SYNTHESIS AND OPTICAL PROPERTIES OF HYPERBRANCHED DONOR - ACCEPTOR CONJUGATED POLYMERS BASED ON PHENOXAZINE, BENZO[C][1,2,5] THIADIAZOLE AND TRIPHENYLAMINE

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1. INTRODUCTION

In recent years, hyperbranched conjugated polymers have attracted much attention for their applications in many organic electronic application such as the efficient hole/electron transport layer in organic solar cells (OSCs), organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), electrochromic devices (EC) due to their good solubility, thermal stability, large area processing.[1-5] Among the building units for synthesis of conjugated polymers, triphenylamine (TPA) and its derivatives have been extensively used in conjugated polymer for hole-transporting polymer layer in photo-electronic application including OSCs, OLEDs, EC devices.[6-10] Yang Liu *et. al* reported the synthesis and photovoltaic characteristics of copolymers containing poly(phenylenevinylene) and triphenylamine moieties with molecular weights M_n = 6,800 g/mol.[11] Jinqing Qu *et. al* also reported the synthesis of hyperbanched copolymers via Sonogashira coupling polycondensation of *N*-octadecyl- and *N*-octyl-3,6-diethynylcarbazoles with tris(4-iodophenyl)amine and 1,3,5-tribromobenzene. The obtained polymers have a molecular weights (M_n) in the range of 3.500 - 21.000 g/mol and exhibited that the polymers were electronically redox-active which can be applied for tunable light-emitting materials based on carbazole-containing polymers.[12] On the other hand, the conjugated polymers based on benzo[c][1,2,5]thiadiazole (BTD), phenoxazine (POZ) also exhibited the narrow band-gap and red-shift absorption and the in the oxidized state owing to the electron-rich N atom in their structure.[13,14] Marri Anil Reddy *et. al* reported the synthesis and fabrication of organic solar cells based on based on phenothiazine and phenoxazine moieties with PCE up to 6%.[12,15-17] Interestingly, Haining Tian *et. al* has reported the small molecular of phenoxazinechromophores based on triphenylamine with phenoxazine containing the vinyl and CN end group that used in organic dye-sensitized solar cells with PCE of 7.7%.[14] Jenekhe's group has fabricated the OFETs based on the alternating phenoxazine-fluorene copolymer (POF2) as a p-channel semiconductor with a hole mobility of 3 x 10^{-4} $cm^2/(V\ s)$.[18] Licheng Sun and his coworkers have synthesized two novel Acceptor-Donor-Acceptor (A-D-A) structured small molecular (SM-) materials containing an electron-rich phenothiazine with the electron-deficient benzothiazole (BTZ) as linker to obtain the hole transport layers materials for OSCs of 7.44%.[19] More recently, Jong Hyuk Bae *et. al* synthesized the phenoxazine dyes with a hexyloxy chain and furan moiety and used in dye-sensitized solar cells that showed the best conversion efficiency of 6.34%.[20] It is worth noting that a phenoxazine moiety includes electron-rich oxygen and nitrogen atoms in a heterocyclic ring and also displays high electron-donating capability therefore it also has suitable as building moieties for a promising organic solar cells application.

In this study, for efficient organic solar cells performance, an alkyl side chain was introduced to the phenoxazine nitrogen atom that would increase the solubility of obtained conjugated copolymers. Following, the hyperbranched donor-acceptor conjugated polymers containing TPA, BTD and POZ moieties have been synthesized and characterized via direct heteroarylation polymerization. The structures of polymers were investigated by FT-IR, ^{1}H-NMR, GPC and XRD spectroscopies. In addition, the optical properties of polymers were characterized via photoluminescence (PL) and UV-vis spectroscopies.

2. EXPERIMENTAL

2.1. Materials

10H-phenoxazine (98%) was purchased from Ark Pharm (USA). Triphenylamine, benzo [c] [1, 2, 5] thiadiazole, tetrahydrofuran (99.9%) and N-bromosuccinimide were purchased from Acros Organics. 2-ethylhexyl bromide (95%), palladium(II) acetate ($Pd(OAc)_2$, 98%), tricyclohexylphosphine tetrafluoroborate ($PCy_3{\cdot}HBF_4$, 97%), 3,3′dibromo-2,2′bithiophene and pivalic acid (PivOH, 99%) were purchased from Sigma-Aldrich/Kantochem and used as received. Potassium carbonate (K_2CO_3, 99%), sodium chloride (NaCl, 99%) were purchased from Acros/Merck. Chloroform (CHCl3, 99.5%) and dimethylacetamide (DMAc, 99%) were purchased from Fisher/Acros and dried using molecular sieves under N_2. Dichloromethane (99.8%), *n*-hexane (99%), methanol (99.8%) and ethyl acetate (99%) were purchased from Fisher/Acros and used as received.

2.2. Characterization methods

^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with TMS as standard, on a Bruker Avance 500 MHz. Fourier transform infrared (FT-IR) spectra, collected as the average of 264 scans with a resolution of 4 cm^{-1}, were recorded from KBr disk on the FT-IR Bruker Tensor 27. Gel permeation chromatography (GPC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with a RI detector, with tetrahydrofuran as the eluent (flow rate: 1.0 ml/min). Molecular weight and molecular weight its distribution was calculated with reference to polystyrene standards. Elemental analyses were performed by the Dumas combustion method, using a Costech ECS 4010 Elemental Analyzer

UV-vis absorption spectra of polymers in solution and polymer thin films were measured on a ASEQ LR1 spectrometer over a wavelength range of 300-1100 nm. Fluorescence spectra were recorded on an Ocean Optics SP-2000.

Differential scanning calorimetry (DSC) measurements were carried out with a DSC 204 F1- NETZSCH instruments under nitrogen flow (heating rate 10°C.min^{-1}). Thermogravimetric analysis (TGA) measurements were performed under nitrogen flow using a STA 409 PC Instruments with a heating rate of 10°C.min^{-1} from ambient temperature to 1000°C.

2.3. Synthesis of 10-(2-ethylhexyl)-10H-phenoxazine

10H-phenoxazine (1000 mg, 5.46 mmol) was dissolved in THF (20 mL) in a 100 mL flask under nitrogen, following by stirring for several minutes. Then, the compound is cooled down to 0°C. 2-Ethylhexyl bromide (1265 mg, 6.55 mmol) and NaOt-Bu (787 mg, 8.18 mmol) were added, and the mixture was degassed via free-pump-thaw cycle three times. Then, the reaction was carried out at 65°C for 24h. After completion of the reaction, the compound was extracted with 50 mL of $CHCl_3$, washed with distilled water, dried over anhydrous K_2CO_3. The mixture evaporated to obtain the crude product, which was purified by silica column chromatography (eluent: *n*-hexane) and dried under vacuum at 50°C in 24h to obtain the compound as a dark green oil (1.08 g, $R_f = 0.7$, yield: 70%).

^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.76 (m, 2H), 6.62 (m, 6H), 3.41 (d, 2H), 1.88 (s, 1H), 1.36 (m, 8H), 0.92 (m, 6H). Analysis calculated for $C_{26}H_{29}NOS$: C, 77.38; H, 7.24; N, 3.47; O, 3.96; S, 7.95. Found: C, 77.82, H, 7.18; N, 3.57; O, 3.85; S, 7.58.

2.4. Synthesis of tris(4-bromophenyl)amine

Triphenylamine (200 mg, 0.82 mmol) and *N*-bromosuccinimide (523 mg, 2.93 mmol) were added to anhydrous THF (10 mL) at 0°C under nitrogen. Then, the compound was stirred at room temperature for 24h. After that, the reactant was extracted by chloroform, washed with NaCl solution and distilled water several times. After solvent had been removed by rotary evaporation, the crude product was purified by silica gel chromatography with *n*-hexane as eluent. A yield of 330 mg of tris(4-bromophenyl)amine ($R_f = 0.75$, yield 84%) was obtain as a white solid.

^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.25 (m, 6H), 6.95 (m, 6H). Analysis calculated for C18H12Br3N: C, 44.85; H, 2.51; Br, 49.73; N, 2.91. Found: C, 45.17; H, 2.71; Br, 49.18; N, 2.94

2.5. Synthesis of hyperbranched polymer based on phenoxazine and triphenylamine moieties (PEHHPTPA) (P1)

10-(2-ethylhexyl)-10H-phenoxazine (100 mg, 0.34 mmol) and tris(4-bromophenyl) amine (109 mg, 0.23 mg) were dissolved in 10 mL DMAc in a 100 mL flask under nitrogen. Then, $Pd(OAc)_2$ (3.80 mg, 0.05 mmol), $PCy_3.HBF_4$ (12.46 mg, 0.10 mmol), PivOH (34.57 mg, 1.00 mmol) and K_2CO_3 (140.35 mg, 3.00 mmol) were added into the flask, the solution was heated at 110°C and stirred for 24h. Then, the mixture was cooled down to room temperature and the polymer was precipitated by addition of 50 ml of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, *n*-hexane, and chloroform. Next, the resulting solution from the chloroform fraction was precipitated in 50 ml of methanol. The polymer was recovered as a greyish solid sample by filtration and dried under vacuum at 50°C for 24h to obtain the final product P1 (68 mg, yield 56%).

^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.5-8.5 (m, 10H), 3.49 (s, 1H), 0.88-1.63 (m, 15H). FT-IR (cm^{-1}): 3045, 2935, 1585, 1491, 1274, 1087, 1014, 812, 720, 621. GPC: M_n = 11.000 g/mol. Đ (M_w/M_n) = 2.27.

2.6. Synthesis of hyperbranched polymer based on phenoxazine, triphenylamine and benzo [c]-1,2,5-thiadiazole moieties (PEHHPTPABT) (P2)

10-(2-ethylhexyl)-10H-phenoxazine (100 mg, 0.34 mmol), tris(4-bromophenyl) amine (109 mg, 0.23 mg) and 4,7-dibromobenzo [c]-1,2,5-thiadiazole (65 mg, 0.14 mmol) were dissolved in 10 mL DMAc in a 100 mL flask under nitrogen. Then, $Pd(OAc)_2$ (3.80 mg, 0.05 mmol), $PCy_3.HBF_4$ (12.46 mg, 0.10 mmol), PivOH (34.57 mg, 1.00 mmol) and K_2CO_3 (140.35 mg, 3.00 mmol) were added into the flask, the solution was heated at 110°C and stirred for 24h. Then, the mixture was cooled down to room temperature, and the polymer was precipitated by addition of 50 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, *n*-hexane, and chloroform. Next, the resulting solution from the chloroform fraction was precipitated in 50 mL of cold methanol. The polymer was recovered as a dark brown solid by filtration and dried under vacuum at 50°C for 24h to obtain the final product P2 (68 mg, yield 53%).

^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.10 (m, 2H), 6.5-7.5 (m, 10H), 3.66 (s, 1H), 0.88-2.14 (m, 15H). FT-IR (cm^{-1}): 3062, 2850, 1585, 1473, 1317, 1213, 1150, 1085, 824, 752, 628. GPC: M_n = 8.000 g/mol. Đ (M_w/M_n) = 2.31.

3. RESULTS AND DISCUSSION

3.1. Synthesis of hyperbranched conjugated polymers

The polymer P1 and P2 was synthesized via direct arylation polycondensation which carried out by catalyst system of $Pd(OAc)_2$ and $PCy_3.HBF_4$ as ligand. The reaction was performed in DMAc solvent at 100°C. In the case of P1, at the early stage of the reaction, the color of mixture was light yellow then changed to the green after 2 h and turned to dark green after 24h. After reaction finished, polymer P1 was dissolved in $CHCl_3$ and filtrated via a celite layer to eliminate the Pd catalyst, and then the polymers were obtained by precipitation in cold methanol. The yields of polymerizations were obtained about 56%. In the case of P2, the color of mixture also was light yellow then change to dark brown after 24h. The P2 was also obtained by precipitation in cold methanol, filtrated and dried in oven. The yield of polymerizations was obtained about 53%. The synthesis route of polymers P1 and P2 was described in Scheme 1. The hyperbranched D-A conjugated polymer P1 and P2 exhibited the good solubility in common solvents such as chlorofoem, THF, dichloromethane and toluene. The polymers P1 and P2 were characterized via the gel permeation chromatography (GPC) to determine the relative number molecular weights of polymers. P1 exhibited the average molecular weight of 11.000 g/mol with polydisperity index (Đ) of 2.27 while P2 exhibited the molecular weight of 8.000 g/mol with Đ of 2.31. It is noted that the molecular weight of P1 is much higher than P2 although in the same polymerization condition. This result can be expained that the P2 which contains benzo[c][1,2,5]thiadiazole moieties that cause the rigid of polymer structure of P2 resulting the decreasing of polymerization degree. In addition, the polymer P2 has a largely insoluble part in the THF solvent that contributed to high molecular weight fraction of polymers. Figure 1 shows the GPC traces of P1 and P2 in THF.

The structures of P1 and P2 were characterized by FTIR and ^{1}H NMR spectroscopies. The FTIR spectra of P1 and P2 displayed the bands between 2850 and 3062 cm^{-1} due to C=C stretching of aromatic structure. The peaks at 1585 cm^{-1} and 1491/1473 cm^{-1} are ascribed to the aromatic C=C stretching and aromatic C-H deformation vibrations, respectively. In addition, the peaks at 1317 cm^{-1} and 1274 cm^{-1} are ascribed to the C-N stretching of triphenylamine units. The bands at 1087 cm^{-1} and 1150 cm^{-1} indicates the presence of C-O stretching vibration. The bands between 621 cm^{-1} and 752 cm^{-1} are ascribed to the long chains methyl rocking vibration.

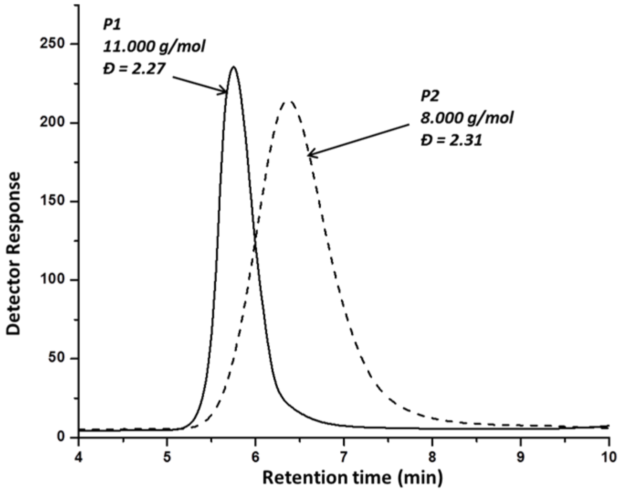
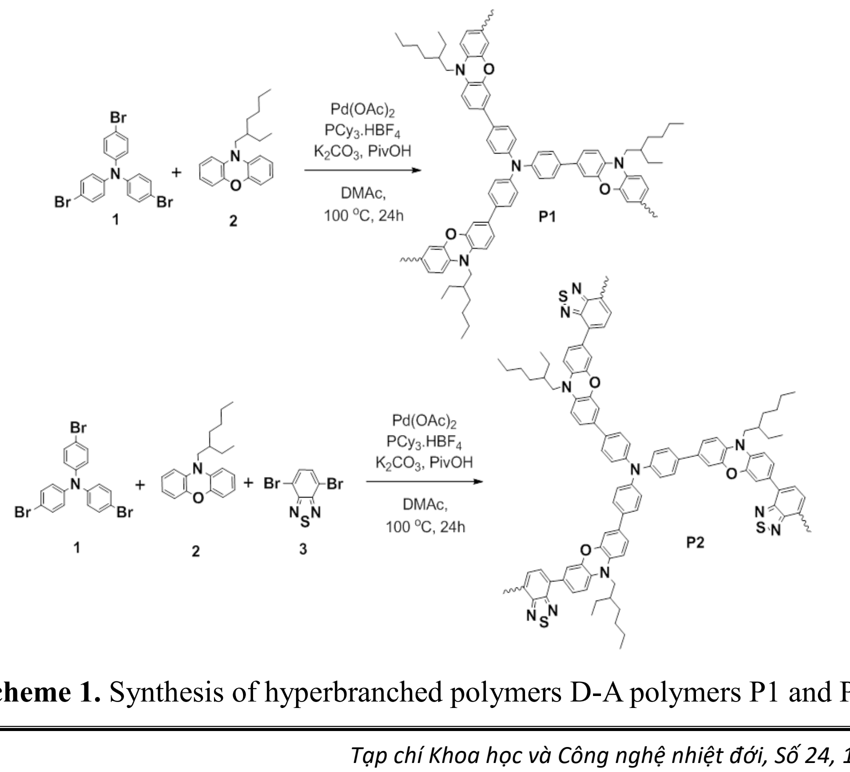


Figure 1. The GPC trace of the hyperbranched conjugated polymers P1 and P2



Scheme 1. Synthesis of hyperbranched polymers D-A polymers P1 and P2

The monomers and polymers structures were characterized by ^{1}H NMR. Figure 2 exhibited the ^{1}H NMR spectrum of monomer EHHP, the peaks from 6.76−6.52 ppm that attributed to the aromatic region and the peak at 3.41 ppm and from 1.88-0.92 ppm ascribed to aliphatic region. The ^{1}H NMR spectra of both polymer P1 and P2 showed all characteristic peaks of the aromatic and aliphatic region. In the ^{1}H NMR spectrum of polymer P1, the peaks from 8.0 to 6.5 ppm are corresponding to aromatic rings in polymer structure including of triphenyl amine and phenoloxazine ring. The peak at 3.49 ppm and the peaks from 2.0 to 0.5 ppm corresponded to alkyl side chain. In the case of polymer P2, the aromatic region was observed from 8.5 to 6.5 ppm which contributed to signals of benzo [c]-1,2,5-thiadiazole, triphenyl amine and phenoxazine moieties. In addition, the signal at 3.66 ppm and the broad peak at 2.5-0.5 ppm exhibited for the alkyl side chain. These results indicated that the new conjugated polymers were successfully synthesized via direct heteroarylation polymerization. In addition, the solubility of polymers can be perform in several solvents such as chroloform, dichromethane, toluene and tetrahydrofurane.

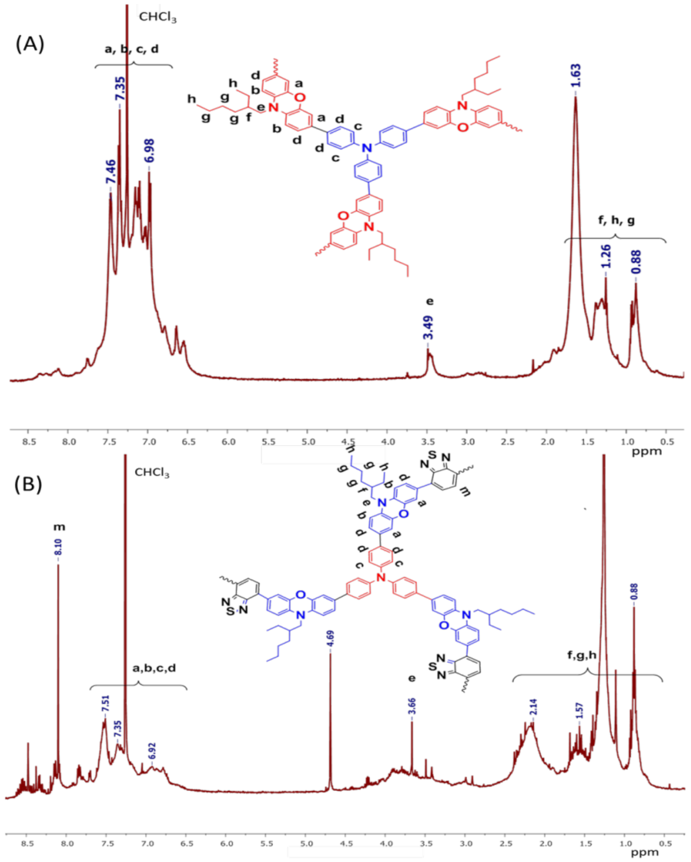


Figure 2. ^{1} H NMR of the hyperbranched conjugated polymer P1 (A) and P2 (B)

3.2. Optical properties of the hyperbranched conjugated polymers

The absorption properties of these hyperbranched conjugated polymers were investigated by UV-Vis spectroscopy in THF solvent and in solid state film. In solution, polymer P1 exhibited the maximum absorption peak at 425 nm while polymer P2 presented the maximum absorption peak at 430 nm. In the case of solid state film, the polymer P1 exhited the maximum absorption peak at 425 nm and onset absorption at 475 nm that corresponding to the optical band gaps (E_g^{opt}) of 2.5 eV. The polymer P2 exhibited the maximum absorption peak at 450 nm and onset absorption at 640 nm in solid state film that corresponding to the optical band gaps (E_g^{opt}) of 1.93 eV. The onset absorption of P2 is much higher than those P1 can be explained by the cooperation of thiadiazole units which referred to strongly acceptor moieties. The UV-Vis absorption of hyperbracnhed conjugated polymers P1 and P2 have ascribled in Figure 3.

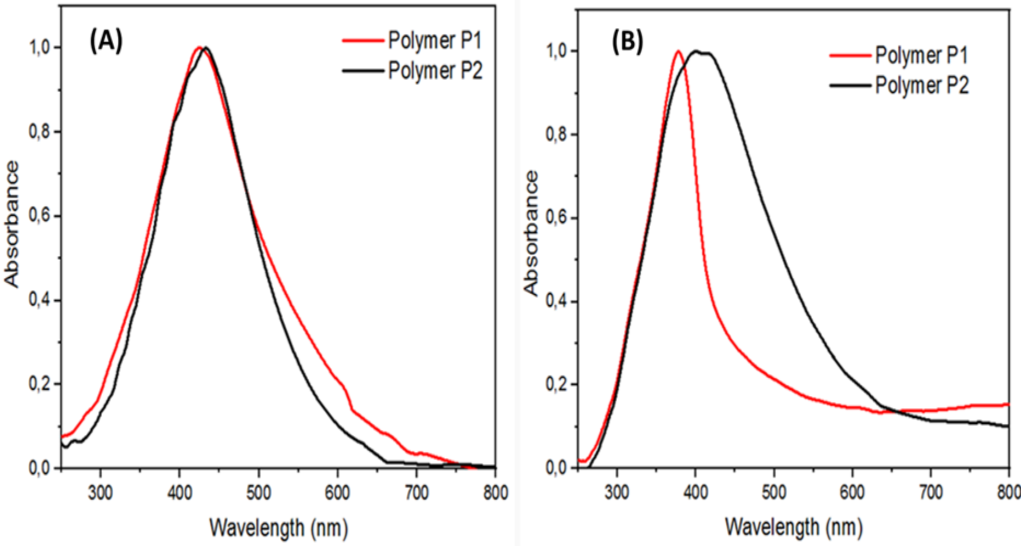


Figure 3. UV-vis absorption spectra of polymers P1 and P2 in THF solution (A) and in solid state film (B)

The hyperbranched conjugated polymers in solutions were investigated by the photoluminiscent (PL) spectra in Fig. 4 that excited at the absoption mamima. In chlorobenzene (CB), polymer P1 displayed doublet emission peaks at 470 nm and 538 nm (Fig. 5A) whereas it exhibited doublet peaks at 470 nm and 610 nm upon excitation at 425 nm (Fig. 5B). Polymer P2 also displayed doublet emission peak at 470 nm, 538 nm (Fig. 5A) in chlorobenzen and doublet emission peaks at 470 nm, 590 nm in THF (Fig. 5B).

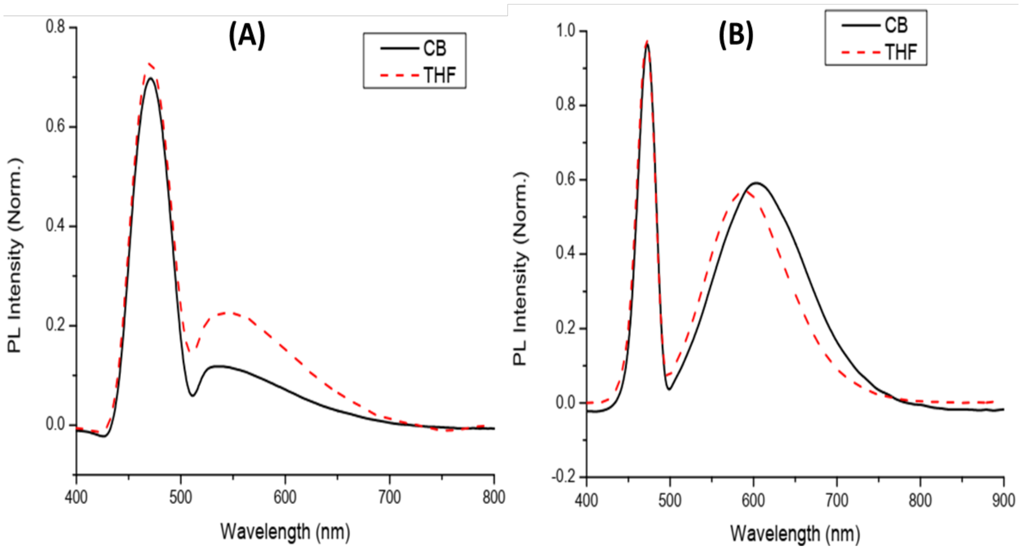


Figure 4. PL spectra of the hyperbranched conjugated polymers P1 and P2 in CB (A) and in THF (B).

The thermal properties of polymer P1 and P2 were investigated by thermogravimetric analysis (TGA). TGA under nitrogen flow was used to evaluate the thermal stability of the purified hyperbranched conjugated polymers in the range from room temperature to 800ºC. Both polymers P1 and P2 showed the thermal threshold decomposition temperature (5% weight loss) around 270ºC (see Fig. 5) and a loss of about 40% wt% at 500ºC. These results suggested that the polymer P1 and P2 have a good thermal stability which could be used in high temperature application.

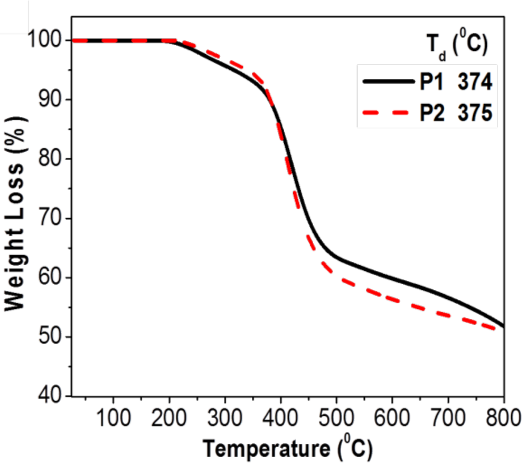


Figure 5. TGA curves of spectra of P1 and P2 with heating rate of 10ºC.min^{-1} under nitrogen atmosphere

4. CONCLUSIONS

In conclusion, the novel hyperbranched conjugated polymers have based on phenoxazine, benzo[c] [1,2,5] thiadiazole and triphenyl amine have been synthesized successfully via direct heteroarylation polymerization in the yield of 53-56%. The conjugated polymers containing the donor- acceptor units and exhibited the good solubility in common solvents that led to processable of thin film component in the electronic devices. The polymers also exhibited the thermal stability up to 350ºC. In addition, the hyperbranched polymers P1 and P2 showed the band gap energy levels of 2.5 eV and 1.93 eV, respectively which are ponential materials for organic solar cell application.

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SUMMARY

SYNTHESIS AND OPTICAL PROPERTIES OF HYPERBRANCHED DONOR - ACCEPTOR CONJUGATED POLYMERS BASED ON PHENOXAZINE, BENZO[C][1,2,5] THIADIAZOLE AND TRIPHENYLAMINE

The novel hyperbranched conjugated polymers containing phenoxazine, triphenylamine and benzo[c] [1,2,5] thiadiazole moieties were successfully synthesized via the direct (hetero) arylation polymerization method. The obtained polymers were characterized via ^{1}H NMR, GPC and FTIR to determine the chemical structure of polymers. In addition, the optical properties of polymers were investigated by UV-vis spectroscopies and fluorescent spectroscopies. The band gap of polymers were estimated about 1.93 to 2.5 eV due to the optical onset absorption of polymers. Moreover, the resulted conjugated polymers exhibited the thermal stability up to 350^{o}C that are suitable for organic solar cells application.

Keywords: *Hyperbranched conjugated polymers, phenoxazine, triphenylamine, benzo[c] [1,2,5] thiadiazole, direct (hetero)arylation polymerization.*

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