Preparation and Oxidative Doping of α,ω-Dithienyl Polyenes

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α,ω-Dithienyl polyenes can be prepared from appropriately substituted 2-thienyl or 3-thienyl carbaldehydes or propenals by condensation with either bis-Wittig reagents or bis-phosphonate esters (Horner–Emmons–Wadsworth modifications) containing one or two double bonds. These polyenes, containing either 3, 4, 5 or 6 conjugated double bonds, can be oxidatively doped with $SbCl_5$, in solution, forming polaronic (radical cation) and bipolaronic (dication) charge states by successive one-electron transfers. In all cases, the bipolaron is the more stable charge state.

During the past 10 years the explosive growth of interest in electroactive materials has led to an ever increasing understanding of the formation and stabilization of charge states and the nature of the insulator–metallic transition upon chemical or electrochemical doping.[1] In general, polymers such as polyacetylene seem to be dominated by polaronic or solitonic species, while polymers such as polythiophene and poly[p-phenylenevinylene] are dominated by bipolaronic species in the conducting state. We have previously reported the syntheses of two series of polyacetylene oligomers containing from 3 to 10 conjugated double bonds, and end-capped with either methyl or phenyl groups.[2–4] Upon oxidative doping with strong oxidizing agents such as $SbCl_5$, in solution, substituted diphenyl polyenes undergo successive one-electron transfers initially forming polaron-like species (P) but, in the presence of excess oxidizing agent, a second oxidation step produces the more stable bipolaronic (BP) change state. The lifetimes of the BP states in solution can be significantly enhanced by mesomeric interaction with electron-donating substituents, with the greatest effect produced by Me_2N substituents.[5] In contrast, polaronic charge states have only been stabilized by MeO groups and careful control of the quantity of oxidizing agent, although in most cases they can be observed spectroscopically (UV–VIS or ESR) as transient intermediates.[6] The BP states generated in this fashion have shown remarkable stability, considering the relatively short delocalization lengths. For example, the BP formed from 1,12-bis(p-N,N-dimethylaminophenyl)dodeca-1,3,5,7,9,11-hexaene in dilute solution (10^{-5} mol dm^{-3} in CH_2Cl_2) can be observed spectroscopically even after 2–3 d in contact with moist air in an open flask. However, less stabilized charge states do decay irreversibly much more quickly under the same conditions.[5] The effect of changing end groups on polaron and bipolaron formation in oligomeric species has not been considered in any great detail. However, the recent observation by several research groups that electroactive materials have large optical nonlinearities has prompted studies of the effect of structural changes upon molecular hyperpolarizability.[7–9] Although it is recognized that the molecular hyperpolarizability γ, or the bulk third order susceptibility $\chi^{(3)}$, are related to the effective conjugation length, it has only recently been shown that the ratio of γ to N, the length of the conjugation sequence, levels off with increasing N.[10–13] For example, Prasad[13] has measured γ for a series of polythiophene oligomers by degenerate four wave mixing (DFWM) in solution and found a power law dependence for γ of four. $\chi^{(3)}$ Measurements for poly(3-dodecylthiophene) showed the same effect, and Prasad concluded that effective conjugation does not extend much beyond 10 repeat units. Similar measurements of poly(p-phenylene) showed that $\chi^{(3)}$ levels off at the terphenyl

level ($N = 3$). With this in mind, we questioned whether phenyl end caps were the best choice for stabilizing charge separation in long polyenes, and decided to investigate the formation and stabilization of BP states in bis-thienyl polyenes.

Synthesis of Bis-thienyl Polyenes.—In a previous publication we outlined a general approach to the synthesis of symmetrically substituted polyenes *via* Wittig or Horner–Emmons–Wadsworth methodology.[14] This approach is outlined in Scheme 1.
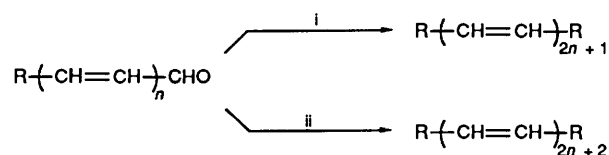
Scheme 1 *Reagents: i*, $Bu_3\overset{+}{P}CH_2\text{+}CH=CH\text{+}CH_2\overset{+}{P}Bu_3$, 2 Cl⁻, NaOEt, EtOH or DMF; *ii*, $Bu_3\overset{+}{P}CH_2\text{+}CH=CH\text{+}CH_2\overset{+}{P}Bu_3$, 2 Br⁻, NaOEt, EtOH or DMF

Thus bis-thienyl polyenes containing 3 and 4 double bonds were prepared in good yield from thiophene-2- or -3-carbaldehydes, while polyenes containing 5 and 6 double bonds were obtained from the corresponding thienylpropenals, as outlined in Schemes 2–4. All thienylpropenals were prepared from the corresponding thiophenecarbaldehydes by the Wittig aldehyde extension methodology developed in our laboratory based on the original suggestion by Cresp. *et al.*[15,16]

| 1 $R^1 = Me$, $R^2 = H$ | 3 $R^1 = Me$, $R^2 = H$ |
| 2 $R^1 = H$, $R^2 = Me$ | 4 $R^1 = H$, $R^2 = Me$ |
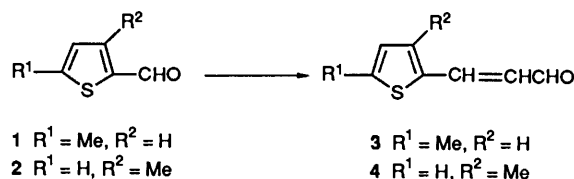
Scheme 2

In the 2-thienyl series, methyl groups were substituted in either the 3- or 5-positions in an attempt to enhance bipolaronic stability, and to determine if the substitution pattern had any real effect (positive or negative) upon BP formation or oxidative stability.

Results and Discussion

When polythiophenes, poly[p-phenylenevinylene](PPV) or poly[2,5-thienylenevinylene] (PTV) are oxidatively doped, the dominant charge carriers are bipolaronic.[17] In model oligo-

Table 1 Polaron (P) and bipolaron (BP) absorption spectra

| Cmpd.[a]	P A/nm[b]	BP A/nm[c]
6	**888**, 1167	720, **776**
8	**881**, 1154	713, **769**
11	705sh, **797**, 1084	653, **713**
12	760sh, **853**, 1154	713, **776**
17	664sh, 741, **797**, 1063	580sh, **636**, 692
18	713sh, **804**, 1067, 1157	633sh, **699**, 773sh

[a] 10^{-5} mol dm^{-3} CH_2Cl_2. [b] Excess of polyene. [c] Excess of $SbCl_5$. Peak of maximum intensity in bold.
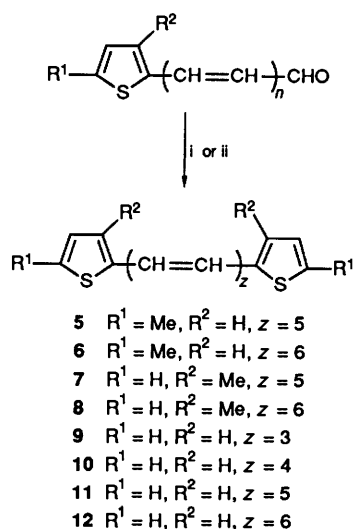
Scheme 3 *Reagents:* see Scheme 1

13 $n = 0$
14 $n = 1$

15 $z = 3$
16 $z = 4$
17 $z = 5$
18 $z = 6$
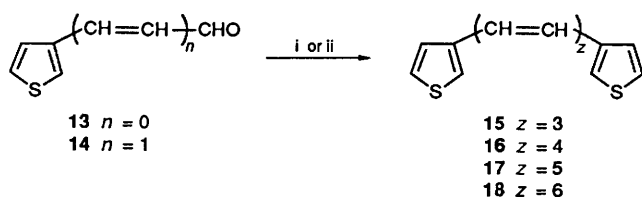
Scheme 4 *Reagents:* see Scheme 1

meric compounds of PPV and PTV, the dominant charge states are similarly bipolaronic, and the intermediary polaronic charge states can sometimes be observed spectroscopically (UV–VIS or ESR), and in some cases stabilized by carefully limiting the quantity of oxidant so that some unoxidized polyene remains.[18,19] Under these conditions no disproportionation of the polaron state is observed (2P→BP + N, where N is a neutral polyene chain).

Bipolaronic charge states, in the diphenyl polyene series, show increased stabilization as the delocalization length increases, as indicated by the rate of decay of the optical absorption signal.[5] Increased stabilization of organic dications as conjugation length increases, thus providing for greater charge separation, has previously been noted by Hünig and co-workers in their many investigations of multistage redox systems.[20,21] Chen, *et al.*[22] have reported a similar tendency to form bipolarons preferentially to polarons as conjugation length increases in the oxidation of conjugated bis(4H-pyrans), bis(4H-thiopyrans) and bis(flavenes). α,ω-Dithienylpolyenes show similar trends when oxidized in CH_2Cl_2 solution with $SbCl_5$, as outlined in Table 1. In the 2-thienyl series ($Z = 3–6$), stable bipolaronic states are formed when $Z = 5$ and 6. As previously observed for the diphenyl polyene series, the $Z = 3$ and 4 delocalization lengths appear to be too short to accommodate two like charges in a stable configuration. Polaronic charge states can be observed as either transient species when excess of oxidant is used, or can be observed as

stable species when the quantity of oxidant is limited to allow only partial oxidation of the original neutral polyene. Thus the sequential formation of P and BP states seems to follow that previously observed for diphenyl polyene, PPV and PTV oligomers,[18,19] as shown in Scheme 5.

Scheme 5
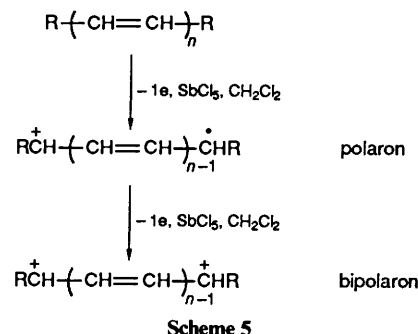
The BP absorption maxima red shift by *ca.* 60 nm in both the 2- and 3-Th series as conjugation length increases from $Z = 5$ to $Z = 6$, however the 2-Thienyl BPs are themselves red-shifted *ca.* 60 nm from the 3-Thienyl BPs of similar conjugation length. Since the delocalization pathlength in the 3-Thienyl series is cross conjugated compared to the 2-Thienyl series, this seems to confirm that BP delocalization involves both thiophene rings, and that the BP absorption maxima is a reliable indication of the delocalization pathway. Thus we would propose that the dominant BP structure for the bis-(2-Thienyl hexaene) would be similar to that shown in Scheme 6.

Scheme 6
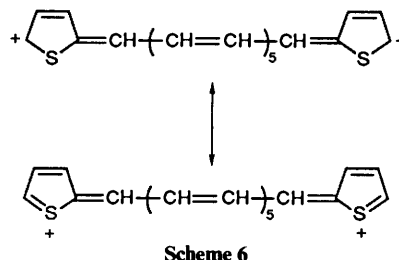
Similar length dependence is seen in the P absorption maxima in both the 2- and 3-Thienyl series. Polaron charge states, as mentioned previously, are attainable by carefully limiting the quantity of oxidant as previously described for donor-substituted diphenyl polyenes.[6] When methyl groups are substituted in either the 5- or 3-positions in the bis(2-Thienyl) polyene series, no further enhancement of BP stability is attained, as indicated by the nearly identical absorption maxima and optical absorption lifetimes (6 and 8 compared to 12), however there is a greater effect on the P absorption spectra, where a *ca.* 30 nm shift in λ_{max} is found, presumably from stabilization of the free radical end of the polaron.

Perhaps the most interesting of the results of this study is the comparison to the diphenyl polyene series. For this series, Ph(CH=CH)$_z$Ph, the $Z = 5$ BP and $Z = 6$ BP have absorption maxima at $\lambda = 612$ and 685 nm compared with 713 and 776 nm for the 2-Thienyl $Z = 5$ and $Z = 6$ counterparts. We interpret this dramatic end group effect on oxidative resistance of the phenyl *vs.* thiophene rings (reflected in their respective band gaps) and the greater ease of charge stabilization in the thiophene ring compared to the quinoid structures of the diphenyl polyene series. We have observed similar behaviour in PPV *vs.* PTV oligomers.[17,18]

The results of this study indicate that the stabilization of charge states and the positioning of optical absorption windows can be controlled by careful choice of end group effects. Thus we can utilize this information to design copolymers in which

electroactive subunits (i.e. oligomeric PTV segments) can be alternated with non-electroactive segments. This approach yields copolymers with sharp absorption bands rather than the extremely broad absorption of such polymers as PPV and PTV. The control of absorption characteristics has been shown to be extremely important in the design of new materials for non-linear optics applications. Most recently, Cao, et al., have demonstrated[23] that $\chi^{(3)}$ can be enhanced in ladder-type polymers by bipolaronic charge states. Since we have now shown that the absorption characteristics of BP states are closely related to the design of the electroactive unit, it should be possible to match carefully the charge state absorption to the laser fundamental and harmonics to allow a choice between resonant and non resonant behaviour.

Experimental

M.p.s were obtained with either a Melt Temp or Electrothermal apparatus and are uncorrected. C,H,N, Analyses were carried out in our laboratory with a Perkin-Elmer Model 240 analyser by Paulanne Rider. UV–VIS spectra were recorded with a Varian Model 2290 as CH_2Cl_2 solutions. ^1H NMR spectra were determined as solutions in $CDCl_3$ or $[^2H_6]DMSO$ (Me_4Si internal reference, J values given in Hz) on an IBM WP-200 spectrometer. In general, no solvent was found that yielded solutions concentrated enough to obtain ^1H NMR spectra for the pentaene or hexaene series. Thiophene-2-carbaldehyde and thiophene-3-carbaldehyde and corresponding methyl-substituted thiophene carbaldehydes were obtained from either Aldrich or Lancaster Chemical Co. Solutions of pure polyenes in CH_2Cl_2 (10^{-5} mol dm^{-3}) were doped by adding $SbCl_5$ in a controlled manner so that the ratio of oligomer to dopant was known accurately. All doping studies were carried out in a 1 cm path-length silica cell, and absorption spectral changes recorded with a Guided Wave Vis-Nir Spectrometer Model 200–25 via fibre-optic cable link to the remote sample cell at a scan rate of 7 nm s^{-1}. Scans were repeated 5–10 times to determine the relative stability of the intermediates, and long-term scans with a 20 min repeat interval were carried out for several hours. In all cases very rapid bleaching of the original π-π^* transition was observed, simultaneous with the appearance of either a polaron or bipolaron band.

1,6-Bis(2'-thienyl)hexa-1,3,5-triene 9.—A solution of potassium tert-butoxide (6 g in 200 cm^3 glyme) was added dropwise to a solution of (E) tetraethyl but-2-ene-1,4-diyldiphosphonate[24] (6.56 g, 0.02 mol) and thiophene-2-carbaldehyde (4.48 g, 0.04 mol) in glyme (100 cm^3) at room temperature. The resulting mixture was stirred for 16 h, heated at 60–70 °C for 2 h, and then poured into cold water (250 cm^3). The crude product was isolated by vacuum filtration and upon crystallization from toluene–dimethylformamide (DMF), yielded 1,6-bis(2-thienyl)hexa-1,3,5-triene 9 as pale yellow crystals, m.p. 212–213 °C (lit.,[25] 198–199 °C) (2.63 g, 54%), λ_{max}/nm ($a_{max}/10^4$ m^{-1}), 404 (4.95), 382 (6.00), 364 (4.25) and 340sh (1.90); δ_H 6.38–6.45 (m, 2 H, vinyl), 6.66–6.72 (m, 4 H, vinyl), 6.95–7.00 (m, 4 H, C$_4$H$_3$S ring) and 7.14–7.19 (m, 2 H, C$_4$H$_3$S ring).

1,8-Bis(2'-thienyl)octa-1,3,5,7-tetraene 10.—A solution of potassium butoxide (6 g, 200 cm^3 glyme) was added dropwise to a solution of (E,E)-tetraethyl hexa-2,4-diene-1,6-diyldiphosphonate[14] (7.08 g, 0.02 mol) and thiophene-2-carbaldehyde (4.48 g, 0.04 mol) in glyme (100 cm^3). The product was isolated as described above for 9, yielding light orange crystals of 10, from toluene–DMF, m.p. 233–234 °C (lit.,[22] 229–230 °C) (2.78 g, 52%), λ_{max}/nm ($a_{max}/10^4$ m^{-1}), 426 (8.20), 402 (9.32), 380 (6.25) and 360sh (3.20); δ_H 6.32–6.48 (m, 4 H, vinyl), 6.62–6.75 (m, 4 H, vinyl),

6.95–7.00 (m, 4 H, C$_4$H$_3$S ring) and 7.14–7.19 (m, 2 H, C$_4$H$_3$S ring).

1,10-Bis(2'-thienyl)deca-1,3,5,7,9-pentaene 11.—A solution of sodium ethoxide (1 mol dm^{-3}; 60 cm^3, 0.06 mol) in ethanol was added dropwise to a solution of 3-(2'-thienyl)propen-2-al[16] (0.04 mol) and (E)-but-2-ene-1,4-diylbis(tributylphosphonium) dichloride[14] (0.02 mol) dissolved in ethanol (200 cm^3). Precipitation of product began after ca. 5 min. The mixture was stirred at room temperature for 16 h, and then at 90 °C for 2 h. Water (50 cm^3) was added to the hot solution to redissolve any co-precipitated NaCl, and the solution cooled to room temperature and vacuum filtered. The crude product was recrystallized from DMF yielding 11, m.p. 252–253 °C (30% from DMF), λ_{max}/nm ($a_{max}/10^5$ m^{-1}) 443 (1.46), 466 (1.56), 395 (1.00) and 385sh (4.1) (Found: C, 72.7; H, 5.9. Calc. for C$_{18}$H$_{16}$S$_2$: C, 72.97; H, 5.41%).

1,12-Bis(2'-thienyl)dodeca-1,3,5,7,9,11-hexaene 12.—A solution of sodium ethoxide (1 mol dm^{-3}; 60 cm^3, 0.06 mol) in ethanol was added dropwise to a solution of 2-(2'-thienyl)-propen-2-al[16] (0.04 mol) and (E,E)-hexa-2,4-diene-1,6-diyl-bis(tributylphosphonium) dibromide[14] (0.02 mol) dissolved in ethanol (200 cm^3). Work-up and isolation were identical with that described above for 11, yielding 12, m.p. 262–263 °C (30% from DMF), λ_{max}/nm ($a_{max}/10^4$ m^{-1}) 461 (8.25), 432 (9.00), 409 (6.40) and 395sh (4.1) (Found: C, 74.2; H, 5.8. Calc. for C$_{20}$H$_{18}$S$_2$: C, 74.53; H, 5.59%).

1,6-Bis(3-thienyl)hexa-1,3,5-triene 15.—The title compound was prepared from thiophene-3-carbaldehyde (0.04 mol) and (E)-tetraethyl but-2-ene-1,4-diyldiphosphonate[24] (0.02 mol) as described above for 9: m.p. 228–230 °C (48% from toluene) λ_{max}/nm ($a_{max}/10^4$ m^{-1}), 366 (5.50), 348 (6.80) and 334 (5.00); δ_H 6.37–6.48 (m, 2 H, vinyl), 6.52–6.80 (m, 4 H, vinyl) and 7.00–7.40 (m, 6 H, C$_4$H$_3$S ring) (Found: C, 70.8; H, 5.3. Calc. for C$_{16}$H$_{14}$S$_2$: C, 71.07; H, 5.22%).

1,8-Bis(3'-thienyl)octa-1,3,5,7-tetraene 16.—The title compound was prepared from thiophene-3-carbaldehyde (0.04 mol) and (E,E)-tetraethyl hexa-2,4-diene-1,6-diyldiphosphonate[24] (0.02 mol) as described above for 10: m.p. 245–247 °C (44% from toluene–DMF), λ_{max}/nm ($a_{max}/10^4$ m^{-1}) 394 (6.30), 372 (7.28) and 354 (5.00); δ_H 6.32–6.47 (m, 2 H, vinyl), 6.60–6.80 (m, 6 H, vinyl) and 7.10–7.40 (m, 6 H, C$_4$H$_3$S ring).

1,10-Bis(3'-thienyl)deca-1,3,5,7,9-pentaene 17.—The title compound was prepared from 3-(3'-thienyl)propen-2-al (0.04 mol) and (E)-tetraethyl but-2-ene-1,4-diylphosphonate (0.02 mol) as described above for 9: m.p. 256–258 °C (65% from toluene–DMF), λ_{max}/nm ($a_{max}/10^5$ m^{-1}), 415 (1.24), 392 (1.26), 372 (0.78) and 352sh (0.38) (Found: C, 72.55; H, 5.9. Calc. for C$_{18}$H$_{16}$S$_2$: C, 72.97; H, 5.41%).

1,12-Bis(3'-thienyl)dodeca-1,3,5,7,9,11-hexaene 18.—The title compound was prepared from 3-(3'-thienyl)propen-2-al (0.04 mol) and (E,E)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium)dibromide[14] (0.02 mol) as described above for 12; m.p. 270–272 °C (46% from DMF), λ_{max}/nm ($a_{max}/10^4$ m^{-1}) 427 (9.20), 411 (9.90), 389 (7.40) and 369sh (5.1) (Found: C, 74.25; H, 5.5. Calc. for C$_{20}$H$_{18}$S$_2$: C, 74.53; H, 5.59%).

1,10-Bis(5'-methyl-2'-thienyl)deca-1,3,5,7,9-pentaene 5.—The title compound was prepared from 3-(5'-methyl-2'-thienyl)-propen-2-al[26] (0.04 mol) and (E)-but-2-ene-1,4-diylbis-(tributylphosphonium) dichloride (0.02 mol) as described above for 11; m.p. 216–217 °C (62% from toluene–DMF), λ_{max}/nm ($a_{max}/10^4$ m^{-1}) 450 (6.37), 425 (7.00) and 399 (4.89) (Found: C, 73.9; H, 6.45. Calc. for C$_{20}$H$_{20}$S$_2$: C, 74.03; H, 6.21%).

1,12-Bis(5'-methyl-2'-thienyl)dodeca-1,3,5,7,9,11-hexaene 6.—
The title compound was prepared from 3-(5'-methyl-2'-thienyl)-propen-2-al[26] (0.04 mol) and (E,E)-hexa-2,4-diene-1,6-diylbis-(tributylphosphonium) dibromide (0.02 mol) as described above for 12: m.p. 236–238 °C (17% from toluene–DMF), λ_{max}/nm (a_{max}/10^4 m^{-1}) 469 (9.92), 441 (10.6), 417 (7.0) and 392sh (3.4) (Found: C, 75.1; H, 6.2. Calc. for $C_{22}H_{22}S_2$: C, 75.38; H, 6.33%).

1,10-Bis(3'-methyl-2'-thienyl)deca-1,3,5,7,9-pentaene 7.—The title compound was prepared from 3-(3'-methyl-2'-thienyl)-propen-2-al[27] (0.04 mol) and (E)-but-2-ene-1,4-diylbis(tri-butylphosphonium) dichloride (0.02 mol) as described above for 11; m.p. 186–187 °C (49% from toluene–DMF), λ_{max}/nm (a_{max}/10^4 m^{-1}), 449 (6.97), 422 (8.08) and 398 (5.35) (Found: C, 74.1; H, 6.05. Calc. for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21%).

1,12-Bis(3'-methyl-2'-thienyl)dodeca-1,3,5,7,9,11-hexaene 8.—
The title compound was prepared from 3'(3'-methyl-2'-thienyl)-propen-2-al[27] (0.04 mol) and (E,E)-hexa-2,4-diene-1,6-diyl-bis(tributylphosphonium) dibromide (0.02 mol) as described above for 12; m.p. 190–191 °C (46% from toluene–DMF), λ_{max}/nm (a_{max}/10^4 m^{-1}), 469 (7.4), 440 (8.5), 416 (6.0) and 392sh (3.3) (Found: C, 74.9; H, 6.75. Calc. for $C_{22}H_{22}S_2$: C, 75.38; H, 6.33%).

Acknowledgements

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