



Effect of alkyl position of pyrrole on structures and properties of conjugated polysquaraines

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ABSTRACT

Poly(1-octylpyrrolyl)squaraine and poly(3-octylpyrrolyl)squaraine were synthesized from squaric acid with 1-octylpyrrole and 3-octylpyrrole under identical conditions of condensation. Visible absorption spectra, photoluminescence spectra, TGA curves, and IR spectra were recorded to characterize the structures of these polymers as synthesized; the measured optical and thermal properties are consistent with backbone structures. The polysquaraine from 3-octylpyrrole possesses mostly zwitterionic repeating units (>97%), but the polymer from 1-octylpyrrole consists of zwitterionic and covalent repeating units in a ratio 2:1. Observations from the visible absorption and photoluminescence spectra in varied solvents, TGA curves, and thermal IR measurements for these two polymers reconciled to their structures. This result indicates that the position of the alkyl group in the pyrrole derivative affects the conformation in the condensation of poly(pyrrolyl)squaraine. These polysquaraines are stable below temperature 155 °C and their visible absorption and photoluminescence properties in hydrogen-bonding solvents exhibit negative solvatochromism.

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1. Introduction

Condensation of squaric acid – 3,4-dihydroxy-3-cyclobutene 1,2-dione – with aromatic compounds rich in electrons yields polysquaraines [1–3]. As the structural backbones of these polysquaraines comprise π -conjugated structures of squaraine dyes, these polymers exhibit intrinsic semi-conducting properties and are classified as conjugated polymers or conducting polymers (CP). Polysquaraines exhibit favorable optical properties and great flexibility for synthetic manipulation, and are suitable for the design of polymers with small optical band gaps [4–10]. The possession of unique optical properties makes polysquaraines suitable materials for several technological applications such as solar cells [11–13], xerographic sensitizers [14], optical data storage [15–17], biomedical applications and sensor [18–24]. Thus, polysquaraines remain at the forefront in many areas of development.

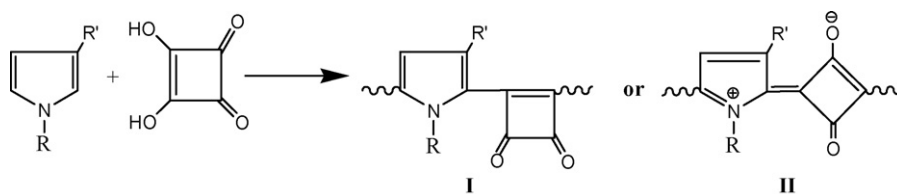
As one polysquaraine, squaric acid reacts with pyrrole derivatives in condensation to form polymeric chains. In this condensation, the pyrrole derivative might react with the squaric acid with 1,2- or 1,3-addition and produce distinct backbone structures of poly(pyrrolyl)squaraines, as shown in Scheme 1. Previous works [25] reported that structural compositions of poly(pyrrolyl)squaraines of two types can thus be generated with formulae **I** and **II** implying the 1,2- and 1,3-reactions, respectively. Poly(pyrrolyl)squaraine containing a repeating backbone in formula **II** features a zwitterionic structure; whereas that in formula **I** adopts a covalent structure. For these polymers, the distinctive bonding character of the backbone structure affects their chemical and physical properties and thus their applications.

In forming the squaraine backbone with squaric acid, the intrinsic nature of pyrrole derivatives might influence the condensation and impinge on the backbone structure in polysquaraine. To improve control of the physical and chemical properties of this polymer, we investigated the effect of derivatives of the pyrrole moiety on the synthesis of polysquaraine by condensation. For this purpose, we focused on the condensation for poly(pyrrolyl)squaraines affected by the position of the alkyl group in the pyrrole derivatives. We synthesized and analyzed poly(pyrrolyl)squaraines from the condensation of squaric acid with 1-octyl- and 3-octylpyrroles having the same molar mass to investigate the products from the same alkyl group linking to separate N- and C-positions.

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Scheme 1. Reaction of a pyrrole derivative with squaric acid in condensation forms repeating units in the structure of poly(pyrrolyl)squaraine of two types, of which formulae **I** and **II** imply the covalent and zwitterionic backbones; respectively. R and R' represent H or an alkyl group.

2. Experimental

2.1. Materials

Reagents 1-octylpyrrole (97.3%), 3-octylpyrrole (99.5%) and squaric acid (99.0%) (all T.C.I. Co.), solvents 1-butanol (99.9%), diethyl ether (99%), benzene (99.8%), and trichloromethane (99.4%) (all Merck Co.), and drying agent anhydrous magnesium sulfate powder (J.T. Baker Co.) were obtained from the indicated suppliers.

2.2. Measurements

^1H NMR and ^{13}C NMR (700 MHz, VARIAN VNMRS-700) spectra were recorded of samples in CDCl_3 with TMS as an internal standard. The molar masses of the polymers were measured with a gel permeation chromatograph (GPC, Viscotek-TDA) at 25°C , using trichloromethane as eluent and polystyrene as the standard reference. IR absorption spectra were recorded with a spectrometer Bomem DA8 FTIR or Nicolet Magna 860 FTIR attached to the IR beamline at the National Synchrotron Radiation Research Center in Taiwan; a HgCdTe or DTGS detector served to span the mid-IR range $500\text{--}4000\text{ cm}^{-1}$ or $400\text{--}4000\text{ cm}^{-1}$, respectively. The IR spectra were typically measured with resolution 0.5 cm^{-1} and 200–512 scans. Samples of polysquaraines were dissolved in trichloromethane. KBr discs were dipped in the samples as saturated solutions and subsequently dried in a vacuum oven to remove the solvent. Elemental analyses (Foss Heraeus CHN-O-Rapid), thermogravimetric analyses (TGA, TA Model, N_2 atmosphere), and visible absorption spectra (Ocean Optics UV-visible spectrophotometer) were performed or measured with the indicated instruments. Photoluminescence spectra were obtained from a Jobin-Yvon Fluorolog-3 spectrophotometer.

2.3. Preparation of poly(1-octylpyrrole-co-squaric acid)

Poly(1-octylpyrrole-co-squaric acid) was synthesized on refluxing 1-octylpyrrole (1.1224 g, 6.26 mmol) and squaric acid (0.714 g, 6.26 mmol) in equimolar proportions in a mixture of 1-butanol (60 mL) and benzene (30 mL) under a continuous flowing N_2 atmosphere for 24 h [25–28]. The dark blue solutions obtained were filtered, and the filtrates were concentrated with vacuum distillation and poured into diethyl ether. The crude products were collected on filtration and washed with diethyl ether, before being redissolved in trichloromethane to yield solutions that were filtered again; the filtrates were evaporated to dryness in an open fume cupboard to eliminate the HCCl_3 . The precipitates were finally washed again with diethyl ether and dried in a vacuum chamber near 295 K for two days.

In this condensation, water contamination might interfere and affect the product generated. We carefully treated water contamination problem in several ways. (1) The solvents were dried with MgSO_4 . (2) The highly pure N_2 was dried further on passing over silica gel. (3) The reaction vessels were fully passivated with copious

amounts of dry N_2 at least 30 min before reagents were admitted. (4) The reaction system was purged a further 30 min a heater was initiated. (5) The reaction mixture was stirred and refluxed with azeotropic solvents at 120°C ; under these conditions, water was removed by the flowing nitrogen. To verify the thorough removal of water, we attached a water trap to the condenser and obtained no liquid water.

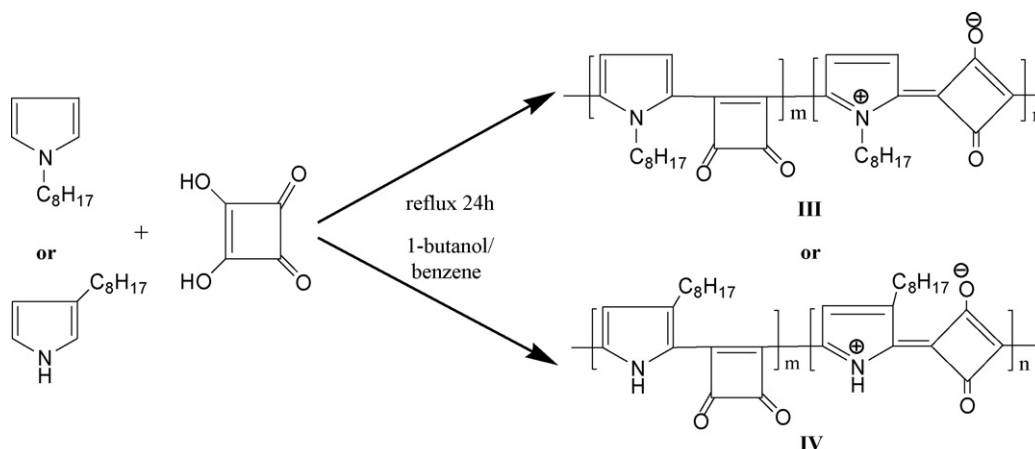
The dark blue product of poly(1-octylpyrrole-co-squaric acid) was obtained with the yield 53%. ^1H NMR (CDCl_3): $\delta = 0.9$ (br s, 3H, CH_3), 1.23 (br s, 10H, CH_2), 1.58 (br s, 2H, CH_2), 3.63 (br s, 2H, CH_2), 4.6–4.8 (br s, 2H), 6.4–6.8 (br s, aromatic). Elemental analysis for $(\text{C}_{16}\text{H}_{19}\text{NO}_2 \cdot \text{H}_2\text{O})_n$ (275.188) $_n$: Calcd. C 69.78, N 5.09, H 7.69; Found C 71.20, N 5.10, H 8.42. IR (KBr): 2956 (as s, CH_3), 2923 (as s, CH_2), 2871 (s, CH_3), 2850 (s, CH_2), 1736 (s, C=O), 1622 (s, C–O), 1482 (ring modes), 1463 (as b, CH_3), 1422 (scissor, CH_2), 1357 (umbrella b, CH_3), 1082 (b, CH), 755 (b, CH), 721 cm^{-1} (r, CH_2). Visible: $\lambda_{\text{max}}/\text{nm}$ (methanol) 539.4, (ethanol) 542.3, (isopropanol) 542.6, (1-butanol) 545.8.

2.4. Preparation of poly(3-octylpyrrole-co-squaric acid)

Poly(3-octylpyrrole-co-squaric acid) was prepared from reaction of 3-octylpyrrole (1.1224 g, 6.26 mmol) and squaric acid (0.714 g, 6.26 mmol) according to the same process used to prepare poly(1-octylpyrrole-co-squaric acid) [25–28]; in which the product was obtained with the yield 66%. ^1H NMR (CDCl_3): $\delta = 0.84$ (s, 3H, CH_3), 1.23 (d, 10H, CH_2), 1.63 (t, 2H, CH_2), 2.51 (s, 2H, CH_2), 6.38 (br s, 1H, aromatic), 10.43 (br s, 1H, NH); ^{13}C NMR (CDCl_3): $\delta = 14.09$, 22.67, 26.63, 27.39, 29.23, 29.28, 29.36, 29.51, 29.69, 30.47, 31.50, 31.79, 31.88, 115.19, 115.45, 125.87, 132.43, 133.12, 143.05, 174.76, 177.13. Elemental analysis for $(\text{C}_{16}\text{H}_{19}\text{NO}_2)_n$ (257.3) $_n$: Calcd. C 74.68, N 5.44, H 7.44; Found C 74.37, N 5.3, H 8.79. IR (KBr): 3350 (s, NH), 3157 (s, CH), 2955 (as s, CH_3), 2922 (as s, CH_2), 2871 (s, CH_3), 2851 (s, CH_2), 1742 (s, C=O), 1600 (s, C–O), 1557 (b, NH), 1539 (b, NH), 1491 (ring modes), 1465 (as b, CH_3), 1429 (scissor, CH_2), 1373 (umbrella b, CH_3), 1112 (b, CH), 936 (b, CH), 882 (b, CH), 775 (b, CH), 726 cm^{-1} (r, CH_2). Visible $\lambda_{\text{max}}/\text{nm}$ (methanol) 538.2, (ethanol) 540, (isopropanol) 541.4, (1-butanol) 542.2.

3. Results and discussion

Squaric acid might react with a pyrrole derivative by 1,2- or 1,3-addition to form poly(pyrrolyl)squaraines of two types, designated as formulae **I** and **II**. Condensation of these two reagents might thus generate poly(pyrrolyl)squaraine possessing both repeating units of formulae **I** and **II** in the polymer chain. The general condensation of squaric acid with 1-octylpyrrole and 3-octylpyrrole is expressed in Scheme 2; the end products poly(1-octylpyrrole-co-squaric acid) and poly(3-octylpyrrole-co-squaric acid) are denoted with formulae **III** and **IV**, respectively. These poly(pyrrolyl)squaraines might contain m repeating units with a covalent backbone and n repeating units with a zwitterionic backbone in their structures; poly(1-octylpyrrole-co-squaric acid) and poly(3-octylpyrrole-co-squaric acid) as we synthesized are named poly(1-octylpyrrolyl)squaraine,



Scheme 2. In the general condensation of squaric acid with 1-octylpyrrole and 3-octylpyrrole, the end product poly(pyrrolyl)squaraines are represented with formulae **III** and **IV**, respectively.

abbreviated **P1**, and poly(3-octylpyrrolyl)squaraine, **P3**, respectively.

The molar masses of as synthesized **P1** and **P3** were determined with a GPC. The values of M_n for **P1** and **P3** are 22 and 20 kDa, and that of M_w for **P1** and **P3** are 63 and 94 kDa, respectively. The polydispersity index (M_w/M_n) of **P3** (4.7) is thus greater than that of **P1** (2.9). The dissimilarity of polydispersity for these two polymers hints of substantial variation of their structures.

Infrared spectra serve to distinguish the chemical characteristics of polymers through their sensitivity to functional groups. Polysquaraines feature strong absorption in the mid-IR range, in which occurs useful information to characterize the structural composition of these polymers. Distinct IR absorption spectra of **P1** and **P3** in the spectral range $400\text{--}4000\text{ cm}^{-1}$ are shown in Fig. 1. Including weak absorption features, the lines in IR spectra of **P1** and **P3** number 27 and 32, respectively. For the analysis of these features, we recorded IR spectra also of the three monomers, as depicted in Fig. 2. IR spectra of the **P1** and **P3** are divided into two regions. The left region, from $2700\text{ to }3400\text{ cm}^{-1}$, contains strong absorptions attributed to C–H and N–H stretching modes. The intense lines observed between $2800\text{ and }3000\text{ cm}^{-1}$ are assigned to C–H stretching modes of the octyl moiety in both polymers. Unlike the octyl group linked to –N atom in **P1**, **P3** has its octyl group linked to a –C atom and shows a signal of the –NH group according to a –NH stretching mode near 3300 cm^{-1} in Fig. 1(b). The right parts of

the spectra, from $400\text{ to }1750\text{ cm}^{-1}$, serve as ‘fingerprints’ of other functional groups and modes. The lines associated with carbonyl (–CO) functional groups in the intrinsic structural backbone of the polymer are typically discernible in the spectra. The covalent and zwitterionic –CO functional groups in polysquaraines have characteristic absorptions near $1750\text{ and }1600\text{ cm}^{-1}$ [29,30], respectively; these values are smaller than the corresponding value 1815 cm^{-1} of squaric acid. As carbonyl moieties of these two kinds are thus distinguished directly in the IR spectra, we derive information about these dissimilar components in polymers on the basis of these lines. For instance, Fig. 1(b) shows a strong absorption at 1600 cm^{-1} and a weak one at 1742 cm^{-1} ; the intensity of the latter attributed to covalent carbonyl is about 3% as that of the former associated with zwitterionic carbonyl. This result demonstrates that **P3** possesses mostly zwitterionic repeating units in the polymer chain, so that its repeating units represented as n in Scheme 2 are about 97%. For a similar analysis applied to the **P1**, the ratio of the intensity for the line attributed to zwitterionic carbonyl about 1622 cm^{-1} to that for the covalent one near 1736 cm^{-1} is approximately 2:1, as shown in Fig. 1(a); hence **P1** includes 1/3 covalent units in its structure [31–36].

The condensation product from a reaction of squaric acid and a pyrrole derivative might retain two basic structural units in the polymer chain, as shown in Scheme 2. The condensation via 1,2- or 1,3-addition is discussed elsewhere and the polymerization reac-

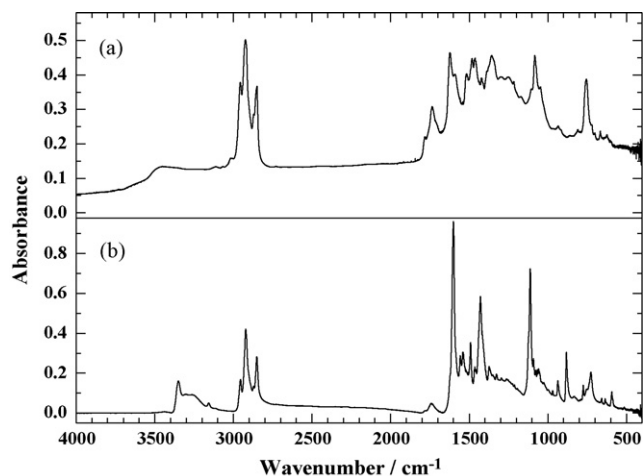


Fig. 1. IR absorption spectra of polysquaraines as synthesized, in the spectral range $400\text{--}4000\text{ cm}^{-1}$: (a) **P1**; (b) **P3**.

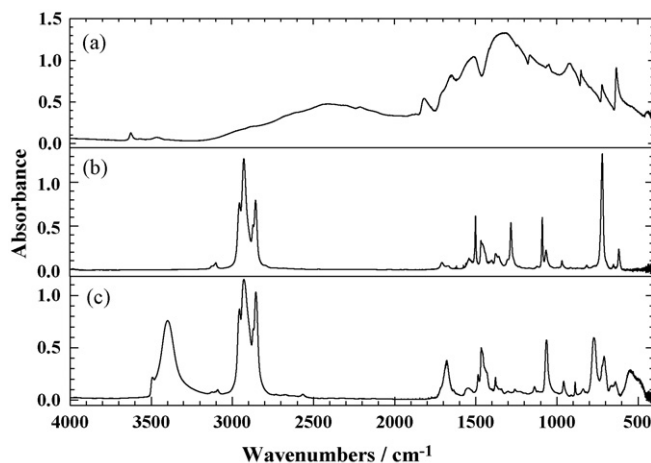


Fig. 2. IR absorption spectra of monomers in the spectral range $400\text{--}4000\text{ cm}^{-1}$ (a) squaric acid; (b) 1-octylpyrrole; and (c) 3-octylpyrrole.

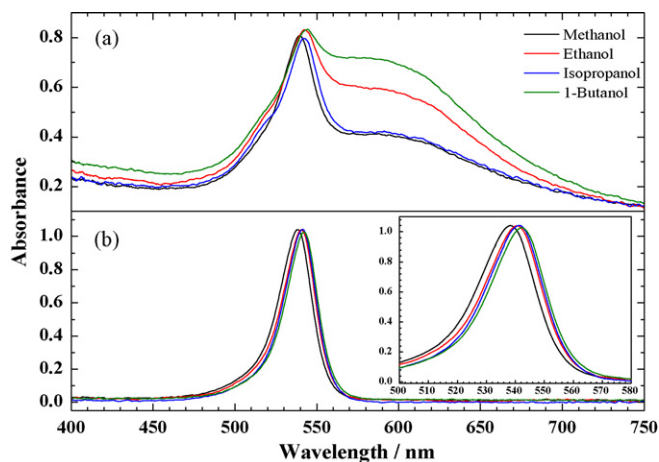


Fig. 3. Visible absorption spectra of poly(pyrrolyl)squaraines, as synthesized, in hydrogen-bonding solvents: (a) **P1**; (b) **P3**.

tion is still under investigation. The reaction and its mechanism might be subject to interference from water contamination in the polymerization and affect the product generated [25]; perhaps the 1,2-addition occurs significantly only in reactions performed in solvent systems from which the produced water is not removed. For the purpose of application as a CP, the poly(pyrrolyl)squaraine has a desired structure predominantly 1,3-squarate. We thus eliminated water as a contamination problem according to several methods described in the experimental section. By this means, we obtained product **P3** from reagent 3-octylpyrrole possessing mostly zwitterionic repeating units (>97%), but polymer **P1** from the reagent 1-octylpyrrole was produced with a backbone ratio 2:1 of the zwitterionic repeating units to the covalent ones. What is the source of this discrepancy in the ratio of structural components for **P1** and **P3**? As we used the same experimental procedures to synthesize the polymers, we conclude that water contamination is not the only factor directing the polymerization. Of the reagents to produce these two polymers, 1-octylpyrrole for **P1** and 3-octylpyrrole for **P3**, both pyrrole derivatives have the same molecular moiety, octyl, but linked at separate positions in pyrrole. As explained above, **P3** from the alkyl group linked to the -C atom in pyrrole comprises mostly a zwitterionic structure, whereas **P1** from the alkyl group linked to the -N atom possesses one-third covalent units in polymer chain. We conclude that the position of the alkyl group in the reagent of the pyrrole derivative affects the structural construction in the condensation of poly(pyrrolyl)squaraine. Regarding Schemes 1 and 2, the condensation of the pyrrole derivative with squaric acid might adopt 1,2- or 1,3-addition to form the covalent and zwitterionic backbones, respectively. For the route of 1,3-addition, the electron cloud of the double bond between positions 2 and 3 in the pyrrole derivative donates to the bond linking to the squaric acid, in which the double bond is eventually formed. The electron donation of the alkyl group in position 3 might thus promote 1,3-addition. 3-Octylpyrrole, that thus possesses an octyl group in the 3 position, can hence contribute to 1,3-addition to yield the most zwitterionic backbones, whereas 1-octylpyrrole that has an H atom in the 3 position engages in both additions in a weighted ratio.

As the polysquaraines have π -conjugated structures that produce intense absorption of visible light, visible absorption spectra serve also to characterize these polymers. We measured the visible absorption spectra of poly(pyrrolyl)squaraines as synthesized in solvents of two classes—hydrogen-bonding (HB) solvents and non-hydrogen-bonding (NHB) solvents, as shown in Figs. 3 and 4, respectively; the poly(1-octylpyrrolyl)squaraine and poly(3-octylpyrrolyl)squaraines as synthesized exhibit distinct fea-

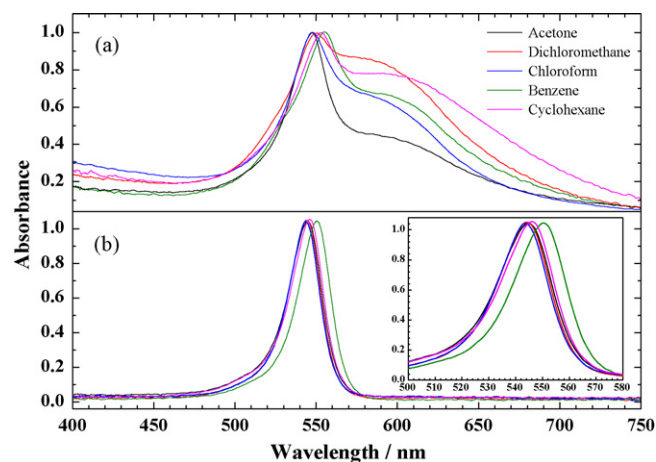


Fig. 4. Visible absorption spectra of poly(pyrrolyl)squaraines, as synthesized, in non-hydrogen-bond solvents: (a) **P1**; (b) **P3**.

tures in their visible absorption spectra. **P3** has a single and narrow visible absorption centered about 538–546 nm depending on the solvent, as displayed in Figs. 3(b) and 4(b), producing a red color in solution, whereas **P1** has a line with maximum absorption at 539–553 nm and a broad shoulder near 600 nm, as depicted in Figs. 3(a) and 4(a), appearing blue in solution. As discussed above, because **P3** possesses mostly zwitterionic repeating units in its structure, the backbones tend to be identical and to bestow on its visible absorption only one narrow band, with maxima in various solvents listed in Table 1, whereas **P1** contains two backbones in its polymer chain, so producing a more complicated absorption in its visible spectra. Through comparison with the narrow absorption for zwitterionic **P3**, we assign the corresponding narrow band of **P1**, of which the maxima are also listed in Table 1, which we attribute to its zwitterionic moiety; the shoulder is due to its covalent part.

The wavelengths of the maximum visible absorptions of the polymers as synthesized varied with the solvent, possibly related to its polarity. The relative permittivity ϵ_r that is a measure of a solvent to separate charge and to orient a dipole is a useful parameter to describe the polarity of the solvent. Relations of the visible absorption maxima of **P1** and **P3** versus relative permittivity of HB solvents are displayed in Fig. 5. As the wavenumbers of maximum absorption exhibit a linear shift with relative permittivity in the HB solvents [37,38], the visible absorption spectra of both polymers as synthesized exhibit significant negative solvatochromism [39–43]; i.e., the absorption exhibits a bathochromic effect with decreasing polarity in alcoholic solvents. The slopes of these relations for **P3** and **P1** are almost the same; the zwitterionic structures in these two polymers are hence similar, but for the same solvent the wave length of maximum absorption of **P3** is blue-shifted relative to **P1**; this phenomenon reflects the fact that the mass ratio of the zwitterionic moiety in **P3** is greater than that in **P1**.

Table 1
Wavelength (nm) of maximum visible absorption of **P1** and **P3**, as synthesized, in various solvents.

Solvent	Relative permittivity	P1	P3
H ₃ COH	32.66	539.4	538.2
C ₂ H ₅ OH	24.55	542.3	540.0
i-C ₃ H ₇ OH	19.92	542.6	541.4
C ₄ H ₉ OH	17.55	543.8	542.2
(CH ₃) ₂ CO	20.56	547.4	544.8
H ₂ CCl ₂	8.93	550.1	544.3
HCCl ₃	4.89	547.9	543.6
C ₆ H ₆	2.27	550.0	550.3
C ₆ H ₁₂	2.02	553.3	546.2

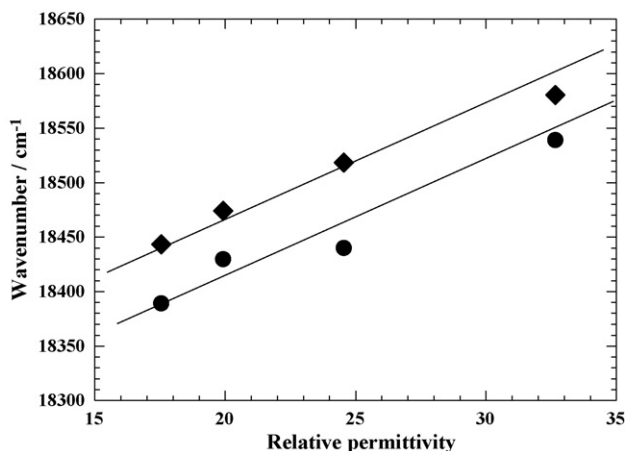


Fig. 5. Wavenumber of absorption maxima of **P1** (solid circle) and **P3** (solid diamond), as synthesized, versus relative permittivity of methanol, ethanol, isopropanol and 1-butanol.

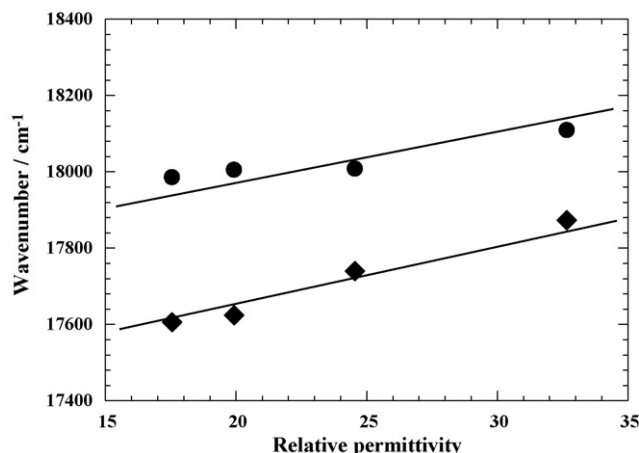


Fig. 7. Wavenumber of emission maxima of **P1** (solid circle) and **P3** (solid diamond), as synthesized, versus relative permittivity of methanol, ethanol, isopropanol and 1-butanol.

Polysquaraines possess π molecular orbitals delocalized along the polymer chain; therefore, it is expected that these polymers have high photoluminescence quantum yields. Fig. 6 shows the photoluminescence spectra of **P1** and **P3** in four HB solvents. In solvents of methanol, ethanol, isopropanol, and 1-butanol, the maximum emission bands of **P1** were observed at 552.2, 555.3, 555.4, and 556.0 nm, respectively; the peaks shift within 4 nm. Whereas, those bands of **P3** were recorded at 559.5, 563.7, 567.4, and 568.0 nm, respectively; the positions of maximum peaks differ in the wavelength range 8.5 nm. Similar to the visible absorptions in HB solvents, the emission bands of **P1** and **P3** undergo hypsochromic shifts with increasing solvent polarity. Relations of the emission maxima of **P1** and **P3** versus relative permittivity of HB solvents are displayed in Fig. 7. As the wavenumbers of maximum emission display a linear shift with relative permittivity in the HB solvents, the photoluminescence spectra of both polymers also possess significant negative solvatochromism. Due to the similar zwitterionic structures in these two polymers, the slopes of these relations for **P3** and **P1** are also the same, as shown in Fig. 7. Compare to the absorptions in the same solvent, the Stokes shifts of **P1** and **P3** are in the ranges 12.2–13.0 cm^{-1} and 21.3–26.0 cm^{-1} , respectively; the values for **P3** are greater than those for **P1**. This occurrence also reveals the phenomenon that the mass ratio of the zwitterionic moiety in **P3** is greater than that in **P1**.

For various applications the thermal stability of these polysquaraines is a matter of concern. As displayed in Fig. 8, the TGA curves of **P1** and **P3** under N_2 were recorded at heating rate 15 $^\circ\text{C}/\text{min}$. Both polymers exhibited no loss of mass at temperature below 155 $^\circ\text{C}$; when temperatures went up to 200.0 $^\circ\text{C}$, the mass loss of **P1** and **P3** were 1.2% and 0.8%, respectively. If we define the temperature at which mass loss is 5% as T_d , we obtain values 259.8 $^\circ\text{C}$ for **P1** and 270.1 $^\circ\text{C}$ for **P3**. Although M_n of both **P1** and **P3** are similar, the M_w of **P3** is greater than that of **P1**; it is hence reasonable that T_d of **P3** is greater than that of **P1**. For a temperature below 304 $^\circ\text{C}$, the extent of mass loss of **P1** is slightly greater than for **P3**, but above 304 $^\circ\text{C}$, the mass loss of **P3** increases more rapidly; this result indicates that the thermal degradation of **P3** under the latter condition is more pronounced than that of **P1**. In the chain of polysquaraine, the covalent backbone is expected to be more stable than the zwitterionic one. As **P1** comprises more covalent moieties than **P3**, **P1** hence tends to resist thermal degradation above 304 $^\circ\text{C}$.

Further evidence of thermal stability for these two polymers was obtained from thermal tests monitored with IR spectra. We dipped polymers on the low-E plates and heated the plates *in situ* for IR measurements in the reflection mode. IR spectra of polysquaraines as synthesized in the spectral range 650–4000 cm^{-1} at various temperatures are shown in Fig. 9. The IR reflection spectra remained constant below 155 $^\circ\text{C}$ for both polymers, but varied

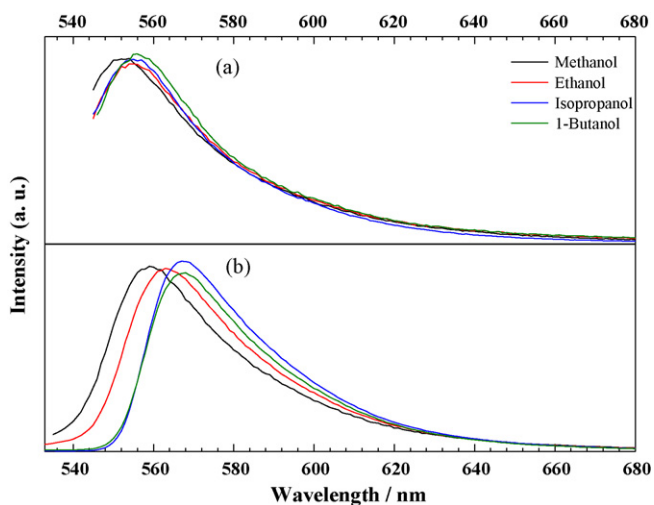


Fig. 6. Photoluminescence spectra of poly(pyrrrolyl)squaraines, as synthesized, in hydrogen-bond solvents: (a) **P1** excited at 540 nm; (b) **P3** excited at 530 nm.

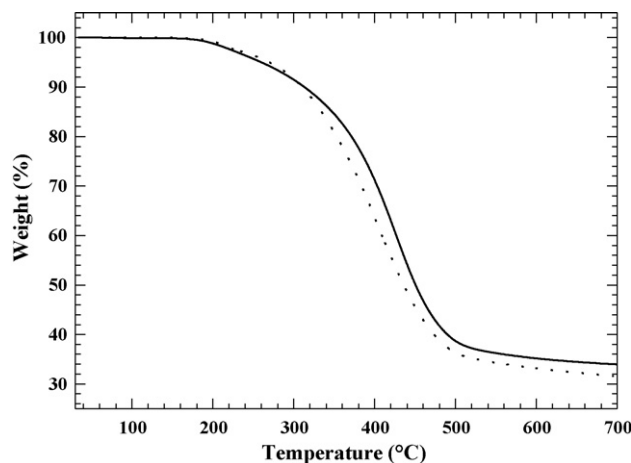


Fig. 8. Thermal gravimetric analysis (TGA) curves of **P1** (solid line) and **P3** (dotted line) as synthesized.

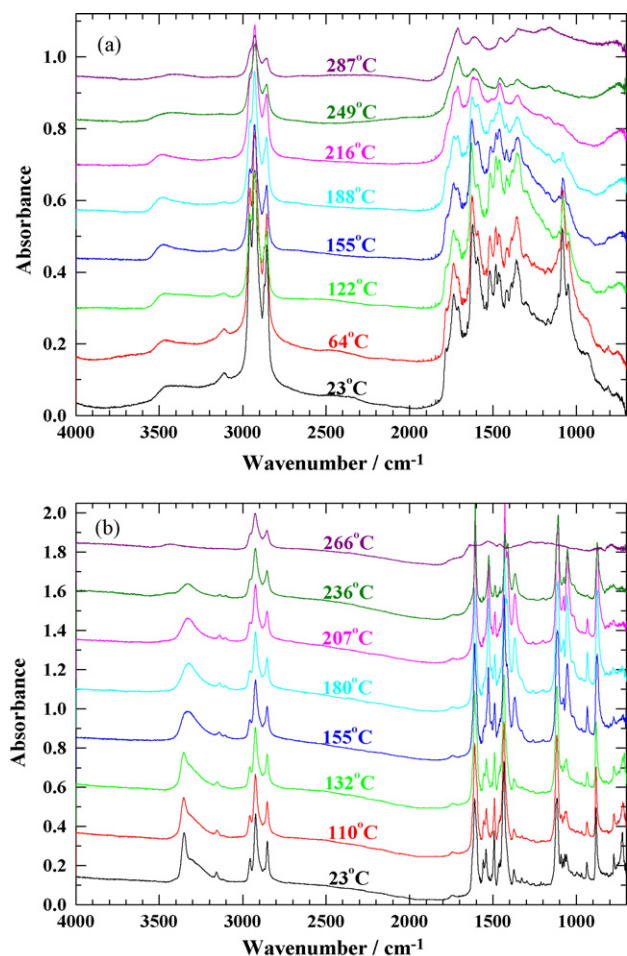


Fig. 9. IR absorption spectra of (a) **P1** and (b) **P3** at various temperatures as indicated.

slightly at 180 °C at which the mass losses were 0.5% and 0.2% for **P1** and **P3**, respectively. The line at 1600 cm^{-1} attributed to the zwitterionic carbonyl of **P3** was present at 236 °C, but vanished by 266 °C in Fig. 9(b), whereas the line at 1736 cm^{-1} attributed to the covalent carbonyl of **P1** was observable at 287 °C in Fig. 9(a). This test is consistent with the thermal stability of the covalent backbone exceeding that of the zwitterionic one in the structure of polysquaraine.

4. Conclusion

Condensation of squaric acid with pyrrole derivatives yields copolymers of the class of polysquaraines. In this condensation, the pyrrole derivative reacts with squaric acid by 1,2- or 1,3-addition and generates covalent or zwitterionic backbones, respectively. The position of the alkyl group in the pyrrole derivative might affect this condensation and result in a distinctive backbone structure for the poly(pyrrolyl)squaraine. We polymerized squaric acid with octyl linked to C- and N-positions in pyrrole derivatives, so effecting a synthesis of poly(1-octylpyrrolyl)squaraine **P1** and poly(3-octylpyrrolyl)squaraine **P3**, respectively. The backbone structures of the covalent and zwitterionic units in these polysquaraines are distinguished by their covalent and zwitterionic carbonyl functional groups having associated IR absorptions near 1750 and 1600 cm^{-1} , respectively. By this means, we deduced that product **P3** from reagent 3-octylpyrrole possesses mostly zwitterionic repeating units (>97%), whereas polymer **P1** from reagent 1-octylpyrrole was produced with backbone ratio 2:1

of zwitterionic repeating units to covalent ones. We hence conclude that the position of the alkyl group in the reagent of pyrrole derivative affects the construction in the condensation into poly(pyrrolyl)squaraine. From the visible absorption and photoluminescence spectra in varied solvents, TGA curves, and thermal IR measurements for these two polymers, the observations of these optical and thermal properties were reconciled to their structures.

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