

# Synthesis of a low-bandgap polymer bearing side groups containing phenoxy radicals

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## Abstract

Poly(isothianaphthene methine) bearing di-*tert*-butylphenoxide in the side chain was prepared by reacting isothianaphthene and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in the presence of POCl<sub>3</sub>. A reference polymer with no hydroxy group in the side chain was also synthesized. Both polymers are characterized by a low-bandgap with value of ca. 1.3 eV obtained by optical absorption spectroscopy, and ca. 1.7 eV estimated from an electrochemical method. After treatment with PbO<sub>2</sub> as an oxidizer, phenoxy radicals were generated by oxidation in the polymer side groups. Optical absorption measurements and electron spin resonance (ESR) showed a characteristic signal due to phenoxy radicals. Magnetic properties of the polymer were examined with ESR and superconducting quantum interference device (SQUID) measurements. The results suggested that the polymer shows paramagnetic behavior.

**Keywords:**  $\pi$ -conjugated polymer; electron spin resonance (ESR); isothianaphthene (ITN); low-bandgap; radical

## Introduction

$\pi$ -conjugated molecules have been studied widely for electronic materials and optical devices [1–10]. A low-bandgap polymer has a notably strong interaction between electrons in the polymer backbone. Applications as transparent electrodes or electrochromic materials have been developed. Specifically, among low-bandgap polymers, isothianaphthene-based polymers have remarkable electronic and optical properties [11–19].

Polymer-based magnetic materials have attracted interest in many fields [20–22]. Magnetism in polymers originated from radicals shows characteristic electrochemical or optical properties. Recent studies have reported synthesis and properties of functional radical polymers and devices using radical compounds such as radical batteries and radical light-emitting diodes [23–26]. We attempt a combination of a low-bandgap polymer based on polyisothianaphthene and stable radical groups for creation of low-bandgap  $\pi$ -conjugated radical polymers.

## Experimental

### Technique

Fourier transform Infrared spectra (FT–IR) of polymers were taken with a JASCO FTIR 300 spectrometer by the KBr method. Fourier transform Raman (FT–Raman) spectra were obtained by using a Nicolet NXR FT–Raman spectrometer with 1064 nm excitation wavelength. Ultraviolet–visible (UV–Vis) absorption spectroscopy measurements were carried out at room temperature by using a HITACHI U–3500 spectrometer with a quartz cell. Cyclic voltammetry (CV) measurements were carried out by repeated potential cycling using an ECO CHEMIE  $\mu$ AUTOLAB TYPE III. The three electrode system consists of a platinum disc working electrode, an Ag/Ag<sup>+</sup> reference electrode, and a platinum wire counter electrode. CV measurements were performed using electrolytic acetonitrile solutions containing 0.1 M of tetrabutylammonium perchlorate at a scan rate of 50 mV/s. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a JASCO HPLC 870–UV detector, with tetrahydrofuran (THF) as the solvent, with the instrument calibrated with polystyrene standards. ESR measurement of the polymer in solid state was carried out with a JEOL JES TE–200 spectrometer and a Bruker EMXPlus9.5/2.7 spectrometer. The polymer was packed into a 5 mm quartz tube. The sample tube was evacuated before sealing. The spin concentration was determined using CuSO<sub>4</sub>·5H<sub>2</sub>O as the internal standard. Magnetic susceptibility measurement for the polymer was performed with a Quantum Design MPMS–3 SQUID magnetometer ( $\pm 5$  T). The polymer was packed into a 5 mm diameter quartz cell connected to Pyrex glass tube. After evacuation, the tube was sealed for SQUID measurements. The magnetic susceptibility was measured from 2 K to 300 K under magnetic fields of 1, 2 and 4 T.

### Polymer synthesis and oxidation

The isothianaphthene monomer 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (1) was synthesized in three steps [27]. The synthetic routes to poly(isothianaphthene methine)s are shown in Scheme 1. A solution of isothianaphthene monomer (1) (0.363 g, 1.00 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (0.237 g, 1.00 mmol) in 1,4-dioxane (8.00 mL) was refluxed at 85 °C in the presence of POCl<sub>3</sub> (2.00 mL) for 24 h.

Then, the solution was poured into a large amount of methanol and the precipitate was collected to obtain an indigotic blue solid followed by centrifugal separation and vacuum drying (0.188 g, Y = 53.6 %). The polymer (poly2) was synthesized under the same conditions used for the preparation of poly1. The isothianaphthene monomer (1) (0.090 g, 0.25 mmol) and 3,5-di-*tert*-butylbenzaldehyde (0.055 g, 0.25 mmol) were dissolved in 1,4-dioxane (2.50 mL), and subsequently the solution was refluxed at 85 °C in the presence of POCl<sub>3</sub> (0.50 mL) for 24 h. After work up 13.2 mg of an indigotic blue solid was obtained (Y=16.0%). Poly1 and poly2 were subsequently neutralized with excess amount of triethylamine.

Next, a suspension of the poly1 (0.051 mg) in toluene (10.0 mL) containing fresh PbO<sub>2</sub> (0.5021 mg) was stirred for 20 min under an argon atmosphere to generate radicals at the side chains [28]. The solution was then filtered and freeze-dried under reduced pressure to yield poly1' as a polyradical. The number average molecular weights ( $M_n$ ) of poly1 and poly2 were found to be 2000 and 1440, respectively; the weight average molecular weights ( $M_w$ ) were 2980 and 1880, respectively, evaluated by GPC with THF as the solvent, against a polystyrene standard (Table 2). The molecular weights seem to be somewhat low because the polymers are poorly soluble in THF, and the GPC measurement thus probably provides results for only the low-weight molecular mass fraction. Therefore, the actual molecular weights of poly1 and poly2 might be larger than the results of the GPC measurements.

## Results and Discussion

### FT-IR and FT-Raman spectroscopy

The FT-IR absorption spectra of poly1 and poly2 are shown in Fig. 1a. The major bands observed on FT-IR and FT-Raman spectra are listed in Table 1. The absorption band at 3431 cm<sup>-1</sup> which corresponds to O-H stretching was observed in poly1, while poly2 showed no signal around 3431 cm<sup>-1</sup>. It indicates that poly1 has OH groups in the side chain. Poly1 and poly2 showed absorption bands associated with C=C vibration of quinonoid isothianaphthene unit at 1588 cm<sup>-1</sup> and 1589 cm<sup>-1</sup>, respectively [16].

Fig. 1b shows the FT-Raman spectra of poly1 and poly2. FT-Raman spectroscopic studies of polyisothianaphthene and poly(isothianaphthene methine) derivatives have been reported [29–31]. The Raman bands of poly1 and poly2 were associated with vibrations of benzenoid and quinonoid isothianaphthene units. This analysis indicates that poly1 and poly2 are copolymers of the isothianaphthene and the benzaldehyde derivatives, and have benzenoid and quinonoid isothianaphthene units in the main chain.

### UV-vis absorption spectroscopy

The UV-vis optical absorption spectra of poly1 (having OH as the substituent) and poly2 (no OH as the substituent) were obtained in CHCl<sub>3</sub> solution (Fig. 2a). Both polymers show wide absorption bands in the visible range. Poly1 shows an absorption maximum ( $\lambda_{max}$ ) at 673 nm and poly2 at 642 nm. From the band-edge of the spectra for these polymers, the band-edge bandgaps are estimated to be 1.3 eV for the both polymers.

Fig. 2b shows the UV-vis absorption spectra of poly1' (having oxyradical as the substituent) obtained from oxidation of poly1. Poly1' exhibits a characteristic peak near 460 nm. Yoshioka et al. [32] have reported that polyacetylenes bearing 2,6-di-*tert*-butyl-4-phenoxy radicals have an absorption band at 495 nm. It should be noted that the absorption band of 460 nm is the phenoxy radical [23–24]. Fig. 2b shows absorption spectra of poly2<sub>PbO<sub>2</sub></sub> after treatment with PbO<sub>2</sub> as a reference (no oxyradical). The absorption spectrum of poly2<sub>PbO<sub>2</sub></sub>, which has no phenoxy radical in the side chain, does not show the characteristic peak at 460 nm. From these results, we conclude that the absorption spectrum of poly1' indicates the presence of phenoxy radicals.

#### Electrochemical measurement

Cyclic voltammetry (CV) measurements were carried out in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 50 mV/s. The cyclic voltammograms for poly1 and poly2 are shown in Fig. 3. An oxidation peak with an onset of  $E_{\text{ox/onset}} = 0.55$  V (vs. Ag/Ag<sup>+</sup>), and a reduction peak with an onset of  $E_{\text{red/onset}} = -1.12$  V (vs. Ag/Ag<sup>+</sup>) were observed for poly1. Poly2 showed similar electrochemical response. The onsets of oxidation and reduction peaks for poly1 and poly2 were calibrated using Fc/Fc<sup>+</sup>. The onset oxidation potential of Fc/Fc<sup>+</sup> measured in the solvent was  $-0.04$  V vs. Ag/Ag<sup>+</sup>, thus  $E_{\text{ox/onset}}$  and  $E_{\text{red/onset}}$  of poly1 and poly2 were calibrated to add 0.04 V to the potentials. These results are summarized in Table 2. Li and Bonardi et al. [33–34] suggested that highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be estimated from CV results. The onset of an oxidation peak (vs. Fc/Fc<sup>+</sup>) was recalculated to electron volts versus vacuum level using a potential value of  $-4.75$  eV [35]. In this study, the energy levels were obtained by adding 4.75 to the potentials (vs. Fc/Fc<sup>+</sup>). For example, the HOMO energy ( $E_{\text{HOMO}}$ ) and the LUMO energy ( $E_{\text{LUMO}}$ ) of poly1 can be estimated as  $E_{\text{HOMO}} = -(E_{\text{ox/onset}} + 4.75)$ , and  $E_{\text{LUMO}} = -(E_{\text{red/onset}} + 4.75)$ , respectively. The bandgap  $E_g(\text{CV})$  is also estimated to be  $E_g(\text{CV}) = E_{\text{LUMO}} - (E_{\text{HOMO}})$ . From these calculations  $E_g(\text{CV})$  is estimated to be 1.67 eV. This bandgap  $E_g(\text{CV})$  is slightly higher than the bandgap of poly1 estimated from the UV-vis optical absorption spectroscopy ( $E_g(\text{opt}) = 1.32$  eV).

#### Magnetic properties

Fig. 4a shows electron spin resonance (ESR) spectra of poly1' and poly2<sub>PbO<sub>2</sub></sub>. Poly1' showed a signal with a  $g$ -value of 2.004 [36], whereas poly2 shows no characteristic signal in the ESR. According to Chen et al. [37] poly(isothianaphthene) synthesized under oxidative conditions intrinsically shows a  $g$ -value of 2.006 due to generation of polarons as charge carriers. This result indicates that oxidation of poly2 with PbO<sub>2</sub> affords no charge carrier along the main chain. Therefore, the  $g$ -value of 2.004 indicates phenoxy radicals in the side chain of poly1'. The ESR spectrum of poly1' was also obtained at low temperature. Fig. 4b shows the ESR spectra for poly1' at 4 – 90 K. The ESR intensity increased with the decrease of temperature. Appearance of hyperfine structure-like signal at 4 K implies that the electron spin of phenoxy radicals interacts with hydrogen on the benzene ring or *tert*-butyl groups in the side chain.

Yoshizawa et al. suggested that the magnetic susceptibility ( $\chi$ ) can be estimated from an ESR spectrum. The  $\chi$  is given as follows:

$$\chi = C \Delta H_{pp}^2 I_{pp} \quad (1)$$

where  $\Delta H_{pp}$  is the peak-to-peak line width,  $I_{pp}$  is the height of the differential curve, and  $C$  is a constant which depends on the measurement conditions such as sensitivity and amplitude of the apparatus [38]. It is noted that  $\chi$  theoretically depends on a temperature ( $T$ ) followed the Currie-Weiss law,

$$\chi = C_{\text{curie}} / (T - \theta) \quad (2)$$

here  $C_{\text{curie}}$  is the Curie constant, and  $\theta$  is the Weiss constant.

The  $\chi$  (estimated from  $\Delta H_{pp}^2 I_{pp}$ ) vs.  $T$  plots and the  $\chi T$  (estimated from  $\Delta H_{pp}^2 I_{pp} T$ ) vs.  $T$  plots for the poly1' are shown in Fig. 5.  $\chi$  decreases with the temperature. This result is observable for general magnetic materials.  $\chi T$  is almost constant against temperature, indicating the polymer shows paramagnetic behavior.

Magnetic behavior of poly1' was also examined with a superconducting quantum interference device (SQUID), as shown in Fig. 6.  $\chi$  value decreases with temperature, whereas  $\chi T$  is almost constant. These are the same trend as these of the ESR results, suggesting the polymer show paramagnetic behavior. However,  $\chi^{-1}$  vs.  $T$  plots for poly1' shows  $\theta < 0$  ( $\theta \approx -5.0$  K). This implies poly1' might have some contents of intra-chain (through the conjugated main chain) antiferromagnetic interaction.

The spin concentration of poly1' was 2% per unit cell determined by ESR spectroscopy. The low spin concentration can be due to the poor solubility of poly1' in the solvent during the radical generation process and the oxidation reaction with  $\text{PbO}_2$  was not sufficient in this experiment. Furthermore, the extinction of radicals and cross-linking of the polymer might occur after oxidation. However, the results in the present study clearly demonstrate the synthesis of low-bandgap polymers having magnetic properties.

## Conclusions

Low-bandgap poly(isothianaphthene methine)s were obtained under oxidative conditions. Poly1 and poly2 showed a broad absorption band at long wavelengths in the optical absorption spectra. Phenoxy radicals in the side-chain of poly1' were generated with  $\text{PbO}_2$ . The generation of the phenoxy radicals was confirmed by the UV-vis optical absorption and the ESR measurements. Although further investigation of the magnetic behavior and improvement of the synthesis to increase the radical concentration of the polymer are required, in this study we successfully synthesized low-bandgap polymers having stable radical groups. This type of polymer may be a useful material of an energy storage application (i.e., radical battery) and could be used for the development of organic magnetic-optical devices.

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**Table 1** FT-IR and FT-Raman bands of poly1 and poly2

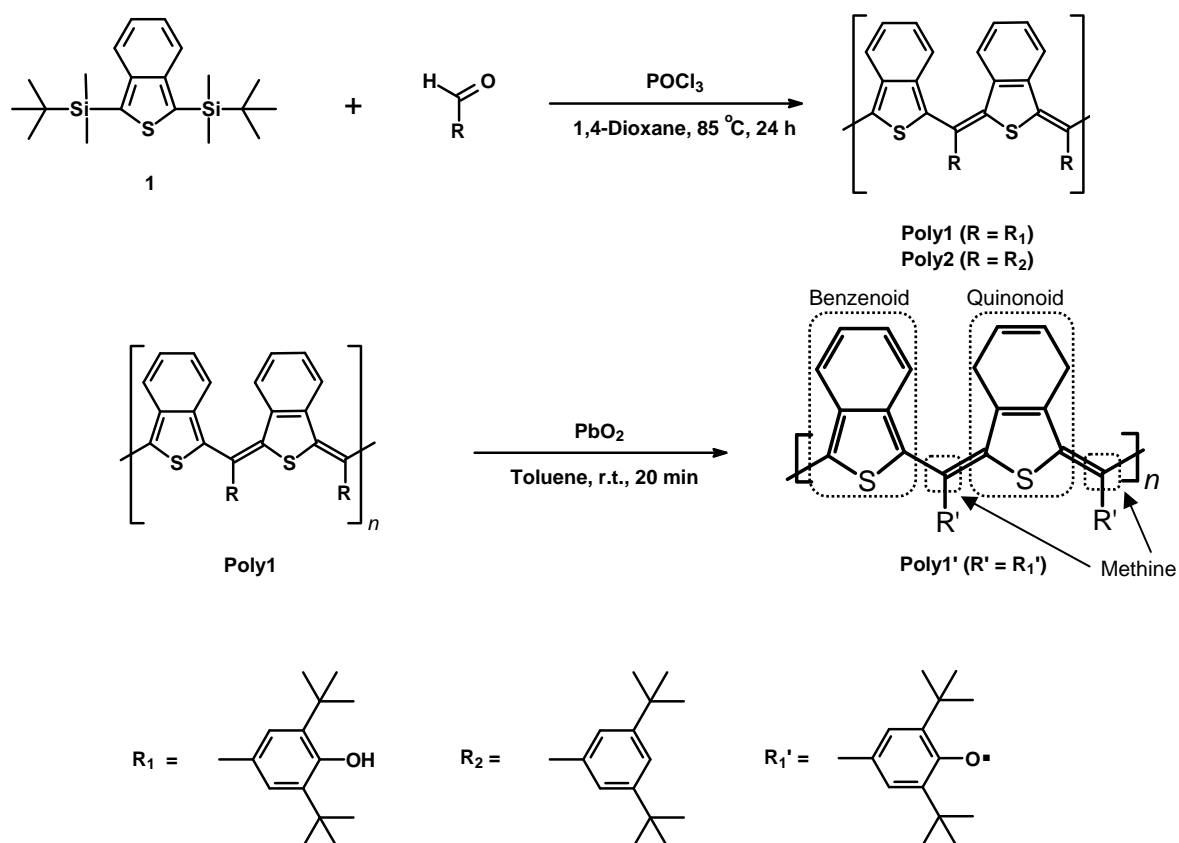
polymer	FT-IR (cm <sup>-1</sup> )	FT-Raman (cm <sup>-1</sup> )	polymer	FT-IR (cm <sup>-1</sup> )	FT-Raman (cm <sup>-1</sup> )
poly1	3431	1464	poly2	2955	1464
	2957	1444		2905	1444
	2909	1304		2865	1304
	2858	1170		1589	1170
	1630	990		1453	990
	1588	446		1391	446
	1393	251		1276	254
	1262			1193	
	1192			1146	
	1144			1047	
	1099			980	
	1044			874	
	976			843	
	807			741	
	743			711	
	517			441	
	441				



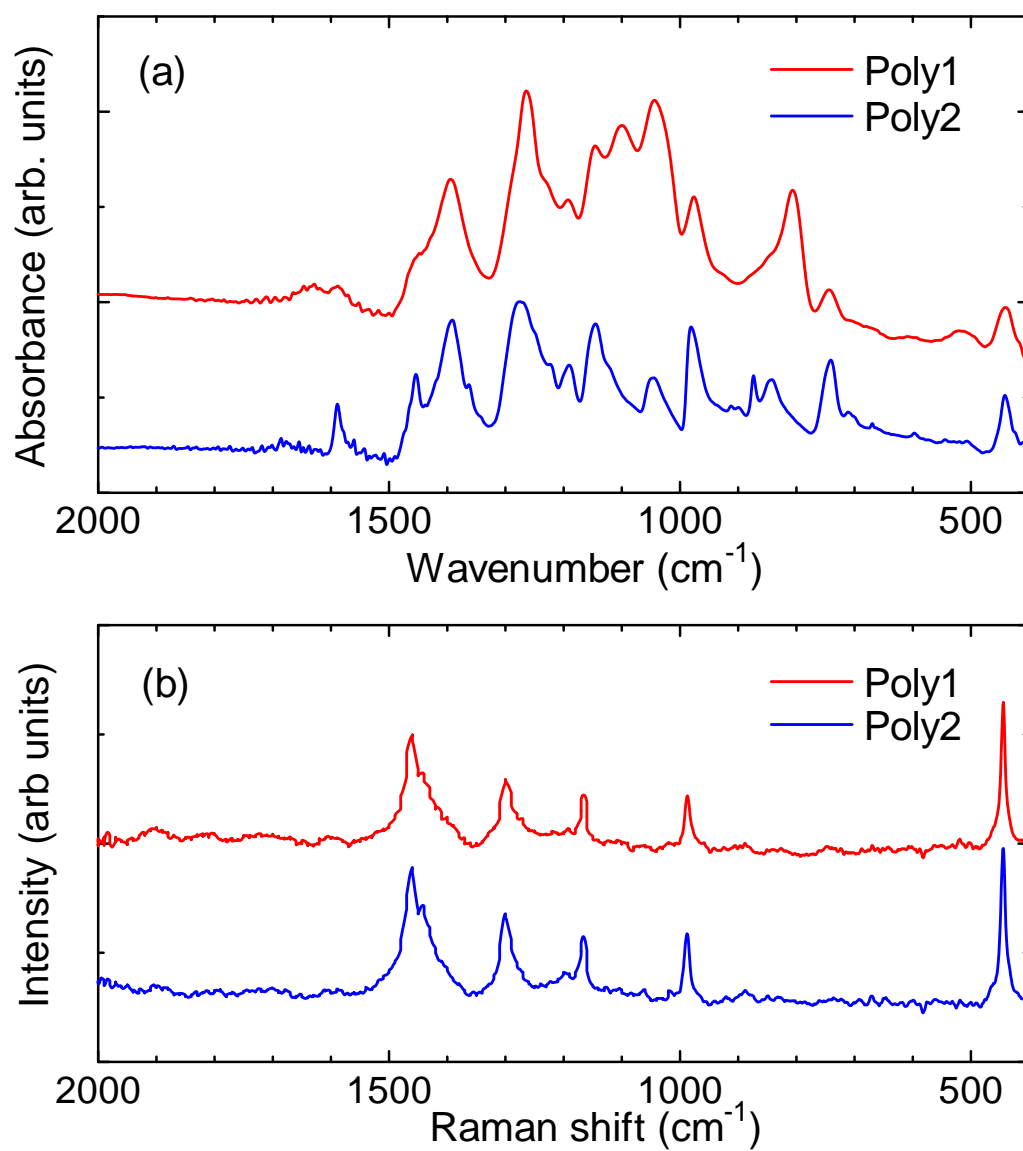
**Table 2** Molecular weights, UV-vis optical absorption spectroscopy, and cyclic voltammetry (CV) measurement results of poly1 and poly2

	$M_n^a$	$M_w^a$	$M_w / M_n$	$\lambda_{\max}$ (nm)	$E_g(\text{opt})^b$ (eV)	$E_{\text{ox/onset}}^c$ (V)	$E_{\text{HOMO}}^d$ (eV)	$E_{\text{red/onset}}^c$ (V)	$E_{\text{LUMO}}^e$ (eV)	$E_g(\text{CV})^f$ (eV)
poly1	2000	2980	1.5	673	1.32	0.59	−5.34	−1.08	−3.67	1.67
poly2	1440	1880	1.3	642	1.33	0.58	−5.33	−1.11	−3.64	1.69

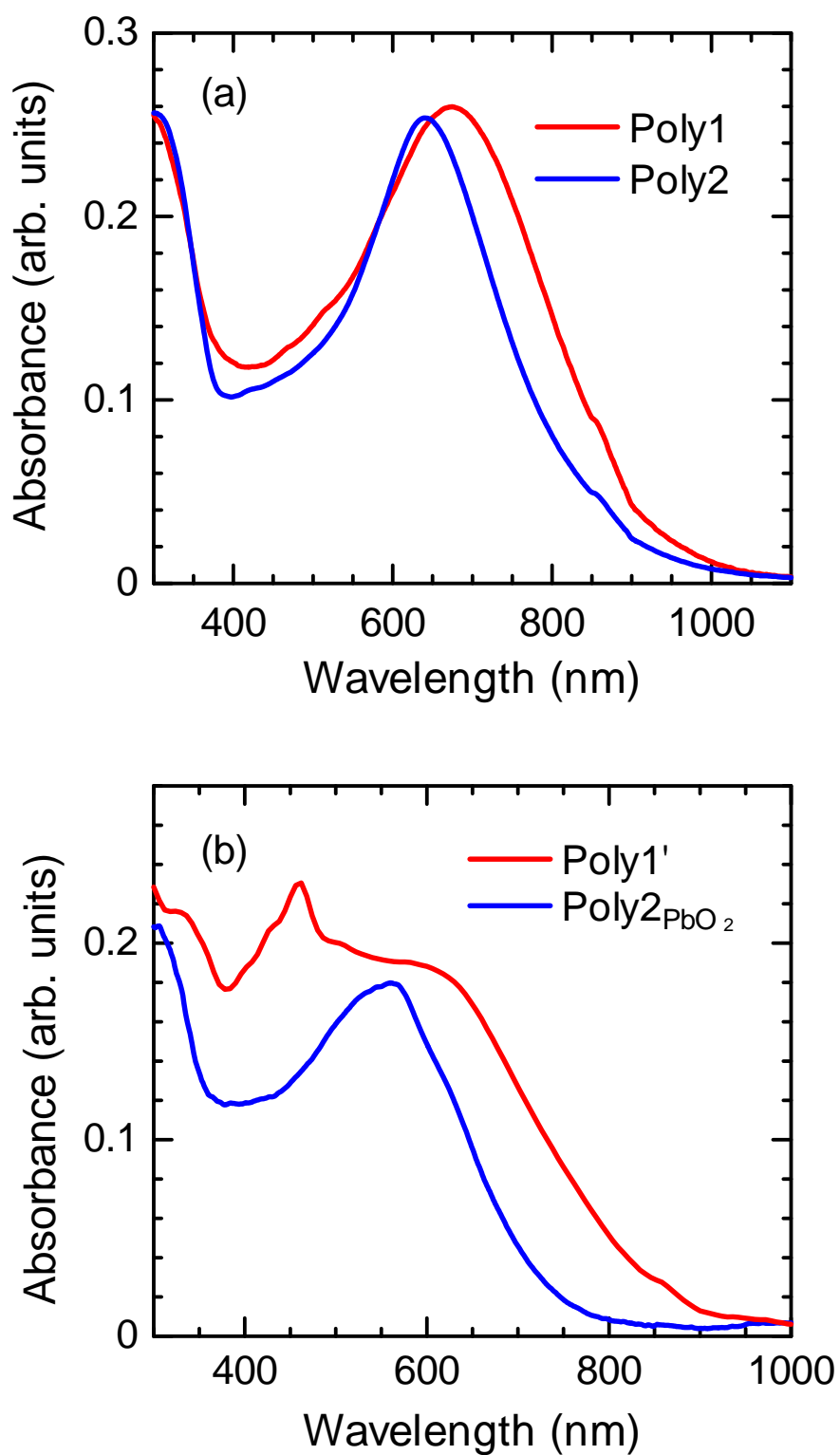
<sup>a</sup> Polystyrene standard, THF as the solvent. <sup>b</sup> Estimated from onsets of optical absorption spectra. <sup>c</sup> Calibrated against ferrocene. <sup>d</sup> Estimated from  $E_{\text{ox/onset}}$ . <sup>e</sup> Estimated from  $E_{\text{red/onset}}$ . <sup>f</sup> Estimated from  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ .



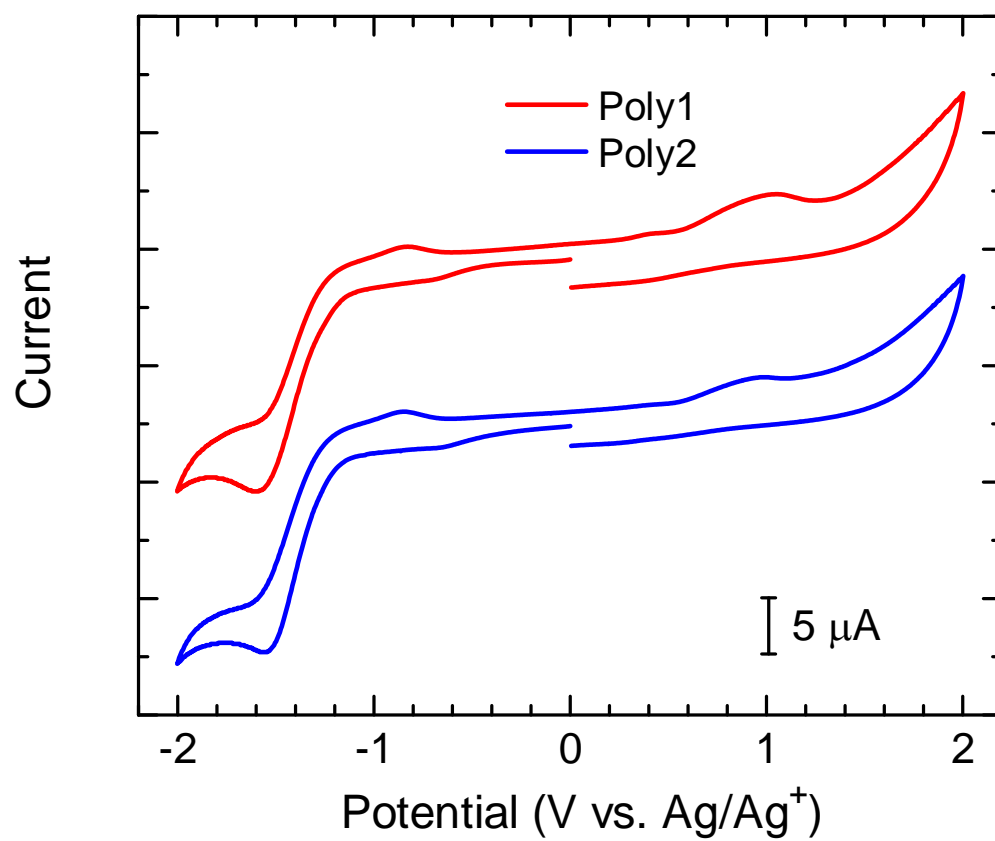
**Scheme 1** Synthetic routes to poly(isothianaphthene methine)s



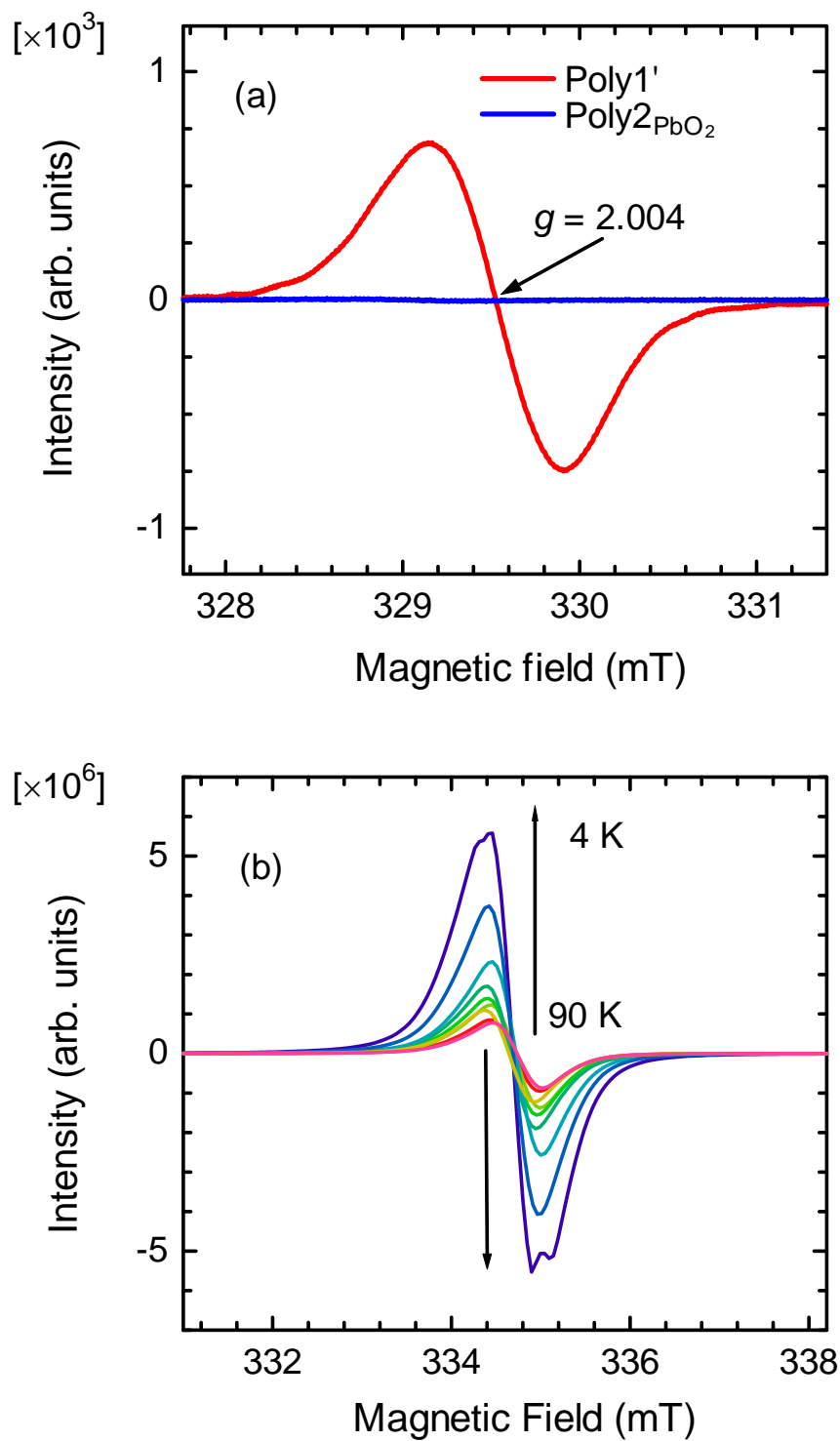
**Fig. 1** FT-IR spectra (a) and FT-Raman spectra (b) of poly1 and poly2



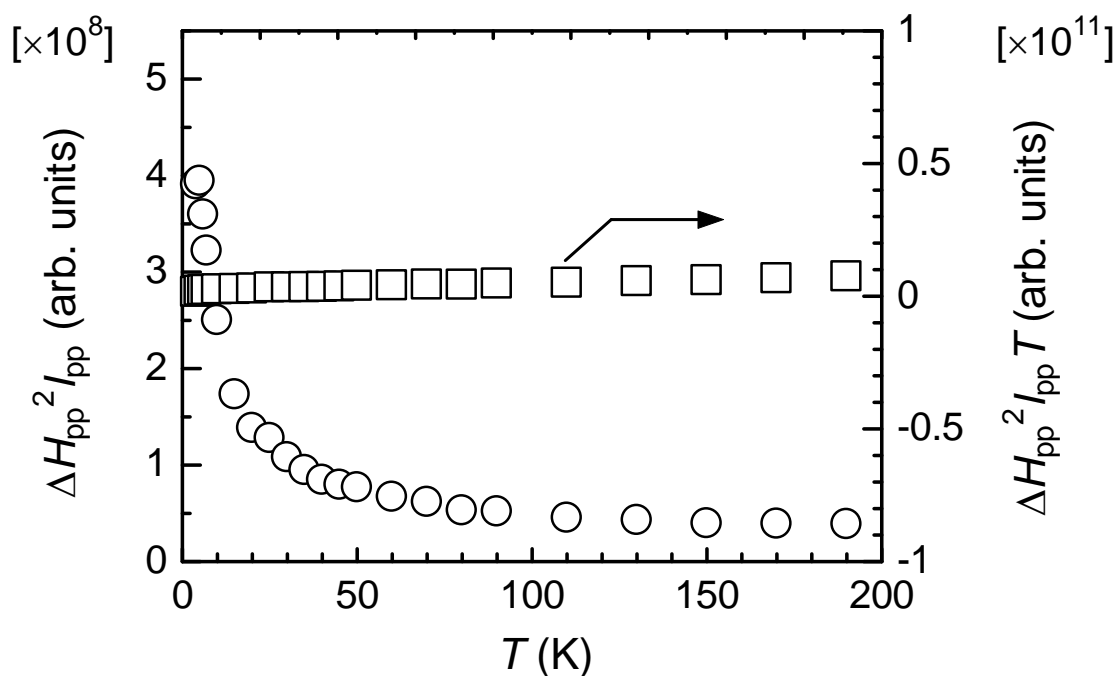
**Fig. 2** (a) UV-vis absorption spectra of poly1 and poly2. (b) UV-vis absorption spectra of poly1' and poly2 after oxidation with PbO<sub>2</sub> (poly2<sub>PbO<sub>2</sub></sub>)



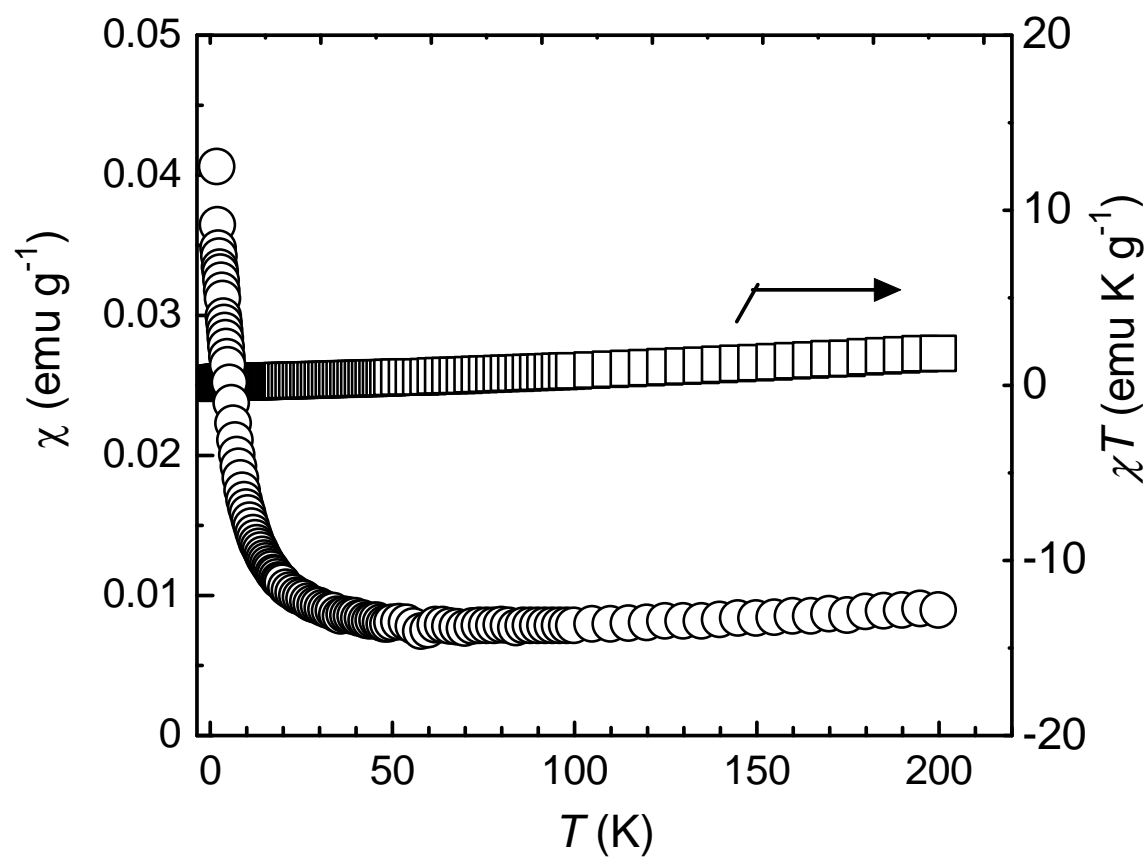
**Fig. 3** Cyclic voltammograms of poly1 and poly2 cast films on a platinum working electrode



**Fig. 4** (a) ESR spectra of poly1' and poly2<sub>PbO<sub>2</sub></sub> at room temperature. (b) ESR spectra of poly1' at 4 – 90 K under a vacuum atmosphere



**Fig. 5**  $\chi$  ( $\Delta H_{pp}^2 I_{pp}$ ) vs.  $T$  plots (circles) and  $\chi T$  ( $\Delta H_{pp}^2 I_{pp} T$ ) vs.  $T$  plots (squares) for poly1' obtained with ESR



**Fig. 6**  $\chi$  vs.  $T$  plots (circles) and  $\chi T$  vs.  $T$  plots (squares) for poly1' obtained with SQUID (1 T)