A low band gap silicon-containing polymer

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Recently, the design and synthesis of low band gap polymers have attracted a great deal of attention due to their intrinsic electrical and optical properties as compared to most conjugated polymers [1, 2]. Generally, powerful approaches to low band gap systems are that one is the introduction of quinoid character into the aromatic conjugated polymer backbone and another is the alternation arrangement of strong aromatic donor and acceptor moieties along the polymer main chain [3–7].

As an exciting class of semiconducting polymers, silicon-containing polymers have become very important in the past two decades. Polysilanes are σ-conjugated polymers with a one-dimensional (1D) Si chain backbone and organic side chain substituents. It has a direct and wide band gap ($\sim$4.0 eV) [8]. Silicon-containing PPV derivatives are polymers with alternating Si and π-electron system, in analogy of the conjugated-non-conjugated block copolymers with aliphatic spacer [9–11]. Compared to the aliphatic segments, the silicon units with an aromatic of flexible group are able to produce the same spacer effects with lower operating voltages. It has been argued that the participation of the d-orbital of the Si atom could assist to increase the effective conjugation length, thus facilitate charge mobility.

In this paper, we report the synthesis of such a kind of poly(heteroarylene methines) containing silicon atoms in the main chain, aiming to promote the interaction of d-orbital of the silicon atoms with thiophene rings and increase the effective conjugated length. In this way, a novel low band gap silicon-containing polymer can be obtained.

The synthetic routes of silicon-containing polymer and its monomers are shown in Scheme 1. Bis(2-thienyl)methylphenylsilane 1 was synthesized by a nickel-catalysed Grignard cross-coupling of methylphenyldichlorosilane with 2-magnisiumbromothiophene [12]. For polymerization of monomer 1, we followed a two-step synthetic route reported by Jenekle [5]. First, the precursor 2 (PDTMPSiB) was prepared by the acid-catalyzed polymerization of monomer 1 with benzaldehyde. Then, precursor 2 was oxidatively dehydrogenated in THF solution using 2,3-dicyano-5,6-dichloro-1,4-benzoquinone-(DDQ). The resulting polymer 3, poly[(2,2′-(methylphenylsilanylene)-bithiophene-5,5′-dily)benz-ylidene-block-((2,2′-methylphenylsilanylene)-bithiop-henequinodimethane-5,5′-dily)] (PDTMPSiBQ), was conformed by IR and ′H-NMR analysis. In FT-IR of PDTMPSiBQ, the methine bridge C-H stretching band, which was observed around 2800–3000 cm^{-1} in the spectrum of precursor PDTMPSiB, almost disappeared, but a strong new band at 1660 cm^{-1} for C=C ring stretching vibration band of the quinoid aromatic rings was found. In ′H-NMR spectrum of PDTMPSiBQ, the characteristic methine hydrogen resonance at 5.90 ppm for precursor PDTMPSiB completely disappeared, but a new proton resonance of 7.5–7.9 ppm was observed, which is characteristic of the formation of the quinoid aromatic rings in the polymer backbone.

The optical absorption spectra of PDTMPSiBQ and its precursor: PDTMPSiB in THF were recorded with a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer, as shown in Fig. 1. For PDTMPSiB, the maximum absorption band is at 300–400 nm, which is assigned to the π-$\pi*$ transition of the aromatic thiophene rings. It is the same as the band of the previously reported poly[(silanylene)thiophene]s [9d], and so for PDTMPSiB, the Si units could be regarded as spacers. While for PDTMPSiBQ, it gives one shoulder at 500–600 nm besides the absorption band at 300–400 nm. The band at 500–600 nm should be assigned to the π-π^* band gap transition [5b], and it means that it has a higher π-electron delocalization and a larger effective conjugated length. To some extent, this may result from the quinoid structure of PDTMPSiBQ to make the interaction of d-obital of silicon atoms with thiophene rings in the polymer main chain. Based on the onset absorption at about 850 nm, the optical band gap can be estimated to be 1.46 eV, which is much lower than that of the previously reported poly[(silanylene)thiophene]s (3.45–3.47 eV) [9d].

The electrochemical properties of the polymer solution were studied by cyclic voltammetry using CHI440 Electrochemical Workstation. It was carried out in 0.1 M tetrabutylammonium perchlorate(TBAP)/dichloromethane, where the polymer concentration was 2–4 mg/mL, with Platium wires as both

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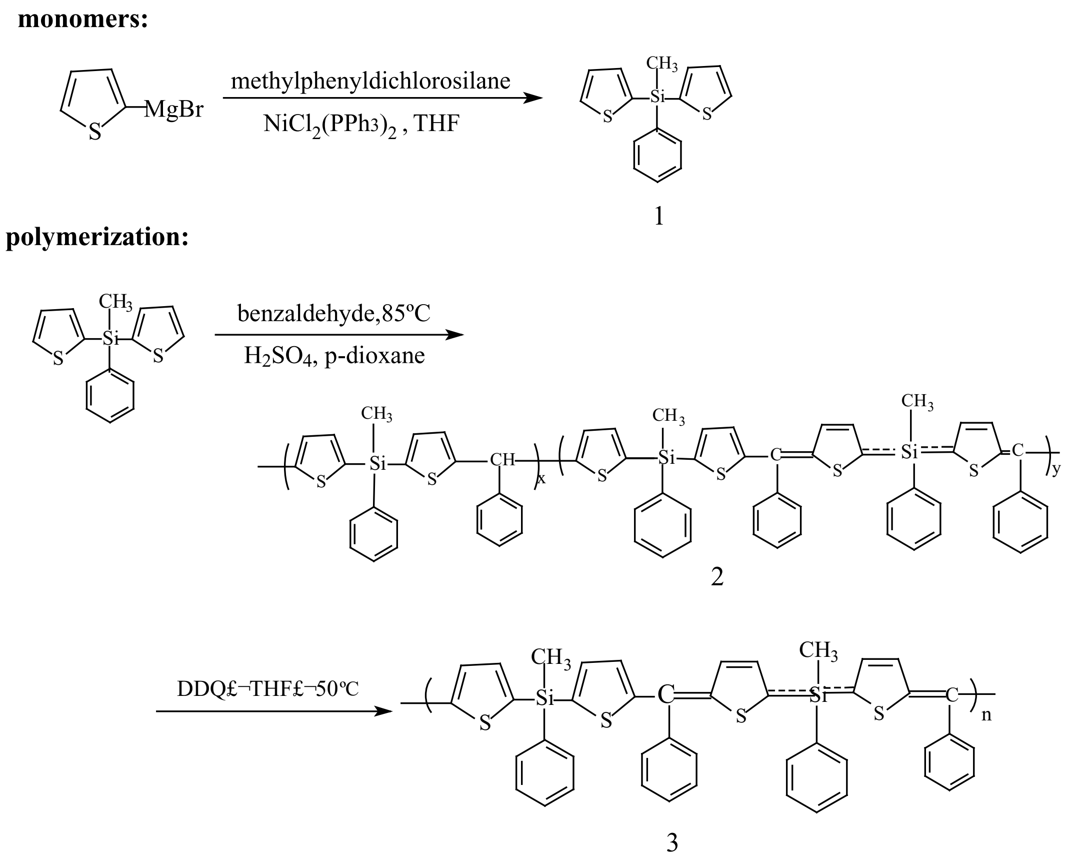
0022-2461
DOI: 10.1007/s10853-006-5313-9



Scheme 1

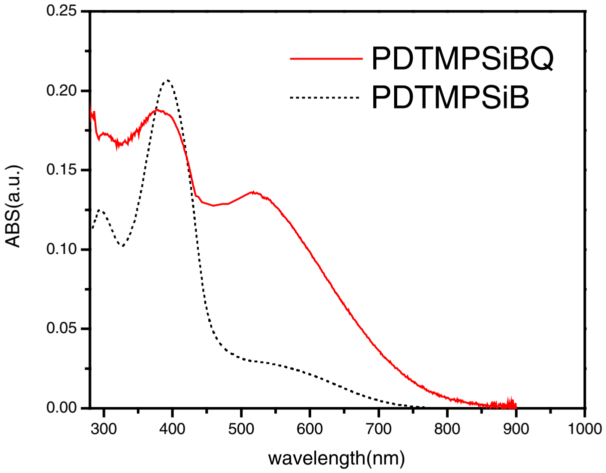


Figure 1 Optical absorption spectra of PDTMPSiBQ and its precursor: PDTMPSiB in THF.

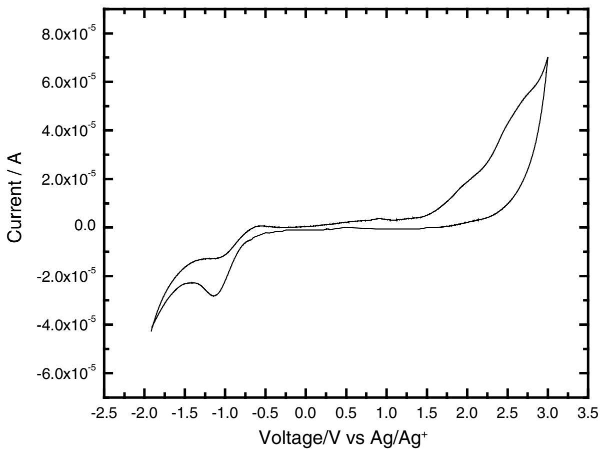


Figure 2 Cyclic voltammetries at 100 mVs-1 of PDTMPSiBQ in $CH_2Cl_2 + TBAP$(0.1 M) from + 3.0 to –2.0 V.

counter and working electrodes, and Ag/Ag^+ as a reference electrode. The IP and EA of the polymer solution were estimated using the following relations [13]: $[E_{on}]^{ox}$ = IP-4.4 and $[E_{on}]^{red}$ = EA-4.4, where the $[E_{on}]^{ox}$, $[E_{on}]^{red}$ are the onset potentials for the oxidation and reduction of polymers versus the reference electrode. Fig. 2 shows the cyclic voltammogram(CV) of PDTMPSiBQ in the potential range of –2.0 to + 3.0 V (vs. Ag/Ag^+ reference electrode). The onset potentials (E_{on}) for electrochemical oxidation and reduction were observed at 1.38 V and − 0.32 V, respectively, which correspond to an ionization potential (IP) of 5.78 eV and an electron affinity (EA) of 4.08 eV. The electrochemical band gap of PDTMPSiBQ calculated from the difference between IP and EA is 1.70 eV, which is higher than its optical band gap, but is still lower than that of poy[5,5′-(dimethylsilylene)-2,2′-bithiophene] and poly[5,5′-(dibutylsilylene)-2,2′-bithiophene] [9d].

In conclusion, a silicon-containing conjugated polymer based on poly(heteroarylene methine), PDTMPSiBQ, has been synthesized. Compared to previously reported poly[(silanylene)thiophene]s, it has a lower optical and electrochemical band gap. And this may result from its quinoid structure to make the interaction of d-obital of the silicon atoms with thiophene rings, and increase its effective conjugated length in the polymer main chain.

Acknowledgments

This project was supported by Nation Natural Science Foundation of China(Grant No. 20274039).

References

1. J. Roncali, *Chem. Rev*. **97** (1997) 173.
2. H. A. M. van Mullekom, J. A. J. M. Vekemans, E. E. Havinga and E. W. Meijer, *Mat. Sci. Eng. R*. **32** (2001) 1.
3. M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl and A. J. J. Heeger, *Chem. Phys*. **82** (1985) 5717.
4. S. A. Jenekle, *Nature* **322** (1986) 345.
5. (a) W. C. Chen and S. A. Jenekle, *Macromolecules* **28** (1995) 454; (b) W. C. Chen and S. A. Jenekle, *Macromolecules* **28** (1995) 465.
6. (a) M. Hanack, U. Schmid, V. Röhrig, J. M. Toussaint, C. Adant and V. Brédas, *Chem. Ber.* **126** (1993) 1487; (b) G. Hieber, M. Hanack, K. Wurst and J. Strähle, *Chem. Ber.* **124** (1991) 1597.
7. E. E. Havinga, W. ten Hoeve and H. Wynberg, *Synth. Met.* **55–57** (1993) 299.
8. S. Hoshino, K. Furukawa, K. Ebata, C.-H. Yuan and H. Suzuki, *J. Appl. Phys*. **88** (2000) 2892.
9. (a) G. G. Malliaras, J. K. Herrema, J. Wildeman, R. H. Wieringa, R. E. Gill, S. S. Lampoura and G. Hadziioannou, *Adv. Mater.* **5** (1997) 721; (b) J. K. Herrema, J. Wildeman, R. H. Wieringa, G. G. Malliaras, S. S. Lampoura and G. Hadziioannou, *Polmer. Prepr.* **34** (1993) 282; (c) K. Yoshino, A. Fujii, H. Nakayama, S. Lee, A. Naka and M. Ishikawa, *J. Appl. Phys.* **85** (1999) 414; (d) J. K. Herrema, P. F. van Hutten, R. E. Gill, J. Wildeman, R. H. Wierings and G. Hadziioannou, *Macromolecules* **28** (1995) 8102.
10. (a) J. Oshita, T. Watanabe, D. Kanaya, H. Ohsaki and M. Ishikawa, *Organometallics* **13** (1994) 5002; (b) K. Nate, M. Ishikawa, H. Ni, H. Watanabe and Y. Saheki, *Organometallics* **6** (1987) 1987; (c) H. K. Kim, M.-K. Ryu, K.-D. Kim, S.-M. Lee, S.-W. Cho and J.-W. Park, *Macromolecules* **31** (1998) 1114.
11. S. H. Lee and W. P. Weber, *Polym. Bull*. **22** (1989) 355.
12. K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato and K. Suzuki, *Tetrahedron* **38** (1982) 3347.
13. R. Cervini, G. W. Spencer, A. B. Holmes, S. C. Moratti and R. H. Friend, *Syn. Met.* **84** (1997) 359.

Received 28 June 2004
and accepted 16 February 2005