

# Synthesis and characterization of novel polyimides with diamines containing thiophene moieties

Mu-Ju Yoon and Tae-Ho Yoon \*

School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST)  
1 Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea

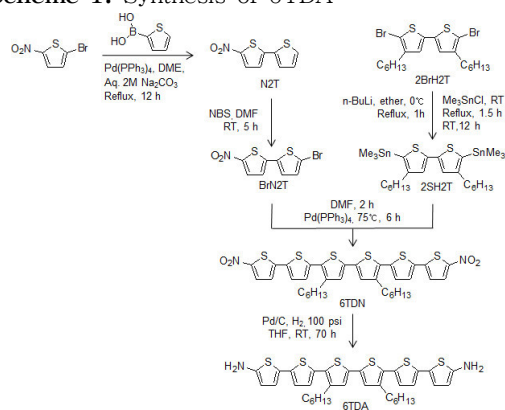
**ABSTRACT:** Noble diamine monomers containing thiophene moiety were prepared, such as 2,5''-diamino-2,2':5', 2''':5'', 2''''-quaterthiophene (4TDA) and 2, 5''''-diamino-3'', 4''''-dihexyl-2,2':5', 2''':5'', 2''''':5''''', 2''''''-sexithiophene (6TDA). Then, these monomers were utilized to prepare polyimides with 3,6-diphenylpromellitic dianhydride (DPPMDA), 3,6-di(4'-trifluoro-methylphenyl)pyromellitic dianhydride (6FPMDA) or 3,6-di(3',5'-bis(trifluoromethyl)phenyl)pyromellitic dianhydride (12FPMDA) via a conventional two-step process. The polyimides were characterized by FT-IR, TGA and DSC, and then subjected CV, UV-vis and PL measurements. The polyimides containing thiophene moiety exhibited high glass transition temperatures (280~310° C) and excellent thermal stability (>420° C) in air as well as green emission (535~586 nm)

During past decades, conjugated polymers have been investigated for optoelectronic applications due to their light weight, flexibility and possible inexpensive solution processing [1]. Thus, a number of conjugated polymers based on thiophene, phenylenevinylene, fluorine, carbazole and triphenylamine have been prepared. However, these polymers exhibited relatively poor optical and/or electrical properties, as well as very poor durability [2] which is being attributed to their low T<sub>g</sub>.

Thus, there has been a great amount of research on increasing the T<sub>g</sub> of conjugated polymers via copolymerization [3], incorporation of bulky side groups [4], or preparation of ladder-type [5]. Unfortunately, however, these approaches exhibited only ~200 °C [4]. Consequently, incorporation of imide moiety was suggested owing to its very high T<sub>g</sub> (> 300 °C) [6], leading to polyimide copolymers with conjugated groups [7-9] or homo-polyimide with conjugated side moiety [10]. Some of these resulted in high T<sub>g</sub>s (~300 °C) [8,10] but their optical and electrical properties are not so good.

In this study, therefore, it was attempted to prepare thiophene-based diamine monomers such as 2,5''-diamino-2,2':5',2''':5'',2''''-quaterthiophene (4TDA) and 2,5''''-diamino-3'',4''''-dihexyl-2,2':5',2''':5'',2''''':5''''',2''''''-sexithiophene (6TDA). Then, these monomers were utilized to prepare polyimides with PMDA-based dianhydrides containing electron withdrawing fluorine groups.

**Scheme 1.** Synthesis of 6TDA



The 6TDA was synthesized via 7-step process (Scheme 1). First, 5-bromo-5'-nitro-2,2'-bithiophene (BrN2T) was obtained by bromination of 5-nitro-2,2'-bithiophene (N2T) which was prepared via Suzuki coupling reaction from 2-thiopheneboronic acid and 2-bromo-5-nitrothiophene [12]. Next, this was reacted with 2,5-bis(trimethylstannyl)-4,4'-dihexyl-2,2'-bithiophene (2SH2T) which was prepared from 2,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene (2BrH2T) [13] via lithiation using *n*-BuLi and then reacting with trimethyltin chloride, resulting in 2,5''''-dinitro-3'',4''''-dihexyl-2,2':5',2''':5'',2''''':5''''',2''''''-sexithiophene (6TDN) which was hydrogenated to afford 6TDA (see Supporting information for detailed synthesis). The product was purified by column chromatography using methylene chloride, providing redish oil (yield 11.9%). <sup>1</sup>H-NMR (DMSO, ppm): 7.21 (s, 2H), 7.05 (d, 2H), 6.91 (d, 2H), 6.84 (d, 2H), 5.97 (s, 4H), 5.83 (d, 2H), 2.71 (t, 4H), 1.62 (t, 4H), 1.35~1.30 (m, 12H) and 0.86 (t, 6H). FT-IR (KBr, cm<sup>-1</sup>): 3380, 3280 (primary amines stretch), 3100~2920 (aryl-H stretching), 2950~2750 (alkyl C-H stretch),

\*To whom correspondence should be addressed.

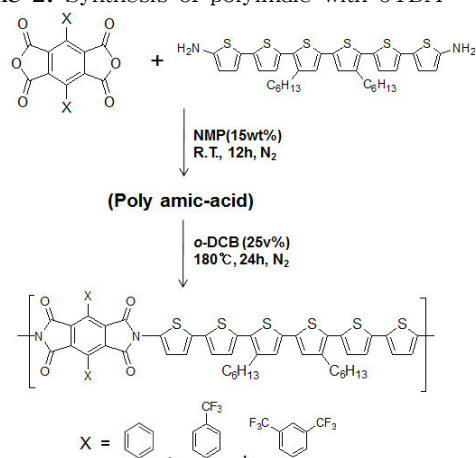
E-mail: [thyoon@gist.ac.kr](mailto:thyoon@gist.ac.kr)

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1690~1560 (N-H bending), 990 (C-N stretch) and 550 (N-H out-of-plane bending).

For comparison, 4TDA was also synthesized via similar chemistry from 5, 5-bis(trimethylstannyl)-2, 2'-bithiophene (2S2T) and 2-bromo-5-nitrothiophene via Stille coupling reaction, resulting in 2,5''-dinitro-2,2':5',2''':5'', 2''-quaterthiophene (4TDN) which was then hydrogenated and purified by recrystallization using chloroform, affording greenish crystals (yield 44.5%). <sup>1</sup>H-NMR (DMSO, ppm): 7.05 (d, 2H), 6.82~6.77 (m, 4H), 5.99 (s, 2H) and 5.81 (d, 2H). FT-IR (KBr, cm<sup>-1</sup>): 3380, 3280 (primary amines stretch), 1690~1560 (N-H bending), 990 (C-N stretch) and 550 (N-H out-of-plane bending).

### Scheme 2. Synthesis of polyimide with 6TDA

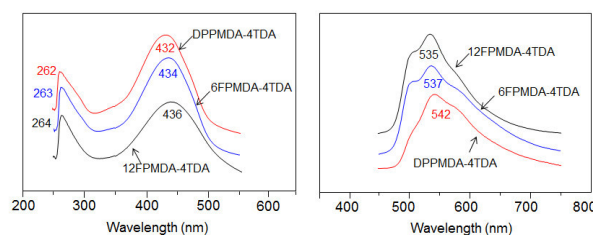


These monomers were utilized to synthesize polyimides with dianhydrides such as 3,6-di(3',5'-bis(trifluoromethyl)phenyl) pyromellitic dianhydride (12FPMDA) [13], 3,6-di(4'-trifluoromethylphenyl) pyromellitic dianhydride (6FPMDA) [14] or 3,6-diphenyl pyromellitic dianhydride (DPPMDA) [15], as shown in Scheme 2. The polyimides were prepared by two-step process; synthesis of poly(amic-acid), followed by solution imidization [13]. The polymerization was conducted in NMP at 15 w/v% solid concentration and the number-average molecular weight was controlled to 25,000g/mole by off-stoichiometry. The solution imidization was performed in the presence of o-DCB (20 v.%) at 180 °C for 24 hr under a nitrogen flow. Upon completion of polymerization, the polymer was isolated by precipitating into methanol and analyzed by FT-IR (KBr), TGA and DSC.

The thiophene-based polyimide, for example 12FPMDA-6TDA, exhibited asymmetric (1760 cm<sup>-1</sup>) and symmetric (1710 cm<sup>-1</sup>) C=O stretching and C-N stretching (1315 cm<sup>-1</sup>), but no amide-carbonyl (C=O) peak at 1650 cm<sup>-1</sup>, indicating successful imidization. In addition, CF<sub>3</sub> stretching-bending absorption (1120 cm<sup>-1</sup>) was also observed, demonstrating presence of fluorine moieties [13]. This polyimide also showed good solubility in NMP, DMF, TCE, THF and CHCl<sub>3</sub>, but slightly poorer solubility was observed with 6FPMDA and DPPMDA (See

supporting information).

The polyimide of DPPMDA-6TDA exhibited very high *T<sub>g</sub>*s of 310 °C, followed by 299 with 6FPMDA and 291 °C with 12FPMDA, while those with 4TDA showed 303, 291 and 281 °C demonstrating the effect of CF<sub>3</sub> moiety, as expected [13], as well as thiophene moiety. These polyimides also exhibited excellent thermal stability (> 420 °C, 5wt% loss temperature) in air in TGA analysis. The best value was obtained with DPPMDA-4TDA (454 °C), demonstrating again the effect of CF<sub>3</sub> and thiophene units.



**Figure 1.** Absorption (left) and PL emission (right) of polyimides with 4TDA.

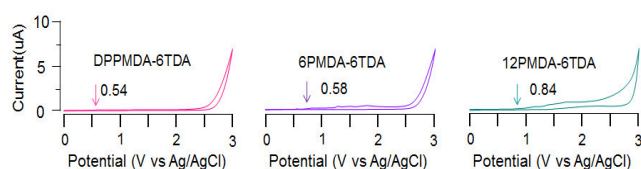
These polyimides exhibited UV-vis absorptions at around 430 nm and 440 nm with 4TDA and 6TDA, respectively (Table 1), while their PL emissions appeared at 530-540 nm and 550-580 nm, respectively. As noted, 4TDA-based polyimide provided shorter wavelength PL emissions compared to those with 6TDA, possibly attributing to destruction molecular packing because of the hydrocarbon attached to 6TDA, while blue shift in PL emission with 6FPMDA and 12FPMDA can be attributed to electron withdrawing nature of CF<sub>3</sub> moiety.

**Table 1.** Optical and electrical properties of polyimides with thiophene moiety.

Polyimide		Abs $\lambda_{abs}$ (nm) <sup>a</sup>	PL $\lambda_{eml}$ (nm) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	Band gap (eV)
4TDA	DPPMDA	262, 432	542	5.38	2.44	2.94
	6FPMDA	263, 434	537	5.42	2.34	3.08
	12FPMDA	264, 436	535	5.75	2.41	3.34
6TDA	DPPMDA	264, 444	586	5.34	2.42	2.92
	6FPMDA	265, 447	568	5.38	2.33	3.05
	12FPMDA	267, 450	554	5.68	2.30	3.34

From the cyclic voltammetry (CV) of these polyimides, onsets of oxidation potentials were measured at 0.54, 0.58 and 0.84 V with DPPMDA-6TDA, 6FPMDA-6TDA and 12FPMDA-6TDA (Table 1), respectively, while slightly higher potential was observed with DPPMDA-4TDA (0.58), 6FPMDA-4TDA (0.62) and 12FPMDA-4TDA (0.95 V). From these values, HOMO level energies were calculated [16], and then LUMO energies were estimated with optical bandgap estimated from UV-vis absorption edge values (Table 1). These values are compatible to those in the literature [9].

In summary, noble diamine monomers, containing thiophene moiety, such as 4TDA and 6TDA were successfully prepared and then utilized to synthesized polyimides with DPPMDA, 6FPMDA or 12FPMDA. The polyimides exhibited very high T<sub>g</sub> (281~310 °C) and excellent thermal stability (5wt% loss temperature of >420 °C) and green emission (535~586nm).



**Figure 2.** Cyclic voltammetry of polyimides with thiophene moiety.

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**KEYWORDS:** thiophene moiety, polyimide, high T<sub>g</sub>, excellent thermal stability, green emission

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#### SUPPORTING INFORMATION

Experimental procedures; synthetic and characterization of the imide compounds are available free of charge via the Internet at <http://rcp.or.kr>

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