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Poly(5-*tert*-butyl)benzothiophene: a soluble form of polyisothianaphthene with a large nonlinear optical response

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A soluble form of polybenzothiophene has been produced and chemically characterised. NMR spectroscopy indicates that there is a large quinoidal character contribution to the ground state of the polymer. The third order nonlinear optical properties of the polymer have been probed and it is found that the response is relatively large in the near-infrared region.

The third order nonlinear optical properties of conjugated organic semiconducting polymers have been the subject of much investigation for the past 15 years. It is expected that such materials will find use in optical switching devices based on planar waveguides.[1]

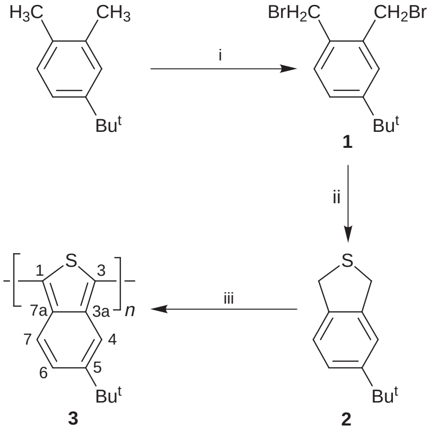
Many different classes of such polymers have been investigated[2] in the search for a material which exhibits a sufficiently large third order nonlinear optical response for use in all optical switching devices. To date, a material which meets all device requirements has still not been identified. For certain applications within telecommunications, materials which exhibit a large and fast third order nonlinearity in the region of 1.3–1.5 μm are required.

More recently, conjugated molecules with absorption in the near-infrared region have attracted attention since it is hoped that the nonlinear optical response will be relatively large. Polyisothianaphthene (PITN) (or polybenzothiophene) is just such a material. It was first produced some years ago in an insoluble form[3] and has been shown to possess a small bandgap[4] (*ca.* 1 eV).

The absence of soluble forms of this polymer has however precluded any study of its nonlinear optical properties in solution or high quality thin film forms. Recently, Pomerantz *et al.* reported the synthesis of a soluble form of a similar polymer in a preliminary communication.[5]

We report here on the synthesis and optical (both linear and nonlinear) characterisation of another soluble form of this polymer, namely, poly(5-*tert*-butyl)benzothiophene.

The route employed to synthesise this polymer is depicted in Scheme 1. The key intermediate **1** was produced by the method of Hanack[6] and the product isolated by careful low pressure distillation. The dihydro precursor **2** was synthesised using the method previously reported for the unsubstituted derivative.[7] The polymerisation is catalysed by 1 equiv. of $FeCl_3$[8].



Scheme 1 *Reagents and conditions*: i, NBS, CCl_4, reflux, 1 h, then room temp., 18 h; ii, Na_2S, EtOH, reflux, 1 h; iii, $FeCl_3$, $CHCl_3$, 50 °C, dry air, 72 h.

NMR analysis of **3** is in good agreement with values reported for PITN[9] and suggests that there is a large degree of quinoidal character in the ground state. The ^1H NMR analysis serves to confirm this observation, the broad signal at δ 8.2–8.6 being assigned to the deshielded environment of the proton attached to carbon 6 (see Scheme 1). The broadness of the signals may also be explained by this observation since a large contribution of quinoidal structure serves to 'rigidise' the polymer backbone, decreasing freedom of rotation about the bonds connecting repeat units.

The product polymer is soluble in polar organic solvents such as chloroform, THF or toluene. Fig. 1 shows the visible/near-infrared absorption spectrum of a 1 g l^{-1} solution of the polymer in chloroform.

The broad absorption shows several vaguely defined shoulders probably indicating a large degree of coupling between electronic transitions and vibrational levels. Temperature dependent absorption studies currently in progress will yield further information regarding this point. An estimate of the optical gap from this spectrum gives $E_g = ca.$ 1.1 eV. This value is in close agreement with that reported by Pomerantz *et al.*[5] and is marginally greater than the value originally reported for the insoluble form.[3]

The experimental method used to determine the microscopic third order nonlinear optical coefficient (γ) of a compound at 1064 nm in solution is described in detail elsewhere.[10] It is based on self-diffraction from transient laser-induced diffraction gratings. Under thin grating conditions,[11] an expression relating the diffraction efficiency, η into the first order, to the

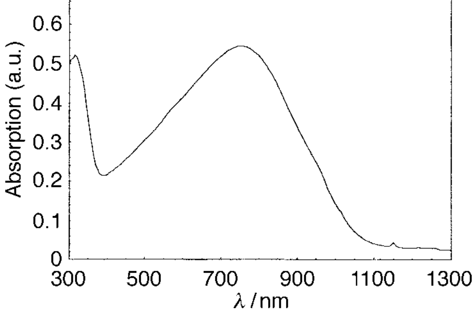


Fig. 1 Electronic absorption spectrum of **3**.

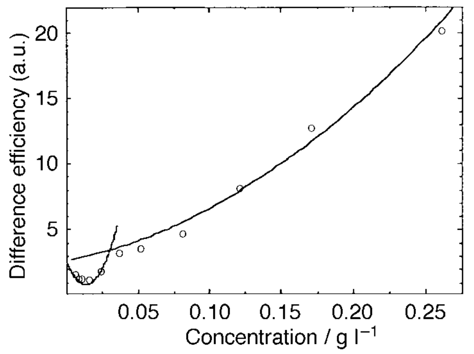


Fig. 2 Concentration dependence of the laser induced grating diffraction efficiency for **3**.

third order material nonlinearity $\chi^{(3)}$ is valid [eqn. (1)],

$$|\chi^{(3)}| = 4\ \varepsilon_o c\ n^2\ \lambda\ \sqrt{\eta}/(3\ \pi\ d\ I_o) \qquad (1)$$

where c is the speed of light, ε_o is the permittivity of free space, n is the refractive index of the sample, d is the sample thickness and I_o is the input pulse intensity. In the experiments reported here, $d = 1$ mm and n is taken to be the refractive index of the solvent, because of the low fractional volume of solute.

The third order nonlinearity $\chi^{(3)}$ for a solvent/solute mixture may be expressed as shown in eqn. (2),

$$|\chi^{(3)}| = [(\chi^{(3)}{}_{\mathrm{solv}} + \mathrm{Re}\ \chi^{(3)}{}_{\mathrm{sol}})^2 + (\mathrm{Im}\ \chi^{(3)}{}_{\mathrm{sol}})^2]^{1/2} \qquad (2)$$

where Re $\chi^{(3)}{}_{\mathrm{sol}}$ and Im $\chi^{(3)}{}_{\mathrm{sol}}$ are the real and imaginary components of the material nonlinearity. By determining the concentration dependence of $|\chi^{(3)}|$, the contribution from $\chi^{(3)}{}_{\mathrm{solv}}$ may be extracted and the magnitude of Re $\chi^{(3)}{}_{\mathrm{sol}}$ and Im $\chi^{(3)}{}_{\mathrm{sol}}$ may be determined. Furthermore, the sign of Re $\chi^{(3)}{}_{\mathrm{sol}}$ may be determined from the concentration dependence of the real part of $|\chi^{(3)}|$.

The γ values of a solute may then be derived [eqn. (3)],

$$\gamma = |\chi^{(3)}|/(N_A\ C\ L_L{}^4) \qquad (3)$$

where C is the molecular concentration (for polymer samples, the repeat unit concentration), N_A is Avogadro's constant and L_L is the Lorentz local field factor, which is taken to be that of a linear molecule (*i.e.* $L_L = 1$).[12].

Fig. 2 shows the concentration dependence of the diffraction efficiency. As already described, theory predicts a parabolic dependence. It is clear however that there is a deviation from such a dependence in this case. At low concentration, the dependence on diffraction efficiency is parabolic. At a certain limit, however, this dependence begins to deviate before returning at higher concentrations to a second parabolic dependence. Such behaviour is not well understood but is clearly due to some form of electronic interaction between polymer chains.

The values of γ measured for **3** from fitting data in the low concentration region are given in Table 1. The γ values obtained for **3** are remarkably high in comparison to other polymers. In comparison to a polythiophene (a structural relative), for example, the values are one order of magnitude greater. This is thought to be due to relatively closer positioning of the electronic absorption band to the wavelength of measurement.

In summary, a soluble form of polyisothianaphthene has been synthesised and characterised. The optical properties of the polymer show that the material possesses a small gap, slightly larger than that of the insoluble form. It is also likely from these spectra that there is a strong degree of coupling between electronic transitions and vibrational states. This last point is the subject of further investigations.

Table 1 Values of γ for **3** compared to those of a polythiophene (ref. 13).

Compound	γ_{Re} (esu)	$\lvert\gamma\rvert_{\mathrm{Im}}$ (esu)	$\lvert\gamma\rvert$ (esu)
3	-7.2×10^{-32}	21.5×10^{-32}	22.7×10^{-32}
Poly(3-butyl)thiophene	-4.3×10^{-33}	7.2×10^{-33}	8.4×10^{-33}

The microscopic nonlinear optical response is larger than that of comparable molecules and polymers. This is most likely due to the closer position of the absorption band to the measurement wavelength.

Experimental

All solvents were dried prior to use using standard methods. All reactions were carried out in an argon atmosphere unless otherwise stated. NMR spectra were recorded on a Bruker MSL 300 spectrometer and TMS was used as an internal reference. IR spectra were recorded on a Nicolet 510-P FTIR spectrometer. GPC analysis was performed using a Waters 600t system.

4-*tert*-Butyl-1,2-dimethylbenzene

106.2 g (1 mol) *o*-Xylene and 92.1 g (1 mol) *tert*-butyl chloride were well mixed (magnetic stirrer). 1.1 g Anhydrous ferric chloride was added slowly (30 min) at room temperature. When the evolution of hydrogen chloride had ceased, excess *tert*-butyl chloride (20.5 g) was added and the mixture stirred for a further 1 h. It was then heated in a water bath for 15 min (turning brown at approx. 65 °C) and filtered through charcoal (125 g). The resulting yellow solution was distilled and various fractions of colourless liquid were collected (bp 155–175, 185–200 and 205–210 °C). The highest boiling fraction was found to be 4-*tert*-butyl-1,2-dimethylbenzene. Yield: 90.6 g (55.8%); δ_H(300 MHz, $CDCl_3$) 1.3 (s, 9H), 2.2 (s, 3H), 2.25 (s, 3H), 7.1 (m, 3H).

1,2-Bis(bromomethyl)-4-*tert*-butylbenzene 1

8.125 g 4-*tert*-Butyl-*o*-xylene (0.05 mol), 17.8 g *N*-bromosuccinimide (0.1 mol), 0.2 g benzoyl peroxide and 50 ml dry carbon tetrachloride were placed in a 250 ml round-bottomed flask and refluxed with magnetic stirring in the dark under argon for 3 h. The mixture was left overnight at room temperature (under argon), then it was filtered (to remove succinimide salts) and concentrated *in vacuo*. The product was collected by vacuum distillation (bp 116–118 °C at 0.12 mmHg). Yield: 4.66 g (29%); δ_H(300 MHz, $CDCl_3$ 1.31 (s, 9H), 4.79 (s, 2H), 4.81 (s, 2H), 7.40 (m, 2H), 7.55 (d, 1H); δ_C($CDCl_3$) 30.53 and 30.56 (CH_2Br), 31.03 (CH_3), 34.86 (Me_3C), 126.83 (CH), 128.66 (CH), 131.53 (CH), 134.39 (quaternary C), 136.88 (quaternary C), 152.95 (quaternary C).

1,3-Dihydro-5-*tert*-butylisothianaphthene 2

1.05 g (0.013 mol) Anhydrous sodium sulfide was dissolved in 75 ml dry ethanol in a 250 ml round-bottomed two-necked flask fitted with a magnetic stirrer and condenser. 3.98 g (0.012 mol) 1,2-Bis(bromomethyl)-4-*tert*-butylbenzene was added dropwise during 30 min. The solution went from pale blue to bright yellow. It was refluxed for 1 h and the ethanol removed *in vacuo*. The remaining brown–black oil was dissolved in CH_2Cl_2 and filtered to remove sodium bromide. The CH_2Cl_2 was removed *in vacuo* and the final product obtained by vacuum distillation (bp 88 °C at 6×10^{-2} mmHg). Yield: 1.53 g (64%); δ_H(300 MHz, $CDCl_3$) 1.33 (s, 9H), 4.25 (s, 2H), 4.28 (s, 2H), 7.18 (dd, 1H), 7.26 (dd, 1H), 7.29 (s, 1H); δ_C($CDCl_3$) 31.30 (CH_3), 34.49 (Me_3C), 37.67 (CH_2), 38.16 (CH_2), 121.41 (CH), 123.97 (CH), 129.32 (CH), 137.38 (quaternary C), 140.28 (quaternary C), 150.02 (quaternary C)(Calc.

for $C_{12}H_{16}S$: Theory: C, 74.94; H, 8.39; S, 16.28. Found: C, 74.71; H, 8.52; S, 16.46%).

Poly (5-*tert*-butyl-1,3-dihydroisothianaphthene) 3

0.7 g (3.6 mmol) 5-*tert*-Butyl-1,3-dihydroisothianaphthene was placed into a three-necked flask equipped with condenser and drying tube, dropping funnel and inlet for dry air. 0.5 g Anhydrous ferric chloride dissolved in 50 ml chloroform was added (20 min). The solution was warmed to 50 °C and stirred for 24 h, with air bubbling through. The resulting black solution was then washed with water to remove $FeCl_3$. Concentrated ammonia (20 ml) was added and the solution stirred for 30 min at room temperature. It was washed several times with water and dried over magnesium sulfate. The solvent was removed *in vacuo* and the low molecular weight fractions removed by Soxhlet extraction with methanol. Yield: 0.25g (36.5%). The experiment was repeated using monomer recovered from the methanol wash giving a total yield of 53.1%. GPC measurement indicated a high molecular weight for the product: $M_w = 49\,362$; $M_n = 10\,842$; $\delta_H(CDCl_3)$ 0.9–1.7 (9H), 7.1–7.6 (2H), 8.2–8.6 (1H); $\delta_C(CDCl_3)$ 30–33, 36–38, 120–127, 137–143; $\nu_{max}(KBr)/cm^{-1}$ 1686, 1595, 1545, 1480, 1458, 1410, 1362, 1254, 1140, 1003, 943 and 843 (Calc. for $C_{12}H_{12}S$: C, 76.57; H, 6.42; S, 17.01. Found: C, 76.06; H, 6.66; S, 17.11%).

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