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13. ABSTRACT (Maximum 200 words)

Described is the synthesis of a zwitterionic pyrrole-derived polymer. The monomer (1) is formally an azomethine ylide and it was synthesized in 3 steps from pyrrole. 1 was polymerized using copper-bronze in DME. The polymer had a strong optical absorbance at 512 nm in THF and an inter-unit ionic interaction is proposed to explain this large red-shifted band. If aqueous NaOH is added to the THF solution, or a Lewis basic solvent used instead of THF/NaOH, then a tremendous bathochromic shift occurs to 881 or 901 nm, respectively. The large shifts are attributed to a dramatic structural change in the polymer induced by hydroxide or Lewis base attack on the iminium unit. This causes a cascade of electron shifts to form a fully conjugated polymer that is fixed into a planar conformation. The planarization process is reversible so that addition of acid or shifting to a weaker Lewis basic solvent causes the polymer to recover its zwitterionic form and its original optical absorption characteristics. Moreover, upon mild reduction of the zwitterionic polymer with Pd/C and H_2 (1 atm), some of the extended conjugation is lost but a polymer forms that has an enormous optical absorption maximum range from the near-UV to the near-IR (λ_{max} = 886 nm) depending on the solvent or hydroxide concentration. Further, a sample of the reduced polymer can be dispersed in platicized poly(vinyl chloride). The flexible polymer composite reversibly changed from dark blue-brown in aqueous hydroxide to bright yellow-orange in aqueous HCl.

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Reversible Optical Absorbances From the UV to the Near-IR

by

Thorsten W. Brockmann and James M. Tour

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Abstract

Described is the synthesis of a zwitterionic pyrrole-derived polymer. The monomer (1) is formally an azomethine ylide and it was synthesized in 3 steps from pyrrole. 1 was polymerized using copper-bronze in DME. The polymer had a strong optical absorbance at 512 nm in THF and an inter-unit ionic interaction is proposed to explain this large red-shifted band. If aqueous NaOH is added to the THF solution, or a Lewis basic solvent used instead of THF/NaOH, then a tremendous bathochromic shift occurs to 881 or 901 nm, respectively. The large shifts are attributed to a dramatic structural change in the polymer induced by hydroxide or Lewis base attack on the iminium unit. This causes a cascade of electron shifts to form a fully conjugated polymer that is fixed into a planar conformation. The planarization process is reversible so that addition of acid or shifting to a weaker Lewis basic solvent causes the polymer to recover its zwitterionic form and its original optical absorption characteristics. Moreover, upon mild reduction of the zwitterionic polymer with Pd/C and H_2 (1 atm), some of the extended conjugation is lost but a polymer forms that has an enormous optical absorption maximum range from the near-UV to the near-IR (λ_{max} = 886 nm) depending on the solvent or hydroxide concentration. Further, a sample of the reduced polymer can be dispersed in platicized poly(vinyl chloride). The flexible polymer composite reversibly changed from dark blue-brown in aqueous hydroxide to bright yellow-orange in aqueous HCl.

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
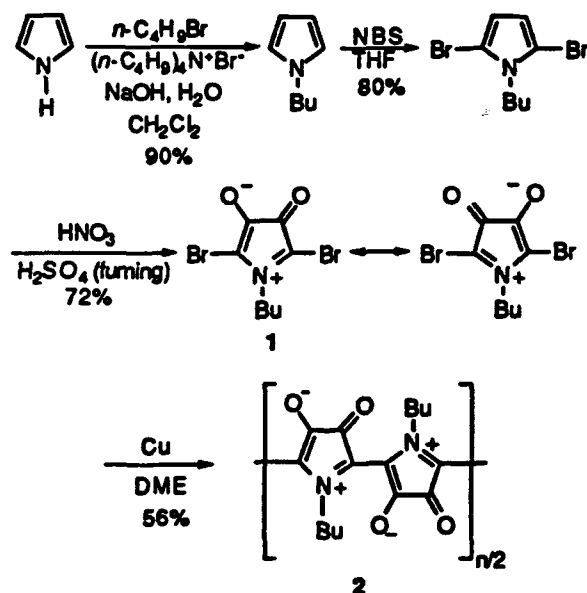
Pyrrole was N-alkylated under standard phase transfer conditions.[4] Bromination[5] and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718 cm^{-1}, with no hydroxyl absorbance), mass spectrum (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, $\lambda = \underline{248}$, 322; NMP, $\lambda = \underline{281}$, 320 (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl), ^{1}H 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, 18 h) 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 = 3,910 (SEC, PS standards).[11] If the reaction was run for 40 h, the molecular weight peaked at M_n = 4,980 with PD = 1.54. Continued heating caused no increase in the molecular weight. Spectral analysis again confirmed the proposed structure: FTIR (film, 1697 cm^{-1}, with no hydroxyl absorbance), elemental analysis (calc'd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.26; found: C, 63.40; H, 6.71; Br, <0.5; Cu, <0.02; N, 8.06), ^{1}H NMR [(300 MHz, $CDCl_3$) δ 3.40 (br s, 2 H), 1.55 (br s, 2 H), 1.27 (br s, 2 H), 0.89 (br t, J = 7 Hz, 3 H)], and ^{13}C NMR [(125 MHz, $CDCl_3$) δ 169.16, 131.07, 39.26, 30.58, 20.08, 13.92]. No detectable bromide content was observed since the excess Cu(0) carries out oxidative additions on nearly all aryl bromide locations with subsequent end group protonations on workup; a commonly observed feature of Ullman reactions.[10b] A macrocyclic structure can not be ruled out, however, to have a pyrrole ring system with all the nitrogen atoms pointing inward would require 10 pyrrole units to complete the ring.[6c] A macrocycle with all the oxygen atoms pointing inward would require even far more pyrrole units, therefore excluding a monomeric Cu-templation driven macrocyclization.

Compound **2** is an intrinsic semiconductor exhibiting an undoped conductivity of 1.4 x 10^{-5} Ω^{-1} cm^{-1} and an iodine doped conductivity of 4.2 x 10^{-4} Ω^{-1} cm^{-1} (4-point probe, pellet). The low doped conductivity of the system may be due to the presence of the carbonyl functionality which can retard polaronic or bipolaronic migrations.[1j] Thermogravimetric analysis (TGA, 10°C/min, N_2) showed 10% weight loss at 318°C and with a rapid weight decrease at 400°C.

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.[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 nm; H_2SO_4, 498 nm (with strong hypochromicity that is indicative of a protonic substitution effect). Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the $\pi-\pi^*$ 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 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

2   3
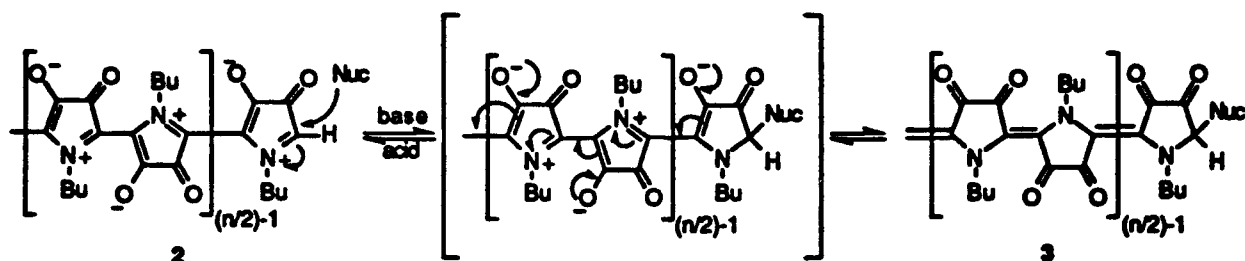
3 is similar to indigo and related indigo-like compounds that possess cross-conjugated vinyligous amides with extraordinarily large values of λ_{max}.[3]

We attempted to get a conductivity of 3 as the diethylamine adduct λ_{max} (Et_2NH solution) 783 nm. Removal of the excess amine and press-formation afforded pellets that were repeatedly too brittle for 4-point probe analysis. This is understandable with these extremely rigid-rod systems. Other analogs with longer alkyl chains may afford less brittle materials that are suitable for conductivity analysis.

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 ^{1}H 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, $\lambda = 886$ nm) (Figure 3). Thus the reduced polymer is soluble in DMSO and it responds most dramatically to solvent changes. When aqueous NaOH (0.05 M) was added dropwise to the reduced polymer in THF, the initial yellow-colored THF solution became green, blue-green, and finally blue as more base was added and a new absorption band appeared at 618 nm. The absorbance could be stabilized at any color along this transition depending on the amount of hydroxide added. Upon addition of aqueous HCl to the THF solution, the color moved back again over the same range before ceasing at the yellow-colored solution with a major absorption peak at < 290 nm. Unlike 3,

the reduced polymer undergoes no noticeable hydroxide-induced decomposition upon the reversible pH shifts. Furthermore, we dissolved the reduced polymer (0.05 wgt % relative to PVC plus plasticizer) in a solution of THF, poly(vinyl chloride) (PVC), and the plasticizer di(2-ethylhexyl) phthalate (DOP). Evaporation of the THF resulted in the formation of a dark green (possibly resulting from a mixture of yellow and blue)[3] transparent flexible film since DOP was acting as a Lewis base. Suspension of the film (250 μm thickness) in aqueous HCl (3 N) (no organic solvent was present) caused the film to become bright yellow-orange while suspension in aqueous NaOH (0.5 M) caused the film to become dark blue-brown, and this process was reversible.

Supplementary Material Available: Detailed synthetic procedures and characterization data for the synthesis and reduction of 2 (3 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) Since size exclusion chromatography (SEC) is a measure of the hydrodynamic volume and not the molecular weight (MW), significant errors in M_n and M_w may result when comparing rigid rod polymers to the flexible coils of polystryrene (PS) standards. Therefore, the values recorded here are given simply as a reference.

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List of figures.

Fig 1

Fig 2

Absorbance

Wavelength (nm)

Fig 3

Scheme 1

1

2
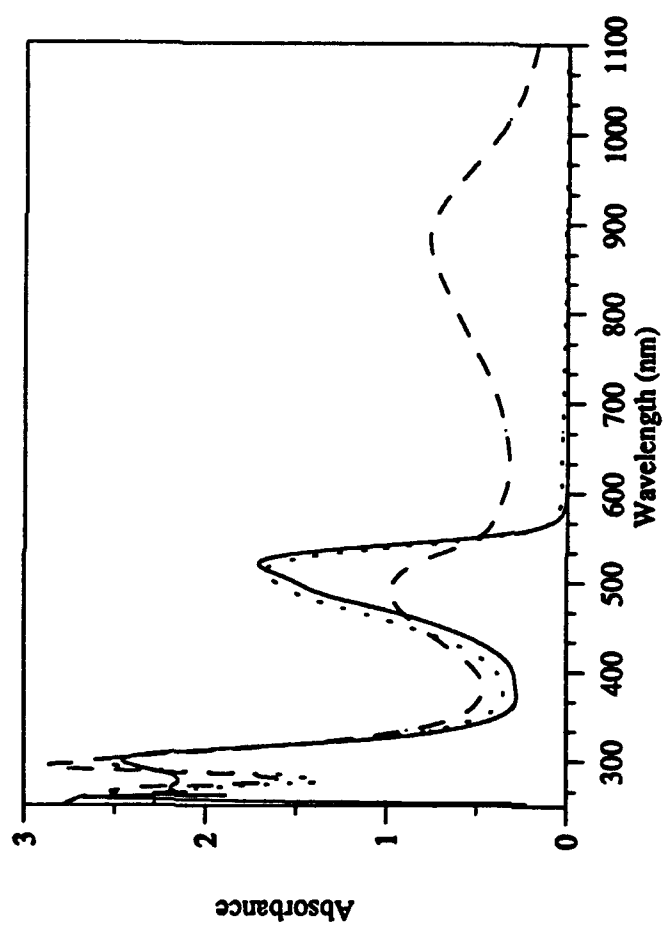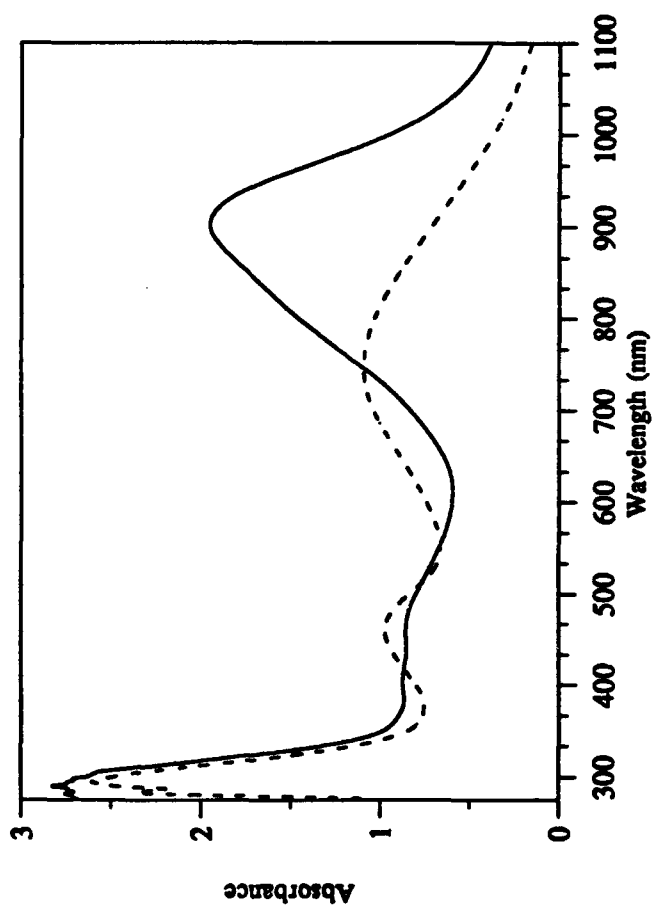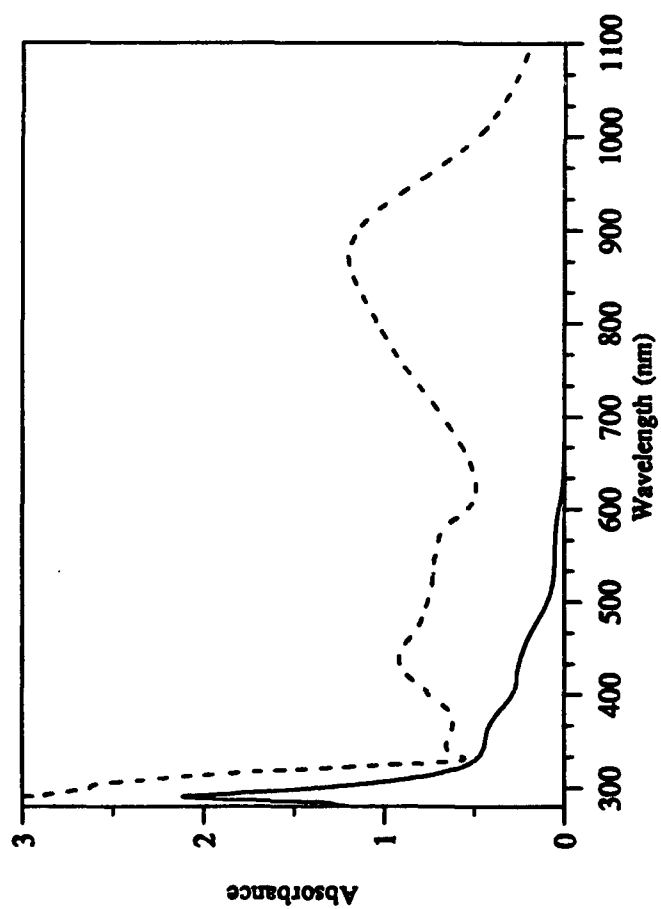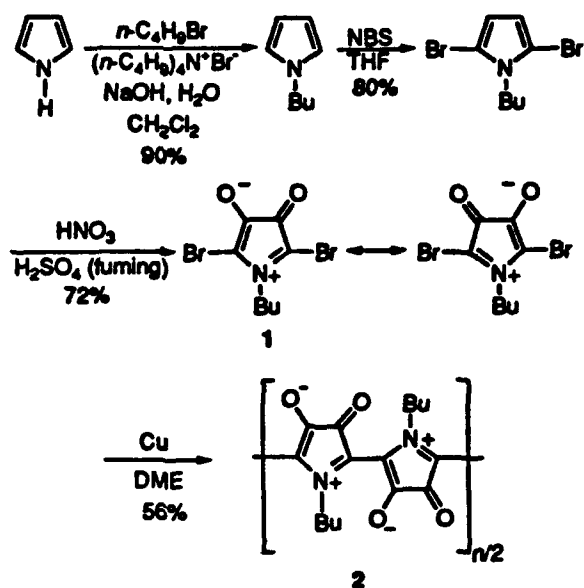
one-column format

Scheme 2

2

3

two-column format