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# Synthesis, characterization and hydrolysis of aromatic polyazomethines containing non-coplanar biphenyl structures

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#### ABSTRACT

New polyazomethines containing electron-withdrawing trifluoromethyl group and non-coplanar biphenyl structures were prepared at room temperature under reduced pressure. It was found that these polyazomethines would undergo hydrolysis in DMSO solution at temperature higher than 50 °C. The hydrolysis, evidenced by <sup>1</sup>H NMR spectra and GPC chromatograms, was resulted from the reverse reaction of azomethine formation and was facilitated at higher temperature. The GPC results also suggested that post-polymerization would be possible if polyazomethine films were heated at elevated temperature (200 °C) under reduced pressure (0.27 torr). The HOMO (-5.69 to -5.96 eV) and LUMO (-3.04 to -3.18 eV) energy levels of the new polyazomethines are much lower than those of other polyazomethines. Combined with the excellent solubility and good thermal stability, non-coplanar biphenyl structure containing electron-withdrawing trifluoromethyl group could be a new candidate as electron acceptor for the structure design of new conjugated polymers.

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# 1. Introduction

Aromatic polyazomethines, containing C=N linkage, exhibit excellent thermal stability, good mechanical properties and, in some cases, liquid crystalline morphology [1]. In addition to high performance fiber and metal-chelating ability [2,3], they have been also investigated for the opto-electrical applications such as holetransport layer for OLED, semiconductor, non-linear optics (NLO) and photovoltaic cell [4-7]. However, these applications have been limited by their poor solubility in common organic solvents and low molecular weights. Besides, the relatively rare availability of new dialdehyde monomers also hindered the chemical structure modifications of polyazomethines. Many strategies have been reported to improve the solubility of polyazomethines. The introduction of flexible alkyl and alkoxy groups as the substituents has been proved to be effective, although at the expense of their thermal stability [8–10]. The incorporations of bulky substituents such as triphenylamine, tetraphenylethylene and diphenylfluorene, have been investigated [11–13]. The copolymerization of electronrich, solubility-enhancing aromatic or heterocyclic units such as thiophene, carbazole and fluorene [14–17], has also been explored. The C=N linkages of polyazomethines are electron-withdrawing group and therefore can be used to tune the HOMO and LOMO energy levels of the electron-rich conjugated polymers to fit the best combination of energy levels and charge mobility in a multilayer device. However, in most cases, the enhancements in solubility of these conjugated polymers are resulted from the long alkyl or alkoxy side chains attached on the electron-rich units, leading to lower thermal stability.

The chemical modifications of polyazomethines are mainly achieved by synthesizing new diamines and then polymerizing them with commercially available dialdehydes. These attempts targeting at either solubility enhancement or investigating their optical and electrical properties are limited by the rare availability of new dialdehyde monomers. Most dialdehyde monomers are prepared by electrophilic substitution (Vilsmeier reaction) on an electron-rich aromatic or heterocyclic ring [18]. The preparation of new dialdehydes by the reduction of cyano group has rarely been reported [19].

Conventionally, polyazomethines are prepared by solution polymerization from diamines and dialdehydes either at room temperature or at higher temperature [20]. The premature precipitation during polymerization, as a result of poor solubility, often leads to low molecular weight products. Even for soluble polyazomethines, it is often difficult to achieve high molecular weight. Several polymerization conditions have been applied. In some cases, LiCl was used as the water absorption agents [21]. It has also been demonstrated that polymerization at room temperature





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under vacuum in weakly acidic *m*-cresol is the best method to obtain the highest molecular weight [13]. However, the reason has not been fully explained. In addition, the formation of azomethine linkage is, like esterification, actually reversible. In the presence of water, hydrolysis might predominate under suitable conditions [22]. However, this issue has never been addressed in polyazomethine study.

In this study, a new aromatic dialdehyde containing electronwithdrawing trifluoromethyl groups at the 2 and 2' positions of biphenyl was synthesized. The aldehyde functionality was achieved by the reduction of cyano groups. Organosoluble polyazomethines were prepared from this dialdehyde with 2,2'-disubstituted-4,4'benzidines, 4,4'-oxydianiline and *p*-phenylenediamine by solution polycondensation at room temperature under reduced pressure. The hydrolysis of azomethine linkages at the presence of trace water was investigated by <sup>1</sup>H NMR spectroscopy and GPC chromatography. The thermal, optical and electrochemical properties of these new polyazomethines were also investigated. The effects of strong electron-withdrawing trifluoromethyl groups and noncoplanar biphenyl structures on the HOMO and LUMO energy levels were also discussed.

# 2. Experimental

# 2.1. Materials

Tetrabutylammonium perchlorate (TBAP) used in cyclic voltammetric measurements was recrystallized twice with ethyl acetate and dried at 120 °C under reduced pressure overnight. All of other reagents were purchased from commercial companies and used as received. All of the solvents used in this study were purified according to standard methods prior to use. 2,2'-Dimethyl-4,4'benzidine (**DMB 6**) and 2,2'-bis(trifluoromethyl)-4,4'-benzidine (**TFMB 7**) were synthesized according to reported procedures with some modifications [23,24].

#### 2.2. Measurements

All melting points were determined on a Mel-Temp capillary melting point apparatus. Proton (<sup>1</sup>H NMR) and carbon (<sup>13</sup>C NMR) nuclear magnetic resonance spectra were measured at 500 and 125 MHz on a Bruker Avance-500 spectrometer, respectively. Infrared spectra were obtained with a Digilab-FTS1000 FTIR. Mass spectroscopy was conducted on a Finnigan TSQ 700 mass spectrometer. Elemental analyses were performed on a Heraeus Vario analyzer. High performance liquid chromatography was performed on a JASCO HPLC system equipped with a UV (254 nm) detector using a Thermo Hypersil column (250 mm  $\times$  4.6 mm, particle size 5  $\mu$ m) with an 80/20 (v/v) acetonitrile/water mixture as the solvent. Inherent viscosities were determined with a Cannon–Ubbelohde No. 100 viscometer at  $30.0 \pm 0.1$  °C in *N*-methyl-2pyrrolidinone (NMP). Molecular weights were measured on a JASCO GPC system (PU-980) equipped with an RI detector (RI-930), a Jordi Gel DVB Mixed Bed column (250 mm  $\times$  10 mm) column, using dimethylacetamide (DMAc) as the eluent and calibrated with polystyrene standards. Thermal gravimetric analyses (TGA) were performed in nitrogen with a TA TGA Q500 thermogravimetric analyzer using a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimeter (DSC Pyris 1) was used to measure the glass transition temperatures under nitrogen at a heating rate of 10 °C min<sup>-1</sup>. UV-visible measurements were carried out on a Cary-100 UV-Visible spectrometer at room temperature. Photoluminescence (PL) measurements were carried out on a Perkin-Elmer F4500 photoluminescence spectrometer. Fluorescence quantum yield  $(\Phi_{\rm PI})$  of the polymer in chloroform was measured by  $10^{-5}$  M quinine sulfate in 1 N H<sub>2</sub>SO<sub>4</sub> as reference standard ( $\Phi_{PL} = 0.546$ ). Cyclic voltammetric (CV) measurements were carried out on a CH Instrument 611C electrochemical analyzer at room temperature in a three-electrode electrochemical cell with a working electrode (polymer film coated on ITO glass), a reference electrode (Ag/Ag<sup>+</sup>, referenced against ferrocene/ferrocium (Fc/Fc<sup>+</sup>), 0.09 V), and a counter electrode (Pt gauze) at a scan rate of 100 mV s<sup>-1</sup>. CV measurements for polymer films were performed in an electrolyte solution of 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. The potential window at oxidative scan was 0–2.5 V and reductive scan was 0 to –2.5 V, respectively. The wide-angle Xray diffraction (WXRD) data were collected on a PANalytical X'Pert PRO X-ray powder diffraction.

#### 2.3. Synthesis of monomers

Monomers (1)–(4) were synthesized by procedures in our previous work [33].

#### 2.3.1. 2,2-Bis(trifluoromethyl)-4,4-biphenyldicarbaldehyde (5)

To a 100 mL, three-neck, round-bottom flask equipped with condenser and mechanical stirrer were added 0.30 g (0.88 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbonitrile (4) and 10 mL of toluene. After 9 mL (10.09 mmol) of diisobutylaluminium hydride (DIBAL-H) (20% in hexane) was slowly added with a syringe under nitrogen atmosphere, the reaction mixture was further stirred at 16 °C for 18 h under nitrogen atmosphere. The reaction mixture was then poured into a vigorously stirred solution of methanol/water (1:1, v/v) and kept at 0 °C with ice bath for 3 h. After 200 mL of 2M HCl solution was added, the mixture was extracted with 200 mL of ether twice. The combined organic phase was collected and washed many times with water and dried with anhydrous magnesium sulfate. The organic phase was evaporated and dried under reduced pressure at 60 °C overnight. The crude product was then sublimated under reduced pressure at 70 °C to afford 0.18 g (59.0% yield) of white crystals: mp 118-120 °C; FTIR (KBr) :  $2757 \text{ cm}^{-1}$  (aldehyde C–H stretching), 1705 cm<sup>-1</sup> (aldehyde C=0 stretching). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 10.17 (s, 2H, aldehyde-H<sub>d</sub>), 8.41 (d, J = 0.8 Hz, 2H, Ar-H<sub>a</sub>), 8.26 (dd, J = 0.8and 8.0 Hz, 2H, Ar $-H_b$ ) and 7.70 (d, J = 8.0 Hz, 2H, Ar $-H_c$ ). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, δ, ppm): CF<sub>3</sub> (q) (C7) 119.99, 122.17, 124.35, 126.54, C-CF3 (q) (C6) 127.63, 127.87, 128.12, 128.37, 127.24 (C5), 131.80 (C2), 132.36 (C3), 136.41 (C4), 141.00 (C1), 191.87 (C8). EIMS (*m*/*z*): Calcd. for C<sub>16</sub>H<sub>8</sub>F<sub>6</sub>O<sub>2</sub>: 346.0428; Found: 346.0 [M] <sup>+</sup>; 344.9 [M – 1]<sup>+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>8</sub>F<sub>6</sub>O<sub>2</sub>: C: 55.50, H: 2.33%; Found : C: 55.51%, H: 2.45%.



#### 2.3.2. 3,3'-Dibromoazoxybenzene

To a 250 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, and a stopper were added 60 mL of ethanol and 21.20 g (530.00 mmol) of sodium hydroxide. The reaction mixture was heated at 70 °C until most of sodium hydroxide was dissolved. After 66.4 mL of ethylene glycol and 10.00 g (49.50 mmol) of 1-bromo-3nitrobenzene were added, the reaction mixture was heated at reflux for 2 h. The warm mixture was poured into 300 mL of ice water and stirred for 30 min. The brown solid that formed was collected by filtration and washed

several times with water. After drying under reduced pressure at 90 °C overnight, 7.71 g (80.0% yield) of crude product was obtained. The crude product was used in the next procedure without further purification. A small portion of crude product was decolorized with charcoal and recrystallized from acetone to afford a yellow powder: mp 114–115 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 8.42–7.25 (m, 8H, Ar–H<sub>a–d</sub>).

# 2.3.3. 2,2'-Dibromo-4,4'-diaminobiphenyl (8)

To a 250 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, and a thermometer were added 18.50 g (12.45 mmol) of 3,3'-dibromoazoxybenzene, 115 mL of tetrahydrofuran and 161 mL of glacial acetic acid. Zinc dust (12.90 g) was added slowly so the temperature of the reaction mixture was maintained below 40 °C. After the addition of zinc dust, 23 mL of 85% phosphoric acid was added slowly so the temperature of the reaction mixture was maintained below 55 °C. After stirring for 30 min, the reaction mixture was filtered to remove zinc dust. The filtrate was poured into 300 mL of water. The aqueous phase was extracted twice with 100 mL of methylene chloride. The combined organic phase was added dropwise to 60 mL of conc. hydrochloric acid at 0 °C and stirred for 30 min. The precipitate that formed was collected by filtration and washed with methylene chloride and then dissolved in 1 L of hot water. After the solution was filtered, the clear filtrate was neutralized with ammonium hydroxide. The precipitate that formed was collected and recrystallized from toluene to afford 9.02 g (56.0% yield) of white crystal: mp 151–153 °C (lit [25]. mp 152–156 °C); <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, δ, ppm): 6.85–6.81 (m, 4H, Ar–H<sub>a.c</sub>), 6.54 (dd, I = 2.0 and 8.2 Hz, 2H, Ar-H<sub>b</sub>) and 5.35 (s, 4H, NH<sub>2</sub>-H<sub>d</sub>).



# 2.3.4. 2,2'-Diphenyl-4,4'-diaminobiphenyl (9)

To a 250 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet were added 3.00 g (8.76 mmol) of 2,2'-dibromo-4,4'-diaminobiphenyl (**8**) and 54 mL of toluene. After the solution was heated at 50 °C under nitrogen and became clear, 4.26 g (40.00 mmol) of sodium carbonate in 18 mL of water and 0.66 g (0.57 mmol) of  $Pd(P(Ph_3))_4$  were added. After the solution was vigorously stirred for 30 min, a solution of 2.70 g (22.14 mmol) of phenylboronic acid in 18 mL of

ethanol was added. The reaction solution was heated at reflux for 24 h under nitrogen. After the reaction mixture was allowed to cool to room temperature, it was filtered to remove insoluble components. The filtrate was collected and washed several times with a saturated NaCl aqueous solution. After dried with anhydrous magnesium sulfate, the combined organic phase was evaporated to dryness under reduced pressure. The crude product was recrystallized from a mixture of water and methanol to afford 2.10 g (71.0% yield) of light-brown crystals. mp 152–153 °C (lit [26]. mp 151–152 °C); <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 7.07–7.03 (m, 6H, Ar–H<sub>f</sub>g), 6.83 (d, *J* = 7.7 Hz, 2H, Ar–H<sub>c</sub>), 6.47 (d, *J* = 6.9 Hz, 4H, Ar–H<sub>e</sub>), 6.66 (d, *J* = 7.7 Hz, 2H, Ar–H<sub>b</sub>), 6.34 (s, 2H, Ar–H<sub>a</sub>) and 5.00 (s, 4H, NH<sub>2</sub>–H<sub>d</sub>).



#### 2.4. Synthesis of polyazomethines

Polvazomethines **PAM-1–7** were prepared by solution polvmerization using equimolar dialdehvde and diamine at room temperature under reduced pressure (0.27 torr). The synthesis of **PAM-2** was used as an example to illustrate the general synthetic procedure. To a 100 mL, three-neck, round-bottom flask were added 0.50 g (1.40 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbaldehyde (5), 0.45 g (1.40 mmol) of diamine (7) and 10 mL of *m*-cresol. After the reaction mixture was stirred at room temperature for 48 h under reduced pressure, it was poured into a mixture of methanol and water (1:1, v/v). The precipitate that formed was collected by filtration and washed with hot ethanol (Soxhlet apparatus) for 12 h and dried at 100 °C overnight under reduced pressure to afford 0.85 g (96.0% yield) of powder. IR (KBr): 3402 cm<sup>-1</sup> (NH<sub>2</sub> end group), 3057 cm<sup>-1</sup> (aromatic), 2735 cm<sup>-1</sup> (aldehyde end group O = C - H stretching), 1702 cm<sup>-1</sup> (aldehyde end group O=C stretching), and 1625 cm<sup>-1</sup> (azomethine C=N stretching). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 10.19 (d, J = 7.0 Hz, 1H, aldehyde end group), 9.02 (d, J = 4.5 Hz, 2H, azomethine HC=N), 8.51 (d, J = 6.0 Hz, 2H, Ar-H), 8.36-8.34 (m, 2H, Ar–H), 7.84 (d, J = 6.0 Hz, 2H, Ar–H), 7.72–7.63 (m, 4H, Ar–H) and



Scheme 1. Synthesis of 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbaldehyde (5).

7.54 (d, J = 7.5 Hz, 2H, Ar–H) and 5.74 (br, 2H, NH<sub>2</sub> end group). The inherent viscosity of the obtained **PAM-2** was 0.50 dL/g (measured at a concentration of 0.5 g/dL in NMP at 30 °C). The other polyazomethines were prepared by the same procedure.

#### 3. Results and discussion

#### 3.1. Synthesis of monomers

The new dialdehyde, 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbaldehyde (5), containing electron-withdrawing trifluoromethyl groups at the 2 and 2' positions of biphenyl, was synthesized by a five-step synthetic route as shown in Scheme 1, 2-Aminobenzotrifluoride was first brominated at the para position by *N*-bromosuccinimide (NBS) in DMF. The aromatic bromide (1) that formed was converted to cyanide compound (2) by copper cyanide in NMP. The amino group of compound (2) was then transformed to aromatic iodide (3) by diazotization then Sandmever reaction. The iodide compound (**3**) was coupled by Ullmann coupling reaction in the presence of activated copper powder in DMF to form 2.2'-bis (trifluoromethyl)-4,4'-biphenyldicarbonitrile (4). The new dialdehyde (5) was then obtained by the reduction of cyano compound (4) using diisobutylaluminium hydride (DIBAL-H) as reducing agent. The as-prepared dialdehyde was purified by sublimation at 70 °C under reduced pressure before polymerization. <sup>1</sup>H NMR spectrum of dialdehyde (5) is shown in Fig. 1(a). The singlet peak at 10.17 ppm was attributed to the aldehyde hydrogen. The other absorption peaks in the aromatic region (7-9 ppm) were assigned to the corresponding hydrogen as shown in Fig. 1(a). IR spectrum of dialdehyde (**5**) is shown in Fig. 2. The absorption peaks at 2757 cm<sup>-1</sup> (aldehyde C–H stretching) and 1705 cm<sup>-1</sup> (aldehyde C=O stretching) also showed the formation of aldehyde group. The spectra of <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR, together with the result of elemental analysis, confirmed the structure of the new dialdehyde (**5**). Several approaches to simplify the synthetic route have been carried out without success. For example, the attempt to direct formylation (electrophilic reaction) of 2,2'-bis(trifluoromethyl)biphenyl by POCl<sub>3</sub> and DMF was unsuccessful. It might be resulted from the electron deficiency of the biphenyl moiety due to the presence of strong electron-withdrawing trifluoromethyl group.

Diamines, 2,2'-dibromo-4,4'-benzidine (**8**) and 2,2'-diphenyl-4,4'-benzidine (**9**) were prepared according to the synthetic route shown in Scheme 2. First, 1-bromo-3-nitrobezene was reduced to azoxy compound, which then underwent benzidine rearrangement in the presence of zinc dust to form 2,2'-dibromo-4,4'-benzidine (**8**). 2,2'-Diphenyl-4,4'-benzidine (**9**) was then obtained by Suzuki coupling reaction between phenylboronic acid and diamine (**8**).

# 3.2. Synthesis of polyazomethines

Polyazomethines **PAM-1**–**7** were prepared in quantitative yields by reacting equimolar diamines and dialdehydes in *m*-cresol at



Fig. 1. <sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> of (a) monomer (5), (b) as-prepared PAM-2 (soluble part) and hydrolysis of PAM-2 with various condition, (c) 50 °C for 12 h in air, (d) 150 °C for 24 h in nitrogen.



Fig. 2. IR spectra of monomers (5), (6) and PAM-1 (KBr).

room temperature under reduced pressure as shown in Scheme 3. Polyazomethines **PAM-1–4** were prepared by using the new trifluoromethyl-containing dialdehyde (**5**) and four substituted benzidines (**6–9**). The substituents of these benzidines included methyl (**PAM-1**), trifluoromethyl (**PAM-2**), bromide (**PAM-3**) and phenyl (**PAM-4**). 4,4'-Oxydianiline (**ODA**) and *p*-phenylenediamine (**PDA**) were also used to prepare polyazomethines **PAM-5** and **PAM-6**, respectively. In comparison to **PAM-6**, **PAM-7** was prepared by reacting terephthalic dicarbaldehyde (**TPDCA**) with 2,2'-bis(trifluoromethyl)-4,4'-benzidine (**TFMB 7**). All the polyazomethines **PAM-1–7** remained in solution without any premature precipitation throughout the polymerization and were prepared in quantitative yields (Table 1). A representative IR spectrum of **PAM-1** is shown in Fig. 2. The characteristic peak appearing at 1615 cm<sup>-1</sup> (C—N stretching) confirmed the formation of azomethine linkage. A representative <sup>1</sup>H NMR spectrum of as-prepared **PAM-2** (soluble part in DMSO-d<sub>6</sub>) is shown in Fig. 1(b). Because of the limited solubility of **PAM-2** in DMSO-d<sub>6</sub>, <sup>1</sup>H NMR sample was prepared by dissolving 0.1% (w/v) as-prepared **PAM-2** in DMSO-d<sub>6</sub> at room temperature and then removing the insoluble part by filtration. The peaks appearing at 9.02 ppm were assigned to the hydrogen of the azomethine linkage. These peaks suggested the existence of *syn* and *anti* configurations in the polymer backbone as reported earlier [27,28]. It was also found from the <sup>1</sup>H NMR spectrum of **PAM-2** 



**Scheme 2.** Synthesis of 2,2'-diphenyl-4,4'-diaminobiphenyl (9).

soluble part that an appreciated amount of chain-end aldehyde (10.19 ppm) remained. However, it was surprising that the absorption peak of amine end groups (5.74 ppm) was almost invisible. It might be resulted from the slow exchange rate of

able 1 hherent viscosity, M <sub>n</sub> , M <sub>w</sub> and yield of polyazomethines.				
	$\eta_{inh}{}^{a} \left( dL/g \right)$	$M_n^b (10^4 \text{ g/mol})$	M <sub>w</sub> <sup>b</sup> (10 <sup>4</sup> g/mol)	
DANG 1	0.70	2.4	75	

				(70)
PAM-1	0.79	2.4	7.5	96
PAM-2	0.50	1.2	2.5	96
PAM-3	0.38	1.3	3.0	98
PAM-4	0.32	1.3	3.0	97
PAM-5	0.33	1.4	3.5	96
PAM-6	0.79	2.0	5.1	96
PAM-7	0.44	1.6	3.7	96

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

<sup>b</sup> By GPC in DMAc (relative to polystyrene standards).

protons on nitrogen and the electrical quadrupole moment of <sup>14</sup>N nucleus. The protons on the nitrogen might respond by giving a broad peak that disappears in the baseline.

# 3.3. Characterizations of polyazomethines

The inherent viscosity and molecular weights (determined by GPC in DMAc and calibrated by polystyrene standards) are reported in Table 1. The as-prepared polyazomethines had inherent viscosity in the range of 0.32–0.79 dL/g (measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C). The number-averaged molecular weights ranged from 12,000 to 24,000 g/mole. These values are high when compared with those of conventional aromatic polyazomethines. The molecular weights estimated from the intensity



Scheme 3. Synthesis of polyazomethines.

Yield

of chain-end aldehyde peak (10.19 ppm) and that of azomethine hydrogen (9.02 ppm) from the <sup>1</sup>H NMR spectra were much smaller than those measured by GPC. It was attributed to the limited solubility of these polyazomethines in DMSO-d<sub>6</sub> solvent. The molecular weights estimated by <sup>1</sup>H NMR spectra represented only the soluble part of polyazomethines in DMSO-d<sub>6</sub>. These polyazomethines were, however, totally soluble in DMAc, the solvent for GPC. Among these polyazomethines, **PAM-1** and **PAM-6**, prepared from the new dialdehyde (**5**) and 2,2'-dimethyl-4,4'-benzidine (**6**) and *p*-phenylenediamine (PDA), respectively, had the highest molecular weights. It might be attributed to the high reactivity of the new aldehyde (**5**) and these two diamines.

Different methods have been reported for the preparation of polyazomethines. These methods involved polymerization at different temperatures, including at toluene-water azeotropic temperature [29], at 160 °C in *m*-cresol [16] or NMP/HMPA [30], and at room temperature with or without reduced pressure [12,13]. In order to find out the best condition to achieve the highest molecular weights, PAM-1 and PAM-2 were prepared for 48 h in m-cresol at room temperature under reduced pressure (condition A), in mcresol at reflux temperature under nitrogen atmosphere (condition B) and in NMP/HMPA (1:1, v/v) at room temperature condition C. Table 2 shows the inherent viscosity and molecular weights of PAM-1 and PAM-2 prepared in different conditions. PAM-1 prepared in *m*-cresol at room temperature under reduced pressure (condition A) had the highest  $M_n$  of 24,000 g/mole. When the temperature was raised to reflux temperature (condition B), PAM-1 had the lowest M<sub>n</sub> of 3000 g/mole. When **PAM-1** was prepared in NMP/HMPA (1:1, v/v) at room temperature for 48 h (condition C), the M<sub>n</sub> was 12,000 g/mole. **PAM-2** experienced the same effect, highest M<sub>n</sub> was obtained by condition A, the lowest M<sub>n</sub> by condition B. From these data, it can be concluded that polyazomethines with the highest M<sub>n</sub> can be obtained by room temperature solution polymerization in *m*-cresol under reduced pressure. It was pointed out that weakly acidic *m*-cresol had an activating effect on the azomethine formation [13]. The dialdehyde was activated by acidic solvents and deactivated by basic solvents. However, too strongly acidic solvent might deactivate diamine. Therefore, weakly acidic solvent such as *m*-cresol might be the best polymerization medium. Table 2 also shows that polyazomethines prepared at room temperature had higher M<sub>n</sub> than at reflux temperature. This phenomenon was to be discussed in the next section (Hydrolysis and Post-Polymerization).

The solubility behavior of these new polyazomethines in different organic solvents is reported in Table 3. All of these polyazomethines can be dissolved (20 mg in 1 mL of solvent) at room temperature in DMF, DMAc, NMP and *m*-cresol and were partially soluble in DMSO and THF. Especially, **PAM-6** and **PAM-7**, containing the most rigid *p*-phenylene structure, were still soluble in polar organic solvents. Conventional aromatic polyazomethines are insoluble in organic solvents. For example, polyazomethine **PAM-8**,

#### Table 2

Inherent viscosity,  $M_n,\,M_w$  and yield of PAM-1 and PAM-2 prepared in different conditions.

	Condition <sup>a</sup>	$\eta_{inh}{}^{b}\left(dL/g\right)$	$M_n^c$ (10 <sup>4</sup> g/mol)	${\rm M_w}^{\rm c}$ (10 <sup>4</sup> g/mol)	Yield (%)
PAM-1	(A)	0.79	2.4	7.5	96
	(B)	0.20	0.3	0.5	98
	(C)	0.53	1.2	2.2	96
PAM-2	(A)	0.50	1.2	2.5	96
	(B)	0.12	0.2	0.3	95
	(C)	0.32	0.4	0.6	96

 $^{a}$  (A) *m*-cresol, at room temperature under reduced pressure for 48 h; (B) *m*-cresol, at reflux for 48 h; (C) NMP/HMPA (1:1, v/v), at room temperature for 48 h.

<sup>b</sup> Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

<sup>c</sup> By GPC in DMAc (relative to polystyrene standards).

Table 3

Solubility	of	polyazomethines.
solubility	of	polyazomethines.

	Solubility <sup>a</sup>							
	m-cresol	NMP	DMF	DMAc	DMSO	THF	Chloroform	Acetone
PAM-1	++	++	++	++	+-	+-	+-	_
PAM-2	++	++	$^{++}$	++	+-	+-	+-	+-
PAM-3	++	++	$^{++}$	++	+-	+-	+-	+-
PAM-4	++	++	$^{++}$	++	+-	+-	+-	+-
PAM-5	++	++	$^{++}$	++	+-	+-	+-	+-
PAM-6	++	++	$^{++}$	++	+-	+-	-	-
PAM-7	++	++	++	++	+-	+-	-	_

Abbreviations: THF, tetrahydrofuran; DMF, dimethylformamide; DMAc, dimethylacetamide; NMP, *N*-methyl-2-pyrrolidinone; DMSO, dimethyl sulfoxide.

<sup>a</sup> The solubility was determined by using 20 mg sample in 1 mL of stirred solvent. ++: soluble at room temperature; +-: partially soluble at room temperature; -: insoluble at room temperature.

containing similar structures with **PAM-6** and **PAM-7**, can be prepared from 4,4'-benzidine with terephthalic dicarbaldehyde (**TPDCA**). It was only soluble in concentrated sulfuric acid [9].



# PAM-8

It has been reported that the C=N linkage of polyazomethine is not in the same plane with the adjacent N-phenyl ring due to the repulsion force between the hydrogen atom of the C=N linkage and the adjacent *N*-phenylene ring [31]. The torsional angle has been calculated to be 30.4°. However, this non-coplanar conformation resulted from C=N linkage alone is not sufficient to provide good solubility for polyazomethines. The excellent solubility of these new polyazomethines PAM-1-7 was resulted from the combined effects of trifluoromethyl groups of the new dialdehyde (5) moiety and the non-coplanar biphenyl structures. The biphenyl structures are forced to adapt a non-coplanar conformation by the bulky substituents at the 2 and 2' positions of biphenyls. Both of trifluoromethyl groups and non-coplanar biphenyls have been incorporated into polyimides [32], polyamides [25] and poly(pbiphenylene-1,3,4-oxidiazole) [33] to enhance the solubility with great success. This enhanced solubility is attributed to the loose interchain packing resulted from the bulkiness of trifluoromethyl groups and non-coplanar biphenyl structures. Furthermore, the same enhancements in solubility of these new polyazomethines were also observed regardless various diamines were used.

Fig. 3 shows the wide-angle X-ray diffraction patterns of polyazomethines **PAM-1–7**. There were no crystalline peaks can be observed, indicating that these new polyazomethines were amorphous in nature. This can be also attributed to their non-coplanar biphenyl structures which might hinder polymer chain packing.

#### 3.4. Hydrolysis and post-polymerization

Because of the limited solubility of these polyazomethines in DMSO- $d_6$ , we attempted to heat the NMR sample tubes to obtain a homogeneous solution. It was found that the aldehyde peaks became more prominent and azomethine hydrogen peaks diminished when the NMR sample tubes were heated, indicating the decrease in molecular weight. The azomethine linkage of small organic molecules has ever been reported for its hydrolysis phenomenon at the presence of water [22]. In some cases, the formation of azomethine (imine) linkage was exploited to protect aldehyde and ketone groups, which were then reclaimed by the following hydrolysis in refluxing organic solvents [34]. However, the hydrolysis of polyazomethines has never been mentioned



Fig. 3. Wide-angle X-ray diffraction patterns of polyazomethines PAM-1-7.

before. In order to study the hydrolysis of these polyazomethines in solution state. **PAM-2** was used as the example. Fig. 1(b) is the <sup>1</sup>H NMR spectrum of as-prepared **PAM-2** soluble part in DMSO-d<sub>6</sub> at room temperature. Fig. 1(c) shows the <sup>1</sup>H NMR spectrum of asprepared **PAM-2** heated at 50 °C for 12 h in air to form a homogeneous DMSO-d<sub>6</sub> solution. It was found that the intensity of the aldehvde peaks (10.19 ppm) increased and that of azomethine hydrogen peaks (9.02 ppm) diminished as temperature increased. From the increased intensity of aldehyde peak, it is obvious that polyazomethines could undergo hydrolysis in DMSO-d<sub>6</sub> solvent even only trace of water (inherently exists in  $DMSO-d_6$ ) is present as depicted in Scheme 4. The amine peak at 5.74 ppm in Fig. 1(c) was broad and not prominent. This might be attributed to the slow exchange rate of protons on nitrogen and the electrical quadrupole moment of <sup>14</sup>N nucleus. Fig. 1(d) shows the <sup>1</sup>H NMR spectrum of the same as-prepared PAM-2 heated at 150 °C for 24 h in DMSO-d<sub>6</sub> under nitrogen atmosphere to form a homogeneous solution. The intensity of the aldehyde and amine peaks was more intense and that of the azomethine hydrogen peaks was decreased. Under nitrogen atmosphere, the amine peaks can be observed at 5.53 and 5.74 ppm. These peaks were attributed to the hydrolyzed diamine monomers and the amino groups of polyazomethine chain-ends, respectively. From these <sup>1</sup>H NMR spectra (Fig. 1), it indicates that the hydrolysis of polyazomethine PAM-2 is more pronounced at elevated temperature. It also implies that the reversed reaction of



Scheme 4. Hydrolysis of polyazomethines in solution state.

azomethine formation is favored at elevated temperature in the presence of even trace amount of water. This is consistent with the results from Table 2. In the same solvent (*m*-cresol), polymerization at room temperature gave higher molecular weights than at reflux temperature.

The hydrolysis of these new polyazomethines was further evidenced by the GPC measurements. Fig. 4 shows the GPC chromatograms of as-prepared PAM-2 after different levels of hydrolysis and post-polymerization. The hydrolysis was carried out by dissolving as-prepared PAM-2 in DMSO (0.1%, w/v) at 150 °C for different periods of time. PAM-2 can be totally dissolved in DMSO at 150 °C. The GPC chromatogram (Fig. 4(a)) of as-prepared PAM-2 was bimodal with number average molecular weight (M<sub>n</sub>) of 12,000 g/mole. When the 0.1% (w/v) of **PAM-2** solution in DMSO was heated at 150 °C for 4 h in air, the GPC chromatogram (Fig. 4(b)) became monomodal and indicated a lower molecular weight  $(M_n)$ of 6000 g/mole. As the hydrolysis lasted to 16 h, Mn decreased to 2000 g/mole Fig. 4(c). After PAM-2 solution was heated at 150 °C for 24 h, it became difficult to determine the molecular weight from its GPC chromatogram due to the low signal intensity (Fig. 4(d)). It indicated that PAM-2 was mostly hydrolyzed to oligomers whose molecular weights were beyond the lower limit of the GPC measurement. Even though water was not added, the trace amount of water in DMSO solvent is enough for the hydrolysis of polyazomethines at 150 °C. Aromatic polyazomethines have been known for their high thermal stability. This is true only for polyazomethines in their solid states. From the <sup>1</sup>H NMR spectra (Fig. 1) and GPC chromatograms (Fig. 4), it suggests that in solution state the polyazomethine could be easily hydrolyzed in the presence of a trace amount of water at temperature even as low as 50 °C.

It has been well know that the molecular weights of polyazomethines are generally lower than those of aromatic condensation polymers such as polyamides and polyimides. In addition to the effects of the chemical structures and the reactivity of monomers, this phenomenon might possibly be resulted from the hydrolysis during sample preparation for GPC measurement. In some cases, heating might be necessary to obtain a homogeneous solution, leading to hydrolysis and thus lower molecular weights.

It has also been reported that polyazomethine can undergo post-polymerization at high temperature [12]. A thin film (ca.  $2 \mu m$ )



**Fig. 4.** GPC chromatograms of **PAM-2** (a) as-prepared, (b) heated at 150  $^{\circ}$ C for 4 h in DMSO, (c) for 16 h in DMSO, (d) for 24 h in DMSO, and (e) thin film heated at 200  $^{\circ}$ C under reduced pressure for 24 h.

was prepared by spin-coating 2% (w/v) of **PAM-2** in DMF solution on glass and heating at 50 °C for 1 h then 200 °C for 24 h under reduced pressure. The GPC chromatogram of this post-polymerized PAM-2 thin film is shown in Fig. 4(d). The M<sub>n</sub> increased from 12,000 to 24,000 g/mole. It was attributed to the post-polymerization from amine and aldehyde groups of as-prepared **PAM-2** chain-ends. It suggests that in solid state polyazomethines can undergo postpolymerization at elevated temperature. The GPC results combined with <sup>1</sup>H NMR spectra suggested that even though hydrolysis can occur in DMSO solution, leading to low molecular weight, polyazomethine films with high molecular weights can be still obtained if the films were prepared at elevated temperature under reduced pressure. In summary, polyazomethines prepared in *m*-cresol at room temperature under reduced pressure had the highest molecular weights. Post-polymerization at elevated temperature (200 °C) in solid film can further increase their molecular weights.

#### 3.5. Thermal properties

The thermal properties of polyazomethines were evaluated by DSC and TGA. The results, including glass transition temperatures (Tg), decomposition temperatures at 5% (T<sub>5%</sub>), 10% (T<sub>10%</sub>) weight loss, and residual weight percent (R<sub>w800</sub>) at 800 °C in nitrogen atmosphere, are summarized in Table 4. The new polyazomethines PAM-1-7 exhibited high glass transition temperatures ranging from 265 to 324 °C. PAM-5 derived from the new dialdehyde (5) and 4,4'-ODA had the lowest glass transition temperature at 265 °C. It might be due to the flexibility of ether linkage on PAM-5 backbone. On the other hand, **PAM-4** derived from the new dialdehyde (5) and diamine (9) containing bulky phenyl substituents had the highest Tg (324 °C). This might be resulted from the fact that **PAM-4** containing phenyl substituents had higher chain rigidity than other polyazomethines. **PAM-2** containing bulky trifluoromethyl groups on both dialdehyde and diamine moieties also exhibited high glass transition temperature at 287 °C. PAM-6 and PAM-7, which had the same chemical structures except the azomethine arrangements, showed similar glass transition temperatures at 272 and 271 °C, respectively. It suggested that the azomethine arrangements of polyazomethines might have little effect on their glass transition temperatures.

Fig. 5 shows the TGA thermograms of PAM-2 as-prepared (Fig. 5 (a)) and after isothermal treatment at 200 °C for 90 min before heating scan (Fig. 5(b)). The as-prepared PAM-2 experienced an initial weight loss starting at around 190 °C. This initial weight loss was attributed to water released from the post-polymerization between chain-end amine and aldehyde groups. When PAM-2 was heated under nitrogen at 200 °C for 90 min, the thermogram (Fig. 5 (b)) shows no trace of post-polymerization and exhibited  $T_{5\%}$  at 482 °C. All the decomposition temperatures of polyazomethines PAM-1–7 were determined after the isothermal treatment (200 °C in nitrogen for 90 min) to exclude the effect of post-polymerization. The decomposition temperatures in nitrogen atmosphere at 5% and

Table 4
Thermal properties of polyazomethines.

	Tg <sup>a</sup> (°C)	T <sub>5%</sub> <sup>b</sup> (°C)	$T_{10\%}^{b}(^{\circ}C)$	Char yield <sup>c</sup> (wt.%)
PAM-1	273	416	470	62
PAM-2	287	482	502	40
PAM-3	270	475	506	63
PAM-4	324	432	468	48
PAM-5	265	438	463	47
PAM-6	272	487	501	42
PAM-7	271	484	498	40

<sup>a</sup> Measured by DSC at a heating rate of 10 °C/min in nitrogen.

<sup>b</sup> Measured by TGA at a heating rate of 10 °C/min in nitrogen.

<sup>c</sup> Residual weight percentage at 800 °C in nitrogen.



Fig. 5. TGA thermograms of PAM-2 (a) as-prepared and (b) isothermal at 200 °C for 90 min.

10% weight loss of **PAM-1–7** were in the range of 416–487 °C and 463-506 °C, respectively. Their residual weights at 800 °C in nitrogen ranged from 40 to 63%. These polyazomethines exhibited high thermal stability without any significant weight loss up to 400 °C. This further confirmed that the enhancement in solubility by non-coplanar biphenyl structures can be achieved without sacrificing the thermal stability.

# 3.6. Optical properties

The optical properties of **PAM-1–7** were investigated by UV–vis and photoluminescence (PL) spectroscopy by using their  $10^{-5}$  M chloroform solution. The results are summarized in Table 5. All the polyazomethines showed azomethine characteristic absorption at 326-360 nm (Fig. 6). Among these polyazomethines, PAM-2 containing electron-withdrawing trifluoromethyl substituents on both diamine and dialdehyde moieties showed the most hypsochromic shift with maximum absorption wavelength at 326 nm. On the contrary, PAM-4 containing electron-rich phenyl substituents on its diamine moiety showed the most bathochromic shift with maximum absorption wavelength at 360 nm. PAM-5 containing ether linkage on its backbone had maximum absorption wavelength at 344 nm. This value is close to those of other polyazomethines in this study if electronic effect is excluded (i.e. PAM-2 and PAM-4). It indicates that the ether linkage and the noncoplanar biphenyl structures might have the similar effect on interrupting the conjugation along the polymer backbones. Compared with polyazomethine PAM-8 prepared from 4,4'benzidine with terephthalic dicarbaldehyde (TPDCA) (maximum

Table 5
Optical properties of polyazomethines

	$\lambda_{abs}^{a}(nm)$	λ <sub>onset</sub> (nm)	$\lambda_{emi}^{b}(nm)$	$\Phi_{\mathrm{PL}}{}^{c}$ (%)
PAM-1	348	398	433	0.13
PAM-2	326	391	425	0.05
PAM-3	357	408	434	0.05
PAM-4	360	410	491	1.45
PAM-5	344	397	431	0.61
PAM-6	345	400	468	1.10
PAM-7	344	401	442	0.05

<sup>a</sup> Measured by UV-vis spectroscopy in chloroform  $(10^{-5} \text{ M})$ . b

Measured by photoluminescence spectroscopy in chloroform  $(10^{-5} \text{ M})$ .

 $^{\rm c}$  Quantum efficiency relative to quinine sulfate (10 $^{-5}$  M quinine sulfate in 1 N  $H_2SO_4$ ).



**Fig. 6.** UV–vis spectra of **PAM-1–7** in chloroform solution  $(10^{-5} \text{ M})$ .

absorption wavelength at 491 nm in concentrated sulfuric acid) [9], **PAM-1**–7 exhibited significant hypsochromic shift due to the interruption of conjugation along the polymer backbones.

Photoluminescence (PL) spectra were recorded by using the maximum absorption wavelength as the excited wavelength in chloroform solution ( $10^{-5}$  M). The representative PL spectra of **PAM-4**, **PAM-5** and **PAM-6** are shown in Fig. 7. All the polyazomethines **PAM-1–7** showed a broad emission peak with emission wavelengths ranging from 425 to 491 nm. PL quantum efficiency of polyazomethines was calculated by using quinine sulfate ( $10^{-5}$  M) in 1 N H<sub>2</sub>SO<sub>4</sub> as standard ( $\Phi = 0.546$ ) [15]. These new polyazomethines had PL quantum efficiency ranging from 0.05 to 1.45%. It was reported that polyazomethines had PL quantum efficiency less than 0.03%, which is much lower than those of the analogous poly(arylenevinylene)s and polyfluorenes [15]. The low PL quantum efficiency limits their applications as the luminescent layers.

# 3.7. Electrochemical properties

The electrochemical properties of these polyazomethines were investigated by cyclic voltammetry (CV). A representative cyclic



**Fig. 7.** PL spectra of **PAM-4**, **5** and **6** in chloroform solution  $(10^{-5} \text{ M})$ .



Fig. 8. Cyclic voltammogram (CV) of PAM-6.

voltammogram of **PAM-6** in 0.1 M n-Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile solution with a scan rate of 100 mV s<sup>-1</sup> is shown in Fig. 8. The values of HOMO, LUMO and energy gap were calculated by similar equations from previous publication [35]. The electrochemical properties are summarized in Table 6. All of the polyazomethines showed an irreversible peak both at oxidation and reduction region. However, the polymer films remained stable during repeating scans and showed essentially the same cyclic voltammograms. The irreversibility, indicating the short lifetime of the formed radical anions and radical cations during electrochemical processes, might be resulted from the short conjugation length of the non-coplanar biphenyls and the electron-withdrawing nature of trifluoromethyl group.

The HOMO and LUMO energy levels were determined to be -5.69 to -5.96 and -3.04 to -3.18 eV, respectively. These values are much lower when compared with those ( $E_{HOMO} = -5.19$  eV,  $E_{LUMO} = -2.46$  eV) of polyazomethine **PAM-8** prepared from 4,4'-benzidine and terephthalic dicarbaldehyde (**TPDCA**) [9]. The LUMO energy level is related to the conjugation length and the electron-accepting ability of polymers. The higher the delocalization of  $\pi$  electrons, the easier the acceptance of an additional electron during reduction process. Although these new polyazomethines had shorter conjugation length due to the interruption of conjugation along the polymer backbones, the presence of strong electron-withdrawing trifluoromethyl group outweighed the effect of short conjugation length, leading to low  $E_{LUMO}$  [33]. The low  $E_{HOMO}$  was

Table 6		
Electrochemical	properties of polyazomethines.	

	Reduction <sup>a</sup> (V)	Oxidation <sup>a</sup> (V)	$E_{HOMO}^{b}(eV)$	$E_{LUMO}^{c}(eV)$	Eg <sup>d</sup> (eV)
	E <sup>Re</sup> onset	E <sup>Oxi</sup> onset			
PAM-1	-1.66	1.10	-5.81	-3.05	2.76
PAM-2	-1.53	1.27	-5.96	-3.18	2.80
PAM-3	-1.65	1.05	-5.76	-3.06	2.70
PAM-4	-1.67	0.98	-5.69	-3.04	2.65
PAM-5	-1.62	1.09	-5.80	-3.09	2.71
PAM-6	-1.57	1.22	-5.93	-3.14	2.79
PAM-7	-1.55	1.21	-5.92	-3.16	2.76

<sup>a</sup> Measured by cyclic voltammetry.

 $^{b}\ E_{HOMO} = -(\tilde{E}^{Oxi}_{onset} + 4.80 - 0.09\ eV)\ [35].$ 

<sup>c</sup>  $E_{\text{LUMO}} = -(E^{\text{Re}}_{\text{onset}} + 4.80 - 0.09 \text{ eV})$  [35].

 $^{d}\,$  Calculated by the equation : Eg =  $E_{LUMO}-E_{HOMO}$  [35].

also resulted from the electron-withdrawing trifluoromethyl group. For example, **PAM-2** containing electron-withdrawing trifluoromethyl group on both diamine and dialdehyde moieties exhibited exceptionally low  $E_{HOMO}$  of -5.96 eV. It can be concluded that trifluoromethyl-containing non-coplanar biphenyls could be regarded as a new electron acceptor when designing a donor-acceptor system for different applications. This electron acceptor can be used to tune the HOMO, LUMO energy levels and charge mobility for electron-rich conjugated polymers.

The electrochemical energy gaps of these new polyazomethines were in the range of 2.65–2.80 eV. It was reported that the energy gap is resulted from the combined effects of the conjugated length of the polymer backbone and the electronic nature of the substituents (electron-rich or electron-withdrawing) [9]. The energy gaps of **PAM-6** (2.79 eV) and **PAM-7** (2.76 eV) were larger than that of **PAM-8** (2.73 eV). **PAM-6** and **PAM-7** with bulky trifluoromethyl group give larger twisted angles than **PAM-8** along the biphenyl structure. The larger twisted angle combined with the electron-withdrawing nature of trifluoromethyl group gives larger energy gaps of **PAM-6** and **PAM-7** compared with that of **PAM-8**. However, for **PAM-1–5**, their energy gaps are difficult to rationalize when compared with that of **PAM-8**. It is probably due to this combined effect of planarity and electronic nature of the substituents on the energy gap.

# 4. Conclusions

A new dialdehyde containing electron-withdrawing trifluoromethyl groups at the 2 and 2' positions of biphenyl was prepared via a five-step synthetic route. The formed polyazomethines exhibited excellent solubility in polar organic solvents such as DMF, DMAc, NMP and *m*-cresol while maintained their high thermal stability. It was found that these polyazomethines would undergo hydrolysis in solution. The hydrolysis, evidenced by <sup>1</sup>H NMR spectra and GPC chromatograms, was resulted from the reverse reaction of azomethine formation and was favored at higher temperature. It was concluded that polyazomethines prepared in *m*-cresol at room temperature under reduced pressure had the highest molecular weights. Post-polymerization of polyazomethine thin films at elevated temperature can further increased their molecular weights. These polyazomethines also had low electrochemical E<sub>HOMO</sub>s and E<sub>LUMO</sub>s. This is resulted from the combined effects of electron-withdrawing trifluoromethyl group and non-coplanar biphenyls. Combined with the excellent solubility and high thermal stability, 2,2'-bis(trifluoromethyl)-4,4'-

biphenyl structure could be a new choice as the electron acceptor for the structure design of new conjugated polymers.

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