Zwitterionic Dye-Based Conducting Polymers. Synthesis and Optical Properties of Pyrrole-Derived Polysquaraines

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One of the major challenges in the area of molecular electronics is focused toward the synthesis of intrinsically conducting and processable materials with novel optoelectronic properties. Therefore, designing of oligomers and polymers having variable optical properties, striking chromic effects, and narrow bandgap energy remains important. Recent studies have shown that copolymerization of aromatic and *o*-quinoid heterocycles or donor−acceptor monomers are efficient strategies for synthesizing low-bandgap oligomers and polymers.[1] However, syntheses of such materials and their precursors are usually laborious and the resultant polymers in most of the cases are insoluble and intractable, thereby limiting their practical applications. In this context, simple methods to synthesize soluble and processable low-bandgap polymers have great significance. In this connection, several efforts have been made recently to design low-bandgap conjugated polymers with enhanced solubility and novel optical properties.[2] Conjugated polymers with controlled optical behavior and chromic effects are good candidates as polymer-based optical sensors.[3] Therefore, synthesis and/or structural modification of conjugated polymers with tunable optoelectronic properties has great significance, particularly in the emerging area of molecular electronics.

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) is known to condense with electron rich aromatic molecules such as *N*,*N*-dialkylanilines, phenols, pyrroles, and benzothiazoles to form highly colored polar (betaine) dyes called squaraine dyes.[4] Even though extensive studies have been reported on the chemistry and properties of squaraine dyes, studies pertaining to their polymer analogues are rather limited. Recently, Havinga et al. have reported the synthesis and conducting properties of some benzobisthiazole and benzobispyrroline based polysquaraines and polycroconaines.[5] Our objective was to use an appropriate, easily available monomer which is commonly employed in conducting polymer synthesis for designing soluble π-conjugated polymers with reduced bandgap energy. Although Treibs et al. earlier reported the formation of a low molecular weight intractable material (dimer or trimer) by the reaction of pyrrole and squaric acid, structural identification and properties could not be explored due to its insoluble nature.[6] In this Communication, we disclose the synthesis, characterization, and optoelectronic properties of soluble donor−acceptor type conjugated copolymers of *N*-alkylpyrroles and squaric acid. These macromolecular betaine dyes are intrinsic semiconductors and show solvatochromism and reversible optical response from UV to the near-IR region, with the solvent polarity and pH of the medium in an analogous manner to several π-conjugated polymers and organic dyes.

Since, the material derived from unsubstituted pyrrole and squaric acid, reported by Treibs et al., is known to be highly insoluble, we thought of improving its solubility by using *N*-alkyl chain substituted pyrroles, thereby providing better opportunity to look into their structure and properties. For this purpose, several *N*-alkyl chain substituted pyrroles were synthesized by the reaction of the corresponding alkyl halides with pyrrole under phase-transfer conditions.[7] Polysquaraine dyes **5a** and **5b** were synthesized by azeotropic removal of water from equimolar amounts of the corresponding N-substituted pyrroles and squaric acid in 2:1 mixture of 1-butanol and benzene as solvent (Scheme 1). The desired products were obtained in 60−65% yields, which were soluble in a range of organic solvents. GPC analyses (polystyrene standards, THF eluent) of the soluble polymers provided the molecular weight corresponding to $M_n = 6000$, with polydispersity (PD) = 1.8 for **5a** and $M_n = 4950$ with PD = 1.6 for **5b**, respectively.[8] Even though the molecular weight and solubility of **5a** and **5b** are not very high at this stage, appreciable improvements could be achieved compared with that of the material which have been originally reported by Treibs et al. Thermogravimetric analysis (10°/min, N_2) of the polymers indicated no appreciable weight loss upto 300 °C. The X-ray diffraction patterns of the polymers revealed the coexistence of both ordered and disordered structures with an interlayer spacing of ∼18.32 Å for **5a**.

The IR spectra of the polymers **5a** and **5b** (film) showed strong absorption band around 1620 cm^{-1}, characteristic of a cyclobutenediylium-1,3-diolate moiety, revealing that the polymers have a resonance-

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[8] Molecular weights were determined using flexible polystyrene standards which are not suitable for rigid rod polymers and hence may not correspond to the exact value. For similar observations, see ref 2b.

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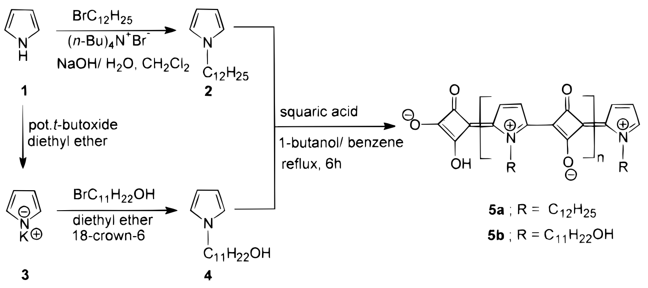
Scheme 1



stabilized zwitterionic structure. The weak carbonyl absorption bands observed at the vicinity of 1730 and 1790 cm^{-1} could be due either to the end functional group or to the formation of a very minor fraction of 1,2-oriented diketonic isomer unit attached to the polymer backbone as a side product. The IR spectral features of the polymers are comparable with that of several squaraine dyes with analogous structures. The ^1H and ^{13}C NMR spectra of the polymers were in agreement with the proposed structures. However, the NMR spectra were complicated with several satellite peaks which could be due to the end functional group of the polymer chain or due to the occurrence of small percentage of the 1,2-oriented diketo isomeric side product which is attached to the polymer backbone as mentioned above in the IR spectra. Comparison of the spectral and elemental analyses data of **5a** with that of the well-established structures of several simple pyrrole-derived squaraine dyes supports the analogous zwitterionic structure to the polymers.[9] Spectral and elemental analyses data[10] of the polymer **5b** were also in agreement with the proposed zwitterionic structure.

The electronic spectra of the new copolymers were found unique from that of a simple dye prepared from 2,4-dimethylpyrrole and squaric acid (λ_{max} in DMSO, 564 nm, sharp). The long-wavelength absorption in the optical spectrum of **5a** in DMSO was broad with a maximum centered around λ = 606 nm. The red shift of ~42 nm of **5a** indicates the extensive conjugation in the polysquaraine. The $\pi-\pi^*$ absorption maxima of **5a** and **5b** showed a significant hypsochromic band shift with increase in solvent polarity and dielectric constant as illustrated by the following data for **5a**: ($CHCl_3$, 586 nm; THF, 580 nm; 1-butanol, 578 nm; MeOH, 562 nm). Similarly, a distinct hypsochromic shift was noticed for **5a** in alcoholic hydrogen bonding donor (HBD) solvents in the order, 1-BuOH (578 nm) > 2-PrOH (571 nm) > EtOH (565 nm) > MeOH (562 nm), which can be explained on the basis of the enhanced acidity of MeOH compared to 1-butanol.[11] However, we could not see such an effect for **5a** and **5b** among various aromatic hydrocarbon solvents with different polarity supporting that hydrogen bonding is mainly responsible for the solvatochromic effect. A plot of the wavenumber (cm^{-1}) of an oligomeric analogue of **5a** versus the solvent Taft polarizability parameter, π^*, is shown in Figure 1. The π^* is the measure of the ability of the medium to stabilize a charge or dipole by virtue of its dielectric effect.[12] The observed negative solvatochromism reveals the decrease of the solute dipole moment upon excitation which is the characteristic property of organic dyes with betaine structure and compounds with inter- or intramolecular charge-transfer absorptions.[13] The negative solvatochromism and its contribution to the nonlinear optical properties of squaraine dyes have been recently reported.[14] Varying solvent polarity will affect the contributions of the neutral and charge-separated resonance structures to the ground and excited states of the molecules, thus changing the $\pi-\pi^*$ absorption

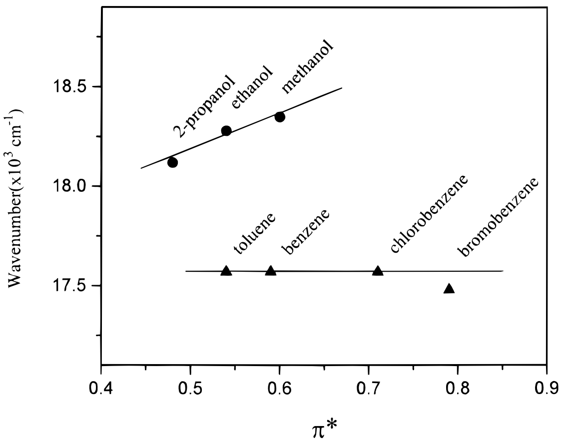


Figure 1. Plot of Taft parameter π^* vs UV/vis absorption maxima of **5a** in different solvents.

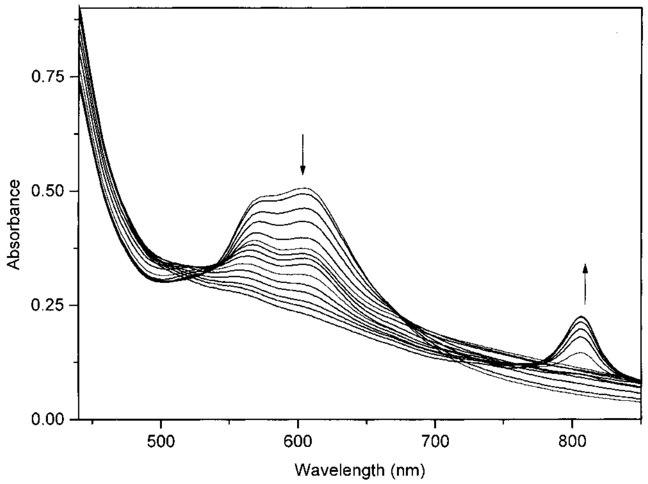


Figure 2. pH-induced spectral changes of **5a** in DMSO on addition of aqueous NaOH (0.1 N).

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(9) IR (neat film): ν = 2961, 2931, 2860, 1732, 1628, 1561, 1486, 1358, 1081 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.7−4.5 (br, s, 2 H), 3.38 (br, s, 2 H), 1.7 (br, s, 2 H), 1.22 (br, s, 18 H), 0.85 ppm (br, s, 3 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 188.9, 167.0, 130.7, 124.54, 123.48, 118.30, 111.50, 108.33, 40.19, 31.89, 31.10, 29.59, 29.48, 29.40, 29.31, 29.22, 26.59, 22.66, 14.09 ppm. UV−vis: λ_{max} = 586 ($CHCl_3$), 578 (1-BuOH), 606 (DMSO). Anal. Calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 75.60; H, 9.36; N, 4.64.

(10) IR (neat): ν = 3434, 2932, 2859, 1770, 1600, 1582, 1414, 1360, 1071 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz) δ = 4.7−4.5 (br, s, 2 H), 3.65 (t, 2 H), 3.4 (t, 2 H), 2.7 (s, 1 H), 1.3 ppm (br, s, 18 H). ^{13}C NMR ($CDCl_3$, 22.4 MHz) δ = 189.88, 167.0, 130.2, 125.01, 123.5, 118.4, 112.6, 110.56, 60.27, 41.0, 31.9, 31.1, 29.59, 29.40, 29.30, 29.14, 26.66, 25.58 ppm. UV−vis: λ_{max} = 577 ($CHCl_3$), 560 (1-BuOH), 601 (DMSO). M_n = 4960, M_w/M_n = 1.6 Anal. Calcd for $(C_{19}H_{25}NO_3)_n$: C, 72.38; H, 7.93; N, 4.44. Found: C, 71.12; H, 8.58; N, 3.99.

(11) Similar effects have been noticed by us for bis(benzothiazolylidene)squaraines. For details, see: Das, S.; Thomas, K. G.; Ramanathan, R.; Kamat, P. V.; George, M. V. *J. Phys. Chem.* **1993**, *97*, 13625.

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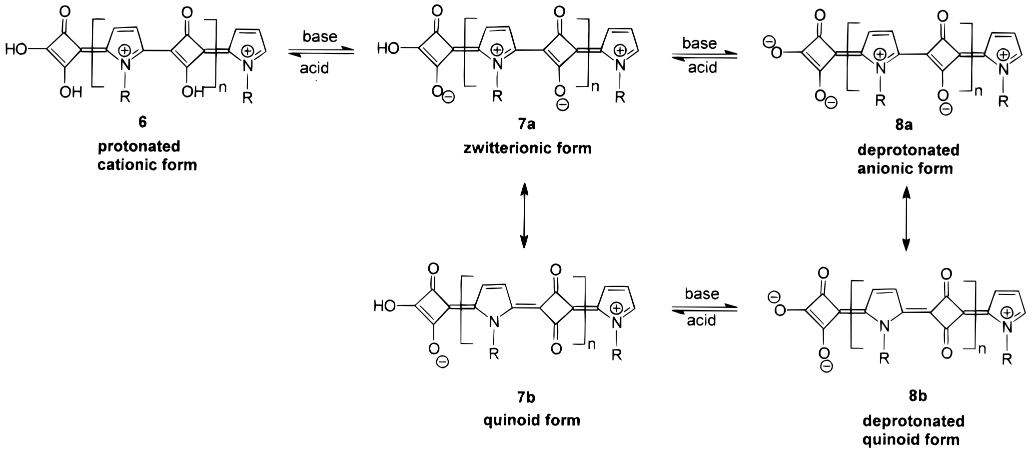
Scheme 2



maximum. The negative solvatochromism observed in HBD solvents implies that in addition to the dipole moment change on excitation, the ability of the solvent to form hydrogen bonds with the ground state of the polysquaraines also plays a major role in shifting the absorption maximum. [15]

The UV/vis spectra of the polymers showed pH-dependent reversible shifts as illustrated in the case of **5a** (Figure 2). Upon slow addition of aqueous NaOH (0.1 M) to a solution of **5a** in DMSO, the initial bluish green color (λ_{max}, 606 nm) was gradually decreased and a broad band appeared in the near-IR region. On continuous addition of base, the 606 nm absorption further decreased with the formation of a new strong band around 806 nm. Thus, Figure 2 clearly indicates that there are some structural changes to the polymer upon the addition of base. When aqueous HCl was added dropwise to the same solution, the initial green color was regained to its original intensity, indicating no decomposition of the polymeric dye. Thus, with change in pH, a unique reversible optical change could be noticed to the polymer, which spans from the UV to the near-IR region.

Even though the structural changes associated with the pH-dependent reversible optical shift is not very clear, it may be the result of the base- or acid-induced structural relaxations of the zwitterionic polymer chain between their protonated cationic form (nonplanar) and deprotonated anionic form (planar) as indicated in Scheme 2. In acids or in protic solvents the polymer could be in its protonated cationic form **6** rather than the original zwitterionic structure. On addition of base, deprotonation occurs, bringing back the polymer to its zwitterionic form **7a** and the mesomeric form **7b**. On further addition of base, a second deprotonation occurs and the polymer changes to its deprotonated anionic form **8a** which can be resonance stabilized to its quinoid form **8b** with long-wavelength absorption at $\lambda = 806$ nm. The polymeric dye **5a** in its deprotonated quinoid form has a solution bandgap of approximately 1.4 eV.

The polymers **5a** and **5b** are intrinsic semiconductors with conductivities (four point probe) of 2.4×10^{-6} and 2×10^{-7} S/cm, respectively. On exposure to iodine, the conductivity of the polymers could be enhanced upto 10^{-3} S/cm which was initially thought to be due to the charge transfer interaction between the squaraine dye unit of the polymer chain and iodine.[16] However, doping with other dopants such as $FeCl_3$ and LiCl further enhanced the conductivity up to 10^{-2} S/cm which support the oxidation of the polymer chain to form polarons and bipolarons thereby improving charge carrier mobility. In conclusion, we have synthesized soluble, alternate donor–acceptor copolymers having zwitterionic squaraine repeat units with interesting optical and electronic properties, which are potential candidates for several optoelectronic applications. Detailed studies on the synthesis and properties of related systems and methods to improve their molecular weights are in progress.

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Supporting Information Available: Detailed synthetic procedures and characterization data of **2**, **4**, **5a**, and **5b** (3 pages). Ordering information is given on any current masthead page.

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