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SYNTHESIS OF BRANCHED CONJUGATED COPOLYMERS BASED ON TRIPHENYLAMINE AND 3-HEXYLTHIOPHENE UNITS

Nguyen Trung Thanh¹, Nguyen Thu Anh³, Nguyen Thi Le Thu¹, Nguyen Ha Tran^{1,2}

¹Faculty of Materials Technology, Vietnam National University, Vietnam

²Materials Technology Key Laboratory, Vietnam National University, Vietnam

³National Key Lab of Polymer and Composite Materials, Viet Nam National University, Vietnam

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ABSTRACT

The branched conjugated copolymer based on triphenylamine and 3-hexylthiophene has been synthesized via Suzuki polycondensation reaction in the presence of $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 as catalytic system. This conjugated polymer named poly(triphenylamine-branched-3-hexylthiophene) (P(TP-b-3HT)). The reaction was carried out at 100°C in 24 hours in the toluene media. The average molecular weight of obtained conjugated polymers was 24000 g/mol by gel permeation chromatography (GPC) with polydispersity index of 1.8. The structure of P(TP-b-3HT) was determined by ^1H NMR and FTIR spectrum, and optical properties of obtained conjugated polymer was characterized via UV-Vis.

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1 INTRODUCTION

The discovery of synthetic chemical materials in the field of organic electronics has created a wealth of functional conjugated organic materials, among which π -conjugated polymer semiconductors are of broad interest for applications in organic electronics and optoelectronics, including light-emitting diodes, chemo- and biosensors, field-effect transistors and photovoltaic cells (Agrawal *et al.*, 1993; McCullough *et al.*, 1993; Chen *et al.*, 1995; Bao *et al.*, 1996; Siringhaus *et al.*, 1998). Conjugated polymers containing 3-hexylthiophene, and triphenylamine in the main chain or side chain have received much attention because of their unique properties derived from those units. These materials exhibited as great organic semiconductors which can be used as hole transporting materials in thin layer electro-optical devices (Chen *et al.*, 1995; Pan *et al.*, 2007; Li *et al.*, 2007; Lim *et al.*, 2011; Chen *et al.*, 2013; Ma *et al.*, 2013). Consequently, incorporation of 3-hexylthiophene or tri-

phenylamine into hyperbranched polymers hopefully leads to the development of optically and electronically functional novel polymers (Bo *et al.*, 2003). However, hyperbranched polymers carrying 3-hexylthiophene and triphenylamine have been scarcely investigated to the best of our knowledge. As reviewed in several articles, many kinds of hyperbranched polymers have been synthesized, with control of the hyperbranched structure as well as the branching degree and molecular weight (Obson *et al.*, 1997; Bharathi *et al.*, 2000; Smet *et al.*, 2002). Conjugated polymers usually possess rigid structure. Therefore, the polymer chains have a tendency to form aggregation or crystallization in solid films and their non-solvents. Aggregation of conjugated polymer chains in thin films leads to weak emission, which considerably reduces the luminescence quantum efficiency. As a result, for light-emitting applications, aggregation or crystallization of polymer chains is unfavorable to their device performance. Hyperbranched conjugated polymers with a tree-like three-dimensional

branched structure can effectively suppress aggregation and thus are restricted from aggregate based fluorescence quenching. The development of hyperbranched polymeric and oligomeric materials based on conjugated monomers has achieved significant progress. Qu *et al.* (2007) reported the synthesis of solvent-soluble hyperbranched polymers based on carbazole and triphenylamine with number average molecular weights (M_n) ranging from 3,500 to 21,000 g/mol via polycondensation of diethynylcarbazoles with tris (4-iodophenyl) amine. Li *et al.* (2007) synthesized hyperbranched polymers with precise conjugated lengths by polycondensation of AB_2 monomers such as 1-(2-(3,5-dibromophenyl) ethynyl)-2,5-bis(dodecyloxy)-4-ethynylbenzene and 1-(2-(4-(2-(3,5-dibromophenyl) ethynyl)-2,5-bis(dodecyloxy) phenyl) ethynyl)-2,5-bis(dodecyloxy)-4-ethynylbenzene. Regarding to hyperbranched conjugated oligomers, Wang *et al.* (2010) reported a series of hyperbranched molecules with 1,3,5-triphenylbenzene as cores with different connecting groups. These molecules exhibited a good solubility and film formation ability, thermal stability as well as necessary physical and chemical properties for use in light-emitting diode (LED) devices.

Here in this paper, it is to report the synthesis of conjugated polymers of 3-hexylthiophene linked with triphenylamine units, named as P(TP-*b*-3HT) as illustrated in Figure 1. The optical and the nanostructures of the obtained hyperbranched conjugated polymers were characterized, and the effect of polymer aggregation on the optical properties was investigated.

2 MATERIALS AND METHODS

2.1 Materials

3-Hexylthiophene was purchased from TCI (Tokyo, Japan). Triphenylamine, tetrahydrofuran (99.9%) and *N*-bromosuccinimide were purchased from Acros Organics. Tetrakis (triphenylphosphine) palladium (0) $Pd(PPh_3)_4$ (99%) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) were purchased from Sigma-Aldrich. Potassium acetate (KOAc), sodium carbonate (99%) and magnesium sulfate (98%) were purchased from Acros and used as received. Chloroform ($CHCl_3$, 99.5%), toluene (99.5%) and tetrahydrofuran (THF, 99 %) were purchased from Fisher/Acros and dried using molecular sieves under N_2 . Dichloromethane (99.8%), *n*-heptane (99%), methanol (99.8%), ethyl acetate (99%) and diethyl ether (99%) were purchased from Fisher/Acros and used as received.

2.2 Characterization

1H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with TMS as an internal reference, on a Bruker Avance 300 MHz. Fourier transform infrared (FT-IR) spectra, collected as the average of 64 scans with a resolution of 4 cm^{-1} , were recorded from KBr disk on the FT-IR Bruker Tensor 27.

Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min. Molecular weight and molecular weight distribution were calculated regarding to polystyrene standards.

UV-vis absorption spectra of polymers in solution and polymer thin films were recorded on a Shimadzu UV-2,450 spectrometer over a wavelength range of 300–700 nm at the room temperature.

2.3 Synthesis of 2,5-dibromo-3-hexylthiophene

3-Hexylthiophene (5 g, 29.7 mmol) and *N*-bromosuccinimide (10.59 g, 59.5 mmol) were added to anhydrous THF (50 mL) at 0°C under nitrogen. The mixture was stirred at 50°C for 2.5 h. Then, 10% aqueous $Na_2S_2O_3$ was added, and the mixture was extracted with diethyl ether and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain the crude product, which was purified by silica column chromatography (eluent: *n*-heptane) to give pure 2,5-dibromo-3-hexylthiophene as a pale-yellow oil (7.3 g, $R_f = 0.8$, Yield: 80%).

1H NMR (300MHz, $CDCl_3$), δ (ppm): 6.97 (s, 1H), 2.52 (t, 2H), 1.56 (q, 2H), 1.32 (m, 6H), 0.89 (t, 3H).

2.4 Synthesis of 2,2-(3-hexylthiophene-2,5-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

2,5-Dibromo-3-hexylthiophene (1.5 g, 4.6 mmol) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.34 g, 9.2 mmol) were dissolved in 45 mL of 1,4-dioxane. To this solution, 531 mg (10 mol%) of $Pd(PPh_3)_4$ and 1.38 g (0.0141 mol) of KOAc were added, and the solution was bubbled by N_2 for 30 min. Then, the reaction was carried out at 85°C for 24 h. After completion of the reaction, 100 mL of ethyl acetate was added for dilution and the mixture was filtered through Celite to remove the Pd catalyst. The obtained solution was washed with distilled water (2 x 100 mL) and with 10% aqueous solution of $Na_2S_2O_3$ (2x100 mL). Afterward, the solution was dried over $MgSO_4$, and the solvent was evaporated to obtain a black liquid

as the crude product. The crude product was purified over silica column with *n*-heptane/diethyl ether (v/v=9.5/0.5) as eluent to obtain a yellow liquid as the pure product of 2,2'-(3-hexylthiophene-2,5-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) ($R_f = 0.4$. Yield: 40%).

2.5 Synthesis of tris (4-bromophenyl)amine

N-bromosuccinimide (2.17 g, 12.2 mmol) and triphenylamine (1 g, 4.08 mmol) were added to anhydrous THF (10 mL) at 0°C under nitrogen. The mixture was stirred at 50°C for 1.5 h. After completion of the reaction, 10 mL of distilled water was added to the reaction mixture, which was extracted with dichloromethane. The organic layer was washed with 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$ and 10% solution of KOH, dried over anhydrous MgSO_4 and concentrated. The product was precipitated in cold *n*-heptane and dried under vacuum to give a white powder ($R_f = 0.6$; Yield: 67%).

^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.35 (d, 6H), 6.95 (d, 6H).

2.6 Synthesis of hyperbranched polymer based on 3-hexylthiophene and triphenylamine moieties (P(TP-*b*-3HT))

200 mg (0.476 mmol) of 2,2'-(3-hexylthiophene-2,5-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 150 mg of (0.311 mmol) tris(4-bromophenyl) amine were dissolved in 5.7 mL of toluene. To the solution, 328 mg (2.38 mmol) of potassium carbonate (K_2CO_3) was added to the monomer solution. Then 1.2 mL of ethanol (EtOH) and 1 mL of distilled water were introduced to the

solution. The mixture was bubbled with N_2 for 30 min, followed by addition of 55 mg of $\text{Pd}(\text{PPh}_3)_4$. The reaction was carried out at 100°C for 72 h. After completion of the reaction, the mixture was extracted with CHCl_3 . The obtained organic layer was passed through Celite to remove the Pd catalyst and the insoluble polymer fraction, subsequently washed with 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$ and distilled water, dried over Na_2CO_3 , concentrated and finally poured into a large amount of cold *n*-heptane to precipitate the polymer. The resulting polymer was isolated by filtration, washed with acetone to remove oligomers and finally dried under reduced pressure at 50°C for 24 h. A yield of 57% was obtained.

^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.63 (broad, 2H), 6.95-7.39 (broad, 3H), 2.51 (t, 2H), 1.2-1.61 (broad, 8H), 0.89 (t, 3H). FT-IR (cm^{-1}): 3059, 2917, 2851, 1584, 1560, 1490, 1436, 1319, 1274, 1183, 1117, 1011, 825, 753, 721, 696, 628, 542.

3 RESULTS AND DISCUSSION

The chemical structures of hyperbranched polymers **P(TP-*b*-3HT)** are shown in Figure 1. The monomers used include 2,2'-(3-hexylthiophene-2,5-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1, Fig. 1) and tris(4-bromophenyl) amine (2, Fig. 1). These monomers underwent Suzuki polycondensation to build hyperbranched polymer structures, which was carried out in a biphasic mixture of toluene and aqueous K_2CO_3 with $\text{Pd}(\text{PPh}_3)_4$ as the catalyst at reflux temperature.

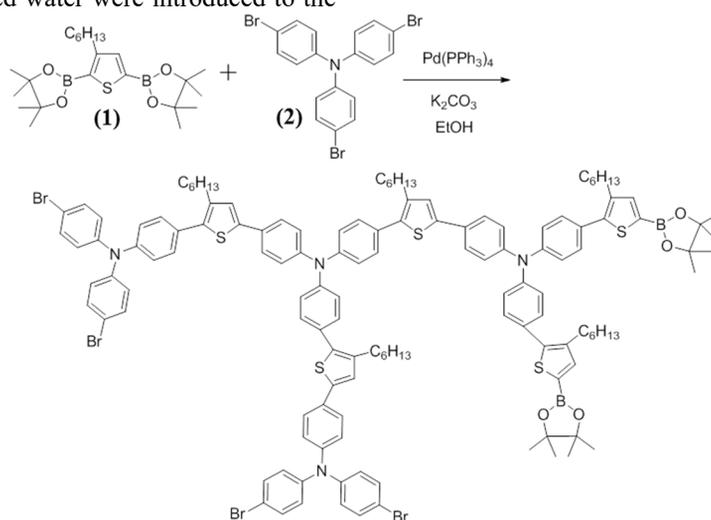


Fig. 1: Polycondensation of 2,2'-(3-hexylthiophene-2,5-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and tris(4-bromophenyl) amine monomers for synthesis of P(TP-*b*-3HT)

The **P(TP-*b*-3HT)** hyperbranched polymer was synthesized by polymerization of a mixture of

monomers (1) and (2), which became pale yellow after 5 h, and gradually turned into brown accom-

panying the appearance of a solvent-insoluble black solid. After 72 h, the hyperbranched polymer was obtained by purification via extraction, catalyst removal, washing and precipitation. The number average molecular weights (M_n) as determined by GPC relative to polystyrene standards of **P(TP-*b*-3HT)** were 24000 g/mol, with polydispersities of 1.8 (Fig. 2). This hyperbranched conjugated polymers were soluble in common organic solvents such as chloroform, THF, toluene and insoluble in acetone, methanol and *n*-heptane. The polymer

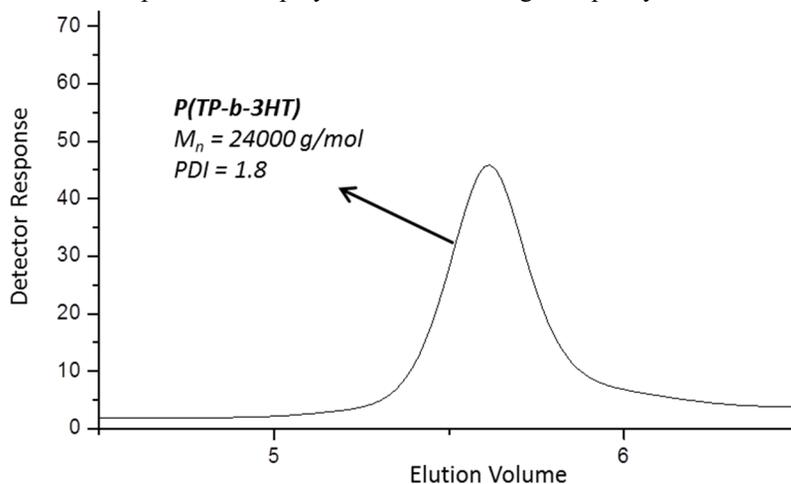


Fig. 2: GPC trace of P(TP-*b*-3HT)

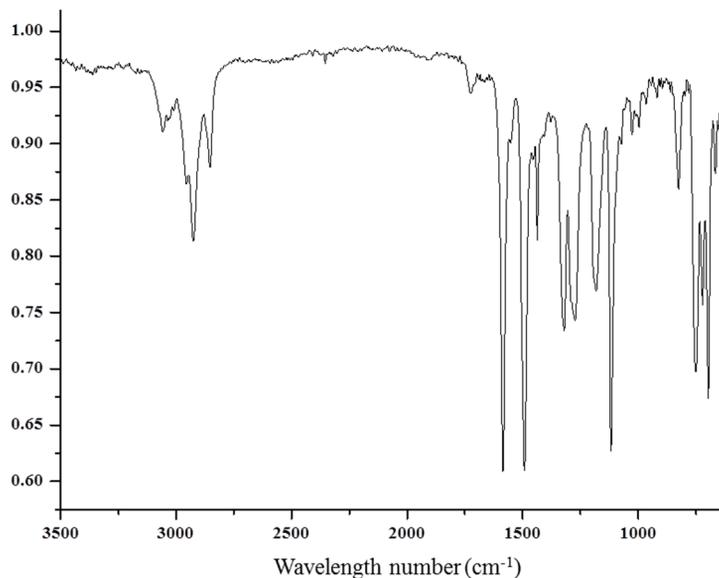


Fig. 3: FT-IR spectrum of P(TP-*b*-3HT)

In the ¹H NMR spectrum of hyperbranched polymer **P(TP-*b*-3HT)** (Fig. 4), a signal was observed 7.63 ppm assignable to the aromatic protons of triphenylamine ring which was originally at 7.35 ppm for the tris(4- bromophenyl) amine monomer. Moreover, the ¹H NMR spectrum of P(TP-*b*-3HT)

structures were characterized by transmission FT-IR and ¹H NMR spectroscopies. The FT-IR spectra (Fig. 3) of **P(TP-*b*-3HT)** displayed several bands between 2850 and 3060 cm⁻¹ due to CH stretching modes of *n*-hexyl groups and ring C-H stretching vibrations. The bands at 1584/1585 cm⁻¹ and 1490/1492 cm⁻¹ are ascribed to the aromatic C=C stretching and aromatic C-H deformation vibrations, respectively, while the bands at 1319/1323 cm⁻¹ and 1273/1274 cm⁻¹ are assigned to the C-N stretching of triphenylamine units.

showed all characteristic peaks of the 3-hexylthiophene and triphenylamine repeating units. However, we could not determine the degree of branching by use of ¹H NMR integration, since the chemical shifts of branching, terminal, and linear units could not be differentiated.

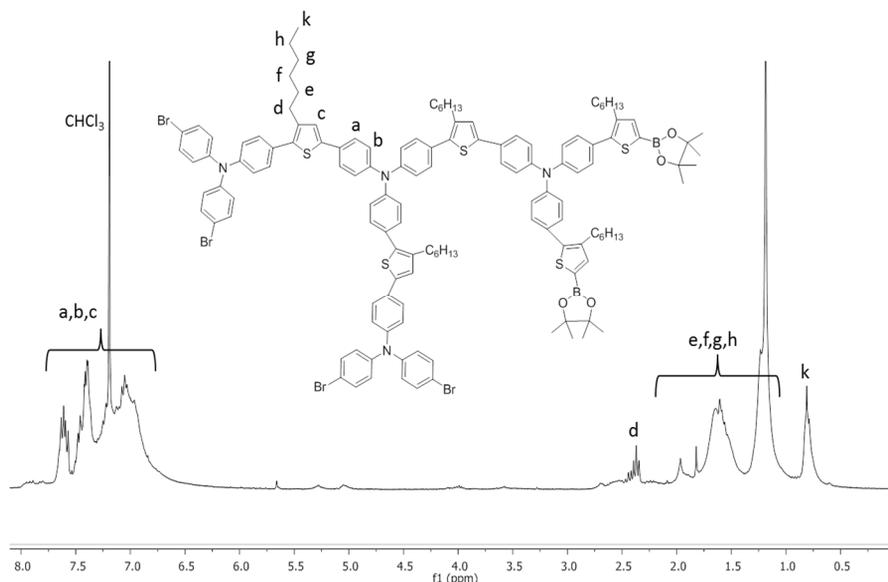


Fig. 4: ^1H NMR spectrum of P(TP-*b*-3HT)

Figure 5 depicts the UV-vis spectra of P(TP-*b*-3HT), measured in different solvents including CHCl_3 , THF, toluene and in solid state films. The P(TP-*b*-3HT) solutions showed an absorption maximum at 340 nm attributable to triphenylamine and

3-hexylthiophene moieties. The solid film of P(TP-*b*-3HT) also showed a similar absorption behavior with an absorption maximum at 350 nm. This indicates the low aggregation degree of P(TP-*b*-3HT) hyperbranched chains in the thin film state.

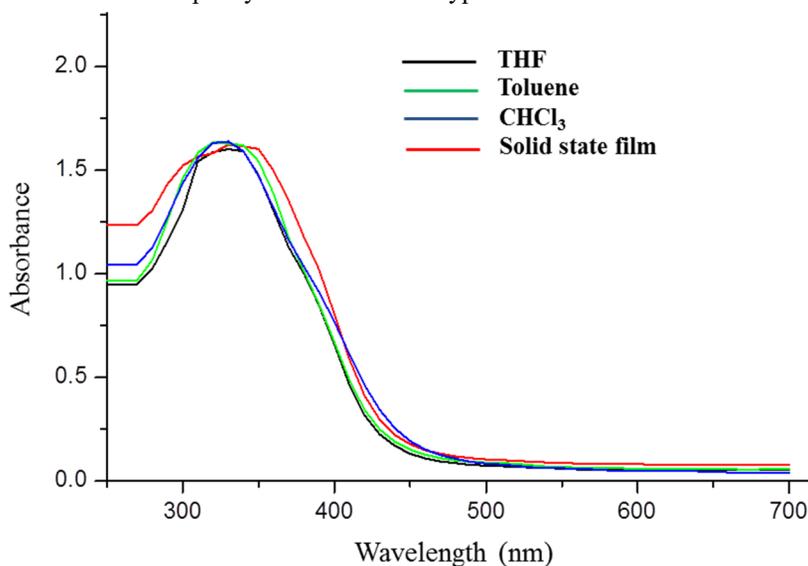


Fig. 5: UV-Vis of P(TP-*b*-3HT)

4 CONCLUSION

In this article, the synthesis of a novel hyperbranched conjugated polymers containing triphenylamine linked with 3-hexylthiophene (P(TP-*b*-3HT)) is demonstrated. The hyperbranched polymers with solvent-soluble properties and M_n of 24000 g/mol were successfully obtained by Suzuki polycondensation of 2,2'-(3-hexylthiophene-2,5-

diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), and tris(4-bromophenyl) amine in 57% yields. The UV-vis absorption of P(TP-*b*-3HT) exhibited an absorption maximum at 350 nm indicating the hyperbranched structure of P(TP-*b*-3HT) effectively decreased chain aggregation which can be used as functional polymer with potential optoelectronic applications.

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