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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 $POCl_3$. 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_2 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.

Introduction

π-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 polyisothianaphtene and stable radial groups for creation of low-bandgap π-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

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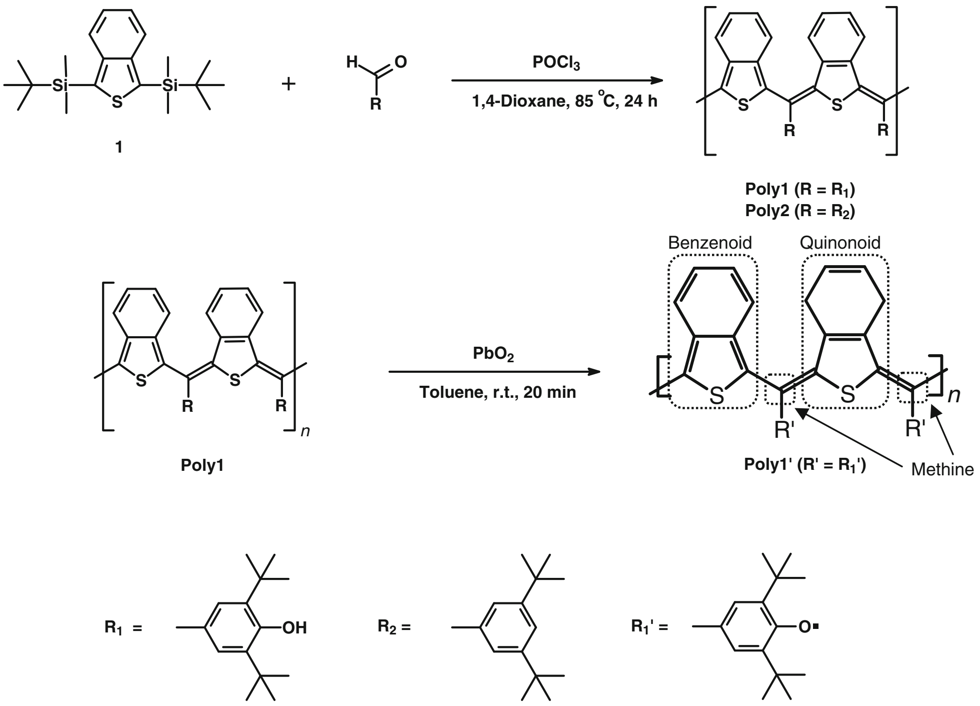
(CV) measurements were carried out by repeated potential cycling using an ECO CHEMIE µAUTOLAB TYPE III. The three electrode system consists of a platinum disc working electrode, an Ag/Ag$^+$ reference electrode, and a platinum wire counter electrode. CV measurements were performed using electrolytic 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 $CuSO_4{\cdot}5H_2O$ as the internal standard. Magnetic susceptibility measurement for the polymer was performed with a Quantum Design MPMS-3 SQUID magnetometer (±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 $POCl_3$ (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 $POCl_3$ (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_2 (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



Scheme 1 Synthetic routes to poly(isothianaphthene methine)s

(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 $\mathrm{cm^{-1}}$ which corresponds to O–H stretching was observed in poly1, while poly2 showed no signal around 3431 $\mathrm{cm^{-1}}$. 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 and 1589 $\mathrm{cm^{-1}}$, respectively [16].

Figure 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.

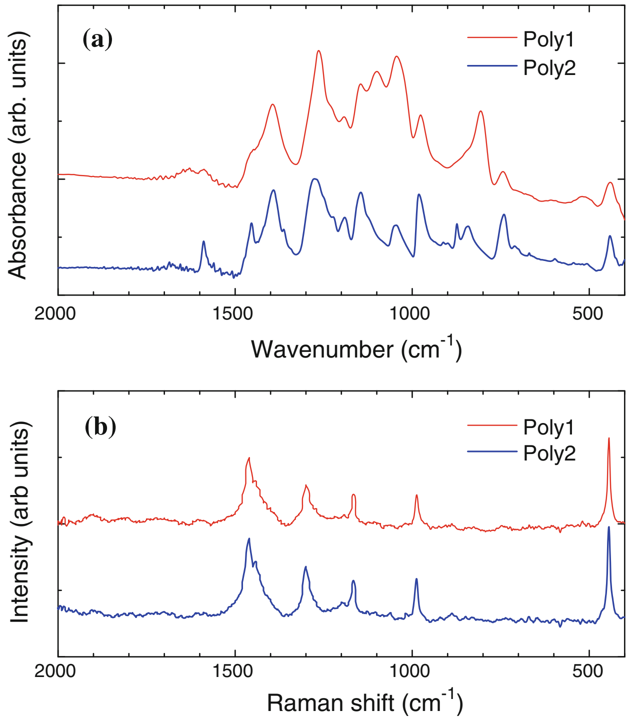


Fig. 1 FT-IR spectra (**a**) and FT-Raman spectra (**b**) of poly1 and poly2

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

Polymer	FT-IR ($\mathrm{cm^{-1}}$)	FT-Raman ($\mathrm{cm^{-1}}$)
Poly1	3431	1464
	2957	1444
	2909	1304
	2858	1170
	1630	990
	1588	446
	1393	251
	1262	
	1192	
	1144	
	1099	
	1044	
	976	
	807	
	743	
	517	
	441	
Poly2	2955	1464
	2905	1444
	2865	1304
	1589	1170
	1453	990
	1391	446
	1276	254
	1193	
	1146	
	1047	
	980	
	874	
	843	
	741	
	711	
	441	

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 $\mathrm{CHCl_3}$ 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.

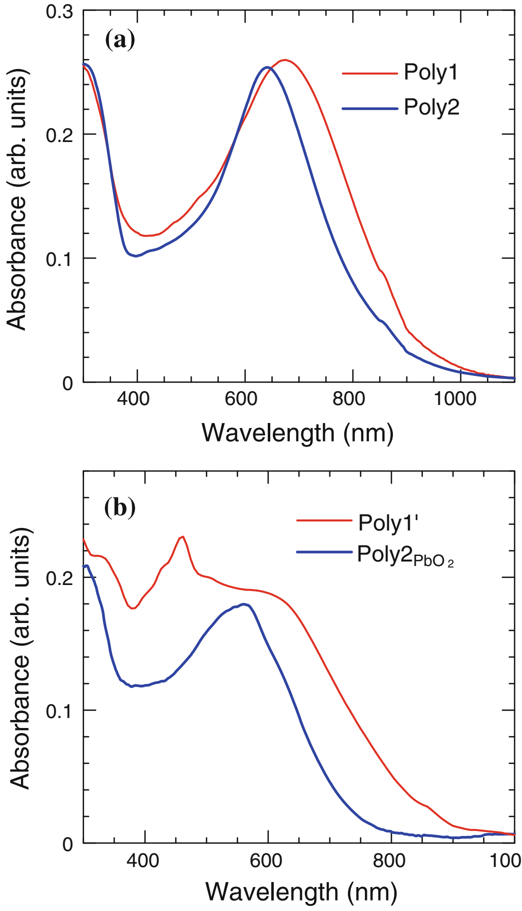


Fig. 2 **a** UV–vis absorption spectra of poly1 and poly2. (**b**) UV–vis absorption spectra of poly1′ and poly2 after oxidation with PbO_2 (poly2_{PbO_2})

Figure 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]. Figure 2b shows absorption spectra of poly2_{PbO_2} after treatment with PbO_2 as a reference (no oxyradical). The absorption spectrum of poly2_{PbO_2}, 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

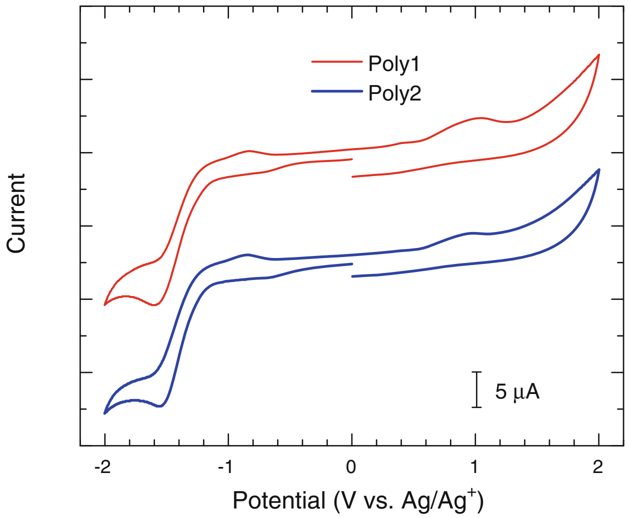


Fig. 3 Cyclic voltammograms of poly1 and poly2 cast films on a platinum working electrode

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 $E_{ox/onset} = 0.55$ V (vs. Ag/Ag$^+$), and a reduction peak with an onset of $E_{red/onset} = -1.12$ V(vs. Ag/Ag$^+$) 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$^+$. The onset oxidation potential of Fc/Fc$^+$ measured in the solvent was −0.04 V vs. Ag/Ag$^+$, thus $E_{ox/onset}$ and $E_{red/onset}$ 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$^+$) 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$^+$). For example, the HOMO energy (E_{HOMO}) and the LUMO energy (E_{LUMO}) of poly1 can be estimated as $E_{HOMO} = -(E_{ox/onset} + 4.75)$, and $E_{LUMO} = -(E_{red/onset} + 4.75)$, respectively. The bandgap E_g (CV) is also estimated to be E_g (CV) = $E_{LUMO} - (E_{HOMO})$. From these calculations E_g (CV) is estimated to be 1.67 eV. This bandgap E_g (CV) is slightly higher than the bandgap of poly1 estimated from the UV–vis optical absorption spectroscopy (E_g (opt) = 1.32 eV).

Magnetic properties

Figure 4a shows electron spin resonance (ESR) spectra of poly1′ and poly2_{PbO_2}. 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

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	λ_{max} (nm)	E_g (opt)^b (eV)	$E^c_{ox/onset}$ (V)	E^d_{HOMO} (eV)	$E^c_{red/onset}$ (V)	E^e_{LUMO} (eV)	E_g (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

[a] Polystyrene standard, THF as the solvent

[b] Estimated from onsets of optical absorption spectra

[c] Calibrated against ferrocene

[d] Estimated from $E_{ox/onset}$

[e] Estimated from $E_{red/onset}$

[f] Estimated from E_{HOMO} and E_{LUMO}

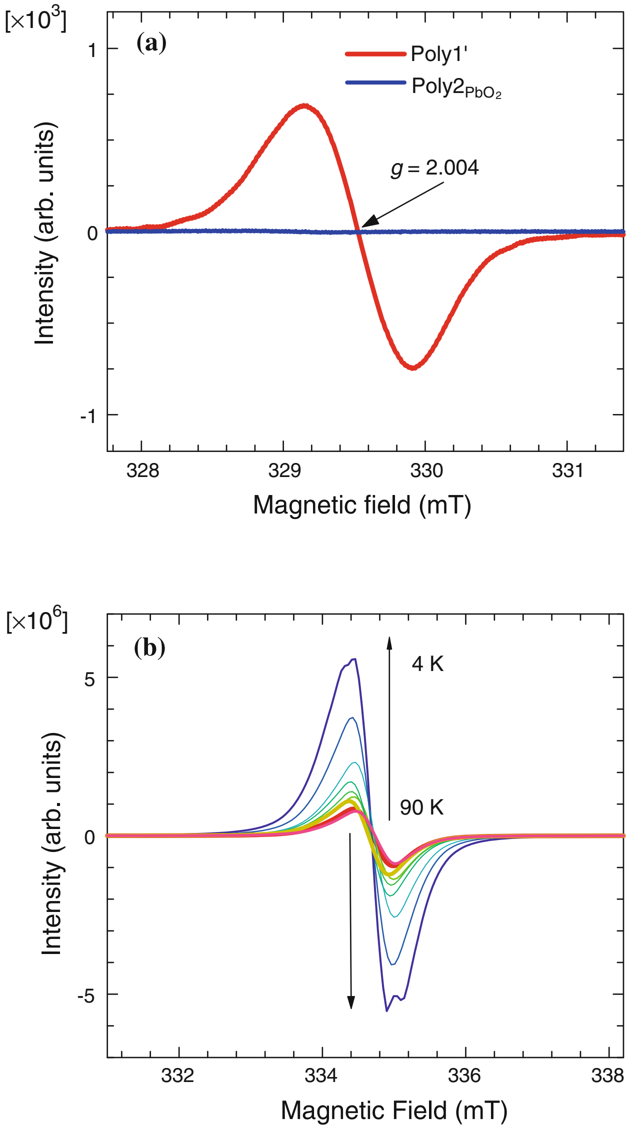


Fig. 4 **a** ESR spectra of poly1′ and poly2$_{PbO_2}$ at room temperature. **b** ESR spectra of poly1′ at 4–90 K under a vacuum atmosphere

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_2 affords no charge career 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. Figure 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 (χ) can be estimated from an ESR spectrum. The χ is given as follows:

$$\chi = C\Delta H_{pp}^2 I_{pp} \tag{1}$$

where ΔH_{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 χ theoretically depends on a temperature (T) followed the Curie–Weiss law,

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

here C_{curie} is the Curie constant, and θ is the Weiss constant.

The χ (estimated from $\Delta H_{pp}^2 I_{pp}$) vs. T plots and the χT (estimated from $\Delta H_{pp}^2 I_{pp} T$) vs. T plots for the poly1′ are shown in Fig. 5. χ decreases with the temperature. This result is observable for general magnetic materials. χT 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. χ value decreases with temperature, whereas χT is almost constant. These are the same trend as these of the ESR results, suggesting the polymer show paramagnetic behavior. However, χ^{-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.

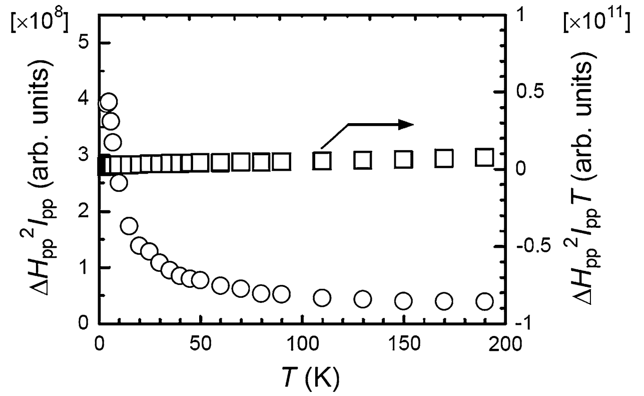


Fig. 5 χ ($\Delta H_{pp}^2 I_{pp}$) vs. T plots (*circles*) and χT ($\Delta H_{pp}^2 I_{pp} T$) vs. T plots (*squares*) for poly1′ obtained with ESR

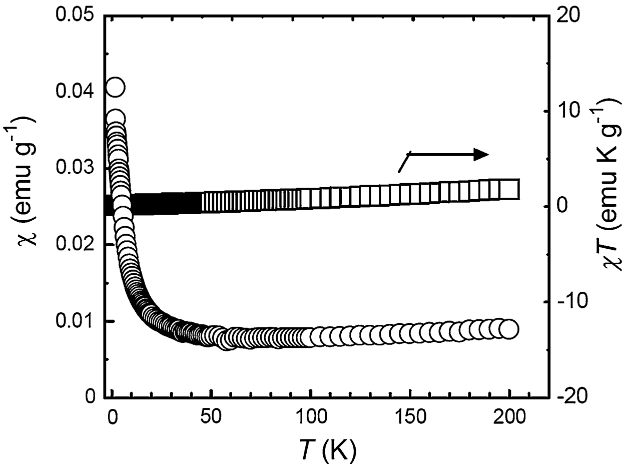


Fig. 6 χ vs. T plots (*circles*) and χT vs. T plots (*squares*) for poly1′ obtained with SQUID (1 T)

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 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 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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