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by

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Described will be the synthesis of a pyrrole-derived polymer that can exist in a zwitterionic form (λ = 520 nm), a partially reduced form (λ = 290 nm), or a planar form (λ = 900 nm). The absorptions are reversible depending on the pH of the medium.

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Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

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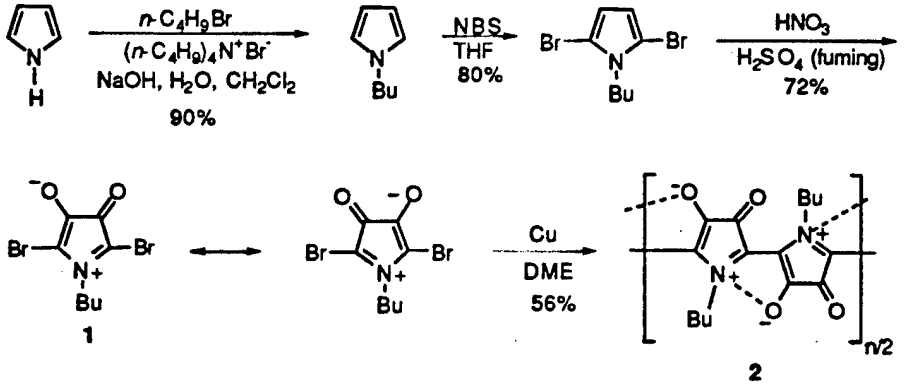
In an effort to maximize the extended π-conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.[1,2] Described here is the synthesis of a unique zwitterionic pyrrole-derived polymer that can reversibly convert to a linear and planar conjugated polymer with a solution band gap of approximately 1.1 eV. The material possesses a reversible and enormous pH-dependent or solvent dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,[2] while polymers with absorbances in the near-IR can serve as dyes for optical data discs.[3]

The synthesis of the new pyrrole-derived zwitterionic polymer is described in Scheme 1.

Scheme 1



1 2

Pyrrole was N-alkylated under standard phase transfer conditions.[4] Bromination[5] and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718 cm^{-1}, with no hydroxyl absorbance), mass spectrum (calc'd for $C_8H_9Br_2NO_2$: 311; found: 311), elemental analysis (calc'd: C, 30.89; H, 2.92; Br, 51.39; N, 4.50; found: C, 30.90; H, 2.92; Br, 51.25; N, 4.48), UV spectrum (CH_2Cl_2, λ = 248, 322; NMP, λ = 281, 320 (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl), ^1H NMR [(300 MHz, $CDCl_3$) δ 3.59 (t, J = 7.3 Hz, 2 H), 1.57 (p, J = 7.1 Hz, 2 H), 1.30 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H)] and ^{13}C NMR [(75 MHz, $CDCl_3$) δ 163.85, 129.24, 39.48, 30.39, 19.82, 13.52] were all consistent with the proposed structure. Note that two resonance forms exist for **1**, therefore there are only six peaks in the ^{13}C NMR spectrum.

We then sought to polymerize **1** using a variety of coupling methods.[6] $(COD)_2Ni(0)$,[7] copper(II) triflate,[8] and Rieke copper[9] failed to afford any polymeric product. Classical Ullman[10] coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine), however, in DME, copper-bronze-promoted polymerization (200°C, screw cap tube) of **1** afforded the desired polymer **2** (Scheme 1) in 56% yield after fractional precipitation (CH_2Cl_2, CH_3OH). The precipitation dramatically sharpened the polydispersity (PD) to 1.15-1.25 with M_n = 3 130 (SEC, PS standards).[11] Spectral analysis again confirmed the proposed structure.

The optical spectra for **2** are most interesting. Polypyrrole has an absorption maximum of 420 nm (solid) but it is intractable. N-alkylated polypyrroles can be soluble, however, the increased steric repulsions between the consecutive aryl units causes a hypsochromic shift to approximately 380 nm.[6] Remarkably, the absorption maximum of **2** exhibits a strong bathochromically shifted absorbance that may be due to ionic interactions that force a diminution in the inter-unit twist angle as depicted in Scheme 1.[2] Solvatochromic effects are consistent with this proposal in that the following trend of S_0-S_1 ($\pi\pi^*$)

absorption maxima are present for **2**: CCl_4, 520 nm; THF, 512 nm (Figure 1); EtOH/THF (1:1), 503 nm; acetone, 482

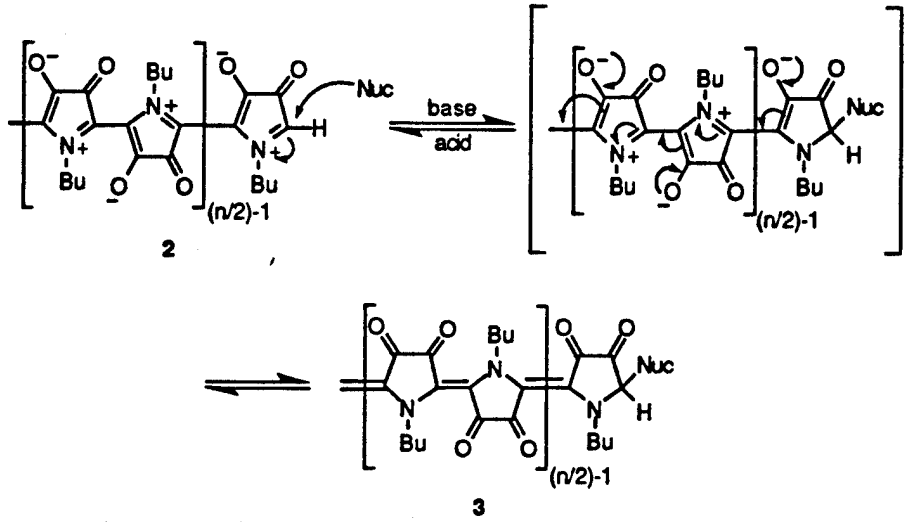
Figure 1. (a) Spectrum of **2** in THF (____). (b) Dissolution of **2** in THF/aqueous NaOH to form **3** (----).

nm. Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absortion shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the π–π^* transition which may exhibit charge transfer character.[3,12] Remarkably, when aqueous NaOH (0.05 M) was added dropwise to **2** in THF, the initial red-colored solution (λ_{max} = 512 nm) became pale-orange and then finally brown (λ_{max} = 881 nm) as more base was added (Figure 1). This pH-dependent shift in the absorption spectrum was reversible but polymer decomposition was detected after a few hours in the hydroxide-containing medium. Equally impressive solution effects occurred upon the dissolution of **2** in strongly Lewis basic solvents[12] such as HMPA (λ_{max} = 901 nm) or NMP (λ_{max} = 746 nm) (**2** was insoluble in DMSO) (Figure 2).[13] No polymer decomposition was

Figure 2. Dissolution of **2** in (a) HMPA (____) and (b) NMP (----).

detected in these Lewis basic solvents. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The ^{13}C NMR spectrum of **2** in HMPA (with 10% $CDCl_3$ added for the lock) showed the butyl signals as well as a broad resonance from 176-163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of π-electron migrations in **2** to afford the planar conjugated polymer **3** (Scheme 2).

Scheme 2



Another interesting feature of **2** is that it could be partially reduced with H_2 (1 atm) over Pd/C (24 h, 23°C) to afford a system that is very similar to the starting polymer by FTIR, and SEC analysis, while the ^1H NMR and ^{13}C NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer can not attain the degree of extended conjugation of **3** (as determined by the optical absorbances), its response range to different solvents can be from the UV region with weak tailing into visible, to the near-IR (DMSO, λ = 886 nm) (Figure 3). Thus the reduced polymer is soluble in DMSO and it responds most dramatically to solvent changes.

Figure 3. Spectrum of the reduction product of **2**. (a) In THF (----) and (b) in DMSO (——).

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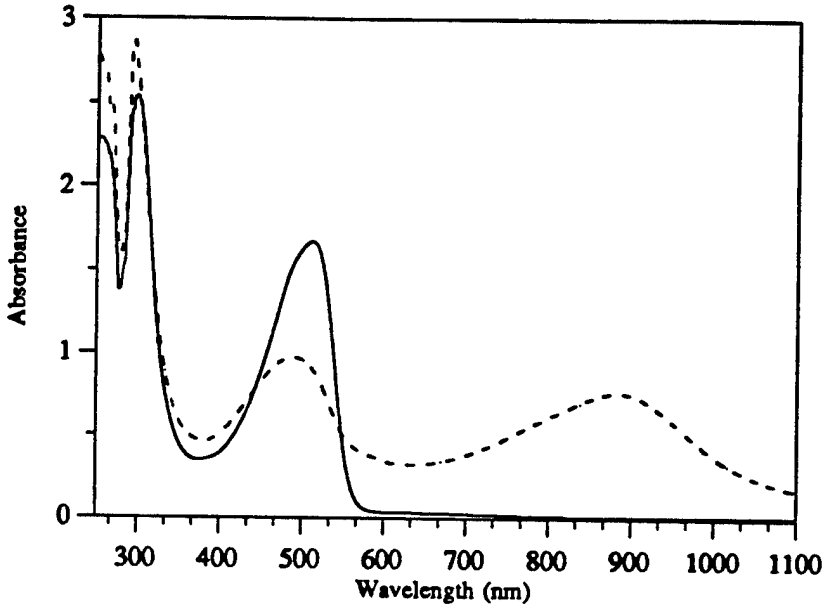
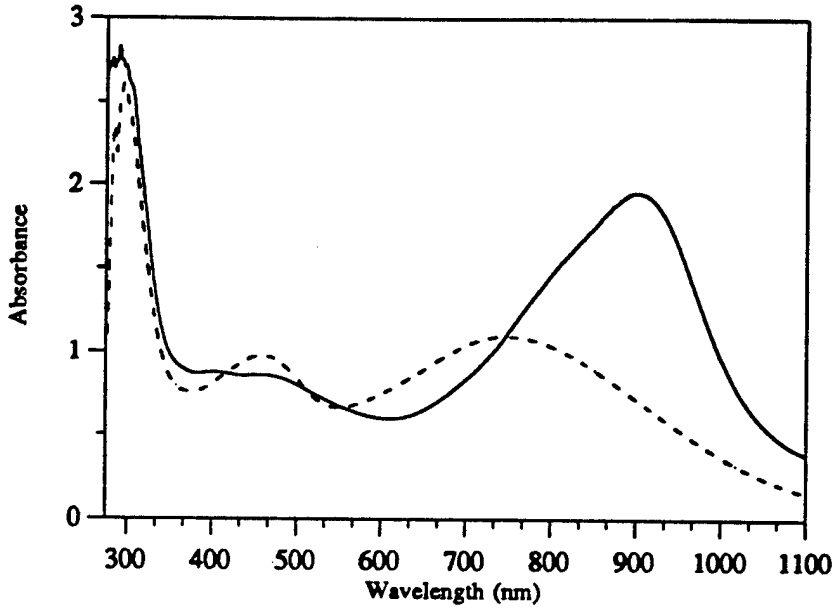

Absorbance
3
2
1
0
300
400
500
600
700
800
900
1000
1100
Wavelength (nm)

Fig 1


Absorbance
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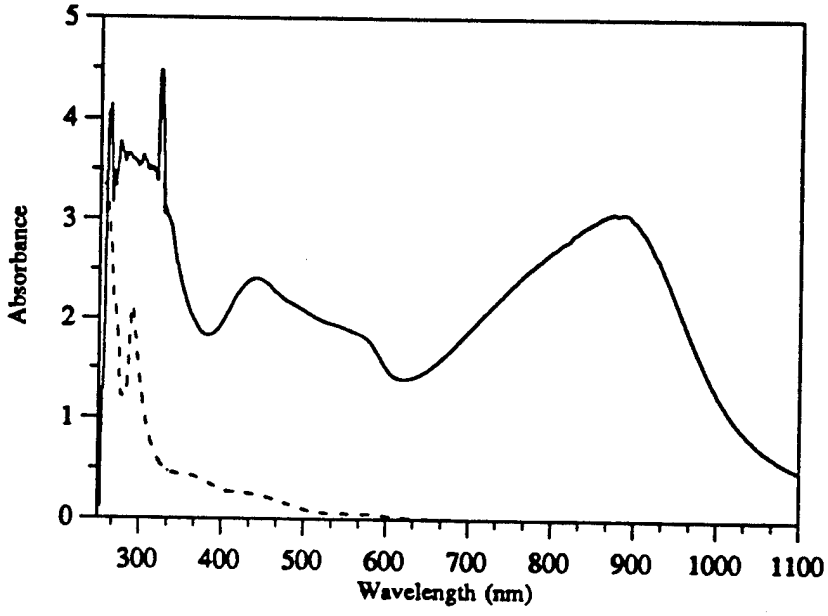
Wavelength (nm)

Fig 2


Absorbance
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1
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4
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Wavelength (nm)

Fig 3