

Synthesis and spectroscopic characterization studies of low molecular weight light emitting PPV segmented copolymers

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ABSTRACT

New tuneable segmented alternating copoly(*p*-phenylene vinylene) (PPV) derivatives were chemically synthesised via the Wittig polycondensation reaction. The chemical and optical properties in solution and in solid state were evaluated. The absorption and photoemission spectra show that incorporating an ethane dioxy spacer limits the conjugation length and produces a blue emitting copolymer, poly[1,2-ethane dioxy 2-methoxy-1,4-phenylene-vinyl 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene] (EDO-PPV-1) **1**. A red shift in the copolymer emission was achieved by adding an electron-donating group, a hexoxo-substituted PPV segment, poly[1,2-ethane dioxy 2-methoxy-1,4-phenylene-vinyl 2,5-dihexoxo 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene] (EDO-PPV-2) **2**. The photophysical properties of these block copolymers was compared with the fully conjugated copolymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) **3**. The absorption band of the $\pi_{deloc}-\pi_{deloc}^*$ transition at 400–500 nm is limited in **1** and **2** indicating that the conjugation is effectively interrupted. The effect of torsional motions on the Stokes shift in these segmented copolymers is discussed. The photoluminescence (PL) efficiency and lifetime of **1** and **2** is different, indicating that the contribution from additional non-radiative decay channels due to interchain interactions is significant. The steady state and time-resolved photophysical characteristics of the thin film form of the copolymers indicates a high order of stacking in copolymer **1** and strong interchain interaction leading to strong excimer emission which may be ascribed to the low folding degree and planarity of the copolymers chemical structure. The spectroscopic time-resolved analysis confirms the interchain interaction.

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1. Introduction

Since the discovery of poly(*p*-phenylene vinylene) PPV as a polymeric electro-luminescent (EL) material in 1990 [1], π -conjugated polymers have attracted many researchers to synthesize new polymers that can be useful for the fabrication of organic light emitting diodes (OLED's). A π -conjugated polymer to be used as an EL material should exhibit good solubility, high chemical stability, high luminescent efficiency and with balanced charge carrier mobility. One of the most interesting characteristics of the conjugated polymers in general and PPV in particular is that these material characteristics can be altered by modifying the chemical structure of the material. Fully conjugated polymers are usually insoluble and not processable in this form, which limits their use in most applications. Processability of these polymers can be achieved by substitution of side groups such as alkyl groups, or

by introducing flexible non-conjugated spacers into the backbone [2]. However, in conjugated homopolymers the actual conjugation length is an average value determined by random conformational or chemical defects in the polymer backbone and is difficult to control. Interrupting the conjugated backbone of the polymer by introducing a non-conjugated spacer not only enhances its efficiency and increase the solubility of the copolymer but also can control the conjugated length and provide a blue shift in the emission due to an increase in the energy band gap [3–5]. Furthermore, if the substituted side group is an electron-donating (electron-rich group) or electron accepting (electron deficient group), the effective conjugated length will also alter [6,7]. Combining spacer and substitution, the photophysical properties of the copolymer can be engineered according to the required application. The first attempt to incorporate a nonconjugated segment into a fully conjugated backbone to obtain a large band-gap polymer emitting blue fluorescence and at the same time confining the excitons was proposed by Burn et al. [3]. These block copolymers confined the excitons within a short segment limiting migration and quenching which leads to fluorescence quantum yield enhancement. Soon

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afterward many workers synthesised different PPV copolymers containing well specified conjugated length with a nonconjugated spacer [8]. Modification of the effective conjugation length of PPV by incorporating electron donating or withdrawing side groups is also synthesized to induce spectrum tuning [9]. Side groups may also induce steric hindrance resulting in interruption of the conjugation length leading to blue shift [10] or may enhance or block the charge carrier mobility [11]. Despite extensive work having been done to study the optical properties of these block copolymers both theoretically and experimentally, the origin of the large Stokes shift observed and the large blue shift in the fluorescence and absorption spectrum compared with the fully conjugated PPV polymer are not fully understood. Therefore it is important to investigate and highlight some photophysical aspects concerning the difference between the block copolymers and a fully conjugated copolymer.

In this work we report the synthesis and study of two new block copolymers (oligomers) incorporating both spacer groups and electron donating group (dihexyloxy) substitution in each segment. The structure and properties of the copolymers have been characterized. The steady state and time-resolved analysis were investigated and the difference in optical properties between the long conjugation polymer such as MEH-PPV **3** and the short block copolymers such as EDO-PPV **1** and **2** has been analyzed. The oligomer emits a blue light and the electron rich alkoxy group induces redshifted emission. The exciton localization induced by the spacer increases the exciton lifetime. Further increase in the lifetime can be induced by the large alkoxy group which enhances solubility and increases the number of isolated copolymer molecules in solution. In thin film form these block copolymers suffer from a high degree of interchain interaction. We have discuss for the first time to the best of our knowledge the difference between the short conjugation block copolymers and the fully conjugated polymers in term of their optical properties and Stokes shift.

2. Experimental

2.1. General details

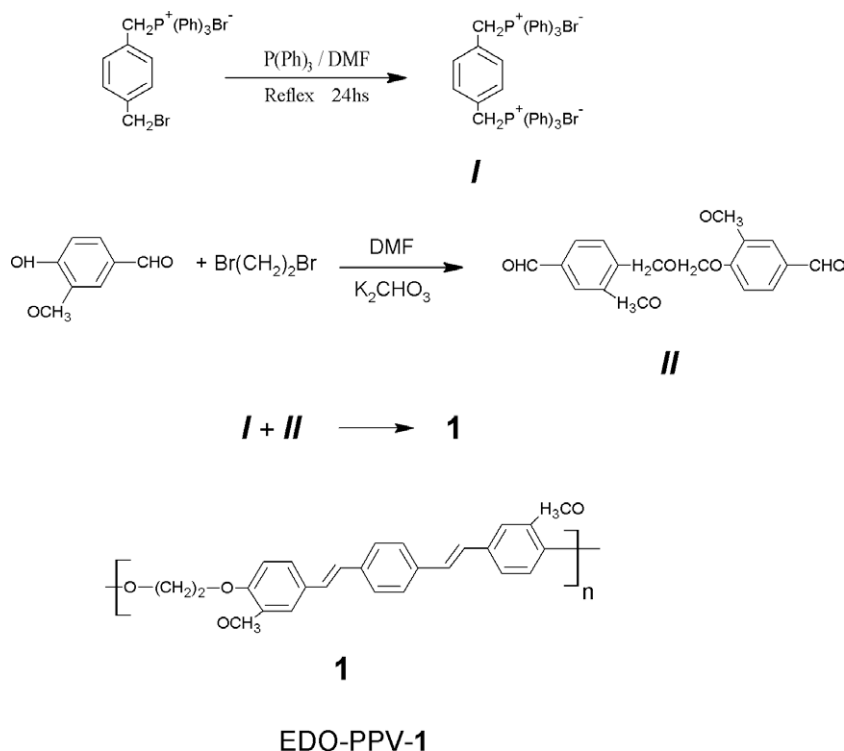
All reactions were performed in air and at room temperature. All reagents were of standard reagent grade and purchased from Aldrich and used as supplied unless otherwise stated. THF was dried and distilled, prior to use, over potassium or sodium metal. FTIR transmission spectra were recorded using Shimadzu 8400s spectrometer. Column chromatography was carried out in silica-gel (40–60 μ m). ^1H NMR spectra were recorded on a Bruker Avance500 at 500 MHz spectrometer using CDCl_3 solvent as the lock and tetramethylsilane as the internal reference. Thermogravimetric analyses (TGA) was performed under nitrogen atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ using Perkin Elmer Thermal Analyser. Glass transition (T_g) and melting temperature of the copolymers were determined by differential scanning calorimetry (DSC) type Universal Q1000.

2.2. Monomer synthesis and polymerization

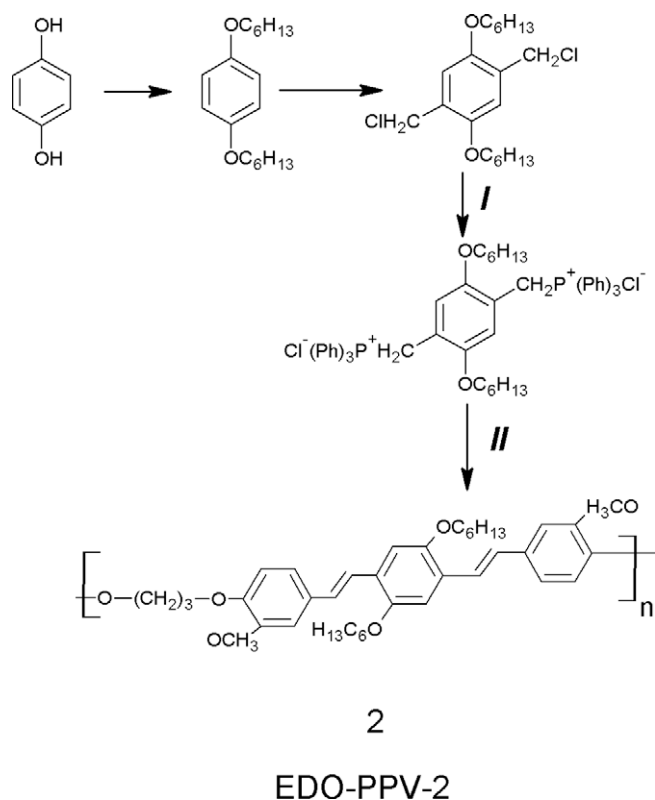
2.2.1. Synthesis of poly(1,2-ethane dioxo 2-methoxy-1,4-phenylene-vinyl 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene) (EDO-PPV-**1**) (*Scheme 1*)

The monomer synthesis was performed according to published procedures [12,13] and the polymer was prepared by Wittig condensation [14].

2.2.1.1. Synthesis of 1,4-xylene bis (tri phenyl phosphonium bromide) (I). A mixture of 1,4-dibenzoyldibromide (0.003 mol), triphenyl phosphine (0.009 mol) and 20 ml of freshly distilled dimethylformamide (DMF) was heated to 95 $^\circ\text{C}$ while stirring for 24 h. After cooling to room temperature, the resulting mixture was dropped into diethyl ether and then stirred. The white solid was filtered washed



Scheme 1. The synthetic route of poly(1,2-ethane dioxo 2-methoxy-1,4-phenylene-vinyl 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene (EDO-PPV-**1**) **1**.



Scheme 2. The synthetic route of poly(1,2-ethane dioxy 2-methoxy-1,4-phenylene-vinyl, 5-dihexyloxy 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene) (EDO-PPV-2), **2**.

repeatedly with diethyl ether to remove the by-products and dried under vacuum to give a white powder, yield, 81%, m.p > 300 °C.

2.2.1.2. Synthesis of dialdehyde monomer 1,2-bis (4-formyl 2-dimethoxy phenoxy) ethane (II). A solution of (0.2 mol) of 4-hydroxy 3-methoxy benzaldehyde and 1.8 g (0.1 mol) of 1,2-dibromoethane in 100 ml DMF was stirred and heated to reflux. A total of 3.5 g of potassium carbonate was added in portion, the solution was stirred and reflux for 6 h. The resulting mixture was poured into 1 L of distilled water and the precipitate was collected after standing 4 h, dried in air at ambient temperature and recrystallization from THF the yield of dialdehyde was 79% with a m.p 183–184 °C.

2.2.1.3. Synthesis of copolymer 1. This copolymer was synthesized by reaction of equal moles of Wittig reagent and dialdehyde in ethanol/chloroform mixture in the presence of sodium ethoxide. IR (KBr, cm^{-1}): 3058, 1510, 1023, 963. ^1H NMR (500 MHz, CDCl_3 , δ (ppm)): 0.8–1.6 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.9 (s, 3H, OCH_3), 7.1 (s, 2H, $-\text{CH}=\text{CH}-$), 7.4–7.8 (s, 6H, C_6H_6), 9.9 (s, 2H, $\text{O}=\text{CH}-$) and finally 7.3 due to solvent.

Table 1
Photophysical properties of copolymers **1**, **2** and **3**.

Co polymer	Mwt Dalton	λ_a max solution (film) nm	λ_f max solution (film) nm	Φ_{PL} solution (film) nm
EDO-PPV-1	3344	315 (316)	431 (484)	0.237 (0.04)
EDO-PPV-2	2132	315, 348 (311, 355)	452 (494)	0.489 (0.21)
MEH-PPV		500	556	

The excitation wavelength, λ_{exc} max is 320 nm.

λ_a max, the absorption maxima in chloroform solution or thin film.

λ_f max, the PL maxima in chloroform solution or thin film.

Φ_{PL} PL quantum yield in chloroform solution.

2.2.2. Synthesis of poly(1,2-ethane dioxy 2-methoxy-1,4-phenylene-vinyl 2,5-dihexyloxy 1,4-phenylene-vinyl 3-methoxy 1,4-phenylene) (EDO-PPV-2), **2 (Scheme 2)**

2.2.2.1. Synthesis of 1,4-bis (hexyloxy)benzene. A mixture of 7.5 g of hydroquinone, 23.5 g hexyl bromide and NaI 21 g, KOH 9.5 g dissolved in 150 ml ethanol and the mixture was reflux for 48 h. The precipitate was collected and washed out for several times with water, then recrystallisation from ethanol to give colorless plates in 68% yield with m.p 44 °C.

2.2.2.2. Synthesis of 1,4-bis (chloro methyl)-2,5-bis (hexyloxy)benzene. A solution of 1,4-dihexyloxy benzene (5 g) and paraformaldehyde 1.3 g in 1,4-dioxane (25 ml), 4 ml of Con. HCl was added then stirred the reaction mixture at 50–60 °C.

Then gaseous of HCl was introduced by bubbling through the reaction mixture for 5 h. After the reaction was complete 12 ml of conc. HCl was added, then cooled the reaction mixture in order to precipitate the product which was washing several time with water and recrystallisation from acetone to give white product in 62% yield with m.p 62–63 °C.

2.2.2.3. Synthesis of 1,4-bis(hexyloxy) 2,5-xylylene bis (triphenyl phosphonium chloride). This molecule is synthesis following reference [13]. A solution of 4.14 gm of 1,4-bis(hexyloxy)benzene and 7.4 g of triphenylphosphine in 150 ml xylene was stirred and heated to reflux for 24 h. After cooling, a white precipitate was obtained which was washed with ether and acetone to give the final product in yield 81%, m.p > 240 °C.

2.2.2.4. Synthesis of the copolymer 2. This copolymer was synthesized by the same procedure as in the case of copolymer 1. IR (KBr, cm^{-1}): 3059, 1508, 1029, 937, 1722. ^1H NMR (500 MHz, CDCl_3 , δ (ppm)): 0.8–1.6 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.9 (s, 3H, OCH_3), 7.1 (s, 2H, $-\text{CH}=\text{CH}-$), 7.4–7.8 (s, 6H, C_6H_6), 9.9 (s, 2H, $\text{O}=\text{CH}-$) and finally 7.3 due to solvent.

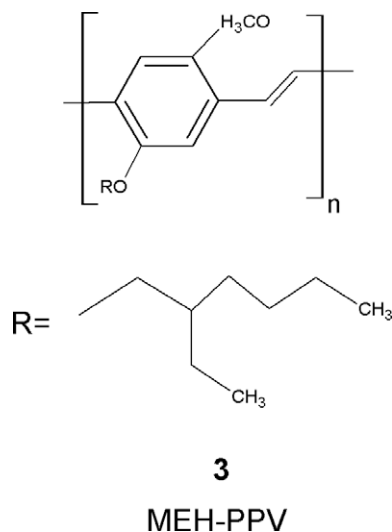
2.2.3. Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) **3 (Scheme 3)**

MEH-PPV copolymer ($M_n = 40,000$) is commercially purchase from Aldrich where its characteristics are shown in Table 1. This copolymer is used without further purification.

2.3. Characterization and instrumentation

2.3.1. Thermal properties

The TGA analysis indicates that the copolymers 1 and 2 are stable up to 275 °C under nitrogen atmosphere (10% weight loss). Between 275 and 350 °C, there is about 70% weight loss, which is a result of the decomposition of the copolymer. Glass transition (T_g) were determined by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 20 °C/min. The copolymers showed that a glass transition appears at 112 °C and 115 for copolymers 1 and 2, respectively.



Scheme 3. The chemical structure of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) **3**.

2.3.2. Steady state photophysical spectroscopy

The absorption and the fluorescence emission spectra of the conjugated copolymers and of the blended mixture were measured using a Perkin–Elmer Lambda 19 spectrophotometer and a Jobin Yvon Fluorolog spectrofluorometer, respectively. The method used to determine the photoluminescence quantum yields (PLQY) is a comparative method. The luminescence standard used as a reference was (1,1,4,4-tetra phenyl-1,3-butadiene) (TPB) its PLQY 0.84 [15]. The PL intensity at this concentration was measured, and the PLQY relative to TPB was calculated.

2.3.3. Time-resolved fluorescence spectroscopy

Time-resolved fluorescence decays were collected using the picosecond time-correlated single-photon-counting (TCSPC) technique (IRF) 21 ps [16]. The excitation source was a MIRA picosecond Ti:Sapphire laser from Coherent Inc. (vertical polarization, wavelength range: 720–1000 nm, 76 MHz repetition rate) coupled to a second-harmonic generator (360–500 nm). Emission collected at the magic-angle polarization is detected through a double subtractive monochromator by a microchannel plate (MCPT) Hamamatsu model R3809U-50. Signal acquisition was performed using a TCSPC module (Becker & Hickl Model SPC-630). Deconvolution of the fluorescence decays was performed using Globals WE software package. To analyze the influence of polymer aggregation which produced fast decay component, we used the single-photon-counting system in high-resolution mode (0.8 ps/channel), and the collected peak counts were greater than 10,000 counts.

3. Results and discussion

3.1. Photophysical characterization

Fig. 1 shows the UV–Vis absorption and fluorescence emission spectra of copolymer **1**, **2** and MEH-PPV **3** in chloroform solution. The optical spectrum for **3** was included for comparison. The absorption peak around 270 nm is most likely associated with localized electronic states within the phenyl rings and is less affected by the differences in π conjugation of the different PPV derivatives. The main absorption peak at 315 nm is observed only in copolymer **1** and **2**, a very weak feature observed in **3** may be a remnant of this absorption, whereas the main absorption peak for **3** appears at 500 nm and is due to a delocalized ($\pi_{\text{deloc}}-\pi_{\text{deloc}}^*$) transition.

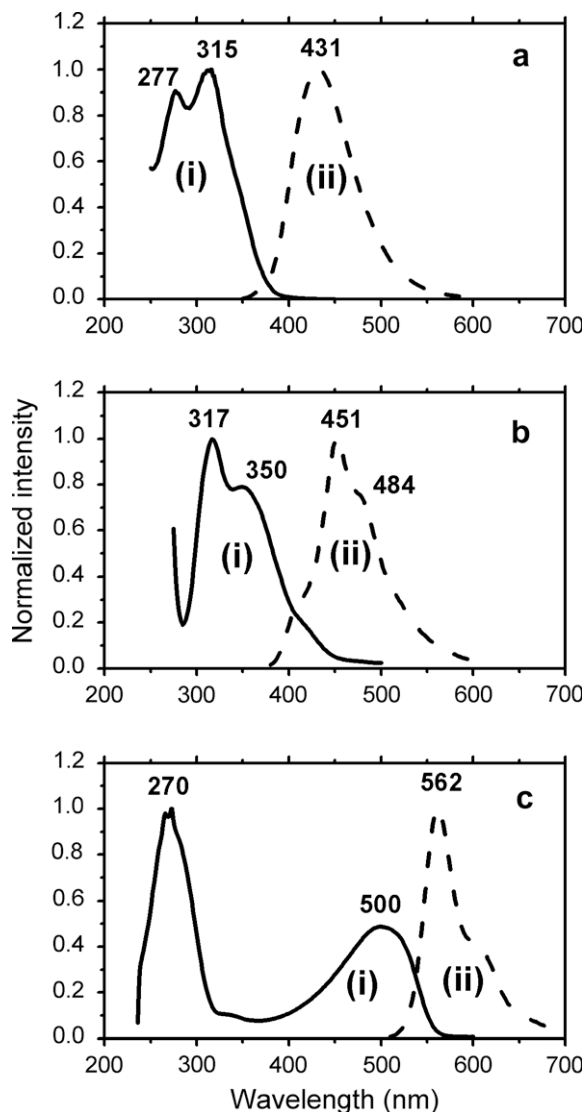


Fig. 1. Normalized absorption (i) and fluorescence (ii) spectra for (a) copolymer **1**, (b) copolymer **2** and (c) copolymer **3** in chloroform (2×10^{-4} M).

Copolymer **1** shows a structural's emission band at 431 nm which is 130 nm blue shifted from the emission of fully conjugated **3** which has its emission peak at 562 nm. This blue shift is a result of the much shorter conjugated length induced by the *ethane dioxy* spacer which effectively interrupts the conjugation length of the PPV backbone **3**. The structureless emission profile of copolymer **1** is indicative that this emission is of an excimer nature. Upon introducing *dihexyloxy* (alkoxy groups) into the second phenyl ring of the copolymer **2** units, the absorption spectra shows a red-shifted peaks at 350 nm and a small knee at 410 nm. The emission band (Fig. 1b) is red-shifted by about 20 nm with respect to **1**, where the emission peak shifts to 451 nm (blue–green emission). This red-shift is due to the electron-donating effect of the alkoxy group which increasing the number of electrons incorporated in the phenylenevinylene unit [6]. Bredas et al. [17] have theoretically calculated the absorption bands of PPV oligomers substituted by electron-donor (methoxy) and/or -acceptor (cyano) groups based on the geometrical and electronic structure. They have divided the $\pi-\pi^*$ transition bands into two categories: the localized and delocalized π -molecular levels, and different absorption peaks ascribed to different transition bands between these π -molecular levels. The three main transition groups lie around 3 eV

(410 nm), 4 eV (310 nm) and 5–7 eV (248–177 nm). The lowest energy absorption feature is assigned to the delocalized HOMO and LUMO levels ($\pi_{\text{deloc}} - \pi_{\text{deloc}}^*$). The second absorption peak results from several configurations involving transitions between delocalized and localized levels. The higher energy peak with the highest intensity has been assigned to transitions between localized levels ($\pi_{\text{loc}} - \pi_{\text{loc}}^*$). The lowest energy absorption band is not clearly shown in our copolymers **1** and **2** where the *ethane dioxy* spacer interrupts the conjugation length of the PPV backbone and limits the delocalization levels (i.e. exciton confinement) Fig. 1a and b. The absence of this absorption band was also found in many other synthesized PPV block copolymers where spacers were introduced to the polymer backbone to interrupt the π -conjugation [8,12,18–22]. In comparison this absorption peak is clearly observed in non-interrupted π -conjugation oligomers and polymers [23–27]. The absence of the $\pi_{\text{deloc}} - \pi_{\text{deloc}}^*$ absorption band in the region 400–500 nm for **1** and is very weak in **2** is clearly shown in Fig. 1. Recently Péres et al. [28] have also shown the difference between the absorption spectra of the fully conjugated halogen substituted PPV and the alternating copolymer with octamethylene segment, where a similar trend is shown in the absorption spectra of the two class of polymers. The other difference between the fully conjugated PPV copolymers and the block PPV copolymers are the magnitude in the shift in absorption and emission. The large difference between the absorption peak and emission peak comprises from the Stokes shift plus other effects that can red shift the emission, and is characteristic of these types of polymers [8,12,18–23]. In conjugated polymers, the Stokes shift is dominated by intramolecular relaxation [29,30]. Low frequency vibrations associated with torsional motions have been shown to be strongly coupled to the excitons [31,32]. Conjugated polymers with low frequency torsional motions are known to exhibit a much larger Stokes shift in comparison to conjugated polymers with restricted torsional degrees of freedom [33]. Tretiak et al. [29] showed that smaller numbers of repeat units in PPV polymer (oligomers) exhibit larger low frequency torsional motions and hence a larger Stokes shift. The calculated Stokes shift varied from 0.55 eV ($\lambda = 100$ nm) for two repeat units and saturated at 0.3 eV ($\lambda = 57$ nm) above 14 repeat units. Therefore the large Stokes shift observed in the block copolymers **1** and **2** compared with **3** may be ascribed to the absence of the delocalization absorption band $\pi_{\text{deloc}} - \pi_{\text{deloc}}^*$ on the one hand as well as the large torsional motions that these copolymer exhibit. We may conclude that introducing a spacer not only interrupts the conjugation length but also reduces the rigidity of the polymer. In highly rigid polymers such as ladder polymers where no conformation changes take place during photoexcitation, the Stokes shift is effectively zero. Therefore, we conclude that the large off-set between the absorption peak and the excitation peak in copolymers **1** and **2** and also that observed in all segmented copolymers [8,12,18–23] is due to the localization of the π -conjugation and the large torsional motion induced by the spacers.

The fluorescence emission of the three polymers collected at different excitation wavelengths shows no change in the emission peak or profile, which indicates single-fluorophore characteristics. Comparing the absorption profiles of **1** with **2**, we conclude that the absorption peak at 316 nm is similar in the two copolymers and it may be attributed to transitions between localized levels ($\pi_{\text{loc}} - \pi_{\text{loc}}^*$). This implies that the side chain (alkoxy group) is not affected by the configuration of the copolymer segment main chain i.e. no steric hindrance or structural distortion to the copolymer conjugated length. Previous characterization of similar copolymers [8,9] indicated that the absorption peak of the $\pi - \pi^*$ band is blue shifted by the side chain substitution due to steric hindrance and that the longer the side chain, the greater the steric hindrance. However, their observation of blue shift is due to the substitution occurring on one side of the fluorophores unit. This unbalanced

chemical structure exerts on torque on the backbone which increases the steric interaction between the substituent and the fluorophores leading to the adjacent phenyls to deviate from coplanarity. The absorption spectrum of the copolymer **2** is broader than **1** and shows extended vibronic peaks at 350 and 410 nm. The extension of the absorption spectrum to the lower energy is due to the electron-donation effect of the alkoxy groups. The resolved vibronic peaks in **2** indicates better solubility and indicates that copolymer **2** in solution has more isolated chains due to the large side alkoxy group which prevents strong chain aggregation. This is also reflected in the value of the quantum yields of copolymer **2** which has higher $\Phi_{\text{PL}} = 0.49$ than **1**, $\Phi_{\text{PL}} = 0.23$. The non-radiative deactivation of singlet excitons by the presence of the alkoxy groups due to spin-orbit coupling, [34] has little effect on the quantum yields of **2**. The value of Φ_{PL} in thin film is significantly less than that in solution as shown in Table 1, and it may be ascribed to the effect of interchain interaction. The absorption spectra of spin cast thin film onto quartz substrate from **1** and **2** is shown in Fig. 2. The absorption and emission spectra are slightly broader than that in solution, indicative of greater disorder, but shows no pronounced peak shift compared with that in the solution. The emission spectra excited at 320 nm show broad peaks that are red-shifted in comparison to those of the copolymer solutions as shown in Fig. 3. This red-shift in the fluorescence emission is partly due to interchain interaction caused by the π - π stacking

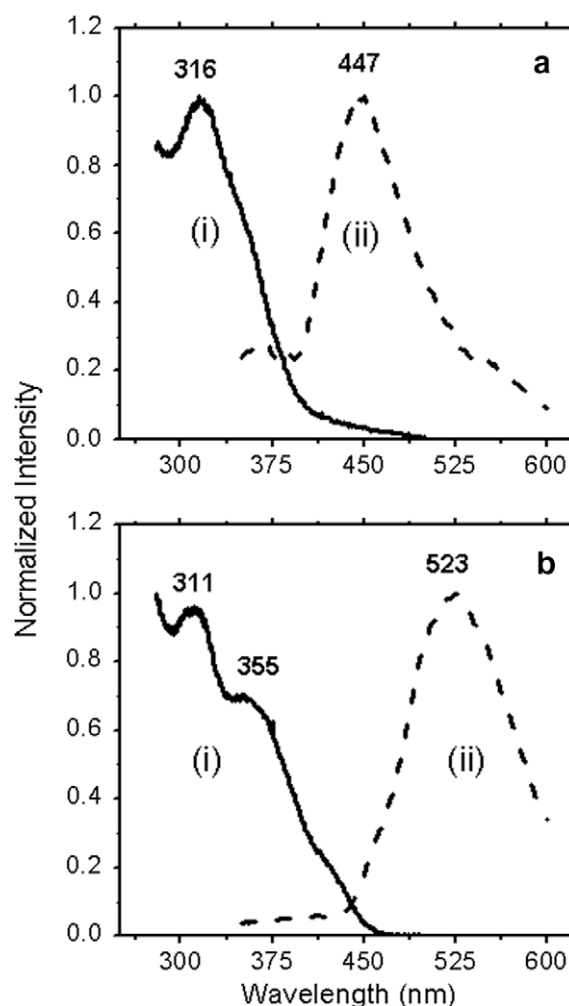


Fig. 2. Normalized absorption spectra of spin coated thin film of **1** (a) and **2** (b) on quartz substrate.

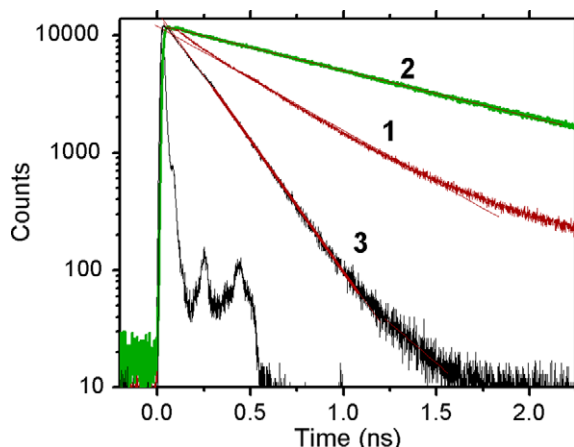


Fig. 3. Fluorescence lifetime decay for copolymers **1**, **2** and **3** measured at their fluorescence peak emission in chloroform solution of 2×10^{-4} M. The excitation wavelength was 374 nm.

between PPV chromophore oligomer segments which generate excimers in the excited state. However, the amount of the red shift due to interchain interaction is hard to estimate since the inner filter effect may influence the shape of the emission spectra due to high absorption at the blue side of the spectrum compared with that at the red side of the spectrum.

3.2. Time resolve analysis

The fluorescence lifetime for the copolymers was measured in chloroform solutions. Fig. 3 shows the decay profile of copolymer **1** and **2** together with that for MEH-PPV **3**. Single-exponential decay is more or less expected in dilute solution due to the absence of strong intermolecular interactions as shown in Fig. 3. However, using the most accurate time-resolved analysis (Global analysis) [35], three exponential decay functions were required to obtain a good fit to the measured data ($\chi^2 \approx 1$).

$$I(t) = \sum_{i=1}^3 a_i \exp(-t/\tau_i) \quad (1)$$

where a_i represent the amplitudes of the components at $t = 0$, τ_i is the decay time of the component i . When the fluorescence decay of fluorophore is multi-exponential the average decay time or fluorescence lifetime can be estimated using [36]:

$$\langle \tau \rangle = \sum a_i \tau_i^2 / \sum a_i \tau_i \quad (2)$$

where the sum runs over the number of exponential terms. The terms a_i , τ_i are proportional to the area under the decay curve for each decay time. The decay profile of copolymer **1** in chloroform solution with the fitting curve and the residual as an example is shown in Fig. 4.

The contribution to the steady state parameter f_i that weight each decay components may defined by [35],

$$f_i = a_i \tau_i / \sum a_i \tau_i \quad (3)$$

The fitting results using global analysis [35] for three decay components together with their contribution to the steady state fluorescence strength for copolymers **1** and **2** and **3** are shown in Table 2. The average fluorescence lifetimes for our copolymers in solution using Eq. (2) are $\langle \tau_{P1} \rangle = 0.5$ ns, $\langle \tau_{P2} \rangle = 1.07$ ns which are significantly longer than the fully conjugated polymer **3** $\tau_{\text{MEH-PPV}} = 180$ ps, this is in agreement with the previously measured lifetime of similar copolymers and monomers of 1–1.8 ns [37,38], compared with that measured for MEH-PPV **3** of $\tau = 270$ –300 ps [39,40]. The reason for the longer lifetimes in the block copolymers and oligomers may be related to exciton confinement, non-radiative decay channels such as exciton diffusion and migration to quenching sites are efficiently inhibited by the blocking units [6]. The time scale for diffusion and migration of the excitons and conformational relaxation are in the femtosecond time scale [41]. Therefore, with our pico- to nano-second system resolution, we only observe the influence of exciton diffusion and migration on the natural life-time of the three copolymers.

Following the analysis used by Al Attar and Monkman [42] for the decay times of luminescent polymers in solution for the emission collected at the blue side of the spectrum, the three exponential components which are described by their discrete lifetimes τ_i and the contribution to the steady state ion, f_i , may be assigned to the aggregated polymer chain (f_1), incomplete soluble (clusters) (f_2) and complete soluble (isolated polymer chain) (f_3). Inspecting

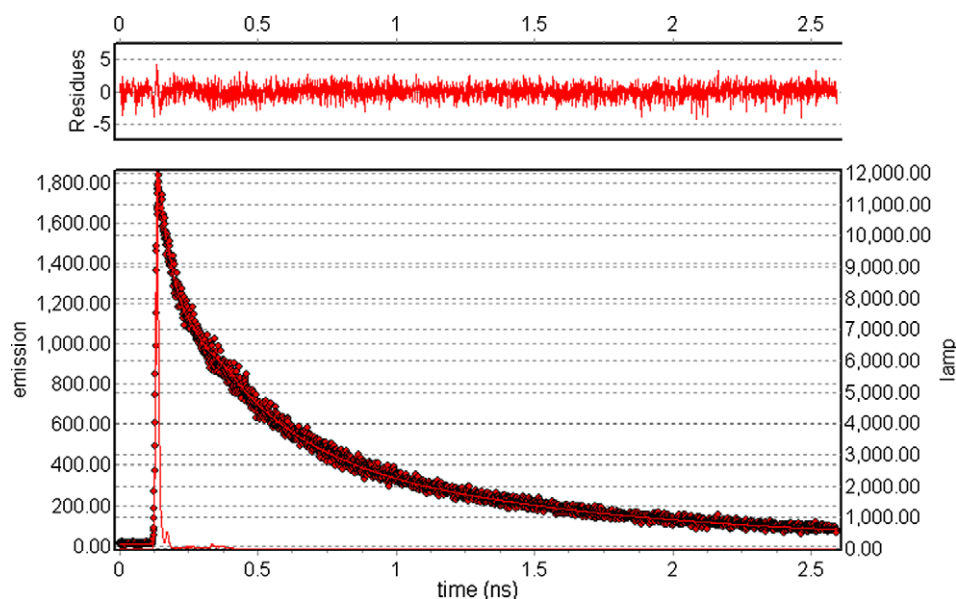


Fig. 4. Decay profile of copolymer **1** in chloroform solution with the fitting curve and the residual.

Table 2
Time-resolved analysis using three terms discrete energy exponential decay for copolymers **1**, **2**, and **3** in chloroform of 2×10^{-4} M. The excitation wavelength was 374 nm.

Polymer	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)	f_1	f_2	f_3	$\langle \tau \rangle$ (ns)
1	24	0.019	38	0.3	8	0.83	0.013	0.62	0.367	0.5
2	16.7	0.018	6.2	0.25	24.5	1.13	0.0057	0.05	0.94	1.07
MEH-PPV 3	17.5	0.016	72	0.18	0.558	0.5	0.02	0.96	0.02	0.18

a_i , τ_i and f_i are the amplitude, time (ns) and the fractional contribution to the steady state. 1, 2 and 3 subscript refer to the three phases which may the polymer exist in the solution.

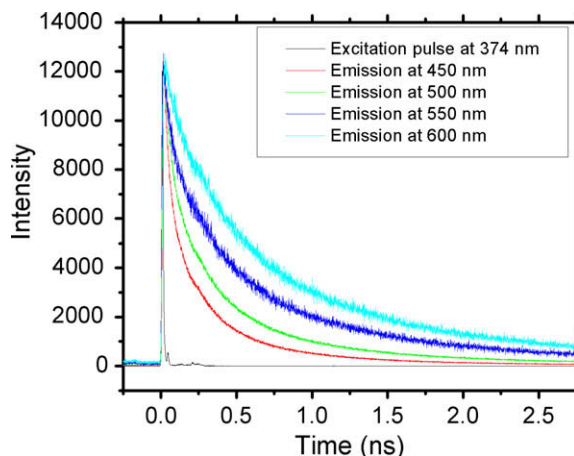


Fig. 5. Wavelength dependence of photoluminescence decay for copolymer **1** shows strong interchain interaction.

Table 2 we found that f_1 is less than 2%, i.e. no strong aggregation in all the copolymers dissolved in organic solvent. We also found that 94% of **2** are isolated chains with a single fluorescence lifetime of 1.13 ns compared to only 36% of **1** is isolated chains and 56% is incompletely soluble with lifetime around 300 ps. The reason for this is that the large alkoxy side group in **2** enhances solubility, leading to higher fluorescence quantum yields and longer lifetime. For MEH-PPV **3** the story is different, 96% of the polymer is completely dissolved having a single lifetime around 200 ps. This relatively short lifetime is not due to solubility but due to longer conjugation lengths having higher non-radiative decay rates, which compete more efficiently with radiative exciton decay.

The wavelength dependence of photoluminescence decay was measured for copolymers **1**, **2** and **3** in solid state. The excitation wavelength was 374 nm and the emission was collected at different wavelengths to evaluate the interchain interaction due to polymer chain stacking. The decay lifetime for copolymer **1** as an example becomes longer at longer emission wavelength which indicates interchain interaction (excimer, aggregates, etc.) species as shown in Fig. 5. Two methods of global analysis were used to understand whether the solid state form of these copolymers are two distinguishable types of emissive species i.e. two decay components (say isolated chains and stacking phase (excimer)), and the different emission wavelengths reflects the percentages of these two species, or whether it is a completely disordered system which yields a continuous change in decay time with emission wavelength, in this analysis we ignored the fast decay component $\tau = 25\text{--}50$ ps which has a very small contribution to the steady state see f_1 . Comparing the two methods we concluded that by allowing all the decay components to vary in the global fitting, the local and the final χ^2 is better than the fit for only two decay components. This reveals that the solid state form of copolymer **1** is a distribution of different stacking orders with a relevant decay time. The average life time for **1**, **2** and **3** calculated using Eq. (2) as a function of emission wavelength is plotted in Fig. 6. Copolymer **1**

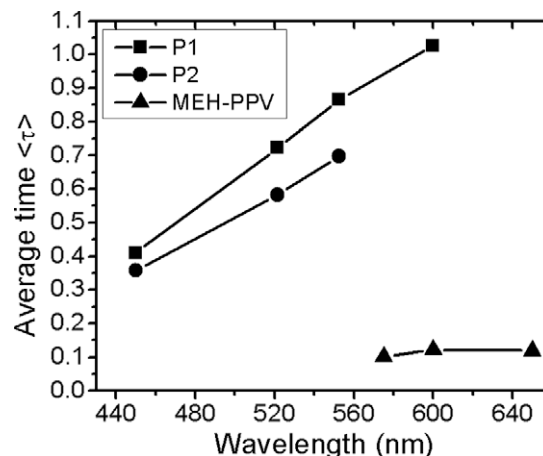


Fig. 6. The change in the average lifetimes as a function of emission wavelength for copolymers **1**, **2** and **3**.

has the highest interchain interaction component, with negligible interchain interaction in MEH-PPV **3**. Copolymer **2** shows lower interchain interaction than **1** due to the existence of the alkoxy side group. From Fig. 6 we conclude that although the enhancement in the quantum yield of these low molecular weight copolymers originate from the exciton confinement by the spacers, interchain interaction by stacking is relatively high due to low polydispersity and low chain length. This implies that low molecular block copolymers required large side group in their chemical structure to prevent aggregation and interchain interaction.

4. Conclusions

Block copolymers are an easy way to obtain precise conjugation length and hence short wavelength emission. Although an enhancement in the quantum yield of these low molecular weight copolymers originate from the exciton confinement by the non-conjugated spacer groups, interchain interactions are relatively high quenching emission which required larger side groups to prevent aggregation and interchain interaction. There is a correlation between the polymer rigidity conjugation length and Stokes shift. Longer conjugation length possesses higher rigidity and smaller torsional motion and hence smaller Stokes shift. The large Stokes shift observed in these block copolymers is thus a combination of exciton localization which eliminate $\pi_{\text{deloc}} - \pi_{\text{deloc}}^*$ transition at lower energy states and the higher torsional motion that such low molecular weight copolymers possess. Furthermore, the strong interchain interaction in these copolymers form excimers which further contributes to the effective Stokes shift.

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