



Polymer Communication

Narrow bandgap and enhanced electroconductivity in a dihydropyrene–thiophene copolymer

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ARTICLE INFO

Article history:

Received 9 January 2009

Received in revised form

12 February 2009

Accepted 16 February 2009

Available online 24 February 2009

Keywords:

Copolymer

Non-benzenoid

Narrow bandgap

ABSTRACT

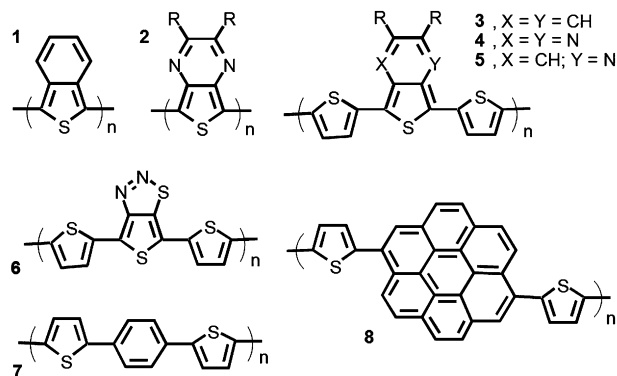
Incorporation of π electron-rich dihydropyrene units into the polymer backbone of polythiophene afforded a conducting polymer with narrow bandgap energy of about 1.0 eV. Doping of this polymer with iodine showed an optimum conductivity of about 1.0 S cm^{-1} . The quinoid character and a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) separation in the dihydropyrene are believed to account for the observed semi-conducting properties of this dihydropyrene–thiophene copolymer. The dihydropyrene unit in the copolymer was found to exhibit a significantly higher thermal stability than the parent molecule.

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1. Introduction

In the design of organic electroactive materials, polymers with narrow bandgaps ($E_{\text{gap}} < 1.5 \text{ eV}$) in their neutral state are desired targets [1]. The significant reduction [2] in bandgap going from polythiophene ($E_{\text{gap}} = 2.1 \text{ eV}$) to polyisothianaphthene **1** ($E_{\text{gap}} = 1.1 \text{ eV}$) and its pyrazino derivative **2** ($E_{\text{gap}} \sim 0.86\text{--}1.02 \text{ eV}$) has been well documented [1d,3]. Attempts to moderate the electronic structure of these materials through copolymers **3** [1d,4], **4** [1d,5] and **5** [6] resulted in relatively larger bandgaps ($E_{\text{gap}} = 1.0\text{--}1.7 \text{ eV}$).

A combination of factors including the coplanarity between adjacent repeat units [1a,2], the quinoid character of the aromatic moieties [7] and the presence of donor and acceptor units [8] is expected to affect the E_{gap} value. The polymer **6** [9] exhibits a narrow bandgap of about 0.9 eV [10]. Incorporating a benzene ring in the polymer backbone as in **7** is expected to reduce the quinoid character in the polymer. This was demonstrated by its relatively larger bandgap of 2.5 eV [11]. The presence of a larger benzenoid such as corene in **8** resulted in a highly insoluble material [12].

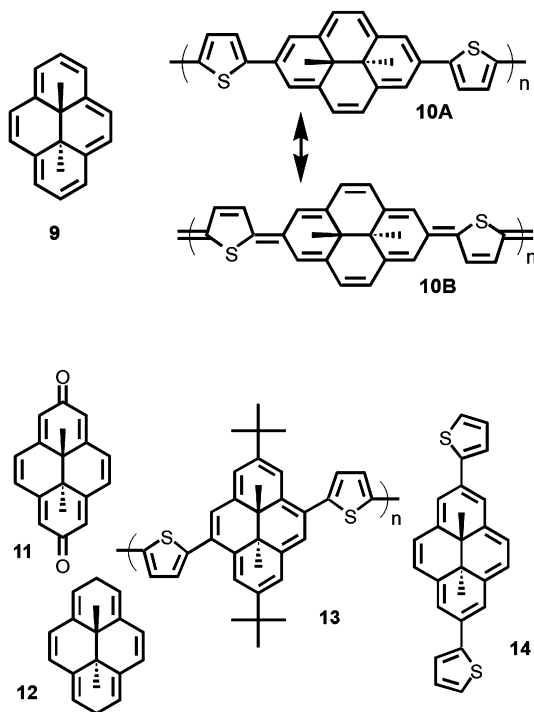


Results from theoretical calculations [13] indicate a large decrease in the HOMO–LUMO separation going from benzene to the 10b,10c-dimethyl-10b,10c-dihydropyrene **9**. Thus going from the polymer **7** to polymer **10** is expected to result in a significant decrease in bandgap. The molecular structure of **9** is essentially planar [14]. The quinone **11** is known and reduction of **10** affords the 2,7-dihydro derivative **12** [15]. The above observation would also suggest a possibility in reducing the energy bandgap through the introduction of quinoid character **10B**. Electrochemical studies [16] of **9** and its reaction with an alkali metal indicated the formation of a dianion [17]. Thus in the polymer **10** the thiophene could serve as an aromatic donor and the dihydropyrene as a quinoid acceptor. A related polymer **13** was reported to exhibit

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interesting optoelectronic properties [18] but it involves a structurally different quinoid-type conjugation compared to that in **10** and may not allow a direct comparison with reported systems such as **7**. We report in this communication the synthesis and properties of 2,7-di(2-thienyl)-10b,10c-dimethyl-10b,10c-dihydropyrene **14** and its polymer **10**.



2. Experimental part

2.1. Characterization and analysis

Ultraviolet–visible (UV–vis) absorption spectra were obtained on a Hewlett Packard 8452A Diode Array Spectrophotometer with a Xenon lamp as light source. Conductivity was measured using a four-point probe connected to Keithley constant-current source system. Thermogravimetric analyses (TGAs) of polymer powders were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ with an air or nitrogen flowing of 75 mL min^{-1} was used with the runs being conducted from room temperature to $1000\text{ }^{\circ}\text{C}$. Electrochemical study was performed on an EG & G 273A potentiostat/galvanostat controlled by EG & G Model 270/250 Research Electrochemistry Software, V. 4.30. A three-electrode system was used, with a Pt disc working electrode (effective area 0.5 cm^2), a platinum foil counter electrode and a silver wire quasi-reference electrode or an Ag/AgNO₃ (0.1 M in dry acetonitrile) reference electrode. The quasi-reference electrode was calibrated against ferrocene/ferrocenium ion and for control also against a saturated calomel electrode (SCE) at the end of measurement.

2.2. Preparations

2.2.1. 2,7-Di(2-thienyl)-10b,10c-dimethyl-10b,10c-dihydropyrene **14**

Pd(PPh₃)₂Cl₂ (100 mg, 0.14 mmol) was added to a solution of 2,7-dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene [19] (336 mg, 0.86 mmol) and (2-thienyl)-tri-(*n*-butyl)tin [20] (0.80 g, 2.16 mmol)

in dry tetrahydrofuran (THF) (35 mL). The mixture was stirred at room temperature for 20 h. During the course of the reaction the color changed from green to red. The mixture was poured into water (150 mL) and extracted with dichloromethane (CH₂Cl₂) (100 mL × 2). The extracts were combined and washed with water, dried (Na₂SO₄), and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with hexane/CH₂Cl₂ (6:1) as eluent to give **14** (260 mg; 76%) as dark purple needles, mp 224–226 °C; FTIR 3029, 2975, 2921, 2856, 1416, 1380, 1053, 878, 852, 823, 692, 661 cm⁻¹. ¹H NMR (300 MHz) δ 8.76 (s, 4H), 8.51 (s, 4H), 7.82 (d, 2H, *J* = 4.2 Hz), 7.43 (d, 2H, *J* = 5.1 Hz), 7.25 (dd, 2H, *J*₁ = 4.2 Hz, *J*₂ = 5.1 Hz), -3.55 (s, 6H); UV–Vis (CH₂Cl₂) λ_{max} 338, 356, 388, 412, 524, 554 nm; MS *m/z* 396 (M⁺, 12), 381 (90), 366 (100), 321 (15), 183 (30); Anal. calcd for C₂₆H₂₀S₂: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.82; H, 5.26; S, 16.40.

2.2.2. Poly[2,7-di(2-thienyl)-10b,10c-dimethyl-10b,10c-dihydropyrene] **10**

The chemical polymerization reactions were carried out in anhydrous solvents at 50 °C under vigorous stirring. A dry argon flow was passed through the reaction medium and the evolved hydrogen chloride gas was trapped in a U-tube with sodium hydroxide. A solution of anhydrous iron(III) chloride (FeCl₃) (186 mg, 1.15 mmol) in nitromethane (2 mL) was added dropwise in 20 min to a solution of **14** (130 mg, 0.33 mol) in carbon tetrachloride (6 mL). The color of the mixture turned dark blue gradually. After stirring the reaction mixture for 10 h, the mixture was poured into methanol. The dark blue solid was filtered and Soxhlet-extracted with methanol until a negative test for iron(III) was achieved with ammonium thiocyanate. The residue was stirred with 10 mL of an ethanol–water solution of hydrazine (40%) for 24 h, filtered and Soxhlet-extracted again with methanol (16 h) followed by acetone (16 h). Polymer **10** was obtained as a dark purple powder with a golden luster (105 mg, 81%). FTIR 3071, 3032, 3017, 2971, 2932, 2855, 1431, 1377, 1342, 1053, 873, 788, 658 cm⁻¹. Anal. calcd for (C₂₆H₁₈S₂)_n: C, 79.15; H, 4.60; S, 16.25. Found: C, 78.32; H, 4.96; S, 16.43. Doped polymer was obtained by placing the polymer disc in an iodine chamber.

The electrochemical polymerization of **10** (10 mg, 0.025 mmol) was carried out in a cell in degassed THF (10 mL) in the presence of *n*-Bu₄NClO₄ (0.42 g, 1.25 mmol) under inert conditions at room temperature using platinum electrodes at 0.5 mA/cm² and a potential of 1 V.

3. Results and discussion

A Stille coupling reaction [21] between 2,7-dibromo-10b,10c-dimethyl-10b,10c-dihydropyrene [19] and (2-thienyl)-tri-(*n*-butyl)tin [20] in the presence of a catalytic amount of Pd(PPh₃)₂Cl₂ afforded the desired monomer **14** in a 76% yield. A comparison of the electronic spectrum of **14** in CH₂Cl₂ (Fig. 1) with that of **9** [22] suggests a strong conjugation effect. Significant bathochromic shifts of the major absorptions are observed going from the parent **9** (λ_{max} at 463, 377 and 338 nm) [22] to **14** (λ_{max} at 554, 524, 412, 388 and 356 nm; Fig. 1). A chemical polymerization of **14** was carried out according to a modified oxidative method (using FeCl₃ as oxidant) generally used for the preparation of polythiophene [23]. A fine powder suspension of the polymer **10** was observed. After dedoping by repeated treatment with dilute aqueous hydrazine solution, the polymer **10** was isolated as a dark blue-violet powder, which was found only sparingly soluble in common organic solvents. The yield of the polymer **10** could be improved significantly by controlling the reaction temperature (5% yield at room temperature; 81% yield at 50 °C). Elemental composition of the neutral polymer as determined from microanalysis of samples

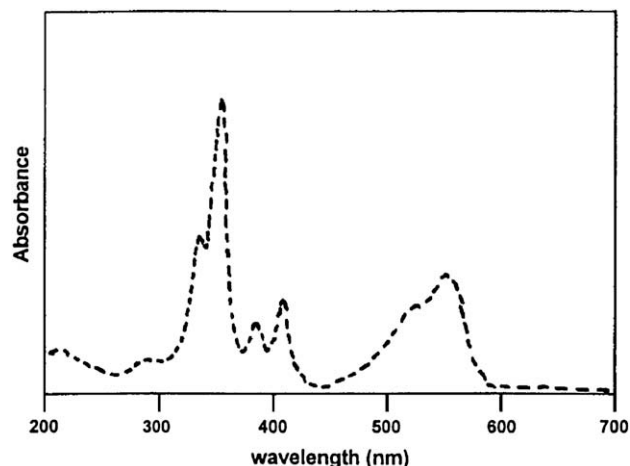


Fig. 1. UV-Visible spectrum of monomer **14** in CH_2Cl_2 .

obtained from different attempts supports the calculated empirical formula (e.g. Calcd for $(\text{C}_{26}\text{H}_{18}\text{S}_2)_n$: C, 79.15; H, 4.60; S, 16.21. Found: C, 78.32; H, 4.96; S, 16.43). Similar results were obtained in repeated analyses. It is common to obtain relatively lower than expected carbon values in combustion analyses of highly unsaturated polymers based on aromatic carbocyclic structures [24]. This is due to incomplete combustion with remaining residues. In most cases, the values for H and S remain reasonably accurate for the polymer **10** with a negligible inorganic content (<0.1 ppm Fe).

The FTIR spectrum of **10** shows a typical absorption at 783 cm^{-1} (out-of-plane bending, H_β) and an observed absorption at 629 cm^{-1} corresponding to H_α of the thiophene ring is consistent with a polymerization process via the α -positions of the thiophene rings in **14** to afford **10**. The monomer **14** could also be polymerized electrochemically either via cyclic voltammetry (CV) or by the galvanostatic method. The monomer and electrolyte ($n\text{-Bu}_4\text{NClO}_4$ in THF) concentrations used were 2.5×10^{-2} and $1.25 \times 10^{-1}\text{ mol dm}^{-3}$, respectively. The resulting polymer films were rinsed carefully with absolute ethanol and acetone and then dried in an argon stream prior to the cyclic voltammetric studies and spectrophotometric analyses. In the CV polymerization approach, film formation was relatively slow although the increase in peak currents observable with the number of scans was indicative of progressive polymer growth on the surface of the electrode. Polymer film prepared via the galvanostatic method exhibited a monomer oxidation potential

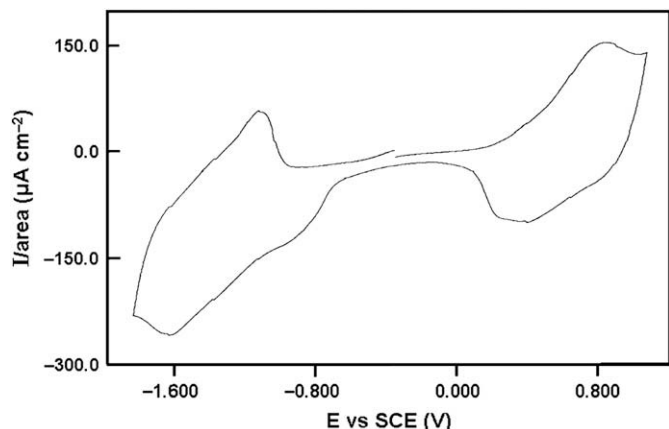


Fig. 2. Cyclic voltammogram of a thin film of polymer **10**.

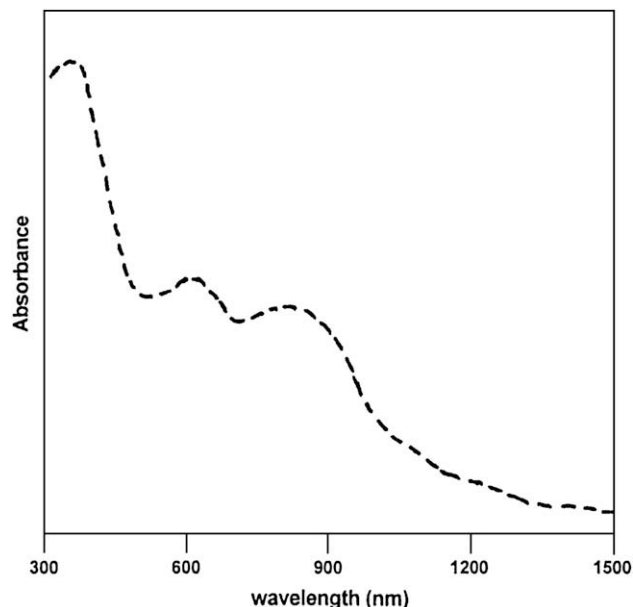


Fig. 3. UV-Visible-NIR spectrum of a dedoped film of the polymer **10**.

of ca. 1.0 V at a current density of $500\text{ }\mu\text{A cm}^{-2}$. Films with good stability on both platinum foil and indium tin oxide (ITO) glass could readily be obtained.

Fig. 2 depicts the cyclic voltammogram of a thin film of polymer **10** deposited on platinum in the potential range of -2.0 to 1.2 V at a scan rate of 100 mV s^{-1} . The polymer **10** remained stable to both p -doping and n -doping after repeated anodic and cathodic cycling. The small difference in threshold potentials for p -doping and n -doping is characteristic of narrow bandgap systems. At scan rates of $40\text{--}100\text{ mV s}^{-1}$, both the cathodic and the anodic peak currents of the n -type redox cycle were found to scale linearly with respect to the scan rate. This suggests that kinetic limitation of the electrochemical reduction of the polymer is not significant [25]. From Fig. 1, the electrochemical oxidation potential was observed to be

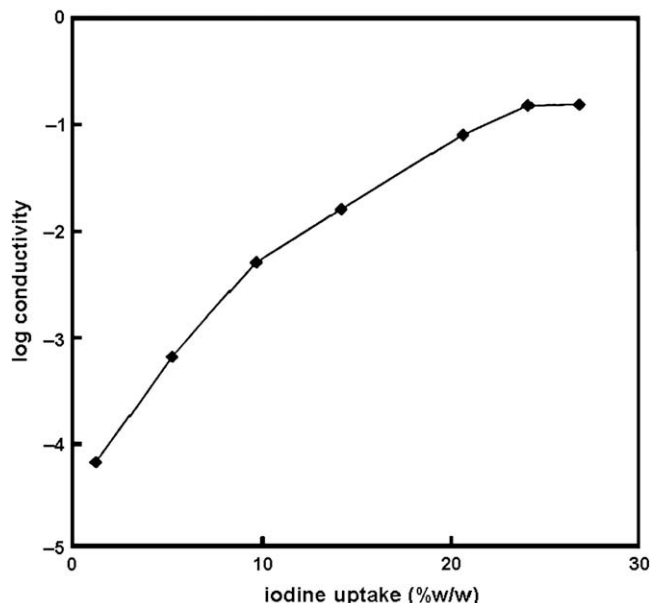


Fig. 4. Changes in conductivity of iodine-doped polymer **10**.

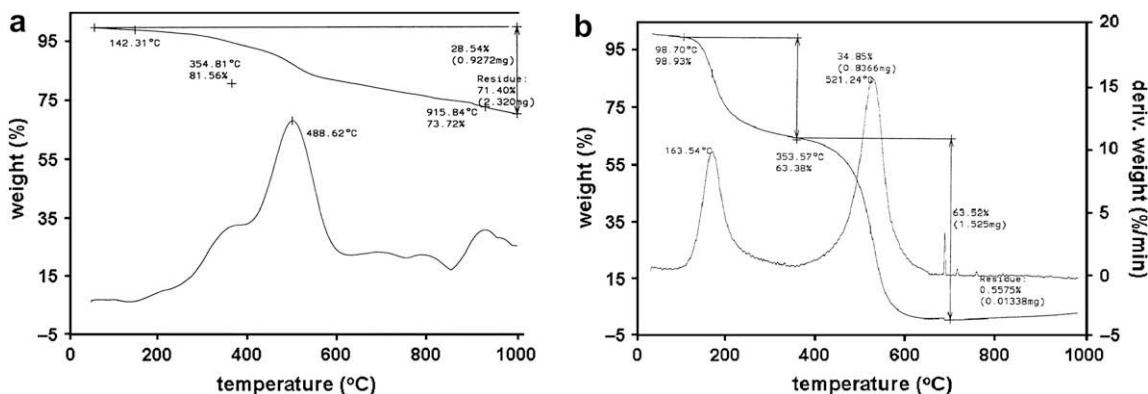


Fig. 5. TGA-DTA study of (a) polymer **10** and (b) iodine-doped polymer **10**.

0.91 V with an onset potential value of 0.19 V. This corresponds to an estimated ionization potential (IP) of 4.59 eV for the polymer **10**. The peak potential for the electrochemical reduction is -1.71 V. The onset potential value could be estimated to be -0.71 V, suggesting that the electron affinity (EA) of polymer **10** is 3.69 eV. The observed electrochemical bandgap (the difference between IP and EA) is thus only 0.90 eV, which is about 1.6 eV lower than that of **7** [11] with a benzene ring as linker.

The UV-Vis-NIR spectrum of a dedoped film of the polymer **10** (Fig. 3) exhibits two absorption maxima (λ_{\max}) at 591 and 851 nm, respectively. Most conjugated polymers reported earlier are generally characterised by a broad absorption band due to its intrinsic energetic disorder derived primarily by the variation of conjugation length in polymer segments. The two maxima observed in the spectrum of **10** could be due to the presence of the dihydropyrene moiety (the monomer **14** exhibits two significant absorption maxima in the range of 500–600 nm; Fig. 1). The bandgap energy of about 1.0 eV of the polymer, as determined from extrapolation of the low energy absorption edge in its UV-vis absorption spectrum (Fig. 2), agrees well with the value estimated by the electrochemical method described earlier. This value places the polymer **10** in the relatively small family of narrow bandgap (≤ 1 eV) conjugated polymers reported so far. Doping of a polymer film of **10** with iodine was carried out in a closed chamber. Four-probe conductivity measurement of the iodine-doped polymer was correlated to the weight uptake of iodine. There was a rapid and continuous upsurge in conductivity as the uptake of iodine increased by weight (Fig. 4). There was a significantly large uptake of iodine up to about 30% by weight and the optimum conductivity, σ , of $0.98 \pm 0.03 \text{ Scm}^{-1}$ was obtained when the iodine uptake reached about 25%.

The thermal properties of the polymer **10** in its neutral and iodine-doped states were analyzed both in air and under nitrogen atmosphere. The neutral polymer was found to be stable under nitrogen with a residual weight of 72% at the end of the transition (1000 °C) (Fig. 5a), indicating that the polymer has a strong backbone. Two weight losses at about 355 °C and 489 °C, respectively, could be attributed to the cleavage of the C–S bond and the elimination of the two methyl groups in the dihydropyrene (Fig. 5b). Unexpectedly only a single-step degradation was indicated by a relatively sharp peak at 515 °C with a final residue of only 7% by weight when a thermal analysis of **10** was carried out in air. When the iodine-doped polymer was studied under similar conditions in air (Fig. 5b), a significant weight loss (of iodine) was observed at 163 °C (at 168 °C under nitrogen) with another relatively sharp peak at 521 °C similar to that observed for the neutral polymer. The weight of the residue was $<1\%$. A possible explanation is that in air

the polymer was degrading and oxidising in such a way that the weight changed only gradually with weight loss being balanced by weight gain brought on by oxygen incorporation until the sample actually ignited.

4. Conclusion

In conclusion the observed properties of the polymer **10** have provided good evidence for the prediction that incorporating aromatic non-benzenoids in the polymer backbone would result in a decrease in bandgap and thus an increase in conductivity. Another significant result derived from our work is that the dihydropyrene moiety in polymer **10** is thermally more stable compared to the parent molecule **9** that was shown to undergo thermal rearrangement at ca. 200 °C. [26]. Many non-benzenoids are known to be thermally unstable but results in this work should provide us with some confidence in further investigations of polymers derived from non-benzenoid aromatic systems.

Acknowledgments

This work was supported by the Singapore Ministry of Education AcRF Tier 1 Grant R-143-000-169-112. The authors thank the staff at the Chemical, Molecular and Materials Analysis Center, Department of Chemistry, NUS, for their technical assistance.

References

- [1] (a) Scholz F, editor. Conducting polymer: a new era in electrochemistry. Berlin: Springer; 2008; (b) Huo L, Tan Z, Wang X, Han M, Li Y. Synth Met 2007;157:690–5; (c) Atwani O, Baristiran C, Erden A, Sonmez G. Synth Met 2008;158:83–9; (d) Rasmussen SC, Pomerantz M. Low bandgap conducting polymers. In: Skotheim TA, Reynolds JR, editors. Handbook of conducting polymers. Conjugated polymers: theory, synthesis, properties, and characterization. 3rd ed. Boca Raton, Florida: CRC Press; 2007 [chapter 12].
- [2] Wudl F, Kobayashi M, Heeger AJ. J Org Chem 1984;49:3382–4.
- [3] (a) Pomerantz M, Chaloner-Gill B, Harding LO, Tseng JJ, Pomerantz WO. Chem Commun 1992:1672–3; (b) Synth Met 1993;55:960–5.
- [4] (a) Lorcy D, Cava MP. Adv Mater 1992;4:562–4; (b) Bäuerle P, Götz G, Emerle P, Port H. Adv Mater 1992;4:564–8; (c) Musmanni S, Ferraris JP. Chem Commun 1993:172–4.
- [5] Kitamura C, Tanaka S, Yamashita Y. Chem Commun 1994:1585–6.
- [6] Ferraris JP, Bravo A, Kim W, Hrnrcr DC. Chem Commun 1994:991–2.
- [7] Bredas JL. Synth Met 1987;17:115–21.
- [8] Havinga EE, Tenhoeve WW, Wynberg H. Synth Met 1993;55:299–306.
- [9] Tanaka S, Yamashita Y. Synth Met 1993;55:1251–4.
- [10] (a) Zhou Z, Parr RG. J Am Chem Soc 1989;111:7371–9; (b) Lambert TL, Ferraris JP. Chem Commun 1991:752–4; (c) Ferraris JP, Lambert TL. Chem Commun 1991:1268–70.
- [11] Ng SC, Xu JM, Chan HSO. Synth Met 1998;92:33–7.
- [12] Thelakkat M, Naarmann H. Synth Met 1995;68:153–5.

- [13] Bock H. *Angew Chem Int Ed Engl* 1977;16:613–7.
- [14] (a) Mitchell RH, Iyer VS, Khalifa N, Mahadevan R, Venugopalan S, Weerawarna SA, et al. *J Am Chem Soc* 1995;117:1514–32;
(b) Hanson A. *Acta Crystallogr* 1965;18:599–604.
- [15] Boekelheide V, Phillips JB. *J Am Chem Soc* 1967;89:1695–704.
- [16] (a) Fry AJ, Chung LL, Boekelheide V. *Tetrahedron Lett* 1974;445–8;
(b) Fry AJ, Simon J, Tashiro M, Yamato T, Mitchell RH, Dingle TW, et al. *Acta Chem Scand Ser B* 1983;37:445–50.
- [17] Mitchell RH, Boekelheide V. *Chem Commun* 1970:1557–8.
- [18] Marsella MJ, Wang Z-Q, Mitchell RH. *Org Lett* 2000;2:2979–82.
- [19] Mitchell RH, Lai Y-H, Williams RV. *J Org Chem* 1979;44:4733–5.
- [20] Gopinatham S, Gopinatham C, Gupta J. *Indian J Chem* 1974;12:623–8.
- [21] (a) Stille JK. *Angew Chem Int Ed Engl* 1986;25:508–24;
(b) Bailey TB. *Tetrahedron Lett* 1986;27:4407–10;
(c) Farina V. *Pure Appl Chem* 1996;68:73–8.
- [22] Mitchell RH, Chaudhary M, Dingle TW, Williams RV. *J Am Chem Soc* 1984;106:7776–9.
- [23] Casa CD, Bertinelli F, Bizzarri PC, Salatelli E. *Adv Mater* 1995;7:1005–9.
- [24] (a) Zhang QT, Tour JM. *J Am Chem Soc* 1997;119:9624–31;
(b) Lamba JJS, Tour JM. *J Am Chem Soc* 1994;116:11723–36;
(c) Stephens EB, Tour JM. *Macromolecules* 1993;26:2420–7;
(d) Wallow TI, Novak BM. *J Am Chem Soc* 1991;113:7411–2.
- [25] Genies EM, Bidan G, Diaz AF. *J Electroanal Chem* 1983;149:101–13.
- [26] Boekelheide V, Sturm E. *J Am Chem Soc* 1969;91:902–8.