Synthesis and Characterization of Soluble and n-Dopable Poly(quinoxaline vinylene)s and Poly(pyridopyrazine vinylene)s with Relatively Small Band Gap

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ABSTRACT: Synthesis and characterization of poly(quinoxaline vinylene)s and poly(pyridopyrazine vinylene)s with linear and branched aliphatic side chains are reported. The electron affinity of the polymers was measured with cyclic voltammetry (CV) and found to be highest for the pyridopyrazine vinylene polymers. Compared to CN-MEH-PPV, the pyridopyrazine vinylene polymers were easier to reduce, while the quinoxaline derivatives were harder. UV−vis absorption measurements showed that the polymers have relatively small band gaps.

Introduction

Many different conjugated polymers have been synthesized since the discovery in 1977 that polymers can conduct electricity when doped.[1] In particular, poly(phenylene vinylene) (PPV) type polymers have been thoroughly studied since electroluminescence was reported for this class of polymers in 1990.[2] Most conjugated polymers synthesized to date have low electron affinity, despite the advantages of high electron affinity for many applications. One example is in light-emitting diodes (LEDs), where high electron affinity allows the fabrication of LEDs with good electron injection from stable cathodes such as aluminum, rather than the low work function metals required for more electron-rich polymers. Other possible applications are n-type field effect transistors (FET)[3] or as the electron-accepting material in photodiodes or solar cells. Since the discovery of photoinduced electron transfer from conjugated polymers to C_{60},[4] fullerene derivatives as the electron-accepting material in conjugated polymer photovoltaic devices have been studied quite extensively.[5,6] Because of the lack of suitable conjugated acceptor polymers, devices with conjugated polymers as acceptor material[7,8] have not been studied as thoroughly even though some of the highest efficiencies for conjugated polymer photovoltaic devices have been achieved with this type.[9]

One way to achieve high electron affinity is to attach electron-withdrawing groups to the polymer, for example cyano groups in CN-MEH-PPV.[10] Another way to get a polymer with high electron affinity is to introduce an electron-deficient heterocyclic unit in the polymer backbone, for example pyridine, pyrimidine, quinoline, oxadiazole, or quinoxaline.[11,12] Quinoxaline is one of the most promising heterocycles for this type of conjugated polymer. Polymers with quinoxaline moieties were first polymerized by a condensation reaction between aromatic bis(*o*-diamines) and bis(1,2-dicarbonyls) for use as heat- and chemical-resistant materials.[13,14] A polymer of this type has later been used as the electron-transporting material in polymer LEDs.[15] More recently, polymers have also been synthesized by dehalogenation polycondensation using nickel complexes, both where quinoxaline rings are connected in positions 2 and 6[16] and where they are bound in the positions 5 and 8.[17,18]

Another nitrogen heterocyclic compound is pyridopyrazine. This heterocycle is expected to be an even better electron acceptor than quinoxaline due to the additional nitrogen atom. Few studies of conjugated polymers containing pyridopyrazine have been reported, although the characteristics of poly(2,3-diphenylpyrido[3,4-*b*]-pyrazine) have been given in comparison with an alternating copolymer of pyrido[3,4-*b*]pyrazine and thiophene.[19]

In this paper, we describe synthesis and some properties of PPV-type polymers with quinoxaline and pyridopyrazine moieties in the polymer backbone (see Scheme 1). To our knowledge, the only previous study of vinylene polymers with quinoxaline heterocycles used copolymers with phenylene moieties,[20] while the use of poly(pyridopyrazine vinylene) derivatives in photovoltaic devices was first reported in 2001.[21] The electron-withdrawing nitrogens give our polymers high electron affinity, while the fused ring system and planar backbone give the polymers absorption at long wavelengths. We chose to make poly(5,8-quinoxaline vinylene) and the pyridopyrazine analogue so that we could easily attach side chains to obtain soluble polymers.

Experimental Section

Instrumentation. NMR spectra were recorded on a Varian VXR300 spectrometer, and mass spectra were recorded on a VG ZabSpec (Fison Instruments) in positive FAB/LSIMS mode with 3-nitrobenzoyl alcohol as matrix material. UV−vis spectra were recorded on a Perkin-Elmer Lambda 20 UV/vis spectrometer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Perkin-Elmer FT-IR spectrum 1000 spectrometer. The spectra were taken from films prepared on BaF_2 substrates.

The molecular weight of the polymers was determined by size exclusion chromatography (SEC) on a Waters WISP 712 with three commercial styragel columns and a Waters 410

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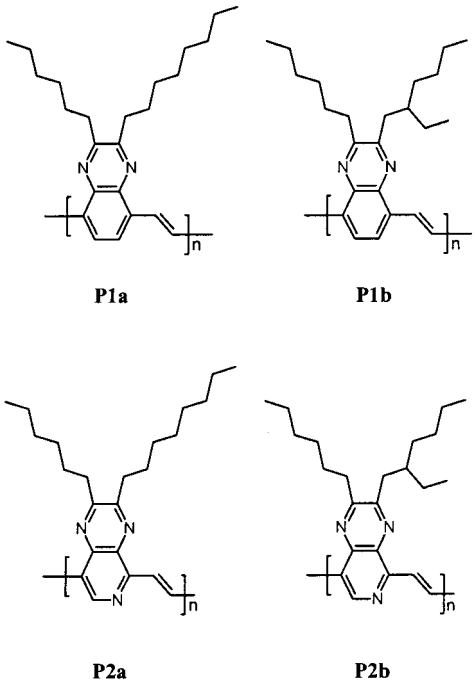
Scheme 1. Prepared Quinoxaline Vinylene (P1a and P1b) and Pyridopyrazine Vinylene (P2a and P2b) Polymers (One of the Possible Configurations)



P1a **P1b**

P2a **P2b**

refractive index detector. A Wyatt Down DSP laser photometer was connected on-line to the SEC. The samples were run at 30 °C with a flow rate of 1.0 mL/min in chloroform with polystyrene standards as references.

Electrochemical measurements of films adsorbed on a Pt wire from a chloroform solution were measured in a single-compartment electrochemical cell with a Pt counter electrode and an Ag/AgCl quasi-reference electrode. Tetrabutylammonium perchlorate (0.1 M) in acetonitrile (dried over molecular 3 Å sieves) was used as the supporting electrolyte. The cell was purged with nitrogen before each measurement. Ferrocene (half-wave potential 0.326 vs Ag/AgCl)[22] was used for calibration of the reference electrode. The sweep rate was 100 mV/s unless otherwise indicated.

Materials. All starting materials are commercially available from Aldrich or Acros. Tetrahydrofuran was distilled over sodium/benzophenone, and DMF was dried by azeotropic distillation with benzene, then over BaO for 15 h, and finally by distillation at reduced pressure. 2,3-Diamino-1,4-dibromobenzene (**3**) was synthesized from 2,1,3-benzothiadiazole, which was brominated to 4,7-dibromo-2,1,3-benzothiadiazole[23] and then reduced to 2,3-diamino-1,4-dibromobenzene.[24] 3,4-Diamino-2,5-dibromopyridine (**5**) was prepared by bromination of 3,4-diaminopyridine.[19] 1,2-Bis(tri-*n*-butylstannyl)ethylene (**7**) was prepared from tributyl(ethynyl)tin and tributyltin hydride with a catalytic amount of α,α′-azoisobutyronitrile.[25,26]

Synthesis. 7-Hexadecyn (1a). 1-Octyne (5 g, 45.5 mmol) was dissolved in tetrahydrofuran (125 mL) and lithiated by adding butyllithium solution (28.45 mL, 1.6 M in hexanes) dropwise at 0 °C under N_2(g). The reaction mixture was raised to room temperature, and 1-bromooctane (8.78 g, 45.5 mmol) was added dropwise. The mixture was refluxed for 68 h. After cooling to room temperature, the solution was extracted with 5% sodium sulfite (aqueous) and water and dried over $MgSO_4$. After distillation (140 °C, 4 mbar) 8.33 g (83%) of colorless oil was obtained.

5-Ethyl-7-tetradecyne (1b). The synthesis was performed in the same way as for 7-hexadecyn (**1a**), but a longer reaction time (4 weeks) was necessary to get high yield. After extraction as described for **1a** and distillation (120 °C, 4 mbar) 7.48 g (73%) of colorless oil was obtained.

7,8-Hexadecandione (2a) and 5-Ethyl-7,8-tetradecandione (2b). The diones were prepared as described by Srinivasan et al.[27]

5,8-Dibromo-2,3-hexyloctylquinoxaline (4a). 2,3-Diamino-1,4-dibromobenzene (0.415 g, 1.57 mmol) was dissolved in 28 mL of ethanol/water (1:0.12) and heated to reflux. 7,8-Hexadecandione (0.40 g, 1.57 mmol) dissolved in warm ethanol (5 mL) was added dropwise. After reflux for 40 h the product had formed as a precipitate. After filtration and recrystallization in acetone 414 mg (55%) was obtained (T_m = 50−60 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82 (s, 2H); 3.07 (t, J = 7.5 Hz, 4H); 1.91 (k, J = 7.5 Hz, 4H); 1.20−1.56 (m, 16 H); 0.91 (t, J = 7.0 Hz, 3H); 0.89 (t, J = 7.0 Hz, 3H). HRMS: Calcd for $C_{22}H_{33}N_2Br_2$: 483.101. Found: 483.094.

5,8-Dibromo-2-(2′-ethylhexyl)-3-hexylquinoxaline (4b). The synthesis was performed in the same way as for **4a**. After reflux for 40 h the solvent was evaporated in vacuo. The product was separated from unreacted material by column chromatography with petroleum ether/chloroform (3:1); 681 mg (75%) of yellow oil was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84 (s, 2H); 3.07 (t, J = 7.5 Hz, 2H); 3.00 (d, J = 6.9 Hz, 2H); 2.14 (m, 1H); 1.91 (k, J = 7.5 Hz, 2H); 1.20−1.56 (m, 14H); 0.94 (t, J = 7.0 Hz, 3H); 0.92 (t, J = 7.0 Hz, 3H); 0.88 (t, J = 7.0 Hz, 3H). HRMS: Calcd for $C_{22}H_{33}N_2Br_2$: 483.101. Found: 483.082.

5,8-Dibromo-2,3-hexyloctylpyrido[3,4-*b*]pyrazine (6a). **6a** was prepared in the same way as **4b**. After drying, 226 mg (62%) of yellow crystals (T_m = 30−40 °C) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.69 (s, 1H); 3.10 (t, J = 7.5 Hz, 2H); 3.11 (t, J = 7.5 Hz, 2H); 1.92 (m, 4H); 1.20−1.56 (m, 16H); 0.91 (t, J = 7.0 Hz, 3H); 0.89 (t, J = 7.0 Hz, 3H). HRMS: Calcd for $C_{21}H_{32}N_3Br_2$: 484.096. Found: 484.097.

5,8-Dibromo-2-(2′-ethylhexyl)-3-hexylpyrido[3,4-*b*]pyrazine and 5,8-Dibrom-2-hexyl-3-(2′-ethylhexyl)pyrido[3,4-*b*]pyrazine (6b). 6b was prepared in the same way as **4b**. After drying, 334 mg (46%) of yellow oil was obtained. In the NMR spectra it was seen that two different isomers were formed in equal amounts. ^{1}H NMR (300 MHz, $CDCl_3$) isomer 1 and 2: δ (ppm) 8.68 (s, 1H); 3.10 (t, J = 7.5 Hz, 2H); 3.03 (d, J = 6.9 Hz, 2H); 2.16 (m, 1H); 1.92 (m, 2H); 1.20−1.56 (m, 14H); 0.84−0.98 (m, 9H) and 8.68 (s, 1H); 3.11 (t, J = 7.5 Hz, 2H); 3.02 (d, J = 6.9 Hz, 2H); 2.16 (m, 1H); 1.92 (m, 2H); 1.20−1.56 (m, 14H); 0.84−0.98 (m, 9H). HRMS: Calcd for $C_{21}H_{32}N_3Br_2$: 484.096. Found: 484.088.

Polymerization. A typical polymerization was performed as follows.

Poly(2(2′-ethylhexyl)-3-hexylquinoxaline vinylene) (P1b). 5,8-Dibromo-2-(2′-etylhexyl)-3-hexylquinoxaline (150 mg, 0.310 mmol), 1,2-bis(tri-*n*-butylstannyl)ethylene (188 mg, 0.310 mmol), and tetrakis(triphenylphosphine)palladium(0) (18 mg, 0.016 mmol) were dissolved in dry DMF under N_2(g). The polymerization was performed at 110 °C for 24 h, whereafter the polymer was precipitated by addition of ethanol and purified by Soxhlet extraction with ethanol for 17 h. The pure polymer was washed out with chloroform. After drying, 110 mg (95%) of dark violet powder was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.7−9.1 (2H); 8.2−8.6 (2H); 2.8−3.4 (4H); 2.1−2.4 (1H); 1.8−2.1 (2H); 1.1−1.8 (14H); 0.6−1.1 (9H). FT-IR (in cm^{-1}): 3053 (m); 2927/2956 (s); 2856/2870 (s); 1615 (m); 1560 (m); 1463/1482 (s); 1378 (m); 1336/1347 (m); 1261 (m); 1143/1161 (m); 1094 (m); 977 (m); 833 (m).

Results and Discussion

Synthesis. The monomers (**4a**, **4b**, **6a**, and **6b**) were prepared by condensation reaction of the diones and diamines as described in the experimental part[28] (see Scheme 2). 2,3-Diamino-1,4-dibromobenzene (**3**) and 3,4-diamino-2,5-dibromopyridine (**5**) were prepared as described in the literature.[19,23,24] The diones (**2a** and **2b**) were synthesized by oxidation of triple bonds with potassium permanganate.[27] The alkyns used (**1a** and **1b**) were synthesized by lithiating 1-octyne with butyllithium and then reacting it with 2-ethylhexyl bromide or 1-bromooctane, respectively, as described in the experimental part.

Scheme 2. Synthesis of the Quinoxaline Vinylene and Pyridopyrazine Vinylene Polymers

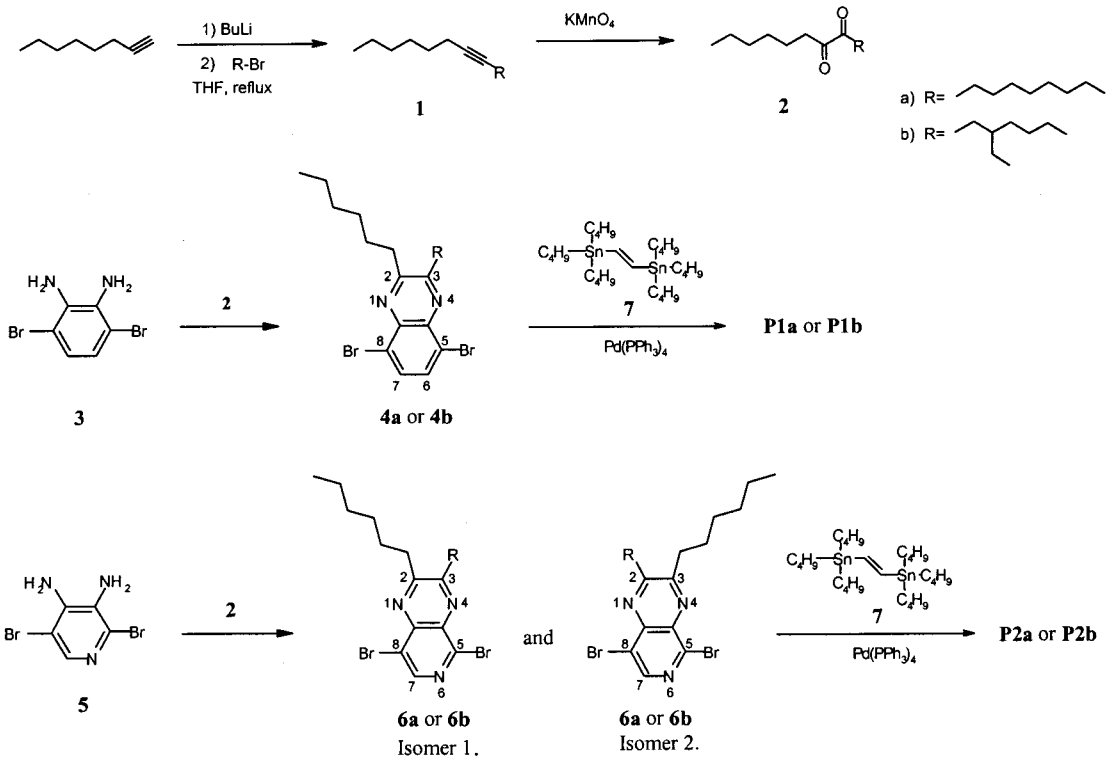


Table 1. Molecular Weights and Yields for Polymerization at Different Times

polymer	polymerization time (h)	$\bar{M}_n$[a]	PD[a]	yield (%)
P1b	15	5800	2.7	65
P1b	24	6100	2.2	95
P1b	62	6800	1.9	68
P1a	62	4900	2.3	75
P2b	24	5800	1.5	39
P2b	62	8700	2.4	22
P2a	62	3100	1.3	40

[a] Measured by size exclusion chromatography relative to polystyrene standards with chloroform as eluent.

Table 2. Solubility for P1b and P2b at Room Temperature

	P1b	**P2b**
p-xylene	partly	partly
toluene	partly	partly
chloroform	yes	yes
THF	partly	yes
diethyl ether	no	partly
DMF	no	no
DMSO	no	no
ethanol	no	no
formic acid	no	yes

In the condensation reaction, two different isomers of the pyridopyrazine monomers (**6**) can be formed. The two isomers could be distinguished in the ^{1}H NMR spectra of **6b,** where they were seen to be formed in equal amounts. In the ^{1}H NMR spectra of **6a**, the two isomers cannot be distinguished, but there is no reason to believe that the monomer only consists of one of the two isomers. Since the two isomers cannot be separated by conventional techniques, they were used together in the polymerization.

The quinoxaline vinylenes and pyridopyrazine vinylenes were polymerized by Stille coupling[29] with 1,2-bis(tri-*n*-butylstannyl)ethylene (**7**), which was prepared from tributyl(ethynyl)tin and tributyltin hydride with a catalytic amount of α,α′-azoisobutyronitrile.[25,26] The polymerization worked well in DMF at 110 °C. A typical polymerization is described in the experimental part.

In Table 1, SEC results and yields are shown for polymers of the four different monomers at different polymerization times. Even though the number of experiments is rather small, it seems like the best polymerization time is about 24 h. At longer times, the yield decreases, which is probably due to formation of insoluble polymer that is lost during workup.

The polymerization of the pyridopyrazine monomers (**P2**) gave lower yields than the quinoxalines. This can be explained by losses at workup because of lower solubility of the poly(pyridopyrazine vinylene)s in chloroform. The additional nitrogen makes the pyridopyrazine polymers more polar. See Table 2 for a summary of the polymers' solubility. The poly(pyridopyrazine vinylene)s are about as soluble in THF as in chloroform, while the poly(quinoxaline vinylene)s are much less soluble in the more polar THF. The poly(pyridopyrazine vinylene)s are also likely to be more soluble in the polar DMF than the poly(quinoxaline vinylene)s. This is probably the reason for the higher molecular weight for **P2b** polymerized for 62 h. An even more drastic difference in solubility between the polymers is seen in formic acid where the poly(pyridopyrazine vinylene)s are about as soluble as in chloroform or THF, and the poly(quinoxaline vinylene)s are insoluble. The solubility in this case is probably due to hydrogen bonds to the nitrogen in position 6 in the pyridopyrazine (see the discussion about protonation in the next section). Even though the higher polarity of the pyridopyrazines makes it harder to get good yields, the solubility can be an advantage for these polymers since they are soluble in a wide range of solvents. The solubility in formic acid can, for example, be useful for preparation of double-layer devices for LEDs or solar cells.

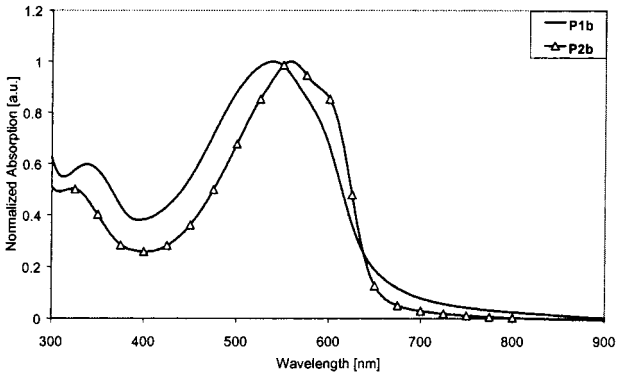
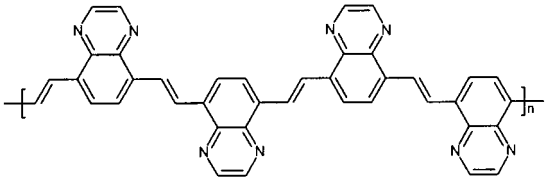


Figure 1. UV−vis absorption spectra for thin films of **P1b** and **P2b**.

Scheme 3. Planar Conformation of Quinoxaline Vinylene Polymers



The high yields for linear side chains compared with branched can be explained by precipitation during the polymerization that prevents polymer of high molecular weight being formed. The lower molecular weights measured for these polymers support this theory. Even though the linear side chains gave higher yields in the polymerization, we chose to use the polymers with branched side chains in the following analysis, because the polymers with linear side chains seem to show a greater tendency to form aggregates. The strongest support for this suspicion was seen with a light scattering detector connected on-line to the SEC. With this detector we could see a fraction of high molecular weight material that was not visible with the refractive index detector, which we believe is caused by aggregates.

UV−vis Absorption. The UV−vis absorption of films of **P1b** and **P2b,** spin-coated from chloroform, are shown in Figure 1. The onset of the absorption is quite similar for the two polymers, but the maximum is slightly red-shifted for the poly(pyridopyrazine vinylene), 558 nm compared to 540 nm for the poly(quinoxaline vinylene). The same difference is seen in chloroform solution where the absorption maxima are at 530 and 517 nm, respectively. A possible explanation for the difference is that the steric hindrance is smaller in the poly(pyridopyrazine vinylene) due to the absence of hydrogen in position 6 on the heterocyclic rings. The low energy for the absorption indicates that the polymers have extended conjugation. Computer models of the polymers, made in Materials Studio version 1.1[30] (with COMPASS[31] as force field), where the energy in the gas phase has been minimized, indicate that the polymers can have a very flat, low-energy conformation with double bonds pointing in the same direction on both sides of the rings, as shown in Scheme 3. This planar conformation is probably important, especially in the solid state.

The electronic properties and UV−vis spectra of nitrogen heterocycles are known to be influenced by protonation. The pyridopyrazine and quinoxaline heterocycles have been reported to have quite different base strengths, with pK_a in water of 0.56 for quinoxaline and 2.47 for the pyridopyrazine.[32] They are both weaker

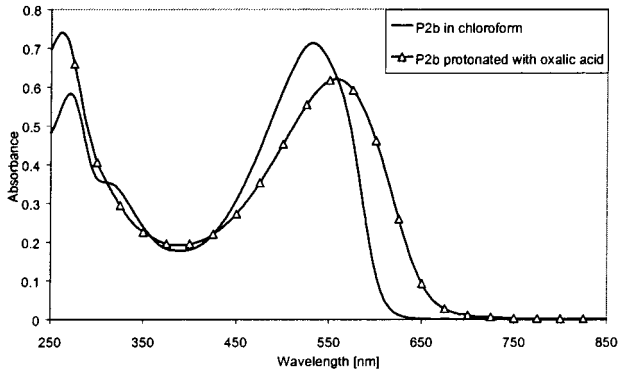


Figure 2. UV−vis absorption spectra for **P2b** in chloroform solution before and after protonation with oxalic acid.

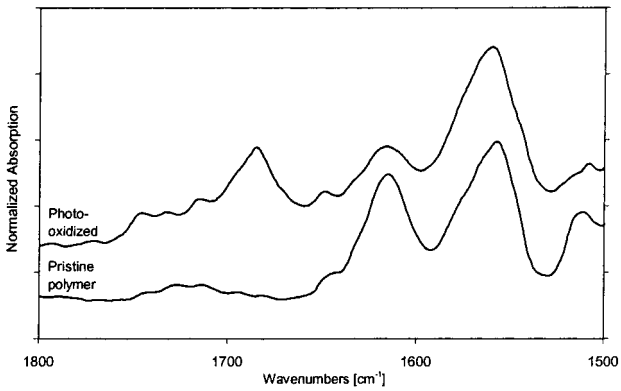


Figure 3. Enlarged FT-IR spectra of **P1b** before and after photooxidation. The spectra have been offset for clarity.

bases than pyridine (pK_a = 5.25) and are for example not protonated by formic acid (pK_a = 3.75). The absorption maximum for **P2b** is the same in formic acid as in chloroform, which indicates that the solubility in formic acid for **P2b** is due to hydrogen bonds. With stronger acids, like oxalic acid for **P2b** and methanesulfonic acid for **P1b**, the UV−vis absorption is red-shifted. The effect is seen in both film and solution. In Figure 2 the protonation of **P2b** in chloroform is shown. The red shift is 27 nm for **P2b** both in film and in chloroform solution and 28 nm for **P1b**. The red shift is accompanied by a decrease in absorption, which is recovered along with the blue shift back to the original absorption by the addition of base (for example ammonia).

Stability. The UV−vis absorption of thin films of all our polymers decreased rapidly when exposed to light and air. For example, when a thin film of **P2b** was exposed to ordinary domestic lighting, it lost most of its color in 2 h. The absorbance, at the absorption maximum, decreased from 0.30 to about 0.25 in 30 min. Thicker films are more stable, and the polymers are much more stable when stored in the dark. No change in absorbance has been seen for films stored dark for several months. When the concentration of nitrogen in air is increased, by repeatedly evacuating to 0.4 mbar and refilling with N_2(g), the degradation is considerably reduced. FT-IR spectra of relatively thick films of **P1b** and **P2b** exposed to light and air for 24 h show formation of carbonyl peaks at 1690 cm^{-1} and a decrease of the peaks at 1615 cm^{-1} (stretch of conjugated double bond) (see Figure 3). This suggests a reaction with oxygen at the double bonds.

In the ^{1}H NMR spectra of degraded polymers we see a decrease and broadening of the peaks in the aromatic region. We also see a decrease, broadening, and slight

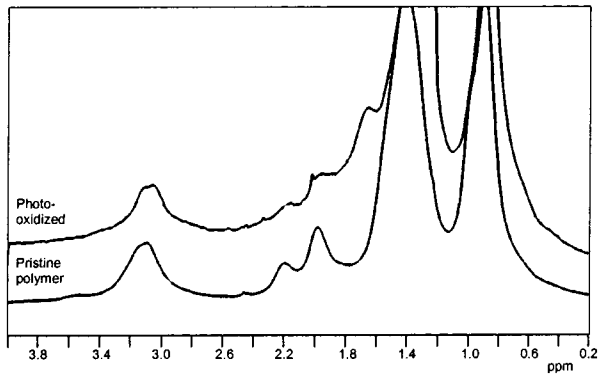


Figure 4. Enlarged ^{1}H NMR spectra of **P1b** before and after photooxidation. The spectra have been vertically scaled so that the peaks at 0.8−1.1 ppm are the same and offset for clarity.

shift of the peak at 2.8−3.4 ppm, a decrease of the peaks at 2.1−2.4 and 1.8−2.1 ppm, and formation of a new peak at 1.7 ppm (see Figure 4). This means that something is happening in the side chains of the polymers as well as to the conjugated backbone. The changes in the NMR spectra can be explained by formation of carbonyl groups in the α position of the side chains, due to abstraction of the labile hydrogens in this position, similar to that seen for alkylthiophenes.[33]

The molecular weight of the polymers, measured with SEC, is lower for photooxidized polymers, but not to the extent that the decline in UV−vis absorption might suggest. There is clearly more than one reaction happening when the polymers are exposed to light and air. The decline in absorption for PPV derivatives has been reported to be due to reaction of the double bond with singlet oxygen.[34−36] This would mean that electron-withdrawing groups increase the stability of the double bond toward the electrophilic singlet oxygen.[37] The stability of **P2b**, with the more electronegative pyridopyrazine ring, is slightly better than that of the quinoxaline analogue (**P1b**), but both polymers are less stable than expected. We think it likely that both the double bonds and the side chains are oxidized in the degradation process. Possible explanations for the low stability compared with other PPV polymers are the labile hydrogens of the side chains[33,38] or the extended conjugation caused by the fused ring.[36]

Cyclic Voltammetry. Cyclic voltammetry of the polymers with branched side chains (**P1b** and **P2b**) showed that the polymers have high electron affinity (see Figure 5). For the quinoxaline (**P1b**) the reduction peak is seen at −1.56 V vs Ag/AgCl and the reoxidation at −1.47 V vs Ag/AgCl. The pyridopyrazine polymer (**P2b**) had a reduction peak at −1.23 V vs Ag/AgCl and a reoxidation peak at −1.14 V vs Ag/AgCl. Earlier reported values for **P2b** differ slightly from these, because different solvent systems were used.[21] The higher electron affinity for the pyridopyrazine is due to the extra nitrogen in the heterocyclic ring. The reduction process is reversible for both polymers and can be repeated many times without any large degradation being noticed. For **P2b** there is however a new reduction peak being formed at −1.04 V vs Ag/AgCl on repeated scanning. The reason for this is unknown, and we do not see any clear reoxidation of this peak.

The oxidation of both polymers is irreversible, with a peak at 0.96 V vs Ag/AgCl for **P1b** and 1.14 V vs Ag/AgCl for **P2b** (sweep rate 5 mV/s). The band gaps calculated from the formal reduction potential (estimated as the average between the reduction and reoxidation peaks to be −1.52 and −1.19 V vs Ag/AgCl, for **P1b** and **P2b**, respectively), and the oxidation peaks are 2.47 eV for **P1b** and 2.32 eV for **P2b**, which is similar to the UV−vis absorption peaks (2.30 and 2.23 eV, respectively).

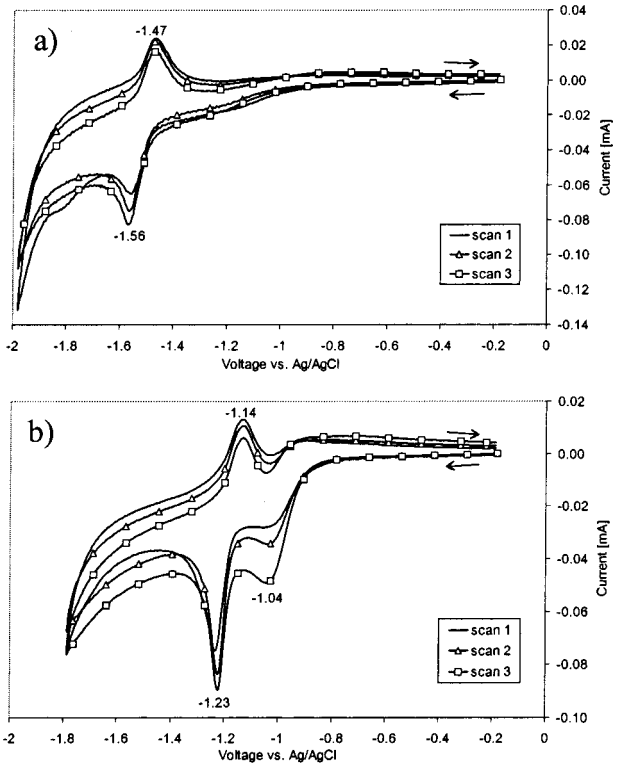


Figure 5. Cyclic voltammogram of (a) **P1b** and (b) **P2b** films on Pt in 0.1 M tetrabutylammonium perchlorate acetonitrile solution.

For comparison, CN-MEH-PPV, synthesized as described in the literature,[39] was measured under the same conditions as **P1b** and **P2b**. The formal reduction potential was −1.30 V vs Ag/AgCl, which is similar to previously reported values;[40] i.e., **P1b** has a lower, and **P2b** a higher, electron affinity than CN-MEH-PPV.

Conclusions

We have synthesized poly(quinoxaline vinylene)s and poly(pyridopyrazine vinylene)s, with linear and branched aliphatic side chains, at different polymerization times. The different monomers gave polymers with different solubility. As a consequence, yields and molecular weights varied. All prepared polymers were soluble in common organic solvents such as chloroform. The poly(pyridopyrazine vinylene)s were also soluble in formic acid. All polymers had UV−vis absorption at long wavelengths due to the fused ring system and planar polymer backbone. Cyclic voltammetry showed that the polymers could be reduced with formal reduction potentials, for **P1b** and **P2b**, of −1.52 and −1.19 V vs Ag/AgCl, respectively, which means that the poly(quinoxaline vinylene) has lower, and the poly(pyridopyrazine vinylene) higher, electron affinity than CN-MEH-PPV. Unfortunately, the photooxidative stability of all polymers is quite poor. The exact reason for this is unknown.

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Supporting Information Available: ^{1}H NMR and FTIR spectra of **P1b** and **P2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shirakawa, H.; Louis, E. J.; MacDiramid, A. G.; Chiang, C. K.; Heeger, A. H. *J. Chem. Soc., Chem. Commun.* **1977**, 578−580.
(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539−541.
(3) Bao, Z. *Adv. Mater.* **2000**, *12*, 227−230.
(4) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474−1476.
(5) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15−26.
(6) Sariciftci, N. S.; Heeger, A. H. *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons Ltd: New York, 1997; Vol. 1, pp 413−486.
(7) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510−4515.
(8) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498−500.
(9) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257−260.
(10) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630.
(11) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1371−1507.
(12) Segura, J. L. *Acta Polym.* **1998**, *49*, 319−344.
(13) Hergenrother, P. M.; Levine, H. H. *J. Polym. Sci., Part A-1* **1967**, *5*, 1453−1466.
(14) Hergenrother, P. M. *Polym. Eng. Sci.* **1976**, *16*, 303−308.
(15) O'Brien, D.; Weaver, M. S.; Lidzey, D. G.; Bradley, D. D. C. *Appl. Phys. Lett.* **1996**, *69*, 881−883.
(16) Saito, N.; Kanbara, T.; Kushida, T.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1993**, 1775−1778.
(17) Kanbara, T.; Yamamoto, T. *Macromolecules* **1993**, *26*, 3464−3466.
(18) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930−3937.
(19) Lee, B.-L.; Yamamoto, T. *Macromolecules* **1999**, *32*, 1375−1382.
(20) Chan, W. K.; Ng, P. K.; Gong, X.; Hou, S. *J. Mater. Chem* **1999**, *9*, 2103−2108.
(21) Jonforsen, M.; Ahmad, I.; Johansson, T.; Larsson, J.; Roman, L. S.; Svensson, M.; Inganäs, O.; Andersson, M. R. *Synth. Met.* **2001**, *119*, 185−186.
(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; John Wiley & Sons: New York, 1980; pp 701−702.
(23) Pilgram, K.; Zupran, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629−633.
(24) Naef, R.; Balli, H. *Helv. Chim. Acta* **1978**, *61*, 2958−2973.
(25) Nesmeyanov, A. N.; Borisov, A. E. *Dokl. Akad. Nauk SSSR* **1967**, *174*, 96−99.
(26) Corey, E. J.; Wollenberg, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5581−5583.
(27) Srinivasan, N. S.; Lee, D. G. *J. Org. Chem.* **1979**, *44*, 1574.
(28) Burton, D. E.; Hughes, D.; Newbold, G. T.; Elvidge, J. A. *J. Chem. Soc. C* **1968**, 1274−1280.
(29) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524.
(30) Distributed by Acceryls Inc.
(31) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338−7364.
(32) Bunting, J. W.; Perrin, D. D. *J. Chem. Soc. B* **1966**, 436−438.
(33) Ljungqvist, N.; Hjertberg, T. *Macromolecules* **1996**, *28*, 5993−5999.
(34) Papadimitrakopoulos, F. Y.; M. Rothberg, L. J.; Katz, H. E.; Chandross, E. A.; Galvin, M. E. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 663−669.
(35) Cumpston, B. H.; Jensen, K. F. *Synth. Met.* **1995**, *73*, 195−199.
(36) Scurlock, R. D.; Wang, B.; Ogilby, P. R.; Sheats, J. R.; Clough, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 10194−10202.
(37) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1969**, *10*, 3609−3612.
(38) Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganas, O.; Andersson, M. R. *Macromolecules* **2000**, *33*, 2525−2529.
(39) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428.
(40) Li, Y.; Cao, Y.; Gao, J.; Wang, D.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243−248.

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