

# Comparisons of Optical Properties on Meta- and Para-Linkages of Copolymers for Poly(phenylene vinylene) and Poly(phenylene azomethine) with Alkylthio Group at the Side Chain

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Received 21 April 2004; accepted in revised form

**Key words:** blue shift, effective conjugation length, excimer, molecular aggregation, PL emission

## Abstract

Three series of soluble copolymers were synthesized: I, poly[m (or p)-phenylene (diacetonitrile) vinylene-co-methoxy-5-(2'-ethylhexylthio)-p-phenylene vinylene] (m-C=C(CN), p-C=C(CN)); II, poly[m (or p)-phenylene azomethine-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenylene azomethine] (m-C=N, p-C=N); III, poly[m (or p)-phenylene vinylene-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenylene vinylene] (m-C=C, p-C=C). Of all these copolymers, the copolymers containing meta-linkage showed glass transition temperatures ( $T_g$ 's) approximately 10 °C to 30 °C lower than those of the corresponding para-linkage copolymers because of lower crystallinity. 5% weight loss of all the copolymers occurred at around 381 to 344 °C.

Copolymers of the meta-linkage also caused a relative asymmetry and irregularity of the copolymer main chain, thus leading to a decrease of effective conjugation length and a reduction of the molecular aggregation: this subsequently led to less excimer formation. These phenomena can be evidenced from the blue-shift of PL emission, 15 to 49 nm for the meta-linkage copolymers compared with the para-linkage copolymers. In addition, due to the lesser electron-donating capability of the sulfur atom, m-C=C, p-C=C and p-C=N containing the alkylthio group indicated a blue shift of 8 to 24 nm, when compared with those copolymers of similar structures containing the alkyloxy group as reported in the literature. Since series II contains strong electron-withdrawing –C=N– at the main chain, and series I contains even stronger electron-withdrawing cyano group, thus, the observed  $\lambda_{max}$  are in the order: series I [m-C=C(CN), p-C=C(CN)] > series II [m-C=N, p-C=N] > series III [m-C=C, p-C=C]. Furthermore, since in series II, the lone pair electrons on the –C=N– main chain would overlap partially with the six  $\pi$  electrons in the phenyl ring, and decrease the coplanar nature of the main chain, thus their PL emission intensities were less than those of series I and III. Finally, a device of the structure (ITO/PEDOT: PSS/m-CC(CN)/LiF/Al) was constructed, and a yellow light of  $\lambda_{max} = 570$  nm was observed.

## INTRODUCTION

Son and Galvin, in 1995, disclosed the coexistence of cis- and trans-forms of poly(phenylene vinylene) (PPV), of which the cis-form distorted the main chain, and shortened the effective conjugation length, leading to a blue shift of  $\lambda_{max}$  at 544 nm. This distortion of polymer chains also decreased the intermolecular aggregation, increased the amorphous region and showed less excimer formation. Thus, a device of (ITO/PPV/Al) showed an increase of internal quantum efficiency by 0.22% [1]. In 1999, Shim reported the meta-linkage of PPV (m-PMEH-PPV) showed a blue shift and stronger intensity than the para-linkage of PPV (p-PMEH-PPV) [2]. Shim also reported that PPV containing a thio group at the side chain (MEHTPPV) showed a blue shift of 40 nm, as compared with a similar PPV containing oxygen at the side chain (MEH-PPV). He interpreted the lower conductivity of MEHTPV than MEH-PPV, attributed to an increased band gap between the valence band and con-

duction band of MEHTPV, because of the lesser electron-donating capability of the sulfur atom [3, 4]. Furthermore, Shim reported the quantum efficiency of MEHTPV was 20 times higher than MEH-PPV [4]. In order to clarify the combined effect of meta-, para-linkages, as well as thio- and oxygen-influences, we therefore synthesized series III to compare their optical properties. Furthermore, Friend et al. in 1993 incorporated a strong electron-withdrawing cyano group onto the conjugated vinylene of PPV (CN-PPV) and found a red shift of the emission wave length [5]. Therefore, we also incorporated a cyano group to series III to study possible further optical changes of series I.

Conjugated aromatic polyazomethines have good thermal and mechanical properties and were applied as electron and emitting layers in OLED by Weaver [6] and Fukuda [7]. In 1996, Fisher applied oligoazomethine films as electron and hole layers in OLED and studied the interfacial phenomenon between the organic and inorganic layers [8]. However, poor solubility is the main drawback for this type of azome-

thine. Nevertheless, Meghdadi et al. reported a soluble azomethine derivative for the OLED device with a good light efficiency [9]. Based on the literature searching, we prepared soluble azomethines, series II ( $-\text{C}=\text{N}-$ ), and compared their optical properties with series I ( $-\text{C}=\text{C}(\text{CN})-$ ) and series III, for *m*- and *p*-linkages of  $-\text{C}=\text{C}-$ .

## Experimental

### Materials

#### 4-(2'-ethylhexylthio)-1-methoxybenzene (Compound 1)

4-methoxy thiophenol (10.00 g, 0.07 mole) in 20 ml of anhydrous EtOH in a reaction vessel, was added drop by drop EtONa (7.56 g, 0.11 mole) in 40 ml of anhydrous EtOH. After stirring for 1 h at an ambient temperature, 2-ethylhexylbromide (16.80 g, 0.08 mole) was added slowly, and refluxed at 85 °C for 24 h. The mixture was extracted with hexane/H<sub>2</sub>O and dried with MgSO<sub>4</sub>, and a pale liquid product with 98% yield was obtained after purification by column chromatography with hexane as eluent.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 7.346 (d, 2H, aromatic), 6.848 (d, 2H, aromatic), 3.792 (s, 3H,  $-\text{OCH}_3$ ), 2.821 (d, 2H,  $-\text{SCH}_2-$ ), 1.462~1.249 (m, 9H, alkylthio), 1.245~0.85 (m, 6H,  $-\text{CH}_3$ ); MS: (M + 1)<sup>+</sup> 253.

#### 1,4-bis(bromomethyl)-5-(2'-ethylhexylthio)-2-methoxybenzene (Compound 2)

Compound 1 (5.00 g, 0.02 mole) and paraformaldehyde (6.36 g, 95%, 0.2 mole) were dissolved in 155 ml of glacial AcOH. HBr (6 ml, 33% in AcOH) was added dropwise. The mixture was stirred at 60 °C, and after 12 h, additional 6 ml of HBr was added twice after every 12 h. After a total 36 h of reaction, the mixture was cooled in a refrigerator for 2 h. A white solid product (6.42 g, 74% yield) with mp of 61–62 °C was obtained after washing with MeOH twice.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 7.424 (s, 1H, aromatic), 6.93 (s, 1H, aromatic), 4.733 (s, 2H,  $-\text{CH}_2\text{Br}$ ), 4.497 (s, 2H,  $-\text{CH}_2\text{Br}$ ), 3.906 (s, 3H,  $-\text{OCH}_3$ ), 2.872 (d, 2H,  $-\text{SCH}_2-$ ), 1.574~1.253 (m, 9H, alkylthio), 0.911~1.0855 (m, 6H,  $-\text{CH}_3$ ); MS: (M + 1)<sup>+</sup> 437.

#### 1,4-dicarboxyaldehyde-5-(2'-ethylhexylthio)-2-methoxybenzene (Compound 3) [10]

Into Compound 2 (5.00 g, 0.01 mole) in anhydrous EtOH, was added EtONa (2.02 g, 96%, 0.03 mole) in 20 ml anhydrous EtOH and 2-nitropropane (4.28 g, 95%, 0.05 mole). After stirring for 24 h at room temperature, the mixture was dried by evaporation of EtOH, and the product was extracted with EA/H<sub>2</sub>O. After purification, a pale yellow liquid (1.85 g, yield of 60%) was obtained.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 10.625 (s, 1H,  $-\text{CHO}$ ), 10.503 (s, 1H,  $-\text{CHO}$ ), 7.963 (s, 1H, aromatic), 7.497 (s, 1H, aromatic), 3.998 (s, 1H,  $-\text{OCH}_3$ ), 2.92 (d, 2H,  $-\text{SCH}_2-$ ), 1.615~1.234 (m, 9H, alkylthio), 0.907~0.85 (m, 6H,  $-\text{CH}_3$ ). MS: (M + 1)<sup>+</sup> 309.

#### 1-(2'-ethylhexylthio)-4-methoxy-2,5-xylenebis(triphenylphosphonium bromide) (Compound 4)

Compound 2 (5.00 g, 0.01 mole) and PPh<sub>3</sub> (3.00 g, 0.01 mole) in 60 ml of toluene was refluxed for 2 days. After cooling and precipitating from ether, a white powder (5.00 g, mp: 207–208 °C, yield of 55%) was obtained.

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 7.752~7.588 (m, 30 H,  $-\text{PPh}_3$ ), 7.1 (s, 1H, aromatic), 6.9 (s, 1H, aromatic), 5.5 (d, 2H,  $\text{CH}_2\text{P}$ ), 5.3 (d, 2H,  $-\text{CH}_2\text{P}$ ), 2.889 (s, 3H,  $-\text{OCH}_3$ ), 2.05 (d, 2H,  $-\text{SCH}_2-$ ), 1.3~1.0 (m, 9H, alkylthio), 0.911 (t, 3H,  $-\text{CH}_3$ ), 0.704 (t, 3H,  $-\text{CH}_3$ ), MS: (M + 1)<sup>+</sup> 747.

#### Poly[m-phenylene(diacetonitril)vinylene-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenylenevinylene] (m-C=C(CN)) [5]

Compound 3 (193.5 mg,  $6.27 \times 10^{-1}$  mmole) and 1,3-phenylenediacetonitril (100 mg, 98%,  $6.27 \times 10^{-1}$  mmole) were dissolved in t-butanol/THF (6 ml/2 ml), and heated to 50 °C. A catalyst containing t-BuOK (3.60 mg, 97%,  $3.11 \times 10^{-2}$  mmole) and Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup> (26 mg, 1 m in MeOH,  $3.14 \times 10^{-2}$  mmole) in 1 ml of THF was prepared. 10 drops of the catalyst was rapidly added to the reaction mixture, which turned immediately to dark red. The mixture was coagulated from 150 ml MeOH containing 1 ml AcOH. The polymer thus obtained was dissolved in THF and coagulated from MeOH. This same procedure was repeated twice, and an orange-red powder thus obtained with a yield of 49% (116.2 mg), GPC ( $M_n = 9,000$ ;  $M_w = 14,000$ ;  $M_w/M_n = 1.56$ ).

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 8.383 (m, 8H, aromatic and  $-\text{CH}=\text{C}(\text{CN})-$ ), 4.053 (s, 3H,  $-\text{OCH}_3$ ), 2.968 (s, 2H,  $-\text{SCH}_2-$ ), 1.596~1.0 (m, 9H, alkylthio), 1.0~1.07 (m, 3H,  $-\text{CH}_3$ ).

#### Poly[p-phenylene(diacetonitrile)vinylene-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenylenevinylene] (p-C=C(CN))

The same procedure as in the preparation of (m-CC(CN)) was followed except compound 3 (193.5 mg,  $6.338 \times 10^{-1}$  mmole) and 1,4-phenylenediacetonitrile (100 mg, 98%,  $6.338 \times 10^{-1}$  mmole) were used as starting material. A red powder was obtained (102.8 mg, yield 34.8%), GPC ( $M_n = 6,800$ ,  $M_w = 11,000$ ;  $M_w/M_n = 1.62$ ).

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 8.4~7.3 (m, 8H, aromatic and  $-\text{CH}=\text{C}(\text{CN})-$ ), 4.008 (s, 3H,  $-\text{OCH}_3$ ), 2.954 (s, 2H,  $-\text{SCH}_2-$ ), 1.578~1 (m, 9H, alkylthio), 1~0.6 (m, 3H,  $-\text{CH}_3$ ).

#### Poly[m-phenyleneazomethine-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenyleneazomethine] (m-C=N)

Compound 3 (285 mg,  $9.24 \times 10^{-1}$  mmole) and 1,3-phenyldiamine (100 mg,  $9.24 \times 10^{-1}$  mmole) were dissolved in DMAc (20 ml) and were rapidly heated to 155 °C. Then the mixture was coagulated from MeOH, a yellow powder was filtered and was purified from MeOH by the same coagulation procedure for additional 2 times. m-CN (138.9 mg, 36% of yield) thus obtained indicated  $M_n = 6,300$ ;  $M_w = 7,400$ ;  $M_w/M_n = 1.17$ .

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 8.966 (s, 1H,  $-\text{CH}=\text{N}-$ ), 8.344 (s, 1H, aromatic), 7.833 (s, 1H, aromatic), 7.19~7.125

(m, 4H, =N-C<sub>6</sub>H<sub>4</sub>-), 4.03 (s, 3H, -OCH<sub>3</sub>), 2.906 (d, 2H, -SCH<sub>2</sub>-), 1.584~1.224 (m, 9H, alkylthio), 0.9~0.7 (m, 6H, CH<sub>3</sub>).

*Poly[p-phenyleneazomethine-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenyleneazome-thine] (p-C=N)*

Exactly the same procedure of preparing m-CN was followed except the use of compound 3 (285 mg, 9.24 × 10<sup>-1</sup> mmole) and 1,4-phenylenediamine (100 mg, 9.24 × 10<sup>-1</sup> mmole) as starting materials. The m-CN polymer thus obtained was an orange color (146.6 mg, yield 38%). GPC ( $M_n = 4,100$ ;  $M_w = 6,100$ ;  $M_w/M_n = 1.49$ ).

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 9.008 (s, 1H, -CH=N-), 8.372 (s, 1H, aromatic), 7.872 (s, 1H, aromatic), 7.5~7.3 (m, 4H, =N-C<sub>6</sub>H<sub>4</sub>-), 4.063 (s, 3H, -OCH<sub>3</sub>), 2.957 (s, 2H, -SCH<sub>2</sub>-), 1.634~1.212 (m, 9H, alkylthio), 0.939~0.823 (m, 6H, -CH<sub>3</sub>).

*Poly[m-phenylenevinylene-co-2-methoxy-(2'-ethylhexylthio)-p-phenylenevinylene] (m-C=C) [2]*

Into compound 4 (670 mg, 7.38 × 10<sup>-1</sup> mmole) and isophthalaldehyde (100 mg, 99%, 7.38 × 10<sup>-1</sup> mmole) in 6 ml of CHCl<sub>3</sub>, t-BuOK (342 mg, 97%, 2.956 mmole) in 2 ml of anhydrous EtOH was rapidly added. The reaction mixture was stirred for 2 days, and was coagulated from MeOH containing 1 ml AcOH. The crude m-CC was purified by the same procedure for 3 additional times, and was a green color (70 mg, 35% of yield) with  $M_n = 4,100$ ;  $M_w = 6,200$ ;  $M_w/M_n = 1.51$ .

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 7.919~6.919 (m, 6H, aromatic), 6.668~6.543 (m, 4H, -CH=CH-), 3.984 (s, 3H, -OCH<sub>3</sub>), 2.828 (d, 2H, -SCH<sub>2</sub>-), 1.574~1.0 (m, 9H, alkylthio), 1.0~0.7 (m, 6H, -CH<sub>3</sub>).

*Poly[p-phenylenevinylene-co-2-methoxy-5-(2'-ethylhexylthio)-p-phenylenevinylene] (p-C=C)*

The same procedure as preparing m-CC was followed except for the use of compound 4 (662 mg, 7.306 × 10<sup>-1</sup> mmole) and terephthalaldehyde (100 mg, 7.306 × 10<sup>-1</sup> mmole) to replace the starting materials. P-CC obtained indicated a yellowish green powder (73 mg, 37% of yield) with  $M_n = 4,500$ ;  $M_w = 6,400$ ;  $M_w/M_n = 1.42$ .

<sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): δ 8.9~7.0 (m, 6H, aromatic), 6.9~6.5 (m, 4H, -CH=CH-), 4.003 (s, 3H, -OCH<sub>3</sub>), 2.821 (d, 2H, -SCH<sub>2</sub>-), 1.6~1.0 (m, 9H, alkylthio), 0.9~0.7 (m, 6H, -CH<sub>3</sub>).

The synthetic procedures are given in the synthetic scheme for monomers and copolymers.

*Polymer Films*

All films were prepared by spin coating on quartz plates (1500 rpm for 9 sec followed by 2,000 rpm for 9 sec) from THF (series I and II) or CHCl<sub>3</sub> (series III). Solutions were pre-filtered through a 0.2 μm pore of filtration. Films with approximately 1000 Å were measured with a surface profiler (Dektak-3030) and were used for UV and PL spectrometry.

Table 1. Comparisons of characterization data for series I, II and III

	Polymers	$M_n^a$	$M_w$	PDI	$T_g$ (°C)	TGA(-5 wt%, °C)
Series I	m-C=C(CN)	9000	14000	1.56	79	344
	p-C=C(CN)	6800	11000	1.62	111	368
Series II	m-C=N	6300	7400	1.17	135	370
	p-C=N	4100	6100	1.49	144	381
Series III	m-C=C	4100	6200	1.51	96	365
	p-C=C	4500	6400	1.42	124	367

<sup>a</sup> $M_n$ ,  $M_w$ , PDI determined by GPC using THF (solvent) and polystyrene (standard).

Table 2. Comparisons of the optical data for series I, II and III

	Polymers	UV $\lambda_{max}$ (nm)	$E_g^a$ (nm/eV)	PL $\lambda_{max}$ (nm)	Thickness of film (Å)
Series I	m-C=C(CN)	359	560/2.21	579	1035
	p-C=C(CN)	386	572/2.17	594	1044
Series II	m-C=N	397	520/2.38	512	1005
	p-C=N	459	555/2.23	536	1014
Series III	m-C=C	382	442/2.81	482	1042
	p-C=C	420	540/2.30	531	1001

<sup>a</sup> $E_g$ : energy gap, LUMO-HOMO = energy gap.

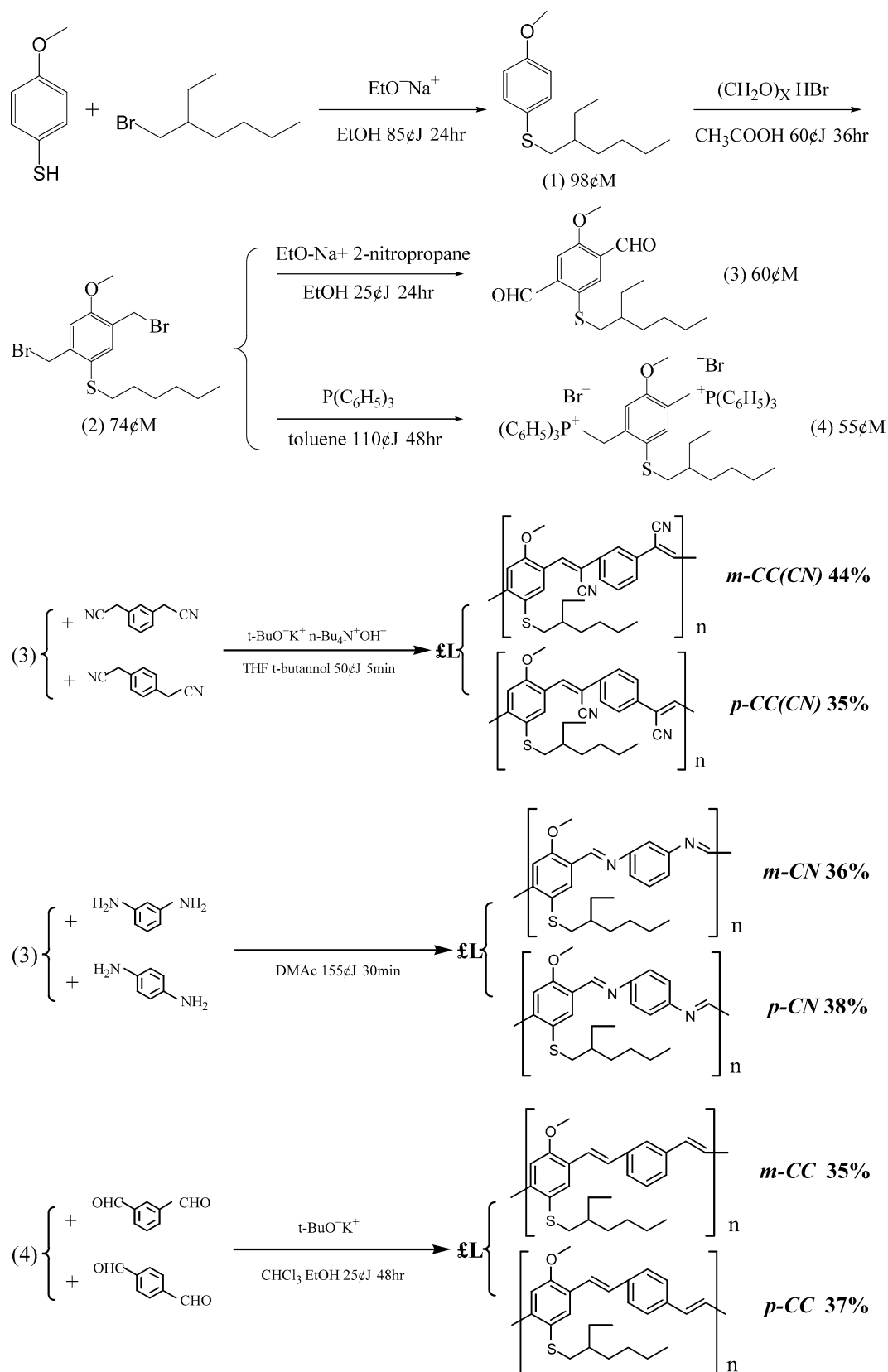
*Fabrication of EL Device*

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) was spin-coated on well cleaned ITO substrate and dried at 120 °C to obtain a film of thickness approximately 700 Å. m-CC(CN) in 1,1,2,2-tetrachloroethane solution and was spin-coated on a (PEDOT:PSS) layer and dried at 50 °C for 30 min. Approximately 700 Å thickness of m-CC(CN) film appeared homogeneous under an optical microscope. LiF (20 Å) : Al (1500 Å) layers as a cathode were formed by using a standard vacuum-vapor deposition procedure.

**Results and Discussions**

The general synthetic route toward the monomers and polymers is outlined in Scheme 1. Series I (m-C=C(CN), p-C=C(CN)) and series III (m-C=C, p-C=C) are soluble in common organic solvents such as THF, DMF, DMAc and chlorinated solvents like CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane. However, series II (m-C=N, p-C=N), indicate the characteristic solubility nature of polyazomethines, and can only be soluble in chlorinated solvents such as CHCl<sub>3</sub>, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane.

Table 1 shows the characterization data of thermal analyses for series I, II and III. Series II have higher  $T_g$ 's and best thermal stability than series I and III. In addition, better meta-linkages (m-C=C(CN), m-C=N, m-C=C) have lower  $T_g$ 's as compared with p-linkages (p-C=C(CN), p-C=N, p-C=C). This is because the asymmetry and irregularity of



Scheme 1. Synthetic scheme of model compounds and polymers.

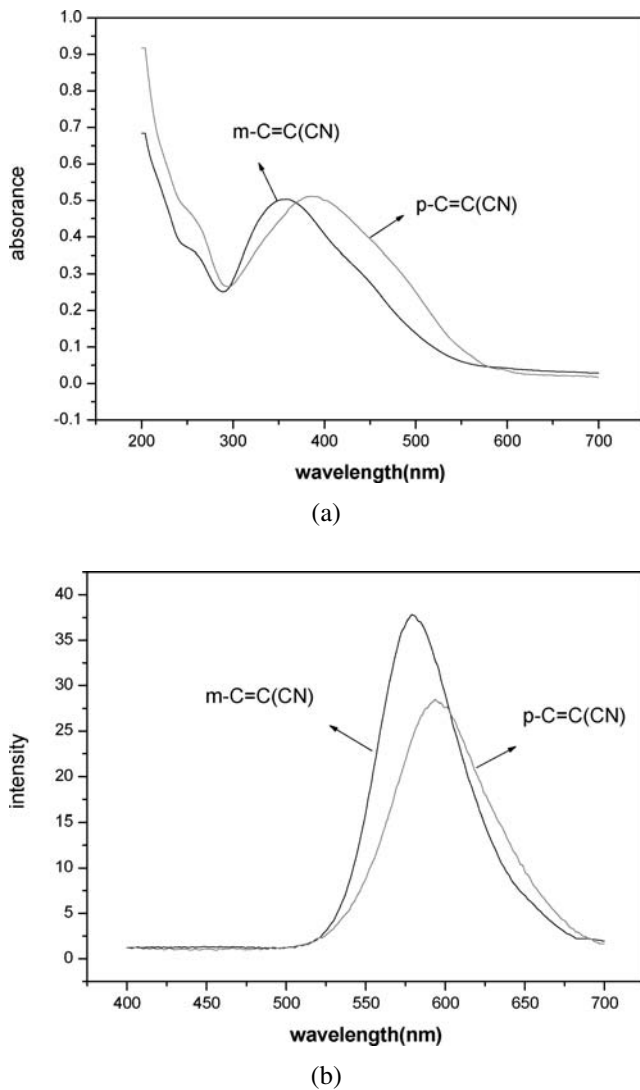


Figure 1. UV absorption (a) and PL emission (b) spectra for series I m-C=C(CN) and p-C=C(CN) copolymer films.

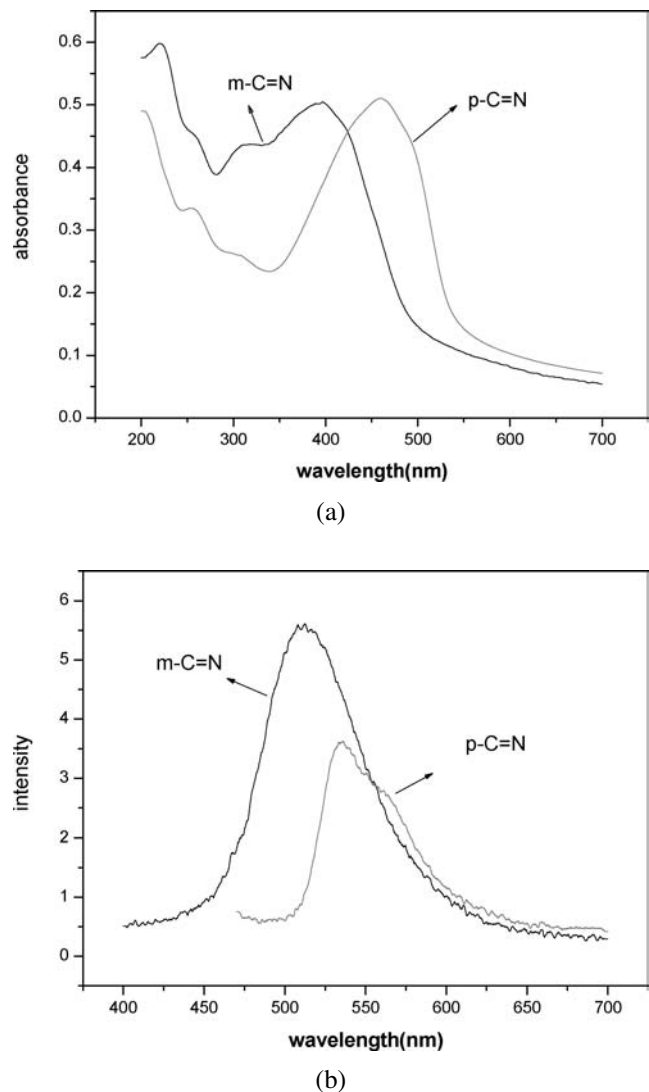


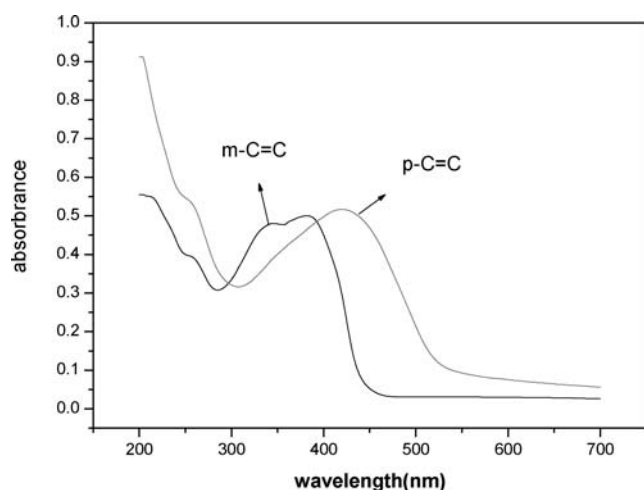
Figure 2. UV absorption (a) and PL emission (b) spectra for series II m-C=N and p-C=N copolymer films.

meta-linkage in the main chain lead to more amorphous portions. Furthermore, for series I and III, the 5% of weight loss occurs at around 344 to 381 °C, lower than reported PPVs containing oxy group (about 400 °C), because our copolymers contain the alkylthio group (713.4 KJ/mol of C-S bond energy), which has lower bond strength than the C-O bond (1076.5 KJ/mol of bond energy) for other PPV derivatives [11].

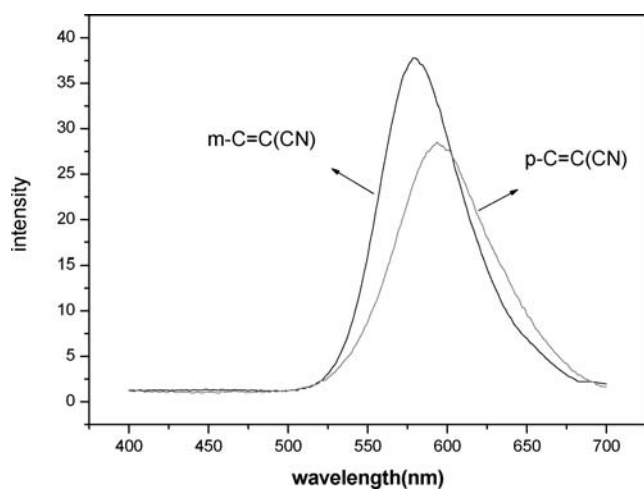
Figures 1, 2 and 3 show the UV absorbances and PL emissions for series I, II and III, respectively. Data were collected from copolymer films on quartz plates about 1000 Å of film thickness and are summarized in Table 2. It appears that all meta-linkages indicate blue shift in the maximum wave length of PL emissions ( $\lambda_{\max}$ ). The  $\lambda_{\max}$  values are: m-C=C(CN), 579 nm; m-C=N, 512 nm; m-C=C, 482 nm which can be compared with all para-linkages: p-C=C(CN), 594 nm; p-C=N, 536 nm; p-C=C, 531 nm. Because the asymmetry and irregularity of the meta-linkages in the main chain have shorter effective conjugation length than the p-linkages, the band gaps in meta-linkages are relatively larger and thus show blue shift [12–16]. Furthermore, all

meta-linkages show stronger PL intensities than the corresponding para-linkages of similar structures, because the asymmetry and irregularity of the molecular array lead to more amorphous portions, less intermolecular aggregation and less excimer formation, thus to interpret the observed phenomena [17, 18]. H. K. Shim and coworkers [2], in their study of the optical properties for o-PMEH-PPV, m-PMEH-PPV and p-PMEH-PPV, found that the order of PL intensity was in the order of m-PMEH-PPV > o-PMEH-PPV > p-PMEH-PPV. A similar conclusion was observed by S. Son et al. in [12].

Shim reported poly[2-(2'-ethylhexylthio)-5-methoxy-1,4-phenylenevinylene] (MEHTPPV) shows a blue shift of the  $\lambda_{\max}$  and less electric conductivity, as compared with MEHPPV [3, 4]. They infer that the sulfur atom in MEHTPPV has less electron donating capability than oxygen and thus broaden the band gap between the valence band and the conduction band and so they interpret the blue shift. All copolymers in this study contain alkylthio group at the side chains. The  $\lambda_{\max}$  for series III show blue shift,



(a)



(b)

Figure 3. UV absorption (a) and PL emission (b) spectra for series III m-C=C and p-C=C copolymer films.

compared with m-PMEH-PPV and p-PMEH-PPV. Anderson reported a  $\lambda_{\max}$  of 570 nm for poly[2-(2'-ethylhexylthio)-5-methoxy-1,4-phenyleneimine] (MEH-PPI), a polyazomethine which also shows a blue shift [19], just like the case of our p-C=N ( $\lambda_{\max}$  of 536 nm). All these results support the inference of Shim and coworkers.

In a comparison of the optical properties for our copolymer systems, it appears that the order of decreasing  $\lambda_{\max}$  of PL are: series I (m- and p-C=C(CN)) > series II (-C=N-) > series III (-C=C-). Compared with series III, series II shows a red shift because of the electron-withdrawing character of the -C=N- bond; series I shows even further red shift because of the stronger electron-withdrawing of the CN group on the -C=C- chain. Such electron-withdrawing groups enhance the electron affinity, subsequently leading to lowering the LUMO energy level and thus decreasing the band gap [5]. Series II (-C=N-) indicates much lower PL intensity than series I and III, presumably because the lone pair electrons on the nitrogen atom partially conjugate with those

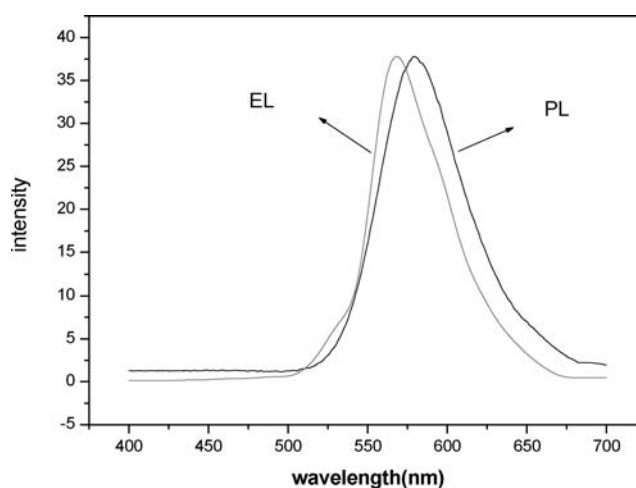


Figure 4. EL and PL emission spectra for the device ITO/PEDOT:PSS/m-C=C(CN)/LiF/Al.

$\pi$ -electrons in the benzene ring, and shorten the effective conjugation length, as interpreted by Jenekne [20].

Although the presence of sulfur in conjugated polymer is not helpful to enhance the EL property of materials, however, an EL device of ITO/PEDOT:PSS (700 Å)/m-C=C(CN) 9700 Å/LiF (20 Å)/Al (1500 Å) was made. A yellow light of  $\lambda_{\max}$  570 nm was observed in the EL under 9 V of driving voltages (Figure 4). The  $\lambda_{\max}$  of EL has a somewhat blue shift compared with the  $\lambda_{\max}$  of PL. I-V and L-V curves were not obtained because of the short lifetime and lack of facility in our laboratory. No EL emission was observed for a similar EL device based on p-C=C(CN) film, presumably because the lifetime and quantum efficiency are too low to be detected.

## Conclusions

Six alkythio-containing soluble copolymers of poly(phenylene vinylenes) and poly(phenylene azomethines) in meta- and para-linkages were synthesized and characterized. Meta-linkage copolymers had more amorphous portions and showed lower  $T_g$ 's than para-linkage copolymers. All alkythio-containing copolymers indicated lower thermal stability than literature reported alkyloxy containing PPVs.

Meta-linkage copolymers showed blue shift and stronger intensity than para-linkage copolymers in their optical properties, presumably because the asymmetry and irregularity of the meta-linkage copolymers shorten the effective conjugation length and have less molecular aggregation and excimer formation. The existence of an alkythio side chain in the copolymers showed blue shift, when compared with those copolymers containing alkyloxy side chain. The PL  $\lambda_{\max}$  showed in the order: series I (-C=C(CN)-) > series II (-C=N-) > series III (-C=C-), indicating the electron withdrawing capability of conjugating -C=N- group lies between -C=C- and -C=C(CN)-, in which the CN group is the strongest. However, series II also showed the weakest PL intensity, because the lone pair electrons on the N atom partially overlap with the six  $\pi$  electrons in the

benzene ring, and thus lead to distortion of the coplanar nature. Finally, a device of the structure ITO/PEDOY:PSS/m-C=C(CN)/LiF/Al was made and showed an EL  $\lambda_{\max}$  of 570 nm.

### Acknowledgement

The authors would like to express their sincere appreciation to the National Science Council for financial support under contract No. NSC 90-2216-E-009-021.

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