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New soluble rigid rod copolymers comprising alternating 2-amino-pyrimidine and phenylene repeat units: Syntheses, characterization, optical and electrochemical properties

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ABSTRACT

A new type – π -conjugated copolymers of 2-amino-pyrimidine was prepared between 2-amino-4,6diiodidepyrimidine and 1,4-dibromo-2,5-dialkoxybenzene by Sonogashira polycondensation. The structures of the copolymers were elucidated by FT-IR, ¹H NMR and ¹³C NMR, fluorescence spectroscopy, gel permeation chromatography, thermal analysis and element analysis. The derived polymers were soluble in common organic solvents and trifloroacetic acid and exhibited good thermal stability. They emitted green light under UV irradiation in solid state and blue or green light in solution phase, respectively. Electrochemical behavior of these new polymers depicted facile *p*-doping and good electron-transporting properties. These polymers displayed bathochromic shift when protonated with CH₃SO₃H acid in chloroform solutions or *m*-cresol solutions and the red-shifted peaks were observed from 490 nm to 652 nm. XRD patterns of copolymers showed that the intensity of peaks was enhanced with increasing alkyloxy chain length.

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1. Introduction

During the past decade, π -conjugated copolymers have been an interesting class of organic materials for optical and electrical applications and a large number of papers have been published on conjugated chains with the linear and rigid structures [1–6].

Although several papers have recently been published on the preparation and properties of the rigid rod conjugated copolymers [7–10], more detailed studies seem to be required for revealing their basic properties. In our work on conjugated-systems, we became interested in copolymers containing electron-deficient heterocycles like 2-amino-pyrimidine [11]. However, π -conjugated copolymers having a 2-amino pyrimidine ring have received less attention, in spite of the presence of a certain number of reports about copolymers of containing pyridine rings [5,12–17]. Because of its electron-deficient nature, pyrimidine could establish charge-transfer (CT) structure with five-membered ring heterocycles such as thiophene and furan which have a π -excessive nature [18,19] and their copolymers had been successfully synthesized. Meanwhile, the linear and rigid rod conjugated chains of copolymers containing pyridine ring have been more attracted for nonlinear optical

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applications [1,2,4]. Subsequently, blue electroluminescent materials containing pyridine ring were reported [5]. In comparison with the pyridine, 2-amino-pyrimidine seemed to be showing more electron-deficient nature, and the amino group was very active [11,18,20].

In this work, we chose 2-amino-pyrimidine to act on the electron density of the conjugated chain by means of an electroactive functional group, electron acceptor attached on the phenyl moiety. We also chose to attach an alkoxy chain on the aryl in order to increase the solubility and the molecular weight. The copolymers reported in this paper are considered to possess linear molecular structures [4,21] without branching since a more convenient method, using a palladium catalyzed polycondensation, has been applied to the synthesis of rigid rod conjugated chains [22,23], more generally known in organic synthesis as a Sonogashira coupling [24–26]. The copolymers which contains 2-aminopyrimidine ring are expected to show interesting chemical and physical properties.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. 2-amino-4,6dicholoro pyrimidine, (PPh₃)₄Pd, Cul, bromine, 1-bromododecane,





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Scheme 1. The procedure for preparation of the copolymers.

Tetrahydrofuran (THF), trimethylsilylacetylene (TMSA), hydroquinone, triphenylphosphine (TPP), dimethylformamide (DMF) were purchased from ACROS(China) Chemical Co. and used as received. 1,4-Dibromo-2,5-bis (dodecanoxy)-benzene [28], 1,4-bis[(trimethylsilyl)ethynyl]-2,6-bis(dodecyloxy) benzene [3], and 1,4-diethynyl-2,5-bis(dialkoxy)benzene [3] were synthesized according to the literature. The acetonitrile and diisopropylamine were distilled from KOH and toluene was dried and distilled from metal sodium powder under a N₂ atmosphere. Both solvents were sparged with N₂ for 2 h and stored under N₂. Other reagents such as methanol and chloroform were commercially available and used as received unless otherwise stated.

2.2. Characterization

¹H NMR and ¹³C NMR spectra were taken with a VARIAN INOVA-400 spectrometer (400 MHz). Photoluminescence and excitation spectra were recorded on a HITACHI F-4500 spectrophotometer. Elemental analyses were made on an FLASH EA series 1112 NCHS-O analyzer. FT-IR spectra of the copolymers were obtained by using a BRUKEREUINOX-55 Fourier transform infrared spectrometer (frequency range 4000–500 cm⁻¹). UV–vis spectra of the copolymers were recorded by using Shimadzu UV-2450 spectrophotometer. UV–vis absorption spectra in powder state were measured at room temperature on a UV-3010 spectrometer equipped with an integrating sphere. The X-ray diffraction studies were performed on a D/Max 2400 X-ray diffractometer by using Cu– K_{α} radiation



Fig. 1. ¹H NMR spectrum of PI.

source ($\lambda = 0.15418$ nm). The scanning rate was 2°/min over a range of $2\theta = 5-60^{\circ}$. Molecular weight determinations were made by Waters Alliance GPC V 2000 at a flow rate of 0.94 ml/min in DMF Waters styragel columns (HT3, HT4, HT6), $T = 65^{\circ}$ C. The thermal stability of the dry sample was determined using Netzsch STA 449C instrument with a temperature range of 26–900 °C at a heating rate of 10 °C/min, using a nitrogen purge at a flow rate of 30 ml/min. The cyclic voltammetry (CV) was performed with a CHI 660A Electrochemical Workstation (CH Instruments, China) in a conventional three electrode cell with a counter electrode (Pt) and a reference electrode (Ag/AgCl), $T = 20^{\circ}$ C. The melting point was measured with a TECH XT-5 melting point apparatus.

2.3. Synthesis of 2-amino-4,6-diiodopyrimidine

2-amino-4,6-diiodopyrimidine was prepared by modifying the literature method [27]. A solution of 2-amino-4,6-dichloropyrimidine (4 g, 24 mmol) in 40% HI (100 mL) was treated with KI (19.2 g, 115 mmol) and stirred for overnight at ambient temperature. The precipitate was filtered, the precipitate was washed with aqueous NaHCO₃ and dried to give the desired product (8 g, 94%). ¹H NMR (CDCl₃) δ : 7.523 (s, 1H), 5.327 (broad s, 2H).

2.4. Synthesis of 1,4-bis (dodecanoxy) benzene

1,4-Bis (dodecanoxy) benzene was prepared by modifying the literature method [4]. To a solution of hydroquinone (7.7 g, 70 mmol)



Fig. 2. ¹³C NMR spectrum of PI.



Fig. 3. ¹H NMR spectrum of PIII in CF₃COOD.

in 140 mL of DMF/toluene mixture (1:1) were added potassium hydroxide (9.52 g, 170 mmol) and potassium carbonate (23.46 g, 170 mmol). The mixture was stirred at room temperature for 30 min. Then 1-bromododecane (38.83 g, 156 mmol) was added dropwise. The mixture was stirred and refluxed under N₂ for 14 h, cooled and the toluene was removed under reduced pressure and the remaining mixture was poured into cold water (210 ml). The brown precipitate was collected by filtration and was recrystallized twice from ethanol to yield a fluffy white material in 96% yield, mp 77–78 °C.

2.5. Synthesis of the copolymers

The poly(2,5-didodecyloxy-1,4-diethynyl-phenylene-*alt*-2-amino-4, 6-pyrimidine) (**PI**), poly(2,5-diheptyloxy-1,4-diethynyl-phenylene-*alt*-2-amino-4,6-pyrimidine) (**PII**) and poly(1,4-diethynylphenylene-*alt*-2-amino-4,6-pyrimidine) (**PIII**) were prepared by modifying the literature method [3] and the procedure for the preparation of **PI** was given as a typical example:

PI: 0.165 mmol of 1,4-Diethynyl-2,5-dialkoxybenzene, 0.165 mmol of 2-amino-4,6-diiodopyrimidine, 0.008 mmol of (PPh₃)₄Pd, and 0.008 mmol of CuI were combined in 3 mL of diisopropylamine and 7 mL of toluene under N₂. The mixture was heated at 80 °C for 10 h. Ammonium iodide salts were formed immediately and the mixture



Fig. 4. FT-IR spectra of copolymers and monomers.



Fig. 5. UV-Vis spectra of PI, PII and PIII in solution or cast film.

was little fluorescent, the emission in the early stages of copolymerization being green and in the later stages more reddish yellow. After cooling the reaction mixture to room temperature it was added dropwise to 100 mL of rapidly stirred acetone. The yellow precipitate was collected and washed repeatedly with acetone, hot EtOH, hot CH₃OH, and recrystallized twice from EtOH/CHCl₃. After drying overnight at 40 °C, copolymer was isolated in 92% yield. GPC analysis (soluble part in DMF) gave M_n of 5951 and M_w of 6119. ¹H NMR (CDC1₃) δ : 7.06–7.088 (m, 2H), 6.82–6.99 (br, 1H), 5.18–5.24 (br, d, 2H), 3.98–4.01 (br, m, 4H), 1.20–1.85 (m, 40H), 0.86 (t, 6H). Anal. Calcd for (C₃₈H₅₅N₃O₂)_n (585.86)_n: C, 77.90; H, 9.46; N, 7.17. Found: C, 77.78; H, 9.65; N, 7.24. UV–vis (CHC1₃) λ_{max} : 415 nm.



Fig. 6. UV-Vis spectra of the monomers and copolymer.



Fig. 7. Fluorescence spectra of copolymers in solution and in powder state.

PII: isolated in 81% yield. GPC analysis (soluble part in DMF) gave M_n of 4798 and M_w of 4969. ¹H NMR (CDC1₃) δ : 6.954–7.058 (m, 2H), 6.802–6.949 (br, 1H), 5.113–5.173 (br, d, 2H), 3.957–3.973 (br, m, 4H), 1.20–1.85 (m, 20H), 0.86 (t, 6H). Anal. Calcd for (C₂₈H₃₅N₃O₂)_n (445.6)_n: C, 75.60; H, 7.71; N, 9.27. Found: C, 75.47; H, 7.92; N, 9.43. UV–vis (CHC1₃) λ_{max} : 423 nm.

PIII: isolated in 75% yield. GPC analysis (soluble part in DMF) gave M_n of 3554 and M_w of 4089. ¹H NMR (CF₃COOH) δ : 7.548–7.969 (m, 4H), 7.156–7.275 (m, 1H). Anal. Calcd for $(C_{14}H_7N_3O_2)_n$ (249.22) $_n$: C, 67.80; H, 2.75; N, 16.72. Found: C, 67.47; H, 2.83; N, 16.86. UV–vis (DMF) λ_{max} : 379 nm.



Fig. 8. UV-vis absorption and fluorescence spectra of PI in powder state.

3. Results and discussion

3.1. Synthesis and characterization of the copolymers

The synthetic procedure of the monomers and copolymers is described in Scheme 1. The precursor of 1,4-bis (dodecanoxy) benzene was prepared via a somewhat different route from the reported route [3,4,28] and the new method gave the precursor in a stabilized higher yield (95%) than the previously reported methods (80–91%).

The chemical structure of the monomers and the copolymers was characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopy and elemental analyses. Fig. 1 presents the ¹H NMR spectrum of **PI** with the assignments of all the protons. The peaks corresponding to the aromatic protons were centered at the interval of 6.82–7.52 ppm. The amide NH₂ protons appear in the region of 5.18–5.24 ppm. The alkyl side-chains are dominating in the region of 0.84–1.86 ppm. The methylene groups adjacent to oxygen are shifted downfield to 4.00 ppm. Fig. 2 represents the ¹³C NMR spectra of **PI**. It shows a signal at 93.5 and 88.11 ppm, assigned to the acetylenic carbons [1]. The aromatic carbons of the pyrimidine ring are detected at 162, 154 and 111 ppm. The aromatic carbons of the benzene ring are detected at 151,117 and 114 ppm. The carbons belonging to the alkoxy side-chains appear as very strong signals at 70 and from 38 to 14 ppm. The peak at 77 ppm is due to CDCl₃.

Fig. 3 presents the ¹H NMR spectrum of **PIII**. The peaks corresponding to the aromatic protons were centered at the interval of 7.15-7.96 ppm. The amide $-NH_2$ protons are not founded in CF₃COOD.

Fig. 4 presents the comparison of FT-IR spectra of monomers and copolymers. For copolymers, the strong peak at 3285 cm⁻¹ corresponding to HC=C-stretching vibration and the weak peak at 2107 cm⁻¹ corresponding to C \equiv C in curve (b) was absent in curve (c), (d) and (e), but a new strong peak at 2212 cm^{-1} which is associated to $C \equiv C$ in copolymers structure was appeared in curve (c), (d) and (e) [29]. According to the IR data, the acetylene group is considered to be affected by the electron-deficient nature of pyrimidine ring and electron-donor nature of phenyl ring. This indicated that the dipoles were instantaneously changed greatly and the stretching vibration of acetylene group was very efficient. The peak at 3278 cm⁻¹ and 3481 cm⁻¹ corresponding to $-NH_2$ in curve (a) was appeared at 3300 cm^{-1} and 3497 cm^{-1} in curve (c), (d) and (e). The typical stretching vibration of alkyl group at 2919 cm^{-1} and 2846 cm^{-1} was also detected at 2922 cm^{-1} and 2851 cm⁻¹ in curve (d) and (e). The characteristic peak of C=N at the pyrimidine ring at 1625 cm^{-1} in curve (a) was detected at almost the same position in curve (c), (d) and (e).

3.2. Optical properties

The chloroform or DMF solutions of copolymers were light yellow and fluoresced blue or green under the irradiation with UV light (365 nm). The films of the polymers were prepared by spincasting the polymers from their solutions in chloroform or DMF. The films of polymers are light yellow. The UV–vis absorption spectra and photoluminescence spectra of the polymers measured from the solution, films and powder state were shown in Figs. 5–7. The peak wavelengths of the spectra and the π – π * band gaps of the polymers estimated from the absorption onset wavelengths are summarized in Table 1. The **PI** and **PII** showed almost identical electronic properties in solution or cast film while **PIII** showed shorter absorbance both in solution and cast film (Fig. 5).

Although all of the three polymers have the same backbone structure, their optical properties are quite different with the variation of substituent. Generally, a substituted group affects the

Table 1			
Optical	properties	of the	polymers.

Polymer	Yield	Color	M _n	UV ar	JV and PL λ (nm) ^a							Optical band			
				Solution $\lambda(nm)$		Stokes' shift	$(\Phi)^{b}$	Powder $\lambda(nm)$		Stokes' shift	Film (nm) ^c		gap (eV)		
				UV	EX	EM ^d			UV	EX	EM ^d		abs λ_{max}	absλ _{onset}	
PI	92%	Yellow	5951	415	429	465	50	0.12	389	-	521	132	438	501	2.48
PI	81%	Yellow	4969	423	458	478	55	0.11	376	-	549	173	439	497	2.49
PIII	75%	Yellow	4089	379	436	495	116	0.07	348	-	554	206	385	445	2.78

^a 10^{-5} M in CHCl₃ or DMF solution.

^b Relative to 9,10-diphenylanthracence (10⁻⁵ M in cyclohexane).

^c Spin-coating from CHCl₃ or DMF solution.

^d The main emission peak, operated at 300 K.

Table 2

Solvents influence on the PL and UV of PI.

Solvents	$\frac{UV}{\lambda_{max}}$	PL EX	$\frac{\lambda_{max}}{EM}$	Stokes' shift (nm)	$PL(\Phi)$
Chloroform	415	429	465	50	0.12
THF	412	418	457	45	0.098
Tetrachloromethane	426	373	436	10	0.081

electronic and optical properties of a conjugated polymer by steric hindrance arising from the substituted group. For polymers, the introduction of dialkoxy groups into the phenylene ring at the 2and 5-positions resulted in a remarkable spectral red or blue shift. In comparison with **PIII** (379 nm), the red shifts of **PI** (415 nm) are 36 nm in absorption spectra and in photoluminescence spectra, **PI** (464 nm) has the blue shifts (31 nm) compared to **PIII** (395 nm).

The **PIII** is a green light-emitting material, whereas polymer **PI** emits blue light. Fig. 6 depicts the UV–vis absorption of the monomers and **PI** in chloroform solution and cast film. The **PI** shows λ_{max} at a longer wavelength (415 nm, log $\epsilon = 2.35$; molarity is based on the repeating unit) than those of the corresponding monomers (**4a**: $\lambda_{max} = 338$ nm and 5: $\lambda_{max} = 302$ nm), indicating that the **PI** has an expanded π -conjugated system. Films of the copolymers showed the UV–vis peak at a somewhat longer wavelength, suggesting the presence of certain intermolecular electronic interaction. However, the degree of the red shift is considerably smaller than those observed with copolymers that take face-to-face stacking [28,30]. Fig. 7 depicts the PL spectrum of copolymers in

solution and powder state. The PI, PII and PIII show different PL peaks in solution and powder state that are summarized in Table 1. For instance, the photoluminescence peak of PI in powder state is observed at 521 nm and shifted by 56 nm to a longer wavelength than chloroform solution. Interestingly, the PL excitation peaks of the all polymers in powder state are not found at the long interval of 300-500 nm and the emission peaks were very easy to find at the interval of 521–554 nm in different intensity. The PL peaks of PI, PII and PIII in solution appear near the onset position of the UV-vis absorption band. The PL spectra, which are attributed to fluorescence on account of the short lifetime of the excited states [5], were obtained by irradiative excitation at the wavelength of the absorption maxima. For polymers, the blue or green fluorescence resulted with emission maxima from ca. 465-495 nm, which correlate approximately with the onset of the absorption band. This is indicative that photoluminescence took place by electrons in a conduction band (π^* level) to a valence band (π level).

Fig. 8 depicts the UV–vis absorption and fluorescence spectra of the **PI** in powder state. The absorption spectra exhibited an absorption maximum (λ_{max}) at ca. 389 and green fluorescence resulted with emission maxima at ca.521 nm.

The quantum yield for emission in solution was determined according to the method described by Davey et al. [5] relative to 9,10-diphenylanthracence (10^{-5} M in cyclohexane). Due to strong self-absorption and excimer formation of the polymers, the determined quantum yields were highly dependent on the concentration, solvents and excitation wavelength upon irradiation. The results are summarized in Tables 1 and 2. All polymers were found



Fig. 9. Changes in the absorption and emission spectra of copolymer $(3.25 \times 10^{-3} \text{ mol } \text{L}^{-1})$ in CHCl₃–CH₃SO₃H mixtures at different concentrations of CH₃SO₃H (mol L⁻¹): (1) 0, (2) 9.1536 × 10⁻⁵, (3) 10.6792 × 10⁻⁵, (4) 12.2048 × 10⁻⁵, (5) 15.256 × 10⁻⁵, (6) 18.3072 × 10⁻⁵, (7) 22.884 × 10⁻⁵, (8) 48.8192 × 10⁻⁵, (9) 140.3552 × 10⁻⁵, (10) 292.9152 × 10⁻⁵, (11) 1360.8352 × 10⁻⁵, (12)15256 × 10⁻⁵; (a) UV spectra; (b) Emission spectra (excitation at absorption maxima).



Fig. 10. Changes in the absorption and emission spectra of copolymer $(0.82 \times 10^{-3} \text{ mol } \text{L}^{-1})$ in *m*-cresol-CH₃SO₃H mixtures at different concentrations of CH₃SO₃H (mol L⁻¹): (1) 0, (2) 1.186×10^{-4} , (3) 1.723×10^{-4} , (4) 2.974×10^{-4} , (5) 1.614×10^{-3} , (6) 1.876×10^{-2} , (7) 1.751×10^{-1} , (8) 2.262×10^{-1} , (9) 1.131, (10) 3.394, (11) 5.085, (12) 8.788, (13) 10.182, (14) 15.274.



Fig. 11. FT-IR spectra of copolymer film on glass. (a) pure copolymer film (CHCl₃ as solvent); (b) copolymer film exposed under CH₃SO₃H ($1.751 \times 10^{-1} \text{ mol } L^{-1}$)/CHCl₃ as solvent; (c) copolymer film exposed under CH₃SO₃H($15.274 \text{ mol } L^{-1}$)/CHCl₃ as solvent; (d) pure CH₃SO₃H.

to be emissive with certain quantum yields. This could be attributable to the rigid structure of the copolymers with the effect that relaxation from the excited state through nonradiative (e.g., thermal) processes will be reduced with consequently certain fluorescence quantum yield [5]. Their optical properties are currently in progress in our laboratory.

With the aim of investigating the effect of protonation on the copolymers, we measured UV–vis and fluorescence spectra of the copolymers in CHCl₃–CH₃SO₃H mixtures. The copolymers showed similar protonation properties in their solution.

Fig. 9 depicts the representative changes in the absorption spectra and fluorescence spectra of PI with increasing concentration of CH₃SO₃H. From Fig. 9a, addition of CH₃SO₃H (0-0.15256 mol L⁻¹) to a CHCl₃ solution of **PI** $(3.25 \times 10^{-3} \text{ mol L}^{-1})$ led to a guick decrease in the intensity of the absorption at 415 nm and, at the same time, an appearance of a new band at 490 nm. From Fig. 9b, in chloroform solution, the emission spectra appeared to be more strongly affected by the addition of CH₃SO₃H than did the UV-vis spectra. The emission maxima were not red-shifted unlike the copolymers based on pyridine [6] when the CH₃SO₃H concentration was increased from 0 to $0.15256 \text{ mol } L^{-1}$. Meanwhile, the emission intensity was disappeared when the CH₃SO₃H concentration was increased from 0 to $9.1536 \times 10^{-5} \text{ mol L}^{-1}$. For the purpose of further investigating the effect of protonation on the copolymers, the representative acidochromism of PI in *m*-cresol is studied. Interestingly, the *m*-cresol solution of **PI** shows different acidochromism with wide range of CH₃SO₃H concentration than chloroform solution.

Fig. 10 depicts the changes in the absorption spectra of **PI** with increasing concentration of CH₃SO₃H in *m*-cresol. From Fig. 10, addition of CH₃SO₃H (0–0.1751 mol L⁻¹) to an *m*-cresol solution of **PI** (3.25×10^{-3} mol L⁻¹) led to a quick decrease in the intensity of the absorption at 440 nm and, at the same time, an appearance of a new band at 499 nm.

With increasing concentration of CH₃SO₃H (0.1751-15.274 mol L^{-1}), the absorption at 499 nm was decreased and, in the meantime, it is possible to observe an appearance of a new band at 652 nm. These results suggested that absorption at a longer wavelength in chloroform or m-cresol solution originates from a π - π ^{*} transition along the main chain. Moreover, this π - π ^{*} transition is strongly affected by the protonation of nitrogen in copolymer, which causes distortion of the inter-ring bonds ascribable to an increase in steric repulsion [20,31]. The difference of acidochromism in the UV–Vis spectral between in chloroform and *m*-cresol might be caused by the acidic and polar properties of the *m*-cresol. The acidochromism of **PI** is carried out in two steps in *m*-cresol solution, the first step is to accept a proton, and the second step is to accept two protons, the first step is relatively easy, while the second reaction was more difficult, because of the existence of the space resistance (space effects). In chloroform solution, **PI** only accept a proton while in *m*-cresol solution, the *m*-cresol solution can offer an acidic and polar environment and these moiety will lead to further protonation of PI and the acidochromism was carried out thoroughly and the PI accept two protons. In the interest of further understanding the protonation of nitrogen in copolymers, the representative FT-IR spectrum of residue was obtained after fully dried the PI in CH₃SO₃H (1.751×10^{-1} mol L⁻¹ or 15.274 mol L⁻¹)/CHCl₃ solution



Scheme 2. Mechanism for the acidochromism



Fig. 12. Changes in the absorption and emission spectra of copolymer $(2.52 \times 10^{-3} \text{ mol L}^{-1})$ in CHCl₃–CH₃OH mixtures at different volume fractions of methanol: (a) 0, (b) 20%, (c) 40%, (d) 60%; (a') UV spectrum; (b') emission spectrum (excitation at absorption maxima).

(Fig. 11). The peak at 3300 cm⁻¹ corresponding to $-NH_2$ in curve (a) was appeared at 3184 cm⁻¹ in curve (b) or (c). The characterization peaks of C=N at the pyrimidine ring and benzenoid units at 1625 cm⁻¹ and 1553 cm⁻¹ in curve (a) was detected at 1591 cm⁻¹ and 1438 cm⁻¹ in curve (b) or (c). The characterization acetylene group was detected at 2212 cm⁻¹ in curve (b) or (c). According to the IR data, the characterization peaks of amino group, pyrimidine ring and benzene ring were shifted to lower wave numbers but the characterization peaks of acetylene group was detected at almost the same position in curve (b) or (c). Since the bands ranging from 3000 cm⁻¹ to 2200 cm⁻¹ which are assigned to vibrations associated with the $-NH_3^+$ group was not observed, the $-NH_2$ group was not protonated but affected by the intermolecular hydrogen bond [32,33]. The representative general chemical structure and proteolytic equilibria of **PI** are shown in Scheme 2 [5,6,34,35].

The representative intermolecular staking properties of the **PI** in solution were investigated in CHCl₃–CH₃OH mixtures. In CHCl₃–CH₃OH mixtures, unlike some substituted polythiophenes which showed strong solvatochromism [36,37], the position of UV–vis maximum absorption slightly shifted to a longer wavelength (ca. 7 nm) with different volume fractions of CHCl₃ and CH₃OH (Fig. 12 (a)). The emission spectrum was nearly dependent on addition of CH₃OH, shifted to a longer wavelength (ca. 19 nm) with the emission intensity diminished rapidly with clear differences at emission energies (Fig. 12(b)).

3.3. The structure of the copolymers in the solid state

XRD patterns of polymers are shown in Fig. 13. As shown in Fig. 13, from **PIII** to **PI**, the intensity of peaks was increased. This indicates tends of crystallinity and the side-to-side distance



Fig. 13. XRD patterns of copolymers in the powder state.



Fig. 14. TG and DTA curves for copolymer with the heating rate of 10 min⁻¹ under dry nitrogen.

Table 3				
Electrochemical	pro	perties	of	polymers.

Polymers	p-doping(V)	n-doping(V)
	$E_{\rm pa}$	Epc	Epc	Epa
PI	0.65	-0.06	-0.65	-1.41
PII	1.36	-0.42	-0.74	-1.13
PIII	1.16	-0.49	-0.70	-1.17

 $E_{\rm pa}$ and $E_{\rm pc}$ stand for anodic peak potential, and cathodic peak potential, respectively.

between the interlayer are increased when the dialkoxy groups were introduced into the phenylene ring at the 2- and 5-positions. The π -conjugated copolymers with long side-chains often give an XRD peak in a low angle region below $2\theta = 10^{\circ}$ (Cu- K_{α}), and the *d* spacing calculated from the peak often corresponds to the distance between the π -conjugated main chains separated by the long side-chains [28,30,38]. When flat plane of the π -conjugated copolymers form a face-to-face stacked assembly, it usually gives another XRD peak corresponding to an interplane distance at about *d* = 3.8 Å [25,26,30]. All-aromatic polyesters with long sidechains also form similar layered structure [21]. Thus, the XRD peak in Fig. 13, For instance, the broad peak of **PIII** at about 24° should be assigned to a side-to-side distance between the interlayer which has a packing-dimension of about 3.7 Å [39].

3.4. Thermal properties

The thermal stability of copolymers was determined using thermogravimetric-differential thermal analysis (TG-DTA) under nitrogen.

The copolymers depicted very good thermal stability with exhibiting an onset of degradation greater than 240 °C in nitrogen atmospheres. A representative TGA and DTA curves of **PI** in nitrogen atmospheres are depicted in Fig. 14 and discussed.

Fig. 14 shows the thermograms for the neutral **PI**, and exhibited an onset of degradation greater than 247 °C under nitrogen with no weight loss at lower temperature. The remaining weight at 900 °C was about 42.6% and it indicates that the char yield of **PI** in nitrogen atmosphere was high even at 900 °C, due to the stability of conjugated backbone [5].

The DTA analysis of the PI showed a broad endothermic peak in the temperature range of 247.8–685.1 °C that was connected with



Fig. 15. CV chart for copolymer cast on a Pt plate in a CH₃CN solution of [Et₄N] [BF₄] (0.10 M) at 20 mVs⁻¹.

an overall weight loss of 57.4% which was consistent with gradually thermal breakdown of the alkyl side-chains adjacent to oxygen [5]. A very strong exothermic stage observed in the temperature range of 751–866 °C was due to phase transition of **PI**.

3.5. Electrochemical redox properties

The electrochemical properties of all three polymers were investigated in an electrolyte consisting of a 0.10 M tetraethylammoniumtetrafluoroborate [Et₄N] [BF₄] in acetonitrile by cyclic voltammetry. The derived polymers were electroactive in both anodic and cathodic region. The electrochemical data of the polymers obtained from their cyclic voltammograms are summarized in Table 3. The *p*-doping process of the polymers is sensitive to the substitution on the phenylene ring. The attachment of dialkoxy groups at the 2- and 5-positions of the phenylene ring resulted in changes of *p*- and *n*-doping process of the polymers is less sensitive to the variation of substituent. Table 3 indicates that all polymers showed similar electrochemical properties.

A representative CV curve of cast film of **PI** on a platinum plate is depicted in Fig. 15. The electrochemical behavior of PI depicted facile *p*-doping and good charge transporting properties attributable to the presence of the easily protonated pyrimidinyl [5,34,35] unit. It is seen that electro- chemical oxidation (or p-doping) starts at about -0.2 V vs. Ag/AgCl and gives *p*-doping peak at 0.058 V vs. Ag/AgCl. However, the anodic peak for PI in the -0.2 to 0.5 V region is similar to those previously reported for polyacetylene [40–47]. This indicated that **PI** may possibly be the same *p*-doping state as ethylene group or phenyl group in some extent and correlate with the acetylenic carbons or phenyl carbons induced by electrondeficient nature of pyrimidine ring (Scheme 3). At the same time the *p*-doping of **PI** was accompanied by obvious color changes (electrochromism) from brown in the neutral film to reddish in the *p*-doped polymer film. The corresponding *p*-undoping peak appears at -0.18 V vs. Ag/AgCl. The color of the film changed from red in the *p*-doped polymer film to brown in the *p*-undoped polymer film. The film did not reveal stability upon repeat scanning of CV and did not give same CV curves. Sweeping to higher potential in the interval of 1.7-3.0 V vs. Ag/AgCl gave no peak, revealing high stability of the PI in this oxidative region. PI gives a reducing (or *n*-doping) at -0.62 V, in contrast to other copolymers comprising electron-deficient heterocycles like pyridine (ndoping peak, -2.49 V; n-undoping peak, -2.21 V) [18], and its corresponding *n*-undoping peak is observed at -0.56 V vs. Ag/AgCl. This indicated that **PI** was more easily reduced or *n*-dopable than other copolymers comprising electron-deficient heterocycles like pyridine.

Optoelectrochemical data of the PI in a 0.10 M [Et₄N] BF₄ dichloromethane solution are shown in Fig. 16. On application of a low potential of 0.04 V, the absorption band of the solution is somewhat changed with a shift of UV-vis peak from 410 nm to 495 nm. The yellow color of the solution turned to red as shown in Fig. 16. After adding Et₃N to this red solution, the red color of the solution turned back to yellow as show in Fig. 16 and the absorption band of the solution is somewhat changed with a shift of UV-vis peak from 495 nm to 401 nm. It is considered that the absorption at a longer wavelength in dichloromethane solution originates from oxidation (or *p*-doping) of the **PI** on anode. Many papers reported that oxidized state of π -conjugated copolymers gave new absorption peak (s) in the wavelength range of 500–1500 nm [28,38]. The absorption peak was as same as UV-vis spectra of the PI in CHCl3-CH₃SO₃H mixtures (Fig. 9, (490 nm)). These results suggested that oxidized state of **PI** has same π - π ^{*} transition as **PI** in CHCl₃-CH₃SO₃H mixtures (Fig. 9, (490 nm)), it is considered that oxidized



Scheme 3. *p*-doping and *n*-doping of pyrimidine.

state of **PI** has coequal electronic energy state with a π - π^* transition along the main polymer chain, moreover, this π - π^* transition is strongly affected by the protonation of nitrogen in polymer. Detailed studies on the relationship between acidochromism of copolymers and their electrochemical properties are currently in progress in our laboratory.

Fig. 17 gives CV of cast film of **PI** in different masses on a platinum plate. The working electrode was a copolymer film electrode prepared by casting the CHCI₃ solution of copolymer on platinum electrode.

The detailed procedure of the film preparation procedure was as following: A certain mass of copolymer will be dissolved in a certain volume of chloroform solution (its concentration could be calculated), and then the chloroform solution is casted carefully with a syringe on Pt and the solution on the Pt was dried very carefully, after that the film electrode was formed. The mass of the copolymer on the Pt was determined by the volume and concentration of chloroform solution (the copolymer was almost insoluble in acetonitrile).



Fig. 16. UV-vis spectra of the copolymer in a dichloromethane solution of 0.10 M [Et₄N] BF₄ at 0.04 V potential.

It has been seen that electrochemical oxidation and deoxidation peak are sensitive to the mass of the **PI** on the Pt plate. With the increasing mass of the **PI** on the Pt plate, the oxidation and deoxidation peaks were moved to higher potential. For instance, the *p*-doping peak was shifted from 0.05 V to 0.65 V and the *p*-undoping peak was shifted from -0.18 V to -0.069 V, while the *n*-doping peak was shifted from -0.62 V to -1.35 V and the *n*-undoping peak was shifted from -0.54 V to -0.75 V.

4. Conclusion

In summary, novel conjugated copolymers comprising of alternating electron donating phenylene units and electron accepting pyrimidinyl units were synthesized by sonogashira coupling reaction. The copolymers depicted good solubility in common organic solvents, such as chloroform, THF and trifloroacetic acid. Our investigation showed that the electronic and optical properties of the copolymers were consistent with a rigid-rod conjugated backbone structure. They showed blue emission in their solution and green emission in powder state. The copolymers in CHCl₃–CH₃SO₃H mixture depicted bathochromic shift. The electrochemical behavior of the copolymers depicted facile *p*-doping and certain electrontransporting properties.



Fig. 17. CV chart for copolymer cast on a Pt plate in a CH_3CN solution of [Et₄N] [BF₄] (0.10 M) at 100 mVs⁻¹: (a) Mass of the copolymer was 6 mg; (b) Mass of the copolymer was 0.03 mg.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.11.010

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