

# Studies of an intrinsically soluble copolymer with well-defined alternating substituted *p*-phenylenevinylene and hexanedioxy blocks

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## Abstract

Intrinsically soluble copolymer with well-defined alternating substituted 2,5 *p*-phenylenevinylene (2.5 PV) and hexanedioxy blocks was synthesized by using the Wittig reaction. The copolymer was characterized with FTIR, <sup>1</sup>H NMR, UV–vis and fluorescence techniques. Thermal properties were investigated with DSC and TGA under nitrogen atmosphere. Time-resolved studies done on the polymer solution and film indicate that the polymer has a recombination time in the region of 20 μs, which is four order of magnitude greater than that reported for the PPV. A single-layer light-emitting diode device having a simple ITO/polymer/Al configuration was fabricated. The forward bias current was obtained and the device shows typical diode behaviour. Photodegradation of the copolymer was also studied by applying high-intensity UV illumination as well as low-intensity irradiation at a fix wavelength to the polymer film. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Photo- and electro-luminescence; Poly(phenylenevinylene); LED

## 1. Introduction

Since the discovery of electroluminescence (EL) in conjugated polymers [1], much interest has been shown in ways of improving device efficiencies and also increasing the range of colours available. Devices fabricated from poly(phenylenevinylene) (PPV) [1] and its derivatives [2,3] have been reported, and typically they show emission in the red to green spectral range. The emission wavelength in these polymers is determined by the energy gap, which is a function of the conjugated backbone, groups substituted onto the backbone and the effective conjugation length.

There is still a big challenge in developing polymer systems to exhibit highly efficient blue-light emission, which cannot be achieved easily from inorganic materials. Very recently, the main efforts have been focused on the developing of blue light-emitting diode materials capable of operating at ambient temperature and low voltages with easy processability and low price [4–8]. There are basically five different approaches in order to develop conjugated polymer systems exhibiting relatively large band gaps that are suitable for blue light emission.

The first approach is to synthesize conjugated polymers

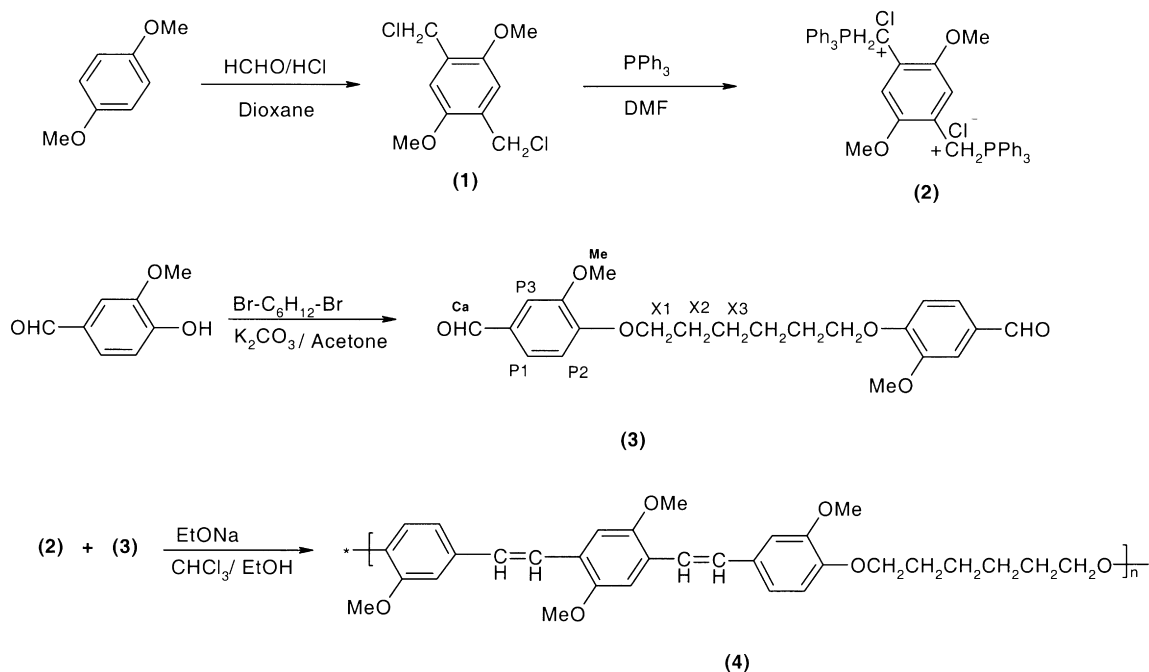
that are able to emit blue light: poly(phenylene) [9,10] and its copolymers with 2,5-dialkoxy-*p*-phenylene blocks [11–13] and phenylene ladder segments [13–17], poly((2,2,5'',5''-tetraoctyl-*p*-terphenyl-4,4''-ylene)vinylene-*p*-phenylenevinylene)[18], poly((2,3-diphenyl-5-*n*-alkyl-*p*-phenylene)vinylene)s [19,20], poly(alkylfluorine)s [10,21–23], and their copolymers containing phenylenebis(divinylene) and their dialkyl-*p*-phenylene units [24,25], poly(3-methyl-4-cyclohexyl-thiophene) [26], poly((3-hexylthiophene-ylene)ethylene)s [27], and poly[*p*-phenylenebenzobis(imidazole)] [28]. By the introduction of such large side groups onto the phenyl ring or vinylene group, the coplanarity of the conjugated π-system will be distorted, thus enlarging the band gaps.

The second approach is to make blue-light-emitting blends from green- and yellow-light-emitting polymers with the blue- or ultraviolet-light-emitting materials: poly(9-vinylcarbazole) blends with PPV and its derivatives and poly(dialkylfluorene) copolymers [29–31].

The third approach is to make blue-light-emitting bilayer or trilayer films from light-emitting polymers with electron-transporting materials: bilayer films of poly(*p*-phenylene-2,6-benzobis(oxazole)) with tris(*p*-tolyl)amine-dispersed poly(bisphenol A carbonate) [32,33] and of PPV with poly(methyl methacrylate) copolymers bearing 2,5-diaryl-1,3,4-oxadiazoles [34,35].

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Scheme 1.

The fourth approach is to disperse blue-light-emitting oligomers, such as oligomeric PPV in polymer matrixes [36].

The final approach is to synthesize polymers composed of conjugated segments as a component of the main chain and/or side chain: alternating co-polymers of short substituted *p*-phenylenevinylene and flexible spacer blocks [37–40], polysilanes consisting of *p*-phenylenevinylene-biphenyl and *p*-phenylenevinylencarbazole derivatives blocks [41], copolymers containing dialkylfluorenes and *N*-alkylcarbazoles [31], polystilbenyl-*p*-methoxystyrene [42], polynorbornenes containing short *p*-phenylenevinylene blocks as side groups [43], and poly(methyl methacrylate)s with distyrylbenzene and oxadiazole side groups [34]. The last two approaches can provide polymers with a well-defined conjugation length. This is highly desired since the large distribution in the conjugation leads to the larger broadness in the emission band [28,34–43].

In this paper, we will discuss on the synthesis and characterization of intrinsically soluble polymer made up of a well defined 2.5 PV derivative unit alternating with the 1,6-hexanedioxy unit.

## 2. Experimental

### 2.1. Synthesis

Synthesis routes of monomers and polymer are as shown in Scheme 1.

#### 2.1.1. Synthesis of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene 1

1,4-Dimethoxybenzene, 20 g (0.14 mol) was dissolved in

250 ml dioxane in a 500 ml 3-necked round-bottom flask. The solution was maintained at below 60°C while dried HCl gas was bubbled into the reaction flask for 3 h and formaldehyde (25 ml, 0.33 mol) was added into the flask. The optimum amount of formaldehyde was generally 2.3 times to the mole of 1,4-dimethoxybenzene. At the end of the reaction, white precipitate was formed. The solid was filtered and washed with distilled water until neutral. The white crude solid was then dried in vacuum oven at room temperature for 24 h. The crude solid was recrystallized in acetone. The yield was 25.86 g (78.6%). Elemental analysis: C: 50.98%, H: 5.11%; calculated: C: 51.06, H: 5.11%. The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) chemical shift: δ = 7.16 ppm (s, 2H, phenylene protons), δ = 4.75 ppm (s, 4H, CH<sub>2</sub>Cl), 3.88 (s, 6H, -OCH<sub>3</sub>).

#### 2.1.2. Synthesis of 1,4-bis(triphenylphosphoniomethyl)-2,5-dimethoxybenzene dichloride 2

A solution of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene (2.88 g, 12.3 mmol) and triphenylphosphine (6.36 g, 24.3 mmol) in 30 ml of DMF was stirred and heated to reflux for 24 h. Half of the volume of DMF was then distilled out under reduced pressure and the reaction mixture was cooled to room temperature to yield white precipitate. The resulting precipitate was filtered off, rinsed repeatedly with dried acetone followed by drying under vacuum at 40°C for 24 h. Yield: 4.83 g (52.4%). Elemental analysis: C: 66.93%, 5.27%; Calculated: C: 67.59%, H: 5.43%. The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) chemical shift: δ = 2.95 ppm (s, 6H, -OCH<sub>3</sub>), 4.75 (d, *J* = 13 Hz, 4H, -CH<sub>2</sub>-), 6.93 (s, 2H, phenylene protons), from 7.63–7.73 (m, 30H, PPh<sub>3</sub> protons).

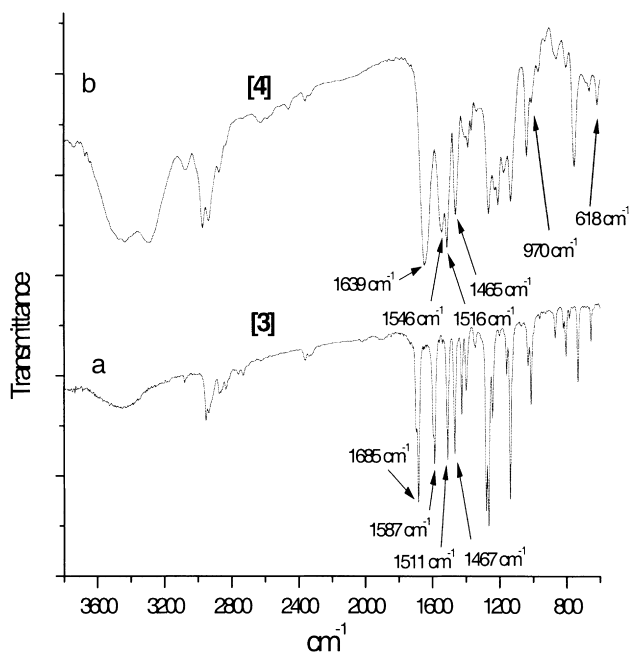


Fig. 1. FTIR spectra of: (a) **3**; and (b) **4**.

### 2.1.3. Synthesis of 1,6-bis(4-formyl-2-methoxyphenoxy)hexane **3**

4-Hydroxy-3-methoxybenzaldehyde, 1.35 g (8.9 mmol), and 1.35 g (9.8 mmol) of anhydrous potassium carbonate were added into a 100 ml 2-neck round-bottom flask equipped with a condenser and a magnetic stirring bar. Reagent grade acetone, 50 ml, was then added into the flask followed by 0.68 ml (4.5 mmol) of 1,6-dibromohexane. The reaction mixture was protected from moisture and refluxed for 48 h. The mixture was then poured into 2 l of distilled water. After 2 h, the precipitate was collected, dried in air at ambient temperature, and recrystallized from ethanol/water (5/1). The yield of **3** was 0.87 g. (25.3%). Elemental analysis: C: 68.01%, H: 6.51%; calculated: C: 68.39%, H: 6.74%. FTIR spectrum (Fig. 1a): 1685–1700  $\text{cm}^{-1}$  (s, C=O stretching), 2750 and 2850  $\text{cm}^{-1}$  (w, aldehyde C–H stretching), 1450–1600  $\text{cm}^{-1}$  (m, phenylene C=C stretching vibration), 1000–1300  $\text{cm}^{-1}$  (m-s, Ph–OCH<sub>3</sub> stretching). The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) chemical shift:  $\delta$  = 9.50 ppm (s, 1H, –CHO), 7.47 [s, 1H, H(P1)], 7.44 [s, 1H, H(P3)], 7.00 [s, 1H, H(P2)], 7.44 [s, 1H, H(Me)] (see Scheme 1 for the numbering of the compound.)

### 2.1.4. Polymer **4**

To a stirred solution of an equimolar amount of 1,6-bis(4-formyl-2-methoxyphenoxy)hexane (0.610 g, 1.58 mmol) and 1,4-bis(triphenylphosphoniomethyl)-2,5-dimethoxybenzene dichloride (1.200 g, 1.58 mmol) in 30 ml of chloroform, was added dropwise 10 ml of sodium ethoxide solution (freshly prepared by dissolving approximately 0.1 g of cleaned sodium metal in 10 ml of “superdry” ethanol) at ambient temperature under a nitrogen atmosphere. The mixture was stirred for 24 h after addition. The yellow

solid was collected at the end of the condensation reaction. The crude polymeric product was filtered followed by washing with ethanol/water (3/1) to remove the byproduct triphenylphosphine oxide and NaCl. The washed product was subsequently dissolved in chloroform and dried with anhydrous sodium sulfate, after which the solvent was completely evaporated off under reduced pressure. In order to eliminate most of the low molecular weight compound remaining in it, the product was washed repeatedly (4–5 times) with dried acetone until the washing became almost colourless. The obtained polymer, **4** was then dried in vacuum oven at 40°C for 2 days. Yield: 0.195 g (23.9%). The solid compound obtained was greenish yellow in colour.

### 2.2. Characterization and instrumentation

FTIR spectra were obtained from the Perkin–Elmer FTIR spectrometer, using KBr discs and as for polymer samples, using films by casting chloroform solution onto the NaCl plate. <sup>1</sup>H NMR spectra were recorded using a Bruker Spectrospin 400 MHz spectrometer in CDCl<sub>3</sub> with a pulse width of 10.2  $\mu\text{s}$ , and chemical shifts were referred to TMS. UV–vis absorption spectra for both the solution and film were taken from the Perkin–Elmer 8540A spectrophotometer. For the acquisition of the polymer film spectra, the film was spin-coated from the 1% solution in chloroform onto a glass plate. Solution and film photoluminescence (PL) analyses were performed by using the Perkin–Elmer fluorometer equipped with a continuous xenon lamp source. The PL decay lifetime of the polymer solution was measured using a Fluorolog 3 spectrometer attached to xenon flash lamp source which flashes for 0.01 ms in each single flash and the slit width applied was 5 nm.

TGA measurements were carried out on an indium-calibrated Setaram TG-DTA/DSC thermal analyzer. The samples were scanned at rates of 5, 10, 15 and 20 K/min under purified nitrogen atmosphere at 20 psi. DSC analyses were performed by using the Perkin–Elmer thermal analyzer under purified nitrogen atmosphere at 20 psi. The elemental analyses were done by using the LECO, CHNS-932 microanalysis analyzer.

### 2.3. Preparation of LED

An indium tin oxide (ITO) coated glass with electrical resistance of 60  $\Omega$  was cleaned by sonication, followed by rinsing in acetone after which, it was dried in a vacuum at room temperature for 4 h. LEDs consist of a polymer layer sandwiched between ITO (anode) and an aluminium layer (cathode). A thin film of the polymer was coated onto ITO glass by spin coating using 1% (w/v) solution in chloroform at 1000 rpm. The residual solvent was evaporated under vacuum at room temperature for 4 h. This was followed by vapour deposition of aluminium through a mask (3 mm in diameter) at a chamber pressure of at least  $5 \times 10^{-6}$  Torr. The top electrode Al was evaporated onto the polymer in a

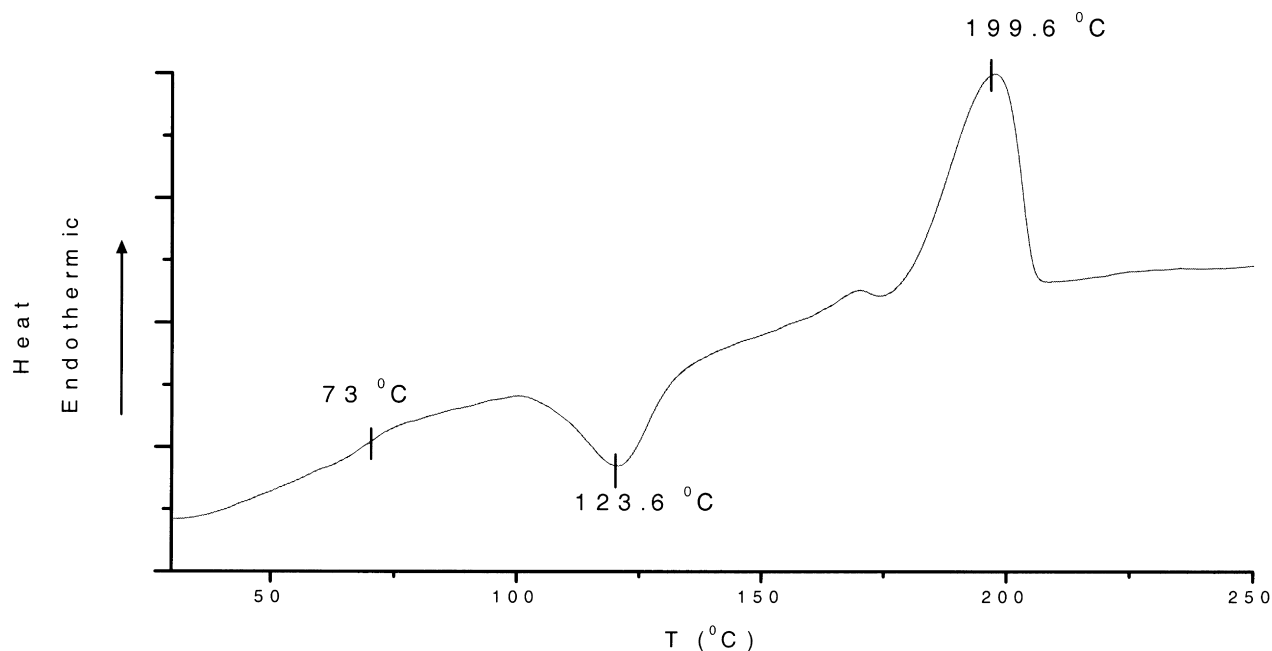


Fig. 2. The DSC heating curve for **4**.

JEOL JEE-400 vacuum evaporator at a rate of 2 to 5 Å/s. The thickness of the Al was about 1000 Å. A typical LED was 3 mm in diameter. The effective area of the LEDs was  $7.07 \times 10^{-2} \text{ cm}^2$ .

Basic electrical characterization involved measurement of the device current as a function of applied voltage. A HP 6282A or a HP 6212B DC power supply supplied the voltage across the device. The current was measured by a Keithley 238 High current source measure unit and a Keithley 614 electrometer which were connected to a computer equipped with Interactive Characterization software. The computer recorded all the current–voltage data.

### 3. Results and discussion

#### 3.1. $^1\text{H}$ NMR spectrum of **2**

The two identical pairs of methylene protons of **2** are split into a pair of doublet peaks ( $J = 13 \text{ Hz}$ ) This is due to the coupling of the hydrogen nucleus with P (spin,  $I = 1/2$ ), its immediate neighbour. It is also noteworthy that the chemical shift of the methoxy protons is shifted upfield by 0.93 ppm compared to **1**. This phenomenon suggests that the methoxy protons are lying well above or below the plane of the benzene ring attached to the phosphorus nucleus. As a result of the shielding effect of the ring current induced in the benzene ring by the applied magnetic field, the chemical shift of the methoxy proton is shifted upfield.

#### 3.2. Characterization of **4**

Wittig condensation was applied to polymerize **2** with **3** to afford about 23.9% yield. The FTIR of polymer **4** is

shown in Fig. 1b. The C=O stretching in the dialdehyde of **3** at  $1680\text{--}1700 \text{ cm}^{-1}$  is no longer noticeable because of the reaction. Three medium to strong peaks extending across the region from  $1510$  to  $1640 \text{ cm}^{-1}$  are attributed to the stretching vibration of both the vinylene and aromatic ring  $\text{--C=C}$ . The peak at  $970 \text{ cm}^{-1}$  is assigned to the out-of-plane bending mode of *trans*-vinylene C–H, whereas the *cis*-vinylene C–H band can be observed at  $618 \text{ cm}^{-1}$ . The absorption bands of the alkoxy groups lie in the region of between  $1000$  and  $1300 \text{ cm}^{-1}$ .

The assignments for the  $^1\text{H}$  NMR spectrum of **4** are as follows:  $\delta$  (ppm) 1.5 (broad, 4H,  $\text{--OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O--}$ ); 1.9 (broad, 4H,  $\text{--OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O--}$ ); from 3.5–4.1 (m, 16 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O--}$  and  $\text{--OCH}_3$ ); 6.6–7.3 (m, 10 H, phenylene C–H and vinylene C–H). There is a series of peaks in  $\delta = 3.5\text{--}4.1$  ppm region, which indicates the existence of *cis*–*trans* isomerism in the polymer structure. This has further confirmed the FTIR interpretation of the *cis*- and *trans*- vinylene C–H. A residual of the aldehyde peak is also observed at the 9.87 ppm region. By comparing the integration of the methylene group at 1.9 ppm and that of the aldehyde peak at 9.87 ppm, a rough number of repeating units can be estimated, which is approximately 10 units.

#### 3.3. DSC and TGA analyses of **4**

The DSC result shown in Fig. 2 indicates that the polymer **4** displays a  $T_g$  at  $\sim 73^\circ\text{C}$ . The exothermic peak that appears at  $123.6^\circ\text{C}$  is due to crystallization and this is followed by a melting peak of the polymer at  $199.6^\circ\text{C}$ .

Thermogravimetric analyses (TGA) were also performed on the polymer at different scan rates (Fig. 3). The percent

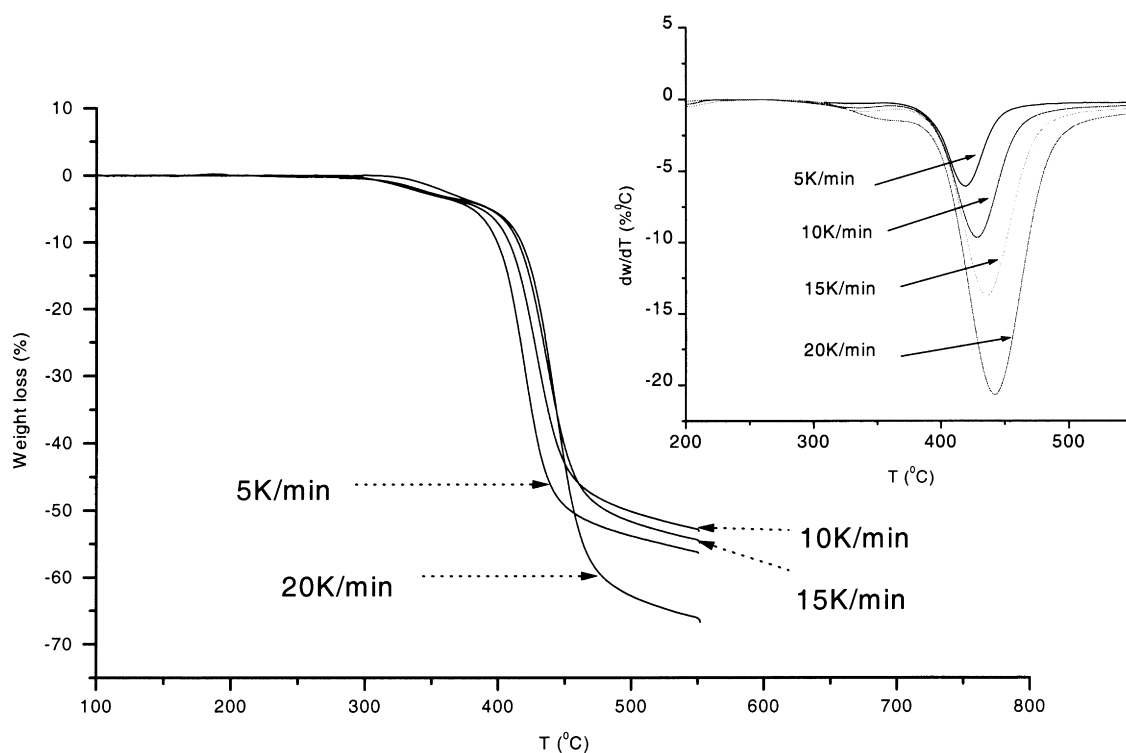


Fig. 3. TGA plots for **4** at heating rate of 5, 10, 15 and 20 K/min. Inset: differential thermogravimetric analysis (DTGA) plots for **4**.

weight loss against the  $T$  plot shows that the polymer is thermally stable up to above  $300^{\circ}\text{C}$  under nitrogen atmosphere. The MHRK method [44] was used to study the thermal decomposition kinetics of the polymer.  $\Delta E$  can be obtained from the slope of a linear plot of  $\ln$  (heat rate) against  $1/T$ . The activation energies,  $E_a$  for the decomposition for the polymer thus obtained are given in Table 1.

### 3.4. Photoabsorption and photoluminescence

The absorption and PL spectra for both the film and solution of the polymer are shown in Fig. 4. The UV–vis absorption for both the film and solution display a pair of structureless spectra. It is evident that the positions of  $\lambda_{\text{onset}}$  and  $\lambda_{\text{max}}$  of the  $\pi$ – $\pi^*$  transition for the film are red-shifted as compared to its solution counterpart (approximately 10 and 20 nm, respectively), the bathochromic shift phenomenon is more prominent in the PL spectra ( $\sim 50$  nm). This bathochromic shift can be attributed to the larger conjugation length because of chain extension in the solid state [45]. From the UV–vis measurement, the  $\pi$ – $\pi^*$  band gap for **4**

was calculated from the  $\lambda_{\text{onset}} = 477$  nm (obtained by taking the maximum of the first derivative of the absorbance against  $\lambda$  plot), corresponds to a band gap of 2.77 eV.

The PL spectra of both the solution and film show two emission maxima at (456, 486 nm) and (509 nm, shoulder at 540 nm), respectively, indicative of an overlapping of two different emission spectra, which could be resulted from the *cis*–*trans* isomers' radiative decay. The half-width of the maximum height of the PL spectra are  $\sim 60$  nm for both the solution and film.

It was found that the UV–vis as well as the PL spectra of **4** was red-shifted ( $\sim 20$  and  $40$  nm, respectively) compared with that of poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] [37]. The bathochromic shift could be due to a higher electron density and hence increased effective conjugation as a result of the introduction of the two electron-donating methoxy groups in the middle phenylene ring of the chromophoric unit (rigid block).

### 3.5. Time-resolved fluorescence experiment

When time-resolved fluorescence studies were performed on the polymer, the PL decay curve of the polymer solution showed an exponential decay with recombination time,  $\tau = 21$   $\mu\text{s}$  at both the emission wavelengths of 450 and 479 nm. Similarly, its film counterpart too displayed a first order fluorescence decay curve at the emission wavelength of 504 nm and the recombination time,  $\tau$  was found to be

Table 1  
Activation energy calculated by using the MHRK method

Weight loss (%)	$E_a$ (kJ/mol)
10	285.7
15	286.4
20	284.1
Average	285.4

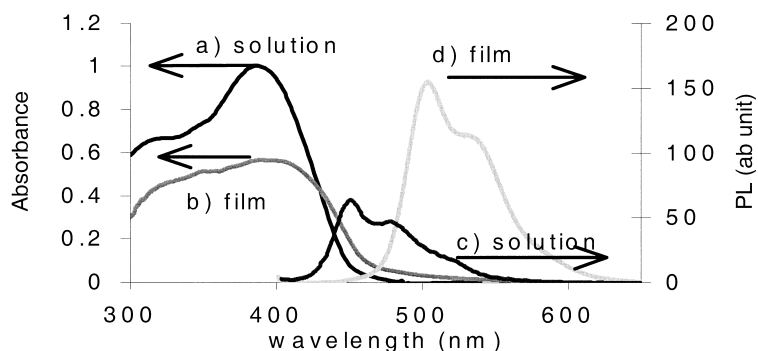


Fig. 4. Absorption and emission spectra of **4**. Absorption: (a) in solution; (b) film and emission; (c) in solution; (d) film.

17  $\mu$ s. The recombination time difference of 4  $\mu$ s obtained when comparing that of solution to the film is negligible. However, these values are about 4 order of magnitude greater than that recorded for the pristine PPV sample [46], evident that the electronically inert spacer (hexanedioxy) between each active chromophore has effectively lengthened the polymer's decay time.

### 3.6. Electroluminescence properties of **4**

The current–voltage ( $I$ – $V$ ) characteristic of the device with the configuration of ITO/**4**/Al was studied. The forward bias current was obtained when the ITO electrode was positively biased and the Al electrode was negatively biased. The current increased with increasing forward bias voltage, which indicates typical diode behaviour. The device has a relatively low turn-on voltage of 5.6 V. The EL, which was in bluish green colour could be easily observed through naked eyes under room light. The diode behaviour of the device suggests that electrons and holes are injected from

the Al and the ITO electrodes, respectively. Injected holes and electrons subsequently form positive and negative polarons in the bulk of the polymer. There, recombination can produce singlet molecular excitations localized at the chromophoric units of the copolymer. The radiative decay of singlet excitation is, in turn, responsible for the EL.

### 3.7. Photo-stability of film **4**

Photo-stability studies were done on the polymer film **4** by constantly illuminating the film sample with UV source. The light source used for the degradation studies was provided by a 150 W Kratos LPS251 HR Xenon lamp, which gave continuous output from UV to IR and has a calibrated intensity of 1016 photons/cm<sup>2</sup> in a 10 nm bandwidth in the 400–700 nm range.

Fig. 5 shows the UV–vis spectra of film **4** before and after various extents of exposure to the UV source in ambient atmosphere. The main absorption peak ( $\lambda_{\text{max}}$ ) of film **4** spin coated with CHCl<sub>3</sub> solution occurs at about 400 nm.

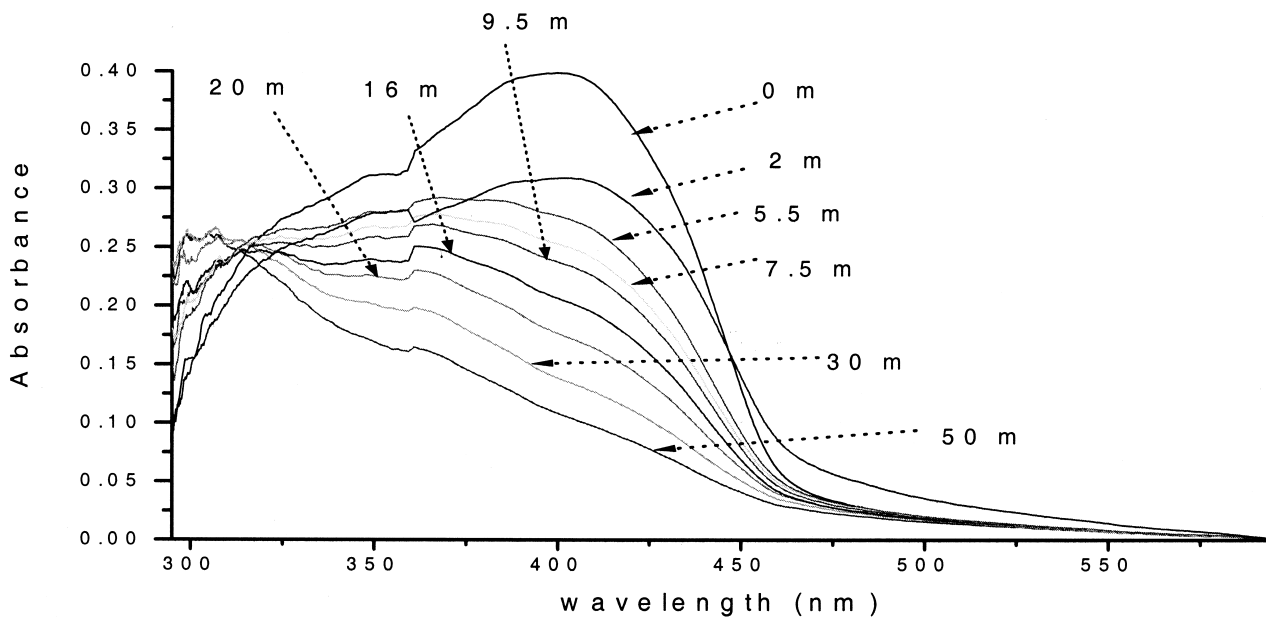


Fig. 5. Absorption spectra for **4** film at different full spectrum high intensity UV illumination time ( $t = 0, 2, 5, 5.5, 7.5, 9.5, 16, 20, 30$  and 50 min). The absorbance at the  $\lambda = 400$  nm region decreases with  $t$ .

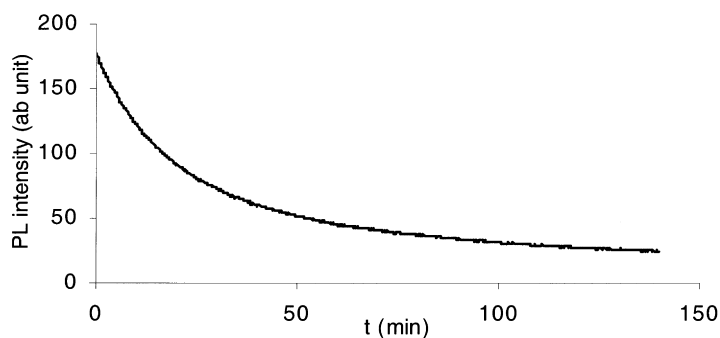


Fig. 6. The PL Intensity at  $\lambda_{em} = 504$  nm corresponds with low intensity irradiation time.

This absorption peak has been attributed to the  $\pi-\pi^*$  electronic transition. The main absorption peak moves towards the shorter wavelengths (hypsochromic shift) with increasing exposure to the light source. In this case, the absorption peak shifts from 400 to 304 nm after 50 min of exposure. The decrease in intensity at  $\lambda = 400$  nm suggests the loss in effective conjugation length or scission of the polymer chain. Attenuation of the C=C stretching peaks at 1515 and 1470  $\text{cm}^{-1}$  were observed in the FTIR spectra. This indicates that polymer chain scission has occurred. In addition, two new peaks with gradual strengthening in intensity with respect to illumination time were also observed in the 1680 and 1720  $\text{cm}^{-1}$  region. These peaks are attributed to C=O stretching of aldehyde and carboxylate group, respectively. The result suggests that oxidation reactions had taken place during the process of irradiation. At the end of the illumination, the colour of the film turned almost colourless. Atreya et al [47] have attributed the photo-degradation to the active participation of oxygen. UV-vis illumination under atmospheric conditions had resulted in the disruption of the  $\pi$ -electron system and a significant loss in the effective conjugation length of the polymer.

### 3.8. Photo-bleaching effect of film 4

PL intensity of the polymer film was measured against time using the fluorometer. The experiment was carried out under ambient atmospheric conditions and the polymer film was irradiated with a low intensity monochromatic light at 397 nm and its emission was measured at 504 nm throughout the whole course of the experiment. Fig. 6 shows the PL intensity change against time. The PL took 84 min to reduce to 20% of its initial intensity.

In order to detect any changes due to the irradiation by low intensity monochromatic light, a spin-coated polymer sample was placed in a UV-vis spectrophotometer. The sample was irradiated by a 400 nm monochromatic light source from the spectrophotometer and the absorbances at  $\lambda = 400$  nm were recorded at fixed interval during the whole course of experiment. The result showed no change in the absorption spectra before and after 2 h of irradiation. This suggests that irradiation at low intensity on the polymer film does not affect the effective conjugation length of the

polymer. The FTIR spectra show no sign of peak attenuation at 1515 and 1470  $\text{cm}^{-1}$ , a further proof that the C=C bonds are well preserved. However, as in the case of high intensity illumination, they register two peaks with growing intensity against irradiation time at 1680 and 1720  $\text{cm}^{-1}$ , a clear indication of an oxidized state on the irradiated spot of the polymer. From the above results, it can be concluded that the photo-bleaching effect of the polymer could have been caused by the oxidation of the polymer prior to the loss in its effective conjugation length.

## 4. Conclusions

A well-defined copolymer with alternating substituted PV rigid block and hexanedioxy soft block was synthesized using the Wittig reaction. The polymer was intrinsically soluble, and homogeneous free-standing film could be obtained from the copolymer solution. The copolymer was thermally stable up to above 300°C under nitrogen atmosphere. DSC analysis showed that the copolymer had a  $T_g$  at  $\sim 73^\circ\text{C}$ . The recombination time of the polymer was about 20  $\mu\text{s}$ , which was four order of magnitude greater than that reported for the fully conjugated PPV. The current-voltage ( $I-V$ ) characteristic of the device with ITO/polymer/Al configuration demonstrates typical diode behaviour and the EL could be easily seen under room light condition. Illumination with high-intensity full spectrum UV light resulted in the chain scission of the polymer. Continual irradiation with low intensity monochromatic light on the polymer film resulted in photobleaching with a loss of PL intensity in spite of the fact that the effective conjugation length of the polymer remained unchanged.

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