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ORIGINAL PAPER

Synthesis, characterization, and OFET characteristics of 3,4-diaryl substituted poly(thienylene vinylene) derivatives

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Abstract Poly(thienylene vinylene) derivatives bearing aryl substituents at 3,4-positions have been synthesized in good yield by Stille-type polycondensation. Two types of aryl substituents, either a 4-octylphenyl or a 5-octyl-2-thienyl, were investigated in this study. The polymers were characterized by ^{1}H NMR, GPC, TGA, UV–vis absorption, and photoluminescence spectroscopy. The polymers (**P1–P4**) showed good to excellent solubility in common organic solvents, and UV–vis absorption spectra in solution exhibit maxima in the range of 511–595 nm. GPC analysis using PPP standards showed a number average molecular weight range of $6.59–8.98 \times 10^3$ g mol^{-1} for the various polymers. The field effect transistors based on these polymers were studied, and the results obtained are correlated to their molecular structure.

Keywords Poly(thienylene vinylene)s · Stille polycondensation · OFETs

Introduction

Semiconducting organic polymers are of considerable interest because of their unique properties and applications in organic electronics and photovoltaics [1–3]. Among the various semi-conducting polymers, polythiophene and its derivatives have been extensively studied as active components in polymeric solar cells, polymer light emitting diodes, chemical sensors, and organic field effect transistors

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(OFET) [4–6]. Regioregular poly(3-hexylthiophene) (rr-P3HT) and alkyl-terminated sexithiophene have been proven to be promising materials for use in OFET because of their high charge carrier mobility resulting from strong inter-chain interaction and high degree of structural regioregularity [7–12]. P3HT exist in well-organized lamellar structures whereby stacks of planar thiophene main chains are uniformly spaced by alkyl side chains [13–15]. Incorporation of conjugated moieties in polythiophenes results in much better oxidative stability and hole mobility [16, 17]. Several reports have been described in literature where polythiophene and poly(thienylene vinylene) derivatives have been modified by conjugated side chains [18–24]. Among these, most of the studies have focused on 3-substituted polythiophene derivatives since they are readily prepared. However, 3,4-diaryl substituted derivatives have been less investigated in part due to steric effects on coupling and conjugation [25, 26]. As part of our ongoing studies into 3,4-diaryl substituted polythiophene derivatives, we report here the synthesis, characterization, and transistor characteristics of new classes of poly(thienylene vinylene) derivatives. The introduction of the vinylene moiety is anticipated to minimize steric effects between neighboring repeat units and improve conjugation and charge transport.

Experimental part

Material and instrumentation

Dry solvents stored in a glove box were used for all reactions except for the Suzuki couplings. Bis(tributylstannyl)ethene was purchased from Aldrich and used as supplied. The synthesis of the monomers (**M1**–**M4**) was reported previously [27]. All the reactions were performed in flame-dried flasks under a nitrogen atmosphere. NMR experiments were measured on a Bruker 300 MHz spectrometer (^{1}H NMR at 300 MHz) in $CDCl_3$ with TMS as internal standard ($CHCl_3$ 7.26 ppm). UV–vis absorption spectra were recorded in THF solution on a Perkin Elmer Lambda 25 Spectrophotometer. Photoluminescence measurements were carried out with a Fluorolog HORIBAJOBIN YVON spectrophotometer using a xenon-arc lamp as a source in THF solution. Thermal degradation was studied by TGA on a Perkin Elmer Pyris 7 thermal analysis system in a dynamic atmosphere of nitrogen at a heating rate of 20 °C min^{-1}. Number average (M_n) and weight average (M_w) molecular weights were determined by gel permeation chromatography (GPC) using poly-*p*-phenylene (PPP) as standard in THF at 30 °C.

Poly[3,4-di-(5′-octyl-2′-thienyl)-2,5-thienylene vinylene] P1

$Pd(PPh_3)_4$ (4.5 mol%, 44 mg) was added to a mixture of monomer **M1** (0.530 g, 0.833 mmol) and bis(tributylstannyl)ethene (0.505 g, 0.833 mmol) in 5.5 mL of dry toluene under N_2 atmosphere. The solution was stirred at 100 °C for 24 h and then poured into methanol, and the resulting blue solid was collected by filtration. The polymer was purified by Soxhlet extraction with methanol followed by re-precipitation from THF solution. The polymer was filtered, dried, and was isolated as a dark blue solid. Yield = 0.375 g (90%). GPC analysis $M_n = 6.96 \times 10^3$ g mol^{-1}, $M_w = 1.23 \times 10^4$ g mol^{-1}, and PDI = 1.7 (against PPP standard). UV–vis (THF): $\lambda_{max} = 595$ nm; δ_H (300 MHz; $CDCl_3$) 7.05 (br, 2H), 6.68 (br, 4H), 2.77 (br, 4H), 1.5–0.81 (m, 30H).

Poly[3,4-di-(4-octylphenyl)-2,5-thienylene vinylene] P2

Polymer **P2** was synthesized using an analogous method as for **P1**. Starting with monomer **M2** (0.510 g, 0.825 mmol), **P2** was isolated as a purple blue solid (0.350 g, 87%). GPC analysis $M_n = 8.98 \times 10^3$ g mol^{-1}, $M_w = 1.85 \times 10^4$ g mol^{-1}, and PDI = 2.0 (against PPP standard). UV–vis (THF): $\lambda_{max} = 588$ nm; δ_H (300 MHz; $CDCl_3$) 7.00–6.87 (br, 10H), 2.56 (br, 4H), 1.5–0.81 (m, 30H).

Poly[3′,4′-di-(octylthienyl)-2,2′:5′,2″-terthiophen-2,5″-ylvinylene] P3

Starting with monomer **M3** (0.415 g, 0.522 mmol) and following the same procedure and reaction times as for **P1**, polymer **P3** was isolated as dark red solid (0.320 g, 92%). GPC analysis $M_n = 8.77 \times 10^3$ g mol^{-1}, $M_w = 4.64 \times 10^4$ g mol^{-1}, and PDI = 5.2 (against PPP standard). UV–vis (THF): $\lambda_{max} = 518$ nm; δ_H (300 MHz; $CDCl_3$) 6.93 (br, 2H), 6.80–6.64 (br, 8H), 2.76 (br, 4H), 1.5–0.81 (m, 30H).

Poly[3′,4′-di-(4-octylphenyl)-2,2′:5′,2″-terthiophen-2,5″-ylvinylene] P4

Monomer **M4** (0.503 g, 0.643 mmol) on polymerization under the same conditions as above gave polymer **P4** as a dark red solid (0.340 g, 82%). GPC analysis $M_n = 6.59 \times 10^3$ g mol^{-1}, $M_w = 2.70 \times 10^4$ g mol^{-1}, and PDI = 4.1 (against PPP standard). UV–vis (THF): $\lambda_{max} = 511$ nm; δ_H (300 MHz; $CDCl_3$) 6.99 (br, 8H), 6.75–6.42 (br, 6H), 2.54 (br, 4H), 1.5–0.81 (m, 30H).

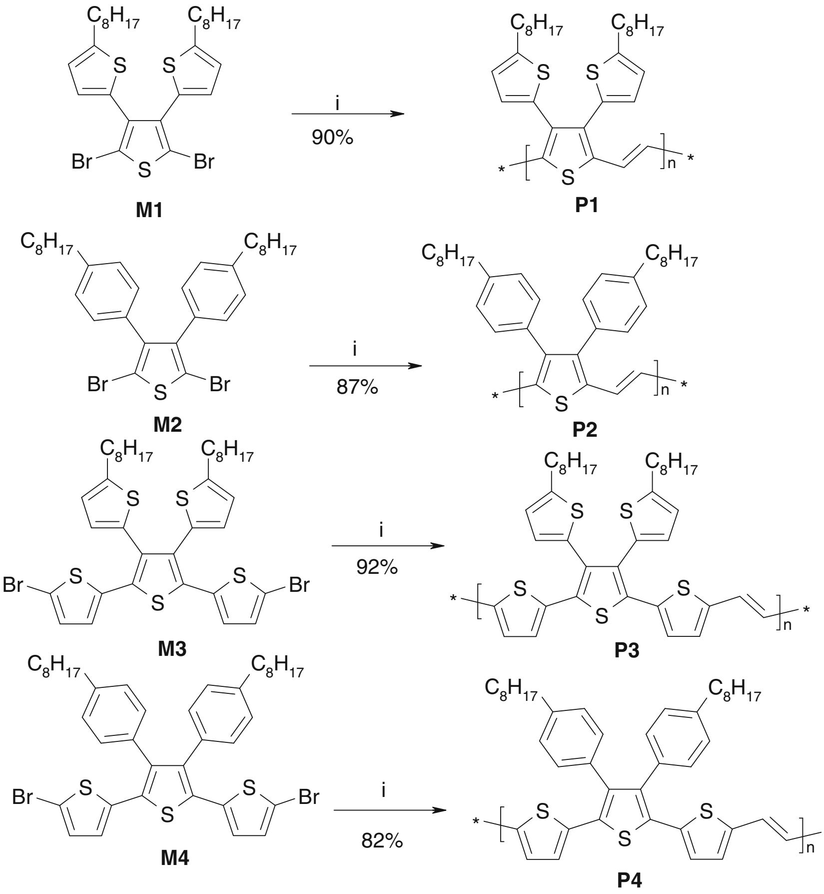
Device fabrication

Field effect transistor

Both top-contact and bottom-contact field effect transistors (FET) were fabricated. However, consistent, reproducible, enhanced, and leakage-free performance was obtained only in bottom-contact FETs. Bottom-contact, top-gate FETs involved an initial process of vapor deposition of Cr–Au electrodes (10^{-6} mbar, 1 Å s^{-1}, 5–25 nm thick) on RCA-treated, clean glass substrates through shadow mask to obtain channels of length (L) 60–80 μm and width (W) of 1–2 mm. Thin film polymer-semiconductor films were deposited inside glove box (<1 ppm H_2O and <10 ppm O_2) in nitrogen atmosphere by spin coating of a 12-mg mL^{-1} solution in chloroform ($CHCl_3$) of the model molecules (**P1**–**P4**) at 1,000 rpm for 1 min on the glass substrate with Au source/drain electrode. The semiconducting films were then annealed at 110 °C for 20 min. After the active film, a dielectric bi-layer of polyvinylidene fluoride (PVDF) and polyvinyl alcohol (PVA) were coated. The PVDF film was coated from a 60-mg mL^{-1} solution in *N*,*N*-dimethylacetamide at 1,000 rpm for 1 min giving a film of thickness of 350 nm (capacitance per unit area 15 nF cm^{-2}). The film was rapidly annealed at 150 °C in vacuum to facilitate the formation of a uniform β-phase [28]. This was followed by a buffer layer of PVA coated from a 20-mg mL^{-1} solution in de-ionized water at 1,000 rpm for 30 s (capacitance per unit area $\sim$10 nF cm^{-2}). The film was then dried in vacuum at 70 °C for 10–12 h to remove traces of water. The Al gate electrode was vapor deposited (10^{-6} mbar, 0.1 Å s^{-1}, 40 nm thick). The bi-layer of dielectric thus formed consisting of PVDF and PVA had effective capacitance, C_0 of 6–8 nF cm^{-2} measured directly using Keithley 4200 semiconductor parameter analyzer for a film of thickness 450 nm. The electrical characterization of the transistor devices were done with two identical source meters Keithley 2400 and high impedance Electrometer Keithley 6514 and cross checked with Keithley 4200 semiconductor parameter analyzer. The saturation region carrier mobility was estimated from the transconductance characteristics of drain-source current, $I_d = (\mu_{FET} WC_0/2L)(V_g - V_t)^2$, where μ_{FET} is the field effect hole mobility, V_g is the gate voltage, and V_t is the threshold voltage.

Results and discussion

The synthetic routes to the four polymers investigated in this study are shown in Scheme 1. Polymers **P1**–**P4** were synthesized by Stille-type polycondensation of their respective dibromides with bis(tributylstannyl)ethene in the presence of catalytic amount of $Pd(PPh_3)_4$ in dry toluene. Polymer **P2** has been synthesized earlier with a different alkyl group by the dithiocarbamate route [29]. All the polymers described above have been characterized by ^{1}H NMR, TGA, GPC, UV–vis absorption, and emission spectroscopy. The initially precipitated polymers were further purified by soxhlet extraction followed by re-precipitation from methanol. The molecular weights of the polymers were determined by GPC against poly-*p*-phenylene (PPP) standards using THF as eluent and are summarized in Table 1. The measured number average molecular weights vary in the range of 6.59–8.98 × 10^3 g mol^{-1} with polydispersity indexes (PDI) in the range of 1.7–5.2. Although the measured molecular weights are not very high, these values correspond to a degree of polymerization of 14 for **P1**, 18 for **P2**, 13 for **P3,** and 10 for **P4**. **P1** and **P2** have excellent solubility in common organic solvents, whereas **P3** and **P4** have limited solubility in common organic solvents which accounts for the relatively high PDI of these polymers [30, 31]. Thermogravimetric analysis (TGA) was carried out to determine the degradation behavior of the polymers. The temperature for 5% weight loss (T_d) is recorded in Table 1. It is found that the polymers are stable up to 375 °C.



Scheme 1 Synthesis of polymers (**P1**–**P4**) via Stille-type polycondensation. Reagents and conditions: (i) bis(tributylstannyl)ethene, Pd(PPh_3)$_4$, toluene, reflux

Table 1 Absorption, emission, molecular weight (THF solution), and T_d values of polymers **P1**–**P4**

Polymer	Absorption λ_{max} (nm)	Emission λ_{max} (nm)[a]	M_n (g mol^{-1})	T_d (°C)[b]	Mobility (10^{-4}) (cm^2 V^{-1} s^{-1})
P1	595	–	6.96×10^3	390	0.43
P2	588	–	8.98×10^3	421	0.12
P3	520	603	8.77×10^3	400	4.2
P4	511	597	6.59×10^3	375	6.0

[a] **P1** and **P2** are non-luminescent, [b]temperature for 5% weight loss

Optical properties

The UV–vis absorption spectra of the polymers **P1**–**P4** and emission spectra of **P3**–**P4** in dilute THF solution are shown in Fig. 1. Polymers **P1** and **P2** show its

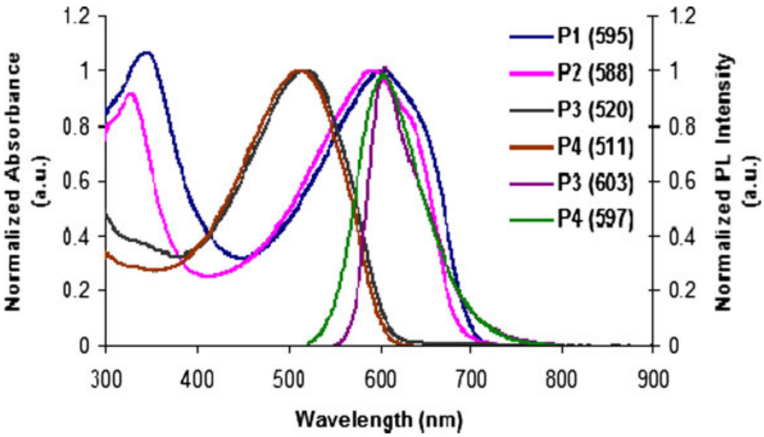


Fig. 1 Normalized UV–vis absorption spectra of polymers **P1**–**P4** and emission spectra of polymers **P3**–**P4** in THF solution

absorption maxima at 595 and 588 nm, respectively. The terthiophene-based polymers **P3** and **P4** exhibit absorption maxima at 520 and 511 nm, respectively. Similar trend in absorption maxima has been reported in literature for poly(thienylene vinylene) polymers, and the observed blue shift for polymers **P3** and **P4** compared to **P1** and **P2** has been attributed to reduction in thiophene to vinylene ratio in the polymer backbone [32, 33]. By increasing the vinylene to thiophene ratio along the polymer backbone, the band gap of the resulting polymers was reduced as clearly evidenced by absorption spectroscopy. The absorption band of poly(thienylene vinylene)s is broader than polythiophenes analogs owing to high degree of coplanarity [34]. The observed absorption maxima values of the polymers (**P1**–**P4**) are comparable with the 3-alkyl and 3,4-diphenyl substituted poly(thienylene vinylene) derivatives reported in literature (both show an absorption maxima at 577 nm) [28, 35].

No photoluminescence was observed for polymers **P1** and **P2**. It is reported in literature that poly(thienylene vinylene)s are non-luminescent due to the fact that an optical transition from the lowest energy excited state ($2A_g$) to ground state ($1A_g$) is forbidden [36–39]. Polymers **P3** and **P4** exhibited emission maxima at 603 and 597 nm, respectively, corresponding to a Stokes shift of 83 and 86 nm, respectively. For a featureless absorption and emission spectra, the measure of Stoke shift is the difference in the wavelength corresponding to the emission and absorption maxima (in energy or wavelength units). In case of conjugated polymers Stokes shift, primarily arises from the electron–phonon coupling, which causes vibrational relaxations upon photoinduced electronic excitation. The magnitude of the Stokes shift in conjugated systems suggests large differences in the conformation of the ground and excited states of the polymer and/or energy migration to minority segments having greater conjugation lengths. For **P3** and **P4**, the spectra are quite simple with single peaks in both absorption and emission.

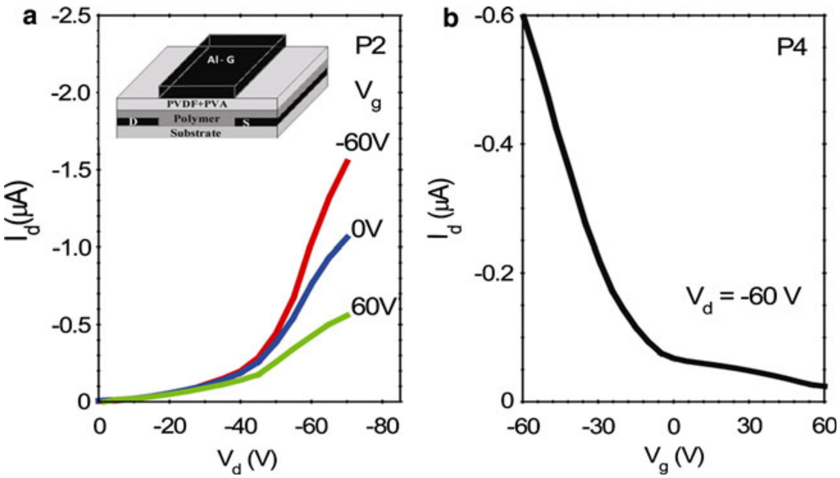


Fig. 2 **a** A typical I_d–V_d characteristic of FET using **P2** at different V_g, similar profiles were obtained for FETs using **P1**, **P3**, and **P4**. *Inset* schematic of the device. **b** Transconductance of FET based on polymer **P4** (see text for device details)

OFET characteristics

It was possible to observe p-type FET characteristics for the devices fabricated using all the four polymer derivatives, as indicated by the V_g dependent I_d–V_d (Fig. 2a). The observations from large number of devices tested indicated a trend where μ_{FET} of **P4** was distinctly larger than **P1** and **P2**. μ_{FET} as high as 6×10^{-4} cm^2 V^{-1} s^{-1} along with V_t of 7 V and ON/OFF ratio of 40 was observed (Fig. 2b). The results are tabulated in Table 1. The performance parameters of the FETs were much lower than rr-P3HT-based FETs which were fabricated in our laboratory in the top-contact geometry using the standard hexamethyldisilizane (HMDS) treatment of glass substrates [40]. This factor can probably arise from the absence of an ordered lamellar structure at the interface, which is not promoted in the bottom-contact, top-gate geometry and is a requisite for efficient field effect transport. Nevertheless, a clear trend where μ_{FET} in **P4** and **P3** is greater than that in **P2** and **P1** is reflective of the importance of the molecular structure in the electrical transport behavior. The transport parameters μ_{FET} and V_t clearly scale with the increasing thiophene to vinylene ratio along the polymer backbone. Introduction of phenylene group in the polymer seems to improve solubility and film morphology indicated by optically clear films.

Conclusions

Four new 3,4-diarylsubstituted poly(thienylene vinylene) derivatives were synthesized by Stille-type polycondensation. The polymers gave satisfactory data by ^{1}H NMR and show varying solubility in common organic solvents. The observed absorption maxima in solution vary between 511 and 595 nm, and seem to have a clear correlation with the thiophene to vinylene ratio which is consistent with literature. The insertion of vinylene spacer in the conjugated polymer backbone profoundly affects the optical properties of polymers. The FETs fabricated from these polymers indicated properties and trends which could be correlated to the modifications in the molecular structure.

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