JOURNAL OF Materials CHEMISTRY

Poly[3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene)]: electrically conducting and fluorescent polymers incorporating a rigid acetylenic spacer

Siu-Choon Ng,[*a] **Teng-Teng Ong**[a] **and Hardy S. O. Chan**[a,b]

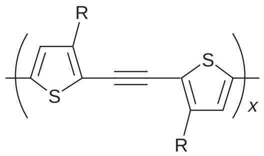
[a] *Department of Chemistry, National University of Singapore, Singapore 119260.*
[†] *E-mail: chmngsc@leonis.nus.edu.sg*
[b] *Department of Material Science, National University of Singapore, Singapore 119260*

Received 27th July 1998, Accepted 2nd September 1998

A series of poly[3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene)]s, comprising a rigid carbon–carbon triple bond between two bithiophene repeating units, were synthesized. The improved rigidity of the polymer backbone led to an increased fluorescent quantum yield in comparison to poly(3-alkylthiophene)s. A generic trend depicting decreasing Stokes shift in the fluorescence spectra with increasing pendant alkyl chain length was observed. The incorporation of the acetylenic spacer also resulted in a significant red shift in the absorption spectra in comparison to poly(3-alkylthiophene)s, corresponding to an increase in effective conjugation over the entire series of polymers. These polymers, upon doping with iodine or ferric chloride, gave electrical conductivity in the range of 10^0 to 10^{-4} S cm^{-1}. Thermochromism studies showed a blue shift in absorption peak as the temperature changes from 25 to 180 °C. The influence of alkyl chain length and the acetylenic spacer on the conductivity and UV–VIS absorption is also discussed. *In situ* electrochemical doping studies were monitored using UV–VIS–near infrared absorption spectroscopy and showed the evolution of polaron bands at around 1.4 eV.

Poly(3-alkylthiophene)s remain attractive candidates for research studies on account of their good chemical stability, processability and high conductivity in the doped state.[1–3] Recently, numerous reports on the light emitting properties of poly(3-alkylthiophene)s[4–8] have aroused our interest in this burgeoning field of research. An ideal organic polymer light emitting diode (LED) should as a first requirement exhibit high fluorescence quantum yields, charge mobility, injection barriers and effective π–conjugation.[9–11] Whilst short chain oligomers are known to limit delocalization by diminishing the effective conjugation, they are nevertheless more rigid, which can result in reducing relaxation from the excited states through non-radiative process with consequently enhanced fluorescence.[12] Although numerous polythiophene derivatives with high fluorescent quantum yield (>50%)[13] have been reported, there has been relatively little research into thiophene-based polymers incorporating rigid acetylene spacers.[14] In conjunction with our ongoing research on structure–property correlation of functional and conducting polymers, we have synthesized a series of symmetrical 3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) monomers which upon chemical oxidative polymerization with $FeCl_3$ afforded polymers that exhibited both electrical conductivity and enhanced fluorescence on comparison with polythiophenes.

The incorporation of the acetylenic spacers into the polythiophene backbone is anticipated to offer several distinct advantages. Thus, they can act as rigid conjugative spacers linking two bithiophene repeating units through the 2,2′-positions on the same plane. The resulting polymer can be expected to afford a more planar conformation through diminished steric effects so that a maximum degree of delocalization of the π-electrons is achieved.[15] In addition, the rigid spacer which helps to minimize neighboring ring interactions in this series should result in a bathochromic shift in the UV–VIS absorption maxima with correspondingly reduced bandgap energy when compared to polythiophene or polyalkylthiophene analogues.[16,17] In regard to these favorable factors which an acetylenic spacer offers, we have successfully synthesized a series of 3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) polymers. We report here our efforts on the synthesis, characterization and properties of these materials.



PEBT	R = H
PDBEBT	R = Bu
PDHEBT	R = C_6H_{13}
PDOEBT	R = C_8H_{17}
PDDEBT	R = $C_{12}H_{25}$

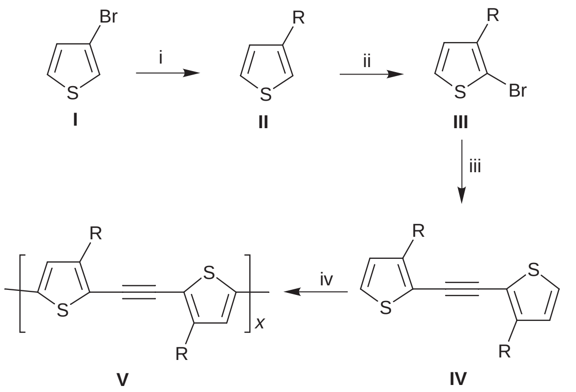
Experimental

Synthesis of monomers

Monomer syntheses were carried out in accordance with the generic approach depicted in Scheme 1. 3-Alkylthiophenes **II** were synthesised from 3-bromothiophene **I** by a nickel catalysed Grignard cross-coupling approach.[18] Bromination of **II** at the 2-position was effected using 1 equiv. of *N*-bromosuccinimide to afford 2-bromo-3-alkylthiophene **III** in nearly quantitative yield.[19] Thereafter a one-pot reaction of **III** with 2-methylbut-3-yn-2-ol in the presence of $Pd(PPh_3)_4$ as catalyst[20] afforded the symmetrical monomer **IV**.

2,2′-(Ethyne-1,2-diyl)bis(thiophene) (EBT)

A mixture of 2-bromothiophene (2.05 g, 12.6 mmol), 2-methylbut-3-yn-2-ol (1.06 g, 12.6 mmol), tetrakis(triphenylphosphine)palladium(0) (0.15 g, 0.333 mmol), benzyltriethylammonium bromide (0.099 g, 0.363 mmol) and cuprous iodide (0.097 g, 0.509 mmol) in 10 ml of benzene was deareated with N_2 for 15 min. Thereafter, aq. NaOH (5.5 M, 10 ml) was added. The resulting reaction mixture, which turned brown–black, was heated at reflux under a nitrogen atmosphere for 18 h, whence a second portion of 2-bromothiophene (2.08 g,



Scheme 1 *Reagents and conditions*: i, RMgBr, Et_2O, Ni(dppp)Cl_2 (cat.); ii, *N*-bromosuccinimide, chloroform, acetic acid, 30 min, 0 °C; iii, Pd(PPh_3)$_4$, 2-methylbut-3-yn-2-ol, benzene, reflux, 48 h; iv, $FeCl_3$, $CHCl_3$, 0 °C.

12.8 mmol) in benzene (10 ml) was added into the reaction mixture. After heating at reflux for a further 16 h, the reaction mixture was allowed to cool, followed by addition of aq. NH_4Cl (5.5 M, 50 ml); it was then stirred for 3 h at room temperature. The crude product was extracted with benzene and purified by flash chromatography to afford white needle shaped crystals in 54% yield; mp 99 °C (lit.,[20] 99.5–101 °C); δ_H(300 MHz, $CDCl_3$) 7.30 (2H, dd, $J_{2,4}=1.1$ Hz, $J_{3,4}=5.1$ Hz), 7.26 (2H, dd, $J_{2,4}=1.1$ Hz, $J_{3,4}=3.6$ Hz), 7.00 (2H, dd, $J_{3,4}=3.6$, $J_{2,3}=5.1$); *m*/*z* 190 (M^+, 100%), 145 (50) (Found: C, 63.3; H, 3.4; S, 33.0. Calc. for $C_{10}H_6S_2$: C, 63.1; H, 3.2; S, 33.6%).

3,3′-Dibutyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) (DBEBT)

Representative procedure. To a mixture of 2-methylbut-3-yn-2-ol (4.20 g, 50 mmol), 2-bromo-3-butylthiophene (11.03 g, 50 mmol), benzyltriethylammonium bromide (0.22 g, 1.02 mmol), cuprous iodide (0.22 g, 1.15 mmol) and tetrakis (triphenylphosphine)palladium (1.50 g, 1.28 mmol) in benzene (80 ml) under a nitrogen atmosphere was added aq. sodium hydroxide (5.5 M, 80 ml). The resulting black mixture was heated under reflux for 72 h whence a second portion of 2-bromo-3-butylthiophene (11.10 g, 50.0 mmol) in benzene (5 ml) was added and heating continued for another 48 h. Upon cooling, aq. ammonium chloride (100 ml) was added and the mixture stirred 3 h at room temperature. The organic phase is separated whilst the aqueous phase is extracted with benzene (2 × 80 ml). The combined organic phases were washed with deionised water (3 × 100 ml) and then dried ($MgSO_4$), whereupon after removal of the solvent the crude compound was obtained as a dark brown viscous liquid which was purified by vacuum distillation; [bp 168–170 °C (0.5 mmHg)] as a pale yellow liquid in 40% yield; δ_H(300 MHz, $CDCl_3$) 7.18 (2H, d, $J=5.1$ Hz), 6.88 (2H, d, $J=5.1$ Hz), 2.75 (4H, t, $J=7.5$ Hz), 1.69–1.32 (4H, m), 0.94 (6H, t, $J=7.5$ Hz); *m*/*z* 302 (M^+, 100%), 217 (97), 273 (60) (Found: C, 71.2; H, 7.2; S, 21.2. Calc. for $C_{18}H_{22}S_2$: C, 71.5; H, 7.3; S, 21.2%).

3,3′-Dihexyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) (DHEBT)

35% yield; bp 180–185 °C (0.2 mmHg); δ_H(300 MHz, $CDCl_3$) 7.20 (2H, d, $J=5.2$ Hz), 6.88 (2H, d, $J=5.2$ Hz), 2.74 (4H, t, $J=7.4$ Hz), 1.70–1.24 (12H, m), 0.87 (6H, t, $J=7.4$ Hz); *m*/*z* 358 (M^+, 100%), 301 (50), 217 (85) (Found: C, 73.8; H, 8.1; S, 18.4. Calc. for $C_{22}H_{30}S_2$: C, 73.7; H, 8.3; S, 17.8%).

3,3′-Dioctyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) (DOEBT)

40% yield; δ_H(300 MHz, $CDCl_3$), 7.19 (2H, d, $J=5.6$ Hz), 6.89 (2H, d, $J=5.6$ Hz), 2.73 (4H, t, $J=2.7$ Hz), 1.67–1.25 (24H, m), 0.86 (6H, t, $J=7.0$ Hz); *m*/*z* 414 (M^+, 100%), 329 (20), 217 (55) (Found: C, 75.1; H, 8.7; S, 15.4. Calc. for $C_{26}H_{38}S_2$: C, 75.3; H, 9.2; S, 15.5%).

3,3′-Didodecyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) (DDEBT)

31% yield; δ_H(300 MHz, $CDCl_3$), 7.18 (2H, d, $J=5.0$ Hz), 6.88 (2H, d, $J=5.0$ Hz), 2.74 (4H, t, $J=7.5$ Hz), 1.66–1.25 (40H, m), 0.87 (6H, t, $J=7.5$ Hz); *m*/*z* 526 (M^+, 100%), 385 (20), 217 (50) (Found: C, 78.0; H, 10.3; S, 11.7. Calc. for $C_{34}H_{54}S_2$: C, 77.5; H, 10.3; S, 12.1%).

Electrochemistry

Polymer films were grafted onto a platinum or an indium tin oxide (ITO) glass electrode *via* spin-coating using chloroform as solvent. Cyclic voltammetry of the polymers was conducted in a three-electrode single compartment electrochemical cell consisting of platinum foil as the working electrode, a platinum wire as the counter electrode and Ag/$AgNO_3$ (0.1 M using dry acetonitrile as solvent) as the reference electrode (0.34 V *vs.* SCE). CVs of polymers were studied under argon atmosphere using tetra-*n*-butylammonium fluoroborate (0.1 M) as electrolyte.

Chemical polymerization

General procedure. A solution of the monomer (0.1 M) in dry chloroform was added dropwise into a reaction vessel containing 4 equiv. of anhydrous ferric chloride at 0 °C for 1 h. Thereafter, polymerisation was terminated by adding an excess amount of methanol. The resulting polymer was subjected to Soxhlet extraction with methanol and then acetone in turn for 24 h each. The resulting polymer was dedoped by stirring the polymer powder in hydrazine hydrate–water (1 : 1 v/v) for 24 h to afford a deep red polymer powder which was dried *in vacuo*. The dedoped polymer was further extracted with chloroform for 4 h to obtain the soluble portion (*ca.* 10%) of the bulk polymer. The soluble portion was adopted for characterisation studies such as solution UV–VIS, fluorescence and nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC).

Chemical doping

Iodine doping of pressed pellets of dedoped polymers was effected by placing them in an iodine chamber for 1 week in the dark. The iodine uptake was monitored by progressive weight gain and increasing electrical conductivity. Solution doping was effected by stirring polymer powder (*ca.* 50 mg) in 0.1 M ferric chloride solution (*ca.* 50 ml) in anhydrous nitromethane under nitrogen for 1 h. Polymer pellets were observed to turn from deep red to deep green when doped.

Instrumentation

Elemental analysis of all monomer and polymer samples was performed at the NUS Microanalytical Laboratory on a Perkin-Elmer 240C elemental analyser for C, H, N and S determination. Halogen determinations were done either by ion chromatography or the oxygen flask method. FT-IR spectra were recorded for monomer and polymer dispersed in KBr disks using a Perkin-Elmer 1600 spectrometer. UV–VIS spectra were obtained for dilute solutions or thin polymer films deposited onto indium tin oxide coated glass plates on a Perkin-Elmer Lamda 900 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker ACF 300 FT-NMR spectrometer operating at 300 MHz, while ^{13}C NMR spectra were recorded at 62.9 MHz. Deuterated solvents were used as indicated and tetramethylsilane (TMS) was used as the internal reference. Mass spectra were obtained using a Micromass VG 7035E mass spectrometer at a source temperature of 200 °C and an ionising voltage of 70 eV. Thermogravimetric analyses (TGA) of polymer powders were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyser. A heating rate of 10 °C min^{-1} with an air flow of 75 ml min^{-1} was used. The runs were conducted from room temperature to 800 °C. Conductivity measurements were carried out on polymer pellets of known thickness using a four-point probe connected to a Keithley constant current source. Conductivities were calculated from at least 10 pairs of consistent readings taken at different points of the pressed pellet. Fluorescence measurements were conducted on a Shimadzu RF5000 spectrofluorophotometer using a xenon lamp as the light source. Standard polymer solutions dissolved in dry chloroform (10^{-5} M) were used for analysis and Coumarin (Aldrich) was used as the calibration standard. *In situ* electrochemical doping studies of polymers were carried out using an EG&G 263A potentiostat together with UV–VIS–near infrared spectrophotometer. GPC analyses were carried out using a Perkin-Elmer Model 200 HPLC system with Phenogel™ MXL and MXM columns (300 mm × 4.6 mm ID) calibrated using polystyrene standards and THF as eluent.

Results and discussion

Physical properties and structural characterization

Elemental composition of the neutral polymers as determined from microanalyses showed good agreement between the expected and calculated empirical formulae, with low iron and chloride contents (Table 1). Table 1 also summarizes the number average molecular weights (M_n) for the dedoped polymers as determined *via* GPC. These polymers have a polydispersity index (PDI) ranging from 1.3 to 1.8 and M_n values in the range 5400 to 6800, corresponding to the existence of 10–18 monomeric repeat units. As the molecular weights obtained from the soluble portion of the bulk polymers possibly represent only the lower molecular weight fractions, the insoluble fractions are expected to have higher molecular weights.[21] This series of polymers was found to be partially soluble (*ca.* 10%) in common organic solvents like chloroform, THF, DMF and DMSO. Purification of these polymers was carried out by first dissolving the polymer in solvent followed by precipitation from cold methanol. Although the soluble portion of these polymers only represents the lower molecular weight fractions, uniform solid thin films could be grafted onto ITO glass plates easily from chloroform solution and used for UV–VIS absorption, cyclic voltammetry, fluorescence spectroscopy and electrochemical doping studies. Currently, we are investigating ways of deriving a suitable polymerization route so as to synthesize higher molecular weight polymers that have good solubility in common organic solvents.

The chemical structure of the monomers and bulk polymers were studied in detail using FT-IR spectroscopy. The FT-IR spectra of the representative 3,3′-dibutyl-2,2′-(ethyne-1,2-diyl)-bis(thiophene) and its corresponding polymer PDBEBT both in its neutral and doped forms are shown in Fig. 1. The presence of the butyl pendants in the monomer is evident from C–H stretching at *ca.* 2850 and 2950 cm^{-1} due to CH_3 and CH_2 groups. A weak rocking bend due to CH_2 group at 718 cm^{-1} is also observed. The C≡C group manifests as a very low intensity stretching band at 2196 cm^{-1}. The thiophene ring depicts C–H stretching at 3101 cm^{-1} and C–H in-plane deformation at 1085 and 1237 cm^{-1}, whilst ring vibrational modes are seen at 1377, 1460, 1517 and 1598 cm^{-1}. The monomer also depict vibrational bands at 721 and 837 cm^{-1} which are ascribable respectively to the C–H_α and C–H_β out-of-plane bending modes of the thiophene rings.[22] In contrast, neutral PDBEBT shows a strong β-CH out-of-plane bend at 826 cm^{-1}, whilst the α-CH out-of-plane bend is relatively insignificant, suggesting that predominant α–α′ coupling of the thiophene ring is inherent in this polymer. Thiophene ring stretches at 1376, 1429, 1528, 1654 and 1718 cm^{-1} remain unchanged with respect to the monomer. The presence of two intense bands at 2852 and 2920 cm^{-1} suggests that the alkyl chain remains intact after polymerization. A weak stretching

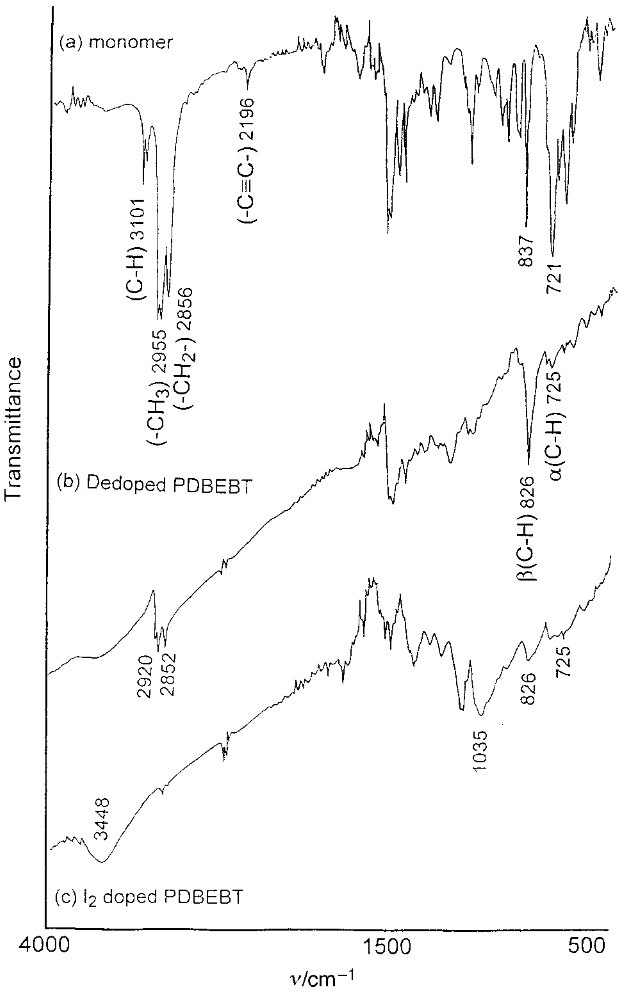


Fig. 1 FTIR of 3,3′-dibutyl-2,2′-(ethyne-1,2-diyl)bis(thiophene) and its corresponding polymer, PDBEBT: (a) monomer, (b) dedoped PDBEBT and (c) I_2 doped PDBEBT.

Table 1 Physical properties of polymers PEBT, PDBEBT, PDHEBT, PDOEBT, PDDEBT including GPC, elemental analysis and conductivity results

	GPC results				Elemental analysis	
Polymer	P_n	PDI	M_n	Conductivity (I_2 doped)/S cm^{-1}	Empirical formula	Found
PEBT	8	1.5	1523	1.5	$C_{10.0}H_{4.0}S_{2.0}$	$C_{10}H_{4.1}S_{2.0}$
PDBEBT	18	1.8	5500	0.03	$C_{18.0}H_{20.0}S_{2.0}$	$C_{18.0}H_{20.4}S_{2.1}$
PDHEBT	18	1.4	6500	0.002	$C_{22.0}H_{28.0}S_{2.0}$	$C_{22.0}H_{27.9}S_{2.1}$
PDOEBT	17	1.3	6900	0.001	$C_{26.0}H_{36.0}S_{2.0}$	$C_{26.0}H_{36.5}S_{2.1}$
PDDEBT	11	1.3	5400	0.0002	$C_{34.0}H_{52.0}S_{2.0}$	$C_{34.0}H_{51.3}S_{2.0}$

attributed to the C≡C group is also observed at 2210 cm^{-1}. The FT-IR spectrum of iodine-doped PDBEBT exhibits dramatic changes in the 1035 to 1438 cm^{-1} region. Here the IR bands are intensified and overlap to constitute a broad band. This broad band is assigned to doping-induced bands attributed to the vibrational modes in the anion-doped (charged transferred) thiophene rings.[23] The low intensity broad band at 3000 to 3800 cm^{-1} is characterized as weakly bonded O–H stretching due to absorbed moisture from the atmosphere.

Conductivity of doped polymers

The dedoped polymers upon doping with iodine or ferric chloride yielded electrical conductivity ranging from 10^0 to 10^{-4} S cm^{-1}. The graphical representation of the variation of conductivity with iodine uptake for the typical polymer PEBT is shown in Fig. 2. As summarised in Table 1, the conductivity of the unsubstituted polymer PEBT is highest followed by a trend of diminishing conductivity with increasing pendant alkyl chain length on going from PDBEBT to PDHEBT, PDOEBT and PDDEBT. These results are consistent with earlier reports by Kaeriyama *et al.*[24] in their study of polyalkylthiophene. It is observed experimentally that with increasing alkyl chain length, the rate of iodine uptake reflected from percentage weight change also decreases. This phenomenon is attributed to the increasing size of the alkyl group, which takes up more of the weight of the polymer, therefore the amount of iodine absorbed is correspondingly smaller. The rate of iodine uptake was found to be progressively slower from PDBEBT to PDDEBT, although the doping period (4 days) was kept consistent for all samples, implying that the doping efficiency was diminished. Elemental analysis of iodine-doped polymers showed that the concentration of I_3^- dopant also decreased on going from PDBEBT to PFHEBT, PDOEBT and PDDEBT. This reduction in rate of doping is largely assigned to significant steric hindrance towards the dopant molecules, which inhibits charge carrier formation during the doping process.[25]

Electronic (UV–VIS) and fluorescence spectroscopy

Standard polymer solutions of 10^{-5} M concentration in chloroform were used for UV–VIS and fluorescence spectroscopic measurements. Fluorescence measurements were compared with Coumarin 334 laser dye (Aldrich) which absorbs at 450 nm and emits at 490 nm. The calculation of fluorescence quantum yield of a solution sample (Φ_s) relative to a reference sample of known quantum yield (Φ_r) is related to eqn. (1),[26]

$$\Phi_s = \Phi_r\ [(A_r/A_s) \times (I_s/I_r)] \qquad (1)$$

where A_s and A_r are the absorbencies of the sample and reference solutions and I_r and I_s are the corresponding relative integrated fluorescence intensities. Table 2 summarises the electronic absorption and emission maxima and the respective polymer fluorescent quantum yields relative to Coumarin 334 laser dye. There is generally little difference in the UV absorption maximum between the parent polymer PEBT and the alkyl-substituted polymers in their solutions UV–VIS spectra. All polymer solutions depicted absorption maxima at *ca.* 476 nm, which is red-shifted in comparison to that of polythiophene at 450 nm.[27] This observation is consistent with enhanced ring conjugation in the polymers attributed to reduced steric effects imposed by alkyl pendants with the introduction of an acetylenic spacer between the thiophene rings. This assumption also correlates well with our experimental data whereby the UV–VIS absorption of PEBT and the alkyl-substituted polymers remain fairly unchanged.

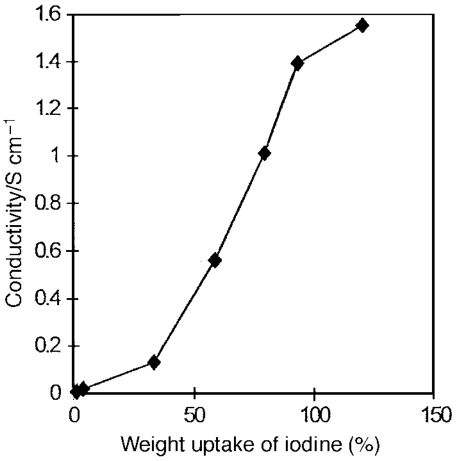


Fig. 2 Conductivity plot of PEBT against uptake of iodine (wt%).

When the alkyl-substituted polymers PDBEBT, PDHEBT, PDOEBT and PDDEBT are spin-coated on ITO glass from chloroform solutions to afford thin polymer films, a red shift of only 20–60 nm with respect to the polymer solution resulted. This bathochromic shift is somewhat less than that observed for poly(3-alkylthiophene)s at between 60–100 nm[28] on going from the solution to the condensed phase, suggesting that the acetylene spacer has imparted a significant amount of rigidity to the polymer backbone. The electrochemically synthesized unsubstituted polymer PEBT, on the other hand, is obtained as a deep red–violet film with an absorption maximum at 519 nm, which is red-shifted from the 496 nm of polybithiophene.[29]

The band gap energies of these polymers (Table 2) can be deduced from the energy absorption edge of the UV–VIS spectrum according to the approach of Johnson *et al.*[30] A reduced band gap energy of 1.7–1.9 eV is observed in this series of polymers in comparison to polythiophene (2.1 eV).[31] Although PDBET (535 nm, 1.7 eV) depicted enhanced ring conjugation compared to PEBT (519 nm, 1.8 eV), the longer alkyl chain polymers PDHEBT, PDOEBT and PDDEBT on the contrary do not exhibit significant red shifts with respect to PEBT.

The fluorescence excitation/emission studies of these polymers from PEBT to PDDEBT showed a green emission in chloroform solution (10^{-4} M) when the polymers were exposed to ultraviolet radiation. These polymers gave an emission peak between 540 and 573 nm with an accompanying decreasing Stokes shift as the chain length of the alkyl substituent increases. The progressively smaller Stokes shift from PEBT to PDDBET implies that the polymer backbone becomes more rigid[32,33] as the alkyl chain length is increased. The increasing rigidity of these polymers must have contributed to the increase in overall fluorescent quantum yield by reducing the extent of non-radiative losses. As the Stokes shift diminishes, the quantum yield becomes progressively higher in the order PEBT < PDBEBT < PDHEBT but decreases again in going to PDDEBT. From the M_n values presented in Table 1, whilst the polymer chains of PDBEBT, PDHEBT and PDOEBT contain a fairly consistent number of monomeric repeat units (17–18) in their soluble fractions, PDDEBT has a significantly smaller degree of polymerisation (DP_n) with only 11 repeat units. Previously, it has been shown with thiophene oligomers that a trend of diminishing fluorescent quantum yields can be correlated with a reduced number of conjugated repeat units in the oligomers.[34] Consequently, arising from this, PDDEBT has a reduced fluorescence quantum yield even though its Stokes shift is the smallest among this series of polymer.

Thermochromism effects

The temperature dependency in the optical absorption spectra of alkyl substituted polymers PDBEBT to PDDEBT were

Table 2 UV–VIS absorption and fluorescence emission data and band gap of various polymers in chloroform solution at 25 °C

Polymer	λ_{max}/nm		Fluorescence/nm		Quantum yield	Stokes shift	Band gap[a]/eV
	Solution	Film	Excitation	Emission			
PEBT	476	519	476	573	22	97	1.8
PDBEBT	475	535	478	568	27	90	1.7
PDHEBT	470	491	470	549	39	79	1.9
PDOEBT	475	492	475	550	37	75	1.9
PDDEBT	471	493	470	540	29	70	1.9

[a]Band gap is derived from UV–VIS spectrum of polymer film coated on ITO glass.

studied. Solid polymer samples spin-coated from chloroform solution onto ITO-coated glass were used in these studies. These polymers undergo a colour change from red to orange upon heating. This is accompanied by a blue shift in the absorption maxima from 535 to 466 (PDBEBT), 491 to 452 (PDHEBT), 493 to 458 (PDOEBT) and 493 to 468 nm (PDDEBT). It is difficult to identify any intermediate phases formed in this series as no clear isosbestic point is observed in the UV–VIS spectra (Fig. 3).[35] Only a gradual blue shift is observed in these polymers upon heating, which is indicative of a decrease in conjugation. The magnitude of the blue shift diminishes with increasing chain length of the pendant alkyl group, with PDDEBT < PDOEBT < PDHEBT < PDBEBT. The blue shift is ascribed to heat-induced disorder in the side chain leading to accentuated steric interaction and concomitant twisting of the polymer chain, reducing the extent of inter-ring conjugation. However, the extent of twisting and consequently the magnitude of blue shift is significantly reduced in comparison to poly(alkylthiophene)s,[36] due to the effect of the spacer unit on the polymer chain, which helps diminish the repulsive intrachain steric interactions exerted by the alkyl pendant groups. Moreover, experimental fluorescence spectroscopy results also show decreasing Stokes shift values in the same order. This corroborates the assumption that substitution with longer alkyl pendants affords polymers with a more rigid structure. This thermochromic behaviour is fully reversible, regaining the initial absorption state upon cooling.

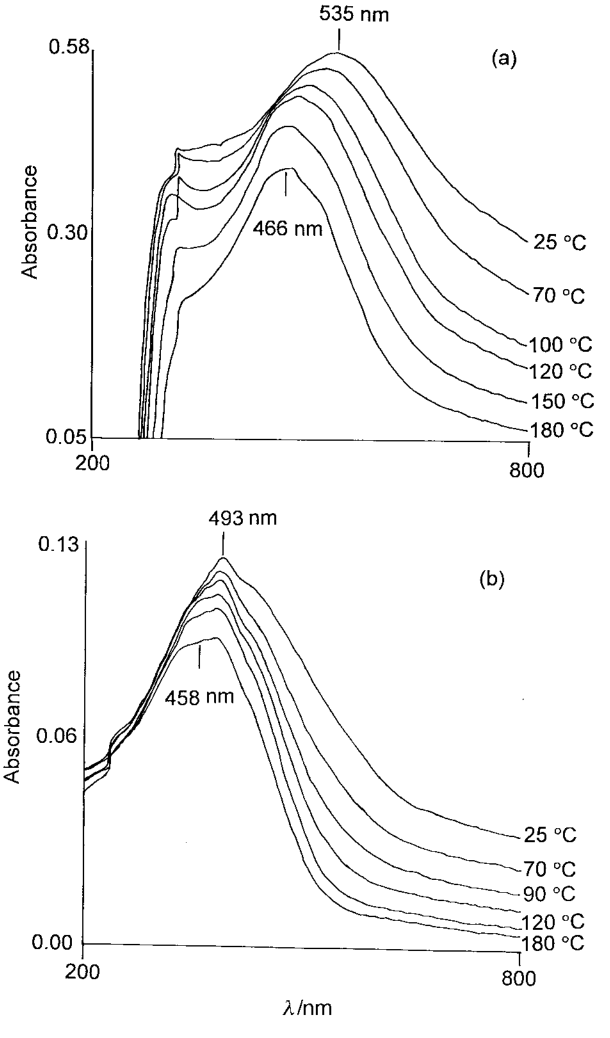


Fig. 3 Variation of absorption maxima in UV–VIS spectra of (a) PDBEBT and (b) PDOEBT upon heating in solid state from 25 to 180 °C.

Electrochemistry

The cyclic voltammograms of various polymers are shown in Fig. 4. The electrochemical oxidation of PEBT is compared with polythiophene (PT) and polybithiophene (PBT). A generally lower monomer oxidation potential (1.43 V) in comparison to PT (1.65 V)[38] is required for generation of PEBT when a current density of 1 mA cm^{-2} is used. PEBT is highly electroactive showing excellent reversibility of its p-doping redox states when subjected to repeated electrochemical cycling between −1.0 to 0.9 V (*vs.* SCE). The p-doped polymer PEBT has a deep green colour which turned red–brown upon electrochemical dedoping. The polymer oxidation potential of PEBT is comparable to polybithophene (1.0 V)[37] but is significantly lower than pristine polythiophene (1.3 V).[38] The effect of lowering the oxidation potential is advantageous as this would prevent over-oxidation of the polymer film when a high oxidising (positive) potential was applied. The film formation process for alkyl-substituted polymers is difficult to achieve as these polymers are slightly soluble in acetonitrile. Therefore electrochemical analysis of these polymers was conducted on chemically polymerized samples which were spin-coated onto platinium electrodes. The p-doping of PDBEBT, PDHEBT, PDOEBT and PDDEBT was observed to be stable, with clearly defined anodic and cathodic peaks. When these polymers were scanned repeatedly using cyclic voltammetry, no significant overoxidation or degradation of the polymer films was observed. The ratio of polymer oxidation potential (E_{pa}) to reduction potential (E_{pc}) showed a slight deviation from unity, suggesting that the doping/dedoping process of these polymers is not absolutely reversible. On varying the scan rates from 20 to 80 mV s^{-1}, the peak current densities of these polymers were observed to scale linearly with increasing scan rates, implying that the doping/undoping processes are non-diffusion controlled reactions.[39]

The E_{pa} values of alkyl-substituted polymers were found to increase with increasing alkyl chain length, whilst the corresponding E_{pc} values shifted towards lower potential. This phenomenon was also observed by Tanaka *et al.*[24] and Yamabe *et al.*[40] in poly(3-alkylthiophene)s. Our findings indicate that the electron donating effect attributed to the butyl groups in PDBEBT ($E_{pa} = 0.92$ V) leads to a lowering of E_{pa} compared to PEBT ($E_{pa} = 0.94$ V) and PBT ($E_{pa} = 1.01$ V),[37] as well as PT ($E_{pa} = 1.30$ V).[38] In PDHEBT, PDOEBT and PDDEBT on the other hand, the E_{pa} values shows a gradual increase

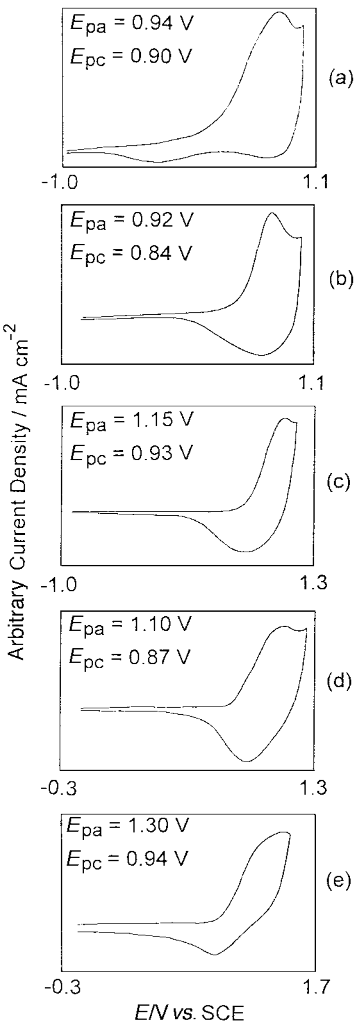


Fig. 4 Cyclic voltammograms of various polymers at scan rate of 20 mV s^{-1}: (a) PEBT, (b) PDBEBT, (c)PDHEBT, (d) PDOEBT and (d)PDDEBT.

with reference to PEBT. The electro-oxidation process involves the removal of one electron from the neutral polymer and the resulting polymer aquires a single positive charge on the sulfur heteroatom. This positively charged species is stabilised electrochemically in the presence of solvated counter anions. It was anticipated that with increasing alkyl chain length, the bulky alkyl group is likely to slow down the rate of mobility of counter anions into and out of the polymer surface, thus resulting in higher oxidation potential.

In summary, the polymer oxidation potentials for this series of polymers lie between 0.92 to 1.30 V, which is comparatively lower than the oxidation potential of polythiophene. Reductive n-doping studies of these polymers were also examined in the potential range 0 to −2.5 V *vs.* SCE. However, no significant n-doping peaks were observed.

In situ electrochemical doping studies of polymers

The UV–VIS-near infrared absorption shifts of doped polymers during electrochemical doping are depicted in Fig. 5. Usually, a low potential of 0.0 V *vs.* SCE was applied to first obtain an undoped polymer spectrum. At this potential, only one main potential corresponding to the π–π^* interband transition is observed at 526, 495, 493 and 494 nm for PDBEBT, PDHEBT, PDOEBT and PDDEBT, respectively. As the applied potential was gradually increased from 0.00 to 0.95 V, the intensity of the π–π^* interband transition decreased slightly with evolution of a new polaronic band in the near infrared region. The position of this polaron band occurs at 880, 860, 840 and 840 nm for PEBT, PDHEBT, PDOEBT and PDDEBT, respectively, which correspond to about 1.4 eV. Therefore when polymers are in lightly doped states within the potential range 0.0 to 1.0 V, two electronic bands corresponding to the π–π^* interband transition as well as the polaron band were observed. When the extent of doping was increased through applying a potential greater than 1.25 V, the polaron band continued to grow in intensity whilst the π–π^* band diminished in intensity until a negative deviation formed. The polymer film appears to be deep blue in this heavily doped state.

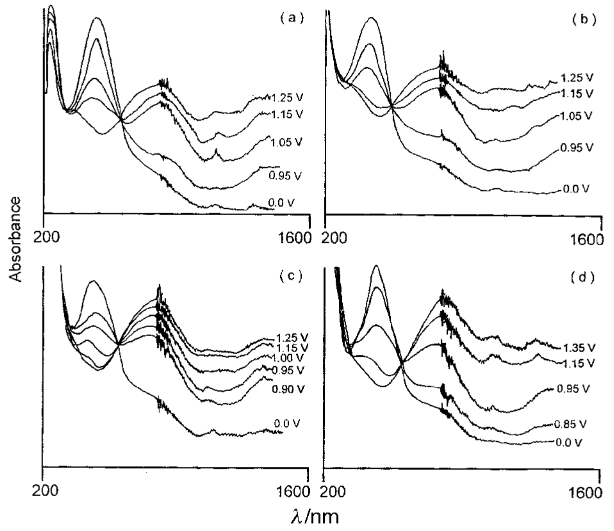


Fig. 5 *In situ* electrochemical doping studies of various polymers: (a) PDBBT, (b) PDHEBT, (c) PDOEBT and (d) PDDEBT.

The calculated electrochemical bandgaps of these polymers were determined from the position where the isosbestic point occurs in the optical spectrum obtained during *in situ* electrochemical doping studies. It has been mentioned by several authors[41] that the relative electrochemical band gap energy can be estimated from the position of the isosbestic point in the optical spectrum using eqn. (2),

$$E\,(\mathrm{eV}) = h\nu = hc/\lambda = 1240/\lambda\ (\mathrm{nm}) \qquad (2)$$

where h is Plank's constant, λ is wavelength in nm and c is the speed of light, and E denotes the band gap energy of the polymer. From Table 3, the evaluated electrochemical band gap energies of PDBEBT, PDHEBT, PDOEBT and PDDEBT are found to be 1.8, 1.9, 1.9 and 1.9 eV, respectively. These readings correlate well with the experimentally determined optical band gap energies.

Thermal stability of neutral and doped polymers

The thermal properties of polymers in both their neutral and doped states were studied in air over a temperature range of 25 to 800 °C. The neutral polymer, PEBT, depicted a single weight-loss step in the temperature range 300 to 500 °C, corresponding to the thermal oxidative degradation of the polymer backbone. All the alkyl-substituted polymers PDBEBT to PDDEBT depicted a two-step weight loss. The first step occurring in the temperature range 220 to 370 °C, corresponded to cleavage of the alkyl chain.[42] The next weight loss step, which took place in the temperature range 370 to 800 °C, was attributed to the degradation of the polymer chain. In most cases, a small residue content of less than 5% was left behind.

The iodine-doped polymers depict different TGA spectra to those of the undoped polymers. The first step, occuring at 100 to 200 °C, is attributed to the expulsion of molecular iodine from the polymer surface. The second weight-loss step, from 200 to 800 °C, due to degradation of polymer chain adopts a gradual weight loss pattern. The thermal dedoping process occurring in the temperature range 100 to 200 °C in doped PDBEBT was closely monitored using FT-IR spectroscopy. These results showed decreasing intensity of the doped induced bands from 1054 to 1458 cm^{-1} as the dopant is expelled at temperatures ranging from 50 to 250 °C. Thus, application of heat can lead to the recovery of the dedoped polymer.

Conclusion

A series of conducting polymers having a rigid backbone through incorporation of an acetylenic spacer, poly[3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene)], was synthesized *via* $FeCl_3$ chemical oxidative polymerization of the respective monomers. Polymerization occurred predominantly α–α', with the doped polymers displaying electrical conductivity in the range of 10^{-4} to 10^{-2} S cm^{-1}. A trend of decreasing Stokes shift in the fluorescence spectra as the alkyl chain length increases indicates an improvement of rigidity of the polymer backbone, which helps to enhance the fluorescence quantum yield. A green emission at 500–570 nm was observed in this series of polymers. The effective conjugation in these polymers was red-shifted as compared to polythiophene. This suggested a smaller twist angle between the neighbouring rings in poly[3,3′-dialkyl-2,2′-(ethyne-1,2-diyl)bis(thiophene)]s compared to pristine polythiophene. Due to the enhanced rigidity and coplanarity of these polymers, thermochromic studies reveals that the extent of blue shift depicted in their UV–VIS spectra was much less than poly(3-alkylthiophene)s when they were heated from 25 to 200 °C. These polymers displayed thermal dedoping behaviour at temperatures ranging from 100 to 250 °C due to explusion of dopants from the surface of the bulk polymer. Degradation of the polymer chain in air showed an onset at 220 °C, the polymer being completely degraded at 600 °C.

We thank the National University of Singapore for financial support through the research grant RP960613. T. T. Ong is grateful to NUS for the award of a research scholarship as well as to ICI for scholarship top-up funding.

References

1 M. A. Sato, T. Shimizu and A. Yamauchi, *Synth. Met.*, 1991, **41**, 551.
2 T. Kawai and M. Nakazono, *J. Mater. Chem.*, 1992, **2**, 903.
3 T. A. Chen and R. D. Rieke, *Synth. Met.*, 1993, **60**, 175.
4 S. A. Chen and C. S. Liao, *Synth. Met.*, 1993, **55**, 4930.
5 Y. Ohmori, M. Uchida and K. Yoshino, *Jpn. Appl. Phys.*, 1991, **10**, 1938.
6 H. Fujimoto, K. I. Iwasaki and S. Matsuzaki, *Synth. Met.*, 1994, **69**, 99.
7 D. A. Santo, C. Quattrochi, R. H. Friend and J. L. Bredas, *J. Chem. Phys.*, 1994, **100**, 3301.
8 J. Mouton and P. Smith, *Polymer.*, 1992, **33**, 4611.
9 M. Sato, S. Tanaka and S. Kaeriyama, *Makromol. Chem.*, 1987, **188**, 176.
10 T. J. Kang, J. Y. Kim, C. Lee and S. B. Rhee, *Synth. Met.*, 1995, **69**, 377.
11 M. Feldhues, G. Kampf, H. Litterer, T. Mecklenburg and P. Wegener, *Synth. Met.*, 1989, **28**, C487.
12 M. T. Vala and J. Haebig, *J. Chem. Phys.*, 1965, **43**, 886.
13 J. K. Tai, Y. K. Jae, J. K. Kyung, J. L. Chang and B. R. Suh, *Synth. Met.*, 1995, **69**, 377.
14 S. C. Ng, S. O. Chan, H. H. Huang, T. T. Ong, A. Sarkar, K. Kumura, Y. Mazaki and K. Kobayashi, *J. Mater. Sci. Lett.*, 1996, **15**, 1684.
15 H. Hotta, T. Hosaka and W. Shimotsuma, *J. Chem. Phys.*, 1984, **80**, 954.
16 A. Bolognesi, C. Botta, Z. Geng, C. Flores and L. Denti, *Synth. Met.*, 1995, **71**, 2191.
17 X. C. Li, F. Cacialli, M. Grumer, R. H. Friend, A. B. Holmes and S. C. Yong, *Adv. Mater.*, 1995, **7**, 898.
18 M. K. Richard, A. P. Schaap, E. T. Harper and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2902.
19 R. L. Elsenbaumer, K. Y. Jen and R. Oboodi, *Synth. Met.*, 1986, **15**, 169.
20 C. Adriano, A. Lessi and R. Rossi, *Synthesis*, 1994, C571.
21 I. Catellani, S. Luzzati and F. Speroni, *Synth. Met.*, 1993, **55**, 1188.
22 S. Hasoon, M. Galtier and L. Sauvajol, *Synth. Met.*, 1989, **28**, C317.
23 Y. Cao, D. Guo, M. Pang and R. Qian, *Synth. Met.*, 1987, **18**, 189.
24 S. Kaeriyama, M. Sato and S. Tanaka, *Synth. Met.*, 1987, **18**, 233.
25 M. R. Anderson, Q. Pei, T. Hjertherg, O. Inganas, O. Wennwestrom and J. E. Osterholm, *Synth. Met.*, 1993, **55**, 1227.
26 A. P. Davey, E. Simon, O. Orla and B. Werner, *J. Chem. Soc., Chem. Commun.*, 1995, 1433.
27 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
28 O. Inganas, W. R. Salaneck, J. E. Osterholm and J. Laakso, *Synth. Met.*, 1988, **22**, 395.
29 R. Claudine and L. Mario, *Chem. Mater.*, 1994, **6**, 620.
30 E. G. Johnson, R. Willardson and A. C. Beer, in *Semiconductors and Semimetals*, Academic Press, New York, 1967, vol. 3, p. 153.
31 K. Iwasaki, H. Fujimoto and S. Matsuzaki, *Synth. Met.*, 1994, **63**, 101.
32 S. Heun, H. Bassler, U. Muller and K. Mullen, *J. Phys. Chem.*, 1994, **98**, 7355.
33 M. Leclerc, C. Roux and J. Y. Bergeron, *Synth. Met.*, 1993, **55**, 287.
34 W. R. Salaneck, O. Inganas, B. Thenmans, J. O. Nilsson, B. Sjogren, J. E. Osterholm and S. Stevensson, *J. Chem. Phys.*, 1988, **89**, 4613.
35 T. Kohji, O. Keiko, M. Yasuhisa and M. Kobayashi, *J. Polym. Sci., Part B: Polym. Phys.*, 1991, **29**, 1223.
36 C. Roux, J. Y. Bergeron and M. Leclerc, *Makromol. Chem.*, 1993, **194**, 669.
37 T. Yamamoto, K. Sanachika and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1497.
38 S. O. Chan, S. C. Ng, S. H. Seow and J. G. Marc, *J. Mater. Chem.*, 1992, **2**, 1135.
39 E. Genies, G. Bidan and A. F. Diaz, *J. Electroanal. Chem.*, 1983, **149**, 113.
40 S. Wang, H. Takahashi, K. Yoshino, K. Tanaka and T. Yamabe, *Jpn. J. Appl. Phys.*, 1990, **29**, 772.
41 M. Onoda, T. Iwasa, Y. Kawai and K. Yoshino, *J. Phys. D: Appl. Phys.*, 1991, **24**, 2076.
42 B. Themans, W. R. Salaneck and J. L. Bredas, *Synth. Met.*, 1989, **28**, C359.

Paper 8/05840G