

Synthesis and Properties of Water-Soluble Squaraine Oligomers Containing Pendant Propanesulfonate Moieties

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Polycondensation of squaric acid with a water-soluble pyrrole derivative containing an *N*-propanesulfonate pendant group gave a water-soluble A–B type oligomer. Similarly, several water-soluble random oligomers were prepared by the polycondensation of pyrrole, sodium 3-(pyrrol-1-yl)propanesulfonate, and squaric acid. Molecular weight analysis of the new oligomers showed a low degree of polymerization ($M_n \sim 1800$ – 2000) due to the premature precipitation of the condensation products in the reaction medium. Comparison of the IR and ^1H NMR spectral data of the new oligomers with those of a model squaraine dye, **9**, revealed the presence of zwitterionic squaraine repeat units. The negative solvatochromic property of the polycondensation products and the model compound **9** was analogous to that of several reported squaraine dyes, indicating their structural similarities. Comparison of the solvatochromic properties of the polycondensation products with that of the model dye **9** revealed the oligomeric nature of the polycondensation products. All new oligomers showed enhanced conductivities without external doping when compared to an analogous material without pendant propanesulfonate groups. For example, the conductivity of the condensation product of squaric acid with pyrrole was 1.1×10^{-6} S/cm, whereas that of the condensation product of squaric acid and sodium 3-(pyrrol-1-yl)propanesulfonate was 3.2×10^{-5} S/cm. The enhanced conductivities of the new squaraine oligomers could be due to enhanced conjugation or due to intramolecular doping by the pendant propanesulfonate groups.

Introduction

Squaraine dyes are the condensation products of 3,4-dihydroxy-3-cyclobutene 1,2-dione (squaric acid) with electron-rich aromatic compounds.¹ They possess a sharp and intense absorption in the visible region in solution. In the solid state, due to the crystal packing and strong charge-transfer interactions, the absorption shows a considerable bathochromic shift to the near-infrared (NIR) region. These optical absorption characteristics have made squaraines suitable materials for several technological applications such as xerography,² optical data storage,³ and solar energy conversion.⁴ Synthesis and properties of several classes of squaraine dyes are well documented in the literature.^{1,2,5} However, synthesis of their macromolecular analogues and studies of their physical and chemical properties are rather limited. Recent theoretical studies by Brocks and

Tol⁶ have predicted the possibility of obtaining low band gap polymers based on squaraine dyes by choosing appropriate starting materials, which attracted our attention in the design of novel materials making use of squaraine chemistry.

It is obvious that condensation of squaric acid with electron-rich aromatic compounds having more than one reaction center may lead to macromolecular analogues of squaraine dyes. Due to the strong charge-transfer interactions associated with the alternate donor–acceptor repeat units, polysquaraines are expected to show interesting optical and electronic properties. The earliest attempt in this direction is the condensation between squaric acid and pyrrole as reported by Triebs and Jacobs.⁷ Due to the insoluble and infusible nature of the condensation product of pyrrole and squaric acid, its structural details and physical properties could not be investigated. Recently we reported the synthesis and

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properties of a few pyrrole-derived soluble polysquaraines which showed several interesting optical and electronic properties.⁸ The electrical conductivities of these polymers are estimated to be on the order of 10^{-6} S/cm, which could be further enhanced upon doping with appropriate dopants.

Synthesis of conventional π -conjugated conducting polymers such as polypyrroles, polythiophenes, and polyanilines is usually accomplished by either chemical or electrochemical routes. The use of certain conducting salts and catalysts during the oxidative polymerization involves the chances of external doping of the resultant polymers, which may decrease their solubility and processibility. On the other hand, use of a polycondensation route to π -conjugated polymers has several advantages over the conventional oxidative polymerization strategies.⁹ This approach is highly useful in the design of π -conjugated polymers with alternate donor-acceptor repeat units.¹⁰ Such polymers are known to have interesting optoelectronic properties such as low band gaps, reversible optical properties, and solvatochromism. Havinga et al. have exploited this strategy in the design of several polysquaraines and polycroconaines with low band gap energies and water solubility.¹¹ We report here the synthesis, characterization, and properties of water-soluble squaraine oligomers derived by the condensation of squaric acid with easily available pyrrole and its *N*-propanesulfonate derivatives.

Results and Discussion

Sodium 3-(pyrrol-1-yl)propanesulfonate (**2**) was prepared using a reported procedure¹² by the reaction of pyrrole (**4**) and 1,3-propane sultone (**6**) in a 76% yield. Condensation of **2** with squaric acid (**1**) in a mixture of 1-butanol and benzene (1:1) with azeotropic removal of water gave a dark precipitate in an 86% yield. The product **3** thus obtained was washed thoroughly with 1-butanol and methanol and dried under vacuum in an oven at 100 °C for 48 h. The IR spectrum of **3** (Figure 1a) showed a strong absorption peak at 1629 cm^{-1} which is characteristic of the zwitterionic structure of cyclobutenediylum-1,3-diolate. In addition, the characteristic absorption peaks of the propanesulfonate group were also present. The broad OH stretching absorption

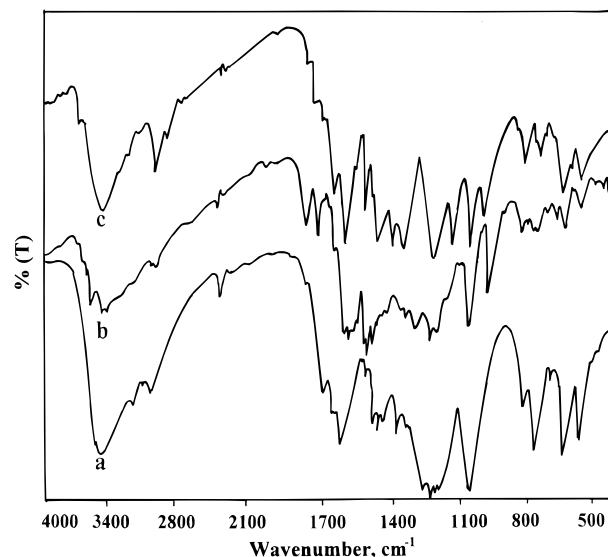


Figure 1. IR spectra of oligomers and model compound. (a) **3**; (b) **5a**; (c) **9**.

peak at 3444 cm^{-1} indicated the presence of adsorbed water due to the hygroscopic nature of **3**. The presence of weak absorptions around 1740 and 1770 cm^{-1} indicates the formation of small amounts of the 1,2-coupled diketonic repeat units.

The ¹H NMR spectrum of **3** in DMSO-*d*₆ is shown in Figure 2a. Most of the expected signals were rather broad without proper resolutions probably due to strong aggregation of the oligomeric dyes in DMSO at higher concentrations. The aliphatic protons attached to the sodium sulfonate moiety appeared as a broad triplet around δ 2.4, whereas the middle CH₂ protons of the propane side chain appeared as a broad multiplet around 1.9. The side-chain protons attached to the pyrrole nitrogen appeared as a broad triplet around δ 4.65, which is 0.88 ppm deshielded from that of the starting pyrrole **2**. The resonance signals of the two aromatic protons attached to the pyrrole ring were observed around δ 6.0 and 6.85 as broad humps. This observation is analogous to the earlier reports of the ¹H NMR spectra of water-soluble polypyrroles in which the signals of the aromatic protons attached to the pyrrole rings are broad and in some cases even difficult to observe.¹³ The elemental analysis data of the oligomer **3** showed a slightly lower value for Na⁺ probably due to partial hydrolysis of the pendant sodium propane-sulfonate to the corresponding acid.

Several water-soluble random oligomers having mixed squaraine dye units were prepared by the cocondensation of **1** and **2** in the presence of pyrrole (**4**) as per the procedure employed for the preparation of **3** (Scheme 2). This reaction can be considered as an $-(A-B)_x-(A-C)_y-$ type polycondensation having a random distribution of A-B and A-C repeat units. The dark green precipitates formed were collected by filtration and washed thoroughly with 1-butanol, methanol, and chloroform. The products **5a-d** were dried under vacuum at 100 °C for 48 h, and their IR and ¹H NMR spectral data were compared with those of **3**. The IR and ¹H NMR spectra of **5d** are shown in Figures 1b and 2b,

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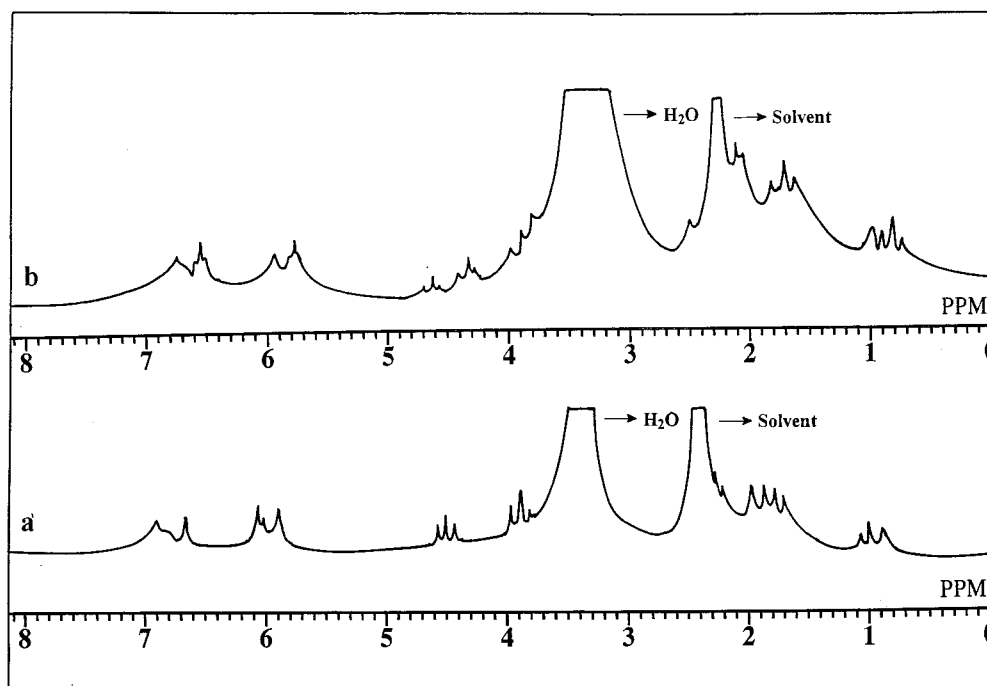
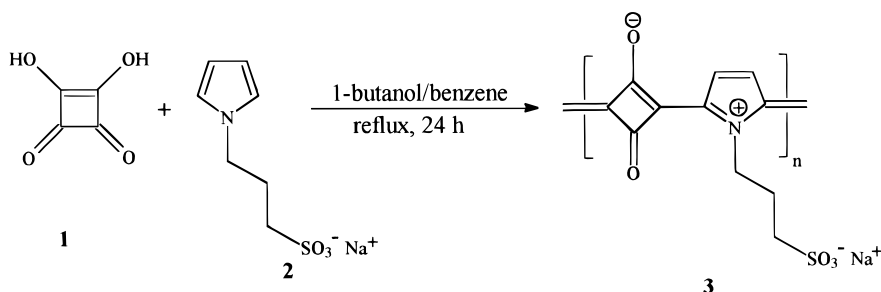


Figure 2. ^1H NMR spectra of oligomers in $\text{DMSO}-d_6$. (a) **3**; (b) **5a**.

Scheme 1

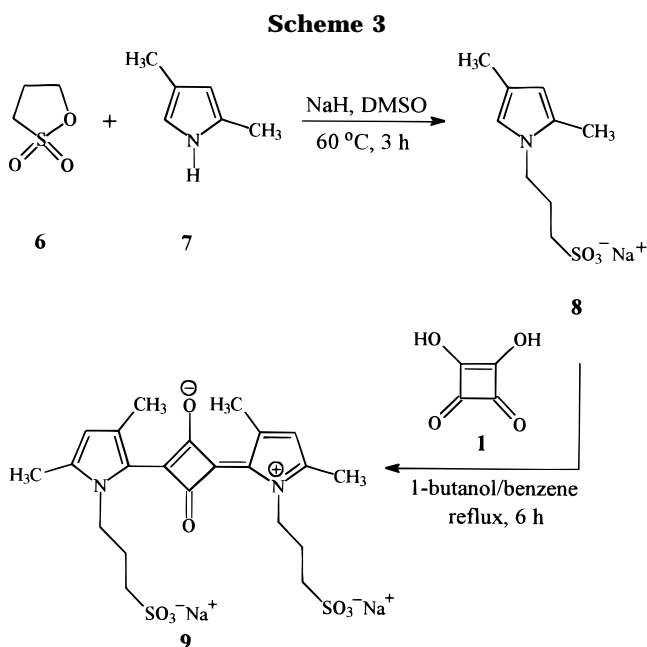
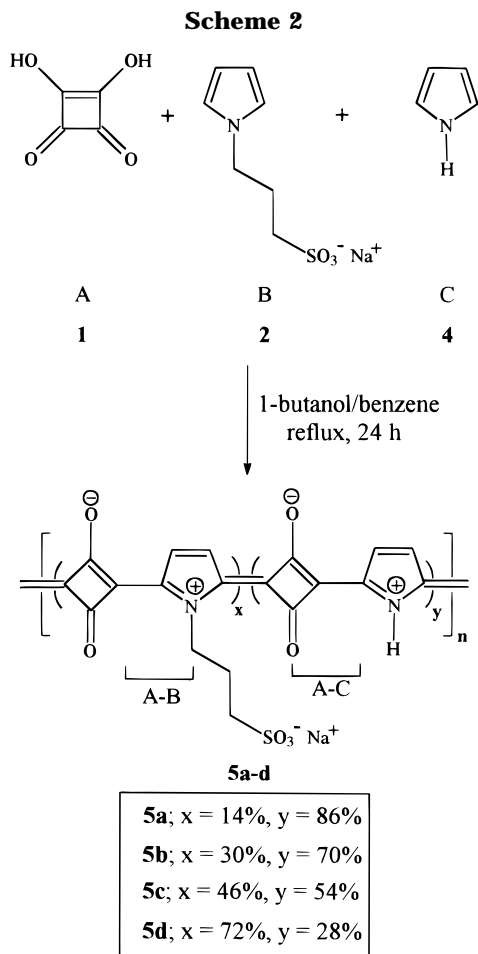


respectively. The compositions of various monomeric units in **5a–d** were determined from the elemental analysis data, which gave approximate values of A–B and A–C repeat units. A plot of the expected and observed mole percentages of the A–B repeat units in **5a–d** is shown in Figure 3, which reveals that the mole percentage of A–B repeat units containing the monomer **2** is slightly lower than the expected value. This observation indicates that the monomer **2** is comparatively less reactive toward squaric acid when compared to the reactivity of pyrrole.

The macromolecular nature of the polycondensation products **3** and **5a–d** was clear from their molecular weight analysis. Molecular weights were determined by gel-permeation chromatography (GPC) using polystyrenes as standards and THF as eluent. Since **3** and **5a–d** were not soluble in THF, they were converted to the corresponding sulfonic acid derivatives with concentrated HCl and precipitated by partial removal of the solvent under reduced pressure. The number average molecular weights of **3** and **5a–d** were in the range of 2800–3000 indicating a low degree of polymerization. This could be due to the poor solubility of the condensation products in the reaction medium, which precipitate after achieving a certain chain length and terminates the condensation process. The molecular weights reported in these cases might not be accurate since flexible

polystyrenes were used as standards for the rigid squaraine oligomers.

Much information on the structure and the oligomeric nature of **3** and **5a–d** could be derived from the synthesis and studies of a model squaraine dye, **9**. This was achieved by synthesizing the pyrrole derivative **8** in which one of the reactive sites is blocked to prevent the polycondensation. The compound **8** was prepared by the reaction of 2,4-dimethylpyrrole (**7**) with propane sultone (**6**) in the presence of NaH in an 88% yield and was characterized by spectral and elemental analyses. The model squaraine dye **9** was prepared in a 73% yield by refluxing **8** with squaric acid in a 1:1 mixture of 1-butanol and benzene with azeotropic removal of water. The IR spectrum of **9** (Figure 1c) is more or less identical to those of the oligomers **3** and **5a–d**, revealing their structural similarities. The absorption peak around 1620 cm^{-1} was characteristic of the cybutenediylum 1,3-diolate anion which is typical of the zwitterionic squaraine dyes in general. The ^1H NMR spectrum of **9** in $\text{DMSO}-d_6$ showed a singlet at δ 6.25 corresponding to the pyrrole rings, a triplet at δ 4.75 of the side-chain proton attached to the pyrrole nitrogen, and a broad multiplet corresponding to the four protons of the two propanesulfonate groups. The remaining four protons of the side chain which are directly attached to the sulfonate groups appeared along with the two singlets



at δ 2.1 and 1.9 of the four CH_3 groups attached to the pyrrole rings. The ^{13}C NMR spectrum of **9** showed eleven signals corresponding to twenty-two carbons indicating that the two halves of the molecule are identical due to its resonance-stabilized zwitterionic structure. Comparison of the spectral features of **9** with those of **3** and **5a–d** clearly indicates their structural similarity.

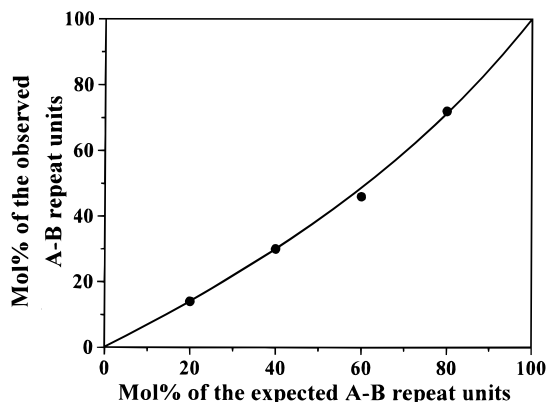


Figure 3. Composition curve of oligomers **5a–d**.

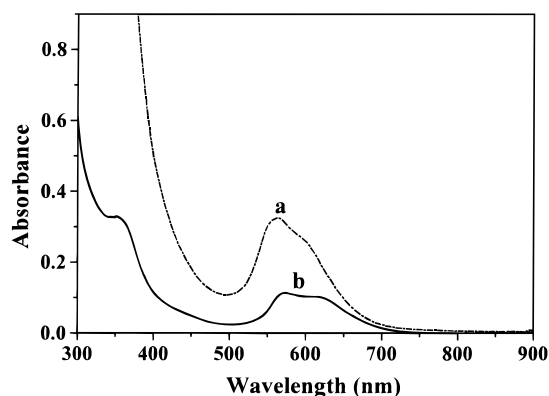


Figure 4. Electronic absorption spectra of oligomer **3** (a) in water and (b) in DMSO.

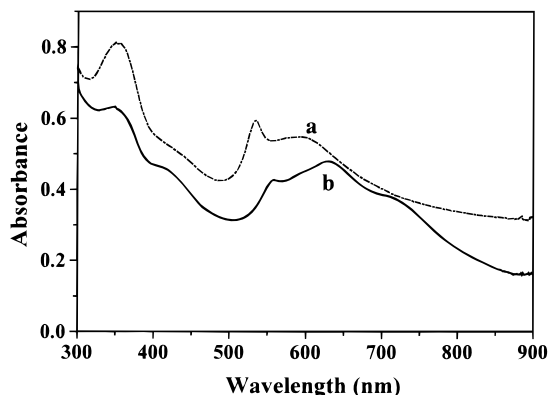


Figure 5. Electronic absorption spectra of the random oligomer **5a** (a) in water and (b) in DMSO.

The electronic absorption spectra of the oligomers **3**, **5a** and the model squaraine dye **9** in water and DMSO are shown in Figures 4–6, respectively. The model dye **9** showed a sharp and intense absorption around 569 nm in water and 584 nm in DMSO. The absorption spectra of the oligomer **3** are considerably broad with less intensity probably due to the presence of oligomeric units of various chain lengths. Despite being less conjugated, the absorption maximum of the model squaraine dye **9** is more or less the same as that of the oligomer **3**. This can be attributed to the strong donor–acceptor interaction of the pyrrole and the cyclobutene moieties due to the presence of the methyl groups in the pyrrole rings of **9**. The electronic absorption spectra of the random oligomers **5a–d** in DMSO and H_2O were broad and red shifted when compared to those of the

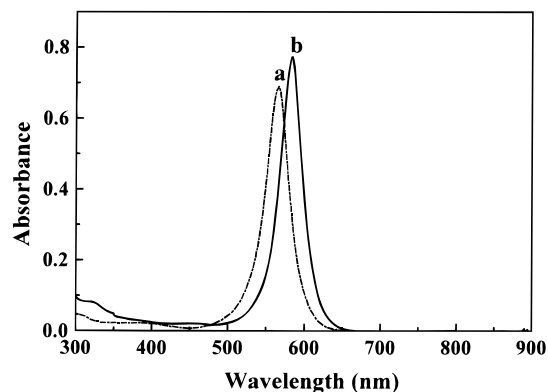


Figure 6. Electronic absorption spectra of the model dye **9** (a) in water and (b) in DMSO.

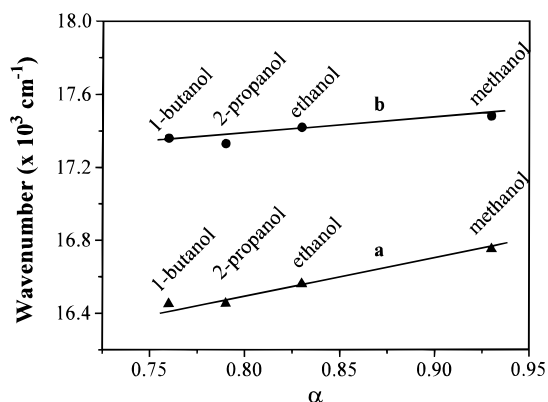


Figure 7. Plots of the solvent acidity parameter vs absorption maxima of the oligomer **3** and the model dye **9** in various hydrogen-bonding solvents. (a) **3**; (b) **9**.

oligomer **3**. For example, the long-wavelength absorption of **5a** in DMSO showed an absorption maximum around 630 nm with two shoulders around 550 and 710 nm (Figure 5).

The zwitterionic structure of the squaraine oligomers and the model squaraine dye can be further supported by their negative solvatochromic behavior against solvents with increasing polarity. In hydrogen-bonding solvents such as MeOH, EtOH, 2-PrOH, and 1-BuOH, a hypsochromic shift of the long-wavelength absorption is noticed for the oligomers **3** and **5a–d** and the model dye **9** with an increase in hydrogen-bonding ability (acidity) of the solvents. Similar negative solvatochromic relationship in hydrogen-bonding solvents is reported for several squaraine dyes.¹⁴ In Figure 7, a comparison of the solvatochromic behaviors of the oligomer **3** and model dye **9** is given which indicates a larger shift in the absorption maximum for oligomer **3** when their absorption maxima (in wavenumbers) were plotted against the acidity parameter (α) of the solvents.¹⁵ This large solvatochromic shift of the oligomer

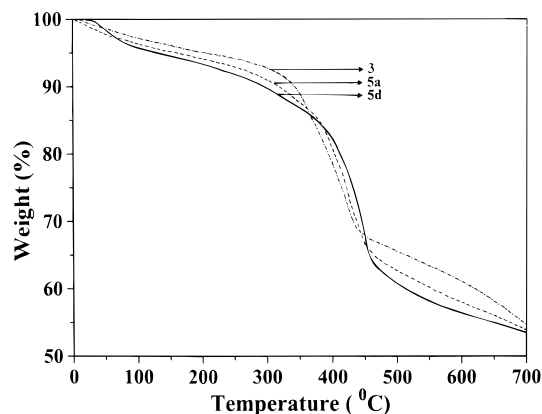


Figure 8. TGA curves of oligomers **3**, **5a**, and **5d** under air.

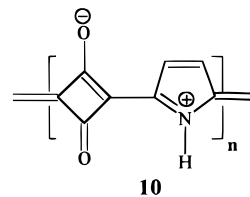
Table 1. Conductivity Values of Oligomers **3**, **5a–d**, and **10**

oligomer	mol % of A–B repeat units	sp conductivity (S/cm)
10	0	1.1×10^{-6}
5a	14	3.6×10^{-6}
5b	30	6.9×10^{-6}
5c	46	1.3×10^{-5}
5d	72	2.3×10^{-5}
3	100	3.2×10^{-5}

3 can be ascribed to its extended π -conjugated oligomeric structure when compared to that of **9**.

The thermograms obtained by the thermogravimetric analysis (TGA) of the oligomers **3**, **5a**, and **5d** are shown in Figure 8. The initial weight loss of nearly 5–10% below 200 °C reveals the presence of adsorbed water molecules in all the oligomers. The thermal decomposition of the oligomer chain occurs between 350 and 450 °C, and in all cases nearly 60% weight loss is noticed at this temperature. Comparison of the thermograms of the various random oligomers with different random compositions did not show much difference in the general pattern of their thermal decomposition. The differential scanning calorimetry (DSC) analysis revealed no melting transition to any of the oligomers under investigation probably due to their zwitterionic structures.

The electrical conductivities of the oligomers **3** and **5a–d** were measured at room temperature by the standard four point probe method using pressed pellets. These values are listed in Table 1. These oligomers showed improved conductivities when compared to that of the squaraine oligomer **10** obtained by the condensa-



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tion of pyrrole with squaric acid. For example, oligomer **10** showed a conductivity of 1.1×10^{-6} S/cm, whereas the oligomer **5d** showed a conductivity of 2.3×10^{-5} S/cm. A plot of the specific conductivities of oligomers **5a–d** versus the oligomer composition is shown in Figure 9, which indicates an increase in conductivity with an increase in the mole percentage of the repeat

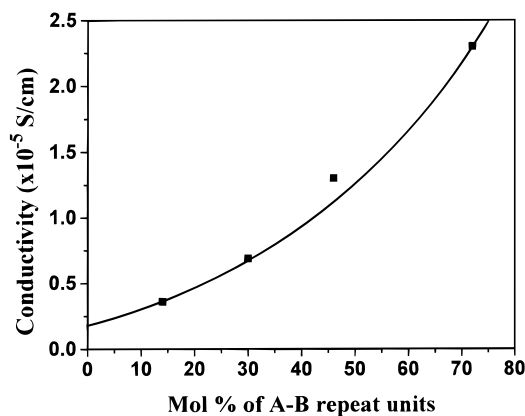
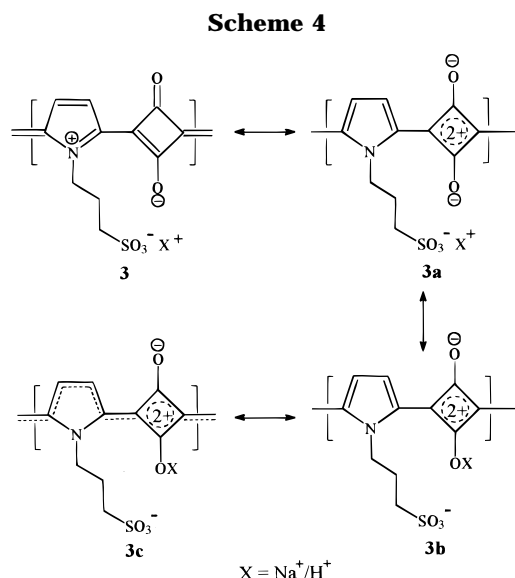
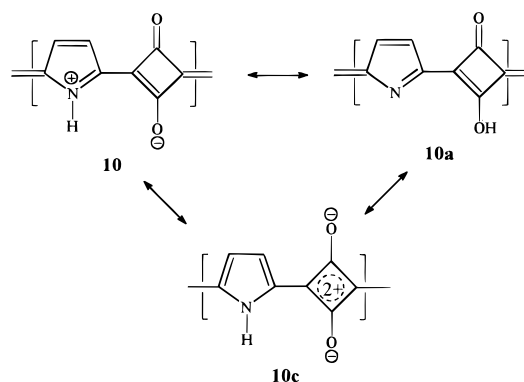


Figure 9. Plot of the conductivities of the random oligomers **5a–d** as a function of their A–B repeat units.



units of monomer **2**. The improved conductivities of the new oligomers could be due to an intramolecular doping (self-doping) of the oligomer backbone by the pendant propanesulfonate group or due to extended conjugation associated with enhanced molecular weight. The shoulder in the long-wavelength absorption in the case of oligomers **5a–d** may be due to charge carriers, indicating that these oligomers are partially doped. Even though the mechanism of self-doping is not very clear, it could be analogous to the self-doping in polypyrroles and polyanilines attached to pendant alkyl sulfonate moieties.¹⁶ A possible mechanism for the improved conductivities in squaraine oligomers containing pendant propanesulfonate moieties is shown in Scheme 4. For example, in the case of the oligomer **3**, the structure can be better represented as **3a** due to its highly resonance stabilized zwitterionic nature. The propanesulfonate moieties which are present as their sodium salt or the corresponding acid (formed during workup or due to adsorbed water molecules) may lead to the structure **3b**, leaving excess charges on the oligomer backbone which lead to the formation of the charge-

Scheme 5



delocalized structure **3c**. On the other hand, even though similar structures can be drawn for polymer **10**, its backbone is electrically neutral (Scheme 5). Further, the electrical conductivity of **10** can be improved by external doping with benzenesulfonic acid indicating that a similar effect can be derived by the presence of covalently attached propanesulfonate moieties in oligomers **3** and **5a–d**.

In conclusion, several π -conjugated water-soluble oligosquaraines have been synthesized by a simple polycondensation strategy. The structures of these oligomers have been determined on the basis of a comparison with the spectral data of a model squaraine dye. The squaraine oligomers and the model squaraine dye showed negative solvatochromism with increases in solvent polarity, which is in accordance with their structural similarities. All squaraine oligomers under investigation showed electrical conductivities in the range of 10^{-5} S/cm without an external doping, which could probably be due to an intramolecular doping by the pendant propanesulfonate moieties.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer model 882 infrared spectrometer. The electronic absorption spectra were recorded either on a Shimadzu UV-2100 spectrophotometer or on a GBC double-beam UV-visible spectrophotometer. The ¹H and ¹³C NMR spectra were recorded on a JEOL EX 90 spectrometer using tetramethylsilane (TMS) as the internal standard. Molecular weights were determined on a Shimadzu LC-8A GPC system equipped with a refractive index detector. Polystyrene was used for calibration, and THF was used as the eluent at a flow rate of 1 mL min⁻¹. Thermogravimetric analyses (TGA) were carried out on a V5.1A Dupont 2000 TGA analyzer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Sodium analyses were carried out on a Digital Flamephotometer, model CI 22 D (Elco Pvt. Ltd., India) with a Na/K filter. The conductivity of the polymers was measured by the standard four point probe method on pressed pellets of about 5 × 1 mm dimensions.

1. Preparation of Sodium 3-(Pyrrol-1-yl)propanesulfonate (2). To a suspension of NaH (20 mmol, 50% suspension in paraffin oil) in dry DMSO (10 mL) under constant stirring and a nitrogen atmosphere was slowly added pyrrole (1.34 g, 20 mmol) in DMSO (20 mL) at 60 °C over a period of 1 h. To this, 1,3-propane

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sultone (2.44 g, 20 mmol) was added dropwise, and the reaction mixture was stirred at 60 °C for 2 h. Addition of acetone precipitated a solid product, which was filtered, washed with hot THF to remove any unchanged sultone, and dried in a vacuum oven at 60 °C for 24 h to give 3.2 g (76%) of **2** as a white solid, mp 200–210 °C (dec). IR ν_{\max} (KBr): 3590, 3137, 3110, 2962, 2890, 1629, 1578, 1504, 1455, 1380, 1285, 1204, 971, 727, 609 cm^{-1} . ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.7–2.0 (2 H, m, CH_2), 2.29 (2 H, t, $J = 6.9$ Hz, CH_2), 3.77 (2 H, t, $J = 7.2$ Hz, $\text{N}-\text{CH}_2$), 5.79 (2 H, t, $J = 2.1$ Hz, aromatic), 6.53 (2 H, t, $J = 2.1$ Hz, aromatic); ^{13}C NMR (DMSO- d_6 , 22.5 MHz) 27.62, 47.73, 48.42, 107.58, 120.65. Anal. Calcd for $\text{C}_7\text{H}_{10}\text{NSNaO}_3$: C, 39.81; H, 4.74; N, 6.64; S, 11.51; Na, 10.9. Found: C, 39.69; H, 4.75; N, 6.62; Na, 10.67.

2. Preparation of Oligomer 3. A flask equipped with an azeotropic reflux condenser was charged with 1-butanol (20 mL), benzene (10 mL), 0.31 g (1.5 mmol) of **2**, and 0.17 g (1.5 mmol) of **1** under a nitrogen atmosphere. The reaction mixture was refluxed for 24 h. It was then cooled, and benzene was evaporated under reduced pressure. The residual mass was treated with chloroform (200 mL), and the precipitated product was washed several times with 1-butanol, methanol, and chloroform. The residue was dried in a vacuum oven at 100 °C for 48 h to give 390 mg (86%) of **3**. IR ν_{\max} (KBr): 3519, 2941, 1725, 1650, 1564, 1198, 1053, 732, 611 cm^{-1} . UV λ_{\max} (DMSO): 574, 612 nm. λ_{\max} (H_2O) 562 and 597 nm. ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.5–1.85 (2 H, m, CH_2), 2.2 (2 H, t, $\text{S}-\text{CH}_2$), 4.65 (2 H, t, NCH_2), 6.0 (1 H, s, br, aromatic), 6.85 (1 H, s, br, aromatic); ^{13}C NMR (DMSO- d_6 , 22.5 MHz) δ 18.49, 26.79, 27.63, 48.42, 56.03, 79.15, 100.42, 107.37, 120.47, 151.38, 157.86. Anal. Calcd for $(\text{C}_{11}\text{H}_8\text{NSNaO}_5)_n$: C, 45.67; H, 2.77; N, 4.84; S, 11.07; Na, 7.96. Found: C, 45.30; H, 2.62; N, 4.61; Na, 7.28.

3. Preparation of Random Oligomers 5a–d. The random oligomers **5a–d** were prepared by adopting methods similar to the synthesis of oligomer **3**. Analytical results and spectral data of the oligomers **5a–d** are summarized below.

5a (58%): M_n , 3800. IR ν_{\max} (KBr): 3406, 2940, 1728, 1588, 1556, 1488, 1288, 1045, 944, 803, 745 cm^{-1} . UV λ_{\max} (DMSO): 556, 628, 720 nm. λ_{\max} (H_2O) 525, 580 nm. ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, $\text{S}-\text{CH}_2$), 4.7 (2 H, t, $\text{N}-\text{CH}_2$), 5.75–5.8 (s, br, aromatic), 6.6–6.9 (s, br, aromatic). Anal. Found: C, 62.71; H, 2.19; N, 8.84; Na, 1.86.

5b (62%): M_n , 3860. IR ν_{\max} (KBr): 3405, 2939, 1788, 1724, 1586, 1563, 1489, 1186, 1046, 945, 737 cm^{-1} . UV λ_{\max} (DMSO): 555, 628, 726 nm. λ_{\max} (H_2O): 534, 600 nm. ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, $\text{N}-\text{CH}_2$), 5.75–5.8 (s, br, aromatic), 6.6–6.9 (s, br, aromatic). Anal. Found: C, 58.06; H, 2.35; N, 7.76; Na, 3.41.

5c (64%): M_n , 3850. IR ν_{\max} (KBr): 3458, 2939, 1781, 1723, 1670, 1569, 1488, 1191, 1045, 805, 735 cm^{-1} . UV λ_{\max} (DMSO): 561, 615 nm. λ_{\max} (H_2O): 595 nm. ^1H

NMR (DMSO- d_6 , 90 MHz): δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, $\text{N}-\text{CH}_2$), 5.75–5.8 (s, br, aromatic), 6.6–6.9 (s, br, aromatic). Anal. Found: C, 54.44; H, 2.47; N, 6.90; Na, 4.57.

5d (74%): M_n , 3900. IR ν_{\max} (KBr): 3526, 3402, 1780, 1583, 1480, 1306, 1047, 814, 714 cm^{-1} . UV λ_{\max} (DMSO) 560, 623 nm. λ_{\max} (H_2O): 540, 595 nm. ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, $\text{N}-\text{CH}_2$), 5.75–5.8 (s, br, aromatic), 6.6–6.9 (s, br, aromatic). Anal. Found: C, 52.24; H, 2.55; N, 6.39; Na, 6.36.

4. Preparation of Sodium 3-(2,4-Dimethylpyrrol-1-yl)propanesulfonate (8). Compound **8** (2.1 g, 88%), mp 160–170 °C (dec), was synthesized from 0.95 g (10 mmol) of 2,4-dimethylpyrrole and 1.22 g (10 mmol) of 1,3-propane sultone, employing the same procedure adopted for the preparation of **2**. IR ν_{\max} (KBr): 3609, 3529, 2981, 2934, 1695, 1625, 1528, 1418, 1210, 1063, 783, 734, 608 cm^{-1} . ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.6–1.9 (8 H, m, CH_3 , CH_2), 1.95 (2 H, s, CH_3), 2.35 (2 H, t, $J = 7.6$ Hz, CH_2), 3.69 (2 H, t, $J = 7.2$ Hz, $\text{N}-\text{CH}_2$), 5.43 (1 H, s, aromatic), 6.25 (1 H, s, aromatic); ^{13}C NMR (DMSO- d_6 , 22.5 MHz): δ 11.78, 12.11, 27.24, 44.69, 48.48, 108.9, 115.70, 117.9, 127.42. Anal. Calcd for $\text{C}_9\text{H}_{14}\text{NSNaO}_3$: C, 45.18; H, 5.86; N, 5.86; S, 13.39; Na, 9.62. Found: C, 45.30; H, 5.82; N, 5.81; Na, 9.92.

5. Preparation of Model Dye 9. A mixture of 0.48 g (2 mmol) of **8**, 0.11 g (1 mmol) of **1**, 20 mL of 1-butanol, and 10 mL of benzene was refluxed for 6 h under nitrogen, and the water formed was removed azeotropically. The reaction mixture was cooled, and benzene was removed under vacuum. This mixture was poured into chloroform (200 mL), and the precipitated product was filtered, dried, and then dissolved in methanol. The solution was filtered, and the filtrate was poured into chloroform (300 mL). The precipitated dye was filtered, dried, and then redissolved in DMSO. The DMSO solution was poured into an excess of chloroform, and the precipitated dye was filtered, washed several times with chloroform, and dried in a vacuum oven at 50 °C for 48 h to give 0.41 g (73%) of **9**. IR ν_{\max} (KBr): 3423, 2933, 1654, 1620, 1510, 1455, 1397, 1349, 1119, 1123, 1048, 975 cm^{-1} . UV λ_{\max} (DMSO): 584 nm. λ_{\max} (H_2O): 562 nm. ^1H NMR (DMSO- d_6 , 90 MHz): δ 1.7–1.95 (4 H, m, CH_2), 2.3 (6 H, s, CH_3), 2.45–2.75 (10 H, m, CH_3 , SCH_2), 4.75 (4 H, t, NCH_2), 6.25 (2 H, s, aromatic); ^{13}C NMR (DMSO- d_6 , 22.5 MHz): δ 27.45, 43.14, 48.12, 119.07, 126.23, 137.48, 147.77, 174.21, 175. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{S}_2\text{Na}_2\text{O}_8$: C, 47.48; H, 4.68; N, 5.03; S, 11.51; Na, 8.27. Found: C, 47.32; H, 4.73; N, 5.23; Na, 8.04.

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