

Synthesis and Characterization of 4-Dodecyloxyphenyl and (4'-Dodecyloxy-4-biphenyl)methylene-Substituted Bispyrrolylvinylthiophene-Based Polysquaraines Having Good Solubility and Very Low Bandgap for Light Absorption

Erfu Huo,¹ Daobin Yang,¹ Zhanyuan Zhang,¹ Zhiyun Lu,¹ Huiqin Sun,² Xing Xin,¹ Yan Huang,¹ Yu Liu,³ Qing Jiang¹

¹College of Chemistry, Sichuan University, Chengdu 610064, China

²Analytical and Testing Center, Sichuan University, Chengdu 610064, China

³Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China

Correspondence to: Z. Lu (E-mail: luzhiyun@scu.edu.cn) or Y. Huang (E-mail: huangyan@scu.edu.cn)

ABSTRACT: In this work, two very low band-gap (~ 1.0 eV) alternate conjugated copolymers bearing bispyrrolylvinylthiophene-based polysquaraine backbone (PVTVPS) have been synthesized. In comparison with their analogous polymer with 2-ethylhexyl side chain on the pyrrole segment, which possesses poor solubility after long-time storage, the two target polymers with 4-dodecyloxyphenyl (PVTVPS-Ph) or (4'-dodecyloxy-4-biphenyl)methylene (PVTVPS-Ph₂) side chains exhibit dramatically improved solubility. Furthermore, PVTVPS-Ph shows unexpected thermochromism in the Vis–near-infrared (NIR) region of 600–1100 nm at 80–160°C in solution and thin film. This may be attributed to the presence of relatively rigid phenyl substituent restricting the free rotation between the D (pyrrole) and A (squaraine) segments of the main chain. To our knowledge, this is the first report on NIR thermochromic polysquaraines. Nevertheless, in the case of PVTVPS-Ph₂, no thermochromism could be observed because of the existence of free-rotating methylene linkage bridge between biphenyl unit and the conjugated polymer skeleton. When compared with PVTVPS-Ph, PVTVPS-Ph₂ has much improved thermostability and broader absorption property. Hence, PVTVPS-Ph₂ is a more prospective candidate as photovoltaic materials. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polysquaraines; substituted PVTVPSs; low bandgap; solubility; thermochromism; conjugated polymers; UV–vis spectroscopy; thermal properties

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INTRODUCTION

Squaraines,^{1,2} the condensation products of squaric acid and electron-rich aromatic or heterocyclic compounds, are relatively old type of dyes with good photochemical and photophysical stability. However, they have been recently renewed because of their potential applications in a variety of technologically relevant fields such as photoconductivity,³ solar cells,^{4–7} two-photon absorbing materials,^{8,9} field-effect transistors,¹⁰ near-infrared (NIR)-emitting fluorescent probes,^{11,12} nonlinear optics,¹³ data storage,¹⁴ and sensitizers for photodynamic therapy.¹⁵ As many small-molecular squaraines exhibit intense absorption in the visible and NIR region, polysquaraines are considered to be suitable candidates for low band-gap semiconducting macromolecules in plastic electronics.^{16,17} Nevertheless, despite of their

excellent optoelectronic properties, the extremely poor solubility of polysquaraines has hampered their further application until Havinga et al.,¹⁸ Eldo and Ajayaghosh,¹⁹ and more recently, Deibel and coworkers⁴ had developed soluble polysquaraines by incorporating long alkyl side chains with the squaraine skeleton. Using this strategy, recently, we had also exploited a series of bispyrrolylvinylthiophene-based low band-gap polysquaraines (PVTVPSs) with broad and strong absorption band in the region of 300–1200 nm.²⁰ However, the resulting macromolecules, though each bears a long-chain alkyl substituent like 2-ethylhexyl, dodecyl, or hexadecyl in its repeating units, are found to show good solubility in common organic solvents only when they are freshly synthesized. After 3 months storage (at room temperature or even at -18°C under protection of argon), the solubility of all these polymers are found to

deteriorate dramatically in similar solvents. Moreover, the molecular weights of these polymers are not satisfied. Therefore, our attempts on manipulating solubility and molecular weight of polysquaraines via the introduction of linear or branched alkyl side chains are still unsuccessful, and thus, the unstable solubility of these macromolecules would extremely hinder their potential application in plastic electronics.

To exploit polysquaraines with good and stable solubility in a variety of common solvents and in satisfied molecular weight as well, herein, we replace the flexible alkyl side chains connecting to the N-atom of pyrrole segments into more rigid phenyl or 1,1'-biphenyl-4-methylene substituents. The phenylpyrrole segment, like biphenyl molecule, may possess a preferred twisted conformation, which is beneficial to the alleviation of π -stacking interactions between the conjugated main chains. Similarly, the presence of rigid biphenyl segment rather than flexible alkyl substituent should also be propitious to the weakening of molecular aggregation via their conjugated backbone. Additionally, as rational control on the film morphology is of great importance for plastic electronics, the alkoxy-substituted biphenyl segment, which is widely used as mesogenic unit in constructing liquid crystalline molecule,^{21,22} is used as side chain to contribute to the solid-state organization.

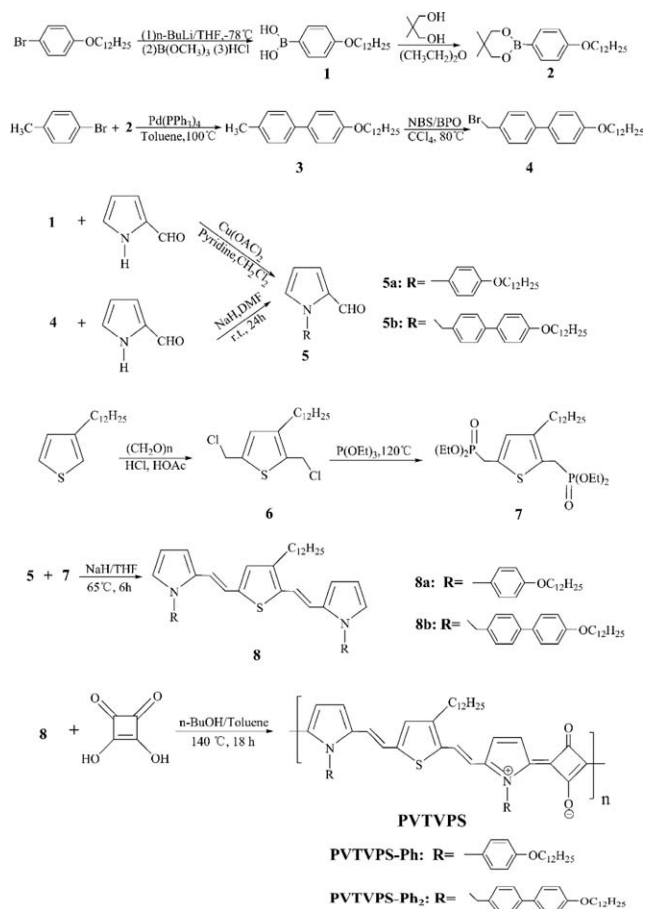
EXPERIMENTAL

Materials

All the materials and reagents were commercially available and used without further purification. Toluene and tetrahydrofuran (THF) were dried from sodium and freshly distilled before use.

Measurements

NMR spectra were measured on a Bruker Avance AV II-400 MHz. FTIR spectra were recorded on a Perkin-Elmer 2000 infrared spectrometer with KBr pellets. UV-Vis-NIR absorption spectra of the polymers in solutions and thin solid films were measured by a HITACHI U-4100 UV-Vis-NIR scanning spectrophotometer. Elemental analysis studies were carried out with a Carlo Erba 1106 elemental analyzer. The molecular weights (M_w) and polydispersity indices (PDI) of the polymers were determined on a PL-GPC (model 210) chromatograph using THF as eluent against polystyrene standards. Thermogravimetry analysis (TGA) was performed on a Perkin Elmer TGA Q500 instrument in an atmosphere of N_2 at a heating rate of $10^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) measurement was carried out on a Perkin Elmer DSC Q100 instrument in an atmosphere of N_2 with a constant heating/cooling rate of $10^\circ\text{C min}^{-1}$. The X-ray diffraction (XRD) studies of the samples were carried out on an X'Pert Pro MPD DY1291 powder diffractometer using the monochromatized X-ray beam from the nickel-filtered Cu K α radiation with a wavelength of 0.15406 nm. Thin film samples of the polymers for the measurements of UV-Vis-NIR absorption spectra were prepared by spin coating (500 rpm, 10 s; 1800 rpm, 30 s) from chlorobenzene solution of the polymers (5 mg mL^{-1}) on quartz substrates. The film of polymers has been annealed at different temperatures for 30 min under nitrogen.



Scheme 1. Synthetic routes of the monomers and polymers.

Synthesis of Monomers and Polymers

The synthetic routes of the monomers and resulting polymers are shown in Scheme 1. Intermediates 1, 2, and 3 were synthesized according to the literature.²³

4-Dodecyloxyphenylboronic Acid (1). Intermediate 1 was obtained as a white solid. Yield: 81%; mp: $62\text{--}65^\circ\text{C}$. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 8.16 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 4.03 (t, $J = 6.0$ Hz, 2H), 1.82 (m, 2H), 1.4–1.3 (m, 20H), 0.88 (t, $J = 6.0$ Hz, 3H).

5,5-Dimethyl-1,3-propanediol-4-dodecyloxyphenylboronate (2). Intermediate 2 was obtained as white-needle crystals. Yield: 87%; mp: $71\text{--}73^\circ\text{C}$. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.72 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.97 (t, $J = 6.0$ Hz, 2H), 3.75 (s, 4H), 1.78 (m, 2H), 1.45 (m, 2H), 1.26 (m, 16H), 1.01 (s, 6H), 0.88 (t, $J = 6.0$ Hz, 3H).

4-(Dodecyloxy)-4'-methylbiphenyl (3). Intermediate 3 was obtained as white crystals. Yield: 92%; mp: $82\text{--}84^\circ\text{C}$. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.52 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 4.00 (t, $J = 6.0$ Hz, 2H), 2.42 (s, 3H), 1.81 (m, 2H), 1.48 (m, 2H), 1.30 (m, 16H), 0.91 (t, $J = 6.0$ Hz, 3H).

4-Bromomethyl-4'-dodecyloxybiphenyl (4). To a solution of 3 (11.65 mmol) in 80 mL of CCl_4 , *N*-bromosuccinimide (NBS,

7.28 mmol) and benzoyl peroxide (BPO, 60 mg) were added under an argon atmosphere. The resulting mixture was stirred and heated at 80°C for 1 h, and then another 5 mmol of NBS and BPO (40 mg) were added followed by stirring at 80°C for 6 h. After the mixture was cooled down to room temperature, the white precipitate was filtered off and the filtrate was concentrated to afford the crude product, which was further purified via recrystallization from hexane to give colorless solid **4** with an yield of 72%; mp: 89–91°C. ¹H-NMR (400 MHz, CDCl₃, δ): 7.53 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 2H), 4.00 (t, *J* = 6.2 Hz, 2H), 1.81 (m, 2H), 1.48 (m, 2H), 1.26 (m, 16H), 0.89 (t, *J* = 6.2 Hz, 3H).

1-(4-Dodecyloxyphenyl)-1H-pyrrole-2-carbaldehyde (5a). Compound **5a** was synthesized according to the reported procedure,²⁴ with **1** as starting material. Yield: 66%; mp: 56–57°C. ¹H-NMR (400 MHz, CDCl₃, δ): 9.56 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.16 (dd, 1H), 7.05 (d, *J* = 2 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.40 (dd, 1H), 4.01 (t, *J* = 6.0 Hz, 2H), 1.83 (t, *J* = 6.2 Hz, 2H), 1.48 (m, 2H), 1.29 (m, 16H), 0.88 (t, *J* = 6.0 Hz, 3H).

1-[(4'-Dodecyloxybiphenyl-4-yl)methyl]-1H-pyrrole-2-carbaldehyde (5b). Compound **5b** was synthesized according to the literature,²⁵ and it was obtained as brownish solid. Yield: 96%; mp: 67–68°C. ¹H-NMR (400 MHz, CDCl₃, δ): 9.58 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 1.2 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.94 (dd, *J* = 1.6 Hz, 1H), 6.28 (dd, *J* = 2.8 Hz, 1H), 5.59 (s, 2H), 3.98 (t, *J* = 6.0 Hz, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.26 (m, 16H), 0.88 (t, *J* = 6.0 Hz, 3H).

3-Dodecyl-2,5-bis(methylenediethylphosphate)thiophene (7). To a solution of paraformaldehyde (50 mmol) in acetic acid (13 mL), dry hydrogen chloride was bubbled under stirring at 60°C for 6 h. Then the mixture was cooled to 0°C, and 3-dodecylthiophene (20 mmol) was added dropwise. The reactant was stirred for 4 h at room temperature and then extracted with ethyl ether. The organic layer was washed with water, saturated NaHCO₃ solution, and brine in sequence, and then dried over anhydrous MgSO₄. After removal of solvent, the pale yellow residue was recrystallized from hexane to afford intermediate **6**. The solution of **6** (19.66 mmol) in triethyl phosphate (12 mL) was heated at 120°C for 4 h and subsequently at 180°C for 1.5 h, and then excessive triethyl phosphate was removed in vacuum. The residue was purified via column chromatography on silica gel using hexane/acetone (3 : 1) as eluent to give **7** as pale yellow oil. Yield: 78%. ¹H-NMR (400 MHz, CDCl₃, δ): 6.74 (s, 1H), 4.07 (m, 8H), 3.25 (m, 4H), 2.48 (t, 2H), 1.54 (m, 2H), 1.34 (m, 30H), 0.90 (t, *J* = 6.0 Hz, 3H).

General Synthetic Procedure of Monomers **8**

To a 100-mL flask, **5** (2.25 mmol), **7** (1.125 mmol), and 10 mL of dry THF at 0°C were added, and then a suspension of sodium hydride (6.6 mmol) in dry THF (30 mL) was added slowly under stirring with protection of argon. The reaction mixture was refluxed for 6 h and then cooled to room temperature, followed by addition of 10 mL of water and 20 mL of dichloromethane. The organic layer was separated, washed with

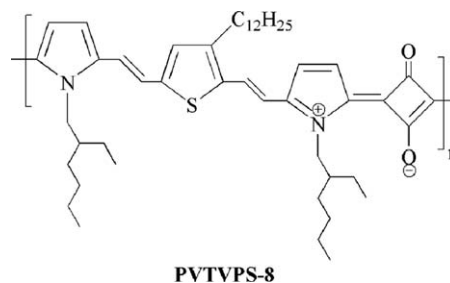
brine (3 × 50 mL), and dried over anhydrous MgSO₄. After removal of solvent under vacuum, the residue was purified via column chromatography over silica gel using hexane/ethyl ether (8 : 1) as eluent.

2,5-Bis[(E)-N-(4-dodecyloxyphenyl)-1H-pyrrol-2-ylvinyl]-3-dodecylthiophene (8a). Compound **8a** was obtained as dark green oil. Yield: 79%. ¹H-NMR (400 MHz, CDCl₃, δ): 7.22 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 4H), 6.79 (s, 2H), 6.75 (t, *J* = 7.6 Hz, 2H), 6.6 (s, 1H), 6.5 (m, 4H), 6.27 (s, 2H), 3.99 (t, *J* = 6.0 Hz, 4H), 2.43 (m, 2H), 1.81 (m, 4H), 1.47 (m, 8H), 1.26 (m, 48H), 0.86 (t, *J* = 6.0 Hz, 9H). ¹³C-NMR (100 MHz, CDCl₃, δ): 158.40, 139.63, 135.24, 132.45, 132.24, 128.15, 127.37, 127.28, 124.10, 123.93, 117.30, 114.86, 109.38, 109.25, 107.76, 107.35, 68.36, 31.94, 30.83, 29.72, 29.65, 29.53, 29.47, 29.38, 29.32, 28.37, 26.11, 22.71, 14.13.

2,5-Bis[(E)-N-(4-((4-dodecyloxyphenyl)phenyl)methyl)-1H-pyrrol-2-ylvinyl]-3-dodecylthiophene (8b). Compound **8b** was obtained as dark green solid. Yield: 67%; mp: 86–88°C. ¹H-NMR (400 MHz, CDCl₃, δ): 7.47 (m, 8H), 7.12 (dd, *J* = 5.2 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 15.2 Hz, 2H), 6.72 (s, 2H), 6.64 (q, 2H), 6.63 (s, 1H), 6.50 (d, *J* = 3.2 Hz, 2H), 6.22 (d, *J* = 2.4 Hz, 2H), 5.17 (d, *J* = 6 Hz, 4H), 3.95 (t, *J* = 6.0 Hz, 4H), 2.47 (t, *J* = 5.8 Hz, 2H), 1.78 (q, 4H), 1.45 (m, 6H), 1.24–1.32 (m, 50H), 0.88 (t, *J* = 6.0 Hz, 9H). ¹³C-NMR (100 MHz, CDCl₃, δ): 158.82, 140.97, 140.25, 140.24, 139.65, 136.24, 136.19, 135.16, 132.89, 131.99, 131.64, 128.49, 128.02, 127.09, 127.02, 126.98, 123.26, 123.22, 119.69, 118.08, 116.28, 115.85, 114.80, 109.13, 109.03, 107.13, 107.04, 68.10, 50.37, 50.27, 31.95, 30.80, 29.70, 29.67, 29.64, 29.62, 29.54, 29.45, 29.38, 29.32, 28.35, 26.09, 22.72, 14.15.

General Synthetic Procedure of the Target Macromolecules PVTVPSs

To a flask equipped with a Dean-Stark apparatus, squaric acid (0.6 mmol), **8** (0.6 mmol), and 120 mL mixture of *n*-butanol and toluene (1 : 2) were added. The reactant was refluxed for 18 h under protection of argon and cooled to room temperature, and then the solvent was removed under vacuum. The sticky residue was poured into MeOH under stirring, and then the black precipitates were filtered. After washing consecutively with acetone and hexane using a Soxhlet extractor, the black solid was dissolved in CH₂Cl₂ followed by precipitation from methanol for three times, then collected and dried under vacuum for 24 h.



Scheme 2. Molecular structure of PVTVPS-8.

Table I. Molecular Weights and Thermal Properties of the Polymers

Polymers	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	PDI	T_d (°C) ^a	T_g (°C) ^b
PVTVPS-Ph	6.47×10^4	2.36×10^4	2.74	321	157
PVTVPS-Ph ₂	2.40×10^4	1.08×10^4	2.22	318	143

^aCarried out in an atmosphere of N₂ at a heating rate of 10°C min⁻¹.

^bCarried out in an atmosphere of N₂ with a constant heating/cooling rate of 10°C min⁻¹.

PVTVPS-Ph. PVTVPS-Ph was obtained as black solid. Yield: 85%. FTIR (KBr, cm⁻¹): 3441 (vs, O—H), 2924, 2853, 1634 (s, C—O), 1510, 1386, 1245, 1138, 1043, 967, 913. ¹H-NMR (400 MHz, CDCl₃, δ): 7.80 (br, 1H), 7.23 (br, 3H), 7.04 (br, 3H), 6.98 (br, 2H), 6.80 (br, 4H), 6.60 (br, 2H), 6.26 (br, 2H), 4.01 (br, 4H), 2.43 (br, 2H), 1.84 (br, 4H), 1.42 (br, 4H), 1.25 (br, 52H), 0.88 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃, δ): 176.55, 159.80, 158.57, 131.86, 129.70, 128.56, 127.34, 126.97, 114.94, 114.72, 113.90, 68.31, 31.92, 30.83, 29.67, 29.46, 29.35, 28.53, 26.19, 26.11, 22.68, 18.95, 14.09, 13.67. Anal. Calcd. for (C₆₈H₉₂N₂O₄S)_{*n*}: C, 79.02%; H, 8.97%; N, 2.71%; S, 3.10%. Found: C, 74.76%; H, 8.92%; N, 2.49%; S, 3.08%.

PVTVPS-Ph₂. PVTVPS-Ph₂ was obtained as black solid. Yield: 93%. IR (KBr, cm⁻¹): 3441 (m, O—H), 2921, 2850, 1625 (m, C—O), 1501, 1375, 1288, 1172, 1092, 909, 805. ¹H-NMR (400 MHz, CDCl₃, δ): 7.40 (br, 10H), 7.17 (br, 4H), 6.99–6.87 (br, 11H), 3.92 (br, 4H), 1.77 (br, 4H), 1.42 (br, 4H), 1.26 (br, 54H), 0.87 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃, δ): 186.73, 175.05, 166.89, 158.71, 139.98, 135.96, 132.74, 127.96, 126.98, 125.05, 114.75, 68.07, 50.16, 31.93, 30.83, 29.65, 29.44, 29.36, 28.55, 26.09, 22.69, 18.89, 14.11, 13.61. Anal. Calcd. for (C₈₂H₁₀₄N₂O₄S)_{*n*}: C, 81.84%; H, 8.64%; N, 2.31%; S, 2.64%. Found: C, 79.49%; H, 8.73%; N, 2.21%; S, 2.82%.

RESULTS AND DISCUSSION

Synthesis and Characterization

Polysquaraine PVTVPSs are synthesized through a multistep strategy (outlined in Scheme 1). The bispyrrole monomers **8** have been prepared in satisfied yields of 67–79% through Wittig reaction²⁶ with phosphonate **7** and pyrrole-2-carbaldehydes bearing different side chains at nitrogen atom (**5a–b**) as reactants. The objective macromolecules PVTVPSs are synthesized by polycondensation reaction using **8** and squaric acid as reac-

Table II. Solubility of the Objective Polymers

Polymers	PVTVPS-8		PVTVPS-Ph		PVTVPS-Ph ₂	
	a	b	a	b	a	b
CH ₂ Cl ₂	++	++	++	++	++
CHCl ₃	++	++	++	++	++
THF	++	+-	++	++	++	++
Chlorobenzene	++	++	++	++	++

'a' is the solubility of the objective polymers freshly synthesized. 'b' is the solubility of the objective polymers after 3 months storage at room temperature in ambient atmosphere. ++ = Very good (30–40 mg mL⁻¹); + = Good (~20 mg mL⁻¹); +- = Partial (5 mg mL⁻¹); = Bad (1 mg mL⁻¹).

tant in a mixture (1 : 2) of *n*-butanol and toluene. In comparison with the well-adopted procedure for preparing squaraine dyes, in which a mixture of *n*-butanol and benzene is generally used as solvents,²⁷ toluene instead of benzene is used to provide higher reaction temperature. Additionally, the composition of the solvents is optimized so that the polymers could show better solubility and hence result in higher molecular weights. As a result, PVTVPS-Ph is determined to have an average M_n of 2.36×10^4 and M_w of 6.47×10^4 and that for PVTVPS-Ph₂ is 1.08×10^4 (M_n) and 2.40×10^4 (M_w), respectively (M_n is number-average molecular weight and M_w is weight-average molecular weight; data are summarized in Table I).

In contrast to the analogous polymers bearing alkyl side chains, we previously reported that,²⁰ which have quite limited solubility in common organic solvents such as CHCl₃, THF, and chlorobenzene after long-term storage in normal atmosphere (for comparison, the polymer PVTVPS-8 bearing 2-ethylhexyl side chain (Scheme 2), with $M_n = 3.8 \times 10^3$, $M_w = 1.86 \times 10^4$, PDI = 4.83, is used as the counterpart here), the two objective polysquaraines are not only readily soluble in common solvents when freshly synthesized but also possess hardly changed solubility after 3 months storage at room temperature in normal atmosphere (Table II). The dramatically improved solubility of the objective macromolecules may be attributed to the alleviated intermolecular interactions and aggregation²⁸ caused by the more rigid phenyl or biphenyl spacing segments connected to the pyrrole moiety.

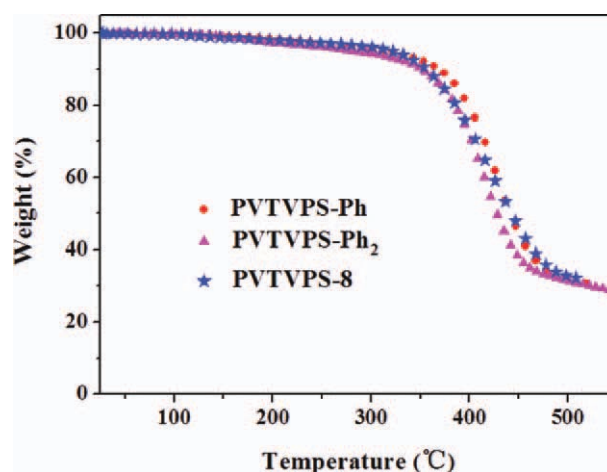


Figure 1. TGA curves of PVTVPSs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

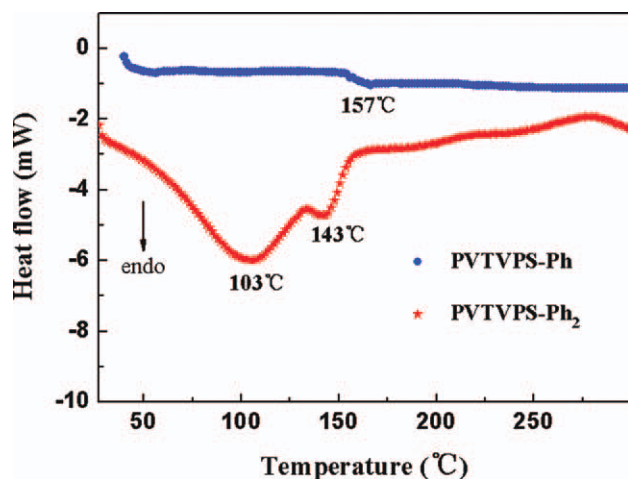


Figure 2. DSC curves of PTVVPSs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties and XRD Studies

TGA results indicate that the two macromolecules and the reference polymer PTVVPS-8 show good thermostability with $T_d > 310^\circ\text{C}$ (5 wt % loss). In accordance with the literature report,²⁰ minor weight reduction in 160–260°C (shown in Figure 1) could be observed in all these three polysquaraines, which should be ascribed to the loss of water. The composition of water is calculated to be 1 : 1 molar ratio in each repeating unit of the polymers, which is further confirmed by the elemental analysis. To investigate the thermal transition characteristics of the objective polysquaraines, DSC analysis is conducted, and the diagrams are depicted in Figure 2. The weak endothermic peaks located at 157°C for PTVVPS-Ph and 143°C for PTVVPS-Ph₂ should be assigned to their glass transition temperatures (T_g). However, differed from PTVVPS-Ph, a distinct strong endothermic peak could be found in PTVVPS-Ph₂ at 103°C during the heating process. As the two polymers have similar backbone structures, the extra strong endothermic peak found in PTVVPS-Ph₂ may originate from the phase transition of dode-

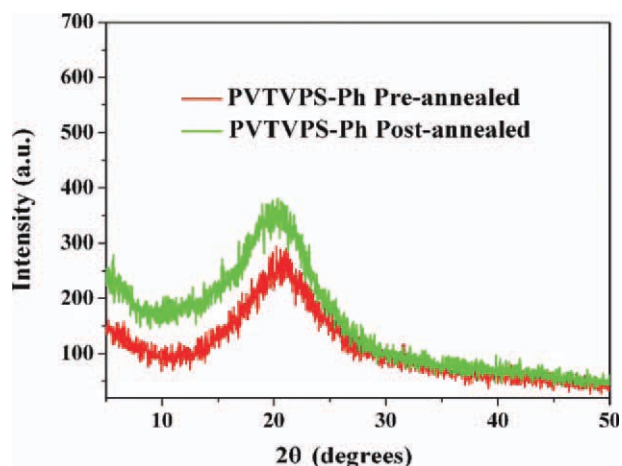


Figure 3. X-ray diffraction patterns of the copolymers PTVVPS-Ph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

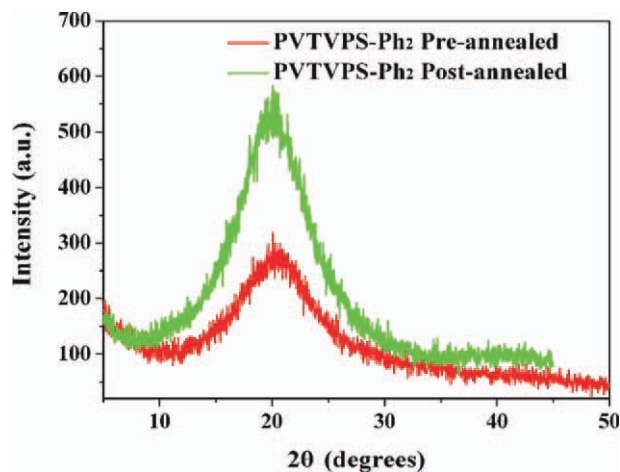


Figure 4. X-ray diffraction patterns of the copolymers PTVVPS-Ph₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cyloxy-substituted biphenyl side chain, implying that there may exist well-ordered structure in PTVVPS-Ph₂ after thermotreatment at $>103^\circ\text{C}$. To gain insight into the molecular-level packing arrangements of the polymers, XRD studies from powder patterns have been conducted. In their pristine state, the two

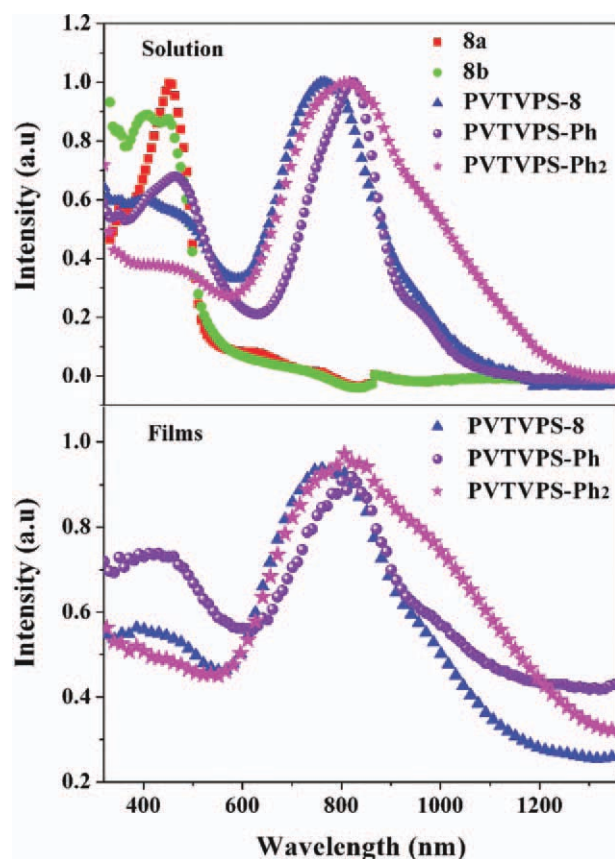


Figure 5. UV-Vis-NIR absorption spectra of PTVVPSs in solution and films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

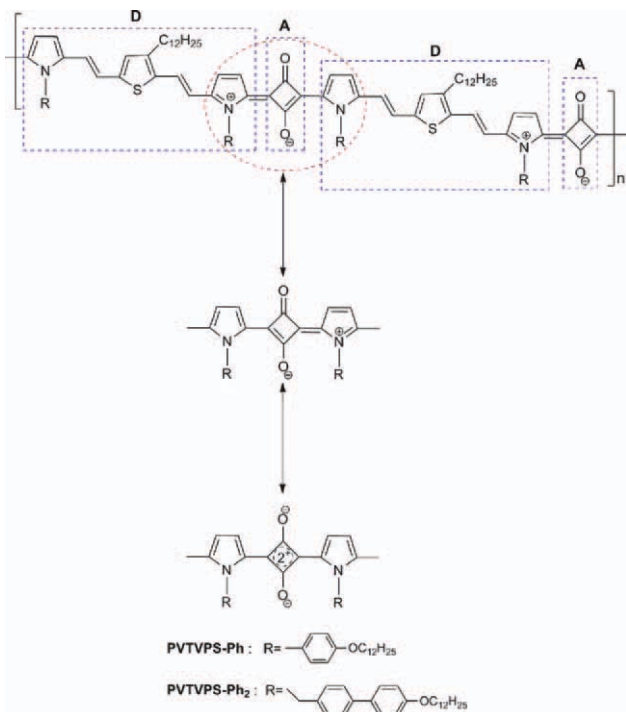


Figure 6. Zwitterionic structure of polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers show nearly identical weak broad peaks at $2\theta \approx 20^\circ$ (Figures 3 and 4), and accordingly, the interlayer π - π stacking distances of the aromatic groups in the polymer chains arranged in the parallel direction are calculated to be 4.3–4.4 Å.²⁷ After being annealed at 160°C (a temperature higher than their T_g) for 30 min, the signal of PVTVPS-Ph₂ is dramatically intensified when compared with that of PVTVPS-Ph, suggesting that the introduction of biphenyl segment is propitious to the formation of more ordered face-to-face packing between main chains with the aid of thermoannealing treatment and consequently may render higher charge carrier mobility.^{29,30}

Optical Properties

The UV–Vis–NIR absorption spectra of the monomers and the polymers in dilute solution (THF, 1×10^{-6} molL⁻¹) are shown in Figure 5. The monomers **8a** and **8b** possess sharp and intense absorption bands with λ_{\max} of ~ 430 nm and extinction coefficients (ϵ_{\max}) of $\sim 8.0 \times 10^5$ L mol⁻¹ cm⁻¹. In contrast, the absorption signals of the resulting macromolecules are considerably broadened and red-shifted, each accompanied with a new broad absorption in the region of 500–1100 nm with λ_{\max} of ~ 810 nm and ϵ_{\max} of 1.0 – 1.1×10^6 L mol⁻¹ cm⁻¹, which is

generally assigned to the donor–acceptor (pyrrole–squaraine) charge-transfer transition in their main chain (Figure 6).³¹ Although when compared with PVTVPS-Ph₂, PVTVPS-Ph may possess more extended conjugation system because the phenyl substituent is connected directly to the pyrrole moiety, the λ_{\max} of the two polymers of both the two bands are quite similar, despite that PVTVPS-Ph even has much higher molecular weight relative to PVTVPS-Ph₂. Therefore, the phenyl substituents in PVTVPS-Ph should contribute little to the elongation of conjugation length. In contrast, the absorption band of PVTVPS-8 is observed to show ~ 60 nm blue shift ($\lambda_{\max} = 750$ nm) when compared with PVTVPS-Ph and PVTVPS-Ph₂. As all these three macromolecules own similar conjugative backbones, the blue-shifted absorption spectrum may arise from the fewer conjugative repeating units in PVTVPS-8 because of its much lower molecular weight. In the case of absorption spectra in thin films, the λ_{\max} of PVTVPS-8 is found to show 55 nm red shift (805 nm) relative to its solution sample, which is a common phenomenon due to the intensified intermolecular interactions in solid state. Nevertheless, the λ_{\max} of both PVTVPS-Ph and PVTVPS-Ph₂ in film samples (spin coated from chlorobenzene solution; Figure 5) are quite similar to those measured in dilute solution (data summarized in Table III), suggesting that the replacement of flexible alkyl group into rigid phenyl or biphenyl segments is beneficial to the alleviation of intermolecular stacking.

In comparison with PVTVPS-8 and PVTVPS-Ph₂, PVTVPS-Ph has the narrowest D–A charge-transfer absorption bands (Table III). This may be attributed to the restricted rotation between D and A moieties of the polymeric backbone due to the existence of rigid phenyl on pyrrole segment. To validate the effect of phenyl substituent on the D–A transition absorption band, UV–Vis–NIR spectra of PVTVPS-Ph films annealed at different temperature have been recorded and shown in Figure 7. With increased thermotreatment temperature, the absorption intensity of D–A charge-transfer band with λ_{\max} of 809 nm decreases gradually, whereas that of the band originating from the $\pi \rightarrow \pi^*$ transition of monomer ($\lambda_{\max} \sim 430$ nm) increases progressively. In solution samples (1,2-dichlorobenzene as solvent), similar result is obtained on heating; moreover, the absorption spectra are restorable on cooling, and this thermochromic transition is found to be reversible. This is quite different from the general observations that the absorption spectra of conjugation polymers usually show hypsochromic effect on heating, which may be attributed to conformational changes,³² reduction of the conjugation length,³³ or breakup of interchain aggregation.^{34,35} Furthermore, in the IR spectrum of annealed PVTVPS-Ph film (160°C, 30 min, measured at room temperature; Figure 8), the

Table III. Optical Properties of the Objective Polymers

Polymers	λ_{\max} (nm)		E_g^{opt} (eV)	Full-width at half maximum in solution (nm)	Full-width at half maximum in film (nm)
	Solution	films			
PVTVPS-8	750	805	1.16	239	245
PVTVPS-Ph	809	809	1.11	171	228
PVTVPS-Ph ₂	806	806	1.01	354	380

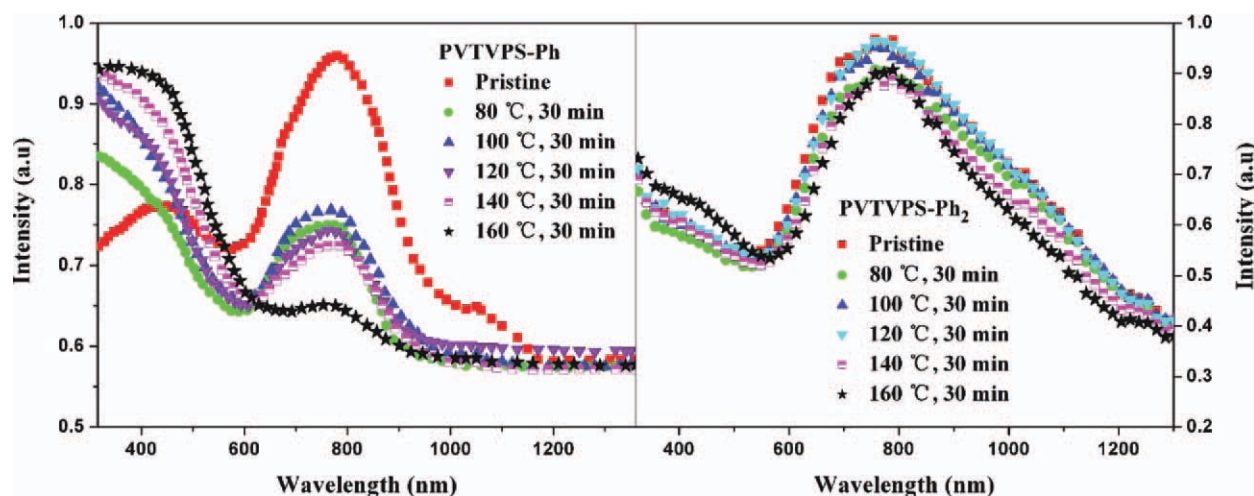


Figure 7. UV-Vis-NIR absorption spectra of PTVVPSs unannealed and annealed films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristic signal of resonance-stabilized zwitterionic 1,3-squaraine²⁷ at 1634 cm^{-1} is found to be much weaker than that of the pristine film, confirming the presence of less D-A charge-transfer species at higher temperature. All these results indicate that on heating, the D-A charge-transfer zwitterionic species in PTVVPS-Ph should reduce in quantity, partially may be due to the intensified steric hindrance between phenyl substituent and squaraine segment, and therefore render dramatically changed absorption spectrum. To our knowledge, this is the first report on thermochromic polysquaraines. Thus, PTVVPS-Ph is a promising NIR thermochromic material.

On the contrary, no similar thermochromism is observed in PTVVPS-Ph₂, for there exists a freely rotating methylene linker between biphenyl unit and the main chain. The charge-transfer absorption band of PTVVPS-Ph₂ is much broader than that of PTVVPS-Ph or PTVVPS-8 in both solution and film, and on heating, no obvious alteration could be found in the absorption

spectra (film samples; Figure 6). Its optical bandgap (E_g^{opt}) is determined to be $\sim 1.0\text{ eV}$ via UV-Vis absorption onset of the film according to the empirical equation ($E_g = 1240/\lambda_{\text{onset}}\text{ eV}$).³⁶ Consequently, PTVVPS-Ph₂ has good thermostability and broad absorption; both are key factors for photovoltaic materials. Detailed studies on the elucidation of polymeric structures of these macromolecular compounds are in progress using quantum-chemical Hartree-Fock method.³⁷

CONCLUSION

By incorporating more rigid phenyl or biphenyl substituents as side chain with pyrrole segment, two novel polysquaraines with good solubility and satisfied molecular weights have been developed. Both the copolymers exhibit intense absorption that covers the entire visible region with tails extended to NIR region, and the bandgaps are as low as $\sim 1.0\text{ eV}$. PTVVPS-Ph with phenyl substituent shows NIR thermochromism, which may be attributed to the restricted free rotation between D and A moieties of the polymer; PTVVPS-Ph₂ exhibits good thermostability, narrow bandgap, and more ordered structure after annealing, indicating it is a prospective photovoltaic material. Therefore, by rational selection of substituents with different electronic and steric effects, the photophysical, morphologic, and thermal properties of the polysquaraines could be readily manipulated.

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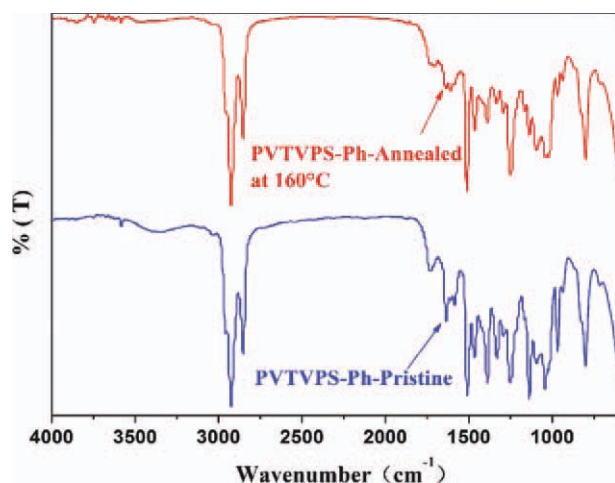


Figure 8. FTIR spectra of PTVVPS-Ph unannealed and annealed films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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