Structure-Property Correlation of Light-Emitting Polymers Containing Alternating Phenylene and Thienylene/Bithienylene Repeating Units

Jingmei Xu, Hardy S. O. Chan, S. C. Ng*

Department of Chemistry, National University of Singapore, Singapore 119260
E-mail: chmcsoh@nus.edu.sg

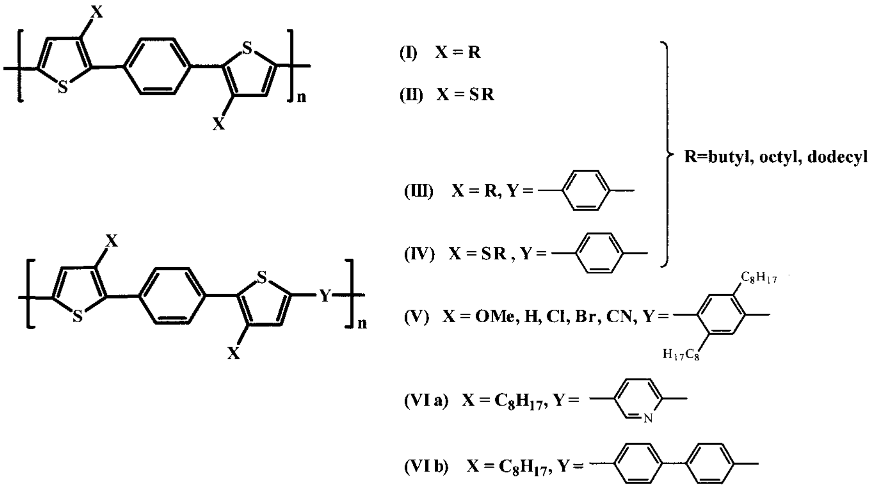
Summary: A number of series of fluorescent and conducting polymers containing alternating 3-functionalized thienylene/ bithienylene and phenylene/ pyridyl/ biphenylene units were synthesized from a number of central symmetric high oligomers and characterized using UV-Vis, photoluminescence, conductivity measurement, thermal analysis, electrochemistry, XRD and XPS. Structural variation of the polymers was realized by both side chain and polymer backbone modifications. Close structure-property correlation of the polymers was observed. This paper mainly reports the results of two families of them, those substituted by alkyl pendant chains and electro-withdrawing and donating groups.

Keywords: conducting polymers; conjugated polymers; electrochemistry; fluorescence; structure-property relations

Introduction

The properties and thus the application possibilities of polymers are greatly influenced by their molecular structures. Polythiophene and its 3-substituted-derivatives represent a family of conjugated conducting polymers which have been well studied.[1,2] For example, alkyl and alkyloxy functionalization have produced polymers which are solution soluble, processible, highly conducting[1,3] or with low bandgaps.[2] Derivatives of polyphenylenes,[4] polyphenylene vinylenes[5] and polyphenylene acetylenes[6] have been reported to be highly fluorescent. We thus designed and synthesized a few families of polymers based on alternating phenylene and thienylene/bithienylene/pyridyl repeating units, as shown below. Structural variations were achieved by both side chain and polymer backbone modifications. The aims are to synthesize a few families of novel conjugated polymers, which are highly fluorescent, conducting and thermally stable, and to examine the structure-property correlations among the polymers.

CCC 1022-1360/00/$ 17,50+.50/0



This paper will mainly report the characterization results for series **(I)**, **(III)** and **(V)**, in which the former two are both substituted by alkyl pendant chains of different lengths but based on phenylene/bithienylene and phenylene/thienylene repeating units, respectively, while the latter is functionalized with electron-withdrawing or –donating groups. Brief comparisons of other series of polymers are made when necessary.

Characterization Results for Polymers (I) and (III)

Polymers **(I)** were prepared by both $FeCl_3$ oxidation and electrochemical methods, while polymers **(III)** were synthesized by Grignard coupling approach, as reported previously.[7-10] They are all yellow powders and all have regioregular structures, as characterized by NMR and FTIR spectra.[8,10] With the increase of side chain length, the solubility of the polymers in common organic solvents decrease. Polymers **(I)** have relatively higher molecular weights but their solubility is lower, in comparison with polymers **(III)**. All the polymers are dopable through $FeCl_3$ or I_2 oxidation. Their color changes from yellow to black upon doping and conductivity increases greatly from un-doped to doped state. The conductivity of the polymers range from 10^{-4} to 10^{-1} S cm^{-1}, but polymers **(I)** have higher conductivities than polymers **(III)**. The doping levels calculated from XPS and elemental analysis suggest that one repeating unit associates with 0.6 dopants.[10] Polymers (**I**) and (**III**) are all p- and n-dopable from cyclic voltammetry (CV). They also all display electrochromism under both oxidation and reduction biases.[10]

The two series of polymers are all highly fluorescent, with emission attainable to the naked eye even under the ordinary laboratory light when dissolved in $CHCl_3$. They absorb blue light but emit in the bluish green range. In $CHCl_3$ solution, their absorption maxima peak in the range of 386 to 388 nm for polymers (**III**) and 398 nm for polymers (**I**), respectively. Emission peak maxima of polymers (**III**) and (**I**) locate at 488 and 494 nm, respectively. In film state, both the absorption and emission maxima shift toward red end. The relative photoluminescence quantum yields of polymers (**I**) and (**III**) in $CHCl_3$ are 19-26 and 48-69%, respectively, with reference to quinine sulphate. The bandgap energies of polymers (**I**) and (**III**) are 2.58 and 2.57-2.68 eV, respectively. It can be seen that polymers (**III**) have higher fluorescence quantum yields and their absorption and emission maxima are blue shifted as compared to those of polymers (**I**). This is ascribable to the higher phenylene to thienylene ratio in the polymer backbone of polymers (**III**) than that in polymers (**I**).[10]

In addition to the differences in physical properties and optical properties, polymers (**III**) have higher thermal stability, lower glass transition temperatures (T_g) and are more crystalline than polymers (**I**).[10] While polymers (**I**) did not show obvious diffraction peaks in XRD pattern, polymers (**III**) all display a few sharp peaks. The interchain spacings from XRD are 8.81, 13.10 and 16.66 Å for the butyl-, octyl- and dodecyl-substituted polymers (**III**). However, these spacings are significantly smaller than those of the butyl-, octyl- and dodecyl-substituted polythiophenes (13.18, 20.53 and 26.43 Å, respectively).[10,11] Figure 1 illustrates a comparison between poly(3-butylthiophene) and polymer (**III**) substituted by butyl pendant chain. Note that the occurrence of side chain interdigitation is impossible in poly(3-butylthiophene), as butyl is too short according to the literature.[11] However, the partially interdigitating structure exists in the polymer (**III**) substituted by butyl pendant chain, although the substituent is also butyl group. This is because of the existence of the unsubstituted phenylene rings. The existence of the unsubstituted phenylene rings also brings high thermal stability of polymers (**I**) and (**III**) than poly(3-alkylthiophene)s[9] and the higher the phenylene content, the better the thermal stability.[10]

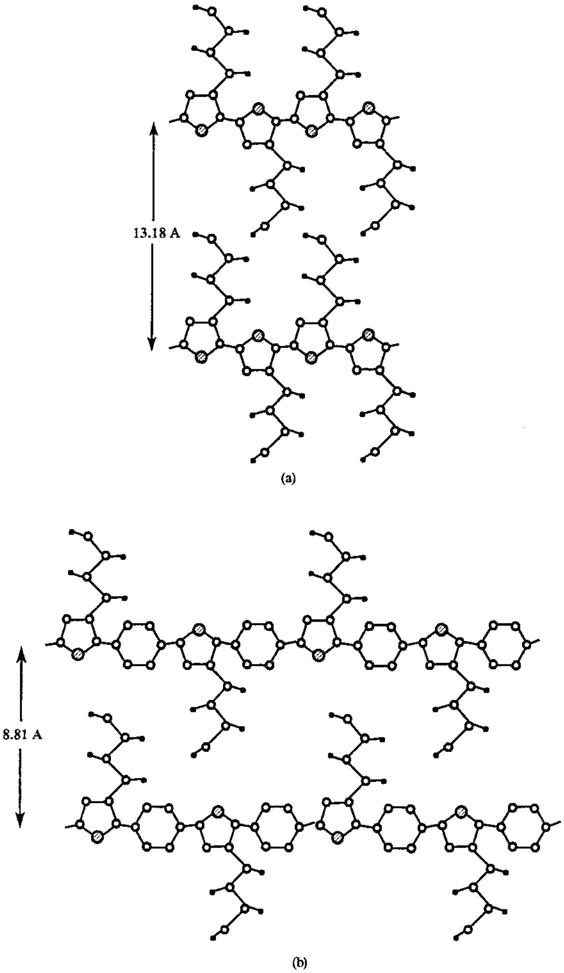


Figure 1. Illustration of interchain spacings in (a) poly(3-butylthiophene); (b) polymer (III) substituted by butyl pendant chain.

Polymers (**II**) and (**IV**) are the alkylthio (SR)-functionalized analogues of polymers (**I**) and (**III**), respectively. Their fluorescence quantum yield are comparable to those of polymers (**I**) and (**III**), but other properties are different.[12] Polymer (**VIIb**) incorporating more phenylene units in the repeating units emits in shorter wavelength range. The optical behavior of polymer (**VIIa**) incorporating electron-withdrawing pyridyl rings suggests the existence of electron transfer and charge transfer phenomena.[13]

Characterization Results for Polymers (V)

Polymers (**V**) were synthesized by Stille coupling.[14] The substituents, OMe, H, Cl, Br and CN, have a direct influence on the polymer properties. All the polymers are highly fluorescent and their absorption and emission maxima are influenced by the substituents, especially OMe and CN. Results from CV suggest that they are all p- and n-dopable.[14] The band structures of polymers (**V**) calculated from CV results are shown in Figure 2.

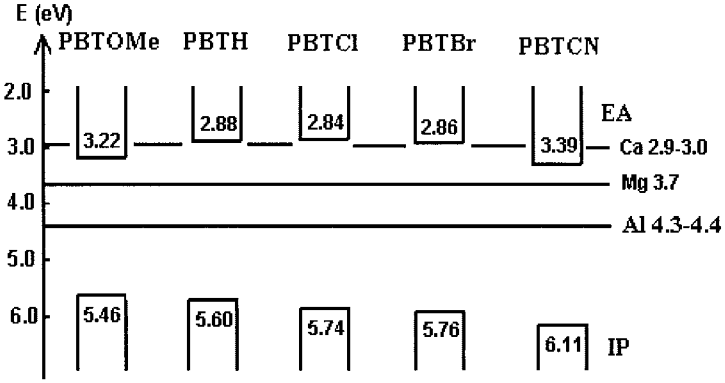


Figure 2. Band structures of polymers (**V**), PBTX (X = OMe, H, Cl, Br, CN). The IP of PBTCN (6.11 eV) is predicted based on the assumption that the electrochemical bandgap of PBTCN is the same as that of PBTH.

The polymer with the strongest electron-donating group, OMe, shows the lowest E_g. That with the strongest electron-withdrawing group, CN, shows an E_g similar to that of H-functionalized polymer, due to the concurrent increase in ionization potential (IP) and electron affinity (EA). The very high EA and IP of PBTCN suggest it to be a good candidate as an electron transport layer (ETL) in a multilayer light-emitting diode (LED) device. PBTOMe, on the other hand, would be a good active material in a single layer device as a balanced electron and hole injection is expected from the analysis of its IP and EA.[14]

Interestingly, the one without any substituent on the thienylene moieties, PBTH, shows the highest conductivity (4 S cm^{-1}) and the highest quantum yield (94%, λ_{em} = 476 nm), amongst all the polymers prepared and studied in this project.[14]

Conclusion

Starting from a few families of high oligomers, a class of novel polymers based on alternating thienylene/bithienylene and phenylene/biphenylene/pyridyl units with properties tunable has been synthesized. These polymers are highly fluorescent and thermally stable. Structural modifications realized by changing the length of the alkyl/alkylthio side chains influences mainly the physical properties, while modifying the electronic properties of side group or polymer backbone influences the properties related to the polymers' electronic structures, such as IP, EA, E_g, ϕ, λ_{max} and λ_{em}. With the increase of phenylene fraction in the polymer backbone, the λ_{max} and λ_{em} blue shift and E_g slightly increases.

[1] R. D. McCullough, S. Tristram-Nagle, S. P., Williams, R. D. Lowe and Jayaraman M., *J. Am. Chem. Soc.* **1993**, *115*, 4910.
[2] K. Faid, M. Leclerc, M. Nguyen and A. Diaz, *Macromolecules* **1995**, *28*, 284.
[3] T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.* **1995**, *117*, 233.
[4] Y. Ohmori, M. Uchida, K. Muro, K. Yoshino, *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
[5] S. T. Kim, D.-H Hwang, X.-C. Li, J. Gruner, R. H. Friend, A. B. Holmes, H.-K. Shim, *Adv. Mater.* **1996**, *8*, 979.
[6] C. Weder, M. J. Wagner, M. S. Wrighton, *Mater. Res. Soc. Symp. Proc.* **1996**, *413*, 77.
[7] S. C. Ng, J. M. Xu, H. S. O. Chan, *Syn. Met.* **1998**, *9*, 33.
[8] S. C. Ng, J. M. Xu, H. S. O. Chan, A. Fujii, K. Yoshino, *J. Mater. Chem*, **1999**, *9*, 381.
[9] S. C. Ng, J. M. Xu, H. S. O. Chan, *Synth. Met.* **2000**, 110, 31.
[10] S. C. Ng, J. M. Xu, H. S. O. Chan, *Macromolecules* **2000**, *33*, 7349.
[11] G. Gustafsson, O. Inganas, H. Osterholm, H. Laakso, *Polymer* **1991**, *32*, 1574.
[12] J. M. Xu, S. C. Ng, H. S. O. Chan, to be published.
[13] J. M. Xu, S. C. Ng, H. S. O. Chan, *Macromolecules* **2001**, *34*, 4314.
[14] J. M. Xu, S. C. Ng, H. S. O. Chan, to be published.