Synthesis and Properties of Alternating Acceptor−Donor Copolymers of Squaric Acid with 1-Dodecyl- and 3-Dodecylpyrroles[†]

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ABSTRACT: Polycondensation between the acceptor−donor monomer combination of squaric acid with 1-dodecyl- and 3-dodecylpyrroles provided conjugated macromolecules having two types of isomeric repeating units, depending upon the reaction conditions employed. Under azeotropic distillation using the 1-butanol−benzene solvent mixture (route A), the most preferred 1,3-zwitterionic repeating units were mostly formed, whereas in DMSO−acetic acid solvent under room temperature (route B), considerable amounts of the isomeric 1,2-diketonic repeating units were also formed along with the zwitterionic repeating units. Evidence for the structural differences of the polycondensation products obtained by routes A and B could be obtained from the detailed IR spectral analysis and studies of their physical properties such as solubility, molecular weight, optical absorption, solvatochromism, and conducting properties. The solubilities and the molecular weights of the polycondensation products having 1,2-diketonic repeating units obtained by route B were significantly enhanced when compared to those obtained as per route A. The UV−vis spectral and solvatochromic properties of the polymers obtained by routes A and B showed distinct differences, which were in accordance with their proposed structures. The electrical conductivities of the polymers obtained from 3-dodecylpyrrole and squaric acid by route B showed better values over polymers obtained through route A.

Introduction

Design of novel π-conjugated macromolecules and investigation of their electronic properties such as optical absorption and electrical conductivity constitute an important area of research in contemporary macromolecular-related materials chemistry. Considerable attention has been paid to the synthesis of soluble and processible π-conjugated oligomers and polymers with low band-gap energies (E_g) due to their intrinsic semiconductivity, NLO activity, and electroluminescent properties.[1] Syntheses of such materials are usually achieved by multistep synthetic procedures. The optical band gap in π-conjugated polymers can be lowered by inducing quinoid character to the polymer or by the rigidification of the repeating units which provide a near-planar conformation to the polymer.[2] However, the resultant polymers in most of the cases are insoluble and intractable, thereby limiting their practical applications. Therefore, the synthesis of soluble and processible π-conjugated polymers having low band-gap energies has attained considerable significance in recent years.

The synthesis of π-conjugated polymers having alternate donor−acceptor repeating units has been an area of intense interest due to their low optical band gaps and unique optoelectronic properties.[3] Organic dye molecules having considerable charge-transfer interactions would be ideal candidates in the design of low-E_g donor−acceptor polymers because of their low HOMO−LUMO separation and interesting optical and electronic properties even at their oligomeric stage. In this context, we have been interested in the synthesis and properties of macromolecular squaraines derived from substituted pyrroles and squaric acid.[4]

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) is known to form highly colored 1,3-disubstituted zwitterionic derivatives with electron-rich aromatic compounds.[5] This class of organic dyes which are commonly referred to as squaraines is known to possess several interesting optoelectronic properties which are useful for several technical applications such as electrophotography,[6] solar energy conversion,[7] optical data storage,[8] and nonlinear optics.[9] Even though the chemistry and physical properties of different classes of squaraines are in the literature, studies pertaining to analogous macromolecular squaraines are relatively few.[10,11] Recent theoretical calculations by Brocks et al. have revealed the possibility of designing low-E_g polysquaraines which have generated tremendous interest in these classes of polymers.[12] The present paper describes the synthesis, characterization, and evaluation of the optical and conducting properties of a few A−B-type polycondensation products of squaric acid with 1-dodecyl- and 3-dodecylpyrroles.

Results and Discussion

1-Dodecylpyrrole (**2**) was prepared under standard phase-transfer conditions according to reported procedures (Scheme 1).[3a,13] 3-Dodecylpyrrole (**5**) was prepared from 1-(phenylsulfonyl)pyrrole (**3**) by the Friedel−Crafts reaction with the corresponding acid chlorides, followed by reduction of the ketone and the subsequent alkaline hydrolysis as depicted in Scheme 1.[14] All pyrrole derivatives were purified by column chromatography and characterized on the basis of reported data and analytical results.

Polycondensation of squaric acid with 1-dodecylpyrrole was performed under two different experimental conditions. According to route A, the squaric acid and pyrrole derivative in a 1:1 ratio was refluxed in a mixture of 1-butanol and benzene (2:1) and the water formed was removed by azeotropic distillation. After 24 h, the deep blue solution formed was concentrated under reduced pressure, and the resulting mixture was poured

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Scheme 1

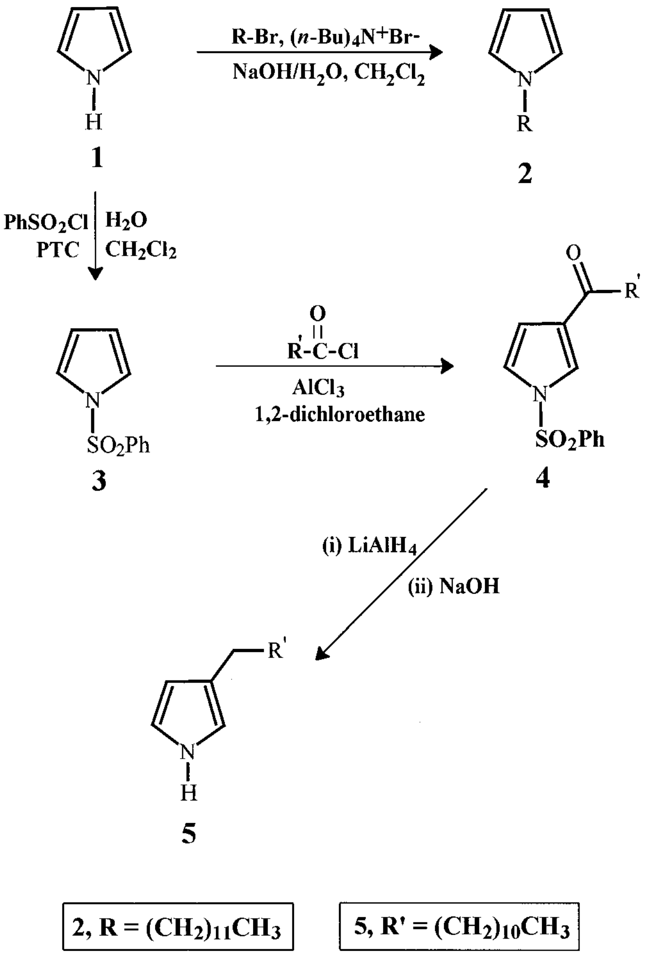


Table 1. Molecular Weights and Solubility[a] of the Polycondensation Products of Squaric Acid with 1-Dodecyl- and 3-Dodecylpyrroles Obtained as per Routes A and B

			solubility			
product	route	$\bar{M}_n$	MeOH	DMF	$CHCl_3$	hexane
7	A	6 000	±	+	+	- -
8	B	14 308	- -	- -	++	++
9	A	4 500	±	+	+	- -
10	B	10 892	- -	- -	++	++

[a] ± = partial; + = good; ++ = very good; - - = bad.

into an excess of diethyl ether. The precipitate formed was collected by filtration, redissolved in DMF, and reprecipitated from diethyl ether. In route B, squaric acid and 1-dodecylpyrrole (1:1) were stirred at room temperature in a mixture of acetic acid and DMSO for 6 days in the dark (Scheme 2). The deep green condensation product **8** was collected by filtration and washed several times with water and methanol. The polycondensation of **5** was carried out as per routes A and B (Scheme 3) as described for the polycondensation of **2** with squaric acid. 3-Dodecylpyrrole was found to be more reactive than 1-dodecylpyrrole toward squaric acid.

Surprisingly, the solubility of the condensation products **7** and **9** obtained through route A was significantly different from that of **8** and **10** obtained by route B. For example, **7** and **9** were soluble in polar protic solvents, whereas **8** and **10** showed better solubility in less polar aprotic solvents (Table 1). Similarly, the molecular weight analysis revealed that **7** and **9** obtained by route A have lower molecular weights than those of **8** and **10** obtained by route B (Table 1). For example, the number-average molecular weight of **7** was 6000, whereas that of **9** was 14 308.[15] The observed anomalies in solubility and molecular weights of the various condensation products indicate some possible structural differences in their repeating units. To gain information on the structures of the condensation products, they were subjected to detailed spectral analyses. In addition, indirect evidence for the structural differences of various condensation products obtained through routes A and B could be derived by the studies of their solvatochromic behavior.

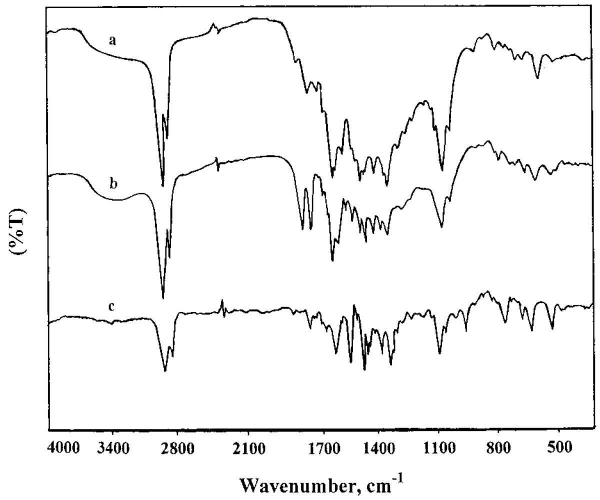
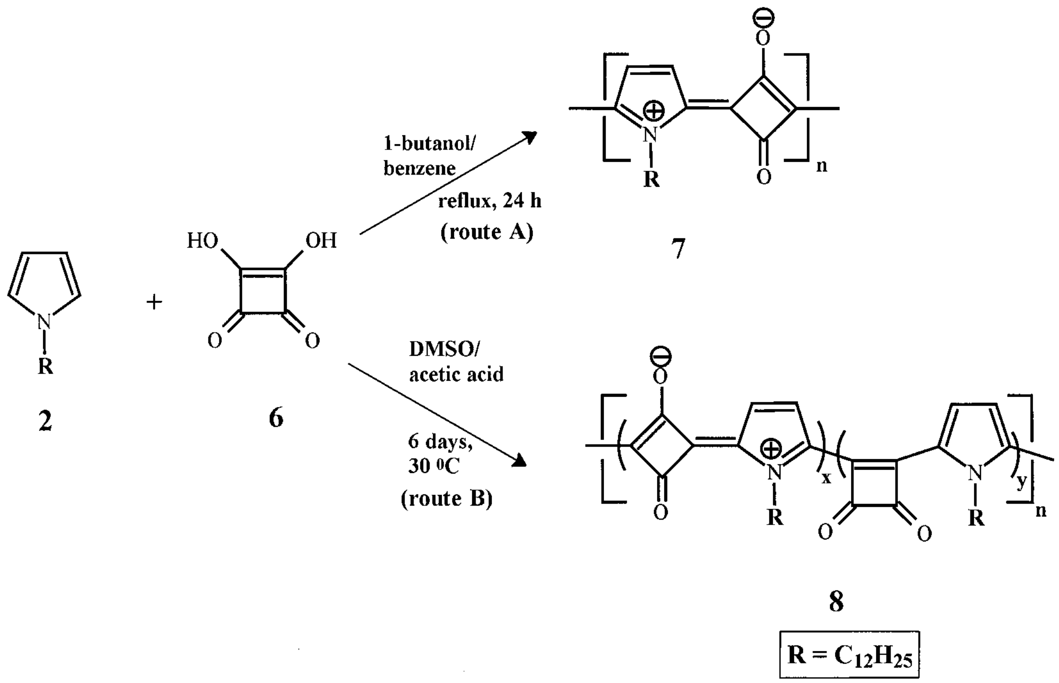


Figure 1. IR spectra of polymers (a) **7** and (b) **8** and (c) model compound **13**.

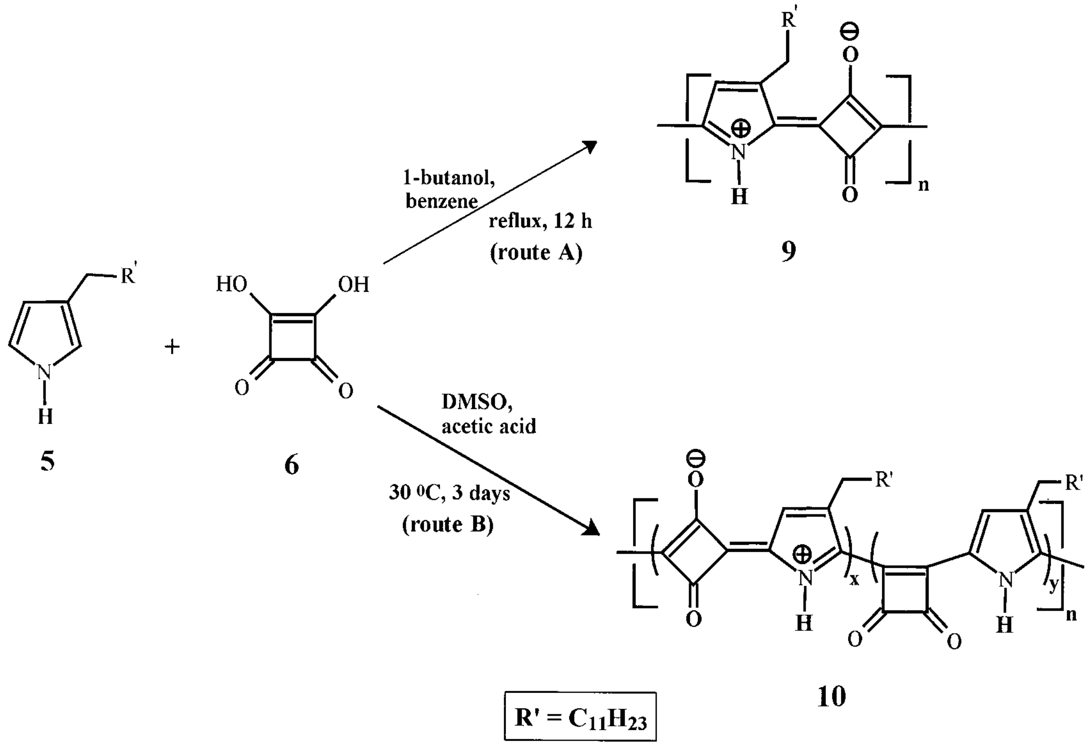
The ^1H NMR spectra of the condensation products **7**−**10** could not provide sufficient evidence for their structures mainly due to the poorly resolved broad resonance peaks. This could probably be due to the limited solubility of the condensation products and due to their strong aggregation in NMR solvents. Nevertheless, the ^1H NMR spectra of **7**−**10** were comparable to that of a model squaraine dye **13**, which has been prepared according to Scheme 4. For example, the $N-CH_2$ protons of the dodecyl chains of **7** and **13** appeared as a broad triplet at 4.7 and 4.8 ppm, respectively. The CH_3 protons of the dodecyl chains of both **7** and **13** gave broad triplets at 0.85 ppm. All other protons of the dodecyl side chains of **7** and **13** were observed as broad singlets at 1.2 ppm. The aromatic protons attached to the pyrrole ring of **7** appeared between 6 and 7 ppm as broad humps as reported in the case of several polypyrroles.[16] The ^1H NMR spectra of **8** and **10** were much more complicated due to the presence of several additional peaks when compared to those of **7** and **9**, thereby revealing the structural complexities of **8** and **10**.

The detailed IR spectral analyses of the condensation products obtained through routes A and B showed significant differences in their structural composition (Figure 1). The IR spectra of **7** and **9** showed strong absorption peaks around 1620−1600 cm^{-1} corresponding to the C−O stretching frequency of a cyclobutenediylium-1,3-diolate moiety. The IR spectrum of the model compound **13** was comparable to those of **7** and **9**, indicating a resonance-stabilized zwitterionic structure. On the other hand, the IR spectra of **8** and **10** showed two strong carbonyl absorptions around 1780

Scheme 2



Scheme 3



and 1720 cm^{-1}, in addition to the C−O stretching frequency at 1610 cm^{-1}. The carbonyl absorption peaks of **8** and **10** are comparable to that of the diketonic model compound **14** (Chart 1), which was reported earlier by Triebs and Jacob.[10a] This observation suggests that the polycondensation products **8** and **10** obtained through route B contain two types of repeating units consisting of a 1,3-substituted zwitterionic and a 1,2-substituted diketonic structure. These structural variations can result from the orientational preference of squaric acid toward the pyrrole derivatives, leading to the formation of the isomeric 1,3- and 1,2-substituted repeating units, the ratio of which may change with the reaction conditions employed for the polycondensation reaction. This observation is analogous to that of an earlier report of the formation of both 1,3- and 1,2-oriented cyclobutene rings during the polyamidation reaction between dimethylsquarate and 1,4-diaminobenzene.[17]

Further evidence for the proposed structural differences in the repeating units of the polycondensation products obtained by routes A and B can be obtained from their electronic absorption spectral properties and solvatochromic behavior. The solvatochromic behavior of organic molecules in various solvents can be related to their structural characteristics. For example, it is

Scheme 4

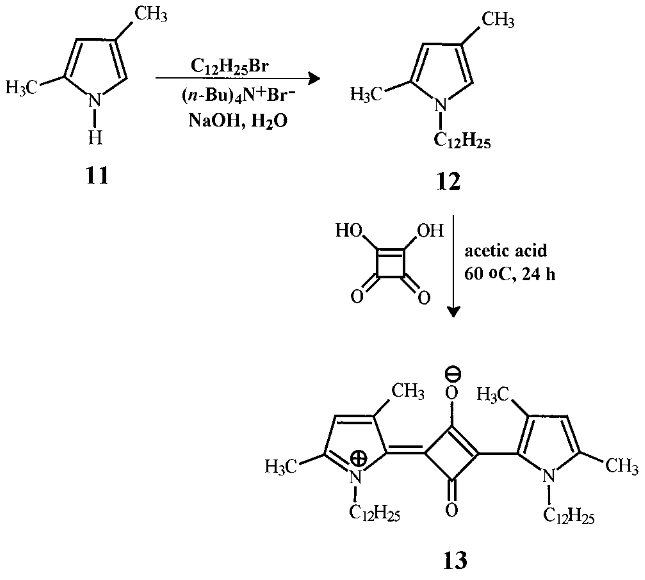
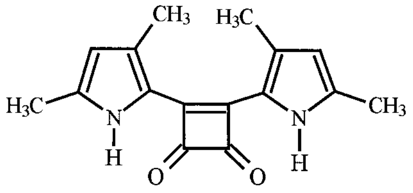


Chart 1



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known in the literature that organic dyes with zwitterionic structures show negative solvatochromism, whereas π-conjugated molecules having strong donor and acceptor groups show positive solvatochromism.[18] The polar zwitterionic structures of squaraine dyes having 1,3-disubstitution of the cyclobutene ring are known to show significant negative solvatochromic properties in solvents having different polarities and dielectric constants.[19] Therefore, if the condensation products obtained by routes A and B have identical squaraine repeating units, they should show similar solvatochromic behavior which has to be again comparable to the model squaraine dye **13** having the zwitterionic 1,3-disubstituted cyclobutene structure. Interestingly, the condensation products **7** and **9** prepared by route A showed negative solvatochromic behavior, which is comparable to that of **13** supporting their zwitterionic structural identity. On the other hand, polymers **8** and **10** prepared through route B showed significantly different solvatochromic behavior when compared to that of **7** and **9**. The absorption maxima of **7** and **8** prepared by routes A and B, respectively, and that of a model squaraine dye **13** in various solvents with an increase in polarity are shown in Table 2 (entries 1−4). The spectral data in Table 2 show a decrease in the absorption maxima of **7** and **13** which is in accordance with the zwitterionic structure of squaraine dyes, whereas **8** did not show any specific trend with an increase in solvent polarity.

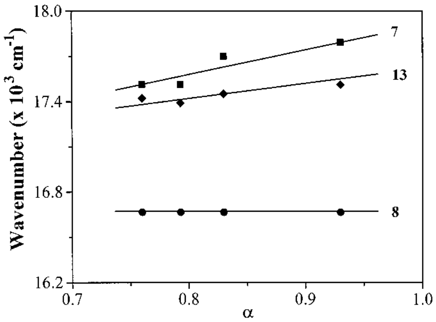

Figure 2. Plot of the absorption maxima of polymers **7** and **8** and model compound **13** versus the acidity parameters (α) of methanol, ethanol, 2-propanol, and 1-butanol.

Table 2. Absorption Maxima of Model Compound 13 and of the Polysquaraines 7 and 8 in Different Solvents

		λ_{max}, nm		
entry	solvent	**13**	**7**	**8**
1	C_6H_6	585	606	600
2	CCl_4	584	592	595
3	$CHCl_3$	580	586	596
4	CH_3COCH_3	577	581	604
5	1-butanol	575	578	600
6	2-propanol	574	571	600
7	C_2H_5OH	573	565	600
8	CH_3OH	571	562	600

In alcoholic hydrogen bond donor (HBD) solvents, polymers **7** and **8** and the model compound **13** showed unique solvatochromic behavior as indicated in Table 2 (entries 5−8). For example, the absorption maxima of **7** and **13** decreased with an increase in the hydrogen bond donating ability (acidity parameter) of the alcoholic solvents, whereas polymer **8** did not show any considerable change in its absorption maximum. Plots of the absorption maxima of polymers **7** and **8** and the model compound **13** in alcoholic hydrogen bond donating solvents against their acidity parameters (α) are shown in Figure 2. A linear increase in absorption maxima could be noticed for polymer **7** and model compound **13**. It is also noticed that the extent of the shift in the absorption maximum of **7** is higher when compared to that of **13**, probably due to the extended π-conjugation of **7** associated with its macromolecular structure. On the other hand, **8** did not show any significant change in its absorption properties with an increase in the acidity parameter of the solvents. Thus, comparison of the observed solvatochromic behavior of **7** with that of **13** lead to the conclusion that they have identical zwitterionic structures. The observed deviation of the solvatochromic property of **8** from that of **7** and **13** could be due to the presence of the 1,2-diketonic units in **8**. The positive solvatochromic behavior of the isomeric diketonic repeating units of **8** may nullify the negative solvatochromic behavior of the 1,3-zwitterionic repeating units, which may be the reason for its observed neutral solvatochromic behavior.

The X-ray diffraction patterns of the solution-cast films of the polycondensation products obtained through routes A and B showed characteristics of partially crystalline, self-organized morphology. The X-ray diffraction patterns of **9** and **10** showed first-order reflections of the 2θ angle at 4.9° and 4.8° which correspond to interlayer spacings of 17.98 and 18.32 Å, respectively (Figure 3). Even though these patterns are characteristic of the well-organized lamellar assemblies similar to those of poly(3-alkylthiophenes), the interlayer distances in polysquaraines are relatively smaller in comparison to those of polypyrroles or polythiophenes containing the same alkyl chains. This close packing in **9** and **10** could be due to the strong dipolar interactions among the 1,3-zwitteronic groups. A broad diffraction centered around 20−25° corresponding to an interlayer

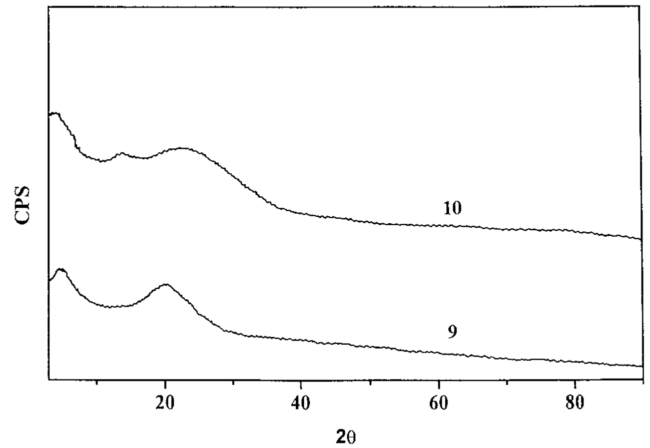

Figure 3. X-ray diffraction patterns of polymers (a) **9** and (b) **10**.

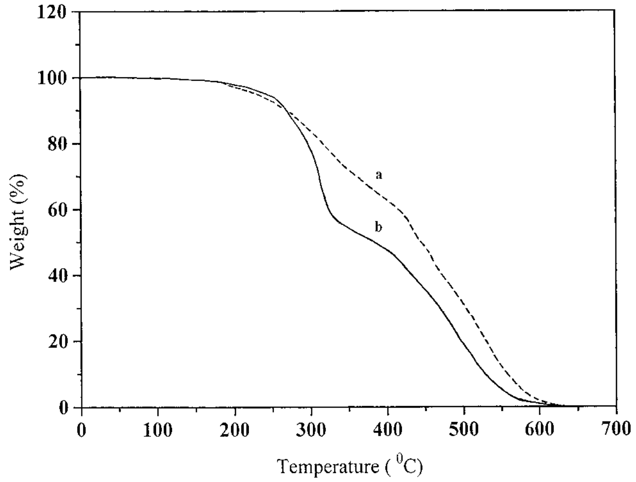

Figure 4. TGA patterns of polymers (a) **9** and (b) **10** under air.

spacing of 4.4–3.5 Å could also be seen in the case of polymer **9**. On the other hand, the corresponding diffraction for polymer **10** was very broad when compared to that of **9**, which can be attributed to the disruption of stacking due to a disordered phase associated with the 1,2-diketonic units of polymer **10**.

Thermogravimetric analysis (TGA) of polymers prepared according to routes A and B showed distinct differences in their degradation patterns (Figure 4). In air, at a heating rate of 20 °C/min, all polymers showed considerable thermal stability up to 200 °C. However, polymers **7** and **9**, having zwitterionic repeating units which are obtained as per route A, showed better thermal stability over polymers **8** and **10**, having both zwitterionic and diketonic repeating units, which showed a sharp weight loss around 250 °C as shown in Figure 4.

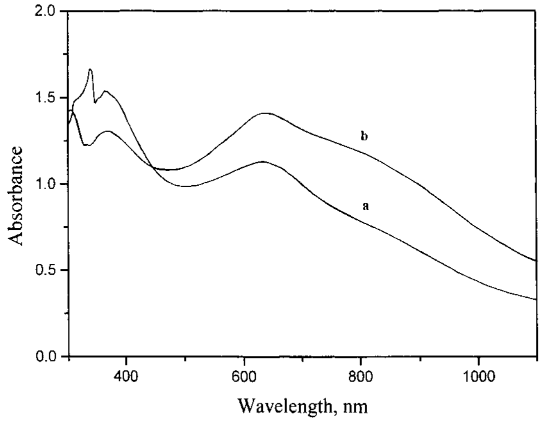

Figure 5. Solid-state UV–vis absorption spectra of polymers (a) **8** and (b) **10**.

The solution and solid-state electronic absorption spectra of polymers obtained by routes A and B showed considerable differences, which reflect their structural dissimilarity. Polymer **9**, having the zwitterionic structure, showed an intense blue color with a λ_{max} around 604 nm in DMSO, whereas polymer **10**, having both zwitterionic and diketonic structure, showed a very broad red-shifted absorption maximum at 639 nm in DMSO. The red shift in the absorption spectra of **10** could be due to its extended conjugation associated with the enhanced molecular weight. The solid-state UV–vis–near IR spectra of polymers **8** and **10** showed very broad and red-shifted absorptions when compared to their solution spectra. The π–π^* transition of **8** occurred at 645 nm with a shoulder around 845 nm, and **10** showed the corresponding absorption peak at 633 nm with a shoulder around 840 nm. In both cases, the solid-state absorptions were tailing beyond 1100 nm (Figure 5). This could be due to the solid-state ordering of the polymer backbone and side chains under slow evaporation of their solutions to form optically transparent thin films. The band-gap energies of polymers **8** and **10** calculated using 1100 nm as the onset of absorption are found to be approximately 1.13 eV.

The electrical conductivities of polymers **7** and **9** obtained through route A were significantly different from those of polymers **8** and **10** which are prepared using route B. The conductivities of polymers **7** and **9** are 2.4×10^{-6} and 8×10^{-6} S/cm, respectively, whereas for polymers **8** and **10**, the corresponding values are 2.5×10^{-6} and 2.3×10^{-5} S/cm. Thus, **10** obtained by the polycondensation of 3-dodecylpyrrole and squaric acid using route B showed the maximum conductivity without an external doping, probably due to its extended conjugation associated with enhanced molecular weight and rigid conformation. However, on doping with iodine, polymers **7** and **9** showed enhanced conductivities in the range of 2.5×10^{-4} and 1×10^{-3} S/cm, whereas polymers **8** and **10** showed 6.0×10^{-4} and 1.8×10^{-3} S/cm.

In conclusion, it has been shown that the polycondensation of 1-dodecyl- and 3-dodecyl-substituted pyrroles with squaric acid lead to the formation of copolymers with isomeric repeating units of 1,3-substituted zwitterionic and 1,2-substituted diketonic structures. Polycondensation in a 1-butanol/benzene mixture under azeotropic reflux conditions gave low molecular weight polymers consisting predominantly of zwitterionic repeating units. On the other hand, polycondensation in acetic acid/DMSO medium under room temperature provides relatively high molecular weight polymers with distinctly different physical properties due to the presence of both zwitterionic and diketonic repeating units. The IR spectral evidence, the observed solubility, the absorption spectral properties, the solvatochromic behavior, and the thermal degradation patterns support the proposed structural differences of the condensation products obtained through routes A and B. The present report is an example of an A–B-type polycondensation between an acceptor–donor monomer combination to form π-conjugated macromolecules containing two isomeric repeating units which control many of their physical properties.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer Model 882 infrared spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-2100 or a GBC double-beam UV–visible spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-90 NMR spectrometer using tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained on a Hewlett-Packard mass spectrometer Model 5971, attached to a 5890 Series II gas chromatography setup, attached with a OV 101 or on a MP–FFAP capillary column and a FID detector. The molecular weights of the oligomers and polymers were determined by gel permeation chromatography (GPC) using polystyrene standards on a Shimadzu LC6A. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1} at 28 °C. Thermogravimetric analyses (TGA) were carried out on a V5.1A Du Pont 2000 analyzer. X-ray diffraction (XRD) patterns were obtained on a Rigaku X-ray diffractometer (Cu Kα = 1.5406 Å, Ni filter). Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The electrical conductivities of the polymers were measured by the standard two-point probe method using pressed pellets. All melting points are uncorrected and were determined using a Mel-Temp-II melting point apparatus. All solvents were dried and distilled before use. 1-Dodecylpyrrole (**2**) and 1-(phenylsulfonyl)pyrrole (**3**) were prepared as per literature procedures.[3a,13,14]

Preparation of 1-(1-Phenylsulfonyl)-3-pyrrolyl-1-dodecanone (4). To a suspension of anhydrous $AlCl_3$ (2.67 g, 20 mmol) in 50 mL of dichloromethane at 25 °C was slowly added lauroyl chloride (4.35 mL, 18.4 mmol), and the resulting solution was stirred at 25 °C for 10 min. To this, a solution of 1-(phenylsulfonyl)pyrrole (3.3 g, 16 mmol) in 10 mL of dichloromethane was added slowly, and the mixture was stirred at 25 °C for 90 min. The reaction was quenched with ice and water, and the product was extracted with dichloromethane. Removal of the solvent followed by column chromatography (silica gel, 100–200 mesh) of the residue, and eluting with 10% petroleum ether/ethyl acetate, gave 5.3 g (82%) of **4,** mp 49–50 °C. IR ν_{max} (KBr) 3147, 2935, 2861, 1680, 1548, 1488, 1456, 1388, 1338, 1285, 1184, 1128, 1099, 805, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, t, CH_3), 1.15–1.85 (18 H, m, CH_2), 2.75 (2 H, t, $COCH_2$), 6.6–6.75 (1 H, m, aromatic), 7.15 (1 H, t, aromatic), 7.45–7.65 (3 H, m, aromatic), 7.75 (1 H, t, aromatic), 7.85–7.95 (2 H, m, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.02, 22.58, 24.28, 29.26, 29.41, 29.53, 31.83, 39.74, 112.50, 121.48, 124.05, 127.06, 129.21, 129.63, 134.46, 138.19, 195.53. Mass spectrum m/z 389 (M$^+$, 3), 305 (25), 291 (15), 277 (20), 249 (24), 234 (17), 192 (6), 141 (27), 94 (12), 77 (100), 66 (5).

Preparation of 3-Dodecylpyrrole (5). To a 1-L, three-necked flask, fitted with a thermometer, a condenser, an argon inlet, and a 150-mL funnel, 1.93 g of lithium aluminum hydride (50 mmol) and 60 mL of THF (dry) were introduced. A solution of **4** (3.9 g, 10 mmol) in 100 mL of dry THF was slowly added. The mixture was refluxed for 1.5 h, cooled, and quenched slowly under argon with brine. The resulting residue was filtered and washed with THF, and the combined organic layer was concentrated under reduced pressure to give 3 g (80%) of the reduced product. To this residue, 2-propanol (70 mL) was added and refluxed with 50 mL of 5 N aqueous NaOH for 8 h. After the solution was cooled to room temperature, 2-propanol was removed under reduced pressure and the aqueous layer was extracted with ether (3 × 10 mL). The combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated to give 1.5 g (68%) of the title compound (**5**) as a colorless liquid. IR ν_{max} (neat) 3404, 2928, 2861, 1678, 1567, 1466, 1066 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.87 (3 H, t, J = 10.7 Hz, CH_3), 1.26 (20 H, m, CH_2), 2.48 (2 H, t, J = 7.6 Hz, CH_2), 6.08 (1 H, m, aromatic), 6.53 (1 H, m, aromatic), 6.65 (1 H, t, J = 2.2 Hz, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.08, 22.70, 26.97, 29.38, 29.59, 29.71, 31.26, 31.95, 108.57, 114.80, 117.55, 124.66. Mass spectrum, m/z 221 (M$^+$, 22), 207 (2), 193 (3), 179 (4), 164 (4), 150 (2), 136 (3), 122 (2), 94 (20), 80 (100), 67 (4).

Preparation of Poly(1-dodecylpyrrole-*co*-squaric acid) (7). A flask equipped with an azeotropic reflux condenser was charged with 1-butanol (20 mL), benzene (10 mL), 1-dodecylpyrrole (**2**) (1.18 g, 5 mmol), and squaric acid (**6**) (0.57 g, 5 mmol) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h with azeotropic removal of water. The dark blue viscous solution obtained was filtered, and the filtrate was collected and concentrated under vacuum. The thick paste of the crude product was poured into diethyl ether. The precipitate obtained was collected by filtration, redissolved in chloroform, and reprecipitated from diethyl ether to give 1.05 g (63%) of **7**. IR ν_{max} (neat) 2961, 2931, 2860, 1732 (w), 1628 (s), 1561, 1486, 1358, 1081 cm^{-1}. UV λ_{max} ($CHCl_3$) 586, (1-butanol) 578, (DMSO) 606 nm. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, br s, CH_3), 1.22 (18 H, br s, CH_2), 1.7 (2 H, br s, CH_2), 3.38 (2 H, br s), 4.5–4.7 (2 H, br s), 6.3 (br s, aromatic), 7.0 (br s, aromatic). 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.

Preparation of Poly(1-dodecylpyrrole-*co*-squaric acid) (8). Squaric acid (57 mg, 0.5 mmol) and 1-dodecylpyrrole (0.12 g, 0.5 mmol) were stirred for 6 days in a mixture of glacial acetic acid (7.5 mL) and DMSO (7.5 mL) under nitrogen atmosphere at room temperature. The contents of the flask were cooled and filtered, and the green solution obtained was poured into water. The precipitated product was washed several times with water, methanol, and diethyl ether. The polymer was redissolved in chloroform and reprecipitated from methanol. Product **8** was obtained in a 60% yield after drying in a vacuum oven at 40 °C for 24 h. IR ν_{max} (neat) 2930, 2860, 1767 (s), 1730 (s), 1639 (s), 1552, 1472, 1355, 1084 cm^{-1}. UV λ_{max} ($CHCl_3$) 596, (1-butanol) 600, (DMSO) 612 nm. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, br s), 1.22 (18 H, br s), 1.7 (2 H, br s), 3.38 (2 H, br s), 6.5–6.7 (2 H, br s, aromatic). Anal. Calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 75.68; H, 9.2; N, 4.4.

Preparation of Poly(3-dodecylpyrrole-*co*-squaric acid) (9). The title polymer (**9**) (90 mg, 60%) was prepared from squaric acid (57 mg, 0.5 mmol) and 3-dodecylpyrrole (0.11 g, 0.5 mmol) according to the procedure used for the preparation of **7**. IR ν_{max} (neat) 3336, 2931, 2859, 1730, 1615, 1550, 1514, 1467, 1159 cm^{-1}. UV λ_{max} ($CHCl_3$) 571, (DMSO) 604 nm. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_2), 1.2 (20 H, m, CH_2), 2.6 (2 H, t, CH_2), 6.35 (1 H, br, aromatic). Anal. Calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 76.20; H, 9.1; N, 4.3.

Preparation of Poly(3-dodecylpyrrole-*co*-squaric acid (10). This compound (90 mg, 58%) was prepared from squaric acid (57 mg, 0.5 mmol) and 3-dodecylpyrrole (0.11 g, 0.5 mmol) under the same conditions as described for **8**. IR ν_{max} (KBr) 3345, 2930, 2859, 1765, 1730, 1610, 1508, 1460, 1112, 876 cm^{-1}. UV λ_{max} ($CHCl_3$) 631, (DMSO) 639 nm. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_2), 1.2 (20 H, m, CH_2), 2.6 (2 H, t, CH_2), 6.35 (1 H, br, aromatic). Anal. Calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.42. Found: C, 76.28; H, 9.1; N, 4.36.

Preparation of 1-Dodecyl-2,4-dimethylpyrrole (12). 1-Dodecyl-2,4-dimethylpyrrole (1.5 g, 57%) was synthesized by the reaction of 2,4-dimethylpyrrole (0.95 g, 10 mmol) and 1-bromododecane (2.5 g, 10 mmol) using tetrabutylammonium bromide as the phase-transfer reagent as per the procedure mentioned for the preparation of **2**. IR ν_{max} (neat) 2931, 2861, 1701, 1678, 1570, 1533, 1510, 1471, 1377, 1265, 952, 719 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.88 (3 H, t, CH_3), 1.03–1.43 (20 H, m, CH_2), 2.04 (3 H, s, CH_3), 2.16 (3 H, s, CH_3), 3.39 (2 H, s, NCH_2), 5.69 (1 H, s, aromatic), 6.31 (1 H, s, aromatic). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 11.75, 11.81, 14.08, 22.67, 26.85, 28.22, 28.79, 29.32, 29.62, 31.47, 31.92, 32.87, 33.80, 46.36, 107.91, 117.55, 127.96, 129.50. Mass spectrum m/z 263 (M$^+$, 5), 249 (4), 192 (3), 179 (4), 150 (6), 122 (24), 100 (100), 94 (20), 67 (9).

Preparation of Bis(1-dodecyl-2,4-dimethylpyrrolyl)-squaraine (13). This compound was prepared by using a reported procedure[11a] from **12** and **6** in a 72% yield. IR ν_{max} (neat) 2934, 2861, 1624, 1563, 1512, 1118 cm^{-1}. UV λ_{max} (CHCl$_3$) 580, (DMSO) 583 nm. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.85 (6 H, t, CH$_3$), 1.2 (40 H, m, CH$_2$), 2.25 (6 H, s, CH$_3$), 2.65 (6 H, s, CH$_3$), 4.65 (4 H, m, NCH$_2$), 6.05 (2 H, br, aromatic). ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 10.41, 13.12, 13.48, 14.11, 22.7, 24.34, 25.95, 26.73, 28.76, 29.05, 29.68, 31.35, 124.11, 138.94, 142.31, 168.18, 181.45.

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