

Copolymerization of 5-[4-(methacryloylamino)phenyl]-10,15, 20-triphenylporphyrin with Styrene: Investigation of Spectroscopic, Structural and Thermal Properties

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ABSTRACT

In this work, tetraphenylporphyrin (TPP) compound was first synthesized by the condensation reaction of pyrrole and benzaldehyde using Adler method. Then, the synthesized tetraphenylporphyrin was nitrated with sodium nitrite. Nitro-functionalized porphyrin (TPP-NO₂) compound was reduced to amine-functional using ammonia and this amine-functionalized porphyrin was reacted with methacryloyl chloride to obtain porphyrin-derived radical monomer (TPP-MAO). Copolymer was synthesized with obtained porphyrin functional monomer and styrene by free radical polymerization method. Structural characterization and spectroscopic studies of the synthesized compounds were carried out by FTIR, H¹-NMR, UV spectroscopy. The molecular weight and thermal properties of the copolymer were determined using gel permeation chromatography (GPC) and thermogravimetry (TG). Tetraphenyl porphyrin containing polymer shows good photoluminescence property.

KEYWORDS: *Porphyrin, Polystyrene, Radical Polymerization, Characterization, Thermal Properties*

1. INTRODUCTION

Porphyrins are heteromacrocyclic structures that result from the attachment of four pyrrole rings by a methyl bridge. Porphyrins are 18 conjugated π electrons systems that conform to the Hückel Rule $(4n+2) \pi$.^[1,2] Furthermore,

non-substituted porphyrins are planar like aromatic systems, which are determined by X-ray crystallography. Nowadays, porphyrin based polymers are widely used in optical sensors,^[3-5] solar cells^[6-8] and photodynamic therapy studies^[9-11]. In a study published in

2015, Wang et al. synthesized amphiphilic acrylamide-based containing porphyrin copolymers and showed that this polymer has high selectivity for mercury by spectroscopy studies. After mercury addition, the color of the aqueous solution of the porphyrin-containing polymer was observed to turn green from brown, and then the difference for mercury was observed in the subsequent absorption studies. It appears that this sensor permits quantitative analysis of mercury to a measurement limit as low as 50 Nm^[12]. Avossa et al. synthesized polyhydroxybutyrate/polystyrene nanofibers doped with graphene and porphyrin for chemiresistor gas sensors using electrospinning method. They reported in this study that the development of a conductive nanofibrous and nanocomposite polymer sensor combined with a free-base tetraphenylporphyrin, having the role of driving the selectivity and sensitivity of the polymer layer^[13]. In another study Hu et al. developed colorimetric and fluorescent sensor based on a porphyrin doped polystyrene nanoporous fiber membrane. They used this sensor for HCl gas detection. According to obtained result, the sensor presented apparent color change from pink to yellow green when exposed to ppm-level of HCl gas at 40 °C^[14]. Tangestaninejad and Mirkhani used the polystyrene-bound Manganese(III) Porphyrin as a Heterogeneous Catalyst for Alkene Epoxidation in their studies. They synthesized a new polymer-bound manganese porphyrin catalyst. This catalyst is very easy to prepare and can be used without degradation in the presence of sodium periodate for alkene epoxidation^[15].

Salatelli et al., in their studies on solar cells in 2016 have derived the polyalkylthiophene chain

with tetraphenylporphyrin and investigated the effect of synthesized porphyrin containing polymer on cell efficiency^[16]. Photodynamic therapy is a method of photochemotherapy based on the principle that the target lesion, which is sensitized by light to the local systematic agents, is irradiated with the light sources of the appropriate wavelength. The most widely used photosensitizers are porphyrins, chlorins and phthalocyanines. In a study by Chang et al. in 2016, the porphyrin compound was covalently bonded to the π -conjugated polymer skeleton as a photosensitizer and polymer-dot-photosynthesis was obtained^[17].

Recently, polystyrene copolymers prepared with porphyrin have created different areas of usage such as gas sensors,^[18,19] fiber membrane,^[20] photo application^[21,22,23].

Here, we describe the synthesis of a polymeric materials made of vinyl-functionalised tetraphenylporphyrin and styrene.

EXPERIMENTAL

Materials

Pyrrole (Merck, reagent grade, 98%), Benzaldehyde (Fluka, purified by redistillation, $\geq 99.5\%$), Propionic Acid (Fluka, ACS reagent, $\geq 99.5\%$), Sodium Nitrite (Merck, ACS reagent, $\geq 97\%$), Trifluoroacetic Acid (TFA) (Merck, reagentplus 99%), Tin (II) chloride dihydrate (Merck, reagent grade, 98%), Hydrochloric Acid (Merck, ACS reagent, 37%), Methacryloyl chloride (Merck, 97%, contains ~200 ppm monomethyl ether hydroquinone as stabilizer), Triethylamine (Merck, $\geq 99.0\%$), Styrene (Merck, ReagentPlus®, contains 4-tert-butylcatechol as stabilizer, $\geq 99\%$), Benzoyl peroxide (Sigma-Aldrich, 75%, remainder water), Magnesium sulphate (Sigma-Aldrich, anhydrous, ReagentPlus®, $\geq 99.5\%$), Silica Gel (Merck,

high-purity grade (Davisil Grade 635), pore size 60 Å, 60-100 mesh), Chloroform (Sigma-Aldrich, contains 100-200 ppm amylenes as stabilizer, $\geq 99.5\%$), Hexane (Sigma-Aldrich, anhydrous ≥ 95), Dichloromethane (Sigma-Aldrich, anhydrous, $\geq 99.8\%$, contains 40-150 ppm amylene as stabilizer), Methanol (Tekkim 99.8%), Tetrahydrofuran (Sigma-Aldrich anhydrous, $\geq 99.9\%$, inhibitor-free).

Instrumentation

$^1\text{H-NMR}$ (NMR, nuclear magnetic resonance) measurements were recorded in CDCl_3 (deuterium chloroform) with $\text{Si}(\text{CH}_3)_4$ as internal standard, using Varian AS-400 (400 MHz) instrument (USA). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a PerkinElmer FTIR Spectrum One-B spectrometer (USA). Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 1 mL/min and a Waters 410 differential refractometer detector (UK). TG measurements of powders polymer samples were obtained on PerkinElmer Diamond TA/TGA (USA) from 25 to 600 °C at 10 °C heating rate under constant flow rate of 100 mL/min of nitrogen atmosphere. The sample weights for all the experiments were taken in the range of 8–10 mg. UV – Visible spectra were on Varian Cary 100 Bio Spectrometer.

Methods

Synthesis of 5,10,15, 20-Tetraphenylporphyrin (TPP)³¹

The pyrrole was distilled before starting the reaction. 250 mL of propionic acid was added to a 500 mL three neck round bottom flask. Then, Benzaldehyde (6.5 mmol) was added to the flask and heated to 141 °C. When the desired temperature was reached, the pyrrole (6.5 mmol) dissolved in 5 ml of propionic acid was added. It was observed that the mixture turned purple color. The mixture was stirred for half hour under reflux. At the end of half hour the mixture was cooled to room temperature (RT) and stirred overnight. The precipitated dark color material washed first with hot water and then methanol. The resulting

purple solid was eluted from the silica gel packed column with chloroform and the first fraction was collected. TPP was crystallized in a chloroform / methanol system.

Synthesis of 5 - (4-nitrophenyl) - 10, 15, 20-Triphenylporphyrin (TPP- NO_2)

TPP (2 mmol) was dissolved in 25 ml of TFA. NaNO_2 (3.6 mmol) was added. The mixture was stirred at RT for 3 minutes. Then, the mixture was added to 150 ml of water and extracted with DCM until the water phase was colorless. The dichloromethane phase was washed with saturated NaHCO_3 then dried over MgSO_4 . Excess solvent was removed in the evaporator. The resulting dark color solid was purified on a plug of silica gel, with dichloromethane / hexane (1: 1). The second fraction was collected.

Synthesis of 5 - (4-aminophenyl) - 10, 15, 20-triphenylporphyrin (TPP- NH_2)

TPP- NO_2 (1,2 mmol) was dissolved in 25 ml concentrated HCl at Ar atm. Then $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3,97 mmol) was added to the reaction medium. The mixture was heated to 65 °C and the reaction was continued overnight. At the end of the reaction, the mixture was slowly added to 100 ml of cold water. Concentrated NH_3 was slowly added to adjust the pH to 8. The water phase was then extracted with chloroform until clear. The organic phase was dried over MgSO_4 . The solvent was removed on the evaporator. The eluted product was chromatographed on silica with DCM. The second fraction was collected and the solvent evaporated. Purple colored solid was obtained.

Synthesis of 5-[4-(methacryloylamino)phenyl]-10, 15, 20-triphenylporphyrin (TPP-MAO)

0,28mmol TPP- NH_2 was dissolved in 15 mL THF at Ar atm 0°C. 0,35 mmol Et_3N was added and the mixture was stirred in the cold for half an hour. Then 0,35mmol methacryloyl chloride was added dropwise over 20 minutes. The mixture was stirred at 0°C. for 10 minutes and then brought to room temperature. The mixture was further stirred at 0°C for 10 minutes and then the reaction was continued for 6 hours at room temperature. At the

end of 6 hours, 25 ml of water was added and extracted with dichloromethane. The organic phase was dried with MgSO_4 . The resulting purple color solid was purified on a plug of silica gel, with dichloromethane / hexane (5: 1). The second fraction was collected. Bright purple solid was obtained.

Synthesis of Poly(Styrene-co-(5-[4-(methacryloylamino) phenyl]-10, 15, 20-triphenylporphyrin)) (Poly(st-co-TPP-MAO))

0,25 mmol TPP-MAO and 0,25 mmol styrene was dissolved in 0,3mL THF. 0,01 mmol BPO was added as initiator and the mixture was heated to 75°C. The reaction was continued for 8 hours under argon atmosphere. At the end of 8 hours the polymer was precipitated in methanol. The product was dried at 40 °C vacuum.

Synthesis of Polystyrene (PS)

To remove the stabilizers, the styrene was poured through the alumina filled-up column. 0.017 mol of styrene was added to the flask at argon atmosphere. 0,51 mmol BPO was added as initiator and the mixture was heated to 70 °C. The reaction was continued for 3 hours. At the end of 3 hours the polymer was precipitated in methanol and it was dried at 40 °C vacuum. A summary representation of all syntheses has been given in figure 1.

RESULTS AND DISCUSSION

In this study, a synthetic copolymer synthesis between vinyl-functionalized porphyrin (TPP-MAO) and styrene has been performed. Structures of synthesized compounds were illuminated by FT-IR and NMR spectroscopy. Thermal behaviors were observed by TG and DTG methods. UV-Visible analysis was performed spectroscopically and the molecular weight of the copolymer (Poly(st-co-TPP-MAO)) was determined with GPC.

Thin Layer Chromatography (TLC) studies were performed using Merck TLC Aluminum sheets 20x20 cm silica gel 60 F254. As a result of the

TLC studies (table 1), suitable column systems were identified and purification procedures were carried out. The yields of the porphyrin compounds synthesized in the study were calculated as in the table 2. In all of the synthesis steps of these compounds, column chromatography was used for purification. A column with a radius of 2.5 cm and a length of 1.20 m was selected for column chromatography. Due to the problem of solubility of porphyrin compounds, these compounds were given in portions to the column. It is thought that Both the size of the column and the fractionation of the compounds into the column affect the % yield.

Infrared spectra were recorded on a Perkin Elmer Spectrum 100 IR spectrometer using KBr pellet technique. Analyzes were made between 450-4000 cm^{-1} . The FTIR spectra of the TPP, TPP- NO_2 , TPP- NH_2 and TPP-MAO were shown figure 2. According to this figure, the most characteristic peaks of the TPP (figure 2-a); secondary amine in the ring stretching at 3316 cm^{-1} , C-H phenyl stretch at 3053 cm^{-1} , C-H stretch at 2954-2852 cm^{-1} , in the ring C = C and C = N at 1354, 1556 and 1472 cm^{-1} , = C-N- at 1356 cm^{-1} , β -pyrrole C-H on the pyrrole ring at 965 cm^{-1} and the pyrrole ring at 798 cm^{-1} . The FTIR spectrum of the TPP- NO_2 compound is as figure 2-b. The most characteristic peaks of this compound are; secondary amine stretch in the ring at 3317 cm^{-1} , C-H phenyl stretch at 3053 cm^{-1} , C-H stretch at 2954-2852 cm^{-1} , C = C and C = N in the rings at 1594 and 1573 cm^{-1} , NO_2 1517 cm^{-1} , = C-N-, at 1346 cm^{-1} , β -pyrrole C-H on the pyrrole ring at 966 cm^{-1} and pyrrole ring at 799 cm^{-1} . The FTIR spectrum of the TPP- NH_2 compound is as figure 2-c. The most characteristic peaks of this

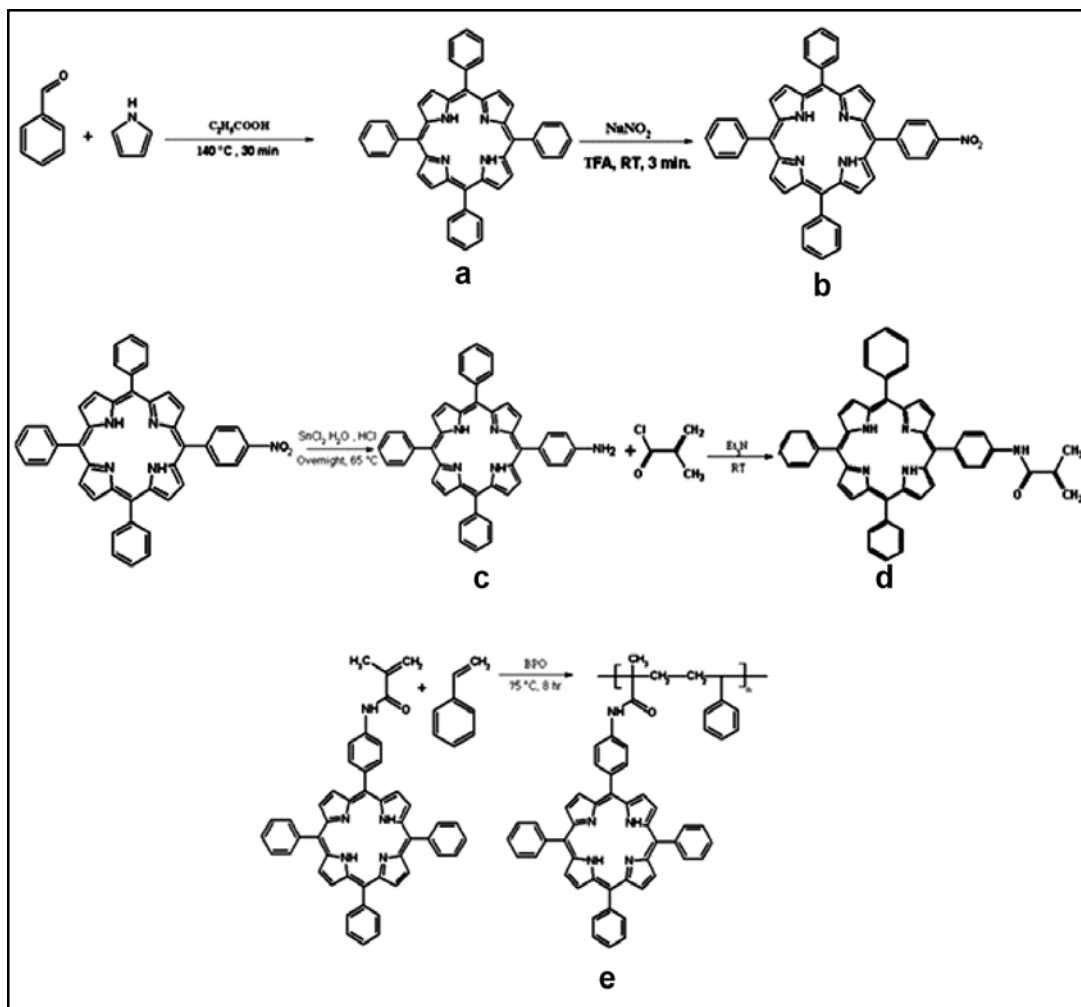


Fig. 1. Synthesis of TPP (a), TPP-NO₂ (b), TPP-NH₂ (c), TPP-MAO (d) and Poly(st-co-TPP-MAO) (e)

TABLE 1. Data of thin layer chromatography

Compound	Solvent System	R _f Value
TPP	DCM	0,97
TPP-NO ₂	DCM:Hexane1:1	0,45
TPP-NH ₂	DCM	0,41
TPP-MAO	DCM:Hexane5:1	0,79

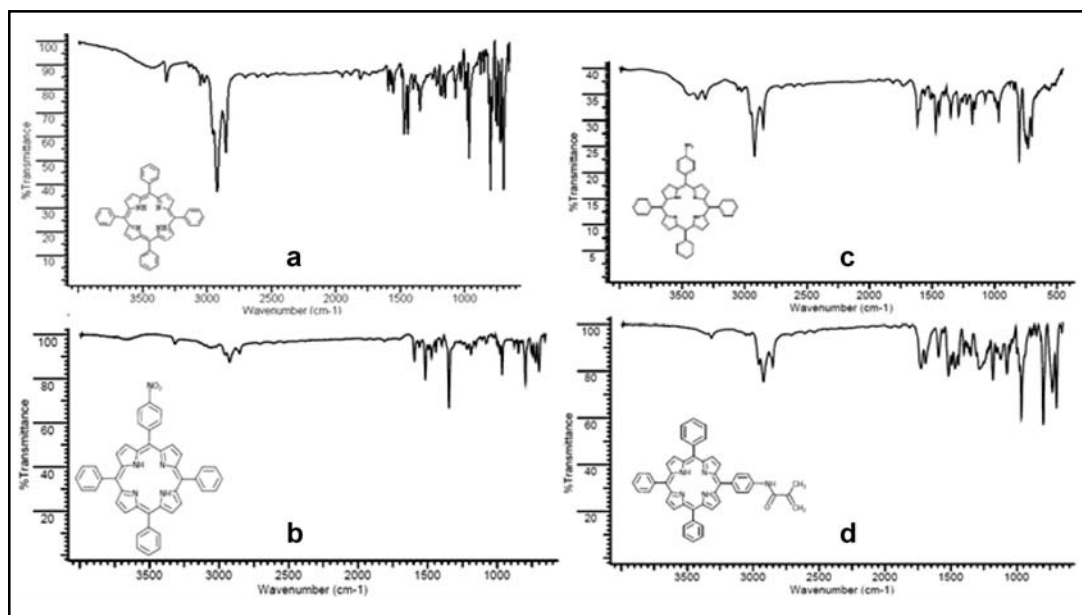
TABLE 2. Closed formulas and physical properties of synthesized compounds

Compound	Closed Formulas	Molecular Weight	Color	Yield %
TPP	$C_{44}H_{30}N_4$	614,74 g/mol	Purple	13%
TPP-NO ₂	$C_{44}H_{29}N_5O_2$	659,73 g/mol	Brownish Purple	58%
TPP-NH ₂	$C_{44}H_{31}N_5$	629,75 g/mol	Purple	55%
TPP-MAO	$C_{48}H_{35}N_5O$	697,82 g/mol	Bright Purple	80%

compound are; Peaks of the NH₂ group at 3446 and 3376 cm⁻¹, secondary amine in the ring stretch at 3316 cm⁻¹, C-H phenyl stretch at 3053 cm⁻¹, C-H stretch at 2954-2852 cm⁻¹, C = C and C = N at 1617 cm⁻¹, NH₂ bending at 1507 cm⁻¹, C-N bending at 1286 and 1179 cm⁻¹, β-pyrrole C-H at 965 cm⁻¹ and pyrrole peaks at 802 cm⁻¹. After reduction of TPP-NO₂ to TPP-NH₂, NH₂ bending at 1507 cm⁻¹ and C-N peaks at 1286 and 1179 cm⁻¹ were

observed in the spectrum of TPP-NH₂. The NO₂ peak at 1517 cm⁻¹ was disappear.

The FTIR spectrum of the TPP-MAO compound is as figure 2-d. The most characteristic peaks of this compound are; Peaks of secondary amine in the ring stretch and secondary amine on methacryloyl group at 3317 cm⁻¹, C-H phenyl stretch at 3055 cm⁻¹, C-H stretch at 2956-2851 cm⁻¹, C=O at 1726 cm⁻¹, C = C

Fig. 2. FT-IR Spectra of TPP (a), TPP-NO₂ (b), TPP-NH₂ (c), TPP-MAO (d)

and C = N at 1617 cm^{-1} , C-N bending at 1287 and 1182 cm^{-1} , β -pyrrole C-H at 965 cm^{-1} and pyrrole peaks at 799 cm^{-1} . The C = O peak, one of the characteristic peaks of the TPP-MAO compound, was observed at 1730 cm^{-1} . Figure 3 shows the FTIR spectrum of the Poly-St-co-(TPP-MAO). The spectra of Poly (St-co-TPP-MAO) and TPP-MAO compounds show similar properties.

$^1\text{H-NMR}$ spectrum of the TPP compound is given figure 4-a. According to this spectrum; Peaks of -NH protons in the porphyrin ring at -2.74 ppm are observed. These peaks are the most characteristic peaks for the porphyrin skeleton. These peaks are the most characteristic peaks for the porphyrin skeleton.

The protons on the pyrrole ring are observed at about 8.8 ppm . Peaks belonging to the benzene ring on the porphyrin ring are observed between $7.7\text{-}8.2\text{ ppm}$. Figure 4-b shows the $^1\text{H-NMR}$ spectrum of the TPP- NO_2 compound. According to this spectrum, the -NH protons in the porphyrin ring are observed at -2.74 ppm , and the protons on the pyrrole and benzene ring are observed between $7.7\text{-}8.9\text{ ppm}$. The $^1\text{H-NMR}$ spectrum of the TPP- NH_2 compound is given in figure 5-a. According to this spectrum, the -NH protons in the porphyrin ring are observed at -2.74 ppm , the $-\text{NH}_2$ protons at 4.02 ppm and the protons over the pyrrole and benzene ring at $7.0\text{-}8.9\text{ ppm}$. Figure 5-b shows the $^1\text{H-NMR}$ spectrum of TPP-MAO compound.

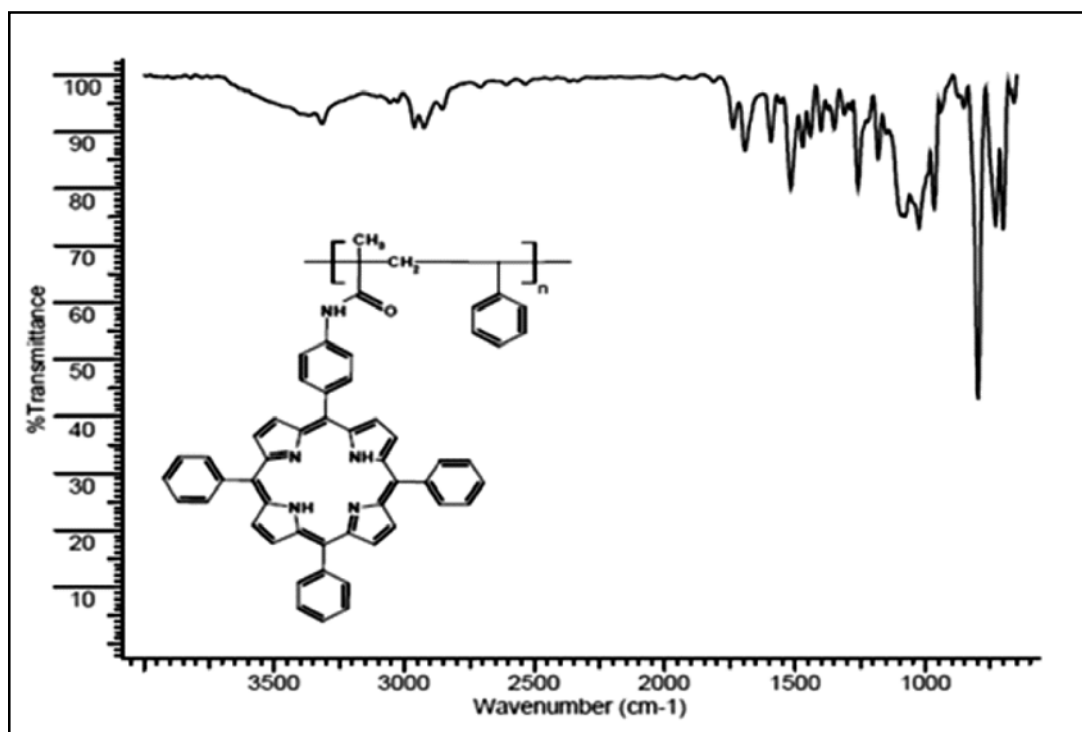


Fig. 3. FT-IR Spectrum of Poly(st-co-TPP-MAO)

According to this spectrum, the -NH protons in the porphyrin ring are observed at -2.74 ppm and the protons over the pyrrole and benzene ring at 7.0-8.9 ppm. It has been observed that the peaks of the NH₂ protons have disappeared as expected. However, the expected C = C protons of 5-6 ppm were not observed. Also, peaks between 1-2.5 ppm are not expected.

The H¹-NMR spectrum of Poly-St-co-(TPP-MAO) compound is in figure 6. According to this spectrum, the -NH protons in the porphyrin ring are observed at -2.74 ppm, aliphatic protons over the polymer backbone at between 1 and 3 ppm and aromatic protons over the polymer backbone at between 7 and 9 ppm.

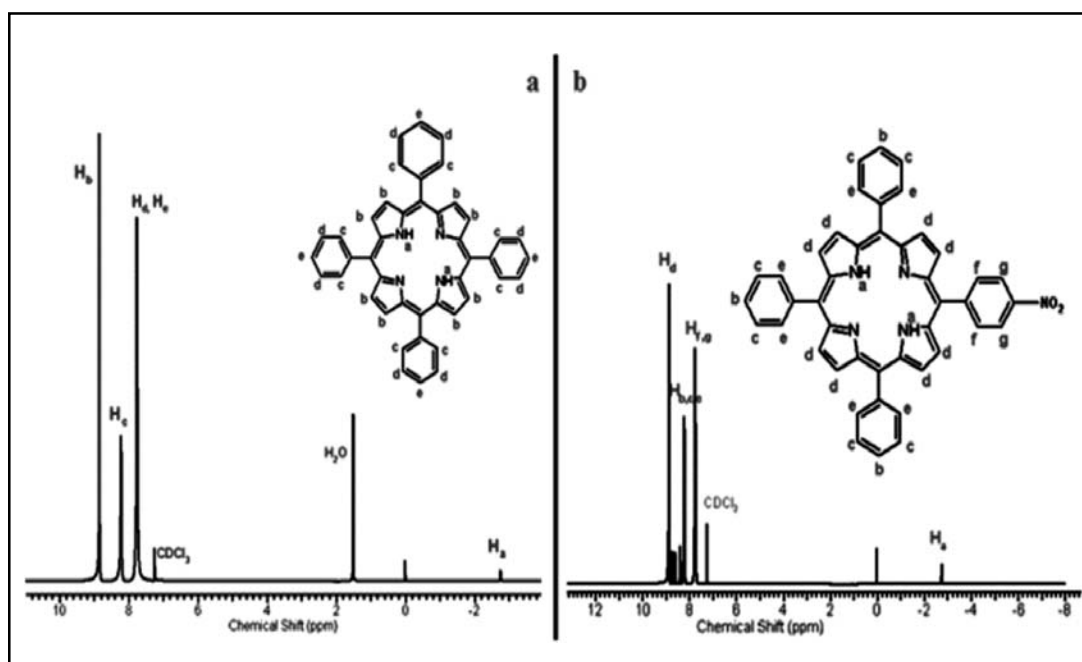


Fig. 4. ¹H-NMR Spectra of TPP (a) and TPP-NO₂ (b)

The thermograms were recorded by heating the samples at a temperature range of 25 to 600 °C under nitrogen atmosphere (10 °C /min). The TG and DTG curves of TPP-MAO, PS and Poly(St-co-TPP-MAO) compounds have been showed at figure 7. As PS is expected, it has degrade at 400-450 °C in one step. It is observed in the DTG curves that both of them are five-decomposition step. The degradation steps of

the TPP-MAO compound are 80-120 °C, 200-250 °C, 250-300 °C and 420-470 °C, respectively. The degradation between 80-120 °C can be from organic solvents or water. Decompositon between 200-250 °C is thought to be caused by the degradation of the pyrrole rings. It is considered that the decomposition between 420-470 °C is caused by the decomposition of benzene rings in the

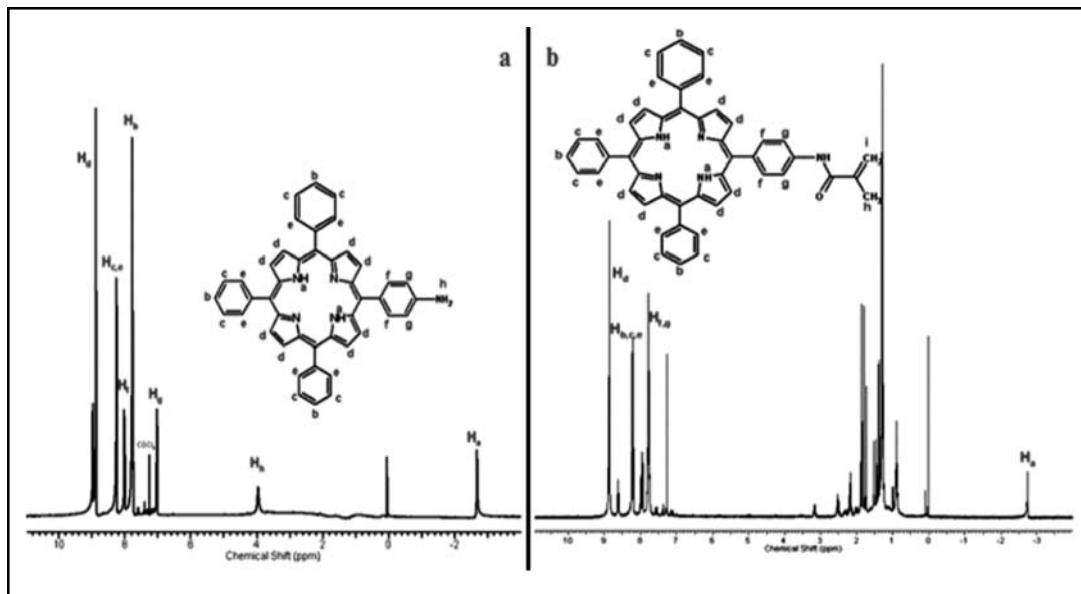


Fig. 5. ¹H-NMR Spectra of TPP-NH₂ (a) and TPP-MAO (b)

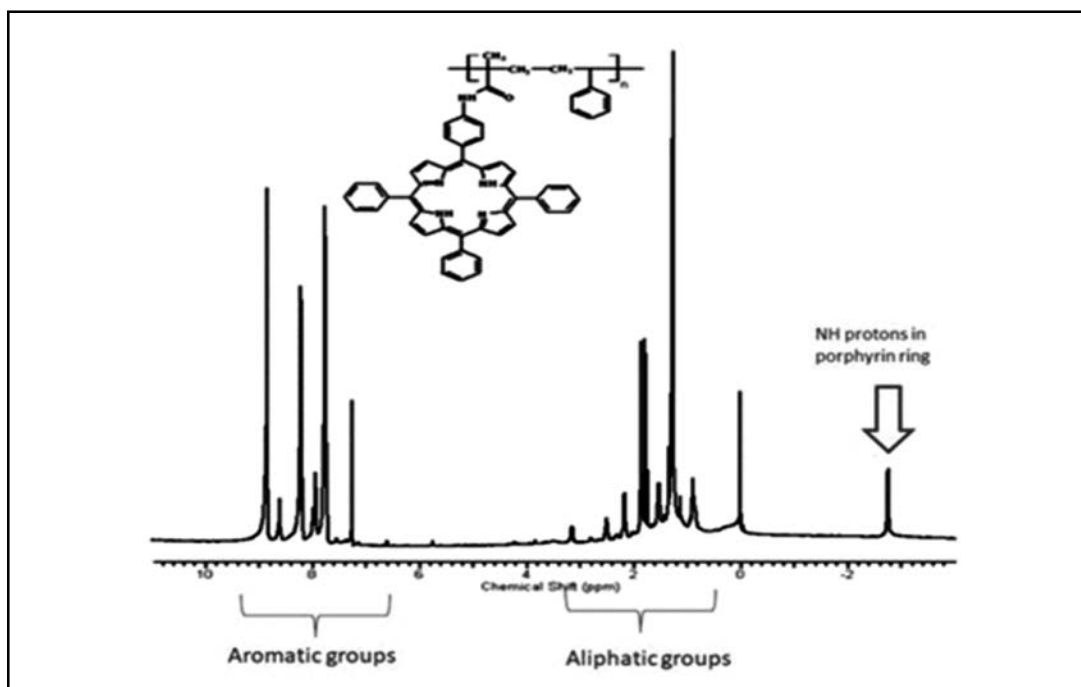


Fig. 6. ¹H-NMR Spectrum of Poly(st-co-TPP-MAO)

structure. The degradation steps of Poly-St-co-(TPP-MAO) compound are 200-250 °C, 300-350 °C and 440-460 °C, respectively. TPP-MAO and Poly(St-co-TPP-MAO) have similar

TG curves. According to previous studies, Poly(St-co-TPP-MAO) is thought to resemble the oligomer structure more^[25]. Also, Figure 7-c shows a significant increase in the remaining

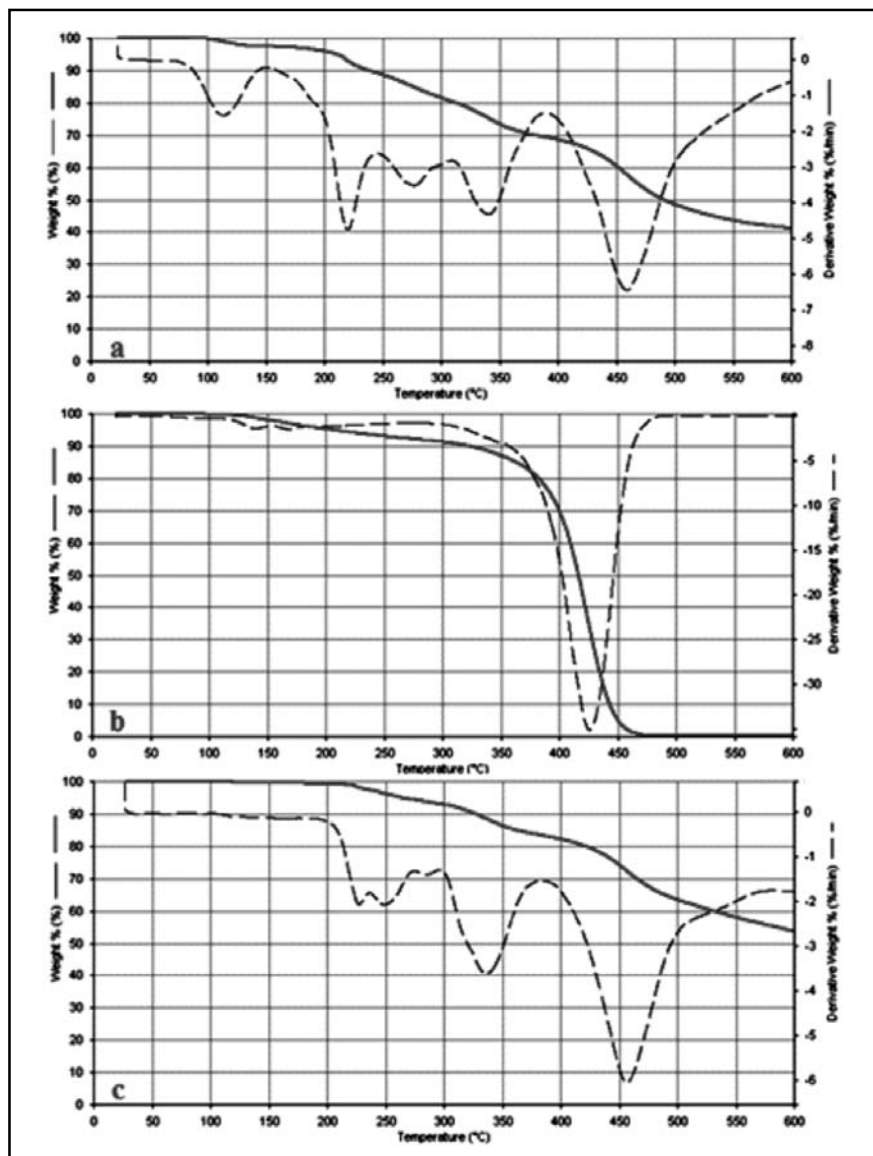


Fig. 7. TG and DTA Curves of TPP-MAO (a), PS (b) and Poly(st-co-TPP-MAO) (c)

mass (55%) of the copolymer (Poly(St-co-TPP-MAO)) at 600 °C^[26,27]. The remaining mass of polystyrene at the same temperature is 0%, the remaining mass of the vinylic porphyrin monomer is 40%. According to the literature,^[26] the thermal stability of the synthesized porphyrin copolymer can be said to be increased.

UV-Absorption Spectra and PL spectra were taken in 1 cm quartz cuvettes with a sensitivity

of ± 2 nm. Measurements were taken after 4×10^{-6} M solutions of the synthesized compounds were prepared with dichloromethane. The UV and PL spectra of porphyrin compounds were given figure 8, 9 and 10, respectively. The absorption and wavelength (nm) values obtained of the porphyrin compounds and polymer are summarized in the table 3. In the UV spectra of the synthesized porphyrin compounds, an intense peak with λ Value of

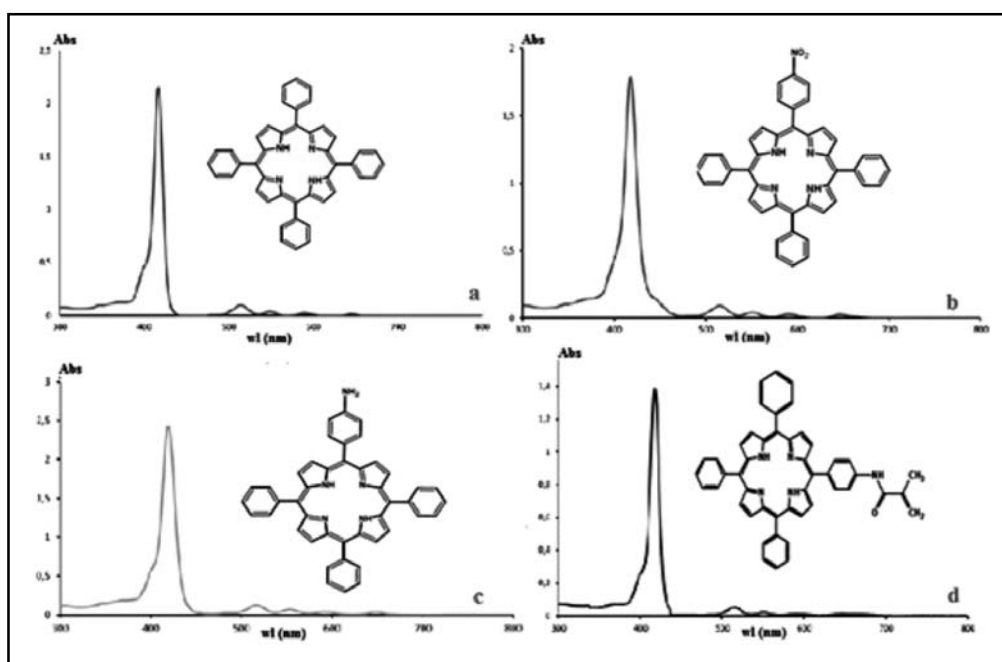


Fig. 8. UV-Visible Spectra of TPP (a), TPP-NO₂ (b), TPP-NH₂ (c), TPP-MAO (d)

about 418 nm was observed. This peak is called the 'Soret Band' and is the most characteristic peak of the porphyrin skeleton. This Soret band arises from the transition of $a_{1u}(\pi) \rightarrow e_g^*(\pi)$. In addition, low intensity four peaks between 513 and 648 nm were observed.

These are called the Q band and are the other characteristic peaks of the porphyrin skeleton and this Q bands attribute to the $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ transition. These results are consistent with previous studies^[28-29]. The different peripheral substituents did not significantly change the

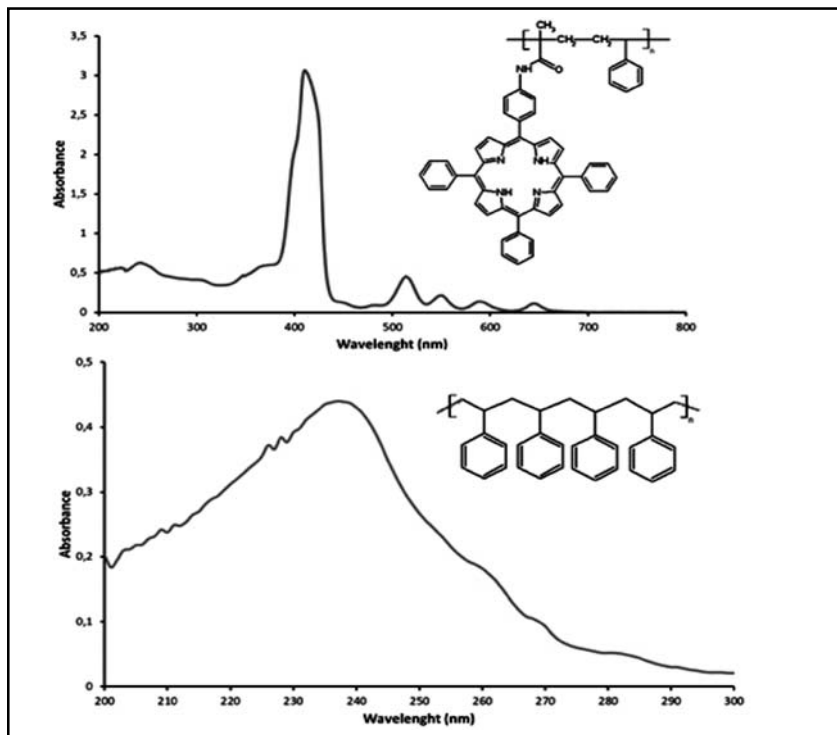


Fig. 9. UV-Visible Spectra of Poly(st-co-TPP-MAO) and PS

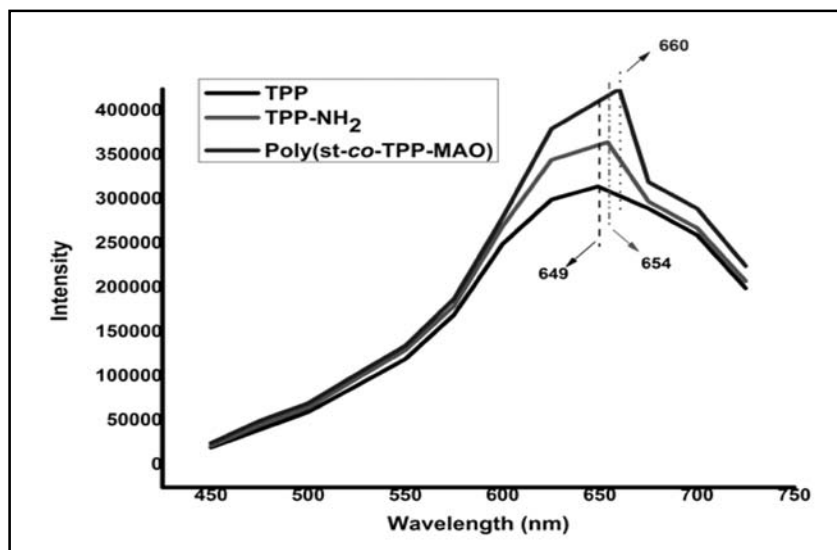


Fig. 10. Fluorescence spectra of the synthesized TPP, TPP-NH₂ and Poly(St-co-TPPMAO)

TABLE 3. UV spectra data of synthesized compounds

Compound	λ (nm)	Abs
TPP	417	2,150
	513	0960
	548	0380
	588	0270
	645	0,021
TPP-NO ₂	418	1,789
TPP-NH ₂	513	0,96
	551	0,042
	590	0,029
	646	0,027
	419	2,424
TTP-MAO	516	0,124
	553	0,070
	591	0,037
	648	0,035
	417	1,383
PS	516	0,053
	552	0,024
	590	0,016
	646	0,019
	226	0,175
Poly-St-co-(TPP-MAO)	238	0,217
	223	0,566
	242	0,628
	411	3,065
	514	0,455
	551	0,214
	589	0,139
	645	0,112

transition mode of the porphyrin molecules. It has been observed that functionalization of porphyrin compounds from meso groups (-NO₂, -NH₂) does not cause any change in UV spectra. Only 1-2 nm chemical shifts were observed in wavelength. According to the figure 9, the absorption spectrum of the copolymer shifts 6-8 nm (blue shift) at the soret band with a dramatically increase of the absorbance. Also Q band absorption values at the copolymer. In addition, the absorption values of the Q band in the copolymer also increased significantly. These absorption values have only been reached in the metal complexes of porphyrin polymers in the literature. Figure 10 shows the fluorescence spectra of the TPP, TPP-NH₂ and Poly(St-co-TPPMAO). According to this figure, the fluorescence intensity of the synthesized Poly(St-co-TPPMAO) is higher than the TPP and TPP-NH₂. It has been observed that 11 nm chemical shift between TPP and polymer is seen.

CONCLUSIONS

We have shown that copolymerization of 5-[4-(methacryloylamino)phenyl]-10,15,20-triphenylporphyrin with styrene. All synthesis were supported by characterization studies. FT-IR, ¹H-NMR, TG-DTG, UV-Visible and GPC techniques were used for identification. According to the GPC results, the number-average molecular weight and the weight-average molecular weight were found 13000 and 18000 g/mol, respectively. After functionalization of porphyrin with -NO₂, -NH₂, chemical shift in wavelength is not been significant but when the UV spectrum of the styrene copolymer with vinyl-functional

porphyrin monomer was examined, a blue shift of 6-8 nm was observed in the soret band. In addition, according to many porphyrin polymers in the literature, the absorption intensity of the soret and Q band belong to copolymer synthesized in this study have been quite high. Thermal stability of the copolymer is higher than according to metal complex non-containing porphyrin polymers. Moreover, this copolymer shows high luminescence property.

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