Poly(2-alkylpyrrolo[3.4-*c*]-1,3-(2*H*,5*H*)-dioxopyrrole-4,6-diyl)s. A Novel Class of Intramolecularly Hydrogen-Bonded, Conjugated Polymers

Steven K. Pollack,* Yousef M. Hijji,[1] and Bethuel Kgobane

Department of Chemistry and the Polymer Science & Engineering Program, Howard University, Washington, D.C. 20059

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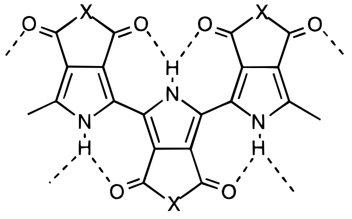
Polypyrrole has long been studied for its unique electronic and optical properties.[2] It is an inherently conducting polymer (ICP) due to both its conjugated π-system and its ready ability to be doped. Numerous studies have focused on its conductivity and nonlinear optical properties. The polymer is typically prepared via two routes. Pyrrole and 3-substituted or 3,4-disubstituted derivatives can be oxidized, either by electrochemical means or through the use of inorganic oxidants such as ferric chloride, to form an insoluble material with high conductivity.[3,4] Alternatively, various 2,5-disubstituted pyrroles can be polymerized through transition metal mediated coupling reactions.[5,6] This latter route typically produces linear oligomers that, depending on other substitution of the pyrrole ring, can have high conductivities and unique optical properties.

Most of the unique electrooptical properties mentioned above derive from the extended π-system present in these polyheteroaromatics. Like most rigid-rod polymers, polypyrrole once formed is not readily processable. Several groups have attempted to add functionality at the 1, 3, and/or 4 position of the pyrrole ring to enhance the solubility of the resulting polymer.[3−6] However, the steric effects of these groups tend to decrease the coplanarity of the polymer backbone, thus compromising its electronic and optical properties. Recently, Tour[7] described a novel polypyrrole based on *N*-alkyl-3-oxopyrrolinium 4-oxides, in which there is the potential of strong favorable Coulombic interactions to stabilize the ring system's coplanarity. This is reflected in UV absorptions extending into the near-infrared. This polymer also exhibits unique solvatochromic behavior. We reasoned that a similar inter-ring interaction, based on self-complementary hydrogen-bonding, might also serve to enhance coplanarity as well as provide for the potential for interesting thermo- and solvatochromic behavior. This work reports on our initial investigation of these new materials.

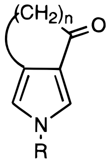
Our approach has been to design a pyrrole monomer capable of hydrogen-bonding through the NH proton to the adjacent monomer units in order to maintain planarity. This suggested a symmetric 3,4-disubstituted system. Using the N−H hydrogen as the hydrogen-bond donor, a 3,4-dicarbonyl system should generate a hydrogen-bonded ladderlike polymer.



For a simple dimer, with $X = NCH_3$, a study of the relative energies of conformers calculated at the AM1 level of semiempirical theory[8] predicted that the minimum energy conformation is antiplanar (as shown above). The syn-planar conformer is predicted to be 15 kcal mol^{-1} higher in energy due to strong steric interactions between carbonyl groups on adjacent monomer units. There is no other conformational minimum predicted. For a trimer, the steric interactions of the two carbonyls on alternate rings and the hydrogen of the central monomer unit causes the system to go out of planarity. The most stable trimer (which we denote as an "r" triad) has a C_2 symmetry, with the C_2 axis going through a line joining the pair of nitrogens on the central ring system, and has the carbonyls of the preceding and following monomer unit lying on opposites sides of the center ring system. The trimer with a mirror plane (and both oxygens on the same side of the N−H, denoted as an "m" triad) is calculated to be 0.5 kcal mol^{-1} higher in energy than the lowest energy trimer, and the planar trimer is calculated to lie 1.0 kcal mol^{-1} higher in energy than the lowest energy conformer. This planar form represents a transition state for interconversion between the two nonplanar trimeric forms. For the lowest energy conformer of the trimer, the inter-ring angle is 8°. For an extended polymer with an all r triad configuration, this would create a 2_1 helical chain with 24 monomers per pitch of helix and a helix period of roughly 80 Å.

This type of hydrogen-bonding structure is similar to the one responsible for the stability of the α-helix in natural proteins and in a number of liquid crystalline polymers.[9] In a similar fashion to those polymers, a helix−coil transition induced by the disruption of the internal hydrogen-bonding network and its effect on the conformation of the polymer backbone should provide a sensitive probe of the polymer's chemical and physical environment. Placements of large alkyl groups at the 2 position should not affect the conformations of the backbone and should serve to enhance solubility and potentially to induce liquid crystallinity in these polymers. Also, suitably chosen chiral substituents at this position might induce a preferred helicity to the backbone, giving rise to unique chirooptical effects.

Wegner has shown that similar monomers[3,4] can be electropolymerized but do not form stable films. We interpret this as being caused be the electron-withdrawing effect of the carbonyl increasing the oxidation potential of the ring system and thereby decreasing the ease with which this system polymerizes. Conversely, electron-withdrawing substituents tend to increase the kinetics of transition-metal-mediated coupling reactions of halo-substituted pyrroles.[7,10] Conjugated polymers derived from such electron deficient monomer units should have the potential for n-doping as a means of inducing conductivity. Given these observations we elected to use Ullman coupling of 2,5-dibromo-substituted systems to form the desired polymers.



Scheme 1 provides an overview for the synthesis of poly(2-octylpyrrolo[3.4-*c*]-1,3-(2*H*,5*H*)-dioxopyrrole-4,6-

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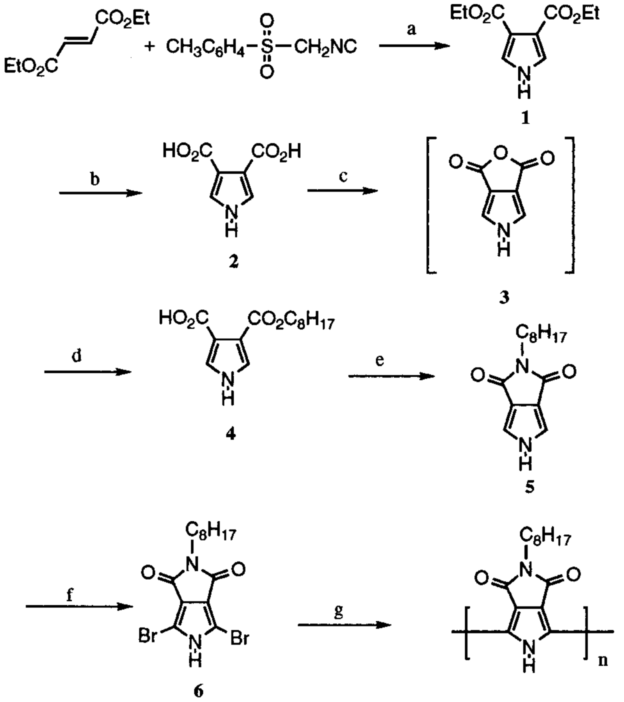
Scheme 1[a]



[a] Key: (a) KOtBu/THF, (b) NaOH, HCl, (c) DCC/THF, (d) octylamine, (e) $SOCl_2$/DMF, (f) NBS/THF, (g) copper bronze/DMF.

diyl) (details of the synthesis are available as Supporting Information).

Arnold and co-workers[11] have described the preparation of 2-substituted pyrrolo[3.4-*c*]pyrrole-1,3-(2*H*,5*H*)-diones (intermediate **5**) for the 2-methyl and 2-benzyl derivatives. The method utilizes the 1,3-dipolar addition of the anion of tosylmethyl isocyanide (TMIC) to diethyl fumarate to form 3,4-diethylpyrroledicarboxylate. This is hydrolyzed to the diacid, cyclyzed to the bicyclic anhydride, reacted with a primary amine to form the amic acid, and then cyclized to the bicyclic imide. In an attempt to enhance the solubility of the ultimate polymer, we utilized octylamine as the primary amine. We obtained the 2-octyl derivative in moderate yield. As these authors also noted, attempts to shorten the synthesis by attempting the cycloaddition of the anion of TMIC with *N*-alkylmaleimide under a variety of conditions led to an intractable black material, which we take to be oligomers due to the anionically initiated polymerization of the maleimide. The 2-octyl derivative is reacted with *N*-bromosucciinmide to afford the 2,5-dibromo compound as a tan solid.[5,6,10] The dibromo compound is then heated in DMF with 2.1 equiv of copper powder.[7,10] The solution immediately turns a dark red. After 2 h, the reaction mixture is quenched in an ice water mixture and the DMF and precipitated copper bromide are washed away with water, leaving a resinous solid that forms emerald green films. Initial NMR data yield an approximate number average degree of polymerization of 8. Infrared spectroscopy indicated the presence of a new NH vibration at 3500 cm^{-1} as well as a new low-frequency shoulder on the carbonyl band. Dissolution of the solid in chloroform produces a dark red solution. Recovery of the solid and dissolution in tetrahydrofuran give a yellow solution. GPC indicates the presence of oligomers up to the 10-mer, with the dominant species being the hexamer. The individual oligomers appear as distinct peaks in the GPC trace (see Supporting Information). UV/vis spectra of this material (Figure 1) indicated that in the strongly hydrogen bonding solvent (THF) the λ_{max} is at 213 nm with a shoulder extending to about 450 nm. The spectrum of the polymer in acetonitrile is nearly identical with that in THF. However, in a weakly hydrogen bonding solvent (chloroform) the λ_{max} undergoes a bathochromic shift to 242 nm and there is the appearance of a new band at 647 nm. Based on the proposed structure of the polymer, its interaction with solvents capable of hydrogen bonding serves to disrupt the internal network of hydrogen bonds along the chain, forcing the rings to adopt more perpendicular conformations. This leads to a reduced conjugation length and the hypsochromic shift in the absorption spectra. Conversely, in non-hydrogen-bonding solvents, the more planar structure is reinforced via the intramolecular hydrogen bonding, leading to the stronger absorbance at longer wavelengths. It is likely that as we increase the molecular weight of this material and therefore increase the conjugation length of the planar form, we would anticipate a greater bathochromic shift. If this does not occur, our hypothesis of the hydrogen-bonding reinforcing planarity will need to be reexamined.

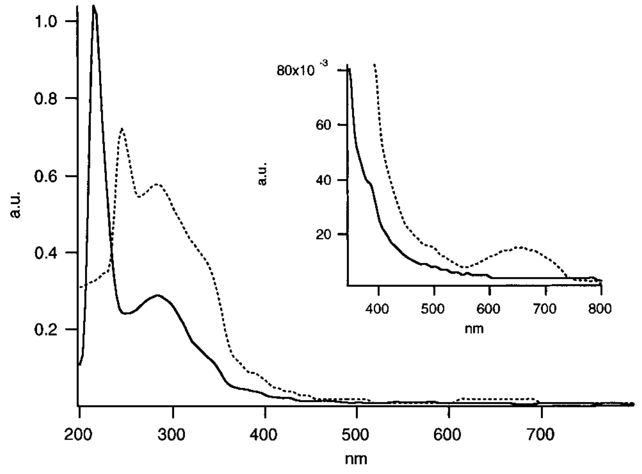


Figure 1. UV/vis spectra of the *N*-octyl olgomer: (solid line) in THF; (dashed line) in chloroform.

We are currently working to optimize the polymerization conditions to increase the molecular weight and the potential conjugation length of the polymer. We are also examining the effect of substituent size and its electronic nature on the optical properties of the polymer. Also under current investigation is the possibility that other influences capable of disrupting hydrogen bonding, such as increased temperature, can serve to affect the optical properties of the material. Finally, we are examining the potential for utilizing chiral amines to induce a preferred helicity to the polymer backbone through interactions of these groups on adjacent monomer units.

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Supporting Information Available: Experimental text for the preparation and characterization of **1**, **2**, and **4**−**6** and the polymerization of **6** and the GPC trace of the polymer (7 pages). Ordering information is on any current masthead page.

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