Vis spectrum of POAE show band at 434 nm and TCMPc core is dominated by two intense bands, the B–band transition at 434 nm and Q–band transition varied depending on metal centre, CoTCPc, NiTCPc and CuTCPc exhibited Q–band transitions at 565, 550 and 580 nm respectively. After grafting of POAE with TCMPc, the ensuing polymers show typical electronic spectra with two absorption regions, one is B–band transition at 434 nm in the blue end of the visible spectrum and other is Q–band transition in the range of 655–
691 nm in the red end of the visible spectrum for different metal centred polymers and this visible region absorption is responsible for the observed green colour of the PETCP 1–9. The CoTCPc, NiTCPc and CuTCPc embedded POAE (PETCP 1–9) exhibited Q–band transitions in the range of 688–691 nm, 656–659 nm and 655–672 nm respectively and the electronic absorption spectra are presented in figure 2. The ensuing PETCP 1–9 exhibit a large shift in Q–band and broad range of absorption was seen as compared to TCMPc. By this we conclude that MPc grafting with polymer results extension of conjugation and more delocalization of π-electrons leads large Q–band shift and broad visible light absorption. Here both B–band and Q–band correlated to π–π* transition of PETCP 1–9. Figure 2 shows some interesting observation, as the variation of TCMPc increases its extinction coefficient increase, but PETCP 3 & 9 shows less extinction coefficient contrast to PETCP 2 & 8 due to certain amount of aggregation of Pc in PETCP 3 & 9, it reduces extinction coefficient of the Q–band to some extent [29]. This can be further confirmed by solubility data, the 30% TCMPc grafted POAE (PETCP 3 & 9) showed insolubility due to some level of aggregation as compare to PETCP 2 & 8.

Optical band gaps of POAE and PETCP 1–9 were determined by the absorption lower edge of the absorption spectrum of each sample in the solid state and the data are summarized in Table 2. Since interactions of TCMPc macromolecules with the polymer chain causes movement of electrons and alter the energy band gap between valence and conduction bands.
Figure 2. Solid-state electronic absorption spectra for the POAE and PETCP 1–9.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peaks $\lambda_{\text{max}}$(nm)</th>
<th>Band gap(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POAE</td>
<td>434</td>
<td>2.12</td>
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<tr>
<td>PETCP1</td>
<td>434, 691</td>
<td>1.79, 1.28</td>
</tr>
<tr>
<td>PETCP2</td>
<td>434, 688</td>
<td>1.70, 1.35</td>
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<tr>
<td>PETCP3</td>
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<td>1.61, 1.24</td>
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</tr>
<tr>
<td>PETCP9</td>
<td>434</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Table 2. Optical band gap data for the POAE and PETCP 1–9.


4.2.3.5. FT-IR spectra

The IR spectrum of PETCP 1–9 displayed the characteristic stretching bands located at 2923–2928 (C–H), 1606–1608 (C=N), 1489 (C=C) and 1166–1168 cm\(^{-1}\) (C–O) were observed at expected frequencies in all the polymeric materials. The characteristic absorption bands appeared at 1271–1273 & 1216–1218 cm\(^{-1}\) due to the presence of aromatic ether (C–O–C) linkages. Even after 30 % TCMPc inclusion into polymer the presence of free acid functionality was confirmed by IR but at low concentration as compare to bare POAE. Its absorption region shift from 3432 cm\(^{-1}\) to somewhat low frequency range around 3398–3424 cm\(^{-1}\) (COO-H) due to hydrogen bonding [30], but the carbonyl stretching of the pendant free carboxylic group at around 1701–1715 cm\(^{-1}\). In this context the oxadiazole formation was clearly confirmed by the absorption bands appearing at 1072–1087 & 1011 cm\(^{-1}\) were characteristic of (C=O=C=) stretching in 1,3,4-oxadiazole rings [13]. IR spectrum PETCP 1–9 demonstrate some additional stretching bands in the range of 842–844 and 738–745 cm\(^{-1}\) due to Pc skeleton vibrations. The assigned absorption bands are reasonably consistent with the suggested structures and for comparison the IR spectra of POAE and PETCP6 presented in figure 3.

**Figure 3.** Comparison of IR-spectra for the POAE and PETCP 6.
4.2.3.6. Thermal Analysis

The thermogravimetric analytical studies of all the polymers were carried out in an air atmosphere (Figure 4). The TGA curves of PETCP 1–9 obtained, demonstrate the decrease in sample mass with linear increase in temperature, exhibited appreciable thermal stability >375 °C. All polymers display two stage degradation pattern, the first stage is the loss of absorbed moisture and solvent from room temperature until around 150 °C. The second weight loss of bare POAE is around 350–596 °C, a large decomposition range was observed. It starts with the loss of carboxylic acids pendants (around 350–400 °C) [29], after complete decarboxylation the main chain degradation starts and it was seen up to 596 °C. The high thermal stability of POAE is due to the presence of thermally inert 1,3,4-oxadiazoles in the polymer backbone. The second major weight loss of PETCP 1–9 shows a varied breakdown temperature range depends on metal centre. All the polymers exhibit a enhanced thermal stability can be attributed by the inclusion of thermally inert MPc. PETCP 1 show decomposition start at 395 °C and varied upto 600 °C results some noticeable improvement of thermal stability compare to bare POAE. As the percentage of TCMPc increases further in PETCP 2 & 3, the stability also increase slightly in the range of 400 to 600 °C and 415 to 600 °C respectively. These steep slopes suggest the decomposition of polymer matrix and Pc ring. The thermal degradation of PETCP 4–9 shows an almost similar pattern as mentioned above, the decomposition temperature ranges of PETCP 4–9 was clearly mentioned in table 3.

Kinetic parameters study of the polymeric materials was determined via thermal techniques to know the thermal oxidative stability (TOS) of the POAE and PETCP 1-9 materials as described in section-1 using Broido’s method [31]. The graphical plots of -Ln(Ln(-1/y)) versus 1/T (where ‘y’ is the fraction of the compound undecomposed)
obtained for POAE and PETCP 1–9 are presented in figure 5. For each step in the decomposition sequence, it was possible to resolve the following thermal parameters such as activation energy ($E_a$), enthalpy ($\Delta H$), entropy ($\Delta S$), free energy ($\Delta G$) and pre-exponential factor ($A$) using Broido’s method and the values are summarized in table 3.

![Figure 4](image1.png)

**Figure 4.** TGA graphs for the POAE and PETCP 1-9

![Figure 5](image2.png)

**Figure 5.** Plots of $-\ln(\ln(-1/y))$ vs $1/T \times 10^{-3}$ for the second step decomposition for the POAE and PETCP 1-9.
Table 3. Kinetic and thermodynamic parameters for the POAE and PETCP 1-9.

### 4.2.3.7. XRD Studies

The X-ray diffraction analysis is a direct method to investigate the crystallinity or amorphous nature of the materials. The XRD pattern of POAE exhibited
characteristic sharp peaks at 15.2°, 17.9° and 25.9° (2θ) corresponding to an interplanar space of 5.80, 4.93 and 3.42 Å respectively reported in section-1 and is presented figure 6. The X-ray diffraction pattern of PETCP 1–9 shows broad peaks. The sharp peaks exhibited POAE is engaged with TCMPc results in extended conjugation and the greater π-electron region influences the stacking of Pc in parallel molecules and the PETCP 1–9 materials were amorphous in nature and for confirmation comparison of XRD pattern of POAE and PETCP 1–3 presented in figure 6.

4.2.3.8. AC electrical measurements

The electrical properties were executed for POAE and PETCP 1–9 in the form of compressed pellet Ag/Polymer/Ag in the frequency range of 50 Hz to 5 MHz utilizing an oscillating voltage with amplitude 1V peak-to-peak. Results have been reported for pellets of polymeric materials maintained under vacuum.

4.2.3.8.1. Frequency dependence of dielectric constant (ε')

Figure 7 shows the decrease of dielectric constant (ε') with frequency for the POAE and PETCP 1–9 at room temperature due to interfacial polarization in the polymeric material described in section-1 [32, 33]. The increase of dielectric constant of a polymer is a main challenge. The POAE show high value of ε' (340 at 50 Hz) reported in section 1. The ε' of POAE is further improved by the insertion of MPC; this can be accomplished by increase in the weight fraction of TCMPc inclusion. The variation of ε’ with different weight fractions of TCMPc as a function of frequency 1 kHz, 10 kHz and 1 MHz are deliberate at room temperature can be seen in figure’s 8, 9 & 10. The PETCP 1–9 show enhanced dielectric constant values in comparison with bare POAE but the dielectric constant imparted TCMPc to the polymer does not increase continuously with increased MPC content, i.e., the relationship is nonlinear.
These high dielectric constant polymers can come forward as suitable candidates in electromechanical fields such as high performance sensors, actuators, artificial muscles, as well as bypass capacitors in microelectronics and energy-storage devices.

**Figure.7.** Variation of dielectric constant with frequency for the POAE & PETCP 1-9.

**Figure.8.** Variation of dielectric constant with composition (wt%) for PETCP 1–9 at constant frequency 1 kHz.
Figure 9. Variation of dielectric constant with composition (wt%) for PETCP 1–9 at constant frequency 10 kHz.

Figure 10. Variation of dielectric constant with composition (wt%) for PETCP 1–9 at constant frequency 1 MHz.
4.2.3.8.2. Frequency dependence of dielectric loss (tanδ)

The variation of dielectric loss (tanδ) with frequency for POAE at different fraction of TCMPc (PETCP 1–9) as depicted in figure 11 shows that tanδ varied rapidly at lower frequencies and slowly at higher frequencies. It is clear from the graph dielectric loss decreases with increasing frequency reaching a constant value at higher frequencies for POAE and PETCP 1–9. The figure 11 also displays the dielectric loss values of the polymers are relatively low over the measured frequency range at room temperature. The POAE exhibit low loss values 0.72–0.0039 in the entire frequency range and for PETCP 1, 4, 5 & 6 initially shows high loss values of 1.41–1.99 at 50 Hz, PETCP 3 & 7 exhibit loss value 1.08–1.09 at 50 Hz frequency and for PETCP 2, 8 & 9 initially show low loss value vary in the range of 0.69–0.82 at 50 Hz and observe the loss value upto 5 MHz and at 5 MHz frequency PETCP 1–9 exhibit the tanδ value in the range of 0.012 to 0.0027. The low dielectric loss results of these polymeric materials can be exploited for the applications in high dielectric constant materials [22].

![Figure 11](image_url)

**Figure 11.** Variation of dielectric loss with frequency for the POAE and PETCP 1–9.
4.2.3.8.3. Frequency dependence of AC conductivity ($\sigma_{ac}$)

Figure 12 displays the frequency dependence of AC conductivity for POAE and PETCP 1–9 at room temperature revealing an increasing trend in the AC conductivity with the increase of frequency, due to an increase in the frequency of the applied field enhances the hopping of charge carriers resulting in an increase in the conduction process thereby increasing the conductivity.

Figure 12. Variation of AC conductivity with frequency for the POAE and PETCP 1-9.

The AC conductivity of all the polymeric materials exhibit same trend and resembles with gradient increase in the frequency from 50 Hz to 1 MHz and start to increase suddenly for further increase in the frequency up to 5 MHz and is found to be highest value at this frequency [34]. At 5 MHz frequency the PETCP 1–3, PETCP 4–6 & PETCP 7–9 shows the AC conductivity in the range of $3.92 \times 10^{-5}$–$4.52 \times 10^{-5}$, $4.27 \times 10^{-5}$–$4.45 \times 10^{-5}$ & $3.92 \times 10^{-5}$–$4.23 \times 10^{-5}$ (S/m) respectively, the variation of conductivity depends on metal centre and MPc% in the polymer matrix. As the TCMPc inclusion (10, 20 & 30 wt%) increases in the polymer, enhancement of AC conductivity
as can be seen clearly in figure's 13, 14 & 15, as a function of frequency 1 kHz, 10 kHz and 1 MHz at room temperature. The observed trends in frequency dependence of AC conductivity can be explained on the basis of electron hopping model [35].

Figure 13. Variation of AC conductivity with composition (wt%) for PETCP 1-9 at constant frequency 1 KHz.

Figure 14. Variation of AC conductivity with composition (wt%) for PETCP 1-9 at constant frequency 10 KHz.
Figure 15. Variation of AC conductivity with composition (wt%) for PETCP 1-9 at constant frequency 1 MHz.
Conclusion

The poly(1,3,4-oxadiazole aryl ether) (POAE) containing carboxylic acid groups is a high dielectric constant high-performance electroactive polymer (340 at 50 Hz reported in section-1). The improvement of dielectric constant of POAE was achieved by grafting with high dielectric constant MPc by a simple PPA assisted condensation followed by cyclization approach with hydrazine sulphate results PETCP 1–9 hybrid materials. The resultant PETCP 1–9 was fruitfully characterized and subjected for AC electrical studies. MPc inclusion polymeric materials expose further enhancement of dielectric constant (~360–700 at 50 Hz) and turn into photoactive by engrossing maximum visible light from 400 to 800 nm with remarkable drop off in optical band gap. The PETCP 1–9 shows better thermal stability compare to bare POAE, because of the insertion of thermally inert MPc in a stochiometric variation (10, 20 & 30 wt%) in to the polymer. The high dielectric constant and low dielectric loss exhibited by these hybrid materials in the measured frequency range of 50 Hz to 5 MHz and make these polymers as potential candidates in advanced studies such as sensors, actuators, artificial muscles, bypass capacitors in microelectronics, energy-storage devices. The AC conductivity for the PETCP 1–9 was explained by electron hopping model and values are in the range of $3.92 \times 10^{-5} - 4.52 \times 10^{-5}$ (S/m) at 5 MHz measured at room temperature.
References


