Novel soluble low band gap polymers

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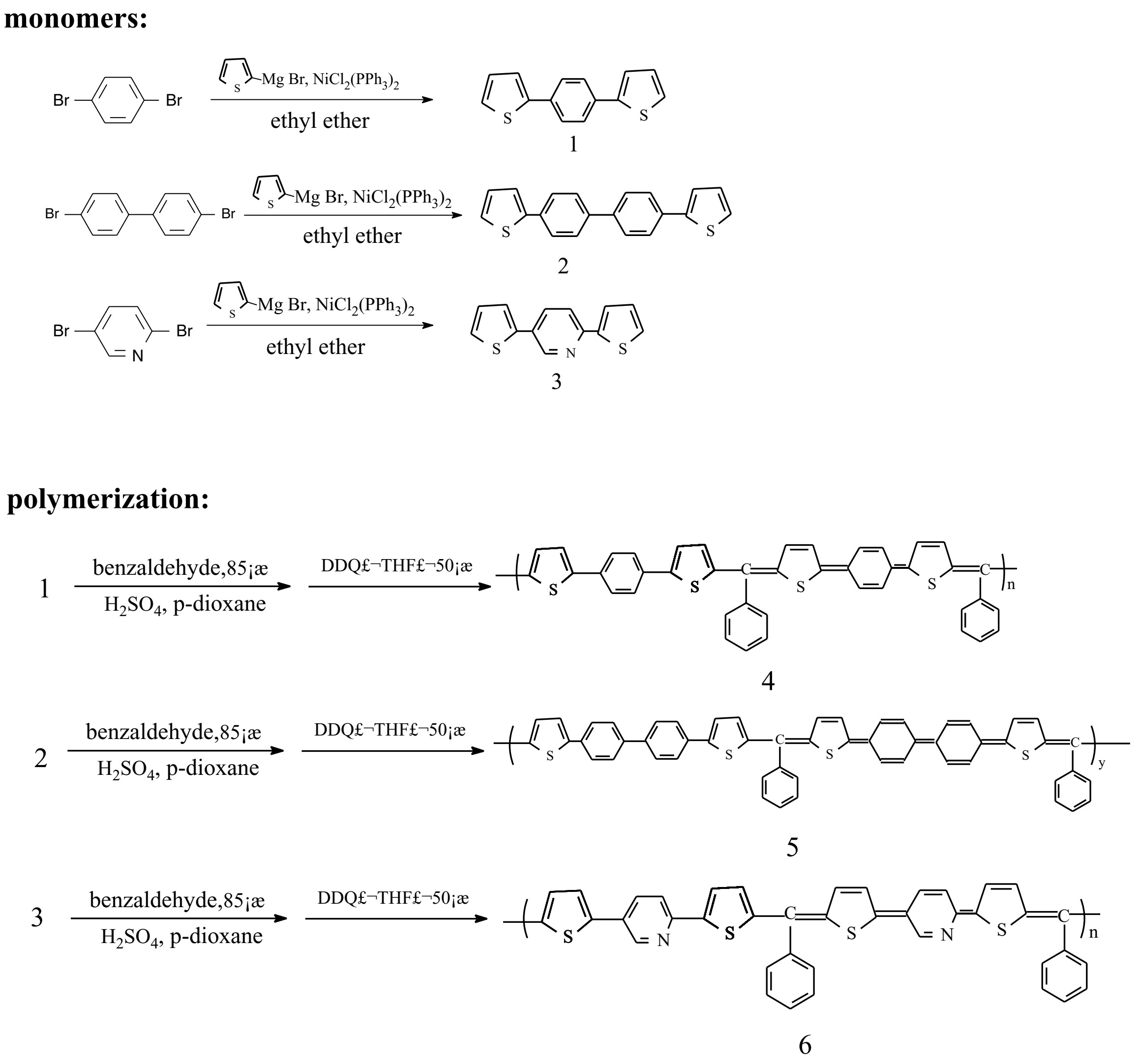
Recently, the design and synthesis of low band gap polymers have attracted a great deal of attention due to their intrinsic electronic, optoelectronic, optical, and nonlinear optical properties as compared to most conjugated organic polymers [1, 2]. One approach involves the introduction of a quinoid character into the acromatic conjugated polymer backbone. Since poly(isothianaphthene) (PITN) having a very small band-gap ($E_g \approx 1.0$ eV) was reported [3], a lot of interest has been attracted to the field. In 1986, S.A. Jenekle proposed a class of small band gap polymers: poly(heteroarylene methines), which directly incorporates quinoid moieties into the conjugated polymer backbone by the methine-bridged structure [4]. Although conjugated poly(heteroarylene methines) could easily be synthesized by a general two-step synthetic route, their solubility and processibility become poor when each repeat unit contains more than three thiophene rings [5].

Here, we have reported some soluble conjugated poly(heteroarylene methines), which have modified methine-bridged polythiophene backbones by inserting



Scheme 1

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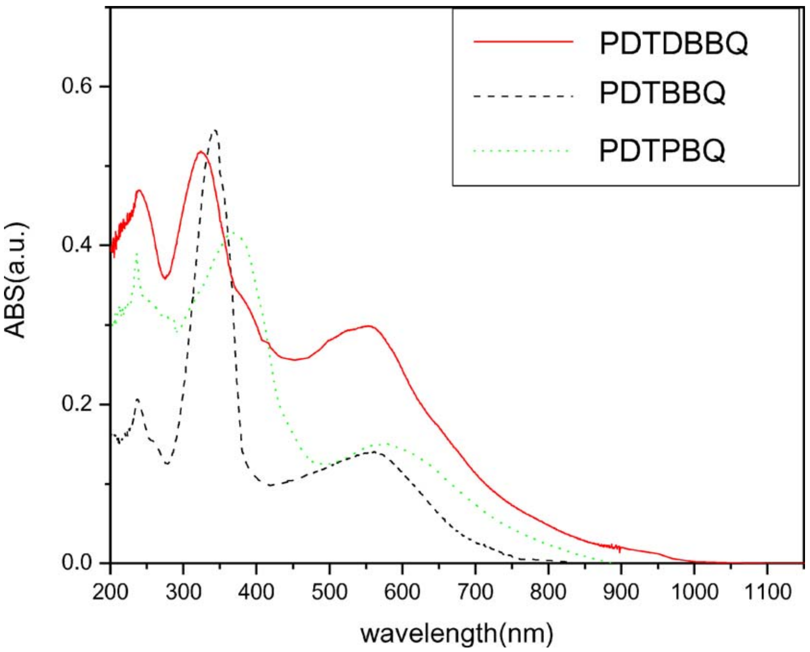

Figure 1 Optical absorption spectra of PDTBBQ, PDTDBBQ and PDTPBQ in THF.

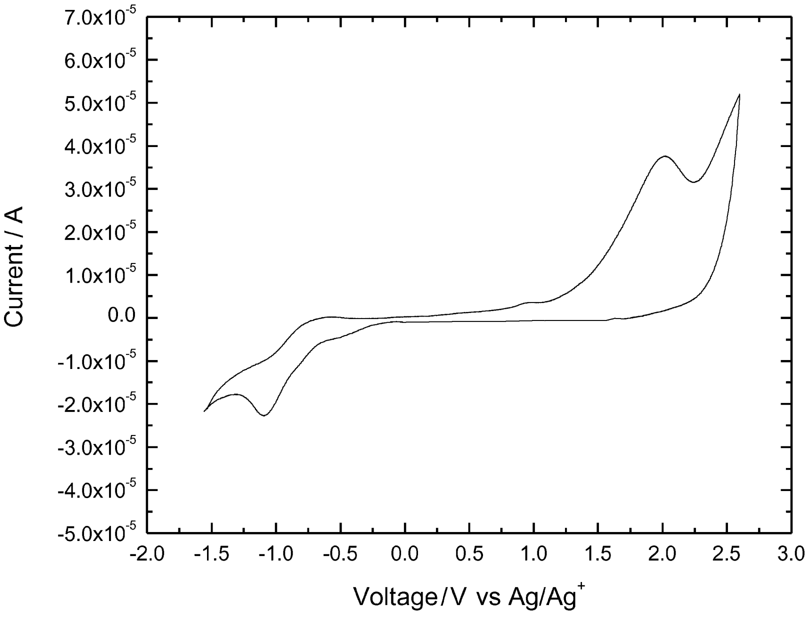

Figure 2 Cyclic voltammetries at 100 mVs^{-1} of PDTDBBQ in CH_2Cl_2 + TBAP(0.1 M) from +3.0 to −2.0 V.

phenylene or pyridine rings between two thiophene rings, and could be soluble in common organic solvents.

The synthetic routes of monomers and corresponding polymers are shown in Scheme 1. For monomers: 1,4-di(α-thienyl)benzene (DTB) 1, 4, 4′-di (α-thienyl) biphenyl (DTDB) 2 and 1,4-di(α-thienyl)pyridine (DTP) 3, were synthesized through the Grignard coupling reaction according to the literature [6]. For polymer: poly[(1′,4′-di(α-thienyl)benzene-5,5″-dily)benzylidene-block-((1′,4′-di(α-thienyl)benzenequinodimethane-5′,5″-dily)) (PDTBBQ) 4, poly [(4′,4″-di(α-thienyl)biphenyl-5,5‴-dily) benzylidene-block-(4′,4″-di(α-thienyl)biphenylquinodimethane-5′, 5‴-dily)] (PDTDBBQ) 5, and poly[(1′,4′-di(α-thienyl) pyridine-5,5″-dily)benzylidene-block-((1′,4′-di(α-thienyl) pyridinequinodimethane-5,5″-dily))](PDTPBQ) 6, were synthesized through a two-step synthetic route reported by S. A. Jenekle [5, 7]. First, the precursors were obtained by the acid-catalyzed polymerization of monomers with benzaldehyde. Then, these precursors were oxidatively dehydrogenated using 2,3-dicyano-5,6-dichloro-1,4-benzoquinone(DDQ) in THF. The resulting polymers were determined by FTIR and ′H-NMR analysis. In FTIR, the methine bridge C—H stretching bands around 2800–3000 cm^{-1} observed in the spectrum of precursors 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, the characteristic methine hydrogen resonance at about 5.90 ppm for precursors completely disappeared, but a new proton resonance of 7.5–7.9 ppm was observed, indicating the formation of the quinoid rings in the polymer backbone. Compared to previously reported poly[(α-terthiophene-5,5′-dily)benzylidene-block-(α-terthiophenequinodimethane-5,5′-dily)] (PTTBQ) [5, 7], the polymers so obtained are readily soluble in common organic solvents, such as chloroform and THF, especially for PDTBBQ and PDTDBBQ.

The UV-vis absorption spectra were recorded with a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer. Fig. 1 shows the optical absorption spectra of polymers: PDTBBQ, PDTDBBQ and PDTPBQ in THF solution. The colors of the polymer solutions were almost grey or black. The absorption spectra in Fig. 1 show two major absorption bands. The band in range of 300–400 nm is assigned to the π-π^* transition of the aromatic heterocycles since it corresponds to the same band as its precursor, and the band in the range of 500–650 nm is assigned to the π-π^* band gap transition [5]. Based on the onset absorption at 800–1000 nm, the corresponding optical band gaps are in the range of 1.55–1.24 eV. Further, we can deduce that the decrease of band gaps is from 1.49 eV for PDTBBQ to 1.40 eV for PDTPBQ and 1.24 eV for PDTDBBQ.

The electrochemical properties of the polymer solutions were studied by cyclic voltammetry using a 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 platinum wires as both counter and working electrodes, and Ag/Ag$^+$ as a reference electrode. The ionization potential (IP) and electron affinity (EA) of the polymer solution were estimated using the following relations [8]: $[E_{\text{on}}]^{\text{ox}} = \text{IP-4.4}$ and $[E_{\text{on}}]^{\text{red}} = \text{EA-4.4}$, where the $[E_{\text{on}}]^{\text{ox}}$, $[E_{\text{on}}]^{\text{red}}$ are the onset potentials for the oxidation and reduction of polymers versus the reference electrode. Fig. 2 shows the cyclic voltammogramm (CV) of PDTDBBQ in THF solution. The onset potentials for oxidation and reduction were obtained at the 0.75 V and −0.18 V, respectively, which correspond to an IP of 5.15 eV and an EA of 4.22 eV. The electrochemical band gap of PDTDBBQ determined from the difference between the IP and EA is 0.93 eV. And the electrochemical properties of poly(heteroarylene methines) are collected in Table I. It reveals that the sequence of the decrease of the band gaps is PDTBBT > PDTPBQ > PDTDBBQ, in agreement with the optical band gaps.

TABLE I Electrochemical properties of poly(heteroarylene methines)

	Oxidation (vs Ag/Ag$^+$)		Reduction (vs Ag/Ag$^+$)		
Polymers	IP (eV)	E_{on} (V)	EA (eV)	E_{on} (V)	E_g (eV)
PDTBBQ	5.55	1.15	3.83	−0.57	1.72
PDTDBBQ	5.15	0.75	4.22	−0.18	0.93
PDTPBQ	5.78	1.38	4.97	−0.03	1.41

In conclusion, we have prepared some soluble conjgugated poly(heteroarylene methines) by modifying the conjugated aromatic backbone through the insertion of other heterocycles between two thiophene rings. Compared to the similar poly(heteroarylene methines), such polymers not only have good solubility, but also have quite low band gap, especially for PDTDBBQ. Such results may serve primarily to illustrate a new strategy to increase the solubility of low band gap polymers through the arrangement of different aromatic heterocycles in conjugated polymer backbones.

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